Thesis Details- (h) Synopsis

Technology helps to improve every aspect of human life and has continued to play an important role in our day today activities. Developing the understanding of magnetism in various new materials could open new and interesting technologies that can become a part of everyday life in the future years to come. Complex magnetic systems like $RMnO_3$ Manganites, Multiferroics and Diluted Magnetic Semiconductors (DMS) etc. are some of the most interesting materials which have opened up a new era for spintronic device applications [1 - 4]. Studies on the electronic states and nature of physics underlying these systems have been a subject of intense research for several decades. The simultaneous presence of ferroelectricity and magnetism in functional materials and the cross-coupling between them can be useful in magnetic storage of data, switching applications, spin valves, spin transistors, field effect devices, etc [5]. $RMnO_3$ [R is the rare earth elements] being the parent compound of the colossal magnetoresistance (CMR) manganite family, shows interesting structural and magnetic behaviour due to the complicated magnetic / spin structure resulting from the presence of two magnetic sub lattices which exhibits multiferroicity [6]. The decrease in ionic radius of R ion tends to increase the cooperative rotation of the MnO_6 octahedra, resulting in the decrease in Mn – O – Mn bond angle which causes a profound effect on the orbital ordering temperature (T_{OO}) and also the magnetic ordering temperature (T_N) such that, T_{OO} increases monotonically while the T_N decreases significantly. Also the A-type antiferromagnetic (AFM) phase becomes E-type AFM phase through an intermediate incommensurate structure that induces multiferroic behaviour [6, 7]. Studies on the parent compound of $RMnO_3$ family, ie, $LaMnO_3$, shows clear evidence of multiferroicity (dielectric anomaly) around magnetic ordering temperature (T_N) due to spin-orbital coupling [8]. On the other hand, in $TbMnO_3$ perovskite, the origin of multiferroicity is due to the onset of incommensurate (IC) spiral magnetic order at $T_{IC} < T_N$, where it breaks, both, spatial and time inversion symmetries simultaneously and exhibit a strong coupling between polarization and magnetization [9]. The earlier research on $RMnO_3$ perovskites has lead to several unanswered questions regarding the origin of magnetism and multiferroic behaviour in them. The interesting physical mechanisms underlying these materials need to be further explored. The main objective of the present work is to study structure-property correlations in mixed valent manganites using Temperature dependent Neutron Diffraction (ND) study and to study its impact on electronic and magnetic properties. Furthermore, an attempt has been made to emphasize the importance of structure-property correlations by growing the high quality thin films and tailoring their properties for various applications.

$RMnO_3$ compounds with R = La, Pr and Nd crystallize in orthorhombic structure [6, 10] with *Pnma* space group while compounds with R = Tb, Ho and Yb crystallize in hexagonal structure with space group $P6_3cm$ [11]. There are several reports available on the factors affecting the properties of $RMnO_3$, such as doping (A-site), sintering temperature, oxygen deficiency etc. These factors are also responsible for the creation of Mn^{4+} and double exchange (DE) interaction between Mn^{3+} - O - Mn^{4+} which results in the antiferromagnetic (AFM) to ferromagnetic (FM) and insulator to metal (I – M) transitions in manganites [12 - 15]. In $RMnO_3$, studies also exist on the Mn site (B-site) doping with transition metal ions resulting in the modifications in their properties possibly due to the weakening of DE interactions. Amongst $RMnO_3$ perovskites, $NdMnO_3$ is an interesting candidate because of competing ferro-antiferromagnetic exchange interactions, the long range AFM ordering and magnetoelastic effect associated with AFM transition temperature T_N (~ 80 K). $NdMnO_3$, as a parent compound for both manganite and multiferroic materials, needs more experimental and theoretical investigations. During the course of this work, the fascinating properties of $NdMnO_3$ compounds have been understood under the light of magnetic exchange interactions between Nd and Mn ions, octahedral and Jahn Teller (JT) distortion etc.

Swift heavy ion (SHI) irradiation is one of the promising tools to engineer the properties of materials in a controlled manner and make them functional for desired applications. Energetic ions, inside a solid, lose their energy due to elastic (S_e) and inelastic (S_n) scattering with the target material. This interaction of highly energetic ions results in the structural transformations and formation of defects in the films, which leads to the modifications in the electronic and magnetic properties of oxide thin films. The ion species, their energy and ion fluence are some of the important parameters required to create defects in the material. Several studies on SHI-irradiation-induced modifications in the properties of functional oxide thin film devices, characterized using X-ray Diffraction (XRD), Rutherford Back Scattering (RBS), Atomic Force Microscopy (AFM), I-V and Raman spectroscopy, SQUID etc. techniques have shown that, deposition of 200 MeV Ag^{+15} ions with higher ion fluence ($> 5 \times 10^{12}$ ions/cm^2) leads to complete amorphization because electric energy (S_e) deposited into the film is larger than the threshold energy (S_{th}) necessary for the creation of ion tracks [16]. In the present work, the results of systematic study on the effect of 200 MeV Ag^{+15} SHI irradiation, with ion fluences ~ 5×10^{10}, 5×10^{11}, 1×10^{12}, 5×10^{12} ions/cm^2 and its effect on structure and transport properties of $NdMn_{1-x}Zn_xO_3$ films have been presented.

Motivation for the work

Main idea behind undertaking this work is to improve the overall structure and magnetic properties of mixed valent doped manganites and to study the magnetic phase segregation, tuned by the substitution of Cu and Zn at Mn – site.

During the course of present work, structure and physical properties of $NdMnO_3$ as a function of -

(A) mangnetic (Cu) and non-magnetic (Zn) doping at Mn-site

(B) different sintering temperatures during synthesis

(C) strain induced due to lattice mismatch in thin films &

(D) ion fluence during SHI irradiation

have been investigated in detail.

The magnetic phase evolution in both the Cu & Zn systems have been investigated using temperature dependent Neutron Diffraction measurements. $NdMnO_3$ perovskites sintered at different temperatures having similar orthorhombic unit cell geometry differ in magnetic, dielectric and transport properties. This sensitivity leads to some important questions which require in-depth understanding. In the form of thin films, it is interesting to study how strain due to doping and irradiation affects the AFM structure of the orthorhombic $NdMnO_3$ which is supposed to modify the magnetic interactions and the transport properties of manganite thin films.

A brief description of the chapters and their contents in this thesis are as below –

Chapter 1: This chapter describes in brief, about the Functional Oxide systems and various factors affecting their properties. Particularly, in manganites, the effect of transition metal doping at B-site and sintering temperature during synthesis, on magnetism and the evolution of magnetic phase has been discussed in detail using Neutron Diffraction technique. This chapter also highlights the effect of strain on the properties of doped manganite thin films. It also includes introduction to SHI irradiation and defects created in the material due to ion beam irradiation. An overview of the research that has been carried out in the past, present scenario and applicability of these materials in various technological aspects is mentioned. The motivation for the present work has been given at the end of chapter.

Chapter 2: The brief idea about various experimental methods used for the synthesis of bulk and thin films of $NdMnO_3$ and doped $NdMnO_3$ manganites has been given in this chapter. Details about various experimental techniques used for characterization of materials under investigation have been explained. The main experimental techniques used in the work viz, magnetization and Neutron Diffraction (ND) have been discussed in detail in this chapter. The chapter also covers the detailed description of the software used to analyze the structure and magnetic structure obtained from XRD and temperature dependent ND. The description of experimental set up of SHI irradiation used is included in this chapter.

Chapter 3: In this chapter, results of the studies on structural, transport and magnetic properties of polycrystalline $NdMn_{1-x}Cu_xO_3$ (x = 0.00, 0.05, 0.10, 0.20) system have been discussed. The effect of magnetic dopant and Mn-site size disorder on the structure, microstructure, dielectric and magnetic properties have been studied. Electronic structure has been investigated using XAS technique. Magnetic phase evolution in Cu-doped $NdMnO_3$ system has been investigated using temperature dependent ND measurements.

Chapter 4: This chapter explains the effect of non-magnetic (Zn) doping on the structural, transport and magnetic properties of polycrystalline $NdMn_{1-x}Zn_xO_3$ (x = 0.00, 0.05, 0.10, 0.20) samples. The effect of sintering temperature on microstructure, dielectric and magnetic properties has been studied. Electronic structure has been investigated using XAS technique. Magnetic spin structure of Zn-doped $NdMnO_3$ system has been investigated using temperature dependent ND measurements.

Chapter 5: This Chapter is devoted to the studies on modifications in magnetism and transport behavior of $NdMn_{1-x}Zn_xO_3$/SNTO thin films. This chapter elucidates the effect of B-site size disorder on the lattice strain, which results in the modifications in microstrostructure, electrical transport and magnetic properties of Zn-doped $NdMnO_3$ films.

Chapter 6: This Chapter presents the results of the studies on the effect of Swift Heavy Ion (SHI) irradiation on the modifications in the properties of Zn-doped NMO thin films. The effect of ion irradiation as a tool to induce defects, by varying ion fluences, results into the modifications in the structural, microstructural and transport properties of thin films under study. At the end, the possible scope for future studies in this field of research has been discussed.

References:

[1] I. A. Abdel-Latif, Journal of Physics Vol. 1 No. 3, 15-31 (2012)

[2] A.A. Mukhin, V.Yu. Ivanov, V.D. Travkin, A.S. Prokhorov, A.M. Balbashov, J. Hemberger, A. Loidl, J. Magn. Magn. Mater., 272-276, 96–97 (2004)

[3] Daniel Khomskii, Physics 2, 20 (2009)

[4] S.K. Kamilla and S. Basu, Bull. Mater. Sci., Vol. 25, No. 6, 541-543 (2002)

[5] J. M. D. Coey, M. Viret, Advances in Physics, Vol. 48, No. 2, 167 – 293 (1999)

[6] T. Kimura, S. Ishihara, H. Shintani, T. Arima, K.T. Takahashi, K. Ishizaka and Y. Tokura, Phys. Rev. B 68, 060403 (2003)

[7] T. Chatterji, B. Ouladdiaf and D. Bhattacharya, J. Phys.: Condens. Matter 21, 306001 (2009)

[8] Parthasarathi Mondal, Dipten Bhattacharya, Pranab Choudhury, and Prabhat Manda, Physical Review B, 76 172403 (2007)

[9] M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S.-W. Cheong, O. P. Vajk and J.W. Lynn, PRL, 95 087206 (2005)

[10] J. M. D. Coey, M. Viret and S. von Molnar, Mixed-valence manganites, Adv. Phys., 48, 167 (1999)

[11] Lev P. Gorkova,b, Vladimir Z. Kresin, Mixed-valence manganites: fundamentals and main properties, Phys. Rep., 400, 149(2004)

[12] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, L.H. Chen, Thousand fold change in resistivity in magnetoresistive La–Ca–Mn–O films, Science, 264, 413 (1994)

[13] V. Caignaert, A. Maignan, B. Raveau, Up to 50 000 per cent Resistance Variation in Magnetoresistive Polycrystalline Perovskites $Ln_{2/3}Sr_{1/3}Mn0_3$ (Ln = Nd ; Sm), Solid State Commun., 95 357 ,(1995)

[14] P.G. de Gennes, Effects of double exchange in magnetic crystals, Phys. Rev., 118, 141 (1960)

[15] M.R. Ibarra, P.A. Algarabel, C. Marquina, J. Blasco, J. Garcia, Large Magnetovolume Effect in Yttrium Doped La-Ca-Mn-0 perovskite, Phys. Rev. Lett., 75, 3541 (1995)

[16] Malay Udeshi, Brinda Vyas, Priyanka Trivedi, Savan Katba, Ashish Ravaiia, P.S. Solanki, N.A. Shah, K. Asokan, S. Ojha, D.G. Kuberkar, Nuclear Instruments and Methods in Physics Research B 365, 560–563 (2015)