

PREFACE

In recent days, the need for device miniaturization has led to immense research activities in the field of material science. It has become essential to discover and design new materials or to modify the existing materials to meet the ever-increasing demand of new multifunctional materials in the industry. In this regard, complex oxides stand out as one of the most promising material classes. In particular, multiferroic materials simultaneously possessing two or more primary ferroic orders (ferromagnetism/antiferromagnetism, ferroelectricity, ferroelasticity) offer advantages over other materials. In this research work, comprehensive studies on polycrystalline material synthesis, thin film growth and characterization pertaining to few such promising multiferroic materials are reported.

Among different types of multiferroics, hexagonal (h) rare-earth manganites (h-RMnO₃, R = Dy-Lu, Sc, Y) form a unique class of materials which exhibit ferroelectricity at room temperature and above by virtue of non-centrosymmetric *P6₃cm* crystal structure. The magnetic structure compatible with the hexagonal crystal symmetry is relatively complex and unique. It consists of triangular non-collinear lattice of Mn atoms in the *ab* basal plane which are magnetically frustrated and results in significantly lower magnetization and magnetic ordering temperatures (T_N in the range of 70-130 K). Below T_N , magnetic and ferroelectric orderings coexist in h-RMnO₃ with evidences of magnetoelectric coupling due to which these materials gained lot of research interest. But, despite their room-temperature ferroelectric behaviour, the h-RMnO₃ series of compounds are not suitable for practical multiferroic applications because their magnetic ordering temperatures are significantly lower than the room temperature. In this context, we have chosen two compounds h-LuMnO₃ and h-ScMnO₃ both possessing high magnetic ordering temperature among the h-RMnO₃ series. Our primary motivation was on increasing the strength of magnetic interactions and the magnetic ordering temperature by doping at either A or B-site while maintaining the polar *P6₃cm* crystal symmetry intact, which yields room temperature ferroelectric properties (as in hexagonal RMnO₃). Interestingly, in addition to the improved multiferroic properties of these doped h-RMnO₃ samples, we observed emergence of new phenomena as a result of doping. Moreover, we found that the substrate induced epitaxial strain in the thin films of doped h-RMnO₃ compounds resulted in new properties which were not discernible in bulk.

Present thesis works can be broadly divided in three parts. The ‘first part’ is on 50% Fe doped LuMnO₃ (i.e. LuMn_{0.5}Fe_{0.5}O₃) compound. Due to higher magnetic moment of Fe³⁺ compared to Mn³⁺, the compound LuMn_{0.5}Fe_{0.5}O₃ possesses improved magnetic nature compared to parent compound LuMnO₃ while holding the polar *P6₃cm* crystal symmetry of LuMnO₃. LuMn_{0.5}Fe_{0.5}O₃ samples were synthesized both in polycrystalline bulk and epitaxial thin film form. Three different types of studies were performed on these samples the results of which are presented in chapters three, four, and five. In the ‘second part’ tetravalent Zr⁴⁺ ion was used for doping at the Sc³⁺ site in ScMnO₃. This resulted in electron doping in the system. Thorough investigations relating to the effect of electron doping in multiferroic behaviour of ScMnO₃ and detailed studies of the emerging new phenomena are given in chapters six and seven. The A-site tetravalent ion doping in ScMnO₃ reduces the magnetic frustration; it induces ferromagnetic behaviour while preserving the polar *P6₃cm* crystal structure. The ‘third part’ of the thesis work is on thin film samples of 50% Ni doped LuMnO₃. In contrast to Fe doping, 50% Ni doping in place of Mn changes the crystal symmetry of LuMnO₃ to monoclinic *P2₁/n* crystal symmetry. The chemical formula of the resultant compound can be written as Lu₂MnNiO₆ as the compound falls under the category of double perovskites. Due to the change in crystal symmetry, the magnetic and other physical properties are

found to be completely different in $\text{Lu}_2\text{MnNiO}_6$ than that in LuMnO_3 . These results are documented in chapter eight. A brief chapter-wise outline of the thesis is given below:

Chapter 1 gives a general introduction to the physics of multiferroics and related phenomena. Brief descriptions of few relevant topics such as anti-phase boundary type crystal growth defects, exchange bias phenomenon, spin-glass, etc are also provided. Motivation for the present research work is included at the end of this chapter.

Chapter 2 summarizes various experimental techniques used in this thesis and their basic working principles. It describes bulk sample preparation processes and thin film growth technique adopted.

Chapter 3 presents detailed experimental characterization of the compound $\text{LuMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (LMFO) with special reference to its multiferroic magnetoelectric properties. X-ray photoemission (XPS) spectra are collected which confirmed the valence state of Mn and Fe to be +3, only. The compound stabilizes in polar hexagonal ($P6_3cm$) crystal symmetry and exhibits long-range antiferromagnetic ordering below $T_N = 103$ K. Additionally, in the magnetization vs. temperature ($M-T$) data, an extra hump-type anomaly was noticed close to room temperature. This is an unseen feature in the related RMnO_3 compounds. By inspection of prevalent magnetic exchange paths existing in the $P6_3cm$ crystal symmetry, we have argued that its origin lies in the intraplane short range spin ordering. Heat capacity of LMFO is also measured and analysed to elucidate the magnetic entropy. This further supports the existence of intraplane spin ordering at higher temperature beyond T_N . Indication of magnetoelectric coupling is obtained from dielectric anomaly at T_N . Room-temperature ferroelectric behaviour is unambiguously probed by Piezo response force microscopy (PFM) and measurement of standard and remnant ferroelectric hysteresis loops. Further, from high-temperature dielectric data, the occurrence of ferroelectric transition above 900 K and relaxation due to Maxwell-Wagner interfacial polarization between grain and grain boundaries is ascertained.

Chapter 4 deals with antiphase boundary (APB) defect induced anomalous weak ferromagnetism, exchange bias effect and large vertical hysteretic shift in the single-phase antiferromagnetic system $\text{LuMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (LMFO). Presence of APB-type defects in LMFO has been probed using ^{57}Fe Mössbauer spectroscopy measurement and high-resolution transmission electron microscopy (HRTEM) technique. At the APB, the bulk super exchange interaction is modified, and the APB spin interaction gives rise to a separate component in Mössbauer spectra having unusually low internal field. From the magnetization measurements, we find that the new APB-induced magnetic interaction persists up to $T^* = 330$ K whereas the intrinsic long-range antiferromagnetic ordering temperature is $T_N = 103$ K. Upon field cooling strong pinning effect of the APB spins lead to large vertical hysteretic shift in LMFO. Finally, post annealing the optimally sintered LMFO sample helps to understand the evolution of defects and their influence on weak ferromagnetism and exchange bias properties. It is observed that the ferromagnetic nature of LMFO becomes more pronounced as the defect content increases and also exchange bias properties of LMFO change accordingly.

Chapter 5 details the results of multiferroic characterization of $\text{LuMn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (LMFO) epitaxial thin film grown by pulsed laser deposition (PLD) technique on cubic (001)- SrTiO_3 (STO) substrate. The films exhibit orthorhombic ($Pnma$) crystal symmetry and show both (0k0) and (h0h) out-of-plane orientations. In addition, HRTEM image revealed that the unit cell of LMFO also has slight monoclinic distortion. The LMFO/STO films are compressively strained along the [100] direction and tensile strained along the [010] and [001] directions. Films display weak-ferromagnetic nature along with the dominant antiferromagnetic interaction. The observed ferromagnetism has been attributed to the substrate-induced epitaxial strain in the film.

Interdigitated gold electrodes were patterned using photolithography and lift-off procedures and in-plane ferroelectric hysteresis loops are measured. PFM measurements are also carried out. Interestingly, the films exhibit room-temperature ferroelectric behaviour which is likely due to the slight monoclinic tilt of the orthorhombic unit cell of LMFO in the epitaxial film.

Chapter 6 reports on multiferroic properties of a series of electron doped multiferroic compound $\text{Sc}_{1-x}\text{Zr}_x\text{MnO}_3$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$). All the doped samples stabilize in $P6_3cm$ structure and, as a result of Zr^{4+} doping, Mn^{2+} is generated at the expense of Mn^{3+} . Detailed analysis of XPS spectra are carried out to confirm the presence of Mn^{3+} , Mn^{2+} , and Zr^{4+} cations. The parent compound ScMnO_3 exhibits long-range antiferromagnetic ordering below $T_N = 130$ K. As Zr^{4+} concentration increases in the doped systems, antiferromagnetic ordering gradually diminishes while shifting to low temperatures and additional ferromagnetic interaction gradually develops. The 20% doped sample showed significant hysteresis with greatly enhanced magnetization. Interestingly, even with zero magnetic moment of Sc^{3+} , a Schottky-like anomaly is observed at 5 K in the heat capacity data of samples with $x = 0.1$ and 0.2 . This we attribute to the highly resistive nature of doped samples. While measuring ferroelectric hysteresis loops, we found that the leakage current contribution is significantly reduced in case of $x = 0.2$ compound compared to ScMnO_3 . Additionally, the compound $x = 0.2$ shows improved dielectric and ferroelectric behaviour. It is proposed that doping of Zr^{4+} compensates for the cation deficiency and consequently eliminates the inherent oxygen vacancies by charge compensation.

Chapter 7 explores electron-doping induced exchange bias effect and cluster glass magnetism in multiferroic $\text{Sc}_{0.8}\text{Zr}_{0.2}\text{MnO}_3$ bulk material. Scanning electron microscopy (SEM) images were collected and microstructure of the sample was investigated which suggested that grain boundaries do not have any significant role in the emergence of exchange bias effect and ferromagnetism in $\text{Sc}_{0.8}\text{Zr}_{0.2}\text{MnO}_3$. Detailed investigations have been carried out to study the influence of temperature, cooling field and training effect on exchange bias parameters so as to obtain insights into the real nature of the observed exchange bias. A comparison of exchange bias properties of $\text{Sc}_{0.8}\text{Zr}_{0.2}\text{MnO}_3$ to the typical phase-separated exchange bias system is presented. We found compelling evidence of cluster glass magnetic nature of $\text{Sc}_{0.8}\text{Zr}_{0.2}\text{MnO}_3$ by dc field dependent magnetic measurements, ac susceptibility measurements, magnetization relaxation experiments and memory tests.

Chapter 8 discusses growth of epitaxial thin films of $\text{Lu}_2\text{MnNiO}_6$ (LMNO) by PLD technique on two different substrates (001)- LaAlO_3 (LAO) and (001)- SrTiO_3 (STO) and compares the structural and magnetic properties of these films. Evidences of simultaneous presence of both (001) and (110) oriented out-of-plane domains are obtained in the epitaxial film of LMNO. We have performed detailed investigation using X-ray diffraction, reciprocal space mapping (RSM) and HRTEM technique and found that there are total six monoclinic twin variants in the film from the (110) and (001) oriented out-of-plane domains. Both films, LMNO/LAO and LMNO/STO showed ferromagnetic behaviour. Due to very good lattice match with LAO substrate, the LMNO/LAO film grows as well-ordered film and the value of saturation magnetization is very close to what has been reported for bulk LMNO with ordered double perovskite structure. Large lattice mismatch with STO substrate resulted in disordered LMNO/STO films. It is found that the magnetic moment (M_s , at maximum field of 70 kOe) is significantly reduced in disordered LMNO/STO ($M_s = 2.4 \mu_B/\text{f.u.}$ at 70 kOe) compared to the ordered LMNO/LAO ($M_s = 4.0 \mu_B/\text{f.u.}$ at 70 kOe). Moreover, along with the dominant ferromagnetic interactions, glassy magnetic interactions are observed in both of the films below their ferromagnetic ordering temperatures.

Chapter 9 provides highlights of major findings in this thesis work and a conclusion to this study. Future prospects are briefly outlined.