Preface

Disorder in materials often brings in new and exotic physical properties along with it. It is thus very important to study different kinds of disorder and their implications on various material properties. In this thesis, we study selected transition metal oxide families of compounds, each being associated with a specific kind of disorder and investigate effects of that disorder on their dielectric and magnetic properties.

In Chapter 1, we have given brief introductions on the origin of magnetic and dielectric properties in materials and have also discussed various mechanisms which give rise to multiferroism in materials which exhibit both spontaneous magnetic ordering and spontaneous electric ordering in the same phase of the material.

In Chapter 2, we describe the various methodologies adopted in this thesis.

In Chapter 3, we mainly study the effect of cationic size-disorder in deciding unusually robust dielectric properties of $Ln_2CuTiO_6$ ($Ln = Y, Dy, Ho, Er, Yb$) family of compounds. We discover that these materials, in addition to possessing large dielectric constant values, also exhibit exceptional stabilities of their dielectric constants with respect to large changes in temperature and frequency. We further find that this class of materials are non-ferroelectrics though it shares the same non-centrosymmetric space group, $P6_3cm$, with the well-known multiferroic YMnO$_3$ that undergoes a ferroelectric transition at 940 K. Using first principles calculations, we establish that exceptional dielectric properties result from a combination of two separate effects. Extensive size disorders at the Cu/Ti $B$-site suppress the expected ferroelectric transition, leading to relatively large values of the dielectric constant for every compound investigated in this series. Additionally, it is shown that the majority contribution to the dielectric constant arises from intermediate-frequency polar vibrational modes, making it relatively stable against temperature variations.
In Chapter 4, we study the effect of cation anti-site disorder on the magnetic, electric and dielectric properties of the solid solution series of $(x)Fe_2O_3 - (1-x)FeTiO_3$ for several values of $x$. For intermediate values of $x$, these solid solution members are found to be strong ferrimagnets. Anti-site cation disorder, between Fe and Ti, however strongly reduces the magnetic moment values. By tuning the degree of cation anti-site disorder, we attain multi-functionality in these samples. We have performed detailed characterizations of valence states of Fe and Ti across the solid solution series using x-ray photoelectron spectroscopy and x-ray absorption spectroscopy. Using x-ray magnetic circular dichroism, we validate the microscopic model of magnetism and suggest a microscopic picture of the anti-site cation disorder for these samples.

In Chapter 5, we study the effects of controlled chemical disorder in SrTiO$_3$ lattice, by performing site-specific doping of Mn in SrTiO$_3$. We find that site specific Mn doping has decisive influence on their dielectric properties with qualitatively and quantitatively different behaviors between these doped samples. Using electron paramagnetic resonance experiments, we establish the site specific doping of Mn in SrTiO$_3$ lattice. We find that while Mn doping at Ti site continues to remain paraelectric, Mn doping at the Sr site becomes a relaxor ferroelectric. We find samples having Mn substituted at both Sr and Ti sites simultaneously to be also relaxor ferroelectrics. Combining experiments with first principles calculations, we understand the origin for the high temperature dielectric properties of various Mn doped SrTiO$_3$ samples. We show that Mn ions doped at the Sr sites off-centers and gives a significant dipolar contribution to their dielectric constants. While demonstrating the superior dielectric properties of Mn doped SrTiO$_3$ ceramics, we also elucidate their magnetic properties in details.

In Chapter 6, we study the effect of cation anti-site disorder on the magnetic and dielectric properties of undoped and Lu doped La$_2$NiMnO$_6$ samples. Using detailed spectroscopic characterizations of these samples with x-ray absorption experiments, coupled with d.c. magnetization and a.c. susceptibility measurements, we demonstrate that while the doped samples are ferromagnetic, the undoped samples exhibit re-entrant spin-glass magnetism. We also show that the dielectric properties of undoped La$_2$NiMnO$_6$, crystallizing in monoclinic and rhombohedral phases are distinctly different and we study their dielectric relaxations in details. We also demonstrate multiferroism in Lu doped La$_2$NiMnO$_6$ samples.
In Appendix A, we study the electronic origin of ferroelectric polarization in the spin spiral compound, MnWO$_4$. Using x-ray absorption spectroscopy on synthesized MnWO$_4$ samples, coupled with configuration interaction calculations, we establish quantitatively a significant population of Mn 3$d$ states beyond the expected half filling and provide a critical insight into the significant presence of spin–orbit coupling and consequent finite polarization in this system.

In Appendix B, we study charge-transfer doping in few-layer graphene covered with electron acceptor (Tetracyanoethylene) and donor (Tetrathiafulvalene) molecules using x-ray photoelectron spectroscopy. We give quantitative estimates of the extent of doping in these samples and thereby elucidate the origin of unusual shifts of their Raman $G$ bands in contrast to electrochemically doping schemes.

In conclusion, we investigate, in this thesis, properties of different classes of compounds in presence of distinctly different kinds of disorder and establish the critical role of disorder in each case in tuning their desirable physical properties.