

Studies on bulk and thin films of MgTiO_3 ceramics for microwave and electronic applications

A THESIS

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STATEMENT

The work contained in the thesis entitled “**Studies on bulk and thin films of MgTiO_3 ceramics for microwave and electronic applications**” has been carried out by me under the supervision of Dr. D. Pamu, Department of Physics, Indian Institute of Technology Guwahati. This work has not been submitted elsewhere for the award of any degree.

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CERTIFICATE

It is certified that the work described in this thesis, entitled “**Studies on bulk and thin films of MgTiO_3 ceramics for microwave and electronic applications**”, done by Mr. T. Santhosh Kumar, a Ph.D. student of Department of Physics, Indian Institute of Technology Guwahati, for the award of degree of *Doctor of Philosophy* has been carried out under my supervision. This work has not been submitted elsewhere for the award of any degree.

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Dedicated to my beloved parents

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Abstract

In recent years, rapid growth of the wireless communication industry has led to a high demand for microwave ceramic components. Commercial wireless technologies such as cellular phones, direct broadcasting satellite (DBS) and global positioning systems (GPS) have been making quick progress due to the improved performance of devices like dielectric resonators (DR) at microwave frequencies. DRs are highly densified ceramic samples of regular geometry, which acts as a resonator at microwave frequencies. They are made of ceramic materials with high dielectric constant (ϵ_r), low value of $\tan\delta$ (hence high-quality factor, Q) and low values of a temperature coefficient of resonant frequency (τ_f). The same materials are also being used for making substrates for microwave integrated circuits (MICs), ceramic filters and low temperature co-fired ceramic (LTCC) based highly miniaturized microwave systems.

In a similar process, high dielectric constant thin films became important in microelectronics. This is mainly due to the fact that for charge storage, materials with higher dielectric constant are essential. As the device dimensions reduce smaller, the frequency of operation of the microelectronic devices goes up and energy dissipation per unit area increases. Hence, thin films with high dielectric constant and low dielectric loss even at higher frequencies and with low temperature dependence is important for such microelectronic applications. Furthermore, due to their good optical properties, dielectric thin films having applications in integrated optical devices with various functions such as optical switching, modulation and coupling in optical communication, optical coatings, and anti-reflection coatings, etc.

Therefore, a suitable DR composition is identified for this study to make both bulk and thin film DRs and characterize the same in the microwave frequencies. This study would confirm the presence of excellent bulk characteristics in thin film as well.

Among the high - ϵ_r and low loss dielectric materials, magnesium titanate MgTiO_3 (MTO) is an excellent material for the applications discussed above in bulk form. The MTO exhibits a dielectric constant of (ϵ_r) ~ 17 , a high $Q \times f_0$ value of $\sim 1,60,000$ GHz (where f_0 is the frequency of measurement in GHz), temperature coefficient of resonant frequency is

~ -50 ppm/°C. However, there are two major disadvantages in preparing MTO ceramics in solid-state reaction method: One is the presence of MgTi₂O₅ as metastable phase, and the other is the requirement of a very high sintering temperature, which limits their practical applications. Therefore, it is essential to search for ways to reduce its sintering temperature and the effect of such processes on the microwave dielectric properties. Another important aspect in the study of DR materials is to understand the factors which influence Q value so that the fabrication conditions can be optimized to improve it. Bernard *et al.* reported the sintering temperature of MTO ceramics as 950°C with the addition of Li-based salts. Zhang *et al.* reported on MTO ceramics with the addition of 5.0mol% Bi₂O₃ - 7 mol% V₂O₅ and 6 wt% CuO - Bi₂O₃ - V₂O₅ sintered at 875°C and 900°C, respectively. Belnou *et al.* studied the addition of bismuth based additives to lower the sintering temperature of MTO ceramics below 1000°C. Nonetheless, the microwave dielectric properties, especially $Q \times f_0$ values are significantly degraded with these additives. On the other hand, few studies were reported on improving the dielectric properties of MgTiO₃ ceramics by partial substitution Mg with Zn , Co or Ni : (Mg_{0.95}Zn_{0.05})TiO₃ ($\epsilon_r \sim 17.1$, $Q \times f_0 \sim 264$ THz, $\tau_f \sim -40.3$ ppm/°C), (Mg_{0.95}Co_{0.05})TiO₃ ($\epsilon_r \sim 16.8$, $Q \times f_0 \sim 244$ THz, $\tau_f \sim -54$ ppm/°C), and (Mg_{0.95}Ni_{0.05})TiO₃ ($\epsilon_r \sim 17.2$, $Q \times f_0 \sim 180$ THz, $\tau_f \sim -45$ ppm/°C). However, the sintering temperature was reported to be always higher than 1400°C.

In addition, MTO thin films have attracted much attention due to its applications in (i) microwave integrated circuits, (ii) as a buffer layer, (iii) as a cladding layer for the growth of epitaxial LiNbO₃ films on Al₂O₃ substrates for the applications of integrated optical devices, (iv) as a high permittivity coating in electric devices, and (v) as a gate oxide for GaN based metal oxide semiconductor devices due to its high-quality factor in the microwave region along with a wide bandgap and refractive index (1.95). Some studies are already available on the thin films of the composition MTO prepared by RF sputtering, pulsed laser deposition (PLD) and chemical vapor deposition (CVD). These reports suggest that these films get lower leakage current as compared to SiO₂ and making them attractive for CMOS technology. Even though a considerable amount of study has gone into the bulk MTO, the systematic investigations on thin films are rather a few. Therefore, an attempt is given to

grow MTO films by a cost-effective process and to compare their properties with that of their bulk counterpart.

As a persistent effort in our research laboratory on microwave materials, we have chosen to investigate the MTO in the bulk form prepared by the solid state reaction method, mechanochemical method and semi alkoxide precursor method. We have attempted different techniques to reduce the sintering temperature to prepare bulk MTO and have been successful to some extent. MTO thin films were prepared by the RF magnetron sputtering. RF reactive magnetron sputtering technique has been used extensively for preparation of various kinds of films as it provides high deposition rates and relatively simple and cost-ineffective as compared to other techniques. The deposition parameters can be optimized to fabricate uniform films with high adhesion to the substrate. We have deposited MTO films from a ceramic target which is prepared using the optimized processing conditions of bulk MTO.

The overall efforts in this study are to enhance the microwave dielectric properties of the bulk samples by improving the microstructure and relative density of this material prepared with different additives. Furthermore, it is proposed to compare the microwave properties of MTO in bulk and thin film forms. In addition, we have also investigated their optical and electrical properties, which could not only be useful in other applications but also helps in arriving at a comprehensive picture of the physics of these materials, and the results were compared with the existing literature. The present thesis contains seven chapters.

Chapter 1 provides the brief introduction to dielectric materials, dielectric resonators (DR) and related areas. A historical background and the evolvement of dielectric resonators (DR) from the physics and device points of view are presented. The basic requirements of a material to be used as DR, a brief overview on DR materials, its mode characteristics and the applications are described. Furthermore, the importance of high dielectric constant and low loss films, the characteristics of SiO_2 in CMOS devices and the difficulties of its replacement are discussed. The basic applications of dielectric thin films were also been discussed. Subsequently, the importance of MgTiO_3 (MTO) as a DR and a brief overview on its crystal structure and microwave dielectric properties are presented. The motivation behind choosing MTO is presented at the end of the chapter 1.

In Chapter 2, the preparation and characterization techniques used for both bulk and thin films of MTO ceramics are presented. MTO ceramics have been prepared using solid-state reaction method, mechanochemical method and semi-alkoxide precursor (sol - gel) methods. The effects of ball milling and sintering mechanism were discussed in detail. Structural properties characterized using x-ray diffraction and microscopy techniques, Apparent densities of the prepared MTO ceramics measured by using Archimedes's method, Dielectric constant (ϵ_r) and the quality factor values (Q) at microwave frequencies measured using the Hakki - Coleman dielectric resonator method as modified and improved by Courtney, the temperature coefficient of resonance frequency (τ_f) at microwave frequency measured in the temperature range 25 - 80°C, the measurement of electrical properties using impedance spectroscopy, and the measurement of magnetic properties using vibrating sample magnetometer (VSM) are discussed. Moreover, an introduction to the RF magnetron sputtering technique for the thin film fabrication, the envelop technique to calculate the optical constants are given in detail. Furthermore, the details on the techniques used for electrical and the low-frequency dielectric properties of the films using a “Metal-Insulator-Metal (MIM) capacitor structure” and microwave dielectric properties of the films using the cavity perturbation technique are also discussed in this chapter.

Chapter 3 describes the preparation of single phase MTO ceramic in two different methods: while the former one is a mechanochemical method, the later one is a solid-state reaction. Since preparing single phase MTO ceramics is difficult in solid-state reaction method due to formation of MgTi_2O_5 as a secondary phase, efforts were made to prepare single phase MTO samples using mechanochemical method by optimizing the process conditions such as milling time, ball to powder ratio, milling speed, sintering temperature and sintering duration. The crystal structure, microstructure, low frequency dielectric and microwave dielectric properties of MTO ceramics are discussed. The best microwave dielectric properties of $\epsilon_r \sim 18.52$, $Q \times f_0 \sim 162$ THz were obtained for the samples milled for 30 h and sintered at 1350°C. On the other hand, in solid-state reaction method, non-stoichiometric MTO ($\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$; $\delta = 0, 0.05, 0.07, 0.10, 0.15$) ceramics are prepared. The effect of excess Mg content on the crystal structure, microstructure and microwave dielectric properties of the MTO ceramics are discussed. The synthesis conditions were optimized to get single phase MTO ceramics and maximum relative density. Samples prepared at $\delta = 0.07$

exhibits a single-phase MTO and exhibits a secondary phase of MgTi_2O_5 (Mg_2TiO_4) for below (above) $\delta = 0.07$. The microstructures of the MTO ceramics were improved with excess Mg content. The optimum microwave dielectric properties of $\epsilon_r \sim 17.68$, $Q \times f_0 \sim 161$ THz at 9.4 GHz were obtained for $\delta = 0.07$ samples sintered at 1350°C for 3 h. In both, the method's dielectric loss mechanisms were discussed, and the obtained results were compared with the earlier reports. Also studied the effect of V_2O_5 addition on the crystal structure, microstructure and microwave dielectric properties of non- stoichiometric MTO ceramics was discussed.

In Chapter 4, a systematic study of the effect of various additives on the densification, microstructure and microwave dielectric properties of MTO are presented. The different types of additives such as CeO_2 nanoparticles, Bi_2O_3 and La_2O_3 (0.5 - 1.5 wt%) were added to MTO. The sintering temperatures and the sintering durations were optimized in each case to get uniform microstructure and higher relative densities. In case of Bi_2O_3 addition, no secondary phase other than MgTi_2O_5 is observed up to 1.5 wt%. However, in case of CeO_2 nanoparticles and La_2O_3 additions, another secondary phase as determined by XRD and confirmed with EDS spectra was observed along with MgTi_2O_5 . The addition of Bi_2O_3 shows higher densification as compared to other two additives at 1200°C whereas other additives did not show much effect on lowering the sintering temperature. The maximum relative densities obtained are 97.5%, 97.6% and 96.9% of the theoretical densities of MTO for the samples added with CeO_2 nanoparticles, Bi_2O_3 and La_2O_3 , sintered at 1300, 1200 and 1300°C, respectively. The decrease in sintering temperature is due to the liquid phase effect and smaller initial particle sizes. Further, the microstructures of the MTO ceramics were improved with the addition of these additives. But, it was found that there is not much change in the dielectric constant and temperature coefficient of the resonant frequency, whereas the quality factor is found to be a significant variable. Also, influence of annealing on the crystal structure, densification, microstructure and microwave dielectric properties of the pure and CeO_2 nanoparticle added MTO samples annealed at 1100°C for 48 h is discussed.

Chapter 5 describes the optimization processing conditions of $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07$) ceramics prepared by semi alkoxide precursor method. The effect of cobalt substitution on the crystal structure, densification, microstructure, broadband dielectric

properties, microwave dielectric properties and magnetic properties were discussed. The calcination temperature and sintering conditions were optimized to obtain the maximum relative density and best dielectric properties. The DSC/TGA curve of as prepared powder shows a crystallization temperature of 600°C and is confirmed with the XRD results. It is revealed that MTO ceramics doped with Co up to be $\delta = 0.05$ exhibit single phase, above that, a small amount of MgTi_2O_5 was observed as a secondary phase. Rietveld refinement was carried out for all the XRD patterns, and the structural properties of the samples were also been discussed. The maximum relative densities for all the samples are obtained at 1200°C, which is attributed to the small initial particle size and larger surface area of the initial powders. The average grain size, relative density and $Q \times f_0$ were improved significantly with the Co^{+2} substitutions. The best dielectric properties of properties $\epsilon_r \sim 17.03$, $Q \times f_0 \sim 170$ THz @ 9.3 GHz and τ_f of -40 ppm/°C was obtained for $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics sintered at 1200°C. The broadband dielectric properties were measured for all the samples in the frequency and of 1MHz to 3GHz as a function of temperature (133 K to 573 K). The broadband dielectric properties show relaxation behavior with frequency and dielectric anomalies observed in the temperature-dependent measurements. Interestingly, at room temperature all the samples showing paramagnetic behavior. Further, it is also found that $x = 0.03$ samples exhibit paramagnetic (PM) to ferromagnetic (FM) and FM to antiferromagnetic (AFM) transitions in temperature dependent magnetization measurements. The correlation between dielectric anomalies and magnetic properties are also being discussed.

In Chapter 6, the optimization of processing conditions of the MTO thin films prepared by RF magnetron sputtering is described. The sputtering target was prepared by optimized processing conditions in the mechanochemical method. MTO thin films were deposited on to various substrates (quartz, amorphous SiO_2 and on platinized silicon ($\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$)) under different oxygen mixing percentage (OMP) in the sputtering gas. The effect of OMP and post annealing temperature on the structural, microstructural, optical and dielectric properties were presented. For the first-time MTO, films were deposited in pure oxygen atmosphere. The as deposited films were amorphous in nature despite the processing conditions and substrates used, but the annealed films at 700°C exhibit crystallinity. Additionally, the optical constants are found to increase with annealing. The annealed films exhibit refractive index of 2.12 - 2.19 at 600 nm with an optical bandgap

value in between 4.11 and 4.19 eV for the films deposited on quartz substrates. On the other hand, films deposited on amorphous SiO₂ substrates exhibit refractive index in the range of 1.98–2.14 at 600 nm with an optical bandgap in the range 4.07 - 4.23eV upon annealing. Raman spectroscopy studies of the films deposited under different conditions were also studied. Metal-Insulator-Metal (MIM) capacitors were fabricated under different OMPs for the films deposited on platinized silicon substrates. The dielectric properties of MTO films were measured in the frequency range of 1 kHz to 1MHz as a function of OMP. The films deposited in pure oxygen atmosphere showed the highest dielectric constant with low loss at 1MHz. The dielectric constant of each film is close to the bulk value whereas the dielectric losses of the films are observed to be higher than the bulk value. The detailed observations, discussion and possible explanations are presented in this chapter.

The sputtering target was prepared by the optimized processing conditions in the semi-alkoxide precursor method. The processing parameters are optimized for the (Mg_{0.95}Co_{0.05})TiO₃ (MCT) thin films using RF magnetron sputtering. MCT thin films are deposited at 300°C on to amorphous SiO₂ and platinized silicon (Pt/TiO₂/SiO₂/Si) substrates under different OMP in the sputtering gas. The effect of OMP on the growth, morphology, optical and physical properties of the thin films is discussed. As deposited films are amorphous, but crystallize after annealing at 700°C. A preferred orientation along (110) has been observed with increasing the OMP. The evolution of the textured growth is explained on the basis of orientation factor (*F*) analysis proposed by Lotgering. The optical constants such as refractive index and bandgap are calculated from the optical transmittance spectra. Upon annealing, it is found that both the refractive index and bandgap values increase and the refractive indices of the annealed films are in the range of 2 – 2.14 at 600 nm with optical bandgap values in between 3.95 to 4.16 eV.

Furthermore, Metal – Insulator - Metal (MIM) capacitors are fabricated under different OMPs. These films exhibit typical semi conducting behaviour with a negative temperature coefficient of resistance. The role of frequency and OMP on the ac conductivity of MgTiO₃ has been studied. These thin films exhibit a maximum relative dielectric permittivity of $\epsilon_r = 12.20$ and low loss ($\tan\delta \sim 1.2 \times 10^{-2}$) over a wide range of frequencies. A progressive increase in relative permittivity ϵ_r values have been noticed up to 75% of OMP

and the properties were observed to be deteriorated on further increasing the OMP. I-V characteristics reveal that the leakage current density decreases from 9.93×10^{-9} to 1.14×10^{-9} A/cm² for OMP 0% to 75%, respectively for an electric field strength of 250 kV/cm.

Chapter 7 describes (i) the correlation between bulk and thin film properties of MTO, (ii) summary of the thesis work, potential applications and (iii) possibilities for further research work.



ABBREVIATIONS

α	Absorption co-efficient
E_a	Activation energy
AFM	Atomic force microscopy, Anti ferromagnetism
D	Average crystallite size
N_A	Avogadro number
E_g	Bandgap
k_B	Boltzmann constant
MCT	Co doped Magnesium titanate ($Mg_{0.95}Co_{0.05}$)TiO ₃
H_C	Coercive Field, Coercivity
σ	Conductivity
ϵ_r	Dielectric constant
DR	Dielectric resonator
EDS	Energy dispersive spectra (X-ray)
FM	Ferromagnetic
FC	Field cooled
P	Fractional porosity
f	Frequency
FWHM	Full width at half maximum (β)
h	Hours
ϵ''	Imaginary part of dielectric permittivity
Z'	Imaginary part of impedance
η	Lattice strain
J	Leakage current density
tanδ	Loss tangent
MTO	Magnesium Titanate (MgTiO ₃)
Z	Number of atoms per unit cell

F	Orientation factor
OMP	Oxygen mixing percentage
PM	Paramagnetic
ppm	Parts per million
$h\nu$	Photon energy
R_p	Profile factor
Q	Quality factor
ϵ'	Real part of dielectric permittivity
Z''	Real part of impedance
χ^2	Reduces chi-square
n	Refractive index
τ	Relaxation time
f_0	Resonant frequency
RT	Room temperature
rms	Root mean square
SEM	Scanning electron micrograph
χ	Susceptibility
TCK	Temperature co-efficient of dielectric constant
τ_f	Temperature co-efficient of resonant frequency
T_c	Transition temperature
WC	Tungsten Carbide
V	Unit cell Volume
VSM	Vibrating sample magnetometer
wt	Weight
XRD	X-ray diffraction
ZFC	Zero field cooled

CONTENTS

Statement	i
Certificate	ii
Dedication	iii
Acknowledgements	iv
Abstract	vi
List of Abbreviations	xiv
List of Figures	xxii
List of Tables	xxx
1. Introduction to High ϵ_r and Low Loss Bulk and Thin Films	1-28
1.1 Introduction to dielectric resonators	1
1.2 History of dielectric resonators	2
1.3 Modes in a dielectric resonator	2
1.4.1 Material requirements of a DR	5
1.4.2 Well known dielectric resonator materials	8
1.4.3 Current state of materials developed for dielectric resonator applications	10
1.4.4 Future requirements of the DR materials	10
1.5 Physics of DR materials	11
1.5.1 Polarization mechanisms in dielectrics	11
1.5.2 Dielectric losses	12
1.5.3 Temperature coefficients	13
1.6 Electronic applications of high (ϵ_r) materials in thin film form	15
1.7 Characteristics of SiO ₂ in MOSFET devices and the difficulties of its replacement	18
1.8 Efforts to replace SiO ₂	19

1.9 Magnesium Titanate (MTO): An interesting system in both bulk and thin film forms	20
1.9.1 Bulk MTO for microwave applications	20
1.9.2 MTO thin film as a possible gate oxide in electronic applications	21
1.9.3 Crystal Structure of MTO	21
1.10 Motivation of study	23
1.11 References	25
2. Preparation Methods and Characterization Techniques	29-70
2.1 Preparation techniques used for bulk MgTiO_3	29
2.1.1 Solid-state reaction method	29
2.1.2 Mechanochemical processing	30
2.1.3 Sol - gel method (Semi Alkoxide Precursor Method)	31
2.1.4 Stoichiometric weighing of reagents	32
2.1.5 Uniform mixing of reagents	32
2.1.6 Calcination stage	33
2.1.7 Particle size reduction	33
2.1.8 Uniaxial Pressing	33
2.1.8a Solid - State Sintering	34
2.1.8b Recrystallization and grain growth	36
2.1.9 Liquid phase sintering	38
2.2 Characterization techniques used for the bulk MTO ceramics:	38
2.2.1 X - ray diffraction	38
2.2.2 Surface area analyzer	39
2.2.3 Particle size analyzer	40
2.2.4 Density Measurement	41
2.2.5 Scanning electron microscopy	41
2.3 Microwave measurements	43
2.3.1 Measurement of dielectric constant (ϵ')	45
2.3.2 Measurement of quality factor (Q)	45

2.3.3 Measurement of temperature coefficient of resonant frequency (τ_f)	47
2.4 Electrical conductivity measurements	47
2.4.1 General theory	48
2.5 Raman Spectroscopy	50
2.6 Vibrating Sample Magnetometer	52
2.7 Thin film preparation techniques	53
2.7.1 Chemical vapor deposition technique	53
2.7.2 Physical vapor deposition technique	54
2.7.2a Thermal Evaporation	54
2.7.2b Sputtering	54
(i) DC sputtering	56
(ii) Magnetron Sputtering	56
(iii) Reactive magnetron sputtering	57
(iv) Mechanism of sputtering	57
(v) RF magnetron sputtering	58
2.8 Thin film characterization techniques	59
2.8.1 Optical properties	60
2.8.2 Surface profilometer	63
2.9 Microwave dielectric properties of thin films using post split dielectric resonator method	63
2.10 Electrical measurements	65
2.11 Atomic force microscope	66
2.12 References	68
3. Mechanochemical and Solid State Synthesis of MgTiO₃ ceramics.	71-94
3.1 Literature review	71
3.2 Experimental details	72
3.2.1 Mechanochemical method	72
3.2.2 Solid state reaction method (non-stoichiometric compositions)	72

3.3 Mechanochemical method	73
3.3.1 Effect of milling time on the phase formation of MTO ceramics	73
3.3.2 Effect of sintering temperature on crystal structure	74
3.3.3 Microstructure	75
3.3.4 Relative density	76
3.3.5 Raman spectra	77
3.3.6 Low frequency dielectric properties	78
3.3.7 Microwave dielectric properties	79
3.4 Preparation of non-stoichiometric $Mg_{1+\delta}TiO_{3+\delta}$ composition and $Mg_{1.07}TiO_{3.07}$ with the addition of V_2O_5 by solid state reaction method.	81
3.4.1 Crystal structure	81
3.4.2 Microstructure	84
3.4.3 Relative density	87
3.4.4 Microwave dielectric properties	89
3.5 Conclusions	92
3.6 References	93
4. Effect of Additives on Microwave Dielectric Properties of $MgTiO_3$ Ceramics	95-120
4.1 Brief literature review of $MgTiO_3$ processing	95
4.1.1 Low temperature sintering of MTO ceramics by chemical processing	95
4.1.2 Low temperature sintering with liquid - phase sintering aids	96
4.2 Experimental Details	97
4.3 Effects of CeO_2 nanoparticles and annealing temperature on MTO ceramics	98
4.3.1 Crystal structure	98
4.3.2 Relative density	100
4.3.3 Microstructural analysis	102
4.3.4 Microwave dielectric properties	104

4.4 Effects of Bi_2O_3 and La_2O_3 additions on MTO ceramics	108
4.4.1 Crystal structure	108
4.4.2 Microstructure of MTO ceramics added with Bi_2O_3 and La_2O_3	109
4.4.3 Effect of Bi_2O_3 or La_2O_3 addition on relative density of MTO ceramics	111
4.4.4 Microwave dielectric properties	114
4.5 Conclusions	117
4.6 References	118
5. Influence of Co Substitution on Microwave and Magnetic Properties of MgTiO_3 Ceramics	121-146
5.1 Brief literature survey	121
5.2 Experimental Details	122
5.3 Phase analysis and crystal structure of gel powders	123
5.4 Crystal structure of sintered pellets	124
5.5 Microstructure and Relative density	126
5.6 Microwave dielectric properties	130
5.7 Low frequency dielectric properties	132
5.8 Magnetic properties	136
5.9 Broadband dielectric properties	138
5.10 Conclusions	141
5.11 References	143
6. Studies on Pure and Co Doped MgTiO_3 Thin Films	147-190
6.1 A brief literature review	147
6.2 Experimental Details	148
6.2.1 Pure MgTiO_3 thin films	148
6.2.2 $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films	149
6.3 MgTiO_3 thin films	149
6.3.1 Structural Characterization of sputtering target	149
6.3.2 Structure and microstructure of MTO thin films	150

6.3.3 Optical Characterization	154
6.3.4 Dielectric studies	159
6.4 (Mg _{0.95} Co _{0.05})TiO ₃ thin films	160
6.4.1 Structural Characterization of sputtering target and thin films	160
6.4.2 Surface morphology	165
6.4.3 Optical properties	166
6.4.4 Impedance spectroscopy	169
6.4.5 Dielectric studies	173
6.4.6 Electrical properties of MCT thin films	176
6.4.7 Microwave dielectric properties of pure MTO and MCT thin films	177
6.5 Conclusions	181
6.6 References	184
7. Summary and Future work	187-190
7.1 Summary	187
7.2 Future scope of the work	189
List of Publications	191

LIST OF FIGURES

Figure no.	Figure description	Page no.
<i>Chapter 1</i>		
1.1	(a) Magnetic field in equatorial plane of the $TE_{01\delta}$ mode. (b) Electric field in equatorial plane of the $TE_{01\delta}$ Mode.	3
	(c) Magnetic and electric field together in a DR (side view).	4
1.2	Commercially available shapes of DRs.	5
1.3	Different types of polarization mechanisms appear in a dielectric.	12
1.4	(a) Crystal structure of $MgTiO_3$ and (b) Schematic representation of a $MgTiO_3$ unit cell.	22
<i>Chapter 2</i>		
2.1	(a) Photographic view of planetary ball mill used to prepare samples and (b) Schematic view of the mechanical milling process	31
2.2	Schematic block diagram of X-ray diffractometer	39
2.3	A schematic block diagram of surface area analyzer.	40
2.4	Schematic diagram of SEM.	42
2.5	QWED Krupka resonator cavity used to measure the Q and ϵ_r .	46
2.6	Complex plane plots of impedance and admittance for R-C circuits.	49
2.7	(a-c) Different types of impedance behaviors observed in solids.	50
2.8	Block diagram of vibrating sample magnetometer	52
2.9	Different regions in a typical glow discharge.	55
2.10	Sputtering process.	57
2.11	Schematic diagram of RF sputtering unit.	59
2.12	Typical transmittance spectrum of the film.	61
2.13	Cross sectional view of SPDR fixture.	64
2.14	Schematic diagram of atomic force microscope.	66
<i>Chapter 3</i>		
3.1	(a) XRD patterns of MgO & TiO_2 oxides milled for 20, 25 and 30 h.	73
	(b) XRD patterns of the $MgTiO_3$ ceramics milled for 30 h and sintered at different sintering temperatures.	74

Figure no.	Figure description	Page no.
3.1	(c) XRD pattern along with Rietveld refinement of MgTiO_3 ceramics sintered at 1350°C . The circles and solid line represent the experimental and the Rietveld refined data, respectively. The blue line at the bottom shows the difference between the experimental and the refined data. The vertical bars correspond to the allowed Bragg's peaks.	75
3.2	SEM image of (a) MTO powder milled for 30 h. The MTO ceramics sintered at (b) 1300°C (c) 1350°C (d) 1400°C .	76
3.3	(a) The variation in relative density as a function of milling time, sintered at 1350°C . (b) Variation in relative density of MTO ceramics as a function of sintering temperature.	77
3.4	Raman spectra of the MTO ceramics sintered at different sintering temperatures.	78
3.5	(a) Dielectric constant (ϵ_r) and (b) loss tangent ($\tan\delta$) measured at different frequencies as a function of temperature of MTO ceramics sintered at 1350°C .	79
3.6	Variation in dielectric constant and $Q \times f_0$ values of MTO ceramics as a function of sintering temperature.	80
3.7	Variation in dielectric constant and $Q \times f_0$ values of MTO ceramics as a function of relative density.	81
3.8	(a) XRD patterns of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ($\delta = 0 - 0.15$) compositions sintered at 1350°C for 3 h. (b) XRD patterns of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ composition added with different amounts of V_2O_5 , sintered at 1100°C for 3 h.	82
3.9	XRD patterns along with Rietveld refinement data of (a) $x = 0.0$ wt% $\text{Mg}_{1.07}\text{TiO}_{3.07}$, sintered at 1350°C , (b-d) different wt% ($x = 0.5 - 1.5$) of V_2O_5 added to $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics, sintered at 1100°C .	83
3.10	SEM images of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics doped with different δ concentrations (a) $\delta = 0$, (b) $\delta = 0.05$ (c) $\delta = 0.07$ and (d) $\delta = 0.15$, sintered at 1350°C for 3 h.	85
3.11	SEM images of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ specimen added with different wt% of V_2O_5 and sintered at 1100°C (a) $x = 0.0$ wt%, (b) $x = 0.5$ wt%, (c) $x = 1.0$ wt% and (d) $x = 1.5$ wt%.	86

Figure no.	Figure description	Page no.
3.12	Variation in relative density of (a) $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ as a function of δ concentration and (b) $\text{Mg}_{1.07}\text{TiO}_{3.07}$ as a function of x wt% at different sintering temperatures.	88
3.13	Dependence of dielectric constant (ϵ_r) on (a) δ concentration in $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics (b) x wt% (V_2O_5) in $\text{Mg}_{1.07}\text{TiO}_{3.07}$ sintered at different temperatures.	89
3.14	Variation in $Q \times f_0$ for (a) $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ as a function of δ concentration and (b) $\text{Mg}_{1.07}\text{TiO}_{3.07}$ as a function of x wt% at different sintering temperatures.	91
Chapter 4		
4.1	X-ray diffraction patterns of MTO ceramics with $x = 0.0 - 1.5$ wt% (a) before annealing (b) after annealing.	99
4.2	SEM images of (a) pure MTO ceramics sintered at 1400°C and MTO - CeO_2 (x wt%) ceramics with (b) $x = 0.5$, (c) $x = 1.0$ and (d) $x = 1.5$, sintered at 1300°C .	102
4.3	SEM images of MTO ceramics with $x = 0.0 - 1.5$ wt% annealed at 1100°C for 48 h (a) Pure MTO ceramics and MTO- CeO_2 ceramics with (b) $x = 0.5$ wt%, (c) $x = 1.0$ wt% and (d) $x = 1.5$ wt%.	104
4.4	Variation in (a) $Q \times f_0$ values and (b) $Q \times f_0$ values of the samples used to optimize the annealing temperature, (c) $Q \times f_0$ values after annealing as a function of sintering temperature for MTO ceramics added with $x = 0.0 - 1.5$ wt%.	106
4.5	(a) XRD patterns of the MTO ceramics added with different wt% of Bi_2O_3 and sintered at 1200°C .	108
	(b) XRD patterns of the MTO ceramics added with different wt% of La_2O_3 and sintered at 1300°C .	109
4.6	SEM images of the MTO - Bi_2O_3 (x wt%) ceramics with (a) $x = 0.5$, (b) $x = 1.0$ and (c) $x = 1.5$.	110
4.7	SEM microstructures of the MTO - La_2O_3 (y wt %) ceramics with (a) $y = 0.5$, (b) $y = 1.0$ and (c) $y = 1.5$. (d) EDS spectra of MTO ceramics added with $y = 1.5$.	111
4.8	Variation in relative densities of the MTO ceramics added with different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.	112

Figure no.	Figure description	Page no.
4.9	SEM microstructure of the pure MTO ceramics milled for 10 h.	113
4.10	Variation in dielectric constants of MTO ceramics with the addition of different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.	114
4.11	Variation in $Q \times f_0$ of MTO ceramics with the addition of different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.	115
Chapter 5		
5.1	DSC / TGA curves of the MTO powders prepared using semi alkoxide precursor method.	123
5.2	(a) X-ray diffraction pattern of MgTiO_3 powder calcined at 600°C . Inset: Application of Williamson-Hall plot method for MTO powders. (b) FESEM image of the MTO powders calcined at 600°C .	124
5.3	(a) X-ray diffraction patterns of the $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ($x = 0.00 - 0.07$) ceramics sintered at 1200°C . (b) Rietveld refinement of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics sintered at 1200°C . (c) XRD patterns of the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics sintered at different sintering temperatures.	125
5.4	SEM images of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics sintered at different sintering temperatures: (a) 1100°C , (b) 1150°C , (c) 1200°C , and (d) 1250°C .	127
5.5	SEM micrographs of $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ doped with different x concentrations: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.03$ and (d) $x = 0.07$, sintered at 1200°C for 3 h.	127
5.6	EDS spectrum for $x = 0.05$ sample sintered at 1200°C for 3 h.	128
5.7	Variations in relative density as a function of sintering temperature for different Co concentrations.	129
5.8	Variations in dielectric constant value as a function of sintering temperature for different Co concentrations.	130
5.9	(a) $Q \times f_0$ values as a function of sintering temperature for different Co concentrations. (b) Dependence of $Q \times f_0$ and average grain size on Co content in MgTiO_3 ceramics.	131

Figure no.	Figure description	Page no.
5.10	Frequency dependent imaginary part of impedance (Z'') for $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample measured at different temperatures.	132
5.11	(a,b) The Nyquist plots (Cole - Cole graphs) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics measured at different temperature (300 - 773 K). The inset of 11(b) shows equivalent circuit model for the Cole - Cole configuration.	133
5.12	The Variation in ac-conductivity (σ_{ac}) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample as a function of frequency (f) measured at different temperatures.	134
5.13	The frequency dependent (a) dielectric constant (ϵ_r) and (b) loss tangent ($\tan\delta$) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample, measured at different temperatures.	135
5.14	Variation in dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample as a function of temperature measured at 10^6 Hz.	136
5.15	(a) $M - H$ loops of MgTiO_3 with different Co concentrations. (b) Magnetic susceptibility of MgTiO_3 ceramics as a function of Co concentration.	137
5.16	$M - T$ curves for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample measured under 100 and 500 Oe applied fields. Insets: (b) $M - H$ curves measured at different temperatures and (c) variation of coercivity with temperature for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.	138
5.17	Frequency dependence of real (ϵ') and imaginary (ϵ'') part of dielectric permittivity at different temperatures for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.	139
5.18	Temperature dependent real (ϵ') and imaginary (ϵ'') parts of permittivity measured at different frequencies for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.	140
5.19	Temperature dependence imaginary part of permittivity (ϵ'') measured at 1GHz and M-T curves measured at 100 Oe and 500 Oe applied fields under ZFC process for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.	141

Figure no.	Figure description	Page no.
<i>Chapter 6</i>		
6.1	XRD pattern along with Rietveld refinement of MgTiO_3 ceramic target sintered at 1350°C . The circles and solid line represent the experimental and the Rietveld refined data, respectively. The blue line at the bottom shows the difference between the experimental and the refined data. The vertical bars correspond to the allowed Bragg's peaks	149
6.2	XRD patterns of MTO thin films deposited under different oxygen mixing percentage and annealed at 700°C for 1h on (a) quartz (b) amorphous SiO_2 and (c) platinized silicon substrates.	151
6.3	The variation in average crystallite size as a function of oxygen mixing percentage.	152
6.4	(a) SEM image and (b) EDS spectrum of the MTO thin film deposited on quartz at 70% OMP and annealed at 700°C for 1 h.	152
6.5	Atomic force microscopic (AFM) images of (a) as - deposited and (b) annealed MTO thin films deposited on quartz at 70% OMP.	153
6.6	Optical transmittance spectrum of as - deposited and post annealed MTO thin films (a) On quartz deposited at 70% OMP and (b) On amorphous SiO_2 substrates at 60% OMP.	154
6.7	(a & b) Variation of refractive index and packing density as a function of OMP.	156
	(c & d) porosity ratio as a function of OMP of as - deposited and annealed MgTiO_3 thin films on quartz and amorphous SiO_2 substrates.	156
6.8	(a) Variation in bandgap as a function of OMP for as - deposited and annealed MTO thin films deposited on quartz substrates.	157
	(b) A Plot of $(\alpha h\nu)^{1/2}$ Vs. $h\nu$ for the MTO thin films deposited at 70% OMP.	157
6.9	(a) Variation in bandgap as a function of OMP for as - deposited and annealed MTO thin films deposited on quartz substrates.	158
	(b) A Plot of $(\alpha h\nu)^{1/2}$ Vs. $h\nu$ for the MTO thin films deposited at 60% OMP.	158
6.10	The variation in bandgap as a function of average crystallite size for MTO thin films deposited onto quartz and amorphous SiO_2 substrates.	158

Figure no.	Figure description	Page no.
6.11	Plots of variation in (a) dielectric constant and (b) loss tangent of MTO thin films deposited at different OMP as a function of frequency.	160
6.12	X-ray diffraction pattern along with the Rietveld refinement of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ target material, sintered at 1200°C for 3 h in air.	161
6.13	X-ray diffraction patterns of post annealed $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films at 700°C deposited on (a) platinized silicon and (b) amorphous SiO_2 substrates at different oxygen mixing percentage (OMP). The peak with asterisk mark indicates the reflection from Si substrates.	162
6.14	The variation of XRD peak intensity of the (104) and (110) reflections as a function of oxygen mixing percentage. Solid symbol indicates films on platinized silicon substrates and open symbol films on amorphous SiO_2 substrates.	163
6.15	The dependence of orientation factor (F) of as a function of oxygen mixing percentage for MCT thin films deposited on (a) platinized silicon and (b) amorphous SiO_2 substrates.	164
6.16	Atomic force microscopic (AFM) images of the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films deposited on platinized silicon substrates. As grown thin films at (a) 25% OMP, (b) 75% OMP. After annealing at (c) 25% OMP (d) 75% OMP.	165
6.17	AFM images of the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films deposited on amorphous SiO_2 substrates. As grown thin films at (a) 0% OMP. After annealing (b) 0% OMP, (c) 25% OMP, (d) 50% OMP (e) 75% OMP and (f) 100% OMP.	166
6.18	(a) Optical transmittance spectra of as - deposited and annealed MCT thin films deposited at 0% OMP.	167
	(b) Variation of refractive index and packing density as a function of OMP.	167
	(c) Porosity ratio as a function of OMP of as-deposited and annealed films on amorphous SiO_2 substrates.	167
6.19	(a) Variation in bandgap as a function of OMP for as deposited and annealed MCT thin films on amorphous SiO_2 substrates.	168
	(b) A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the MCT thin films deposited at 0% OMP.	168

Figure no.	Figure description	Page no.
6.20	(a) Frequency dependence of the imaginary component of impedance ($-Z''$) spectra recorded at different temperature of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films deposited at 25% OMP on platinized silicon substrates.	169
	(b) The Nyquist plots (Cole- Cole graphs) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ films deposited at 25% OMP.	169
6.21	(a) Experimental and calculated Nyquist fittings of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films deposited at 25% OMP at different temperatures for the equivalent circuit model given in the inset. Solid symbol indicates experimental data while open symbol indicates fitted data.	170
	(b) The variation of relaxation time (τ) as a function of $1000/T$.	170
6.22	(a) The ac-conductivity (σ_{ac}) versus frequency (f) at different temperatures.	172
	(b) The variation of $\ln\sigma_{dc}$ versus $1000/T$ plot of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ the films deposited at 25% OMP on platinized silicon substrates.	172
6.23	(a,b) The variation of dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of MCT thin films deposited at different OMP on platinized silicon substrates. The inset of (b) shows the variation of ϵ_r and $\tan\delta$ for different values of OMP measured at 1.0×10^6 Hz.	173
6.24	(a) Temperature dependence of dielectric constant (ϵ_r) and loss tangent ($\tan\delta$, inset) recorded at a constant ac driving frequency of 10^6 Hz for 0 and 75 % OMP. (b) shows variation of temperature co-efficient of dielectric constant (TCK) as a function of OMP measured at constant $f = 1 \times 10^6$ Hz.	175
6.25	(a) The I-V characteristics of the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ films deposited at different oxygen mixing percentage.	176
	(b) Leakage current density versus electric field of 50%, 75% OMP deposited thin films and its corresponding fits.	176
6.26	(a) Microwave dielectric constant and (b) Loss tangent of the MCT thin films as a function of OMP.	177

LIST OF TABLES

Table no.	Table description	Page no.
<i>Chapter 1</i>		
1.1	Some of the DR materials that are known for DR applications.	8
1.2	Comparison of EOT for different materials.	18
1.3	List of high - ϵ_r material candidates.	20
1.4	The atomic co-ordinates, Wyckoff positions and occupancy of MTO system	22
<i>Chapter 3</i>		
3.1	Lattice parameters of $\text{Mg}_{1.07}\text{TiO}_{3.07} + x$ wt% of V_2O_5 obtained from the Reitveld refinement.	84
3.2	The EDS spectra results of $\delta = 0$ and $\delta = 0.15$ doped $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ samples, sintered at 1350°C .	86
3.3	The EDS spectra of $\text{Mg}_{1.07}\text{TiO}_{3.07} + x = 1.5\text{wt}\%$ V_2O_5 sample, sintered at 1100°C .	87
<i>Chapter 4</i>		
4.1	The calculated lattice constants of the as - prepared and annealed samples.	100
4.2	Relative density, measured microwave dielectric constant (ϵ_r) and dielectric constant corrected for porosity (ϵ_m) values of pure and MTO ceramics added with CeO_2 nanoparticles.	101
4.3	EDS spectra of as prepared MTO ceramics with $x = 1.0$ wt%, sintered at 1300°C .	103
4.4	EDS spectra of MTO ceramics with $x = 1.0$ wt% CeO_2 nanoparticles, sintered at 1300°C and annealed at 1100°C for 48 h.	104
<i>Chapter 5</i>		
5.1	Lattice constants (a, b, and c) and unit cell volume (V) for $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ($x = 0 - 0.07$) ceramics sintered at 1200°C for 3 hours.	126

Table no.	Table description	Page no.
5.2	Shrinkage percentage, relative density, measured microwave dielectric constant, dielectric constant corrected for porosity values and $Q \times f_0$ for Co doped MTO ceramics, sintered at 1200°C.	130
<i>Chapter 6</i>		
6.1	The required and obtained percentages of elements in MTO films.	153
6.2	The values of grain resistance (R_g) and capacitance (C_g) of 25% OMP deposited MCT films measured at different temperatures.	171
6.3	The evaluated values of exponent factor “s” and pre - exponent factor logA measured at different temperatures for the films deposited at 25% OMP.	173
6.4	The comparison of microwave dielectric properties of MTO and MCT ceramics in both bulk and thin film form.	180
6.5	The comparison of optical, dielectric properties of both pure MTO and MCT thin films.	181



Chapter 1

Introduction to High ϵ_r and Low Loss Bulk and Thin films

Introduction to Dielectric Resonators

1.1 Introduction to dielectric resonators

Dielectric resonator (DR) is an electromagnetic component which functions as a resonant device by reflections at the high (ϵ_r) dielectric - air interface.

In recent years, the rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. Commercial wireless technologies such as cellular phones, direct broadcasting satellite (DBS) and global positioning systems (GPS) have been making swift progress due to the improved performance of dielectric resonators at microwave frequencies [1, 2]. These materials are primarily used in the microwave integrated circuits (MIC) as resonator elements, substrates, coaxial resonators and ceramic filters. These unique technologies demand materials, which have their own specialized requirements and functions. The requirements of these materials are high dielectric constant (ϵ_r), high quality factor (Q , low loss) and close to zero value of the temperature coefficient of resonant frequency (τ_f). High dielectric constant is important, since it is the key for miniaturization because the size of the resonator depends on the inverse of the square root of the dielectric constant of the material. Higher the quality factor ($Q = 1/\tan\delta$) lower will be the insertion loss and steeper the cut - off frequency. Close to zero parts per million (ppm)/ °C value of τ_f ensures temperature stable operation of MICs [1, 2]. In the ancient microwave devices quartz, metallic and microstrip resonators were used.

The quartz resonators are not attractive at microwave frequencies due to the small signal to noise ratio available with frequency multiplication to microwave frequencies. The metallic cavity resonators are bulky and difficult to integrate with the microwave integrated circuits. The microstrip resonators have emerged, but they have high dielectric loss and poor thermal stability. Ceramic DRs possess the convenience of being more miniaturized as compared to conventional microwave cavities, and have considerably low loss. Further, DRs have succeeded cavity resonators in most microwave and millimeter wave applications due to their cost - effectiveness, size, stability, toughness and ease of use.

1.2 History of dielectric resonators

Lord Rayleigh [3] showed that an infinitely long cylinder of a dielectric material can serve as a guide for electromagnetic waves at certain frequencies, which means that the dielectric has the effect of causing the electromagnetic wave to be confined to the cylinder and its vicinity. In 1939, Ritchmyer [4] proved that unmetallized dielectric materials could function as electrical resonators, which he called as dielectric resonators (DRs).

The primary reason for confinement of microwaves in and in the vicinity of a DR is its large value of permittivity (ϵ_r). The dielectric air boundary will be a perfect reflector of microwaves if the angle of incidence is greater than the critical angle $\theta_c = \sin^{-1} (1/\epsilon_r)$. For large value of ϵ_r , θ_c is totally internally reflected. Depending on the geometry, the waves will undergo multiple total internal reflections. The reflection coefficient approaches unity as the dielectric constant increases. For this reason, Kajfez [5] considered the dielectric air boundary of a high dielectric material as an interface closer to a perfect magnetic conductor (PMC), in which the magnetic field tangential to its surface is zero. As the dielectric constant increases, the electric and magnetic fields are confined in and near the resonator resulting in small radiation losses.

1.3 Modes in a dielectric resonator

As in the case of resonant cavities, there are many possible resonant modes that can be excited in a DR. The modes are divided into three main families.

- Transverse Electric Modes (TE)
- Transverse Magnetic Modes (TM)
- Hybrid Electromagnetic Modes (HEM)

The lowest hybrid mode is $HEM_{11\delta}$. Its resonant frequency can come even lower than that of the widely used $TE_{01\delta}$ mode. Its proximity to $TE_{01\delta}$ mode is governed by the aspect ratio of the DR and the proximity of perturbing metallic surfaces to the DR. Proximity of $HEM_{11\delta}$ mode to $TE_{01\delta}$ mode is not preferred as the former exhibit a very low value of Q . The $HEM_{21\delta}$ mode also has lower resonant frequency, which falls right between $TE_{01\delta}$ and $TM_{01\delta}$

modes. Thus, when operating in either of these modes, $\text{HEM}_{21\delta}$ modes can cause difficulties. Coupling to TM modes needs different arrangement compared to TE modes. However, HEM modes can get coupled to both the TE and TM coupling arrangements, as they have both components. HEM modes are highly leaky (i.e., radiative) and can cause difficulties in using TE and TM modes with their inherent Q values. The complexity of HEM modes increases as the integers m and n take higher values. An aspect ratio of 2.5 makes $\text{TE}_{01\delta}$ well separated from all the neighboring modes.

The resonant modes of a cylindrical resonator can be divided into constituent modes with azimuthal variation given by $\cos(m\phi)$ or $\sin(m\phi)$, where $m = 0, 1, 2, 3, \dots$. For $m = 0$ (i.e. axial symmetric modes) the set of modes can be divided into TE_{mnp} and TM_{mnp} . The first subscript m refers to azimuthal dependence of modes in ϕ . Second subscript n is radial mode number and the third subscript p denotes the axial mode number. They refer to the field extremes within the DR in the radial and axial directions. Due to the evanescent field effects in a DR, it is customary to replace p with $\ell + \delta$, where $\ell = 0, 1, 2, 3, \dots$ and $0 < \delta < \ell$ which means that there are ℓ number of half period variations and a fraction of a period of field variation in the DR along the axial direction.

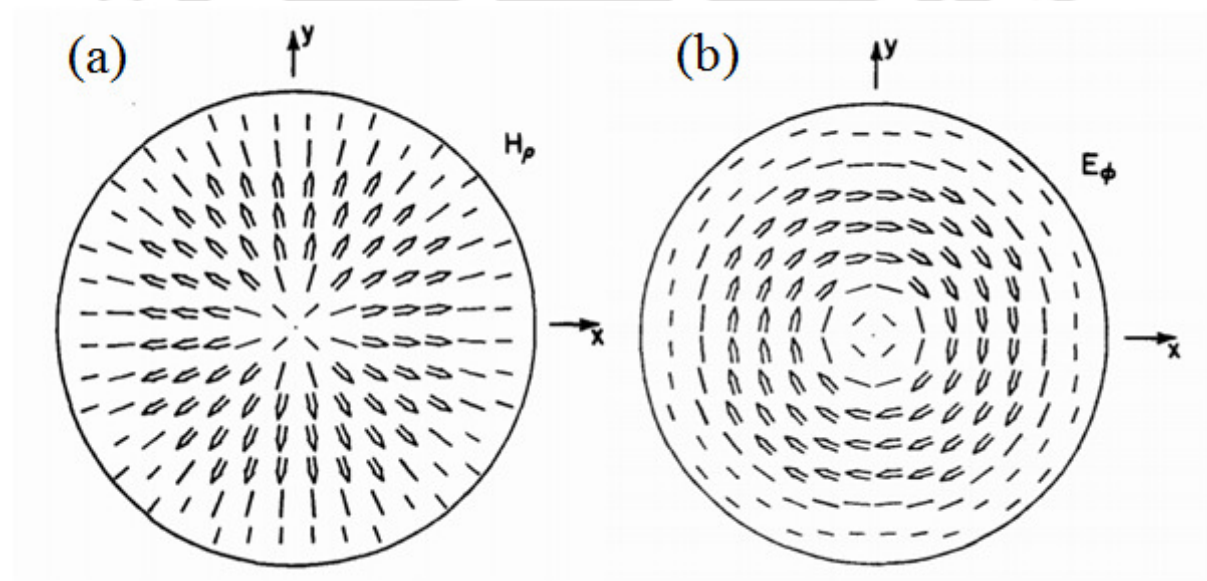


Figure 1.1: (a) Magnetic field in equatorial plane of the $\text{TE}_{01\delta}$ mode. (b) Electric field in equatorial plane of the $\text{TE}_{01\delta}$ Mode [5].

The most commonly used mode in the resonator is $TE_{01\delta}$. The magnetic field and electric field lines for this mode are shown in Figure 1.1(a) and 1.1(b). The magnetic and electric field together for the $TE_{01\delta}$ mode in a DR is shown in Figure 1.1(c).

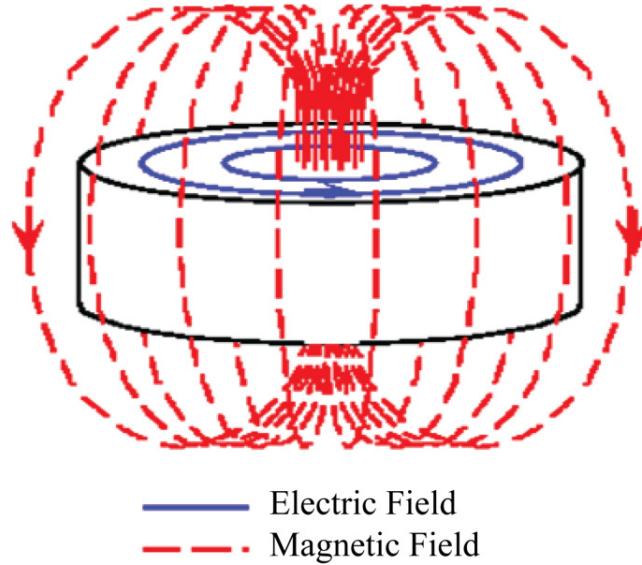


Figure 1.1(c): Magnetic and electric field together in a DR (side view) [3].

The electric field lines are simple circles concentric with the axis of the cylinder. When the relative dielectric constant is around 40, more than 95% of the electric energy of the $TE_{01\delta}$ mode as well as more than 60% of the magnetic energy is stored inside the DR. The remaining energy is distributed in the air around the DR, decaying rapidly with distance away from the DR vicinity. Although the geometrical form of a dielectric resonator is extremely simple, an exact solution of the Maxwell's equations is considerably more difficult for an isolated DR. To find out the resonant frequencies of a DR with known value of dielectric constant, and having a diameter (D) to the height (L) ratio D/L (aspect ratio), standard mode charts are available.

Kobayashi and Tanaka [6] reported a mode chart for a dielectric rod resonator short circuited at both ends. Mode chart graphically represents the variation of the factor $\epsilon_r (D/\lambda_0)^2$ as a function of $(D/L)^2$ for all the resonant modes. Where λ_0 is the free space wavelength corresponding to the resonant frequency of the mode. From the mode chart, the resonant frequencies of the all resonant modes of a DR can be found using its ϵ_r , D and L values. Furthermore, one can find out the order in which various modes appear in frequency

spectrum using the mode chart. This is important because the proximity of some leaky modes to the mode which is being used can lead to degradation of its performance. From the mode chart, one can find out the aspect ratio which must be used for a DR with given value of ϵ_r , to get maximum isolation for the mode of interest. For an approximate estimation of the resonant frequency of the isolated DR, the following simple equation can be used [5].

$$f_{GHz} = \frac{34}{D_{mn}\sqrt{\epsilon}} \left[\frac{D}{L} + 3.45 \right] \quad (1.1)$$

where D is the radius and L is the height of the DR.

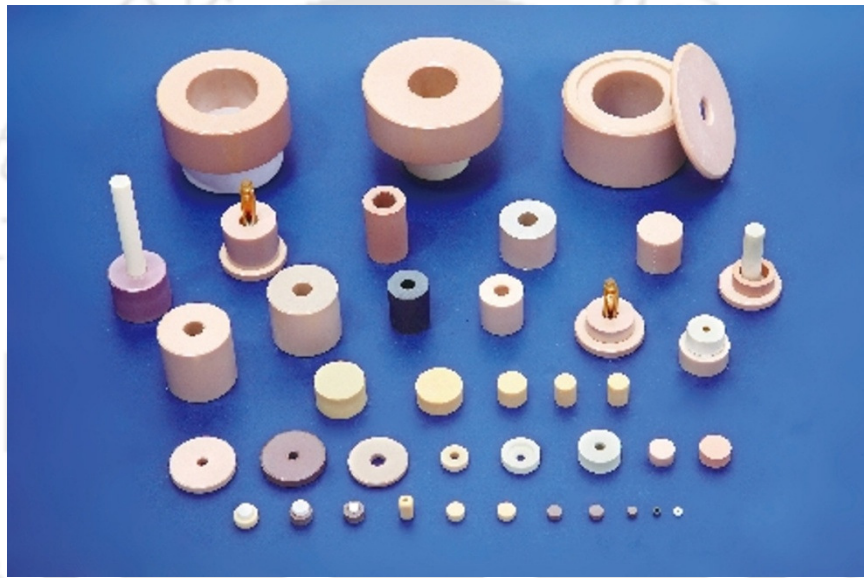


Figure 1.2: Commercially available shapes of DRs.

The size of a DR is considerably smaller than the size of an empty resonant cavity operating at the same frequency. The shape of a DR is usually a cylinder but one can also find tubular, spherical and parallelepiped shapes as shown in Figure 1.2.

1.4.1 Material requirements of a DR:

The important characteristics to be satisfied by a material for DR application are:

(i) High dielectric constant

The dielectric constant of the dielectric resonator material is important because it will ultimately determine the size of the DR. A cylindrically shaped DR sustains an

electromagnetic standing wave within its volume because of the reflection at the dielectric air interface. The wavelength of the standing wave is about equal to the diameter of the cylinder and is given by, $D \sim c/(f_0 \epsilon_r^{1/2})$ [5] where D is the diameter of the resonator, c is the velocity of the electromagnetic waves; f_0 is the resonant frequency and ϵ_r is the permittivity of the resonator. Therefore, it is more important to have the dielectric constant as high as possible in order to reduce the size of the DR.

(ii) Quality factor (Q)

The quality factor is the figure of merit in assessing the performance of a resonator, which is a measure of the energy loss or dissipation per cycle as with respect to the energy stored in the fields inside the resonator and is defined by

$$Q = 2\pi (\text{maximum energy stored}) / (\text{average energy dissipated per cycle})$$
$$Q = \frac{\omega_0 W_0}{p} \quad (1.2)$$

where, W_0 is stored energy, p is power dissipation and ω_0 is the resonant angular frequency.

Perfect dielectrics have no losses since its electrical conductivity is zero, but the real dielectric materials are partially conducting. Therefore, electromagnetic signal loses power as it goes through a dielectric material. For DR applications, Q factor is important and the losses should be minimum. When a DR is coupled to a microwave circuit, from the resonance curve, the loaded Q -factor can be calculated as,

$$Q_l = \frac{f_0}{\Delta f} \quad (1.3)$$

where f_0 is the resonant frequency and Δf is the half power bandwidth at resonant frequency. A higher Q value provides a better signal to noise ratio. This Q - factor is called the unloaded quality factor (Q_u).

$$Q_u = \frac{Q_l}{(1 - \beta_c)} \quad (1.4)$$

where, β_c is the coupling coefficient. To get accurate value of Q_u , weakly coupled case ($\beta_c < 1$) is preferred [5]. For a resonator structure there are number of factors that affect the Q_u

including: dielectric itself, conduction in the walls of the enclosure and radiation, which are referred to as Q_d , Q_c and Q_r , respectively. The losses of the dielectric itself can be divided into two categories: intrinsic and extrinsic losses. The intrinsic losses are dependent on the composition and the crystal structure of the material. The extrinsic losses are determined by impurities, vacancies, grain boundaries, porosity, oxygen non-stoichiometry, dislocations etc. The intrinsic losses are arising from the absorption of microwave field by the optical phonons and their eventual degeneration into thermal phonons [7]. It is well known that the Q - factor of a composition is highest in its single crystal form as it will be free from many of the imperfections of a ceramic.

There are three main mechanisms for microwave absorption: 1) losses in perfect (ideal) crystals because of anharmonic lattice forces which mediate interaction between crystal lattice and phonons 2) losses in real but homogeneous crystals caused by the periodicity defects (isotopes, dopant atoms, vacancies, etc.) and 3) losses in real inhomogeneous ceramics by extended dislocations, grain boundaries, pores and secondary phases. The first category of loss can be influenced by modifying the composition itself by changing the crystal structure. The other categories of loss depend on many extraneous factors and hence could be influenced by additives and processing conditions.

(iii) Temperature coefficient of the resonant frequency (τ_f)

The temperature coefficient of resonant frequency determines how well a resonator will function when there are fluctuations in temperature. This includes the ambient temperature as well as heating by microwave absorption in the resonator structure. The τ_f is a combination of three independent factors: temperature coefficient of the dielectric constant (τ_ϵ), thermal expansion of the material (α_L) and the thermal expansion of the environment in which the resonator is mounted. Assuming that the third factor is negligible, the τ_f is given by [5].

$$\tau_f \approx -(\tau_\epsilon/2 + \alpha_L) \quad (1.5)$$

Changes in temperature can cause changes in the dielectric constant and the volume of the resonator and hence the resonant frequency. The acceptable range of values of τ_f for microwave circuit applications is close to zero ppm / °C (± 3 ppm / °C). A material with a small positive value of τ_f variation can often be combined with another material with a small

negative τ_f variation to make the resonator temperature stable. τ_f is calculated by using the relation given below,

$$\tau_f = \frac{1}{f_0} \times \frac{\Delta f}{\Delta T} \text{ ppm/}^\circ\text{C} \quad (1.6)$$

Where, Δf is the change in resonant frequency over a temperature difference of ΔT , and f_0 is the resonant frequency at room temperature (25°C).

1.4.2 Well known dielectric resonator materials

Various materials are reported for DR applications. These include ceramic mixtures, glass ceramic systems and single-phase compounds.

Table 1.1: Some of the DR materials that are known for DR applications.

Sl.No	Composition	Structure	ϵ_r	$Q \times f_0$ (GHz)	τ_f (ppm/°C)	Ions within the Octahedra	Ref. No.
1	(Mg,Ca) TiO ₃	Perovskite	21	56,000	0	Ti	[8]
2	Ba(Zn _{1/3} Ta _{2/3})O ₃	Complex perovskite	27-33	1,20,000	2	Zn, Ta	[9]
3	Ba(Co,Zn) _{1/3} Nb _{2/3} O ₃	Complex perovskite	34	90,000	0		[10]
4	(Zr _{0.8} Sn _{0.2})TiO ₄	α -PbO ₂	38	50,000	0	Zr, Sn, Ti	[11]
5	Ba ₂ Ti ₉ O ₂₀	Perovskite like Hollandite structure	40	32,000	2	Ti	[12]
6	ZrTiO ₄ -ZnNb ₂ O ₆	α -pbO ₂	44	48,000	0	Ti, Nb	[10]
7	CaTiO ₃ -NdAlO ₃	Perovskite	45	45,000	0		[13]
8	0.5BaTiO ₃ -0.5 La(Mg _{1/2} Ti _{1/2})O ₃	Perovskite	61	10,000	-2	Ti, Mg	[14]
9	Bi ₂ (Zn _{1/3} Nb _{2/3}) ₂ O ₇	pyrochlore	76.2	3000		Zn, Nb	[15]
10	Ba ₄ Nd _{9.333} Tu ₁₈ O ₅₄	Perovskite/ Tetragonal tungsten bronze	80	10000	0	Nd, Ti	[16]
11	BaO-PbO-Nd ₂ O ₃ - TiO ₂	Multiphase system	90	5000	0	Nd, Ti	[17]

They give the required characteristics by optimizing the processing conditions and in some cases with the addition of trace quantity of additives. The characteristics of some of these compositions are given in Table 1.1. All these compositions have oxygen octahedra as their basic building block. The ions, which occupy the sites inside the octahedra, are indicated separately.

The above-tabulated DR compositions can be classified as

- a) Low ϵ_r and high Q compositions (S.No.1-3)
- b) Medium ϵ_r compositions (S.No. 4-7)
- c) High ϵ_r compositions (S.No. 8-11)

Some compositions in the first set can be used in millimeter range applications, and the second sets are utilized in the widely used in 4 - 12 GHz range whereas the last group is efficient for use in the lower frequency ranges.

An observation of the structure of these DR compositions reveals that all of them have either perovskite or perovskite related structure. In these structures, oxygen octahedra is the basic building block in all the compositions and in all these cases, they enclose a highly transition metal ion at their centre. Octahedra shares only corners in most of the cases. In most of the cases, the octahedra do not get aligned along a straight line.

Reany *et al.* [10] observed that when $\log_{10} Q \times f_0$ is plotted against ϵ_r , it gives a straight line for the commercial DR ceramics. It illustrates the fundamental physical principle that dielectric loss and dielectric constant are not independent parameters.

Colla *et al.* [18] showed that a major factor controlling τ_f was the onset of octahedral tilt transitions. Tilt transitions occur when corner shared oxygen octahedra rotate either in phase or anti phase around the major axes of the perovskite structure. A combination of phase transitions, typically involving rotations of the oxygen octahedra, and modifying permittivity by adjusting the polarizability per unit volume are routinely used to control temperature co-efficient of dielectric constant (τ_e). Maintaining a high Q value while adjusting τ_f is more problematic [10].

For complex perovskites, the order / disorder behavior is important. Complex perovskites that exhibits 1:2 ordered cell usually has highest Q values. To induce 1:2 ordering, the temperature of the order / disorder phase transition needs to be determined, and the sample annealed below this temperature. Optimization of processing parameters to avoid porosity, inhomogeneity, secondary phases, impurities and processing defects in general result in enhanced Q values.

1.4.3 Current state of materials developed for dielectric resonator applications:

Initially, a number of materials have been explored in the attempts to develop suitable microwave dielectric materials. The first generations of ceramic resonators were based on $(\text{Mg,Ca})\text{TiO}_3$, ZrTiO_4 and $\text{Ba}_2\text{TiO}_9\text{O}_{20}$. In the beginning of the 1990's the ceramic technology for handsets and base stations diverged. At present, $\text{Ba}_4\text{Nd}_{9.333}\text{Ti}_{18}\text{O}_{54}$ (BNT) based compounds are used primarily for digital television receivers while CaTiO_3 - NdAlO_3 (CTNA) and ZrTiO_4 - ZnNb_2O_6 (ZT - ZN) based ceramics dominates the base station resonator market. $\text{Ba}(\text{Co,Zn})_{1/3}\text{Nb}_{2/3}\text{O}_3$ (BCZN) based ceramics are a recent entrant, and they are cheaper replacement for the more expensive materials [10].

1.4.4 Future requirements of the DR materials:

In order for microwave dielectric ceramics to be used in base stations, they must inevitably offer a commercial advantage over competing technologies. In particular, metal cavities offer an alternative to ceramic resonators. $Q \times f_0$ factors of metal cavities are considerably lower (~ 6000 GHz) but they are two orders of magnitude cheaper. The high cost of ceramics comes from the often - expensive raw materials such as Nb_2O_5 and Ta_2O_5 , and the complex manufacturing processes needed to ensure optimum properties. Therefore, ceramics are only used where high Q is paramount and miniaturization is necessary. At the same time, the efforts are focused on to improve Q , particularly by minimizing the extrinsic losses.

Ceramics offer a distinct advantage over competing technologies in the use of irregular geometries to induce multimode resonance, by reducing cost and space. The unusual shapes and designs lay down new challenges to ceramists to control τ_f , ϵ_r and Q , despite the processing stages required [10].

The microwave ceramic resonator market for base station technology has matured, and industry is focusing primarily on improvement on Q and its cost [10]. New applications for low loss microwave ceramics are constantly emerging such as global positioning systems, low temperature co - fired ceramics for embedded microwave circuitry, tunable filters and applications in advanced radar technology [10].

1.5 Physics of DR materials

1.5.1 Polarization mechanisms in dielectrics

Polarization is an ordering in space of an electrically charged unit under the influence of an external electric field. This causes the formation of an electric moment in the entire volume of the dielectric and in each separate polarizing unit (atom, ion or molecule). Linear dielectrics show a direct proportionality between the induced electric dipole moment p acquired by the polarizable unit during the process of polarization and the intensity E of the field acting on it as given by $p = \alpha E$. α is known as the polarizability. Polarizability reflects the properties of individual polarizable unit and not of a certain volume of matter and is the most important microscopic electrical parameter of a dielectric. During polarization, the charges that are displaceable will be brought in to motion. Piling up of mobile charge carriers at physical barriers such as grain boundary causes interfacial polarization or space charge polarization. At low frequencies (~ 1 kHz) this mechanism gives rise to a high dielectric constant. Dipolar polarization occurs due to the molecules containing permanent dipole moment or by the rotation of dipoles between two equilibrium positions, and this relaxes around 10^3 to 10^6 Hz. The ionic polarization occurs due to the displacement of the positive and negative ions against each other, and it relaxes in the frequency range of 10^{12} to 10^{13} Hz. Electronic polarization occurs due to the displacement of electrons with respect to the atomic nucleus, and it relaxes at high frequencies $\sim 10^{15}$ Hz. The mechanisms of these four polarizations are shown schematically in Figure 1.3. Each of these involves a short - range motion of charge and contributes to the total polarization of the material, and at microwave frequencies ionic and electronic polarizations contribute to the dielectric properties [19].

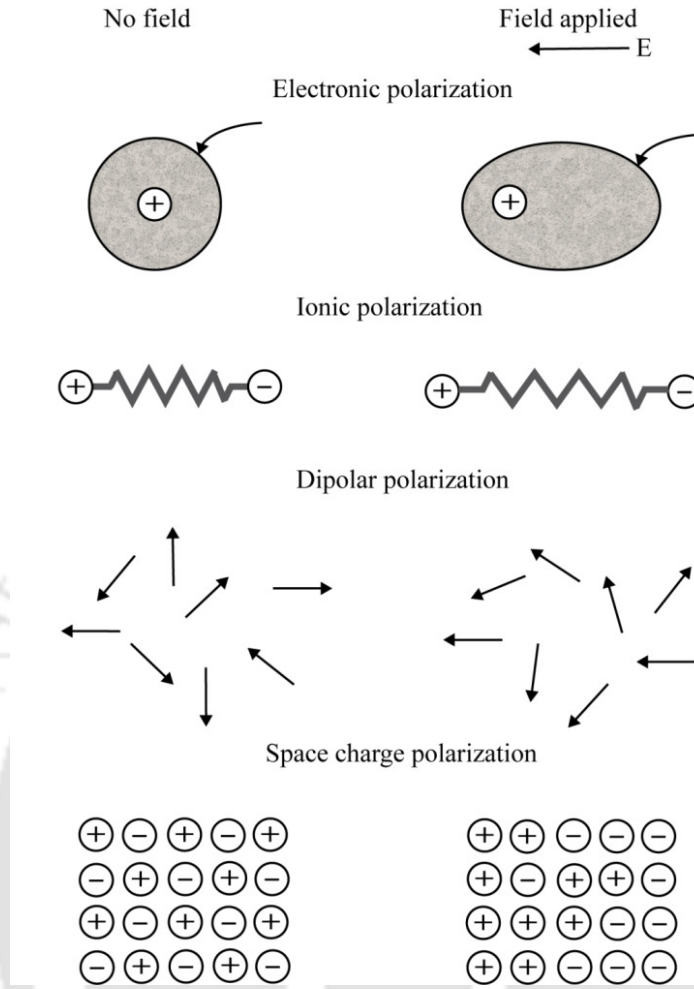


Figure 1.3: Different types of polarization mechanisms appear in a dielectric [19].

1.5.2 Dielectric losses

According to the material requirements for DRs, the dielectric losses and temperature dependence of dielectric properties assumes more significant.

Generally, three mechanisms can be distinguished for dielectric losses at microwave frequencies [7].

The dielectric losses related to phonon damping are usually described in the framework of classical dielectric function

$$\epsilon(\omega) = \epsilon_{\infty} + \sum_j \frac{j}{\omega_{jTO}^2 - \omega^2 + i\gamma_j\omega} \quad (1.7)$$

where, ϵ_∞ is the permittivity at optical frequencies, ω_{jTO} are the frequencies of the transverse optical (TO) lattice modes, and f_j and γ_j are their oscillator strengths and damping constants, respectively. The dielectric loss at microwave frequencies ($\omega \ll \omega_{jTO}$, i.e. $\omega = 0$) can be calculated from equation (1.7) as

$$\tan \delta = \omega \sum_j \frac{j}{\epsilon(0)} \frac{\gamma_j}{\omega_{jTO}^4} \quad (1.8)$$

For the practically important case of $k_B T$ being larger than the phonon energy, the anharmonic interactions between phonons caused by the third and fourth order terms of the lattice potential lead to $\gamma_j \propto T$ and $\gamma_j \propto T^2$, respectively [20]. The dominating dampening process among these is the decay of one *TO* phonon into two acoustical (thermal) phonons [21]. Equation 1.8 shows that, in cases of dominating intrinsic losses, the product of quality factor ($Q = 1/\tan \delta$) and frequency f ($\omega = 2\pi f$) is expected to be constant, a rule which holds, at least approximately for many ceramics. Recent days, it is widely accepted that intrinsic losses can be determined by far - infrared (FIR) spectroscopy, and therefore this method is now often used for the characterization of classical microwave ceramics and related compounds [22]. FIR spectroscopy greatly simplifies the search for new low loss ceramics because in the FIR frequency range, intrinsic losses outnumber extrinsic ones, and thus FIR data are much less sensitive to processing than the losses measured at microwave frequencies.

Understanding the intrinsic loss mechanisms are useful to examine the extent to which the losses of microwave ceramics can be reduced to the small intrinsic values by using advanced processing methods [23]. It is also interesting to note that the intrinsic losses are closely related to the value of permittivity a power law, $\tan \delta \propto \epsilon^a$ with $a = 4$ [7].

1.5.3 Temperature coefficients

To obtain temperature stable oscillators and filters, it is necessary that the resonant frequency (f_0) of a resonator does not change much over a large temperature range (generally

in the range of -20 to + 80°C). The temperature coefficient of resonant frequency τ_f is given by [7]

$$\tau_f = \frac{1}{f_0} \cdot \frac{\partial f}{\partial T} \approx \frac{1}{f_0} \cdot \frac{\Delta f_0}{\Delta T} \quad (1.9)$$

where T is the temperature. Because the resonant frequency of a resonator depends on its size and on ϵ , the following equation holds true [7].

$$\tau_f \approx -(\tau_\epsilon/2 + \alpha_L)$$

where τ_ϵ is defined according to τ_f in equation (1.9) and α_L is the linear thermal expansion coefficient, i.e. the temperature coefficient of one of the resonator dimensions (eg. length, l). The requirement that $\tau_f = 0$ translates then in to $\tau_\epsilon \approx -2\alpha_L$. In addition, it is often necessary that the τ_f in a material system be variable between positive and negative values by virtue of variation of the materials composition. This enables one to set the temperature drift of the composite element containing a resonator equal to zero [7].

From the equation 1.10, the discussion on temperature coefficients can be restricted to consider only the temperature coefficient of permittivity τ_ϵ and τ_ϵ is defined as [7]

$$\tau_\epsilon = \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{\epsilon_r} \left[\frac{v}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_T \alpha_L + \frac{1}{3\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_v - \alpha_L \right] \quad (1.10)$$

The above equation directly follows from the Clausius-Mosotti equation, which takes the long-range coulomb interactions into account. From the equation 1.11 it is important to note that the polarizability α equals the sum of polarizabilities of all atoms in a unit cell with volume v only if all the atoms in the structure have a cubic environment. This is the case for alkali halides but not for complicated structures. However, the additional dipole fields can be taken in to account by an effective polarizability α so that both the Clausius - Mosotti equation and equation 1.11 are valid. In the case of perovskites, for example, the effective polarizability α is obtained by adding an extra ionic polarizability $\Delta\alpha^i$ to the electronic and ionic polarizabilities of all atoms in the unit cell. This supplemental

polarizability $\Delta\alpha^i$ caused by the structure contributes an additional term proportional to $-\alpha_L$ $\Delta\alpha^i$ in equation 1.11 [7].

In materials with more complicated structures, the additional ionic polarizability $\Delta\alpha^i$ is not only raises ϵ_r value but also shifts τ_ϵ to negative values [7]. Both strong electronic polarizabilities and $\Delta\alpha^i$ also give rise to a softening of the lattice modes [7]. Thus the anharmonic contribution $\left(\frac{\partial\alpha}{\partial T}\right)_v$ to τ_ϵ increases and makes τ_ϵ more negative. In the case of microwave dielectrics, ionic polarizability dominates ϵ_r and thus τ_ϵ is affected [7].

1.6 Electronic applications of high (ϵ_r) materials in thin film form

Thin film science and technology play an important role in present day electronic industries. Thin film technology has been developed primarily for the need of the integrated circuit industry. The demand for development of smaller and smaller devices with higher speed, especially in new generation of integrated circuits requires advanced materials and modern processing techniques suitable for future giga scale integration (GSI) technology. In this regard, physics and technology of thin films can play an important role to achieve this goal. The production of thin films for device purposes has been developed over the past 40 years. Thin films as a two - dimensional system are important to many real - world problems. Their material costs are very small as compared to the corresponding bulk material and they perform the same function when it comes to surface processes. Thus, knowledge and determination of the nature, functions and properties of thin films can be used for the development of new technologies for future applications.

Thin film technology is based on three foundations: fabrication, characterization and applications. Some of the important applications of thin films are in microelectronics, communication, optical electronics, catalysis, surface coating of all kinds and in energy generation and conservation strategies.

Since 1997, a consortium of industry representatives has developed and customized the International Technology Roadmap on Semiconductors (ITRS): a publication on the projected equipment, design, and material requirements needed to maintain the rapid

evolution of integrated circuit (IC) technology. The 1999 ITRS publication projected the need for superior high dielectric constant (ϵ_r), low leakage current materials to replace SiO_2 in gate stacks in complementary metal - oxide semiconductor (CMOS) and dynamic random - access memory (DRAM) devices by the year 2005. Since then, it has become apparent that advanced high speed ICs are being developed much faster than the ITRS forecasts. The revised 2000 roadmap stated that “while developmental progress in this area has been significant, it becomes increasingly probable that chip production with high - ϵ_r gate stacks will be very difficult to achieve (even) in the 2005 time frame, and therefore, appears unlikely in the more accelerated time frames suggested by the new proposed gate length scaling forecasts. Consequently, a major 2001 task is the analysis of the current quickened trend, and the identification of design, device and material alternatives imposed by the difficulties of accelerated high ϵ_r / dual metal gate CMOS integration” [24].

For 40 years, SiO_2 has been used as the gate dielectric material in silicon based CMOS devices. Demand for greater speed and increased storage capacity has driven the feature size shrinkage of CMOS - based circuits and storage devices. With the shrinkage of metal - oxide semiconductor field effect transistor (MOSFET) devices, channel lengths and gate dielectric thickness have been scaled to maintain performance and turn - on voltage characteristics. SiO_2 has been scaled down to attain the desired capacitance, but a roadblock exists in how thin the SiO_2 layer can be made without exceeding the leakage current requirements. Below ~ 0.7 nm the leakage current of SiO_2 through electron tunneling becomes too high, to maintain device requirements. The leakage current is particularly significant for logic devices, which must maintain tightly controlled turn - on and turn - off voltages. The leakage current, although prominent for storage devices, does not require a stringent design rule for dynamic memory devices since the data must be periodically re-written to the bit in the operation. Data is re - written on the order of every two to three hundred milliseconds. [25]. Leakage current is considerably more important for static memory devices. New high ϵ_r materials that meet varying requirements are fervently being sought to replace SiO_2 by the projected time frames for the production of future generation devices. With higher dielectric materials, the required capacitance can be maintained with thicker gate layers thereby keeping leakage current under control.

The equation for capacitance is typically written in terms of t_{eq} , the equivalent oxide thickness (EOT). EOT represents the theoretical thickness of SiO_2 required to achieve the same capacitance as the high ϵ_r replacement material. If the dielectric material is SiO_2 ($\epsilon_r = 3.9$), then

$$t_{eq} = 3.9 \times \epsilon_0 \left(\frac{A}{C} \right) \quad (1.11)$$

Assuming a capacitance density $(C/A) = 34.5 \text{ fF}/\mu\text{m}^2$, then $t_{eq} = 1 \text{ nm}$. For an alternative dielectric material to achieve the same capacitance density equivalent to $t_{eq} = 1 \text{ nm}$,

$$t_{high-k} = \frac{\epsilon_{high-k}}{3.9} \times t_{eq} \quad (1.12)$$

A material with dielectric constant $\epsilon_r = 25$ would require a physical thickness of 6.4 nm to achieve the same capacitance density as SiO_2 with $t_{eq} = 1 \text{ nm}$. Often, a thin SiO_2 interfacial layer is produced either during the deposition of the higher ϵ_r material or during post deposition annealing treatments. The incorporation of interfacial layers between the silicon substance and the high - ϵ_r material effectively reduce the overall dielectric constant of the material. The series capacitance of two dielectrics in contact is given by,

$$\frac{1}{C_{total}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1.13)$$

where C_1 and C_2 are the capacitances of the two dielectric materials present. The equivalent oxide thickness can then be given by

$$t_{eq} = t_{\text{SiO}_2} + \left(\frac{3.9}{\epsilon_{high-k}} \right) \times t_{high-k} \quad (1.14)$$

From equation 1.15, it can be seen that when an interfacial SiO_2 layer is present, the minimum achievable EOT is that of the lower dielectric constant material. This is true whether the dielectric material is SiO_2 , a silicide, or a silicate. Table of EOT comparison for different films is tabulated in table 1.2

Table 1.2: Comparison of EOT for different materials.

Name of the Material	ϵ_r	EOT (nm)	Name of the Material	ϵ_r	EOT (nm)
Si ₃ N ₄	7.5	1.79	Ta ₂ O ₅	25	6.66
Al ₂ O ₃	9.1	2.30	La ₂ O ₃	28	7.69
HfSiO _x	10	2.82	Pr ₂ O ₃	30	7.94
Y ₂ O ₃	16	3.84	ZrTiO ₄	38	9.74
MgTiO ₃	17	4.35	(Zr,Sn)TiO ₄	38	9.74
HfO ₂	18	5.38	TiO ₂	100	20.51
ZrO ₂	22	6.40			

From the above table it is clear that, higher the dielectric constant, higher is the EOT.

1.7 Characteristics of SiO₂ in MOSFET devices and the difficulties of its replacement

The use of SiO₂ on silicon for producing MOSFETs offers several key advantages that can be split between two categories: (1) fundamental properties and (2) device properties. The principal properties of SiO₂ include dielectric constant, barrier height, stability in contact with silicon, and morphology. Device properties include: processing, integration and performance issues such as interface quality, method compatibility, device lifetime and reliability [26]. SiO₂, the current gate dielectric material in FET devices has proven to be an extremely difficult material to replace, since it has several characteristics that make it advantageous as the gate dielectric for silicon based FET devices. Among them, SiO₂ is a thermodynamically stable, self - passivating, amorphous oxide that acts as a water insoluble barrier. The density of the oxide can be tailored such that it effectively impedes the diffusion of contaminants and impurities to the underlying silicon. Growth of SiO₂ is so thermodynamically favorable that growth of SiO₂ on pristine silicon surfaces in ambient conditions is impossible to avert. Thick, high purity films have been thermally grown on silicon substrates with a low fixed charge density ($< 5 \times 10^{10} \text{ cm}^{-2}$) and an interface with silicon that exhibits a low density of states ($< 5 \times 10^{10} \text{ cm}^{-2} \text{ eV}$) reproducibly. While SiO₂ is

one of the thinnest components of the device, it routinely and reliably withstands the highest electric field (~ 1 MV/cm). Additionally, it exhibits a small amount of low-frequency C - V hysteresis and frequency dispersion (< 10 mV). Furthermore, the dielectric exhibits tiny amounts of stress - induced leakage currents (SILC) resulting from voltage stress, high surface mobility at the interface, and is considerably reliable after years of high - field stress (~ 10 years). SiO_2 is thermally, chemically and mechanically compatible with Si and heavily doped poly - Si doping, and anneals at $950 - 1050^\circ\text{C}$, without noticeable loss of the intrinsic properties noted above. For SiO_2 , the leakage current changes from 1×10^{-12} A/cm² at 3.5 nm to 10 A/cm² at 1.5 nm. The band gap of SiO_2 is 8.9 eV with band offsets relative to Si greater than 1 eV. Today, the silicon oxide layer is doped with nitrogen to form silicon oxynitrides SiO_xN_y , to prevent diffusion of boron dopants in adjacent poly - Si layers and to increase the dielectric constant to ~ 6.5 [27 - 29]. Achievement of all these characteristics with another dielectric layer of comparable or better properties is an extremely difficult task.

1.8 Efforts to replace SiO_2

Table 1.3 lists several materials and their properties, including dielectric constants that have been studied as possible replacement for SiO_2 . Before the discussion begins, it is important to understand the requirements for differing device applications. For memory / storage applications, significant attention has been focused on Ta_2O_5 , SrTiO_3 and Al_2O_3 . Static memory applications require a very low leakage current ($J < 10^{-8}$ A/cm²) and high charge storage density. In this case, thermodynamic stability of the high - ϵ_r material on silicon is not as critical since the dielectric material is sandwiched by the electrodes, poly-Si or metal. It attempts to minimize interfacial reactions are solely to maximize charge density storage capacity [30]. Additionally, unlike MOSFET applications, no electric field penetration below the bottom electrode is required allowing the use of metal or heavily doped poly-Si as the lower electrode. Furthermore, current transport along the dielectric interface is not important as in MOSFET applications. Ultimately, the bottom dielectric interface is not as critical in storage applications.

A significant research has been done on the materials listed in Table 1.3, but these materials don't possess all the requirements needed for the replacement of SiO_2 . Studies of

ternary and quaternary oxides and silicates have been the next frontier for finding an adequate replacement. It is well understood that transition metal oxides can offer higher dielectric constants due to their higher polarizabilities. The use of mixed transition metal oxides had been studied as an approach to acquiring higher dielectric constants while attaining other required properties such as low leakage current and high stability.

Table 1.3: List of high - ϵ_r material candidates.

Material	ϵ_r	Bandgap (eV)	Crystal Structure
TiO ₂	100	3.4	Tetragonal (Rutile, Anatase)
La ₂ O ₃	30	4.3	Hexagonal, Cubic
Ta ₂ O ₅	26	4.5	Orthorhombic
HfO ₂	25	5.7	Monoclinic, Tetragonal, Cubic
ZrO ₂	25	5.9	Monoclinic, Tetragonal, Cubic
Pr ₂ O ₃	26	3.5	Amorphous
MgTiO ₃	17	4.0	Rhombohedral
Y ₂ O ₃	15	5.6	Cubic
Al ₂ O ₃	9	8.7	Amorphous
Si ₃ N ₄	7	5.1	Amorphous
SiO ₂	3.9	8.9	Amorphous

1.9 Magnesium Titanate (MTO): An interesting system in both bulk and thin film forms

1.9.1 Bulk MTO for microwave applications

Dielectric materials based on the MgO-TiO₂ binary systems are attractive for applications in the microwave domain due to their high dielectric constant, low loss, and low temperature coefficient of the permittivity. Hence, it offers a great stability to specific applications such as frequency discriminators, low phase-noise dielectric resonator

oscillators, duplexers and filters and other applications. They are also useful as a substrate for microwave integrated circuit (MIC) substrates.

1.9.2 MTO thin film as a possible gate oxide in electronic applications

The search for materials with high dielectric constant as an alternative to SiO_2 in CMOS gate oxide and ULSI (Ultra Large Scale Integrated) dynamic random - access memory (DRAM) applications have been the subject of intense research in recent years as described in the previous section.

As mentioned in the previous section, the physical and electrical properties of MgTiO_3 thin films as reported by other researchers have good characteristics such as a high dielectric constant, low dielectric loss and high temperature stability. These properties make MTO thin film a noteworthy material in integrated electronics as well as in high frequency applications.

1.9.3 Crystal Structure of MTO

The crystal structure of MgTiO_3 is an ilmenite type structure and belongs to $R\bar{3}$ space group, is shown in Figure 1.4(a). The ilmenite structure is an ordered derivative of the archetype corundum structure. Typically, $\text{A}^{2+}\text{Ti}^{4+}\text{O}_3$ (where A is a first order transition metal, *Fe, Mn, Zn* and *Mg*) compounds adopts an ilmenite structure when the ionic radii of ${}^{\text{vi}}R_{\text{A}}$ and ${}^{\text{vi}}R_{\text{Ti}}$ are similar and ${}^{\text{vi}}R_{\text{A}}$ is much smaller than the radius of the oxygen anion resulting in a Goldschmidt tolerance factor [31] close to 0.75 [32] is defined as

$$t = \frac{(R_{\text{A}} + R_{\text{O}})}{\sqrt{2}(R_{\text{B}} + R_{\text{O}})} \quad (1.15)$$

where R_{A} , R_{B} and R_{O} are the ionic radii of A, B and O, respectively.

The tolerance factor value of 0.96 [33] is reported for MTO system, which indicates a negative temperature co-efficient of resonant frequency for MTO ceramics. The crystal structure and schematic representation of MgTiO_3 unit cell is shown in Figure 1.4(a) and (b), respectively. The structure is based on hexagonally close-packed oxygen layers with cations occupying two-thirds of the available octahedral interstices. In contrast to the fully disordered corundum structure (space group $R\bar{3}c$), the ilmenite structure contains equal

amounts of di- and tetravalent cations, ordered along the octahedral layers and alternating along the c-direction of the unit cell. A pair of MgO_6 and TiO_6 octahedra share a (001) face, and each octahedron in the ilmenite structure shares one edge with the same type of octahedral and three edges with the other octahedral (Figure 1.4(a)). The stacking sequence along $[001]_h$ of this structure is “Mg-Ti-[]-Ti-Mg-[]” and either “Ti-Ti-[]” or “Mg-Mg-[]” parallel to (111), resulting in a centrosymmetric $R\bar{3}$ rhombohedral cell [34]. The typical lattice parameters of MTO are $a = b = 5.0567(4) \text{ \AA}$ and $c = 13.9034(2) \text{ \AA}$, with number of atoms per unit cell (Z) = 8. The atomic coordinates, Wyckoff position and occupation of MTO system are given in Table 1.4.

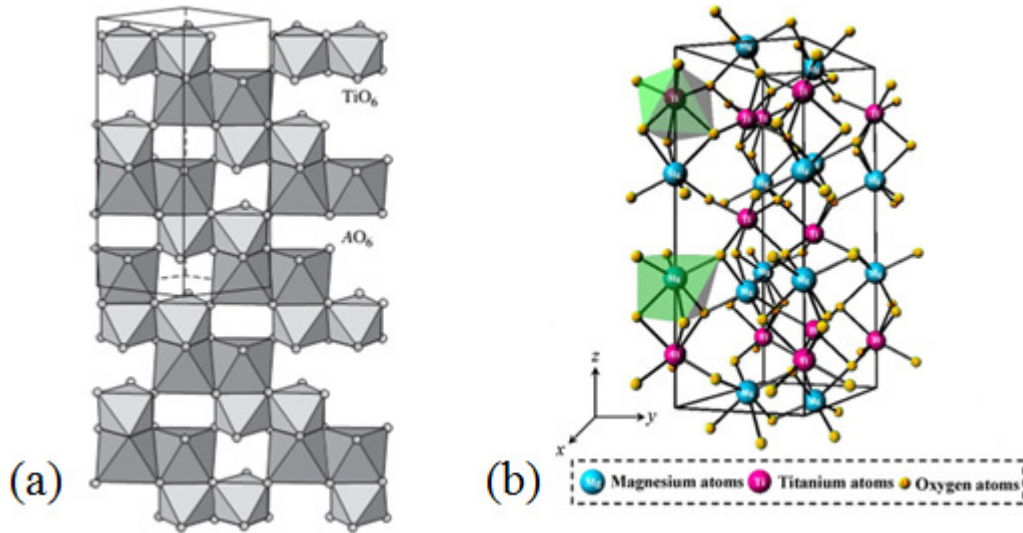


Figure 1.4 :(a) Crystal structure of MgTiO_3 (b) Schematic representation of a MgTiO_3 unit cell. (Taken from Ref [34, 35])

Table 1.4: The atomic coordinates, Wyckoff position and occupation of MTO system.

Atoms	Wyckoff positions	x	y	z	Occupation
Mg	6c	0.0	0.0	0.35682	1
Ti	6c	0.0	0.0	0.14528	1
O	18f	0.31922	0.02030	0.24702	3

1.10 Motivation of this study

Among the high ϵ_r and low loss dielectric materials magnesium titanate (MTO) MgTiO_3 has been found to be an excellent material for the applications discussed above in bulk form. The bulk MTO has a dielectric constant of 17, a high $Q \times f_0$ value of $\sim 1,60,000$ GHz (where f_0 is the frequency of measurement in GHz), temperature coefficient of resonant frequency is ~ -50 ppm/ $^\circ\text{C}$ [36]. There are two major disadvantages in preparing MTO ceramics in solid - state reaction method. One is the presence of MgTi_2O_5 metastable phase in the final MTO composition and the other is, it requires very high sintering temperature, which limits their practical applications [37]. Therefore, it is interesting to look for ways to reduce its sintering temperature and the effect of these procedures on the microwave dielectric properties. Another important aspect in the study of DR materials is to understand the factors which influence Q value and to look for ways to improve it. Bernard *et al.* [38] reported the sintering temperature of MTO ceramics as 950°C with the addition of Li - based salts. Zhang *et al.* reported the preparation of MTO ceramics with the addition of 5.0 mol% Bi_2O_3 - 7 mol% V_2O_5 and 6 wt.% $\text{CuO-Bi}_2\text{O}_3$ - V_2O_5 sintered at 875°C and 900°C , respectively [39, 40]. Belnou *et al.* [41], studied the addition of bismuth based additives to lower the sintering temperature of MTO ceramics to below 1000°C . Nonetheless, the microwave dielectric properties, especially $Q \times f_0$ values are significantly degraded with the additives. On the other hand, few studies were reported on improving the dielectric properties of MgTiO_3 ceramics by partial substitution Mg with Zn , Co or Ni : $(\text{Mg}_{0.95}\text{Zn}_{0.05})\text{TiO}_3$ ($\epsilon_r \sim 17.1$, $Q \times f_0 \sim 264$ THz, $\tau_f \sim -40.3$ ppm/ $^\circ\text{C}$) [42], $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ($\epsilon_r \sim 16.8$, $Q \times f_0 \sim 244$ THz, $\tau_f \sim -54$ ppm/ $^\circ\text{C}$) [43], and $(\text{Mg}_{0.95}\text{Ni}_{0.05})\text{TiO}_3$ ($\epsilon_r \sim 17.2$, $Q \times f_0 \sim 180$ THz, $\tau_f \sim -45$ ppm/ $^\circ\text{C}$) [44]. However, the sintering temperature was reported to be always higher than 1400°C .

Also, MTO thin films have attracted much attention due to its applications in (i) microwave integrated circuits [45], (ii) as a buffer layer, (iii) as a cladding layer for the growth of epitaxial LiNbO_3 films on Al_2O_3 substrates for the applications in integrated optical devices [46], (iv) as a high permittivity coating in electric devices [47] and (v) as a gate oxide for GaN based metal oxide semi conductor devices due to its high quality factor in the microwave region, and refractive index (1.95). Some aspects are already available on the thin films of the composition MTO prepared by RF sputtering, pulsed laser deposition (PLD)

and chemical vapour deposition (CVD) [48, 49]. Those reports suggest that these films have lower leakage current compared to SiO_2 , making them attractive for CMOS technology. Even though the considerable amount of study has gone into bulk MTO, studies on thin film are rather few. This work is an attempt in that direction by growing MTO films by a cost effective process and to compare their properties with that of their bulk counterpart.

As a continuing effort in our laboratory on microwave materials, we have chosen to investigate the MTO in the bulk form prepared by the solid - state reaction, mechanochemical method, and semi alkoxide precursor methods. Thin films were prepared by the RF magnetron sputtering. We have tried different approaches to reduce the sintering temperature to prepare bulk MTO and have been successful to some extent. RF reactive magnetron sputtering technique has been used extensively for preparation of various kinds of films as it gives high deposition rates and is a relatively simple and cheaper technique compared to PLD techniques and other chemical routes. One can optimize the deposition parameters resulting in good thickness uniformity of films and their high adhesion to the substrate. We have prepared MTO films from a ceramic target which was prepared using the optimized processing parameters of MTO.

The overall main effort in this study is to prepare the MTO ceramics with different additives to enhance the microwave dielectric properties of the bulk samples by improving the microstructure and relative density and temperature treatments. Another interest is to compare microwave properties of MTO in bulk as well as in thin film form in order to see whether these properties become better or not. In addition, we have also investigated their optical, electrical properties and impedance spectroscopy, which could not only be useful in other applications but also helps in arriving at a comprehensive picture of the physics of these materials, and the results were compared with the existing literature.

1.11 References

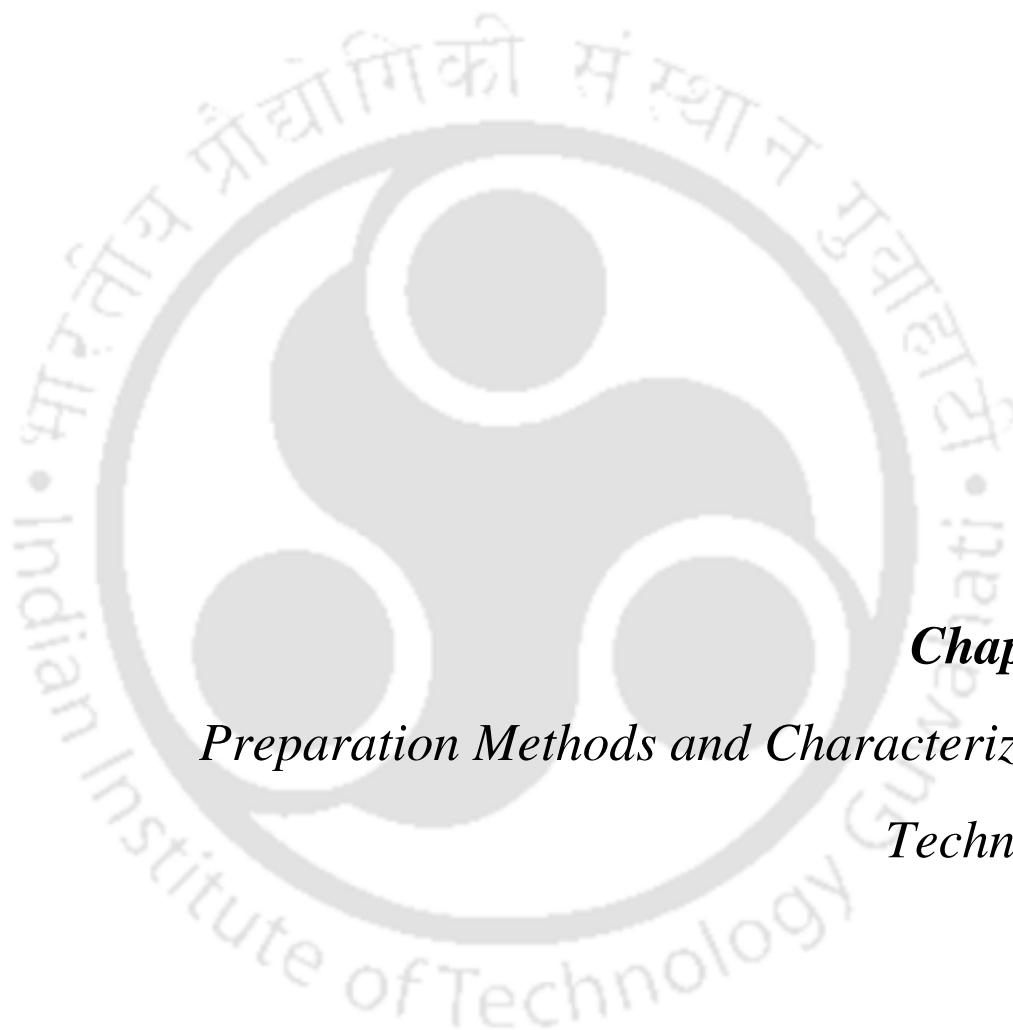
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Chapter 2

Preparation Methods and Characterization Techniques

Preparation and Characterization Techniques Used for Bulk and Thin Films of MgTiO_3

This chapter describes the preparation and characterization techniques used for both bulk and thin films of MgTiO_3 .

Section 2.1 and its subsequent sections describe the preparation of MTO ceramics by solid - state reaction method, sintering mechanisms, measurement techniques used for estimating microwave dielectric properties and impedance spectroscopy. Section 2.7 and its following sections describe the preparation of MgTiO_3 films by RF magnetron sputtering. The characterization techniques used for measuring the optical, electrical and dielectric properties of these films are also described.

2.1 Preparation techniques used for bulk MgTiO_3

This section deals with the preparation and characterization techniques used for the bulk MTO composition. Since this material has to be characterized for its DR properties in the microwave range, it has to be prepared in a regular geometry with highest possible densification. This being an oxide material, the available methods for its preparation are (a) solid - state reaction method (or ceramic method) (b) Chemical methods and (c) Mechanical methods [1-3]. In the present study, all the above three different methods were used to prepare MTO ceramics in bulk form.

2.1.1 Solid-state reaction method

Ceramics are polycrystalline, materials having fine crystalline grains and imperfections like grain boundaries, impurities segregated in the grains and grain boundaries, pores, etc. Since they are in general brittle refractories, shaping them and densifying without cracks and deformation is a challenge. The solid-state reaction method is used for forming the MTO composition from the initial reagents. The shaping and densification are separate processes, which are described in subsequent sections.

The conventional solid - state reaction method involves the following steps: (a) Uniform mixing of the initial reagents (b) Phase formation of the required compound at a

high temperature which is called the calcination stage. The main disadvantages of this method are that it needs high processing temperatures in order to achieve best properties, and this process increases the particle size. However, cost - effectiveness and simplicity are the major advantages of this process.

2.1.2 Mechanochemical processing

Mechanochemical processing (MCP) is a process in which chemical reaction and phase transformations (phase formation) take place and make the material finer due to the application of mechanical energy. A simple difference between mechanically activated processes and MCP methods is that no chemical reactions or phase transformation takes place during the mechanical activation, whereas these do occur in MCP. Contrast to the solid - state reaction methods no calcination stage is required in MCP. Generally, ceramics prepared to use solid - state reaction method requires high sintering temperature and repeated heat treatments. This is a convenient method for the synthesis of wide range of nanosized metallic and ceramic powders in an efficient and economical manner [4]. Physicochemical changes occur due to the efficient transformation of the mechanical energy of the grinding media to the material particles and the intensive mechanical force during the milling process. MCP can provide the means to substantially increase the reaction kinetics of the reduction reactions. This is because the repeated cold welding and fracturing of powder particles. This in turn increases the area of contact between the reactant powder particles by repeatedly forms new surfaces into contact due to a reduction in particle size during milling. This allows the reaction to proceed without the necessity for diffusion through the product layer. As a consequence, reactions that normally require high temperatures occur at lower temperatures during MCP or even without any externally applied heat. The planetary ball mills are generally used for mechanochemical processing. The photographic view of a planetary ball mill is shown in Figure 1.1 (a) and the schematic view of MCP process is shown in Figure 1.1(b). The planetary ball mill owes its name to the planet like movement of its vials. These are arranged on a rotating support disk and a special drive mechanism causing them to rotate around their own axes while revolving in a circle. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk, both act on the vial contents, consisting of material to be ground and grinding balls added inside the vial.

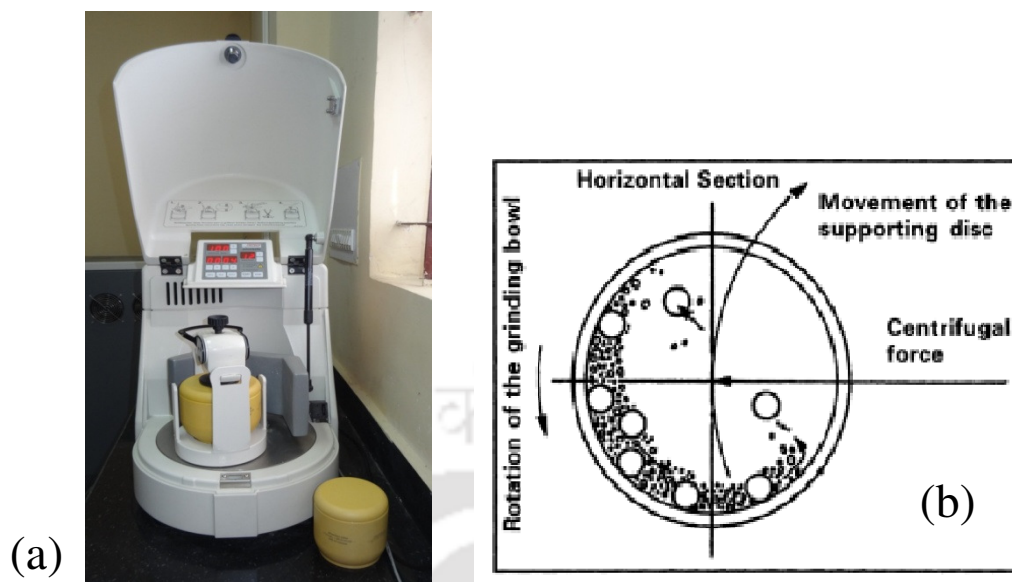


Figure 2.1: (a) Photographic view of planetary ball mill used to prepare samples and (b) Schematic view of the mechanical milling process

There are several processing variables that determine the final size of the particles, after milling process and reaction, such as type of mill, milling vial, milling speed, milling time, size distribution of the milling medium, ball to powder ratio, extent of filling of a vial, milling atmosphere, process control agent and temperature of milling [4, 5]. In the present study, planetary ball mill (Fritsch Pulverisette 6, Germany) was employed for mechanochemical process. The zirconia and tungsten carbide vials and different diameters of spherical 5 & 10 mm zirconia / tungsten carbide balls are used. The ball to powder ratio of 10:1 and rotating speed 500 rpm maintained during the milling process. In order to avoid excess heating it is programmed to stop for 15 minutes after every 15 min of continuous milling up to phase formation.

2.1.3 Sol - gel method (Semi Alkoxide Precursor Method)

The sol - gel process is a versatile solution process for preparing ceramic materials. In general, the sol - gel process involves the transition of a system from a liquid sol (mostly colloidal) into a solid gel phase. With further drying and heat - treatment, the gel is converted into dense ceramic or glass articles. The motivation behind selecting the sol - gel process is the higher purity and homogeneity of the product and the lower processing temperatures associated with the method compared to traditional ceramic powder methods. In the sol - gel

synthesis, two simultaneous reactions – hydrolysis and poly condensation - take place when metal alkoxide reacts with solvents. These two reactions are sensitive to many experimental parameters such as water concentration [6], pH [7], type and amount of solvent [8], reaction temperature [9] and mixing conditions. Semi alkoxide precursor method is known to be sol-gel method in which initial ingredients used are metal alkoxides.

In the present work, nanocrystalline ($\text{Mg}_{1-x}\text{Co}_x$) TiO_3 ($x = 0.00 - 0.07$) samples were prepared in this method. Initially, the stoichiometric ratio of magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved in the isopropanol at room temperature. Prescribed amount of titanium isopropoxide is slowly added to isopropanol solution and stirred it for 2 h in air. Subsequently, the temperature of the mixture was increased slowly to produce the sol and then gel. The obtained gel was heated to 110°C for 24 h to get the initial powders. Further prepared powers were calcined to get the phase formation and sintered to densify the MTO ceramics.

2.1.4 Stoichiometric weighing of reagents



The required ratios of the reagents as per the above chemical equation are weighed. The purity $> 99.99\%$, (Aldrich Chemicals, USA) of the initial reagents is important to achieve control over impurities in the product and to maintain reproducible microwave dielectric properties. An electronic balance (Mettler Toldo Model no. AG135) is used to weigh the reagents, which has accuracy up to 0. 01 milli gram.

2.1.5 Uniform mixing of reagents

The individual reagents are to be mixed uniformly in order to increase the point of contacts between the reagents, which will act as product layer formation centres. Therefore, the initial stoichiometric reagents mixture must be mixed uniformly with a suitable mixing medium. The powders were mixed (at 150 rotations per minute for 5 h) using a planetary ball mill (Fritsch Peverisette 6, Germany) in a zirconia jar with 5 & 10 mm diameter of zirconia balls. Deionized water was used as a mixing medium.

2.1.6 Calcination stage

The solid state diffusion controlled chemical reaction between the initial reactants resulting in the desired phase formation is called calcination. It is the intermediate heat treatment at lower temperatures prior to sintering. Calcination could involve chemical decomposition reactions in which a solid reactant is heated to produce a new solid phase and to remove the gases which are commonly associated with the initial metal oxide compounds such as carbonates, hydroxides, nitrides, sulphates, acetates and other metal salts. The parameters of calcination stage such as temperature, duration of heating and atmosphere are important factors influencing shrinkage during sintering. In the present case, the reagents being oxides do not undergo any decomposition. With the help of the X - ray diffraction pattern of the calcined products, the completion of reaction, desired phase formation and presence of impurity or secondary phases are identified.

2.1.7 Particle size reduction

The particle size reduction (milling) of the complex oxides after the calcination stage is important to homogenize the formed phase. It is well known that the smaller initial particle size reduces the sintering temperature and enhances the density of the ceramics. The planetary ball mills are generally used for milling the powders to achieve particle size reduction. In the present study, planetary ball mill was employed to achieve the initial stoichiometric mixing before the calcination and to reduce the particle size of the calcined ceramic powders. Zirconia / tungsten vials and different diameters of spherical 5 & 10 mm diameter zirconia balls are used. All the processing parameters were optimized to achieve smaller particle sizes. In the milling process, the particle experiences mechanical stresses at their contact points due to compression, shear with the milling medium or with other particles. The mechanical stress leads to elastic and inelastic deformation. If the stress is exceeding the ultimate strength of the particle, it will fracture the particles.

2.1.8 Uniaxial Pressing

After reducing the particle size of the calcined powder, the fine powder is compacted into cylindrical specimens (green pellets) by uniaxial pressing. The compaction of the powder should be done slowly to facilitate the escape of the entrapped air. To make the green

pellets of the ceramic powder, a rigid dies, which is rust free is used. To make the inner walls of the die smooth, stearic acid is used as an internal lubricant. The pressure gradient on the die as a function of the distance from the upper punch is given by the equation

$$P_x = P_a e^{\frac{-4\mu KL}{D}} \quad (2.2)$$

where, μ is the coefficient of friction, P_a is the applied pressure, L is the length and D is the diameter of the die and K is a constant [10].

2.1.8a Solid - State Sintering

In ceramics, porosity is an important parameter which governs many of its properties. For maximizing properties such as the dielectric constant, quality factor, mechanical strength, translucency and thermal conductivity, it is desirable to eliminate as much of porosity as possible. The purpose of sintering is the reduction of porosity in the compact. The development of microstructure and densification during sintering is a direct consequence of mass transport through several possible paths and one of these paths is usually predominant at any given stage of sintering [10]. The sintering phenomena are of two types: solid state sintering and liquid phase sintering. In the former one, the densification is achieved through the change in particle shape, without particle rearrangement. In the liquid phase sintering, some liquid is present at sintering temperature that aids densification.

During, liquid phase sintering process, significant diffusion and viscous flow occurs when a liquid phase is present or produced by a chemical reaction. The driving force for the sintering is the capillary pressure associated with surface curvature where the particles come into contact. In order to reduce the surface area, atoms diffuse to the points of contact, permitting contact flattening. Contact flattening involves the removal of matter between particle centers by volume diffusion or diffusion through a liquid phase [11]. These mechanisms must be promoted for the pores to shrink and eventually to get eliminated. Coarsening mechanisms such as surface diffusion or evaporation - condensation must be minimized as they only redistribute matter around surfaces. There are three major stages in sintering. In the initial stage, there is surface smoothening of the particles, neck growth and rounding of interconnected open pores. Diffusion of active, segregated dopants can occur and

the porosity decreases by about 12%. The initial density of the green ceramics is around 60% and after initial stage, the density will be around 70% of theoretical density (TD). However, in the initial stage, the 10% densification spreads quickly in few minutes after reaching to higher sintering temperature, because of the large surface area and high driving force for sintering [11]. In the intermediate stage, there is a formation of neck growth as densification proceeds, particle centers approach one another, resulting in further shrinkage of the compact. The shrinkage in this stage can result in about 90% of TD.

In the final stage of sintering, isolated pores are eliminated by mass transport from the grain boundary at the pore, and the uniform grain growth takes place. Pore on a grain boundary gets eliminated by grain boundary or lattice diffusion, but pores within the grains can be eliminated by lattice diffusion only, which can be a problem since volume diffusion often has higher activation energy. The complete elimination of porosity in the final stage of sintering can at most happen when all openings are connected to fast and short diffusion paths along the grain boundaries. In most ceramics, the lattice diffusivity of the slower rate - limiting constituent is eventually too slow for effective annihilation of pores that got trapped in grains. To achieve higher densities, the elimination of pores attached at the grain boundary is important.

In the initial stage, there are a number of competing paths for material to be transported to the neck area. Some of these paths will lead to densification, which is a shrinkage process that requires the centers of particles to approach each other. Other paths will lead to coarsening, which is the growth of a neck between the particles leading to a reduction in specific surface area without shrinkage. These different paths of diffusion are competitive paths of transport. The mechanism that gives the fastest rate of neck growth will dominate and cause either densification or coarsening. Surface diffusion is the general transport mechanism that can produce surface smoothing, particle joining and pore rounding without volume shrinkage. In materials where vapor pressure is high, sublimation and vapor transport to surfaces of lower vapor pressures also produces these effects. In contrast, grain boundary diffusion and lattice diffusion produce neck growth and volume shrinkage. At high temperatures, grain boundary diffusion and lattice diffusion tend to dominate and therefore, promote densification. Firing at lower temperatures can cause coarsening without significant

densification and can be useful in making mechanically strong but porous materials. Therefore, to improve the densification in DR materials requires dopants that enhance volume and grain boundary diffusion at lower temperatures without affecting the microwave dielectric properties.

Solid - state sintering of mixed cation oxides that are used in DRs is an ambipolar diffusion process in which anions and cations must be transported from the source to sink without kinetic de - mixing. The rate limiting mechanism will be slowest moving species along the fast path. Therefore, rate of sintering depends a great deal on the diffusivities and additives that influence diffusion. Additives often help to decrease the rate of coarsening in the earlier stages of sintering, increase the rate of densification and decrease the rate of grain growth.

2.1.8b Recrystallization and grain growth

In general, two types of crystallization processes occur. Primary and secondary recrystallization processes. Primary recrystallization is the process by which nucleation and growth of a new generation of strain - free grains occur in a matrix which has been plastically deformed [11]. Grain growth is the process by which the average grain size of the strain released or nearly strain free material increases continuously during heat treatment without change in the grain size distribution. Secondary recrystallization, sometimes called abnormal or discontinuous grain growth, is the process by which a few large grains are nucleated and enlarge at the expense of fine grained, but essentially strain free matrix.

Primary recrystallization process has its driving force in the increased energy of a matrix which has been plastically deformed. If the isothermal change in grain size of strain free crystals in a deformed matrix is measured after an initial induction period, there is a constant rate of grain growth for the new strain free grains. If the grain size is d [11],

$$d = U(t - t_0) \quad (2.3)$$

where, U is the growth rate (cm/sec), t is the time and t_0 is the induction period. The induction period corresponds to the time required for unstable embryos present to grow to the size of a stable nucleus. For a nucleus to be steady, its size must be larger than some critical

diameter at which the lowered free energy of the new grain is equal to the increased surface free energy. If an unlimited number of sites are available, the rate of nucleation increases to some constant rate after an initial induction period. As the temperature increases, the rate of nucleation increases exponentially.

The growth rate remains constant until the grains begin to impinge on one another. The growth rate becoming constant results from the constant driving force (equal to the difference in energy between the strained matrix and strain free crystals). The final grain size is determined by the number of nuclei formed, i.e. the number of grains presents when they finally impinge on one another.

Since both the nucleation and growth rate are strongly temperature dependent, the overall recrystallization changes quickly with temperature. As the temperature is raised, the final grain size is larger, since the growth rate increases more rapidly than the rate of nucleation. However, at higher temperatures recrystallization is completed more rapidly so that the greater grain size observed can be due to the greater time available for grain growth following the recrystallization [11].

In general, it is observed that (1) some minimum deformation is required for recrystallization, (2) with the small degree of deformation a higher temperature is required for recrystallization to occur, (3) an increased annealing time lowers the temperature of recrystallization and (4) the final grain size depends on the degree of deformation, the initial grain size and the temperature of recrystallization. In addition, continued heat after the completion of recrystallization leads to the prolongation of grain growth [11].

Grain growth: Whether or not primary recrystallization occurs, an aggregate of fine - grained crystals increases in average grain size when heated at elevated temperatures. As the grain size increases, it is obvious that some grains must shrink and disappear. An equivalent way of looking at grain growth is the rate of disappearance of small grains. Then the driving force for the process is the difference in energy between the fine - grained material and the larger grain size product resulting from the decrease in grain boundary area and the total boundary energy [11].

2.1.9 Liquid phase sintering

When a wetting liquid is present, bulk viscous flow can cause volume shrinkage [11]. When liquid coats at each grain, the material can often be sintered to a higher density at lower temperatures with less of a tendency for exaggerated grain growth. Less than 1 vol% liquid phase is sufficient to coat the grains, if the liquid is distributed uniformly and grain size is about 1 μm . The wetting liquid concentrates at the particle contacts and forms a meniscus, which exerts an effective compressive pressure on the compact. There is a rapid rearrangement of particles into higher density configuration. After the initial rearrangements, further densification takes place as particle contacts flatten under the compressive stress applied to the point contacts by capillary pressure. The contact flattening occurs through dissolution at the particle contacts and transport of the materials towards stress free interfaces. This leads to appreciable grain growth compared to solid state sintering.

2.2 Characterization techniques used for the bulk MTO ceramics

2.2.1 X - ray diffraction

Powder X - Ray Diffraction (XRD) is a powerful non - destructive method for determining a range of physical and chemical characteristics of materials. The applications include the type and quantities of phases present in the sample (phase analysis), the crystallographic unit cell and crystal structure, crystallographic texture, crystallite size, macro - stress and micro-strain and also electron radial distribution functions.

X - ray diffraction results from the interaction between X - rays and electrons of atoms. Depending on the atomic arrangement, interfaces between the scattered rays are constructive when the path difference between two diffracted rays differs by an integral number of wavelengths, which is described by the Bragg's equation (Bragg's law)

$$2d \sin \theta = n\lambda \quad (2.4)$$

where, λ is the wavelength, d is the spacing between the planes and θ is the Bragg angle, which is the angle between incident and reflected beam [12]. The schematic block diagram of X - ray diffractometer is shown in Figure 2.2.

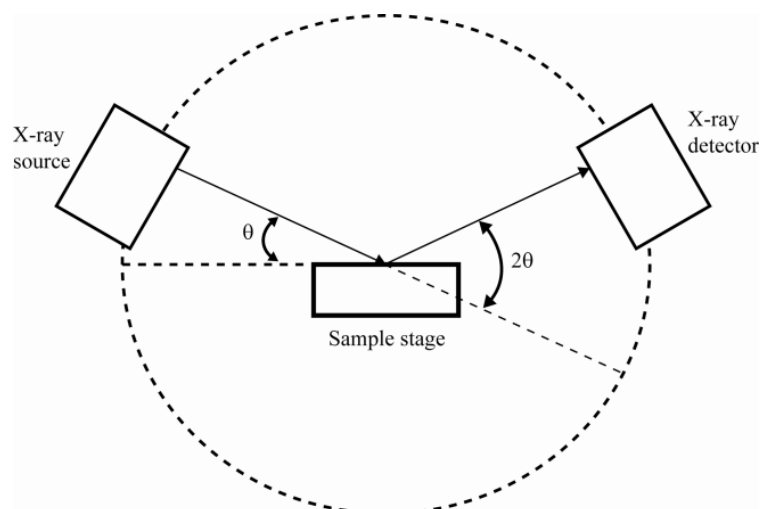


Figure 2.2: Schematic block diagram of X-ray diffractometer

In the present work, two types of X - ray diffractometers were used to characterize the samples. One is Seifert X - ray diffractometer (XRD) with CuK_α ($\lambda = 1.5406 \text{ \AA}$) radiation operating at 40 kV and 30 mA (1.2 kW). The other one is Rigaku (TTRAX-III, 18 kW) X-ray diffractometer with CuK_α ($\lambda = 1.5406 \text{ \AA}$) radiation. Calibration using a Si standard was done to account for the instrumental line broadening and the value was approximately 0.15° .

The XRD patterns were analyzed with the help of Reitveld refinement method using Fullprof program [13]. The background was refined using a polynomial function.

2.2.2 Surface area analyzer

The surface area of the prepared nanopowders was measured using the Brunauer, Emmett and Teller (BET) theory by gas adsorption [14]. The schematic block diagram of a surface area analyzer is shown in Figure 2.3. The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid. The amount of adsorbed gas was calculated corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (Vander waals forces) between the adsorbed gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen (77 K) so - called adsorption isotherms (BET isotherm). The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure. Before determining the specific surface area of the sample, it is

necessary to remove gases and vapors that may have become physically adsorbed onto the surface after manufacture and during treatment, handling and storage are called out gassing. In the present work, surface area of the samples prepared in semi alkoxide precursor method were obtained using surface area analyzer Autosorb iQ automated gas sorption analyzer (Quantachrome instruments).

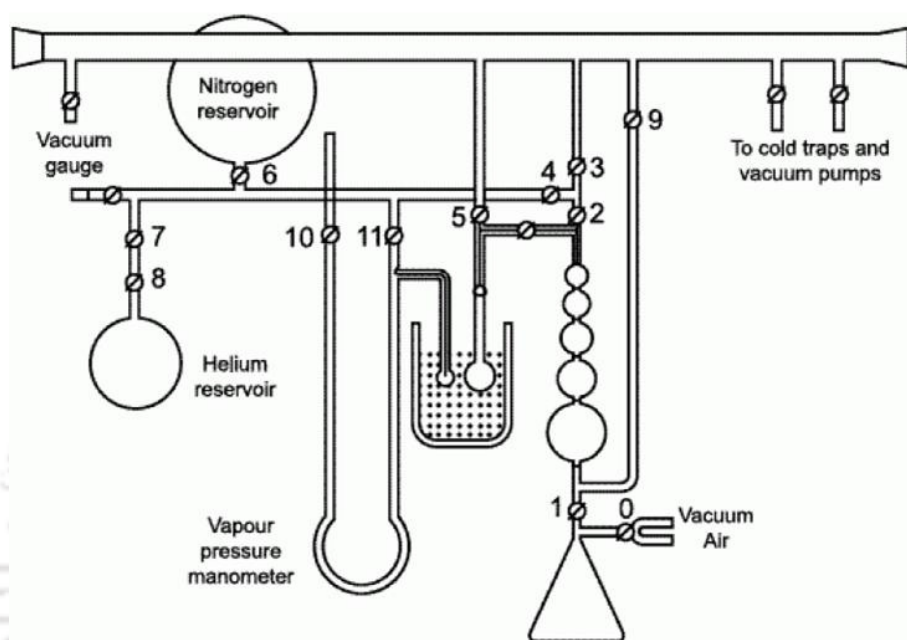


Figure 2.3: A schematic block diagram of surface area analyzer.

2.2.3 Particle size analyzer

The particle size distribution of calcined powders was measured using electrophoretic light scattering method [15]. It is the method used to determine the velocity of the particles suspended in a liquid medium under an applied electric field. In order to determine the speed of the particles movement, the particles are irradiated with a laser light, and the scattered light emitted from the particles is detected. Since the frequency of the scattered light is shifted from the incident light in proportion to the speed of the particles movement, the electrophoretic mobility of the particles could be measured from the frequency shift of the scattered light. In the present work, Delsa Nano C (Beckman coulter, Model no: A53878) was used to measure the particle size of the calcined powders using semi alkoxide precursor method.

2.2.4 Density Measurement

The densities of the sintered samples were measured by Archimedes's setup along with weighing machine. According to Archimedes's principle, when a body is immersed partially or fully in a fluid, it experiences an upward force (buoyant force) that is equal to the weight of the liquid displaced by it. The apparent densities of the sintered pellets calculated using the following expression

$$\rho_a = \left(\frac{w_1}{w_2 - w_3} \right) \times \rho_w \text{ gm/cm}^3 \quad (2.5)$$

where w_1 is the weight of the sintered pellet in air,

w_2 is the weight of the sintered pellet immersed in liquid medium (distilled water)

w_3 is the weight of the sintered pellet after removed from liquid medium (distilled water)

and ρ_w density of liquid medium (water = 1 gm/cm³). The relative densities of sintered pellets were calculated using the formula

$$\text{Relative density} = \frac{\rho_a}{\text{Theoretical density}} \quad (2.6)$$

2.2.5 Scanning electron microscopy

The schematic block diagram of Scanning Electron Microscope (SEM) is shown in Figure 2.4. In SEM, electrons are thermionically emitted from a tungsten cathode and are accelerated towards an anode. Alternatively, electrons can be emitted via field emission (FE). The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a fine focal spot size of 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam in a raster fashion over a rectangular area of the sample surface. Through these scattering events, the primary electron beam effectively spreads and fills a teardrop - shaped volume, known as the interaction volume, extending from less than 100 nm to around 5 μ m into the surface. Interactions in this region lead to the subsequent emission of electrons which are then detected to produce an image. X - rays, which are also produced by the interaction of electrons with the sample, may as well be detected in an SEM equipped for energy-dispersive

X - ray spectroscopy or wavelength dispersive X - ray spectroscopy. The most common imaging mode monitors low energy (< 50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. The electrons are detected by a scintillator -photomultiplier device, and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a digital image. This process relies on a raster - scanned primary beam.

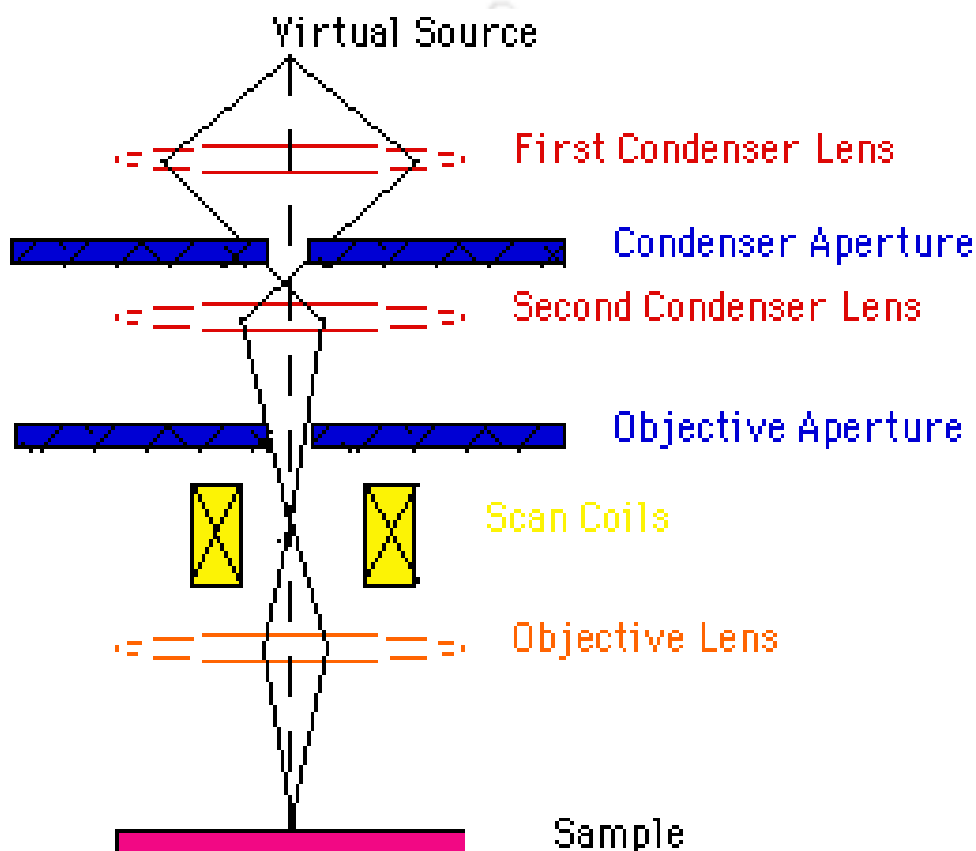


Figure 2.4: Schematic diagram of SEM.

The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well - defined, three - dimensional appearance. Using this technique, resolutions less than 1 nm is possible.

In addition to the secondary electrons, backscattered electrons can also be detected. Backscattered electrons may be used to detect contrast between areas with different chemical compositions.

2.3 Microwave measurements

Miniaturization of microwave circuits is possible with the help of low loss, temperature stable dielectric resonators. These dielectric resonators are used to replace waveguide filters in such demanding applications as satellite communications where microstrip and stripline resonators cannot be used because of their inherently high losses [16]. The most accurate measurement methods for low loss dielectric materials at microwave frequencies are resonance methods employing cavity, dielectric or open resonators [17]. The presence of air gaps is one of the most important factors limiting the measurement accuracy of high - permittivity solid materials, unless the electric field of the mode of interest does not have a component perpendicular to the surfaces of the sample. This is the situation for TE_{0np} modes of cylindrical cavities and dielectric resonators; Therefore, methods employing these modes are considered to be among the most accurate [18]. The quasi- $TE_{01\delta}$ mode of operation (often called the TE_{011} - mode) is the mode most commonly used by manufacturers of dielectric materials for making dielectric loss tangent measurements. In this work, a resonant structure, which can excite the TE_{011} mode in the reflection mode and having geometry as shown in Figure 2.4 is used. Samples should not have dimensions smaller than $1/4^{\text{th}}$ of appropriate cavity dimensions.

The important characteristics of a DR are dielectric constant, loss tangent and temperature dependence of resonant frequency. The permeability of most of these materials is equal to that of free space, as they are non - magnetic materials. A parallel - plate dielectric resonator structure known as Courtney set up is used to measure the dielectric constant of the bulk dielectric material. The principle involved in the measurement is rather simple. The resonant frequency of a $TE_{01\delta}$ mode is measured for a dielectric resonator radius ' a ' and height ' L '. Afterwards, the dielectric constant is computed using the Courtney procedure [18]. Hakki and Coleman first introduced the procedure. The error analysis and investigation of temperature effects were later made by Courtney [19]. Another cylindrical cavity made of invar is used to measure the temperature coefficient of resonant frequency of the cylindrical

DR. The negligible coefficient of thermal expansion of invar material helps to increase the accuracy of this measurement.

Theory

Consider a circular cylindrical rod of relative dielectric constant ϵ_r , permeability μ_0 , length L , and radius a placed between two large perfectly conducting plates. If the dielectric material is isotropic, then the characteristic equation for this resonant structure operating in the TE_{0nl} mode is

$$\alpha \frac{J_0(\alpha)}{J_1(\alpha)} = -\beta \frac{K_0(\beta)}{K_1(\beta)} \quad (2.7)$$

where, $J_0(\alpha)$ and $J_1(\alpha)$ are the Bessel functions of the first kind of orders zero and one, respectively, $K_0(\beta)$ and $K_1(\beta)$ are the modified Bessel functions of the second kind of orders zero and one, respectively. The parameters α and β depend on the geometry, the resonant wavelength, and dielectric properties. Thus

$$\alpha = \frac{2\pi a}{\lambda_0} \left[\epsilon_r - \left[\frac{c}{v_p} \right]^2 \right]^{1/2} \quad (2.8)$$

$$\beta = \frac{2\pi a}{\lambda_0} \left[\left(\frac{c}{v_p} \right)^2 - 1 \right]^{1/2} \quad (2.9)$$

‘ c ’ being the velocity of light and v_p the phase velocity in the structure so that

$$\frac{c}{v_p} = \left(\frac{l\lambda_0}{2L} \right) \quad (2.10)$$

where, l is the number of longitudinal variations of the field along the axis, and λ_0 is the free space wavelength. It is seen that the characteristic equation is a transcendental equation and hence, a graphical solution is necessary. The resulting mode charts are given by Hakki *et al.* [18] where each value of β_l corresponds α_l .

2.3.1 Measurement of dielectric constant (ϵ_r)

The measurement can be done using transmission method introduced by Hakki and Coleman [19]. This setup is having two parallel plates with an adjustment for varying distance between the two plates. Two bent monopoles (rigid coaxial cables) are provided for coupling electromagnetic waves to the DR and are mounted in such a way that, they can be moved in any of the x , y and z directions. One can identify the modes of the DR by moving the bent monopoles in all three directions. The number of standing waves in z - directions indicates the third subscript of resonant mode. By rotating the rigid coaxial cables around its own axis, one can find if the field is maximum in horizontal direction or vertical direction. Then the first subscript can be found by placing the coaxial cable at different angles in the plane of parallel plates. Once the resonant frequency of $TE_{01\delta}$ mode is measured using the procedure explained above, the relative dielectric constant for the dielectric resonator with known dimensions can be calculated using the equations (2.11) and (2.12).

$$\beta_l = \frac{2\pi a}{\lambda_0} \left[\left(\frac{l\lambda_0}{2L} \right)^2 - 1 \right]^{\frac{1}{2}} \quad (2.11)$$

$$\epsilon = \left(\frac{\alpha_n \lambda_0}{2\pi a} \right)^2 + \left(\frac{l\lambda_0}{2L} \right)^2 \quad (2.12)$$

Here β_l corresponds to α_n , which can be obtained from the mode chart given in [20] one of the characteristic equation.

2.3.2 Measurement of quality factor (Q)

Once the mode of operation and dielectric constant are determined, it is simple to derive the loss tangent of the dielectric material from a measured value of the unloaded Q_u value of the structure. The unloaded Q_u of the cavity is defined as 2π times the ratio of the maximum energy stored to the energy lost in one cycle. This measurement is done using reflection method with a cylindrical cavity having 10 mm height and 24 mm diameter (inner dimensions). The rigid coaxial cable is provided at the center of the cavity as shown in Figure 2.5 for electromagnetic field coupling, and it can be moved in and out for adjusting between weak and strong coupling.



Figure 2.5: QWED Krupka resonator cavity used to measure the quality factor and dielectric constant.

The cavity is connected to the Vector Network Analyzer (VNA, Rohde & Schwarz, Model no: ZVA24) through a rigid coaxial cable with connectors on both the ends (THRU). The network analyzer is set in S_{21} mode and performs calibration. The coaxial cable is adjusted in such a way that weak coupling exists between the rigid coaxial cable and DR. By identifying the TE_{018} mode, the resonant frequency can be obtained and -3 dB width of the spectrum to calculate loaded Q - factor (Q_l). One can assume that the unloaded Q - factor is equal to loaded Q - factor if coupling is weak (S_{21} at resonance < 45 dB, and couplings are symmetric). The unloaded Q_u value is calculated using the coupling coefficient β_c , and loaded Q value using the relation [21],

$$Q_u = \frac{Q_l}{(1 - \beta_c)} \quad (2.13)$$

where, β_c is the coupling coefficient is equal to $10^{\frac{-S_{21}}{20}}$. Further rigorous electromagnetic analysis must be performed to evaluate the dielectric constant of the sample under test. Rayleigh-Ritz's method has been used in the computer program used for calculating the dielectric constant. Accuracy in the measurement is

$$\frac{\Delta \epsilon}{\epsilon} = T \cdot \frac{\Delta h}{h} + (2 - T) \frac{\Delta d}{d} \text{ for } 0 < T < 2$$

where h is the diameter and d is the height of the sample.

$$\Delta \tan \delta = \pm 2.0 \times 10^{-6} \text{ or } \pm 0.03 \cdot \tan \delta$$

2.3.3 Measurement of temperature coefficient of resonant frequency (τ_f)

The temperature dependent resonant frequency can be measured using the cavity made up of invar material. Invar material has the least thermal expansion coefficient. The temperature is varied from room temperature to 80°C to obtain the temperature coefficient of resonant frequency by using the equation (2.14)

$$\tau_f = \frac{1}{f_0} \frac{\Delta f}{\Delta T} \text{ ppm/}^\circ\text{C} \quad (2.14)$$

where f_0 is the resonant frequency at room temperature and Δf is the change in resonant frequency for a variation in temperature of ΔT .

2.4 Electrical conductivity measurements

Direct current (DC) measurement cannot yield the exact resistance of the samples due to the choice of electrode and polarization at the electrode - material interfaces. The equivalent circuit of a metal – insulator - metal structure consists of circuit elements such as resistance (R), capacitance (C), inductance (L). The contribution of at least one component will be dependent on the frequency measurement [22, 23]. Complex impedance analysis is a technique in which the circuit elements are determined from the data obtained over a wide range of frequencies [24, 25]. It involves the plotting of the real and imaginary parts of the complex electrical quantities such as

- (a) Z^* - Complex Impedance
- (b) Y^* - Complex Admittance
- (c) ϵ^* - Complex Permittivity and
- (d) Complex Modulus

These plots are characteristics of particular equivalent circuits and consist of a combination of semi circles and straight lines. The component values correspond to the intercepts with the real axis [26, 27]. The modulus and permittivity complex plane plots are used for representing the response of the dielectric systems.

2.4.1 General theory

The applied voltage and the measurement current in an electrical network are given by

$$V(t) = V_0 \exp(i\omega t) \quad (2.15)$$

$$I(t) = I_0 \exp(i\omega t + \phi) \quad (2.16)$$

where $\omega = 2\pi f$, f is the frequency and ϕ is the phase angle.

$$\begin{aligned} Z^*(\omega) &= |Z| \exp(-i\phi), \\ &= |Z| \cos(\phi) - i |Z| \sin(\phi) \\ &= Z'(\omega) - i Z''(\omega) \end{aligned} \quad (2.17)$$

where, $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary parts of the complex impedance. The relationships between various related quantities are:

$$|Z| = [Z'(\omega)^2 + Z''(\omega)^2]^{1/2} \quad (2.18)$$

$$\tan\phi = Z'(\omega) / Z''(\omega) \quad (2.19)$$

$$\text{Admittance } Y^*(\omega) = 1/Z^*(\omega) = G(\omega) + i B(\omega) \quad (2.20)$$

$$\text{Conductance } G(\omega) = Z'(\omega) / [Z'(\omega)^2 + Z''(\omega)^2] = 1/R \quad (2.21)$$

$$\text{Susceptance } B(\omega) = Z''(\omega) / [Z'(\omega)^2 + Z''(\omega)^2] = \omega C \quad (2.22)$$

The real and imaginary parts of the impedance / admittance of the samples are plotted and their frequency dispersion curves possess information about the electrode - material interface, bulk resistance etc. The idealized plots for certain lumped circuit elements are shown in Figure 2.5. For parallel RC combination, we have

$$Z'(\omega) = R/(1 + (\omega RC)^2) \text{ \& } Z''(\omega) = \omega R^2 C/(1 + (\omega RC)^2) \quad (2.23)$$

Elimination of ωRC leads to

$$(Z' - R/2)^2 + Z''^2 = (R/2)^2 \quad (2.24)$$

This is the equation of a semi circle, with radius = $R/2$ and center at $(R/2, 0)$.

Consider a solid capacitor, its equivalent circuit consists of a capacitance (C) in parallel with the sample resistance (R). The corresponding impedance and admittance plots are shown in Figure 2.6. The intercept of the dispersion curve on the real axis gives the bulk resistance / conductance. In addition to sample capacitance and resistance, for any real system there will be grain boundary and electrodes effects. Figure 2.7 (a-c) shows the complex plane plots with electrode and grain boundary contributions.

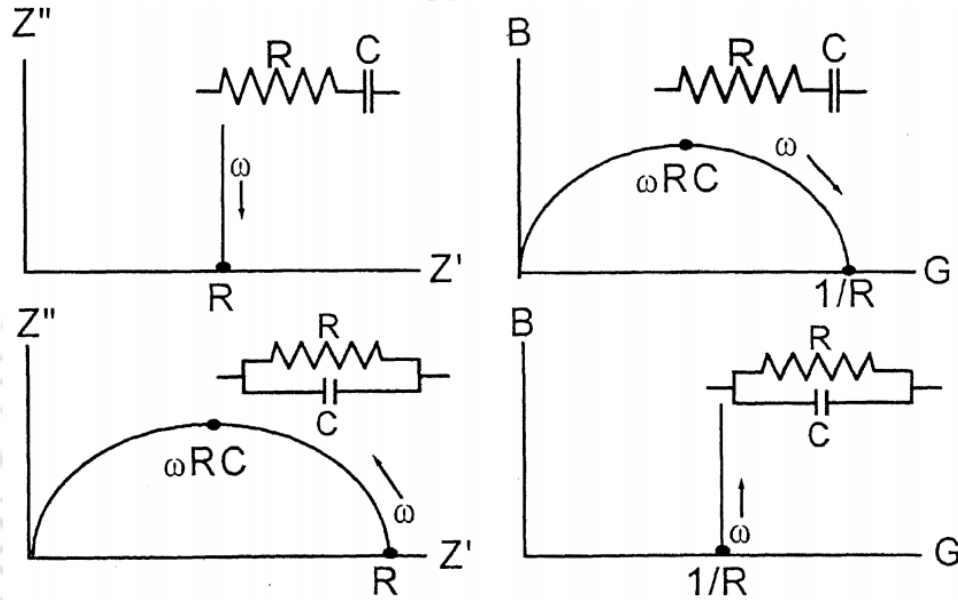


Figure 2.6: Complex plane plots of impedance and admittance for R-C circuits.

For example, in Figure 2.7(a), in addition to a semi circle, a straight line at low frequencies is observed which is characteristic of the double layer capacitance. In polycrystalline samples, there may be a contribution to the impedance from the presence of grain boundaries also. The grain boundary may act as a hindrance to ion transport, or it may besides provide a high conducting path (since the defect density may be larger in the interface region). Studying grain size effects on conductivity could help in identifying the conduction mechanism. Another common observation in the complex impedance is the depression of a semi circle in the high frequency region, i.e. the center of the circle is situated at the real axis as shown in Figure 2.7(c). The depression in the semi circle is accounted by introducing a constant phase element (CPE) connected in parallel with the bulk resistance [25]. In the present study, the RF impedance analyzer (Agilent Technologies, Model : 4991

A) equipped with temperature attachments (M/s Novocontrol, GmbH. Germany) has been used to obtain the broadband dielectric properties of MTO ceramics in the frequency range of 1 MHz - 1GHz.

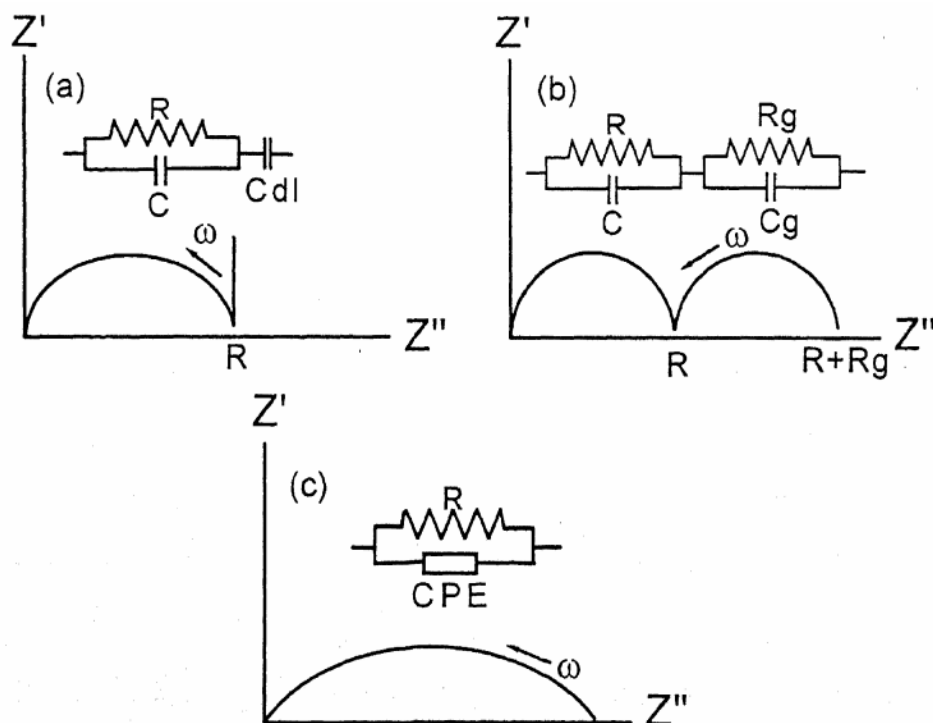


Figure 2.7 :(a-c) Different types of impedance behaviors observed in solids.

2.5 Raman Spectroscopy

Raman spectroscopy is related to vibrational spectroscopy which gives information about the vibrations of atoms of the constituent molecule and the nature of the atomic bonding. A molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as vibrational frequency. A non-linear molecule having N- atoms per primitive cell have $3N - 6$ normal modes of frequency of vibration. An axis is not visible. At room temperature, all molecules are in their lowest energy levels with quantum number $n = 0$. For each normal mode, the most probable vibrational transition is from this level to the next higher level ($n = 0 \rightarrow 1$) and they are called as the fundamental bands. For transitions into next higher levels such as for $n \geq 2$ are called overtone bands. The vibrational excitation occurs similar to that of the electronic excitation. Here the excitation

particle is a phonon and its energy, a measure of vibrational energy is quantized. So, it occurs in different energy states. Vibrational transitions are strongly related to photon - photon coupling and follow the Franck - Cardon selection rules [28]. When the vibrational transition occurs during the scattering of light by molecule, it comes under Raman spectroscopy. Depending on the nature of symmetry and asymmetry of a molecule, the mode of vibration can be either Raman active or IR active. Raman active materials, exhibits a change in polarizability (α), when the molecule vibrates. The asymmetric stretching and bending in a center of a symmetry molecules do not give rise to change in polarizability and hence such molecules are Raman inactive. Whereas in symmetric stretching things will be just the opposite. However, for molecules without having the center of symmetry, the vibrational mode could be either IR active, Raman active, both or neither.

There are two types of scattering of light namely elastic and inelastic scattering. Elastic scattering is generally quite strong and the frequency of scattering light has the same frequency as that of the incident light (ν_0) and such scattering is generally known as Rayleigh scattering. In inelastic scattering, the frequency of scattered light can be either more or less than the incident wave. Raman scattering is a type of inelastic scattering and the scattering wavelengths fall in two categories namely anti Stokes lines and Stokes lines. The Raman scattering phenomenon was first observed by Sir. C. V. Raman in 1928, for which he got the Nobel prize in 1930.

In infrared (IR) spectroscopy, a photon is completely absorbed to excite a molecular vibration, where as in Raman spectroscopy, high energy photons are used, and some energy is lost from the photon to excite a vibration. The intensities and energy of the photons that have been lost energy to excite the vibrations are measured in order to get a spectrum. An integrated Raman system (HR 800) used for all our samples to obtain the Raman spectra. The microscope coupled confocally to a 800 nm focal length spectrograph equipped with two switchable gratings. The excitation photon can be supplied by using two sources namely. He -Ne laser of 20 mW power with 632.817 nm wave length (or) Argon of wave length 488 nm. If the particular sample used is fluorescence acted to certain wave length, then next high wavelength is used, in order to observe the Raman spectra. The laser beam is totally reflected by the beam splitter, which splits the beam into two equal parts. The beam was allowed to

fall on the sample, and it undergoes both Reyleigh and Raman scattering. The notch filter, allows only the Raman scattered wavelength while it blocks the incident wavelength. The inelastic scattered light was allowed to pass through the grating and electron which in turn resolve the weak inelastic scattered wavelength coming from the sample more effectively. Further, the beam was allowed to enter into a charge couple device when it detects the change in polarizability of the sample from the change in wave length and converts into the intensity. We could see intensity versus wave number graph in the computer screen. In the present study, the Raman spectrum was recored using LABRAM HR800 Raman spectrometric analyzer developed by Horiba Jobin Yvon with a He - Ne source.

2.6 Vibrating Sample Magnetometer

DC magnetization as a function of temperature and field was measured by using the vibrating sample magnetometer (VSM) Lakeshore (model no. 7410).

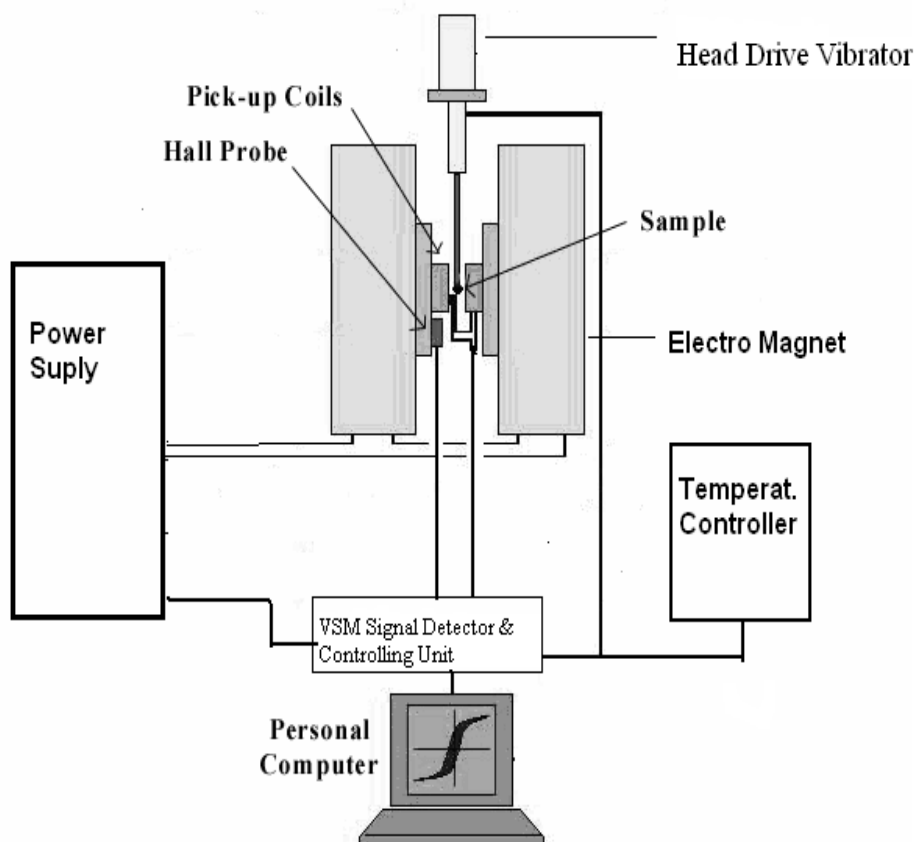


Figure 2.8: Block diagram of vibrating sample magnetometer.

The vibrating sample magnetometer (VSM) is an important equipment for the rapid and reliable measurement of the magnetic moment for a large variety of magnetic materials. The VSM developed originally by Foner [29], is widely used experimental setup for measuring temperature and field dependent magnetization of magnetic solids at ambient, higher and lower temperatures up to a moderately high field. It has a flexible design and combines high sensitivity with ease of sample mounting and exchange. Samples can be changed rapidly, even at any operating temperature. Using a vibrating sample magnetometer, one can measure the DC magnetic moment as a function of temperature, magnetic field and time. So, it allows performing susceptibility and magnetization studies. Magnetic moments as small as 5×10^{-5} emu can be measurable with a VSM [29].

The temperature variations of magnetization (M) were measured by using a vibrating sample magnetometer. The temperature variation down to 20 K was achieved using a CCR cryostat (OXFORD, model X 74019-044) along the temperature controller. The magnetic field was produced by using a 10" electromagnet. The magnetization loop was measured by varying B up to 2T. Calibration of the vibrating sample magnetometer was done by measuring the magnetic moment of a standard pure Ni sample. Block diagram of vibrating sample magnetometer is shown in Figure 2.8.

Preparation and characterization techniques for thin films

2.7 Thin film preparation techniques

Thin films are three dimensional solids, on which one dimension called the thickness which is several orders of magnitude lower than the other two dimensions. Thin films range in thickness from a monolayer to several hundreds of nanometers. The properties of thin films are governed by the deposition method. In general, the preparation techniques of thin films are broadly classified into two categories. (a) Chemical vapor deposition techniques (CVD) and (b) Physical vapor deposition techniques (PVD).

2.7.1 Chemical vapor deposition technique

This method is suitable when a volatile compound of the substance to be deposited. In this technique, the material to be deposited is vaporized, and the vapor is thermally

decomposed into atoms or molecules and reacted with other gases, vapors or liquids on the substrate surface to yield non - volatile reaction products on the substrate.

2.7.2 Physical vapor deposition technique

This is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces. The coating method includes purely physical processes such as high temperature vacuum evaporation or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in the case of chemical vapor deposition technique.

Physical Vapor Deposition (PVD) is divided into two categories:

2.7.2a Thermal Evaporation and 2.7.2b Sputtering.

2.7.2a Thermal Evaporation

The solid materials vaporize when heated to sufficiently high temperatures. The condensation of vapor on to a substrate yields a thin solid film. Thermal evaporation of a material can be achieved by a variety of physical methods

- (a) Pulsed laser deposition (PLD)
- (b) Molecular beam epitaxy (MBE)
- (c) Resistive heating
- (d) RF heating
- (e) Exploding wire technique
- (f) Arc evaporation
- (g) Flash evaporation
- (h) Electron bombardment

2.7.2b Sputtering

Grove first discovered the sputtering phenomenon in 1852. The ejection of atoms from the surface of a material (target) when bombarded with energetic particles is called sputtering. If the ejection of atoms is due to positive ion bombardment, it is referred to as a cathodic sputtering.

A simple source of ions for sputtering is provided by the glow discharge due to an applied electric field between two electrodes at low pressures. The gas breaks down to conduct electricity when a certain value of voltage is reached. The glow discharge maintains itself at a constant voltage and referred to as a normal glow. The region where voltage and current increase together are called abnormal glow. A luminous layer, which covers the cathode partially in the normal glow and completely in the abnormal glow, is known as a cathode glow. A fairly well defined region of relatively low luminosity known as Crookes or cathode dark space is found next to it. A bright negative glow region, Faraday dark space and then a positive column region follows this in sequence. The cathode dark space is the most important region. Most of the applied voltage is dropped (cathode fall) across it. Ions and electrons created at the breakdown are accelerated across this region. The different regions in the discharge are shown in Figure 2.9.

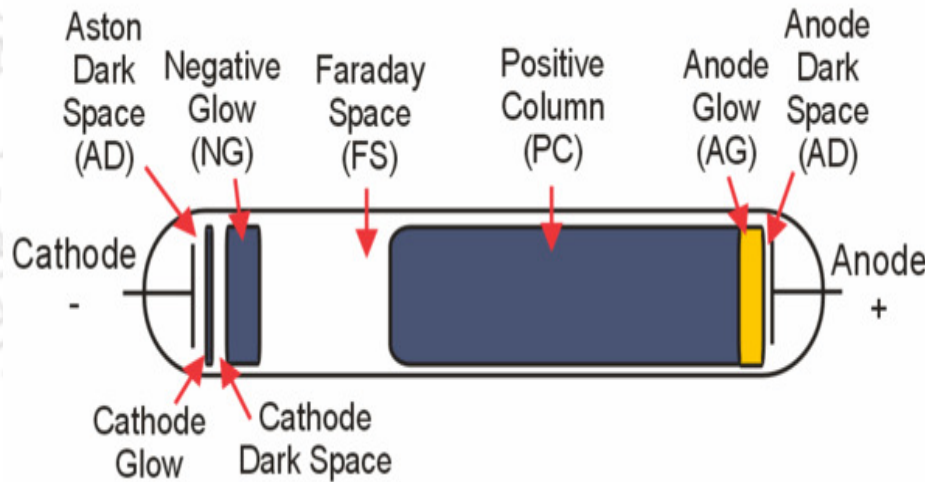


Figure 2.9: Different regions in a typical glow discharge.

The energetic electrons produce more ions by collision with the gas atoms in the negative glow, and the energetic ions strike the cathode to produce sputtered flux and secondary electrons, which are essential to sustain the glow. The effective sputtering is possible only when both the number of ions and their energy are large and controllable.

Several sputtering techniques are proposed for thin film deposition, including DC diode, RF diode and ion beam sputtering [30].

(i) DC sputtering

This technique is the simplest among the sputtering techniques. In this method, the system consists of a pair of planar electrodes (cathode and anode). The front part of the cathode is covered with a target material, which is to be deposited, and the substrate is placed at an anode. The sputtering chamber is filled with an inert gas (in general argon gas), and the glow discharge is maintained under the application of dc voltage between the electrodes. The Ar^+ ions generated in the glow discharge are accelerated at the cathode fall and eject the atoms from the target resulting in the deposition of the thin film on to the substrate. In the DC sputtering technique, the target is composed of metal because the glow discharge is maintained between metallic electrodes.

Sputtering has attracted great attention because of low - temperature crystallization, thickness uniformity and control, high deposition rates, high adhesion and large throughput. However, sputtering has some disadvantages too. In general, the DC sputtering needs higher voltages ($\sim 2 - 3$ KV) in order for sputtering to take place and the films cannot be deposited at lower pressures. Reduced deposition rates for oxide films and re-sputtering effects are other two difficulties.

(ii) Magnetron Sputtering

In a magnetron - sputtering configuration, both an electric field (E) and a magnetic field (B) are used to confine the electrons to be near the cathode surface where electrons are emitted. An electron moving with a component of velocity perpendicular to the magnetic field will spiral around the magnetic field lines and will be confined by the magnetic field. Both the frequency and the radius of spiraling motion depend on the strength of the magnetic field. The interaction of an electron with the electric and magnetic fields depends on the magnitude and the orientation of the field as $E \times B$. If the magnetic field is parallel to the cathode surface and the electric field is normal to the surface, an electron leaving the surface will be accelerated towards the anode and will spiral around the magnetic field lines. The magnetic field is oriented such that these drift paths for electrons form a closed loop. This electron trapping effect increases the collision rate between the electrons and the sputtering gas molecules. In addition, the increased ionization efficiency achieved in the magnetron

sputtering allows the discharge to be maintained at lesser pressures of operation and at lower operation voltages. In the present work, RF magnetron sputtering is used to deposit the thin films.

(iii) Reactive magnetron sputtering

When a reactive gas species such as oxygen or nitrogen is introduced in to chamber, thin films of compounds such as oxides and nitrides are deposited by the sputtering of the appropriate metal targets, and this process is known as reactive magnetron sputtering. This process is used in practice for high rate of deposition of insulating metal oxide films.

(iv) Mechanism of sputtering

Two models have been proposed for sputtering:

- (i) Thermal vaporization theory: The surface of the target is heated enough to be vaporized due to bombardment of energetic ions.
- (ii) Momentum transfer theory: Surface atoms of the target are emitted when kinetic momentum of incident particles is transferred to target surface atoms [31, 32].

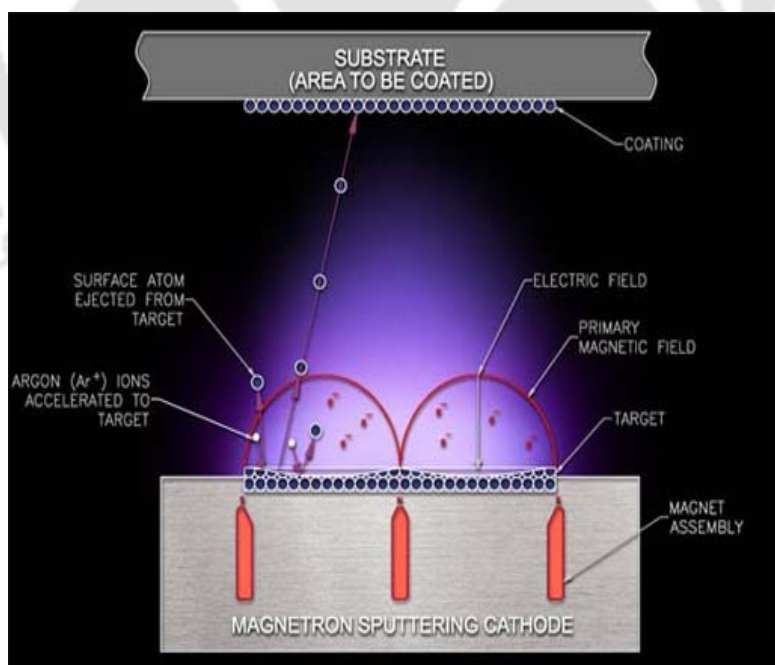


Figure 2.10: Sputtering process [33].

A sputtering process is initiated by the first collision between incident ions and target surface atoms followed by the second and third collisions between the target surface atoms. The displacement of target surface atoms will be more isotropic due to successive collisions, and atoms may finally escape from the surface. The sputtering collision on the target surface is shown in the Figure 2.10.

(v) RF magnetron sputtering

When insulating / dielectric targets (such as oxides or nitrides) are sputtered using DC voltages, the negative charge applied to the target is neutralized by the *Ar* ions. Eventually, due to positive charge built - up on the cathode (target), the *Ar* ions will not be attracted anymore by the target to carry out sputtering. Very high potential differences (around 10^8 volts) between the electrodes are required to sputter insulators, and this creates practical difficulties. To overcome this, an alternating current in the radio frequency (RF) regime is used rather than DC. Since the ions are heavy and less mobile as compared to electrons, they cannot follow radio frequencies. On the otherhand, the electrons follow RF and acquire sufficient energy to cause ionizing collisions in the space between the electrodes and thus maintain the plasma. When an electrode is capacitively coupled with the RF source, an alternating (positive and negative) potential appears on the surface. In the one - half cycle, at which the target is negative, the ions are accelerated towards the target with sufficient energy to cause sputtering while, in the next positive half cycle; the electrons reach the target surface to prevent any charge built - up. Since the substrate and chamber make a very large electrode, not much sputtering occurs at the substrate. RF sputtering can be performed at lower *Ar* pressures (1 to 15 mTorr). More lines of sight deposition occur due to a fewer gas collisions. The processing parameters such as substrate temperature, RF power, deposition time, target to substrate distance, *Ar/O₂* flow ratio, and working pressure significantly affects the thickness of the film and consequently, thin film properties.

In the present study we have chosen reactive RF magnetron sputtering (Advanced Process Technologies, India) to deposit films in the MgTiO_3 system. The schematic diagram of RF sputtering unit is shown in Figure 2.11. This consists of vacuum system, which is equipped with conventional mechanical pump and turbo molecular pump and mass flow controllers. They are used to evacuate, to achieve a base pressure to 10^{-6} Torr.

There are very few reports on as grown nanocrystalline MgTiO_3 thin films, while there are no reports on *Co* doped MgTiO_3 thin films by RF magnetron sputtering. Significantly all the films were deposited using a single cathode from homemade MTO, and *Co* doped MTO ceramic targets prepared from the optimized conditions in bulk & discussed in chapter 3. Interestingly, there were no reports on the deposition of these films in pure oxygen atmosphere.

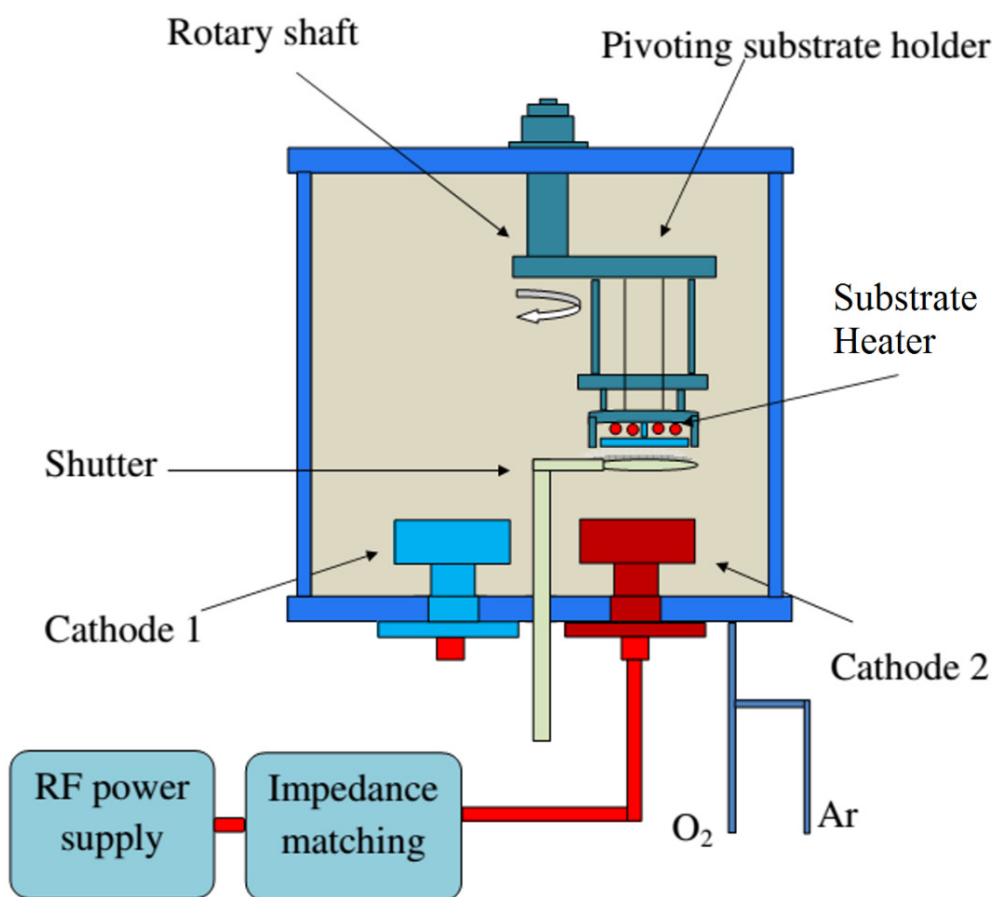


Figure 2.11: Schematic diagram of RF sputtering unit.

2.8 Thin film characterization techniques

In the case of thin films also, XRD has been used to find out the crystalline phase of the films.

2.8.1 Optical properties

The optical constants of the thin films were calculated using the envelope technique [34]. The spectral transmission characteristics in the wavelength range 190 -1500 nm were measured using a (UV 3101PC, SHIMADZU) UV-VIS-NIR spectrophotometer.

When the light is incident on a film of refractive index n , coated on to a substrate of refractive index s , then at the air - film, film - substrate and substrate - air interfaces, part of the incident light is reflected and part of it is transmitted. Since the reflected and transmitted beams originate from a single coherent source, the beams exhibit interference effects. The condition for constructive interference in such a case is given by

$$2nd = m\lambda \quad (2.25)$$

where, n is the refractive index of the film at a wavelength λ and m is the order of interference, d is the thickness of the film that can be calculated from the derived values of refractive indices.

In general, the transmission T , is given by the expression

$$T = \frac{Ax}{B - Cx \cos \phi + Dx^2} \quad (2.26)$$

where $A=16n^2s$

$$B=(n+1)^3 (n+s)^2$$

$$C=2(n^2-1) (n^2-s^2)$$

$$D=(n-1)^3 (n-s^2)$$

$$\phi=4\pi nd/\lambda$$

$$x = e^{-\alpha d}$$

For such a system, at the points of constructive and destructive interference the transmittance T_M and T_m , respectively are given by

$$T_M = \frac{Ax}{B - Cx + Dx^2} \quad (2.27)$$

$$\text{and } T_m = \frac{Ax}{B + Cx + Dx^2} \quad (2.28)$$

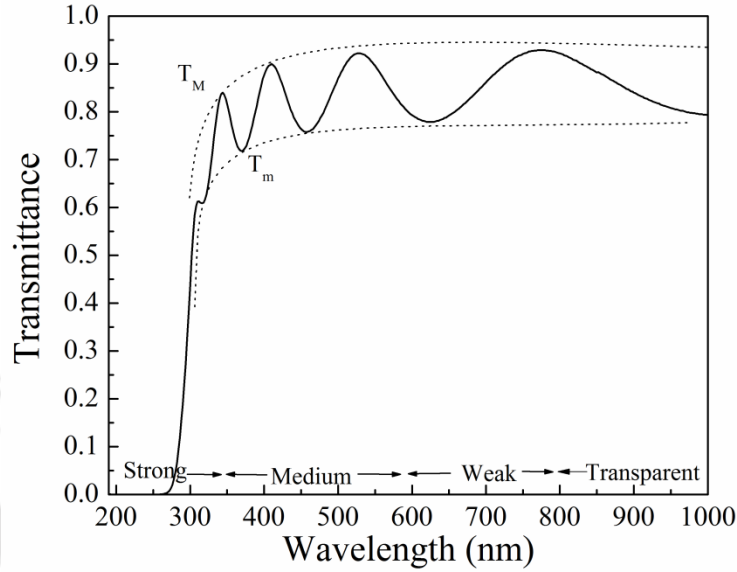


Figure 2.12: Typical transmittance spectrum of the film.

For simplicity it can be assumed that the transmission is a continuously varying function of wavelength which can be approximated by drawing the envelope across the spectrum, connecting all the maximas and minimas as shown in the Figure 2.12.

$$n = \left[N + (N^2 - n_s^2)^{1/2} \right]^{1/2} \quad (2.29)$$

where, N is a constant, n_s is the refractive index of the substrate used and n is the refractive index of the film at that particular wavelength.

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \quad (2.30)$$

On adding the reciprocals of the equations 2.27 and 2.28 yields,

$$\frac{2T_M T_m}{T_M + T_m} = \frac{Ax}{B + Dx^2} \quad (2.31)$$

and solving for x we get,

$$x = \frac{F - F[F^2 - (n^2 - 1)(n^2 - n_s^4)]^{1/2}}{(n - 1)^3(n - n_s^2)} \quad (2.32)$$

$$\text{where } F = \frac{8n^2n_s}{T_i} \quad (2.33)$$

$$\text{and } T_i = \frac{2T_M T_m}{T_M + T_m} \quad (2.34)$$

where, T_M is the maximum of the transmission on the envelope at a wavelength λ and T_m is the minimum in transmission on the envelope at the same wavelength. The T_M and T_m at each wavelength can therefore be read off from the envelope and the refractive index can be derived at each wavelength.

From the equation of constructive interference, it can be seen that for two successive maxima occurring at λ_1 and λ_2 , the equation becomes

$$2n_1d = m_1 \lambda_1 \text{ and} \quad (2.35)$$

$$2n_2d = m_2 \lambda_2 \quad (2.36)$$

Also $|m_1 - m_2| = 1$.

$$\text{Therefore, } d = \frac{\lambda_1 \lambda_2}{2(n_1 \lambda_2 - n_2 \lambda_1)} \quad (2.37)$$

In the strong absorption region, from Beer - Lambert's law given by

$$I = I_0 e^{-\alpha d} \quad (2.38)$$

where I_0 is the incident intensity =1

I is the intensity at a given wavelength λ

d is the thickness of the film and

α is the absorption coefficient in cm^{-1} .

Since d is known from previous calculations and I is a measured quantity (i.e. transmission at a wavelength λ), the absorption coefficient α can be calculated. Knowing α from the expression for the so-called “Tauc gap”, the fundamental absorption edge of the material can be determined. The expression for the Tauc gap is given by

$$\alpha h\nu = \text{constant} \times (h\nu - E_g)^2 \quad (2.39)$$

X - intercept of the extrapolation of the linear region in a plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ will give the value of bandgap E_g . The error associated with the measurement of k , n and d is ± 0.005 , ± 0.02 and ± 10 nm respectively.

2.8.2 Surface profilometer

The thickness of the films deposited on to transparent substrates were calculated using envelop technique and verified using the surface profilometer. The thickness of the thin films deposited on platinized silicon substrates were measured using stylus profiler (Veeco-Dektak 6M). A diamond - tipped stylus is used to measure the thickness of the films. A precision x - y stage moves the sample under the stylus, and vertical displacements in the stylus are converted into an electrical signal corresponding to the dimensions of the feature. These electrical signals are then converted to a digital format where they can be displayed on a computer screen and manipulated to determine various analytical information about the substrate. Scan length and scan speed can be fine - tuned to increase or decrease analysis time and resolution. Additionally, the stylus force can be varied to be compatible with either hard or soft surfaces.

2.9 Microwave dielectric properties of thin films using post split dielectric resonator method

The microwave dielectric properties of thin films were determined using an vector network analyzer Agilent 8722 ES by employing the split post dielectric resonator based measurement technique (SPDR) [35]. Split - post dielectric resonator measurement technique is a highly accurate technique for measurement of complex permittivity of dielectric substrates and thin films at spot frequencies in the frequency region of 1- 20 GHz. This method is attractive for accurate non - destructive measurements of low - loss substrates.

Low loss materials are nearly non dispersive so that the dielectric constant and loss tangent will stay constant over a range of frequencies. The required thickness of sample depends on dielectric constant of material. Material with high dielectric must have less thickness. The fixture air gap and the active area dimension of the fixture depend on the operating frequency of resonator. It is possible to measure the relative permittivity with uncertainty of approximately $\pm 0.5\%$ or better and the dielectric loss tangent with a resolution of 2×10^{-5} for properly chosen sample thickness. The cross section view of the SPDR is shown in Figure 2.12.

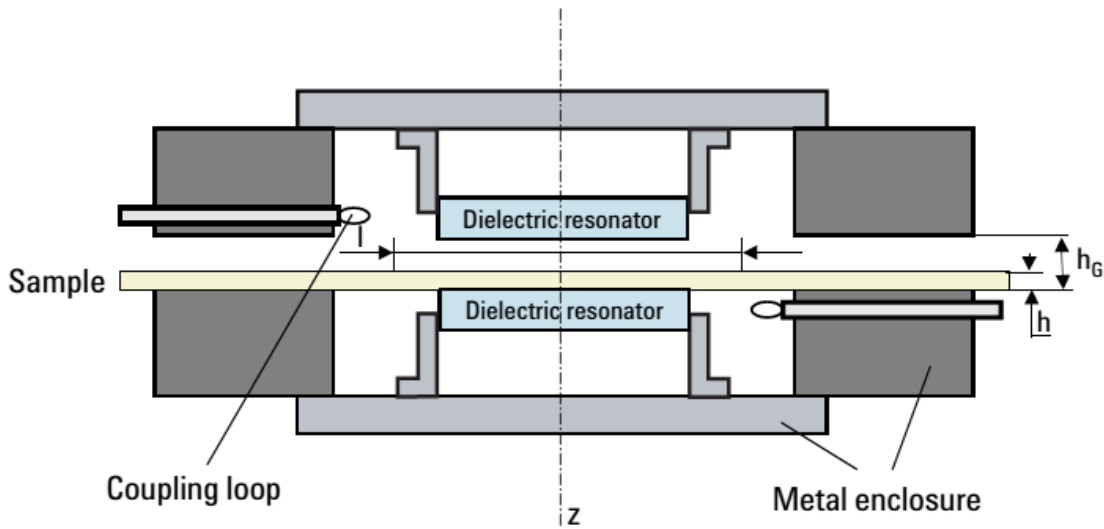


Figure 2.13: Cross sectional view of SPDR fixture [35].

For thin films deposited on a substrate, the frequency shift due to the film has to be separated from the overall frequency shift of the film substrate. For this purpose one has to measure the resonance frequency and quality factor (f_{01} , Q_{01}) of the empty resonator and do the same (f_0 , Q_0) with the substrate. After the film deposition, the resonance frequency and quality factor of the (f_s , Q_s) substrate coated with the film have to be measured again. The SPDR typically operates in the $TE_{01\delta}$ mode that has only an azimuthal electric field component, so that the electric field remains continuous on the dielectric interfaces. This makes the system insensitive to the presence of air gaps perpendicular to the z - axis of the fixture. The real part of permittivity of the sample is found on the basis of the measurements of the resonant frequencies and thickness of the sample as an iterative solution to Eq. (2.40).

$$\epsilon' = \frac{1 + (f_0 - f_s)}{hf_0 K_s(\epsilon', h)} \quad (2.40)$$

Here, h is the sample thickness, f_0 is the resonance frequency of the SPDR with the substrate, and f_s is the resonance frequency of the SPDR with the film coated substrate. K_s is a function of the sample's dielectric constant ϵ_r and thickness h . Since K_s is a slowly varying function of ϵ_r and h , the iterations using the formula (2.40) converge rapidly. The loss tangent is computed using the Eq. (2.41):

$$\tan \delta = \frac{Q^{-1} - Q_{Dr}^{-1} - Q_c^{-1}}{P_{es}} \quad (2.41)$$

where, Q is the unloaded quality factor of the SPDR containing the dielectric sample and P_{es} is the electrical energy-filling factor of the sample. Q_c is the Q factor depending on the metal losses for the SPDR containing the dielectric sample and Q_{Dr} is the Q - factor depending on the dielectric losses in the dielectric resonators. The unloaded Q - factors depends on conductor and dielectric lossess and all other related parameters. The dielectric parameters can be derieved using basis of measurements for high frequency applications. The accuracy of this measurement is

$$\frac{\Delta \epsilon}{\epsilon} = \pm \left(0.0015 \pm \frac{\Delta h}{h} \right), \text{ where } h \text{ is the thickness of the film}$$

$$\Delta \tan \delta = \pm 2.0 \times 10^{-5} \text{ or } \pm 0.03 \cdot \tan \delta, \text{ whichever is higher}$$

2.10 Electrical measurements

For the electrical characterizations, metal insulator metal (MIM) type test structures were fabricated. All the oxide thin films (pure and *Co* doped MgTiO_3) were deposited on Pt-coated Si-substrates. 100 nm thick Ag top electrodes were deposited on to the oxide layer through a shadow mask so as to define a capacitor structure (the diameter of a top electrode is 1.0 mm). The low frequency impedance and dielectric spectroscopy at zero dc bias from 100 Hz to 1 MHz were performed by using an LCR meter (Wayne Kerr Electronics Pvt. Ltd., Model 1J43100). The I - V characteristics of these test structures were measured using parameter Analyzer (Keithely 4200 Semiconductor Systems) connected with a probe station (J Microtechnology LMS 2709 DC).

2.11 Atomic force microscope

The microstructures of the deposited films were obtained using atomic force microscope (AFM). The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip of radius of curvature of the order of nanometers. When the tip is brought into the proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces, solvation forces etc. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. The AFM can be operated in a number of modes, depending on the application. The primary modes of operation are static (contact) mode and dynamic mode [36].

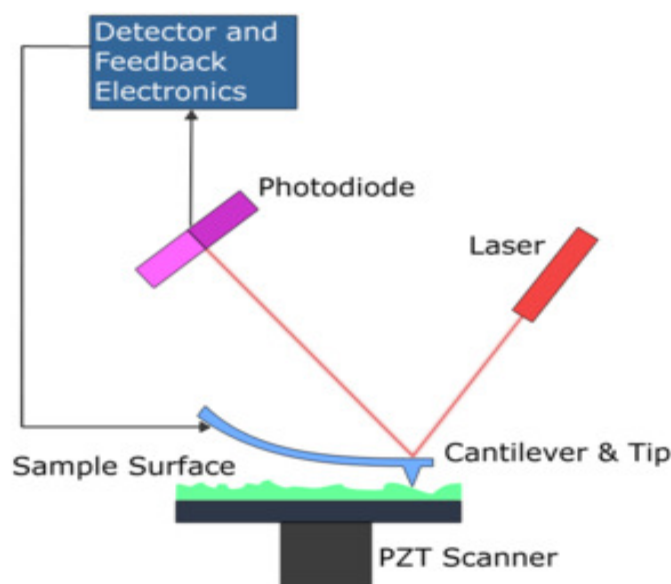


Figure 2.14: Schematic diagram of atomic force microscope.

In the static mode operation, the static tip deflection is used as a feedback signal. Because the measurement of a static signal is prone to noise and drift, low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces can be quite strong, causing the tip to 'snap - in' to the surface. Thus

static mode AFM is almost always done in contact where the overall force is repulsive. Consequently, this technique is typically called 'contact mode'. In contact mode, the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection through feedback circuitry.

In the dynamic mode, the cantilever is externally oscillated at or close to its resonance frequency. The oscillation amplitude, phase and resonance frequency are modified by tip - sample interaction forces. These changes in oscillation with respect to the external reference oscillation provide information about the sample's characteristics. Schemes for dynamic mode operation include frequency modulation and the more common amplitude modulation. In frequency modulation, changes in the oscillation frequency provide information about tip-sample interactions. Frequency can be measured with very high sensitivity and thus the frequency modulation mode allows for the use of very stiff cantilevers. In the present study, the AFM images were obtained using Agilent atomic force microscope (Agilent technologies, Model 5500 series) and analyzed using WSXM software [37]

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Chapter 3

Mechanochemical and Solid State Synthesis of

MgTiO₃ ceramics

It is well known that it is difficult to eliminate subordinate phases in MgTiO₃ ceramics prepared by conventional solid state reaction method due to the hygroscopic nature of MgO. Hence, in this study, we have chosen to prepare the MTO ceramics using mechano-chemical synthesis and non-stoichiometric composition of MgTiO₃ by adding extra *Mg* in to the parent composition using solid state reaction method. Investigate the impact of these processes on the structural, microstructural and microwave dielectric properties of MTO ceramics.

3.1 Literature review

MgTiO₃ ceramics are promising due to their excellent microwave dielectric properties. However, there are two major disadvantages in preparing MgTiO₃ (MTO) ceramics by solid state reaction method. One is the presence of MgTi₂O₅ meta-stable phase in the final MgTiO₃ composition and the other is, it requires a very high sintering temperature, which limits their practical applications [1]. To overcome the above difficulties in preparing single phase MTO, alternative approaches such as complex polymerization [2], auto igniting combustion [3], sol-gel [4, 5], and mechanochemical processing [6, 7] methods were adopted. However, the densification of MTO ceramics remains a challenge and hence various novel approaches such as addition of low melting point additives, smaller initial particle sizes, and the liquid phase sintering aids [8 - 10] were utilized to reduce the sintering temperature. But with this addition of the sintering aids the microwave dielectric properties deteriorated drastically. Hence the present work discusses the preparation of single phase MTO ceramic in two different methods: (i) mechanochemical and (ii) solid - state reaction method with the addition of excess MgO to MTO. In mechanochemical method, the processing conditions such as milling time, ball to powder ratio, milling speed, sintering temperature and sintering duration were optimized to achieve single phase MTO ceramics. The crystal structure, microstructure, low frequency and microwave dielectric properties of MTO ceramics were investigated.

In solid-state reaction method, to recompense the *Mg* deficiency in MTO by addition of excess mole concentration of MgO has been added to MTO. The non-stoichiometric Mg_{1+ δ} TiO_{3+ δ} (δ = 0, 0.05, 0.07, 0.10 and 0.15) ceramics were prepared. The synthesis conditions were optimized to get single phase MTO ceramics, maximum relative density and best microwave dielectric properties. The effect of excess *Mg* content on the crystal structure, microstructure and microwave dielectric properties of the MTO ceramics are discussed. The

best composition which formed single phase MgTiO_3 was chosen and different wt% of V_2O_5 is added. The effect of V_2O_5 addition on the crystal structure, microstructure and microwave dielectric properties of non - stoichiometric MTO ceramics is discussed. Furthermore, in both the methods dielectric loss mechanisms were discussed, and the obtained results were compared with the earlier reports.

3.2 Experimental details

3.2.1 Mechanochemical method

MgTiO_3 ceramics were prepared from high purity reagents MgO (Sigma Aldrich 99.99%) and TiO_2 (Sigma Aldrich 99.99%). These powders were weighed according to stoichiometry and the powders were ball milled for 30 h using a planetary ball mill (Fritsch GmbH, Germany). After drying and sieving, the samples were uniaxially pressed into pellets with dimensions of 10 mm in diameter and 4 - 5 mm in thickness isostatically. The pellets were sintered in the range of 1250 - 1400°C for 3 h in air.

3.2.2 Solid state reaction method (non-stoichiometric compositions)

Samples with compositions $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ($\delta = 0, 0.05, 0.07, 0.10$ and 0.15) in the magnesium titanate system were prepared using solid state reaction method. MgO (Sigma Aldrich 99.99%) and TiO_2 (Sigma Aldrich 99.99%) compounds were used for preparation of these samples. The stoichiometry amounts of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ compounds were weighed and mixed in a planetary ball mill (Fritsch GmbH, Germany) for 5 h using zirconia vial and distilled water as milling medium. The prepared mixtures were dried and calcined at 1100°C for 2 h. The calcined powders were re-milled for 10 h to reduce the particle size. The powders were added with an organic binder (PVA) and pressed into pellets with 10 mm in diameter and 4-5 mm in thickness under a pressure of 2000 Kg/cm^2 isostatically. The pellets were subsequently sintered at 1100 -1400°C for 3 h in air.

From the above compounds best composition has been identified ($\text{Mg}_{1.07}\text{TiO}_{3.07}$) for further studies. After calcination $\text{Mg}_{1.07}\text{TiO}_{3.07}$ powders were re - milled with an inclusion of 0.5, 1.0 and 1.5 wt% of V_2O_5 (Sigma Aldrich, USA) and pressed in to pellets. The pellets were sintered in the temperature range of 1050 - 1200°C for 3 h in air with a heating rate of

$10^\circ\text{C}/\text{min}$. A soak time of 30 min at 600°C is given while heating to expel the binder. After sintering, the samples were cool down to room temperature at a rate of $1^\circ\text{C}/\text{min}$.

3.3 Mechanochemical method

3.3.1 Effect of milling time on the phase formation of MTO ceramics

To see the effect of ball milling on the initial powders, XRD patterns were recorded for different milling time. Figure 3.1(a) shows the XRD patterns of the MgO and TiO_2 oxides milled for 20, 25 and 30 h.

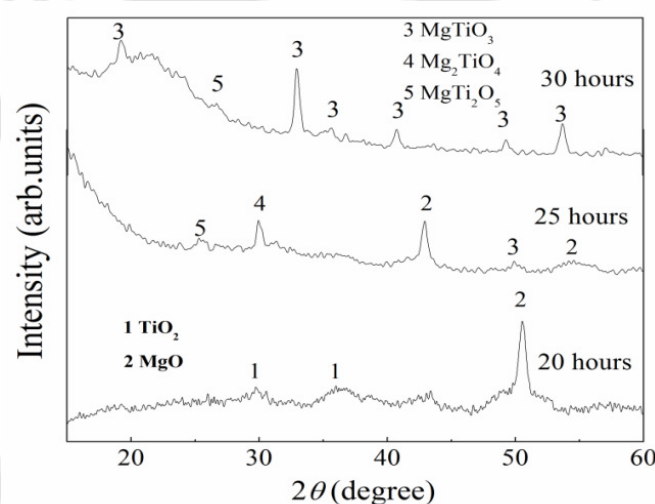


Figure 3.1: (a) XRD patterns of the MgO and TiO_2 oxides milled for 20, 25 and 30 h.

The patterns indicate that the intensities of the MgO and TiO_2 weaken gradually with increase in ball milling time upto 20 h. As the milling time increases further upto 25 h along with MgO and TiO_2 phases MgTi_2O_5 and Mg_2TiO_4 phases were also appeared. After 30 h milling, all the peaks of the parent oxides disappear; strong diffraction peaks of MgTiO_3 were observed clearly. From the XRD patterns, it is expected that after 30 h of ball milling, surface crystal structures of the oxide particles contain lattice distortion, dislocations and defects. In the mechanochemical synthesis process, the crystal structures of MgO and TiO_2 are heavily deformed and even become amorphous which results in a dramatic increase of the internal energy of the solid particles. These highly reactive MgO and TiO_2 particles can easily shed ions with diffusion ability at high temperature which promotes the formation of

MgTiO_3 [11]. The formation of the heterogeneous phases comprising MgTi_2O_5 and Mg_2TiO_4 in the $\text{MgO} - \text{TiO}_2$ system, mainly due to the differences in the degree of the incipient mechanochemical reaction. It is observed that with increase in milling time the crystallite sizes of the MTO ceramics decreases and are in the range of 30 - 50 nm.

3.3.2 Effect of sintering temperature on crystal structure

Figure 3.1(b) shows the XRD patterns of the MTO ceramics sintered at different sintering temperatures. All the samples exhibited single - phase crystalline MTO peaks which are in agreement with PDF 79-0831. It is interesting to note that all the heterogeneous phases were completely suppressed during the sintering process. Figure 3.1(c) shows the x-ray diffraction pattern along with the Rietveld refinement of MgTiO_3 ceramics sintered at 1350°C for 3 h. The Rietveld refinement was performed through Fullprof program [12]. The refinement was carried out by considering $R\bar{3}$ space group and by refining the lattice parameters, position of the *Mg*, *Ti* and *O* atoms, occupancy, and thermal parameters. The obtained lattice parameters are found to be $a = b = 5.0567$ (12) Å, $c = 13.9056$ (9) Å. From the Rietveld refinement, it is confirmed that there is no secondary phase. The values of χ^2 , R_{Brag} factor and R_f factor were found to be 1.09, 14.26 and 12.53, respectively. The above XRD analysis results are in agreement with those reported by Ferri *et al.* [2].

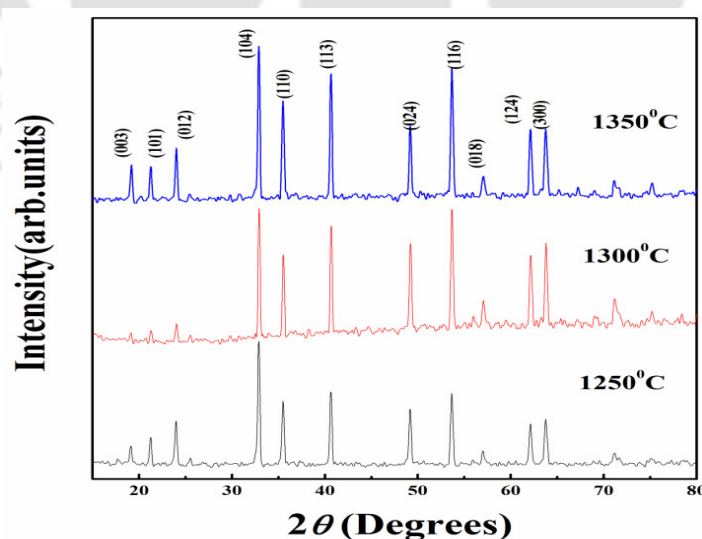


Figure 3.1(b): XRD patterns of the MgTiO_3 ceramics milled for 30 h and sintered at different sintering temperatures

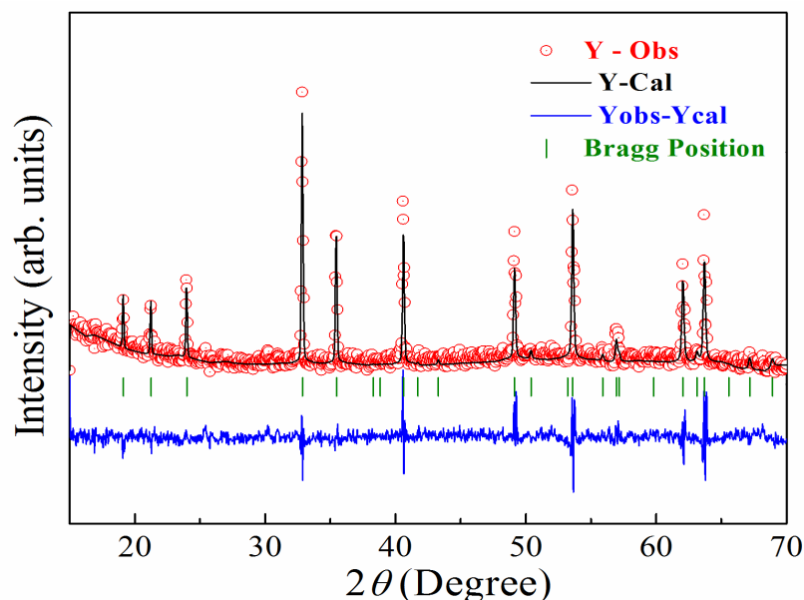


Figure 3.1(c): XRD pattern along with Rietveld refinement of MgTiO_3 ceramics sintered at 1350°C . The circles and solid line represent the experimental and the Rietveld refined data, respectively. The blue line at the bottom shows the difference between the experimental and the refined data. The vertical bars correspond to the allowed Bragg's peaks.

3.3.3 Microstructure

The scanning electron microscopic (SEM) image of the MTO powder milled for 30 h is shown in Figure 3.2(a). It is observed that all the particles exhibited nearly spherical shape and the mean particle size is around 100 nm. The SEM image of the MTO ceramics sintered at different sintering temperatures for 3 h are shown in Figure 3.2(b - d). As the milling time increases, the particles would be finer and highly reactive. When an aggregate of fine grained crystals is heated at high temperatures, recrystallisation takes place and the average grain size increases. As the initial particle size decreases, the driving force for the process increases, because the increased surface area enhances the relative density and the grain size. The bigger grain size reduces the grain boundary area. The average grain size of the MTO ceramics ranged between 1.5 to $8\ \mu\text{m}$. Further, MTO ceramics sintered at 1350°C showed larger grain sizes. From the SEM pictures, it can be surmised that initial particle size plays an important role in the densification and grain size, both of which lead to the differences in the dielectric properties of MTO ceramics.

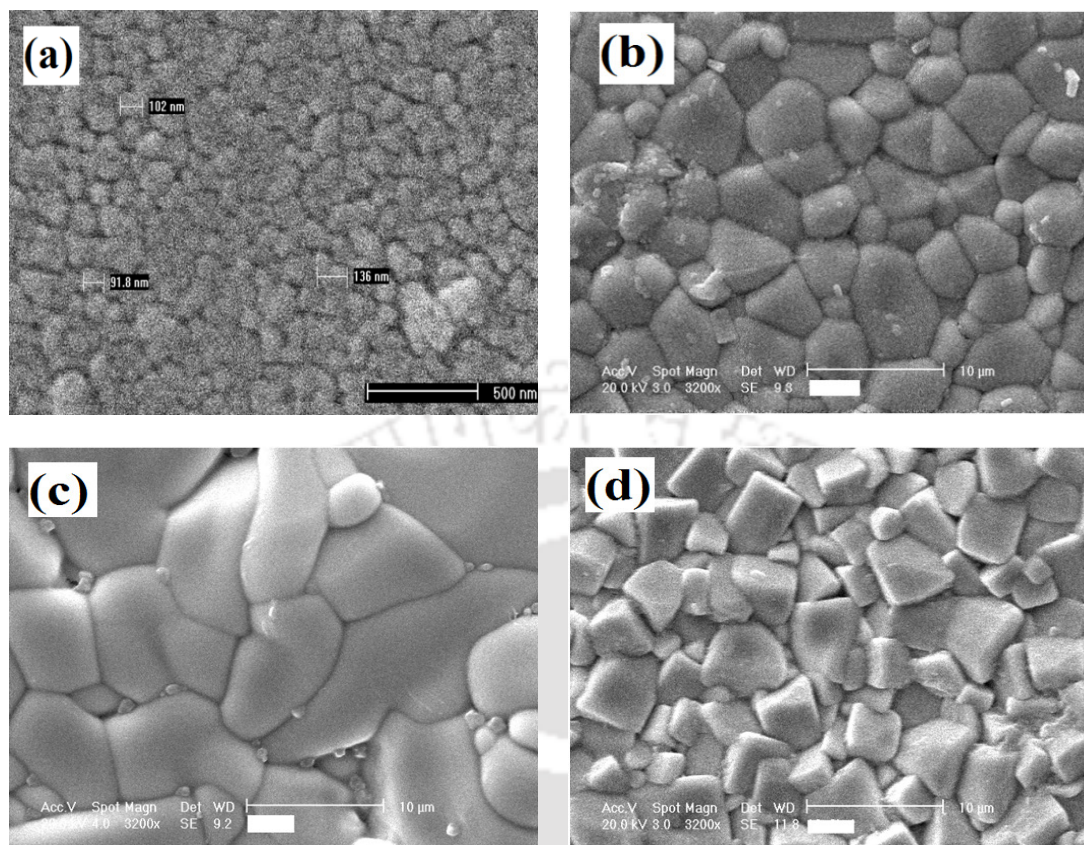


Figure 3.2: SEM images of (a) MTO powder milled for 30 h. The MTO ceramics sintered at (b) 1300°C (c) 1350°C (d) 1400°C.

3.3.4 Relative density

The variation in relative density as a function of milling time, sintered at 1350°C is shown in Figure 3.3(a). It is found that the density of the MTO ceramics increases linearly with increasing milling time. The SEM image of the MTO ceramics milled for 30 h is shown in Figure 3.2(a) and it is observed that the particle size of the powders is 100 nm. The initial particle size of the powders is $> 2 \mu\text{m}$. From the SEM image and Figure 3.2(b), it is clear that mechanochemical synthesis reduces the initial particle size of the MTO ceramics along with the phase formation. The initial particle size plays an important role on the densification of MTO ceramics and it is well known that the microwave dielectric properties are heavily influenced by the density of the ceramics (Figure 3.7). To optimize the sintering temperature of MTO ceramics, the sintering temperature is varied and the variation in densities as a function of sintering temperature is shown in Figure 3.3(b). It is again confirmed that the MTO ceramics exhibited highest density at 1350°C.

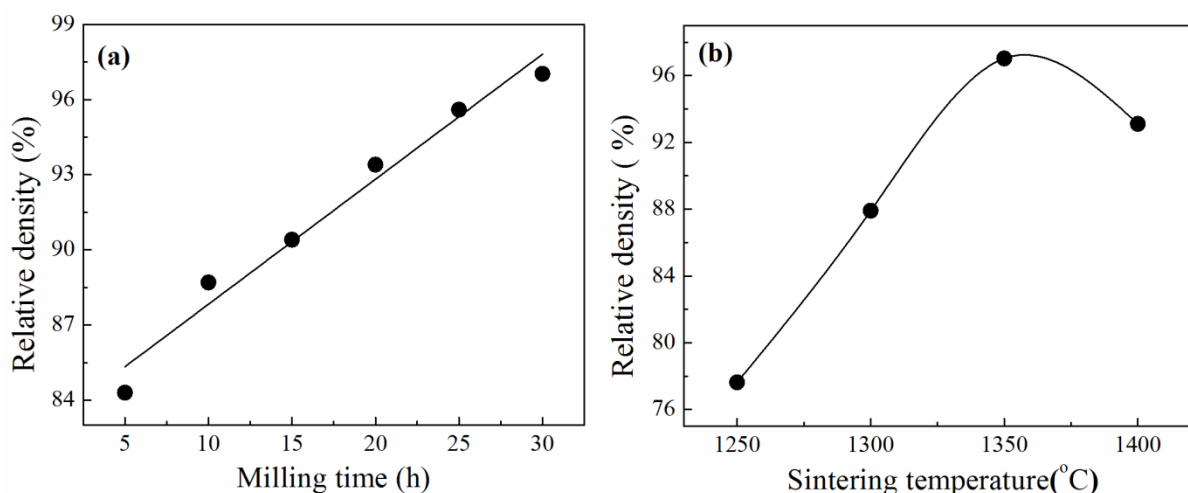


Figure 3.3: (a) The variation in relative density as a function of milling time, sintered at 1350°C. (b) Variation in relative density of MTO ceramics as a function of sintering temperature.

It was observed that as the temperature increases, the densities of the MTO ceramics increase up to 1350°C and above that started decreasing. The maximum relative density of 97.1% was obtained for the sample sintered at 1350°C for 3 h. The decrease in relative density at higher sintering temperatures may be due to non-uniform grain growth which is observed from SEM images (Figure 3.2(d)). The decrease in sintering temperature in this study can be attributed to the smaller initial particle sizes. It is well known that fine particles have tremendous surface areas and surface energies. The finer the particles are, the higher is the surface energy which leads to a faster densification rate. The larger grains and higher densities obtained in the present study can be due to uniform mixing of the powders and smaller particle sizes.

3.3.5 Raman spectra

Raman spectroscopy is a standard technique which is used to characterize the lattice-vibrational properties of crystals. The Raman spectra of MTO ceramics, sintered at different temperatures for 3 h are shown in Figure 3.4. It is observed that all ten Raman peaks theoretically expected appear distinctly. The results obtained in the present study agree very well with the previously reported data [13, 14]. From the Raman spectrum, it is clear that all atoms are involved in each vibrational mode. The A_g (220 cm^{-1}) and A_g (302 cm^{-1}) modes mainly originated from the vibrations of Mg^{2+} and Ti^{4+} ions along the z axis, while the A_g

(394 cm^{-1}), A_g (498 cm^{-1}), and A_g (712 cm^{-1}) modes are mainly contributed by the vibrations of O^{2-} ions. For the A_g (498 cm^{-1}) and A_g (712 cm^{-1}) modes, the six O^{2-} ions show breathing like vibrations, but each of them corresponds to different liberation directions of oxygen octahedra. The A_g (394 cm^{-1}) mode can be primarily represented as the combination of $a_g^{(1)}$ and $a_g^{(3)}$ that make the mode a nearly isotropic stretching vibration. In the case of E_g modes, the E_g (278 cm^{-1}) mode can be essentially considered as the anti - symmetric breathing vibration of the oxygen octahedron. The E_g (323 cm^{-1}) and E_g (349 cm^{-1}) modes can be approximately described as the twisting of the oxygen octahedron with the vibrations of the Mg^{2+} and Ti^{4+} ions parallel to the xy plane. The E_g (481 cm^{-1}) and E_g (636 cm^{-1}) modes are predominantly due to the anti - symmetric breathing and twisting vibrations of the oxygen octahedra with the cationic vibrations parallel to the xy plane. For the E_g (481 cm^{-1}) mode, both Mg^{2+} and Ti^{4+} ions are involved in the vibration, while for the E_g (636 cm^{-1}) mode, the cation vibrations are dominated by that of Ti^{4+} ion [15].

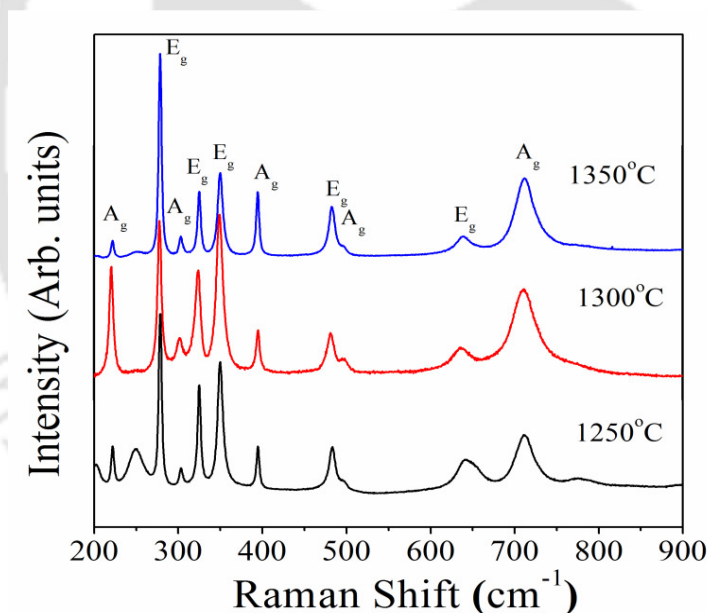


Figure 3.4: Raman spectra of the MTO ceramics sintered at different sintering temperatures.

3.3.6 Low frequency dielectric properties

The dielectric constant and dielectric loss of the MTO ceramics sintered at 1350°C for 3 h were measured as a function of temperature and measured at different frequencies were shown in Figure 3.5(a) and 3.5(b), respectively. It is observed that as the temperature

increases both the dielectric constant and dielectric loss is found to increase and also as the frequency increases both the dielectric constant and dielectric loss decreases. The dielectric constant and dielectric losses were in the range of 18.5 to 24.7 and 7×10^{-5} to 1.5×10^{-2} in the temperature range of RT to 500°C . At low temperatures, the molecules cannot orient themselves in polar dielectrics. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. At high temperatures, the dielectric losses caused by the dipole mechanism reach their maximum value and the degree of dipole orientation increases. Apart from dipole losses electrical conduction also increases with increase temperature. These factors would cause the increase in both dielectric constant and dielectric loss of MTO ceramics with increase in temperature [16].

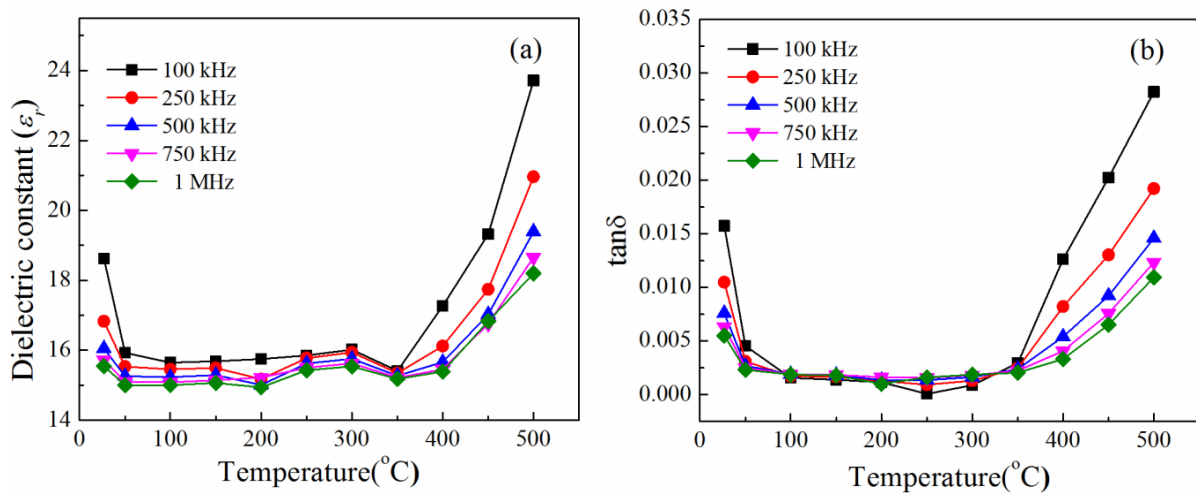


Figure 3.5: (a) Dielectric constant (ϵ_r) and (b) loss tangent ($\tan\delta$) measured at different frequencies as a function of temperature of MTO ceramics sintered at 1350°C .

3.3.7 Microwave dielectric properties

Figure 3.6 shows the microwave dielectric constant and $Q \times f_0$ of MTO ceramics as a function of sintering temperature. Both the dielectric constant and $Q \times f_0$ followed the same trend as a function of temperature. The ϵ_r values of MTO ceramics ranged between 15.95 - 18.52. The increase in ϵ_r values are due to the simultaneous increase in the relative density of the samples because higher relative density means lower porosity. The variation in dielectric constant and $Q \times f_0$ values as a function of relative density was shown in Figure 3.7. In both the cases, it was observed that both the dielectric constant and $Q \times f_0$ increases with increase

in relative density, especially at higher values of relative density. The product of the quality factor (Q) and resonant frequency (f_0) is considered as a tool for evaluating the quality of dielectric materials. The $Q \times f_0$ values increased with an increase in sintering temperature up to 1350°C above that started decreasing and the values $Q \times f_0$ are in the range 61.5 - 162.3 THz. These values are much higher compared to the values reported by Baek *et al.*, [17] and the samples were prepared by the high energy ball milling method. The obtained dielectric properties are $\epsilon_r = 17.1$ and $Q \times f_0 = 100$ THz; sintering temperature: 1350°C for 2 h.

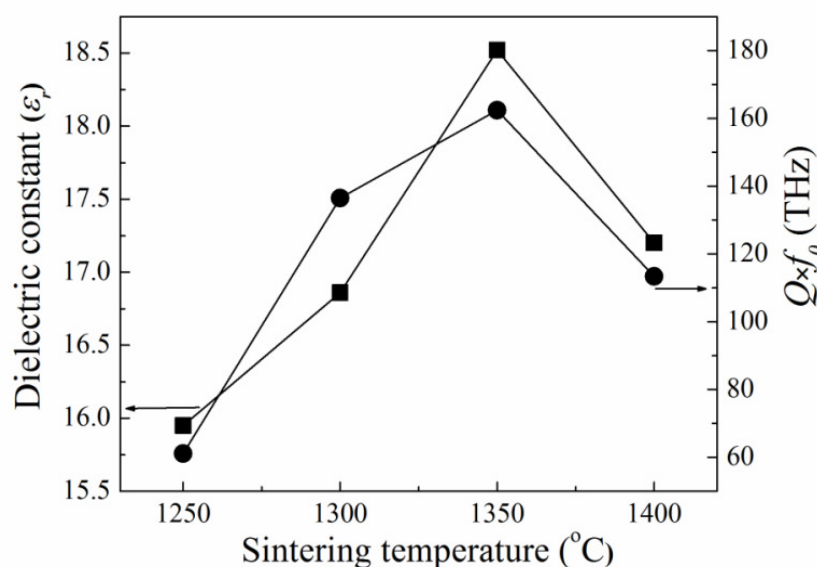


Figure 3.6: Variation in dielectric constant and $Q \times f_0$ values of MTO ceramics as a function of sintering temperature.

The maximum $Q \times f_0$ value is found to be 162.3 THz for the samples sintered at 1350°C for 3 h. Many microwave dielectric loss mechanisms are suggested including intrinsic and extrinsic [18]. Intrinsic losses in crystals arise because of anharmonic lattice forces that mediate the interaction between the crystal and phonons. This leads to damping of the optical phonons and therefore of the microwave field. Losses in ceramics caused by extended dislocations, grain boundaries, inclusions and secondary phases are termed extrinsic. These losses are caused by either dipole relaxations of impurities concentrated at interfaces or relaxations of space charge polarizations present at interfaces. The increase in $Q \times f_0$ value is primarily attributed to the increase in uniform grain size and higher densities. The decrease in $Q \times f_0$ values at higher temperatures can be attributed to the lower densities and the non-

uniform grain growth. Since the grain boundary is a plane defect, it probably decreases the $Q \times f_0$ value. The specimens with large grains are expected to have a high $Q \times f_0$ value because growth decreases the grain boundary area. In the present study, it is clear that under favorable conditions, grains grow uniformly to larger sizes leading to the well - densified MTO ceramics behaving like a single crystal which show that the $Q \times f_0$ values were strongly dependent both on the uniform grain size and relative density.

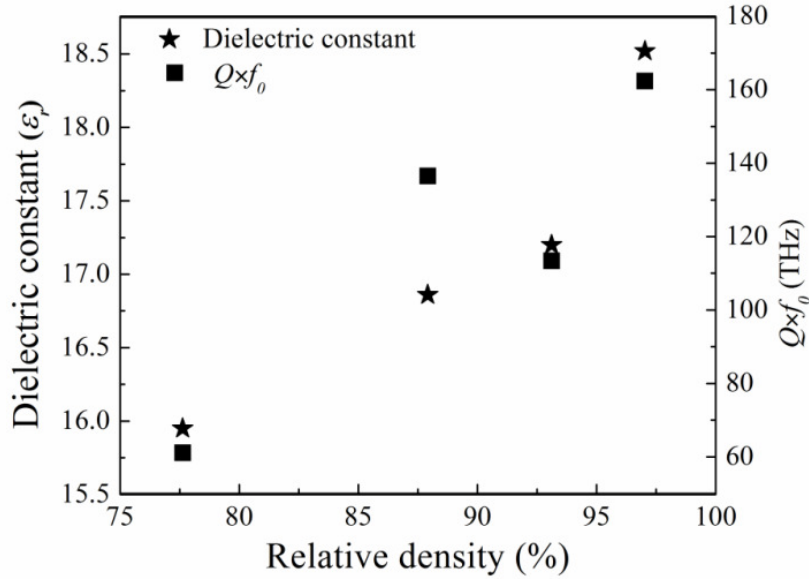


Figure 3.7: Variation in dielectric constant and $Q \times f_0$ values of MTO ceramics as a function of relative density.

3.4 Preparation of non - stoichiometric $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ composition and $\text{Mg}_{1.07}\text{TiO}_{3.07}$ with the addition of V_2O_5 by solid state reaction method.

3.4.1 Crystal structure

Figure 3.8(a) shows the X-ray diffraction patterns of excess mol concentration of MgO ($\delta = 0, 0.05, 0.07, 0.1$ and 0.15) doped in MgTiO_3 ceramics sintered at 1350°C . It is found that all the samples exhibited rhombohedral MgTiO_3 as a main crystalline phase (ICCD: 06-0464). For $\delta = 0$ samples (parent MTO), along with MgTiO_3 the presence of MgTi_2O_5 secondary phase is also observed. MgTi_2O_5 is usually formed in the MgTiO_3 matrix when prepared using solid state reaction method and which is difficult to eliminate from the sample [19].

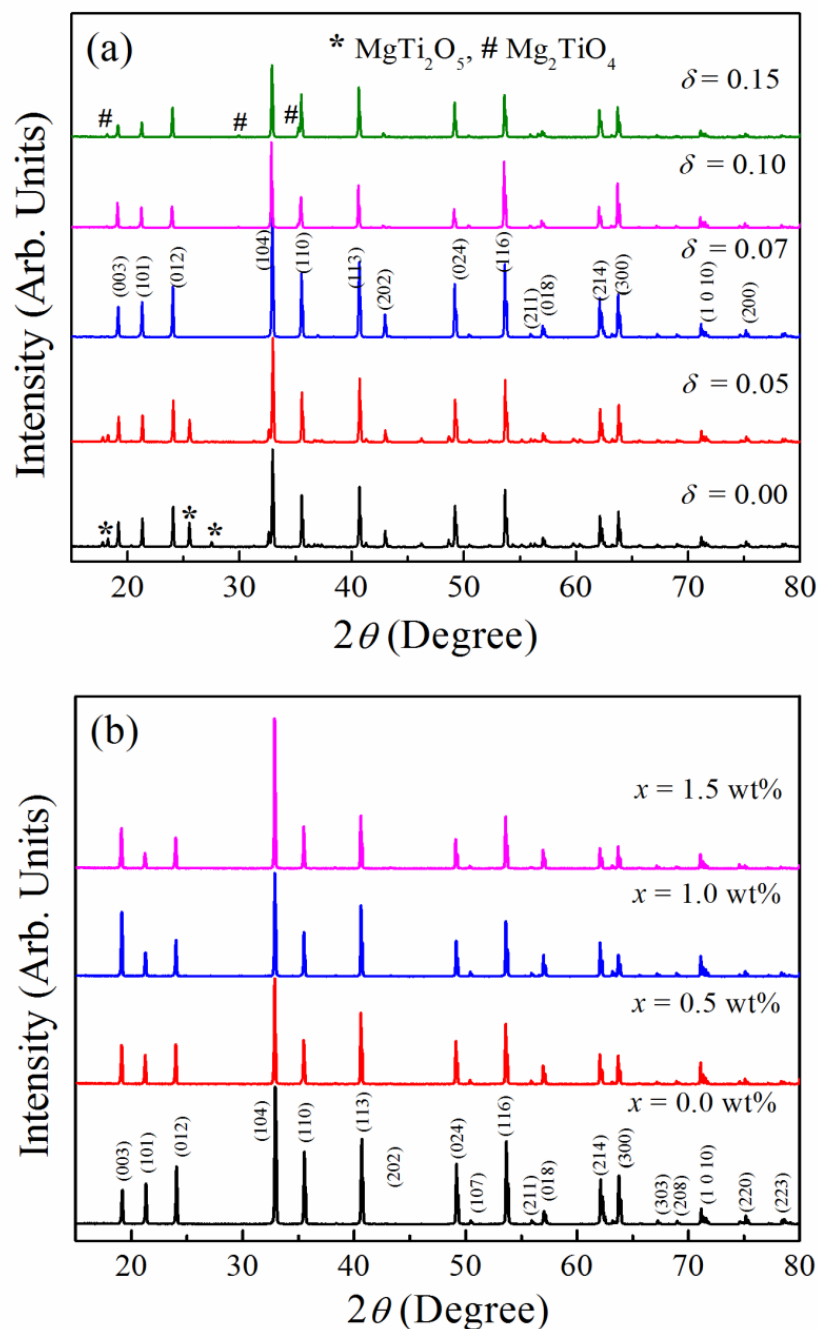


Figure 3.8: (a) XRD patterns of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ($\delta = 0 - 0.15$) compositions sintered at 1350°C for 3 h. (b) XRD patterns of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ composition added with different amounts of V_2O_5 , sintered at 1100°C for 3 h.

The secondary phase peak intensity was suppressed with increases in δ concentration and at a critical concentration of $\delta = 0.07$ sample exhibiting a pure MgTiO_3 phase. With increase in the δ beyond 0.07, a presence of Mg_2TiO_4 phase was observed along with MgTiO_3 and the intensity of Mg_2TiO_4 is improved with further increase in δ . The presence of

MgTi_2O_5 secondary phase at $\delta = 0$ may be due to the high hygroscopic nature of MgO , which absorbs moisture from the environment gives rise to deficiency in stoichiometry. From these results, one can conclude that excess MgO concentration plays a significant role in the formation of phase pure MgTiO_3 ceramics. Similar results were observed in the case of MgTiO_3 samples prepared from $\text{MgCO}_3 \cdot 0.2708 \text{ H}_2\text{O}$ as initial powder and were reported by Huang *et al.* [20]. Also, the presence of MgTi_2O_5 ($\epsilon_r \sim 17.4$, $Q \times f_0 \sim 47,000 \text{ GHz}$, $\tau_f \sim -66 \text{ ppm/}^\circ\text{C}$) [21] and Mg_2TiO_4 ($\epsilon_r \sim 14$, $Q \times f_0 \sim 150,000 \text{ GHz}$, $\tau_f \sim -50 \text{ ppm/}^\circ\text{C}$) [22] are expected to influence the microwave dielectric properties of MTO ceramics significantly. The composition with $\delta = 0.07$ is considered for the further study owing to the formation of phase pure MTO ceramics.

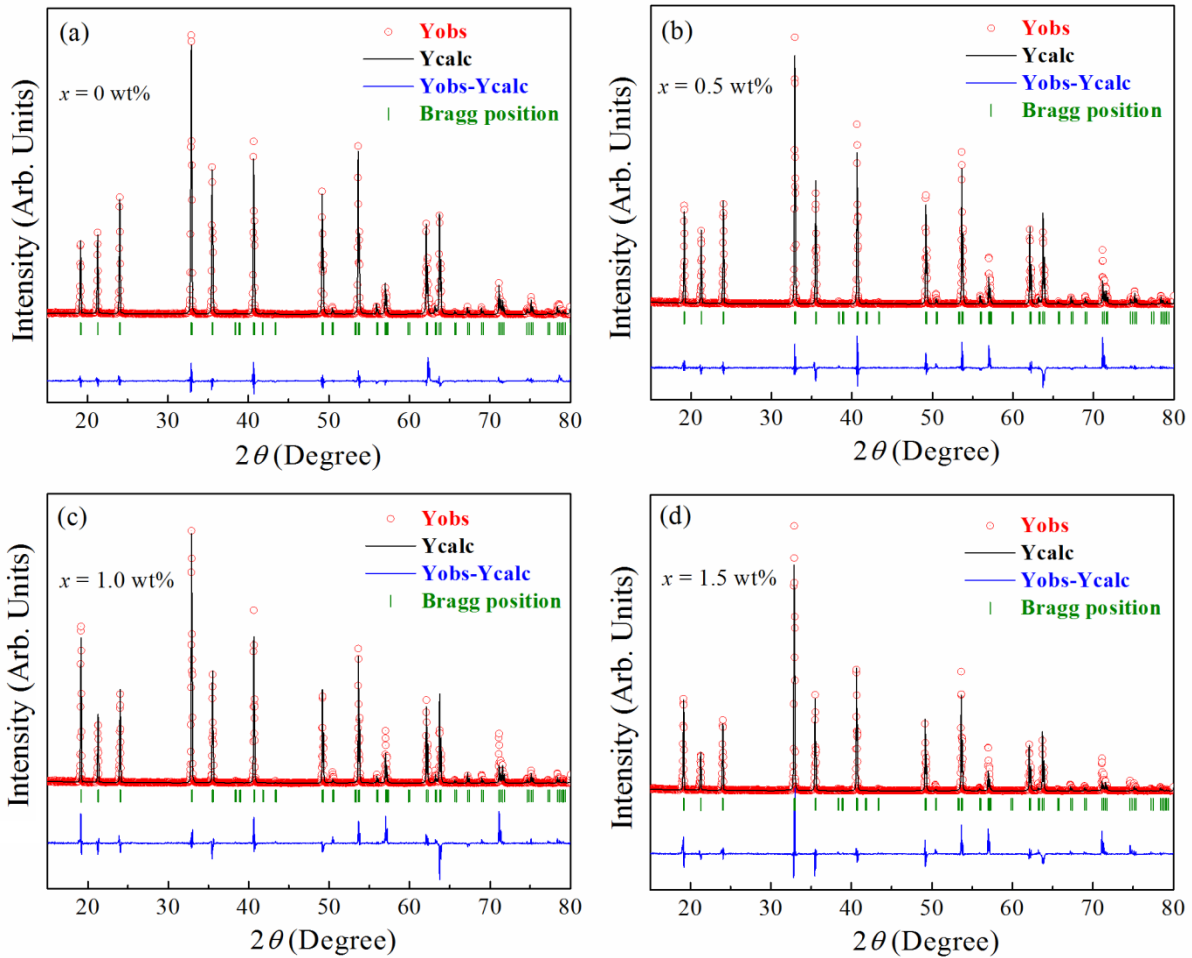


Figure 3.9: XRD patterns along with Rietveld refinement data of (a) $x = 0.0 \text{ wt\%}$ $\text{Mg}_{1.07}\text{TiO}_{3.07}$, sintered at 1350°C , (b-d) different wt% ($x = 0.5 - 1.5$) of V_2O_5 added to $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics, sintered at 1100°C .

Figure 3.8(b) shows the $\delta = 0.07$ (considered as a pure MTO with single phase for the addition of V_2O_5) and V_2O_5 ($x = 0.5 - 1.5$ wt%) added $\text{Mg}_{1.07}\text{TiO}_{3.07}$ samples sintered at 1350°C and 1100°C , respectively. It is observed that all the samples exhibited a rhombohedral MgTiO_3 phase without any secondary phase. To see the influence of V_2O_5 addition on crystal structure on $\text{Mg}_{1.07}\text{TiO}_{3.07}$ samples, all the samples were refined by considering rhombohedral $R\bar{3}$ space group. The Rietveld refinement of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ samples added with different wt% of V_2O_5 are shown in Figure 3.9.

The lattice parameters were calculated and were summarized in Table 3.1. The lattice parameters were found to decrease with the addition of V_2O_5 addition, and this indicates that V_2O_5 forms a solid solution with $\text{Mg}_{1.07}\text{TiO}_{3.07}$. This can be explained as follows V^{5+} can be substituted for tetravalent ions in $\text{Mg}_{1.07}\text{TiO}_{3.07}$, because the ionic radii of V^{5+} ($0.54 \text{ \AA}$) is smaller than Ti^{4+} ($0.605 \text{ \AA}$) in co-ordination number 6 [23, 24]. Further, as the x wt% increases, the volume of the unit cell decreases, this shows that V^{5+} has entered in to the MTO lattice.

Table 3.1: Lattice parameters of $\text{Mg}_{1.07}\text{TiO}_{3.07} + x$ wt% of V_2O_5 obtained from the Reitveld refinement.

Composition in x (wt %)	$a = b$ ($\text{\AA}$)	c ($\text{\AA}$)
0.0	5.0539 (20)	13.8954 (15)
0.5	5.0539 (21)	13.8940 (29)
1.0	5.0535 (18)	13.8933 (27)
1.5	5.0533 (23)	13.8923 (32)

3.4.2 Microstructure

The SEM images of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics with different concentration of MgO (δ) doped samples sintered at 1350°C are shown in Figure 3.10. It revealed a porous and non - uniform microstructure for $\delta = 0$ sample. Furthermore, small rods like grains were observed at grain boundary of larger grains, with an average grain size of $3.2 \mu\text{m}$. An EDS analysis was performed to investigate the chemical composition of these grains, and the results were

enlisted in Table 3.2. From the EDS spectra, the larger (spot A) and small grains (spot B) were confirmed as MgTiO_3 and MgTi_2O_5 , respectively. Whereas a uniform grain growth and improved grain size were observed with an increase in δ up to $\delta = 0.07$ (Figure 3.10(b, c)). The average grain size of 9.1 and 10.2 μm were observed for $\delta = 0.05$ and $\delta = 0.07$ samples, respectively. Further, increase in MgO (i.e., $\delta = 0.15$), porous grain morphology and two different sized grains are observed with reduced grain size (Figure 3.10(d)). The EDS spectra results confirm that the larger grains (spot A) having a chemical composition of MgTiO_3 and smaller size grains (spot B) exhibited a chemical composition of as Mg_2TiO_4 and the obtained results were given in Table 3.2. This EDS result complements the XRD results which are discussed in section 3.4.1. This indicates that *Mg* concentration enhances the uniform grain growth and grain size up to 0.07 concentrations and later they start decreases. The improvement in grain size and uniform grain growth corresponds to the formation of phase pure MgTiO_3 . The non-uniform grain growth for other samples was due to the formation of subordinate phases.

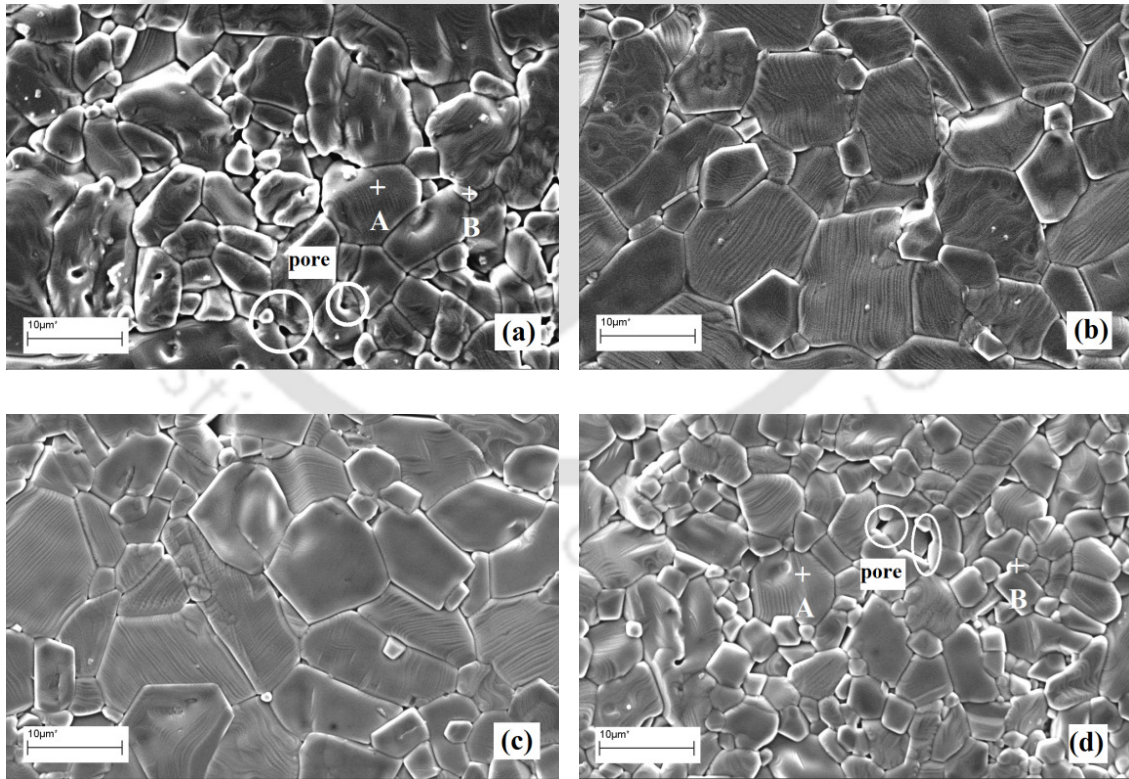


Figure 3.10: SEM images of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics doped with different δ concentrations (a) $\delta = 0$, (b) $\delta = 0.05$ (c) $\delta = 0.07$ and (d) $\delta = 0.15$, sintered at 1350°C for 3 h.

Table 3.2: The EDS spectra results of $\delta = 0$ and $\delta = 0.15$ doped $Mg_{1+\delta}TiO_{3+\delta}$ samples, sintered at $1350^\circ C$.

Spot	Atom (%)		
	Mg K	Ti K	O K
For $\delta = 0$			
A	19.94	19.84	60.23
B	12.71	23.93	64.51
For $\delta = 0.15$			
A	17.48	19.48	60.61
B	28.33	14.21	57.46

Figure 3.11 demonstrates the SEM images of $x = 0.0$ -1.5 wt% of V_2O_5 added $Mg_{1.07}TiO_{3.07}$ ceramics, sintered at $1100^\circ C$. For $x = 0.0$ wt% ($Mg_{1.07}TiO_{3.07}$) sample exhibit a highly porous microstructure with no prominent grains. With the addition of V_2O_5 , the grain growth has been enhanced and formed a rod like grains with dense microstructure.

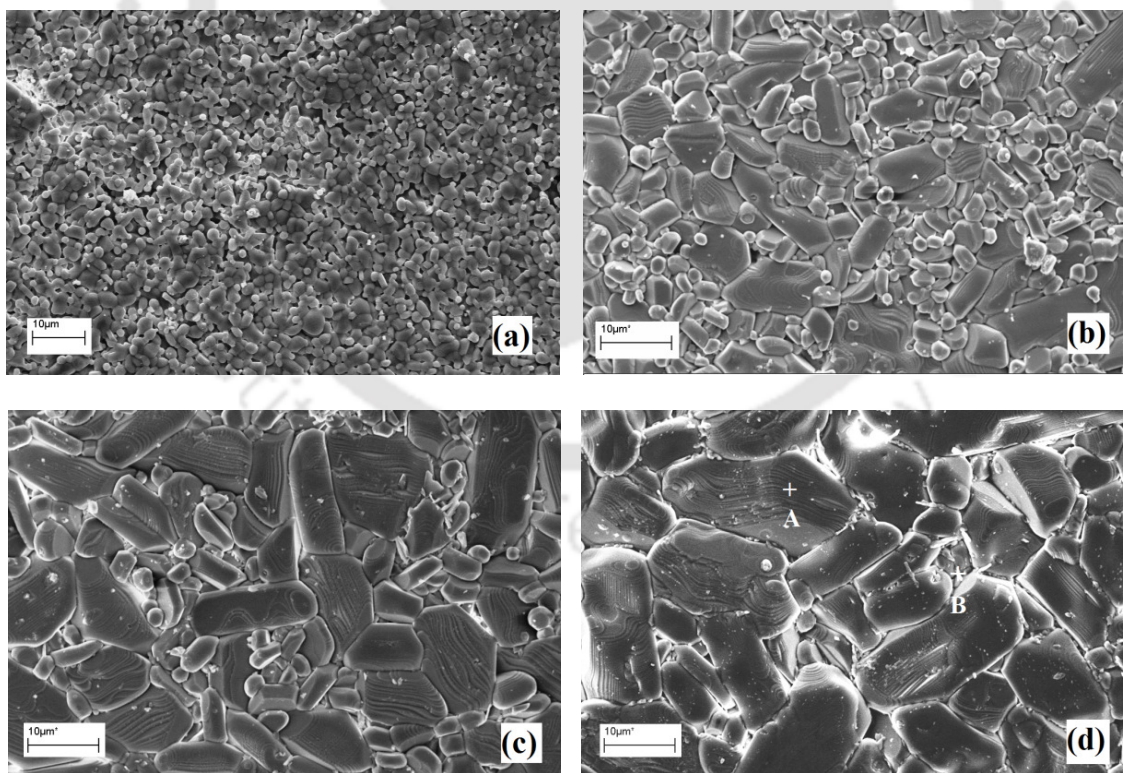


Figure 3.11: SEM images of $Mg_{1.07}TiO_{3.07}$ specimen added with different wt% of V_2O_5 and sintered at $1100^\circ C$ (a) $x = 0.0$ wt%, (b) $x = 0.5$ wt%, (c) $x = 1.0$ wt% and (d) $x = 1.5$ wt%.

The average grain size increases with the addition of V_2O_5 addition and were in the range 1.1 - 16 μm for $x = 0.0 - 1.5$ wt%. For higher concentration ($x = 1.5$ wt%) of V_2O_5 addition, a minor brown colored liquid phase has been observed at the grain boundary (Figure 3.11(d)). In order to understand the chemical composition of this phase, EDS analysis was performed on the $x = 1.5$ wt% added sample and the results were summarized in Table 3.3. The larger grains (spot A) found to be the chemical composition of MgTiO_3 with a composition of small amount of V presents in the grains, whereas the brown colored phase (spot B) showed a V-rich phase. However, XRD patterns could not identify this phase, because the detection of minor phases by means of XRD is extremely difficult. Valant *et al.* [25] reported that liquid phase may disappear or may resident in the final stage of the sintering process. In the present case, a small amount of V is soluble into $\text{Mg}_{1.07}\text{TiO}_{3.07}$ matrix and remaining is resides at the grain boundary. Similar results were observed for the $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$ and zinc titanate ceramics added with V_2O_5 [26, 27]. From all these observations, one can conclude that V_2O_5 additive and its concentration plays an important role in densification and enhancement of grain size of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics.

Table 3.3: The EDS spectra of $\text{Mg}_{1.07}\text{TiO}_{3.07} + x = 1.5\text{wt}\% \text{V}_2\text{O}_5$, sintered at 1100°C .

Spot	Atom (%)			
	Mg K	Ti K	V K	O K
A	21.35	17.38	0.28	60.99
B	28.06	1.14	13.20	57.61

3.4.3 Relative density

Figure 3.12(a) demonstrates the relative density of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics as a function of δ concentration ($\delta = 0 - 0.15$) sintered at different sintering temperatures. The relative density increases with an increase in δ concentration up to 0.07 and decreases thereafter. The obtained relative densities were in the range of 90.2 - 97.8 % for all the samples sintered in the temperature range of 1250 - 1400°C . The maximum relative density of 97.8% is observed for $\delta = 0.07$ samples sintered at 1350°C for 3 h. The improvement in the relative density is due to the excess MgO, which promotes the uniform grain growth, and the formation of the single phase MgTiO_3 with an increase in grain size (see Figure 3.10(c)). Above $\delta = 0.07$, the

reduction in relative density corresponds to the formation of Mg_2TiO_4 phase (theoretical density 3.54 gm/cm^3 which is lower than MgTiO_3), small grain size and porosity. Furthermore, it is found that with an increase in sintering temperature the relative densities increase firstly up to 1350°C and then decreases. This increase in relative densities with sintering temperature up to 1350°C is due to enhancement of uniform grain growth and improved grain size. Beyond 1350°C the decrease in relative density is because of abnormal grain growth and the formation of secondary phase.

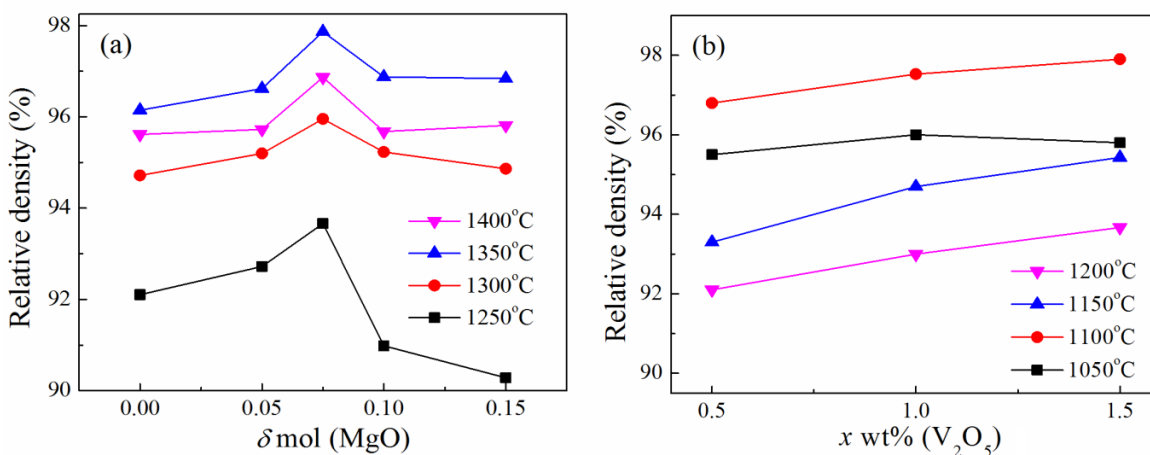


Figure 3.12: Variation in relative density of (a) $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ as a function of δ concentration and (b) $\text{Mg}_{1.07}\text{TiO}_{3.07}$ as a function of x wt% at different sintering temperatures.

To study the effect of V_2O_5 addition on densification of pure MgTiO_3 ceramics prepared from optimized condition of $\delta = 0.07$, the relative densities of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ added with V_2O_5 were determined using Archimedes method. Figure 3.12(b) shows the variation in relative densities of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics as a function of V_2O_5 ($x = 0.5 - 1.5$ wt%) sintered at different sintering temperatures. The relative density increases with increase in sintering temperature up to 1100°C and decreases slightly for the samples sintered at 1150°C . Also, with addition of V_2O_5 , the relative density of the sample increases linearly up to maximum of 1.5 wt%. The maximum relative density of 97.9% is obtained for $x = 1.5$ wt% added samples and sintered at 1100°C . It is important to note that the sintering temperature of MTO ceramics was reduced to 1100°C from 1400°C with the addition of V_2O_5 . However, the relative density of pure $\text{Mg}_{1.07}\text{TiO}_{3.07}$ is only 70% when sintered at 1100°C which is due to high porosity and insufficient sintering temperature (see Figure 3.11(a)). The reduction in the

sintering temperature with the addition of V_2O_5 can be explained as follows. The melting point of V_2O_5 is 690°C , which forms a liquid phase during the sintering process. In liquid phase sintering, the liquid spreads to cover the solid surfaces, works as liquid bridge between particles. This decreases the friction between the MTO particles and exerts a capillary force, which can be used to rearrange the particles more easily and enhance the densification process to get maximum packing [28]. From all the results, it is demonstrated that addition of V_2O_5 is not only decreases the sintering temperature but also improves the grain growth of the MTO ceramics.

3.4.4 Microwave dielectric properties

Figure 3.13(a) demonstrates the δ dependent dielectric constant (ϵ_r) of $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics, sintered at different sintering temperatures. The variation in ϵ_r exhibits almost a similar behavior as that of relative densities with sintering temperature and δ doping concentration. There is a slight increase in ϵ_r with increase in δ concentration up to $\delta = 0.07$ and the dielectric constants are in the range of 16.4 -17.4 for all the δ doped samples. A maximum ϵ_r of 17.4 was obtained for $\delta = 0.07$ samples, sintered at 1350°C . The improvement in the dielectric constant with x concentration and sintering temperature are due to formation of single phase MgTiO_3 , highest relative densities and the uniform grain growth. Above $\delta = 0.07$ the decrease in dielectric constant with δ concentration is due to the presence of Mg_2TiO_4 ($\epsilon_r \sim 14$) which is having lower ϵ_r than MgTiO_3 .

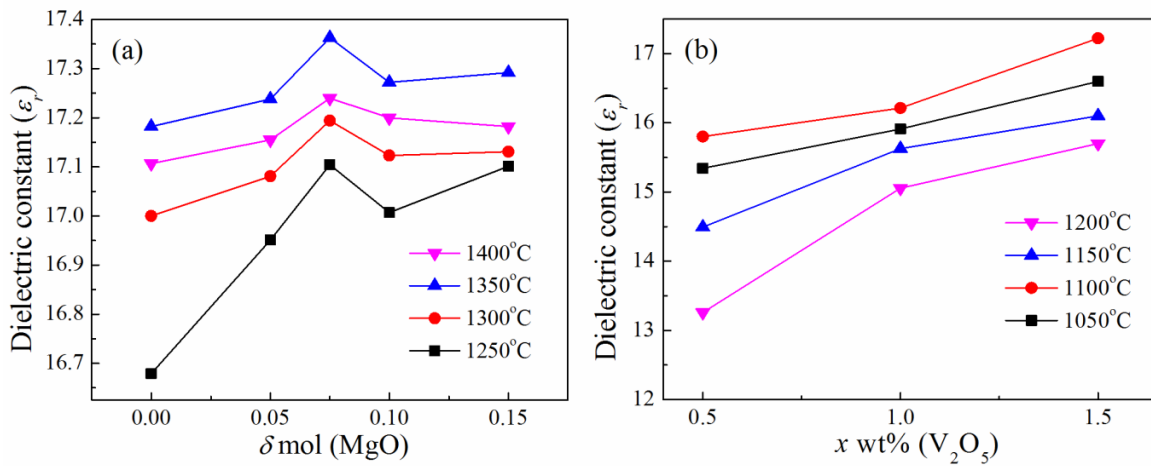


Figure 3.13: Dependence of dielectric constant (ϵ_r) on (a) δ concentration in $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics (b) x wt% (V_2O_5) in $\text{Mg}_{1.07}\text{TiO}_{3.07}$ sintered at different temperatures.

Figure 3.13(b) shows the variation in dielectric constants (ϵ_r) of $\text{Mg}_{1.07}\text{TiO}_{3.07}$ as a function of V_2O_5 (x wt%) sintered at different temperatures. The variation in ϵ_r is consistent with that of the relative density as a function of V_2O_5 and as a function of sintering temperature. The improvement in the dielectric constant with addition of V_2O_5 and sintering temperature are due to uniform grain growth and large grain size. The maximum dielectric constant of 17.3 is observed for $x = 1.5$ wt% samples, sintered at 1100°C .

The product of quality factor (Q) and resonance frequency (f_0) is the tool for evaluating the performance of a dielectric resonator material. Figure 3.14(a) demonstrates the variation in $Q \times f_0$ values for $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ ceramics as a function of δ concentration ($\delta = 0 - 0.15$) at different sintering temperatures. The $Q \times f_0$ exhibits similar behavior as that of relative density and dielectric constant as a function of δ concentration and as well as sintering temperature. Nevertheless, the obtained $Q \times f_0$ values were in the range 59 - 161 THz for the $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ samples, sintered in the sintering temperature range of $1250 - 1400^\circ\text{C}$. In general, the microwave dielectric losses arise from the two mechanisms (i) intrinsic and (ii) extrinsic losses [29, 30]. Intrinsic losses arise due to the anharmonic forces that mediate the interaction between crystal lattice modes and electromagnetic radiation, which leads to damping of the optical phonons. On the other hand, extended dislocations, grain boundaries, grain size, densification or porosity, oxygen vacancies, secondary phases and sample processing conditions are responsible for the extrinsic losses. At lower δ concentration, the lower $Q \times f_0$ values are due to the presence of MgTi_2O_5 ($Q \times f_0 \sim 47,000$ GHz), which deteriorates the microwave dielectric properties of the MTO ceramics. However above $\delta = 0.07$, samples exhibited low $Q \times f_0$ values even the secondary phase Mg_2TiO_4 ($Q \times f_0 \sim 150,000$ GHz) has comparable $Q \times f_0$ with MTO. This is attributed to the reduction in grain size and the presence of pores (see Figure 3.9(d)) in the prepared samples. In the present case, secondary phase and grain size significantly influenced the microwave dielectric properties of the MTO ceramics. The maximum $Q \times f_0$ value of 161 THz is obtained for the $\delta = 0.07$ sample, sintered at 1350°C is owing to the formation of phase pure MgTiO_3 with larger grain size and maximum relative densities. Djuniadi *et al.* [31] reported that the increase in average grain size reduces the porosity and the grain boundary area which controls the microwave loss of the ceramics. Because, grain boundary is a plane defect as a result microwave dielectric loss increases.

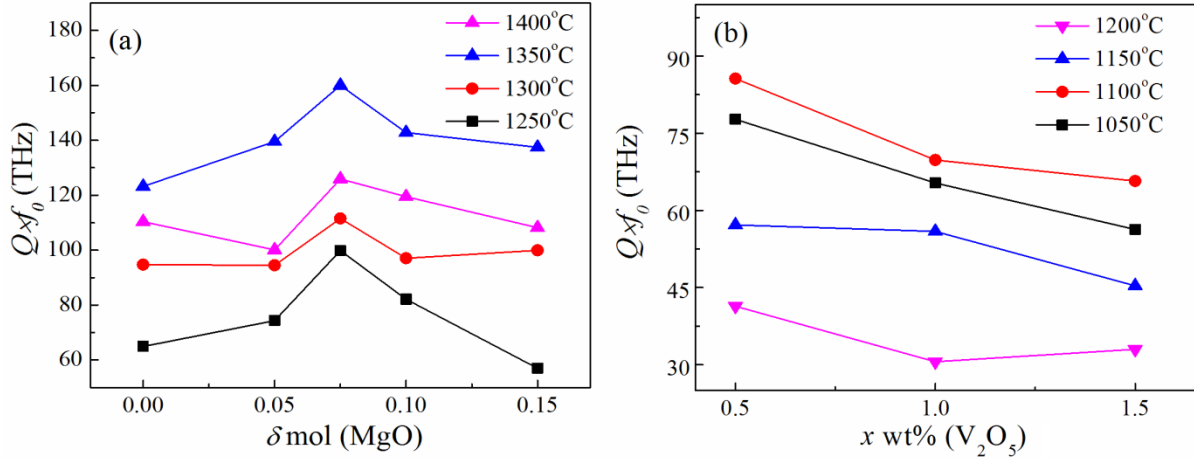


Figure 3.14: Variation in $Q \times f_0$ for (a) $\text{Mg}_{1+\delta}\text{TiO}_{3+\delta}$ as a function of δ concentration and (b) $\text{Mg}_{1.07}\text{TiO}_{3.07}$ as a function of x wt% at different sintering temperatures.

Figure 3.14(b) shows the V_2O_5 dependent $Q \times f_0$ values for $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics, sintered at different temperatures. The $Q \times f_0$ values follow the similar trend as that of relative density and dielectric constant with sintering temperature and opposite trend with x wt%. The pure $\text{Mg}_{1.07}\text{TiO}_{3.07}$, sintered at 1100°C exhibits very low $Q \times f_0$ value of 42 THz at 9.3 GHz. Interestingly, with the addition of V_2O_5 , the $Q \times f_0$ values decreases even though the grain size of the sample are large. The obtained $Q \times f_0$ values were in the range 30.6 - 85.6 THz for the $\text{Mg}_{1.07}\text{TiO}_{3.07}$ ceramics, sintered in the temperature range of 1050-1200°C. For $x = 0.5$ wt% of V_2O_5 , the maximum $Q \times f_0$ of 85.6 THz is obtained at 1100°C. The improvement in the $Q \times f_0$ with lower wt% addition of V_2O_5 is due to reduction in oxygen vacancies by the substitution of V^{5+} with Ti^{4+} which is confirmed from the XRD results. When a V^{5+} ion substitutes for a Ti^{4+} , V^{5+} ion introduces one extra positive charge. A single positive charge is eliminated from the sample to maintain the electroneutrality and acts as a donor, the reaction can be expressed as [27]



The reduction in oxygen vacancies influence the anharmonic interaction: consequently, there is an increase in $Q \times f_0$. Similar reports are available on the improvement in $Q \times f_0$ with the addition of V_2O_5 to $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$ and Mg_2TiO_4 ceramics [26, 32]. With the increase in the V_2O_5 addition, the decrease in $Q \times f_0$ values can be due to the presence of V - rich liquid phase

at grain boundary and abnormal grain growth, which is confirmed from SEM images and EDS spectra. Ferreira *et al.* [33] reported that a smaller concentration of pentavalent oxides improves the $Q \times f_0$ values in MTO ceramics. The $Q \times f_0$ values obtained in this case are much higher than the MTO ceramics added with V₂O₅ - Bi₂O₃ [34]. From the above results the excess of Mg doping and V₂O₅ addition have greatly influenced the microwave dielectric properties of MTO ceramics.

3.5 Conclusions

- We successfully prepared single phase MgTiO₃ ceramics by mechanochemical synthesis and by the addition of excess MgO to MTO ceramics by solid state reaction method by optimizing the processing conditions.
- In the mechanochemical method, the dielectric constant and $Q \times f_0$ values were in the range of 15.85 to 18.52 and 61.5- 162.3 THz, respectively. The increase in $Q \times f_0$ values was attributed to the increased uniform grain size and maximum relative density.
- The best microwave dielectric properties of $\epsilon_r \sim 18.52$, $Q \times f_0 \sim 162$ THz were obtained for the samples milled for 30 h and sintered at 1350°C.
- On the other hand, samples prepared with at $\delta = 0.07$ exhibits a single-phase MTO and exhibits a secondary phase of MgTi₂O₅ (Mg₂TiO₄) for below (above) $\delta = 0.07$.
- The optimum microwave dielectric properties of $\epsilon_r \sim 17.68$, $Q \times f_0 \sim 161$ THz at 9.4 GHz were obtained for $\delta = 0.07$ samples, sintered at 1350°C for 3 h is attributed to the larger grain size, phase pure MgTiO₃ and highest relative density.
- The addition of V₂O₅ not only decreased the sintering temperature of about 300°C but also improved the grain growth of Mg_{1.07}TiO_{3.07} ceramics due to the formation of liquid phase.
- The good dielectric properties of $\epsilon_r \sim 15.8$ and $Q \times f_0$ of 85.6 THz at 9.3 GHz were obtained for the MTO ceramics doped with V₂O₅ sintered at 1100°C.
- Low concentration of V₂O₅ improves the $Q \times f_0$ of MTO and is attributed to the reduction in oxygen vacancies.

3.6 References

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The logo of the Indian Institute of Technology Guwahati is a circular emblem. It features a central stylized 'S' or 'Om' symbol composed of three interlocking circles. The outer ring of the logo contains the text 'Indian Institute of Technology Guwahati' in English and its Hindi equivalent 'भारतीय प्रौद्योगिकी संस्थान गुवाहाटी' in Devanagari script.

Chapter 4
*Effect of Additives on Microwave Dielectric Properties
of MgTiO_3 Ceramics*

MgTiO_3 (MTO) is one of the promising dielectric materials being used as dielectric resonators in microwave and in type-1 capacitor applications. Generally, MTO ceramics were prepared by solid-state route, which requires higher sintering temperature; as a result it limits their practical applications. Several approaches have been adopted to reduce the sintering temperature of microwave ceramics such as chemical processing [1], addition of glassy phases [2], liquid phase sintering [3] and by use of smaller particle as starting materials [4]. The additives which are used to improve sinterability should not degrade the microwave dielectric properties. Hence it is necessary to optimize the concentration and additive and the processing parameters to achieve best microwave dielectric properties at lower sintering temperatures, and hence this study.

4.1 Brief literature review of MgTiO_3 processing

4.1.1 Low temperature sintering of MTO ceramics by chemical processing

In order to improve the microwave dielectric properties of MTO ceramics, expensive and energy consuming physical treatments are generally needed. Therefore, wet chemical methods such as sol-gel and auto-igniting combustion were developed to obtain ultra fine and homogeneous powders which exhibit maximum densities at lower sintering temperatures.

Miao *et al.* [5] investigated the processing and microwave characteristics of pure MTO ceramics by sol-gel technique using metal nitrate and butyl titanates as starting materials. The prepared MgTiO_3 nano-powders have been calcined at 600°C . The dense pellets showed the microwave properties of $\epsilon_r = 16.6$, $Q \times f_0 = 62,600 \text{ GHz}$ ($f_0 = 7 \text{ GHz}$) and $\tau_f = -41 \text{ ppm}/^\circ\text{C}$ at 1200°C . Wu *et al.* [6] prepared uniform MTO nanoparticle using aqueous sol-gel method. They reported that, the higher the specific surface area of MTO powders enhances the densification and improves the microwave dielectric properties ($\epsilon_r = 17.8$, $Q \times f_0 = 156,300 \text{ GHz}$ and $\tau_f = -44.2 \text{ ppm}/^\circ\text{C}$). Suresh *et al.* [7] studied the synthesis and characterization of MTO ceramics through auto - igniting combustion method. This method has two advantages. (a) Reaction takes place at low temperatures and (b) the obtained particle size distribution is narrow. The samples prepared by this method were sintered at 1200°C for 3 h. However, the prepared samples exhibited inferior microwave dielectric properties of $\epsilon_r = 16.7$, $Q \times f_0 = 73,700 \text{ GHz}$ at 6.5 GHz and $\tau_f = -44.2 \text{ ppm}/^\circ\text{C}$.

Wang *et al.* [8] prepared B₂O₃ doped MTO ceramics by using sol-gel method from Mg(NO₃)₂·6H₂O, Ti(C₄H₉O)₄ and H₃BO₄, ethanol and acetic acid. The particle size was in the range of 20 - 120 nm and sintered at 1100°C. The dielectric properties of the samples were found to be $\epsilon_r = 17.63$, $Q \times f_0 = 33,768$ GHz and $\tau_f = -48$ ppm/°C these Q values are rather low. Partasarathy *et al.* [9] prepared MTO nanopowders with 20 - 40 nm crystallite sizes using co - precipitation method. However, the microwave dielectric properties were not reported. Ferreira *et al.* [10] prepared MTO ceramics from pechini method (chemical route). They reported MTO ceramics sintered below 1150°C and the dielectric properties were $\epsilon_r = 17.5$, $Q = 21,200$ at 8 GHz.

4.1.2 Low temperature sintering with liquid - phase sintering aids

In the quest for improving sinterability of MTO without degrading the dielectric properties many sintering aids were identified. It is well known that, it is difficult to fully densify the MTO ceramics using solid-state reaction method. Therefore, sintering aids have been invariably added to achieve maximum densification at temperatures between 1000 - 1400°C. Bernard *et al.* [11] reported the sintering temperature of MTO ceramics as 950°C with the addition of Li-based salts. Belnou *et al.* [12] studied the addition of bismuth based supplements such as Bi₂O₃ - B₂O₃ and Bi₄Ti₃O₁₂ to MTO ceramics and reported sintering temperature below 1000°C from the dilatometric curves. However, they did not report the dielectric properties. Tseng *et al.* [13] reported 1.5 wt% CuO added Mg(Zr_{0.05}Ti_{0.95})TiO₃ sintered at 1300°C due to liquid phase sintering effect. The reported dielectric properties were $\epsilon_r = 20.6$, $Q \times f_0 = 223,000$ GHz.

Microwave ceramics are increasingly used for resonators, filters, duplexers and antenna systems for wireless communications. Especially, multilayer microwave devices are being investigated to let those devices increase volume efficiency. Multilayer chip inductors (MLCI) are one of the key surfaces mounted devices and have been extensively developed in recent years. These components are fabricated by lamination of ferrite and Ag electrode paste alternately and then co - fired to form a monolithic structure [14]. To keep up with the trend in miniaturization of electronic devices and related components, particularly with the rapid development of integrated circuits and surface mounting technology, the demand for multilayer ceramic capacitors is increasing drastically [15]. Accordingly, low temperature co-

fired ceramics (LTCC) technology becomes more important for cost effectiveness. Often LTCC is used as a substitute for multi chip modules (MCM). Integration proceeds by combining thick film and LTCC materials [16]. The sintering temperatures of microwave dielectrics such as MTO are too high to use low melting point electrodes. It was imperative to lower the sintering temperature of these microwave ceramics in order to use silver or copper electrodes. i.e., the sintering temperature of co firing with high conductivity metals should be lower than the melting temperature of Ag (961°C) or Cu (1064°C) [17-19].

Zhang *et al.* [20] reported MTO ceramics with 5.0mol% Bi_2O_3 - 7mol% V_2O_5 additions and were sintered at 875°C . The reported microwave dielectric properties were $\epsilon_r = 20.6$, $Q \times f_0 = 10,240$ GHz at 6.3 GHz. Furthermore, same group reported with the addition of 6 wt% CuO - Bi_2O_3 - V_2O_5 the sintering temperature of MTO ceramics were lowered to 900°C . These samples exhibited the dielectric properties of $\epsilon_r = 18.1$, $Q \times f_0 = 20,300$ GHz and $\tau_f = -57$ ppm/ $^\circ\text{C}$ [21]. The low sintering temperature for the above additives is due to the liquid phase sintering effect. However, the quality factor for these samples was very low. Nonetheless, the microwave dielectric properties, especially $Q \times f_0$ values are significantly degraded with these additives.

It is well known that the additives and their concentration play an important role on the densification, microstructure and on the microwave dielectric properties, especially on the quality factor of the MTO ceramics. In the present study CeO_2 nanoparticles (Smaller initial particle size), low melting additives Bi_2O_3 and La_2O_3 oxides were added to MTO ceramics to see their effect on the sinterability, microstructure and on the microwave dielectric properties of MTO ceramics.

4.2 Experimental Details

MgTiO_3 ceramics were prepared by the conventional solid-state reaction method using the high-purity oxide powders ($> 99.99\%$): MgO and TiO_2 (Sigma Aldrich, USA). The starting materials were combined according to the stoichiometry of MgTiO_3 , and the mixture was grinded under distilled water for 5 h by using a planetary ball mill (Fritsch GmbH, Germany). The prepared mixtures were dried and calcined at 1100°C for 2 h in air. The calcined powders were re - milled with an inclusion of 0.5, 1.0 and 1.5 wt% of different

additives such as CeO₂ nanoparticles or La₂O₃ or Bi₂O₃ (Sigma Aldrich, USA). The CeO₂ nanoparticles with an average particle size of 80 nm were procured from M/S Alfa Aesar, USA. Further, the powders were added with an organic binder (PVA) and pressed into pellets with 10 mm in diameter and 4 - 5 mm in thickness under a pressure of 2000 Kg/cm² isostatically. The pellets were subsequently sintered at 1100 - 1400°C for 3 h in air. To optimize the annealing conditions, pure and CeO₂ nanoparticle added samples were annealed separately at 1000°C, 1100°C and 1200°C for 48 h followed by a cooling rate of 1°C per minute.

4.3 Effects of CeO₂ nanoparticles and annealing temperature on MTO ceramics

4.3.1 Crystal structure

The XRD patterns of $x = 0.0$ wt% MgTiO₃ ceramics sintered at 1400°C and with $x = 0.5$ to 1.5 wt%, sintered at 1300°C for 3 h are shown in Figure 4.1(a) and for $x = 0$ to 1.5 wt% annealed at 1100°C for 48 h are shown in Figure 4.1(b). It is observed that the samples with $x = 0$ wt% reveal MgTiO₃ as a main crystalline phase along with a minor secondary phase of MgTi₂O₅. On the other hand, the secondary phases for the MTO ceramics with $x = 0.5$ to 1.5 wt% are found to be Ce₂TiO₅ and MgTi₂O₅. The crystal structure of MgTiO₃ is found to be trigonal (ICDD # 06-0464). The intensity of the peaks corresponding to Ce₂TiO₅ phase is found to enhance with an increase in x wt%. MgTi₂O₅ usually forms as an intermediate phase, and it is difficult to eliminate in the samples prepared by the mixed oxide route. The MgTi₂O₅ phase exhibits a dielectric constant of 17, $Q \times f_0$ value of 41,000 GHz (at 9 GHz) and a τ_f value of -66 ppm/°C [22]. The lattice constants of pure and MTO + x wt% ceramics were calculated. No appreciable variations in lattice constants with an increase in x wt% are observed and it suggests that CeO₂ nanoparticles are not forming a solid solution with MTO matrix and the obtained lattice constants of the as prepared and annealed samples are tabulated in Table 4.1. This is expected due to the mismatching of ionic radii of Ce⁴⁺ ions (1.02 Å) with Mg²⁺ (0.72 Å) and Ti⁴⁺ (0.605 Å) ions. Hence the Ce⁴⁺ ion can not be substituted in the Mg²⁺ and Ti⁴⁺ sites. The annealing gives rise to reduction in the intensity of XRD peaks of MgTi₂O₅ impurity phase in $x = 0$ sample and the intensities of both Ce₂TiO₅

and MgTi_2O_5 impurity phases in $x = 0.5$ wt% samples. However, the intensities of Ce_2TiO_5 and MgTi_2O_5 phases are found to increase up on annealing for $x = 1.0$ and 1.5 wt%.

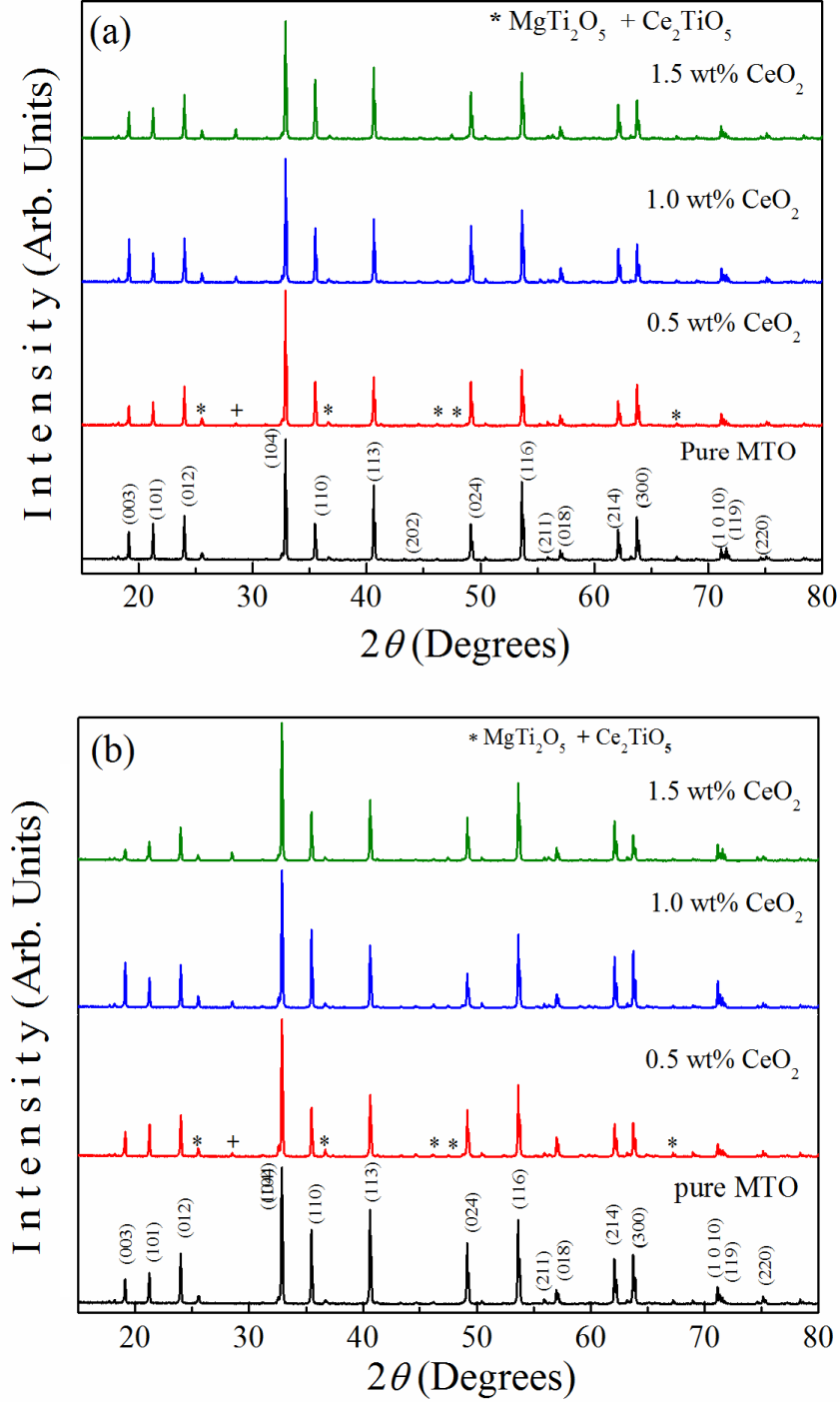


Figure 4.1: X-ray diffraction patterns of MTO ceramics with $x = 0.0 - 1.5$ wt% (a) before annealing (b) after annealing.

Table 4.1: The calculated lattice constants of the as - prepared and annealed samples

Composition	Obtained lattice parameters (Å)	
As prepared		
Pure MTO	a = b = 5.0547 (11)	c = 13.9003 (07)
MTO+0.5 wt% of CeO ₂	a = b = 5.0554 (08)	c = 13.9001 (09)
MTO+1.0 wt% of CeO ₂	a = b = 5.0562 (13)	c = 13.9010 (11)
MTO+1.5 wt% of CeO ₂	a = b = 5.0559 (07)	c = 13.9008 (13)
After annealing		
Pure MTO	a = b = 5.0554 (07)	c = 13.9000 (12)
MTO+0.5 wt% of CeO ₂	a = b = 5.0561 (14)	c = 13.9012 (07)
MTO+1.0 wt% of CeO ₂	a = b = 5.0555 (06)	c = 13.9014 (08)
MTO+1.5 wt% of CeO ₂	a = b = 5.0543 (12)	c = 13.9009 (10)

4.3.2 Relative density

The relative densities of MTO ceramics sintered at different sintering temperatures with $x = 0.0 - 1.5$ wt% were measured using the Archimedes method and are given in Table 4.2. The improvement in the relative densities of MTO ceramics with an increase in x wt% is observed with the increase in the sintering temperature up to 1300°C , and beyond that it is found to decrease. However, pure MTO ceramics exhibited the maximum density of 97.5 % of theoretical density only at 1400°C . Further, the values of relative density of MTO ceramics are found to decrease with an increase in x wt% beyond $x = 0.5$ wt%. The maximum relative density of 97.4% was obtained for the sample with $x = 0.5$ wt%, and sintered at 1300°C . The relative density values are found to be in the range of 97.5 to 94.2% for all the samples sintered in the temperature range of $1250 - 1400^\circ\text{C}$. The optimum sintering temperature for the maximum relative densities for MTO + x wt% ceramic is 1300°C and the reduced density for the samples sintered above 1300°C could be due to the possible evaporation of CeO_2 nanoparticles, secondary phases and non-uniform grain growth (SEM image Figure 4.2(d)). The reduction in sintering temperature can be explained as follows: It is known that nanoparticles have more surface to the volume ratio than the bulk materials, and the higher surface energy lowers the melting point [23]. Moreover, sintering velocity is inversely

proportional to particle size, i.e., sintering is faster for the finer particles. In addition, the sintering velocity gets enhanced, when the diffusion across the grain boundary increases. Therefore, during the sintering process, surface defect atoms of powders tend to become normal atoms with lower energy within the crystalline grains.

Table 4.2: Relative density, measured microwave dielectric constant (ϵ_r) and dielectric constant corrected for porosity (ϵ_m) values of pure and MTO ceramics added with CeO_2 nanoparticles.

Material composition	Sintering temperature	Percentage of relative density	ϵ_r (measured)	ϵ_m (corrected)
MgTiO_3	1400°C	97.50	17.21	17.82
	1350°C	95.90	17.04	17.70
	1300°C	95.10	16.95	17.80
	1250°C	94.22	16.80	17.95
$\text{MgTiO}_3 + 0.5$ wt% of CeO_2 nanoparticles	1400°C	96.50	16.70	17.54
	1350°C	96.66	16.96	17.80
	1300°C	97.40	17.12	17.76
	1250°C	95.05	16.69	17.91
$\text{MgTiO}_3 + 1.0$ wt% of CeO_2 nanoparticles	1400°C	95.56	16.60	17.67
	1350°C	96.05	16.67	17.63
	1300°C	96.47	16.77	17.63
	1250°C	95.58	16.52	17.59
$\text{MgTiO}_3 + 1.5$ wt% of CeO_2 nanoparticles	1400°C	95.07	16.52	17.72
	1350°C	95.59	16.58	17.65
	1300°C	95.97	16.59	17.56
	1250°C	95.25	16.35	17.49

When the CeO_2 nanoparticles (80 nm) were added to MTO powders (1.2 μm), the high temperature accommodates external activation energy to release the internal energy contained in powders thus enabling the mass transfer and reduction in surface energy [24]. Similar studies of reduction of sintering temperature by the addition nanoparticles were

reported by Pamu *et al.* [25], and Shanker *et al.* [26]. In order to prove the effect of CeO_2 nanoparticles, we have also prepared by adding bulk CeO_2 powder (average particle size is $\sim 1.5 \mu\text{m}$) of different wt% and by sintering at 1300°C and 1350°C . It is found that the densities of these samples are found to be in the range of 82 - 88%. Thus, CeO_2 nanoparticles play a crucial role in enhancing the density of MTO ceramics.

4.3.3 Microstructural analysis

The SEM images of pure MTO ceramics, sintered at 1400°C is shown in Figure 4.2(a) and MTO ceramics with $x = 0.5 - 1.5 \text{ wt\%}$, sintered at 1300°C for 3 h are shown in Figure 4.2(b-d).

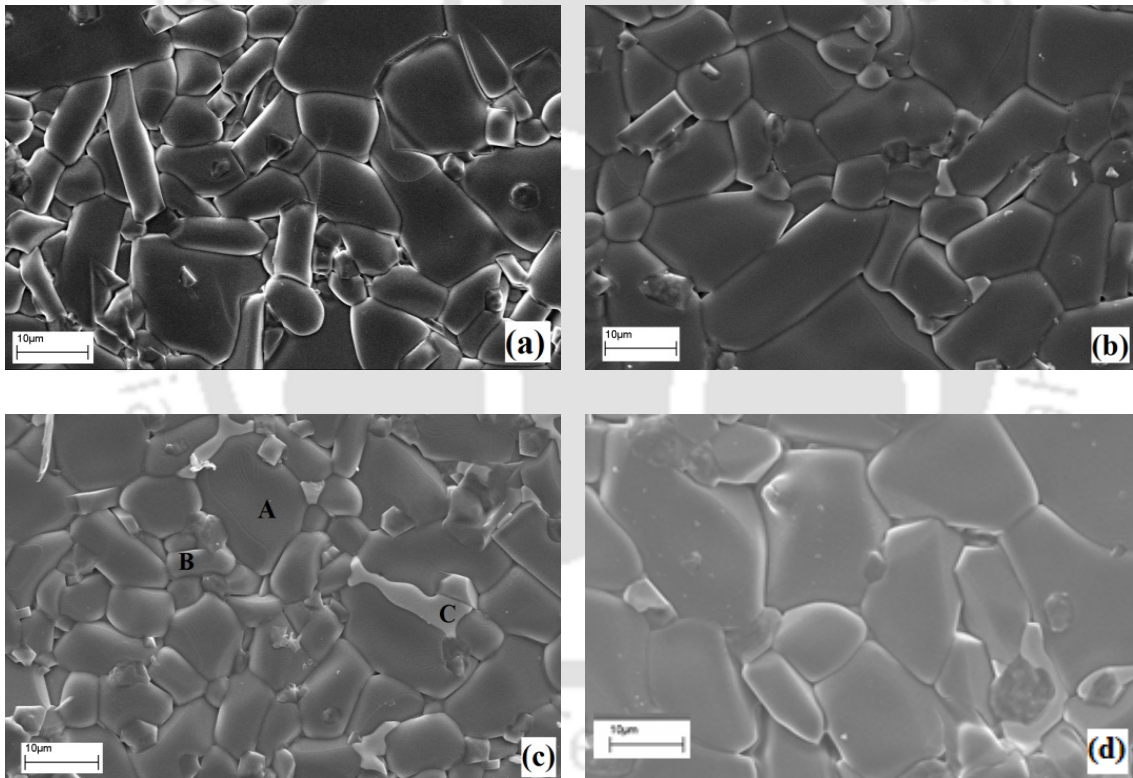


Figure 4.2: SEM images of (a) pure MTO ceramics sintered at 1400°C and MTO - CeO_2 ($x \text{ wt\%}$) ceramics with (b) $x = 0.5$, (c) $x = 1.0$ and (d) $x = 1.5$, sintered at 1300°C .

The microstructures revealed that all the samples are crack free and highly densified and the samples with $x = 0.5 \text{ wt\%}$ exhibited a microstructure with mixed grain sizes. Further, as the $x \text{ wt\%}$ increases, grain morphology of dense MTO ceramics exhibited two different

types of grains: at the grain boundary of the large grains, a segregation of brown and white colored grains was observed. In order to understand the chemical compositions of these contrast phases, EDS analysis was performed. The chemical composition for $\text{MTO} + x = 1.0$ wt% (Figure 4.2(c)) contrast phases obtained from EDS is shown in Table 4.3. The larger grains (spot A) exhibit the chemical composition of MgTiO_3 , whereas the chemical compositions of spot B and spot C correspond to MgTi_2O_5 and Ce_2TiO_5 , respectively. Further, as the amount of x wt% increases, magnitude of the secondary phase is intensified, and the grain growth is non uniform. The average grain sizes of the sintered specimens for $x = 0.5, 1.0, 1.5$ wt% are 8.7, 7.1 and 9.7 μm , respectively.

Table 4.3: EDS spectra of as prepared MTO ceramics with $x = 1.0$ wt%, sintered at 1300°C .

Spot	Atom (%)			
	Mg K	Ti K	Ce L	O K
A	19.66	19.79	-	60.55
B	12.21	23.93	-	63.86
C	-	11.86	24.95	63.19

To see the effect of annealing on the microstructure of $\text{MTO} + x = 0.0 - 1.5$ wt%, SEM micrographs of the samples were obtained. The microstructures of MTO ceramics annealed at 1100°C are shown in Figure 4.3(a-d) for different values of x . Where (a) corresponds to pure and MTO ceramics, (b) with $x = 0.5$, (c) with $x = 1.0$ and (d) with $x = 1.5$ wt%, respectively. Pure MTO ceramics did not show any noticeable change in the microstructure. However, in the case of MTO ceramics with $x = 0.5 - 1.5$ wt%, segregation of secondary phases at the grain boundary was clearly observed. The chemical compositions of contrast phases obtained from EDS for $\text{MTO} + x = 1.0$ wt% (Figure 4.3(c)) annealed at 1100°C for 48 h is shown in Table 4.4. During the annealing process, the secondary phases were segregated on to the surface of the samples through the grain boundary which is confirmed from SEM images (Figure. 4.3(b-d)). This is in good agreement with the earlier reports on similar systems [27]. Further, in the case of as prepared samples, all the secondary phases may be dispersed /suppressed in MTO matrix. After annealing, the secondary phases precipitated on to the surface of MTO ceramics.

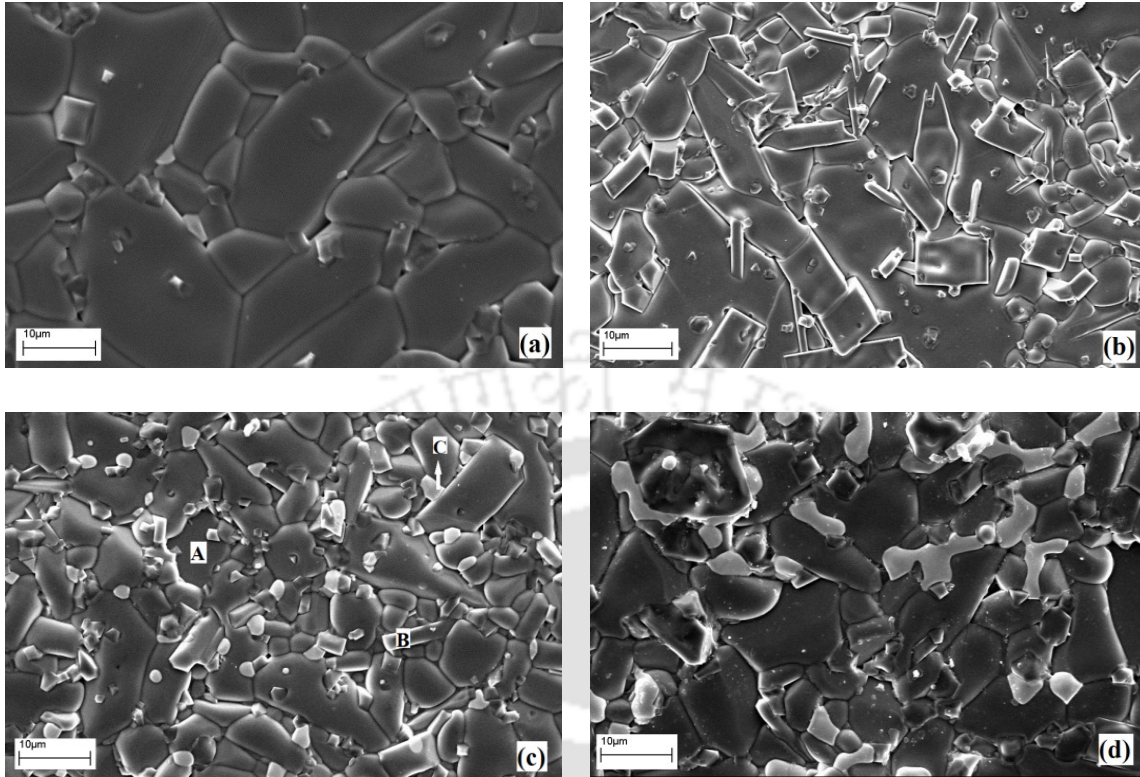


Figure 4.3: SEM images of MTO ceramics with $x = 0.0 - 1.5$ wt% annealed at 1100°C for 48 h (a) Pure MTO ceramics and MTO- CeO_2 ceramics with (b) $x = 0.5$ wt%, (c) $x = 1.0$ wt% and (d) $x = 1.5$ wt%.

Table 4.4: EDS spectra of MTO ceramics with $x = 1.0$ wt% CeO_2 nanoparticles, sintered at 1300°C and annealed at 1100°C for 48 h.

Spot	Atom (%)			
	Mg K	Ti K	Ce L	O K
A	19.45	19.23	-	61.32
B	13.23	24.91	-	61.86
C	-	11.98	25.32	62.90

4.3.4 Microwave dielectric properties

To comprehend the influence of CeO_2 nanoparticles on MTO ceramics, microwave dielectric properties were measured. The measured dielectric constants and the porosity corrected dielectric constants are tabulated in Table 4.2. As the sintering temperature

increases up to 1300°C, the dielectric constant increases and beyond that it decreases. Further, pure MTO ceramics exhibit the maximum value of dielectric constant only after sintering at 1400°C. On the other hand, MTO with $x = 0.5$ wt% showed the highest value of dielectric constant after sintering at 1300°C. The relationship between ϵ_r and sintering temperature follows the same trend as that of relative density Vs. sintering temperature, and it shows the dependence of dielectric constants with relative densities. The measured values of dielectric constants are in the range of 16.35 - 17.21. To see the effect of porosity on the dielectric constant, the measured values of the microwave dielectric constants corrected for porosity using the following equation:

$$\epsilon_r = \epsilon_m \left(1 - \frac{3P(\epsilon_m - 1)}{2\epsilon_m + 1} \right) \quad (4.1)$$

where ϵ_m is the dielectric constant corrected for porosity, ϵ_r is the experimental dielectric constant and P is the fractional porosity [28]. The obtained values are tabulated in Table 4.2.

The dependence of $Q \times f_0$ values of MTO + x wt% ceramics as a function of sintering temperatures are shown in Figure 4.4(a). The $Q \times f_0$ values of pure MTO ceramics are found to increase with an increase in sintering temperature, and the maximum value is achieved at 1400°C. However, for MTO with $x = 0.5 - 1.5$ wt% the best $Q \times f_0$ value is obtained for samples sintered at 1300°C. The trend of relative density as a function of sintering temperature is found to comparable to that of $Q \times f_0$. The maximum $Q \times f_0$ values obtained for the pure MTO and MTO+ $x = 0.5$ wt% were found to be 140.8 and 140.3 THz, respectively. Besides, it is also observed that for a particular sintering temperature the value of $Q \times f_0$ is found to decrease with the increase in x wt%, and it is due to the presence of secondary phase of Ce₂TiO₅. Further, it is also noticed that $Q \times f_0$ values did not show considerable dependence on average grain sizes.

To optimize the annealing conditions, four sets of samples with maximum relative densities and the best microwave dielectric properties (pure MTO sintered at 1400°C and MTO + $x = 0.5 - 1.5$ wt% sintered at 1300°C) were chosen. Each set was annealed at 1000, 1100 and 1200°C for 48 h separately. After annealing, the microwave dielectric properties

were measured again. It was found that the best microwave dielectric properties were obtained for the samples annealed at 1100°C . It was observed that the samples annealed at 1100°C exhibited the maximum $Q \times f_0$ values compared with other conditions and the measured $Q \times f_0$ values are depicted in Figure 4.4(b). The variations of $Q \times f_0$ as a function of sintering temperature after annealing at 1100°C for $\text{MTO} + x \text{ wt}\%$ ceramics are shown in Figure 4.4(c). No significant change in relative density and dielectric constant values were observed upon annealing whereas $Q \times f_0$ values strongly affected. On annealing, pure MTO ceramics exhibited large $Q \times f_0$ values compared to MTO ceramics with $x \text{ wt}\%$ and they are found to be in the range of 59.9 to 165.5 THz. It is interesting to note that as prepared pure MTO ceramics and MTO with $x = 0.5 \text{ wt}\%$ exhibit almost the same dielectric properties. Nevertheless, on annealing, pure MTO ceramics exhibited the best microwave dielectric properties as compared to MTO with $x \text{ wt}\%$.

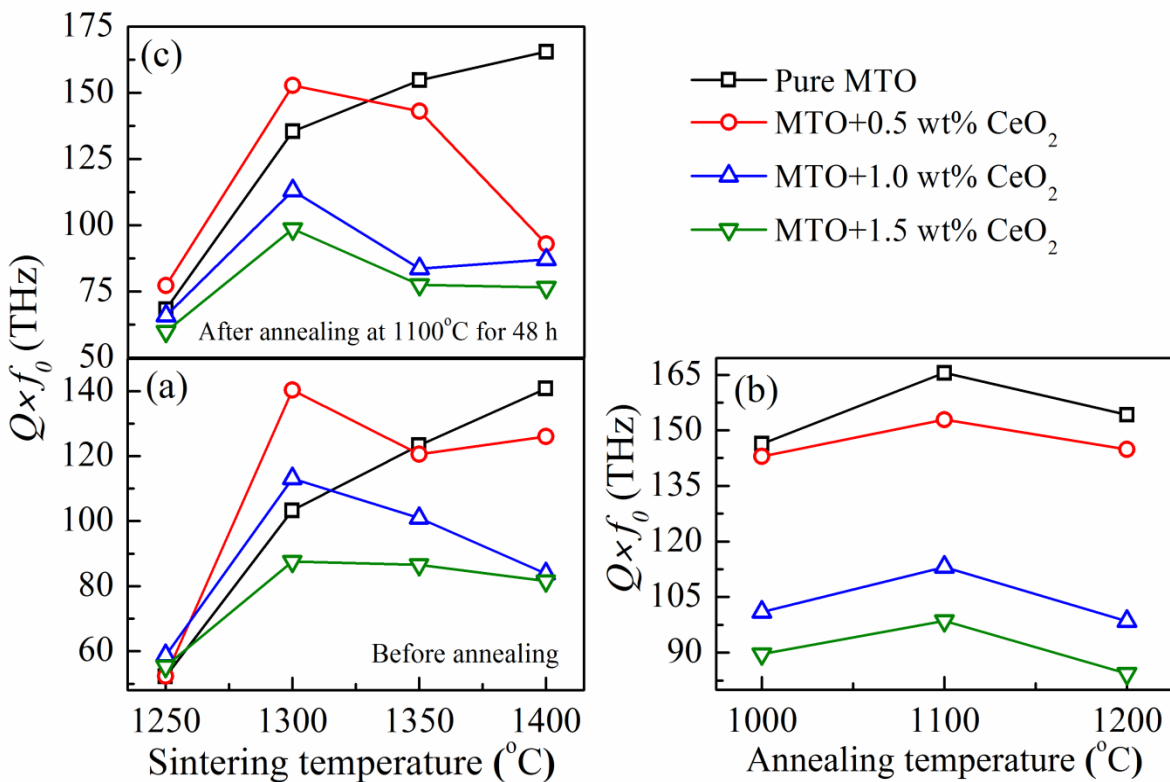


Figure 4.4: Variation in (a) $Q \times f_0$ values and (b) $Q \times f_0$ values of the samples used to optimize the annealing temperature, (c) $Q \times f_0$ values after annealing as a function of sintering temperature for MTO ceramics added with $x = 0.0 - 1.5 \text{ wt}\%$.

In order to understand the effect of the strain on the $Q \times f_0$ values, the strain in the samples was estimated using the Williamson-Hall plot method. The strain values of the samples correspond to the as prepared and the annealed samples are found to be in the order of 10^{-3} and 10^{-4} , respectively. Further, it is well known that the slow rate of cooling improves the $Q \times f_0$ values [29]. The strain values in the annealed samples are found to be lower compared to those of the as prepared samples, and it could influence the dielectric loss. The improvement in $Q \times f_0$ values of pure MTO ceramics after annealing can be described as follows: When MTO ceramics are sintered at elevated temperatures, oxygen loss occurs due to the defect equilibrium. Further, these oxygen vacancies may trap the electrons which partially reduce Ti^{4+} to Ti^{3+} as expressed as follows,



The above equations imply that the frozen defects of oxygen vacancies, electrons and Ti^{3+} produced during the sintering process are a result of oxygen loss. On annealing, these oxygen vacancies would be reduced, and it leads to increase in $Q \times f_0$ values [30 - 33]. In addition, the increase in $Q \times f_0$ values can also be attributed to the relaxation of strain and slow cooling rate [29]. On annealing, the microwave dielectric loss in pure MTO ceramics considerably is decreased as compared to MTO ceramics with CeO₂ nanoparticles. The increase in microwave dielectric loss is due to the precipitation and diffusion of secondary phases during the annealing process.

The temperature coefficient of resonant frequency (τ_f) is known to be related to the composition and the presence of secondary phase in the material. The pure MTO exhibited a negative value of τ_f -49 ppm/°C and the τ_f values for the samples with the addition of CeO₂ nanoparticles are in the range of - 30 to - 44 ppm/°C. The variations in the τ_f values can be attributed to the presence of secondary phases.

4.4 Effects of Bi_2O_3 and La_2O_3 additions on MTO ceramics

4.4.1 Crystal structure

Figure 4.5(a) and (b) shows the XRD patterns of MTO ceramics added with ($x = 0.5$, 1.0 & 1.5 wt% of Bi_2O_3) Bi_2O_3 , sintered at 1200°C and ($y = 0.5$, 1.0 & 1.5 wt% of La_2O_3) La_2O_3 sintered at 1300°C , respectively.

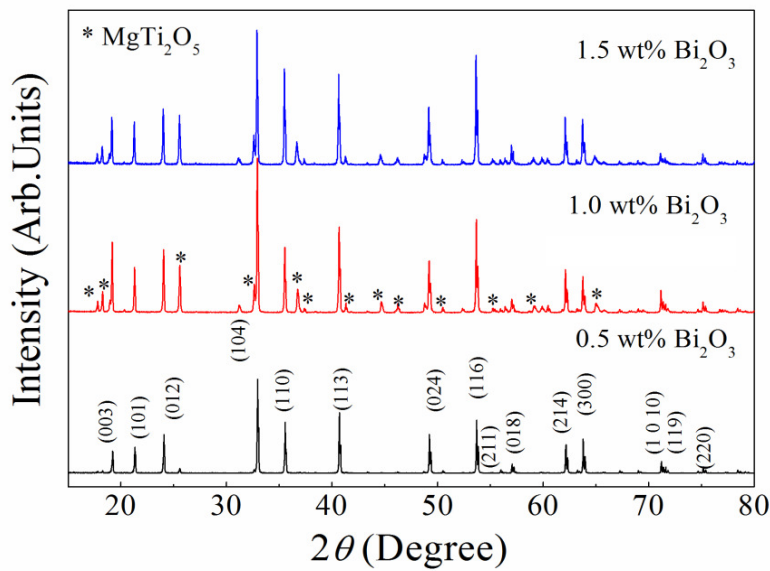


Figure 4.5(a): XRD patterns of the MTO ceramics added with different wt% of Bi_2O_3 and sintered at 1200°C .

It was observed that all the samples were exhibited trigonal MgTiO_3 as main crystalline phase (ICDD: 06-0464) and MgTi_2O_5 as a minor secondary phase. Moreover, with an increase in wt% of the additives, the percentage of secondary phases also increased. However, the MTO ceramics added with $x = y = 0.5$ wt% of Bi_2O_3 or La_2O_3 exhibited only two negligible peaks of MgTi_2O_5 , with the further addition in the additional wt%, the number of secondary planes of phases increased beside their peak intensities. MgTi_2O_5 usually formed as minor phase and is difficult to eliminate completely from the samples prepared by the mixed oxide route. Furthermore, the determined lattice constants of the MTO ceramics supplemented with these additives revealed that there is no deviation for the values compared to pure MTO ceramics, because the ionic radii of the La^{3+} and Bi^{3+} is larger than the Mg^{2+} .

and Ti^{4+} . This implies that these additives do not enter crystal lattice of MTO matrix, but remained at the grain boundary.

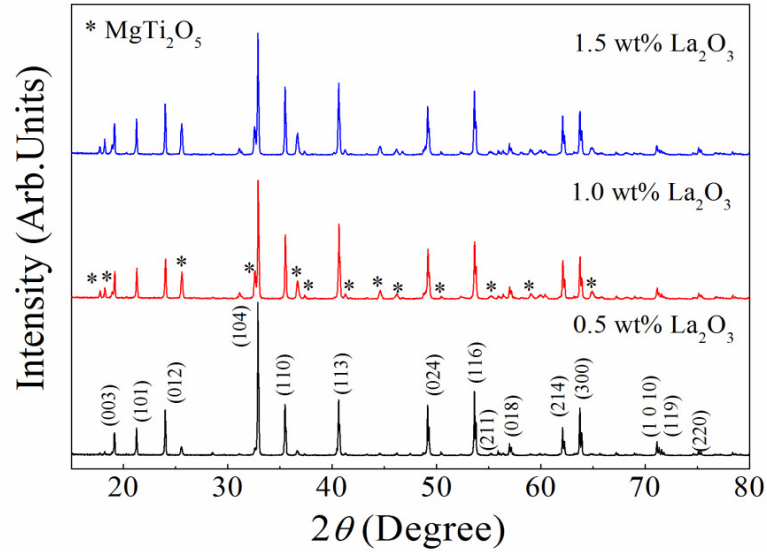


Figure 4.5(b): XRD patterns of the MTO ceramics added with different wt% of La_2O_3 and sintered at 1300°C .

4.4.2 Microstructure of MTO ceramics added with Bi_2O_3 and La_2O_3

To perceive the effect of these additives on the microstructure of MTO ceramics, micrographs of the samples were obtained by SEM. Figure 4.6(a-c) and Figure 4.7(a-c), shows the SEM images of the MTO ceramics added with $x = 0.5 - 1.5$ wt% of Bi_2O_3 and $y = 0.5 - 1.5$ wt% of La_2O_3 , respectively. In both the cases, it was observed that all the samples were crack free and exhibited uniform dense microstructures. The mean grain sizes of the samples added with Bi_2O_3 were found to decrease with an increase in Bi_2O_3 wt% whereas the MTO ceramics with La_2O_3 exhibited larger average grain sizes with an increase in its concentration. In addition, the samples added with $x = 0.5$ wt% exhibited larger average grain sizes with identical microstructures while the samples with $y = 1.5$ wt% exhibited uniform microstructures with greater average grain sizes. Moreover, in the case of MTO ceramics added with $y = 1.5$ wt%, smaller grains were observed at the grain boundaries of the large grains. Further, as the y wt% increases, grain morphology of dense MTO ceramics exhibited two different types of grains: at the grain boundary of the large grains, a segregation of white colored phase was observed. In order to understand chemical compositions of this contrast

phase, EDS analysis was performed. The chemical composition for $\text{MTO} + y = 1.5 \text{ wt\%}$ (Figure 4.7(c)) contrast phase obtained EDS spectra is shown Figure 4.7(d). The larger grains (spot A) exhibit the chemical composition of MgTiO_3 , whereas white layer (spot B) showed the chemical composition of $\text{La}_2\text{Ti}_2\text{O}_7$, and the similar effect was observed by Ferreira *et al.* [34]. However, this phase could not be identified from XRD patterns because the detection of minor phases by XRD is extremely difficult. The average grain sizes of the samples were in the range of $8.1 - 2.5 \mu\text{m}$ and $10.2 - 3.2 \mu\text{m}$ for the samples added with Bi_2O_3 and La_2O_3 , respectively. This observation indicates that the addition of Bi_2O_3 did not promote grain growth and average grain size whereas the La_2O_3 enhanced both grain growth and average grain size of MTO ceramics.

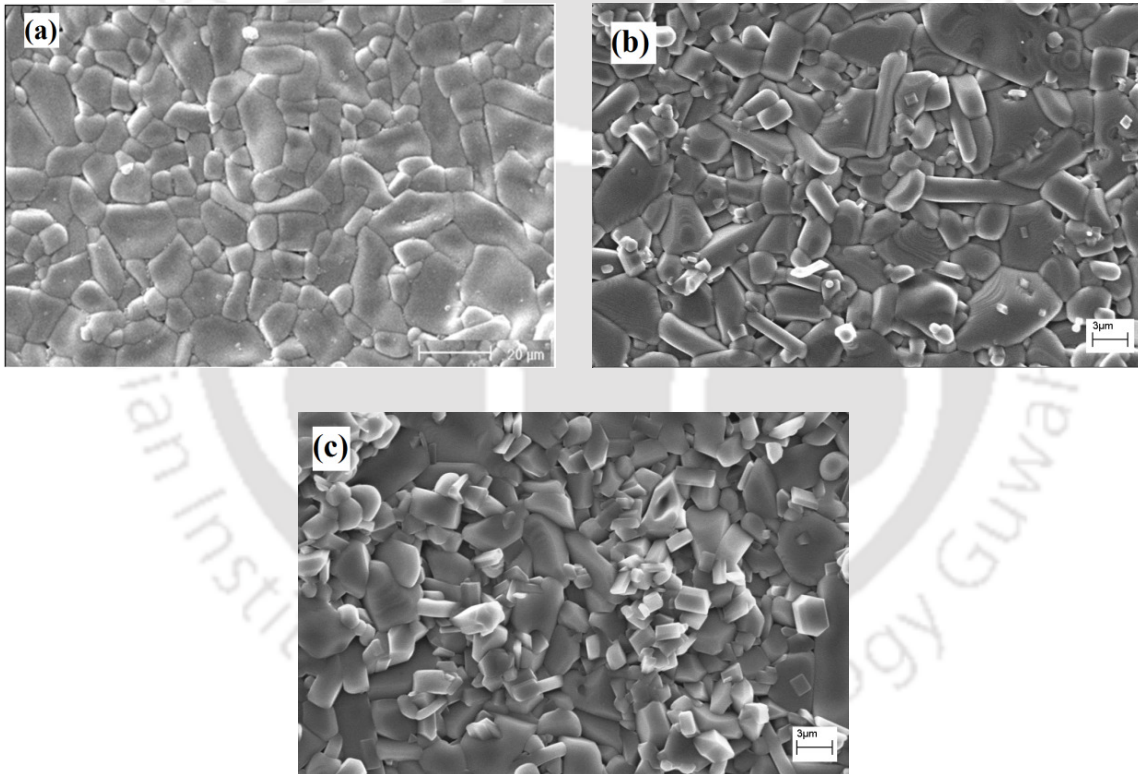


Figure 4.6: SEM images of the $\text{MTO}-\text{Bi}_2\text{O}_3$ ($x \text{ wt\%}$) ceramics with (a) $x = 0.5$, (b) $x = 1.0$ and (c) $x = 1.5$.

In addition, the obtained similar average grain size of the MTO ceramics added with $x = 0.5 \text{ wt\%}$ is due to the identical grain growth, microstructure and the presence of a small amount of MgTi_2O_5 phase. The reduction in average grain size and non uniform

microstructures can be attributed to the presence of secondary phases, and the segregation of liquid phase observed within the grain boundaries. Further, increase in x wt% enhanced the growth of MgTi_2O_5 , which resulted in smaller grain sizes and non uniform grain growth. In the case of the MTO ceramics added with La_2O_3 , in addition to MgTi_2O_5 phase, $\text{La}_2\text{Ti}_2\text{O}_7$ also observed, which enhanced the grain size and grain growth (see Figure 4.7(c)). Microstructure analysis reveals that the nature of the additive and its concentration plays an important role during the development of uniform microstructure and the average grain sizes of the MTO ceramics.

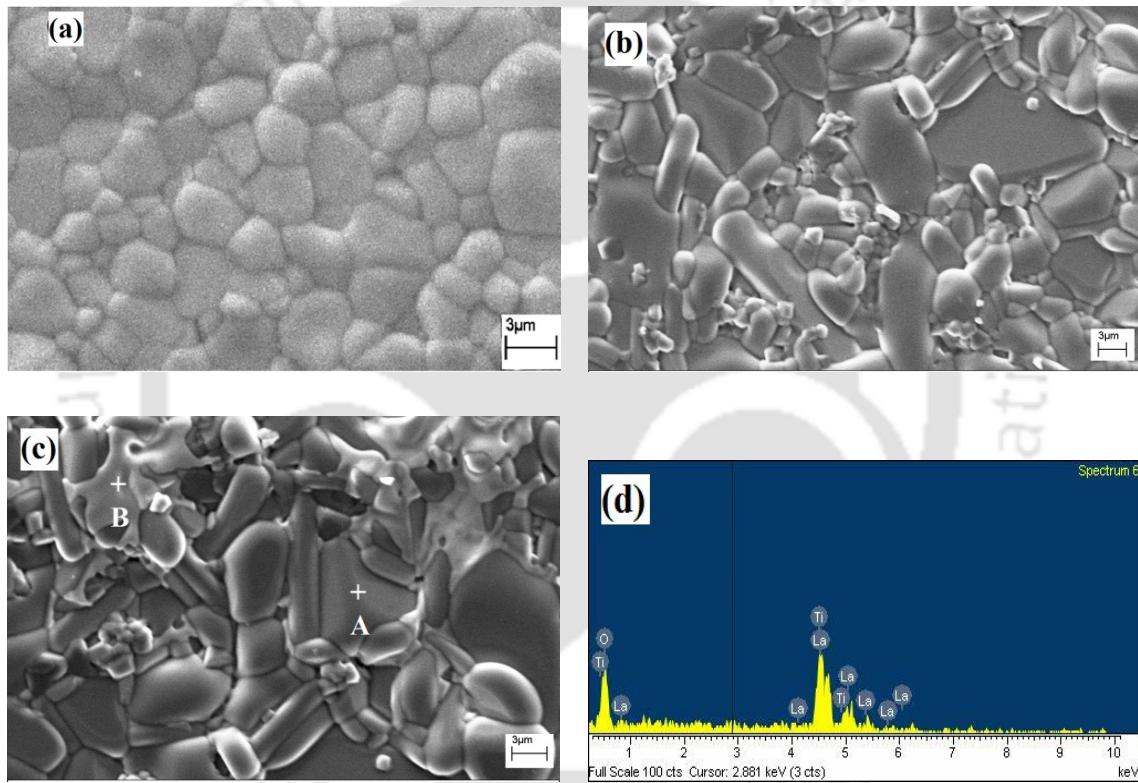


Figure 4.7: SEM microstructures of the MTO - La_2O_3 (y wt %) ceramics with (a) $y = 0.5$, (b) $y = 1.0$ and (c) $y = 1.5$. (d) EDS spectra of MTO ceramics added with $y = 1.5$.

4.4.3 Effect of Bi_2O_3 or La_2O_3 addition on relative density of MTO ceramics

To understand the effect of these additives on the densification of MTO ceramics, the relative densities of MTO ceramics mixed with different weight percentages of Bi_2O_3 and La_2O_3 were measured. The variation in relative densities of MTO ceramics added with Bi_2O_3 and La_2O_3 as a function of sintering temperatures were illustrated in Figure 4.8(a) and (b),

respectively. While the MTO ceramics added with Bi_2O_3 shows a continuous increase in relative density from 86.5 to 97.5 % with an increase in sintering temperature from 1100°C to 1200°C. The maximum of 97.5 % of the theoretical density was obtained for the sample added with $x = 0.5$ wt%. Further, the relative density found to decrease with an increase in x wt%. The decrease in the relative densities with higher x wt% can be attributed to the non-uniform grain growth and the presence of secondary and liquid phases (Figure 4.6(b) & (c)). Nevertheless, the decrease in density above 1200°C may be due to the evaporation of Bi_2O_3 , which causes the non-uniform growth (Figure 4.6(c)).

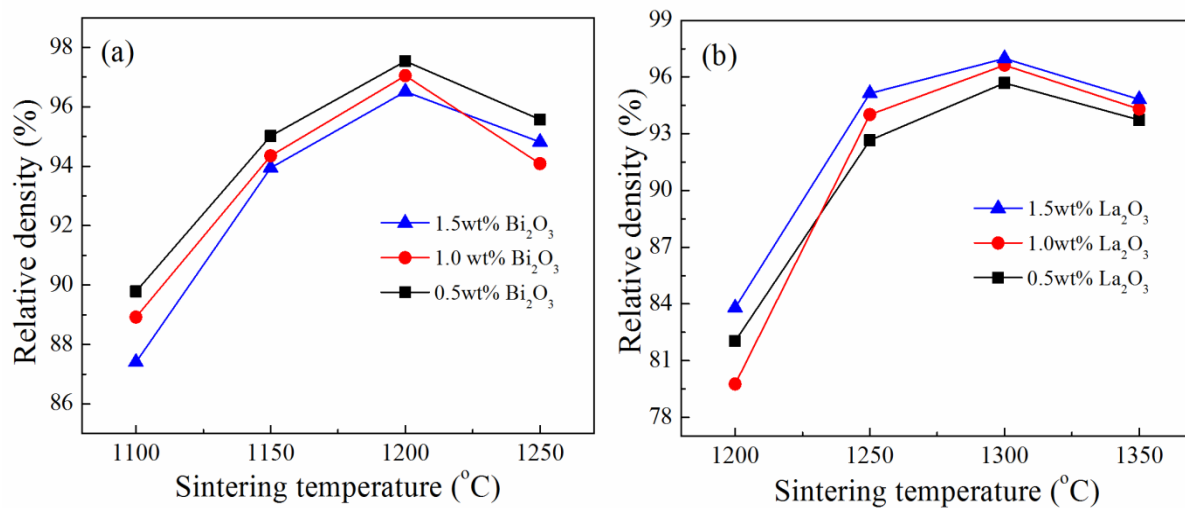


Figure 4.8: Variation in relative densities of the MTO ceramics added with different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.

The addition of Bi_2O_3 reduced the sintering temperature from 1350°C to 1200°C. However, MTO ceramics with La_2O_3 revealed the maximum density of 96.9 % at 1300°C. In addition, at a given temperature, the relative densities of the samples increased with an increase in $y = \text{wt}\%$. The increase in relative densities with the increase in y wt% can be correlated to the enhancement of uniform grain growth and average grain size. Ferreira *et al.* [34] reported the sintering temperature of the MTO ceramics mixed with La_2O_3 as 1350°C. Nevertheless, in the present study, the MTO ceramics added with La_2O_3 achieved higher densities at 1300°C, whereas pure MTO ceramics exhibited maximum density of 96.4 % at 1350°C. These results confirm that the densification of MTO ceramics without the sintering aid is considerably difficult.

The addition of La₂O₃ could not reduce the sintering temperature much because La³⁺ controls the grain growth and the solubility limit for La in MTO ceramics could be very low because of the La₂Ti₂O₇ secondary phase. In the present study, the obtained lower sintering temperatures are a collective effect of liquid phase and smaller initial particle sizes. The effects of these additives and sintering temperature on the improvement of the relative density and microstructure can be described by the following mechanism: In the liquid phase sintering, the liquid spreads to cover the solid surfaces, will be separated by the liquid bridge. This decreases the friction between the MTO particles and exerts a capillary force, which can be used to rearrange the particle more easily and enhances the densification process to get the maximum packing [35]. Furthermore, the sintering would be faster as the particle size decreases, since the diffusion distances are shorter and curvature stresses are longer. In the arrangement stage, a small particle size improves the role of rearrangement because of a large capillary force even though the amount of friction is increased. Similarly, in the solution re-precipitation stage, a little particle size improves the densification rate [36]. Figure 4.9 shows the initial particle sizes of the MTO ceramics milled for 10 h. It is revealed that the average initial particle size is around 700 nm. However, pure MTO ceramics exhibited highest densities of 82% and 92% of theoretical densities, sintered at 1200°C and 1300°C, respectively, and pure MTO ceramics exhibited maximum density of 96.4 % at 1350°C for 3 h. This comparison shows that the obtained maximum densities are the combined effect of liquid phase and initial particle size because initial particle size alone did not increase the densities of the MTO ceramics.

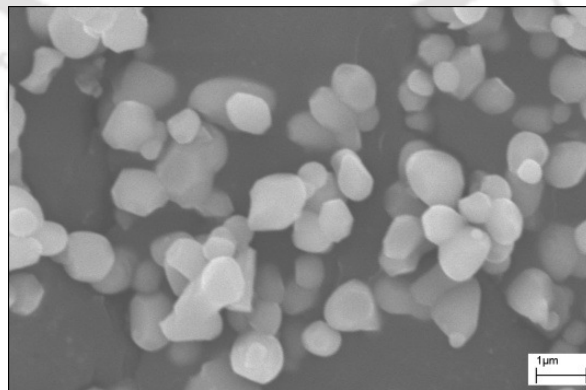


Figure 4.9: SEM microstructure of the pure MTO ceramics milled for 10 h.

4.4.4 Microwave dielectric properties

To observe the influence of these additives on the microwave dielectric properties of MTO ceramics, we have measured the dielectric constant and quality factor at microwave frequencies for all the samples and depicted in Figure 4.10. In both the cases, it is clearly seen that dielectric constant (ϵ_r) as a function of sintering temperature followed a similar trend as that of the relative density as a function of sintering temperature suggesting that the dielectric constants of the investigated MTO ceramics can be enhanced by increasing the densification, which results in reduction in the porosity. The dielectric constants of the MTO ceramics added with Bi_2O_3 are ranged from 14.7 to 16.6 where as the samples added with La_2O_3 , exhibited in the range of 12.8 to 16.9. The obtained lower values of dielectric constants can be attributed to the lesser relative densities and secondary phases. The resonant frequency of the measured samples is around 10.5 GHz.

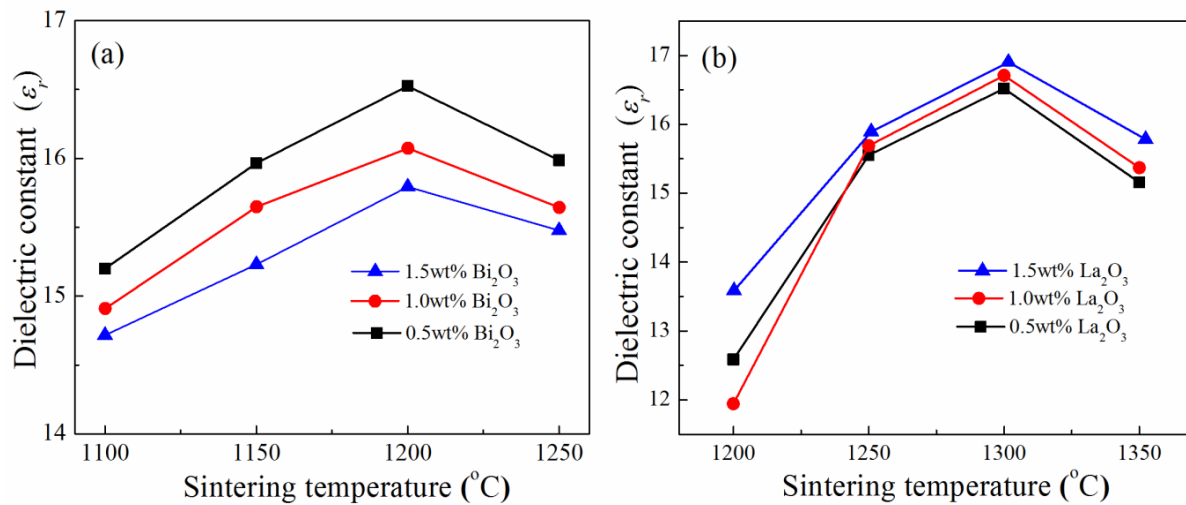


Figure 4.10: Variation in dielectric constants of MTO ceramics with the addition of different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.

The variation in $Q \times f_0$ of the MTO mixed with Bi_2O_3 and La_2O_3 as a function of sintering temperature is shown in Figure 4.11. In the case of the MTO ceramics with Bi_2O_3 , the $Q \times f_0$ values increased up to 1200°C thereafter started decreasing and follows the same trend as that of the relative density and ϵ_r as a function sintering temperature. A maximum $Q \times f_0$ value of 71.9 THz (at 10.5 GHz) is obtained for the sample with $x = 0.5$ wt%, sintered at 1200°C. In addition, $Q \times f_0$ values found to decrease with an increase in x wt%. Kim *et al.*

[37] proposed that the dielectric loss arose in the $(\text{Zr}_{0.8}\text{Sn}_{0.2})\text{TiO}_4$ ceramics with the addition of Bi_2O_3 is due to the substitution of Bi^{3+} ions in Ti site, which creates the oxygen vacancies. However, this loss mechanism is not applicable to the present situation. Since the ionic radii of Bi^{3+} ion in the ilmenite structure is $1.03 \text{ \AA}$, because both A and B sites belong to the coordination 6. Hence the Bi^{3+} ion cannot be substituted in the Mg^{2+} ($0.72 \text{ \AA}$) and Ti^{4+} ($0.605 \text{ \AA}$) sites. This would complement the obtained lattice constants' calculations that these additives did not enter the MTO matrix but remained at the grain boundary. The decrease in the $Q \times f_0$ values of MTO ceramics with the higher concentration of Bi_2O_3 may be due to increase in the oxygen vacancies which increase the anharmonic interactions, lower densities and decrease in the average grain size.

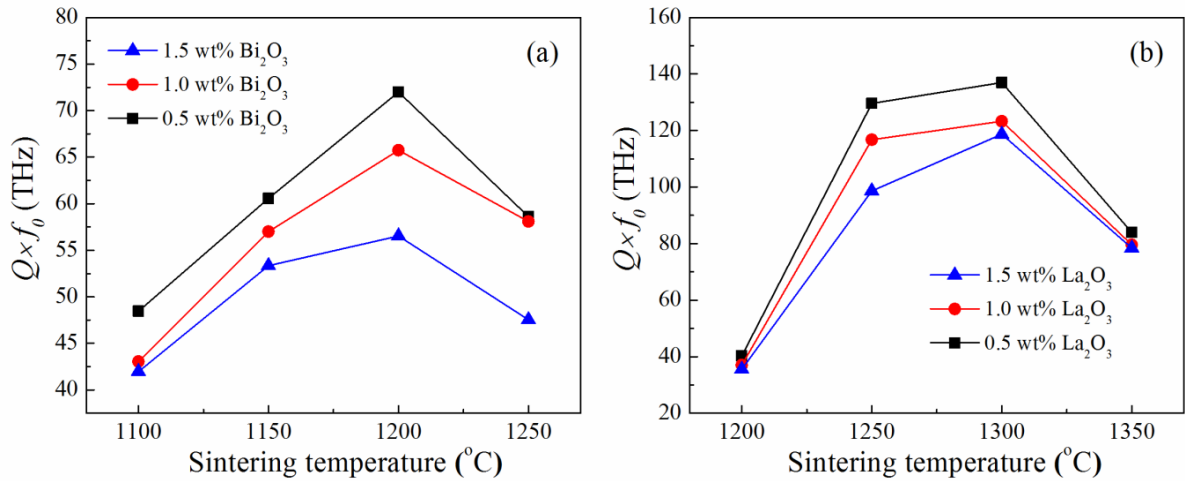


Figure 4.11: Variation in $Q \times f_0$ of MTO ceramics with the addition of different wt% (a) Bi_2O_3 , (b) La_2O_3 as a function of sintering temperature.

In the case of MTO ceramics with La_2O_3 , the $Q \times f_0$ values found to increase with an increase in sintering temperature up to 1300°C and decreased thereafter. The maximum values of $Q \times f_0$ (136.9 THz) were obtained for MTO ceramics added with $y = 0.5 \text{ wt\%}$, sintered at 1300°C . In addition, it was also observed that with an increase in the $y \text{ wt\%}$, although there is an improvement in the density, enlargement in average grain size but the $Q \times f_0$ values decreased drastically. The lower $Q \times f_0$ values were due to the presence of $\text{La}_2\text{Ti}_2\text{O}_7$ and MgTi_2O_5 , which result in the absorption of electromagnetic radiation. The MgTi_2O_5 exhibits inferior microwave dielectric properties, which deteriorate in the

microwave dielectric loss of the MTO ceramics [38]. The best $Q \times f_0$ values, obtained from the samples added with $y = 0.5$ wt% can be due to the absence of $\text{La}_2\text{Ti}_2\text{O}_7$ in these samples which is confirmed from EDS spectra. Although La_2O_3 - TiO_2 system has the ability to form the eutectic liquids around 1300°C but it's not observed in the present study. Further, it can be concluded that the La^{+3} also cannot be substituted for Mg^{2+} and Ti^{4+} ion sites because ionic radii of La^{+3} ($1.061 \text{ \AA}$) is larger compared Mg^{2+} and Ti^{4+} ion sites. In the case of MTO ceramics with La_2O_3 , the microwave dielectric loss was heavily influenced by the secondary phases and is independent of grain size and relative densities. However, the observed $Q \times f_0$ values obtained with these additives were found be lower compared to pure MTO ceramics sintered at 1350°C for 3 h. The pure MTO ceramics exhibited ϵ_r of 18.52 and $Q \times f_0$ 162.3 THz. In both the cases, it is clearly observed that there is not much variation in ϵ_r values were as the $Q \times f_0$ values are heavily influenced. Because the higher concentrations of these additives create local impurities, defects and secondary phases, which result in absorption of electromagnetic radiation that leads to the increase in microwave dielectric loss. The addition of Bi_2O_3 and La_2O_3 reduced the sintering temperature and exhibited maximum relative densities, but could not improve the microwave dielectric loss as compared to pure MTO ceramics.

The microwave dielectric losses arise from the two mechanisms (i) intrinsic and (ii) extrinsic losses [39, 40]. Intrinsic losses arise due to the enharmonic forces that mediate the interaction between crystal lattice modes and electromagnetic radiation, which leads to damping of the optical phonons. On the other hand, the extrinsic losses are caused by the extended dislocations, grain boundaries, porosity, oxygen vacancies and secondary phases, which are heavily dependent upon the processing conditions. These losses are caused mainly by the dipolar relaxation of the defect oriented polarizations concentrated at the interfaces. Generally, the specimen with larger grain size expected to have a high $Q \times f_0$ because the grain growth decreases the grain boundary area [41]. From the present study, it is clearly evident that the microwave dielectric properties of MTO ceramics are strongly influenced by the additives and their concentrations. Further, it is significant to note that the MTO ceramics with these additives exhibited the best microwave dielectric properties at lower sintering temperatures, which qualify this material for resonator and type I capacitor applications.

4.5 Conclusions

- MTO ceramics with different type and amount of additives has been reported and in each case, their densification dependence on sintering conditions has been studied systematically.
- The influence of annealing temperature on the crystal structure, densification, microstructure and microwave dielectric properties of the pure and CeO₂ nanoparticle added MTO samples, annealed at 1100°C for 48 h are discussed.
- In case of Bi₂O₃ addition, no secondary phase other than MgTi₂O₅ is observed up to 1.5wt%. However, in case of CeO₂ nanoparticles and La₂O₃ additions, extra phases determined by XRD and confirmed with EDS spectra was observed along with MgTi₂O₅.
- The microstructures of the MTO ceramics are getting modified with the addition of these supplements. It is observed that the nature of the additive, and its concentration played an important role on the sintering temperature and relative density.
- The decrease in sintering temperature is due to the liquid phase effect and smaller initial particle sizes. Further, the microstructures of the MTO ceramics were improved with the concentration of these additives.
- By the addition of different additives, it was found that there is not much change in the ϵ_r and temperature coefficient of the resonant frequency, whereas the quality factor is significantly affected.
- The increase in quality factor is primarily attributed to the increase in uniform grain size, reduction in porosity (improvement in density) and the reduction in oxygen vacancies.

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Chapter 5

Influence of Co Substitution on Dielectric and Magnetic Properties of MgTiO_3 Ceramics

Due to the hygroscopic nature of MgO, it's difficult to prepare phase pure MTO ceramics by solid state reaction method. Further, it is also well known that small initial particle sizes reduce the sintering temperature. Also it is reported that partial substitution of Co enhance the microwave dielectric properties, however, there is no systematic study on concentration of Co substitution of MTO ceramics using semi Alkoxide precursor method. In this chapter we have investigated effect of Co substitution on dielectric and magnetic properties of MTO ceramics.

5.1 Brief literature survey

MgTiO₃ (MTO) ceramics are prepared by solid-state reaction method involving a repeated milling of powders and calcination at high temperatures. This causes the agglomeration of crystals with different particle sizes, which eventually require high sintering temperatures ($> 1350^{\circ}\text{C}$) to achieve maximum density. Nevertheless, these samples cannot be obtained in pure single phase MgTiO₃ ceramic [1, 2] due to the hygroscopic nature of MgO and often exhibit additional phase of MgTi₂O₅ after the sintering process. To overcome the above difficulties in preparing single phase MTO, alternative approaches such as complex polymerization [3], auto igniting combustion [4], sol-gel [5, 6], and mechanochemical processing [7, 8] methods were adopted. However, the densification of MTO ceramics remains a challenge and hence various novel approaches such as addition of low melting point additives, smaller initial particle sizes, and the liquid phase sintering aids [9-12] were utilized to reduce sintering temperature. Also, few studies were reported on improving the dielectric properties of MgTiO₃ ceramics by partial substitution Mg with Zn, Co or Ni and Ti with Zr or Sn : (Mg_{0.95}Zn_{0.05})TiO₃ ($\epsilon_r \sim 17.1$, $Q \times f_0 \sim 264$ THz, $\tau_f \sim -40.3$ ppm/ $^{\circ}\text{C}$) [13], (Mg_{0.95}Co_{0.05})TiO₃ ($\epsilon_r \sim 16.8$, $Q \times f_0 \sim 244$ THz, $\tau_f \sim -54$ ppm/ $^{\circ}\text{C}$) [14], and (Mg_{0.95}Ni_{0.05})TiO₃ ($\epsilon_r \sim 17.2$, $Q \times f_0 \sim 180$ THz, $\tau_f \sim -45$ ppm/ $^{\circ}\text{C}$) [15], Mg(Ti_{0.95}Sn_{0.05})O₃ ($\epsilon_r \sim 17.4$, $Q \times f_0 \sim 322$ THz, $\tau_f \sim -54$ ppm/ $^{\circ}\text{C}$) [16] and Mg(Ti_{0.95}Zr_{0.05})O₃ ($\epsilon_r \sim 18.1$, $Q \times f_0 \sim 380$ THz, $\tau_f \sim -50$ ppm/ $^{\circ}\text{C}$) [17]. Conversely, the sintering temperature was reported to be always higher than 1350°C .

On the other hand, stoichiometric MgTiO₃ was reported as paramagnetic [18] and metallic when sintered in the reduced atmosphere [19]. Furthermore, all pure ilmenites,

except MgTiO₃, exhibit antiferromagnetic (AFM) nature with the Néel temperature below 80 K [18]. Shirane *et al.* [20] have reported that in AFM ilmenites, the magnetic moment was parallel to the hexagonal *c* - axis. Interestingly, the electrical resistivity was found to increase exponentially with decreasing temperature below 30 K in the *Ti* - rich MgTiO₃ ilmenites [21]. Fujioka *et al.* [22] reported that non-stoichiometric solid solution of Mg_{1-x}Ti_{1+x}O₃ exhibits itinerant electron ferromagnetism below 260 K and correlated that entering of excess *Ti* into the *Mg* - *O* octahedral layer is responsible for the existence of magnetism. It was also described that the cation substitution is a practical technological way to control magnetization in ilmenites. However, there are no detailed reports correlating between magnetic and dielectric properties in MgTiO₃ ceramics available in literature.

Therefore, in this study, we prepared *Co* substituted single phase MTO ceramics [(Mg_{1-x}Co_x)TiO₃ (*x* = 0 - 0.07)] using semi alkoxide precursor method at reduced sintering temperature with enhanced microwave dielectric properties. Semi alkoxide precursor method is a simple method to prepare single phase MTO ceramics. Hence, in the present study, we have systematically investigated the structural, microstructural and microwave dielectric properties of (Mg_{1-x}Co_x)TiO₃ (*x* = 0 – 0.07) ceramics and compared the results of the samples prepared using other techniques. Also, effect of *Co* doping on the magnetic and dielectric properties of MgTiO₃ and understand the correlation between magnetic and dielectric properties were studied for the first time.

5.2 Experimental Details

Nanocrystalline (Mg_{1-x}Co_x) TiO₃ (*x* = 0.00 - 0.07) samples were prepared by using semi alkoxide precursor method. Magnesium nitrate hexahydrate (Mg(NO₃)₂.6H₂O, Sigma Aldrich, >99.0%), Cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O) and Titanium isopropoxide (Ti(OC₃H₇)₄) were used as starting materials and isopropanol was used as solvent. Initially, the stoichiometric ratio of Mg(NO₃)₂.6H₂O and Co(NO₃)₂.6H₂O were dissolved in the isopropanol at room temperature. Prescribed amount of titanium isopropoxide is slowly added to isopropanol solution and stirred it for 2 h in air. Subsequently, the temperature of the mixture was increased slowly to produce the sol and then gel. The obtained gel was heated to 110°C at a rate of 5°C / min and maintained at 110°C for 24 h. The prepared samples were calcined at 600°C (with heating rate of 5°C) for 5 h. The calcined powders

were well grinded and added with PVA to bind. The powders were pressed into pellets of 10 mm diameter and 5 mm height, which were sintered between 1100°C to 1250°C for 3 h with a heating rate of 10°C/min. A soak time of 30 min at 600°C is given while heating to expel the binder. After sintering, the samples were cool down to room temperature at a rate of 1°C / min.

5.3 Phase analysis and crystal structure of gel powders

Figure 5.1 depicts the DSC / TGA plots of the nanocrystalline MTO powders obtained from the gel. It is observed that powders decompose through two endothermic stages: one is at 80°C and the other one is at 340°C. While the former one can be attributed to the removal of residual moisture, the latter one can be correlated to the decomposition of $TiO(OH)_2$ [23]. In addition, a distinct exothermic peak observed at 585°C is mainly due to the crystallization of MTO.

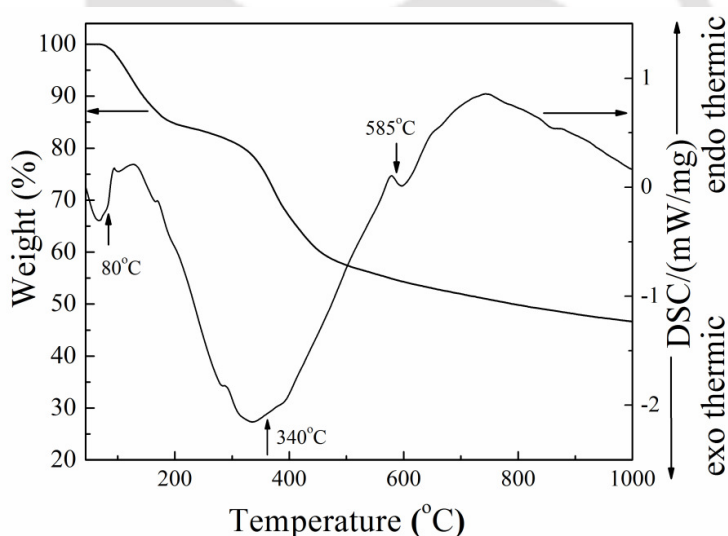


Figure 5.1: DSC / TGA curves of the MTO powders prepared using semi alkoxide precursor method.

To confirm the crystallization, the powders were calcined at 600°C for 5 h and the resulting crystal structure analyzed using XRD is shown in Figure 5.2(a). All the diffraction peaks can be identified using ICDD # 06-0494, confirming the formation of single phase MTO ceramics with rhombohedral crystal structure and $R\bar{3}$ space group. As the effective XRD peak broadening is caused by lattice strain and fine crystallites, these parameters can be

estimated by utilizing the Williamson - Hall plot method [24], where the plot between $\beta \cos \theta$ and $\sin \theta$ as given in eqn.(5.1)

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\eta \sin \theta \quad (5.1)$$

where β is the full width at half maximum, k is a constant, λ is the X-ray wavelength, D is average crystallite size and η is lattice strain, yields a straight line. The applicability of Williamson - Hall plot for the presently investigated MTO powders calcined at 600°C is shown in inset of Figure 5.2(a). The slope and the calculated strain are found to be 0.00352 and 1.3×10^{-3} , respectively. The average size of the crystallites obtained from the intercept is 39 nm. Figure 5.2(b) displays the microstructure of MTO powders calcined at 600°C for 5 h. It is observed that the particle size is in the range of 80 - 120 nm confirming that each particle observed in SEM micrograph consists of few fine nanocrystals oriented randomly. Further, the average particle sizes of the powders obtained from the particle size analyzer are in the range of 90 - 110 nm.

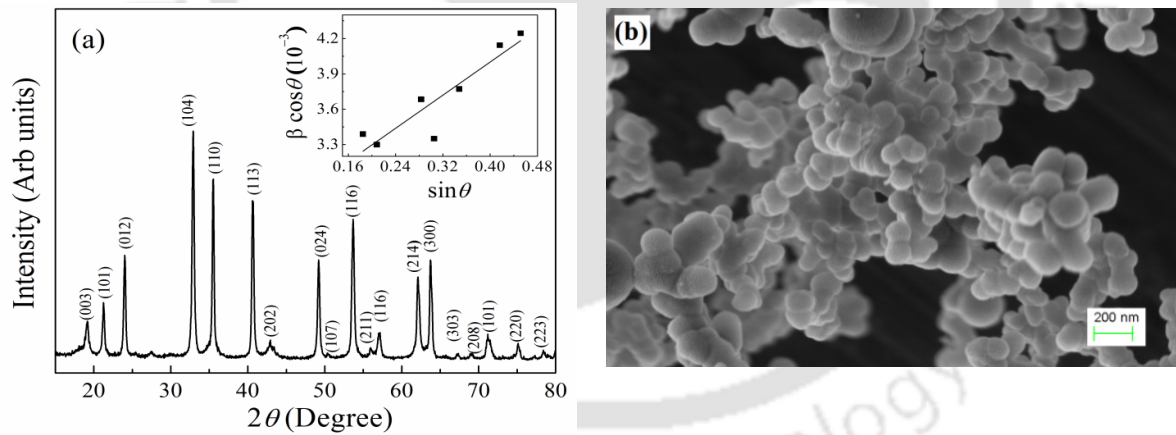


Figure 5.2: (a) X-ray diffraction pattern of MgTiO₃ powder calcined at 600°C. Inset: Application of Williamson - Hall plot method for MTO powder. (b) FESEM image of the MTO powders calcined at 600°C.

5.4 Crystal structure of sintered pellets

To study the effect of Co doping on crystal structure of MTO ceramics, room temperature XRD patterns were obtained for all the Co doped samples [(Mg_{1-x}Co_x)TiO₃, $x = 0.00 - 0.07$] sintered at 1200°C and depicted in Figure 5.3(a). The observed XRD patterns

could be refined by using rhombohedral $R\bar{3}$ space group as shown in Figure 5.3(b). It is revealed that MTO ceramics doped with Co up to $x = 0.05$ exhibit single phase (ICDD: 06-0494). On further increasing Co , a small amount of $MgTi_2O_5$ phase was observed as a secondary phase. In addition, we observed a significant peak shift towards lower angles and peak broadening, as depicted in inset of Figure 5.3(a).

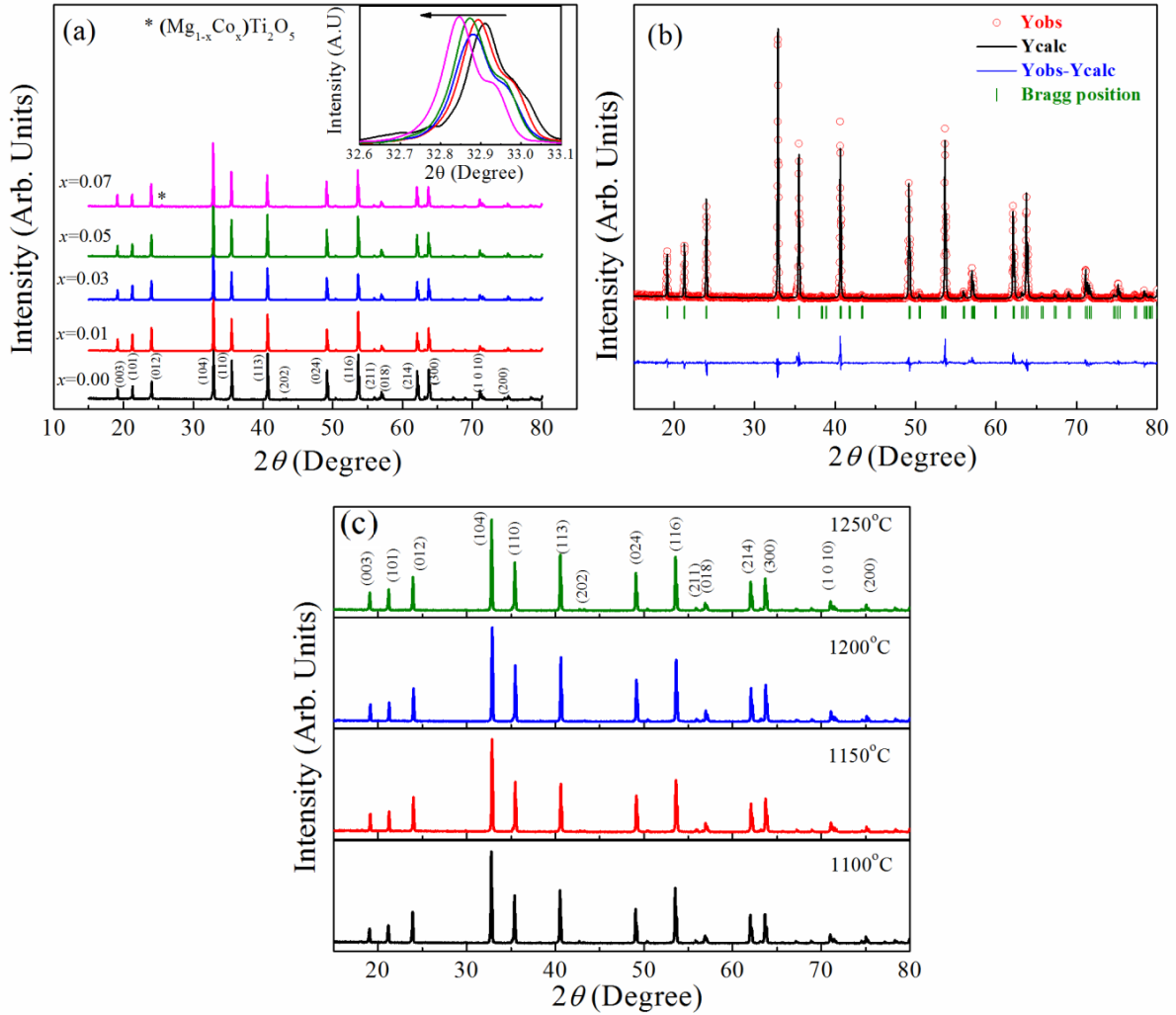


Figure 5.3: (a) X-ray diffraction patterns of the $(Mg_{1-x}Co_x)TiO_3$ ($x = 0.00 - 0.07$) ceramics sintered at $1200^\circ C$. (b) Rietveld refinement of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at $1200^\circ C$. (c) XRD patterns of the $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at different sintering temperatures.

To understand the formation of solid solution with more details, the lattice parameters calculated using Rietveld analysis are summarized in Table 5.1. It is observed that the lattice constant and the volume of the unit cell are found to increase with increasing Co content,

which is in good agreement with the earlier reports [14]. The increase in lattice parameter can be correlated to the larger ionic radii of Co^{2+} as compared to Mg^{2+} [25]. Figure 5.3(c) shows the XRD patterns of (Mg_{0.95}Co_{0.05})TiO₃ ceramics sintered at different temperatures for a constant duration of 3 h. All the samples exhibit single phase (Mg_{1-x}Co_x)TiO₃ phase and the intensity of the diffraction peaks are improved with increasing sintering temperature. The formation of secondary phases was not observed with increasing sintering temperature up to 1250°C. These results show that Co^{2+} form a solid solution with MgTiO₃ which is in good agreement with earlier reports [26]. Further it was also shown that Co^{2+} substitute for Mg^{2+} rather than Ti^{4+} [27].

Table 5.1: Lattice constants (a , b , and c) and unit cell volume (V) for (Mg_{1-x}Co_x)TiO₃ ($x = 0-0.07$) ceramics sintered at 1200°C for 3 hours.

Co Content (x)	$a = b$ (Å)	c (Å)	V (Å ³)
0.00	5.0524	13.8968	307.2139
0.01	5.0532	13.8979	307.3355
0.03	5.0541	13.8994	307.4782
0.05	5.0555	13.9007	307.6774
0.07	5.0563	13.9029	307.8234

5.5 Microstructure and Relative density

To understand the effects of Co doping on the evolution of microstructure of MTO ceramics, surface morphology of the sintered MTO ceramics were analyzed using SEM as depicted in Figure 5.4. For $x = 0.05$ sintered at 1100°C, the microstructure displays a small grain structure with finite pores. However, with increasing sintering temperature up to 1200°C, the average grain size increases with an enhancement in compactness along with the uniform microstructure. The average grain sizes were found to be 3.1, 4.0 and 7.4 µm for the samples sintered at 1100°C, 1150°C and 1200°C, respectively. Figures 5.5 (a - d) displays the SEM images of samples doped with different Co content and sintered at 1200°C for 3 h. All the samples are showing dense and pores free uniform microstructures. The average size of the grains increases with increasing Co doping up to $x = 0.05$, which indicates that Co doping up to $x = 0.05$ in MTO ceramic promotes the grain growth. The maximum grain size in the

range of 5.5 - 7.4 μm is achieved for the sample with $x = 0.05$. To study the chemical composition of the prepared samples, EDS spectra were obtained. A typical EDS spectrum for $x = 0.05$ sample is shown in Figure 5.6 and the chemical composition is found to be ($Mg: Co: Ti: O = 18.58: 1.03: 19.81: 60.59\%$) ($Mg_{0.95}Co_{0.05}TiO_3$).

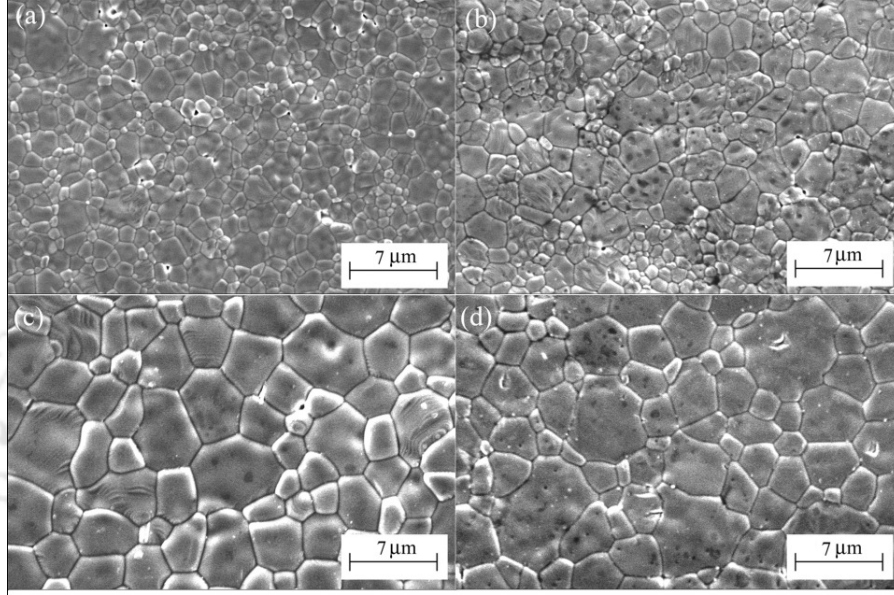


Figure 5.4: SEM images of $(Mg_{0.95}Co_{0.05})TiO_3$ ceramics sintered at different sintering temperatures: (a) 1100°C, (b) 1150°C, (c) 1200°C, and (d) 1250°C.

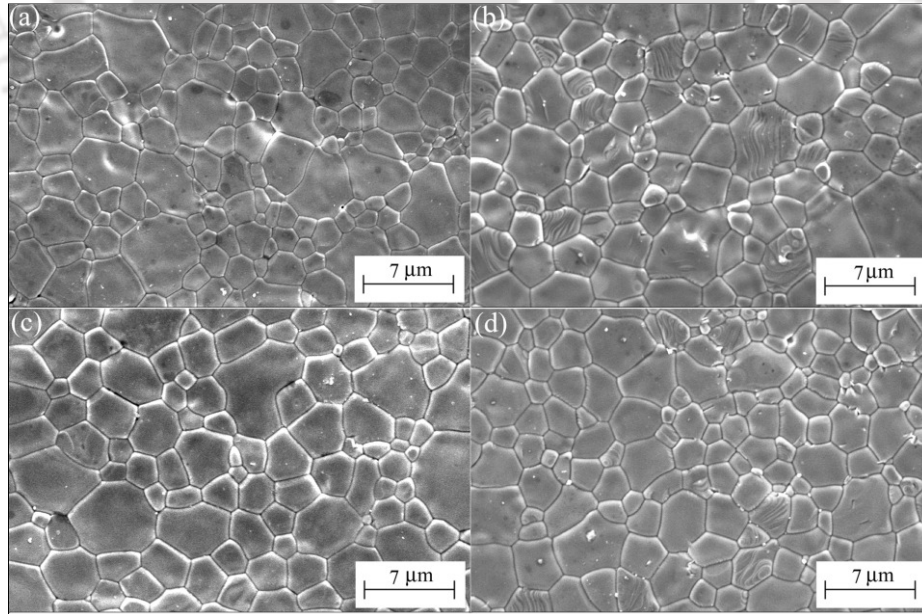


Figure 5.5: SEM micrographs of $(Mg_{1-x}Co_x)TiO_3$ doped with different x concentrations: (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.03$ and (d) $x = 0.07$, sintered at 1200°C for 3 h.

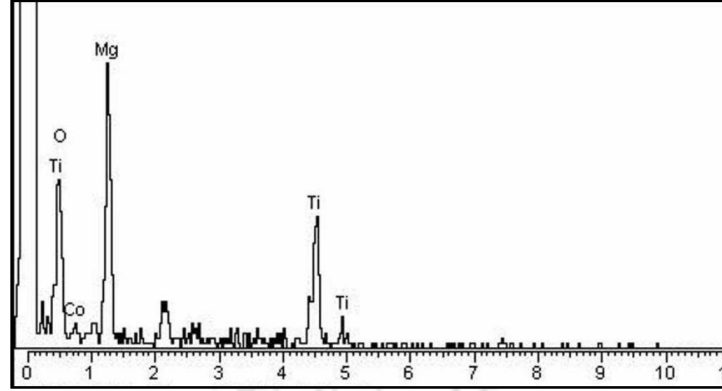


Figure 5.6: EDS spectrum for $x = 0.05$ sample sintered at 1200°C for 3 h.

To study the improvement in density of MTO ceramics with *Co* doping, the relative density was calculated using the Archimedes method. At first, we have calculated theoretical densities of (Mg_{1-x}Co_x)TiO₃ ceramics using

$$\rho_{theo} = \frac{ZM}{N_A V} \quad (5.2)$$

where Z is the number of atoms per unit cell, M is the molecular weight (g/mol), N_A is the Avogadro number (6.023×10^{23} atoms per mol), and V is the volume of the unit cell (in cm³). The theoretical densities of pure and *Co* - doped MTO ceramics are 3.89, 3.89, 3.90, 3.91, 3.92, and 3.93 gm/cm³, respectively.

Figure 5.7 shows the variations in relative densities of (Mg_{1-x}Co_x)TiO₃ ($x = 0.00 - 0.07$) ceramics as a function of sintering temperature. The relative density increases with increasing sintering temperature up to 1200°C and decreases slightly for the samples sintered at 1250°C. The maximum relative density of 97.26% is obtained for $x = 0.05$ sintered at 1200°C for 3 h and is attributed to the reduction in porosity, increase in average grain size and uniform microstructure. The decrease in relative densities of the samples with $x = 0.07$ may be due to the presence of finite amount of secondary phase. The obtained relative density values were in the range of 82.40 - 97.26% for all the samples sintered in the temperature range of 1100 – 1250°C. It is important to note that the processing temperature of MTO ceramics is reduced from 1350°C to 1200°C and sintering temperature is much lower as compared to those reported temperatures for the chemical processes [6, 28].

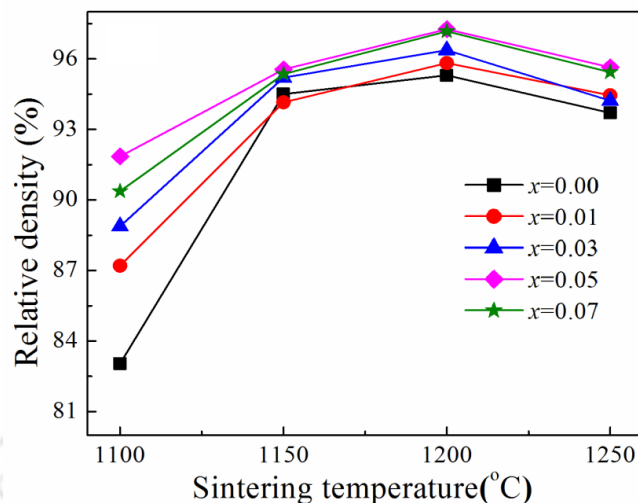


Figure 5.7: Variations in relative density as a function of sintering temperature for different Co concentrations.

This can be attributed to the use of finer initial particles (see Figure 5.2(b)) and understand as follows: Nanoparticles have larger surface area resulting higher surface energy, which promotes the sintering process significantly [29]. Furthermore, it is well known that the sintering velocity depends upon the nature of the powder, particle size and sintering temperature. Nanoparticles exhibit distinctive contact necks in the powder and form different inter particle boundaries. Therefore, at lower sintering temperature, most of the sintering mechanisms would be active as a result of the increased sintering velocity, leading to a maximum relative density and larger uniform grain size [30]. It is also observed that relative density of $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ceramics increased with x concentration up to $x = 0.05$. This can be understood from the fact that Co doping forms a solid solution with MgTiO_3 and promotes uniform grain growth. To understand our results carefully, we have carried out surface area analysis using surface area analyzer. It is observed that the surface area of the powder increases with increasing x mol% and the values are in the range of $13.49 - 17.87 \text{ m}^2/\text{g}$. This increase in surface area certainly supports the enhancement of densification at lower sintering temperatures. For the samples with $x > 0.05$, density starts decreasing due to the presence of secondary phase. The relative density values and the shrinkage % for the $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ($x = 0.00 - 0.07$) ceramics sintered at 1200°C are given in Table 5.2. The obtained higher shrinkage values propose that these samples are also promising for the multilayer ceramic capacitor technology.

Table 5.2: Shrinkage percentage, relative density, measured microwave dielectric constant, dielectric constant corrected for porosity values and $Q \times f_0$ for Co doped MTO ceramics, sintered at 1200°C.

Co Content (x)	Shrinkage (%)	Relative density	ϵ_r (measured)	ϵ_m (porosity corrected)	$Q \times f_0$ (THz)
0.00	20.47	94.30	16.49	17.89	126.6
0.01	20.96	94.82	16.65	17.93	147.3
0.03	20.57	95.37	16.78	17.92	159.1
0.05	21.73	96.26	17.03	17.95	170.0
0.07	20.70	96.17	16.84	17.78	163.7

5.6 Microwave dielectric properties

Figure 5.8 shows the dependence of microwave dielectric constants (ϵ_r) of (Mg_{1-x}Co_x)TiO₃ ($x = 0.00 - 0.07$) ceramics on sintering temperature. The variation of ϵ_r exhibits almost a similar behavior of relative densities with sintering temperature.

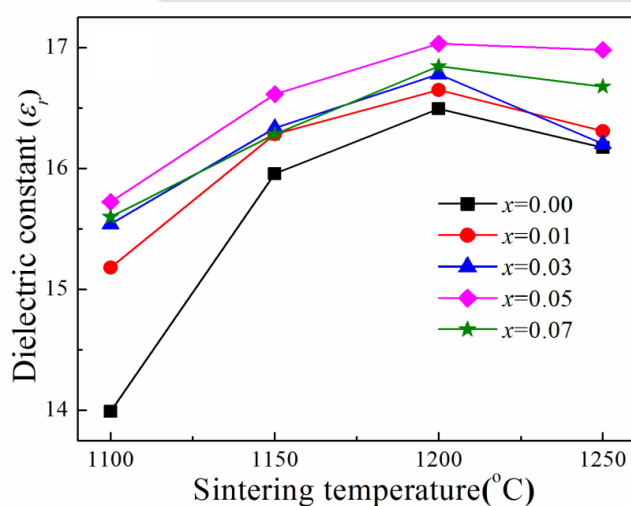


Figure 5.8: Variations in dielectric constant value as a function of sintering temperature for different Co concentrations.

Furthermore, there is a slight increase in ϵ_r with increasing Co concentration upto $x = 0.05$ and the measured dielectric constant is in the range of 14.00 - 17.03 for Co doped MTO ceramics. A maximum ϵ_r of 17.03 was obtained for $x = 0.05$ sample sintered at 1200°C for 3 h. The increase in dielectric constant can be attributed to the higher ionic polarizability of

Co²⁺ ion (1.65 Å³) as compared to Mg²⁺ ion (1.32 Å³) [31]. To obtain the true values of microwave dielectric constant, the measured values of ϵ_r were corrected for porosity using the relation given as [32],

$$\epsilon_r = \epsilon_m \left(1 - \frac{3P(\epsilon_m - 1)}{2\epsilon_m + 1} \right) \quad (5.3)$$

where ϵ_m is dielectric constant corrected for porosity, ϵ_r is the experimental dielectric constant and P is the fractional porosity. The porosity corrected values are given in Table 5.2, and these values are slightly higher than the experimentally measured values.

Figure 5.9(a) shows the $Q \times f_0$ values of (Mg_{1-x}Co_x)TiO₃ ($x = 0.00 - 0.07$) ceramics as function of sintering temperature. Interestingly, $Q \times f_0$ values also follow a similar behavior as that of relative density and ϵ_r as a function of sintering temperature. A maximum $Q \times f_0$ value of 170 THz was obtained for $x = 0.05$ specimen. Nevertheless, the observed $Q \times f_0$ values are in the range of 72 -170 THz for the (Mg_{1-x}Co_x)TiO₃ samples sintered in the temperature range of 1100°C -1250°C.

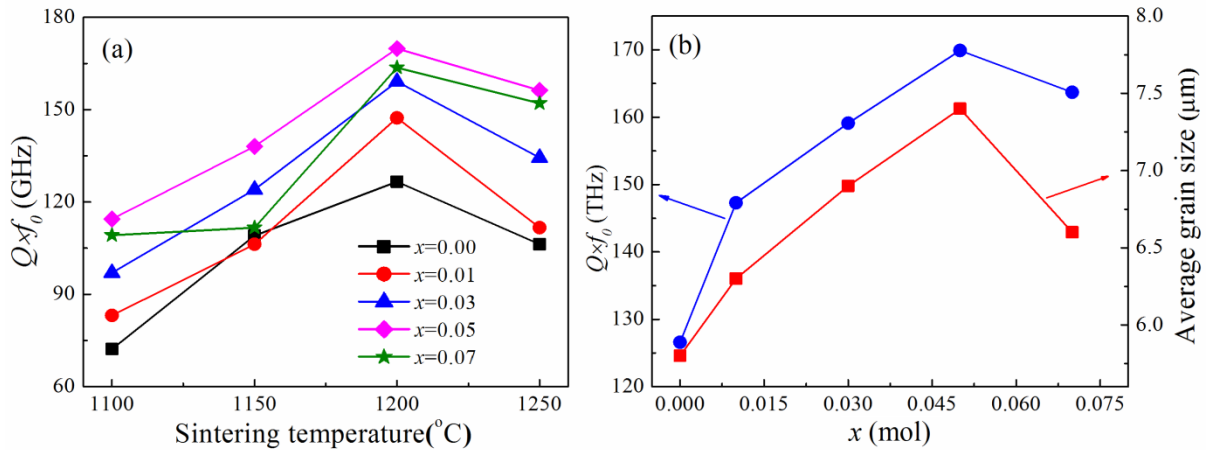


Figure 5.9: (a) $Q \times f_0$ values as a function of sintering temperature for different Co concentrations. (b) Dependence of $Q \times f_0$ and average grain size on Co content in MgTiO₃ ceramics.

To understand the correlation between the structural properties and improvement in microwave dielectric properties with Co addition, we also plotted the dependence of average grain size as a function of Co doping along with the quality factor in Figure 5.9(b). It may be

noted that the extrinsic losses occur generally due to the presence of secondary phases, oxygen vacancies, non-uniform grain growth, defects, and porosity, etc. However, it is clear from the Figure 5.5 that the average size of the grain increases along with the uniform microstructure, resulting in a reduction of porosity, grain boundary, and lattice imperfections. In addition, the doping of *Co* in MTO modulates the crystal structures such that the interaction between the TiO_6 octahedra and MO_6 octahedron layer is minimized in the ilmenite structure resulting an enhancement in Q values [15, 33]. With increasing the sintering temperature above 1200°C , the microwave dielectric loss is increased due the presence of MgTi_2O_5 phase. Furthermore, the pure MTO sample exhibited a negative value of τ_f of $-49 \text{ ppm}/^\circ\text{C}$, which decreases with increasing *Co* doping and found to be in the range of -40 to $-45 \text{ ppm}/^\circ\text{C}$.

The best microwave dielectric properties obtained for $x = 0.05$ doped MTO sample and this composition was chosen for further thin film study. The low frequency dielectric and impedance properties were studied for the $x = 0.05$ samples to compare with the thin films results.

5.7 Low frequency dielectric properties

The frequency dependence of imaginary part of impedance ($-Z''$) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics measured at different temperatures is shown in Figure 5.10.

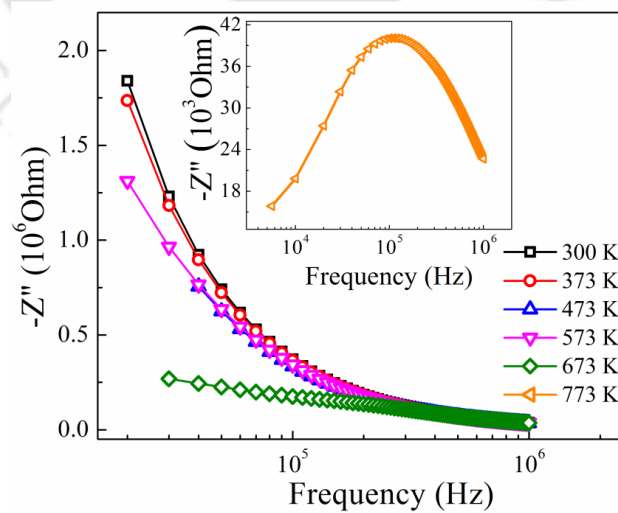


Figure 5.10: Frequency dependent imaginary part of impedance ($-Z''$) for $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample measured at different temperatures.

The value of Z'' exhibits a very high value at low frequencies and decrease monotonically with increase in frequency (f) in the temperature range of 300 - 673 K. However at 773 K, a broad peak in Z'' (f) is observed at 110 kHz. All the curves merge into single curve for frequencies > 400 kHz for all the investigated temperatures. This relaxation process may be due to the presence of immobile species at low temperature and formation of defects at high temperatures.

Figure 5.11(a) and (b) shows the Nyquist plots of the complex impedance spectrum of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample measured at different temperatures. In the temperature range of 300 - 673 K the plots of Z' vs. $-Z''$ linearly lineup towards Z'' axis indicating high resistivity of the sample. But at 773 K, these curve almost semi circular arc with non - zero high frequency intercept has been observed.

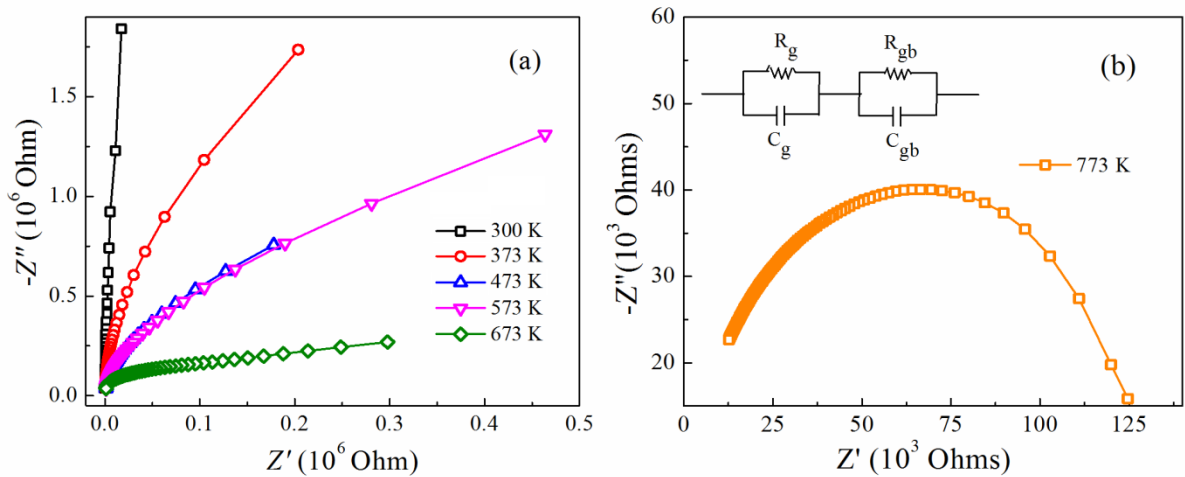


Figure 5.11: (a, b) The Nyquist plots (Cole - Cole graphs) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ ceramics measured at different temperature (300 - 773 K). The inset of 11(b) shows equivalent circuit model for the Cole - Cole configuration.

Generally, the semicircle behavior of complex impedance plots can be explained on the basis of an equivalent circuit model (Cole- Cole) as shown in the inset of Figure 5.11(b). In this model, the high frequency intercept provides the value of the series resistance and the magnitude of semi circle diameter gives the electrical dc - resistivity of the sample at a specified temperature. The maximum value corresponds to the relaxation frequency $\omega = 2\pi f = 1/RC$. The present $-Z''$ and Z' Cole-Cole configuration represents two parallel RC combination circuit $[(R_g C_g) (R_{gb} C_{gb})]$ elements connected in series, serves as the equivalent

circuit. The semi circle arc at low frequency circuit corresponds to grain boundary resistance (R_{gb}) and the high frequency arc indicates the contribution from grains (R_g). The data at 773 K is well match with the single RC circuit and the relaxation time (τ) is calculated by substituting ω in the equation: $\tau = 1/\omega$ as 1.4×10^{-6} sec. Similar results of high temperature Cole - Cole plots measured at 800°C was reported by Kuang *et al.* [34] for MgTiO₃ ceramics.

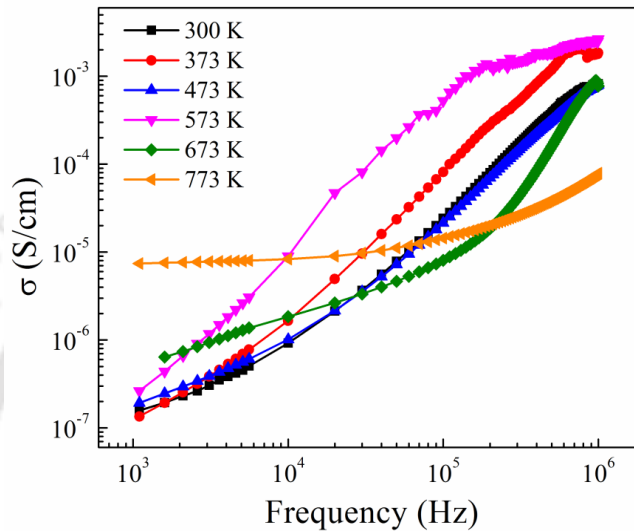


Figure 5.12: The Variation in ac-conductivity (σ_{ac}) of $(Mg_{0.95}Co_{0.05})TiO_3$ sample as a function of frequency (f) measured at different temperatures.

The ac-conductivity (σ_{ac}) of $(Mg_{0.95}Co_{0.05})TiO_3$ sample as a function of frequency measured at various temperatures is shown in Figure 5.12. For $T < 673$ K, the conductivity is almost varies linearly with the frequency and no dc-plateau region has been observed within the frequency range of $10^3 - 10^6$ Hz. On the otherhand, at 773 K, frequency independent conductivity (plateau) is observed at low frequencies ($f < 30$ kHz), due to the contribution of dc conduction mechanism. Beyond a critical frequency the conductivity follows linearly with frequency which is expected due to the contribution of grains [35]. The dependence of ac - conductivity on the frequency is generally described using Jonscher power law [36]

$$\sigma(\omega) = \sigma(0) + A\omega^s \quad (4)$$

where $\sigma(\omega)$ is the total conductivity of the system, $\sigma(0)$ is the contribution from dc conductivity (frequency independent part), ω is the angular frequency of the ac signal ($\omega = 2\pi f$) and “s” and “A” are the temperature dependent characteristic parameters. The term $A\omega^s$

contains the ac dependence and characterizes all dispersion phenomena [37]. The calculated “s” and “A” are found to be 1.16 and 0.74, respectively at 773 K. Usually, the value of “s” should lie between 0 and 1. In the present case slightly higher values of “s” is noticed. The similar results were reported for chalcogenide materials [38].

Figure 5.13(a) and (b) shows the frequency dependent dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample measured at different temperatures. Both the dielectric constant and $\tan\delta$ are found to decrease with increase in applied frequency. The decrease in dielectric constant with increase in frequency is a typical characteristic of the linear dielectric. The obtained dielectric constant and loss tangent values are in the range between 6454 -15.35 and 0.93 - 0.0011 respectively for the measured temperatures in between 300 K - 773 K. The obtained dielectric constant at 10^6 Hz is identical to the value measured at microwave frequencies ($\epsilon_r \sim 17.3$) for the same sample. The dispersion in dielectric constant with frequency can be explained on the basis of Maxwell - Wagner two layer and koop's phenomenological theory [39]. These models demonstrates that as the frequency increases, the electrons reverse their direction of motion more often which decreases the probability of electrons reaching the grain boundary which results the reduction in polarization therefore decreasing the dielectric constant. This variation in loss at lower frequencies may be due to the contributions from metal electrode and the electrode interfaces.

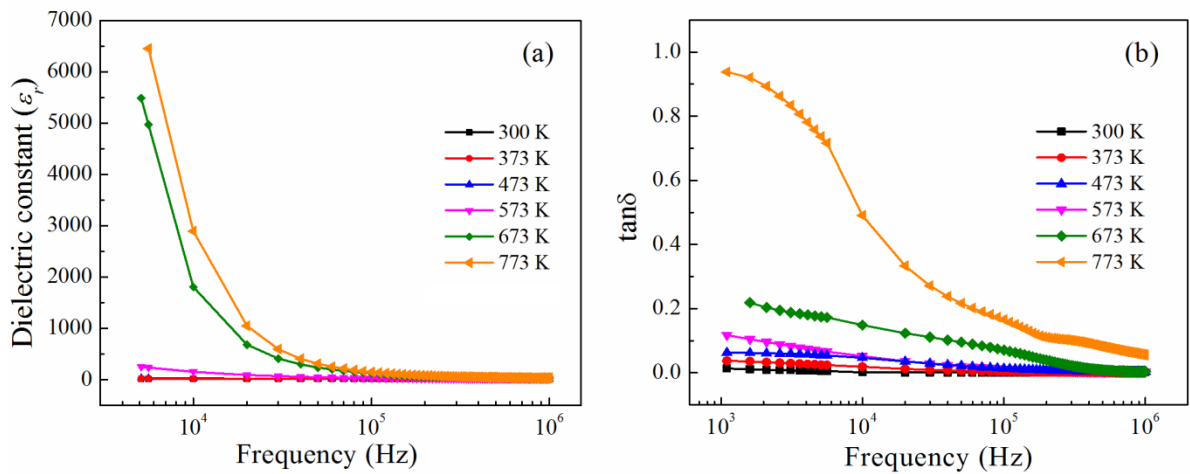


Figure 5.13: The frequency dependent (a) dielectric constant (ϵ_r) and (b) loss tangent ($\tan\delta$) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ sample, measured at different temperatures.

Figure 5.14 shows the variation in dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of (Mg_{0.95}Co_{0.05})TiO₃ sample as a function of temperature measured at 10⁶ Hz. Both the dielectric constant ϵ_r and $\tan\delta$ increases linearly with temperature. This can be explained as, at low temperatures the molecules cannot orient themselves in polar dielectrics. When the temperature rises, the orientation of dipoles is facilitated and this increases dielectric constant. At high temperatures, the dielectric losses caused by the dipole mechanism reach their maximum value and the degree of dipole orientation increases. Apart from dipole losses electrical conduction also increases with increase in temperature. These factors would cause the increase in both dielectric constant and dielectric loss of (Mg_{0.95}Co_{0.05})TiO₃ ceramics with increase in temperature [40].

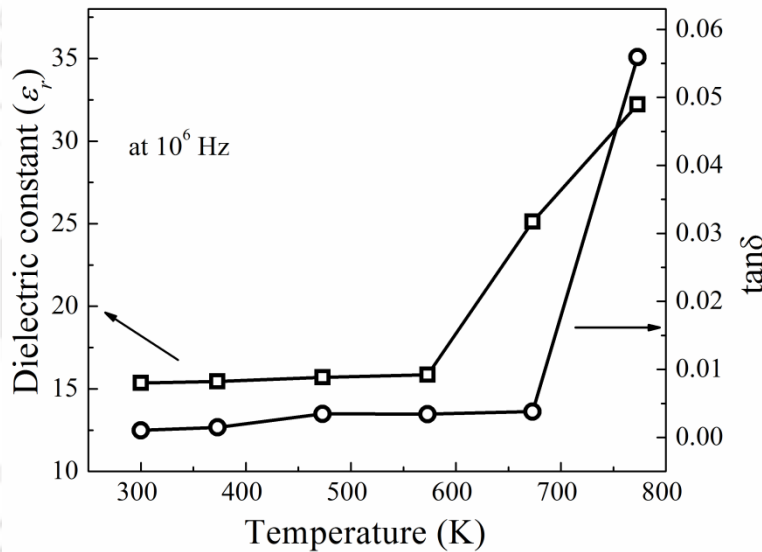


Figure 5.14: Variation in dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of (Mg_{0.95}Co_{0.05})TiO₃ sample as a function of temperature measured at 10⁶ Hz.

5.8 Magnetic properties

To see the effect of Co doping on MTO ceramics, magnetic properties were measured. To study the magnetic properties of Co doped MgTiO₃ samples, room temperature *M-H* loops were recorded and are shown in Figure 5.15(a). It is observed that all the as sintered samples show paramagnetic nature at room temperature. The magnetic susceptibility calculated from the paramagnetic *M-H* loops and depicted in Figure 5.15(b) increases with Co upto 0.03 and decreases with a further increase in Co content. A maximum susceptibility of 6.25×10⁻⁶ (emu/g-Oe) is obtained for *x* = 0.03 sample. Although the structural properties

analyzed using XRD revealed a single phase formation for x up to 0.05, the magnetic susceptibility was observed to decrease for the samples with $x > 0.03$. This could be attributed to the strong dependence of magnetic susceptibility on the Co substitution, which is altered by the initiation of secondary phase formation, but not probed by the XRD due to its limitation. Nevertheless, the existence of MgTi_2O_5 secondary phase was clearly evident for $x = 0.07$ sample. Hence, we have taken only $x = 0.03$ sample for further investigations.

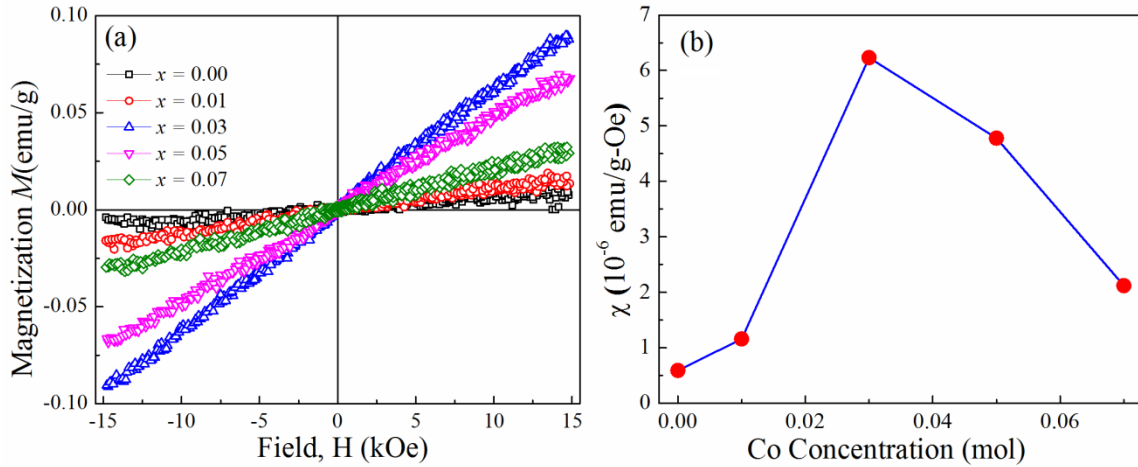


Figure 5.15: (a) M - H loops of MgTiO_3 with different Co concentrations. (b) Magnetic susceptibility of MgTiO_3 ceramics as a function of Co concentration.

Figure 5.16(a) shows the M - T curves of $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions in the temperature range 20 - 300 K under different applied fields. It is observed that (i) with decrease in temperature, the sample exhibits a sudden increase in magnetization below 228 K revealing a magnetic phase transition from paramagnetic (PM) to ferromagnetic (FM) state. (ii) On further lowering temperature, both ZFC and FC increases until a certain temperature, which is sensitive to the applied fields. A bifurcation was observed between ZFC and FC data, which shifts to lower temperature from 170 to 150 K with increasing the applied field. These results suggest that $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ ceramic displays a successive PM - FM - antiferromagnetic (AFM) transitions upon cooling down to low temperature due to magnetic ordering. It is well known that the cobaltites ($\text{EuBaCo}_2\text{O}_{5.4}$ or $\text{GdBaCo}_2\text{O}_{5.4}$) exhibit intriguing magnetic behavior of PM - FM - AFM transitions [41 - 44]. A similar transition could be occurring in the present investigated system.

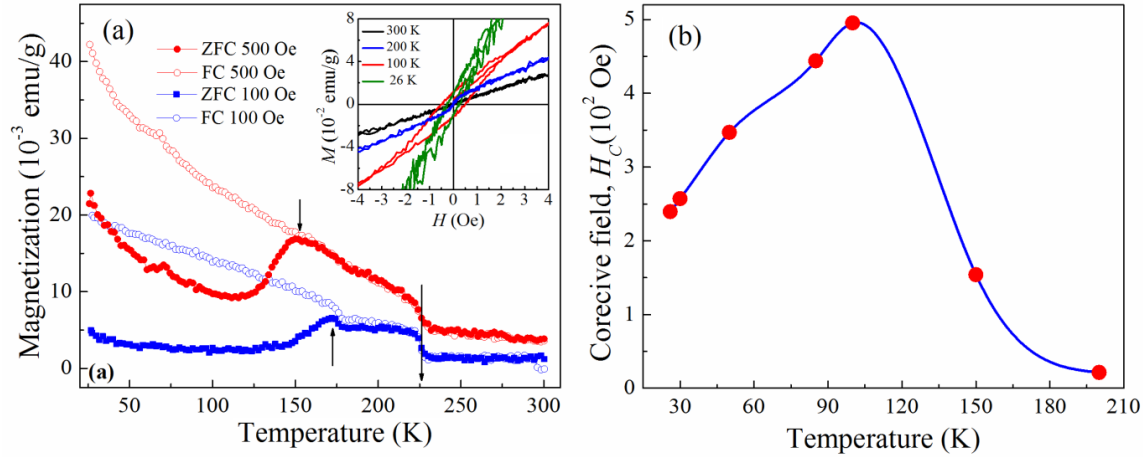


Figure 5.16: M - T curves for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample measured under 100 and 500 Oe applied fields. Insets: (b) M - H curves measured at different temperatures and (c) variation of coercivity with temperature for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.

Inset of Figure 5.16(a) display temperature dependent unsaturated hysteresis loops in which the magnetization increases progressively with decreasing the temperature. The extracted values of Coercive field ($H_C(T)$) shown in the Figure 5.16(b), reveal a peak at 100 K and decreases continuously to zero at Curie temperature (T_C) $\sim$ 228 K. Also, the sudden decrease of magnetization below 150 K can be ascribed to a transition from a canted AFM state to a normal AFM state where the magnetic moments of cobalt sublattices can cancel out with each other. Nevertheless, M - H curves recorded at low temperatures ($T < T_C$) do not show any saturation behaviors.

5.9 Broadband dielectric properties

To see whether there is any correlation between magnetic properties and dielectric properties, the dielectric properties of MTO ceramics were measured in the frequency range of 1 MHz to 1 GHz at different temperatures. Figure 5.17 represents the real (ϵ') and imaginary (ϵ'') part of dielectric permittivity as a function frequency in the range 1 MHz -1 GHz for $(\text{Mg}_{0.7}\text{Co}_{0.3})\text{TiO}_3$ sample at different temperatures. The real (ϵ') part of dielectric permittivity shows a constant value about 18.3 up to a frequency 7 MHz, beyond this dispersion in ϵ' with increase in frequency reaches a low value of 16.2. However, a sharp peak in imaginary (ϵ'') part of dielectric permittivity at a critical frequency $f_c = 300$ MHz and

which is considered as relaxation frequency. From room temperature (300 K) to low temperature there is no shift in relaxation frequency observed. It can be understood as follows: At lower frequencies (in MHz region), all polarization mechanisms respond easily to time varying electric field. With increasing frequency, relaxation of dipole polarization takes place [45] and increases ionic conductivity. This causes an increase in ϵ'' and decrease in ϵ' , respectively.

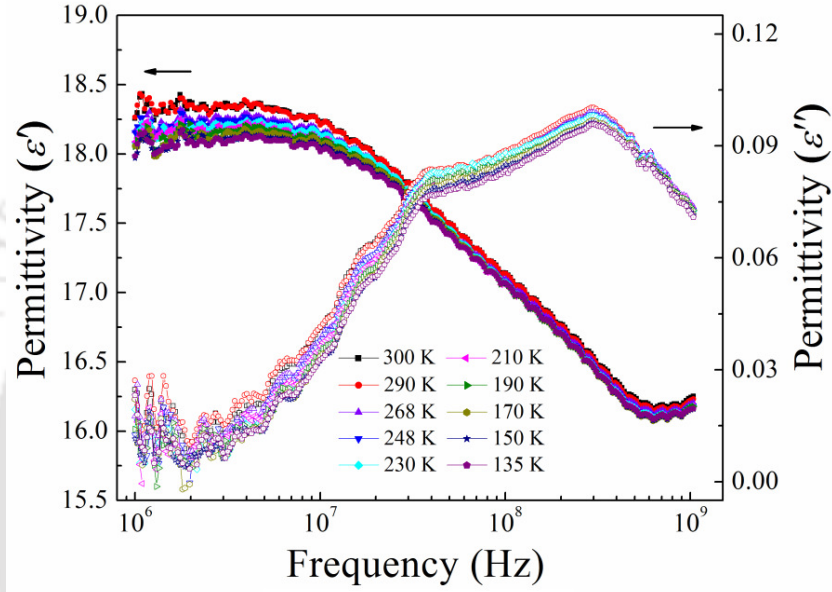


Figure 5.17: Frequency dependence of real (ϵ') and imaginary (ϵ'') part of dielectric permittivity at different temperatures for $(Mg_{0.97}Co_{0.03})TiO_3$ sample.

Figure 5.18 illustrates the temperature dependence of real (ϵ') and imaginary (ϵ'') parts of permittivity for $x = 0.03$ sample. It is observed that as the measurement frequency increases, the ϵ' decreases and ϵ'' increases. Furthermore, both ϵ' and ϵ'' are enhanced with increasing the temperature from 133 to 300 K. The obtained values of ϵ' and ϵ'' are in the range of 18.5 - 16.2 and 0.010 - 0.006 in the temperature range 133 - 300 K, respectively. There are two types of losses that dissipate energy within a dielectric and are classified as intrinsic, while the other is extrinsic losses. Intrinsic loss originates from the anharmonicities of the lattice vibration, and the extrinsic loss is mainly because of porosity, grain boundary, secondary phases and impurities. Conduction loss also causes energy dissipation due to the flow of charge through the material. As the temperature increases, the anharmonic forces mediate the interaction between the lattice modes and applied field resulting an increment in

damping factor. With decreasing temperature, the damping of the optical phonon also reduces [46]. The increase in both ϵ' and ϵ'' values with an increase in temperature can be explained as follows: The molecules cannot orient themselves in polar dielectrics in the low temperature region. When the temperature rises, the orientation of dipoles is facilitated, which in-turn increases the dielectric constant. At high temperatures, dielectric losses caused by the dipole mechanism reach maximum value and the degree of dipole orientation increases. Apart from the above factors, electrical conduction also increases with increasing temperature [40].

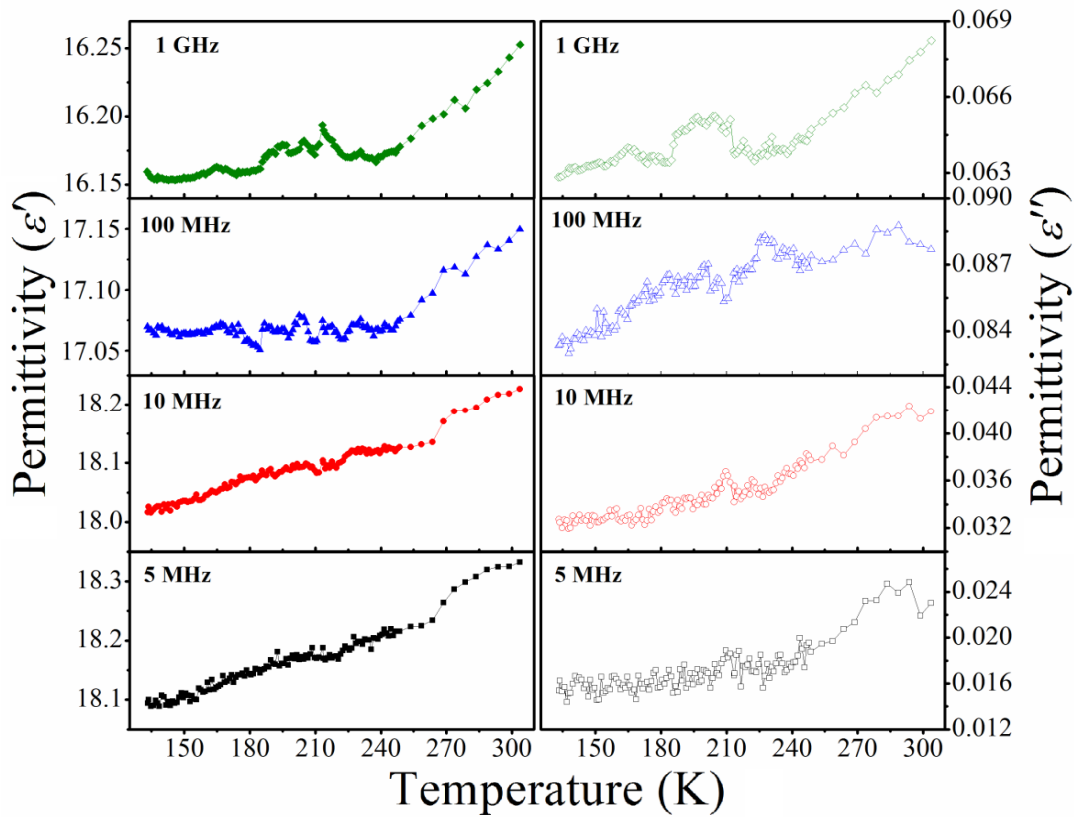


Figure 5.18: Temperature dependent real (ϵ') and imaginary (ϵ'') parts of permittivity measured at different frequencies for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.

In order to correlate the dielectric and magnetic properties in Co doped MTO ceramics, the temperature variation of imaginary part of dielectric permittivity $\epsilon''(T)$ measured at 1 GHz is compared with $M - T$ curve in Figure 5.19. Interestingly, we observed a dielectric anomaly across the onset of AFM to FM transition. It is clearly seen that the step transition observed in $\epsilon''(T)$ across the field induced transition is also realized in $M - T$. This can be associated to

the structural changes occurring in bulk $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ polycrystals. However, the response of domains in $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ is significant only at high frequency spectrum.

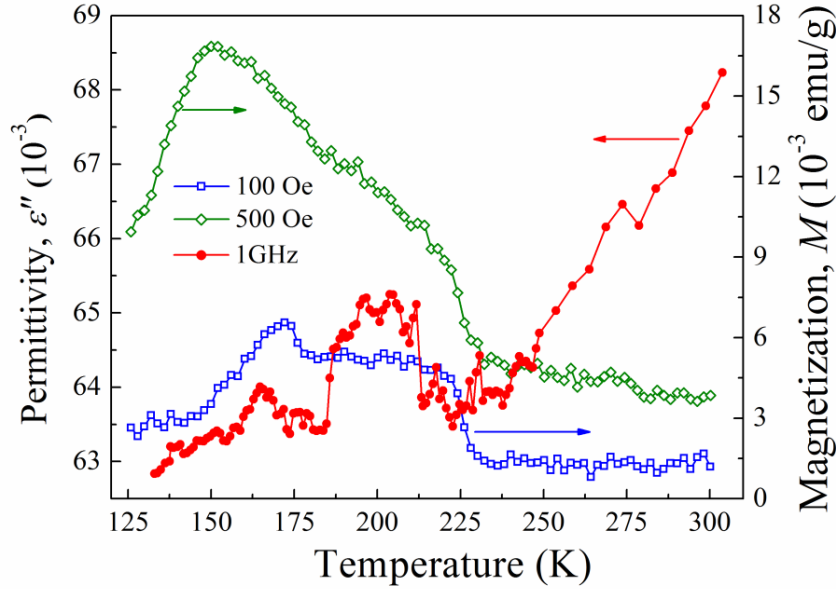


Figure 5.19: Temperature dependence imaginary part of permittivity (ϵ'') measured at 1GHz and M - T curves measured at 100 Oe and 500 Oe applied fields under ZFC process for $(\text{Mg}_{0.97}\text{Co}_{0.03})\text{TiO}_3$ sample.

5.10 Conclusions

- $(\text{Mg}_{1-x}\text{Co}_x)\text{TiO}_3$ ($x = 0.00 - 0.07$) ceramics were successfully prepared by semi alkoxide precursor method.
- The processing conditions were optimized to obtain a single phase ilmenite structure, highest density, uniform microstructure and good microwave dielectric properties.
- Due to the small initial particle size, the maximum relative density was obtained at 1200°C . This sintering temperature is around 150°C lower than the usual sintering temperature of 1350°C .
- The maximum shrinkage %, relative density of 97.17%, ϵ_r of 17.03, $Q \times f_0$ value of =170 THz and τ_f of -40 ppm/ $^\circ\text{C}$ were obtained for $x = 0.05$ samples sintered at 1200°C for 3 h, providing as one of the promising dielectric materials for low-loss and millimeter-microwave and multilayer capacitor applications.

- Interestingly, all the sintered samples exhibit paramagnetic nature at room temperature and a maximum susceptibility of 6.25×10^{-6} (emu/g-Oe) was obtained for $x = 0.03$ sample.
- Thermomagnetization measurements revealed a ferromagnetic to paramagnetic phase transition with T_C around 228 K for (Mg_{0.97}Co_{0.03})TiO₃ ceramic and a field dependent bifurcation point around 170 K.
- The temperature dependent dielectric properties revealed that both ϵ' and ϵ'' were linearly increased with temperature measured at 5, 10, 100 MHz and 1 GHz frequencies and dielectric anomalies observed at all frequencies.
- The observed anomalies were similar to the transitions observed in magnetic properties and were correlated with magnetic properties.

5.11References

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Chapter 6

Studies on Pure and Co Doped MgTiO_3

Thin Films

The MTO ceramics prepared by mechanochemical synthesis and semi alkoxy precursor method exhibited pure crystalline phase both after calcinations and sintering. Hence, we have decided to deposit the MTO thin films from the sputtering targets prepared from these methods. Thin films were deposited using RF reactive magnetron sputtering and studied their structural, microstructural, optical, electrical and dielectric properties systematically.

6.1 A short literature review

Recent past, MgTiO_3 (MTO) has been investigated in the thin film form due to its promising optical, dielectric and electrical properties. MTO thin films can be used as a buffer layer for high-purity LiNbO_3 grown epitaxially on the c -axis oriented Al_2O_3 substrates for the applications of integrated optical devices [1]. Furthermore, Lee *et al.* [2] studied the application of MTO thin films as the buffer layer by using electron-beam evaporation. Surendran *et al.* [3] reported that Zn^{2+} and Ni^{2+} substitution into Mg^{2+} sites significantly improves the dielectric response of this system. The corresponding values were $\tan\delta \approx 1.1 \times 10^{-2}$, 1.9×10^{-2} for 5 at% Ni and Zn substitution in MgTiO_3 . Pure MTO thin films prepared by soft chemistry method displays the temperature co-efficient of dielectric constant (TCK) $\sim +260$ ppm/ $^\circ\text{C}$ [4]. Ho *et al.* [5] studied the effect of crystal orientation on photoluminescence of pure MTO thin films deposited on P - type Si(111) oriented substrates. They reported that after annealing at 800°C , MTO grain growth occurred along (003) orientation by varying Ar and O_2 ratio.

Ferri *et al.* [6] prepared MTO thin films by the polymeric precursor method with posterior spin - coating deposition on Pt(111)/Ti/SiO₂/Si(100) substrates. Effect of annealing temperature on the degree of structural order - disorder, optical properties, and morphology of the MTO thin films were investigated. A very intense distinct blue and red photoluminescence (PL) emission was found in MTO thin films. They reported that the PL behavior can be associated with extrinsic and intrinsic effects: oxygen vacancies and distortions of $[\text{MO}_6] - [\text{MO}_6]$ ($\text{M} = \text{Mg}, \text{Ti}$) complex clusters [6]. However, MgTiO_3 thin films grown by PLD method on c - axis oriented Al_2O_3 substrates are highly oriented along (003) direction and exhibit very high dielectric constant 24 at 1 MHz frequency [7]. Zeng *et al.* [8] reported (012) oriented MTO thin films grown on SrTiO_3 substrates and studied the optical properties.

Huang research group has studied the MTO thin films deposited on n-type Si(111) oriented substrates using RF magnetron sputtering. They have varied different processing parameters such as RF power, substrate temperature, and working pressure and studied their effect on crystal structure; dielectric and electric properties [9-11]. Recently, they again reported the electrical properties of the MgTiO₃ based metal - insulator - metal (MIM) devices at various temperatures. Consequently, the MIM capacitor fabricated at 200°C with 210 nm thick MgTiO₃ shows very high density of capacitance $\sim 1.2 \text{ nF}/\mu\text{m}^2$ and low leakage current $1.51 \times 10^{-9} \text{ A/cm}^2$ at 5V [12]. Nevertheless, no author mentioned the processing details and phase purity of the sputtering target. However, there is no systematic study on the structural, electrical, optical and dielectric properties of pure MTO thin films sputtered from the target which is prepared using mechanochemical synthesis method. Nevertheless, up to now no report is available on the Co doped MgTiO₃ system in the form of thin film nanostructures. In addition, no systematic study on optical and dielectric properties of MTO thin films have been reported, which motivated us to pursue this study. In this chapter, the MgTiO₃ and (Mg_{0.95}Co_{0.05})TiO₃ thin films were deposited under different oxygen mixing percentage (OMP) by RF magnetron sputtering from the homemade sputtering target. The effects of processing parameters and post annealing on the structural, microstructural, optical, electrical and dielectric properties were studied systematically.

6.2 Experimental Details

6.2.1 Pure MgTiO₃ thin films

The MgTiO₃ (MTO) sputtering target was prepared by mechanochemical reaction method and the detailed experimental procedure of preparation of sputtering target was discussed in chapter 3. MTO thin films were deposited on to quartz, amorphous SiO₂ and platinized silicon (Pt/TiO₂/SiO₂/Si) substrates at ambient temperature using RF magnetron sputtering. The base pressure in the chamber was 1.0×10^{-6} mbar. The processing gas was a mixture of high pure argon (99.99%) and oxygen (99.99%) and the sputtering pressure 1×10^{-2} mbar maintained constantly throughout the deposition by varying the oxygen mixing percentage (OMP) in the sputtering gas. All the thin films were deposited at a fixed RF power of 80W and for 3 h. The as - deposited MTO thin films were annealed at 700°C for 1 h.

6.2.2 $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films

RF magnetron sputtering method has been employed to deposit the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ (MCT) thin films on amorphous SiO_2 , platinized silicon ($\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$) substrates at 300°C deposited at a fixed RF power of 40W. Initially, a sputtering target material of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ is prepared by semi alkoxide precursor method detailed methodology is discussed in chapter 5. The deposition chamber is maintained up to a base pressure of 1.0×10^{-6} m bar before the deposition. The substrate to target distance was kept at 5 cm. A mixture of high purity argon (99.99%) and oxygen (99.99%) and is then introduced in order to chamber using mass - flow controllers. The sputtering pressure of 1×10^{-2} mbar are maintained constantly throughout the deposition process by varying the oxygen mixing percentage from 0 -100% in the sputtering gas. The target was pre-sputtered in argon ambient for 10 minutes to clean the surface. The rate of deposition under different OMPs has been optimized to achieve the constant thickness of the film. The thickness of all the reported films is of the order of 280 ± 10 nm. As deposited MCT thin films are post annealed at 700°C for 1 h to obtain good crystallinity.

6.3 MgTiO_3 thin films

6.3.1 Structural Characterization of sputtering target

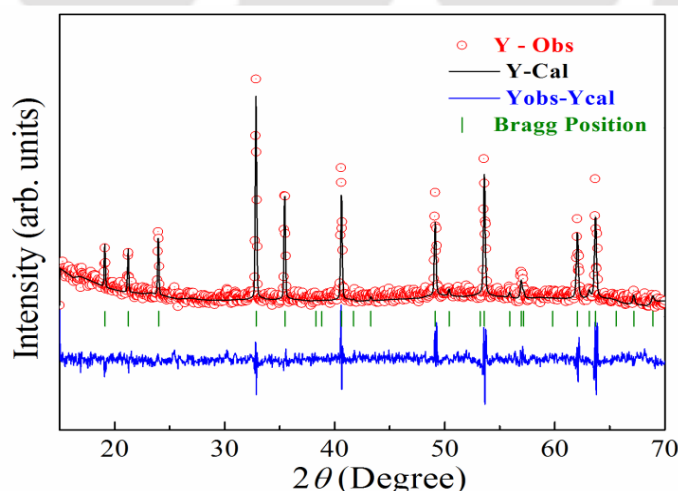


Figure 6.1: XRD pattern along with Rietveld refinement of MgTiO_3 ceramic target sintered at 1350°C . The circles and solid line represent the experimental and the Rietveld refined data, respectively. The blue line at the bottom shows the difference between the experimental and the refined data. The vertical bars correspond to the allowed Bragg's peaks.

Figure 6.1 shows the XRD pattern of the MTO sputtering target along with a Rietveld refinement result. The XRD pattern clearly indicates the formation of single phase MTO without any impurities. The Rietveld refinement was performed through fullprof program by varying cell parameters, position of the Mg, Ti, and O atoms, their occupancy and thermal parameters. The lattice parameters derived from the XRD pattern are found to be $a = b = 5.0557(12) \text{ \AA}$, $c = 13.9003(9) \text{ \AA}$. The values of χ^2 , R_{Bragg} factor and R_f factor were found to be 1.09, 14.26 and 12.53, respectively. The obtained refinement results are in agreement with the earlier reports [13].

6.3.2 Structure and microstructure of MTO thin films

All the as - deposited films were found to be amorphous and become crystalline after the post - deposition annealing at 700°C for 1 h irrespective of substrates used. It is well known that the oxide films grow naturally in an amorphous form unless the required activation is provided either in the form of the temperature or the ion bombardment to initiate the crystal growth. Upon annealing at 700°C for 1 h, the MTO thin films exhibited evidence of conversion from an amorphous state to polycrystalline trigonal phase. The XRD patterns of the MTO films deposited onto quartz and amorphous SiO₂ under different OMP are shown in Figure 6.2. Along with trigonal phase a secondary phase MgTi₂O₅ is observed for the films deposited on amorphous SiO₂ substrates. These results indicate that the intensities of the (104), (113) and (116) peaks were decreasing gradually with increasing OMP for MTO films on both the substrates. The average crystallite size of the annealed films was estimated using Scherrer's equation [14].

$$\text{Crystallite size } D = \frac{K\lambda}{\beta \cos \theta} \quad (6.1)$$

where K - Scherrer constant, where λ is wavelength of X - ray ($=1.5406 \text{ \AA}$) , β is full width and half maxima, θ is Bragg's angle. Figure 6.3 shows the variation in crystallite size as a function of OMP for the films deposited on quartz, amorphous SiO₂ and platinized silicon substrates. One can observe that a decrease in the average crystallite size with an increase in OMP from 33 to 19 nm, 29 to 21 nm and 27 to 21 nm for quartz, amorphous SiO₂ and platinised silicon substrates, respectively. This indicates that films deposited at higher OMP

were less crystalline. This may be due to the decrease in rate of deposition, which causes lowering of thickness of thin films.

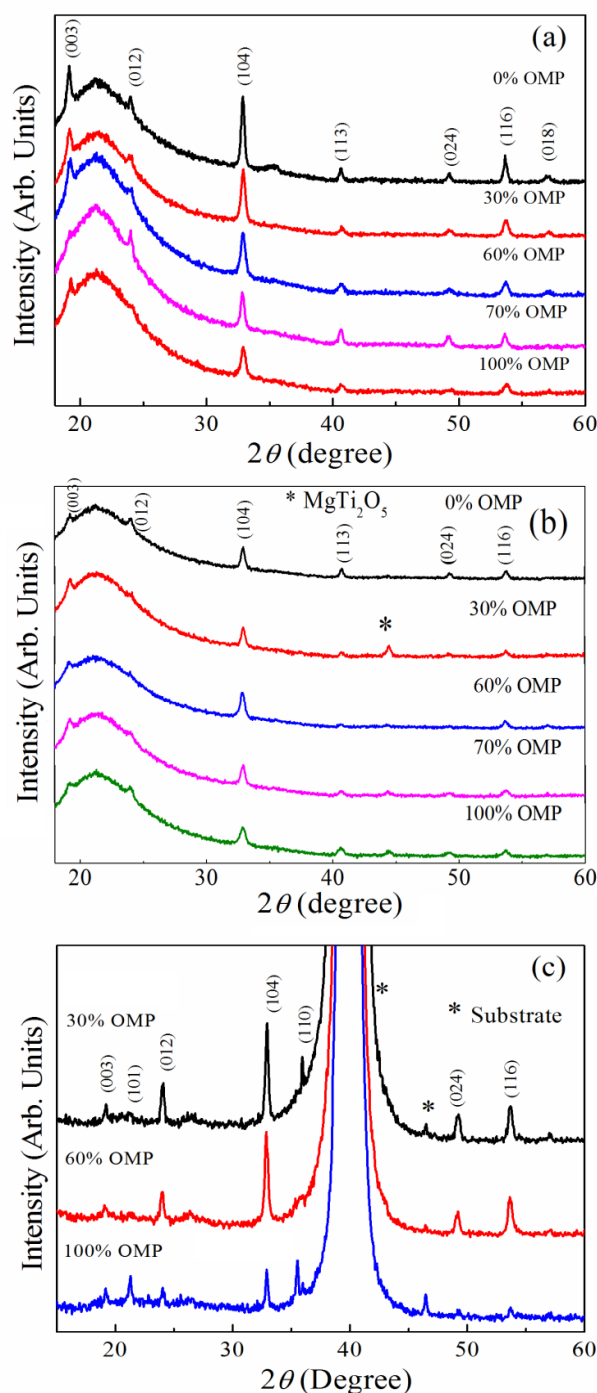


Figure 6.2: XRD patterns of MTO thin films deposited under different oxygen mixing percentage and annealed at 700°C for 1h on (a) quartz (b) amorphous SiO_2 and (c) platinized silicon substrates.

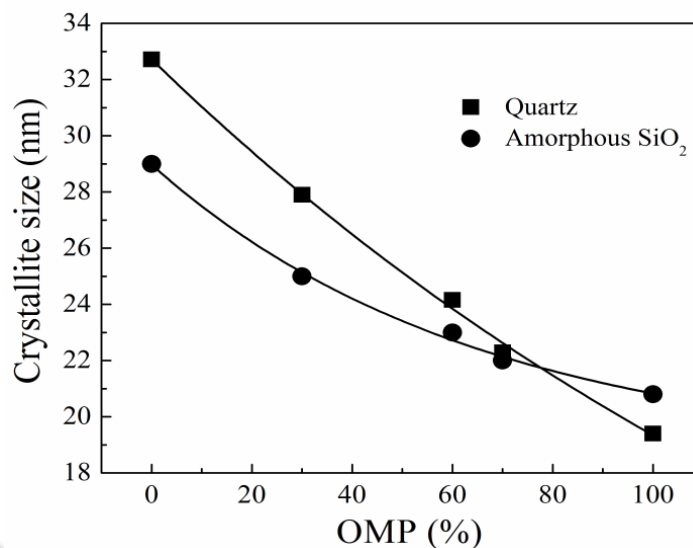


Figure 6.3: The variation in average crystallite size as a function of oxygen mixing percentage.

In order to confirm the chemical composition of the deposited MTO thin films, energy dispersive spectroscopy (EDS) analysis was performed on the films deposited on quartz substrates.

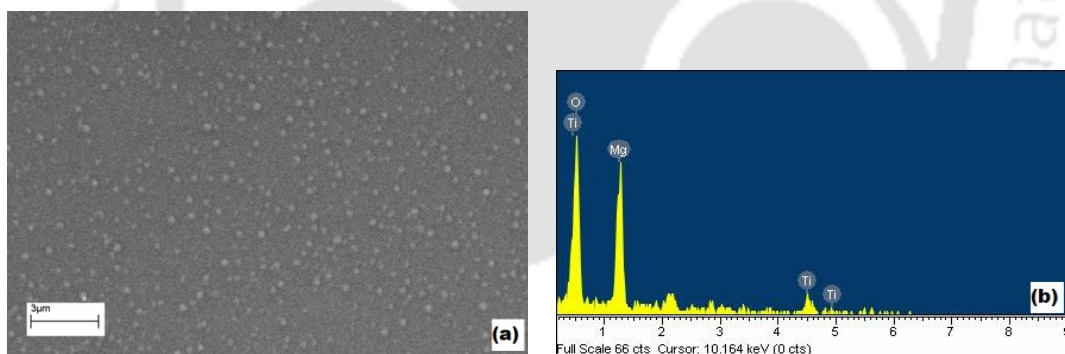


Figure 6.4: (a) SEM image and (b) EDS spectrum of the MTO thin film deposited on quartz at 70% OMP and annealed at 700°C for 1 h.

Figure 6.4(a) and 6.4(b) shows the microstructure and EDS spectrum of annealed MTO thin film deposited at 70% OMP, respectively and the elemental percentages are summarized in Table 6.1. It is found that the composition of the target is nearly achieved in the deposited thin films. The rate of deposition of Mg atoms is slightly higher than Ti atoms because Ti atomic weight is higher than Mg atoms. The slight deficiency of the oxygen can be due to the high sintering temperature of the sputtering target. The present study confirms that the

multicomponent materials can be easily grown in the stoichiometric state by using RF sputtering technique.

Table 6.1: The required and obtained percentages of elements in MTO films

Element	Weight (%)	Atomic (%)	Required	Obtained
O K	39.13	58.84	3	2.94
Mg K	21.72	21.50	1	1.08
Ti K	39.15	19.66	1	0.98
Total	100.00			

The AFM images of as - deposited and annealed MTO films deposited on quartz substrates were shown in Figure 6.5(a) and 6.5(b), respectively. It is evident that the as - deposited film does not show any apparent grain structure. On the other hand, the annealed films reveal the homogeneous nano - sized grain morphology with an average grain size of about 35 - 40 nm. Post deposition annealing enhanced the roughness and improved the grain growth which improves the packing density of the films. The magnitudes of rate of deposition of the films are 2.6 - 2 nm per minute. With an increase in the OMP, the rate of deposition and the thickness of the thin films were decreased. The thickness of the thin films was in the range of 460 - 350 nm and 380 - 305 nm for the as - deposited and annealed films, respectively.

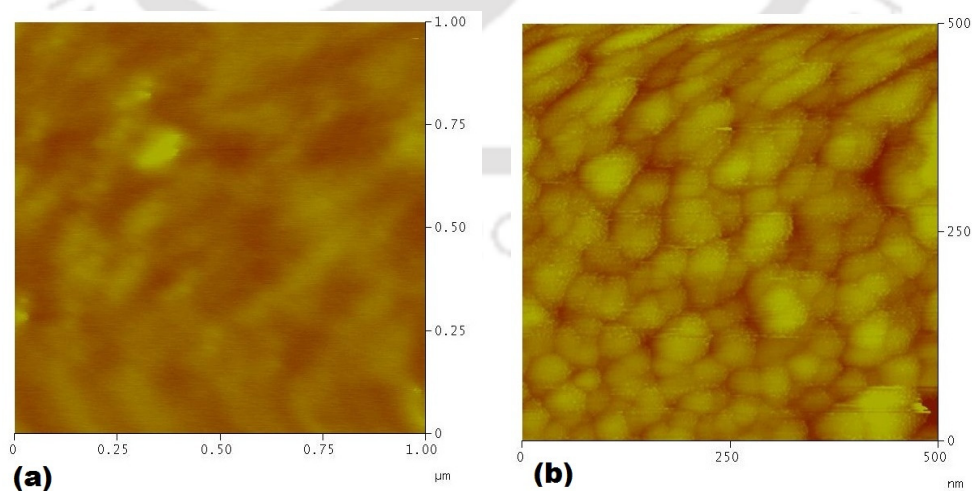


Figure 6.5: Atomic force microscopic (AFM) images of (a) as - deposited and (b) annealed MTO thin films deposited on quartz at 70% OMP.

6.3.3 Optical Characterization

To study and understand the optical behaviour of MTO thin films the optical constants were obtained from the transmittance spectra. The optical transmittance spectra of as - deposited and annealed MTO films deposited on quartz at 70% OMP and amorphous SiO_2 at 60% OMP is shown in Figure 6.6(a) & (b), respectively. The sharp fall in transmission and the disappearance of fringes at shorter wavelengths are due to the fundamental absorption of the films. All the transmittance spectra show interference fringes, which originate due to the interference at the air and substrate - film interfaces. The average transmittances of the as - deposited films were in the range between 70 - 98% above 400 nm which indicates the high quality of the deposited thin films. It was observed that the annealed MTO films exhibited lower transmittance compared to as - deposited films. The post deposition annealing causes an increase in average grain size of a film which scatters the light on grain boundaries. The packing density of the films increases upon annealing. This does not allow the light to pass through and hence the reduction in the transmittance and is also confirmed from AFM images (Figure 6.5(b)). It was also observed that the absorption edge of the annealed films shifted to the lower wavelengths.

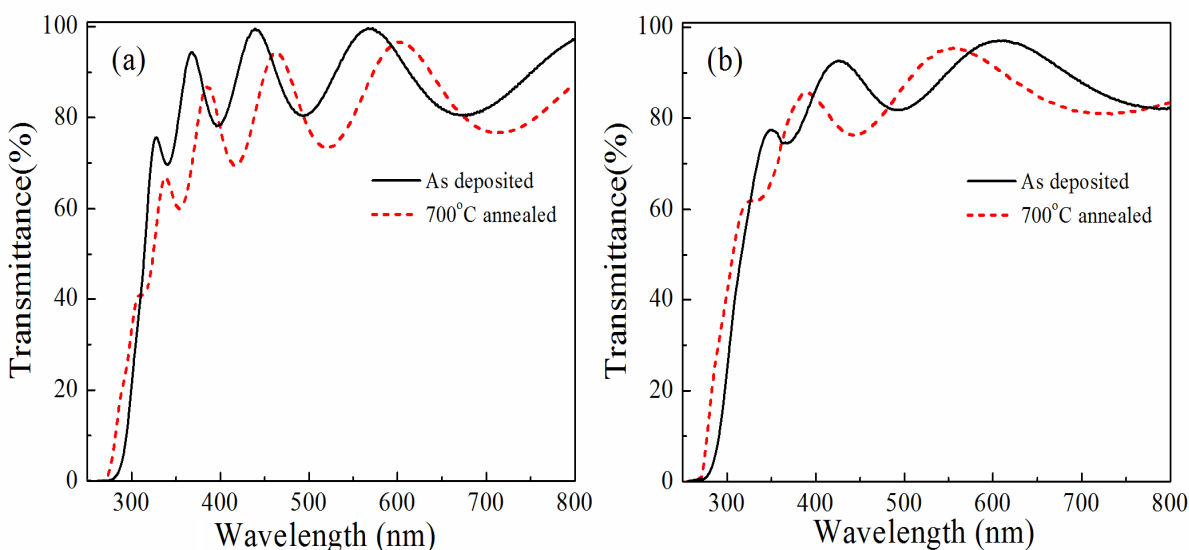


Figure 6.6: Optical transmittance spectrum of as - deposited and post annealed MTO thin films (a) On quartz deposited at 70% OMP and (b) On amorphous SiO_2 substrates at 60% OMP.

The optical packing density (P) of the films is calculated using the relation [15],

$$P = \left(\frac{n_f^2 - 1}{n_f^2 + 2} \right) \left(\frac{n_b^2 + 2}{n_b^2 - 1} \right) \quad (6.2)$$

The porosity ratio (the volume of pores per volume of film) of the films obtained using the following expression [16]

$$P = 1 - \left(\frac{n_f^2 - 1}{n_b^2 - 1} \right) \quad (6.3)$$

Where n_f and n_b are the film and bulk refractive index of MgTiO₃ (single crystal refractive index = 2.31) [17], respectively.

The variation in refractive index and packing density of as - deposited and annealed MTO thin films deposited on quartz and amorphous SiO₂ substrates as a function of OMP was shown in Figure 6.7(a, b). Porosity ratios as a function of OMP for as - deposited and annealed films were shown in Figure 6.7(c, d), respectively. It was observed that the refractive index of the MTO thin films decreased with an increase in OMP concentration both in as - deposited and annealed films. The decrease in refractive indices with an increase in OMP has been related to the packing density and crystallinity of the MTO films. The refractive index of MTO films increased with annealing, which can be attributed to the increase in the packing density, crystallinity, reduction in porosity ratio, and the improvement in morphology. The refractive index and packing densities of the as - deposited films were in the range of 2.00 - 2.06 @ 600 nm and 0.85 - 0.87, respectively and on annealing it increases to 2.12 - 2.18 and 0.90 - 0.94, respectively for MTO films deposited on quartz substrates. Whereas as-deposited MTO films on amorphous SiO₂ substrates exhibited refractive index and packing density in the range of 1.84 - 0.96 @ 600 nm and 0.75 - 0.82, respectively and on annealing increases to 1.98 - 2.14 and 0.83 - 0.92, respectively. Upon annealing, both the refractive index and packing density exhibited a similar behavior as a function OMP. The porosity ratios were found to decrease on annealing, which complements the increase in refractive index and packing density of the films. It is known that the refractive index of a transparent thin film is directly proportional to its electronic

polarization, and the electronic polarization is in turn inversely proportional to the inter - atomic separation [18]. Post deposition annealing causes a reduction in the inter - atomic spacing due to crystallization that leads to higher densification, improvement in morphology and hence an increase in the refractive index. The as - deposited films are highly disordered due to their amorphous nature resultant in lower film density and low adatom mobility, which in turn results in the lower refractive index. The packing density of the films depends on the energy of the deposited particles at higher OMP [19]. Since the momentum transfer process is lower at higher OMP due to this one can expect low deposition rate. This leads to a reduction in thickness, increase in porosity and hence decrease in refractive index.

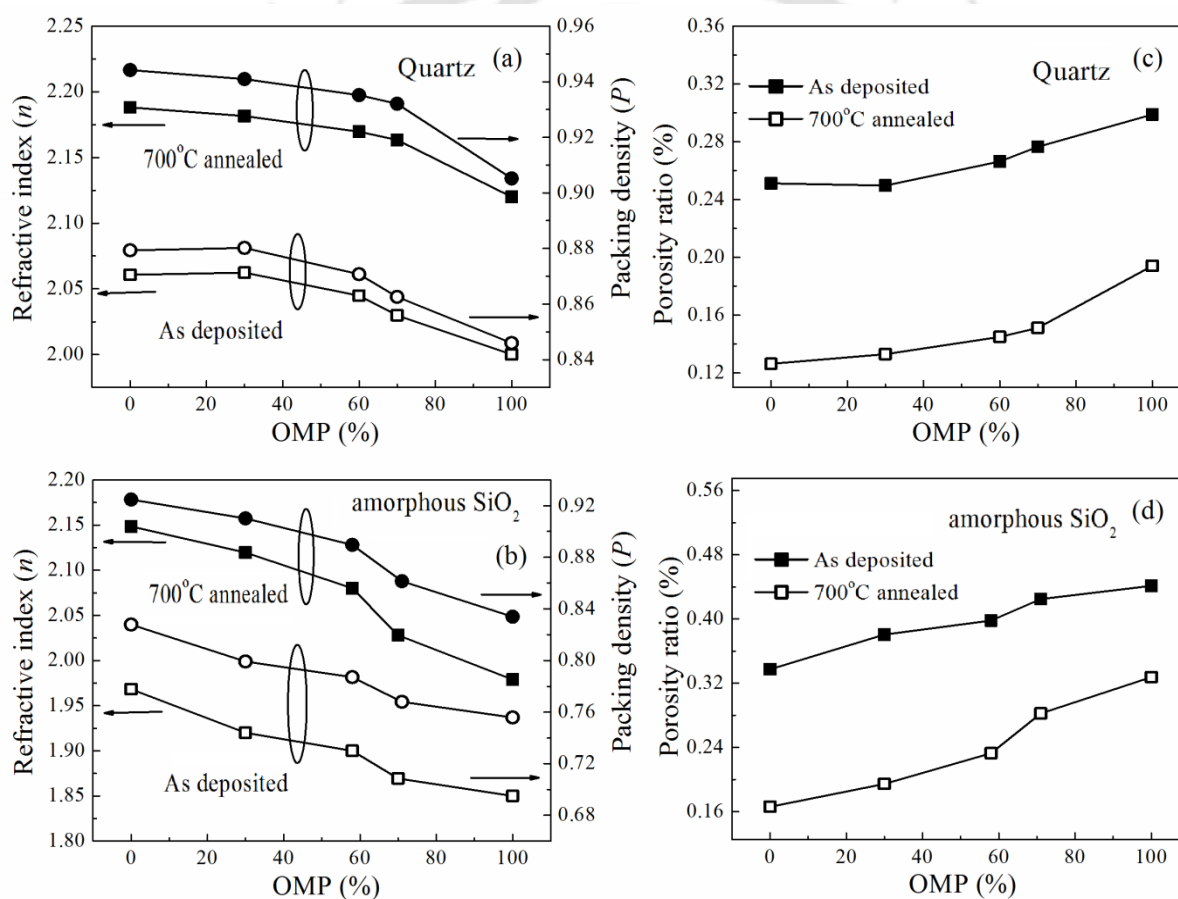


Figure 6.7: (a & b) Variation of refractive index and packing density as a function of OMP and (c & d) porosity ratio as a function of OMP of as - deposited and annealed MgTiO_3 thin films on quartz and amorphous SiO_2 substrates.

The variation in optical bandgap as a function of OMP for the as - deposited and annealed MTO films on quartz and amorphous SiO_2 substrates is shown in Figure 6.8(a) and

6.9(a), respectively. The optical band gap (E_g) for all the thin films was calculated using the Tauc equation [20], which was given by

$$(\alpha h\nu) = C(h\nu - E_g)^\gamma \quad (6.4)$$

where C is a constant, α is an absorption coefficient, $h\nu$ is the incident photon energy and $\gamma = 0.5, 1.5, 2$ or 3 for allowed direct, forbidden direct, allowed indirect and forbidden indirect electronic transitions, respectively. In the present case, the band gap energy has been estimated by assuming $\gamma = 2$. The bandgap energy (E_g) of the films was obtained by extrapolating the linear portion of the plot of $(\alpha h\nu)^{1/2}$ against $h\nu$ to $(\alpha h\nu)^{1/2} = 0$. It is known that the disordered titanates are characterized by an indirect allowed electronic transition [21]. The obtained bandgap values for as - deposited and annealed films were in the range of 3.72 - 3.77 eV and 4.11 - 4.19 eV on quartz substrates and 3.72 - 3.76 eV and 4.07 - 4.23 eV on amorphous SiO₂ substrates. It was observed that the bandgap values were found to increase for the annealed films, which is in good agreement with the earlier report by Ferri *et al.* [13].

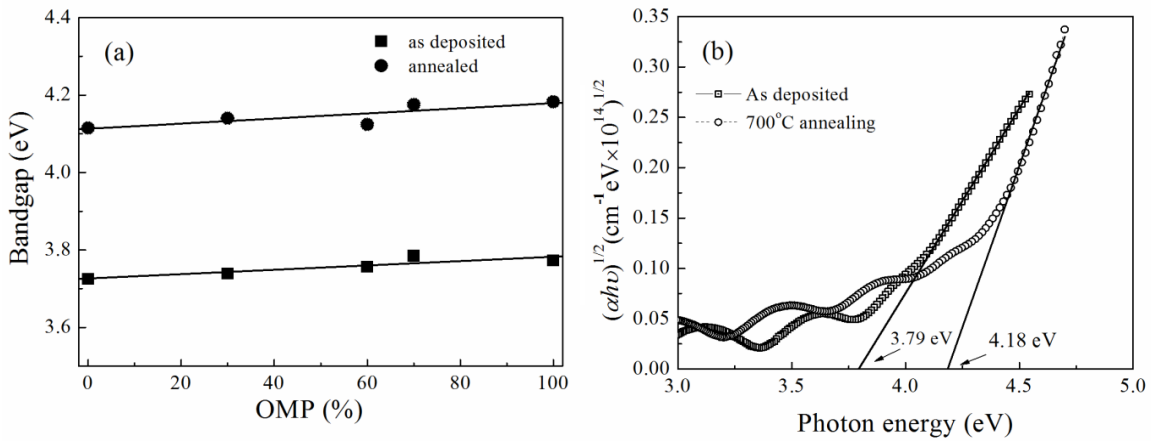


Figure 6.8: (a) Variation in bandgap as a function of OMP for as - deposited and annealed MTO thin films deposited on quartz substrates. (b) A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the MTO thin films deposited at 70% OMP.

The increase in bandgap values associated to decrease of intermediary energy levels within the optical bandgap and was confirmed from optical transmittance spectra (Figure 6.6(a) and 6.6(b)). The shift in the absorption edge to a lower wavelength indicates an increase in the bandgap upon annealing. Figures 6.8(b) and 6.9(b) shows $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the MTO thin films deposited at 70% OMP on quartz and 60% OMP on amorphous SiO₂

substrates, respectively. A slight increase in the bandgap is observed with the increase in OMP. Although the bandgap energy is a constant for a material in the bulk form, it is known to vary in thin films. The dependence of optical bandgap on crystallite size MTO thin films on various substrates is shown in Figure 6.10. It was observed that the films with smaller crystallite exhibit larger bandgap energy than those with larger crystallite size. It is demonstrated in the number of other oxide films that the bandgap decreases with an increase in crystallite size exhibiting approximately $1/d^2$ dependence where d is the crystallite diameter [22].

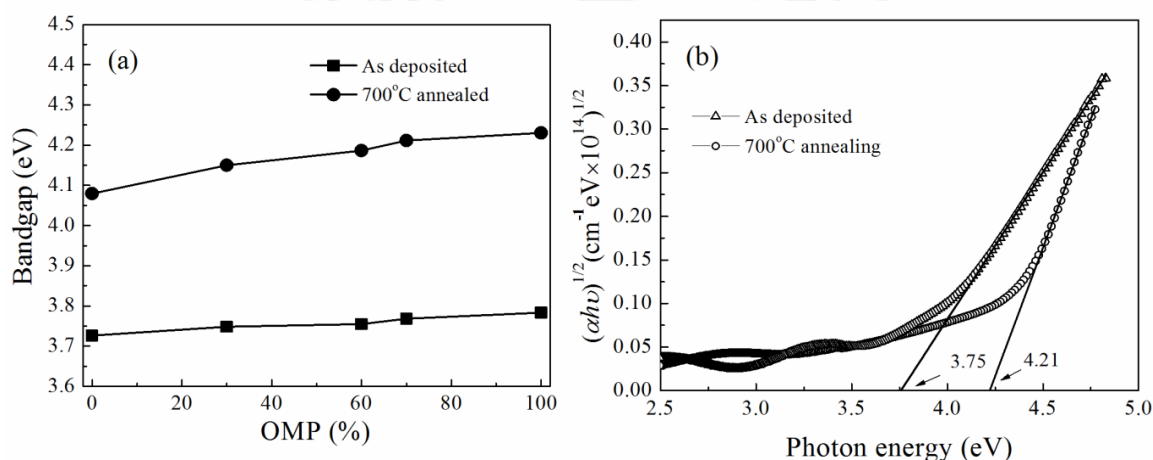


Figure 6.9: (a) Variation in bandgap as a function of OMP for as - deposited and annealed MTO thin films deposited on quartz substrates. (b) A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the MTO thin films deposited at 60% OMP.

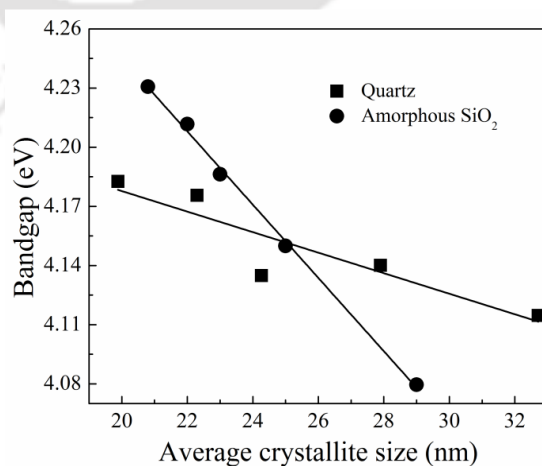


Figure 6.10: The variation in bandgap as a function of average crystallite size for MTO thin films deposited onto quartz and amorphous SiO_2 substrates.

6.3.4 Dielectric studies

To investigate effect of processing parameters on the dielectric response of MTO thin films, MIM capacitors were fabricated. Figure 6.11(a) and 6.11(b) shows the variation in dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of the MTO films deposited under different OMP. Both the dielectric constant and $\tan\delta$ are found to decrease with an increase in applied frequency. The dielectric constant and loss tangent values are in the range between 31.11 - 13.68 and 0.124 - 0.006, respectively. The decrease in dielectric constant with the increase in frequency is a typical characteristic of the linear dielectric. It is observed that the dielectric constant and loss values were found to be higher at low frequencies. The dispersion in dielectric constant with frequency can be explained on the basis of Maxwell - Wagner two layer and koop's phenomenological theory [23]. These models demonstrate that as the frequency increases, the electrons reverse their direction of motion more often, which decreases the probability of electrons reaching the grain boundary, which results in the reduction in polarization leading to a decrease in the dielectric constant. It is observed that as OMP increases, both the dielectric constant and loss tangents are improved, and the films deposited at 100% OMP exhibited maximum dielectric constant and lowest loss. It is natural that films deposited at lower OMP may have some oxygen vacancies, which lead to a high dielectric loss. The dielectric loss arises from interfacial dead layers, possibly existing at a film - electrode interface and the interface dead layer may occur due to impurities, vacancies and the lattice disorder. The dielectric dispersion at low frequencies occurs due to the space charges arising from vacancies or charged defects, and the structural disorder is likely to be the primary cause for dielectric loss. The improvement in dielectric properties with the increase in OMP has been correlated to the reduction in oxygen vacancies, increase in crystallinity and grain size of the films. Chen *et al.* [9] reported $\epsilon_r = 15.91$ and $\tan\delta = 0.05$ at 1MHz for MTO thin films deposited at 350°C by RF sputtering while Choi *et al.* [17] reported dielectric properties: $\epsilon_r = 21$ and $\tan\delta = 0.02$ at 100 KHz and the films were prepared by metal organic solution deposition method. Surendran *et al.* [24] reported the dielectric properties ($\epsilon_r = 16.3$ and $\tan\delta = 0.0021$ at 1MHz) of MTO thin films deposited at 700°C by Non - Methoxyethanol route. In the present study, the observed values are $\epsilon_r = 15.4$ and $\tan\delta = 0.006$ at 1MHz and are in agreement with the reported values. The microwave dielectric properties of bulk MTO ceramics ($\epsilon_r = 15.85$ and $Q \times f_0 = 162,300$ GHz) were reported by the

current authors [25]. The obtained results for both bulk and thin films of MTO ceramics are almost comparable.

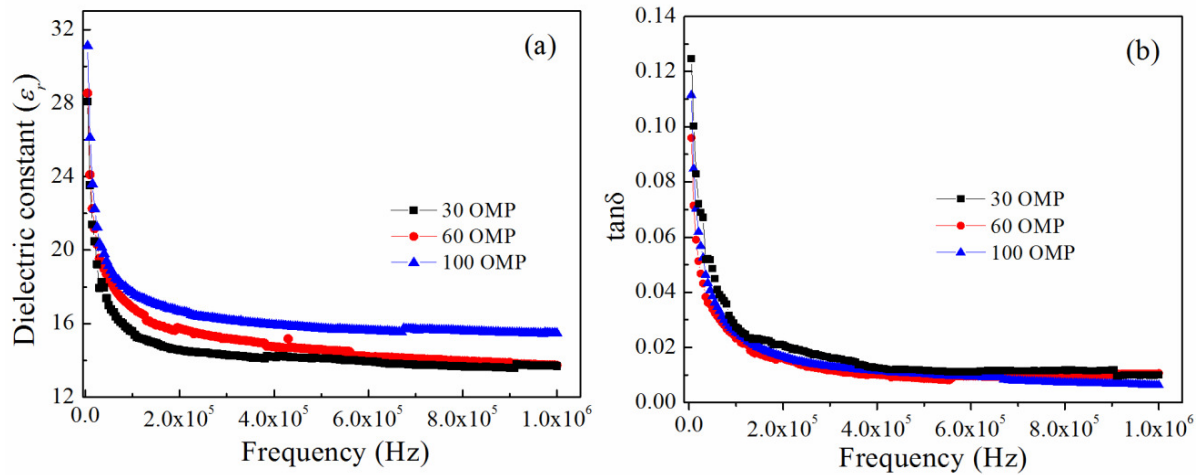


Figure 6.11: Plots of variation in (a) dielectric constant and (b) loss tangent of MTO thin films deposited at different OMP as a function of frequency.

The low dielectric losses in the case of bulk MTO ceramics may be due to the large grain sizes, and the reduction in strain of the crystallites results from high sintering temperature. In the case of thin films, the small grain sizes results in large grain boundary area and these differences could cause the deviation from the bulk properties. The grain boundary regions are interconnected in all directions, and their properties may dominate or severely influence the effective dielectric response of the whole system even if their volume concentration is relatively small [26]. From the present study, it is clear that the obtained optical and dielectric properties of MTO thin films show that these films are one of the potential candidates for applications in integrated circuits and optical devices.

6.4 $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films

6.4.1 Structural Characterization of sputtering target and thin films

To study effect of Co substitution on the crystal structure, microstructure, optical, electrical and dielectric properties of MTO ceramics and to compare these properties with pure MTO thin films, this study is initiated. The x-ray diffraction pattern along with the Rietveld refinement data of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ (MCT) sputtering target, sintered at 1200°C for 3 h is shown in Figure 6.12. The refinement was carried out by considering $R\bar{3}$ space

group [27]. The lattice parameters, atomic positions of the Mg , Ti , Co and O atoms, and occupancy are refined. The corresponding estimated values being $a = b = 5.053 \pm 0.001 \text{ \AA}$, $c = 13.898 \pm 0.002 \text{ \AA}$. The fitting parameters (i) $\chi^2 \approx 2.09$, (ii) R_{Brag} factor ≈ 2.86 and (iii) R_f factor ≈ 3.08 for MCT target system.

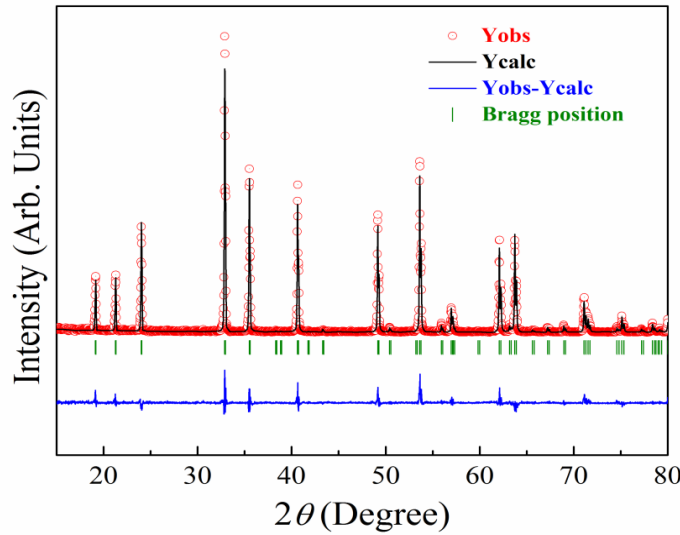


Figure 6.12: X-ray diffraction pattern along with the Rietveld refinement of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ target material, sintered at 1200°C for 3 h in air.

MCT thin films deposited at 300°C under various oxygen mixing percentages depict amorphous nature. However, after annealing at 700°C for 1 h in air all the thin films exhibit rhombohedral crystal structure, which is consistent with the earlier reports [28]. Figure 6.13(a) and 6.13(b) shows the X-ray diffraction pattern of post annealed MCT thin films deposited under various oxygen mixing percentages on platinized silicon and amorphous SiO_2 substrates, respectively. Significant changes have been noticed in the peak intensities of (104), (110) and (003) reflections. The peak intensities of (003), (012), (211) and (104) reflections suppressed while (101), (110), (013) and (024) peaks were enhanced with increasing in OMP up to 75% and decreases beyond for MCT thin films on both the substrates. The variation in the peak intensities of (104) and (110) reflections as a function of oxygen mixing percentage is shown in Figure 6.14. One can clearly observe an opposite trend of peak intensities with an increase in OMP level. The peak intensity of (110) increases progressively up to 75% of OMP confirming the preferred orientation of grains along (110) direction. Such kind of favoured orientational growth with the increase of oxygen content has also been observed in various other systems also [29-31].

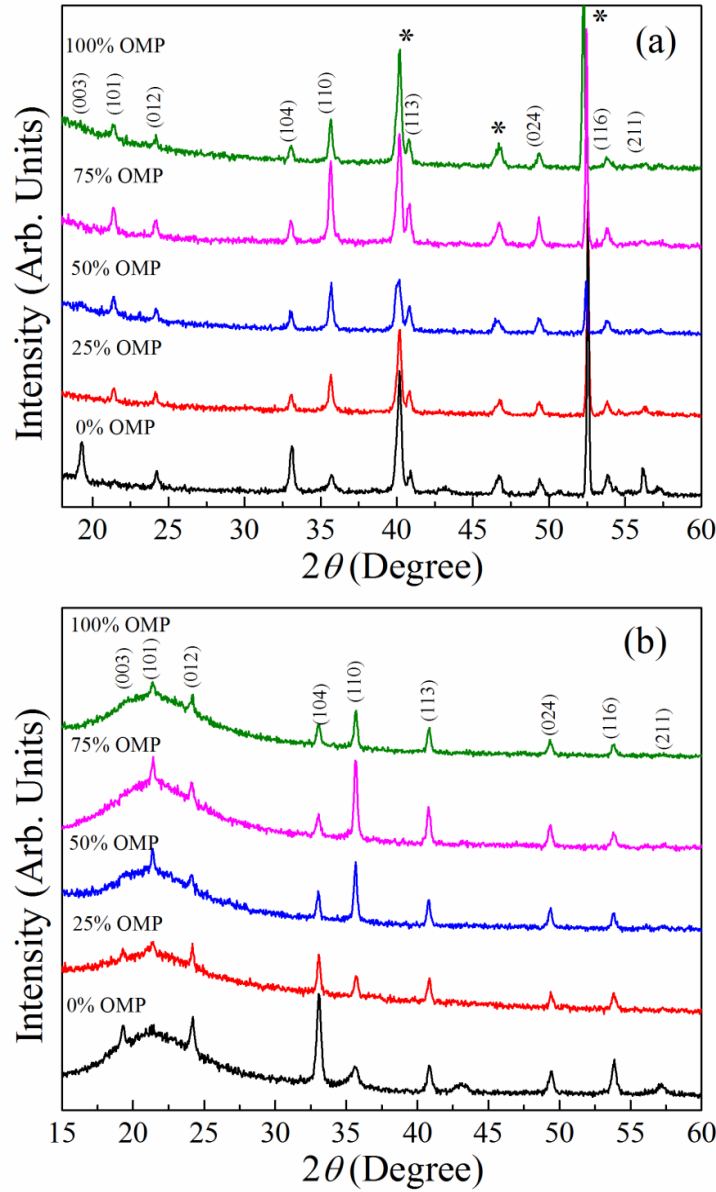


Figure 6.13: X-ray diffraction patterns of post annealed $(Mg_{0.95}Co_{0.05})TiO_3$ thin films at $700^\circ C$ deposited on (a) platinized silicon and (b) amorphous SiO_2 substrates at different oxygen mixing percentage (OMP). The peak with asterisk mark indicates the reflection from Si substrates.

The preferred oriented growth can be explained on the basis of Lotgering analysis [32] of the orientation factors (F) with respect to a reference plane (abc) defined as

$$F = \frac{(P - P_0)}{(1 - P_0)} \quad (6.5)$$

$$P = \sum I_{(abc)} / \sum I_{(hkl)} \quad (6.6)$$

where abc denotes the Miller indices, P represents the ratio of sum of intensities of the investigated reflections (abc) to the sum of all reflections of the textured thin film. The value “ P_0 ” stands for the equivalent ratio for the ceramic powder of the target with random orientation. Usually, the value of the orientation factor for preferred orientation should lie in the range 0 to 1. Thus, $F = 0$ denotes a film with randomly oriented grains, while $F = 1$ denotes a perfect epitaxial growth. In the present case, all the diffraction peaks lie in the range $2\theta = 15^\circ - 60^\circ$ has been used to calculate the P and P_0 . The P_0 values obtained from the MCT sputtering targets are found to be 0.30 and 0.12 for the (104) and (110) planes, respectively. Consequently, the calculated orientation factors for the (104) and (110) reflections of the MCT thin films on both substrates are plotted as a function of oxygen mixing percentage, which is shown in Figure 6.15.

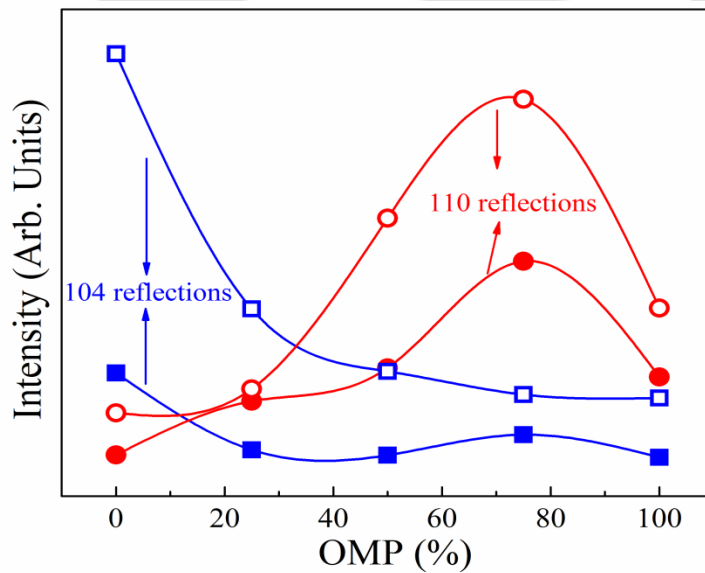


Figure 6.14: The variation of XRD peak intensity of the (104) and (110) reflections as a function of oxygen mixing percentage. Solid symbol indicates films on platinized silicon substrates and open symbol films on amorphous SiO_2 substrates.

For lower OMP values the orientation factor for both (104) and (110) reflections turns out to be close to the zero indicating that the films grown under pure Ar ambient are randomly oriented. With an increase in OMP, the $F(104)$ goes to negative value and $F(110)$ increases continuously, which indicates that the MCT thin films grown under high OMP is

textured along (110) direction. The maximum value of $F(110) \approx 0.32$ and 0.30 is observed for 75% OMP deposited films on platinized silicon and amorphous SiO_2 substrates, respectively beyond, which $F(110)$ values start decreasing. Identical results obtained for both the substrates confirms that the growth of (110) orientation is independent of substrate used, but it depends strongly on oxygen mixing percentage. Similar results were reported by C. L. Huang *et al.* [11, 33] for the highly (110) oriented pure MgTiO_3 thin films prepared by using RF magnetron sputtering.

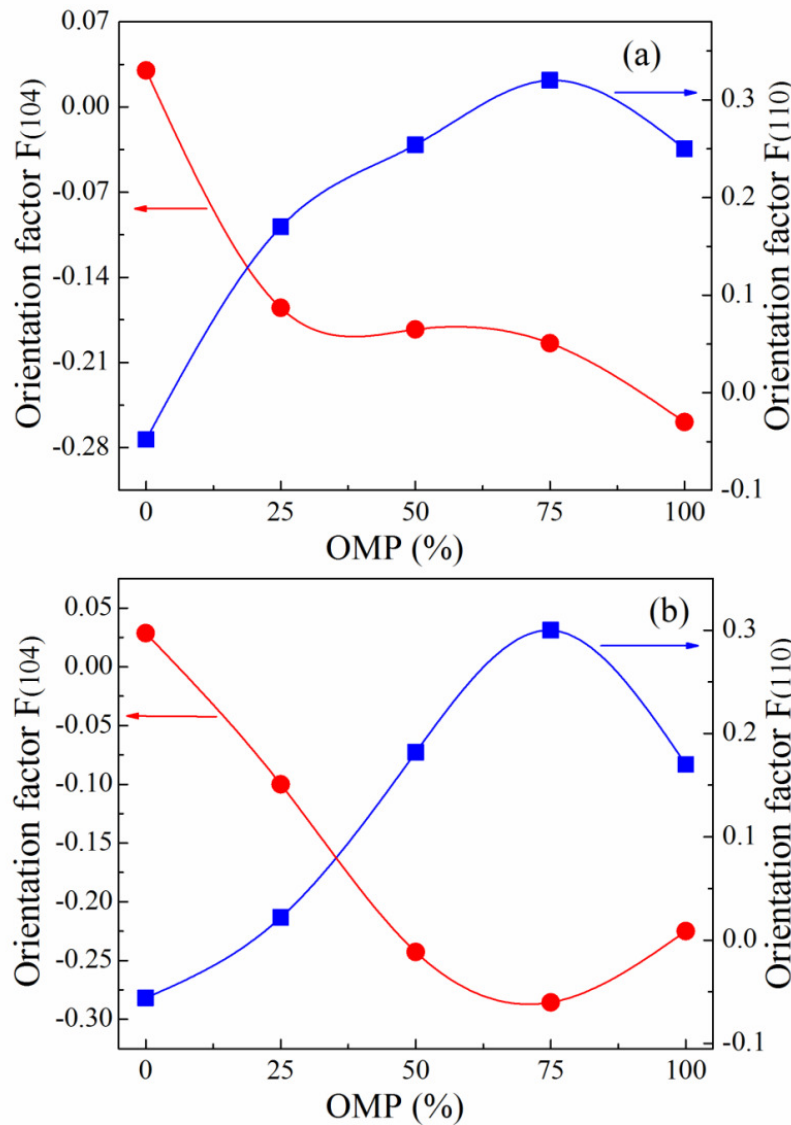


Figure 6.15: The dependence of orientation factor (F) of as a function of oxygen mixing percentage for MCT thin films deposited on (a) platinized silicon and (b) amorphous SiO_2 substrates.

6.4.2 Surface morphology

Figure 6.16 and 6.17 shows the atomic force microscopic images of as deposited and post annealed MCT thin films deposited under different OMP on platinized silicon and amorphous SiO_2 substrates, respectively.

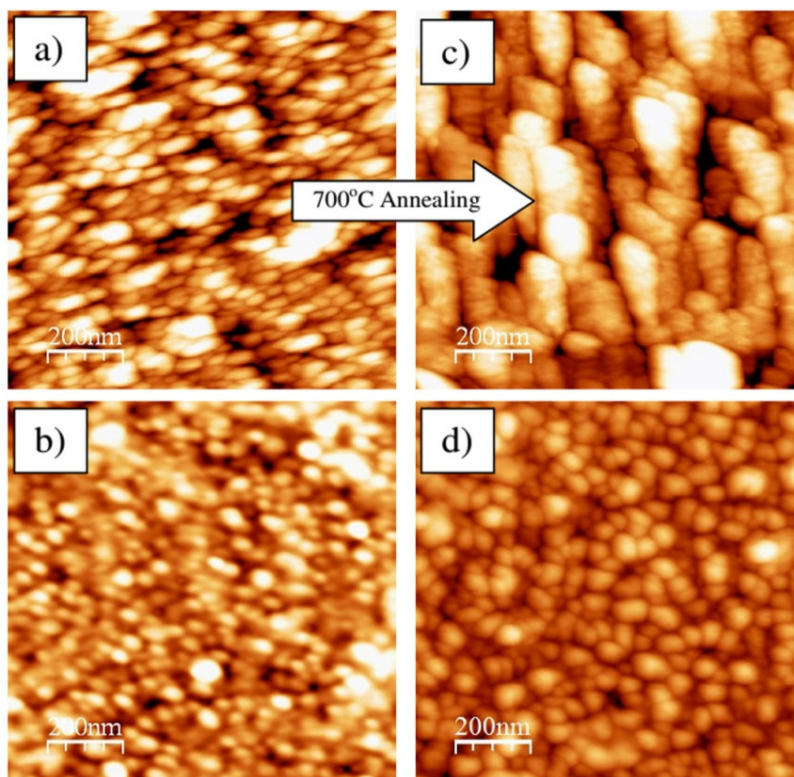


Figure 6.16: Atomic force microscopic (AFM) images of the $(Mg_{0.95}Co_{0.05})TiO_3$ thin films deposited on platinized silicon substrates. As grown thin films at (a) 25% OMP, (b) 75% OMP. After annealing at (c) 25% OMP (d) 75 % OMP.

Different surface morphologies and roughness have been noticed with the variation in OMP and annealing conditions. Thin films deposited at $300^\circ C$, could enhance the surface diffusion during deposition and forms small and uniform grains. The root means square (rms) surface roughness of as - grown MCT films deposited, at 25% and 75% OMP was 8.8 nm and 7.5 nm, respectively for platinized silicon substrates, whereas films deposited on amorphous SiO_2 substrates and deposited in pure Ar atmosphere is found to be 8.2 nm. However, the post annealed films shows larger grains with pronounced grain boundaries due to diffusion. With increasing the oxygen content, the rms surface roughness of the films

decreases from 15.3 nm to 9.3 nm and 12.6 to 3.4 nm for platinized silicon and amorphous SiO_2 substrates, respectively. For the films deposited under pure Ar ambience one can expect an abnormal grain growth and high surface roughness as compared to the oxygen environment. This is due to large momentum transfer process (heavier Ar atoms) as compared to the lighter gas such as oxygen, where relatively fewer rms roughness sputtering yields can be expected [34].

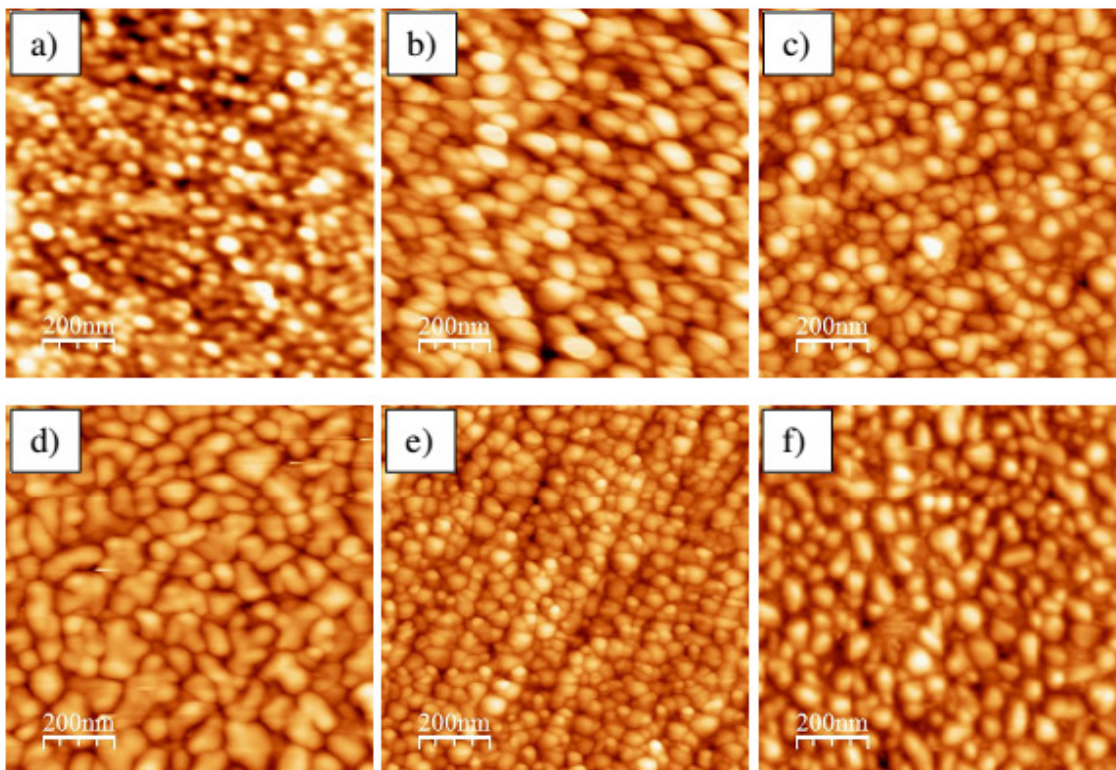


Figure 6.17: AFM images of the $(Mg_{0.95}Co_{0.05})TiO_3$ thin films deposited on amorphous SiO_2 substrates. As grown thin films at (a) 0% OMP. After annealing (b) 0% OMP, (c) 25 % OMP, (d) 50% OMP (e) 75 % OMP and (f) 100% OMP.

6.4.3 Optical properties

The optical transmittance spectra of as - deposited and annealed MCT thin films deposited in pure Ar atmosphere on amorphous SiO_2 substrates is shown in Figure 6.18(a). All the transmittance spectra show interference fringes, which originate due to the interference at the air and substrate - film interfaces. The sharp fall in transmission and the disappearance of fringes at shorter wavelengths are due to the fundamental absorption of the

films. The transparency of the films increases sharply at a wavelengths 280 nm and 300 nm for annealed and as - deposited films, respectively. The average transmittance values for the as - deposited films were in the range between 65 - 98% above 350 nm, which indicates that the high quality of the deposited thin films. On annealing a slight decrease in transmittance, it may be attributed to the improvement of grains, which causes light scattering effects at grain boundaries and was confirmed from the AFM images (Figure 6.17).

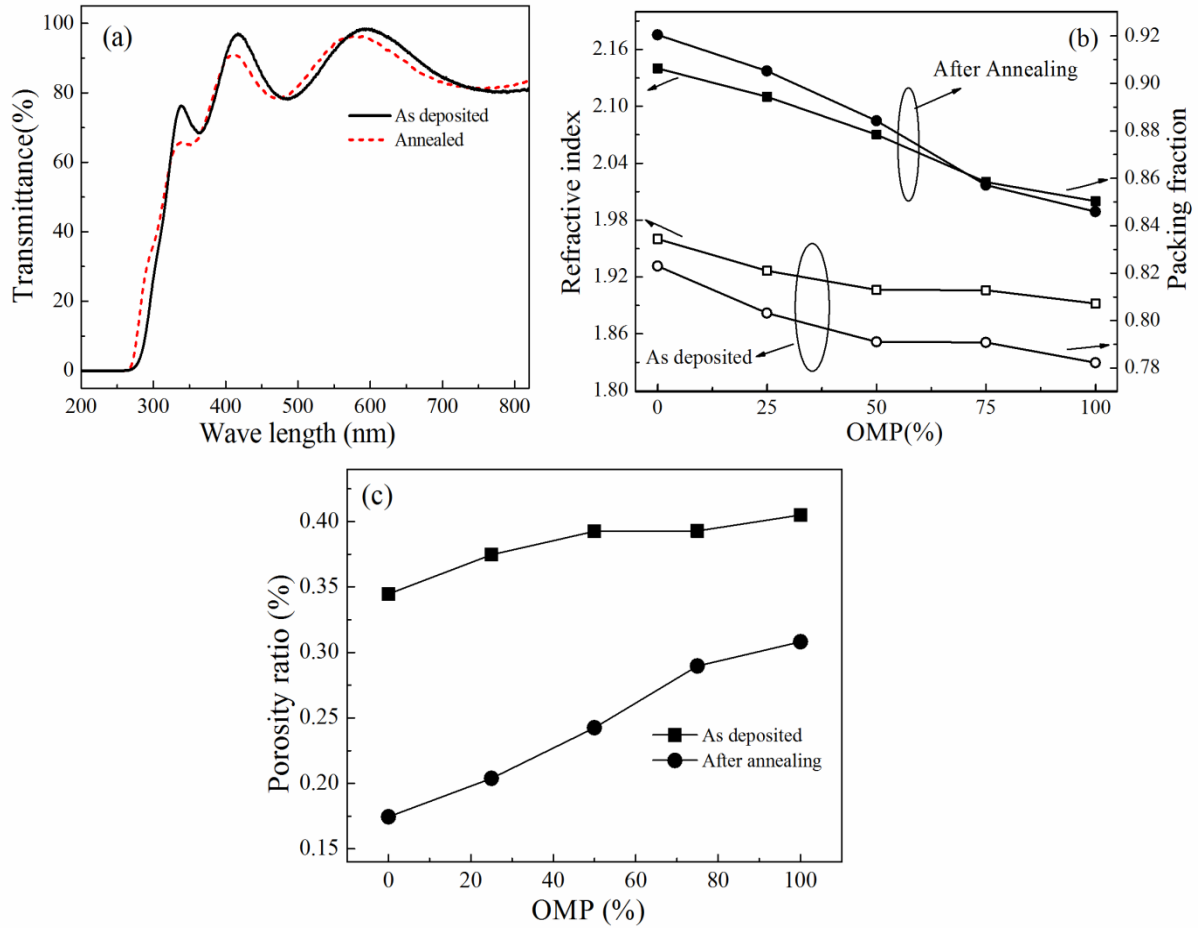


Figure 6.18: (a) Optical transmittance spectra of as - deposited and annealed MCT thin films deposited at 0% OMP. (b) Variation of refractive index and packing density as a function of OMP and (c) porosity ratio as a function of OMP of as-deposited and annealed films on amorphous SiO_2 substrates.

The variation of refractive index, packing density and porosity ratio of as - deposited and annealed MCT thin films deposited on amorphous SiO_2 substrates as a function of OMP are shown in Figure 6.18(b) and 6.18(c), respectively. It was observed that, refractive index of the thin films decreases with OMP concentration and increase with annealing. Both the

refractive index and packing density exhibited a similar behaviour as a function OMP. This behavior is similar to the behaviour of optical properties of MTO thin films with OMP which is already discussed in previous sections. The refractive index and packing densities for the as deposited films were in the range of 1.89 - 1.96 @ 600 nm and 0.78 - 0.82, respectively and on annealing increases to 2 - 2.14 and 0.84 - 0.92, respectively. The porosity ratio was found to decrease on annealing, which complements the refractive index and packing density as a function of OMP. The increase in the refractive index on annealing can be attributed to the decrease in porosity ratio and improvement in crystallinity. On annealing, there is a reduction in the inter - atomic spacing due to crystallization that leads to higher densification, improvement in morphology and hence an increase in the refractive index. The as - deposited films are highly disordered due to their amorphous nature resulting in lower film density, which in turn results in the lowering of the refractive index.

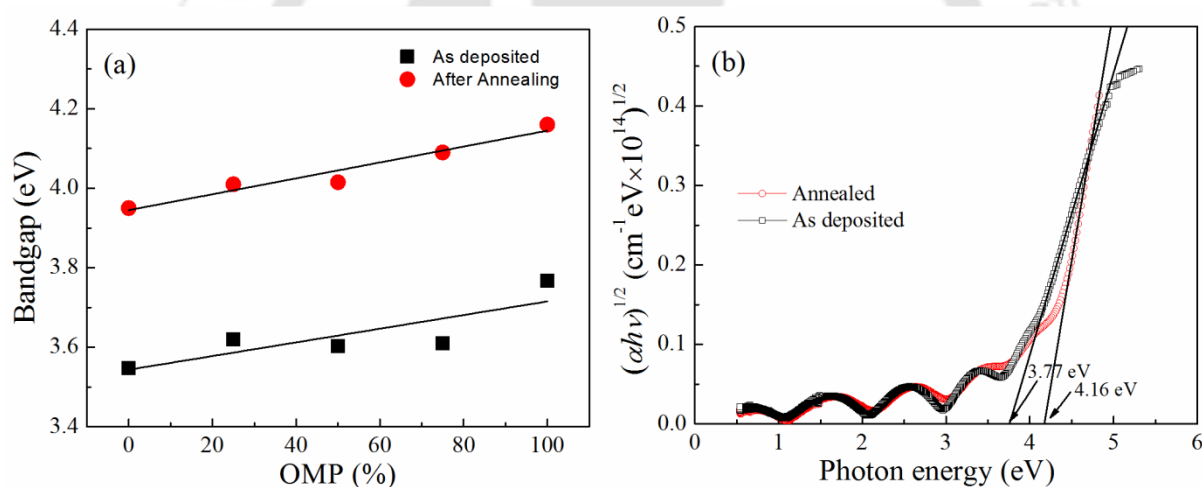


Figure 6.19: (a) Variation in bandgap as a function of OMP for as deposited and annealed MCT thin films on amorphous SiO_2 substrates. (b) A plot of $(ah\nu)^{1/2}$ versus $h\nu$ for the MCT thin films deposited at 0% OMP.

The variations in bandgap as a function of OMP for the as - deposited and annealed MCT thin films were shown in Figure 6.19(a). The optical band gap (E_g) for all the thin films was calculated using the Tauc equation [20]. The obtained bandgap values were in the range 3.55 - 3.77 eV and 3.95 - 4.16 eV for as - deposited and annealed MCT films, respectively. It was observed that the bandgap values found to increase on annealing and with OMP. The similar behaviour is observed for the pure of MTO films which is discussed in previous section. The increase in bandgap values associated to decrease of intermediary energy levels

within the optical bandgap and was confirmed from optical transmittance spectra (Figure 6.18(a)), the absorption edge was shifted to a lower wavelength which shows that on annealing the bandgap of the films increases. Figure 6.19(b) shows $(\alpha h\nu)^{1/2}$ versus $h\nu$ for the MTO thin films deposited at 0% OMP.

6.4.4 Impedance spectroscopy

Figure 6.20(a) shows the frequency variation of imaginary part of impedance ($-Z''$) recorded at different temperatures in the range 300 K - 493 K for 25% OMP of MCT deposited on platinized silicon substrates. For $T < 383$ K, Z'' exhibit a very high magnitude which decreases monotonically with an increase in ac - driving frequency (f). As the temperature increases beyond 383 K, a cusp like behavior is observed in the $Z''(f)$. The maximum values of Z'' occurs at 2.1×10^3 Hz, 3.1×10^3 Hz, 4.1×10^3 Hz, and 5.1×10^3 Hz at 413 K, 443 K, 468 K and 493K, respectively. The peak value of Z''_{max} shifts towards the higher frequency side with decrease in the magnitude of the peak implying that the electrical relaxation phenomenon is thermally activated [35]. For frequencies above 25 kHz, all the curves merge into a single curve at the investigated temperature range. The relaxation process may be due to the presence of immobile species at low temperature and may be due to the formation of defects at the high temperatures.

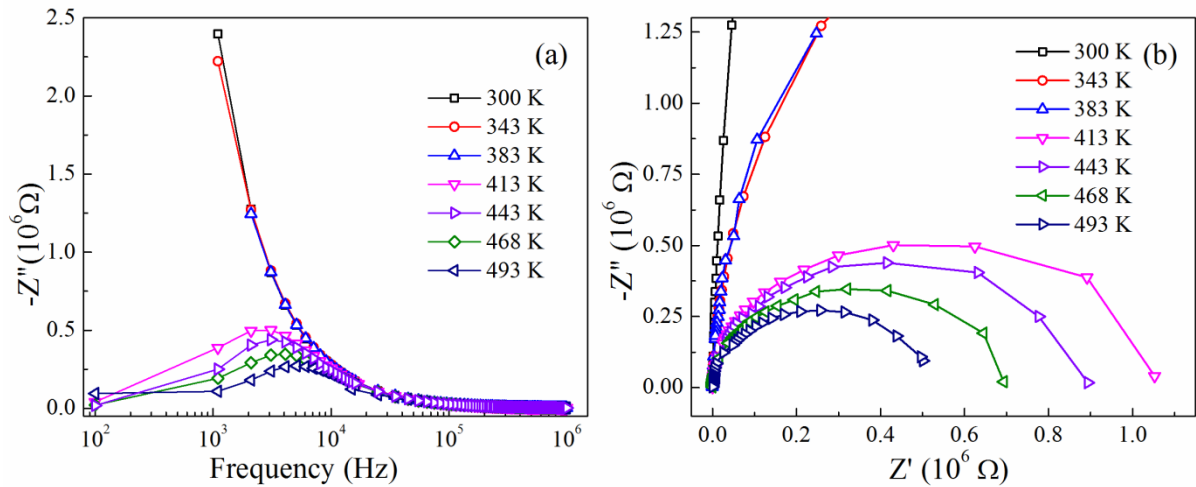


Figure 6.20: (a) Frequency dependence of the imaginary component of impedance ($-Z''$) spectra recorded at different temperature of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films deposited at 25% OMP on platinized silicon substrates. (b) The Nyquist plots (Cole - Cole graphs) of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ films deposited at 25% OMP.

Figure 6.20(b) shows the Nyquist plots of a complex impedance spectrum of MCT thin films deposited at 25% OMP, measured at different temperatures. At low temperature range 300 - 383 K the plots of Z' vs. $-Z''$ linearly line up towards the $-Z''$ axis indicating the higher resistance of the samples. With increasing the temperature above 383 K, these curves become almost semi circular arcs with non-zero high frequency intercept. Generally, the semicircle behaviour of complex impedance plots can be explained on the basis of an equivalent circuit model as shown in the inset of Figure 6.21(a). In such equivalent circuit model, the high frequency intercept provides the value of the series resistance, and the magnitude of semi circle diameter gives the electrical dc - resistivity of the sample at a specified temperature. The maximum value corresponds to the relaxation frequency $\omega = 1/RC$. For the present $-Z''$ and Z' Cole-Cole configuration two parallel RC combination circuit $[(R_g C_g) (R_{gb} C_{gb})]$ elements connected in series serves as the equivalent circuit. The semi circle arc at low frequency circuit corresponds to grain boundary resistance (R_{gb}) and the high frequency arc indicates the contribution from grain (R_g).

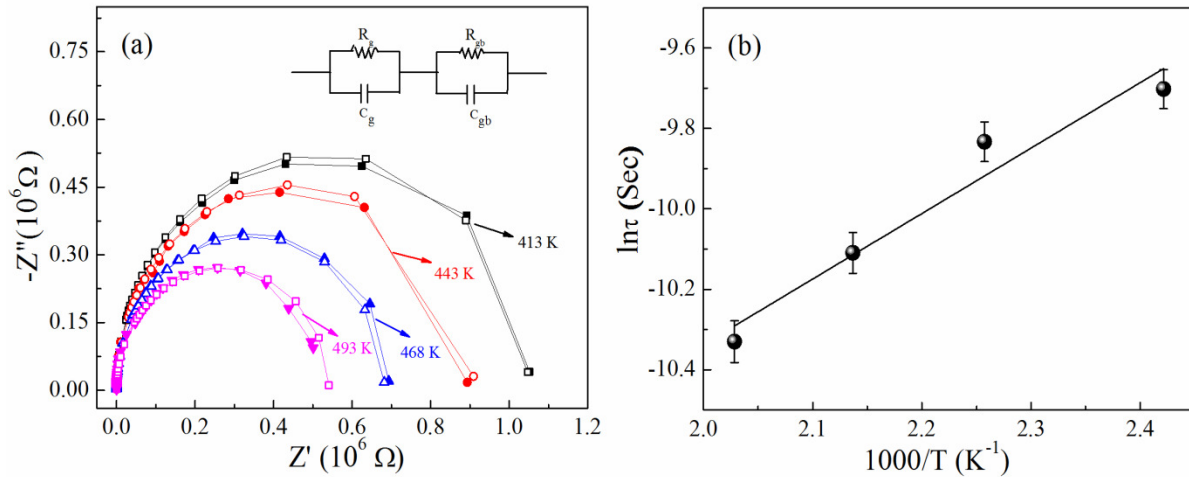


Figure 6.21: (a) Experimental and calculated Nyquist fittings of $(Mg_{0.95}Co_{0.05})TiO_3$ thin films deposited at 25% OMP at different temperatures for the equivalent circuit model given in the inset. Solid symbol indicates experimental data while open symbol indicates fitted data. (b) The variation of relaxation time (τ) as a function of $1000/T$.

Figure 6.21(a) shows the Z' vs. $-Z''$ plots after fitting experimental data with equivalent circuit model. The open symbol represents the fitted data while the solid symbol shows the experimental data. The calculated R_g and C_g values were given in Table 6.2. Using these

values the relaxation time (τ) is calculated by substituting it in the equation: $\tau = 1/\omega = R_g C_g$. Figure 6.21(b) shows the variation of $\ln \tau$ as a function of $1000/T$. All these plots show that the data is following the Arrhenius law.

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (6.7)$$

where τ_0 is the prefactor, E_a is the activation energy for the response and k_B is Boltzmann constant. From the linear fit, we have obtained the slope value which in turn gives the activation energy (E_a) ~ 0.14 eV of MCT thin films deposited 25% OMP.

Table 6.2: The values of grain resistance (R_g) and capacitance (C_g) of 25% OMP deposited MCT films measured at different temperatures.

Temperature (K)	Grain resistance R_g (k Ω)	Grain capacitance C_g (pF)
413	1049.2	58.29
443	910.5	58.89
468	682.6	59.63
493	541.4	60.34

Figure 6.22(a) shows the ac - conductivity (σ_{ac}) as a function of frequency measured at various temperatures for MCT film deposited at 25% OMP. The dependence of ac - conductivity on the frequency is generally described using Jonscher power law [36],

$$\sigma(\omega) = \sigma(0) + A\omega^s \quad (6.8)$$

where $\sigma(\omega)$ is the total conductivity of the system, $\sigma(0)$ is the contribution from dc conductivity (frequency independent part), ω is the angular frequency of the ac signal ($\omega = 2\pi f$) and “s” and “A” are the characteristic parameters. Both “A” and “s” are temperature dependent parameters. The term $A\omega^s$ contains the ac dependence and characterizes all dispersion phenomenons [37- 40]. For $T < 383$ K, the conductivity almost varies linearly with the frequency, and no dc-plateau region has been observed within the frequency range $100 - 10^6$ Hz. On the other hand, above 383 K, frequency independent conductivity (plateau) is observed at low frequencies ($f < 2$ kHz), due to the contribution of dc conductivity

mechanism. Beyond a critical frequency, the conductivity follows linearly, which is expected due to the contribution of grains [41]. The values of an exponent “s” and pre-exponent factor “A” for various temperatures above 383 K and are enlisted in Table 6.3.

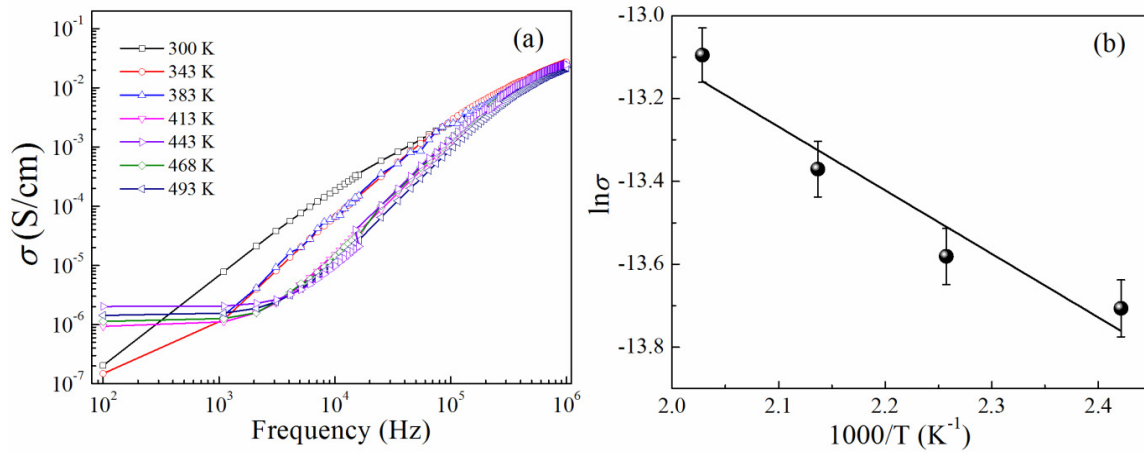


Figure 6.22: (a) The ac-conductivity (σ_{ac}) versus frequency (f) at different temperatures. (b) The variation of $\ln \sigma_{dc}$ versus $1000/T$ plot of $(Mg_{0.95}Co_{0.05})TiO_3$ the films deposited at 25% OMP on platinized silicon substrates.

It is observed that, with increasing temperature, the value of “s” increases where as $\log A$ decreases significantly. Usually, the value of “s” should lie between 0 and 1. In the present case slightly higher values of “s” than the unity has been noticed, which are typically observed in chalcogenide materials [42]. It is expected that the higher values of “s” are the indicative of more complicated frequency dependent behavior of the conductivity. Accordingly, it is likely that frequency dependence of conductivity is following the double power law behavior

$$\sigma'(\omega) = \sigma_0(dc) + B_1\omega^{s_1} + B_2\omega^{s_2} \quad (6.9)$$

(as proposed by Funke and Barranco *et al.*)[43-45]. In the above equation, the first exponent s_1 characterizes the low frequency region connected with the translational hopping of ions. While the second exponent characterizes the high frequency region due to the contribution of localized charge carrier conductivity of the reorientation ionic hopping [46]. Figure 6.22(b) shows the logarithmic variation of conductivity as a function inverse of the temperature measured at constant frequency $f \sim 1$ kHz. The linear behavior of these plots indicates that the dc conductivity follows Arrhenius relation given by

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (6.10)$$

The activation energy (E_a) calculated from the linear portion of the curve results $E_a \approx 0.132$ eV which is in excellent agreement with those values obtained from the relaxation time analysis as discussed in previous section. The oriented growth along (110) direction in-turn causes activation energy to increase from 0.14 to 0.4eV for 25 to 75 % OMP, respectively.

Table 6.3: The evaluated values of exponent factor “s” and pre - exponent factor logA measured at different temperatures for the films deposited at 25% OMP.

Temperature (K)	413	443	468	493
s	1.39	1.45	1.59	1.66
logA	-9.81	-10.10	-10.79	-11.32

6.4.5 Dielectric studies

Figure 6.23(a,b) shows the frequency variation of the dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of the MCT thin films deposited at different OMP recorded at 300 K. The obtained dielectric constant and loss tangent values lies in the range 19.5 - 8.56 and 0.06 - 0.0012, respectively.

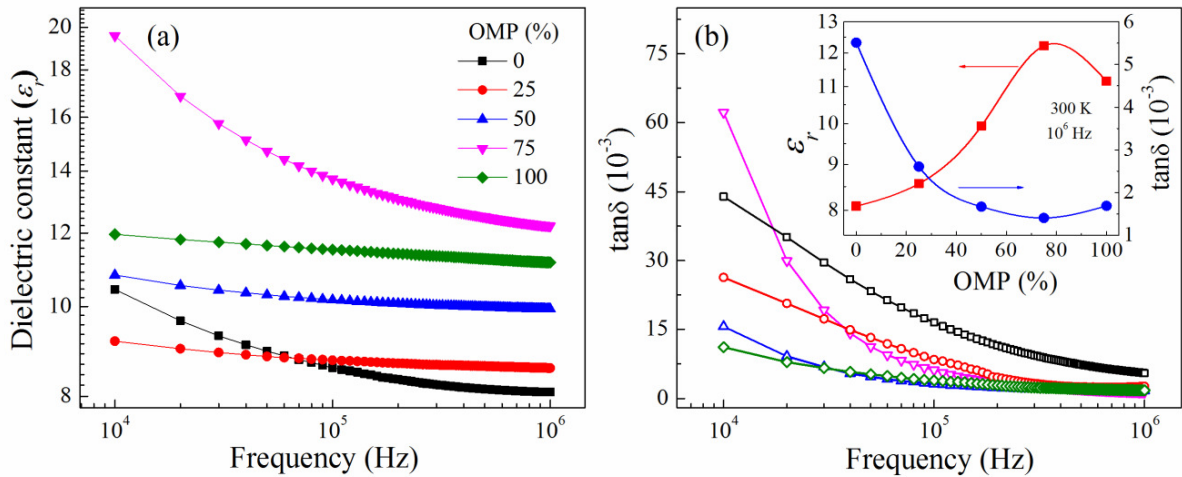


Figure 6.23: (a,b) The variation of dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of MCT thin films deposited at different OMP on platinized silicon substrates. The inset of Figure 6.23(b) shows the variation of ϵ_r and $\tan\delta$ for different values of OMP measured at 1.0×10^6 Hz.

These ϵ_r values are higher compared to the values reported by Chen *et al.* [10] for the pure MgTiO₃ thin films deposited on n-type silicon substrates using RF magnetron sputtering under O₂ rich ambient. These values are still lower than the values ($\epsilon_r \approx 24$ at 1MHz) reported by Kang *et al.* who deposited (003) oriented MgTiO₃ on c - axis oriented Al₂O₃ substrates using PLD [7]. Usually dispersion in ϵ_r with the frequency can be explained on the basis of Maxwell - Wagner approach and koop's theory [23, 47]. These models demonstrate that as the frequency increases, the probability of electrons reaching the grain boundary decreases which in turn results in the reduction of polarization finally leading to a significant decrease of ϵ_r [48]. It is possible that the interfacial dead layers may exist across the interface of electrodes and the thin film which in turn leads to dielectric losses. The inset of Figure 6.23(b) shows the variation of the ϵ_r and $\tan\delta$ as a function of different values of OMP, measured at 10⁶ Hz. As the OMP increases from 0% to 75%, the ϵ_r values increases progressively up to 75% OMP, beyond which it starts decreasing. Such variation in the dielectric properties with OMP strongly suggests the role of oxygen vacancies and crystallographic orientations [49, 50]. The improvement in dielectric properties of the films deposited up to 75% OMP can be attributed to the following factors: (i) the preferred orientation of grains along (110) direction, may enhance the polarizability and increase in the degree of crystallinity of the films. (ii) From the AFM images, it was clear that the films were highly densified with a uniform grain size, and (iii) films deposited below 75% OMP have some oxygen vacancies and can be explained according to the equation



where O_0 , $V_0^{\bullet\bullet}$, and e' represents the oxygen ion on its normal site, oxygen vacancy, and electron, respectively. The oxygen vacancies may cause significant changes in the dielectric behaviour of the deposited films. However, for the films deposited at 75% OMP, the number of oxygen vacancies reduces, which causes the improvement in the dielectric properties [50 - 52]. In the present case, the thin films deposited in pure oxygen atmosphere (OMP > 75%) may result in the target poisoning during sputtering, which may cause the reduction in the rate of deposition as a result smaller grain size and lower densities occur. Further, the preferred orientation in films along (110) is less as compared to the films deposited at 75% OMP. These factors may significantly deteriorate the dielectric properties of the films

deposited in pure oxygen atmosphere. In the present case, the optimum values of ϵ_r and $\tan\delta$ being 12.20 and 0.0012 were obtained for the films deposited at 75% OMP and 700°C and annealed at 700°C for 1 h.

Figure 6.24(a) shows the temperature dependence of ϵ_r and $\tan\delta$ for 0% and 75% of OMP of MCT thin film measured at $f = 1 \times 10^6$ Hz in the temperature range 300- 433 K. Both dielectric constant and $\tan\delta$ linearly increases with temperature. Usually, at low temperatures, the molecules cannot orient themselves in polar dielectrics [53]. However, as the temperature increases, the orientation of dipoles is facilitated, and cause increase in the dielectric constant [45]. We have estimated the temperature stability of dielectric permittivity by evaluating the temperature coefficients of dielectric constant (TCK) of MCT thin films. The TCK was determined using the following equation [53, 4]

$$TCK = \frac{\Delta\epsilon_r}{\epsilon_0 \Delta T} (ppm/^{\circ}C) \quad (6.12)$$

where $\Delta\epsilon_r$ is the change in ϵ_r with respect to the value ϵ_0 ($T = 300$ K) and ΔT is the change in temperature relative to 300 K.

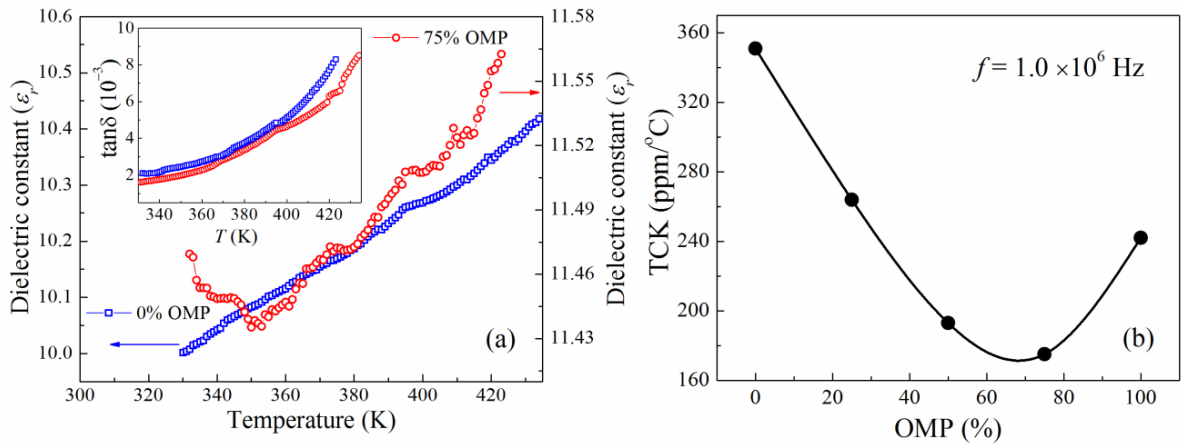


Figure 6.24: (a) Temperature dependence of dielectric constant (ϵ_r) and loss tangent ($\tan\delta$, inset) recorded at a constant ac driving frequency of 10^6 Hz for 0 and 75 % OMP. (b) Variation in temperature co - efficient of dielectric constant (TCK) as a function of OMP measured at constant $f = 1.0 \times 10^6$ Hz.

Figure 6.24(b) shows the variation of TCK as a function of oxygen mixing percentage. From this figure one can say that all the MCT films show a positive TCK values across 10^6

Hz. It is evident that as the oxygen availability increases, the TCK of MCT films decreases up to 75% and starts increasing for OMP > 75%. The obtained TCK values lies in the range 350 - 175 ppm/ °C. It is clear from the figure, that the 75% OMP gives better thermal stability (minimum TCK) of the dielectric properties.

6.4.6 Electrical properties of MCT thin films

The I-V characteristics of MCT films deposited at different OMP were measured and depicted in Figure 6.25. The leakage current characteristics show relatively low leakage current density ($J = 1.14 \times 10^{-9} \text{ A/cm}^2$ at 250 kV/cm^2 for OMP = 75%) for the investigated thin films. Chen *et al.* [10] reported the leakage current characteristics of pure MgTiO_3 thin films deposited on n - type silicon substrates. They attributed that the low leakage current ($I \approx 1.3 \times 10^{-8} \text{ A/mm}^2$ at 75% Ar/ O_2 ratio) is due to the improvement of grain sizes (fewer defects due to the increased annealing temperatures).

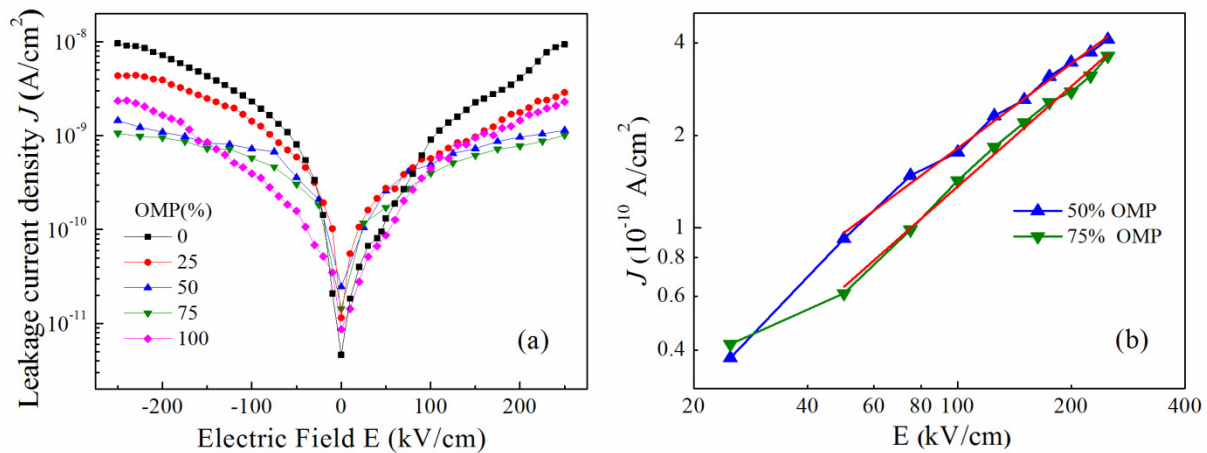


Figure 6.25: (a) The I-V characteristics of the $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ films deposited at different oxygen mixing percentage. (b) Leakage current density versus electric field of 50%, 75% OMP deposited thin films and its corresponding fits.

Usually the leakage current density depends on the grain sizes, the average crystallinity, and the rms surface roughness [54, 36]. We attribute that the decrease in leakage current density with an increase in OMP is due to the lower rms surface roughness and more structured grain boundaries in the MCT thin films. In the present case, the values of slope for the leakage current versus electric field curves are close to unity (1.08 for 50% OMP and 1.12 for 75% OMP), which indicates that the leakage mechanism is considered to be due to

ohmic conduction [55]. For OMP values near to 50 and 75% the J versus E curves exhibits linear behavior confirming the ohmic conduction mechanism. However, for OMP values < 50% and more than 75% no linear behavior of J(E) is observed indicating that the ohmic conduction is not responsible for the leakage current in MCT thin films. These electric and dielectric properties of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films can make this material for suitable gate oxide material in for CMOS applications.

6.4.7 Microwave dielectric properties of pure MTO and MCT films

To investigate and to compare the microwave dielectric properties of both in bulk and thin films, the microwave dielectric properties of pure MTO and MCT films were measured using split post resonator technique [19]. This is a non-destructive and accurate method for measuring the complex permittivity of dielectric substrates and thin films at spot frequencies. The microwave dielectric constant and dielectric loss of the as - deposited and annealed pure MTO and MCT films deposited on amorphous SiO_2 substrates have been measured at some spot frequencies (at 10 and 20 GHz). The dielectric constant and loss tangent of the MCT films as a function of OMP for as - deposited and annealed are shown in Figure 6.26(a) and (b), respectively.

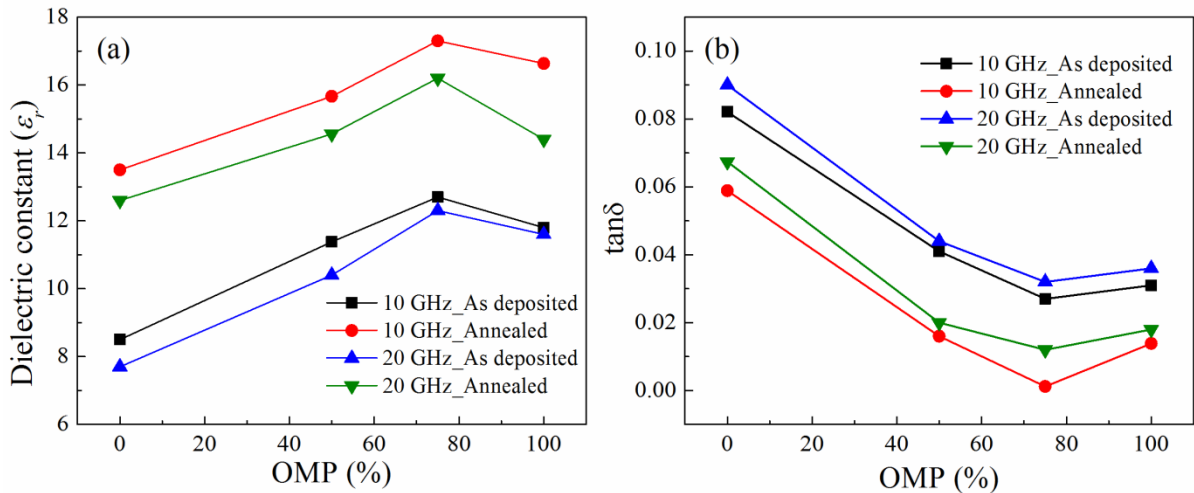


Figure 6.26: (a) Microwave dielectric constant and (b) Loss tangent of the MCT thin films as a function of OMP.

It is observed that as the OMP is increases up to 75% of OMP, the dielectric constant of the films increases whereas the loss decreases. Above that dielectric constant decreases but

the loss increases. Furthermore, the dielectric constants of the annealed films increase whereas the loss decreases as compared to the as deposited films. In all the cases, it is observed that the dielectric constant slightly decreased with an increase in frequency, whereas the dielectric loss enhanced with increment in frequency. This variation in dielectric constant indicates the presence of a feeble dipolar relaxation in the films around this frequency range. Since oxygen partial pressure is the processing variable in these samples, it is quite possible that dipoles associated with oxygen deficiency are responsible for this weak relaxation. Similarly, the observed microwave dielectric properties for the pure MTO films are found to be $\epsilon_r = 18.1$, $\tan\delta = 1.2 \times 10^{-3}$ and $\epsilon_r = 17.21$, $\tan\delta = 3.0 \times 10^{-3}$ of measured at 10 GHz and 20 GHz, respectively. The similar behavior is also observed when the dielectric properties of the films measured in the parallel plate capacitor structure.

The dielectric properties of MCT thin films at microwave frequencies were not previously reported. For pure MTO films, Lee *et al.* [56] reported the microwave dielectric properties for spin coated MTO films on Pt(111)/Ti/SiO₂/Si substrates with different annealing temperatures. The dielectric constant and $\tan\delta$ were found to be 16 and 8.0×10^{-4} at 6 GHz, respectively. Significantly, MTO films in the current study exhibit a maximum dielectric constant value of 17.3, indicating porosity driven reduction in dielectric constant.

In the present study, the microwave dielectric properties of MCT films are also studied in bulk form. In bulk MCT, it is found that large grains give lower $\tan\delta$ because grain growth decreases the grain boundary area. However, in MCT films, the simultaneous occurrence of higher dielectric constant and lower loss at 75% OMP is due to the preferred orientation of the films along the (110) direction, increase in crystallinity and reduction in oxygen vacancies. In an oxide, observation of high dielectric constant with low dielectric loss is possible when the structure gets favorably disposed towards higher dielectric constant, and the vibrations of polar optic phonons are within their harmonic limits. However, oxygen stoichiometry is known to play a key role as it heavily influences the occurrence of many extrinsic loss mechanisms. It is also observed that the dielectric constant slightly decreased with an increase in frequency, whereas the dielectric loss increases. This variation indicates the presence of dipolar relaxation in MCT films around this frequency region, which is absent in their bulk counterparts. This again highlights the role of oxygen stoichiometry in

these films, as it is known that oxygen deficiency could lead to defect based dipole formation, which could exhibit a dipolar relaxation [57] influencing the dielectric properties heavily.

The dielectric properties of pure MTO and MCT are measured both at lower (100 kHz - 10 MHz) and at microwave frequencies (10 - 20 GHz). In both the cases and in both the frequency regions, films deposited with 100% and 75% OMP showed higher dielectric constants with smaller loss, respectively. In the case of MCT, above 75% OMP, the dielectric constants decreased where as the dielectric loss increased. The variation in dielectric constant and dielectric loss also followed the variation in rate of depositions as a function of OMP except at 75% of OMP. Interestingly, the uniform crystallinity, grain size and preferred orientation of all the films with 75% OMP are higher compared to the films deposited at other OMPs. It was observed that the dielectric properties of all these films are dependent on the microstructure, preferred orientation and crystallinity of the films.

The dependence of optical bandgap and dielectric constant on the OMP appears to follow similar trends. It is known that oxygen stoichiometry can affect optical bandgap as well as dielectric properties. It is seen that OMP changes the rate of deposition, microstructure, crystallite size, optical packing density and thereby porosity as well as crystallographic strain. However, from the current study, it is not possible to unambiguously establish, which of these variable quantities is dominant in determining the observed differences in physical properties over the frequencies. Of particular interest is the critical behavior in dielectric properties at 75% OMP. It correlates well with morphological changes such as grain size, crystallite size and also crystal orientation. Although, stoichiometry variations may be one of the causes for the variations in the observed dielectric and optical properties. However, the role of morphological changes should not be underestimated. A more detailed study is required to establish the exact causes for the observed dielectric properties. It may be noted that studies with microwave dielectric properties of thin films are not widespread in these types of linear dielectrics. From all the above observations, it is confirmed that pure MgTiO₃ and (Mg_{0.95}Co_{0.05})TiO₃ samples exhibited comparable microwave dielectric properties in both bulk and thin films form.

Table 6.4: The comparison of the microwave dielectric properties of MTO and MCT ceramics in both bulk and thin film form.

	Dielectric constant (ϵ_r)	$\tan\delta = (1/Q)$	Measured frequency
Bulk pure MgTiO_3	18.52	5.7×10^{-5}	9.3 GHz
MgTiO_3 thin film	18.1	1.2×10^{-3}	10 GHz
deposited at 100% OMP	17.21	3.0×10^{-3}	20 GHz
Bulk $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$	17.03	5.5×10^{-5}	9.4 GHz
$(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin	17.3	1.1×10^{-3}	10 GHz
film deposited at 75% OMP	16.2	1.4×10^{-3}	20 GHz

From the above Table 6.4, it is clear that there is not much change in the dielectric constants of the bulk and thin films of the pure MTO and MCT. However, the dielectric loss is higher in films as compared to bulk form. The obtained higher dielectric losses in the films can be explained as follows: The low dielectric losses in the case of bulk MTO ceramics with sizeable grains is also attributed to the reduction in the strain of the crystallites in ceramics prepared at higher sintering temperatures. In the case of thin films, the grain size is much smaller compared to the bulk, resulting in large grain boundary area. This could cause deviation from the bulk properties. In the presence of applied electric field, the depolarization fields generally appear at grain boundaries, which influence the fields inside the grains and the dielectric response of the film changes. On the other hand, the grain boundary regions are interconnected in all directions, and their properties may dominate or severely influence the effective dielectric response of the whole system even if their volume concentration is very small [58].

Table 6.5: The comparison of optical, dielectric properties of both pure MTO and MCT thin films.

Deposition conditions	Optical bandgap (eV)		Refractive index		ϵ_r at 1 MHz	$\tan\delta$ at 1MHz
	As deposited	After annealing	As deposited	After annealing	After annealing	After annealing
MgTiO_3 thin films						
0% OMP	3.73	4.11	2.06	2.19	-	-
30% OMP	3.74	4.14	2.06	2.18	13.68	0.010
60% OMP	3.76	4.12	2.04	2.17	13.72	0.009
70% OMP	3.79	4.18	2.03	2.16	-	-
100% OMP	3.78	4.18	2	2.12	15.47	0.006
$(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films						
0% OMP	3.54	3.95	1.96	2.14	8.08	0.050
25% OMP	3.62	4.01	1.93	2.11	8.58	0.0026
50% OMP	3.60	4.05	1.91	2.07	9.93	0.0016
75% OMP	3.61	4.09	1.90	2.02	12.21	0.0014
100% OMP	3.77	4.16	1.89	2	11.15	0.0017

From the above table, it can be seen that there is not much variation in optical constants whereas the dielectric constants of MCT films are slightly lower as compared to pure MTO films.

6.5 Conclusions

- MgTiO_3 and $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ thin films were grown on different substrates by RF magnetron sputtering at various oxygen mixing percentages (OMP) have been investigated.
- The as - grown films were structurally amorphous nature and after post annealing at 700°C for 1 h in air induced the crystallinity for both MTO and MCT thin films.

- From the XRD patterns, it is found that the crystallite size decreases with increases in OMP indicates films deposited at higher OMP were less crystalline for pure MTO thin films.
- The structural analysis on MCT films reveals that all the grains are orientated along (110) preferred direction as OMP increases from (0-75%) with reduced rms roughness observed on platinized silicon and amorphous SiO₂ substrates.
- For both the MTO and MCT as deposited and annealed films, the refractive index and packing density of the films are found to decrease where as the bandgap increases with an increase in OMP.
- On annealing both refractive index and bandgap increased where as the porosity ratio decreases. The improvement in the refractive index attributed to improvement in crystallinity, packing density and reduction in the porosity ratio.
- The MIM structures were fabricated and the dielectric constant and loss tangent values were strongly depended on the OMP in both the pure MTO and MCT films. The MTO and MCT thin films exhibited the high dielectric constant and low loss tangent for deposition conditions 100% and 75% OMP, respectively.
- The MTO films deposited under pure oxygen atmosphere exhibited best dielectric properties of dielectric permittivity ($\epsilon_r = 15.56$), low losses (0.006) attributed to the reduction in oxygen vacancies.
- The MCT films prepared under 75% of OMP provides high dielectric permittivity ($\epsilon_r = 12.2$), low losses (0.0012) and low temperature co-efficient of dielectric constant (175 ppm/°C) due to the preferred orientation of grain growth along (110) direction.
- The frequency dependent ac conductivity of MCT films follows the Jonscher power law, and the activation energies estimated from the Arrhenius relation are in good agreement with those estimated from dc conductivity analysis.
- The oriented growth along (110) direction in-turn causes activation energy to increase from 0.14 to 0.4eV for the O₂ variation window of (25 to 75%).
- The leakage current analysis ($J \sim 1.14 \times 10^{-9}$ A/cm² at 250 kV/cm) reveals that the ohmic conduction mechanism is dominated in MCT films prepared at 50 - 75% of OMP range.

- It was observed that the post annealing temperature and OMP heavily influenced the structural, microstructural, optical, electrical and dielectric properties of both pure MTO and MCT thin films.



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Chapter 7

Summary and Future Scope

7.1 Summary

This chapter presents the overall summary of the studies carried out. Especially the correlations between the bulk and thin films counter parts of the MTO ceramics. In summary, dielectric resonators (DR) of single phase MgTiO_3 (MTO) ceramics have been prepared by solid - state reaction, mechanochemical synthesis, and semi alkoxide precursor methods. The effect of various additives, substitutions, their concentrations and processing parameters on crystal structure, microstructure and on microwave dielectric properties are studied systematically. Successful efforts were made to reduce the sintering temperature from 1450 to 1100°C without affecting the microwave dielectric properties of the MTO ceramics by reducing the initial particle size and supplementing different type of additives. In solid-state reaction method the excess mol MgO concentration plays an important role in formation of single phase MTO ceramics with high densities. In mechanochemical method, initial powders of MgO and TiO_2 were milled for 5, 10, 15, 20, 25 and 30 h. The 30 h milled powders sintered at 1350°C exhibited pure MgTiO_3 phase.

It is well known that the addition of liquid phase sintering aids reduces the sintering temperature without affecting the microwave dielectric properties. The effect of various additives such as CeO_2 nanoparticles, La_2O_3 , Bi_2O_3 and V_2O_5 of 0.5 – 1.5 wt% have been added to MTO ceramics and studied their effect on structure, microstructure and on the microwave dielectric properties. In case of CeO_2 added samples, effect of annealing temperature on structure, microstructure and on the microwave dielectric properties were also been studied. In all the cases, it is found that the dielectric constant is not affected much where as the Q factor changed drastically. The improvements in Q factor are attributed to the improvements in density, increase in uniform grain size and reduction in oxygen vacancies.

It is well noted that partial substitution of suitable elements improves the microwave dielectric properties of ceramics. A small amount of Co ($x = 0 - 0.07$) was substituted for Mg site and studied the crystal structure, surface morphology, microwave dielectric properties and magnetic properties of MTO ceramics. The samples were prepared in semi alkoxide precursor method and all samples were sintered at 1200°C exhibited highest relative density due to tiny initial particle and Co enhances the grain growth. The maximum dielectric properties were observed for MTO doped with $\text{Co} = 0.05$ concentration. Further, the Co

doped sample exhibited good magnetic properties and temperature - dependent magnetic properties exhibited a paramagnetic transition (T_C) 228 K has been observed. The temperature - dependent dielectric properties showed dielectric anomalies at measured frequencies. The observed anomalies were similar to the transitions observed in magnetic properties and were correlated with magnetic properties.

Thin films of pure MgTiO_3 (MTO) and $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ (MCT) have been deposited by RF reactive magnetron sputtering from the targets prepared from mechanochemical processing and semi alkoxide precursor methods, respectively. The processing parameters such as the substrate to target distance, working pressure, oxygen mixing percentage (OMP) and power density, etc. were optimized to get best structural, microstructural, optical, electrical and dielectric properties. The effect of OMP and annealing temperature on crystal structure, morphology, optical, impedance spectroscopy and dielectric properties were investigated systematically. For the first time, all these films were deposited in pure oxygen plasma. In both the cases, the crystallinity was induced by post annealing process. The crystallite sizes of the films decreased with an increase in OMP for pure MTO thin films whereas the MCT thin films exhibited a change in preferred orientation grain growth. The microstructure of these films exhibited spherical shaped grains on quartz, amorphous SiO_2 and $\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$ substrates. The grain size is improved upon annealing, and small grains were observed with higher OMPs.

The optical properties of the films in the MgTiO_3 (MTO) system have been studied. It was noticed that as the OMP increases the refractive index decreases whereas bandgap improved. The bandgap decreased with an increase in crystallite size exhibiting approximately $1/d^2$ dependence, where ' d ' is the diameter of crystal. The electrical properties of the films were measured and found that the films with optimized conditions showed lower leakage currents. The leakage currents were dependent on processing parameters, crystallinity and microstructure.

The dielectric properties of MTO and MCT films were measured both at low frequency and at microwave frequencies. At lower frequency range, the dielectric constant and loss decreased with an increase in frequency. At microwave frequencies, the dielectric constant decreases with enhancement in frequency while loss increased. The dielectric constant and

loss showed enormous dependence on OMP and the resulting variation in crystallite size and bandgap. Interestingly the dielectric loss of the films showed profound dependence on crystallographic strain in the deposited films. For these films, the microwave dielectric properties are reported for the first time.

In the present study DRs and thin films of MTO and MCT have been prepared by mechanochemical method, semi alkoxide precursor and RF reactive magnetron sputtering respectively. In bulk form MTO dielectric constant of 18.52, $Q \times f_0$ of 162.8 THz were observed for the sample sintered at 1350°C where as in thin film form dielectric constant of 18.1 and $\tan \delta = 0.0012$ were observed at 10 GHz. Similarly, for MCT, the dielectric constant of 17.03, $Q \times f_0$ of 170 THz were observed for the sample sintered at 1200°C whereas in thin film form, the dielectric constant of 17.3 and $\tan \delta = 0.0011$ were observed at 10 GHz. The microwave dielectric properties of thin films were inferior compared to that of bulk.

From the present study, the obtained excellent microwave dielectric properties of pure MTO and MCT ceramics makes this material appropriate for type - 1 capacitor and dielectric resonators. Furthermore, the optimized best optical, electrical and dielectric properties of pure and MCT thin films are suitable for optoelectronic, antireflection, integrated electronic and CMOS applications.

7.2 Future scope of the work

To tune the temperature co-efficient of resonant frequency (τ_f) of the MTO ceramics, composite systems will be prepared with positive τ_f systems such as CaTiO_3 and SrTiO_3 . The effect of these additions makes τ_f of MTO to zero (temperature stable material) and study the crystal structure, microstructure and microwave dielectric properties for practical applications.

Furthermore, the effect of initial particle size of the MTO ceramics can be studied further systematically to farther and reduce the sintering temperature. We have supplemented different types of additives to reduce the sintering temperature and to improve the microwave dielectric properties. During this process, the microstructure of MTO ceramics changes significantly. To find out whether these additives entered into the matrix of MTO or remained at the grain boundary, a composition analysis across the microstructure with a

facility like Electron probe Micro Analysis (EPMA) will be useful. We have focused on to reduce microwave dielectric losses that are extrinsic in nature by process optimization. However, we have not studied the intrinsic loss mechanisms and can be studied with far IR reflectivity spectroscopy.

In the case of thin films, since the crystallinity and microstructure are playing an important role on optical, electrical and microwave dielectric properties, a systematic study of the films by varying the substrate temperature during deposition will be beneficial. A detailed compositional analysis of MTO films deposited at different temperatures and pressure are needed to explain the loss mechanisms of the films. Films deposited with same OMP but having different microstructures can be obtained by annealing or heating during deposition. A detailed compositional analysis with independent control over the microstructure will help in interpreting the observed variations in optical and dielectric properties with changes in OMP during deposition.

An accurate determination of crystallographic strain using X- Ray reflectivity measurements will help in establishing the discovered correlations between crystallographic strain and $\tan\delta$ at microwave frequencies. In addition, it is interesting to see whether indentation measurements using a nanoindenter throws more light into the observed possible correlation between strain in the films and the microwave dielectric loss in this linear dielectric.

The dielectric properties of these films are measured only at a few spot frequencies in the microwave range. It will be interesting to do a broad - band measurement of dielectric constant and $\tan\delta$ of these films spanning over a few bands to ascertain the loss mechanisms in these films at such frequencies.

List of Publications

- 1) **T. Santhosh Kumar**, Pallabi Gogoi, S. Thota, D. Pamu, Structural and Dielectric Studies of *Co* Doped MgTiO_3 Thin Films Fabricated by RF - Magnetron Sputtering. Accepted in *AIP advances*, **4**, 067124 (2014).
- 2) **T. Santhosh Kumar**, Pallabi Gogoi, Bhagban Kisan, A. Perumal, P. Sharma, D. Pamu, Magnetic Properties of *Co* Doped MgTiO_3 Ceramics. *Physica B*, **448**, 330 (2014)
- 3) **T. Santhosh Kumar**, Pallabi Gogoi, A. Perumal, P. Sharma, D. Pamu, Effect of Cobalt Doping on the Structural, Microstructural, and Dielectric Properties of MgTiO_3 Ceramics Prepared by Semi Alkoxide Precursor method. *Journal of American Ceramic Society*, **97**[4], 1054 (2014).
- 4) **T. Santhosh Kumar**, D. Goswami, D. Pamu, Effect of CeO_2 Nanoparticles and Annealing Temperature on the Microwave Dielectric Properties of MgTiO_3 ceramics, *Ceramics International*, **40**, 1125 (2014).
- 5) **T. Santhosh Kumar**, D. Goswami, D. Pamu, Influence of Bi_2O_3 and La_2O_3 on Densification, Microstructure and Microwave Dielectric Properties of MgTiO_3 Ceramics. *Journanl of Ceramic Science and Technology*, **4**, 145 (2013).
- 6) **T. Santhosh Kumar**, R. K. Bhuyan and D. Pamu, Effect of Processing Parameters and Post Annealing Temperature on Structural and Optical Properties of MgTiO_3 Thin films Deposited by RF magnetron sputtering, *Springer Proceedings in Physics*, **143**, 291 (2013).
- 7) **T. Santhosh Kumar**, R. K. Bhuyan, D. Pamu, Effect of Post Annealing on Structural, Optical and Dielectric Properties of MgTiO_3 Thin films Deposited by RF Magnetron Sputtering. *Applied Surface Science*, **264**, 184 (2013).
- 8) **T. Santhosh Kumar**, Ajeet Kumar, A. R. James, D. Pamu, Enhanced Microwave Dielectric Properties of MgTiO_3 Ceramics Prepared by Mechanochemical Method. *Journal of Australian Ceramic Society*, **48**[1], 96 (2012).
- 9) **T. Santhosh kumar**, A. R. James, D. Pamu, Dielectric and Raman Studies on MgTiO_3 Ceramics Prepared by Mechanochemical Processing Method. *AIP Conference Proceedings*, **1372**, 107 (2011).

- 10) **T. Santhosh Kumar**, Pallabi Gogoi, D. Pamu, Optical Properties of (110) oriented Co Doped MgTiO_3 Thin Films Prepared by RF Magnetron Sputtering (Submitted).
- 11) **T. Santhosh Kumar**, Pallabi Gogoi, D. Pamu, Effect of V_2O_5 Addition Structural, Microstructure and Microwave Dielectric Properties of Non - stoichiometric MgTiO_3 Ceramics (Submitted).

Conferences and workshops

- 1) **T. Santhosh Kumar**, Pallabi Gogoi, Pramod Sharma, D Pamu, Effect of Processing parameters on Preferred Orientation, Optical and Dielectric Properties of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ Thin Films, Accepted for presentation in *Asian Meeting on Ferroelectricity (AMF-9) and the 9th Asian Meeting on Electroceramics (AMEC-9)*, (AMF-AMEC-2014), 26-30 Oct 2014, Shanghai, China.
- 2) **T. Santhosh Kumar**, Pallabi Gogoi, Pramod Sharma, D. Pamu, Effect of V_2O_5 on Structural, Microstructural and Microwave Dielectric Properties of Non - stoichiometric MgTiO_3 Ceramics, Accepted for presentation in *Asian Meeting on Ferroelectricity (AMF-9) and the 9th Asian Meeting on Electroceramics (AMEC-9)*, (AMF-AMEC-2014), 26-30 Oct 2014, Shanghai, China.
- 3) Participated in “*Advanced Workshop on Dielectric Impedance Analyzer*”, held at University of Delhi, India during 17 - 18th Jan 2014.
- 4) **T. Santhosh Kumar**, Pallabi Gogoi, Bhagban Kisan, A. Perumal, P. Sharma, D. Pamu, Magnetic Properties of Co Doped MgTiO_3 Ceramics, Presented in *International Conference on Magnetic Materials & Applications (MagMA 2013)*, 5-7 Dec 2013, IIT Guwahati, India.
- 5) **T. Santhosh Kumar**, Pallabi Gogoi, D. Pamu, Effect of Ar/ O_2 Mixing on Crystallinity Dielectric and Electrical Properties of $(\text{Mg}_{0.95}\text{Co}_{0.05})\text{TiO}_3$ Thin films Prepared by RF Magnetron Sputtering, Presented in *3rd International Conference on Advanced Nanomaterials and Nanotechnology (ICANN 2013)*, 1- 3 Dec 2013, IIT Guwahati, India.
- 6) Participated in “*Indo-US Workshop on Functional Materials Processing & Characterizations*” held at NIT Rourkela during 3rd - 6th Jan 2012, Orissa, India.
- 7) **T. Santhosh Kumar**, R. K. Bhuyan, S. Thota, D. Pamu, Effect of Annealing on the Structural and Optical Properties of Nanocrystalline MgTiO_3 Thin Films, Presented in

International conference on Nano Science and Technology (ICONSAT-2012), 20 - 23rd Jan 2012, Hyderabad, India.

- 8) Participated in “*INUP Familiarization Workshop Nano Fabrication Technologies*” held at IIT Guwahati, during 28 - 29th Sept 2012.
- 9) **T. Santhosh Kumar**, D. Goswami, D. Pamu, Effect of CeO₂ Nanoparticle Addition on Microstructure and Microwave Dielectric Properties of MgTiO₃ Ceramics, Presented in *International Conference on Materials science and Technology (ICMST-2012)*, 10 - 14th June 2012, Kottayam, India.
- 10) **T. Santhosh Kumar**, Ajeet Kumar, A. R. James, D. Pamu, Enhanced Microwave Dielectric Properties of MgTiO₃ Ceramics Prepared by Mechanochemical Method, Presented in *PacRim 9th International Meeting of Pacific Rim Ceramics Societies*, 10-14th July 2011, Cairns, Australia.
- 11) **T. Santhosh Kumar**, R. K. Bhuyan, S. Ravi, D. Pamu, Structural and Dielectric Studies of MgTiO₃ Thin Films Deposited by RF magnetron Sputtering, Presented in *International Thin Films Conference (TACT-2011)*, 20 - 23th Nov 2011, Kenting, Taiwan.
- 12) **T. Santhosh Kumar**, A. R. James, D. Pamu, Dielectric and Raman studies on MgTiO₃ Ceramics Prepared by Mechanochemical Processing Method, Presented in *National Seminar on Ferroelectrics and Dielectrics - XVI*, 2- 4th Dec 2010, Bilaspur, India.
- 13) Participated in Quality Improvement Program “*Smart Materials and Devices*” held in IIT Guwahati, during 9 -13th Aug 2010, Assam, India.

Outside thesis work

Journal publications

- 1) R. K. Bhuyan, **T. Santhosh Kumar**, D. Pamu, J. M. Renehan and M. V. Jacob, Low Temperature and Broadband Dielectric Properties of V₂O₅ doped Mg₂TiO₄ Ceramics, *Materials Express*, **4**, 349 (2014).
- 2) D. Pamu, **T. Santhosh Kumar**, B. Sreedhar, Anil K. Bhatnagar, Optical, Dielectric and X - ray Photoelectron Spectroscopy Studies on Nanocrystalline Ba(Zn_{1/3}Ta_{2/3})O₃ Thin Films Deposited by Pulsed Laser Deposition. *Proceedings in National Academy of Sciences, India, Section A: Physical Sciences*, **84**[3], 457 (2014).

- 3) R. K. Bhuyan, **T. Santhosh Kumar**, A. R. James, D. Pamu, Structural and Microwave Dielectric Properties of Mg_2TiO_4 Ceramics Synthesized by Mechanical Method *International Journal of Applied Ceramic Technology*, **10**[S1], E18 (2013).
- 4) R. K. Bhuyan, **T. Santhosh Kumar**, A. R. James, A. Perumal, D. Pamu, Enhanced Densification and Microwave Dielectric Properties of Mg_2TiO_4 Ceramics Added with CeO_2 nanoparticles. *Materials Science and Engineering B*, **178**, 471 (2013).
- 5) R. K. Bhuyan, **T. Santhosh Kumar**, A. Perumal, S. Ravi, and D. Pamu, Optical Properties of Ambient Temperature Grown Nanocrystalline Mg_2TiO_4 Thin Films Deposited by RF Magnetron Sputtering, *Surface and Coatings Technology*, **221**, 196 (2013).
- 6) R. K. Bhuyan, **T. Santhosh Kumar**, A. Perumal, P. Saravanan and D. Pamu, Effect of Annealing and Atmosphere on the Structure and Optical Properties of Mg_2TiO_4 Thin Films Obtained by the Radio Frequency Magnetron Sputtering Method. *Journal of Experimental NanoScience*, **8**, 371 (2013).
- 7) R. K. Bhuyan, **T. S. Kumar**, D. Goswami, A. R. James, D. Pamu, Liquid Phase Effect of La_2O_3 and V_2O_5 on Microwave Dielectric Properties of Mg_2TiO_4 Ceramics. *Journal of Electroceramics*, **31**, 48, (2013).
- 8) **T. Santhosh Kumar**, Y. Sarath Kanth, D. Pamu, Temperature Dependent Dielectric Properties of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ Ceramics. *AIP Conference Proceedings*, **1372**, 20 (2011).

Conference Presentations

- 1) **T. Santhosh Kumar**, Pallabi Gogoi, Pramod Sharma, D. Pamu, Structural, Broadband and Microwave Dielectric Properties of Ni Doped MgTiO_3 Ceramics, *Asian Meeting on Ferroelectricity (AMF-9) and the 9th Asian Meeting on Electroceramics (AMEC-9)*, (AMF-AMEC-2014), 26-30 Oct 2014, Shanghai, China.
- 2) **T. Santhosh Kumar**, Pallabi Gogoi, D. Pamu, Optical, Dielectrical and Impedance Spectroscopic Analysis of Zr Doped MgTiO_3 Thin Films, Presented in *International Conference on Nano Science & Engineering Applications (ICONSEA-2014)*, 26 - 28th June 2014 in Hyderabad, India.

- 3) Pallabi Gogoi, **T. Santhosh Kumar**, D. Pamu, Microstructural Studies and Optical Properties of Zr Doped MgTiO_3 Thin Films, Presented in *International conference on Nano Science and Technology (ICONSAT-2014)*, 3 - 5th Mar 2014, Chandigarh, India.
- 4) R. K. Bhuyan, **T. Santhosh Kumar**, D. Pamu, Effect of La_2O_3 and V_2O_5 Addition on Sintering Behavior and Microwave Dielectric Properties of Mg_2TiO_4 Ceramics, Presented in *International Conference on Materials science and Technology (ICMST-2012)*, 10 - 14th June 2012, Kottayam, India.
- 5) R. K. Bhuyan, **T. Santhosh Kumar**, D. Pamu, Optical Studies of Ambient Temperature Grown Nanocrystalline Mg_2TiO_4 Thin Films Deposited by RF Magnetron Sputtering, Presented in *International Thin Films Conference (TACT-2011)*, 20 - 23rd Nov.2011, Kenting, Taiwan.
- 6) **T. Santhosh Kumar**, Y. Sarath Kanth, D. Pamu, Temperature Dependent Dielectric Properties of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ Ceramics, Presented in *National Seminar on Ferroelectrics and Dielectrics-XVI*, 2nd - 4th Dec 2010, Bilaspur, India.

Awards & Honours:

- 1) “**Best poster presentation certificate**” in *International Conference on Nano Science & Engineering Applications (ICONSEA-2014)*, 26 - 28th June 2014 in JNTU Hyderabad, India.
- 2) “**Certificate of Appreciation**” for worked as volunteer in successful completion of *Inter IIT Sports meet*, during 16 - 29th Dec 2013, IIT Guwahati.

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