Chapter 3

Multiferroic BiMn$_2$O$_5$: An insight

3.1 Introduction

The multiferroic series RMn$_2$O$_5$ ($R^{3+}$ Mn$^{3+}$ Mn$^{4+}$ O$_5^2$; where R is rare-earth, Y or Bi), a family of materials which order antiferromagnetically followed by a ferroelectric transition around $\sim$ 40 K, has created a lot of interest in recent years [7, 11, 52, 64, 95-107, 115, 132]. In these materials the ferroelectric transition occurs at a lower temperature compared to the magnetic transition, which is unusual. This can be visualized by the generation of electrical polarization with the application of an external magnetic field. At this juncture, it is interesting to investigate the origin of ferroelectric polarization in these materials. Now the question is, whether the polarization may arise or not spontaneously due to the presence of
internal magnetic fields by certain magnetic ordering inside the material? In this sequence, acentric spin density waves, which are the most probable magnetic structure for this class of materials, have been reported to be responsible for the ferroelectricity in these systems [100]. Further, in general, the magnetic twist for ferroelectricity has now been classified depending upon their ground state spiral magnetic structure and interactions [8, 11]. Some efforts have also been made to solve this puzzle using structural anomalies during transitions [96, 101]. In order to make clear understanding about these transitions, one must have exact information regarding their electronic structures, explicitly responsible for all sorts of properties.

The detailed structure and unit cell parameters of single crystals of RMn$_2$O$_5$ was investigated by Quezel-Ambrunaz et al [53] and Bertaut et al [54]. At room temperature, these systems show mixed valence Mn-sites (Mn$^{3+}$/Mn$^{4+}$), having orthorhombic symmetry described by the space group $Pbma$ (No. 55) and $Z = 4$. Figure 3.1 shows a unit cell structure of pure BiMn$_2$O$_5$, which have four different oxygen sites (O1, O2, O3 and O4). In unit cell, Bi$^{3+}$ and O2 are coordinated at 4g ($x,y,0$); Mn$^{4+}$ at 4f ($0, \frac{1}{2}, z$); Mn$^{3+}$ and O3 at 4h ($x,y, \frac{1}{2}$); O1 at 4e (0,0,z) and O4 at 8i ($x,y,z$). Since the manganese ions occupy two sites with different oxidation states of +3 and +4, the Mn$^{4+}$ ($t_{2g}^3e_g^0$, $S=3/2$) ions located at 4f site are octahedrally coordinated to oxygen (in cyan). These Mn$^{4+}$O$_6$ octahedra share edges via O2 and O3 to form infinite chains along the c axis. The Mn$^{3+}$ ($t_{2g}^3e_g^1$, $S = 2$) ions positioned at 4h site are coordinated to five oxygens present at the apex of a distorted tetragonal pyramid (in red). Mn$^{3+}$O$_5$ pyramids interconnect to the Mn$^{4+}$O$_6$ octahedra along the c axis via O3 and O4. The larger R$^{3+}$ ions (in green) surrounded by eight oxygen atoms form RO$_8$ units. In this polyhedron, the measured values of two nearest Bi-O4 distances (obtained from Rietveld refinement) i.e. 2.37 Å and 2.77 Å, are in agreement with earlier report [64] but sensibly different from the other members of R. For example, La-O4 bond lengths are 2.49 Å and 2.56 Å as testified by others [98]. The BiO$_8$ polyhedral units in Fig. 3.1 are slightly more distorted than other RO$_8$ units in RMn$_2$O$_5$ due to the influence of Bi lone pair electrons and is consistent with earlier report by Prellier et al [20]. In orthorhombic RMn$_2$O$_5$, the spins
of the Mn$^{4+}$ and Mn$^{3+}$ ions and R$^{3+}$ are coupled together via the predominantly AFM super-exchange (SE) interactions giving rise to a complex magnetic phase diagram [102].

Fig. 3.1: Schematic crystal structure of BiMn$_2$O$_5$ and magnetic structure in $ab$ plane along the $c$ axis.

The common features for all RMn$_2$O$_5$ are having a transition to a high-temperature Neel phase with two component incommensurate (IC) magnetic modulation characterized by a wave vector $\vec{q} = (q_x, 0, q_z)$ at $T_{N1} \approx 39$ K and followed by a lock-in transition into a commensurate (CM) phase with $\vec{q} = (0.5, 0, 0.25)$ at $T_{C1}$. Another transition at $T_{C2}$ (lower than $T_{C1}$) [107] is accompanied by a change in the polarization and is often referred to as a second FE transition (not observed in BiMn$_2$O$_5$). Variation in transition temperatures due to lattice in connection with the size of R (for Sm, Dy and Y) has been studied by Tachibana et al [95]. They have concluded that transition temperatures increase monotonically with the decreasing size of R. In some rare earth compounds (e.g., HoMn$_2$O$_5$, DyMn$_2$O$_5$), additional magnetic anomalies have been observed, which are yet to be explored [105, 106].
This thesis is all about BiMn$_2$O$_5$ multiferroic; more precisely the effect of Ti substitution as well as effect of swift heavy ion (SHI) irradiation have been studied. This Chapter is aimed to provide detailed insight information on BiMn$_2$O$_5$ multiferroic only, before proceeding to next chapters, where the effect of Ti substitution and SHI irradiation are discussed. Structural, magnetic, dielectric and heat capacity data of BiMn$_2$O$_5$ presented in this chapter are in good agreement with the previously reported data. In order to understand the origin of multiferroicity in orthorhombic BiMn$_2$O$_5$, it is essential to investigate the electronic structure including the valence states of functioning ions. In principle, these investigations are possible by employing the soft x-ray absorption spectroscopy (XAS). There is no experimental report on the electronic structure of RMn$_2$O$_5$ family of materials, possibly due to difficulties arising in the electron spectroscopy studies as these systems are good insulators. Along with confirmation of multiferroic anomalies, data on the O 1s XAS, and Mn 2p XAS of polycrystalline BiMn$_2$O$_5$ samples at room temperature are presented. Mn 2p XAS spectra has been compared to those of reference materials having different formal valences of Mn in the compounds MnO, MnO$_2$ and KMnO$_4$. All the possible hybridization of O 2p and Mn 3d orbital incorporated with the participation of Bi 6s and 6p orbital is presented.

3.2 Results and discussion

Figure 3.2 (a) represents the Reitveld refinement x-ray pattern for BiMn$_2$O$_5$, the parameters extracted from this analysis [structure Orthorhombic, s. g. Pbam, $a = 7.5642$ Å, $b = 8.53055$ Å, $c = 5.7895$ Å, volume = 371.22433 Å$^3$, $\chi^2$=1.6] are in agreement to the reported results [13 JAP]. The site symmetry analysis [108] of the Pbam structure of BiMn$_2$O$_5$ yields a total 96 $\Gamma$-point phonon modes, out of these 48 phonon modes are Raman-active ($\Gamma_{\text{Raman}} = 13A_g + 13B_{1g} + 11B_{2g} + 11B_{1g}$). Figure 3.2 (b) shows the unpolarized Raman spectra for BiMn$_2$O$_5$. All the 19 Raman peaks were identified at 185, 195, 200, 235, 245, 280, 300, 325, 345, 360, 405, 445, 480, 510, 545, 565, 595, 610 and 655 cm$^{-1}$ for the spectra collected between 100 to 800 cm$^{-1}$. These Raman modes are in agreement to the earlier report by Garcia Flores et al [96] for BiMn$_2$O$_5$ and correspond to single phase character.
Fig. 3.2: (a) Reitveld profile analysis for BiMn$_2$O$_5$. (b) Room temperature Raman spectrum of BiMn$_2$O$_5$. 
Fig. 3.3: (a) Temperature vs. dc susceptibility ($\chi$) and its reciprocal measured under 0.5 kOe, in ZFC and FC conditions (Inset shows isothermal dc magnetization curve at $T = 5$ K) (b) Temperature vs. dielectric constant at fix frequency of 100 kHz and (c) Variation of specific ($C$) heat with temperature at 0, 9 and 14 T magnetic fields.
Fig. 3.3 (a), 3.3 (b) and 3.3 (c) represent the characteristic phase transitions namely antiferromagnetic, ferroelectric and specific heat anomaly corresponding to the magnetic/ferroelectric transitions respectively. Isothermal magnetization curve in inset of Fig. 3.3 (a) confirms presence of antiferromagnetism at 5 K. Further specific heat data has no variation even with the application of 14 T magnetic field (Fig. 3.3 (c)), due to the strongly correlated electron behaviour of this system. The low temperature specific heat (LTSH) data has been fitted (not shown here, discussed in detail in Chapter 5) by the expression

\[ C = \gamma T + \beta T^3 + BT^\delta \]  

(3.1)

The linear term is associated with the charge - carrier contribution; the \( \beta T^3 \) term corresponds to the lattice contribution and the last term \( BT^\delta \) (\( \delta = 3/2 \) for ferromagnetic contribution and 2 for 2D antiferromagnetic) is related to the spin-wave excitations. First the data were tried to fit using all three terms in Eq. (3.1) resulting in negative value of parameters. By considering the data from 2 K to 16 K, the best fit is obtained if the linear term is neglected and \( \delta = 2 \). The fitted parameters for lattice contribution, \( \beta \) (0.0012 J/mol K\(^4\)) and magnon contribution, \( B \) (0.0049 J/mol K\(^3\)) well matches with the data by Munoz et al [64]. The Debye temperature \( \Theta_D \) (~ 235 K) is calculated from \( \beta \) through the expression \( \Theta_D = (12\pi^4 nR / 5\beta) \), \( R \) being the gas constant and \( n \) the number of atoms per formula unit.

An active role of the orbital degrees of freedom in the lattice and electronic response can be most typically observed in manganese perovskite oxides. As a matter of fact, such properties appear to have their origin in the unique electronic structure derived from the hybridized Mn 3d and O 2p orbitals in the particular structural and chemical environment of a perovskite. Therefore, the resulting intra-atomic exchanges and the orbital degrees of freedom of Mn 3d electrons play essential roles in this constellation. XAS spectra were assessed at the Mn L-edges and O K-edges for BiMnO\(_3\) samples. The former directly proves the unoccupied Mn 3d states via Mn 3d → 2p transitions. Nevertheless, the later establishes the unoccupied O 2p states via O 1s → 2p dipolar transitions to provide information on the Mn 3d occupancy on the hybridization between the O 2p and Mn 3d orbitals.
Mn 2p (L3,2 -edge) NEXAFS spectra of BiMn2O5 and comparison to the reference compounds KMnO4 (Mn 7+) , MnO2 (Mn 4+) and MnO (Mn 2+) having different formal valences are shown in Fig. 3. It is well known that peak position and line shape of Mn 2p NEXAFS spectra depend upon the local electronic structure of the Mn ion, so that the Mn 2p XAS spectra provides information about the valence state of the Mn ion [109]. The spin orbit interaction of the Mn 2p core states splits the spectrum into two broad multiplet, namely L3 (2p3/2) and L2 (2p1/2) are ~ 11 eV apart. Each of these two regions further split into t2g and e_g orbital features because of crystal field effect of ligand ions. The spectral shape in case of transition metal ions changes drastically with either the strength of the crystal field or the relative magnitudes of the exchange and 3d spin-orbit interactions [110, 111]. These observations show that peak position shifts towards the higher energy as the valence state of the Mn ions increase in the respective reference compounds. In MnO2, Mn ions have 4+ oxidation state with all the e_g subbands empty, so the intensity due to e_g subbands is more than the t2g subbands. However, in MnO, Mn (2+) ions having 3 t2g subbands and 2 e_g subbands empty, so due to more unoccupancies in t2g, the peaks due to it are much more intense. Similar is the case in BiMn2O5 where e_g subbands are more unoccupied than the t2g subbands. BiMn2O5 spectra looks almost similar to the MnO2 (4+) with an admixture of Mn 3+, arising from the fact that they both are having the same geometrical structure around Mn ion. For MnO3, the L3 edge peaks are ~ 1.5 eV lower than the (from Ref.112) that of MnO2 L3 edge peaks. This is because of the difference in 3d spin-orbit interaction in MnO3 and MnO2. For Mn L3 and L2 edge separation is ~ 1 eV more in case of BiMn2O5 than that of MnO2 due to the presence of Mn3+. Further, the ligand environment decides the crystal field splitting (10Dq) and the characteristic crystal field splitting effect is clearly seen at Mn L3 edge of BiMn2O5, which is narrow in comparison to MnO2 L3 edge. This narrowing can be attributed to Mn3+ ions in BiMn2O5, which are in pyramidal geometry with oxygen ions, where the four oxygens are in-plane and one oxygen is in apical arrangement that has less crystal field splitting than the Mn4+ octahedral geometry. Therefore, for Mn, on the basis of the comparison with the spectra of the manganese oxides, the spectral shape which looks more closer to MnO2 in shape has dominant Mn3+ feature in spin-orbit interaction and crystal field splitting. Although
multiplet structure makes the spectra quite complicated, this imbalance of the spectral weight at different energies can be used, in principle, to disentangle the contribution of the two manganese sites by comparing with multiplet calculations. This would give a deeper understanding of the magnetic properties of manganese at two sites, for example, the antiferromagnetic coupling in this compound below 39 K. It is to be pointed out that the above mentioned approach is quite delicate and will improve the understanding of the knowledge of the local symmetries at the two sites. The overall spectral shape can be attributed to the high degree of covalency of the Mn (+4) - O bond.

Fig. 3.4: Comparison of normalized Mn L edge XAS spectra of BiMn$_2$O$_5$ to those of KMnO$_4$, MnO$_2$, and MnO.
Figure 3.5 shows the O K-edge spectra along with the entire reference compounds. They exhibit the considerable difference even in case of MnO$_2$ and BiMn$_2$O$_5$, in contrast to their Mn L-edge spectra, which reflects the difference in the electronic structure of these two compounds. It arises from the fact that lifetime broadening in the oxygen 1s core-hole potential is considerably smaller than the Mn 2p core-hole state. Oxygen 1s XAS spectra represents the transitions from the oxygen 1s state to the unoccupied O 2p state which are hybridized with the other orbitals of Mn atom as well as of Bi atom, participating in all type crystal field splitting responsible for the non-degenerate states. So it provides the reasonable estimate of the unoccupied conduction bands [113]. Within this framework, in O K edge spectra of BiMn$_2$O$_5$, four main features are leveled as A, B, C and D in the energy range from 528 to 545 eV. Peaks A and B are attributed to the O 2p – Mn 3d hybridization. The O 2p derived states lie predominantly in the valance band and the presence of O 2p derived states in the conduction band is due to coupling with cation orbitals. Peak A at 528.5 eV is related to the hybridization between O 2p-Mn t$_{2g}$ and B is due to the hybridization between O 2p-Mn e$_g$ orbitals. Peak C and D are identified due to the as hybridization between O 2p – Bi 6s and O 2p- (Bi 6p + Mn 4sp) respectively. Peak D is broader than others showing unoccupancies is not in specified subbands, from here the oxygen p symmetry primarily arising due to hybridization with various neighbouring atoms can be probed by the dipole selection rule during the transition of electron from 1s state to the 2p state. The actual assignment of Mn 3d orbitals is still a matter of controversy in mixed valance state. The peak A may be an admixture of t$_{2g}$ and e$_g$, whereas the peak B is only due to e$_g$. Intensity of B is greater than A, thus indicating that the e$_g$ states are more unoccupied. The properties of peak C at 533 eV depends upon the behaviour of highly polarizable 6s$^2$ lone pair of Bi$^{3+}$ ion. The hybridization of Bi-6s orbital with the oxygen 2p orbital can produce a local distortion which avoids the inter network transfer of e$_g$ electrons from one network of Mn-O-Mn to another Mn-O-Mn network, which results the room temperature insulator property in BiMn$_2$O$_5$. However, the inter network SE interactions become active at low temperature and gives the antiferromagnetic ordering at low temperature.
Fig. 3.5: Comparison of normalized oxygen K edge XAS spectra of BiMn$_2$O$_5$ to those of MnO$_2$, MnO and Bi$_2$O$_3$. 

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3.3 Conclusions

In conclusion, single phase polycrystalline BiMn$_2$O$_5$ shows antiferromagnetic transition at temperature around $T_N \sim 39$ K and ferroelectric transition at temperature around $T_C \sim 35$ K, well matched with its single crystal data available in literatures. Anomaly observed in heat capacity measurements clearly represents the temperature dependent transitions arising due to ordering of Mn ions. Mn L$_{3,2}$ as well as O K edge XAS data show that $e_g$ states are more unoccupied than the $t_{2g}$ states in Mn ion. Spectral shape of Mn L edge in BiMn$_2$O$_5$ shows similar outline as of MnO$_2$ (Mn$^{4+}$) with an admixture of Mn$^{3+}$, whereas the Mn$^{3+}$ presence is dominated in spin orbit interaction and crystal field splitting (10Dq).