

## Module 8: Multiferroic and Magnetoelectric Ceramics

### Introduction

A ferroic material is basically a material which exhibits either ferroelectric or ferromagnetic or ferroelastic ordering, a feature typically demonstrated by the presence of a well defined hysteresis loop when the material is switched electrically, magnetically or mechanically. More recently there has been another ordering mechanism proposed which is called as ferrotoroidic ordering. Magnetoelectric coupling in the materials, on the other hand, is a more general phenomenon irrespective of the state of magnetic and electrical ordering. For example, it could occur in paraelectric ferromagnetic materials or it can be mediated by other parameter such as strain.

Hence, the term multiferroic would mean a material exhibiting two or more of the above ordering mechanisms. More recently, multiferroic materials have become of tremendous interests because of potential device applications. For example, one can have multi-state memory element or sensors which can be operated in multi-mode or spintronic devices. However, there are challenges in finding a material that would act as a perfect multiferroic. Most multiferroic materials are not naturally occurring and are made in the laboratory. There are problems with respect to their fabricability, while their transition temperatures are often impractical. Despite these challenges, research is on to find a material which would emerge as a potential device material. In this module we discuss some of the basic aspects of multiferroics and a few multiferroic materials.

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Suggested Reading:

- N. A. Hill, J. Phys. Chem. B, 104, 6694-6709 (2000)
- M. Fiebig, J. Phys. D: Appl. Phys., 38, R123-R152 (2005)
- W. Eerenstein, N. D. Mathur and J. F. Scott, Nature, 442, 759 (2006)

## 8.1 Ferroic Material

Multiferroics are materials which possess more than one type of primary ferroic ordering in a single phase. The general features are

- Ferroics are materials like ferroelectrics, ferromagnetic or ferroelastics which exhibit a large change in the properties of the materials across a critical temperature and show a characteristic hysteresis loop with two equivalent response states at zero value of stimuli.
- The critical temperature, in general, is also accompanied with a symmetry breaking.
- Typically known orderings are ferroelectric (coupling of charge polarization and electric field), ferromagnetic (coupling of magnetic moment and magnetic field) and ferroelastic (coupling of stress and strain) ordering. Another proposed ordering mechanism is ferrotordicity which exhibit arrangement of magnetic vortices in an ordered manner, called tordozation.

Figure 8.1 explains the various possible scenarios. While there are a large number of magnetically and electrically polarizable materials, there are only a few materials which show ferroelectric and ferromagnetic ordering. Magnetoelectric materials are those materials which are simultaneously electrically and magnetically polarizable, while Multiferroics are strictly those materials which show ferroelectric and ferromagnetic ordering.

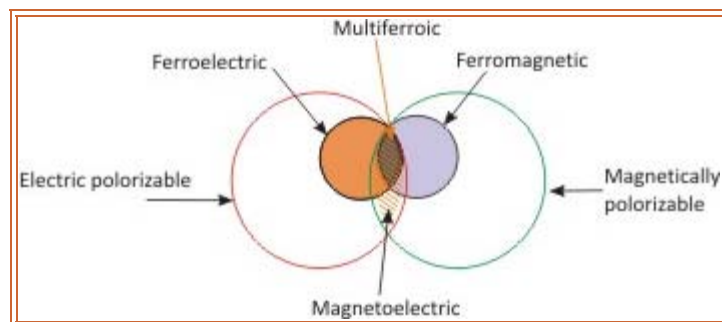


Figure 8.1 Classification of multiferroic and magnetoelectric materials

While, strictly speaking multiferroism means only for those materials in which there is coupling of more than one order parameter, now a days, researchers have also started including antiferromagnetism as well as ferrimagnetism also with multiferroic materials.

The multiferroic materials are either rare earth manganites or ferrites or transition metal perovskite oxides. The examples are  $\text{TbMnO}_3$ ,  $\text{TbMn}_2\text{O}_5$ ,  $\text{HoMn}_2\text{O}_5$ ,  $\text{LuFe}_2\text{O}_4$ ,  $\text{BiFeO}_3$ ,  $\text{BiMnO}_3$  and  $\text{YMnO}_3$ . Some non-oxides are also multiferroics such as  $\text{BaNiF}_4$  and spinel chalcogenides, e.g.  $\text{ZnCr}_2\text{Se}_4$ .

Given that the multiferroic materials show more than one ferroic ordering, the envisaged applications are numerous. Some of these applications can be future memory devices with multiple degree of control, sensors and actuators that be controlled by more than one type of stimuli, spintronic devices where spin of electron can be controlled electrically.

Recent reports also classify the multiferroics into Type I and Type II multiferroics. Type I

multiferroics are those materials in which the source of ferroelectricity and magnetism is different and the effects are fairly independent of each other, albeit with a small degree of coupling. In contrast, type II materials are those where magnetism causes the existence of ferroelectricity attributed to the strong coupling between two states. However, the magnitude of polarization in these materials remains very small, typically less than  $10^{-2} \mu\text{C}/\text{cm}^2$ .

There are no text books yet on Multiferroics, however there are a few good reviews<sup>1,2,3,4</sup> in the international journals which can be referred for an elaborate reading. These reviews have also been source of much of the basic information in this module.

<sup>1</sup>N. A. Hill, J. Phys. Chem. B, 104, 6694-6709 (2000)

<sup>2</sup>M. Fiebig, J. Phys. D: Appl. Phys., 38, R123–R152 (2005)

<sup>3</sup>W. Eerenstein, N. D. Mathur and J. F. Scott, Nature, 442, 759 (2006)

<sup>4</sup>D. Khomskii, Physics, 2, 20 (2009)

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## 8.2 Historical Perspective

Magnetoelectric effect was first observed by Rontgen in 1888 and by Pierre Curie in 1894 in two independent studies. Rontgen found that a dielectric when moved in an electric field, became magnetized and conversely it became polarized when moved in a magnetic field. In contrast, Curie pointed out the magnetoelectric effect based on symmetry considerations. The term magnetoelectric was first used by Debye in 1926.

The first material with magneto-electric switching was  $\text{Cr}_2\text{O}_3$  with small magnitudes of induced polarization and magnetization. Subsequently the research was carried on various materials and it is now established that more than 80 compounds including  $\text{Ti}_2\text{O}_3$ ,  $\text{GaFeO}_3$ , boracites, phosphates showed magnetoelectric effect.

The first ever discovered multiferroic material that was simultaneously ferroelectric and ferromagnetic, was nickel iodine boracite,  $\text{Ni}_3\text{B}_7\text{O}_{13}\text{I}$ . Subsequently many studies were made on various boracite compounds. However, most of them had quite complex crystal structures and materials were not very useful from technological viewpoint.

This was followed by studies on mixed perovskites, essentially solid solutions of two perovskite oxide compounds. Russian scientists took the lead in these investigations where they replaced some of the  $d^0$  type cations in the ferroelectric perovskite oxides with magnetic  $d^n$  type elements in order to induce magnetic ordering. One of first such compounds to be discovered was a solid solution of  $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$  and  $\text{Pb}(\text{Mg}_{1/2}\text{W}_{1/2})\text{O}_3$ . In this compound, ferroelectricity was caused by diamagnetic Mg and W atoms while magnetic ordering is caused by  $\text{Fe}^{3+}$  ions. Some other candidates were lead based Fe or Co doped tungstates or tantalates which showed ferroelectricity and antiferromagnetic ordering. However, most of these materials had either very low Curie temperatures or Neel temperature which prevented further research on these.

Subsequently, the research focus was on other perovskite materials which are either manganites or ferrites and have been more promising than previously research materials and will be discussed later in this module.



### 8.3 Requirements of a Magnetoelectric and Multiferroic Material

There are many material requirements which need to be fulfilled for a material to be called as multiferroic. For instance, for ferroelectricity, a material must be non-centrosymmetric to possess spontaneous electrical polarization and there are only a limited number of point groups (out of 32) which allow an unique polar direction. Similarly, spontaneous magnetic moment is permitted by 31 point groups. Out of these, 13 point groups allow occurrence of both the properties simultaneously. Since this is not a small number; it is probably unlikely that symmetry plays an important role in determining a multiferroic.

Electrically, while a ferroelectric material must be an insulator, it is not a constraint for a ferromagnetic material. For most ferromagnets, electronically speaking, the conductivity is due to high density of states at the Fermi level while the same is not true for ferroelectrics and insulators. However, there are a few magnetic oxides, such as half metallic magnets and ferrimagnetic oxides which show reasonable spontaneous magnetism while simultaneously being semiconducting or insulating.

As far as the chemistry of the material is concerned, most ferroelectrics require ions whose shells are filled and in case of perovskites the B-atom at the centre of  $\text{BO}_6$  octahedra must have  $d^0$  type electron configuration. In contrast, magnetic systems require d-orbitals to be partially occupied for magnetic ordering to develop. Latter also puts constraints to maintaining the center of symmetry in these systems.

Among type I multiferroics, multiple mechanisms of ferroelectricity have been proposed<sup>5</sup>. For example, in mixed perovskites, it has been suggested that  $d^0$  ions being ferroelectrically active shift from the center of  $\text{O}_6$  octahedra while magnetic order is maintained by  $dn$  ions. In contrast, in materials like  $\text{BiFeO}_3$ , ferroelectricity is believed to arise due to the ordering of lone pairs of Bi in one direction such as [111]. Another proposed mechanism for ferroelectricity is charge ordering i.e. if after charge ordering has occurred, the sites have different charges and bonds turn out to be of unequal lengths. This is seen in materials like  $\text{TbMn}_2\text{O}_5$ . Finally, materials like  $\text{YMnO}_3$  exhibit geometric ordering due to tilting of rigid  $\text{MnO}_5$  polyhedra, resulting in Y and O atoms coming closer to each other forming dipoles.

Another factor that could be analyzed is the size of small cation, especially in the perspective of perovskites. However, upon comparison, one finds that this is not a valid argument as sizes vary considerably for different kinds of compounds.

Another contrast between ferroelectric and ferromagnetically ordered systems is that the way structure is distorted. While ferroelectrics undergo a phase transition as temperature changes, low temperature phase being non-centrosymmetric, ferromagnetic materials show significant Jahn-Teller distortion arising from partially filled d-shells. The latter is almost absent in most ferroelectrics as it has been postulated that Jahn-Teller distorted structure may have less driving force for off-center displacement of B-ions in the octahedra.

Another condition which ferroelectric materials show is that they possess a time reversal symmetry but do not exhibit a space inversion symmetry (i.e. polarization reverses in space). On the other

hand, ferromagnetic materials possess space inversion symmetry but do not exhibit time inversion symmetry.

So, in summary, while there is no constraint on various material parameters which prevent materials from being multiferroic i.e. simultaneously ferroelectric and ferromagnetic, a multiferroic does not possess either time reversal or space inversion symmetry.

<sup>5</sup>D. Khomskii, Physics, 2, 20 (2009)

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## 8.4 Magnetoelectric Coupling

Landau theory describes the magnetoelectric effect in a single phase material through expansion of the free energy expression as

$$F(E, H) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j - \alpha_{ij} E_i H_j + \frac{\beta_{ijk}}{2} E_i H_j H_k + \frac{\gamma_{ijk}}{2} H_i E_j E_k + \dots \quad (8.1)$$

where E and H are the electric and magnetic field respectively. Here  $\epsilon$  and  $\mu$  are the dielectric permittivity and magnetic permeability respectively. The second and the third term in Equation (8.1) are the temperature dependent electrical polarization,  $P_i^S$ , and magnetization,  $M_i^S$ . Fourth and fifth terms describe the effect of electrical and magnetic field on the electrical and magnetic behavior respectively, while sixth term consisting of  $\alpha_{ij}$  describes linear magnetoelectric coupling. The next two terms consisting of  $\beta_{ijk}$  and  $\gamma_{ijk}$  are third rank tensors and represent higher order coupling coefficients.

Differentiation of Equation (8.1) with respect to electric and magnetic fields respectively leads to polarization and magnetization which are as follows:

$$P_i = - \frac{\partial F(E, H)}{\partial E_i} = P_i^S + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{\beta_{ijk}}{2} H_j H_k + \dots \quad \text{and}$$

$$M_i = - \frac{\partial F(E, H)}{\partial H_i} = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_i + \beta_{ijk} E_i H_j + \dots \quad (8.2)$$

In most cases, we are interested to know about the linear magnetoelectric coefficient,  $\alpha_{ij}$ , as magnetoelectric effect is linear in most compounds. This coefficient basically quantifies the dependence of polarization on magnetic field or of magnetization on the electric field. In case of multiferroics, although many linear magnetoelectric effects are expected because these materials often possess large susceptibility and permeability respectively, this is not a necessary condition as some ferroelectrics and ferromagnets do show small dielectric susceptibility and magnetic permeability.

In addition to direct coupling, there may be instances of indirect coupling mediated by strain. This is likely to arise in two phase systems where two components are couple via strain. However, more recently, in cubic  $\text{SrMnO}_3$  and  $\text{EuTiO}_3$ , strain mediated ME effect is observed in single phase.

Indirect measurements of magnetoelectric coupling include measurement of changes in the magnetization near the magnetic transition temperatures or changes in dielectric constant near the magnetic transition temperature. However, such measurements do not provide any mechanistic insight into the coupling constant. Direct measurements measure magnetic response of material to an applied electric field or electric response to an applied magnetic field.





## Module 8: Multiferroic and Magnetoelectric Ceramics

### Type I Multiferroics

#### 8.5 Type I Multiferroics

There are a few type I single phase multiferroics. As mentioned earlier, Type I multiferroics are the materials which have different sources of ferroelectricity and magnetism with the two effects being quite independent of each other. However, a small degree of coupling cannot be ruled out.

In this section, we will mainly have a look at most studied compounds:

- [Bismuth Ferrite \( \$\text{BiFeO}\_3\$ \)](#).
- [Bismuth Manganite \( \$\text{BiMnO}\_3\$ \)](#) and
- [Hexagonal Manganites](#)

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### 8.5.1 Bismuth Ferrite ( $\text{BiFeO}_3$ )

One of the most studied multiferroic is Bismuth ferrite or  $\text{BiFeO}_3$  (BFO), primarily because it has very high ferroelectric transition temperature ( $T_C = 1100 \text{ K}$ )<sup>6</sup> and shows G-type antiferromagnetism with cycloidal spin structure with Neel temperature ( $T_N$ ) of  $\sim 650 \text{ K}$ .<sup>7</sup>

In its ferroelectric state, as shown in Figure 8.2, BFO possesses a rhombohedrally distorted  $\text{ABO}_3$  type perovskite structure with space group  $R3c$  having lattice parameters,  $a_r = 3.965 \text{ \AA}$  and  $\alpha_r = 89.4^\circ$  at room temperature.<sup>8</sup> Above the Curie temperature, the structure changes to a high symmetry cubic phase.

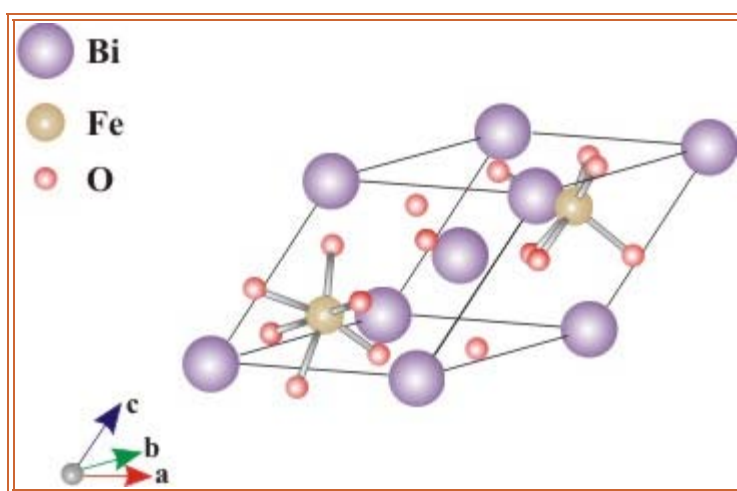


Figure 8.2 Schematic diagram of the crystal structure of  $\text{BiFeO}_3$

The material has been shown to be ferroelectric at room temperature in both single crystal and thin film form high remanent polarization, more than  $50 \mu\text{C}/\text{cm}^2$ .<sup>9,10</sup> However, polycrystalline thin films can be leaky depending upon the methods of preparation and other conditions.<sup>11</sup> On the other hand, while magnetic character of pure phase in single crystal form is antiferromagnetic, there have been a few controversies on magnetism in thin films. Often, impurities like  $\text{Fe}^{2+}$  and other iron borne impurities as well as deoxygenation can result in significant magnetism.<sup>12</sup> The material is also prone to containing defects as well as difference valencies of Fe which can alter the material properties.

The periodic spin spiral results in zero magnetic moment and hence linear magnetoelectric effects average to approximately zero. However, properties of  $\text{BiFeO}_3$  can also be altered by making chemical substitutions. For example substitution of A-site cation (Bi) by ions such as Ba or Nd<sup>13</sup> gives rise to significant magnetism in the compound while substitution of B-site cation (Fe) by elements such as Zr<sup>14</sup> results in alteration in the defect chemistry as well as change in the leakage characteristics of the material. These effects are attributed to the breaking of spin spiral upon doping. Similarly, epitaxial constraints can also result in this breaking of spin spirals.

<sup>6</sup>R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* 8, 1073 (1970)

<sup>7</sup>P. Fischer, M. Polomska, I. Sosnowska, and M. Szymanski, J. Phys. C 13, 1931 (1980)

<sup>8</sup>G Catalan and J.F. Scott, Advanced Materials, 21, 2463 (2009).

<sup>9</sup>D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, Phys. Rev. B 76, 024116 (2007).



<sup>10</sup>J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, Science 299, 1719 (2003)

<sup>11</sup>A. Z. Simoes, A. H. M. Gonzalez, L. S. Cavalcante, C. S. Riccardi, E. Longo, and J. A. Varela, J. Appl. Phys. 101, 074108 (2007).

<sup>12</sup>H. Bea, M. Bibes, A. Barthelemy, K. Bouzehouane, E. Jacquet, A. Khodan, J. P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson and M. Viret, Applied Physics Letters 87 (7), 072508 (2005).

<sup>13</sup>V. A. Khomchenko, D. A. Kiselev, M. Kopcewicz, M. Maglione, V. V. Shvartsman, P. Borisov, W. Kleemann, A. M. L. Lopes, Y. G. Pogorelov, J. P. Araujo, R. M. Rubinger, N. A. Sobolev, J. M. Vieira, and A. L. Kholkin, J. Magn. Magn. Mater. 321, 1692 (2009).

<sup>14</sup>S. Mukherjee, R. Gupta, A. Garg, V. Bansal, and S. Bhargava, J. Appl. Phys. 107, 123535 (2010)

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### 8.5.2 Bismuth Manganite ( $\text{BiMnO}_3$ )

Bismuth manganite is an interesting multiferroic material with a perovskite structure. It is a low temperature ferromagnet and a room temperature ferroelectric. The material shows ferromagnetic ordering below 105 K attributed to the orbital ordering of B-site ions *i.e.*  $\text{Mn}^{3+}$  ions and a magnetization of  $3.6 \mu_B$  per formula unit.<sup>15</sup> The material has a perovskite triclinic structure which changes to monoclinic structure at  $\sim 450$  K and then to a non-ferroelectric orthorhombic phase at  $\sim 770$  K.<sup>16</sup> However, the trouble with this material for device application has been its low resistivity, especially in polycrystalline form. The bulk form of material has been shown to exhibit multiferroic behavior near 80 K<sup>17</sup> and negative magneto-capacitance effect in the vicinity of magnetic transition temperature ( $T_m$ ) with -0.6% change in the dielectric constant near  $T_m$ .<sup>16</sup> The problem which arises with this material is that it requires high pressures in bulk form<sup>17</sup>. In contrast, recent work has shown that it can be made resistive in thin film form which can be prepared with much ease.<sup>18</sup>

<sup>15</sup>H. Chiba, T. Atou, and Y. Syono, Journal of Solid State Chemistry, Volume 132, 139-143 (1997)

<sup>16</sup>T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, Physical Review B, Volume 67, 180401(R) (2003)

<sup>17</sup>A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham, C. N. R. Rao, Solid State Communications, 122, 49-52 (2002)

<sup>18</sup>W. Eerenstein, F. D. Morrison, J. F. Scott, and N. D. Mathur, Appl. Phys. Lett. 87, 101906 (2005)

### 8.5.3 Hexagonal Manganites ( $\text{TbMnO}_3$ , $\text{YMnO}_3$ )

Hexagonal manganites are another interesting class of manganites and are depicted by the general formula  $\text{RMnO}_3$  where R is typically a rare earth ion such as Y and Ho. These materials simultaneously exhibit ferroelectricity and antiferromagnetic ordering of magnetic Mn ions. In general, rare earth elements having smaller ionic radii, tend to stabilize hexagonal phase of manganites,  $\text{RMnO}_3$ <sup>19</sup> (R = Sc, Y, Ho, Er, Tm, Yb, Lu) with space group  $\text{P6}_3\text{cm}$ .<sup>20</sup> In spite of having a chemical formula,  $\text{ABO}_3$ , similar to the perovskites, hexagonal manganites have altogether different crystal and electronic structure. In contrast to the conventional perovskites, hexagonal manganites have their  $\text{Mn}^{3+}$  ions with 5-fold coordination, located at the center of an  $\text{MnO}_5$  trigonal bi-prism. R ions, on the other hand, have 7-fold coordination unlike the cubic coordination in perovskites. The  $\text{MnO}_5$  bi-prisms are two dimensionally arranged in space and are separated by a layer of  $\text{R}^{3+}$  ions. Figure 8.3 shows a schematic representation of  $\text{YMnO}_3$  unit cell showing ionic arrangements within the structure.

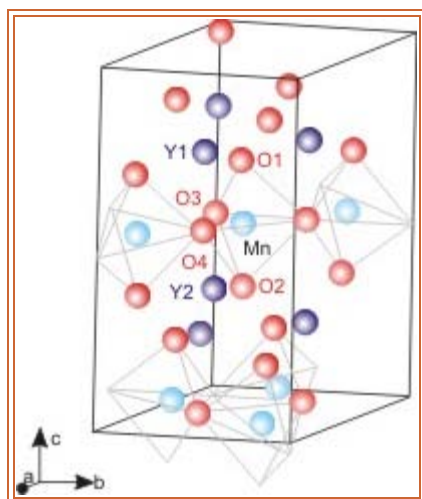


Figure 8.3 Crystal structure of hexagonal  $\text{YMnO}_3$ .<sup>21</sup>

Crystal field level scheme of  $\text{Mn}^{3+}$  ions in hexagonal  $\text{RMnO}_3$  is also different from that of  $\text{Mn}^{3+}$  ions with octahedral coordination. Here, the  $d$ -levels are split into two doublets and an upper singlet. As a result, four  $d$ -electrons of  $\text{Mn}^{3+}$  occupy two lowest lying doublets and unlike  $\text{Mn}^{3+}$  ion in octahedral coordination, there is no degeneracy present. Consequently,  $\text{Mn}^{3+}$  ions in these compounds are not Jahn-Teller ions.<sup>22</sup>

Hexagonal  $\text{RMnO}_3$  are found to possess considerably high ferroelectric transition temperature ( $> 500$  K). However, their Neel temperature is far below the room temperature. Table 1 lists the ferroelectric and magnetic transition temperatures, spontaneous polarization ( $P_S$ ) and effective paramagnetic moment  $\mu_{\text{eff}}$  of some common  $\text{RMnO}_3$  along with their structural parameters.

The mechanism of ferroelectricity in these compounds also differs from that of the conventional perovskite oxides. In case of  $\text{YMnO}_3$ , it was observed that off-centering of  $\text{Mn}^{3+}$  ion from the center of

the  $\text{MnO}_5$  biprism is very small and cannot be considered to contribute toward ferroelectricity. Apparently it turns out that R ions (Y, here) contributes most toward ferroelectricity by having large R-O dipole moments. However, in reality, ferroelectricity in these materials has different origin and can be considered as accidental by-product. Similar to  $\text{BO}_6$  octahedra in perovskite oxides ( $\text{ABO}_3$ ),  $\text{MnO}_5$  trigonal biprism in  $\text{RMnO}_3$ , tilts and rotates in order to ensure closest packed structure. Such tilting of  $\text{MnO}_5$  trigonal biprism results in loss of inversion symmetry in the structure and brings about ferroelectricity.<sup>22</sup> Since the mechanisms of ferroelectric and magnetic ordering in the above materials are quite different in nature, giant effect of magnetoelectric coupling is understandably not present.<sup>22</sup>

Table 8.1 Lattice parameters, Neel temperature ( $T_N$ ) and ferroelectric Curie ( $T_C$ ) temperature, effective paramagnetic moment ( $\mu_{\text{eff}}$ ) and spontaneous polarization ( $P_S$ ) of some common hexagonal manganites.<sup>23,24,25</sup>

Compound	a(Å)	c(Å)	$T_N$ (K)	$T_C$ (K)	$\mu_{\text{eff}}$ (in $\mu_B$ )	$P_S$ ( $\mu\text{C}\cdot\text{cm}^{-2}$ )
ScMnO <sub>3</sub>	5.833	11.17	129	-	-	-
YMnO <sub>3</sub>	6.139	11.39	80	920	89	5.5
HoMnO <sub>3</sub>	6.142	11.42	76	873	11.1	5.6
ErMnO <sub>3</sub>	6.112	11.40	80	833	10.5	-
TmMnO <sub>3</sub>	6.092	11.37	86	>573	8.6	0.1
YbMnO <sub>3</sub>	6.062	11.36	87	993	6.4	5.5
LuMnO <sub>3</sub>	6.042	11.37	96	>750	5.2	7.5

<sup>19</sup>S. Lee, A. Pirogov, M. Kang, et al., Nature 451, 805 (2008)

<sup>20</sup>H. L. Yakel, W. C. Koehler, E. F. Bertaut, et al., Acta. Crystallogr. 16, 957 (1963)

<sup>21</sup>M. Zaghrioui, V. Ta Phuoc, R. A. Souza, et al., Physical Review B 78, 184305 (2008)

<sup>22</sup>D. I. Khomskii, Journal of Magnetism and Magnetic Materials 306, 1 (2006)

<sup>23</sup>J. G. Park, 1st APCTP Workshop on Multiferroics (2008)

<sup>24</sup>K. Uusi-Esko, J. Malm, N. Imamura, et al., Materials Chemistry and Physics 112, 1029 (2008)

<sup>25</sup>L. J. Wang, S. M. Feng, J. L. Zhu, et al., Applied Physics Letters 91, 172502 (2007)

## 8.6 Type II Multiferroics

This class of multiferroics is of the materials which show ferroelectricity in their magnetically ordered state and that too of a particular type. Moreover, very strong coupling between ferroelectric and magnetic order parameters has also been observed. In 2003, Kimura et al. reported<sup>26</sup> presence of spontaneous polarization in the magnetized state of the  $\text{TbMnO}_3$ .  $\text{TbMnO}_3$  has various magnetic structures: it is an incommensurate antiferromagnet between 27 and 42 K and is commensurate antiferromagnet between 7 and 27 K. It is in the commensurate state between 7 and 27 K, the material show ferroelectricity. This discovery was followed by observation of similar effect in  $\text{TbMn}_2\text{O}_5$  by Hur *et al.*<sup>27</sup> Subsequently variety of other materials have also been investigated such as  $\text{Ni}_3\text{V}_2\text{O}_8$ ,  $\text{MnWO}_6$  showing this effect. Magnetic spin structure can be either a spiraling cycloid type or a collinear type.

<sup>26</sup>T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima and Y. Tokura, Nature, 426, p55, (2003)

<sup>27</sup>N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha and S-W. Cheong, Nature 429, 392-395 (2004)

## 8.7 Two Phase Materials

Another method to for achieving high degree of magnetoelectric coupling is to mix ferroelectric (e.g. BaTiO<sub>3</sub>) and ferromagnetic (e.g. CoFe<sub>2</sub>O<sub>4</sub>) materials and utilize the strain between two phases to introduce magneto-electric coupling. Such a coupling requires that two phase have good contact between them i.e. to have an interface through which properties can coupled such as in the form of composites, epitaxial multilayers and laminates. For a few systems, the data is shown in the table below.

Table 8.2 Magnetoelectric coupling constant data for selected two-phase magnetoelectric systems

Type of system	Materials	Coupling constant (mV/cm-Oe)
Composite <sup>28</sup>	BaTiO <sub>3</sub> and CoFe <sub>2</sub> O <sub>4</sub>	50
Laminated composite <sup>29</sup>	Terfenol-D in polymer matrix and PZT in polymer matrix	3,000
Laminate <sup>30</sup>	Terfenol-D/PZT	4,800
Laminate <sup>31</sup>	La <sub>0.7</sub> Sr <sub>0.3</sub> MnO <sub>3</sub> and PZT	60
Laminate <sup>32</sup>	NiFe <sub>2</sub> O <sub>4</sub> and PZT	1,400
Epitaxial thin film structures <sup>33</sup>	BaTiO <sub>3</sub> and CoFe <sub>2</sub> O <sub>4</sub>	--
Epitaxial thin film structures <sup>34</sup>	BiFeO <sub>3</sub> and CoFe <sub>2</sub> O <sub>4</sub>	--

In two phase structures, as evident from some of references, one can create large changes in the magnetization owing to strain due to the ferroelectric phase transition of the ferroelectric material during film growth or one can also attempt to alter the magnetic structure by applying a field the piezoelectric material which thereby generates a strain in the magnetic material in the vicinity. Epitaxial growth of layers allows very good interfacial contact between two materials as shown in case of BaTiO<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> which has potential to improve the coupling of parameters

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## Module 8: Multiferroic and Magnetoelectric Ceramics

### Summary

#### Summary

Multiferroic and magnetoelectric materials are a new class of materials which show interdependence of magnetic and electric properties on each other. Moreover, multiferroics simultaneously exhibit ferroelectric and magnetic ordering in a single phase with some degree of coupling between order parameters. While a multiferroic material has to be a single phase material, magnetoelectric materials can be single phase as well as a mixture of two phases showing interface mediated magnetoelectric coupling. These materials have the potential for a variety of exciting applications such as dual memory devices, spintronic devices, high frequency applications etc. However, the applications are realized yet due to lack of materials and difficulty in achieving the desired effects in the available materials. The single phase materials which have been studied well enough in both bulk and thin film form are  $\text{BiFeO}_3$ ,  $\text{BiMnO}_3$  and hexagonal manganites while two phase mixture studies include  $\text{BaTiO}_3$  and  $\text{CoFe}_2\text{O}_4$ .

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