

Bismuth Ferrite

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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, high-quality BFO thin films, and ceramics brought back researchers into BFO. It is an ABO_3 type perovskite compound that crystalizes into the 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 (TC) of BFO is as high as ~ 1103 K and antiferromagnetic Neel temperature (TN) is ~ 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

Keywords: magnetoelectric coupling ; bismuth ferrites

1. Introduction

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][5][6][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. ^{[1][2][4][5][6][7][14]}

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 that marked the discovery of the magnetoelectric effect (ME) effects:

1. Röntgen 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. Schematic representation of interrelation between electric and magnetic fields with respect to their polarization.

2. Bismuth Ferrite: Historical Background and Properties

It was not until the early 2000s that the research in single crystals ^[11], high-quality BFO thin films ^[12] and ceramics ^[13] 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 ~1103 K and antiferromagnetic Neel temperature (T_N) is ~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.

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

3. Applications

Presently, applications of BFO main 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 ^[15].

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 ^[16].

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 ^[17], 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 ^[18]

3.1 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 ^[19] 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.

3.2 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.

3.3 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 ^[20].

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 ^[21] . Recently, Mg ^[22] and Al ^[23] doped bismuth ferrite has also seen application in anti—bacterial studies.

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