Synopsis Report

High-permittivity magneto-dielectric materials and their composites have drawn a tremendous attraction in recent past due to their versatile applications such as in piezoelectric transducers, low-power CMOS devices, sensors and spintronics [1-11]. Apart from the Perovskite systems (Pb[Zr,Ti]O_3, $CaCu_3Ti_4O_3$, $KNaNbO_3$, etc.), lead-free 3*d* transition metal oxide based magnetic ceramics with static dielectric constant (ε_r) more than 1000 are very limited in the literature [12-17]. Compounds such as $La_{1-x}Ca_xMnO_3$, $BaTiO_3$, $YBa_2Cu_3O_6$, and $FeTiTaO_6$ are considered as important systems because of their negligible temperature variation of ε_r and relaxor-like ferroelectric behavior [18-25]. There has not been enough attention paid to the high-frequency dielectric behavior of alkali metal (Na or Li) doped nonperovskite wide-bandgap oxides such as ZnO and NiO, and their composites. Among various lead-free 3*d* transition metal oxide systems Li and Ti doped wide-bandgap Mott insulators are the best known examples because of their colossal dielectric permittivity and temperature independent behavior of ε_r [12, 26]. Internal grain-boundary layer mechanism and thermally excited relaxation process are the key sources for such enhanced ε_r and non-zero dipole moment [26]. Dielectric relaxation in Fe, Mg, Al, Co, Zr and V doped wide-bandgap oxides are also widely investigated aiming to understand the ac-conductivity, space-charge polarization (Maxwell–Wagner type) at low frequencies and defect-dipole induced polarization mechanism at high frequency regions [27-30]. The present research work has primarily motived to develop the two-phase composite systems of $Zn_{1-x}Ni_xO$/NiO and $Ni_{1-x}Na_xO$ whose physical properties are comparable to those of Li, Ti doped NiO. When we initiated this problem no report was available focusing on the structural, dielectric and magnetic properties of above composites either in the form of both bulk or nanostructures. Hence, an attempt was made to understand the growth mechanism and other physical properties of the above mentioned composites. The detailed layout of the thesis is as follows:

Chapter 1 provides a brief introduction to the High-κ dielectrics and their significance in microelectronics. This chapter also presents an important up-to-date research on the dielectric properties of alkali metal doped ZnO and NiO. This chapter reviews few important concepts like: Mott-Insulators, Lyddane-Sachs-Teller relation $\left[\frac{\epsilon_0 - S'}{\epsilon_\infty} = \left(\frac{\omega_l}{\omega_t}\right)^2\right]$, Debye relaxation, various dielectric polarization mechanisms including Maxwell–Wagner–Sillars and defect-dipole polarization with special emphasis on the influence of domain-wall displacement, microstructure, depletion and depolarization effects. In addition, a brief introduction to molecular field theory of antiferromagnetism in transition metal oxides which crystalizes in rock salt type crystal structure was presented. Finally, a detailed description of the research problem and its approach is illustrated in this chapter.

Chapter 2 describes a detailed overview of various experimental techniques employed in this research work including the synthesis procedure of $Zn_{1-x}Ni_xO$/NiO and $Ni_{1-x}Na_xO$ based on low-temperature sol-gel processing and standard solid-state reaction method. This chapter also demonstrates various characterization techniques including structural characterization using X-ray and electron diffraction techniques and thermal properties using

thermogravimetric-analysis (TGA) and differential scanning calorimetry (DSC). For a detailed crystal structure analysis, we performed the Rietveld refinement of diffraction data using Fullprof and Powder-cell softwares. Particulars of elemental analysis performed by the X-ray photoelectron spectroscopy (XPS) was described thereafter. Morphological characterization techniques such as transmission electron microscopy (TEM) has also been discussed. In the subsequent sections we presented the details of various characterization tools employed in this work such as: (*i*) frequency and temperature dependence of dielectric measurements, (*ii*) Raman spectroscopy to understand the vibrational excitation, (*iii*) electron-spin resonance technique to probe the local atomic environment, and (*iv*) magnetic measurements using superconducting quantum interference device (SQUID) based magnetometer and vibrating sample magnetometer.

Chapter 3 presents a detailed structural and dielectric properties of polycrystalline wurtzite h.c.p $Zn_{1-x}Ni_xO$ and cubic NiO two-phase composites. In this chapter we demonstrated that these composites exhibit a dielectric anomaly across the transition temperature (T^*) ~ 541 K associated with the changeover from antiferro to paramagnetic ordering of NiO. Such transition is accompanied by the change in crystal structure from rhombohedral to cubic phase. For $T > T^*$, a giant dielectric cusp was observed across 683 K (410˚C) for $x = 1$ together with the above mentioned anomaly at T^* close to the antiferromagnetic Néel temperature T_N of NiO. For $T > T^*$ the dielectric permittivity cusp obeys the empirical scaling law based on the equation $(\varepsilon_A/\varepsilon_r = 1+0.5(T-T_A)^2/\delta^2)$ with the shape parameter value 'δ' ~ 88 and 39.73 ˚C for the compositions $x = 0.30$ and 0.163, respectively. Dynamic variation of the dispersion in ε_r at temperatures close to T^* follows the Vogel–Fulcher law with Debye frequency $\nu_0 \sim 1.33 \times 10^9$ Hz and 1.33×10^6 Hz, freezing temperature $T_g \sim 181$˚C and 240˚C, and activation energy $E_A = 0.11$eV and 0.023 eV for $x \sim 0.30$ and 0.16, respectively. Diffuseness exponent 'γ' = 1.91 and 1.77 estimated from the experimental data for the compositions $x = 0.30$ and 0.163, respectively are close to 'γ' = 2 usually exhibited by an ideal relaxor ferroelectric system. These results are further supported by the butterfly loop characteristics of C-V curves. The relaxor behavior (mixed phase ferroelectric–glass) for heavily doped $Zn_{1-x}Ni_xO$/NiO system is mainly driven by the compositional heterogeneity. The temperature dependence of ac-resistivity $\rho_{ac}(T)$ provide strong evidence of variable-range-hopping of charge carriers between the localized states through a mechanism involving spin-dependent activation energies. The temperature variation of carrier hopping energy $\varepsilon_h(T)$ and nearest-neighbor exchange-coupling parameters $J_{ij}(T)$ are evaluated for all the compositions using small-Polaron model. For all the composite systems, $J_{ij\text{-Average}}$ nearly equals to 70 meV which is slightly greater than the exciton binding energy 60 meV of pure zinc-oxide. A systematic comparative analysis of the above results with the Na doped NiO system is presented.

Chapter 4 focuses on the nature of magnetic exchange interactions in $Zn_{1-x}Ni_xO$-NiO composites. The magnetic exchange constants $|J_1|$ and $|J_2|$ for the two-sublattices have been evaluated using both molecular-field approximation ($J_1 \sim 0.15$ meV and $J_2 \sim 1.15$ meV for $x = 1$) and Green's-function theory ($J_1 \sim 0.78$ meV and $J_2 \sim 1.77$ meV for $x = 1$). Magnitudes of these exchange constants determined from the Green's-function analysis are

compared systematically with the values obtained from the spin-wave dispersion curves ($J_1 \sim 0.137$ meV and $J_2 \sim 1.90$ meV for $x = 1$) and Raman scattering ($J_2 \sim 1.98$ meV). Additionally, the carrier activation energies 'ε_h' and nearest-neighbour exchange coupling parameters 'J_{ij}' (~1.61 meV) calculated from the temperature dependence of ac-resistivity $\rho_{ac}(T)$ across T_N of NiO. Such analysis is based on the small-polaron model involving spin dependent activation energies. These results are compared with the theoretical estimations performed by the Green's-function theory. Furthermore, the role of oxygen stoichiometry on the temperature variation of J_{ij}, ε_r, ρ_{ac}, and unit-cell volume 'V_C' have been discussed for both $Zn_{1-x}Ni_xO$/NiO and $Ni_{1-x}Na_xO$.

Chapter 5 is devoted to the growth and characterization of low-dimensional nanostructures of $Zn_{1-x}Ni_xO$/NiO. First two sections of this chapter are dedicated to the formation mechanism, crystal structure and morphology. These preliminary studies are followed by a detailed investigation of the electron-spin-resonance (ESR) and Raman spectroscopic studies. The temperature variation of X-band ESR parameters viz. resonance field $H_R(T)$ and line-width $\Delta H_{PP}(T)$ was analyzed using the power-law variation ($\delta H_R = (\Delta H_{PP})^n$) of Nagata and Ishihara model. This model was used to understand the orientation of statistical ensemble of particles with respect to a given direction of the anisotropy axis. This analysis yields the exponent 'n' $\simeq$ 2.13 and 2.85 for the nanocomposite system $Zn_{1-x}Ni_xO$/NiO and pure NiO suggesting the presence of partial and randomly oriented ellipsoidal nanocrystallites, respectively. Further, the Raikher and Stepanov model has been employed to probe the role of amorphous Ni^{3+} clusters on the observed ESR spectra. The vibrational excitations obtained from the Raman spectroscopy reveals that after Ni substitution in wurtzite ZnO, a new zone-boundary phonon mode was emerged at 129 cm^{-1} for all the compositions. Such phonon mode is usually forbidden in the first-order Raman scattering of ZnO. In addition to the 2M Magnon mode, two extra modes appear at 558 and 900 cm^{-1} due to the increased volume fraction of NiO within the $Zn_{1-x}Ni_xO$ matrix. A systematic correlation of all the above results with the magnetic anisotropy of the nanocomposites is discussed.

Chapter 6 presents a brief summary of important findings of our experimental results. In this chapter we also identify some open issues which are potentially interesting for the future studies.