Multiferroic Bismuth Ferrite-based Materials for Multifunctional Applications: Ceramic Bulks, Thin Films and Nanostructures

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Abstract: Among the different types of multiferroic compounds, bismuth ferrite (BiFeO₃; BFO) stands out because it is perhaps the only one being simultaneously magnetic and strongly ferroelectric at room temperature. Therefore, in the past decade or more, extensive research has been devoted to BFO-based materials in a variety of different forms, including ceramic bulks, thin films and nanostructures. Ceramic bulk BFO and their solid solutions with other oxide perovskite compounds show excellent ferroelectric and piezoelectric properties and are thus promising candidates for lead-free ferroelectric and piezoelectric devices. BFO thin films, on the other hand, exhibit versatile structures and many intriguing properties, particularly the robust ferroelectricity, the inherent magnetoelectric coupling, and the emerging photovoltaic effects. BFO-based nanostructures are of great interest owing to their size effect-induced structural modification and enhancement in various functional behaviors, such as magnetic and photocatalytic properties. Although to date several

review papers on BFO and BFO-based materials have been published, they were each largely focused on one particular form of BFO. There have been very few papers addressing the different forms of BFO in a comprehensive manner and providing a comparison across the different forms. As BFO has been extensively studied over the past more than one decade especially in the past several years, there have been new phenomena arising more recently. Naturally they were not included in the early reviews. Here, we provide an updated comprehensive review on the progress of BFO-based materials made in the past fifteen years in the different forms of ceramic bulks, thin films and nanostructures, focusing on the pathways to modify different structures and to achieve enhanced physical properties and new functional behavior. We also prospect the future potential development for BFO-based materials in the cross disciplines and for multifunctional applications. We hope that this comprehensive review will serve as a timely updating and reference for researchers who are interested in further exploring bismuth ferrite-based materials.

Keywords: Bismuth ferrite; Multiferroic; Bulks; Thin films; Nanostructures

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1. Introduction

Multiferroics are one class of unique functional materials that possess two or more ‘ferroic’ orders, such as ferroelectricity, ferromagnetism, ferroelasticity and ferrotoroidicity.¹⁻²² They have attracted considerable interest owing to the coexistence of at least two switchable states (e.g., polarization, magnetization and strain), which promises a wide range of applications in multifunctional devices. More interestingly, the coupling among the different order parameters can induce new physical effects, such as the electric field control of magnetism or vice versa.^{1-3,9-14} One of the most desirable features for multiferroics is to achieve two or more ‘ferroic’ orders at room-temperature for device applications. In nature, however, there are very few single-phase multiferroic compounds simultaneously showing (anti-) ferromagnetism and ferroelectricity at room temperature,² among which bismuth ferrite (BiFeO_3 , BFO) is the most well-known one.^{23-104,107-160,163-264,266-387,389-419,421-450,452-494,496-506,515-542,567-571,573-614,618-644,646-858}

BFO is shown to exhibit extremely versatile crystal structures and a broad palette of physical properties,^{112-115,411,606} as revealed by the vast number of studies since its first discovery in 1957 by Royen *et al.*⁶⁰⁵ A significant breakthrough was made in 2003, when a large ferroelectric polarization of $\sim 60 \mu\text{C}/\text{cm}^2$ was demonstrated for the first time by BFO epitaxial thin films.^{27,97} Since then, BFO, in its various forms such as ceramic bulks, thin films, and nanostructures, have been extensively studied. Many interesting findings have therefore been reported.²³⁻⁷⁶⁴ For example, the P_r value can exceed $>150 \mu\text{C}/\text{cm}^2$ in BFO-based thin films, as result of the substrate or lattice strain, composition tuning, and effect of buffer layer.^{5,23,48,78,87,349} In particular, the crystal structures and physical properties of BFO thin films are very sensitive to

substrate strain due to the strong interplay between different degrees of freedom (lattice strain, charge, spin and orbital). The strain engineering has been widely used to manipulate the crystal structure and properties.^{78-83,99} For BFO-based ceramics, they can be made with much suppressed leakage current, high d_{33} value (~ 50 pC/N) and high T_C of >700 °C,⁸⁸⁻⁹⁰ which are superior to those of bismuth layer-structured ones. More recently, a remarkably enhanced d_{33} of ~ 402 pC/N and a high T_C of ~ 454 °C have been demonstrated in the BiFeO₃-BaTiO₃-BiGaO₃ ceramic system by forming a rhombohedral-tetragonal (R-T) phase boundary similar to the morphotropic phase boundary (MPB) in lead zirconium titanate (PZT).¹¹⁸ Low dimensional BFOs have exhibited dramatic differences in functional properties as compared to the corresponding ceramic bulks and thin films, due to the great enhancement in surface area and creation of surface states. For example, the surface-induced and uncompensated spins by nanosizes can enhance the magnetization of BFO.^{504,505,649} The visible-light photocatalytic ability of BFO nanostructures are significantly enhanced due to the modulation in band gap and larger surface area,^{10,12,505} thus promising the widespread applications in production of hydrogen through solar water splitting.⁶⁵⁰ In addition, several novel physical effects have also been discovered in the BFO-based materials. For example, both diode effect and switchable photovoltaic current were reported for BFO single crystals by Choi *et al.*,⁹⁸ and several physical mechanisms were then proposed to account for the origin of the photovoltaic effect in BFO.¹⁰⁵⁻¹¹⁰ Thanks to these new findings, the research enthusiasm on the BFO-based materials remains undiminished in recent years and it will continue in the future.

Fig 1. (a) Publications on multiferroic and BiFeO₃ in refereed journals in the time window of 2000 to 2015, and (b) publications on BiFeO₃ in 2000~2015.

Fig 2. Statistics of refereed publications on the properties of BFO over the period of 2000 to 2015.

Fig 3. (a) Publications on BiFeO₃ bulks, thin films, and nanostructures in refereed journals in the time period of 2000 to 2015.

Figure 1(a) shows the statistic data on refereed publications from 2000 to 2015 searched using the keywords “multiferroic” and “BiFeO₃”. Publications on “BiFeO₃” make up ~42.97% of those on “multiferroic”. As a result, the research on BiFeO₃ plays a central role in the development of multiferroic materials as a whole. There is a gradually increasing trend in the number of publications on “BiFeO₃”, as shown in Fig. 1(b). The statistical data indicate that BFO-based materials have received an increasing attention.²³⁻⁷⁶⁴ By further analyzing the data, it can be found that most of the researches have focused on the ferroelectric, magnetic, magnetoelectric, piezoelectric, and more recently photovoltaic properties of BFO-based materials. Figure 2 shows the statistic data on the refereed publications concerning the above mentioned properties over the time period from 2000 to 2015. Those studies on “ferroelectric” and “magnetic” dominated the researches of BFO-based materials. Considerable attention was also paid to the magnetoelectric, piezoelectric, and more recently photovoltaic properties. Figure 3 shows the publications on BiFeO₃ ceramic bulks, thin films, and nanostructures in refereed journals for the time period of 2000 to 2015, where one can see that thin films take up about 50 % of the total share due to the rich variation in tunable structures and properties.

Over the past fifteen years, several research groups have summarized the advances of BFO-based materials at the different stages of development and from different angles,^{2,14,15,17,19,20,92-96,493,632,775-810} which have greatly promoted the research progresses and led to some of the major breakthroughs. For example, in their review, Ramesh *et al.*^{805,807,810} concentrated on the function of multiferroic bismuth ferrite in electric field control of ferromagnetism. Scott *et al.*¹⁷ emphasized the fundamental physics of bismuth ferrites as well as their potential device applications in spintronics

and memory devices that could be addressed both electrically and magnetically. Silva *et al.*⁹² provided an account on the preparation methods (e.g., oxide precursors and wet chemical) and the related properties of BFO-based ceramics. Yuan *et al.*⁹³ stressed the ferroelectric and piezoelectric properties of rare earth elements-doped BFO ceramics prepared by liquid-phase sintering method. Rojac *et al.*⁹⁴ visited the major processing issues of BFO-based ceramics, and their physical mechanisms in the formation of secondary phases and electrical properties. Chu *et al.*⁹⁵ introduced the growth of BiFeO₃ thin films and emphasized the use of piezoresponse force microscopy and X-ray reciprocal space mapping to characterize their crystal structure and domain structure, and illuminated the ferroelectric switching mechanisms. Sando *et al.*⁹⁶ discussed the influences of thickness and strain on the crystal structure and properties of BFO epitaxial films and highlighted the various types of devices based on BFO. In other reviews and summaries,^{2,14,15,19,20,493,632,779-803,807-809} BFO-based materials were discussed as part of the multiferroic materials. In most of the previous reviews, BFO-based materials were considered largely in several specific aspects and/or as a particular class of multiferroic materials.^{92-96,776-778,804-806,810} Additionally, previous review papers on BFO were each largely restricted to one particular form of BFO. There have been few papers addressing the different forms of BFO in a comprehensive manner and providing a comparison across the different forms. Furthermore, there has been considerable progress over the very recent years, where several new phenomena concerning the structures and properties of BFO-based materials have been derived, which have not been properly covered by the previous reviews. It would therefore be of considerable value to provide a systematic account including the most recent progress that has been made as well as the future prospects of these materials in the forms of ceramic bulks, thin films and nanostructures,

focusing on the effective pathways to modify the different structures and to achieve enhanced functional properties as well as new physical phenomena. We also prospect the future potentials of the rapid development of BFO-based materials in the cross disciplines and for multifunctional applications. We hope that this comprehensive review will serve as a timely updating and reference for researchers who are interested in further exploring bismuth ferrite-based materials.

Fig. 4. Outline of this review

Figure 4 shows the outline of this review. In the first part, we give a general introduction to the background and basic physics of BFO, emphasizing the structures, properties and their physical origins. In the second part, we focus on the progress and prospects of BFO in various forms (i.e., ceramic bulks, thin films, and nanostructures), and systematically look into the relationships among chemical modifications,

structures and properties. Emphasis is given in some specific aspects, e.g., the relationship between phase boundary and piezoelectricity of BFO ceramic bulks, the epitaxial strain-induced phase structures of BFO thin films, and the size effect on physical properties in BFO nanostructures. In the third part, we will address several key physical properties, discuss certain existing challenges, suggest possible methods for further improvement, and provide conclusions arising.

2. General considerations

2.1 Structure

Fig. 5. R3c structure of BiFeO₃ represented with (a) hexagonal unit cell; (b) two pseudocubic unit cells along the [111] direction with different rotations of oxygen octahedra; and (c) 2×2×2 super cell [112-115,411,606].

BFO is known to be the only single-phase ABO₃-type perovskite compound which possesses multiferroic properties at room temperature, and is thus considered to be the most promising candidate among various multiferroic materials for applications in the next generation memories and spintronics.^{17,97} The first BFO sample was synthesized in the late 1950s,⁶⁰⁵ and the crystal structure was characterized a few years later.⁷⁶⁴

BFO exhibits a rhombohedral R3c space group (R phase) in bulk form, in which

$a=3.965 \text{ \AA}$ $\alpha=89.45^\circ$, and the FeO_6 octahedra tilting angle is about 11° .^{411,606} Figure 5 shows the R3c structure of BFO expressed in three common ways. The structure of BFO is remarkably flexible, which can be easily modified by many factors, such as temperature, strain and composition modification. At higher temperatures (e.g., $\sim 1100 \text{ K}$), BFO endures a first-order phase transition from R phase to a GdFeO_3 -like Pbnm phase and a (probable) orthorhombic γ phase.¹¹²⁻¹¹⁵ The crystal structure of epitaxial BFO films can be modulated by imposing the strain using different substrates, into monoclinic (M_A , M_B , M_C),^{402,403} tetragonal or tetragonal-like,^{48,99,400} rhombohedral,^{24,330,609} orthorhombic,^{406,610} and even triclinic;⁶¹⁴ Different phase structures or phase boundaries can also be established by doping foreign elements or forming solid solutions.^{118,125,128,130,137,144-146}

2.2 Ferroelectricity and Origin

Fig. 6. Evolution of ferroelectric properties in BFO materials from 2003~2015 [5,23,26,78,97,274,330,349,416,417].

In 1970, a weak spontaneous polarization of $3.5 \mu\text{C}/\text{cm}^2$ was first measured for BFO single crystal along the $\langle 001 \rangle$ direction of pseudocubic unit cell,²⁷⁸ in which the high

leakage current was considered to suppress the presence of saturated P - E hysteresis loops. Although efforts were then made to reduce the leakage current for attaining a good P - E loop, little progress was made over the following two to three decades. Until 2003, the Science paper published by Ramesh's group reported a large P_r in epitaxial BFO thin films at room temperature.⁹⁷ It was the first time to document such a large P_r in BFO-based materials, which aroused considerable interest in the research of BFO thin films [See Fig. 6].^{5,23,26,78,97,274,330,349,416,417} In 2005, a larger P_r of 90-100 $\mu\text{C}/\text{cm}^2$ was predicted in BFO-based materials with space group $R3c$ along the $\langle 111 \rangle$ direction by density functional theory within the local spin-density approximation (LSDA) and the LSDA+ U method.⁸ The origin of the polarization was further revealed to be the large ionic Bi displacement induced by stereochemically active 6s lone pairs.⁴²³ After that, the predicted giant P_r was experimentally demonstrated in the BFO thin films and single crystals,^{23,273} confirming that the large P_r value is an intrinsic behavior of BFO. There have been considerable efforts in tuning the structure and physical properties of BFO-based thin films for the past decade. More recently, the super-tetragonal phase of BFO has become a research focus,⁴²¹ because its giant polarization predicted is very attractive. The BFO-based thin films with super-tetragonal phase were shown to exhibit a giant P_r up to $\sim 230 \mu\text{C}/\text{cm}^2$ ^{248,78,99,109,349} which may be attributed to the giant c/a ratio of ~ 1.25 .

2.3 G-type Antiferromagnetism and ME Coupling

The magnetic structure of BFO is G-type antiferromagnetic below $T_N \sim 673 \text{ K}$ ^{102,765} with a modulated cycloidal spin structure having a long periodicity of 62 nm.¹⁰⁴ In addition, a weak ferromagnetism with the Dzyaloshinskii and Moriya (DM) type has been confirmed in BFO using the density functional theory within LSDA and

LSDA+U methods.⁷ Some theories also suggested that the weak ferromagnetism resulted in canting of antiferromagnetic moments in BFO [See Fig. 7], and the canting angle was calculated to be $\sim 1^\circ$ and would lead to a weak magnetization of $\sim 0.05 \mu_B$ per unit cell.⁷ A large number of researches focused on promoting the magnetic properties by various ways, for example, control of spiral magnetic ordering, site engineering, and introduction of strong ferromagnetic phases.^{97,113,448-504,536,616-620}

Fig. 7. Magnetic structure of BiFeO₃: G-type antiferromagnetic ordering and the formation of the weak ferromagnetic moment [632]

Magnetoelectric (ME) coupling is one of the most appealing aspects of multiferroic materials, because it provides additional degrees of freedom for manipulating the polarization/magnetization in multifunctional devices, such as actuators, sensors, and data storage devices.¹⁰ In BFO, the ferroelectricity and magnetism mainly originate from Bi and Fe, respectively. The coupling of ferroelectricity with magnetism is among the main interests, which has been investigated extensively by both theoretical and experimental studies.^{7,9, 805,807}

Fig. 8: Schematic diagram of (001)-oriented BiFeO₃ crystal structure and the ferroelectric polarization (bold arrows) and antiferromagnetic plane (shaded planes). (a) Polarization with an up out-of-plane component before electrical poling. (b) 180° polarization switching mechanism with the out-of-plane component switched down by an external electrical field. The antiferromagnetic plane does not change with the 180° ferroelectric polarization switching. (c) 109° and (d) 71° polarization switching mechanisms, with the out-of-plane component switched down by an external electrical field. The antiferromagnetic plane changes from the orange plane to the green and blue planes upon 109° and 71° polarization switching, respectively [9].

Fig. 9. Photoemission electron microscopy (PEEM), and in-plane PFM images of a BiFeO₃ film in the same area before and after electrical poling. (a,b) PEEM images before (a) and after (b) poling. (c,d) In-plane PFM images before (c) and after (d) poling. Regions 1 and 2 correspond to 109° ferroelectric switching, Regions 3 and 4

correspond to 71° and 180° switching. In regions 1 and 2 the PEEM contrast reverses after electrical poling. (e) A superposition of in-plane PFM scans shown in (c) and (d) used to identify the different switching mechanisms that appear with different colors and are labeled in the figure [9].

Bulk BiFeO_3 is a room-temperature ferroelectric with a large spontaneous polarization along the $[111]$ axes¹¹¹ [See Fig. 8(a)]. Its ferroelectric polarization exhibits eight possible orientations, corresponding to positive and negative orientations along four body diagonals. The polarization direction can be switched by 180° , 109° , and 71° [See Figs. 8(b)-(d)]. In particular, the polarization switching by 109° or 71° induces a change in the rhombohedral axis, and thus a switching of ferroelastic domain state takes place. The antiferromagnetic ordering belongs to the G-type, where nearest neighbour Fe moments are aligned antiparallel to each other in three cartesian directions.¹⁰² The preferred orientation of the individual spins is perpendicular to the rhombohedral axis (also the polarization direction), as suggested by the first principles calculations of the magnetocrystalline anisotropy energy.⁷ There is a sixfold degeneracy for (111) plane, effectively leading to an ‘easy magnetization plane’ for the orientation of magnetic moments. As the plane is perpendicular to the $\langle 111 \rangle$ axis, i.e., the ferroelectric polarization direction, there is a coupling between the antiferromagnetic sublattice and the ferroelastic strain state. Furthermore, the polarization switching by 71° or 109° can give rise to reorientation of the easy magnetization plane. The ME coupling is well recognized in BFO,⁶³³ where the electric control is demonstrated for magnetic domains in BFO thin films at room temperature, i.e., ferroelectrically-induced antiferromagnetic switching [See Fig. 9], which is of considerable value for device applications.^{9,97,805,807,810} The coupling arises

from both antiferromagnetic and ferroelectric domains due to the underlying ferroelastic domain structure. Such interesting phenomenon has intrigued the investigation into the ME coupling of BFO-based materials.^{513-543,766,805,807,810}

3. Forms of bismuth ferrite and recent advances

3.1 Ceramic Bulk

Fig. 10. Research publications on BFO-based ceramics over the period of 2000~2015.

In several previous studies, BFO ceramic bulks have earned a place due to application potentials, as shown in Fig. 10. The polarization of BFO is dominated mainly by the Bi^{3+} lone pair ($6s^2$ orbital), and its magnetization results from Fe^{3+} .⁴⁹³ Therefore, the physical behavior can be enhanced by introducing different ions to *A* or/and *B* sites of bismuth ferrite. In this section, we focus our attention on discussing the chemical modifications in BFO as well as the key resultant phenomena, by ion substitution and alloying with ABO_3 compounds.

It is difficult to prepare a single-phase stoichiometric BiFeO_3 ceramic bulk due to the loss of Bi^{3+} during the sintering process, and the occurrence of some secondary phases (e.g., Bi_2O_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, and $\text{Bi}_{25}\text{FeO}_{39}$).^{86,94,103,119-121} Even if a single-phase BFO bulk

can be attained, a high leakage current resulting from the presence of Fe^{2+} and oxygen vacancies makes it difficult to be electrically poled.^{94,119-121} As a result, it is necessary to look into the chemical modifications and preparation methods for BFO ceramic bulks. They can significantly affect the electrical properties of BFO ceramic bulks.

3.1.1 Ion Substitution

For improvement in electrical properties, ion substitution is one of the most common approaches for BFO ceramic bulks, including substitutions at either Bi or Fe or both sites. It is now well known that the ion substitution for Bi site can modify the ferroelectric and piezoelectric properties by decreasing the leakage current.^{88,122,124,126,127,129,130,132,138} The effects known by ion substitutions in BFO for different sites are described in detail below.

3.1.1.1 Substitution for Bi Site

Table 1 Structure and properties of BFO ceramics with ion substitutions in Bi site

Material system	Phase structure	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/g	Ref.
BiFeO_3	R	27	~10	~70	-	122
$\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$	R	-	0.51	16.6	0.078	123
$\text{Bi}_{0.875}\text{Sm}_{0.125}\text{FeO}_3$	Triclinic	29	15.1	90	0.071	124
$\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3 (x=0.125)$	R	45	40	150	-	125
$\text{Bi}_{0.95}\text{Dy}_{0.05}\text{FeO}_3$	-	-	31	120	0.021	126
$\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$	R~R-O	12-40	6.1~15	60~110	-	127
$\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$	R-Triclinic-Pseudo-T	-	9~1.9	-	0~0.23	128
$\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$	R	28	-	-	-	129
$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$	R-Triclinic-Pseudo-T	>25	9.8	-	0.20	130
$\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$	R	-	~6.0	-	-	131
$\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$	Pseudocubic	27.7	12	60	0.0744	132
$\text{Bi}_{1-x}\text{Ce}_x\text{FeO}_3 (x=0.15)$	R	-	8.4	60	-	133
$\text{Bi}_{0.95}\text{Ho}_{0.05}\text{FeO}_3$	-	-	1.59	5.45	0.736	134
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{FeO}_3$	R	-	12.5	63	0.028	135
$\text{Bi}_{1-x}\text{Yb}_x\text{FeO}_3$	R	-	8.5	~50	-	136
$\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$	R- R-O	-	-	-	0.075	137

(x=0.10)						
(Eu,Gd,Tb,Dy)-BiFeO ₃	R	48~49	21~35	106~117	0.016~ 0.044	138
Bi _{1-x} Pr _x FeO ₃	R	-	-	-	0.0051	139
Bi _{1-x} Sr _x FeO ₃	Triclinic	-	-	-	0.09	140
Bi _{0.74} Ba _{0.30} FeO ₃	Pseudo-tetragonal	-	-	-	0.16	141
Bi _{1-x} Ba _x FeO ₃	-	-	~5.5	-	~0.75	142
Bi _{1-x} Ca _x FeO ₃	R-Triclinic	-	-	-	~0.034	143
Bi _{1-x-y} Sm _x La _y FeO ₃	R	50	1.38	58.5	-	88

The substitution at Bi site strongly affects the ferroelectric and surprisingly even magnetic properties of BFO ceramic bulks, as the polarization is mainly induced by Bi site.⁴⁹³ Table 1 lists the phase structure, electrical and magnetic properties of BFO ceramics with ion substitutions in Bi site.^{88,122-143} One can see that the substitution by rare earth elements plays an important role in the improvement of electrical properties of BFO ceramics. The substitution by common rare earth elements (e.g., Sm,^{88,123-125} Nd,^{128,129} Dy,^{126,127,138} La,^{101,131,132} Ce,¹³³ Ho,^{134,135} Yb,¹³⁶ Eu,¹³⁷ Gd,¹³⁸ Eu,¹³⁸ Gd,¹³⁸ Tb,¹³⁸ and Pr¹³⁹) in Bi site can effectively suppress the leakage current of BFO ceramics, resulting in the enhancement of piezoelectric^{122,124,125,127,129,130,132,138} and ferroelectric^{124,132,135,138} properties. For example, Wu *et al.*⁸⁸ reported that a high d_{33} of ~50 pC/N for Bi_{1-x-y}Sm_xLa_yFeO₃ ceramics, due to the greatly decreased leakage current. In addition, a relatively large P_r of 20~35 $\mu\text{C}/\text{cm}^2$ was observed in BFO ceramics doped with Sm, Dy, Eu, Gd, Tb, etc.^{88,122,124-127,130,132,135,136,138} The decrease in leakage current caused by doping on Bi site could undoubtedly improve ferroelectric and piezoelectric properties. There are phase structure changes caused by ion substitution at Bi site, which can also play an important role. Therefore, one has to analyze the influences of different ion substitutions on the phase structure of BFO ceramics.

As can be seen from Table 1, the phase structure of BFO ceramics can be affected by doping with some elements into Bi site,^{124,125,127,128,130,132,137,140,141,144,145} accompanied by the change of their properties.^{124,125,127,130} BFO compounds doped with rare earth elements undergo phase transition from rhombohedral structure to others, and the phase structures are strongly dependent on the type and amount of doped rare-earth elements.^{113,127,128,628-631} For example, Yuan *et al.* found that the $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ceramics underwent a phase transformation from rhombohedral structure ($x=0$) to triclinic structure ($x=0.05\text{--}0.15$) and then to pseudotetragonal structure ($x=0.175\text{--}0.2$). Due to the continuing collapse of the space-modulated spin structure,¹²⁸ the magnetic behavior was also affected. Their ferroelectric properties were however deteriorated with increasing x due to the occurrence of the non-ferroelectric phases. At room temperature, $\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$ ceramics exhibit a rhombohedral structure at $x=0\text{--}0.12$, coexistence of triclinic and orthorhombic phases at $x=0.125\text{--}0.20$, and then paraelectric orthoferrite-type phase at $x=0.25$. A large d_{33} of 42 pC/N was observed in the two-phase region of triclinic and orthorhombic phases ($x=0.125$),⁴ due to the high piezoelectric activity at MPB.^{124,125} By further doping with La, the ceramic system of $\text{Bi}_{1-x-y}\text{Sm}_x\text{La}_y\text{FeO}_3$ with R phase exhibited an enhanced d_{33} of 50 pC/N.⁸⁸ Other rare earth elements (e.g., Dy,¹²⁷ Nd,¹²⁸ Eu,^{137,144} Gd,¹⁴⁵ Tb¹⁴⁶) have also been studied in inducing the phase transitions in BFO. The addition of certain Group II elements (Sr,¹⁴⁰ Ba,¹⁴² Ca¹⁴³) can change the phase structure and thus give rise to the enhanced properties. For example, in $\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$, the original R3c structure was distorted to a monoclinic or tetragonal structure as x varied. The pseudo-tetragonal structure led to an improved magnetic behavior ($M_s=0.75$ emu/g).¹⁴² The addition of Sr resulted in a structural transition from rhombohedral to triclinic, together with an enhanced magnetization, which may well be due to the suppression in inhomogeneous magnetic

spin structure as well as the increased canting angle.¹⁴⁰ However, it was observed that some elements (e.g., Ce,¹³³ Yb,¹³⁶ Pr,¹³⁹ Ho^{134,135,147-149}) could not induce the phase transitions in BFO ceramics. The enhancement of the ferroelectric properties induced by these elements was mainly attributed to suppressing leakage current.^{133-136,139,147-149}

Fig. 11. Relationship between phase structures and piezoelectric properties of Sm or Eu-doped BFO ceramics fabricated by the quenched method.

Recently, we have further developed Sm or Eu-modified BFO ceramics by a quenched method and have studied the effects of phase structures on their piezoelectric properties, the results of which are shown in Fig. 11. A higher d_{33} of 45~46 pC/N was obtained in the ceramics with a pure R phase, while the formation of mixed phases or other phases results in a lower d_{33} . Therefore, the R phase indeed exhibited better piezoelectric activity when Sm and Eu were used to modify BFO in ceramic form. In this case, “MPB” may not be necessarily needed for the improvement of piezoelectric effect of BFO ceramics. According to the available data, it is difficult to construct an MPB similar to that in PZT for the A-site modified BFO ceramics. Their electrical properties (especially ferroelectric and piezoelectric

behavior) were largely affected by the leakage current. As a result, the substitution ion type is very critical for the property modification.

3.1.1.2 Substitutions for Fe Site

Table 2 Structures and properties of BFO ceramics with ion substitutions for Fe site

Material system	Phase structure	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/g	Ref.
$\text{BiFe}_{0.75}\text{Ti}_{0.25}\text{O}_3$	-	0.081	2.571	0.025	150
$\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$	R	-	-	0.7	151
$\text{BiFe}_{0.95}\text{Zn}_{0.05}\text{O}_3$	-	-	-	-	152
$\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$	R	3.99	19.79	-	153
$\text{BiFe}_{1-x}\text{Ti}_x\text{O}_3$	R-R-O	-	-	-	154
$\text{BiFe}_{1-x}\text{Sc}_x\text{O}_3$	R	-	-	0.24~1.7m	155
$\text{BiFe}_{1-x}\text{Ta}_x\text{O}_{3+x}$	-	0.22	-	0.06	156
$\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$	-	-	-	0.015	157
$\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$	R	-	-	-	158
$\text{BiFe}_{1-x}\text{Ho}_x\text{O}_3$	R	8.4	~75	0.0258	149

Similar to the substitution in Bi site, the ion replacement on Fe site also affects the phase structure and relevant properties of BFO ceramic bulks. Table 2 lists the structures and some key properties of selected BFO ceramics with ion substitution for Fe site.¹⁴⁹⁻¹⁵⁹ One can see from Table 2 that the phase structure of BFO remains almost unchanged by the addition of several elements studied (e.g., Ho,¹⁴⁹ Co,¹⁵¹ Zn,¹⁵² Mn,¹⁵³ Sc,¹⁵⁵ Nb,¹⁵⁷ and Ni¹⁵⁹). However, the addition of Ti induced the formation of R-O phase boundary in BFO ceramic bulk.¹⁵⁴ Contrary to the Bi-site substitution (see Table 1), the ion substitution for Fe site often resulted in poorer ferroelectric and piezoelectric behavior¹⁴⁹⁻¹⁵⁹ and yet with some enhanced magnetic behavior.^{150,151,155,156,159} According to the available references,¹⁴⁹⁻¹⁶⁰ the degradation in electrical properties (ferroelectric and piezoelectric) may well be caused by the presence of dopant-induced secondary phases, e.g., Co, Nb, Sc, Zn, Zr, Ni. The magnetic properties of BFO ceramics could indeed be enhanced by doping some

magnetic elements (e.g., Co and Ni).^{151,159,604} For example, the addition of magnetic element Ni increased the remanent magnetization (M_r) of BFO ceramic bulk from 0.006 emu/g to 0.10 emu/g, which was due to the FM super-exchange interaction between Fe^{3+} -O- Ni^{2+} .^{161,162} Another example is that the Co substitution induced a rhombohedrally distorted structure with compressive lattice distortion in $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$, where its magnetic properties were significantly enhanced ($M_r \sim 0.7$ emu/g).¹⁵¹ While the magnetic properties can be generally improved by the substitution of an appropriate magnetic element for Fe site, it is still a challenging to make a trade-off between magnetic and ferroelectric properties in BFO ceramics.

3.1. 1.3 Substitution for Both Bi and Fe Sites

Table 3 Structures and properties of BFO ceramics with ion substitutions for Bi and Fe sites

Material system	Phase structure	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/g	Ref.
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.98}\text{Mn}_{0.02}\text{O}_3$	R3c-P4mm	-	31	110	0.075	58
$\text{Bi}_{0.8-x}\text{Sr}_x\text{La}_{0.2}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{O}_3$	O	-	-	-	-	163
$\text{Bi}_{1-x}\text{Nd}_x\text{Fe}_{1-x}\text{Mn}_x\text{O}_3$	R3c-Pnam-	-	-	-	0.023-0.033	164
$\text{Bi}_{0.85}\text{La}_{0.15}\text{Fe}_{0.9}\text{Ti}_{0.1}\text{O}_3$	R-T	-	-	-	0.25	165
$\text{Bi}_{1-x}\text{Ba}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$	Pseudo-Cc	-	-	-	2.59	167
$\text{Bi}_{0.74}\text{Ba}_{0.30}\text{Fe}_{0.95}\text{Ti}_{0.05}\text{O}_3$	Pseudo-T	-	-	-	0.15	141
$\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$	O	-	-	-	0.0195	168
$\text{Bi}_{0.80}\text{La}_{0.20}\text{Fe}_{1-x}\text{Nb}_x\text{O}_3$	R	-	-	-	0.06~0.20	169
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.98}\text{Zr}_{0.02}\text{O}_3$	R	-	-	-	0.013	170
$\text{Bi}_{0.87}\text{La}_{0.05}\text{Tb}_{0.08}\text{FeO}_3$	R	-	-	-	0.05/ 0.3	171
$\text{Bi}_{0.8}\text{La}_{0.2}\text{Fe}_{0.95}\text{Mg}_{0.05}\text{O}_3$	R	-	-	-	-	172
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.05}\text{O}_3$	R	-	0.4	20	0.242	173
$\text{Bi}_{1-x}\text{Ca}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$	R	-	0.28	-	0.18	174
$\text{Bi}_{1-x}\text{Zn}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$	R	-	0.1	7.5	1.5	175
$\text{Bi}_{0.8}\text{Ca}_{0.2}\text{Fe}_{1-x}\text{Mg}_x\text{O}_3$	R	-	-	-	0.6038	176
$\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$	R	-	-	-	0.1824	177
$\text{Bi}_{1-2x}\text{Ba}_{2x}\text{Fe}_{1-x}\text{Nb}_x\text{O}_3$	R	-	-	-	0.03933	178
$\text{Bi}_{0.9}\text{Gd}_{0.1}\text{Fe}_{1-x}\text{Ti}_x\text{O}_3$	R	-	-	-	~0.02	179
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{Fe}_{0.97}\text{Ni}_{0.03}\text{O}_3$	R	-	-	-	0.2280	180
$\text{Bi}_{0.85}\text{Y}_{0.15}\text{Fe}_{0.95}\text{Zr}_{0.05}\text{O}_3$	R	-	0.21	-	0.4150	181
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$	-	-	-	-	0.23	182
$\text{Bi}_{0.75}\text{Ba}_{0.25}\text{Fe}_{1-x}\text{Ni}_x\text{O}_3$	-	-	0.63	-	0.70	183

$\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Zr}_x\text{O}_3$	-	-	-	-	0.1234	184
$\text{Bi}_{0.925}\text{La}_{0.05}\text{Sm}_{0.025}\text{Fe}_{0.95}$	R	50	-	-	-	185
$\text{Bi}_{1-y}\text{Sm}_y\text{Fe}_{1-x}\text{Sc}_x\text{O}_3$	R	51	14.2	53.1	-	89

Fig. 12. (a) Piezoelectric properties of BLAFMO ceramics as a function of A and M elements, and (b) backscattering electron images of BLSFMO ceramics with M=Ga [185].

There have been studies of using different elements to simultaneously replace both Bi and Fe sites in BFO ceramic bulk,^{58,141,163-184} and their influences on the phase structure and physical properties. In BFO, the Bi 6s lone pair electrons are responsible for ferroelectricity and the partially filled d orbitals of Fe lead to magnetic moment.^{13,14} As a result, proper chemical modifications in both sites can promote the electrical (i.e., ferroelectric and piezoelectric) and magnetic properties. As shown in Table 3, different phase structures can be formed in BFO ceramic bulk by doping different elements to both Bi and Fe sites.^{58,141,163-168} For example, $\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.98}\text{Mn}_{0.02}\text{O}_3$ ceramics were reported to exhibit a structural transition from rhombohedral (R3c) to tetragonal (P4mm) phase, due to the addition of both Nd and Mn, together with enhanced ferroelectric properties being observed.⁵⁸ In addition, different phase boundaries were reported in other BFO-based ceramics with both sites being doped,^{58,141,163-168} such as R-T by La&Ti,¹⁶⁵ R-Pbnm by Ca&Nb,¹⁶⁶ R-

pseudotetragonal by Ba&Ti,¹⁴¹ and O by Pr&Ti.¹⁶⁸ On the other hand, it can also be seen from Table 3 that the phase structure of BFO remains almost unchanged when combinations of some elements are doped,¹⁶⁹⁻¹⁸⁴ such as La & (Nb,¹⁶⁹ Zr,¹⁷⁰ Fe,¹⁷¹ Mg¹⁷²), (Ho,¹⁷³ Ca,¹⁷⁴ Pr,¹⁷⁵ Gd¹⁷⁹) & Ti, Zn&Ni,¹⁷⁵ Ca & Mg,¹⁷⁶ Ho & Ni,¹⁸⁰ Y & Zr,¹⁸¹ Ba & Ni,¹⁸³ and Sm & Co.⁶⁰⁴ Poor ferroelectric and piezoelectric behavior were generally observed in spite of the enhancement in magnetic behavior.¹⁶⁹⁻¹⁸⁴ Recently, we have noted that certain element substitutions for both Bi and Fe sites can improve the piezoelectric activity of BFO ceramic bulk if the leakage current is well controlled.¹⁸⁵ For example, Bi_{0.925}La_{0.05}A_{0.025}FeO₃ (i.e., A: Sm, Yb, Ho, Y, Nd, Pr, Dy, Gd) and Bi_{0.925}La_{0.05}Sm_{0.025}Fe_{0.95}M_{0.05}O₃ (i.e., M: Sc, In, Al, Ga, Ni, Co) ceramics fabricated by the modified quenched method,¹⁸⁵ demonstrated an apparent dependence of piezoelectric behavior on the types of A and M ions [See Fig. 12(a)]. Some of these ions (e.g., A=Sm, Yb, Ho, and Y) could lead to both a single phase structure and relatively good piezoelectricity ($d_{33} \geq 40$ pC/N), while most of the M ions (e.g., In, Al, Ga, Ni, Co) were unable to help suppress the formation of impurity phases, leading to a degradation in piezoelectricity, as shown in Fig. 12(b).¹⁸⁵ By suppressing the secondary phases, Bi_{0.925}La_{0.05}Sm_{0.025}Fe_{0.95}Sc_{0.05}O₃ was demonstrated with a high d_{33} value of ~47 pC/N.¹⁸⁵ Their ferroelectric and piezoelectric properties can be simultaneously improved by choosing an optimal combination of element types on both sites. For example, a high d_{33} of ~51 pC/N and a low dielectric loss of ~0.25% were attained in the (1-x)Bi_{1-y}Sm_yFeO₃-xBiScO₃ ceramics with x=0.05 and y=0.05, together with a saturated P - E loop with $P_r \sim 14.2$ $\mu\text{C}/\text{cm}^2$ and $E_C \sim 53.1$ kV/cm.⁸⁹ One can also see from Table 3 that the ceramic compositions containing magnetic elements (i.e., Ni,^{175,183} Co^{167,182}) possess a higher M_r value with respect to

others. For example, $\text{Bi}_{1-x}\text{Zn}_x\text{Fe}_{1-y}\text{Ni}_y\text{O}_3$ with $x=y=0.1$ shows a high M_r value of >1.5 emu/g under the magnetic field of 800 Oe.¹⁷⁵

3.1.2 Addition of ABO_3

3.1.2.1 BiFeO_3 - BaTiO_3 Solid Solutions

Table 4 Structures and properties of BFO- BaTiO_3 -based ceramics.

Material system	Phase structure	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	E_c kV/cmm	M_r emu/g	T_c °C	Ref.
$(1-x)\text{BiFeO}_3$ - $x\text{BaTiO}_3$ ($x=0.33$)	R-Pseudocubic	0.15%	19.6	29	-	-	186
0.65BiFeO_3 - 0.35BaTiO_3	Pseudocubic	104	30.6	27.9	0.07	414	187
0.75BiFeO_3 - 0.25BaTiO_3	R-c	-	12.95	-	0.1	310	188
0.8BiFeO_3 - 0.2BaTiO_3 (N_2)	R	98	25.7	74.6	-	632	189
$(1-x)\text{BiFeO}_3$ - $x\text{BaTiO}_3$ - $0.6\text{wt}\%, \text{MnO}_2$ ($x=0.275$)	R-T	136	-	-	-	-	190
0.75BiFeO_3 - 0.25BaTiO_3 -Mn	R	116	22.9	39.3	-	619	191
$(1-x)\text{BiFeO}_3$ - $x\text{BaTiO}_3$ - CuO - MnO_2 ($x=0.325$)	R-P	170	18	30	-	485	193
0.71BiFeO_3 - 0.29BaTiO_3 - $0.6\text{wt}\%, \text{MnO}_2$	Pseudocubic	131	20	-	-	463	194
$(0.725-x)\text{BiFeO}_3$ - 0.275BaTiO_3 - $x\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -1 mol% MnO_2 ($x=0.02$)	R-T	140	27.4	-	0.19	-	195
0.8BiFeO_3 - 0.2BaTiO_3 - x wt.% SiO_2 ($x=0.15$)	R	86	-	-	-	-	196
$(1-x)(0.65\text{BiFeO}_3$ - $0.35\text{BaTiO}_3)$ - $x\text{Nb}_2\text{O}_5$	Pseudocubic	-	5.33	-	-	-	197
$(0.725-x)\text{BiFeO}_3$ - 0.275BaTiO_3 - $x\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$ - MnO_2 ($x=0\sim 0.02$)	R-T	129~135	~11	~32	-	559~610	198
$(0.75-x)\text{BiFeO}_3$ - 0.25BaTiO_3 - $x\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3$ -1 mol% MnO_2 ($x=0.01$)	R-O	112	7.69	33.9	-	-	199
$(1-y)\text{BiFe}_{1-x}(\text{Mg}_{0.5}\text{Ti}_{0.5})_x\text{O}_3$ - $y\text{BaTiO}_3$ ($y=0.29$, $x=0.03$)	Pseudocubic	155	~16	25	-	425	200
0.69BiFeO_3 - $0.02\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ - 0.29BaTiO_3 -0.3wt% MnO_2	Pseudocubic	115	25.4	40	-	509	201
$(0.70-x)\text{BiFeO}_3$ - 0.30BaTiO_3 - $x\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ - MnO_2 ($x=0.05$)	-	139	28.1	-	-	~530	203
$(0.75-x)\text{BiFeO}_3$ - 0.25BaTiO_3 - $x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - 1 mol% MnO_2 ($x=0.05$)	R- Pseudocubic	120	18.7	-	-	-	205
$(1-x)\text{BiFeO}_3$ - $x\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ -1mol% MnO_2 ($x=0.275$)	R	106	24.5	—	0.00135	425	206
$0.71\text{Bi}(\text{Fe}_{1-x}\text{Ga}_x)\text{O}_3$ - 0.29BaTiO_3 ($x=0.015$)	Pseudocubic	157	8	23	-	464	207
$0.71(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$ - 0.29BaTiO_3 - MnO_2 ($x=0.02$)	-	168	16.0	-	-	400	208
$0.71\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ - 0.29BaTiO_3 ($x=0.6\%$)	Pseudocubic	167	-	-	-	488	209

0.75Bi _{1-x} Nd _x FeO ₃ -0.25BaTiO ₃ -1mol%MnO ₂	R-Monoclinic	113–121	16.5–17.5	-	0.127–0.138	473–482	210
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As discussed above, ion substitutions can effectively improve the electrical properties of BFO ceramic bulk. There are several well studied oxide perovskites, such as BaTiO₃ and PbTiO₃,¹⁸⁶⁻²¹² some of which have been employed to form the solid solutions with BFO. The BiFeO₃-BaTiO₃ is one typical example,¹⁸⁶⁻²¹² where the structure and properties can be effectively tailored by changing the BaTiO₃ contents. Indeed, BiFeO₃-BaTiO₃ solid solutions have been shown with several structural transitions with increasing BaTiO₃ contents. For example, a rhombohedral structure was formed when BFO was up to 67 mole % in the solid solution. A tetragonal structure appeared for the compositions with BFO content being below 6 mole %. In between these two critical compositions, the cubic phase was dominant.²¹³ Similar phases were observed by other researchers for the same system, although at different BTO contents, i.e., rhombohedral phase (0.0~0.30), pseudo-cubic phase (0.30~0.95), and tetragonal phases (0.95~1.0).^{214,215} Table 4 summarizes the electrical properties of BFO-BTO-based ceramics,¹⁸⁶⁻²⁰⁹ where one can see that their piezoelectric and ferroelectric properties can be effectively strengthened, in connection with the above mentioned phase transitions.^{186-188,190,193,198,199,201,210} To further enhance their electrical properties, several approaches have been taken,¹⁹⁰⁻²¹⁰ including for example introducing certain additive oxides,¹⁹⁰⁻¹⁹⁷ elements,²⁰⁷⁻²¹⁰ and other additional ABO₃ compounds.¹⁹⁸⁻²⁰⁶

For improving the *dc* resistivity and other electrical and magnetic properties, oxide additives (e.g., MnO₂, CuO, etc) were used to modify the BFO-BTO ceramics.^{191,194,218-220} For example, the magnetic properties were enhanced by doping MnO₂ into BFO-BTO.²¹⁰ 0.7BiFeO₃-0.3BaTiO₃-*x*wt.%MnO₂ (*x*=0~0.5) ceramics

were shown to exhibit enhanced M_r , which increased up to 0.15 emu/g for 0.5 wt.% MnO_2 . Such a M_r enhancement was due to the decrease in crystal symmetry as well as the creation of lattice defects.²¹⁹ Within CuO-doped BFO-BTO ceramics, there was a transition being observed from relaxor to normal ferroelectric with increasing CuO content, as a result of the structural transition from pseudocubic to R phase as well as the domain configuration changing from nanodomains to macrodomains.²²⁰ Recently, MnO_2 and CuO were studied as co-dopings to modify the behavior of BFO-BTO ceramics, where both T_C of 170 °C and d_{33} of 485 pC/N were obtained, in connection with both rhombohedral lattice distortion and enhanced densification.¹⁹³ There is no doubt that the addition of appropriate oxides helps improve the overall electrical properties of BFO-BTO ceramics.

Adding certain ABO_3 compounds, such as $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$,^{192,200,221} $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$,²⁰⁵ $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$,¹⁹⁵ $\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$,¹⁹⁸ $\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3$,¹⁹⁹ and $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$,²⁰³ has been shown to be able to tailor the electrical properties of BFO-BTO ceramics. For example, $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ improved the piezoelectric activity of BFO-BT, due to changes in nanodomains, while there was no formation of phase boundaries.^{192,200,221} In contrast, the multicomponent system of $(0.75-x)\text{BiFeO}_3-0.25\text{BaTiO}_3-x\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3-1\text{mol}\%\text{MnO}_2$ ($x=0.025$) was demonstrated to possess a large d_{33} of 126-135 pC/N, where the coexistence of rhombohedral and pseudocubic phases was observed.²⁰⁵ The addition of $\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3$ and $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ did not lead to much change in the phase structure of BFO-BTO ceramics.^{199,203} The $\{(0.75-x)\text{BiFeO}_3-0.25\text{BaTiO}_3-x\text{Bi}_{0.5}(\text{Na}_{0.8}\text{K}_{0.2})_{0.5}\text{TiO}_3-1\text{mol}\%\text{MnO}_2\}$ ceramics with $x=0.01$ showed enhanced ferroelectric and piezoelectric properties ($d_{33}=112-114$

pC/N, $k_p=30\text{--}30.3\%$, and $P_r=7.1\text{--}7.7\text{ }\mu\text{C}/\text{cm}^2$), because of the high sintered density and good electric insulation.¹⁹⁹ Improved ferroelectric and piezoelectric properties ($P_r=21.9\text{--}28.1\text{ }\mu\text{C}/\text{cm}^2$, $d_{33}=125\text{--}139\text{ pC}/\text{N}$, $k_p=30.1\text{--}32.4\%$, and $T_C=523\text{--}565^\circ\text{C}$) were also observed in the $(0.70-x)\text{BiFeO}_3\text{--}0.30\text{BaTiO}_3\text{--}x\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3\text{--}1\text{mol}\%\text{MnO}_2$ system with $x=0.05$.²⁰³ The phase boundaries in BFO-BTO ceramic bulk can be induced by doping certain ABO_3 compounds. For example, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was shown to promote the formation of R-T phase boundary in the BFO-BTO system, which was demonstrated with good ferroelectricity ($P_r=27.4\text{ }\mu\text{C}/\text{cm}^2$), piezoelectricity ($d_{33}=140\text{ pC}/\text{N}$, $k_p=31.4\%$), and ferromagnetism ($M_r=0.19\text{ emu/g}$).¹⁹⁵ Similarly, the ceramic bulk of $\{(0.725-x)\text{BiFeO}_3\text{--}0.275\text{BaTiO}_3\text{--}x\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3\text{--}1\text{mol}\%\text{MnO}_2\}$ composition with $x=0\text{--}0.02$ possessed a dense microstructure (relative density: $\sim 94.9\text{--}96.3\%$), strong piezoelectricity ($d_{33}=129\text{--}135\text{ pC}/\text{N}$), and a high Curie temperature ($559\text{--}610^\circ\text{C}$) due to the presence of the R-T phase boundary.¹⁹⁸ However, further studies are needed to verify whether the phase boundaries play an important role in the piezoelectricity and other electrical properties of the BFO-BTO system^{192,195,198-200,203,205,221}.

Certain elements (such as Ga, La and Co) have been shown to promote the piezoelectric properties of BFO-BTO ceramics,²⁰⁷⁻²⁰⁹ although some of these doping elements appear to not change the phase structure.²⁰⁷⁻²⁰⁹ Therefore, the microstructure evolutions have been considered as among the key parameters in affecting the piezoelectric activity. Microstructural parameters, such as the grain size and degree of densification of BFO-BTO ceramics, were dependent on the doping level of Ga²⁰⁷ or Co,²⁰⁹ which were considered among the factors leading to the enhanced d_{33} (~ 157 or

167 pC/N) and high T_C (467 or 488 °C). Doping with an optimum amount of La_2O_3 effectively enhanced the piezoelectric properties, including d_{33} up to 168 pC/N.²⁰⁸

Fig. 13. d_{33} and T_C of selected piezoceramic systems.

The formation of MPB can effectively improve the ferroelectric and piezoelectric properties of BFO-BTO ceramics, similar to what has been demonstrated for PZT-based ceramics. For example, Lin *et al.* observed that there was a MPB of rhombohedral and monoclinic phases in $0.75\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\text{-}0.25\text{BaTiO}_3\text{-}1\text{mol.}\%\text{MnO}_2$ with $x=0.05$, giving rise to a d_{33} value of 113–121 pC/N.²¹⁰ Recently, a high piezoelectric activity of ~402 pC/N has been attained in the BiGaO_3 -doped BFO-BTO ceramics prepared by the water-quench method [Fig. 13].¹¹⁸ The d_{33} values measured for these ceramics were comparable with those PZT ceramics, and their T_C values were even higher.

3.1.2.2 $\text{BiFeO}_3\text{-PbTiO}_3$ Solid Solutions

Table 5 Electrical and magnetic properties of BFO-PbTiO_3 -based ceramics.

Material system	Phase structure	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/g	T_C $^{\circ}\text{C}$	Ref.
(1-x) BiFeO ₃ -xPbTiO ₃ (x=0.3)	R-T	-	-	-	-	-	222
	(Intermediate phase)						
(1-x)BiFeO ₃ -xPbTiO ₃ (x=0.20~0.28)	T-M	-	-	-	-	-	223
(1-x)BiFeO ₃ -xPbTiO ₃	R-T	87	63	45	-	600	224
(1-x)BiFeO ₃ -xPbTiO ₃ (x=0.30-0.35)	R-T	-	62	-	-	610	225
(1-x)[0.9BiFeO ₃ -0.1DyFeO ₃]-xPbTiO ₃	R-T	-	20.2	39	0.782(10K)	-	226
(1-x)(0.7BiFeO ₃ -0.3CoFe ₂ O ₄)-xPbTiO ₃	R3c	-	-	-	6.88-13.63	-	227
(1-x-y)BiFeO ₃ -yBi(Zn _{1/2} Ti _{1/2})O ₃ -xPbTiO ₃	R-T	30	-	-	-	560	228
0.511BiFeO ₃ -0.326PbZrO ₃ -0.163PbTiO ₃	R-T	101	-	-	-	431	229
0.648BiFeO ₃ -0.053PbZrO ₃ -0.299PbTiO ₃	R-T	64	15	-	-	560	230
(1-x-y)BiFeO ₃ -x Bi _{0.5} K _{0.5} TiO ₃ -yPbTiO ₃	R-T	228	-	36.4	-	427	231
(0.8-x)BiFeO ₃ -0.2BaZrO ₃ -xPbTiO ₃	R-T	270	~25	~15	-	270	232
0.575BiFeO ₃ -0.15(K _{0.5} Bi _{0.5})TiO ₃ -0.275PbTiO ₃	R-T	205	34	40	-	575	233
(0.9-x)BiFeO ₃ -xPbTiO ₃ -0.1BaTiO ₃ (x=0.22)	R-T	100	60	51	-	600	234
(1-x) BiFeO ₃ -xPb(Zr _{0.52} Ti _{0.48})O ₃ (x=0.30)	Monoclinic	-	6.464	-	~0.46	-	235
(0.6BiFeO ₃ -0.4PbTiO ₃)-wt% La	R-T	-	10	-	0.075	-	236
0.63(Bi _{0.94} La _{0.06})(Ga _{0.05} Fe _{0.95})O ₃ -0.37PbTiO ₃	R-T	63	30	45	-	532	237
0.7Bi(Fe _{1-x} Ga _x)O ₃ -0.3PbTiO ₃	R-T	-	3.5	55	-	-	238

BFO-PbTiO₃ is another typical solid solution for BFO-based ceramic bulks, which has been extensively investigated.²²²⁻²⁴³ Table 5 shows the phase structure and electrical properties of BFO-PTO ceramics.²²²⁻²⁴³ One can see from Table 5 that the phase boundary (e.g., R-T) can be easily constructed in the BFO-PTO binary ceramics or ternary materials doped with other types of ABO₃ compounds. The addition of PTO drives the formation of phase boundaries, promoting piezoelectric properties.^{222,225,239-243} However, there are some disputes concerning the phase compositions in (BiFeO₃)_x-(PbTiO₃)_{1-x}.^{222,239,240,242,243} In as early as 1964, Fedulov *et al.*²⁴² observed the coexistence of R-T two phases in (BiFeO₃)_x-(PbTiO₃)_{1-x} for $x=0.66\sim0.73$. Subsequently, Woodwarda *et al.*²²² further confirmed the existence of an intermediate phase bridging the R-T phases by electron diffractometer patterns for the composition of $x=0.70$. In addition, Ye *et al.*²⁴³ also observed that there was a

R-O-T MPB in the solid solutions with $x=0.72\sim0.80$ by using X-ray diffraction. Bhattacharjee *et al.*^{239,240} confirmed the existence of O phase in the MPB by the refinement method. The composition region and exact phase boundaries in $(\text{BiFeO}_3)_x\text{-(PbTiO}_3)_{1-x}$ have been further investigated by several other studies.^{222,239,240,242,243} By engineering the phase compositions in MPB, their electrical properties can be enhanced.

3.1.2.3 Other Solid Solutions

Table 6 lists electrical and magnetic properties of BFO ceramics modified by other ABO_3 compounds, in addition to BaTiO_3 and PbTiO_3 .²⁴⁴⁻²⁵⁵ The phase structures were strongly dependent on the type of doping compounds. For example, the addition of SrTiO_3 ²⁴⁷ or NaNbO_3 ²⁴⁸ induced the phase transition from R to pseudocubic and cubic. However, the piezoelectric properties were degraded²⁴⁴⁻²⁵⁵ due to a high leakage current.²⁴⁵ Similar behavior was demonstrated with $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$,²⁵² $\text{CuCa}_3\text{Ti}_4\text{O}_{12}$,²⁵³ YCrO_3 ²⁵⁴ or $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$.²⁵⁵ The magnetic properties of BFO ceramics can be greatly enhanced by doping magnetic compounds (e.g., CoFe_2O_4 ²⁴⁵ and $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ²⁴⁹).

Table 6 Electrical and magnetic properties of BFO ceramics modified by other ABO_3 .

Material system	Phase structure	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/g	T_C °C	Ref.
$(1-x)\text{BiFeO}_3\text{-}x\text{BiZn}_{1/2}\text{Ti}_{1/2}\text{O}_3$ ($x=0.01$)		-	20	0.7	-	-	244
$(1-x)\text{BiFeO}_3\text{-}x\text{GdCrO}_3$	R-O	-	10.1	84	0.118	-	245
$(1-x)\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3\text{-}x\text{CoFe}_2\text{O}_4$ ($x=0.4$)	R-C	-		-	11.30	-	246
$(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$ ($x=0\text{-}1.0$)	R (≤ 0.2)	-	7.3	-	0.1	-	247
	Pseudo-C(0.2~0.8)		($x=0.3$)		($x=0.2$)		
	C (0.8-1.0)						

$(1-x)\text{BiFeO}_3\text{-}x\text{NaNbO}_3$	R3c (0.1)	-	0.9-1.3	-	0.14	-	248
	Pseudo-C (0.3)				($x=0.1$)		
	C (0.5)						
$x\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3\text{-(}1-x\text{)BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$	R-Monoclinic	-	0.3	-	0.539	-	249
$x\text{BiFeO}_3\text{-(}1-x\text{)SrBi}_2\text{Nb}_2\text{O}_9$		-		-	-	-	250
$x\text{BiFeO}_3\text{-(}1-x\text{)K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ($x=0.6$)	R	37	12	38.5	-	441	251
$(1-x)\text{BiFeO}_3\text{-}x\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$	R-T ($x=0.15$)	-	1.83	11.2	-	-	252
$(1-x)\text{BiFeO}_3\text{-}x\text{CuCa}_3\text{Ti}_4\text{O}_{12}$	R- Pseudo-T	-		-	0.2	-	253
$(1-x)\text{BiFeO}_3\text{-}x\text{YCrO}_3$	R-O	-	14.9	-	-	-	254
$(1-x)\text{BiFeO}_3\text{-}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ($x=0.30$)	R-Pseudo-C	-	1.49	-	-	-	255

3.1.3. Preparation Techniques

Several techniques have been developed to fabricate BFO ceramic bulks to overcome the issues such as the formation of secondary phases as well as the occurrence of high leakage current. When BFO bulks are prepared by the conventional solid-state reaction method using oxides as the starting materials, a large number of unexpected phases ($\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{25}\text{FeO}_4$, Bi_2O_3) can be formed. Wet chemical methods and the use of proper oxide precursors could effectively suppress the formation of secondary phases and improve the quality of overall microstructures. In addition to the conventional sintering, liquid phase sintering and spark-plasma sintering have also been explored. Techniques of preparing single crystals have been investigated.

3.1.3.1 Liquid Phase Sintering

Table 7 Electrical and magnetic properties of BFO-based ceramics prepared by liquid phase sintering

Material system	d_{33}	P_r	E_C	M_r	Ref.
	pC/N	$\mu\text{C}/\text{cm}^2$	kV/c	emu/g	
BiFeO_3	36	-	-	-	Our work
BiFeO_3	-	2.5	40	-	256
BiFeO_3	-	4.0	39	-	120

$\text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$	-	3.99	-	-	153
$0.67\text{BiFeO}_3\text{-}0.33\text{BaTiO}_3\text{-Mn}$	-	12.8(11.75)	-	-	257
$\text{Bi}_{0.85}\text{La}_{0.15}\text{Fe}_{0.97}\text{V}_{0.03}\text{O}_3$	-	1.26	39.0	-	55
$\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$	28	-	-	-	129
$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$	25	9.8	-	0.20~0.25	130
$\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$	35~42	12	-	-	258
$\text{Bi}_{1-x-y}\text{Sm}_x\text{La}_y\text{FeO}_3$	50	1.38	58.5	-	88

Fig. 14. Preparation process and piezoelectric properties of 0.67BFO-0.33BTO ceramics fabricated by the water quenched method [854].

It is well known that certain secondary phases (e.g., $\text{Bi}_{25}\text{FeO}_{40}$ and $\text{Bi}_2\text{Fe}_4\text{O}_9$) are easy to form in both undoped and doped-BFO ceramics prepared by the conventional solid-state reaction method^{86,119}. Due to the high conductivity of these secondary phases, a properly saturated P - E loop cannot be attained and the ceramics cannot be fully poled. It is necessary to fabricate a high-resistivity BFO ceramic in order to further investigate the electrical properties. One attempt was to leach the impurity phases with dilute nitric acid.²⁶⁰ Unfortunately, the as-prepared samples thus prepared showed poor ferroelectric loops due to the low density. It was reported that the liquid phase technique could be used to sinter the dense BFO ceramics.^{55,88,120,129,130,153, 256-258} The initial steps of these processes are similar to the solid-state route, where the

pressed powder samples are sintered at a given temperature for a short period of time. Table 7 shows electrical and magnetic properties of BFO-based ceramics prepared by liquid phase sintering. One can see from Table 7 that some of the electrical and magnetic properties of BFO-based ceramics can be effectively improved by the processing control. In 2004, a rapid liquid-phase sintering method developed by Wang *et al.*¹²⁰ was used to prepare BFO ceramics with single phase structure and high resistivity. The Bi₂O₃-based liquid phase accelerated the reaction due to its low melting point (817 °C), and therefore a single-phased BiFeO₃ ceramic could be attained by sintering at 850 °C. By using this method, defect concentrations (i.e., oxygen vacancies and Fe²⁺) could be greatly suppressed, leading to a high electrical resistivity. Therefore, the electrical characterization of BFO ceramics became possible. After that, Yuan *et al.*^{129,130,258} further optimized this method to prepare the high-quality BFO-based ceramics by controlling the particle size in the starting materials. Recently, we have further improved the piezoelectric properties of these liquid-sintered BFO-based ceramics by using both ion substitution and further modification in liquid phase sintering.^{88,185} For example, a d_{33} value of ~50 pC/N was obtained for Bi_{1-x-y}Sm_xLa_yFeO₃.

We have also investigated the relationships between preparation parameters and piezoelectric properties of 0.67BFO-0.33BTO ceramics developed using the quenched method,⁸⁵⁴ as shown in Fig. 14. The quenched method could effectively promote the piezoelectric properties of the ceramics.⁸⁵⁰⁻⁸⁵⁴ By optimizing the processing conditions, the resultant ceramics possess a large piezoelectricity (d_{33} ~170 pC/N) as well as enhanced ferroelectricity (P_r ~22 μ C/cm²), together with a high Curie temperature (T_C ~457 °C). Therefore, the liquid phase sintering technique is an effective pathway

to tune the phase compositions and boundaries of BFO-based ceramics and to further achieve improved performance.

3.1.3.2 Spark-Plasma Sintering

BFO is known to slowly decompose into $\text{Bi}_2\text{Fe}_4\text{O}_9$ when the temperatures rise from 675 to 830 °C, and then quickly transforms to $\text{Bi}_2\text{Fe}_4\text{O}_9$ at above 830 °C.²⁷² It is thus difficult to obtain a dense single-phase BFO ceramic by the conventional solid-state method. To overcome this problem, spark plasma sintering (SPS) technique has been used to develop single-phased BFO ceramics with relatively high density²⁶¹⁻²⁶⁵ where both the Bi loss and the valence shift of Fe are suppressed. In this technique, the ceramic is quickly densified at a relatively low temperature over a very short period of time (usually in a few minutes).²⁶⁵

Table 8 Electrical properties of BFO-based ceramics prepared by spark-plasma sintering

Material system	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	M_r emu/g	P_s $\mu\text{C}/\text{cm}^2$	Ref.
BiFeO_3	4.2	-	-	-	261
BiFeO_3	-	7.5	0.0057	10.4	262
$\text{Bi}_{0.87}\text{La}_{0.05}\text{Tb}_{0.08}\text{FeO}_3$	12.8	17	0.71	19	263
$0.75\text{BiFeO}_3\text{-}0.25\text{BaTiO}_3$	-	10	-	-	264

BFO-based ceramics fabricated by SPS exhibit a high bulk density of up to 96% theoretical density^{263,266-270}. Therefore, their ferroelectric, piezoelectric and magnetic properties are improved with respect to those of the conventionally sintered ones.²⁷⁰

Table 8 shows the electrical and magnetic properties of BFO-based ceramics prepared by SPS. One can see that SPS can promote the ferroelectric and piezoelectric properties.²⁶¹⁻²⁶⁴ For example, Nan *et al.* fabricated dense $\text{Bi}_{0.87}\text{La}_{0.05}\text{Tb}_{0.08}\text{FeO}_3$ ceramics using SPS, and obtained rather good electrical and magnetic properties

($P_r \sim 17 \mu\text{C}/\text{cm}^2$, $d_{33} \sim 12.8 \text{ pC}/\text{N}$ and $M_s \sim 0.71 \text{ emu}/\text{g}$).²⁶³ Dense BiFeO₃-based ceramics with nanosized grains ($\sim 40 \text{ nm}$) were prepared using SPS, with the starting materials of nanopowders synthesized by both sol–gel method and high energy ball milling. The Curie point shifts to a lower temperature (from 697°C to 655°C) due to the internal stress and a single ferroelectric domain structure. These nanocrystalline BFO-based bulk ceramics possess active magnetic ($M_s \sim 0.18 \text{ emu}/\text{g}$) and ferroelectric ($P_r \sim 7.5 \mu\text{C}/\text{cm}^2$) properties.^{262,271}

In general, a rapid sintering followed by quenching process leads to a high density and improved properties for BFO-based ceramics because the loss of Bi can be decreased and the valence shift of Fe^{3+} - Fe^{2+} can be suppressed by such a sintering technique.^{55,88,120,129,130,153, 256-258} In addition, there are several other attempts to improve the fabrication and electrical properties of BFO-based ceramics, such as by the reactive templated grain growth, control in starting materials/precursor by glycol reaction, Pechini method and chemical methods, use of sintering aid and control of sintering atmosphere. Detailed reviews on this aspect are referred to the literature.⁹²

3.1.3.3 Single Crystal

Table 9 Electrical properties of BFO-based single crystals

Material system	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	P_s $\mu\text{C}/\text{cm}^2$	Ref.
BiFeO ₃	-	60	-	273
BiFeO ₃	-	-	100	274
BiFeO ₃	-	70(190K)	-	276
BiFeO ₃	16pm/V	-	-	277
BiFeO ₃	-	6.1(77K)	-	278
BiFeO ₃	-	40~50	-	280
0.67BiFeO ₃ -0.33PbTiO ₃	-	0.1	-	275

BFO single crystals are expected to exhibit superior dielectric, ferroelectric and piezoelectric properties over polycrystalline ceramics.²⁷³⁻²⁸⁰ Different methods have therefore been used to grow BFO single crystals. Single crystals are free from defects in association with grain boundaries and are desirable for investigations of properties arising from the anisotropic crystal structure of BFO. Yet in most of the reported works, they are too conductive at room temperature and therefore it is difficult to characterize some of the key electrical properties.

In 1970, a poor spontaneous polarization of $3.5 \mu\text{C}/\text{cm}^2$ was first observed in BFO single crystal along $\langle 001 \rangle$ direction of pseudocubic unit cell due to the high leakage.²⁷⁸ In 2007, Lebeugle *et al.* developed resistive BFO single crystals by using a flux growth method, and a large spontaneous polarization of $\sim 100 \mu\text{C}/\text{cm}^2$ was measured.²⁷³ Due to the minimization in defect concentrations, the measured polarization value was close to the predicted value.⁸ Similar to polycrystalline ceramic bulks, different phases have been observed when BFO single crystals are doped with other perovskite compounds. For example, Ye *et al.* grew $0.67\text{BiFeO}_3\text{-}0.33\text{PbTiO}_3$ single crystals from high-temperature solution using $\text{Bi}_2\text{O}_3\text{-PbO}$ flux,²⁷⁵ and they found that tetragonal, orthorhombic, and rhombohedral phases could coexist.^{275,279} Recently, several new phenomena have been reported for BFO single crystals.⁹⁸ For example, a diodelike effect was shown in BFO crystals with single ferroelectric domain structures, where a substantial zero-bias PV current was induced by visible light. The switchable diode and photovoltaic effects in BFO single crystal reveal some of the unusual and intriguing charge transport behavior.⁹⁸

3.1.4 Phase Structure vs. Piezoelectricity

Table 10 Piezoelectric, ferroelectric and magnetic properties of BFO-based ceramics with different phase structure

Material system	Phase boundary type	d_{33} pC/N	P_r $\mu\text{C}/\text{cm}^2$	M_r/M_s emu/cm^3	Ref.
$\text{Bi}_{1-x}\text{Sm}_x\text{FeO}_3$	R(<0.125)/R(Triclinic)	42	12	-	258,
	-O(0.125-0.175)	(0~0.125)	(0~0.12)		438
	Paraelectric O (0.25)				
$\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$	R-Triclinic (0.05~0.15)	-	9	0.227	128
	Pseudo-T (0.175-0.2)				
$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$	R-Triclinic (0.05~0.15)	25	9.8	0.204–	130
	Pseudo-T (P4 mm) (0.2)			0.246	
	Pseudo-T (P4/mmm)(0.25)				
$\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$	R (0.08)	35	55	0.313	439,
	R-O (0.10~0.25)		(0.05)	(0.05)	440
$\text{Bi}_{1-x}\text{Eu}_x\text{FeO}_3$	R (<0.15)/O (>0.2)	-	11 ^[442]	0.0347 ^[442]	144,441,
			(0.1)	(0.1)	442
$\text{Bi}_{1-x}\text{Pr}_x\text{FeO}_3$	R (<0.12)/ O(Pnam)	-	-	-	443
	(0.16-0.25)/ O(Pnma) (0.28)				
	R3c-Pnam-Pnma				
$(1-x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$	R-O-T	-	-	-	243
$0.7\text{BiFeO}_3\text{-}0.3\text{PbTiO}_3$	R-T-intermediate phase	-	-	-	222
$0.675\text{BiFeO}_3\text{-}0.325\text{PbTiO}_3$	R-T	-	62		225
$0.675\text{BiFeO}_3\text{-}0.325\text{PbTiO}_3$	R-T	-	63	87(d_{33})	224
$(1-x)\text{BiFeO}_3\text{-}x\text{PbTiO}_3$ ($x=0.3$)	R-T	160 pm/V	-	-	444
$0.7\text{Bi}_{1-x}\text{La}_x\text{FeO}_3\text{-}0.3\text{PbTiO}_3$ ($x=0.15$)	R-T	278	26.1	-	445
$0.67\text{Bi}_{1.05}\text{Fe}_{1-x}\text{Ga}_x\text{O}_3\text{-}0.33\text{BaTiO}_3$	R-T	402/454 °C	-	-	118

0.511BiFeO ₃ -0.326PbTiO ₃ -0.163PbZrO ₃	R-T	101	-	-	229
0.675BiFeO ₃ -0.325BaTiO ₃ -MnO ₂ -CuO	R-Pseudocubic	~160	-	-	193

Composition modification in *A* or *B* site or both sites in ABO₃-type perovskite ferroelectrics has been thought as an effective route to construct the desired MPB with enhanced functional properties.⁸⁶¹ The construction of an appropriate phase boundary improves the electrical properties of functional ceramic materials.⁸⁶¹ For the relationship between phase structure and electrical properties of BFO bulk, one would need to look at compositions close to MPB.⁸⁶¹ Table 10 summarizes the piezoelectric, ferroelectric, and magnetic properties of BFO-based ceramics with different phase structures. Firstly, the strong effects of ion substitutions on the phase structure have been demonstrated by several groups.^{128,130,144,258,438-443} The addition of certain rare earth elements can induce a dramatic change in phase structure,^{128,130,144,258,438-443} where the ferroelectric phase and paraelectric phase can coexist.^{128,130,144,258,438-443} For example, the phase structure of BFO-based ceramics was tailored by doping with Sm, Co, Pr, Nd, La, Dy or Eu.^{128,130,144,258,438-443} However, the piezoelectric activity was not improved significantly (typically below ~50 pC/N) in spite of the existence of MPBs in doped BFO-based ceramics.^{130,258,438-440}

Table 11 Phase compositions of (1-*x*)BiFeO₃-*x*PbTiO₃ ceramics with MPB^{222,240,242,243,447}

Materials	MPB range	Preparation method	Research group
(1- <i>x</i>)BiFeO ₃ - <i>x</i> PbTiO ₃	<i>x</i> =0.27~0.34	Solid state route	Fedulov
(1- <i>x</i>)BiFeO ₃ - <i>x</i> PbTiO ₃	<i>x</i> =0.3~0.4	Solid state route	Woodward
(1- <i>x</i>)BiFeO ₃ - <i>x</i> PbTiO ₃	<i>x</i> =0.27~0.31	Solid state route	Bhattacharjee
(1- <i>x</i>)BiFeO ₃ - <i>x</i> PbTiO ₃	<i>x</i> =0.2~0.28	Solid state route	Zhu
(1- <i>x</i>)BiFeO ₃ - <i>x</i> PbTiO ₃	<i>x</i> =0.25~0.35	Solid state route	Correas

In order to construct the phase boundaries with MPB similar to those in PZT, investigations have been conducted into BFO solid solutions with other ABO_3 .^{118,193,222,224,225,229,243,444,445} As mentioned earlier, PbTiO_3 and BaTiO_3 are the two typical ABO_3 compounds that have been used to modify BFO. In the phase diagram of $(1-x)\text{BiFeO}_3-x\text{PbTiO}_3$, ferroelectric rhombohedral (R3c) and tetragonal (P4mm) phases are shown to coexist by changing x , giving rise to the enhanced electrical properties.⁴⁴⁶ The addition of other elements or ABO_3 can also promote piezoelectric activity by modifying the ratio of R and T phases. For example, the ceramic composition of $0.511\text{BiFeO}_3-0.326\text{PbZrO}_3-0.163\text{PbTiO}_3$ in the rhombohedral-rich side of MPB possess a $d_{33}\sim 101$ pC/N.²²⁹ The addition of La further enhances the d_{33} to ~ 278 pC/N.⁴⁴⁵ Nevertheless, there are rather different MPB composition regions of BFO-PTO ceramics,^{222,240,242,243,447} as shown in Table 11.

$(1-x)\text{BiFeO}_3-x\text{BaTiO}_3$ has been given considerable attention, as it is considered as one of the potential lead-free piezoceramics.^{117,193,215} The phase structure is strongly dependent on the compositions, where $x=0.92\sim 1.00$, $0.33\sim 0.92$, and $0\sim 0.33$ correspond to tetragonal, cubic, and rhombohedral phases, respectively.²¹⁵ A high d_{33} of 116 pC/N together with high T_C of ~ 619 °C have been observed in Mn-doped $(1-x)\text{BiFeO}_3-x\text{BaTiO}_3$ ($x=0.25$) lead-free system.¹⁹¹ Similarly, a high $d_{33}\sim 170$ pC/N with T_C of 450 °C has been reported for 0.65BF-0.35BT ceramics by doping both MnO_2 and CuO .¹⁹³ Recently, a very large d_{33} of 402 pC/N and high T_C of 454 °C have been shown by the ternary lead-free ceramic system of $0.67\text{Bi}_{1.05}(\text{Fe}_{1-x}\text{Ga}_x)\text{O}_3-0.33\text{BaTiO}_3$ ($x=0.03$). The d_{33} value is indeed comparable to those of PZT ceramics,¹¹⁸ and moreover the T_C value is higher.

3.2 Thin films

Fig. 15. Publications on the BFO-based thin films over the period of 2000 to 2015.

As mentioned earlier, the intrinsic ferroelectric properties of BFO bulks are difficult to achieve, due to the nature of polycrystalline structure and involvement of high leakage current.^{24,94,119-121,278} Considerable attentions have therefore been focused on the BFO-based thin films, because generally high quality thin film samples can be well fabricated by choosing appropriate deposition techniques and tuning processing parameters. They also promise a wide range of applications, such as in memories and the next generation spintronic devices. In 2003, Wang *et al.*⁹⁷ prepared epitaxial BFO thin films on SRO/STO substrates and first reported a large P_r of $\sim 60 \mu\text{C}/\text{cm}^2$. This was the first time to demonstrate such a high P_r in BFO-based materials, and the big gap between experimental value and the theoretically expected P_r value was significantly narrowed down.⁸ After that, many investigators conducted careful works in tuning the structures and electrical properties of BFO-based thin films, by several different approaches.^{5,26,29,33,42,45,50,54,56,57,59,66,67,87,281-347} Figure 14 shows the publications on BFO-based thin films. One can see that the dramatic rise of interest in

BFO thin films since 2003.

3.2.1 BiFeO₃ Thin Films

Table 12 Ferroelectric properties of BFO thin films

Material system	Substrate	Preparation technique	P_r $\mu\text{C}/\text{cm}^2$	E_C (kV/cm)	Ref.
BiFeO ₃ (100)	SrRuO ₃ /Si/SrTiO ₃	PLD	60	~150	97
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	0.83	-	281
BiFeO ₃ (001)	SrRuO ₃ /Si/SrTiO ₃	PLD	55	-	282
BiFeO ₃ (101)	SrRuO ₃ /Si/SrTiO ₃	PLD	80	-	282
BiFeO ₃ (111)	SrRuO ₃ /Si/SrTiO ₃	PLD	100	-	282
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	68	-	284
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	35.65	62.5	285
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	146(90K)	-	5
BiFeO ₃	SrRuO ₃ /SrTiO ₃	CVD	55-60	220*	286
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	CSD	0.5	-	287
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	102	271	289
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	152(80K)	308(80K)	289
Strained BiFeO ₃ (77 nm)	SrRuO ₃ /SrTiO ₃	PLD	62	-	291
Strained BiFeO ₃ (77 nm)	SrRuO ₃ /SrTiO ₃	PLD	115	-	291
BiFeO ₃ (111)	SrRuO ₃ /Pt/Ti/SiO ₂ /Si	RF	98.55	270.55	23
BiFeO ₃ (001)	SrRuO ₃ /SrTiO ₃	CSD	50(80K)	300	57
BiFeO ₃	Pt/Ti/SiO ₂ /Si	CSD	100(80K)	400	295
BiFeO ₃ (0001)	GaN	CVD	90	470	297
BiFeO ₃ (111)	SrRuO ₃ /SrTiO ₃	RF	118.3	295	66
BiFeO ₃ (110)	SrRuO ₃ /SrTiO ₃	RF	78.7	356	66
BiFeO ₃ (100)	SrRuO ₃ /SrTiO ₃	RF	63.2	193	66
BiFeO ₃ Poly	SrRuO ₃ /SrTiO ₃	RF	69	308	66
BiFeO ₃	ITO/glass	SOL-GEL	2.0	-	299
BiFeO ₃	Pt/Ti/SiO ₂ /Si	CSD	31	560	305
BiFeO ₃	Pt/Ti/SiO ₂ /Si	SOL-GEL	90(80K)	-	313
BiFeO ₃	LaNiO ₃ /Si	SOL-GEL	14.3	-	315
BiFeO ₃ (111)	BaPbO ₃ /Pt/Ti/SiO ₂ /S	RF	102.5	337.5	317
BiFeO ₃	La _{0.7} Sr _{0.3} MnO ₃ /SrTi	PLD	55	-	321
BiFeO ₃	LaNiO ₃ /Si	SOL-GEL	6.4	-	322
BiFeO ₃	SrRuO ₃ /SrTiO ₃	RF	82	255	326
BiFeO ₃ (111)	SrTiO ₃ (111)	PLD	95	-	330

After the breakthrough of Wang *et al.*⁹⁷ in demonstrating the high P_r for BFO thin

films, considerable pursue is directed towards a high P_r comparable to the theoretical value.^{5,26,29,33,42,45,50,54,56,57,59,66,67,87,281-347} Table 12 lists the ferroelectric properties of several types of BFO thin films, which were prepared by different preparation techniques and on different substrates. One can see from Table 12 that their ferroelectric properties are strongly affected by several factors, such as types of substrates,^{23,97,281,297,299,321,322} preparation techniques^{57,66,97,286,322} and use of buffer layers.^{23,97,315,317,321} In addition, there are orientation modifications induced by some of these factors, which play a big role in the ferroelectric properties of BFO thin films.^{66,282} For example, Wu *et al.*⁶⁶ investigated the orientation [e.g., (111), (100), (110)] dependence of ferroelectric properties of BFO thin films. A giant ferroelectric polarization ($2P_r=196.9 \mu\text{C}/\text{cm}^2$) was shown in the (111)-oriented BFO thin film, and the film possessed an almost fatigue-free behavior up to 5.25×10^7 switching cycles under a frequency of 100 kHz. For R3c BFO thin films, [111] is the polarization axis, and therefore there have been considerable efforts in orientation engineering to tune the ferroelectric properties of BFO thin films.^{8,282} On the other hand, the ferroelectric properties can be properly characterized only when there is a low leakage current. In general, there have been quite a few studies successfully attaining a high P_r value of $>90 \mu\text{C}/\text{cm}^2$ in BFO thin films at room temperature.^{5,289,295,313} In addition to these studies, there were also reports that ferroelectric properties were characterized at low temperatures to minimize the influence of high leakage current at high temperatures. For example, Yun *et al.*⁵ prepared a polycrystalline BFO thin film deposited on Pt/TiO₂/SiO₂/Si substrate by pulsed-laser deposition. A remarkably giant saturation polarization of $158 \mu\text{C}/\text{cm}^2$ with remnant polarization of $146 \mu\text{C}/\text{cm}^2$ were observed when the film was measured at 90 K.⁵ However, for device applications at room temperature, the high leakage currents in BFO thin films grown on Pt-coated silicon

substrates need to be suppressed. For this purpose, several studies have shown a dramatic decrease in the leakage current by inserting an oxide buffer layer (e.g., SrRuO₃,⁶⁶ BaPbO₃,³¹⁷ LaNiO₃³²¹ and La_{0.7}Sr_{0.3}CoO₃^{315,322}) between the thin film and Pt-coated silicon substrate, leading to a high P_r of $\sim 100 \mu\text{C}/\text{cm}^2$ being observed.^{23,317} For example, a high P_r of $\sim 98.5 \mu\text{C cm}^{-2}$ was shown by the (111)-oriented BFO thin film grown on SrRuO₃/Pt/TiO₂/SiO₂/Si(100) substrates by off-axis radio-frequency magnetron sputtering,²³ where the SrRuO₃ buffer layer not only decreased the leakage current but also induced the BFO (111) orientation. Controls in use of buffer layer and substrate straining and their combination can significantly enhance the overall ferroelectric properties of BFO thin films.^{297,299,315,321,322}

In addition to macroscopic ferroelectricity, epitaxial BFO thin films have some unique features regarding the microscopic domain structures.^{773,820-827} BFO is known to exhibit rhombohedral symmetry with eight polarization variants [Fig. 16(a)]. Different domain configurations, including 71° , 109° and 180° domains, can thus be formed [Fig. 16(a)]. For example, an 1D periodic structure of ferroelectric domains was observed in an epitaxial BFO thin film.⁷⁷³ The formation of 1D stripe domains was attributed to the anisotropic in-plane strain imposed by the underlying DyScO₃ (110) single-crystal substrate, and also to the step-flow growth mode of the SrRuO₃ (SRO) bottom electrode. Chu *et al.*⁸²¹ further found that the formation of a specific domain pattern was dependent not only on the elastic strain but also on the electrostatic boundary conditions. Their results showed that when a thick (~ 50 nm) SRO layer was introduced, the 71° domain pattern was favored [Fig. 16(b) and (c)]; however, when the SRO layer was absent, the 109° domain pattern became prevailing [Fig. 16(d) and (e)]. Recently, Chen *et al.*⁸²⁷ observed 180° stripe domains in

(110)-oriented BFO films grown on GdScO_3 (001)_O substrates [Fig. 16(f) and (g)]. This particular domain pattern was achieved by using the compressive strain from GdScO_3 (001)_O substrates to suppress the in-plane domain variants of BFO and hence stabilize the out-of-plane domain variants. Besides the stripe domains, other topological domain structures were also reported in BFO thin films, such as vortex and antivortex domains, and center-type domains.^{823,825} The 2D domain walls, and also 1D topological defects (like vortex core) were found to possess many interesting functionalities, such as enhanced strain, magnetization and conductance.^{821,822,826} Moreover, a great deal of efforts have been devoted to realizing the deterministical control of the domain patterns by external stimulus, e.g., the electric field. Balke *et al.*¹ reported that by carefully controlling the lateral motion and the applied bias of a PFM tip, a reversible switching between different domain patterns could be realized.

Fig. 16. (a) Schematics of domain variants and domain walls. (b), (d), and (f) Out-of-plane PFM phase images of BFO films with 71°, 109°, and 180°, respectively. (c), (e), and (g) In-plane PFM phase images of BFO films with 71°, 109°, and 180°.

respectively [821, 826].

3.2.2 Chemical Modification

3.2.2.1 Substitution for Bi Site

Table 13: Electrical and magnetic properties of BFO thin films by ion substitutions for Bi site

Material system	Substrate	Preparation technique	d_{33} pm/V	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r/M_s emu/cm ³	Ref.
$\text{Bi}_{1.05}\text{La}_{0.05}\text{FeO}_3$	$\text{BaPbO}_3/\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$	RF	-	90	216	3.2	29
$\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	SOL-GEL	-	50	-	-	291
$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	CSD	-	44(10K)	598	-	292
$\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	-	21	-	-	293
$\text{Bi}_{0.95}\text{La}_{0.05}\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	-	102	380	15	59
$\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$	SrTiO_3/Si	PLD	45	45	~150	-	298
$\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$	$\text{SRO}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	-	55	540	-	314
$\text{Bi}_{0.9}\text{Nd}_{0.1}\text{FeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	MOD	-	-	-	46	288
$\text{Bi}_{0.825}\text{Nd}_{0.175}\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	-	34	235	-	54
$\text{Bi}_{0.97}\text{Gd}_{0.03}\text{FeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	MOD	-	79	361	-	290
$\text{Bi}_{0.75}\text{Ba}_{0.25}\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	-	2.4	67	1.2*	294
$\text{Bi}_{0.94}\text{Ce}_{0.06}\text{FeO}_3$	$\text{SnO}_2\text{-F(FTO)}/\text{glass substrates}$	CSD	-	46.15	382	-	309
$\text{Bi}_{0.9}\text{Eu}_{0.1}\text{FeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	PLD	-	74	250	3.5	319
Sm-BFO	$(\text{LaAlO}_3)_{0.3}\text{SrAl}_{0.5}\text{Ta}_{0.5}\text{O}_3)_{0.7}$	PLD	110	-	-	-	320
$\text{Bi}_{0.8}\text{Ce}_{0.2}\text{FeO}_3$	$\text{Pt}/\text{TiN}/\text{Si}_3\text{N}_4/\text{Si}$	SOL-GEL	-	2.04	-	-	327
$\text{Bi}_{0.89}\text{Tb}_{0.11}\text{FeO}_3$	Indium tin oxide/glass	MOD	140	~60	~400	-	329
$\text{Bi}_{1.1}\text{Sr}_{0.1}\text{FeO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	-	50(80K)	-	1.43	335
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{FeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	CSD	-	-	-	-	341
$\text{Bi}_{0.86}\text{Sm}_{0.14}\text{FeO}_3$	SrTiO_3	PLD	110	70	~230	-	623

It is commonly known that the high leakage current of BFO originates from some defects, such as oxygen vacancies, as shown in Eq. (1) below.^{24,185} In addition, the high leakage may also be due to the valence change from Fe^{3+} to Fe^{2+} .

In the past, the ion substitution has been employed as an effective way to improve ferroelectric properties of BFO by depressing leakage current. The effects of site engineering and element doping types on electrical properties of BFO thin films have

been extensively investigated. Table 13 summarizes the electrical and magnetic properties of BFO thin films modified by different ions for Bi site. In general, ions substitutions for Bi site mainly include La,^{29,59,291-293,298,314} Nd,^{54,288,292} Gd,²⁹⁰ Ba,²⁹⁴ Ce,³⁰⁹ Eu,³¹⁹ Sm,^{320,623,855,856} Tb,³²⁹ Sr,³³⁵ and Ho.³⁴¹ As shown in Table 13, the ions substitution at Bi site can effectively improve the overall ferroelectric properties of BFO thin films. For example, Yan *et al.*⁵⁹ prepared La-doped BiFeO₃ thin films grown on Pt/TiO₂/SiO₂/Si substrates using pulsed laser deposition, and it was shown that La-doping greatly decreased leakage current and thus a giant P_r of 102 $\mu\text{C}/\text{cm}^2$ was achieved. In addition, it was found that the addition of Sm or Tb could also improve the ferroelectric and piezoelectric activity of BFO thin films.^{320,329,623} For example, well-saturated P - E loops were observed in the Bi_{0.89}Tb_{0.11}FeO₃ films deposited on indium-tin-oxide/glass substrates because oxygen vacancies (V_{O}^{2-}) were suppressed by doping Tb.³²⁹ The Tb-doped BFO films also exhibited high values of out-of-plane piezoelectric coefficient ($d_{33}\sim 140$ pm/V) and saturated magnetization ($M_s\sim 22.2$ emu/cm³).³²⁹ The phase boundary between rhombohedral and pseudo-orthorhombic phases results in the enhancement of piezoelectric effect ($d_{33}\sim 110$ pm/V) in Bi_{0.86}Sm_{0.14}FeO₃ films, which was comparable to that of epitaxial (001)-oriented PbZr_{0.52}Ti_{0.48}O₃ thin films with MPB.⁸¹⁵

3.2.2.2 Substitution for Fe Site

Table 14: Electrical and magnetic properties of BFO thin films by ion substitutions for Fe site

Material system	Substrate	Preparation technique	d_{33} pm/V	P_r $\mu\text{C}/\text{cm}^2$	E_C (kV/c)	M_r/M_s emu/cm ³	Ref.
BiFe _{1-x} Ga _x O ₃ ($x=0.1$)	LaNiO ₃ /glass	CSD	-	230	500	-	349
BiFe _{0.6} Ga _{0.4} O ₃	LaNiO ₃ /NdCaAlO ₄	RF	-	150	-	-	78
BiFe _{0.95} Mn _{0.05} O ₃	Pt/Ti/SiO ₂ /Si(100)	CSD	-	100	330	-	26
BiFe _{0.95} Mn _{0.05} O ₃ (111)	SRO/Pt/Ti/SiO ₂ /Si	CSD	-	70	300	-	308

BiFe _{0.95} Mn _{0.05} O ₃	ITO/glass	MOD	-	58	337	-	318
BiFe _{0.95} Ru _{0.05} O ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	-	99	-	16.53	56
BiFe _{0.97} Cr _{0.03} O ₃	Pt/TiO ₂ /SiO ₂ /Si	CSD	-	61	290	-	33
BiFe _{0.97} Cr _{0.03} O ₃	Pt/Ti/SiO ₂ /Si	SOL-GEL	-	100	260	-	331
BiFe _{0.5} Cr _{0.5} O ₃	SrRuO ₃ /SrTiO ₃	PLD	-	56 (77K)	-	-	302
BiFe _{0.9} Ti _{0.1} O ₃	Pt/Ti/SiO ₂ /Si	SOL-GEL	40	-	-	-	300
BiFe _{0.9} Ti _{0.1} O _{3+δ}	LaNiO ₃ /SiO ₂ /Si	SOL-GEL	-	1.9	-	-	323
Bi _{1.1} Fe _{0.9} Zn _{0.1} O ₃	Pt/TiO ₂ /SiO ₂ /Si	PLD	-	73(80K)	-	0.6	335
BiFe _{0.9} Co _{0.1} O ₃	Pt/Ti/SiO ₂ /Si	CSD	-	-	-	2.9	338
BiFe _{0.98} Ti _{0.02} O _{3+δ}	Pt/Ti/SiO ₂ /Si	CSD	-	19	404	-	341
Bi _{0.9} Nb _{0.1} FeO ₃	Pt/Ti/SiO ₂ /Si	Polymeric	38	22	70	-	346
		Precursor					
Bi(Fe _{0.95} Mn _{0.03} Ti _{0.02})O	Pt/SrTiO ₃	PLD	-	75	310	-	42
Bi(Fe _{0.98} Zn _{0.01} Ti _{0.01})O ₃	Pt/Ti/SiO ₂ /Si	MOD	-	84	285	-	45
Bi(Fe _{0.93} Mn _{0.05} Zn _{0.02})	SRO/Pt/Ti/SiO ₂ /Si	RF	-	118	306	-	87

Ion substitutions for Fe site have been shown to improve the overall ferroelectric properties of BFO thin films by decreasing defect concentrations. Table 14 shows electrical and magnetic properties of BFO thin films with ion substitutions for Fe site.^{26,33,42,45,78,87,300,302,323,331,338,341,346,349} The ferroelectric properties of BFO thin films could be improved by the ion substitutions for Fe site, such as by Ru,⁵⁶ Mn,^{26,308,318} Cr,^{33,331} Ti,^{300,323,341} Zn,³³⁵ Co,³³⁸ and Nb.³⁴⁶ For example, a low leakage current was observed under a high applied electric field (>0.6 MV/cm) when 3%–5% Mn was doped to BFO, where well saturated *P-E* loops with $P_r \sim 100 \mu\text{C}/\text{cm}^2$ were observed.²⁶ A well-saturated *P-E* loop with $P_r \sim 99 \mu\text{C}/\text{cm}^2$ was found in the Ru-doped BFO films due to the reduced concentration of defects and the changes in domain structures, together with a saturated magnetization of $M_s \sim 16.53 \text{ emu}/\text{cm}^3$ due to the distorted spin cycloid and canting moment of Fe ions.⁵⁶ The addition of Cr suppressed leakage current in the high electric field region and then resulted in an increased P_r ($\sim 100 \mu\text{C}/\text{cm}^2$).³³¹ The addition of quadrivalent elements is expected to eliminate oxygen vacancies and shift Fe³⁺ to Fe²⁺, whereas the doping with bivalent elements can

increase the concentrations of oxygen vacancies and suppress the formation of Fe^{2+} . In one of our previous studies, the addition of both bivalent (Zn^{2+} , Mn^{2+}) and quadrivalent (Mn^{4+} , Ti^{4+}) elements in Fe site was shown to enhance ferroelectric properties ($P_r=70\sim118 \text{ } \mu\text{C}/\text{cm}^2$) of BFO thin films.^{42,45,337} For example, within (111)-oriented $\text{Bi}(\text{Fe}_{0.93}\text{Mn}_{0.05}\text{Zn}_{0.02})\text{O}_3$ thin films deposited on SRO-buffered silicon substrate, a $2P_r\sim235 \text{ } \mu\text{C}/\text{cm}^2$ value was demonstrated together with an almost fatigue-free behavior.^{337, 348} Giant P_r values of 150 ³⁴⁹ and $230 \text{ } \mu\text{C}/\text{cm}^2$ ⁷⁸ have been recently shown in the Ga-doped BFO thin films, due to a change in phase structure (super-tetragonal-like structure⁸⁸ or coexistence of R3c and Cm phases⁸⁹).

3.2.2.3 Substitution for Bi&Fe Sites

Table 15 Electrical and magnetic properties of BFO thin films by ion substitutions for Bi&Fe

Material system	Substrate	Preparation technique	P_r $\mu\text{C}/\text{cm}^2$	E_C (kV/cm)	M_r / M_s emu/cm^3	Ref.
$\text{Bi}_{0.975}\text{La}_{0.025}\text{Fe}_{0.975}\text{Ni}_{0.025}\text{O}$	Pt/Ti/SiO ₂ /Si	CSD	70	-	-	50
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$	SRO/Pt/TiO ₂ /SiO ₂ /Si	RF	105	263	18	67
$\text{Bi}_{0.9}\text{Ca}_{0.1}\text{Fe}_{0.90}\text{Mn}_{0.10}\text{O}_3$	Pt/Ti/SiO ₂ /Si	SOL-GEL	89	-	-	303
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.98}\text{Mo}_{0.02}\text{O}_3$	Pt/Ti/SiO ₂ /Si	PLD	43	210	-	306
$\text{BiPb}_{0.05}\text{Fe}_{0.97}\text{Cr}_{0.03}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	CSD	62	235	-	310
$\text{BiNd}_{0.05}\text{Fe}_{0.97}\text{Mn}_{0.03}\text{O}_3$	Pt/SrTiO ₃	PLD	100	250	-	311
$\text{Bi}_{0.95}\text{Nd}_{0.05}\text{Fe}_{0.97}\text{Cr}_{0.03}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	CSD	98	300	-	312
$\text{Bi}_{0.95}\text{Sm}_{0.05}\text{Fe}_{0.97}\text{Cr}_{0.03}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	CSD	94	285	-	312
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.95}\text{Ti}_{0.05}\text{O}_3$	LaNiO ₃ /Pt/Ti/SiO ₂ /Si	RF	51.3	269	-	316
$\text{Bi}_{0.85}\text{Pr}_{0.15}\text{Fe}_{0.95}\text{Mn}_{0.05}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	CSD	67	203	-	325
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.96}\text{Mg}_{0.04}\text{O}_3$	SRO/Pt/TiO ₂ /SiO ₂ /Si	RF	35	300	-	334
$\text{Bi}_{1.1}\text{Sr}_x\text{Fe}_{0.9}\text{Zn}_{0.1}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	PLD	58(80K)	801	1.1	335
$\text{Bi}_{0.90}\text{La}_{0.10}\text{Fe}_{0.95}\text{Zn}_{0.05}\text{O}_3$	Pt/TiO ₂ /SiO ₂ /Si	RF	65.8	248	-	336
$\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_3$	Pt/Ti/SiO ₂ /Si	CSD	66	-	5.9	338
$\text{Bi}_{0.95}\text{Sr}_{0.05}\text{Fe}_{0.975}\text{Nb}_{0.025}\text{O}_3$	SrRuO ₃ /Si	RF	27	-	17.4	339
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{Fe}_{0.98}\text{Ti}_{0.02}\text{O}_{3+\delta}$	Pt(111)/Ti/SiO ₂ /Si	CSD	26	443	-	341
$\text{Bi}_{0.9}\text{Ho}_{0.1}\text{Fe}_{0.99}\text{Ni}_{0.01}\text{O}_{3-\delta}$	Pt(111)/Ti/SiO ₂ /Si(100)	CSD	32	395	-	342
$\text{Bi}_{0.94}\text{Ce}_{0.06}\text{Fe}_{0.97}\text{Ti}_{0.03}\text{O}_3$	Pt/Ti/SiO ₂ /Si	SOL-GEL	65	500	-	343
$\text{Bi}_{0.85}\text{Sm}_{0.15}\text{Fe}_{0.97}\text{Cr}_{0.03}\text{O}_3$	FTO/glass	CSD	77	-	-	344
$\text{Bi}_{0.92}\text{Tb}_{0.08}\text{Fe}_{0.99}\text{Cr}_{0.01}\text{O}_3$	FTO/glass	CSD	52	-	-	345
$\text{Bi}_{0.9}\text{Nd}_{0.1}\text{Fe}_{0.975}\text{Zn}_{0.025}\text{O}_{3-\delta}$	Pt(111)/Ti/SiO ₂ /Si	CSD	30	386	0.037	347

There have been investigations into the effects of ion substitutions for both Bi and Fe sites and their impacts on the electrical and magnetic properties of BFO thin films [Table 15], such as by La and Ni⁵⁰/Mn⁶⁷/Ti³¹⁶/Zn³³⁶/Co³³⁸/Mg³³⁴, Ca and Mn,³⁰³ Nd and Mo³⁰⁶/Mn³¹¹/Cr³¹²/Zn³⁴⁷, Pb and Cr,³¹⁰ Pb³¹⁰/Sm³¹²/Tb³⁴⁵ and Cr, Dy and Mn,³⁴⁰ Sr and Zn³³⁵/Nb³³⁹, Ho and Ti³⁴⁰/Ni³⁴¹, and Ce and Ti.³⁴³ Among those, the doping with La&Mn $\{(\text{Bi}_{0.90}\text{La}_{0.10})(\text{Fe}_{0.95}\text{Mn}_{0.05})\text{O}_3, \text{BLFMO}\}$ could well improve ferroelectric and magnetic properties of BFO thin films, when deposited on $\text{SrRuO}_3/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}(100)$ substrates,⁶⁷ giving rise to $2P_r \sim 210.0 \text{ } \mu\text{C}/\text{cm}^2$. The BLFMO thin films also exhibited the enhanced magnetic behavior due to the canting of antiferromagnetically ordered spins. However, not all doped BFO films showed enhanced electrical behavior when the Bi and Fe sites were substituted by different ions. For example, a P_r value of $>50 \text{ } \mu\text{C}/\text{cm}^2$ could be observed in the Sr and Zn-codoped BFO thin films $\{(\text{Bi},\text{Sr})(\text{Fe},\text{Zn})\text{O}_3\}$ only when they were measured at far below room temperature (80 K).^{335,339} In order to obtain a good ferroelectricity at room temperature, La & Zn were co-doped to BFO thin films, which showed a high $2P_r$ value of $\sim 131.7 \text{ C}/\text{cm}^2$ at room temperature together with greatly suppressed leakage current.^{336,337} With La doping decreasing leakage current and Co improving magnetic properties, $\text{Bi}_{1-x}\text{La}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ polycrystalline thin films prepared by CSD method showed saturated ferroelectric hysteresis loops ($P_r=44\sim 66 \text{ } \mu\text{C}/\text{cm}^2$) and large saturation magnetization ($M_s \sim 5.9 \text{ emu/g}$, $x=0.1$).³³⁸

3.2.2.4 Addition of ABO_3

In general, the BFO epitaxial films possess a larger polarization,^{87,97,295,349} while the polycrystalline films often suffer from a high electrical leakage due to Fe valence fluctuation and the existence of some secondary phases.²⁸⁵ Among the many methods

proposed to overcome the leakage current in polycrystalline BFO thin films, one is to develop the BFO solid solutions with certain ABO_3 structured perovskite oxides^{296,301,304,324,350-358} (e.g., $PbTiO_3$,^{296,301,304,324,350-354} $Bi_{0.50}Na_{0.50}TiO_3$ ³⁵⁵ and $BaTiO_3$ ³⁵⁶⁻³⁵⁸). By alloying BFO with ABO_3 in thin film forms, MPB can be formed^{324,351,352,355,357,358} giving rise to a decrease in leakage current, as shown in Table 16. For example, a high remnant polarization ($2P_r \sim 100 \mu C \text{ cm}^{-2}$) can be attained in bismuth ferrite-lead titanate thin films in the region of MPB.³²⁴ Ren *et al.* found that the addition of Ti could further decrease the leakage current of $0.72Bi(Fe_{0.98}Ti_{0.02})O_3-0.28PbTiO_3$ thin films by replacing Fe^{3+} with Ti^{4+} .³⁵¹ They measured a P_r value of $\sim 45 \mu C/\text{cm}^2$. It was known that the $(1-x)BiFeO_3-xPbTiO_3$ films possessed enhanced ferroelectric behavior and weak ferromagnetism when the compositions were located at the tetragonal and rhombohedral phase boundary region.³²⁴ Lu *et al.*^{352,353} found that the doping with Sc^{3+} could suppress the formation of Fe^{2+} in $0.7BiFe_{0.5}Sc_{0.5}O_3-0.3PbTiO_3$ thin films, and also modulate the spin cycloid structure, resulting in the enhanced ferroelectric and magnetic properties.^{352,353} Recently, Wu and Wang *et al.*³⁵⁵ reported a giant remnant polarization of $2P_r \sim 198.3 \mu C/\text{cm}^2$ in $(1-x)BiFeO_3-x(Bi_{0.50}Na_{0.50})TiO_3$ thin films with (111) orientation and decreased leakage current. In general, ferroelectric and magnetic properties of BFO thin films can well be improved by introducing ABO_3 additives due to the formation of phase boundaries,³²⁴ modification in film orientation,³⁵⁵ decrease in leakage current^{351,352,355,357,358} and possible changes in spin cycloid modulation and spin canting angle.^{352,353}

Table 16: Electrical and magnetic properties of BFO thin films modified by ABO_3

Material system	Substrate	Preparation technique	P_r $\mu C/\text{cm}^2$	E_C (kV/cm)	M_r /Ms emu/cm^3	Ref.
$0.7BiFeO_3-0.3PbTiO_3$	Pt/TiO _x /SiO ₂ /Si	CSD	50	150	0.31	301

$\text{BiFeO}_3\text{-PbTiO}_3$	Pt/Si	PLD	50	230	-	296
$0.7\text{BiFeO}_3\text{-}0.3\text{PbTiO}_3$	Pt/TiO _x /SiO ₂ /Si	CSD	60(-190)	230	-	304
$0.1\text{BiFeO}_3\text{-}0.9\text{PbTiO}_3$	Platinized silicon	PLD	30(-10°C)	132	-	351
$0.72\text{BiFe}_{0.98}\text{Ti}_{0.02}\text{O}_3\text{-}0.28\text{PbTiO}_3$	Pt/TiO ₂ /SiO ₂ /Si	PLD	45(92)	-	-	350
$0.7\text{BiFe}_{0.5}\text{Sc}_{0.5}\text{O}_3\text{-}0.3\text{PbTiO}_3$	Pt/TiO ₂ /SiO ₂ /Si	PLD	40	250	12	352
$0.7\text{BiFe}_{0.5}\text{Sc}_{0.5}\text{O}_3\text{-}0.3\text{PbTiO}_3$	LaNiO ₃ /SiO ₂ /Si	PLD	38	165	-	353
$(1-x)\text{BiFeO}_3\text{-}x\text{BaTiO}_3$	R3c to P4mm	Sol-gel	27	50	1.46	356
$0.7\text{BiFeO}_3\text{-}0.3\text{BaTiO}_3$	-	PLD	2.5	533	0.2	358
$0.7\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\text{-}0.3\text{BaTiO}_3$	-	CSD	27	150	7.5	357
$(1-x)\text{BiFeO}_3\text{-}x\text{Bi}_{0.50}\text{Na}_{0.50}\text{TiO}_3$	SrRuO ₃ /SrTiO ₃	RF	99	150	2.5	355

3.2.3. Multilayer Structure

The construction of multilayer structure is among the most promising on-going topics in the field of thin films and devices, where both the growth and physical properties can be strongly influenced by the coupling and interactions among the different constituent layers.^{60,61,70,359-384} BFO-based multilayer structures have been shown to promote the desired electrical properties and/or new physical phenomena,^{60,61,70,71,77,110,359-384} such as a larger remnant polarization, improved magnetoelectric coupling, and photovoltaic behavior.

3.2.3.1 Heterojunction Multilayer Structure

Table 17 lists the electrical and magnetic properties of some of the BFO heterojunction multilayers that have been reported. The multilayers combining BFO with either ferroelectric or nonferroelectric layers have all been extensively studied.^{61,70,366-384,772,848,849} Although some of the properties of BFO thin films can be improved by forming the heterostructure, the P_r value is often limited to below 60 $\mu\text{C}/\text{cm}^2$ ^{60,70,366-375,377-379,381,383,384} due to the additive layers having lower or even zero P_r values. There have been surprisingly large P_r values reported for the heterostructure films consisting of BFO and non-ferroelectric layers.^{61,379,380,382,383} For example, $\text{BiFeO}_3/\text{ZnO}$ ³⁸⁰ and $\text{BiFeO}_3/\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ³⁷⁹ thin films possessed a P_r of

~60~80 $\mu\text{C}/\text{cm}^2$, owing to the orientation modification induced by ZnO or $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.

Table 17 Electrical and magnetic properties of BFO heterojunction multilayers

Material system	Substrate	Preparation technique	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/cm^3	Ref.
$\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3/\text{Bi}_{1.05}\text{La}_{0.05}\text{FeO}_3$	$\text{CaRuO}_3/\text{SrTiO}_3$	PLD	39.1	207	-	366
$\text{PbZrTiO}_3/\text{BiFeO}_3$	$\text{ZnO}/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	CSD	~60		-	367
$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{BiFeO}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	Metal Alkoxide	41.3	151	-	368
$\text{BiFeO}_3/\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	CSD	12		2.0	60
$\text{BiFeO}_3/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	Metal Alkoxide	13.86	37	-	369
$\text{BiFeO}_3/\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	26.1	277	48	370
$\text{BiFeO}_3/(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF/SOL-GEL	39.8	386.3	-	70
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{Bi}_{0.9}\text{La}_{0.1}\text{Fe}_{0.9}\text{Mn}_{0.1}\text{O}_3$	p-type Si(100)	CSD	42.3		28.6	371
$\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3/\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	PLD	13.2	185	0.78	373
$[\text{BiFeO}_3/\text{BaTiO}_3]_2$	$\text{Pt}/\text{SiO}_2/\text{Si}$	PLD	29.68	68.4	56.88	374
$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}/\text{BiFeO}_3/\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	CSD	-	-	3.6	375
$\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3/\text{CoFe}_2\text{O}_4/\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$	$\text{SrRuO}_3/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	85.9	384	218	376
$\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\text{-BiFeO}_3\text{-PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$	Pt/Si	Sol-gel	3	115	-	377
$\text{BaTiO}_3/\text{BiFeO}_3/\text{BaTiO}_3$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ (100)	RF	6.75	-	61 emu/cc	378
$\text{BiFeO}_3/\text{Zn}_{1-x}\text{Mn}_x\text{O}$	$\text{SrRuO}_3/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	65.3	-	15.2	379
$\text{BiFeO}_3/\text{ZnO}$	$\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	76.8	438.1	5.0	380
$\text{BiFeO}_3/\text{CoFe}_2\text{O}_4$	$\text{SrRuO}_3/\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$	RF	72.1	389	61.2	61
$\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3/\text{CoFe}_2\text{O}_4$	$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$	PLD	4.2		11.4	381
$\text{Bi}_{0.85}\text{Nd}_{0.15}\text{Fe}_{0.98}\text{Mn}_{0.02}\text{O}_3/\text{CoFe}_2\text{O}_4$	FTO	CSD	117	410	60	382

BiFe _{0.93} Mn _{0.04} Cr _{0.03} O ₃ /NiFe ₂ O ₄	FTO/Glass	Sol-gel	55	-	27.04	383
BiFeO ₃ /BiCrO ₃	LaAlO ₃	PLD	-	-	13 emu/cc	384

One particular type of the heterojunction multilayers is the multiferroic composite thin films, in which the magnetic and ferroelectric phases are purposely combined. They are promising for achieving greatly enhanced magnetic properties without significantly sacrificing the ferroelectricity, and more importantly for achieving prominent ME effects at room temperature. Some researchers have introduced magnetic layers such as CoFe₂O₄,^{61,381,382} NiFe₂O₄,³⁸³ and BiCrO₃³⁸⁴ to couple with BFO thin films in order to improve its magnetic properties and further achieve strong ME coupling.^{61,381-384} For example, bilayer thin films consisting of Bi_{0.85}Nd_{0.15}Fe_{0.98}Mn_{0.02}O₃ and CoFe₂O₄ show both good ferroelectric ($P_r \sim 117 \mu\text{C}/\text{cm}^2$, $E_c \sim 410 \text{ kV}/\text{cm}$) and ferromagnetic ($M_r \sim 60 \text{ emu}/\text{cm}^3$, $H_c \sim 1050 \text{ Oe}$) properties at room temperature.³⁸² However, a high coercive field of $E_c \sim 410 \text{ kV}/\text{cm}$ is shown, as the electric field is applied to the additional non-ferroelectric layers.⁶¹ In terms of the magnetoelectric properties, they will be discussed in detail in Section 4.4.

Recently, considerable interest has been aroused in the BFO/semiconductor multilayers, mainly for field-effect transistor applications and opto-electrical functionalities.³⁸⁸ The BFO/semiconductor multilayers could realize non-volatile memory by reading the conductance of the semiconductor channel which can be tuned by ferroelectric polarization.³⁸⁹ In addition, theories predicted the bulk photovoltaic effect with above-band-gap photovoltage in BiFeO₃ using the first-principles shift current theory, which were then supported by experimental results.¹¹⁰ The multilayer structures consisting of BFO and photo-active semiconductors have demonstrated

promising photovoltaic properties.^{71,77} For example, Wang *et al.*⁷¹ have investigated the photovoltaic effects in In₂O₃-SnO₂/ZnO/BiFeO₃/Pt multilayer films, where a short-circuit current density (J_{sc}) of 340 $\mu\text{A}/\text{cm}^2$ and an energy conversion efficiency of ~0.33% under blue monochromatic illumination were observed. There were abundant $e-h$ pairs generated from ZnO while the BFO layer could ensure a satisfactory photovoltage.

3.2.3.2 Homojunction Multilayer Structure

Table 18 Electrical and magnetic properties of BFO homojunction multilayers

Material system	Substrate	Preparation technique	P_r $\mu\text{C}/\text{cm}^2$	E_C kV/cm	M_r emu/cm^3	Ref.
BiFeO ₃ /Bi _{0.90} La _{0.10} Fe _{0.85} Zn _{0.15} O ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	69.1	329	-	359
Bi _{0.95} Gd _{0.05} FeO ₃ /BiFe _{0.95} Mn _{0.05} O ₃	SrRuO ₃ /Pt/TiO ₂ /SiO ₂ /Si	RF	73.8	343.6	-	360
BiFeO ₃ /BiFe _{0.95} Mn _{0.05} O ₃	SrRuO ₃ /Pt/TiO ₂ /SiO ₂ /Si	RF	82.6	209	-	361
BiFe _{0.95} Mn _{0.05} O ₃ /Bi _{0.90} La _{0.10} Fe _{0.85} Zn _{0.15} O ₃	SrRuO ₃ /Pt/TiO ₂ /SiO ₂ /Si	RF	94.7	-	-	362
Bi _{0.9} La _{0.1} Fe _{0.9} Zn _{0.1} O ₃ /Bi _{0.9} La _{0.1} Fe _{0.9} Sn _{0.1} O ₃	SrRuO ₃ /Pt/TiO ₂ /SiO ₂ /Si	RF	80.1	-	-	363
BiFeO ₃ /(Bi,Gd)FeO ₃	SrRuO ₃ /Pt/TiO ₂ /SiO ₂ /Si	RF	69	361	-	364
BiFe _{0.95} Mn _{0.05} O ₃ /Bi _{0.90} La _{0.10} FeO ₃	SrRuO ₃ / SrTiO ₃	RF	77.6	167.8	15.6	365

Recently, we have investigated the homostructures of BFO thin films by avoiding the weak (or even zero) ferroelectricity of an additional layer.³⁵⁹⁻³⁶⁵ P_r values of ~69.0-94.7 $\mu\text{C}/\text{cm}^2$ were demonstrated. Table 18 shows electrical and magnetic properties of BFO homojunction multilayers selected. For example, the bilayered thin films consisting of BFO and Bi_{1/2}Na_{1/2}TiO₃ nanolayers were deposited on the

Pt/TiO₂/SiO₂/Si substrates by RF sputtering, giving rise to enhanced physical properties ($2P_r=52.2$ C/cm², $2E_c=554.0$ kV/cm, $2M_s=96.0$ emu/cm³, $2H_c=253.2$ Oe) and reduced leakage current.³⁷⁰ In addition, in order to gain a large remnant polarization, BFO homostructure films have to be tuned into appropriate film orientation.³⁵⁹⁻³⁶⁵

3.2.4. Buffer Layer

Table 19 Electrical and magnetic properties of BFO –based thin films with different buffer layers

Material system	Buffer layer	Substrate	Preparation technique	P_r μC/cm ²	E_c kV/cm	M_r/M_s emu/cm ³	Ref.
BiFeO ₃ (111)	SrRuO ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	98.5	263	-	23
BiFeO ₃ (110)	SrRuO ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	72	193	1.92	390
Bi _{0.90} La _{0.10} Fe _{0.95} Mn _{0.05} O ₃ (111)	SrRuO ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	105	263	18	67
BiFeO ₃ (110)	LaNiO ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	73	286	-	69
BiFe _{0.6} Ga _{0.4} O ₃ (001)	LaNiO ₃	NdCaAlO ₄	RF	150	600	-	78
BiFeO ₃	La _{0.8} Sr _{0.2} MnO ₃	Si	CSD	13.5	-	113	391
BiFeO ₃ (111)	La _{0.67} Sr _{0.33} MnO ₃	Pt/TiO ₂ /SiO ₂ /Si	RF	105.3	218	89.5	392
BiFeO ₃	La _{0.5} Sr _{0.5} TiO ₃	Ni	CSD	75	1050	-	393
BiFeO ₃ (Random)	La _{0.5} Sr _{0.5} TiO ₃	Ni (200) tapes	CSD	70	1050	-	393
BiFeO ₃ (001)	Sr _{0.33} Ca _{0.67} RuO ₃	SrTiO ₃ (001)	PLD	15.5	176	-	394
Mn-doped BiFeO ₃ (001)	SrTiO ₃	GaAs (001)	PLD	46	186	6.5	395
BiFeO ₃ (111)	BaPbO ₃	Pt/Ti/SiO ₂ /Si	RF	42.8	500	-	328
BiFe _{0.95} Mn _{0.05} O ₃	Bi ₂ O ₃	Pt/Ti/SiO ₂ /Si	SOL-GEL	78	255	-	396

Conductive oxide buffer layers have often been used to grow bismuth ferrite thin films and improve their properties^{23,67,69,78,225,328,390-396} by controlling the film texture

as well as tuning the leakage current.^{23,67,69,78,225,328,390-396} Table 19 lists the main electrical and magnetic properties for some of the BFO thin films that were reported with different conductive oxide buffer layers,^{23,67,69,78,225,328,390-396} such as SrRuO₃,^{23,67,390} (La,Sr)(Mn/Ti)O₃,³⁹¹ Sr_xCa_{1-x}RuO₃,³⁹⁴ SrTiO₃,³⁹⁵ BaPbO₃,³²⁸ Bi₂O₃,³⁹⁶ and PbO.⁸⁵⁷ Among these buffer layers, the SRO is particularly effective. For example, P_r values of 72~105 $\mu\text{C}/\text{cm}^2$ were measured in the BFO-based thin films with SRO buffer layer due to the improvement in film quality and (111)/(110) orientation.^{23,67,225,390} More recently, Wang and Fan *et al.* have successfully demonstrated the predicted giant polarization ($\sim 150 \mu\text{C}/\text{cm}^2$) in (001)-oriented BiFe_{0.6}Ga_{0.4}O₃ thin films with super-tetragonal (-like) phase by the conventional $P-E$ hysteresis measurement at room temperature.⁷⁸ Such giant P_r is partly attributed to the (001) orientation induced by the LaNiO₃ bottom electrode. In general, the orientation and leakage current of BFO can be greatly modified by inserting a conductive oxide buffer layer between the film and substrate, and thus enhanced ferroelectric properties can be attained for BFO-based thin films.

3.2.5 Strain Effect

Table 20 Ferroelectric properties of BFO-based thin films with different phase structures

Material system	Substrate	Phase boundary type	P_r $\mu\text{C}/\text{cm}^2$	Ref.
BiFeO ₃	LaAlO ₃ -YAlO ₃ -SrTiO ₃	R-T	-	99
BiFeO ₃	LNO/(001)LaAlO ₃	R-T	-	397
BiFeO ₃	-	R-T	-	398
BiFeO ₃	LaAlO ₃ (001)	R _(MI) -T _(MII,tilt)	-	399

BiFeO ₃	-	R- M_A - M_C -T	-	400
BiFeO ₃	SrTiO ₃	Monoclinic	-	401
BiFeO ₃	SrTiO ₃	Monoclinic	-	402
BiFeO ₃	PrScO ₃	Monoclinic (M_B)	85	403
BiFeO ₃	SrTiO ₃ (001)	Pseudo tetragonal	-	39
BiFeO ₃	Yttria-stabilized Zirconia	Tetragonal	-	404
BiFeO ₃	Pt/TiO ₂ /SiO ₂ /Si	Tetragonal	166	289
BiFeO ₃	SrTiO ₃	Rhombohedral	63-98	405
BiFeO ₃	NdScO ₃ (110)	Orthorhombic		406
BiFeO ₃	La _{0.3} Sr _{0.7} MnO _{3-δ} /SrTiO ₃ (001)	T_R -T- M_C -R	-	407
Bi _{1-x} Sm _x FeO ₃	SrRuO ₃ /SrTiO ₃	ferroelectric-to-antiferroelectric	70	408
BiFe _{0.6} Ga _{0.4} O ₃ (001)	LaNiO ₃	Super-tetragonal	150	78
BiFe _{0.9} Ga _{0.1} O ₃	LaNiO ₃ /glass	$R3c$ - C_m	230	349
0.6BiFeO ₃ -0.4PbTiO ₃	-	-	80	296
[BiFeO ₃ /(Bi _{1-x} Sm _x)FeO ₃] _n	-	R-O	-	409

Strain effect, which arises from the mismatching in lattice parameters and/or thermal expansion between the film and the substrate, is an effective approach to change the structure and tailor the physical properties of functional oxide thin films.⁴¹⁰ It may lead to the structure and properties of thin films significantly different from those of the bulk counterpart. Bulk BFO exhibits a rhombohedrally distorted perovskite structure with $R3c$ space group ($a=3.965$ Å and $\alpha=89.4^\circ$),⁴¹¹ and however the symmetry can be steadily changed due to the strain when BFO is grown on different substrates. Table 20 thus summarizes the rich phase structures and corresponding ferroelectric properties of BFO films grown on different substrates.

A more effective way to impose strain is perhaps by growing BFO epitaxially on single-crystal substrates, which is also known as “strain engineering”. There is a wide range of single-crystal substrates with different lattice parameters, orientations and miscuts available commercially. Table 21 lists the lattice information of the single-crystal substrates that have been commonly used for the epitaxial growth of BFO thin films. Therefore, different types and amounts of strain can be provided for BFO thin films. By varying the strain, a series of phases (i.e., rhombohedral, tetragonal, orthorhombic, monoclinic and mixed phases) have been reported in BFO thin films.^{99,400,412-414} A rich phase diagram for strain varying from -7% to +6.3% is shown in Fig. 17. One can see that BFO endures a phase transition from monoclinic (M_A) to monoclinic (M_C , super-T) and tetragonal (T) phase as the in-plane compressive strain increases, while the increasing tensile strain drives the phase transition of BFO from M_A to M_B , and then to orthorhombic (O) phase.^{24,48,330,400,402,403,406,6416,418,608-613} In particular, as the compressive strain exceeds 4.5%, there is a phase transition from pseudo-rhombohedral (R phase) to pseudo-tetragonal (T phase) and.^{416,421} It was theoretically predicted that the pseudo-tetragonal structure of BFO could exhibit an extremely large polarization of $\sim 150 \mu\text{C}/\text{cm}^2$.^{48,415-417} Okuyama *et al.*²⁸⁹ first observed such a giant ferroelectric polarization values, i.e., 110 and 166 $\mu\text{C}/\text{cm}^2$ at room temperature and 80 K, respectively. Since then, several researchers have focused on the investigations into the pseudo-tetragonal phase ($c/a \sim 1.25$) in BFO films which can be grown on the substrate with compressive misfit strain greater than 4.5%.^{413,414,416,418,419} A giant P_r of $\sim 130 \mu\text{C}/\text{cm}^2$ was reported in the BFO films grown on LAO substrates, because of the strain-induced super-tetragonal phase having large ionic displacements arising from both the stereochemically active Bi 6s

lone pair electrons and the off-center motions of Fe.⁴¹⁷ It was also found that the super-tetragonal BiFeO₃ phase could be stabilized at a low growth rate when using Bi₂O₃ as a buffer layer, which was confirmed by *ab initio* calculations.⁸² Chu *et al.*^{412,413,420} further suggested that these BFO films possessed pseudo-tetragonal structures instead of a real tetragonal structure,⁴⁰⁴ and then they fabricated the BFO thin films with a tetragonal phase by choosing the yttria-stabilized zirconia substrates, as identified by a combination of X-ray diffraction, scanning transmission electronic microscopy, X-ray absorption spectroscopy, and Raman spectroscopy.

Table 21 Lattice parameters of the substrates commonly used for epitaxial BFO films

Substrate materials	Phase structure	Lattice parameters (Å)	Misfit strain (BFO)	Strain types
NdCaAlO ₄	T	3.685(a=b)/12.12(c)	-7.0%	Compressive Strain
YAlO ₃	O	3.69(a=b=c)	-6.9%	
LaSrAlO ₄	T	3.755(a=b)/12.6(c)	-5.2%	
LaAlO ₃	R	3.79(a=b=c)	-4.4%	
NdGaO ₃	O	5.426(a)/5.496(b)/7.707(c)	-2.8%	
SrTiO ₃	C	3.905(a=b=c)	-1.5%	
KTaO ₃	C	3.989(a=b=c)	+0.6%	Tensile Strain
NdScO ₃	O	5.575(a)/5.776(b)/8.003(c)	+1.2%	
MgO	C	4.216(a=b=c)	+6.3%

Fig. 17. Effects of strain on phase structure of epitaxial BFO films [24,48,330,400,402, 403,406,6416,418,608-613]

Besides substrates, other factors which could induce strain, such as film thickness, and chemical strain, also play a role in tailoring the phase structures and properties of BFO. For example, Saito *et al.* observed that the films thickness strongly affected the phase structure of BFO thin films. More specifically, BFO films fabricated on $\text{SrRuO}_3/\text{SrTiO}_3$ substrates with a thickness of <50 nm exhibited a tetragonal phase, but a monoclinic phase was found for the film thickness of >50 nm.⁴²² Wang *et al.*⁷⁹ found that three phases (i.e., orthorhombic-like, tetragonal-like, and rhombohedral-like phase) coexisted in the (110) BFO films as the films thickness increases from 10 to 190 nm, as confirmed by high resolution synchrotron X-ray diffraction. It was also reported that chemical strain could strongly affect the phase transition of BFO thin films, and then enhanced electrical properties can be attained. For example, for highly strained La-modified BFO films, the addition of La changed the energy landscape between the tetragonal-like and the rhombohedral-like polymorphs due to the chemical pressure imposed by the La substitution.⁴³⁷ An increase in La doping induced the polar instability for the in-plane polarization component, which was correlated with the vanishing of in-plane ferroelectric domain

structures. The transition sequence of the in-plane ferroelectric polarization was consistent with the one which was previously reported for the bulk-like rhombohedral phase of BFO under continuous La doping, indicating the universality of the chemical strain effect on the ferroelectric order.⁴³⁷

There is no doubt that the phase structures of BFO thin films are very sensitive to the type and level of strain as modified by substrate (particularly in epitaxial growth), film thickness, and chemical doping. A good understanding of the correlations between them will benefit the development of BFO thin films with the desired phases and corresponding properties.

3.3 Nanostructures

Fig. 18. Publications on BFO-based nanostructures over the period of 2000 to 2015.

Nanoscaled ferroelectric materials has been an interesting research topic, which is very important for the development of future electronics and information technologies because of their unique properties and diverse application ranges such as in memories and tunnel junctions.⁶⁴²⁻⁶⁴⁵ The dimensional downscaling also allows for the desired high-density integration of nanostructured ferroelectric devices.

In Sections 3.1 and 3.2, we have looked at many interesting aspects of BFO-based ceramics and thin films. Due to both the size effect and large surface to volume ratio, BFO nanostructures often exhibit different properties from those of the bulk counterparts, especially in magnetic and photocatalytic behavior [See Fig. 18].^{17,30,46,53,143,466,472,482,486,504,505,516,519,528,534,646-763,845-847} For example, both the Néel and Curie temperatures of BFO decreased with decreasing the particle sizes to the nanometer level.^{647,648} The enhanced magnetization of BFO nanostructures was considered to be partially originated from the uncompensated spins at surfaces.^{504,505,649} The visible-light photocatalytic ability was also significantly enhanced by modulation in band gap and increase in the surface area.⁵⁰⁵ BFO nanoparticles have been demonstrated for use in production of hydrogen through solar water splitting.⁶⁵⁰ The 1-3 vertical CFO-BFO nanocomposites, which were fabricated by the self-assembly method, have been demonstrated with enhanced magnetoelectric properties.^{516,519,651-661} . In this section, we will look into the details of fabrication methods, size effects and properties of nanostructured BFO materials.^{17,30,46,53,143,466,472,482,486,504,505,516,519,528,534,646-763}

3.3.1 Synthesis of BFO-based Nanostructures

Due to the size effects on structure and functional properties, considerable efforts have been devoted to the controllable synthesis of low-dimensional BFO nanostructures with various morphologies. According to their dimensions, four types of BFO nanostructures can be defined: (i) zero dimension (nanoparticles or dots), (ii) one dimension (nanowires, nanorods, and nanotubes), (3) two dimension (thin films

and nanoislands), (4) three dimension (nanocomposites consisting of nanowires, nanotubes arrays).

Table 22 Synthesis methods and morphologies of BFO nanostructures

Compounds	Experimental methods	Nano-morphology
BiFeO ₃	Sol-gel, ^{53,505,680,686,693,695,699,700,702,704,705,710,711,713-715,717,719,720}	Rod, ⁶⁸⁵ Island, ⁶⁸⁴ Wire, ^{30,668} Belt,
	PLD, ^{516,656-661} Hydrothermal, ^{670,703,706} Soft electron beam	Tube, ^{53,702,723} Cube, ^{665,666}
	lithography, ⁶⁷² Combustion reaction, ⁶⁸² Microwave	Particle, ^{46,466,505,672,679-683,686,687,693,}
	Synthesis, ⁶⁸³ Sonochemical, ⁶⁸⁷ Co-precipitation, ⁶⁹⁴	^{694,698-701,703-711,713-720} Dot array, ⁶⁶⁹
	Electrospinning, ⁶⁹⁷ Self-combustion, ⁶⁹⁸ Solution	Sheet, ⁷⁶³ Plate, ⁶⁷⁰ Fiber, ^{695,697,712}
	combustion, ^{486,696,701,729} Pechini, ⁶⁸¹ Solution evaporation, ⁷²⁵	Nanocomposite, ^{516,656-661} etc.
	Auto-combustion, ^{727,742} Molten salt, ⁷³⁶ Solvothermal, ⁷³⁸	
	Dip-pen nanolithography, ⁶⁶⁹ Top-down lithographic, ⁶⁵⁸	
	Lift-off nanoimprint lithography, ⁷⁵⁴ etc.	

Table 22 lists some of the synthesis methods and morphologies of BFO nanostructures that have been reported. One can see that different nano-morphologies can be fabricated through different synthesis methods, including deposition by PLD and CVD, electron beam lithography, dip-pen nanolithography, top-down lithographic, lift-off nanoimprint, sol-gel, hydrothermal, combustion reaction, microwave synthesis, co-precipitation, electrospinning, and molten salt growth.^{53, 486,}

^{505, 516,656-661,669,670, 672, 680-683,686,687,693-706, 710,711,713-715,717,719,720,725,727,729,736,738,742,754}

Among those methods reported, two chemistry-based approaches (i.e., sol-gel and hydrothermal method) have been more commonly employed than others.^{3,505,670,680,686,693,695,699,700,702-706,710,711,713-715,717,719,720} Indeed, a wide range of nano-morphologies have been developed by these techniques, including nanoparticles,^{46,466, 505,672,679-683,686,687,693,694,698-701,703-711,713-720} nanocubes,^{665,666}

nanotubes,^{53,702,723} nanowires,^{30,668} nanodots,⁶⁶⁹ nanosheet,⁷⁶³ nanoplate,⁶⁷⁰ and nanoislands.⁶⁸⁴

3.3.2 Undoped Nanostructured BFO

Table 23 Magnetic and electrical properties of nanostructured BFO

Material system	Form	Preparation technique	M_r / M_s emu/g	E_g eV	Ref
BiFeO ₃ nanoparticle	(<100nm)	Electron beam lithography	10		672
BiFeO ₃ nanotube array	(200nm/6μm)	Sol-gel			53
BiFeO ₃ nanoparticle	(10-150nm)	Spray pyrolysis	0.5-2.5		679
BiFeO ₃ nanoparticle	73.7nm	Sol-gel		2.18	680
BiFeO ₃ nanoparticle	21-68nm	Pechini sol-gel	0.1-7.5		681
BiFeO ₃ nanoparticle	23/26nm	Combustion reaction	0.64	2.27/1.66	682
BiFeO ₃ nanoparticles	30-50nm	Microwave synthesis	0.045μ _B /Fe		683
BiFeO ₃ islands	250nm	Ion beam milling	0.42/1.23		684
BiFeO ₃ nanorods		Hydrothermal	0.0245μ _B /Fe(10K)		685
BiFeO ₃ nanoplates	20-160nm	Hydrothermal	0.6		670
BiFeO ₃ nanosheets	20nm(thickness)	Chemical solution	3.1		763
BiFeO ₃ nanodot	27nm(D)/13nm(d)	Dip-pen nanolithography			669
BiFeO ₃ nanoparticles	18-248nm	Sol-gel			686
BiFeO ₃ nanoparticles	46-58nm	Sonochemical	0.2		687

Fig.19. Selected examples of morphologies of BFO nanostructures [505,646,670-672,673-675,763]

Figure 19 shows selected examples of morphologies of BFO nanostructures prepared by different techniques.^{505,646,670-672,673-675,763} These nanomorphologies can be well modulated by the processing technique and parameters chosen for fabrication. Table 23 lists magnetic properties for selected BFO nanostructures.^{53,669-672,679-692} Compared with the forms of thin films or ceramic bulks, they possess stronger magnetism,^{676,677} depending on the corresponding morphological features.^{53,669-672,679-692} Previous studies have also revealed the two major factors largely responsible for the enhanced magnetic properties:⁵⁰⁴ (i) large degree of suppression of magnetic structure (period length of ~ 62 nm) with decrease in nanoparticle size, and (ii) uncompensated spins and strain anisotropies at surface.

Fig. 20. (a) Size-dependent M - H loops at 300 K for BiFeO₃ nanoparticles. (b) Strong size-dependent Néel temperature (T_N) and polarization behavior of BiFeO₃ nanoparticles [647].

Figure 20(a) shows the size effect of M - H loops of BFO nanoparticles, measured at 300 K.⁶⁴⁷ Compared with those of ceramic bulks, nanoparticles show better magnetic behavior. The magnetic response increases rapidly with the decrease in particle size. In particular, there is a dramatic increase in M_r for sizes below 62 nm (the period length of the spiralmodulated spin structure of BiFeO₃) due to the modification in

long range spiral-modulated spin structure.⁵⁰⁴ It is seen from Fig. 20(b) that the decrease in size gives rise to a decrease of T_N because of phenomenological scaling relations and possible correlations with decreasing polarization.⁶⁴⁷ In addition, the magnetic properties are also dependent on the morphologies of BFO nanostructures. For example, BFO nanorods show a maximum magnetization of 0.277 emu/g under an applied field of 8 kOe, which is inferior to that ($M_S \sim 0.534$ emu/g) of nanowires but higher than that ($M_S \sim 0.125$ emu/g) of nanotubes.^{30,678} The variation in magnetism with morphologies may well be correlated to the shape anisotropy, magnetocrystalline anisotropy and different amounts of defects present in the different nanoforms.

3.3.3 Chemical Modification in Nanostructured BFO

3.3.3.1 Ion Substitution for Bi Site

Table 24 Electrical and magnetic properties of BFO nanostructures with ion substitution for Bi site

Material system	Form	Preparation technique	E_g eV	M_r / M_s emu/g	Ref.
$\text{Bi}_{0.9}\text{Dy}_{0.1}\text{FeO}_3$ nanoparticles	300-600nm	Sol-gel	2.22	5.5	693
$\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ nanoparticles	30-70nm	Co-precipitation		0.47/0.84	694
$\text{Bi}_{1-x}\text{Dy}_x\text{FeO}_3$ nanofibers	13-27nm	Electrospinning	2.45	0.40-1.17	695
$\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ nanocrystallites	26-74nm	Solution combustion		0.044	696
$\text{Bi}_{1-x}\text{Ca}_x\text{FeO}_3$ nanofibres	147-169nm	Electrospinning		0.6	697
$\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ nanoparticles	22-23nm	Self-combustion		0.35-0.73	698
$\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_3$ nanoparticles	27-52nm	Sol-gel	1.8-2.3	0.54-1.37	699
$\text{Bi}_{1-x}\text{In}_x\text{FeO}_3$ nanoparticles	30-42nm	Sol-gel		1.98-3.2	700
$\text{Bi}_{1-x}\text{Al}_{2x}\text{Fe}_{1-x}\text{O}_3$ nanoparticles	13-20nm	Solution combustion	2.78-2.93		701
$\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$ nanotubes	200nm/20nm	Sol-gel		5	702
$\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ nanoparticles	100nm	Hydrothermal		0.194	703
$\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ nanocrystallines	20-70nm	Sol-gel		2.681	704
$\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ nanoparticles	50-200 nm	Sol-gel	2.02-2.47	0.76	705
$\text{Bi}_{1-x}\text{Ba}_x\text{FeO}_3$ nanoparticles	88-104nm	Hydrothermal		7.24/12(1.6T)	706
$\text{Bi}_{1-x}\text{Pr}_x\text{FeO}_3$ nanoparticles	25nm	Propylene glycol-gel		0.1	707
$\text{Bi}_{1-x}\text{Ho}_x\text{FeO}_3$ nanoparticles	60-75nm	Soft chemical		1.8	708
$\text{Bi}_{1-x}\text{Ho}_x\text{FeO}_3$ nanoparticles	55-71nm	Sol-gel	2.01-2.11	1.5	709
$\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ nanoparticles	21-34nm	Polyol-mediated		2.23	466
$\text{Bi}_{1-x}\text{Na}_x\text{FeO}_3$ nanoparticles	50nm	Sol-gel	2.08-2.16	0.2	710
$\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ nanoparticles	42-59nm	Sol-gel	2.29-2.36	0.1	711
$\text{Bi}_{1-x}\text{Gd}_x\text{FeO}_3$ nanofibers	150-250nm	Electrospinning		2.4-4.12	712

Bi _{1-x} Lu _x FeO ₃ nanoparticles		Sol-gel	0.67	713
Bi _{1-x} Co _x FeO ₃ nanoparticles	22nm	Sol-gel	3.5	714
Bi _{1-x} Ce _x FeO ₃ nanoparticles	30-50nm	Sol-gel	1.766	715
Bi _{0.99} Y _{0.01} FeO ₃ nanoparticles	29nm	Pechini technique	1.97-2.29	716
Bi _{0.9-x} La _{0.1} Ca _x FeO ₃ nanoparticles	19-24nm	Sol-gel	0.25-0.33	717
Bi _{0.9} La _{0.075} Ce _{0.025} FeO ₃ nanoparticles	25nm	Combustion method	1.045	718
Bi _{1-x-y} Er _x Ba _y FeO ₃ nanoparticles	50-100nm	Sol-gel	0.98	719
Bi _{0.8} Ca _{0.2-x} Ba _x FeO ₃ nanoparticles	20-28nm	Sol-gel	1.10-1.64	720

Site engineering is able to tailor the physical properties of BFO nanostructures.^{466,693-720} The substitution at Bi site in nanostructured BFO could produce significant effects on the Bi 6s² lone pair and the lattice structure,⁸¹⁷ which affects both the ferroelectric and magnetic behaviors. Table 24 shows the electrical and magnetic properties of BFO nanostructures with the modification of Bi site. The band gap, magnetism, and photocatalytic properties can be modified. There are several important notes that are worthy to mention. Firstly, an appropriate amount of additives in nanostructure can benefit the magnetic properties of BFO.^{466,693,700,702-715} For example, the Ba-doped nanocrystals⁷⁰⁴ possessed a higher H_c value than ceramic bulk^{818,819} at the same doping concentration, due to the magnetic anisotropy induced by size effect.⁷⁰⁷ In addition, the morphology of BFO nanostructures was changed by the level of Ba doping [See Figs. 21(a)-(c)]. As can be seen from Figs. 21(a)-(c), the compositions with $x=0$, 0.1 and 0.2 show the cylindrical, cylindrical and hexagonal shapes, respectively.⁷⁰⁶ The hexagonal-shaped sample demonstrates a maximum M_s value of ~12.74 emu/g, as shown in Fig. 21(d).

Fig. 21. FE-SEM images of Bi_{1-x}Ba_xFeO₃ samples with (a) $x=0$, (b) $x=0.1$, and (c) $x=0.2$. (d) Composition dependence of M - H loops [706].

Secondly, the type of doping elements at Bi site affects the magnetic properties. For example, Pr-modified BFO nanoparticles showed a higher M_r value than those doped with nonmagnetic elements of La, Ca or Ba.^{143,528,721} Divalent ion doping benefit both magnetic and photocatalytic properties of nanostructured BFO.^{46,695,697,698,709,711} The enhancement of magnetic properties of Bi_{1-x}Dy_xFeO₃ nanofibers was attributed to the rhombohedral distortion in the FeO₆ octahedron along the [111] direction and the formation of magnetic domains. The decrease in band gap and the enhancement in ferroelectricity promoted photocatalytic efficiency.⁶⁹⁵ Thirdly, the bang gap of BFO nanostructures can be effectively narrowed by certain types of dopants, giving rise to effective promising photocatalysis for potential applications. For example, the band gap of BFO is narrowed by doping with Dy,⁶⁹⁵ Sr,⁶⁹⁹ Ba,⁷⁰⁵ Na,⁷¹⁰ Gd⁷¹¹ and Y⁷¹⁶. The increases in Fe–O–Fe angle as well as the impurity-induced energy levels inside the forbidden gap region, may be responsible for the narrowed band gap of Bi_{1-x}Na_xFeO₃ nanoparticles.⁷¹⁰

3.3.2 Ion Substitution for Fe and Bi & Fe Sites

Table 25 Magnetic properties of BFO nanostructures with ion substitution for Fe site [467,472,722-726]

Material system	Form	Preparation technique	M_r / M_s emu/cm ³	Ref.
BiFe _{1-x} Mn _x O ₃ nanoparticles	50-100nm	Sol-gel	0.04-0.25	472
BiFe _{0.95} Co _{0.05} O ₃ nanotubes	200nm/20nm	Sol-gel	0.021	723
BiFe _{1-δ} Co _δ O ₃ nanocrystallites	39nm	Solution evaporation	0.42(5K)	725
BiFe _{0.9} Sc _{0.05} Ti _{0.05} O ₃ nanoparticles	18±1nm	Sonochemical synthesis	0.36	726

Table 26 Magnetic properties of BFO nanostructures with ion substitution for both Bi and Fe sites [482,727-735]

Material system	Form	Preparation technique	M_s / M_r emu/cm ³	Ref.
Bi _{0.95} Ce _{0.05} Fe _{1-x} Cr _x O ₃ nanoparticles	20-50nm	Auto-combustion	2.63	727
Bi _{0.9} Eu _{0.05} La _{0.05} Fe _{0.95} Co _{0.05} O ₃ nanoparticles		Sol-gel	1.15/0.35	728
Bi _{1-x} Sm _x Fe _{1-y} Mn _y O ₃ nanoparticles	16nm	Solution combustion	5.4/0.175	729
Bi _{1-x} Ca _x Fe _{1-y} Co _y O ₃ nanoparticles	20-70nm	Sol-gel	0.811	730
Bi _{1-x} Ba _x Fe _{1-y} Nb _y O ₃ nanoparticles	27/32nm	Sol-gel	2.94/0.36	731
Bi _{0.9} Nd _{0.1} Fe _{1-x} Co _x O ₃ nanoparticles	50-70nm	Sol-gel		732
Bi _{1-x} Eu _x Fe _{1-y} Co _y O ₃ nanoparticles	13nm	Sol gel	9.04	482
Bi _{0.8} La _{0.2} Fe _{1-x} Co _x O ₃ nanoparticles	46-49nm	Sol-gel	0.568	734
Bi _{1-x} Gd _x Fe _{1-y} Co _y O ₃ nanoparticles	~60nm	Pechini sol-gel	2.36/0.37	735

In BFO, the *d* shell is partially filled, giving rise to magnetism.⁸¹⁶ Therefore, the multiferroic properties of nanostructured BFO can be tuned by controlling over the *d* shell configuration through chemical substitutions. Tables 25 and 26 show the magnetic properties of BFO nanostructures with ion substitution for Fe^{467,472,722-726} and both Bi & Fe^{482,727-735} sites, respectively. Similar to the substitution at Bi site, magnetic properties can be well modified by introducing foreign elements to Fe site. For example, BiFe_{0.95}Co_{0.05}O₃ (BFC) nanotube arrays, prepared using the AAO templates,⁷²³ showed smooth tubular characteristics with wall thickness of ~20 nm [See Fig. 22(a)]. A saturated *M-H* loop of ~0.021 emu/g was obtained for BFC

nanotubes, which was superior to undoped BFO nanotubes [See Fig. 22(b)], indicating that the Co doping enhanced the magnetic properties due to the possible breakage in space-modulated spin cycloid induced by Co doping. In addition, the enhancement in magnetic properties has also been demonstrated for Mn,⁴⁷² Cu,⁷²⁴ Sc⁴⁶⁷ and Sc-Ti⁷²⁶ doped BFO nanostructures.

Fig. 22. (a) SEM and TEM images of $\text{BiFe}_{0.95}\text{Co}_{0.05}\text{O}_3$ (BFC) nanotubes, and (b) M - H hysteresis loops of BFO and BFC nanotubes [723].

Fig. 23. (a) TEM image of $\text{Bi}_{0.95}\text{Ce}_{0.05}\text{Fe}_{0.9}\text{Cr}_{0.1}\text{O}_3$ nanoparticles. (b) M - H loops of pure and Ce, Cr doped BFO nanostructures, measured at room temperature [727].

One can see from Table 26 that the substitutions at both A and B sites can improve the magnetic properties of BFO nanostructures, such as by the combination of Ce&Cr,⁷²⁷ (Eu,La)&Co,⁷²⁸ Sm&Mn,⁷²⁹ Ca&Co,⁷³⁰ Ba&Nb,⁷³¹ Nd&Co,⁷³² Sm&Co,⁷³³ Eu&Co,⁴⁸² La&Co,⁷³⁴ and Gd&Co.⁷³⁵ For example, $\text{Bi}_{0.95}\text{Ce}_{0.05}\text{Fe}_{0.9}\text{Cr}_{0.1}\text{O}_3$ was

shown to exhibit irregular-shaped and agglomerated nanoparticles of ~28 nm [Fig. 23(a)], and the enhancement in magnetic properties ($M_S=2.63$ emu/g) observed in [Fig. 23(b)] was attributed to the transition metal cation Cr^{3+} as well as small particles size.⁷²⁷ The changes in the Fe–O–Fe angle induced by Ce^{3+} and the Ce–O–Fe spin coupling may also modify the spin cycloid structure.

3.3.4 Nanocomposites

Table 27 ME, E_g and magnetic properties of BFO nanostructures doped with ABO_3 [516,656,661,736-751]

Material system	Form	Preparation technique	ME	E_g eV	M_S/M_r emu/cm ³	Ref.
(BiFeO ₃) _x -(BaTiO ₃) _{1-x} nanocube	150-200nm	Molten salt			0.32-0.75	736
(BiFeO ₃) _{1-x} (PbTiO ₃) _x nanocrystallite	7-35nm	Solution combustion			~0.15	486
BiFeO ₃ /(100-x)NiO nanocomposite	11nm	Solvothermal process			2.2emu/gm	738
(1-x)BiFeO ₃ -xNiFe ₂ O ₄ nanocomposite	3.6-14nm	Sol-gel			6-10	739
(1-x)BiFeO ₃ -xNiFe ₂ O ₄ nanocomposite	200nm	Sol-gel			34/7	740
(1-x)BiFeO ₃ -xDyMnO ₃ nanoceramic	30nm	Auto-combustion			0.5	742
BiFeO ₃ -(Na _{0.5} Bi _{0.5})TiO ₃ nanopowder	40-100nm	Sol-gel		2.08	0.36	745
Ni ₈₀ Fe ₂₀ /BiFe _{0.95} Co _{0.05} O ₃ core-shell	300nm	Electrodeposition				746
(1-x)BiFeO ₃ -xNaNbO ₃ nanocomposite		Pechini method	0.13	1.9-2.8		748
TiO ₂ /BiFeO ₃ nanoheterostructure	2-8nm	Wet chemical				750
BiFeO ₃ /poly nanocomposite	40nm	Auto combustion			0.91	751
CoFe ₂ O ₄ -BiFeO ₃ nanocomposite		PLD	60		3.4 $\mu\text{B/f.u.}$	516
CoFe ₂ O ₄ -BiFeO ₃ nanocomposite		PLD				661
CoFe ₂ O ₄ -BiFeO ₃ nanocomposites		PLD				656

Multiferroic (ME) nanocomposites offer a unique approach for integrating ferroelectricity and ferromagnetism together, which have been widely studied in recent years [Table 27]. Several types of ME nanostructures have been constructed, examples of which include the vertical-type, horizontal-type, and particulate-type composites [Fig. 24]. Figure 24 is a schematic illustration of these three types of ME nanocomposite structures.⁸⁰¹ The 0-3 nanocomposite consists of single-phase

nanoparticles embedded in a matrix of another phase, and the 2-2 horizontal and 1-3 vertical heterostructures consist of ferroelectric and magnetic phases aligned horizontally and vertically, respectively. For BFO-based nanocomposites, one of the appealing types is the self-assembled nanostructure of ferromagnetic nanopillars being embedded in a ferroelectric matrix and vice versa.

Fig. 24. Schematic illustration of three types of ME nanocomposites: (a) 0-3 particulate nanocomposites, (b) 2-2 horizontal heterostructures, (c) 1-3 vertical heterostructures [801].

3.3.4.1. Preparation of $\text{CoFe}_2\text{O}_4\text{-BiFeO}_3$ Vertical Nanocomposite

Among the vertical nanocomposites that have been reported,^{516,656-661} the $\text{CoFe}_2\text{O}_4\text{-BiFeO}_3$ (CFO-BFO) vertical nanocomposite is of particular interest due to the strong ME coupling. In this system, the 1-3 vertical nanocomposite exhibits a phase segregation of CFO and BFO when they are co-deposited via physical vapor deposition at high temperatures on an (001)-oriented SrTiO_3 substrate.^{657-661,755} A self-assembly process was often used to fabricate the CFO-BFO vertical nanocomposites.

Fig. 25. (a) Flow chart showing the fabrication process of CFO-BFO nanocomposites. (b) Pillar topographies with 100 nm, 150 nm, and 200 nm center-to-center distance [658].

A patterned CFO-BFO nanocomposite was prepared by self-assembly process, where CFO islands were patterned on Nb-doped STO for direct self-assembly of the nanocomposites, producing square arrays of CFO pillars.⁶⁵⁸ Figure 25(a) illustrates the detailed preparation process, where a top-down lithographic process was employed to pattern CFO islands on the substrate surface, followed by a bottom-up self-assembly to produce the ordered CFO-BFO nanocomposite. Figure 25(b) shows AFM images of the arrays with pillar pitches of 100, 150, and 200 nm. CFO fluxes deposited in 100 nm and 150 nm pitch arrays segregate to pillars at the template sites, confirming that CFO deposits within the patterned regions are absorbed by the template pillars, without the formation of interstitial defect pillars.⁶⁵⁸

Fig. 26. (a) Preparation procedure: (1) mask transfer on the substrate, (2) deposition of CFO through mask, (3) formation of nucleation centers by removal of the hard mask, (4) growth of ordered multiferroic composite by deposition from a mixed target. (b) TEM image evidencing the shape of CFO pyramids to be consistent with the usual self-assembly growth; (c) 52° tilted SEM image of the same sample, selected area electron diffraction pattern, and AFM phase image [659].

A novel nucleation-induced self-assembly process was devised to successfully fabricate large areas of highly ordered CFO nanopillars embedded in BFO matrix [See Fig. 26(a)]. In the work reported by Alexe *et al.*⁶⁵⁹ SrRuO₃/SrTiO₃(001) single crystals were used as the substrates. Detailed preparation procedure includes: (1) hard mask (i.e., anodic aluminum oxide and lithography-defined gold membranes) for inducing nuclei is transferred onto the substrate; (2) nuclei are attained by depositing CFO pillars through hard mask at high temperatures by PLD; (3) hard mask is removed, leaving the nucleation centers on substrate; (4) BFO-CFO nanocomposites are then formed by the self-assembly process from a mixed target using PLD technique. In addition, two types of pillar shapes (square and rectangular) can be simultaneously obtained, due to the in-plane crystallographic direction [See Fig. 26(c)]. As expected, CFO pillars protrude through the surface of BFO matrix and

exhibit a pyramidal shape. The pillars outside the matrix are about 65 nm in height and their square lateral size is around 110 nm [See Fig. 26(b)].⁶⁵⁹

Fig. 27. Schematic illustration of the fabrication process of a templated BFO/CFO vertical nanocomposite [661].

Recently, Ross *et al.* have developed BFO/CFO vertical composite films by using a self-assembled linear triblock terpolymer as the etch mask to pattern the substrate [See Fig. 27]. It owned the advantages of being able to pattern large areas at low cost and over short period of process time.⁶⁶¹ More importantly, it could produce a periodicity as small as 44 nm for BFO/CFO composites.

3.3.4.2 Morphologies Control of CoFe_2O_4 - BiFeO_3 Vertical Nanocomposite

The morphology of the CFO-BFO vertical nanocomposites can be controlled. It was reported that the morphology of CFO pillars in CFO-BFO could be modified by changing the substrate orientation.⁶⁵² In BFO-CFO vertical nanocomposites [Figs. 28(a) and (b)], the (111) SrTiO_3 substrate gives rise to the formation of BFO nanopillars embedded in CFO matrix, while CFO forms nanopillars embedded in BFO matrix on the (001) SrTiO_3 substrate due to the surface energy anisotropy.⁶⁵² In addition, it can be seen from Fig. 28(c) that the substrate orientation greatly modifies

the morphology of CFO nanopillars, where three types of CFO pillars (square, stripe, and triangular) can be formed in BFO matrix on the (001)-, (110)-, and (111)-oriented STO substrates, respectively.⁷⁵⁵

Fig. 28. Z-contrast images from a plan-view TEM showing the morphology of $\text{BiFeO}_3\text{-CoFe}_2\text{O}_4$ nanostructures grown on: (a) (001)-oriented, and (b) (111)-oriented SrTiO_3 substrates [652]. (c) Schematic of phase architectures for differently oriented BFO-CFO thin films on SrTiO_3 substrate, and SEM images with square, stripe, and triangular CFO features [755].

3.3.4.3 Structure Modification of $\text{CoFe}_2\text{O}_4\text{-BiFeO}_3$ Vertical Nanocomposite

Figure 29(a) shows the substrate effects on the crystal structure of BFO. With increasing lattice parameters of substrate,⁶⁵⁷ the crystal structure of BFO undergoes a phase transition from T-phase (on LAO) to R-phase (on LNO and STO), and finally decomposes (on MgAl_2O_4 and MgO). It shows a rotation of ferroelectric polar axis from [111] to close to the [001] direction. Figures 29(b)-(d) shows the magnetic properties of CFO-BFO nanocomposites. One can see that they all display a similar saturation, and however their magnetic anisotropy is significantly different. The

magnetic anisotropy of CFO is tuned from parallel to perpendicular by controlling the strain applied to CFO by the substrate.

Fig. 29. (a) Sketch of T-BFO, R-BFO, and CFO crystal structures, and 3D view as a result of combining different filtered SEM images. Magnetization hysteresis loops measured at room temperature with the field applied in the plane (circles) and out-of-plane (rhombi) for nanocomposites deposited on (b) LNO/LAO(001), (c) LAO(001), and (d) STO(001) [657].

3.3.4.4 ME Effect of CoFe₂O₄-BiFeO₃ Vertical Nanocomposite

Figure 30 shows the magnetic, ferroelectric, and ME properties of CFO-BFO vertical nanocomposites.⁹⁷ From Fig. 30(a), one can see that a saturated moment of 3.4 $\mu\text{B}/\text{f.u.}$ is obtained in the in-plane or out-of-plane direction, which matches well with the reported value for CFO.⁸⁵⁹ The nanocomposites possess a saturated P_s of 62 $\mu\text{C}/\text{cm}^2$ [Fig. 30(b)], which is comparable to the previously reported value in epitaxial (001) BFO films.⁹⁷ More importantly, a high α_{31} of ~ 60 mV/cm Oe at a magnetic field of ~ 6 kOe is attained [Fig. 30(c)], which is superior to the reported values ($\alpha_{33} \sim 16$ mV/cm

Oe) of the 0-3 structured $\text{NiFe}_2\text{O}_4\text{-PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ composites.⁸⁶⁰ As a result, the CFO-BFO nanocomposites exhibit the overall enhanced ferroelectric, magnetic, and ME properties.

Fig. 30. (a) M - H loops, (b) J - E and P - E loops, and (c) α_{31} and α_{33} of CFO-BFO nanocomposites [97].

3.3.4.5 Electric field Induced Switching of Magnetization

To effectively control ferromagnetism at room temperature by an electric field is of considerable interest, both scientifically and technologically, for which BFO-based nanocomposites offers a possible solution. Electric field induced switching of magnetization is often observed in BFO-based nanocomposites at room temperature.^{579,651,654,766,805,807,810,843,844} For example, as shown in Figs. 31(a) and (b), MFM images indicate that the magnetic configuration of CFO pillars can be changed by applying an electric field,⁶⁵¹ implying a ME coupling between the two ferroic components. The ME coupling between BFO matrix and CFO pillars is calculated to be about 1.0×10^{-2} G cm/V according to the equation of $\alpha = \Delta M / \Delta E$ [Figs. 31(c) and

(d)], which is attributed to the strong elastic coupling between the two ferroic constituents as a result of the three-dimensional heteroepitaxy.

Fig. 31. Magnetic force microscopy (MFM) images of $(\text{BiFeO}_3)_{0.65}\text{-(CoFe}_2\text{O}_4)_{0.35}$ films: (a) after magnetization in an upward oriented 20 kOe perpendicular field, and (b) after electrical poling at +12 V. (c) Magnetization curves taken before (black curves), and after (red curves) electrical poling of ~10% of the total film area. (d) Enlarged view of the central part of a [651].

The electric field control of magnetization and vice versa were also realized in BFO-CFO nanodots.^{828,829} For example, Gao *et al.*⁸²⁹ reported the well-ordered array of isolated epitaxial $\text{BiFeO}_3/\text{CoFe}_2\text{O}_4/\text{SrRuO}_3$ heterostructured nanodots fabricated by nano-porous anodic alumina (AAO) template method. Figure 32(a) shows the detailed preparation AAO method, and three main processes are included: (i) AAO mask transfer, (ii) materials deposition by PLD, and (iii) mask removal. By this method, the nanodots with average lateral size of 70 nm and neighboring dot-dot distance of ~110 nm can be attained. There is an enhancement of piezoelectric effects induced by

applying magnetic field in a single nanodot because of the strong ME coupling [Fig. 32(b)].⁸³⁰ More importantly, a large ME coefficient (α_{31} 1.2×10^4 mV/cm Oe) can be observed in 0-0 type nanodots of this work, which is superior to the quasi 0-3 type nanocomposite heterostructures and comparable to those of PZT/CFO core-shell nanofiber structure.⁸⁵⁸ The release of substrate clamping effect may be responsible for the enhanced ME effect. In addition, it is found that the magnetization can be well switched under the electric field because of the reverse ME effect [Fig. 32(c)].

Fig. 32. (a) Fabrication process of BiFeO₃/CoFe₂O₄/SrRuO₃ heterostructured nanodot array. (b) Effects of magnetic field on piezoelectric properties for single nanodot. (c) MFM image superimposed with its corresponding 3d topology image [829]

3.3.5 Size effect

Low dimensional multiferroics exhibit a dramatic difference in physical properties as compared to the corresponding ceramic bulks, due to the enhancement in surface or

interfacial area. Extensive investigations have focused on the nanosize effects in tuning the physical and chemical properties of multiferroics over the past decade, motivated by the potential applications in various nanoscale devices.

3.3.5.1 Size Effect of Magnetic Properties

Fig. 33. (a) Magnetization of BFO nanoparticles with different sizes [504]. (b) M-H loops of BFO nanoparticles of different sizes, and the inset in (b) shows size-dependent M_s and H_c [686]. (c) Size dependency of critical temperatures in BFO nanodots.⁷⁵⁶ (d) Variation in T_N , M_s , and H_c with particle sizes [44,677].

Figure 33 shows the size dependence of magnetic properties of selected BFO nanostructures.^{504,677,686,756} It is observed that the M_s increases with decreasing particle sizes [See Figs. 33(a), (b) and (d)]. The incomplete spiral of magnetic order in particles of less than 62 nm in sizes is largely responsible for the enhanced magnetic properties.⁵⁰⁴ BFO nanoparticles with sizes close to the spiral spin period of 62 nm possess exceptionally enhanced ferromagnetism, as shown in Fig. 33(b). A structural

anomaly (i.e., an enhanced rotation distortion of FeO_6 octahedron) arises when the particle size is close to the spiral spin period.⁶⁸⁶ Figure 33(c) shows the theoretic prediction of critical temperatures (T_C and T_N) as a function of particle sizes in the nanometer range.⁶⁷⁷ The critical temperature decreases with the decrease in particle size, which has been supported by experimental results [Fig. 33(d)].

3.3.5.2 Size Effect of Photocatalytic Properties

TiO_2 -based photocatalysts response to UV irradiation due to the high band gap of ~ 3.2 eV, while BFO nanostructures show the unique advantages of being photocatalytic in the visible-light region due to the small band gap (< 2.7 eV), which is important in the pursue of photocatalytic reaction under the visible sunlight. Besides the small band gap, the good chemical stability of BFO also contributes to the promising applications of BFO in the visible-light photocatalysis, such as hydrogen generation by water splitting. In addition, the degradation of organic pollutants by BFO nanostructures has also been demonstrated.^{663,758,759} The self-polarization induced electric field in BFO can induce a high separation efficiency of photogenerated electrons and holes.⁵⁴⁹ Below we will summarize the dependence of the photocatalytic efficiency of BFO nanostructures on the parameters such as the particle size, morphology, and type and level of dopants.

3.3.5.2.1 Morphologies and Photocatalytic Activity

The small band gap and high surface area in BFO nanoparticles are responsible for the enhanced photocatalytic activity. Gao *et al.*⁵⁰⁵ prepared spherical and well-dispersed nanopowders with particle sizes of 80~120 nm [Fig. 34(a)]. As shown in Fig. 34(b), the methyl orange (MO) was almost unchanged after 15 h UV-vis irradiation without

BFO nanoparticles, while more than 90% of MO was decolorized after 8 h under UV-vis irradiation when BFO nanoparticles were used as the photocatalyst. In addition, in the presence of BFO nanoparticles, more than 90% of MO was decolorized after 16 h of visible light irradiation, confirming the efficient photocatalytic activity of BFO nanoparticles under visible light. As compared with the nanoparticles, BFO bulks only led to ~70% MO degradation after 16 h UV-vis irradiation.

Fig. 34. (a) SEM image of BFO nanoparticles with the TEM image as the inset, and (b) photocatalysis of BFO nanoparticles and bulk counterpart on degradation of methyl orange under UV-vis light irradiation and visible light irradiation [505].

It is commonly known that the morphology and particle size of BFO nanostructures significantly influence the photocatalytic activity. Firstly, for different morphologies,⁶⁶³ efforts were made to control them for attaining better photocatalytic activity.^{556,663,758,767,768} For example, a hydrothermal process was used to modify the morphologies of BFO nanostructures [Figs. 35(a)-(c)], where BFO microcubes showed better photocatalytic activity than microspheres for degradation of Congo red under visible light irradiation⁶⁶³, which may well be due to the difference in band gap arising from different morphologies [Fig. 35(d)]. BFO with $\{111\}_c$ dominant pills and rods exhibits a better visible light response with respect to the $\{100\}_c$ dominant

cubes.⁷⁶⁸ Secondly, the photocatalytic property of BFO nanostructures is strongly related to the particle size. Better photocatalytic activity ($k=0.0692 \text{ min}^{-1}$ at pH=0.5) was achieved in BFO nanoparticles (e.g., 35 nm) as compared with that of ceramic bulk in the degradation of rhodamine B.⁷⁵⁸

Fig. 35. SEM images of different BiFeO_3 morphologies: (a) microspheres, (b) microcubes, and (c) submicrocubes. (d) Morphologies dependence of photodegradation efficiencies of Congo red (CR), as a function of irradiation time under visible-light [663].

3.3.5.2.2 Dopants and Photocatalytic Activity

The addition of a proper dopant has been commonly used to improve the photocatalytic activity of semiconductors by adjusting the band gap, in addition to tuning in surface area. Chemical modification has indeed been confirmed to be able to enhance the photocatalytic activity of BFO nanostructures due to the modulation in

band gap,^{46,695,711,760,769} such as by Dy,⁶⁹⁵ Gd,^{46,711} Ca,⁶⁹⁷ Na_{0.5}Bi_{0.5}TiO₃,⁷⁴⁵ La.⁷⁶⁹ For example, Gd substitution at the Bi site induced a dramatic enhancement in photocatalytic activity of BFO under visible light.^{46,711} Ca doping in BFO showed similar behavior under visible light, which will be briefly reviewed below.⁶⁹⁷

Fig. 36. (a) SEM image of the as-spun Bi_{1-x}Ca_xFeO₃ nanofibres with $x=0$, 0.05, 0.10, and 0.15. (b) Degradation of Congo red upon visible light irradiation for 2 h [697].

From Fig. 36(a), it is seen that the morphology of Bi_{1-x}Ca_xFeO₃ nanofibres changes little with the increase in Ca content, while the average diameters of nanofibers with $x=0$, 0.05, 0.10, and 0.15 are 155 nm, 169 nm, 151 nm, 147 nm, respectively.⁶⁹⁷ The significantly improved photocatalytic activity, measured by degradation of Congo red as a trial organic pollutant [Fig. 36(b)], is due to the increased concentration of free carries together with large surface area of the nanofibres.⁶⁹⁷ However, some conflicting results of the photocatalytic behavior of doped BFO nanoparticles have been observed with different types and amounts of dopants, as new recombination centers may also be formed.⁶⁹⁷

3.3.5.2.3 Nanocomposite and Photocatalytic Activity

BFO-based nanocomposites consisting two or more types of constituent materials

show enhanced photocatalytic properties.⁸¹¹⁻⁸¹⁴ To promote the photocatalytic activity of BFO nanostructures, several types of nanocomposites have been investigated, including Ag/BFO,⁷⁴³ Au/BFO,⁷⁴⁴ BFO/grapheme,^{747,761} BFO/ γ -Fe₂O₃,⁷⁵² BFO/TiO₂,⁷⁵⁰ SrTiO₃/BFO core/shell.⁷⁵⁷ For example, in the nanocomposite consisting of BFO and Fe₂O₃, electrons and holes were photogenerated as a result of the absorption of visible-light photons with energy equal to or higher than the band gap of BFO or Fe₂O₃.⁷⁵² The excited electrons in conduction band of BFO move to that of Fe₂O₃, and meanwhile holes in the valence band of Fe₂O₃ shift to valence band of BFO, because of the band offset. Therefore, the recombination of electron and hole is restrained and the resulting photocatalytic properties are improved. Recently, BFO/graphene nanohybrids were demonstrated with enhanced photocatalytic performance in the visible light activity.⁷⁶¹ H₂ could be generated in the presence of SrTiO₃/BFO core/shell structures under visible-light irradiation.⁷⁵⁷ Hydrothermally synthesized BFO/TiO₂ nanocomposites showed a high visible-light photocatalytic activity for photodegradation of Congo red.^{673,750}

Fig. 37. (a) TEM image of Ag/BiFeO₃ nanocomposites. (b) Photodegradation efficiencies of methyl orange (MO) as a function of irradiation time under visible

light. (c) Recycle experiment of Ag-BFO-3 (the molar ratio between BiFeO_3 and AgNO_3) photocatalyst in the decomposition of MO under visible light irradiation. (d) Photocatalytic mechanism of Ag/ BiFeO_3 nanocomposites [743].

Both irregular and monodispersed Ag nanoparticles of 20-50 nm in sizes were dispersed on the surface of BFO [Fig. 37(a)]. The resultant nanocomposite exhibited a higher photocatalytic efficiency than that of BFO alone.⁷⁴³ The photocatalytic activity is further enhanced by increasing the Ag dosage [Fig. 37(b)], which is attributed to the localized surface plasmon resonance and Schottky barriers, induced by the electronic effect of Ag nanoparticles [Fig. 37(d)]. The Ag/BFO nanocomposites showed a stable and effective visible light photocatalysis for decomposition of organic pollutant [Fig. 37(c)].

Fig. 38. (a) Schematics for synthesis of BiFeO_3 -graphene nanohybrids, and SEM images of the supernatant nanohybrids and the precipitant BiFeO_3 particles. (b) photodegradation efficiencies of CR as a function of irradiation time under visible-light [761].

Figure 38(a) shows schematics for the synthesis of BFO-graphene nanohybrids by a facile hydrothermal process.⁷⁶¹ Graphene was shown to effectively modify the

morphology and band structure ($E_g \sim 1.78$ eV) of BFO.⁷⁶¹ Figure 38(b) shows the photodegradation efficiency of CR as a function of irradiation time under visible-light. BFO nanoparticles alone degrade 30% CR, and a remarkable 75% of CR degradation was observed for the BFO/graphene nanocomposite, due to the combined effects of low band gap and coupling between BFO and graphene. In addition to control in morphology and use of dopants, there are other parameters can be considered to further enhance the photocatalytic activity of BFO in nanocomposite structures.^{663,758,747} Overall, there have been a considerable number of studies focusing on modification in morphology, chemical composition and interfaces in nanocomposite structures, in order to modulate their properties.

4. Manipulation of properties of bismuth ferrite

As discussed in Section 3, some of the physical and chemical properties of BFO can be effectively tuned by several different approaches. In this section, we will look into recent advances in manipulating these properties, with particular emphasize on ferroelectric, piezoelectric, magnetic, magnetoelectric, photovoltaic and ferroelectric resistive switching properties.

4.1. Ferroelectric Properties

Fig. 39. Ferroelectric properties of BFO-based materials: (a) thin films; and (b) ceramic bulks.

There is no doubt that the ferroelectric properties are the best advantages of BFO-based materials, because of giant P_r values that have been reported for different forms. Figure 39(a) summarizes the remanent polarization of BFO-based materials in the form of thin films and bulks. Considerable efforts and attempts have been made to effectively promote the ferroelectricity of BFO thin films by decreasing their leakage currents, strain modification, control in film orientation, and interfacial coupling and construction of phase boundaries. Among those approaches, ion substitution, construction of multilayer structure, formation of solid solutions with ABO_3 -type perovskite, and use of oxide buffer layers are well documented. Use of a proper oxide buffer layer together with one or more other approaches can simultaneously tailor the leakage current as well as growth orientation. Several types of oxide buffer layers have been studied to promote the ferroelectric properties of BFO thin films. For example, the (111) orientation is of particular interest as has been confirmed by both experimental and theoretical studies. As shown in Fig. 39(a), a high P_r of $>90 \mu\text{C}/\text{cm}^2$ was attained in the BFO-based thin films.^{5,23,26,56,66,67,78,87,289,297,317,331,349,355,362,382} Giant P_r values of $130\sim 230 \mu\text{C}/\text{cm}^2$ (the largest P_r reported so far) have been further achieved in the Ga-doped BFO thin films,^{78,349} which may be attributed to change in the phase structure (super-tetragonal-like structure or coexistence of $R3c$ and Cm phases). Figure 39(b) shows P_r values of BFO-based ceramics. One can see that the ferroelectric properties of BFO-based ceramics can be improved by ion substitution or the formation of solid solutions with other ABO_3 -type perovskite. As discussed earlier, these two methods can effectively suppress the high leakage current.^{58,124,138,189,224,225}

Phase boundary plays a critical role in the ferroelectric properties of BFO ceramics.^{58,224,225,234} For example, a rather rectangular-shaped polarization hysteresis loop and P_r value of as high as $31 \mu\text{C}/\text{cm}^2$ were observed in 15% Nd and 2% Mn co-doped BFO (BNFM) ceramics with the structure transition from rhombohedral R3c to orthorhombic P4mm.⁵⁸ Square-shaped hysteresis loop with P_r as high as $60\sim 63 \mu\text{C}/\text{cm}^2$ was shown in the $\text{BiFeO}_3\text{-PbTiO}_3$ ceramics, owing to the formation of MPB between multiferroic polymorphs with rhombohedral and tetragonal symmetries.^{224,225,234} Although in BFO ceramic bulks, the ferroelectric properties can be improved by ion substitution or constructing MPB, they are not yet comparable to those of the corresponding thin films [Fig. 39(b)].

4.2. Piezoelectric Properties

Fig. 40. Piezoelectric properties of BFO-based materials in thin film and ceramic bulk forms.

For applications in piezoelectric devices, temperature-dependent piezoelectric properties are among the main pursuits in search for high-temperature piezoceramics. Ferroelectric bismuth layer-structured materials are considered to be potential

candidates for high-temperature piezoceramic applications. However, the d_{33} values of bismuth layer-structured materials are typically lower than 30 pC/N, and thus there is big room for further improvement and this stimulates the research interest in BFO-based materials. BFO-based materials possess a high T_C of $\sim 830^\circ\text{C}$,^{8,17} which is far beyond the required temperature for high-temperature devices ($>500^\circ\text{C}$). Several approaches have been taken to further improve the piezoelectricity of BFO-based materials, such as optimization of preparation process, addition of a second phase, ion substitution, and strain modification. Figure 40 summarizes the piezoelectric activities for some of these materials, where one can see that enhanced d_{33} values together with a high T_C of $>700^\circ\text{C}$ have been observed. The ion substitution for Bi^{3+} and/or Fe^{3+} sites is popular to promote the piezoelectric activity, such as by La^{3+} ,^{130,132} Sm^{3+} ,^{124,125,320,623} Dy^{3+} ,^{127,138} Nd^{3+} ,¹²⁹ Eu ,¹³⁸ Gd ,¹³⁸ Tb ,^{138,329} Ti ,³⁰⁰ Nb ,³⁴⁶ $\text{La\&Sm}$,^{88,185} $\text{La\&Sc}$,⁸⁹ $\text{La\&Yb/Ho/Y}$.¹⁸⁵ Among the ion substitutions, La^{3+} or/and Sm^{3+} in Bi^{3+} site can well enhance the piezoelectric effect of BFO thin films or ceramic bulks.^{124,125,130,132,320,623} For example, a $d_{33}\sim 50$ pC/N value and a reduction in leakage current were observed in these systems.^{88,185} Tb ³²⁹ or Sm ^{320,623} modified BFO thin films exhibit a large piezoelectric coefficient of 95~140 pm/V, which is superior to the corresponding ceramic bulks.^{124,125,138} Note that there was no MPB formed in the above doped-BFO thin films and ceramics, implying that d_{33} values may be further improved by introducing MPB. In order to develop the desired MPB, similar to that in PZT, other ABO_3 compounds shall be introduced to BFO. It has been widely found that the R-T phase boundary could be formed by tailoring the type and amount of ABO_3 compounds.^{118,167,168,193,200,207,231-233} For example, BFO-BT^{118,167,168,193,200,207} or BFO-PT²³¹⁻²³³ ceramics have been extensively studied for enhanced piezoelectricity by forming the desired R-T phase boundaries. Kim reported a giant d_{33} value of ~ 405

pC/N in Ga -modified BFO-BTO ceramics by forming R-T phase boundary.¹¹⁸ These impressive piezoelectric activities were attributed to the phase boundary,^{118,621,622} together with the effects of rare-earth element doping.^{320,329,623}

4.3. Magnetic Properties

Fig. 41. Magnetic properties of BFO-based materials in various forms

BiFeO₃ is G-type antiferromagnetic below $T_N \sim 673$ K,^{104,116} and thus also exhibits a weak magnetization. In the past, several approaches have been used to enhance its magnetic properties, including growth in different forms, chemical modification and coupling with other magnetic materials. Figure 41 shows magnetic properties of BFO-based materials in various forms (thin films, ceramic bulks, and nanostructures), where one can see that the magnetic properties are largely dependent on morphologies and compositions of BFO-based phases. In terms of morphologies, the undoped or ion-modified BFO nanostructures exhibit much better magnetic behavior than the corresponding bulks.^{482,672,686,693,700,704,706,712,726,727,731,735} For the compositions, a number of doping elements have been investigated to modify the magnetic properties, such as Ho,^{134,148,709} Nb,¹⁵⁸ Cu,⁴⁵⁰ Co,^{448-450,714} Ni,^{159,450,451} Sm,^{452,453} Y,^{454,455} La,^{456-458,702,703} Cr,^{459,460} Eu,^{144,461-464} Gd,^{465,466,466,711,712} Sc,⁴⁶⁷ Nd,^{468,696} Er,⁴⁶⁹ Mn,^{153,450,470-472,472} Ti,^{473,474} Ce,^{475,715} Dy,^{476,693-695} Ca,⁶⁹⁷ Sr,^{698,699} Ba,⁷⁰⁴⁻⁷⁰⁶ Pr,⁷⁰⁷

Na,⁷¹⁰ Lu,⁷¹³ Ba&Nb,¹⁷⁸ Ho&Ni,¹⁸⁰ Y&Zr,¹⁸¹ Nd&Zn,³⁴⁷ Ti&Co,⁴⁷³ Pr&Co,⁴⁷⁷ La&Co,⁴⁷⁸ La&Nd,⁴⁷⁹ La&Mn,^{67,480} Pr&Zr,⁴⁸¹ Eu&Co,⁴⁸² Pr&Cr,⁴⁸³ In&Mn,⁴⁸⁴ Ce&Cr,⁷²⁷ Ca&Co,⁷³⁰ Gd&Co⁷³⁵ Their magnetic properties can be further enhanced by introducing certain compounds to BFO, either magnetic or non-magnetic, such as Pb(Zr_{0.52}Ti_{0.48})O₃,²³⁵ GdCrO₃,²⁴⁵ Bi_{0.5}Na_{0.5}TiO₃,^{355,370} La_{0.67}Sr_{0.33}MnO₃,³⁹² BaTiO₃,^{187,214,216,483} PbTiO₃,⁴⁸⁶ CoFe₂O₄,^{61,376,487,488,516} and NiFe₂O₄.⁷⁴⁰

There have been studies on the physical mechanisms to explain the enhanced magnetic properties of BFO: (i) coexistence of Fe²⁺ and Fe³⁺,^{29,90,453,489,634} where Eerenstein *et al.* considered that a substantial Fe²⁺ fraction could induce a large saturation magnetization,⁹⁰ (ii) structure change,^{187,486} where the magnetism of BFO films can be tailored by the structure changes by the addition of different types of dopants at varying concentrations. For example, introducing Pr and Nd favors the ferromagnetism of BFO films due to the development of mixed orthorhombic and tetragonal phases,^{356,489} (iii) spatial homogenization of spin arrangement,^{32,178,294,476,478,490,491} (iv) distorted spin cycloid structure,^{59,134,181,347,453,455,458,481,492-495} where for example, the Mn substitution at Fe site could destroy the unique spin cycloid structure and lead to net magnetization;⁴⁹³ (v) varied canting angle of Fe–O–Fe bond,^{187,486} and (vi) addition of magnetic elements or materials,^{66,180,376,449,487,488} where for example, Co can improve magnetic properties as a result of the strong magnetic coupling between Fe³⁺ and Co³⁺ under 180° super-exchange interaction.⁴⁴⁹

Note that the above different mechanisms responsible for the enhancement of magnetic properties may coexist in a single BFO-based material system.^{29,496-500} For

example, the Tb concentration at Fe site was found to strongly affects the magnetic properties.⁴⁹⁷ The ferromagnetic coupling between Tb^{3+} and Fe^{3+} was induced by decoupling the antiferromagnetic interactions across the Fe^{3+} due to the spininteractions between Tb^{3+} and Fe^{3+} for $x < 0.06$ ⁴⁹⁷ as well as the different bond interactions between $4f$ and $5d$ orbitals of Tb-O and $6p$ orbitals of Bi-O.⁴⁹⁸ Doping with Tb also led to a high lattice strain and then results in higher spin canting, generating strong ferromagnetism.⁴⁹⁹ The phase transition (i.e., rhombohedral-pseudotetragonal) in the film with $x > 0.06$ played an important role in the magnetic properties.^{500,501} The addition of La gave rise to an increase in the macroscopic magnetization of BFO thin films,²⁹ which was attributed to the formation of Fe^{2+} ,^{90,634} a suppressed inhomogeneous magnetic spin structure,³² and an increased canting angle.⁶³⁴

For BFO-based thin films, the strain effects, in connection with substrate, film thickness, and interface strain coupling, play a big role in influencing the magnetic properties.⁴⁷¹ There have been reports on the thickness-dependent magnetism in the compressively strained BFO thin films.⁵⁰² Xu *et al.*⁵⁰³ found that the use of different substrates affected the magnetic properties of BFO thin films. For example, a stronger saturation magnetization was found in the BFO films deposited on Pt/Ti/SiO₂/Si substrates than those of the samples prepared on LiNbO₃ substrates, because of the stress induced by substrate.⁵⁰³ Wang and Wu *et al.*³⁷⁰ reported a high saturated magnetization of $2M_s = 96.0 \text{ emu/cm}^3$ in (111)-oriented BiFeO₃/(Bi_{1/2}Na_{1/2})TiO₃ (BFO/BNT) films, which was higher than both BFO-only and BNT-only films. This was attributed to the interface strain coupling induced enhancement in magnetism.

For BFO nanoparticles, the size effect plays the major role in modifying the magnetic properties, especially when the particle size is less than the period length (62 nm) of the spiral modulated spin structure.^{464,467,483,504,505} Perhaps the uncompensated spins mainly appear in the surface regions of BFO-based nanoparticles,^{464,504} and thus the ferromagnetic surface is the major origin of enhanced magnetic properties.⁴⁶⁷

4.4. Magnetoelectric Coupling

The magnetoelectric coupling between electric dipoles and magnetic dipoles at room temperature has been demonstrated by measuring the effects of electric poling on magnetic hysteresis loop and the change in dielectric constant with an external magnetic field.^{15,20} It enables several types of device designs (e.g., highly sensitive magnetic-field sensors, low-power read heads for magnetic hard disks, and magnetic energy harvesters).^{20,506-512} BFO-based materials have widely used in composites, bilayers, trilayers, and multilayered structures, consisting of both piezoelectric (ferroelectric) and magnetic phases, to achieve strong magnetoelectric coupling at room temperature.^{4,513}

Fig. 42. Magnetoelectric properties of selected BFO materials (unit of ME coupling: $\text{mV cm}^{-1} \text{Oe}^{-1}$)

As reviewed in Section 2.3, the ferroelectric polarization and weak magnetization is coupled in single-phase BFO. This has also been confirmed by the first-principles density functional theory.⁸ However, the magnetoelectric coupling coefficient of single-phase BFO is rather small, only $\sim 0.067 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ at $\sim 9.5 \text{ kOe}$.⁵¹⁴ Kimura *et al.* recently⁵¹⁵ showed that the ME coupling of BFO at RT could be enhanced by the strategies such as: (a) destroying the long range spin cycloid, and/or (b) shifting the transition temperature T_C or T_N toward room temperature. Other attempts were made to enhance the ME coupling in BFO by: (i) construction of layered or nanosized bulk composites or multiferroic film heterostructures;⁵¹⁶⁻⁵²⁵ (ii) chemical substitution with diamagnetic (Ca^{2+} , Sr^{2+} , Ba^{2+}), rare earth (La^{3+} , Gd^{3+} , Nd^{3+} , Dy^{3+} , Sm^{3+}) elements at the A-site, and magnetic (Mn^{3+} , Cr^{3+}), non-magnetic dopant (Zr^{4+} , Ti^{4+}) elements at B-site;^{294,4833,526-530} (iii) formation of BFO solid solutions with other compounds;^{213,518,531-533} and (iv) development of BFO nanoparticles with crystallite size less than the periodicity of helical order via various chemical routes.^{472,534}

Figure 42 shows the ME coefficients of BFO-based materials in comparison to other materials. The largest ME coupling of BFO-based materials was achieved in $0.3\text{Co}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4\text{-}0.7\text{Bi}_{0.9}\text{La}_{0.1}\text{FeO}_3$ nanocomposites as reported by Yadav *et al.*⁵³⁸ A maximum ME coefficient as high as $315 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ at 50 kHz was obtained, due to the high piezomagnetic and piezoelectric coefficient induced by small grain sizes. However, the ME coefficient of BFO-based materials is still inferior, compared with those of other materials.⁵⁴³⁻⁵⁴⁵ For example, Nan *et al.*⁵⁴³ prepared a $\text{Pt}(30\text{nm})/\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3(400\text{nm})/\text{Pt}/\text{Ni}$ multiferroic film heterostructure, which showed a large a_{E31} of $\sim 772 \text{ mVcm}^{-1} \text{ Oe}^{-1}$ at the low *dc* magnetic bias field of 86 Oe.

Therefore, there is still a large scope to improve the ME coefficient of BFO-based materials. Perhaps forming nanocomposites consisting of a strong magnetic phase and BFO, in which the piezoelectric properties of BFO could be further enhanced, may lead to a high ME coefficient.

It is worth noting that although the ME coefficient matters, the deterministic control of magnetism by ferroelectric switching is perhaps more critical to realize the practical device applications. This research topic has attracted tremendous research interests over the past few years and most of the relevant works have been comprehensively summarized in an excellent review paper.⁸⁰⁵ To avoid repetition, we will restrict ourselves to the most representative results. In most of previous works, the electric field control of magnetism was realized in BFO/ferromagnet heterostructures, where the ferromagnet materials were either transitional metals (e.g., $\text{Co}_{0.9}\text{Fe}_{0.1}$.^{766,831} and Permalloy⁸³² or oxides (e.g., $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ^{18,843}). These heterostructures take advantages of the intrinsic ME coupling in BFO and the interface exchange coupling between BFO and the ferromagnetic layer. In BFO/LSMO heterostructures, the exchange bias was reversibly switched between two stable states with opposite exchange bias polarities upon ferroelectric switching of BFO, as examined by magnetotransport measurements.⁸⁴³ Unfortunately, such an effect could only be observed at <30 K. In BFO/ $\text{Co}_{0.9}\text{Fe}_{0.1}$ heterostructures, however, the electric field control of magnetization could be realized at room temperature. The X-ray magnetic circular dichroism (XMCD)–photoemission electron microscopy (PEEM) revealed that the reversal of magnetization of $\text{Co}_{0.9}\text{Fe}_{0.1}$ was 90° ⁷⁶⁶ and was later promoted to 180° .⁸³¹ Note that the above two studies applied the electric field with the in-plane electrode geometry, which may not be suitable for memory

applications. A very recent study successfully demonstrated that even by applying vertical electric fields, the 180° reversal of magnetization of $\text{Co}_{0.9}\text{Fe}_{0.1}$ could also be achieved.⁸⁴⁴ By a combination of time-dependent, dual-frequency piezoresponse force microscopy (PFM) and first-principles calculations, authors in Ref. 844 demonstrated that the application of a vertical electric field induced two-step sequential rotation of polarization [Fig. 43(a)]. Through the two-step switching and owing to the ME coupling, the Dzyaloshinskii–Moriya (DM) vector and weak ferromagnetism of BFO would be switched by 180° . As a result, the $\text{Co}_{0.9}\text{Fe}_{0.1}$ magnetization would in principle be reversed by 180° even by applying a vertical electric field. Then, the XMCD-PEEM technique was used to experimentally probe the magnetic moment change of $\text{Co}_{0.9}\text{Fe}_{0.1}$ induced by vertical electric field. As shown in Figs. 43(b) and (c), after the application of 6 V (10 ms) pulse, the net $\text{Co}_{0.9}\text{Fe}_{0.1}$ magnetization is switched by 180° . Moreover, the 180° electric-field induced reversal of $\text{Co}_{0.9}\text{Fe}_{0.1}$ moments within each domain can be clearly observed [Fig. 43(d)], confirming the predicted coupling between the DM vector and ferroelectric polarization. Although substantial progress has been achieved in the electric field control of magnetism in BFO/ferromagnetic heterostructures, some important issues, e.g., switching reliability, still remain challenging.⁸⁰⁵ Further studies are therefore of great demand to validate the practical applications.

Fig. 43. (a) Magnetoelectric device consisting of $\text{Co}_{0.9}\text{Fe}_{0.1}$ or $\text{Co}_{0.9}\text{Fe}_{0.1}/\text{Cu}/\text{Co}_{0.9}\text{Fe}_{0.1}$ spin value on BFO. Initial and final (after applying 6 V) directions of in-plane $\text{Co}_{0.9}\text{Fe}_{0.1}$ moments with components viewed (b) perpendicular and (c) parallel to the stripe domains. (d) Images of initial and final states merged near the centre of $\text{Co}_{0.9}\text{Fe}_{0.1}$, with the components viewed parallel to stripe domains [844].

4.5. Photovoltaic Activity

Ferroelectric materials have been recently reported as one of the promising candidates for photovoltaic materials.^{98,108,109,546-549} Several typical types of ferroelectric oxide perovskites have been extensively investigated for their photovoltaic effects, such as LiNbO_3 ,^{550,551} BaTiO_3 ,^{552,553} $\text{Pb}(\text{Zr,Ti})\text{O}_3$,⁵⁵⁴ and BFO.^{98,108,109,555,556} Among them, the typical oxide ferroelectric perovskites (i.e., LNO, BTO, and PZT) exhibit a gap of more than 3 eV.⁵⁵⁷⁻⁵⁵⁹ In comparison, the band gap of BFO is ~2.2 eV for single crystal⁹⁸ and 2.7 eV for thin films because of the presence of partially filled d orbitals in Fe^{3+} .^{505,560,561}

Table 28 Summary of PV performance of BFO-based materials

Structure	V_{oc} (V)	J_{sc} $\mu\text{A cm}^{-2}$	Light intensity mW cm^{-2}	Light wavelength nm	Efficiency (%)	Ref.
Pt/BFO/Pt	16	120	285	W-light	$10^{-3}(\text{IQE})$	108
Pt/BFO/Pt	0.014	50	100	W-light	10 (IQE)	546
Pt:Pt/BFO/ Pt:Pt	6-30	$10^{-7}-10^{-8}$	40000	405	40(IQE)	597
ITO/BFO/FTO	0.65	130	100	300-900	$2.73 \times 10^{-2}\%$	592
Au/BFO/ FTO	0.21	63.9	100	Xe bulb	-	603
Au/BFO/Au	0.7	1.58	20	532	1.5(EQE)	556
Pt/BFO/Pt	0.33	71.2	5	Purple	$1.1 \times 10^{-2}\%$	598
ITO/BFO/SRO	0.8-0.9	1500	285	W-light	10(IQE)	599
Au/BFO/NSTO	0.04	6000	285	W-light	$3 \times 10^{-2}\%$	586
Grapheme/BFO/Pt	0.20-0.44	25-2800	100	W-light	$2.5 \times 10^{-3}\%$	600

ITO/BFSO/LNO	0.6	-	22.3	435	-	75
Au/BCFMO/ITO	0.4	33-241	15-160	405	0.02%(95)	575
Ag/Pr-BFO NTs/Ag	0.21	-	10	Sunlight	0.5%	602
ZnO:Al/BLFTZO/Pt	0.018-0.022	650-700	10 ⁶	-	-	576
ZnO:Al/BLFTO/ Pt	0.20	1350	100	-	-	574
Graphene/BFSiO/ITO	0.35-0.45	630-750	100	-	-	571
Au/BNaFO/FTO	0.66	1.26	100	Xe bulb		573
ITO(Au)/BFO/NBT-BT/FTO	0.5-0.71	18.9-45	100	-	-	583
Pt/YCO-BFO/Pt	0.32-0.51	0.44-1.48	150	Xe bulb		577
Au/BFO/BTO/Pt	1.25	318.4	160	405	0.067%	591
ITO/ZnO/BFO/Pt	0.165-0.225	110-340	22.3	435	0.1-0.33%	71
Glass/ZnO:Al/BFO/LSCO	0.22	4000	1	W-light	-	585
Pt/BFO/LSMO/PMNPT	0.2	0.7		405	2.18	772

To achieve high-efficiency photovoltaic effects, ferroelectrics with small band gap, robust polarization and good *dc* conductivity, such as BFO, are of general interest. Many parameters of ferroelectric and electrode materials can affect the photovoltaic output, including crystallographic orientations,⁵⁶⁷ band gap,^{75,573,555,575,596} electrical conductivity,⁵⁶² remnant polarization,⁵⁶³ domain walls,¹⁰⁸ ferroelectric/electrode interface,¹⁰⁹ microstructure,⁵⁶⁴ distance between two opposite electrodes.⁵⁶⁵ With these understandings, some attempts have been made to enhance the photovoltaic efficiency of BFO-based devices [Table 28], for example by band gap engineering,^{75,573,555,575,596} selection of the interface and electrode materials,^{71,386,578-586} domain engineering,⁵⁸⁷⁻⁵⁹⁰ construction of multilayer structure.^{591,592} The overall photovoltaic efficiencies have been improved significantly over the past several years.^{71,578,602} For

example, By modifying the Fe/Cr cationic ordering and engineering the domain size, a band gap as low as ~ 1.5 eV was achieved in $\text{Bi}_2\text{FeCrO}_6$ (BFCO) double perovskites.^{555,596} Hence, the BFCO double perovskites could exhibit an unprecedented photovoltaic efficiency of 8.1%. The photovoltaic efficiency the FTO/BFO/ZnO(Nanorod)/PEDOT:PSS/Au heterojunction has been demonstrated with a high conversion efficiency of $\sim 0.17\%$, in relation to the polarization-induced FTO/BFO Schottky barrier, the low-resistance ZnONR/PEDOT:PSS contact as well as the superior carrier transportation characteristics of the ZnONRs.⁵⁷⁸ Fan *et al.* recently reported a giant energy conversion efficiency of up to 0.33% under blue monochromatic illumination in a metal/semiconductor/ferroelectric/metal heterostructure of $\text{In}_2\text{O}_3\text{-SnO}_2/\text{ZnO}/\text{BiFeO}_3/\text{Pt}$.⁷¹

Besides the tremendous efforts made to enhance the photovoltaic efficiency, the origins of photovoltaic effects in BFO and other ferroelectrics have also attracted a lot of research enthusiasm. So far, various origins have been proposed, such as the bulk photovoltaic effect,¹¹⁰ depolarization field driven photovoltaic effect,^{105,109} schottky barriers,⁵⁹⁴ and domain wall theory.^{16,108} However, there are still a lot of disputes and controversy on the photovoltaic origins and they deserve further studies undoubtedly.

4.6 Ferroelectric Resistive Switching

The non-destructive readout of binary information become possible by bipolar switching between high and low conductances of a metal/ferroelectric/metal capacitor under two opposite polarizations.⁸³³ Recently, ferroelectric resistive switching has been widely observed in BFO films, including reversible diode effect in thicker films and tunnel electroresistance effect in ultrathin films.^{40,834-836} More excitingly,

ferroelectric resistive switching has also been demonstrated in high-density and well-ordered BFO nanodots, showing the great potentials for applications in high-density non-volatile memories with non-destructive readout.^{646,828,837} The most striking feature of ferroelectric resistive switching behavior in BFO-based diodes or tunnel junctions is the giant ON/OFF ratio (could even reach 10^5),⁸³⁵ which may be attributed to the large polarization of BFO. However, the reported switching speeds were limited to the microsecond level,^{834,835} which seemed to be unsatisfactory because the speed of intrinsic ferroelectric switching could reach the nanosecond level.⁸³⁸ In addition, the highest switching endurance reported so far was still less than 10^7 cycles,⁸³⁵ which could not yet compete with conventional ferroelectric random access memory.⁸³⁹ It also should be pointed out that the defect-mediated mechanisms can also induce resistive switching in BFO,^{840,841} and this shall be distinguished from the ferroelectric resistive switching. For example, Lin *et al.*⁸⁴² observed that both the switchable diode behavior induced by polarization reversal, and the bipolar resistive switching behavior induced by oxygen vacancies migration and/or carrier trapping/detrapping mechanisms, coexisted in the Au/BFO/SRO structure. Therefore, it is of great necessity to understand the real mechanism underlying the observed resistive switching as this will be the first step toward improving the reliability of resistive switching in BFO.

5. Outlook and future work

Over the past two decades, there has been a large and consistent pursue in BFO multiferroic materials and devices, as clearly indicated by the large numbers of published references during 2000~2015 [Figs. 1 and 2]. As has been reviewed above, great progress has been made in the understanding of different structures, ferroelectric,

piezoelectric, magnetic, magnetoelectric, and photovoltaic properties in various forms of BFO and BFO-based materials. As compared to other multiferroic materials, bismuth ferrite exhibits some unique advantages, such as a giant remnant polarization ($100\sim 230\text{ }\mu\text{C}/\text{cm}^2$), high Curie temperature ($\sim 830\text{ }^\circ\text{C}$), the coexistence of ferroelectric and magnetic properties at room temperature, and relatively low band gap ($<2.8\text{ eV}$). In order to fully explore some of these unique characteristics, considerable efforts have been made in the modifications of electrical and magnetic properties in BFO materials by different approaches. Firstly, suppressing the leakage current of BFO is very critical for the improvement of the overall ferroelectric and piezoelectric properties. It is well known that a high leakage current induced by the loss of Bi and the valence variation of Fe^{3+} seriously hinder the development towards device applications. Leakage current in BFO thin films and ceramic bulks have been addressed, to a large degree, by the site engineering, use of proper buffer layer, selection of substrates, and choices of preparation techniques. Secondly, there is high expectation to promote the electrical properties by constructing the desired phase boundaries, similar to those in PZT. The strain-induced MPB is an interest topic, where chemical modification is often used to tailor the wanted phase structures. In addition, the control in film orientation can further promote the electrical and magnetic properties, as well as construction of homojunction multilayer structure. Thirdly, nanostructured BFO materials exhibit several new physical effects and some excellent properties, which are of great interest and achieved by the size effect-induced modifications in structures and properties. Indeed, some of them have been demonstrated with significant enhancement in selected functional properties, such as magnetic and photocatalytic properties. Pursue for large remnant polarization and high piezoelectric activity has been driven by the memory, sensor and actuation

applications, e.g., ferroelectric random access memories (FeRAMs) and ferroelectric tunnel junctions, piezoelectric sensors and actuators. For example, a giant P_r of 230 $\mu\text{C}/\text{cm}^2$ was recently achieved in the Ga-doped BFO thin films with super-T phase. Ga-doped BFO-BTO ceramic shows a high d_{33} of 402 pC/N together with a high T_C of 454 °C with R-T phase boundary. On the other hand, there is a rapid increase of research into other novel aspects. Magnetoelectric coupling in BFO is attractive and promising, because of the coexistence of the large ferroelectric polarization as well as weak magnetization at room temperature,^{97,283} where the control of magnetic properties can be realized by electric fields.^{9,97,624} Due to a relatively low band gap of <2.7 eV, BFO-based materials have been considered as a promising candidate for photovoltaic activity.

On the basis of the progress presented in this review, further efforts are still needed for the following challenges:

(i) Further improvement of ferroelectric and magnetoelectric properties. There is no doubt that BFO exhibits the highest polarizations among all ferroelectrics. Given the rich variety of structures, can the ferroelectric polarization of BFO further go up above 230 $\mu\text{C}/\text{cm}^2$? More interestingly, can BFO be engineered to show a large magnetoelectric response at room temperature? The strain, site engineering, and nanocomposites or their combination may realize the objective.

(ii) Enhancement of piezoelectric activity. BFO-based materials are considered as a class of reasonable high-temperature piezoelectrics, due to the high T_C of ~830 °C. They can be modified by different approaches in order to improve the d_{33} and other key piezoelectric properties with respect to those of bismuth layer-structured materials used in the high-temperature piezoelectrics. However, one also sees that it has been

difficult to attain a high piezoelectric activity matching that of PZT, although a few breakthroughs have been achieved in BFO-based ceramics. Among these methods to be further developed, the construction of phase boundaries may be the most effective way to further promote the piezoelectric activity. Can the piezoelectric response be enhanced to qualify BFO as viable replacement for lead-based ones? How to drive the formation of phase boundaries similar to PZT is very critical for the promotion of piezoelectric properties.

(iii) Other effects. There is a rather long way for BFO-based materials to go in terms of being applied in magnetoelectric and photovoltaic devices, given the generally poor ME switching reliability and low PV efficiencies as observed, respectively. However, it would be useful to further investigate the key and related properties, by understanding the physical mechanisms behind. For example, the discovery of enhanced magnetism and finite conductivity at domain walls in BFO has triggered the potential application of domain wall nanoelectronics. Nanostructured BFO-based materials shall be further studied for new physical effects and novel functional properties.

(iv) Phase-property relations. The phase structure is a useful approach to enhance the functional properties of BFO-based materials. There are however some disputes on the phase compositions in the phase boundary region. A clear and generally valid relationship between phase structure and properties should be established. This is essential for the design of high-performance BFO-based materials with tailored properties linked to different applications.

6. Conclusions

Development of multiferroic materials for different applications is one of the focus areas in functional materials research community. The investigations into multiferroic bismuth ferrite materials have seen great growth in the past fifteen years. In this review, we have visited the progress and prospects of the BFO-based materials in the different forms of ceramic bulks, thin films and nanostructures, where thorough fundamental understandings in phase structures and key properties are shown. By the systematical review, we hope to provide an updated overview on the understanding and also highlighting of the existing issues that hinder the further development of BFO-based materials.

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