# *Chapter 5 Room temperature large exchange bias in hard-soft antiferromagnetic composite BiFeO3-TbMnO3*

## **5.1 Introduction**

Since its discovery by Meiklejohn and Bean in 1956 the Exchange bias (EB) phenomenon has been the focus of extensive theoretical and experimental analysis and more recently it is attracting researchers for its potential application in devices like giant magnetoresistance, highdensity data storage, electrically controllable spin-polarized currents, magnetic sensors and spin valve devices [47, 105, 106]. Conventional exchange bias (CEB) is observed at the interface between ferromagnetic and antiferromagnetic materials when cooled in a field through the Neel temperature  $(T_N)$  of the hard magnetic material [46, 107]. Apart from interacting interfaces between FM and AFM materials, the effect has so far been observed in different types of heterostructures, such as, ferromagnetic–antiferromagnetic, ferromagnetic–spin glass– antiferromagnetic, ferromagnetic–ferrimagnetic, ferromagnetic–dilute antiferromagnetic, etc. in different geometries like bilayers, core-shell nanostructures, granular composites and super lattices [47, 80].

In recent years  $BiFeO<sub>3</sub>$  has emerged as one of the most significant materials for investigating the EB as well as multiferroicity. It is the only perovskite material which shows multiferroic behavior at room temperature (Neel temperature  $T_N \approx 643$  K and Curie temperature  $T_C \approx 1100$  K) [14, 31]. Different low dimensional  $BiFeO<sub>3</sub>$  systems, such as nanoparticles and nanotubes are known to display weak ferromagnetic behavior at room temperature and spin glass type behavior at low temperature [108, 109]. The EB and its origin in  $BiFeO<sub>3</sub>$  based systems are in discussion in recent times [108, 110, 111]. It was found to persist at room temperature in some nanodimensional systems consisting  $BiFeO<sub>3</sub>$  and was ascribed to the spin pinning at the interface between the AFM and weak FM layers present in those structures [108] Dong *et al*. have

demonstrated that SEB exists in  $BiFeO<sub>3</sub>$  nanocrystals with a non-monotonic temperature dependence of H<sub>SEB</sub>. They proposed that the formation of a diluted antiferromagnetic phase and its interaction with the hard AFM moments was the mechanism responsible for the hightemperature behavior of  $H<sub>SEB</sub>$ . The low-temperature  $H<sub>SEB</sub>$  were explained by suggesting the formation of super spin-glass (SSG) type structure and related interactions [112]. Manna *et al.* have reported H<sub>EB</sub> above the SSG transition within their  $BiFe_{0.8}Mn_{0.2}O_3$  nanoparticles and have explained the EB on the basis of the interaction between antiferromagnetic core and a diluted antiferromagnetic (DAFF) shell .Zhang *et al*. have also shown room temperature exchange bias in BiFe $O_3$  nanocrystals and explained the phenomenon as a consequence of the interaction between antiferromagnetic core and DAFF shell*.* Recently, Maity *et al*. on the other hand found EB only when an SSG-type structure is formed at low temperature in  $BiFeO<sub>3</sub>-Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>$ nanostructures, and the phenomenon was linked to pinning of glassy spins to the remaining antiferromagnetic spins. [110]. A skin layer different from its bulk is also reported in single crystalline BiFe $O_3$  which influences several of its properties including the EB [113].

Several attempts have been made to induce chemical pressure in the  $BiFeO<sub>3</sub>$  lattice by substituting Bi or Fe ions with rare earth and transition metal atoms respectively. Substitution is known to modify the magnetic behavior and enhance the EB [111]. Attempts have also been made to integrate  $BiFeO<sub>3</sub>$  in heterostructures, and composite systems containing other perovskite materials like,  $BaTiO<sub>3</sub> and SrTiO<sub>3</sub> [75, 114]$ . However, a clear understanding of the mechanism which leads to the EB effect is still missing. Although, the EB effect has been investigated for many years, obtaining a large H<sub>EB</sub> at room temperature and within the bulk, the state remains an ongoing task since room temperature EB is more attractive for device applications.

In this context, we decided to incorporate  $TbMnO<sub>3</sub>$  (which shows very strong magneto-electric coupling) into  $BiFeO<sub>3</sub>$ . TbMn $O<sub>3</sub>$  is a promising material to induce strain at the single-phase interfaces in the system [115] TbMnO<sup>3</sup> possesses a perovskite structure (space group *Pbnm*), and the lattice mismatch between the two materials in the composite system is sufficient to create strain [115]. In this article we examine composites of  $0.7BFO-0.3TMO$  (70% BiFeO<sub>3</sub> and 30%) TbMnO<sub>3</sub>) and 0.8BFO-0.2TMO (80% BiFeO<sub>3</sub> and 20% TbMnO<sub>3</sub>). We found (i) a large exchange bias both near room temperature and low temperatures (ii) a non-monotonic variation of exchange bias with temperature. We propose an exchange interaction initiated by the strainmediated strong magnetoelectric coupling which is the result of lattice mismatch between the two materials. Further, we demonstrated by means of XMCD that the canted nature of antiferromagnetic ordering in BFO, exchange interaction between Fe and Mn ions present in the system and the pinning layer at the interface play a vital role in determining the amplitude and temperature behavior of the EB.

## **5.2 Experimental methods**

The synthesis of magnetoelectric multiferroics composite consisting of  $BiFeO<sub>3</sub>$ in bulk via solid state reaction is a difficult task because it commonly leads to the formation of thermodynamically stable impurities  $Bi_2Fe_4O_9$ ,  $Bi_{25}FeO_{39}$  and  $Bi_{46}Fe_2O_{72}$  due to the volatile nature of  $Bi_2O_3$  [28]. In this work, we have used high purity oxides  $Bi_2O_3$ ,  $Fe_2O_3$ ,  $Mn_2O_3$  and  $Tb_4O_7$  as starting materials. First, polycrystalline  $TbMnO_3$  was prepared through a solid state reaction as described in our previous report [116]. Then stoichiometric amounts of the materials  $Bi<sub>2</sub>O<sub>3</sub>$  (5% excess), Fe<sub>2</sub>O<sub>3</sub> and TbMnO<sub>3</sub> were mixed for 3-4 hours and then the mixture was

calcined at 1173 K for 1 hour to prepare composites with two different ratios (7:3 and 8:2) namely, 0.7BFO-0.3TMO and 0.8BFO-0.2TMO. The calcined powder was ground and pressed into pellets and sintered for 2 hours at 1273 K with some mixture of calcined powder as a spacer to reduce the loss of  $Bi<sub>2</sub>O<sub>3</sub>$  during synthesis.

The structural analysis of the composite was carried out using an X-ray diffractometer (Model: Miniflex-II, Rigaku, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) in step size of 0.002 with a scan speed of 2°/min. For their magnetic properties, the composites were investigated using a commercial superconducting quantum interference device [Magnetic Properties Measurement System XL-7, Quantum Design, Inc.] magnetometer. [X-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements at Mn  $L_{2,3}$ -edge and Fe  $L_{2,3}$ -edge at 300 K and 180 K were performed with polarized X-rays at beamline from Hsinchu Synchrotron center, Taiwan.

## **5.3 Results and discussion**

### **5.3.1 Structure and Morphology**

Figure 5.1 shows the Rietveld refinement of the X-ray diffraction profile for the composite 0.7BFO-0.3TMO in the 2θ range from 20° to 80°.A closer look at the 2θ value 32° which corresponds to 110 planes of BFO in *R3c* phase reveals that the peak is shifted to the higher angle side as well as split into multiple peaks which hints towards the existence of multiple phases of BFO. Rietveld refinement using the FULLPROF package was employed to index the XRD pattern for analyzing the crystal structure and structural phase transition from the intensities of overlapping reflections in the XRD pattern. The difference between experimental and theoretical pattern as well as Bragg positions are shown at the bottom of the plot. From the refinement result it was found that in the composite,  $TbMnO_3$ crystallizes as in its native bulk structure, i.e., orthorhombically distorted perovskite structure with space group *Pbnm*. BiFeO<sub>3</sub>, on the other hand,is found to co-exists in two very similar phases consisting of rhombohedral and orthorhombic symmetry  $(R3c+Pbnm)$ . Rare-earth orthoferrites  $RFeO<sub>3</sub>(R=$  rare earth), manganites and the high-temperature phase of BFO is known to undergo a structural transition from the rhombohedral *R3c* structure to an orthorhombic (*Pnma or Pbnm*) structure when sintered at higher temperature [117]. The observation of the existence of dual phases,i.e., rhombohedral (*R3c*) and orthorhombic (*Pnma or Pbnm*) in rare earth (RE)-modified BFO has previously been reported [118].

Recent reports show that BFO in solid solution with rare earth manganites  $(RMnO<sub>3</sub>)$ , i.e.,  $BiFeO<sub>3</sub>-RMnO<sub>3</sub>$  ( $R=La$ , Gd, Ho,and Dy), and  $(1-x)BiFeO<sub>3</sub>-xYMnO<sub>3</sub>$  undergo a structural phase transition from *R3c* to *R3c + Pnma* over a wide compositional range [32-34]. This structural transition to dual phases was accompanied by a significant improvement of multiferroic properties within BFO. Lotey *et al*. reported complete structural transformation from rhombohedral ( $R3c$ ) to the orthorhombic ( $Pn2<sub>1</sub>a$ ) phase at 15% of Tb-doping in BFO nanoparticles] [119].The existence of both rhombohedral and orthorhombic phase in the composite can, therefore, be attributed to (a) the deficiency of  $6s^2$  lone pair in Tb<sup>+3</sup>alsohinders the stereochemical activity of the lone pair of  $Bi^{+3}$  ions in the structure (b)  $Mn^{+3}$  weakly destabilizes *R3c* phase whereas  $Fe^{3+}$  stabilizes it (c) chemical pressure of Tb<sup>3+</sup> is much smaller than for  $Bi^{3+}$  as the ionic radii of  $Bi^{3+}$  and Tb<sup>3+</sup> are 1.31 A $^{\circ}$  and 1.17 A $^{\circ}$ , respectively, for highspin eight-fold coordination [41]. The two phases in our sample correspond to bulk (*R3c*) and

interfacial (*Pbnm*) phase at the interface with  $TbMnO<sub>3</sub>$ . The interfacial regions of the  $BiFeO<sub>3</sub>$ crystals face strain due to the presence of  $Tb^{3+}$  and Mn<sup>3+</sup> and the interface structure changes to the *Pbnm* phase.

The microstrain of the sample is evaluated from Williamson-Hall (W-H) equation where microstrain  $(\epsilon)$  and FWHM are related as;

$$
\beta \mathcal{C}os\theta \propto 4\varepsilon \mathcal{S}in\theta \tag{5.1}
$$

Thus, from the intercept and slope of β Cosθ vs.  $4\sin\theta$  plot (inset of figure 6.1(a)) the τ and ε are calculated. All the parameters calculated from the XRD are given in Table–5.1. The surface morphology and microstructure of the 0.7BFO-0.3TMO composite were characterized by field emission scanning electron microscope (FESEM) shown in Figure 6.1(b). The microstructure of composite is observed to be closely packed with non-uniform and randomly oriented (both in size and shape) grains with clear grain boundaries. For the composite system, it is hard to get a homogenous microstructure because of the large difference in sintering temperature and thermal expansion coefficient of the different phases.



Figure 5.1. Rietveld refinement of the XRD data of the composite 0.7BFO-0.3TMO. Inset shows the Williamson-Hall plot to calculate the microstrain.



Table 5.1Parameters calculated from the XRD pattern and the Williamson-hall plot.

## **5.3.2 AFM/MFM analysis**

In order to visualize surface morphology and magnetic structure, AFM and corresponding MFM measurements of the sintered 0.7BFO-0.3TMO composite were performed. Figure 5.2 a and b show the AFM and the corresponding MFM image of the composite over a surface area of  $10\times10\mu$ m<sup>2</sup>. It is clear from the Figure that composite exhibits grainy–like surface with uniformly and non-homogenously distributed grains. The average grain size was calculated by line scan sectional analysis to be of  $\sim$  180 nm which is consistent with the crystallite size

calculated from the XRD pattern. Further, composite also display larger grains growth due to the agglomeration of smaller grains [120].

The corresponding MFM image which was taken at a lift height of 200 nm is presented in Figure 2b. From the Figure disappearance of grains can be seen as compared to the AFM image of composite and contrasting dark and bright images were found to display the domain structure. Since short-range force between the sample and magnetic tip is ascribed to the light and dark contrast areas represents the magnetic domain of the composite, these spots correspond to the attractive and repulsive force between the magnetic tip and the sample [[121]. Thus, from the image microscopic domains can be seen which is evident for the antiferromagnetic materials[122]. The surface of the grains thus appeared to be antiferromagnetic in nature. The average domain size and the magnetic signal strength was calculated using the sectional scan analysis.



Figure 5.2. AFM (left) and MFM (right) image of the 0.7BFO-0.3TMO Composite.

#### **5.3.3 Magnetic Properties**

Figure 5.3 a and 5.3 b depicts the temperature dependence of field cooling (FC) and zero field cooling (ZFC) dc-magnetization for composite 0.7BFO-0.3TMO and 0.8BFO-0.2TMO, respectively. The two different compositions show similar behaviors in the ZFC-FC magnetization where the ZFC and FC values increase with decreasing temperature at low temperatures. In this plot (Figure 5.3a), the magnetization (both FC and ZFC) for the composition 0.7BFO-0.3TMO is observed to decrease with decreasing temperature in the temperature range  $215 - 300$  K which is expected for an antiferromagnetic material below its Neel temperature.

Further, on decreasing the temperature below 215 K  $(T^*)$ , FC and ZFC magnetization curves show upturns. To get clear view of the anomaly the dM/dT vs. T is plotted in the insets of the Figure 5.3a and b from where it is found that in case of 0.7BFO-0.3TMO the slope of the dM/dT vs. T curves changes abruptly at  $\sim$  215 K whereas for the other composite the transition temperature was found to be 169 K. Similar trends have previously been reported as a result of reorientations of spins with the involvement of electro-magnons, similar to that observed in orthoferrites [61, 73, 116]. The transition is reported to be of magnetic origin and not related to structural deformation or transition [116]. Although the spin reorientation transition is reported well above the room temperature and just below the  $T_N$  for different composite systems such as  $BiFeO<sub>3</sub>$ -PbTiO<sub>3</sub> and BiFeO<sub>3</sub>-BaTiO<sub>3</sub>, T<sup>\*</sup> has been reported in the temperature range of 150-200 K for pure BiFeO<sub>3</sub> [69, 116]. Recently, A. Kumar *et al.* have also observed such a spin reorientations transition in pure and  $0.3\%$  MnO<sub>2</sub> doped BiFeO<sub>3</sub> powders in the same temperature range [114]. Further decreasing the temperature, FC and ZFC magnetization curves of 0.7BFO-

0.3TMO show very low bifurcation from 95 K to 2 K as the two curves deviate from each other very slowly towards lower temperatures. Although there is bifurcation in the plots, we have not found any traces of long range or short range ordering from either the dM/dT vs. T plots or AC susceptibility measurements (not shown here) in both the samples. Moreover, as it is observed from Figure 3b no bifurcation is observed in the FC and ZFC magnetization of 0.8BFO-0.2TMO. TbMnO<sub>3</sub> is known to exhibit AFM ordering below 40 K in the bulk, but feature is also not traceable in M-T plots.



Figure 5.3. ZFC and FC magnetization vs. temperature plots for **(a)** 0.7BFO-0.3TMO and **(b**) 0.8BFO-0.2TMO composites under an applied magnetic field of 1000 Oe. Inset: the dM/dT vs T plots for the respective sample. The arrows in the insets point towards the spin reorientation transition temperature T\*.

Figure 5.4 presents the M-H loop of the composite 0.7BFO-0.3TMO at different temperatures after cooling from a higher temperature in the presence of a magnetic field 1 T. The M-H loop at room temperature shows a linear variation of magnetization with an applied magnetic field which is typical for an antiferromagnetic material. Around the zero field, a deviation of nonlinearity is observed which indicates the existence of FM ordering too. Furthermore, a close view

around the zero field (inset of Figure 5.4) reveals that the loops, measured at 275 and 80 K, are asymmetric in nature, yielding exchange bias (SEB) for 0.7BFO-0.3TMO at all the temperatures. The presence of massive loop shift in the room temperature M-H loop can be quantified as exchange bias field,  $H_{SEB} = [(H_{C1}+H_{C2})/2]$ , where  $H_{C1}$  and  $H_{C2}$  are the points in the field axis where magnetization value becomes zero. The coercivity has also been estimated from the M-H loop as  $H_C = [(H_{C1}-H_{C2})/2]$ . H<sub>EB</sub> estimated at different temperature are plotted in Figure 5.5 from which it becomes evident that  $H_{EB}$  exhibits clear temperature dependence. The measured exchange bias increases with increase in the temperature from 5 K to 275 K. The similar variation in exchange bias has also been observed in 0.8BFO-0.2TMO composite (not shown).



Figure 5.4. The M-H loop of **(a)** 0.7BFO-0.3TMO and composite measured at different temperature across 5-300 K after field cooling (1 T) from a higher temperature. Insets **(a)** and **(b)** show close view of the M-H loops around zero field measured at 275 K and 80 K respectively.



Figure 5.5 The temperature dependence of exchange bias field  $(H_{\text{SEB}})$  and coercivity of 0.7BFO-0.3TMO.

### **5.3.4 Isothermal remanent magnetization**

Recently, isothermal remanent magnetization (IRM) measurement is being used as a fingerprinting technique to differentiate different magnetic states such as DAFF, spin glass, and others as it identifies the nature of the irreversible magnetization contributions [123]. We have performed IRM vs. field measurements to look out for the presence of any interface pinning containing hard antiferromagnet  $BiFeO<sub>3</sub>$  and possible dilute antiferromagnet. To measure the IRM a field is applied to the sample for a concise time  $($   $\sim$  60 s) after cooling it from a high temperature, and then the remanent magnetization is immediately recorded. It is expected that a

pure AFM material shows zero IRM value for all fields and all temperatures as the reversible magnetization becomes zero for a pure AF state. From Figure 5.6, it can be seen that the IRM value observed is very low and increases little when the field is raised to 1.5 T where the virgin curve increases sharply and linearly with the field. This behavior is consistent with an AFM state. However, the IRM is not showing a typical behavior of a 3D dilute antiferromagnet as it is not expected to increase at all. This type of behavior of IRM has been found for  $Co<sub>3</sub>O<sub>4</sub>$ nanowires where the nature of the particle is found to be of 2D DAFF [124].The 2D DAFF layer is attributed to the formation of a  $2<sup>nd</sup>$  phase (*Pbnm*) of BFO at the interfacial regions other than that of core BFO (*R3c*). The antiferromagnetic ordering in the two phases is expected to be different [113].However, the origin of the DAFF layer remains in doubt as it could be formed either due to BFO skin layer or due to the TMO spins which could be coupled to the interfacial spins of the BFO.

The BFO/TMO interface is likely to be responsible for the EB and is expected to exhibit a complex interface structure, including charge transfer, atomic spin, and orbital configurations. At the interface of the composite two different phases are combined at the atomic level which results in an increased magnetoelectric (ME) coupling due to the strain-mediated ME effects across the interfaces [53]. This enhanced ME coupling can modify the lattice structure through spin reconstruction at the interface as seen from the XRD results. From the calculation of magnetic coupling across the interface of  $BiFeO<sub>3</sub>$  and other manganites, it has been found that both charge and orbital ordering at the interface results in developing a magnetic moment of Fe ions at the BFO-TMO interface [63]. Another possibility can be the presence of an orbital reconstruction which will lead to a strong hybridization between Fe  $d_{3z2-r2}$  orbital and Mn  $d_{x2-y2}$ 

via an oxygen-mediatedsuper-exchange [105]. According to the Anderson-Goodenough-Kanamori rules, the exchange interaction between Fe and Mn cations are expected to be ferromagnetic and the Mn-O-Mn interaction to be antiferromagnetic [51]. Thus, there lies a competition between the interfacial interaction of the Fe and Mn spins and the bulk antiferromagnetic interaction of the BFO which results in the canting of the interfacial spins. The exchange bias can be understood due to the pining and canting of the interfacial spins to the core antiferromagnetic spins to BFO. Moreover, the possibility of charge flow across the interface can be neglected as there is a large difference between the energy level of BFO and TMO, as estimated from atomic stacking  $[(BiO)^+-(FeO_2) - (BiO)^+-(MnO_2) - (TbO)^+]$  equation for BFO/TMO [125]. The strain mediated ME coupling also produces a very thin layer of BFO with the different structure as seen from the XRD results which can be the reason behind getting the 2D DAFF layer at the interface observed from the IRM measurement (Figure 6) which also plays a significant role in getting the exchange bias. Thus, the large coercivity can also be explained on the basis of interfacial ferromagnetic super-exchange interaction. At room temperature, the value of exchange bias got reduced from the maximum value at 225 K due to the large thermal fluctuations of spins resulting into less interfacial coupling [112].

The origin of exchange bias in  $BiFeO<sub>3</sub>$  based systems has been an argued mechanism in recent years. As mentioned during the introduction, some  $BiFeO<sub>3</sub>$  based systems exhibit EB only below super spin glass (SSG) transition temperatures where the explanation was the presence of SSG moments. The SSG moments at the core generate a random field that can induce a variation in the anisotropy of the AFM moments including biaxiality with respect to the direction of the applied field and set the uniaxial anisotropy via RKKY interaction. Our ZFC-FC M-T data shows little bifurcation below ~95 K for 0.7BFO-0.3TMO suggesting weak frustration in the system, but in case of 0.8BFO-0.2TMO there is no bifurcation in the ZFC-FC data. We also could not find signals of any relaxation phenomena from our AC susceptibility measurements for both the samples (not shown here).

Therefore, we could rule out the possibility of any kind of SSG mediated phenomena happening to give rise to the EB effect. Thus, the results obtained from our study cannot be explained within the model given by Maity *et al*. [110, 126]. Manna *et al*. found room temperature and low-temperature exchange bias in their Mn-doped  $BiFeO<sub>3</sub>$  nanoparticles. The results were understood on the basis of a core-shell model of hard antiferromagnetic core and dilute antiferromagnet shell where the spins of DAFF gets pinned to the core"s spins when a magnetic field is applied, thus, setting the uniaxial anisotropy in the system. Zhang *et al.* also found a DAFF layer to influence the magnetic property of the  $BiFeO<sub>3</sub>$  nanoparticles. Therefore, to verify the compatibility of this model with our system confirmation of the type of interaction between the different ions present in the composite in different temperature is necessary. To this end, we have recorded X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD) spectra of Fe and Mn  $L_{2,3}$  edge.



Figure 5.6 Isothermal remnant magnetization (IRM) and the virgin loop of magnetization vs. magnetic field of the composite 0.7BFO-0.3TMO.

### **5.3.5 XAS and XMCD Results**

The synchrotron-based XAS is a spectroscopic technique which probes electronic states of a matter. In x-ray absorption spectroscopy (XAS), an x-ray is made to incident on the core level electrons to excite them to unoccupied valence levels. The transition from core to valence level is governed by the dipole selection rules. Thus XAS has a direct correspondence with an

unoccupied density of states (DOS). As it has a direct correlation with the unoccupied density of states (DOS) numerous information regarding oxidation states, local symmetries, and the spin and orbital magnetic moments of the Fe and Mn ions and interaction between them in the composite can be investigated by means of XAS and XMCD measurements.

The XMCD signal at the Mn and Fe  $L_{2,3}$  edges (excitation from filled 2p $\rightarrow$ 3d transition) is obtained from the difference between the two XAS spectra, taken as the difference between XAS spectra recorded with left and right hand circularly polarized light ( $\Delta \mu = \mu^+ - \mu^-$ ) in presence of a magnetic field of 0.6T. XMCD measurements were performed in total electron yield (TEY) mode at 180 K, and 300 K. Figures 5.7a-d depicts the XAS and XMCD spectra of Fe  $L_{2,3}$  of the two composites measured at 300 K and 180 K. The spectral shape and energy position in the Fe L<sub>2,3</sub>-edge splits due to spin-orbit coupling at L<sub>3</sub>(2P<sub>3/2</sub>) at ~710eV and L<sub>2</sub>(2P<sub>1/2</sub>) at ~722eV corresponding to the absorption edge of  $Fe^{3+}$ ions. The  $L_3$  and  $L_2$  peaks are also split due to the crystal field to doubly degenerate  $e<sub>g</sub>$  and triply degenerate  $t<sub>2g</sub>$  levels [127]. The shape of the XAS peak of BFO matches well with the  $Fe^{3+}$  signal previously seen in BiFeO<sub>3</sub> based systems [83]. The shape of the spectral lines for the composites matches with the calculated spectrum taking the high spin configuration of Fe<sup>3+</sup> ions ( $t_{2a}^3 e_q^2$ ) and with the measured Fe<sup>3+</sup> XAS signal [128]. A closer look at the  $L_3$  edge of the composites (inset of Figure 5.7a) when compared with the Fe  $L_3$ edge of standard  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> reveals that the spectral shape of the t<sub>2g</sub> peak of the L<sub>3</sub> edge is diminished and shifted to the higher energy side for the composites. The overall spectra of the composites are also broader in comparison to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. These features of the t<sub>2g</sub> can arise from the presence of either different crystalline coordination of the Fe ions or of different valence states of Fe in the sample. The  $L_2$  edge of the composites shows Fe<sub>3</sub>O<sub>4</sub> like diminished  $L_2$  edge

from where one might get the indication of mixed valence state of Fe. But, a closer inspection of the  $L_2$  edge (inset of Figure 5.7b) supports the fact that Fe ions are in mixed crystal coordination as the peaks are not shifted to the lower energy side [129] which should have been the case for mixed valence state. From the XAS study, Fe ions are thus, found to be in a trivalent state with octahedral and another crystalline coordination.

The bottom panels of Figure 5.7 (a-d) show the XMCD spectra of Fe ions of the composite 0.7BFO-0.3TMO. The XMCD signal in the composite system is weak and in Figure5.7 the XMCD signals are magnified five times for clear visualization. BiFe $O_3$  is antiferromagnetic at room temperature, and hence it is not dichroic; thus, the absence of the XMCD signal of the composites at room temperature can be understood. Interestingly, The Fe XMCD spectrum at 180 K for the 0.8BFO-0.2TMO shows clear dichroic signal similar to that of previously observed in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, BiFeO<sub>3</sub> thin films, and La<sub>2</sub>FeCrO<sub>6</sub> [130]. It has been shown that in BiFeO<sub>3</sub> weak ferromagnetism can be developed due to spin canting as a result of Dzyaloshinski - Moria interaction in the lattice. A similar XMCD spectrum has been reported by Kuoet al., to describe the weak ferromagnetism in  $BiFeO<sub>3</sub>$  thin films due to canted antiferromagnetic ordering [130]. Gray *et al.* have also shown similar Fe  $L_{2,3}$  XMCD signal in case of canted antiferromagnetic double perovskite La<sub>2</sub>FeCrO<sub>6</sub> [130]. In the case of γ-Fe<sub>2</sub>O<sub>3</sub>the weak ferromagnetism arises as a result of the alignment of spins of tetrahedral sites which is canted in nature [129]. It is significant to mention here that in the *Pbnm* phase there are two sites available for Fe ions  $(O<sub>h</sub>)$ and  $T_d$ ) whereas in *R3c* phase only  $O_h$  sites are available for Fe. Thus, the interfacial secondary *Pbnm* phase can also be responsible for the XMCD signal at Fe edge of 0.8BFO-0.2TMO at 180

K. The dilute antiferromagnetic (2D DAFF) layer can be understood to be due to the interaction between Fe ions in the *Pbnm* phase which was observed from the IRM measurements.

The canting of Fe spins close to the interface could arise due to the lattice strain at the interface as introduced by the TMO phase. This, however, should not affect the spin orientation further away from the interface. Gruber *et al.* have recently shown that the interfacial pinning plays a vital role in attaining the XMCD signal in Co/Mn Pc interface [50]. From the thickness dependent study of the layered structure, it has been shown that the XMCD signal varies when the pinning layer varies. [50]From the XMCD spectra at 300 K and 180 K, it can be conferred that as we decrease the temperature from 300 K spin canting in the system increases in the system down to the spin reorientation temperature. Below the transition temperature, the spins reorient in such a way that the weak ferromagnetism due to spin canting vanishes in the system. Thus, the XMCD signal can only be observed for 0.8BFO-0.2TMO composite at 180K as the spin reorientation transition temperature (T<sup>\*</sup> = 169 K) is lower than 180 K whereas it is (T<sup>\*</sup> = 215 K) higher than that of the XMCD measurement temperature (180 K) of 0.7BFO-0.3TMO.



Figure 5.7 Fe  $L_{2,3}$  XAS and XMCD spectra of (a) 0.7BFO-0.3TMO at 300 K (b) 0.8BFO-0.2TMO at 300 K (c) 0.7BFO-0.3TMO at 180 K (d) 0.8BFO-0.2TMO at 180 K. XMCD signal was multiplied by 5 in all the cases for better visualization. Inset in (a) and (b) shows the comparison of  $t_{2g}$  peak of  $L_3$  edge and  $L_2$  edge of the composites with standard  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> respectively.

Figure 5.8 (a-d) represents the Mn  $L_{2,3}$ -edge XAS and XMCD spectra of the two composites (0.7BFO-0.3TMO and 0.8BFO-0.2TMO) at 300 K and 180 K. The XAS spectra of the composites exhibit two broad spin-orbit split peaks of L<sub>3</sub> (2P<sub>3/2</sub>) at ~ 64eV and L<sub>2</sub> (2P<sub>1/2</sub>) at ~ 652eV separated by spin-orbit splitting energy ( $\Delta E = \sim 11$ eV). The XAS spectra of the composites are compared with that of standard MnO sample from which it can be easily

concluded that the  $L_3$  and  $L_2$  peaks are shifted to higher energy side for the presence of higher valence state of Mn ions [131]. Interestingly, the composites show distinct behavior at  $L_3$  and  $L_2$ edges where the shape of the spectra does not match exactly with  $Mn_2O_3$  in which Mn lie in 3+ state, rather it matches well with Mn XAS spectra observed in La0.7Sr0.3MnO3 thin films in which Mn lie in a mix valence state [127]. The main peak observed at  $\sim 640$  eV is due to the presence of  $Mn^{3+}$  as the position matches well with Mn signal obtained from  $Mn_2O_3$  in a tetragonally distorted  $D_{4h}$  crystal field and from TbMnO<sub>3</sub>. The high-intensity peak  $2P_{3/2}$  observed at  $\sim$  640eV shows distinct shoulder peaks at  $\sim$  638 eV (marked by a blue star) and 642 eV (marked by red arrow) indicating the existence of multivalent oxidation states of Mn. The spectral shape of any  $L_{2,3}$  edge depends on different factors such as local crystal field effects, multiplet structure given by the Mn 3d-3d and 2p-3d Coulomb and exchange interactions and the hybridization with the O 2p ligands [131]. The peaks can be assigned to the presence of  $Mn^{2+}$ and  $Mn^{4+}$  respectively as has been done by several authors in Mn XAS spectra [127, 132]. To maintain the charge neutrality affected by oxygen vacancy present in the lattice, the mixed oxidation states can evolve in the system. The co-valency can also arise from the charge transfer effect between the Mn 3d orbitals and O 2p ligand orbitals commonly observed in Mn-based systems The valence instability of  $Mn^{3+}$  ions can also give rise to the creation of  $Mn^{4+}$  and  $Mn^{2+}$ species which is known to modify the bulk magnetic and electrical properties of different manganite systems [127]. Oxygen vacancies present in the composites which are observed in XPS analysis (not shown here) of the composite can change the effective super-exchange (SE) interaction between Mn ions. Yang *et al*. reported the change in the magnetic spin structure of TbMnO<sub>3</sub> due to the alternation in SE between next-nearest-neighbor Mn ions mediated through O ion [133].

The XAS spectra of the 0.8BFO-0.2TMO (Figure 5.8 b and d) show more pronounced shoulder peaks due to the presence of  $Mn^{2+}$  and  $Mn^{4+}$  ions (marked by a blue star and red arrow). From the spectra, it can be concluded that in this composite the 2+ state of Mn ion dominated over other valence states. Moreover, the intensity ratio of the  $L_3$  and  $L_2$  (i.e.,  $L_3/L_2$ ) edges is also a significant parameter to determine the dominating oxidation states of transition metal and their oxides (TMs) with 3d occupancy [72, 134]. For the transition metals which have  $d^0$  to  $d^5$ occupancy (i.e., up to half-filled occupancy) the increment in  $L_3/L_2$  intensity ratio signifies a reduction in the oxidation state of the TMs [72, 73, 134, 135]. Larger  $L_3/L_2$  intensity ratio for Mn ion in 0.8BFO-0.2TMO composite than the other reveals that the dominating state of Mn is  $Mn^{+2}$ . The presence of large amount of  $Mn^{2+}$  and  $Mn^{4+}$  in this composite is understood to be due to the large lattice strain experienced by the  $TbMnO<sub>3</sub>$  due to a higher concentration of BFO in the 0.8BFO-0.2TMO composite. Lattice strain is known to create oxygen vacancies in a lattice which in turn creates the mix valence state of Mn ion in the composites [136]

Mn  $L_{3,2}$  edge XMCD signals of the composites are shown in the bottom panel of Figure 8 (a-d). The room temperature XMCD signal has been multiplied by 5 for better visualization which showsweak XMCD signal at  $L_3$  and  $L_2$  edge. Although the XMCD signals are weak and noisy at room temperature, XMCD peaks can be found in opposite polarity for  $Mn^{2+}$  with respect to that of  $Mn^{3+}$  and  $Mn^{4+}$  for both the composite which show the opposite alignment of  $Mn^{2+}$ ionswith respect to  $Mn^{3+}$  and  $Mn^{4+}$ . Interestingly, the 180 K XMCD spectrum of 0.8BFO-0.2TMO shows prominent signal just like its Fe counterpart. The signal for  $Mn^{2+}$  is opposite in nature to the signal of  $Mn^{3+}$  and  $Mn^{4+}$  showing the antiferromagnetic coupling between them. Further, it is found that the magnitude of the Mn dichroism is almost diminished at 180K for the composite 0.7BFO-0.3TMO due to the spin reorientation transition occurring at a higher temperature (225 K). This reduction of the Mn dichroism could be understood by taking into account spinreorientation transition near ~200K observed from the magnetization measurement. Interestingly, the 180 K XAS signal of 0.7BFO-0.3TMO shows an increase in the intensity of the shoulder peak at ~638 eV which signifies the increase in the charge transfer process between Mn ions at low temperature.



Figure 5.8 Mn L2,3 XAS and XMCD spectra of **(a)** 0.7BFO-0.3TMO at 300 K **(b)** 0.8BFO-0.2TMO at 300 K **(c)** 0.7BFO-0.3TMO at 180 K **(d)** 0.8BFO-0.2TMO at 180 K. XMCD signal was multiplied by 5 in case of **(a)** and **(b)** for better visualization. Inset in **(a)** shows the comparison between XAS spectra from 0.7BFO-0.3TMO, 0.8BFO-0.2TMO and standard  $α$ -Fe<sub>2</sub>O<sub>3</sub> sample.

The contribution of spin moments and the orbital moments to XMCD signal are calculated following the XMCD sum rule. It is found that the contribution of orbital momentum is not negligiblein comparison to the spin momentum in all the cases. This massive orbital momentum can break the local symmetry in the proximity of the BFO/TMO interface, leading to strongly

enhanced unidirectional anisotropy energy [137]. This local anisotropy energy is strong enough to induce effective exchange imbalance at the interface, which tries to rotate spin moments by spin-orbit- coupling (SOC) [138].Recently, Nistor et al. have reported that the exchange bias in their system arises from the coupling of the Mn spins to the uncompensated spin at the interface [138].Thus, in our sample also there might be a coupling of Mn spins to the uncompensated Fe spins at the interface. In addition to the coupling of Mn and Fe spins there are also exchange coupling between Mn-Mn ions. This coupling of Mn-Mn and Mn-Fe ions would give rise to a layer of pinned magnetic moments at the interface. However, the detection and measurement of pinned magnetic moments cannot be done following the simple XMCD measurement protocol [137].

Thus, analyzing XAS and XMCD spectra of all the  $L_{3,2}$  edges, it can be concluded that charge transfer between Mn ions occurs due to oxygen vacancy and instability of the  $Mn^{3+}$  oxidation state. The charge transfer results in a mix valence state of Mn ions in the composite. As a result of the transfer and mix valence state of the TM ions band gets reconstructed at the interface and the band gap of the material is decreased. The presence of mixed valence state creates different superexchange interaction between TM ions across the interface and in bulk. The result indicates the coupling of the Mn spins to the uncompensated spin of Fe which forms a pinned layer of spin moments at the interface of the two components (BFO and TMO). This weak ferromagnetic layer is stabilized against the thermal fluctuations through exchange coupling to the 2D DAFF layer and/or to the core canted antiferromagnetic spins of BFO. On lowering the temperature from 300 K the spin canting increases as a result the uniaxial antiferromagnetic anisotropy decreases (seen from XMCD results). Thus, the exchange bias is developed as a result of pinning of the interfacial ferromagnetic spins to the core antiferromagnetic BFO spins. Due to the dual phase structure of BFO a thin layer of DAFF is formed at the skin of BFO core which also favours the formation of canted antiferromagnetic ordering of the BFO lattice.

# **5.4 Conclusion**

In this chapter, we have studied the origin of exchange bias induced in  $BiFeO<sub>3</sub>-TbMnO<sub>3</sub>$ composite (7:3 and 8:2 stoichiometric ratio) prepared via solid state reaction. In the prepared composite  $BiFeO<sub>3</sub>$  has the rhombohedral distorted perovskite  $(R3c)$  structure at the core and orthorhombically distorted *Pbnm* structure at the shell or skin whereas TbMnO<sub>3</sub> has orthorhombically distorted perovskite (*Pbnm*) structure. We observed exchange bias at room temperature and low temperatures which could not be explained on the basis of the pinning or a super-spin-glass state at low temperatures. Different models explaining the EB have been investigated, such as core-shell of hard and dilute antiferromagnet and charge transfer between Fe and Mn ions present at the interface of the two materials in the composite. The charge transfer between the Mn-Mn ions at the interface takes place due to the oxygen vacancy and instability of  $Mn^{3+}$  ions.

The presence of mix charge state creates different exchange interaction between the TM ions (Ferro and antiferromagnetic). The strong magnetoelectric coupling between the two materials initiates canting and pinning of the interfacial BFO or TMO spins. From the IRM measurement signatures of the presence of 2D dilute antiferromagnet has been found which plays a significant role in obtaining the exchange bias. The 2D DAFF layers are the result of the formation of the interfacial phase of BFO (*Pbnm*) in which the antiferromagnetic ordering is

different from that of the  $R3c$  phase in bulk. As a result, the Fe edge shows  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> like XMCD signal. The EB obtained at different temperatures also shows non monotonic variation with temperature. The decrease in AFM anisotropy due to spin canting and increase in FM ordering in the pinned layer with a decrease in the temperature have been found to influence the temperature dependence of the EB. The role of interfacial pinning layer which influences the exchange bias in the system has also been confirmed from the IRM results and XMCD spectra of Fe and Mn  $L_{2,3}$  edge.