Magnetoelectric Coupling in Bismuth Ferrite—Challenges and Perspectives

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Abstract: Multiferroic materials belong to the sub-group of ferroics possessing two or more ferroic orders in the same phase. Aizu first coined the term multiferroics in 1969. Of late, several multiferroic materials’ unique and robust characteristics have shown great potential for various applications. Notably, the coexisting magnetic and electrical ordering results in the Magnetoelectric effect (ME), wherein the electrical polarization can be manipulated by magnetic fields and magnetization by electric fields. Currently, more significant interests lie in significantly enhancing the ME coupling facilitating the realization of Spintronic devices, which makes use of the transport phenomenon of spin-polarized electrons. On the other hand, the magnetoelectric coupling is also pivotal in magnetic memory devices wherein the application of small electric voltage manipulates the magnetic properties of the device. This review gives a brief overview of magnetoelectric coupling in Bismuth ferrite and approaches to achieve higher magnetoelectric coupling and device applications.

Keywords: magnetoelectric coupling; bismuth ferrites; strain engineering; doping

1. Introduction

Magnetoelectric coupling has a long history; it has not only been a topic of theoretical interest for researchers but is also being used as a tool for a variety of practical applications. Hence, it is crucial to realize past discoveries, present challenges and strategize for the future. The relation between the electric and magnetic subsystems can vary among the materials and also existing conditions; for instance, Bismuth ferrite theoretically, at room temperature shows quadratic and higher-order relation, while a linear behavior is observed at application with high electric fields or magnetic fields around 10–18 T [1,2], for the bulk and about 3–6 T for thin film samples depending upon their substrate [3]. Recently there have been many review papers related to Bismuth ferrite (BFO) [4–7] and its magnetoelectric coupling but this paper stands out from the rest in providing theoretical background and practical knowledge needed in a way that could be understood by a reader who is even new to the topic. Most review papers do not provide any information regarding measurement techniques employed for magnetoelectric coupling and hence this review aims to bridge this gap so that a reader can acquire both theory and practical knowledge at the same time.

The interrelation between the electric and magnetic leading to the magnetoelectric effect is schematically represented in Figure 1. There are two main important events in history which marked the discovery of magnetoelectric effect (ME) effects:

1. Röntegen discovered in 1888 that the moving dielectric was magnetized in the electric field [8] and the converse effect of polarization in the magnetic field by Wilson [9].
2. Later in 1894, Curie suggested a possible existence of magnetoelectric behavior in crystals with only symmetry conditions [10].

![Figure 1](image-url)  
**Figure 1.** Schematic representation of interrelation between electric and magnetic fields with respect to their polarization.

It was Debye who first coined the term ‘magnetoelectric’ [11], followed by many unsuccessful efforts to demonstrate the same. For decades, researchers had failed to recognize the need for time-asymmetric media for exhibiting the ME effect, for instance, in the presence of a magnetic field or like the experiments of Röntegen. Ultimately, it was Dzyaloshinskii [12] who showed the manipulation of magnetization by the application of electric field and vice versa for antiferromagnetic Cr$_2$O$_3$. Since then, many materials were subjected to investigations for magnetoelectric behavior. Some of these materials along with bismuth ferrite are listed in Table 1.

**Table 1.** List of some materials showing magnetoelectric behavior and the property/condition essential for the same.

| Material              | Molecular Formula | Property/Condition                                                                 | Ref       |
|-----------------------|-------------------|------------------------------------------------------------------------------------|-----------|
| Bismuth ferrite       | BiFeO$_3$         | Coexistence of weak ferromagnetic and ferroelectric nature                         | [1]       |
| Manganese iodine      | (Mn$_3$B$_2$O$_{13}$I) | Low Temperature                                                                     | [13,14]  |
| boracite              |                   |                                                                                    |           |
| Yttrium manganese     | (YMn$_2$O$_3$)    | Low temperature                                                                     | [15,16]  |
| oxide                 |                   |                                                                                    |           |
| Bismuth oxide         | (Bi$_2$O$_3$)     | Low temperature                                                                     | [17]      |
| Terbium molybdate     | Tb$_2$ (MoO$_4$)$_3$ | Interaction of magnetoelectric and ferroelectric subsystems based on magnetostriction | [18]      |
| Gadolinium molybdate  | Gd$_2$ (MoO$_4$)$_3$ | Interaction of magnetoelectric and ferroelectric subsystems based on magnetostriction | [18]      |
| Lithium cobalt        | LiCoPO$_4$        | Orthorhombic magnetic point group and possesses the spontaneous magnetization direction parallel to the direction of the spin. | [19]      |
| phosphate             |                   |                                                                                    |           |
| Lithium nickel        | LiNiPO$_4$        | Orthorhombic magnetic point group and possesses the spontaneous magnetization direction parallel to the direction of the spin. | [20]      |
| phosphate             |                   |                                                                                    |           |
| Terbium phosphate     | TbPO$_4$          | Has magnetic point group 4/m/m/m                                                   | [21]      |

ME effect in chromium oxide was one of the main reasons for the excitement behind the 1st International Conference on Magnetoelectric Interaction Phenomena in Crystals (MEIPIC-1) conference held in 1973. However, the enthusiasm was soon lost, as most of the strategies which came out of the conference failed to give any significant results. Consequently, the second MEIPIC conference was
held after 20 years. During this time, the revival of interest in ME coupling was mainly due to newer experimental techniques, novel synthesis methods and also updated theoretical concepts [22].

This brief review on the ME effect of Bismuth ferrite deals with past discoveries, present investigations and future strategies for complete utilization into device application.

2. Bismuth Ferrite: Historical Background and Properties

The idea of the existence of ferromagnetic and ferroelectric crystals originated from investigations of Pierre Curie in the 1900s [10]. Ferroelectric switching was discovered by Valasek in 1920 [23] and magnetoelectricity was first understood theoretically by Dzyaloshinskii [12] for Cr$_2$O$_3$ and was experimentally discovered later by Astrov [24]. However, Cr$_2$O$_3$ failed to realize practical applications as it was paraelectric and antiferromagnetic, leading to discoveries into boracites. Unfortunately, even boracites were impractical for application as they had low symmetry with large unit cells and magnetoelectricity was exhibited only in low temperatures. A possible candidate to have all the features was Bismuth ferrite (BFO), whose study was pioneered by Smolenskii’s group in Leningrad in 1958–1960 (Now, its St. Petersburg) [25].

Bismuth ferrite was first discovered to harness its ferroelectric and magnetoelectric properties; the bulk BFO prepared in the 1960s–1970s were marred with high conductivity and secondary phases, which resulted in the loss of motivation over the years. It was not until the early 2000s that the research in single crystals [26], high-quality BFO thin films [27] and ceramics [28] brought back researchers into BFO. It is an ABO$_3$ type perovskite compound that crystalizes into rhombohedral R3c group, hence possessing multiferroic properties due to its noncentrosymmetric nature. In ABO$_3$, perovskite A is Bismuth (Bi) and occupies the corner of the perovskite unit cell, B is iron (Fe), the central atom with an oxygen octahedral arrangement. There is a tilting of oxygen octahedral, which doubles the pseudocubic unit cell giving rhombohedral unit cell. There is an equivalence between pseudocubic unit cell, rhombohedral and hexagonal unit cell representation and hence Figure 2 gives the hexagonal representation. The ferroelectric Curie temperature (T$_C$) of BFO is as high as $\sim$1103 K and antiferromagnetic Neel temperature (T$_N$) is $\sim$643 K. It exhibits a weak net magnetization as the G-type magnetic ordering with an incommensurate cycloidal spin structure having a periodicity of 62 nm. The chemical substitution of A and B sites are considered as one of the alternatives for enhancing the net magnetization via disruption of the cycloidal chain. Few basic properties of BFO are listed in Table 2.

![Image of Crystal Structure](https://example.com/image.png)

**Figure 2.** The crystal structure of Bismuth ferrite with hexagonal coordinates, drawn using BURAI software (software development credit: Satomichi Nishihara).
3. Bismuth Ferrite: Historical Background and Properties

The magnetic symmetry in BFO can be described as G-type antiferromagnet, which is distorted to break the symmetry inducing a small canting, resulting in net magnetization via Dzyaloshinskii—Moriya interaction. A ferroelectrically induced spin cycloid appears because of polarization’s coupling with magnetization gradients (Figure 3), averaging the canted net magnetism \( \beta - \frac{1}{2} \) differently low for single-phase BFO (see in accordance to experiments in Reference [30]). The presence of the spin cycloid also negates any linear ME coupling present between polarization \( P \) and magnetization \( M \) and hence only higher-order ME effects are found up to several Tesla of an applied field. The complete ME tensor was characterized in Reference [30], with \( P_3 \) parallel to spontaneous polarization in the hexagonal coordinate axis is given as:

\[
P_1 = \beta_{111}(H_1^2 - H_2^2) + \beta_{113}H_1H_3 \\
P_2 = \beta_{111}H_2H_3 - 2\beta_{113}H_1H_2 \\
P_3 = \beta_{333}(H_1^2 - H_2^2) - \beta_{333}H_3^2,
\]

where \( \beta \) is the nonlinear (quadratic) ME susceptibility and \( H \) is the magnetic field. Where \( \beta_{111} = 5.0 \times 10^{-19} \text{ s} \cdot \text{A}^{-1} \), \( \beta_{113} = 8.1 \times 10^{-19} \text{ s} \cdot \text{A}^{-1} \) and \( \beta_{333} = 2.1 \times 10^{-19} \text{ s} \cdot \text{A}^{-1} \) in accordance to experiments in Reference [30].

![Figure 3](image_url)

**Figure 3.** Resultant spins of antiferromagnetic moments which average to zero over a period of 62–64 nm forming the spin cycloid, contained in the polarization plane usually seen in bulk material \( P [111] \).

| Property                              | Reported Value | Ref  |
|---------------------------------------|----------------|------|
| Lattice parameter (a) in nm           | 0.3965         | [31] |
| Rhombohedral angle                    | 89.3–89.4°     | [31] |
| Fe—O—Fe angle                        | 154–156°       | [32] |
| Curie temperature in K                | 1103           | [33] |
| Neel Temperature in K                 | 643            | [33] |
| Refractive index                      | 2.62           | [34] |
| Dielectric constant (room temperature) at GHz radiation | 30            | [35] |
| Bandgap in eV                         | 2.2–2.8        | [36–38] |
| Young’s modulus at 1000 μN in GPa     | 26             | [39] |
| Magnetoelectric coupling coefficient α in V cm\(^{-1}\)·Oe\(^{-1}\) | 0.010 (sol-gel) | [40] |
| \( \frac{dE}{H} \)                    | 0.144 (Dy doped) | [40] |
| 3 (epitaxial thin film)               |                | [27] |

From Equation (4) in the following pages, it can be seen that the magnetoelectric coupling is dependent on both ferromagnetic as well as ferroelectric nature (susceptibilities). Due to the contrasting origins of these ferroic behaviors, the ME coefficient is inherently low for single-phase BFO (see in Table 2 for values). This low coupling is detrimental to applications as it eliminates the advantage of having a multiferroic nature.
The multiferroic nature of BFO, with ferroelectricity arising from Bi and ferromagnetism arising from Fe, was extensively studied both theoretically and experimentally and few of the possible strategies to enhance ME coupling are as follows.

3.1. Strain-Induced ME Coupling

The strain calculations can be done using Hooke’s law

$$\Delta \varepsilon = \frac{\sigma}{E'},$$

where $\Delta \varepsilon$ is the strain, $\sigma$ is the stress and $E'$ is Young’s modulus. The Young’s modulus can be taken from reported studies like in Reference [39]. The lattice strain for a- ($\Delta \varepsilon_a$) and c- ($\Delta \varepsilon_c$) axes can be calculated as

$$\Delta \varepsilon_a = \frac{a' - a}{a},$$
$$\Delta \varepsilon_c = \frac{(c' - c)}{c}. (3)$$

Here $a'$ and $c'$ are the bulk lattice constants of BFO, $a$ and $c$ are lattice constants of BFO in thin film state. It was reported in Reference [41] that the $\sigma$ for the c-axis changed sign for the films grown using the spin coating method, which meant that the film changed from being under compressive strain to being partially tensile strained after a particular concentration. Few known methods of synthesis of BFO thin films are summarized in Table 3, along with their advantages and disadvantages.

In 2005, Ederer and Nicola Spaldin showed theoretically, through first-principle calculations, the effect of strain and oxygen vacancies on the ME coupling in BFO [17]. This paper held great importance as strain was considered to be one of the remedies for enhancing ME coupling. Strain effects in conventional ferroelectrics can enhance polarization and changes in the Curie temperature [42].

Magnetic properties like saturation magnetization can also be affected by strain. In thin films, experiments conducted also showed significant dependence of magnetic and ferroelectric properties on the film’s thickness; possible explanations were due to increased strain with decreased thickness and the concentration of defects such as oxygen vacancies [27,43]. The DFT calculations showed that spontaneous polarization increased marginally with increasing compressive strain; however, the observed increase is as large as other conventional ferroelectrics. This meager change in ferroelectric properties was mainly due to the weak dependence of strain on ionic displacements and the possible causes of this weak dependence are:

- The driving mechanism of ferroelectricity in BFO is different from other conventional ferroelectrics.
- The oxygen octahedra rotate around the polar axis in the presence of strain and the resulting condition is less favorable for ionic displacements.
- The general ‘high stability’ of ferroelectrics with high Curie temperature and large energy displacements between the centrosymmetric reference and ground state.

In thin films oriented in (001) direction, theoretically, if the in-plane stress is large, there will be substantial out-of-plane relaxation, leading to an increased out-of-plane polarization component even with relatively small strain. Experimentally, the out-of-plane component was relatively small in thicker films (400 nm: about 5 emu·cm$^{-3}$) when compared to thinner films (70 nm: about 150 emu·cm$^{-3}$) as seen in Reference [27].

The magnetization in BFO is mainly dependent on the Fe-O-Fe bond angle, the oxygen octahedral; therefore, the changes in the magnetization of BFO due to oxygen vacancies and strain [44] cannot elucidate the large increase in the observed magnetization in BFO films (nearly 1 $\mu_B$ per unit cell) [27].

3.2. Doping Induced ME Coupling

The canting and the suppression of the spin cycloid can also be done through chemical substitution. Substitution of Bi ions by lanthanides is preferred as they result in a change in the parent structure. The introduction of rare-earth dopants increases the anisotropy constant to a level where the existing
spatially modulated structure tends to become energetically unfavorable. The dysprosium doped BFO prepared through sol-gel method showed maximum ME constant of $\alpha = 0.144 \text{ V cm}^{-1}\text{Oe}^{-1}$ while undoped BFO showed about $0.010 \text{ V cm}^{-1}\text{Oe}^{-1}$ [40]. However, epitaxial thin films have shown a larger magnetoelectric effect with $\frac{dE}{dH} = 3 \text{ V cm}^{-1}\text{Oe}^{-1}$ [27].

The A-site doping alters the structure leading to the suppression of the spin cycloid. It was in Reference [45], where the authors used Ca, Sr, Pb and Ba for doping BFO and found that the crystal structure remained noncentrosymmetric (R3c) but, it showed spontaneous polarization and the magnetic states were dependent on the ionic radius of the dopant, a larger dopant with bigger ionic radius showed better suppression of the spin cycloid.

Another way would be to directly substitute aliovalent transition metal ions in place of Fe to suppress the spin cycloid or cant the antiferromagnetic moments. Ions of Ti [46], Nd [47] are commonly preferred to increase resistivity and boost ferroelectric properties. In Reference [46], the Ti substituted BFO was used to understand the effect of poling (magnetic) on the ferroelectric hysteresis and the dielectric variation with the magnetic field. The high dielectric constant in the presence of the magnetic field was attributed to the field-induced stress, which is piezoelectric in turn generating the electric field.

Uniyal and Yadav [48] showed that in Pr co-doped BLFO (lanthanum doped BFO) prepared using solid-state reaction technique, the resistivity increased and the successful observation of polarization hysteresis loop was reported. Further, the observed spontaneous magnetic moment in all the films was enhanced with the lowering of temperature. A strong dependency of remnant polarization and dielectric constant on the magnetic field’s strength is direct evidence of enhancing the ME effect with Pr doping. This dependence comes from the ferroelectricity, which is accompanied by ferroelastic strain distorting the lattice and hence switching of polarization will also result in ferroelastic domains state. In BFO, the antiferromagnetic moments are coupled to the ferroelastic strain-state that is always perpendicular to ferroelectric polarization. Hence with the switching of polarization, there is also switching of antiferromagnetically ordered spins and vice versa [49]. It is important to note that just by switching of polarity, there will not be a change in the orientation of magnetic easy planes but there needs to be a change in the polarization direction. It was seen that by switching the polarization to an angle other than 180° (it can shift by either 71° or 109° in a rhombohedral system), the magnetic easy planes also rotated. This observation is of great importance as it paves the way for exploring voltage-controlled magnetization for device application.

Future strategies would be to investigate effective co-dopants resulting in a better ME effect than undoped or singly doped counterparts.
Table 3. Popular methods to produce Bismuth ferrite (BFO) thin films.

| Method                          | Advantages                                                                 | Disadvantages                                                                 | Ref  |
|--------------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------|------|
| Pulsed Laser Deposition        | Versatile and straightforward process. High deposition rates compared to techniques like molecular beam epitaxy. Stoichiometric evaporation is possible. Reasonable control over the film quality and orientation. | Non-conformal coverage, too complex models can hinder theory-based improvements and needs a vacuum environment. | [47] |
| Chemical Vapor Deposition      | Versatile method due to its application to many base materials like ceramics, glass, metal and metal alloys. It can be used to coat irregular surfaces evenly. Can produce films with high purity and density as numerous parts of the film are simultaneously coated. | Operates at a relatively higher temperature. By-products from the precursors can be toxic. A large number of parameters need to be controlled to reproduce condition for the production of the film. | [50] |
| Molecular Beam Epitaxy (MBE)   | Good control over doping profile and concentration. Single crystalline epitaxial films can be easily grown with minimum or no secondary phases. | Needs ultra-high vacuum. Relatively expensive than other CVD methods. The growth rate is slow and hence deposition can be time-consuming. | [51] |
| Magnetron Sputtering           | Low substrate temperatures. Epitaxial, highly oriented single crystalline films can be obtained which are devoid of secondary phases. Good film density with moderate to high stresses. | Vacuum requirement. Relatively expensive and is complex. High energy target material can cause substrate heating. | [52] |
| Sol-gel                        | Manipulation of chemical composition is relatively easier along with the doping composition. A relatively more straightforward method with no need for a vacuum. | Variety of factors like $p^{11}$, annealing temperature, number of layers, concentration, precursors, etc., play a vital role. It is challenging to obtain phase-purity. Relatively rough films as compared to films produced using the physical method. | [53] |
| Spray Pyrolysis                | Low-temperature deposition. Manipulation of chemical composition and doping is relatively straightforward. A relatively simpler method with no need for a vacuum. | The one-step reaction to produce the film can be a double-edged sword; BFO being metastable, secondary phases in the films are unavoidable. | [54] |
3.3. Enhancement of ME Coupling with the External Field

3.3.1. Electric Field

The ME effect is expected to occur when the derivative of antiferrodistortion vector (AFD) with respect to electric field undergoes critical behavior [55] and is supported by the fact that certain magnitudes of external fields lead to a reorientation of antiferromagnetic structure [56]. In critical fields, this AFD vector tends to infinity and leads to an unlimited increase of the ME effect in theory. However, a limiting condition still exists, which fixes the electric field’s upper limit to ensure the system is thermodynamically stable [57].

\[ \alpha_{ij}^2 < 4\pi(\chi_{ii}\kappa_{jj}) \]  

(4)

Here, \( \alpha_{ij} \) is ME coefficient, \( \chi_{ii} \) and \( \kappa_{jj} \) are the electrical and magnetic susceptibilities. The enhancement mechanism results from the softening mode of reorientation of the antiferrodistortion vector, which may also occur due to elastic stresses in heterostructures.

3.3.2. Magnetic Field

Above a threshold magnetic field, the ME polarization changes, reflecting a transformation in the spin configuration. Early reports suggested a required field to be only 0.5 T [58], which was later proved not reproducible as many agree that the critical field to be about 15 T–20 T [1] for the bulk BFO while for thin films, it depends on the substrate on which it is grown, for example, it is about 4 T, 6 T and 4 T for BFO grown on DyScO\(_3\), GdScO\(_3\) and SmScO\(_3\) respectively [3]. (as seen in Figure 4). This variation in the critical fields between bulk and thin films is mainly due to the different magnetoelastic coupling coefficients in both cases. It follows quadratic strain dependence in the thin film case. Due to which the cycloid previously assumed (type -1) is only applicable for bulk and the type—2 cycloid (applicable for strained films) has relatively less critical field than type -1 [3] (see Figure 5). It must also be noted that there is a dependency of piezoelectric and elastic parameters on the orientation and the spatial anisotropy of the elastic stiffness (\( c_{ij} \)) and the piezoelectric coefficient (\( d_{ij} \)) on the asymmetrical characteristics of the rhombohedral R3c BFO (with 3 m space group) [59].

![Figure 4](image-url). Low-energy Raman fingerprint of spin cycloid at 295 K of BFO grown on (a) DyScO\(_3\), (b) GdScO\(_3\) and (c) SmScO\(_3\), respectively. The magnetic field was applied normally to the film plane as seen in Reference [3].
Crossing the threshold field would give rise to a linear ME effect suggesting the suppression of the spin cycloid. Few implications of this are, firstly, the magnetization induced by the field jumps to a greater value. Secondly, even with no lattice mismatch, other factors like the finite-size effect, change in the symmetry can easily influence the strain gradient. Thirdly, even though the strain on its own is incapable of destroying the cycloid as previously believed, it can affect the factors that can destroy the cycloid, resulting in significant opportunities for the application of strained BFO thin films [3] as seen in Figure 5. Doping of elements like Mg can also be used for getting better magnetization due to distortion of the spin cycloid [60].

![Figure 5](image_url) Schematic representation of spin cycloids in (a) Bulk, (c) In thin films, (b) gives the projection of cycloid k vectors along a plane oriented at (001) plane. (d) Gives the projection of spin cycloid k’ vectors in the thin film along (001) orientation. As seen in Reference [61].

3.4. Alliance through the Formation of Composites

The physical properties of composite material depend not only on the individual single-phase constituents but also on their interaction. This interaction can result in synergistic effect (enhancement of properties), scaling effect (averaging of properties) or product effect (novel properties evolve which are not seen in the constituents). The ME effect hence can be achieved through the composite of a magnetostrictive and a piezoelectric material. The magnetic field applied will induce strain, which is carried to its composite partner, which produces an electric polarization and vice versa [62].

A simple way to express this idea is through [9]

\[
\text{ME effect} = \frac{\text{electrical}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}
\]  

(5)

One of the first composite to be extensively studied was a composite formed using BaTiO₃ (ferroelectric and piezoelectric) and CoFe₂O₄ (ferromagnetic and piezomagnetic); the reported magnetoelectric coefficient was 130 mV cm⁻¹·Oe⁻¹ [63] and is much superior to a single-phase compound [64].
4. Applications

Presently, applications of BFO mainly revolve around magnetoelectric and spintronic behavior (other than gas sensing, photovoltaic application). One of the most significant advantages of BFO-based memory devices is that memory can be stored using voltages and read using a magnetic field, resulting in reduced voltage requirement for the device. The two necessary conditions for this to be met are that the device should be electrically switchable and magnetically readable. The first condition of electrical switchability is relatively easier to achieve, while magnetic readability poses problems. The reading of the antiferromagnetic domain is rather difficult and hence a ferromagnetic layer on top of antiferromagnetic material is applied for magnetic readability. Upon application of voltage, the antiferromagnetic domains influence the ferromagnetic layer. Therefore, the changes in the magnetic hysteresis loop are observed, which is an indirect method for reading antiferromagnetic domains on which there is an application of voltage [65].

Bismuth ferrite is also known to show terahertz radiation when excited with femtosecond laser pulse; this can be used in telecommunication. The response depends on the poling state of the film. Hence, it provides a non-destructive and faster method for ferroelectric memory readout. It should also be noted that this response works independently from leakage current and thus one of the most significant obstacles of BFO is easily eliminated [66].

Another important line of work is the use of BFO as sandwiching material between ferromagnetic material. With electrical switchability, the BFO layer can be used to control the magnetic state of the ferromagnetic layers and hence would result in a tunneling device [67], which can be controlled both by voltage and magnetization. A challenge for many of the applications of BFO is the leakage current. It depends mainly on phase-purity, size of the particles and defects like oxygen vacancies [53].

4.1. Energy Harvesters

Energy harvesters are devices that can generate energy from unconventional sources like radio waves, light, wind, sound, vibrations and so forth, which are gaining focus as researchers head towards new and renewable energy sources. ME composites are more preferred over single-phase material due to enhanced ME coupling coefficient. One popular method is to derive energy from small magnetic fields using the principle magneto-mechano-electric mechanism [68]. It involves the magnetostrictive layer producing vibrations when placed in the AC magnetic field, which would then strain the piezoelectric layer, giving out an output voltage.

4.2. Field Sensors

ME based field sensors can play a vital role in future technology as they are promising candidates to replace SQUIDs, Hall sensors and others. The advantage of using the ME field sensor is that they are relatively cost-effective compared to SQUIDs and Hall sensors but this is possible only when the magnetoelectric coupling is possible at room temperatures, sensitive of pT and even at lower operating frequencies. The direct magnetoelectric coupling (DME) would facilitate sensing magnetic fields (AC or DC) by sensing the output electrical signals.

4.3. Magnetoelectric Random Access Memory

ME materials are multiferroic. Hence, they can be suitably applied for either ferroelectric random access memory (Fe RAM), which stores the information using polarization states or magnetic random access memory (MRAM), which stores data using magnetic states. A significant disadvantage of both the RAM’s is that they need reset operations (due to destructive read in FeRAM) and large current (for the magnetic reversal in MRAM). Hence ME material can be a solution to this problem, as it provides the opportunity to use control of magnetic state and polarizations either with electric or magnetic fields. They are also advantageous because they have better thermal stability, greater memory density and lower power consumption [69].
These are the few popular applications of ME materials; other applications include current sensors, phase shifters, inductors and so forth, discussed in detail, along with the applications mentioned above in Reference [70]. Recently, Mg [60] and Al [71] doped bismuth ferrite has also seen application in anti—bacterial studies.

5. Measurement of Magnetoelectric Coupling Coefficient

Most researchers tend to calculate indirect evidence of magnetoelectric coupling rather than the actual coefficient itself. Some examples are the thermal measurement under a large magnetic field, the variation in the dielectric constant at transition temperatures of the magnetic phase, changes in the resistivity and magnetization of the magnetic phase due to interfacial strain at the structural phase boundary [72–76]. Hence it is essential to distinguish between indirect evidence and actual calculations.

Due to the magnetoelectric coupling, the electric polarization is affected by an external magnetic field (Equation (6)) and magnetization is affected in an external electric field (Equation (7)) and it is numerically quantized through magnetoelectric coefficient $\alpha$

$$\alpha_{ij}^E = \left( \frac{\delta B_i}{\delta E_j} \right)$$

$$\alpha_{ij}^H = \left( \frac{\delta P_i}{\delta H_j} \right).$$

In accordance with the Maxwell equation, $\alpha_{ij}^E$ and $\alpha_{ij}^H$ are thermodynamically equal. The $\alpha$ is a second rank tensor and the components are usually dependent on the crystal symmetry, sample size and even the geometry of the applied external field. Hence, on most occasions, most of the components are zero. With further manipulation of Equation (7), we can get a more practical unit for ME coefficient in terms of the voltage

$$\alpha_{ij}^H = \left( \frac{\partial V}{\partial H} \right)_{t, \varepsilon_0, \varepsilon_r}.$$

The SI unit of $\alpha_{ij}^H$, $\alpha_{ij}^E$ are (s m$^{-1}$) while $\alpha_{ij}^H$ is given in terms of (V·A$^{-1}$) or (V cm$^{-1}$·Oe$^{-1}$) in CGS.

Few of the measurement methods for the ME coefficient are as follows:

5.1. To Find $\alpha_{ij}^H$

As seen in Equation (7), the magnetically induced magnetoelectric coefficient can be indirectly calculated through (8). It is evident that the measured voltage, $V = \alpha_{ij}^H \cdot H \cdot t$, here, the sample’s thickness is $t$ (or thickness of the ferroelectric layer in composites), the amplitude of the external magnetic field is $H$. It must be noted that the applied AC magnetic field has to be large or a DC bias field has to be coupled to produce a pseudo—piezo—magnetic response.

Initially, the sample is kept in an optimal DC biased magnetic field and the AC magnetic field is applied at a suitable angle to the DC field. The voltage responses are then noted for varied amplitudes of the AC field while keeping DC bias and frequency of the AC field fixed. The measured values are then plotted as a function of AC amplitudes and the slope $V$ is the product $\alpha_{ij}^H$ and $t$. It is important to note that the actual measurement is more complicated than what is reviewed here as the optimal DC field, which needs to be applied has to be found. The system must allow simultaneous AC and DC magnetic fields and the induced signals are amplified. Frequency response is detected through a spectrum analyzer or the amplitude measurement through a lock-in amplifier (Figure 6).
The magnetoelectric coefficient has a non-linear behavior with DC magnetic field bias, as seen in Figure 7. The strain increases as the applied magnetic field increases and it saturates at saturation field, beyond which strain remains constant with increasing magnetic field. The piezo-magnetic coefficient is non-linear. The piezo-magnetic coefficient again contributes to the magnetoelectric coefficient, which is the reason for the behavior, as seen in Figure 7. The optimum DC bias field is the point of the largest gradient of magnetic strain with respect to the field corresponding to the maximum piezo-magnetic coefficient results in the maximum magnetoelectric voltage response.

A fine example of this technique in practical usage is reported in Reference [79]. For the magnetoelectric device application, the frequency region where the magnetoelectric coefficient remains constant is usually preferred. For the compounds (BiFeO$_3$)$_{1-x}$-(BaTiO$_3$)$_x$ and (Bi$_{1-x}$Nd$_x$FeO$_3$), this threshold frequency was 2 kHz while it was about 5 kHz for (Bi$_5$Ti$_3$FeO$_3$).

The (BiFeO$_3$)$_{1-x}$-(BaTiO$_3$)$_x$ sample showed $\alpha^H$ to be equal to 2.84 mV·cm$^{-1}$·Oe$^{-1}$ when electrically poled at 3 kV mm$^{-1}$ with a constant magnetic field of 600 Oe at 368 K. The (Bi$_{1-x}$Nd$_x$FeO$_3$) sample showed $\alpha^H$ to be around to 2.5 mV·cm$^{-1}$·Oe$^{-1}$ for similar conditions with $x = 0.2$. The (Bi$_5$Ti$_3$FeO$_3$) ceramic nearly showed $\alpha^H$ to be equal to 20 mV·cm$^{-1}$·Oe$^{-1}$ under similar conditions as seen.
in (B\textsubscript{1}Fe\textsubscript{2}O\textsubscript{3})\textsubscript{1-x}-(BaTiO\textsubscript{3})\textsubscript{x}. These results confirmed that electrically poled samples show greater magnetoelectric than non-poled samples.

5.2. To Find \(a^E\)

Equation (6) on most occasions can be expressed as \(a^E_{ij} = \left(\frac{\partial M}{\partial E}\right)\), the measurement of \(a^E\) involves magnetic measurement of the sample when placed in an external electric field at zero magnetic fields; this gives the magnetization induced as a function of an electric field. Again, the measurement requires a large enough AC field or DC coupled AC field. It is also important to note that the applied electric field needs to be greater than the ferroelectric phase’s coercive field. The final calculation can be done through

\[
M = a^E \cdot E = a^E \cdot V \cdot t. \quad (9)
\]

The sample is placed in a modified magnetometer, which is capable of applying an electric field simultaneously. While keeping the external magnetic field at zero, the external electric field is applied. The magnetization \(M\) is then measured by varying the applied AC electric field and the plot of \(M\) v/s \(E\) is drawn. The slope of the plot gives the product of the \(a^E\) and the thickness of the dielectric material. The measurements can be done at various temperatures as well. It is important to note that there is a frequency dependence of \(a^E\) similar to as seen in Figure 7, magnetically induced coupling is maximum when the AC electric field’s frequency matches the electro-mechanical resonance frequency of the sample.

5.3. To Find \(\alpha\) from Piezoelectric Measurements.

The magnetoelectric coefficient through piezoelectric measurement can be found for samples that show piezoelectric behavior as well as magnetoelectric coupling. With the application of the external field and stress, the polarization obtained would be a function of an electric field, magnetic field and stress. Exerting short circuit conditions, we get polarization to be equal to electric displacement and the electric field is zero.

\[
D_i = d_{im} \sigma_m + \alpha_{ij}^{eff} H_j, \quad (10)
\]

where \(\sigma\) is the mechanical stress applied, \(d\) is the piezoelectric coefficient. The instrument measures the \(d\) and hence the equation can be rearranged in terms of \(d\). It can be observed the measured \(d\) is a function of \(H\) and the equation can be differentiated as

\[
\alpha_{ij}^{eff} = -\sigma \left(\frac{\partial d_{ij}^{p}}{\partial H_j}\right). \quad (11)
\]

Here the \(\alpha_{ij}^{eff}\) obtained will be in terms of \((C \ m^{-2} \ Oe^{-1})\).

The sample is placed in a modified piezoelectric testing instrument (like the Berlincourt instrument, which can apply both AC and DC magnetic fields). The piezoelectric coefficient is measured at different amplitudes of the AC magnetic field and a fixed optimal DC bias field. The graph of \(d\) v/s \(H\) is drawn and from the slope of this linear graph, the \(\alpha\) is found as seen in (11).

5.4. To Find \(\alpha\) from Thermal Measurements

The \(\alpha\) can be found in multiferroics using temperature change to produce adiabatic responses in volume, strain, magnetization and polarization; this effect is called a multicaloric effect. In multiferroics, it can merge multiple calorific effects into a single adiabatic response. A cooling effect is seen whenever there is depolarization or demagnetization. The efficiency of such cooling can be increased by using base temperature to be equal to ferroic transition temperatures. A prerequisite of this method is that the transition temperatures need to be different. The contribution of change in temperature at different transition temperatures can be calculated as seen in (12) and (13).
When magnetic transition temperature $T_m >$ electric transition temperature $T_e$, we have:

$$\alpha^H = \varepsilon_0 \chi^e \frac{\Delta T_H}{\Delta E} \frac{\Delta H}{\Delta E}, \quad (12)$$

When magnetic transition temperature $T_m <$ electric transition temperature $T_e$, we have:

$$\alpha^E = \mu_0 \chi^m \frac{\Delta T_H}{\Delta T_E} \frac{\Delta E}{\Delta H}, \quad (13)$$

where $\varepsilon_0, \mu_0$ are electric permittivity and magnetic permeability in the vacuum, $\chi^e$ and $\chi^m$ are electric and magnetic susceptibility, $\Delta T_E$ and $\Delta T_H$ are change in temperature when depolarization and demagnetization, $\Delta H$ and $\Delta E$ are the demagnetization and depolarization, respectively.

The working method is as follows; the sample is placed in the vacuum chamber in adiabatic condition, where the instrument is capable of applying both electric field $E$ and magnetic field $M$ (as seen in Figure 8) and also measure accurate temperature changes when the $E$ is on and $T_m > T_e$, the operating temperature in the reservoir was set to $T = T_e$. The thermal link is then shut and the $E$ is reduced to zero, resulting in depolarized cooling. The temperature change $\Delta T_H$ is noted. Then the system is brought back to operating temperature $T = T_e$, in order to measure demagnetized cooling and a large magnetic field is thus applied. The temperature change $\Delta T_E$ is calculated by reducing the applied magnetic field to zero. By using the relation (12), we can calculate $\alpha^H$.

![Figure 8](image_url). Schematic of multicaloric testing system. Image modified and adapted from Reference [80].

If $T_m < T_e$, then the operating temperature $T = T_m$ and the procedure is repeated to get $\alpha^E$ from (11). The complete derivation of the multicaloric effect can be found in Reference [81]. The details of some of the techniques mentioned above can be found in detail in Reference [78].

6. Conclusions

In summary, manipulating structure and spin cycloid through strain, doping, external factors like the electric field, magnetic field have facilitated the enhancement of magnetoelectric coupling in BFO. We list the following conclusions of this brief review:

- Many first principles studies have shown that strain might directly affect magnetoelectric coupling but the strains caused by substrates can affect the critical magnetic field needed to destroy spin cycloid. Thus, confirming that strain does have an indirect influence over magnetoelectric coupling.
Doping can affect both ferroelectric and ferromagnetic behavior but its importance lies in the fact that it affects the structure and spin cycloid, which can be utilized to enhance the magnetoelectric effect.

Critical fields like electric fields can influence the antiferrodistortion vector, which ultimately manipulates the magnetization but there is an upper limit that depends on the susceptibility.

The critical magnetic field affects the spin cycloid and hence through manipulation of the spin cycloid, there is an indirect control of the magnetic field over magnetoelectric coupling.

Even with more than a century’s theoretical and experimental background, research into the ME effect is still not complete. Over the years, the researchers are slowly mastering the synthesis, manipulation and control of the ME effect by forming composites, heterostructures and even in thin-film form and are slowly reaping the benefits, especially in the field of sensors and magnetic memory devices. The investigations are still underway, either enhancing the ME effect or achieving a more straightforward and effective route. The frustrated systems can achieve a lower ground state via ME contributions in systems in the vicinity of phase transitions where magnetic phase can be controlled using electric field and vice versa, which is a sure sign of an evolving subject.

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