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Chapter

Synthesis and Characterization of Multiferroic BiFeO$_3$ for Data Storage

Kuldeep Chand Verma

Abstract

Multiferroic BiFeO$_3$ deals with spintronic devices involved spin-charge processes and applicable in new non-volatile memory devices to store information for computing performance and the magnetic random access memories storage. Since multiferroic leads to the new generation memory devices for which the data can be written electrically and read magnetically. The main advantage of present study of multiferroic BiFeO$_3$ is that to observe magnetoelectric effects at room temperature. The nanostructural growth (for both size and shape) of BiFeO$_3$ may depend on the selection of appropriate synthesis route, reaction conditions and heating processes. In pure BiFeO$_3$, the ferroelectricity is induced by $6s^2$ lone-pair electrons of Bi$^{3+}$ ions and the G-type antiferromagnetic ordering resulting from Fe$^{3+}$ spins order of cycloidal (62-64 nm wavelength) occurred below Neel temperature, $T_N = 640$ K. The multiferroicity of BiFeO$_3$ is disappeared due to factors such as impurity phases, leakage current and low value of magnetization. Therefore, to overcome such factors to get multiferroic enhancement in BiFeO$_3$, there are different possible ways like changes dopant ions and their concentrations, BiFeO$_3$ composites as well as thin films especially multilayers.

Keywords: electric-driven magnetic switching, chemical synthesis, magnetoelectric, ferroelectric polarization

1. Introduction

Spintronic devices that electrically store non-volatile information are the potential candidates for high-performance, high-density memories due to their interdependence between magnetization and charge transport phenomenon. Since the capacitor stored information in the form of charges and the electric field moved these charges to transmit information. However, the magnetic recording is caused when the magnetic field used to read or write the information stored in the form of magnetization by measuring local orientation of spins. The behavior started to change in 1988, when the discovery of giant magnetoresistance provides a way for efficient control of charge transport through magnetization [1, 2], for example, the hard-disk recording. Hard disk drives (HDD) with a capacity of 10 MB were sold for ~$5300 in the 1980s, and were unaffordable for many during Apple and IBM PC era. However, HDDs with 16 TB capacity are available at the time of writing (2020). The computers in 1980s had memory of hundreds of kB that recently 8 GB random access memory (RAM). Even mobile gadgets have a dynamic random access memory (DRAM) capacity of ~4 GB, at the time of writing. This is possible by use of
charge property of the electron as well the spintronics devices make use of the spin property of an electron. Flash memory is an example, as it is a non-volatile memory as used in mobile applications [3]. However, the electrically induced bistable magnetization switching at room temperature - a necessary requirement for magnetic data storage - is the multiferroics [4]. The room-temperature manipulation of magnetization by an electric field using the multiferroic BiFeO$_3$ represents an essential step toward magnetoelectric (ME) control for spintronics devices [5].

1.1 Multiferroic memories for data storage

Multiferroic might hold the future for the ultimate memory device. The demonstration of a four-state resistive memory element in a tunnel junction with multiferroic barriers represents a major step in this direction [6–9]. For example, the thin films of lanthanum bismuth manganite remain ferromagnetic and ferroelectric down to thicknesses of 2 nm and, when used as a multiferroic tunneling junction, act as a four-state resistive system. Their spin-filter device as shown in Figure 1(a) is the tunnel junctions, which has tunnel barrier height is spin dependent because the bottom level of the conduction band in the ferromagnetic barrier is spin-split by exchange model. This allows the tunneling of electrons that to be efficiently filtered according to their spin. Gajek M et al. [10] suggested the large tunnel magnetoresistance in junctions that have a ferromagnetic electrode. The combination of these two effects - magnetoresistance plus electroresistance - yields a four-state resistive memory element. In comparison to the information stored in a capacitor, the resistive memories, on the other hand, can be read more simply, for example, by monitoring the source-drain current in a field-effect transistor. In order to make a multiple-state ME memory, one must be able to access the four states formed by electric polarization P and magnetization M, i.e. $(+P, +M)$, $(+P, -M)$, $(-P, +M)$, and $(-P, -M)$ [6].

1.2 Spin-transfer-torque magnetic random access memory

The spin-transfer-torque magnetic random access memory (STT-MRAM) devices stored information due to use of magnetic orientation in the ferromagnetic
nanoparticles. For example, hard disk drives (use magnetic states to store information). In addition to hard disk drives, the STT-MRAM is a device that written and read electrically without any moving parts. The function of spin-transfer is to write information and such information is read by measuring the device resistance. The magnetoresistance plays role to measure percentage change in resistance between parallel and antiparallel magnetic spins of the electrodes of the magnetic tunnel junction. Such magnetic tunnel junction is made up by a ferromagnetic metal/insulator/ferromagnetic material [7]. Figure 1(b) shows a 1-bit STT-MRAM cell constituted by free layer and reference layer that are magnetized perpendicular to the plane of the junction [7]. The cell is constituted with a word line with a transistor that required for each cell. The biasing voltage could operate the cell with respect to bit lines and such read bias voltage measured the cell resistance to determine the bit state to be low of 100 mV. However, the write bias voltage is higher to allow the magnetic moment of the free layer taken to be reversed by using spin transfer torque.

1.3 Multiferroic BiFeO$_3$

The multiferroic BiFeO$_3$ (BFO) has high Curie temperature, $T_C \sim 1103$ K and Neel temperature, $T_N \sim 643$ K results into simultaneously ferroelectric and antiferromagnetic orders at room temperature. The ferroelectricity in BFO is originated by 6s$^2$ lone pair electrons of Bi$^{3+}$ via structural distortion, however, magnetism resulted with Fe-O-Fe superexchange interactions [11]. But the reported study pointed out BFO with low spontaneous polarization and saturation magnetization because superimposition of a spiral spins structure of BFO by antiferromagnetic order. In such spiral spin structure, the antiferromagnetic axis rotates BFO crystal with 62 nm long wavelength, which cancels out the macroscopic magnetization as well as affects ME coupling value. The superexchange between the octahedrally coordinated Fe$^{3+}$ through the O ligand is responsible for the resulting antiferromagnetism. The presence of oxygen vacancies and the valence fluctuation (Fe$^{2+}$/Fe$^{3+}$) believed to be the main disadvantages causing large electrical leakage in BFO.

1.3.1 BiFeO$_3$ structure

The BFO structure is characterized with two distorted perovskite units connected by their body diagonal to build a rhombohedral unit cell as shown in Figure 2(a). For such BFO structure, the two octahedral oxygen connected along (111) plane are rotated clockwise and counterclockwise at 13.8°. However, Fe ion is shifted 0.135 Å along same axis from oxygen that present at the octahedral position. The large displacement of Bi ions with respect to the FeO$_6$ responsible to induced ferroelectric polarization [12–14]. The spins in this BFO structure are incommensurate to form antiferromagnetic order. There is also some canting moments to give weak ferromagnetism due to Dzyaloshinskii-Moriya (DM) effect because the moments may oriented perpendicular to the (111) polarization direction to influence symmetry properties.

1.3.2 Lone-pair mechanism supporting multiferroicity

The spatial asymmetry that caused by anisotropic unbounded valence electrons around Bi$^{3+}$ might to give lone pair mechanism (Figure 2(b)) responsible into room temperature ferroelectric polarization of BFO [12]. In BiFeO$_3$, a pair of Bi$^{3+}$ valence electrons of the 6s orbital not involved sp hybridization to generates a local dipole which resulting into $\sim$100 μC cm$^{-2}$ ferroelectric polarization below $T_C = 1103$ K. A long-range periodic antiferromagnetic structure arises below $T_N = 643$ K. The main
driving force of the ferroelectric phase transitions seems to be the stereochemical activity of the Bi 6s lone-pair, resulting into a displacement of Bi and O sublattices. However, the Fe sublattice is also displaced and makes a sizeable contribution to the total electric polarization.

1.3.3 Ferroelectric and magnetic order in BiFeO$_3$

Bulk BiFeO$_3$ crystallized into a slightly distorted rhombohedral structure which commonly described by the pseudocubic unit cell (Figure 2(c)). The displacement of Bi ions relative to the FeO$_6$ octahedra gives rise to a strong ferroelectric polarization (100 $\mu$C cm$^{-2}$) along one of the [111] directions [13]. However, the magnetization in BiFeO$_3$ involved G-type antiferromagnet order with a cycloidal wavelength, $\lambda \sim 62-64$ nm was investigated by high-resolution neutron diffraction. As shown in Figure 2(d), the normalized position of the spin cycloid propagation and the ferroelectric polarization vector might to induce ME coupling effect.

2. Synthesis of multiferroic BiFeO$_3$

The some synthesis methods used for BiFeO$_3$ are summarized in Table 1. Some of the listed methods are the derivatives of wet-chemical that deals with chemical reactions in the solution phase using precursors at proper stoichiometric conditions. Each wet-chemical synthesis route differs from the others in the sense that one cannot find a general rule for these kinds of synthesis approaches. Such wet-synthesis schemes mostly used for fabrication of 2D nanomaterials. The wet-chemical processes offer a high degree of controllability and reproducibility of the 2D nanostructures. The solvothermal synthesis, template synthesis, self-assembly, oriented attachment, hot-injection, and interface-mediated synthesis are wet-chemical routes. However, the solvothermal and hydrothermal processes are mostly used to synthesize 2D nanostructures due to their simple and scalable steps.
<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Reaction time</th>
<th>Precursor salts</th>
<th>Reaction condition</th>
<th>Shape control</th>
<th>Shape/size</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet chemical methods</td>
<td>Hours</td>
<td>Bi(NO₃)₃·3H₂O, Fe(NO₃)₃</td>
<td>HNO₃ used to adjust pH, Ethylene glycol &amp; carboxylic acid are a polymerizing agent, annealed at 400°C/2 h</td>
<td>Good</td>
<td>13-70 nm particles</td>
<td>[15, 16]</td>
</tr>
<tr>
<td>Sol-gel method</td>
<td>Hours/day</td>
<td>Bi₃H₂N₂O₁₀₂₆, Fe(NO₃)₃</td>
<td>Precursor concentration adjusted in 0.05-0.2 M using acetic acid &amp; ethylene alcohol, annealed at 200-500°C</td>
<td>Good</td>
<td>10 nm particles</td>
<td>[17]</td>
</tr>
<tr>
<td>Co-precipitation method</td>
<td>Minutes</td>
<td>Fe(NO₃)₃·9H₂O, Bi₂O₃</td>
<td>NaOH used as a precipitating agent, maintain pH 12, annealed at 400-600°C/1 h</td>
<td>Poor</td>
<td>200-250 nm particles</td>
<td>[18]</td>
</tr>
<tr>
<td>Hydrothermal process</td>
<td>Hours/days</td>
<td>Bi(NO₃)₃·3H₂O, FeCl₃·6H₂O</td>
<td>Precursor salts dissolved in acetone, pH adjusted 10-11 by ammonia solution, Precursor solution transferred into teflon-lined steel autoclave and heated at 180°C for 72 h</td>
<td>Very good</td>
<td>45-200 nm diameter wires</td>
<td>[19]</td>
</tr>
<tr>
<td>Solution evaporation method</td>
<td>Hours</td>
<td>Fe(NO₃)₃·9H₂O, Bi(NO₃)₃·3H₂O, HNO₃</td>
<td>Tartaric acid and nitric acid used as precipitating and oxidizing agent, crystallization of the final powder take-place at 650°C/2 h</td>
<td>Good</td>
<td>22-31 nm particles</td>
<td>[20]</td>
</tr>
<tr>
<td>Microwave-assisted hydrothermal synthesis</td>
<td>Minutes</td>
<td>Bi(NO₃)₃·3H₂O, Fe(NO₃)₃·9H₂O</td>
<td>NaOH solution and polyethylene glycol were added to the precursors to obtain brown precipitates, solution irradiated by 300 W of MW irradiation for 30 min at 190°C with 2450 Hz</td>
<td>Good</td>
<td>20 nm diameter wires</td>
<td>[21, 22]</td>
</tr>
<tr>
<td>Self-catalyzed fast reaction process</td>
<td>Hours</td>
<td>α-Fe₂O₃, Bi₂O₃</td>
<td>5 mol of tartaric acid (C₄H₆O₆) added to the precursors and heated at 250°C to begin to ignite and violently burn, final powder annealed at 650°C/2 h</td>
<td>Poor</td>
<td>100 nm particles</td>
<td>[23]</td>
</tr>
<tr>
<td>Conventional solid state</td>
<td>Hours/days</td>
<td>Bi₂O₃, Fe₂O₃, Co₃O₄</td>
<td>Synthesis of BiFeO₃ powder from Bi₂O₃</td>
<td>Poor</td>
<td>100-200 nm particles</td>
<td>[24]</td>
</tr>
<tr>
<td>Synthesis method</td>
<td>Reaction time</td>
<td>Precursor salts</td>
<td>Reaction condition</td>
<td>Shape control</td>
<td>Shape/size</td>
<td>Ref.</td>
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</tr>
<tr>
<td>reaction and thin film deposition of BiFeO₃, CoFe₂O₄</td>
<td>and Fe₂O₃ and heated at 800°C, CoFe₂O₄ powder prepared from Co₃O₄ and Fe₂O₃ using ball milling for 24 hours and heated at 1200°C/3 h, RF magnetron sputtering used for thin film deposition</td>
<td></td>
<td>Poor</td>
<td>50-500 nm nanostructures</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td>Chemical combustion method</td>
<td>Hours</td>
<td>Bi(NO₃)₃, Fe(NO₃)₃</td>
<td>Precursor solution mixed in polyethylene glycol, Urea added at 70°C and the combustion take-place, annealed at 600°C/5 h</td>
<td>Very good</td>
<td>1-D nanoparticles-assembled microrods</td>
<td>[25]</td>
</tr>
<tr>
<td>Polymer-directed solvothermal</td>
<td>Hours</td>
<td>Bi(NO₃)₃, Fe(NO₃)₃, Mn(OOCCH₃)₂, Cr(NO₃)₃</td>
<td>Porous nanochannel alumina (NCA) templates used, precursor salts mixed in nitric acid to get transparent, Citric acid &amp; deionized water added, pH adjusted to be natural by using ammonia, urea added in 1/20th ratio, NCA templates added and heated at 80°C/20 h and annealed at 650°C/5 h</td>
<td>Very good</td>
<td>Nanotubes 150-190 nm</td>
<td>[26]</td>
</tr>
<tr>
<td>Sol-gel template process</td>
<td>Hours/ days</td>
<td>Bi(NO₃)₃, SH₂O, Fe(NO₃)₃, 9H₂O</td>
<td>In sonicated solution of Bi and Fe, add 5 ml of tetraethylene glycol and sonicated for 10 min, pH adjusted to 8 by adding ammonia and irradiated with a high intensity (100 W cm⁻²)</td>
<td>Good</td>
<td>Nanorods diameter 20-50 nm</td>
<td>[27]</td>
</tr>
<tr>
<td>Sonochemical technique</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
3. Results and discussion

3.1 Structural analysis of BiFeO$_3$

3.1.1 X-ray diffraction of Pb substituted BiFeO$_3$

Figure 3(a) shows the X-ray diffraction (XRD) pattern of Bi$_{1-x}$Pb$_x$FeO$_3$ [$x = 0$ (BFO), 0.05 (BPFO5), 0.075 (BPFO75) and 0.1 (BPFO10)] nanostructures measured at room temperature [11]. All reflections are indexed to a rhombohedral structure of R3c space group. This is based on the character of the single (012) peak at around 22° and the splitting of the (104) and (110) peaks around 32°. The splitting of XRD peaks indicates the structural distortion due to tilting of FeO$_6$ octahedrons. The calculated lattice constants are $a$ (Å) = 5.578, 5.577, 5.573 and 5.574 and $c$ (Å) = 13.862, 13.893, 13.905 and 13.915, respectively for BFO, BPFO5, BPFO75 and BPFO10. The increase in lattice constant, $c$ and decrease in $a$ may be due to change in Fe-O bond lengths and Fe-O-Fe bond angles which have a significant effect on multiferroic properties.

### Table 1.

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Reaction time</th>
<th>Precursor salts</th>
<th>Reaction condition</th>
<th>Shape control</th>
<th>Shape/size</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodized alumina template technique</td>
<td>Hours</td>
<td>Bi(NO$_3$)$_3$ ·$\text{SH}_2$O, Fe(NO$_3$)$_3$ ·$\text{H}_2$O</td>
<td>Precursor salts are mixed in 2-methoxyethanol, pH 4-5 by adding 2-methoxyethanol and nitric acid, anodized aluminum oxide template immersed in precursors for 12 h and heated at 750°C/12 h</td>
<td>Very good</td>
<td>Wires ~50 nm in diameter</td>
<td>[28]</td>
</tr>
<tr>
<td>Sol-gel based electrospinning</td>
<td>Hours</td>
<td>Bi(NO$_3$)$_3$ ·$\text{SH}_2$O, Fe(NO$_3$)$_3$ ·$\text{H}_2$O</td>
<td>Precursor salts are neutralized with 2-methoxyethanol, pH 3-4 adjusted with Ethanolamine, Ethanol, glacial acetic acid, and poly vinyl pyrrolidone (PVP) added, solution was electrospun and the ultrafine fibers spun were collected in glass flake or Pt/Ti/SiO$_2$/Si substrate, final heating at 550°C/2 h</td>
<td>Very good</td>
<td>Nanofiber diameter in 100-300 nm</td>
<td>[29]</td>
</tr>
</tbody>
</table>

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DOI: http://dx.doi.org/10.5772/intechopen.94049
3.1.2 Crystalline structure of BiFeO$_3$/BaTiO$_3$ bilayer interface

Glancing angle XRD patterns, recorded at incident angle 1°, on different BFO/BTO bilayer thin films sputtered on Pt/TiO$_2$/SiO$_2$/Si(100) substrates shown in Figure 3(b) [30]. Both BFO and BTO layers were found to be polycrystalline in nature without any impurity phase. The (110) plane of BFO appeared in θ mode only which was not be observed in GAXRD mode. It can be inferred that the bottom BTO layer promotes the formation of pure perovskite phase and high degree of (110) orientation in film texture.

3.1.3 Raman spectra of BiFeO$_3$ nanoparticles

The Raman spectrum of BFO obtained using 488 nm excitation wavelength depicted in Figure 3(c) [31]. The spectra have been deconvoluted into 10 individual components for BFO (3 A modes and 7 E modes). It was studied by DFT calculation of first principle that the low frequency Raman modes below 167 cm$^{-1}$ are due to Bi atoms, and the modes between 152 and 262 cm$^{-1}$ are due to Fe atoms [31].
However, oxygen atoms dominated with higher frequency modes above 262 cm\(^{-1}\). The shifting and broadening of Raman modes with standard values suggests the presence of disorder and oxygen vacancies, and the internal microstrain due to Fe ions which might to change resulting magnetism.

### 3.2 Microstructural studies of BiFeO\(_3\)

#### 3.2.1 FESEM image of Bi\(_{0.9}\)Pb\(_{0.1}\)FeO\(_3\)

**Figure 4(a)** shows the FESEM image of Bi\(_{0.9}\)Pb\(_{0.1}\)FeO\(_3\) nanostructure [11]. The diameter of the nanorods, D = 125 ± 4 nm, and length, L = 900 ± 20 nm. However for pure BFO, the nanoparticles (D = 75 ± 2 nm) are formed [11]. This morphological variation with Pb doping into BFO is explained due to variation in the valence states of Fe ions due to oxygen vacancies. The substitution of Pb\(^{2+}\) into Bi\(^{3+}\) ions induces Fe\(^{2+}/Fe^{3+}\) ions in the BFO matrix that can influence lattice defects (oxygen vacancies) in the rhombohedral BFO phase. It results into an anisotropic growth along the c-axis.

#### 3.2.2 BiFeO\(_3\)-CoFe\(_2\)O\(_4\) self-assembled nanocomposite

**Figure 4(b)** shows a top-view SEM image of a square array with period 83 nm [32]. The bright rectangular islands visible in this image correspond to (111)-faceted tops of the CoFe\(_2\)O\(_4\) pillars, while the darker area corresponds to single crystal
BiFeO$_3$ matrix. This BFO-CFO nanocomposite was grown by pulsed laser deposition. The film thickness was between 50 and 100 nm.

### 3.2.3 Atomic force microscopy images of BTO/BFO thin films

The BiFeO$_3$ and BaTiO$_3$ were used to grow homogeneous composite thin films and multilayer heterostructures with 15 double layers by pulsed laser deposition [33]. The thin films are composites grown directly from mixed PLD targets with 67 wt\% BTO/33 wt\% BFO (BTO67/BFO33) and 33 wt\% BTO/67 wt\% BFO (BTO33/BFO67), respectively. Figure 4(c) and (d) are the AFM surface images of these two different composite films and the nanoparticle sizes are in the ranges 40-100 nm and 100-200 nm, respectively.

### 3.2.4 Scanning transmission electron microscopy (STEM) of BaTiO$_3$-BiFeO$_3$

Multiferroic (BaTiO$_3$-BiFeO$_3$)$\times$15 multilayer heterostructures show high ME coefficients, $\alpha_{\text{ME}}$ up to 24 V cm$^{-1}$ Oe$^{-1}$ at 300 K [34]. The STEM and SAED mapping results of the (BaTiO$_3$-BiFeO$_3$)$\times$15 multilayer are depicted in Figure 4(e). The STEM cross section is shown 15 double layers BaTiO$_3$-BiFeO$_3$ at smooth interfaces. The octahedral tilt involves both clockwise and counter clockwise rotations around [111], which is parallel to ferroelectric dipole displacements to $R3m$ phase. The difference between the lattice parameters of the tetragonal BaTiO$_3$ and rhombohedral BiFeO$_3$ layers can be detected by reflection splitting along the growth direction (inset in Figure 4(e) top).

### 3.3 Ferroelectric behavior of BiFeO$_3$

The BiFeO$_3$ is a rhombohedrally distorted perovskite material, which means that the ferroelectric polarization can have orientation along the four pseudo-cubic diagonals (〈111〉) [35–38]. The largest relative displacements are those of Bi relative to O, consistent with a stereochemically active Bi lone pair that might induce ferroelectricity of BiFeO$_3$.

#### 3.3.1 Ferroelectric polarization of Pb doped BiFeO$_3$ nanoparticles

The ferroelectric polarization of multiferroic Bi$_{1-x}$Pb$_x$FeO$_3$ nanostructures is given in Table 2 [11]. In BFO, the lone-pair orbital of Bi$^{3+}$ (6s$^2$) is stereochemically active and responsible for ferroelectric distortion. Here, the distortion is induced by Pb doping and therefore, by tuning the lone-pair activity. Generally, the ferroelectric behavior is weakened due to an increase in oxygen vacancies that form more

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_s$ ($\mu$C cm$^{-2}$)</th>
<th>$P_r$ ($\mu$C cm$^{-2}$)</th>
<th>$E_c$ (kV cm$^{-2}$)</th>
<th>$J$ ($\mu$A cm$^{-2}$)</th>
<th>$\varepsilon$</th>
<th>MC (%)</th>
<th>$T_{FE}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 kHz</td>
<td>1 MHz</td>
<td>1 kHz</td>
</tr>
<tr>
<td>BFO</td>
<td>0.75</td>
<td>0.35</td>
<td>7.66</td>
<td>10.31</td>
<td>6.2</td>
<td>5.1</td>
<td>0.68</td>
</tr>
<tr>
<td>BPFO5</td>
<td>1.76</td>
<td>0.63</td>
<td>6.03</td>
<td>6.27</td>
<td>1.9</td>
<td>1.8</td>
<td>2.56</td>
</tr>
<tr>
<td>BPFO75</td>
<td>3.55</td>
<td>1.57</td>
<td>8.55</td>
<td>2.72</td>
<td>13</td>
<td>10.6</td>
<td>3.61</td>
</tr>
<tr>
<td>BPFO10</td>
<td>6.73</td>
<td>2.63</td>
<td>5.06</td>
<td>1.57</td>
<td>34</td>
<td>12</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 2. Values of spontaneous polarization ($P_s$), remanent polarization ($P_r$), electric coercivity ($E_c$), current density ($J$) at 20 kV cm$^{-1}$, dielectric constant ($\varepsilon$) and MC at 1 kHz and 1 MHz, and ferroelectric phase transition ($T_{FE}$) at 1 MHz for Bi$_{1-x}$Pb$_x$FeO$_3$ [x = 0 (BFO), 0.05 (BPFO5), 0.075 (BPFO75) and 0.1 (BPFO10)] nanostructures [11].
free electrons. It resulting into a higher conductivity and hence have a harmful influence on the ferroelectricity. The Pb doping into BFO could increase the grain size as well the oriented growth (nanorod-type) in the samples. From Table 2, there is a considerable reduction in the leakage current of BFO upon Pb$^{2+}$ doping, which indicates reduction in oxygen vacancies.

3.3.2 Ferroelectric and piezoelectric properties of epitaxial BiFeO$_3$ thin film

Figure 5(a) and (b) shows the ferroelectric polarization and piezoelectric behavior of epitaxial BiFeO$_3$ thin film [35]. The films display a room-temperature spontaneous polarization (50 to 60 μC cm$^{-2}$) almost an order of magnitude higher than that of the bulk (6.1 μC cm$^{-2}$). These results leads to the observations of
heteroepitaxial, in-plane compressive stress imposed by the epitaxial bottom electrode allows growth of a monoclinic crystal structure in BFO, and the degree of compressive stress progressively decreases with increasing BFO thickness. The piezoelectric hysteresis loop shows a remanent out-of-plane piezoelectric coefficient ($d_{33}$) value 70 pm V$^{-1}$, representing the piezoresponse of the film in the fully clamped state.

3.3.3 Ferroelectric hysteresis of BaTiO$_3$/BiFeO$_3$/BaTiO$_3$

Figure 5(c) represents polarization hysteresis loops of trilayer films of BaTiO$_3$/BiFeO$_3$/BaTiO$_3$ measured at 50 kV cm$^{-1}$ applied electric field frequency of 10 kHz [36]. This trilayer thin film was prepared by RF-magnetron sputtering technique at different thicknesses of BiFeO$_3$ layer. The thickness of BTO layer is 20 nm at the top and bottom, and the middle layer BFO is deposited with thicknesses of 20 nm (B-2), 40 nm (B-4), 60 nm (B-6), and 80 nm (B-8), respectively. The film showed maximum remnant electric polarization ($2P_r$) of 13.5 $\mu$C cm$^{-2}$ and saturation magnetization ($M_s$) of 61 emu cc$^{-1}$ at room temperature. The ferroelectric polarization was found to be improved with increasing thickness of BFO layer may be attributed to the reduced oxygen vacancies.

3.4 Dielectric properties of BiFeO$_3$

3.4.1 Frequency dependent dielectric properties of Bi(Co$_{0.4}$Ti$_{0.4}$Fe$_{0.2}$)O$_3$

Figure 5(f) correlates the dielectric permittivity versus frequency plot at temperatures from 300 to 773 K of Bi(Co$_{0.4}$Ti$_{0.4}$Fe$_{0.2}$)O$_3$ multiferroic [37]. As the value of dielectric permittivity decreases upon increasing frequency, its nature could be described by Koop’s hypothesis and Maxwell-Wagner mechanism. The nano grains with highly resistive grain boundaries might exist in an inhomogeneous medium from which the application of electric field constructs space charge polarization. With low frequency, the grain boundaries influence is more dominant to cause dispersion in dielectric properties. However, the higher frequency reduces the space charge polarization impact because the slow traveling species are not capable to trace an applied electric field.

3.4.2 Temperature dependent dielectric permittivity of Pb:BiFeO$_3$

Figure 5(d) and (e) shows the temperature dependent relative permittivity ($\varepsilon_r$) for BiFeO$_3$ and Bi$_{0.925}$Pb$_{0.075}$FeO$_3$ (BPFO75) multiferroics [11]. The value of $\varepsilon_r$ starts to increase with temperature because of $T_N$ for pure BFO is 1103 K. This change in $\varepsilon_r$ at 600-650 K for both Pb:BFO samples occurs due to occurrence of $T_N$. For pure BFO, the value of $T_N$ is 643 K. The value of the ferroelectric phase transition ($T_{FE}$) is 644 and 649, respectively, for BFO and BPFO75. This observation is an anomaly in the phase transition; $T_{FE}$ around $T_N$ confirms the ME coupling, which must be correlated with inverse DM-type interactions and Landau-Devonshire theory of phase transition. The variation in phase transition temperature with frequency for Pb:BFO nanostructures (inset of Figure 5(d) and (e)) indicates the emergence of the relaxor behavior which explained with an increase cation disorder in the B-site and Bi-site substitution by Pb$^{2+}$.

3.5 Magnetization in BiFeO$_3$

The magnetization of BiFeO$_3$ is reported in the refs. [39–44]. The cycloidal model of spin ordering in BFO is distorted at low temperatures. Any break to the
cycloidal spin structure could induce uncompensated spins, enhancing the magnetization [45].

3.5.1 Magnetization in multiferroic BiFeO$_3$ and Bi$_{0.9}$Pb$_{0.1}$FeO$_3$

The ferromagnetic behavior of Pb substituted BiFeO$_3$ is reported in ref. [11] that the maximum value of magnetization, $M = 4.73, 8.41, 2.62$ and $8.99$ emu g$^{-1}$, respectively, for BFO, BPFO$_5$, BPFO$_75$ and BPFO$_{10}$. The origin of the variation of magnetization is analyzed with temperature dependent zero field (ZFC) and field cooled (FC) magnetization is shown in Figure 6(a). The splitting of the ZFC/FC curves usually appears as the co-existent system of the antiferromagnetic and ferromagnetic phases. With nanostructural dimensions of less than 62 nm, there is a possibility of modification to the cycloidal spin structure of BFO, and that can lead to weak room temperature ferromagnetism. The sharp cusp observed around 65 and 79 K, respectively, for BFO and BPFO$_{10}$ nanostructures in the ZFC curve is represented by the blocking temperature ($T_B$) which may attribute via superparamagnetic relaxation, glass transition, $T_N$ for antiferromagnetic-

![Figure 6](image-url)

Figure 6.
(a) Magnetization ($M$) as a function of temperature ($T$) following ZFC and FC at $H = 500$ Oe for BiFeO$_3$ (BFO) and Bi$_{0.9}$Pb$_{0.1}$FeO$_3$ (BPFO$_{10}$) multiferroics. The respective insets are $\chi^{\prime\prime} (T)$ following Curie-Weiss law. (a: right) The temperature dependent real part of the ac magnetic susceptibility ($\chi^{\prime \prime}$) at $T = 5\sim 200$ K ($H_{ac} = 2.5$ Oe without any dc field bias) [11]. (b) Magnetic hysteresis at 300 K for BiFeO$_3$ nanoparticles with different nano-sizes. Inset shows the corresponding magnetization at 50 kOe as a function of $1/d$. (c) Respect ZFC and FC curves at 200 Oe [39]. (d) Magnetic hysteresis of BiFeO$_3$ nanoparticles grafted on graphene nanohets (BiFeO$_3$-g-GNS) [40].

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ferromagnetic transition). The enhancement in magnetization is explained by Coey JMD et al. [46] model of F-center exchange mechanism where spin-polarized electrons were trapped at oxygen vacancies to cause higher magnetic moments. The upward curvature in FC curve of M(T) measurements of Pb:BFO suggested a Curie-Weiss like behavior Figure 6(a) (inset). The estimated value of $\theta$ is found to be negative which indicate to the formation of antiferromagnetic interactions.

The $ac$ magnetic susceptibility of Pb substituted BFO is measured at 1 Hz, 100 Hz, 1 kHz 10 kHz, and the temperature dependent real ($\chi_{\text{ac}}^\prime$) $ac$ magnetic susceptibility ($\chi_{\text{ac}}$) is shown in Figure 6(a) (right). The applied oscillating field, $H_{\text{ac}} = 2.5$ Oe without any $dc$ bias in $T = 5$-200 K. A quite sharp cusp is observed in both the samples. This $ac$ magnetic measurement at different frequencies revealed the peak positions of $\chi_{\text{ac}}^\prime$($T$) curve shift toward higher temperature and the peak magnitudes drop down with rising frequency. Such behavior is expected for a spin glass system. The dynamic susceptibility measurements can thus be used to confirm such spin glass or superparamagnetic by using frequency dependence of $T_{\text{f}}$($\omega$) in the expression, $\Delta p = \frac{\Delta T_{\text{f}}}{T_{\text{f}} \log(10\omega)}$. The calculated peak shift ($\Delta p$) per decade of frequency shift has a value 0.014 and 0.019, respectively, for BFO and BPFO10. These values of $\Delta p$ are lower than those observed for superparamagnetic system ($\Delta p$ is $\sim 0.154$).

3.5.2 Nano size dependent magnetism of BiFeO$_3$

The SQUID results as shown in Figure 6(b) suggest that a magnetic response in BiFeO$_3$ can be initiated when the size of the system is less than about 95 nm [39]. A plot of the magnetization, measured at the maximum applied field of $H_{\text{appl}} \sim 50$ kOe as a function of $1/d$, is given (inset of Figure 6(b)). Neel L [47] attributed the magnetic moment of small antiferromagnetic particles for the incomplete magnetic compensation between these two spin sublattices. For single-domain antiferromagnetic particles, the magnetization is expected to scale as $1/d$ (diameter), that is, as the surface to volume ratio [39]. For particles ranging in diameter from 95 to 41 nm, a linear dependence is observed, indicating that the simple Neel model is applicable [48]. The smallest nanoparticle is 14 nm that deviates from the expected behavior which indicates that such 14 nm nanoparticle may diminish the model for superposition of an antiferromagnetic core and a ferromagnetic surface. The maximum magnetization, obtained as $M_s$ $\sim 1.55$ emu g$^{-1}$ for the 14 nm particles. Figure 6(c) shows the magnetization measurements as a function of temperature at an applied field strength of 200 Oe following ZFC and FC process. It is noted that the apparent sharp cusps observed in the magnetization curves at 50 K are reproducible for BFO samples with particle dimensions over 95 nm (e.g. 245 nm and bulk). For BiFeO$_3$ nanoparticles possessing diameters of $\leq 95$ nm, associated data curves exhibit a broad magnetization maximum around $T_{\text{max}} = 85$ K. $T_{\text{max}}$ represents a spin-glass-like freezing temperature due to high packing volume fraction as well as a complex interplay between finite size effects, interparticle interactions, and a random distribution of anisotropy axes.

3.5.3 Temperature dependent magnetization of BiFeO$_3$-g-GNS nanoparticles

Magnetic properties of BiFeO$_3$ grafted on graphene nanosheets (BiFeO$_3$-g-GNS) is studied using SQUID VSM with an applied field of 5 T at different 10, 297 and 380 K Figure 6(d) [40]. Magnetic moments of nanoparticles get distorted at higher temperature. The maximum observed value of magnetization is 2.52 emu g$^{-1}$ at 10 K, while the minimum is 1.78 emu g$^{-1}$ at 380 K. At room temperature,
magnetization measured to be 1.98 emu g$^{-1}$. These values well matched with reported data [49]. It means the magnetic properties of BiFeO$_3$ are not compromised on GNS grafting.

3.5.4 Magnetization of BiFeO$_3$-CoFe$_2$O$_4$ (BFO-CFO) bulk heterojunction

Figure 7(a) exhibits the magnetic hysteresis in isotropic magnetic behavior along in plane and out of plane directions [41]. The value of $M_s$ of BFO-CFO/mica is $\sim$237 emu cm$^{-3}$ with $H_c \sim 2$ kOe, which is smaller than from epitaxial CFO/STO ($\sim 3$ kOe). This may due to the effect of an effective relaxation of clamping from the mica substrate.

3.5.5 Ferromagnetism in BiFeO$_3$/BaTiO$_3$ bilayer interface

Figure 7(b) shows the ferromagnetic behavior of BiFeO$_3$/BaTiO$_3$ (BTO thickness = 100 nm; BFO = 50 nm (BFBT-5), 100 nm (BFBT-10), 150 nm (BFBT-15), and 200 nm (BFBT-20) films [30]. The observed ferromagnetism in the bilayer thin films can be interpreted due to creation of unbalanced spins at the interface. Maximum magnetization value $M_s \sim 33$ emu cc$^{-1}$ was observed in BFBT-5. The value of saturation magnetization is 20 emu cc$^{-1}$ for BFBT-10 sample which is higher than for those observed in BFBT-15 (15 emu cc$^{-1}$) and BFBT-20 (8 emu cc$^{-1}$). This is because with smaller antiferromagnetic nanoparticles, the size reduction has incomplete surface compensation of long-range antiferromagnetic ordering which result into increase magnetic moment at comparatively smaller size nanograins.

Figure 7.
(a) $M$-$H$ hysteresis for BiFeO$_3$-CoFe$_2$O$_4$ composite at room temperature [41]. (b) $M$-$H$ loops of bilayer BiFeO$_3$/BaTiO$_3$ thin films [30].

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3.6 Magnetocapacitance

The ME behavior due to Magnetocapacitance (MC) effect in BiFeO$_3$ is given in the refs. [50–54]. The MC effect is the change in the capacitance with an external applied magnetic field. This MC/magnetodielectric effect has a resistive origin that arises from the Maxwell-Wagner effect and magnetostriction [55].

3.6.1 Dielectric constant and MC of Pb substituted BiFeO$_3$

Table 2 shows the magnetic field affected dielectric constant of Pb:BFO nanostructures measured at room temperature. The frequency dependent relative permittivity ($\varepsilon_r$) of Pb:BFO in the frequency region 20 Hz-10 MHz under dc magnetic field (H = 0, 1 kOe) is given [11]. From Table 2, the improvement in dielectric constant with the substitution of Pb$^{2+}$ for Bi$^{3+}$ provides a larger vibration space to a larger dipole moment. Besides the oxygen vacancies due to ionic formation of Fe$^{2+}$/Fe$^{3+}$ valence states, the shape/size of BFO grains might influence the dielectric behaviors [11]. It is also observed from Table 2 that the capacitance varies with applying magnetic field of 1 kOe, which indicate a positive/negative MC effect. The applied magnetic field leads to local stresses (or strains) and consequently changes in the polarization of the ferroelectric phase due to the piezoelectric effect. The values of MC ($\varepsilon(H) - \varepsilon(0) = \Delta\varepsilon/\varepsilon(0)$) at a frequency of 1 MHz is 0.61, 1.59, 0.36 and 0.11%, respectively, calculated for BFO, BPFO5, BPFO75 and BPFO10 multiferroic.

3.6.2 Magnetocapacitance effect in BiFe$_{0.95}$Sc$_{0.05}$O$_3$

The magnetic field dependent capacitance for BiFe$_{0.95}$Sc$_{0.05}$O$_3$ system to induce MC effect at 30 kHz is shown in Figure 8(a) [50]. The value of MC is 0.04% at applied magnetic field of 5 T which is higher than from pure BFO (0.007%). This type of MC behavior might be correlated with $P^2M^2$ in a Ginzburg-Landau free energy leads to a quadratic dependent dielectric constant in respect to magnetization. The observed results of MC in Figure 8(a) have magnetization-linear dielectric behavior which may proportional to $P^2M$ of a linear MC effect.

3.6.3 Piezoelectric properties of BiFeO$_3$/Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ composite films

Lead-free BiFeO$_3$/Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ (BFO/NBTO) composite films were deposited on Pt(100)/Ti/SiO$_2$/Si substrates using chemical solution deposition [51]. A giant ME voltage coefficient has maximum $\alpha_E = 136$ mV cm$^{-1}$ Oe$^{-1}$ at $H_{bias} = 8.0$ kOe. Figure 8(b) shows the piezoelectric coefficient ($d_{33}$) and surface displacement ($d$) vs. applied voltage (V) for BFO/NBTO films. A typical butterfly curve from D-V characteristics shows maximum value 4.06 nm at 15 V of 2.63% highest ratio of strain. The occurrence of $d_{33}$-V piezoelectric hysteresis from D-V curve is the result converse piezoelectric effect. The $d_{33}$-V loop clearly shows that BFO/NBTO composite films are switchable and the ferroelectricity is retained. The piezoelectric coefficient $d_{33}$ of BFO/NBTO films is as high as 285 pm V$^{-1}$ at 20 V, which suggests the strong piezoelectric effect for BFO/NBTO films.

3.6.4 Magnetostriction of BiFeO$_3$-BaTiO$_3$, Bi$_{0.8}$FeO$_{2.7}$-BaTiO$_3$, and BaFe$_{12}$O$_{19}$

The magnetostriction of BFO-BTO, B$_{0.8}$FO$_{2.7}$-BTO, and BaFe$_{12}$O$_{19}$ ceramics was measured using a resistive strain gauge when a dc magnetic field was applied to the materials (Figure 8(c)) [52]. A contraction induced by the magnetic field is
observed, and at 6 kOe, the contraction is approximately 20 ppm. BaFe$_{12}$O$_{19}$ is a ferromagnetic material and can have a magnetostrictive response. However, due to the weak ferromagnetic nature of the BFO-BTO ceramics, it was difficult to detect the strain below 6 kOe. Because only a small amount of BaFe$_{12}$O$_{19}$ is generated in the Bi-deficient ceramics, the magnetostriction is also very small in the materials.

3.6.5 ME coupling: ferroelectric polarization in an applied magnetic field

The mechanism for the spin driven ferroelectricity must be involved the spin-current model or inverse DM interaction due to the local electric polarization, \( p \propto e_{ij} \times (S_i \times S_j) \), where \( e_{ij} \) is the unit vector of adjacent spins, \( S_i \) and \( S_j \) [56]. These cycloidal spin structures produced the macroscopic electric polarization \( P \) due to helicity of spins. The ferroelectric hysteresis under an external magnetic field and the flop near 0.6 T reveal a strong ME coupling in BFO-BTO multiferroics as shown
in Figure 8(d) [53]. Without applying H, values of $P_{\text{max}} = 24.80 \mu \text{C cm}^{-2}$, $P_r = 15.13 \mu \text{C cm}^{-2}$ and $E_c = 53.6 \text{kV cm}^{-1}$ are observed. Switching from $+P_r$ to $-P_r$ by E, and magnetic switching from $+P_r$ to zero at 0.6 T have been observed. The inset of Figure 8(d) shows a low polarization response with lossy hysteresis of BFO-BTO composite at 0.6 T, which may cause by the electrode. When a magnetic field is applied to a ME material, the material is under strain to induce a stress on the piezoelectrics (ferroelectric) to orient ferroelectric domains, leading to enhance polarization.

3.6.6 ME effect in BiFeO$_3$ by PFM

Figure 8(e) shows AFM, out of plane piezoresponse amplitude of the BFO thin film which leads to agglomeration of the nanoparticles of average size 10 nm [55]. It can be seen from Figure 8(f) that BFO nanoparticles exhibits positive and negative polarization components and the ferroelectric domains are constrained at grain boundaries. The PFM amplitude under bias voltage is shown in Figure 8(g). It observed ferroelectric hysteresis for dc voltage sweeps in $+0.5 \text{ V to } -0.5 \text{ V to } +0.5 \text{ V}$ which indicates that sub - 5 nm BFO nanoparticles retains their ferroelectric behavior that might be usable for read-write operation.

3.7 Magnetoelectric (ME) coupling

3.7.1 ME coupling in Bi$_{0.88}$Dy$_{0.12}$Fe$_{0.97}$Ti$_{0.03}$O$_{3+\delta}$ (BDFO) and BiFeO$_3$

The ME effect of BFO and BDFO was measured, and the results are shown in Figure 9(a) [57]. It can be seen that the pure BiFeO$_3$ exhibits no ME signal under bias magnetic field because spatially incommensurately modulated spin structure that cancels out the linear ME effect. In contrast, BDFO exhibits a strong ME signal under bias magnetic field at 300 K due to the ME coefficient $\alpha_E$-magnetic field ($\alpha_E$-H) hysteresis to include the features of saturation at field of 250 Oe. This is because the switching of electric polarization by either $10^9$ or $71^\circ$ leads to switching of the ferroelastic domain states [58–60]. The incorporation of Dy$^{3+}$ into BFO suppresses the spiral spin structure, leads to weak ferromagnetism. Because the magnetic moment lags behind the variation of magnetic field, the electric polarization induced by magnetic field through ME effect is also lagged behind the variation of magnetic field, giving $\alpha_E$(H) hysteresis.

3.7.2 ME coupling of 15 x (10 nm BaTiO$_3$-5 nm BiFeO$_3$)

The ME coefficient was measured as a function of dc bias field in Figure 9(b) for 15 x (10 nm BaTiO$_3$-5 nm BiFeO$_3$) [58]. The ME coefficient reaches its maximum, off - resonance, value of 60.2 V cm$^{-1}$ Oe$^{-1}$ at a bias field of 2 T. This higher value is described due to the rotation of the oxygen octahedra with the antiferro-distortion vector $\Omega$ and shows that the linear ME effect depends on the derivative of $\Omega$ with respect to the external field. This leads to giant values of $\alpha_{\text{ME}}$.

3.7.3 ME coupling of 15 x [BaTiO$_3$/BiFeO$_3$] multilayer

The effect of strain and interfaces on the ME coupling in BiFeO$_3$ was studied for a number of thin films and multilayers of 15 x [BaTiO$_3$/BiFeO$_3$] as shown in Figure 9(c) [33, 59]. To this end, a direct longitudinal ac method was used to measure the ME coefficient $\alpha_{\text{ME}}$ as a function of static magnetic field. It is clear that $\alpha_{\text{ME}}$ of the multilayer is notably larger than that of the BFO film. Since the
multilayer additionally contains piezoelectric/piezomagnetic interfaces, an extra ME coupling in multilayers may occur via the horizontal interfaces through strain-mediated interface coupling. The magnetostrictive stress is produced in the weak ferromagnetic BiFeO$_3$ layer and is transferred to ferroelectric BaTiO$_3$ layer through the interface (Figure 9(d)). This mechanical stress generates an electric potential difference in the ferroelectric layer via a piezoelectric effect.

3.7.4 Magnetoimpedance and ME effects of BaTiO$_3$/BiFeO$_3$/BaTiO$_3$ heterostructure

The ME effect for BaTiO$_3$/BiFeO$_3$/BaTiO$_3$ heterostructure is also investigated by analyzing complex impedance ($-Z''$ vs. $Z'$) as well as complex modulus plots ($M''$ vs. $M'$) under applied magnetic fields (Figure 9(e)) [36]. The data were fitted with an equivalent circuit of two series RC-elements. Two well resolved semicircles
<table>
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<th>BiFeO₃ composition</th>
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<th>Phase structure</th>
<th>Nano-structure</th>
<th>Pₓ/Pᵧ (μC cm⁻²)</th>
<th>M (emu g⁻¹)</th>
<th>MC (%)</th>
<th>αₓₑₑ mVcm⁻¹ Oe⁻¹</th>
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<tr>
<td>BiFeO₃−BaTiO₃</td>
<td>RF-magnetron sputtering</td>
<td>(110) plane: high degree</td>
<td>50 nm thick BiFeO₃</td>
<td>15.5/9</td>
<td>33</td>
<td>4.96</td>
<td>61</td>
<td>[30]</td>
</tr>
<tr>
<td>0.7BiFeO₃/0.3MgLa₀.02Fe₁.97O₄</td>
<td>Sol-gel auto combustion</td>
<td>distorted R</td>
<td>D = 56 nm</td>
<td>0.28/0.08</td>
<td>5.28</td>
<td>—</td>
<td>—</td>
<td>[80]</td>
</tr>
<tr>
<td>0.9BiFeO₃−0.1PbTiO₃</td>
<td>Sol-gel solid state</td>
<td>R/T</td>
<td>—</td>
<td>3.8 × 10⁻⁵</td>
<td>0.06</td>
<td>—</td>
<td>0.2</td>
<td>[81]</td>
</tr>
<tr>
<td>BaFe₃O₉/BiFeO₃</td>
<td>Mechano-chemical</td>
<td>H/R</td>
<td>D = 588 nm</td>
<td>~2.8/1.4</td>
<td>~28</td>
<td>—</td>
<td>11.9</td>
<td>[82]</td>
</tr>
<tr>
<td>BiFeO₃/CoFe₂O₄</td>
<td>Solvothermal</td>
<td>R/spinel</td>
<td>D = 285 nm</td>
<td>2.1/1</td>
<td>30.1</td>
<td>—</td>
<td>8.5</td>
<td>[83]</td>
</tr>
<tr>
<td>0.7BiFeO₃/0.3PbTiO₃</td>
<td>Solid-state</td>
<td>R/T</td>
<td>D = 37 nm</td>
<td>~1.1/0.2</td>
<td>AF</td>
<td>—</td>
<td>—</td>
<td>[84]</td>
</tr>
<tr>
<td>0.67BaTiO₃−0.33BiFeO₃</td>
<td>Pulsed laser</td>
<td>R/T</td>
<td>1850 nm thick film, D = 40 nm</td>
<td>400/230 × 10⁻² Cm⁻²</td>
<td>2 × 10⁻⁵ μ₀T</td>
<td>—</td>
<td>20.75</td>
<td>[33]</td>
</tr>
<tr>
<td>BaTiO₃/BiFeO₃/BaTiO₃</td>
<td>RF-magnetron sputtering</td>
<td>R/T</td>
<td>BTO = 20 nm BFO = 40 thick thin film</td>
<td>~8/3.2</td>
<td>37</td>
<td>5.95</td>
<td>457</td>
<td>[36]</td>
</tr>
<tr>
<td>Bi₀.₃Fe₂O₉−BaTiO₃</td>
<td>Solid-state</td>
<td>R/T</td>
<td>D = ~1 μm</td>
<td>~48/30.2</td>
<td>~5.5</td>
<td>—</td>
<td>~120</td>
<td>[52]</td>
</tr>
<tr>
<td>BiFeO₃/Nb₂O₅Bi₄Ti₄O₁₅</td>
<td>Chemical solution deposition</td>
<td>R/O</td>
<td>BFO = 879 nm NBT = 545 nm</td>
<td>62.1/38.7</td>
<td>4.68</td>
<td>—</td>
<td>136</td>
<td>[51]</td>
</tr>
</tbody>
</table>

Table 3.
Summary of multiferroic properties of BiFeO₃ (phase structure (monoclinic (M), rhombohedral (R), tetragonal (T), orthorhombic (O), cubic (C), hexagonal (H)), nanostructural size (diameter (D) and length (l)), ferroelectric spontaneous polarization (Pₛ), remanent polarization (Pᵣ), saturation magnetization (M), antiferromagnetic (AF), magnetocapacitance (MC), and magnetoelectric coefficient (αₘₑ)).
representing increase in both grain and grain boundary resistance ($R_g$ and $R_{gb}$) with applied magnetic field are shown. A maximum 20% increase in grain capacitance ($C_g$) with applied magnetic field of 2 kG to represent an intrinsic ME effect. The bonding between Fe and Ti atoms at interface results into ME interaction between BFO and BTO at both interfaces. This interaction to change grains/boundaries resistances with the application of magnetic field induced magnetoimpedance/MC effect which is explained with Maxwell-Wagner model consisting of two leaky capacitors connected in series.

The ME coefficient, $\alpha_{ME}$ was measured in trilayer BaTiO$_3$/BiFeO$_3$/BaTiO$_3$ film by dynamic method (Figure 9(f)) and the detailed measurement set-up is given [36]. The $\alpha_{ME}$ was calculated using equation, $\alpha_{ME} = \delta V/\delta H.t$, where $\delta V$ is the measured output voltage, $\delta H$ is applied ac magnetic field, and $t$ is the film thickness. The maximum $\alpha_{ME}$ of $\sim$515 mV cm$^{-1}$ Oe$^{-1}$ is observed for B-2 film. By increasing the thickness of BFO layer, $\alpha_{ME}$ found to be reduced to 457 mV cm$^{-1}$ Oe$^{-1}$ for B-4, 400 mV cm$^{-1}$ Oe$^{-1}$ for B-6, and to 318 mV cm$^{-1}$ Oe$^{-1}$ for B-8. The enhancement in ME coupling for trilayer films may the effect of bonding between Fe and Ti atoms at both interfaces via oxygen atom. The reduction in oxygen vacancies with increasing thickness of BFO layer results into decreasing $\alpha_{ME}$ value.

### 3.8 Comparison of multiferroic properties of BiFeO$_3$

In Table 3, we have reported the list of multiferroic properties such as synthesis method, phase structure, nanostructures, ferroelectric behavior, magnetization, magnetocapacitance and ME coefficient of BiFeO$_3$. It is observed that the single phase BiFeO$_3$ has multiferroic behavior enhanced due to different doping from transition and rare earth ions. For the composites of BiFeO$_3$, there are moderate improvements in ME coupling. However, for multilayer BiFeO$_3$ with BaTiO$_3$ or ferrites has remarkable value of ME coupling. The Magnetocapacitance effect study on BiFeO$_3$ is hardly reported. Therefore it is summarized that the different multilayers perovskites structures of BiFeO$_3$ may give much advancement to the multiferroic behaviors.

### 4. Conclusion

Multiferroic BiFeO$_3$ becomes a suitable material for spintronic application of data storage. Wet chemical methods, hydrothermal, Polymer-directed solvothermal, sol–gel template process, sonochemical, anodized alumina template, sol–gel based electrospinning and microwave synthesis are the best synthesis routes to control the shape and size of BiFeO$_3$ nanostructures. These nanostructural shape and size of BiFeO$_3$ has much impact to control the magnetism and leakage current of BiFeO$_3$. In addition to change dopant level and composites with other materials (such as ferrites and other perovskites like BaTiO$_3$), the BiFeO$_3$ thin films especially multilayers gives remarkable results of ferroelectric polarization and ME voltage.

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Synthesis and Characterization of Multiferroic BiFeO₃ for Data Storage

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