Multiferroic properties of Mn doped $La_{0.8}Bi_{0.2}FeO_3$ system and effect of SHI irradiation

THESIS ABSTRACT

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Abstract

Multiferroics, defined for those multifunctional materials in which two or more kinds of fundamental ferroicities (ferroelectricity, ferromagnetism, antiferromagnetism and/or ferroelasticity) coexist, have become one of the hottest topics of condensed matter physics and materials science in recent years. This thesis describes the research work performed by me in last few years as a Ph.D research scholar. Magnetic and ferroelectric materials pervade almost every aspect of contemporary science and technology. Although ferroelectricity and magnetism have been the focus of condensed matter physics/material science since their discovery, quite a number of challenges have emerged in dealing with multiferroicity within the framework of fundamental physics and technological applications. Nevertheless, simple approaches do allow ferroelectricity and magnetism in one system, but may not necessarily offer strong magneto-electric coupling, partially because the microscopic mechanisms responsible for ferroelectricity ($d^0$ orbitals) and magnetism (partially filled d orbitals) are physically very different. There are, in principle, two basic issues to address in order to make multiferroicity physically understandable. The first is the coexistence of electric dipole order and spin order in one system. The second is an efficient magneto-capacitive coupling between the two orders in a multiferroic system which seems to be even more important than their coexistence. This is because such a magneto-electric coupling represents the basis for multi-control of the two orders by either an electric field or a magnetic field. Investigations have demonstrated that a realization of such strong coupling is even more challenging and thus, the core of recent multiferroic researches.

However, these types of material are very few in nature or synthesized in laboratory. Syntheses of such type of materials mostly lead to a mixture of the main phase along with other impurity phases which is another demanding assignment. It should be mentioned here that most multiferroics synthesized so far are transition metal oxides (TMO) based with perovskite structures. They are typically strongly correlated electronic systems in which the correlations among spins, charges/dipoles, orbitals and lattice/phonons are significant. Therefore, intrinsic integration and strong coupling between ferroelectricity and magnetism are essentially related to the multi-latitude landscape of interactions between these orders, thus making the physics of multiferroicity extremely complicated. Nevertheless,
it is also clear that multiferroicity provides a more extensive platform to explore the novel physics of strongly correlated electronic systems. It now offers us the opportunity to explore some important issues which have rarely been reachable. Multiferroics are likely to offer a whole range of new applications and phenomena. The ability to couple the electric polarization with the magnetization allows an additional degree of freedom in device design. Other applications include multiple-state memory elements, in which data are stored both in the electric and magnetic polarizations, and novel memory media, which might allow the writing of a ferroelectric (FE) data bit and reading of the magnetic field generated by association. Motivated from the above mentioned facts, we have tried to achieve a single phase multiferroic system by solid state reaction method without any pressure. This thesis topic includes the development of new multiferroic system. For that, we have introduced the compositional disorder which becomes obliging in achieving improved dielectric, magnetic, and magneto-electric properties. In order to implement this idea, we choose LaFeO$_3$ which is a rare earth TMO having orthorhombic perovskite structure with space group (sp.gp) $Pnma$. This compound is antiferromagnetic (AF) in nature with $T_N \sim 750$ K. The steadiness of the perovskite structure $A^{3+}FeO_3$ (where A is a rare earth element) depends on the tolerance factor ‘$t$’. In LaFeO$_3$, $t$ is less than 1. Therefore, the cubic structure transforms into the orthorhombic one and pilots to the deviation of Fe–O–Fe bond angle from 180$^\circ$. This divergence in Fe–O–Fe bonds further leads to a distortion in FeO$_6$ octahedra. Consequently, properties can be altered/modified precisely by the choice of suitable doping element at La$^{3+}$ and Fe$^{3+}$ site, respectively.

In the present study, we have substituted Mn at Fe site in LaFeO$_3$ with Bi being in fixed proportion at La site i.e., La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (LBFMO, 0.0 ≤ $x$ ≤ 0.4). 20% Bi at La site is substituted in order to introduce lone pair of electrons responsible for FE and to get single phase samples. For any technological application, thin films with good electrical and magnetic properties are desired. Therefore, the fabrication of thin films for oxides holds the final key to any of its properties. Main obstacle in integrating thin-film devices and in the growth of multiferroic thin films is to grow high-quality films with proper base electrodes that satisfies requirements not only as an electrode but also as an intermediate layer between the multiferroic thin films and the substrate. The specific characteristics of LaNiO$_3$ (LNO) like its conductivity and Pauli paramagnetic nature down to very low temperature favor its integration as electrode with other functional oxides and a variety of perovskite-based multiferroic films. The thin film growth of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ (LBFMO3) and LNO
is being carried out using radio frequency (RF) sputtering technique and the optimization of the growth parameters has been done prior to its growth. We have also studied the effect of swift heavy ion (SHI) irradiation in these materials in thin film form with the suitable substrate and appropriate buffer layer. The changes due to the irradiation induced local strain and disorder in the lattice of the samples have been studied using different characterization techniques. The present thesis contains the synthesis and characterization of LBFMO (0.0 \leq x \leq 0.4) single phase multiferroic system. Then structural, dielectric, magnetic, electronic structure, surface morphology and magneto-electric properties of the samples in bulk and thin film form are studied. Theoretical analyses are also carried out in order to corroborate the results from the simulations. All of the above mentioned characterizations were also done after performing SHI irradiation of LBFMO3 films deposited on LaAlO$_3$ (LAO, 100) substrate with LNO (100) buffer layer. The thesis is divided into eight parts, which can be read independently. Each of them is covered in a single chapter. A large number of references are quoted throughout. All of them are listed at the end of each chapter.

Structural studies using **X-ray diffraction** (XRD) of the samples were performed using Bruker X-ray diffractometer to confirm the single-phase formation of LBFMO (0.0 \leq x \leq 0.4) samples. Data were taken in 2θ range of 20° - 80° for bulk samples and 20° - 60° in case of thin films of LBFMO3 with LNO as buffer layer and LAO substrate. The XRD data of all the samples were analyzed using POWDERX and Rietveld refinement FULLPROF code. We limit our discussion only up to x = 0.4 composition since impurity phase starts occurring at this level. It is evident from the XRD analysis that there is no change in structural symmetry (orthorhombic) and sp.g.p (Pnma) with Mn substitution at Fe site and Bi at La site in base system LaFeO$_3$ except the changes in lattice parameters and reduction in unit cell volume. Single phase (101) oriented thin film of LBFMO3/LNO/LAO has been synthesized using RF sputtering technique. XRD data results of LBFMO3/LNO/LAO thin film confirm the (101) oriented growth with no traces of impurity. Thin films of LBFMO3/LNO/LAO have been irradiated using Ag$^{15+}$ SHI beam of 200 MeV with the fluence values of 5x10$^{11}$ and 5x10$^{12}$ ions/cm$^2$. The unit cell parameters are found to increase with SHI compared to that of unirradiated thin films.

Electronic structure studies using **X-ray absorption spectroscopy** (XAS) provides the fundamental basis for understanding the electronic structure. Near edge X-ray absorption fine structure (NEXAFS) study has been performed to know the local environment, exact valence state, symmetry and crystal field splitting of the ions present in
LBFMO \((0.0 \leq x \leq 0.4)\) system. NEXAFS spectra of \(\text{O K-}, \text{Mn L}_{3,2-}, \text{Mn K-}, \text{Fe L}_{3,2-}\) and \(\text{La M}_{4,5-}\) edges along with the spectra of reference compounds at room temperature had been taken at the beam line 7B1 XAS KIST of the Pohang Light Source (PLS), Korea. It was found that Mn ions in samples are present in mixed valence states. Mn ions are mainly in +3 states along with a small admixture of +2 and +4 state. Though, Fe ion remains in the +3 state for all doping values, \(\text{M}_{3,5-}\) edges spectra of La confirm the +3 state of La ions in the system. Atomic multiplet calculations on \(\text{Fe L}_{3,2-}, \text{Mn L}_{3,2-}\) and \(\text{LaM}_{4,5-}\) edges further substantiate these valence specific arrangements of the respective ions in the LBFMO \((0.0 \leq x \leq 0.4)\) samples. In LBFMO3/LNO/LAO thin film electronic structure studies reveal almost identical results to that of the bulk LBFMO3 sample with only increase in hybridization of Bi \(6s^2\) lone pair of electrons as is exhibited from \(\text{O K-edge}\) demonstrating the better ferroelectricity than the bulk. Valence state of Mn and Fe ions are also found to be in accordance with the magnetization data of thin film. After SHI irradiation, the NEXAFS observation of LBFMO3/LNO/LAO thin films at \(\text{Mn L}_{3,2-}\) edge illustrates the evolution of \(\text{Mn}^{2+}\) in a network of \(\text{Mn}^{3+}/\text{Mn}^{4+}\) with fluence value of \(5 \times 10^{12}\) ions/cm\(^2\). \(\text{Fe L}_{3,2-}\) edge gives the signature of distortion in \(\text{FeO}_6\) octahedra.

Surface studies using the **field emission scanning electron microscopy** (FESEM) has been performed for LBFMO \((0.0 \leq x \leq 0.4)\) bulk samples to probe the surfaces and micro structural characterization at a scale of 10\(\mu\)m. Results suggest an overall increase in grain size along with two different types of distribution of grains. As the Mn content is increased, number of larger grains (average grain size \(\sim 5.75\ \mu\)m) increases at the expense of smaller particles (average grain size \(\sim 1.50\ \mu\)m). **Atomic force microscopy** (AFM) studies have been performed for finding the surface topology of LBFMO3/LNO/LAO thin film and the results propose the presence of strain in them. After SHI irradiation of LBFMO3/LNO/LAO thin film at different fluence values \((5 \times 10^{11} \text{ and } 5 \times 10^{12} \text{ ions/cm}^2)\), the AFM results are observed to be in harmony with XRD results and show an increase in root mean square (rms) surface roughness value with irradiation amid the increase in grain size.

**Transport studies** using the frequency \((75 \text{ kHz} \text{ – } 4 \text{ MHz})\) and temperature \((200 \text{ – } 475 \text{ K})\) dependent dielectric measurement had been preformed with Agilent 4285A precision LCR meter. Room temperature dielectric constant for LBFMO \((0.0 \leq x \leq 0.4)\) bulk samples have been found to increase with the increase in Mn concentration. At higher frequencies (above 500 kHz), these exhibit frequency independent behavior up to \(x=0.3\) concentration. Frequency responses of these LBFMO \((0.0 \leq x \leq 0.4)\) multiferroic bulk
samples have been analyzed carefully, in the light of “universal dielectric response” (UDR) model. Results suggest that it is in good agreement with UDR in low frequency region (< 500 kHz) while in high frequency region this is not the case which authenticate that dielectric property is due to weak ferroelectric nature of these samples in high frequency region (> 500 kHz).

**Capacitance vs voltage (C-V)** measurement performed at room temperature with applied frequency of 100 kHz and voltage varying in the range of –20 to +20 volts for bulk samples and -5 to +5 volts in thin film form further establishes this fact. In LBFMO3/LNO/LAO thin film although the value of \( \varepsilon' \) is small with respect to bulk, it is quite appreciable as far as properties are concerned in thin film form. A notable feature is that the lower value of \( \tan\delta \) is conducive for the practical applications using the film. The asymmetric (different values) C vs V loop of capacitance on the two sides of curve may be due to the difference in electrode effect. The two surfaces of the films have two different electrodes, silver on the top and LNO at the bottom. LBFMO3/LNO/LAO thin films irradiated with 200 MeV Ag\(^{15+}\) ions at different fluences (5 \( \times 10^{11} \) and 5 \( \times 10^{12} \) ions/cm\(^2\)) exhibit improvement in the ferroelectric properties with enhanced \( \varepsilon' \) and decreased \( \tan\delta \) compared to the unirradiated thin film.

**Temperature and magnetic field dependent magnetization** for LBFMO (0.0 \( \leq x \leq 0.4 \)) samples have been measured in the temperature range of (5 - 320 K) with physical properties measurement system (PPMS). It demonstrates the favorable effect of Mn substitution with enhanced magnetization. Magnetic behavior of these samples has been briefly discussed on the basis of “Exchange bias” (EB) model for granular systems and it illustrates the presence of EB in the samples. Magnetic measurement for LBFMO3/LNO/LAO thin film has been carried out using commercial Quantum Design MPMS XL superconducting quantum interference device (SQUID) magnetometer. Magnetization of LBFMO3/LNO/LAO films exhibit ferrimagnetic nature along with unsaturated behavior even up to 1 tesla. Magnetization data exhibit ferrimagnetic nature along with unsaturated behavior even up to 1 tesla. Irradiation induces EB phenomena in LBFMO3/LNO/LAO thin film which is not present prior to SHI irradiation.

**X-ray magnetic circular dichroism (XMCD)** study has been done for unirradiated LBFMO3/LNO/LAO thin film and films irradiated at different fluences (5 \( \times 10^{11} \) and 5 \( \times 10^{12} \) ions/cm\(^2\)). XMCD data further show considerable contribution to magnetization from Mn ions in irradiated thin films after irradiation at dose value of 5 \( \times 10^{12} \) ions/cm\(^2\) with
minimal contribution from Fe ions which are in concurrence with electronic structure results. Overall, one may conclude that these studies present noteworthy outcomes and observations in the field of research in multiferroic materials from both aspects i.e. fundamental physics as well as for application view point.

**Thesis on multiferroic properties of Mn doped La$_{0.8}$Bi$_{0.2}$FeO$_3$ system and effect of SHI irradiation is divided as follows:**

1. **Chapter 1** puts forward the basic understanding and history of multiferroic materials along with their applications.

2. **Chapter 2** envelops the indispensable explanation of experimental techniques used for the structural, electrical, electronic, surface and magnetic properties of the La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4) samples along with an overview about the SHI irradiation such as its production and applications.

3. **Chapter 3** deals with the theoretical approach of various models for simulation used in fitting and finding the approximate values.

4. **Chapter 4** gives the details of structural, dielectric, magnetic and surface properties of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4) bulk samples prepared by the solid-state reaction technique.

5. **Chapter 5** provides an insight on the magneto- capacitive coupling and electronic structure studies of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ (0.0 ≤ x ≤ 0.4) multiferroic system.

6. **Chapter 6** includes the thin film deposition using RF sputtering and all the characterizations done as in case of bulk samples discussed in Chapter 4 and 5.

7. **Chapter 7** comprises of the irradiation studies on the La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ thin films using Ag$^{15+}$ ions. This chapter also includes the comparative studies on unirradiated and irradiated films.

8. **Chapter 8** presents an overview of results concluded from all previous chapters and scope of future work on the studied materials.

The thesis ends with my list of publications in internationally reputed journals and papers presented in different national/international conferences along with attended workshops/schools.
Publication in peer reviewed journals

1. NEXAFS Studies of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ ($0.0 \leq x \leq 0.4$) Multiferroic System using X-ray Absorption Spectroscopy; G. Anjum, R. Kumar, S. Mollah, P. Thakur, S. Gautam and K. H. Chae, J. Phys. D: Appl. Phys. 44 075403 (2011).

2. Enhanced Ferromagnetic Insulating State in La$_{0.85}$Ca$_{0.15}$Mn$_{1-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.1$); S. Mollah, G. Anjum, Z. Zainab, Alamgir and R. A. Jawafi, accepted for publication in AIP proceeding (2011).

3. Structural, Dielectric and Magnetic Properties of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ ($0 \leq x \leq 0.4$) Multiferroics; G. Anjum, R. Kumar, S. Mollah, D. K. Shukla, S. Kumar and C. G Lee, J. Appl. Phys. 107 103916 (2010).

4. Magneto-electric Coupling in Multiferroic La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ Ceramic; G. Anjum, S. Mollah, D. K. Shukla and R. Kumar, Mater. Lett. 64 2003 (2010).

5. Conductivity of Ca$_{1-x}$Na$_x$MnO$_3$ ($0 \leq x \leq 0.3$) Perovskite; S. Mollah and G. Anjum, Integrated Ferroelectrics 119 33 (2010).


7. Transport and Magnetic Properties of La$_{0.85}$Ca$_{0.15}$Mn$_{1-x}$Al$_x$O$_3$ Manganites; G. Anjum and S. Mollah, Asian Journal of Chemistry. 21 S086-090 (2009).

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9. Effect of Doping on the Properties of Ferromagnetic Insulating La$_{0.85}$Ca$_{0.15}$Mn$_{1-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.1$) Perovskites; S. Mollah, D. K. Shukla, G. Anjum, S. M. Amir, A. Das and R. Kumar, Matel Materials and Processes 20 229 (2008).

10. Growth and Characterization of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ Multiferroic Thin Film on LaNiO$_3$ Buffer Layer; G. Anjum, Ravi Kumar, S. Mollah, S. K. Sharma and M Knobel, submitted to Mater. Lett. (2011).

11. Swift Heavy Ion Irradiation Modified Multiferroic Properties of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$/LaNiO$_3$ Thin Film with LaAlO$_3$ Substrate; G. Anjum, R. Kumar and S. Mollah, submitted to J. Appl. Phys. (2011).

12. NEXAFS and XMCD Studies of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ Multiferroic Thin Film and Effect of Swift Heavy Ion Irradiation; G. Anjum, P. Thakur, Ravi Kumar, N. B. Brookes and S. Mollah, submitted to Appl. Phys. lett. (2011).

**International/National Conferences and Workshops**

1. Structural and Dielectric Properties of BiFe$_{0.7}$Mn$_{0.3}$O$_3$; G. Anjum, D. K. Shukla, S. Mollah and R. Kumar, 52$^{nd}$ Solid. State. Physics, DAE-SSPS University of Mysore, Mysore Dec. 27-31 (2007).


4. Magnetoelectric Multiferroic La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$ Ceramic; G. Anjum, S.Mollah, D. K. Shukla, Ravi Kumar, International Conference on Multifuntional Oxide Materials (ICMOM), H. P. University, Shimla April. 16 – 18 (2009).

5. Multiferroic Materials: La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ System; G. Anjum National Workshop on Oxide Materials, Aligarh Muslim University, Aligarh May 12- 13 (2009).

6. Electronic Structure Studies of La$_{0.8}$Bi$_{0.2}$Fe$_{1-x}$Mn$_x$O$_3$ ( 0.0 ≤ x ≤ 0.4 ) Multiferroic; G. Anjum, R. Kumar, S. Mollah, P. Thakur, S. Gautam and W. K. Choi, International Conference on Electroceramics (ICE), University of Delhi, New Delhi Dec 13- 17 (2009).

7. National Seminar on Frontiers of Condensed Matter Physics; Aligarh Muslim University, Aligarh March 27 (2010).

8. School on Nano science and Nanotechnology (NANO-2010); National Institute of Technology, Hamirpur May 31- June 4 (2010).

9. AONSO School on Neutron Scattering; Bhaba Atomic Research Centre, Mumbai Oct 4 - 9 (2010).

10. Characterization of La$_{0.8}$Bi$_{0.2}$Fe$_{0.7}$Mn$_{0.3}$O$_3$/LaNiO$_3$ Multiferroic; G. Anjum, R. Kumar, S. Mollah, International Conference on Magnetic Materials (ICMM), Saha Institute Nuclear Physics, Kolkata Oct 25 -29 (2010).

11. 5$^{th}$ DST School on Nanoscience and Nanotechnology; Indian Institute of Science, Bangalore Jan 17 -23 (2011).

13. Workshop on Nanoscience and Nanotechnology; Aligarh NANO-1, Aligarh Muslim University, Aligarh March 26 – 27 (2011).

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