PREFACE

Semiconducting high-κ dielectric and ferroelectric materials have technological applications in optoelectronic devices for uses in optical communication, memory, displays, and coherent optical processing. In semiconducting materials, high-κ dielectricity and ferroelectricity are a result of the delicate balance between a long-range dipole–dipole interaction and a short-range interaction. Slight distortion of electron cloud due to structural changes in dielectrics gives rise to dipole moments. The ferroelectric phase transitions are associated with a structural phase transition from the high-symmetry paraelectric phase to the low-symmetry ferroelectric phase. Therefore, new materials with a simple structure are not only preferable for understanding the microscopic origin of ferroelectricity but are also important for integrating into modern ferroelectric devices with the utilization of novel ferroelectric/piezoelectric/relaxor and multiferroic materials that do not contain environmental hazards such as Pb and Bi.

Also, there is an interest in bringing d^0 and d^n ($0 \leq n \leq 10$) transition metal atoms together in a simple oxide matrix to realize multiferroic properties. Further altering of the relative iconicity and bonding character in M-O bond by structural anisotropy or introducing different electronic state cations in a single lattice to result in entropy-driven relative net polarization in the lattice can also act as an effective way to develop high-κ dielectric and relaxor-type ferroelectrics. For the development of high-κ dielectrics and relaxor-type ferroelectrics, in this thesis, the role of oxygen vacancy, and doping of multiple cations to develop structural anisotropy and to alter the ionic strength or iconicity in M-O to develop net polarization in the lattice are explored.

Chapter 1 presents the introduction of dielectricity and its application to modern electronics and a way forward to develop superior high-κ dielectric and ferroelectrics and understand the origin of high-κ dielectricity and ferroelectricity.

Chapter 2 deals with synthesis schemes and characterization techniques utilized in the study and the use of impedance spectroscopy to measure the dielectric properties of the material.

Chapter 3 presents the investigation of Cu^{+} ion substituted ZnO and the role of d^{0}-d^{10} interaction in the wurtzite structure and the effect of relative iconicity in M-O (M = Zn and Cu) bond to result in effective net polarization in the lattice. Cu^{+} ion substitution on Zn^{2+} sites not only resulted in net polarization but also opened the path for strong polarization between O-2p and filled d^{10} Zn/Cu 4p orbital in tetrahedral coordination. Up to 8% of Cu^{+} ions were substituted in the ZnO lattice and the highest dielectric constant (~6300) was obtained at 600°C for $Zn_{0.95}Cu_{0.05}O_{1-\delta}$ at 100 KHz frequency. The materials $Zn_{0.95}Cu_{0.05}O_{1-\delta}$ also exhibit ferroelectricity at room temperature with remnant polarization Pr and Vc equal to $9.60*10^{-03}$ μC/cm^2 and $3.83*10^{+02}$ V/cm respectively.

Chapter 4 presents the investigation of dielectric properties of bulk pristine Cu^{2+} and Li^{+} co-doped ZnO. $Zn_{0.92}Cu_{0.05}Li_{0.03}O_{1-\delta}$ and $Zn_{0.9}Cu_{0.05}Li_{0.05}O_{1-\delta}$ ceramics samples were prepared by the modified sol-gel method. The complex impedance spectroscopic study of Cu and Li co-doped ZnO confirms the high dielectric constant and low dielectric loss at high temperatures and high frequency compared to ZnO. T_m was found to increase with increasing frequencies suggesting the relaxor nature of dielectricity in the sample. The bulk pristine $Zn_{0.9}Cu_{0.05}Li_{0.05}O_{1-\delta}$ also exhibits ferroelectricity and paramagnetic properties at room temperature. Bulk pristine $Zn_{0.9}Cu_{0.05}Li_{0.05}O_{1-\delta}$ also exhibits

ferroelectricity at room temperature with remnant polarization Pr and Vc equal to $4.20*10^{-02}$ μC/cm^2 and $4.1*10^{+03}$ V/cm at (30KV, 500 Hz) respectively. Bulk pristine $Zn_{0.9}Cu_{0.05}Li_{0.05}O_{1-\delta}$ also shows the dilute paramagnetic behavior with a coercivity and saturation magnetization reaching 114 Oe and 7.43 memu/g at 5K.

Chapter 5 presents the synthesis of single-phase Fe-doped ZnO and Fe/Li co-doped ZnO and the investigation of the dielectric behavior of the materials. The complex impedance spectroscopic study of Fe-doped and Fe/Li co-doped ZnO shows a high dielectric constant and low dielectric loss at high temperatures and high frequency compared to ZnO. The Fe and Fe/Li doping depresses the concentration of the intrinsic donor and impedes the conduction mechanism resulting in the dielectric constant (ε_r') equivalent to 612 for $Zn_{0.9}Fe_{0.1}O_{1+\delta}$ and 90000 for $Zn_{0.8}Li_{0.1}Fe_{0.1}O$. at 1000 Hz frequency at 400^{o}C. Also with an increase in frequency, the dielectric constant and dielectric loss were found to decrease.

Chapter 6 presents the investigation of single-phase Ti^{4+} ion substituted $CoNb_2O_6$ in the form of $CoNb_{2-x}Ti_xO_6$. Ti^{4+} substitution in the Trirutile $CoNb_2O_6$ lattice enhances the dielectric constant of the material. Similar to well-known PZT type high κ Ferroelectrics, Ti^{4+} ion substitution in novel Trirutile $CoNb_2O_6$ lattice resulted in high κ dielectricity and overall turned Trirutile into a new family of ferroelectrics as smaller Ti^{4+} can vibrate from its mean position in Trirutile octahedral resulting in net polarization in the octahedral. The dielectric constant (ε_r') for $CoNb_2O_6$ was found to be 500, $CoNb_{1.95}Ti_{0.05}O_6$ is 700 and $CoNb_{1.9}Ti_{0.1}O_6$ is 14000 respectively at 100 Hz frequency at 200^{o}C and then decreases, clearly shows relaxor type behavior. Samples also exhibit ferroelectric behavior with remnant polarization Pr and Vc at 50Hz frequency equal to

0.05 μC/cm^2 and 8*10^{+03}V/cm for $CoNb_{1.95}Ti_{0.05}O_6$ and 0.05 μC/cm^2 and 10*10^{+03}V/cm for $CoNb_{1.9}Ti_{0.1}O_6$.

Chapter 7 provides the conclusions drawn from the investigation and presents the role of structural anisotropy or multiple cations doping to alter the relative ionic strength or ionicity of the M-O bond in the lattice to generate effective net polarization and long-range dipole-dipole interaction for the development high-κ dielectric and relaxor type ferroelectrics. Insight for future investigation and a way forward to develop high-κ dielectric and ferroelectrics.