Progress and Perspectives on Aurivillius-Type Layered Ferroelectric Oxides in Binary Bi₄Ti₃O₁₂-BiFeO₃ System for Multifunctional Applications

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Abstract: Driven by potentially photo-electro-magnetic functionality, Bi-containing Aurivillius-type oxides of binary Bi₄Ti₃O₁₂-BiFeO₃ system with a general formula of Biₓ+1Feₓ₋₃Ti₅O₁₆₋₃, typically in a naturally layered perovskite-related structure, have attracted increasing research interest, especially in the last twenty years. Benefiting from highly structural tolerance and simultaneous electric dipole and magnetic ordering at room temperature, these Aurivillius-phase oxides as potentially single-phase and room-temperature multiferroic materials can accommodate many different cations and exhibit a rich spectrum of properties. In this review, firstly, we discussed the characteristics of Aurivillius-phase layered structure and recent progress in the field of synthesis of such materials with various architectures. Secondly, we summarized recent strategies to improve ferroelectric and magnetic properties, consisting of chemical modification, interface engineering, oxyhalide derivatives and morphology controlling. Thirdly, we highlighted some research hotspots on magnetoelectric coupling, which can offer the possibility of manipulating the magnetic state by an electric field or vice versa inside a uniform structure, thus having the potential for a variety of functional applications including quantum controlling, signal processing, and information storage. Finally, we provided an updated overview on the understanding and also highlighting of the existing issues that hinder further development of the multifunctional Biₓ+1Feₓ₋₃Ti₅O₁₆₋₃ materials.

Keywords: layer oxide; multiferroic; ferroelectric; Aurivillius-phase; ME effect; PV effect; catalytic

1. Introduction

In single-phase crystals, magnetic moment (un-paired localized electrons in the partially filled d-orbital) and electric dipole (the empty d orbitals rule) are often mutually exclusive [1–3]; however, the discovery of multiferroics as a favorable topics in condensed matters and materials physics, breaks the principle of this exclusion. Importantly, a combination of ferroic orders (ferromagnetism, ferroelectricity, ferroelasticity, or ferrorotoroidicity) in the multiferroics can lead to coupling between them, so that one ferroic property can be manipulated with the conjugated field of the other, such as the magnetoelectric (ME) coupling, which can offer the possibility of manipulating the magnetic state by an electric field or vice versa inside a uniform structure, thus having the potential for a variety of functional applications including quantum controlling, signal processing, and information storage [4]. To date, BiFeO₃ and TbMnO₃, belonging to different types (type-I and type-II) of multiferroics, have been extensively studied not only for their ME performance but also more for their representativeness leading to new physics of multiferroicity [5–8]. Many other single-phase materials including type-I: HoMnO₃, YMnO₃, LuFeO₃ and type-II: TbMn₂O₅, DyFeO₃, CaMn₇O₁₂, have been studied [9], however, the majority of mentioned materials possess ferroelectric (FE) and ferromagnetic (FM) orderings at low temperatures, which is far below room temperature (RT). Therefore, in order to simultaneously meet large FE and FM responses and a detectable and low field responsive ME coupling above RT, finding new material systems or seeking new techniques is a significant subject to understand fundamental physics, tailor functional properties, or develop materials for specific applications.
BiFeO$_3$ can show large spontaneous polarization and G-type antiferromagnetic order above RT, stimulating the extensive research in bulk, thin film, and nano-size forms till today [10]; however, the notorious leakage and defects hampered its practical applications. Availability of single phase multiferroic material functional at RT poses a big challenge. In the effort to battle against this challenge, the researchers are turning their attention from a simple perovskite-type structure to the layered oxide structures now, driven by great potential for tailoring specific properties by varying different ionic compositions or even the number of layers. Most layered structures and the number of experimentally-proven and theoretically-predicted layered materials were reported in Ref [11]. Obviously, the layered structures in Aurivillius, Ruddlesden-Popper, and Dion-Jacobson families exhibit the same basic perovskite motif, but the layers of anions and cations may be stacked in multiple ways. Such structural intricacy provides many opportunities to turn and tweak the design, for example, layer-thickness and -number, multi-selective chemical substitution, and inducing stress-strain applied to the crystal.

Aurivillius-type layered ferroelectrics, which were firstly studied by Bengt Aurivillius [12], have attracted increasing research interest, especially in the last twenty years, due to their promising electrical properties as new lead-free piezoelectric materials operating at high temperatures. For instance, the well-known Bi$_5$Ti$_3$O$_{12}$, presents large polarization, anisotropy, and high FE Curie temperature and wide applications in the electronic industry, capacitors, transducers, nonvolatile FE memories, piezo-electric sensors, and optical devices [13–15]. In view of the above, to increase functionality of Bi$_5$Ti$_3$O$_{12}$ modification with BiFeO$_3$ is very promising, which is a methodology for constructing single-phase multiferroics in which ferroelectricity and magnetic ordering are coupled near RT. Combining these two materials exhibiting different physical properties can create a kind of novel material and achieve functionality. It is commonly known that the Bi$_{n+1}$Fe$_{n-3}$Ti$_3$O$_{3n+3}$ (BFTO-$n$) compounds of binary Bi$_5$Ti$_3$O$_{12}$-BiFeO$_3$ system combine FE, magnetic and ME properties, making the potentially attractive for producing advanced materials for information processing and storage applications [16–18]. More intriguingly, such oxides exhibit important characteristics as follows: (i) structure breaks the spiral spin canting superposed onto the G-type antiferromagnetic order as well as can accommodate different magnetic ions realizing strong magnetic interactions; (ii) the origin of the ferroelectricity is a combination of oxygen octahedral rotations and polar distortions; (iii) different layer numbers in the perovskite slabs show a larger difference on physical properties.

In the last decade, numerous pieces of research focused on the BFTO-$n$ with integer $n$, for example, Bi$_5$Fe$_2$Ti$_3$O$_{15}$, Bi$_6$Fe$_2$Ti$_3$O$_{18}$, and Bi$_7$Fe$_2$Ti$_3$O$_{21}$. The reported studies have mainly embodied two aspects: (i) doping ions into A-sites [19–29] and/or substituting magnetic transition ions into B-sites [30–43] inside the layered perovskite structure to realize a significant enhancement in the multiferroic performances, and (ii) controllable synthesis of materials in ceramics [44–46], thin films [47–52], nano-crystallines [53–58] and single crystals [59–61] to observe the growth process [62–65] and understand the correlations between structure and properties. To enable potential RT industrial applications, numerous attempts have been made to further improve the FE, FM, and ME properties. Encouragingly, there have been two new important advances: a maximum ME coefficient as high as 400 mV@Oe$^{-1}$cm$^{-1}$ was reported in the BFTO-based composite films [66] and the available control of FE domain by magnetic field and control of magnetic domain by electric field were demonstrated on the BFTO-$n$ thin film at RT [67–69]. However, it should be noted that, in this system, the underlying physics to explain the resulting enhancement or coupling mechanisms are still unclear, the part correlations between structure and special properties remain ambiguous, and new methods for developing new RT-functioning single-phase multiferroics are still needed. There is thereby an urgent need to conduct various efforts to boost the study of the BFTO-$n$, of course, it is indeed very important and meaningful. In order to further push forward the research frontier of this exciting area, a timely review addressing the new achievements on Aurivillius-type ferroelectric BFTO-$n$ becomes imperative. Unfortunately, until now, few review articles covering the
major progress on this system are available. Therefore, in this review, recent progress in the fields of the synthesis of the BFTO-\(n\) with various architectures, modifications of electrical, and magnetic responses by different approaches, and their extraordinary properties for promising applications are discussed to present a roadmap for the advance of the BFTO-\(n\) oxides.

2. Basic structure and Morphology

2.1. Aurivillius-Phase Layered Structure

The BFTO-\(n\) oxides are layered perovskite structures, in which fluorite-like Bi-O layers alternate with \(n\) perovskite-like layers. Figure 1a shows the prototype of the Aurivillius-phase structure as a function of the number of perovskite layers. The layered compounds form a natural structural-stack and, ideally, form as a single-phase. In the limiting case \(n = \infty\), the repeated cell is the pure perovskite and can be regarded as a structure of BiFeO\(_3\), which has a rhombohedral distorted perovskite unit cell. The atomic-scale layered structure of the BFTO-\(n\) oxides can be visualized by the state-of-the-art aberration corrected scanning transmission electron microscopy high angle annular (STEM-HAADF) image carried out on scanning transmission electron microscope, as shown in Figure 1b. In the STEM-HAADF image, the orderly arranged bright spots all belong to the Bi atoms, and four layers of Bi atoms (Ti/Fe atoms are neatly arranged between layers) sandwiched by two closely stacked Bi layers (namely the fluorite-type Bi-O layers) can be understandable as corresponding to 5-layer perovskite slabs, which presents typical Aurivillius-type layered structures.

Figure 1. (a) Prototype of Aurivillius-type structure for the BFTO-\(n\) as a function of the number of layers (examples of each case are Bi\(_4\)Ti\(_3\)O\(_{12}\), Bi\(_5\)FeTi\(_3\)O\(_{15}\), Bi\(_6\)Fe\(_2\)Ti\(_3\)O\(_{18}\), and Bi\(_7\)Fe\(_3\)Ti\(_3\)O\(_{21}\)); (b) scanning transmission electron microscopy high angle annular (STEM-HAADF) image of the BFTO-5 as an example. The orderly arranged bright spots in the STEM-HAADF image all belong to the bismuth atoms.

Up to now, the single-phase BFTO-\(n\) compounds with integer \(n \leq 9\) have been synthesized by using the different methods, whereas the synthesis of the pure compounds with \(n > 9\) are still a big challenge, due to kinetic or thermodynamic reasons and produced reaction intermediates or impurity phase [70]. Of particular interest is that \(n\) may take fractional values, confirmed by some works [71–75]. The compounds with fractional \(n\) have a mixed-layer structure alternating perovskite layers of different thicknesses. For examples, Bi\(_{11}\)Fe\(_3\)Ti\(_6\)O\(_{33}\), is made up of alternating \(n = 4\) and \(5\) perovskite layers, so that the average number of its perovskite layers per unit cell is \(n = 4.5\) [76]. It should be emphasized that the mixed-layer structure is disorder rather than order in most cases. The difference of the order and disorder Aurivillius-type intergrowths are shown in Figure 2.
Figure 2. Aurivillius-type intergrowths: Order and Disorder. Examples of the Order and Disorder are \( n = 2 \) and \( 3 \) for Bi\(_7\)Ti\(_4\)NbO\(_{21}\), and \( n = 4 \) and \( 5 \) for Bi\(_{11}\)Fe\(_3\)Ti\(_6\)O\(_{33}\), respectively.

To elucidate mechanisms for the compound formation with various perovskite slabs and obtain new compounds including mixed-layer structure in the Bi\(_4\)Ti\(_3\)O\(_{12}\)-BiFeO\(_3\) system, in earlier research, major attention was paid to structure and thermal behavior and researchers from Russian Academy of Sciences [70–73,77–80]. All of the BFTO-\( n \) compounds were found to have orthorhombic structures. Analysis of phase changes for the compounds with different \( n \) can reveal a number of general trends: (1) with increasing \( n \), the peak occurring at 15°–20° shifts toward the higher angle while the peak at 30°–35° shifts toward lower angle, the peak spacing between two peaks at 45°–50° gradually become larger, and two peaks separated clearly at 50°–55° gradually overlap each other [79]; (2) As \( n \) increases, the \( c \) cell parameter rises almost linearly, the best fit straight line \( c = 8.22n + 8.16 \) and the average thicknesses of one perovskite layer and the fluorite-like layer is 4.11 Å and 4.08 Å, respectively [80]; (3) The compounds are close in chemical composition and subject to the general tendency, as a rule, the degree of ordering in the layer stacking can be assessed for new materials with fractional \( n \) values. In addition, recent studies found an abrupt decrease in the temperature of their decomposition when \( n > 6 \), possibly caused by thermal instability of BiFeO\(_3\) (exceeds 70 mol %) in considered temperature range. Moreover, the BFTO-\( n \) compounds at \( n > 6 \) are distinguished by the slight differences in the solidus and liquidus temperatures, being in a state close to indifferent equilibrium. This noteworthy feature correlates with considerable structural alterations in them at \( n > 6 \) [80]. In a word, the high BiFeO\(_3\) percentages and the abrupt decrease in the thermal stability affect the stability of the BFTO-\( n \) (\( n > 6 \)), probably resulting in the occurrence of the complicated mixed-layer structure.

2.2. Controllable Synthesis and Morphological Features

The main approaches to making BFTO-\( n \) materials include the conventional solid state reaction method, sol-gel method or chemical solution deposition method or Pechini’s method, coprecipitation method, hydrothermal synthesis method, molten salt method, and micro-pulling down method. The general pathways of these methods are present in Figure 3.
2.2.1. Ceramics

Layer-structure determines the growth habit for the BFTO-$n$. They grow with anisotropic shapes, as platelets with the minor dimension in parallel to the c-axis. This is a disadvantage for the sintering process to obtain dense bulk ceramics but favors the grain alignment that allows the texture and the crystal orientation, as shown in Figure 4a–c, carried out by different means, such as hot pressing, tape-casting, template grain growth or others. Because of lower cost and the possibility of obtaining high amount of materials, the ceramic method is the most used route for the processing of materials with Aurivillius structure. However, a major drawback for this method is that the lamellar crystal growth makes the compaction of precursor ceramic powder more difficult. The reduced mass transport during sintering easily led to porous ceramics, higher than ~10 % of porosity. Fabrication of the BFTO-$n$ ceramics generally follows the procedures of pre-sintering for powders and sintering of the hot/cold-pressed green pellets.

2.2.2. Thin Films

In order to drive device applications, the BFTO-$n$ materials in the form of thin films are required. Currently, polycrystalline BFTO-$n$ thin films were successfully prepared by typical chemical solution deposition method or sol-gel method [81–90], which consists of the solution preparation and spin coating processing. The practical substrate usually adopts
the Pt/Ti/SiO$_2$/Si substrate [81–86], fused quartz substrate [90], sapphire substrate [25], and so on. Figure 4d,e shows the field emission scanning electron microscope (FE-SEM) images of surface and fracture morphologies of the BFTO-$n$ thin film. Yet, owing to the almost equal Gibbs free energies and the increased inner constraint of crystalline structures, it is difficult to synthesize BFTO-$n$ ($n > 6$) with a homogeneous layer-structure by using the existing methods. The fabrication of single crystal epitaxial thin films of the BFTO-$n$ has been a long-standing challenge due to their thermodynamic phase-instability and the large stacking layer number. Through the long-continued efforts, little work has been done on the high-quality single-crystalline BFTO-$n$ thin films [91–96]. For example, BFTO-8 epitaxial films were obtained on TiO$_2$-terminated SrTiO$_3$ (001) substrates using pulsed laser deposition with a KrF excimer laser [49]; the epitaxial growth of BFTO-5 on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrate and LaNiO$_3$ conductive buffer layer was done, using laser molecular-beam-epitaxy employing a KrF excimer laser [96].

**Figure 4.** (a) SEM image of BFTO-6 ceramic from fresh fracture surface. (b) The photo of hot-pressed BFTO-6 ceramics. (c) Cross-section SEM images of BFTO-6 ceramic prepared by dry pressing the nanoplates and subsequently sintering without pressure. Reproduced with permission from Ref. [97]. Copyright 2015, Elsevier Ltd. The FE-SEM images of (d) surface and (e) cross-sectional morphologies of BFTO-4 thin film on (111) Pt/Ti/SiO$_2$/Si substrate. (f) SEM, TEM, and HRTEM images of the BFTO-8 nanobelts. Reproduced with permission from Ref. [98]. Copyright 2017, the Royal Society of Chemistry. SEM images of (g) BFTO-4 nanoshelf or nanoflower and (h) individual BFTO-4 nanoplate. (i) TEM image of BFTO-4 plate on the ab plane. Reproduced with permission from Ref. [62]. Copyright 2017, the Royal Society of Chemistry.

2.2.3. Nanostructures and Single Crystals

Because of specific surface effect, small size effect, quantum effect, etc., the nanophase materials show manifold excellent performances and have broad applications in the fields of environmental pollution and shortage of clean energy. So, the BFTO-$n$ in the
form of nanostructure attracted extensive attention worldwide in recent years and diverse nanostructures of them including nano-shelves [54], nano-belts [97,98], nano-fibers [63], nano-sheets [62], nano-plates [59], and nano-flowers [53] were synthesized and applied as catalysts for photo-degradation, visible-light-driven water splitting, and oxygen evolution reaction. Morphology of the BFTO-$n$ nanobelts synthesized via electrospinning is shown in Figure 4e. These nanobelts present belt morphology with well-developed crystallization, but the belts could become rougher with the size of particles and pores increased with increasing the calcination temperature [98]. The BFTO-4 nanoflowers and truncated tetragonal bipyramid BFTO-4 nanoplates are shown in Figure 4f,g, respectively. In fact, the previous work found that various morphologies such as nanoflowers, nanosheets, and microplates can be synthesized successfully by a hydrothermal method adopted different operate technology and process [62–64]. The concentration of MOH (Na$^+$ or/and K$^+$) solution as mineralizer and citrate acid as adjuvant play a critical role for the morphology control of the nanostructure. Whatever hierarchical morphology stacked by regular nanosheets or individually crystalline nanoplates, there are some different exposed facets which may produce different numbers of reactive sites and carrier migration ability, thus presenting diversified physicochemical performances. The selected area electron diffraction (SAED) patterns taken from four corns of one BFTO plate from the sample in Figure 4h exhibit almost identical diffraction spots corresponding to (200) and (020) plane, confirming the single-crystalline nature (Figure 4i). More importantly, this individual single-crystalline nanoplate can verify intrinsic FM and FE properties of Aurivillius-type BFTO-$n$ compounds [59]. Apart from the nano-crystals, single crystals of the BFTO-$n$ were grown by using modified micro-pulling down method [60]. The growth system uses mirror halogen lamps and a Pt tube, and the type of heater lamp, tube diameter, heating power, molten zone properties, and rotation speed are key factors and should be adjusted for different crystal types.

3. Strategies for the Improvement of Properties

The BFTO-$n$ compounds have FE property with very high FE transition temperatures. The origin of ferroelectricity is from a combination of octahedral rotations and polar distortions in the perovskite layers, where lone pair electrons of Bi$^{3+}$ ions induce Ti (Fe) ions to deviate from the center of Ti(Fe)-O octahedral along an axis. Birenbaum et al. [99] calculated that the BFTO-4 had a FE polarization of ~55 $\mu$C/cm$^2$, which is similar in magnitude to Bi$_4$Ti$_3$O$_{12}$ (~50 $\mu$C/cm$^2$) [14]. Recently reported remanent polarization (2$P_r$) values from the forms of thin films or ceramics are recorded and shown in Table 1, and vary from 6.1~75.6 $\mu$C/cm$^2$. There exists a great discrepancy in the observed polarization and the reason could be that, on one hand, the polarization depends strongly on the synthesis method and annealing conditions in most cases, on the other hand, it is difficult to obtain fully saturated P-E loops, or saying that substantial numbers of the obtained P-E loops are not saturated or leaky. As presented in Table 1, the 2$P_r$ value from the films is about two to three times higher than that from the ceramics, except a few individual exceptions. Song et al. [51,100,101] had obtained well-saturated FE hysteresis loops with 2$P_r$ up to 50 $\mu$C/cm$^2$ in the BFTO-$n$ ($n$ = 4, 5 and 6) thin films. Pulsed positive-up-negative-down polarization (PUND) measurements further confirm that the obtained remanent polarization is from the intrinsic FE domain switching contribution. Their FE fatigue and retention properties were also tested, and the polarizations approached a near steady-state value after a retention time of $2 \times 10^4$ s and the switchable polarization loss after read/write switching $1 \times 10^{10}$ cycles is lower than 20%, which implied favorable fatigue and stable retention. These above results revealed obviously that authentic and larger remanent polarization can be obtained in the BFTO-$n$ oxides with un-doping or doping in the A or/and B sites.
Table 1. Multiferroic properties of the BFTO-$n$ ceramics (C) and thin films (F) with ion substitutions for A or B sites.

| Materials | Form | 2Pr ($\mu$C/cm$^2$) | Applied E (kV/cm) | Ref. |
|-----------|------|---------------------|-------------------|-----|
| Bi$_{5}$Fe$_{13}$O$_{15}$ | C | 35 | 270 | 127 |
| Bi$_{5}$Fe$_{13}$O$_{15}$ | F | 51.2 | 600 | 51 |
| LaBi$_{4}$Fe$_{23}$O$_{15}$ | C | 32.3 | 220 | 27 |
| NdBi$_{4}$Fe$_{23}$O$_{15}$ | C | 6.1 | 90 | 29 |
| SmBi$_{4}$Fe$_{23}$O$_{15}$ | F | 48 | 800 | 28 |
| YBi$_{4}$Fe$_{23}$O$_{15}$ | F | 53.6 | 1300 | 21 |
| Tb$_{0.4}$Bi$_{5.6}$Fe$_{23}$O$_{17}$F | F | 44 | 250 | 25 |
| Sr$_{0.5}$Bi$_{4.5}$Fe$_{23}$O$_{15}$F | C | 60 | 180 | 143 |
| Bi$_{6}$Fe$_{0.5}$Co$_{0.5}$Ti$_{15}$ | C | 15 | 270 | 127 |
| Bi$_{5}$Fe$_{0.5}$Ni$_{0.1}$Ti$_{15}$ | F | 49.3 | 900 | 39 |
| Bi$_{5}$Fe$_{0.75}$Mn$_{0.25}$Ti$_{15}$ | F | 34.2 | 800 | 41 |
| Bi$_{4}$Fe$_{1.4}$Ni$_{0.6}$Ti$_{15}$ | C | 75.6 | 475 | 44 |
| Bi$_{6}$Fe$_{1.4}$Co$_{0.6}$Ti$_{15}$ | F | 35.2 | 700 | 81 |
| Bi$_{3}$Fe$_{2}$Ni$_{1.5}$Ti$_{15}$ | F | 36.4 | 625 | 86 |
| Bi$_{2}$Fe$_{2}$Co$_{1.5}$Ti$_{15}$ | F | 38.6 | 600 | 142 |
| Gd$_{0.75}$Bi$_{4.25}$Fe$_{0.5}$Co$_{0.5}$Ti$_{15}$ | C | 10.6 | 180 | 136 |
| LaBi$_{4}$Fe$_{0.5}$Co$_{0.5}$Ti$_{15}$ | F | 42 | 1000 | 88 |
| La$_{0.4}$Bi$_{4.5}$Fe$_{1.4}$Co$_{0.6}$Ti$_{15}$ | F | 37.4 | 700 | 89 |
| SrBi$_{5.5}$Fe$_{0.5}$Co$_{0.5}$Ti$_{15}$ | C | 52.4 | 170 | 137 |
| Sm$_{0.85}$Bi$_{6.15}$Fe$_{2}$Co$_{1.5}$Ti$_{15}$ | F | 27 | 600 | 142 |

The BFTO-$n$ ($n \leq 6$) are paramagnetic (PM) or antiferromagnetic (AFM) states at RT, while both AFM and weak FM states are possible for the compounds with $n > 6$ [102–104]. The origin of the magnetism was proposed by the spin canting of sub-lattices via Dzyaloshinskii-Moriya interaction [99]. With a low concentration of magnetic cations, there is a strong AFM coupling between Fe$^{3+}$ cations in nearest-neighbor positions, whereas the coupling between further neighbors is rather weak. When it has a higher concentration, the FM properties are mainly from the presence of a small inhomogeneous magnetic Fe ion distribution in a nano-region, leading to a short-range magnetic order (FM behavior) [105]. It was also proved that when the BFTO-$n$ have higher integer or fractional $n$ values, the Fe/Ti ions are inhomogeneously distributed in octahedral positions of the perovskite blocks and structural inhomogeneity easily exists in these layered structure, which lead to strong effects on the magnetic properties [106].

3.1. Chemical Modification

Great attention was paid to the BFTO-$n$ materials due to an amazing variety of both structural and physical properties that can be achieved by substituting other cations into the A-site and B-site as well as changing the number of perovskite units ($n$). Normally, the Bi atom in the perovskite layer (A-site) can be replaced by ions with ionic radii in the range of 1.1–1.3 Å, and the Ti$^{4+}$ or Fe$^{3+}$ (B-site) will be substituted by ions with 0.58–0.65 Å. Experimentally, tolerance factor and mismatch or inter-strain are two basic factors for structural stability of the Aurivillius compounds. The ion substitution would influence the inter-strain and tolerance factor. The A-site can be occupied by large cations such as Na$^+$ [20], K$^+$ [107], Ca$^{2+}$ [108], Sr$^{2+}$ [46], Ba$^{2+}$ [26], Pb$^{2+}$ [109], Y$^{3+}$ [21], Bi$^{3+}$ and Ln (La [27], Nd [22], Sm [23], Gd [24], Ce [110–112], Tb [25], Dy [113], Ho [114], Er [115,116], Eu [56], Yb, Th [117], Pr [118]), the B-site can accommodate hetero-valent elements (Ti$^{4+}$, W$^{6+}$ [36], Nb$^{5+}$ [43], Ta$^{5+}$ [119], V$^{5+}$, Cu$^{2+}$ [120], Mo$^{6+}$ [121], and Mg$^{2+}$ [43]) and a variety of magnetic elements (Fe, Cr, Mn, Co, and Ni) [32–44,52], which will create the possibility of magnetic ordering. More interestingly, the halogen or nitrogen elements substitution on the O-sites was accomplished [122,123]. The compounds by F/Cl/Br modification will become Sillen-Aurivillius oxides described as [(Bi$_2$O$_2$XBi$_2$O$_3$)$_3$ $^n$(A$_{n-1}$Bi$_n$O$_3$)$_{n+1}$]$^3$]$^-$ $(X = F, Cl, Br)$, for example, Bi$_7$Fe$_2$Ti$_2$O$_{17}$Cl [123], in which perovskite layers are sandwiched by Sillen slabs.
Ion substitution is one of the most common approaches for the BFTO-\(\text{n}\) to improve their electric and magnetic properties. In the past, the ion substitution for Bi site was employed to improve FE and piezoelectric properties [124–126] by depressing the leakage current. Recently, a large number of research focused on A-site substitution and confirmed the ion substitution at Bi site can strongly affect the FE and even magnetic properties for materials, especially the substitution by common rare earth elements. One can see that a relatively large 2\(P_r\) was observed in BFTO-\(\text{n}\) doped with La, Sr, Y, Sm, Tb, etc. (Table 1), but, weak magnetism was detected too. Li et al. [21] reported the coexistence of FE and weak FM properties with the 2\(P_r\) \(~\sim\)53.62 \(\mu\)C/cm\(^2\) and the saturated magnetization \(~\sim\)0.5 emu/cm\(^3\) for YBi\(_4\)FeTi\(_3\)O\(_{15}\) thin films at RT, due to the decreased leakage current density and the lattice distortion. Contrary to the Bi-site substitution, ion substitution for Fe/Ti site often resulted in poorer FE behavior (Table 1) and yet with some enhanced magnetic behavior [30–40]. The degradation in the FE property may be caused by the presence of dopant-induced secondary phases or defects resulting in the higher leakage current. Most studies have confirmed that the magnetic property of the BFTO-\(\text{n}\) could indeed be enhanced by doping some magnetic elements, e.g. Co, Ni, Cr and Mn. For examples, the addition of Ni increased remanent magnetization (2\(M_r\)) of Bi\(_6\)Fe\(_{2-x}\)Ni\(_x\)Ti\(_3\)O\(_{18}\) from almost 0 emu/g to 1.06 emu/g (\(x = 0.6\)) [44]. The Co substitution showed a higher 2\(M_r\) \(~\sim\)0.26 emu/g for Bi\(_5\)Fe\(_{1-x}\)Co\(_x\)Ti\(_3\)O\(_{15}\) [127], compared with the value \(~\sim\)\(10^{-3}\) emu/g for the un-doped BFTO-4 ceramic. Liu et al. [81] found that the Bi\(_6\)Fe\(_{2-x}\)Co\(_x\)Ti\(_3\)O\(_{18}\) thin film with \(x = 0.3\) showed a higher 2\(M_r\) of 16.8 emu/cm\(^3\). These studies indicated that the different magnetic element doping can effectively enhance the magnetic properties, due to the possible magnetic exchange interactions and spin canting behavior of the AFM coupling. In addition, it is necessary to mention that despite there are some controversies about the origin of magnetism in the early days [128–130], the intrinsic RT magnetism properties of Mn-, Ni-, and Co-doped BFTO-\(\text{n}\) were clearly determined by impedance spectroscopy [131], magnetic domain investigations [67], magnetic thermogravimetric analysis [132], and polarized neutron reflectivity [133]. Moreover, the intrinsic FM nature of individual single-crystalline Bi\(_5\)Fe\(_{0.9}\)Co\(_{0.1}\)Ti\(_3\)O\(_{15}\) nanoplate was visualized by electron holography [59].

Ion substitution for both Bi and Fe sites can have a greater impact on the electric and magnetic properties than that of the substitution for Fe site, such as the co-doping of Nd and Ni [134], Nd and Co [135], Gd and Co [136], and Sr and Co [137]. Among those, Sr and Co co-doped SrBi\(_5\)Fe\(_{0.5}\)Co\(_{0.5}\)Ti\(_4\)O\(_{18}\) ceramic [138] could improve FE and FM properties, giving rise to 2\(P_r\) \(~\sim\)52.4 \(\mu\)C/cm\(^2\) at the electric field of 170 kV/cm and 2\(M_r\) \(~\sim\)2.24 emu/g (Figure 5). However, not all doped BFTO-\(\text{n}\) compounds showed enhanced electric behavior when the Bi and Fe sites were substituted by different ions. For example, a 2\(P_r\) \(~\sim\)10.6 \(\mu\)C/cm\(^2\) was observed in Bi\(_{4.25}\)Gd\(_{0.75}\)Fe\(_{0.5}\)Co\(_{0.5}\)Ti\(_3\)O\(_{15}\) at 180 kV/cm [136]. Owing to decreasing leakage current (La /Sr-doping) and improving magnetic properties (Co-doping), La /Sr and Co co-doped BFTO-\(\text{n}\) ceramics or films have recently become a focus of attention [139–143], and can show saturated FE hysteresis loops with 2\(P_r\) \(~\sim\)20–50 \(\mu\)C/cm\(^2\) and large saturation magnetization with \(~\sim\)10 emu/cm\(^3\) for film and \(~\sim\)1 emu/g for ceramic.
Figure 5. Multiferroic properties of the SrBi$_5$Fe$_{0.5}$Co$_{0.5}$Ti$_4$O$_{18}$ (SBFCT) ceramic. (a) P-E hysteresis loop at room temperature (RT). The inset shows the electric field dependence of remanent polarization. (b) Plot of $\pm \Delta P_r$ versus the testing electric field in a standard pulsed positive-up-negative-down polarization (PUND) measurement. (c) Normalized polarization in the fatigue test. (d) Magnetization versus magnetic field (M-H) loop at RT. (e) Temperature dependencies of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization at a magnetic field of 500 Oe. The ferromagnetic (FM) Curie temperature is about 436 K. Reproduced with permission from Ref. [138]. Copyright 2015, the Royal Society of Chemistry.

3.2. Interface Engineering

Considerable efforts and attempts have been made to effectively promote multiferroic properties of the BFTO-$n$ by strain modification, interfacial coupling, decreasing leakage currents, control in orientation, and construction of similar phase boundaries. Among those approaches, construction of interfaces in heterojunctions or super-lattices, use of oxide buffer layers in thin films, and formation of layer-modulated interfaces of the layered structure are well documented, as shown in Figure 6. Oxide interface can easily influence electric, magnetic, and structural functionalities of the perovskite oxides, arising from chemical, strain, polarization discontinuity, and so on [144–146].

3.2.1. Interface from Film Heterojunctions

Aurivillius-type composite films are increasingly being paid attention in recent years. Tang et al. [66] synthesized Bi$_5$FeTi$_3$O$_{15}$ (BFTO-4)/Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ (NBT) composite film using a sol-gel technique and investigated FE, piezoelectric, FM, and ME properties. As a result, this composite film endowed with good FE polarization, and the P-E loops with $2P_r \sim 182 \mu$C/cm$^2$ at 696 kV/cm meets the standard of FE property without obvious asymmetrical phenomena and severe polarization degradation at the range of the electric field. The piezoelectric coefficient $d_{33}$ reached $\sim 235$ pm/V, suggesting that the composite films endow with a good electrostrictive and piezoelectric effect (Figure 6a,b). Moreover, the BFTO-4/NBT composite film possessed weak FM property and the values of $2M_r$ and saturation magnetization are similar with those of pure BFTO-4 film, implying that the magnetism mainly comes from the BFTO-4. In addition, in Zhao’s group, the multiferroic properties of bilayer Bi$_4$Ti$_3$O$_{12}$/BFTO-4 [147], BiFeO$_3$/BFTO-4 [148], CoFe$_2$O$_4$/BFTO-4 [149], and NiFe$_2$O$_4$/BFTO-4 [150] composite films were reported too, which were all prepared by the chemistry solution deposition.

3.2.2. Interface between Substrate and Thin Film

Apart from the interface from heterojunctions, the study of the interface between substrate and thin film is of importance and interest. Firstly, thin films on different substrates
could present different properties due to the chemical and structural strain. To study the growth and multiferroic responses of strain modified thin films, high-quality thin films of varying thickness usually were fabricated at optimized growth temperature and oxygen partial pressure. For example, Ramana et al. [93] grew SrBi$_{4.25}$La$_{0.75}$Ti$_4$FeO$_{18}$ polycrystalline thin films 80–330 nm thick, and observed that the 1.66% strain of the film with 80 nm gradually decreases with the thickness to 0.04% for thickest film with 330 nm and the crystal structure shows an orthorhombic distortion. Secondly, because the thermal-equilibrium energies of various phases with different number of layers approach a constant value when $n > 6$, this chemical nature of Aurivillius oxide and the strain from the substrate can result in experimentally observed intergrowths, as shown in Figure 6c,d. In general, thin films are a mixed-layer structure [94,151–153] and the coexistence of the mixed layers with different strain states and possible point defects at (Bi$_2$O$_2$)$^{2+}$ layers could result in distortions, especially Jahn-Teller distortions, [154] which strongly affects magnetic property. Campanini et al. [94] proved that epitaxial strain is released by the formation of out-of-phase boundaries (seeing point defects in Figure 6d) and the Fe dopant atoms are distributed with a preferential mixed configuration, that is, occupying one inner and one outer site of the four perovskite blocks. Keeney et al. [153] also found a marked preference for Mn to partition to the central layer in the five-layer Bi$_6$Ti$_x$Fe$_y$Mn$_z$O$_{18}$ system, due to defect regions of the mixed-layer structure. Thirdly, in order to find a way to fabricate high-quality single-crystalline Aurivillius-type compound films. A buffer layer may be adapted to improve preparation conditions or performances. In previous work [96], the Bi$_6$FeCoTi$_3$O$_{18}$ films were grown on LSAT insulating substrate and a conducting LaNiO$_3$ buffer layer on the LSAT, as shown in Figure 6e. It is found that the conductive buffer layer can assist the growth of Aurivillius oxide thin films, resulting in a significantly enhanced epitaxial quality. Importantly, it was inferred that the enhanced epitaxial quality was closely correlated to a uniform and sharp interface due to the screening of the interface ionic dipole. Yang et al. [155] used the LaNiO$_3$ layer to fabricate Bi$_6$Fe$_2$Ti$_3$O$_{18}$/LaNiO$_3$/Si thin films and studied the annealing temperature effect. Kim et al. [156] reported electrical and structural properties of metal-ferroelectric-insulator-semiconductor Au/Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$/HfO$_2$/Si structure as the nonvolatile-memory field-effect transistors, by varying the HfO$_2$ buffer layer thickness. Zhu et al. [157] found that the $2P_r$ and coercive field ($E_c$) of the BFTO-4/CuO films are 29.40 $\mu$C/cm$^2$ and 54 kV/cm, respectively, while the values for the BFTO-4 film are 46.32 $\mu$C/cm$^2$ and 146 kV/cm, respectively. Obviously, $2P_r$ and $E_c$ are significantly reduced after the introduction of the CuO buffer layer, due to the good conductivity of the CuO.

3.2.3. Interface Inside the Layered Structure

The BFTO-$n$ has many one-dimensional layer-stacked interfaces. Engineering these interfaces inside the layered structure is an important and significant subject to either find new fascinating phenomena or realize a large enhancement of resulting performances. Minor interface modulation has been usually done via chemical modification, including doping alkaline-earth or rare earth metal ions into A-sites or substituting magnetic transition metal ions into B-sites inside the perovskite-like structure. This interface modulation indeed could realize certain levels of property enhancements; however, the symmetry of the periodic structural unit was not apparently broken. In order to make a large modulation capability to the structure, the symmetry of interfaces in layered structures should be better broken by using different perovskite slabs. Hence, the mixed-layer Aurivillius oxides, uniquely with different layers sandwiched by the (Bi$_2$O$_2$)$^{2+}$ layers, are as candidates to study.

A structural evolution from high-layer homogeneous phase to low-layer homogeneous phase in the BFTO-$n$ was induced by excessive Co substitution for Fe sites, and layer-structural transformation easily produces and modulates correlated interfaces of two different layer phases with different strain states. For instance, in early work, we observed two structural transformations (changing the material gradually from the originally de-
signed six-layer architecture down to five-layer and then four-layer) in Bi$_7$Ti$_3$Fe$_{3-x}$Co$_x$O$_{21}$ (BFCT-x) ceramics, by continuously increasing the Co content [158]. The mixed-layer structure and enhanced multiferroic properties occurred at the two boundaries. To understand the correlation between structure and properties, we studied the one transformation by making more compositions in the BFCT-x [159]. Large physical effects and an abnormal magnetic transition related to the enhanced magnetic property were observed inside this special structural transformation region. We also observed the structural evolution of Sr-doped Bi$_7$Fe$_1.5$Co$_{1.5}$Ti$_3$O$_{21}$ ceramics [137] and SrBi$_5$Fe$_{3-x}$Co$_x$Ti$_4$O$_{18}$ films [160]. In addition, Zhang et al. [22] reported Bi$_4$NdTi$_3$Fe$_{1-x}$Co$_x$O$_{15}$ compounds suffer a structural evolution from the four-layer phase to three-layer phase with increasing Co doping level from 0 to 1, and they found the compounds with different ratios of four- and three-layered structure present a significant variation of FE and magnetic properties. Wang et al. [161] reported that Bi$_5$Ti$_3$Fe$_{1-x}$Co$_x$O$_{15}$ forms single four-like layer perovskite structures for $x < 0.67$, while three-like layer perovskite begins to arise for $x > 0.67$, suggesting a structural transformation, and the weak RT FM properties only exist in the materials with the mixed-layer structure, as shown in Figure 6g.

Figure 6. Interface from heterojunction, e.g., (a) SEM image, (b) P-E loops and piezoelectric coefficient curves of the Bi$_5$FeTi$_3$O$_{15}$/Na$_{0.5}$Bi$_{4.5}$Ti$_4$O$_{15}$ composite films. Reproduced with permission from Ref. [66]. Copyright 2019, Elsevier B.V. Interface between substrate and film, e.g., epitaxial strain induces structural and polar properties or a buffer layer. (c,d) High-resolution HAADF-STEM images of Bi$_5$FeTi$_3$O$_{15}$ thin film on an NdGaO$_3$ (001)-oriented substrate. Reproduced with permission from Ref. [94]. Copyright 2019, American Chemical Society. (e) XRD and AFM images of Bi$_6$FeCoTi$_3$O$_{18}$ films grown on LSAT and on LaNiO$_3$/LSAT. Reproduced with permission from Ref. [96]. Copyright 2015, AIP Publishing LLC. Interfaces inside Aurivillius-type layered structure, e.g. the control of the number of intergrowth interfaces in mixed-layer structure. (f) A mixed-layer structure, (g) Evolution of microstructure and magnetic properties of Bi$_5$Ti$_3$Fe$_{1-x}$Co$_x$O$_{15}$ by continuously increasing Co. Reproduced with permission from Ref. [161]. Copyright 2017, American Chemical Society.
The interfaces from the mixed-layer structure and point defects can be induced by breaking the homogeneous structure of long-period Aurivillius oxides through a simple Fe/Ti content modulation. The $\text{Bi}_9\text{Fe}_5\text{Ti}_3\text{O}_{27}$ (BFTO-8) and $\text{Bi}_{10}\text{Fe}_{6}\text{Ti}_{3}\text{O}_{30}$ (BFTO-9) by modulating the Fe/Ti mole ratio present the fantastic intergrowth structures with different layer numbers in neighboring layers [162]. The Neel temperatures of the homogeneous BFTO-8 and BFTO-9 is below 290 K, while it is approximately 320 and 360 K for $\text{Bi}_9\text{Fe}_{5.4}\text{Ti}_{2.6}\text{O}_{27}$ and $\text{Bi}_{10}\text{Fe}_{6.6}\text{Ti}_{3}\text{O}_{3}$, respectively, which have the disordered mixed-layer structure. Keeney et al. [153] distinguished the differences of the atomic layer-structures between $\text{Bi}_6\text{Ti}_{3.04}\text{Fe}_{1.42}\text{Mn}_{0.54}\text{O}_{18}$ (less magnetic cations) and $\text{Bi}_6\text{Ti}_{2.99}\text{Fe}_{1.46}\text{Mn}_{0.55}\text{O}_{18}$ (more magnetic cations), as shown in Figure 7a–c. Some regions of two samples display out-of-phase boundaries (OPB) defects, where there is displacement by a fraction of the 6-layer. However, in Figure 7c, some OPBs regions can be accompanied by an insertion of an extra perovskite block, namely the stacking fault defects, where there are sub-unit-cell intergrowths of 4- and 6-layer and can terminate in an OPB. They also revealed that Ti content is increased and Mn content is drastically decreased locally at the stacking fault defect, compared with the defect-free average. Faraz et al. [163] reported the FE property of the mixed-layer $n=5/6\text{Bi}_6\text{Ti}_{2.7}\text{Fe}_{1.5}\text{Mn}_{0.8}\text{O}_{18}$ (57.42~67.94 $\mu\text{C/cm}^2$) is better than that of $\text{Bi}_6\text{Ti}_{2.9}\text{Fe}_{1.5}\text{Mn}_{0.6}\text{O}_{18}$ (23.66~24.69 $\mu\text{C/cm}^2$).

Figure 7. (a) HAADF-STEM image of a 5-layer Aurivillius phase structure (Fe/Ti ratio ~2/3) in a defect-free region. Representative HAADF-STEM images of (b) $\text{Bi}_6\text{Ti}_{3.04}\text{Fe}_{1.42}\text{Mn}_{0.54}\text{O}_{18}$ (lower Fe/Ti ratio) and (c) $\text{Bi}_6\text{Ti}_{2.99}\text{Fe}_{1.46}\text{Mn}_{0.55}\text{O}_{18}$ (lower Fe/Ti ratio). The numbers displayed in red designate the number of layers ($n$) in the region designated by the red bar. Yellow arrows demonstrate the position of the OPBs and blue rectangles indicate stacking fault regions. Reproduced with permission from Ref. [153]. Copyright 2017, Nature Publishing Group.

Direct interface modulations inside Aurvillius-type mixed-layer compounds can easily influence structural deformation, electron density and magnetic structure, thus giving rise to novel physical properties potentially. As mentioned earlier, we synthesized polycrystalline Bi$_{11}$Fe$_3$Ti$_6$O$_{33}$ (BFTO-4.5) compound, which is an inhomogeneous phase and disordered intergrowths of the 4- and 5-layer, and observed its physical properties [76]. Based on this material, a very minor Co-doping was adopted to modulate their layer-stacked interfaces [164]. Structural transformation, gradually changing from the originally phase-modulated structure composed of both 4- and 5-layer phases to a new homogeneous 4-layer structure, was clearly observed, as shown in Figure 8. Interestingly, larger magnetic coercive field from the M-H loop at low temperature only exists in these mixed-layer materials. This abnormal phenomenon arises from intrinsic 1D phase-modulated structure and the utilization of minor Co-doping, which could generate structural distortions at interfaces of two different phases and give rise to some weak FM regions forming strong FM-AFM interaction. In short, nanoscale structural transformation easily modulating correlated interfaces of two different layer phases, plays a key role in enhancing properties and reveals potential via chemically-driven symmetry controlling and structurally-driven strain controlling to give rise to novel structural, electronic, and magnetic behaviors.
3.3. Oxyhalide Derivatives

Individual units for materials are responsible for different functions. The $(\text{Bi}_2\text{O}_2)^{2+}$ slabs in the layered structures play a key role as both space-charge compensation and charge insulation. In recent years, considerable interest was aroused in these fluorite-like layers. Insertion of one or several halide layers between the $(\text{Bi}_2\text{O}_2)^{2+}$ slabs can get a plethora of complex intergrowth structures, which sufficiently widened the window of layered functional materials. Some derivatives with perovskite-based intergrowth structures as examples are shown in Figure 9. Sillen-Aurivillius (S-A) type layered oxyhalide derivatives, corresponds to a general formula $[(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})]^3-$, with alternate stacking of Aurivillius-type perovskite blocks $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$ and Sillen blocks $(\text{Bi}_2\text{O}_2)^{2-}$. A series of S-A type bismuth-based layered oxyhalides were shown to stably and efficiently oxidize water under visible-light [166–169]. For instance, $\text{Bi}_4\text{NbO}_8\text{Cl}$ as a research focus, belongs to a $n=1$ member of S-A type oxyhalides and possesses a narrow bandgap $\sim 2.4$ eV, while it can place a conduction band minimum more negative than the water reduction potential for $\text{H}_2$ generation [170]. However, for the S-A type materials with electrical and magnetic orders, it is a question whether more magnetic cations could be incorporated into the S-A structures. The perovskite blocks reflected by the $\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}$ formula are oxygen-excessive in the Aurivillius-type or S-A type structures, which favors the $d^0$ cations with large charges and restricts the fraction of the transition metal cations with smaller charges ($\text{Fe}^{3+}$, $\text{Cr}^{3+}$, or $\text{Co}^{3+}$). The Sillen block requires one less positive charge for charge compensation due to the intercalation of Cl anions between two $(\text{Bi}_2\text{O}_2)^{2-}$, which can

![Figure 8](image_url) Nanoscale structural transformation. (a) Structural transformation and (b) low-temperature magnetic response of $\text{Bi}_{11}\text{Fe}_{3-x}\text{Co}_x\text{Ti}_6\text{O}_{33}$. Reproduced with permission from Ref. [164]. Copyright 2018, Nature Publishing Group.

![Figure 9](image_url) Perovskite-based intergrowth structure: (a) Aurivillius-type structure $(\text{Bi}_2\text{O}_2)(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$, (b) Sillen-Aurivillius-type structure $(\text{Bi}_2\text{O}_2)_2(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})\text{Cl}$, (c) Ruddlesden-Popper-type $\text{A}_{n+1}\text{B}_n\text{O}_{3n-1}\text{Cl}_2$ and (d) hematophanite-type $\text{A}_{n+1}\text{B}_n\text{O}_{3n-1}\text{Cl}$. Reproduced with permission from Ref. [165]. Copyright 2015, American Chemical Society.
effectively reduce the total valence of the B-site and thus improve the content of magnetic ions in the perovskite slab, e.g., 3-layer Bi₆Ti₂FeO₁₄Cl [171]. In addition, the Sillen block could depress the interaction of magnetic ions existing in neighboring perovskite slabs.

A new S-A phase Bi₇Ti₂Fe₂O₁₇Cl with highly orientated texture was studied and its complex spin structure and magnetic anisotropy were found [123]. This 4-layer S-A phase structure and magnetic anisotropy are shown in Figure 10a–c. Interestingly, two broad peaks observed in the ZFC curve, based on large temperature gap between them, suggests the existence of two magnetic glass-like behaviors (the AFM do-main wall pinning effect from adjacent domains and the blocked spin glass). Batuk et al. [165] observed new layered oxychlorides corresponding to the [PbBiO₂] An⁺¹BnO₃n−₁Cl2 (A = Pb/Bi, B = Fe/Ti), e.g., Pb₂BiFe₃O₁₀Cl₂ (n = 3), Pb₃Bi₂Fe₄O₁₃Cl₂ (n = 4), and Pb₅BiFe₃TiO₁₃Cl₂ (n = 4), which are built as a stacking of truncated An⁺¹BₙO₃n−₁ perovskite blocks and α-PbO-type [A₂O₂]²⁺ (A = Pb, Bi) blocks combined with chlorine sheets. These structural blocks can be represented as an intergrowth between the hematophanite and Sillen phases. The 4-layer structure of the Pb₅Bi₂Fe₄O₁₃Cl₂ (n = 4) and Pb₅BiFe₃TiO₁₃Cl₂ (n = 4) are shown in Figure 10d,e, and their magnetic ordering is G-type AFM state (the Neel temperatures are around 400–600 K).

Figure 10. S-A type structure and magnetic properties of Bi₇Ti₂Fe₂O₁₇Cl: (a) atomic structure model, (b) STEM-HAADF image, and (c) ZFC-FC curves for the in-plane, out-of-plane, and sloping plane (45° with the field directions) directions (the inset shows the complete ZFC-FC curves). Reproduced with permission from Ref. [123]. Copyright 2019, Elsevier Ltd. (c) HAADF-STEM image of Pb₅Bi₂Fe₄O₁₃Cl₂ taken along the [100] zone axis. Arrowheads indicate the chlorine layers and asterisks indicate the [PbBiO₂] slabs. The insets show simulated images calculated using the structural parameters. (d) HAADF-STEM image of Pb₅BiFe₃TiO₁₃Cl₂ take along the [100] zone axis, (e) individual Pb, Bi, Fe, Ti, O, and Cl atomic resolution STEM-EDX elemental maps, Fe/Ti mixed map, and the Fe and Ti signal intensity profiles. The dots correspond to the experimental data, the black lines to the fitting curves. Reproduced with permission from Ref. [165]. Copyright 2015, American Chemical Society.

3.4. Morphology Controlling

Due to size effects on structure and properties, considerable efforts have been devoted to the controllable synthesis of low-dimensional BFTO-n nanostructures with various morphologies, such as BFTO-4 microflowers [53], BFTO-6 nanoshelf [54], and BFTO-4 nanosheets [62], by modulating the processing techniques and parameters chosen for
fabrication. These BFTO-n nanostructures often exhibit different properties from those of the bulk counterparts, especially in the magnetic and photocatalytic behavior, which may well be correlated to the shape anisotropy, the uncompensated spins at surfaces and different amounts of defects present in the different nanoforms. In this part, besides modifying the morphologies of the BFTO-n nanostructures, other controlling types such as anisotropic ceramics and thin films and nanocomposites will be discussed.

3.4.1. Anisotropic Ceramics and Thin Films

Grain-oriented BFTO-n ceramics were fabricated as following: typical hydrothermal synthesis nanoplates, then dry pressing the nanoplates at rather low pressure, and subsequently sintering the green compacts without applied pressure [97]. Comparing to randomly oriented ceramics, grain-oriented ceramics have attractive anisotropic magnetism. For example, Chen et al. [134] reported the synthesis and magnetic anisotropy of Bi₄NdTi₃Fe₀.₇Ni₀.₃O₁₅-oriented ceramics. Anisotropic electrical and magnetic properties of textured BFTO-4 [172] and grain-oriented Bi₄Ti₃O₁₂-La₀.₅Sr₀.₅MnO₃ [173] ceramics were reported too. The morphology of the films could be modified by changing the substrate orientation. For example, highly c-axis-oriented BFTO-4 thin film was deposited on (100) Si substrates by atomic vapor deposition [174]. This oriented film can show only (00l) peaks in the XRD patterns, up to (0024), and present a strong in-plane piezoelectric response. Faraz et al. [175] reported the FE property of c-axis oriented BFTO-5 films on c-plane sapphire substrates, grown by liquid injection chemical vapor deposition (LI-CVD) too.

3.4.2. Nanocomposites

Aurivillius oxide-based nanocomposites consisting of two or more types of constituent materials show enhanced physicochemical properties, especially photo- or electrocatalytic activity [176–182]. To promote the activity of the BFTO-n nanostructures, several types of nanocomposites have been investigated, including nanoplates/BiCoO₃ [176], nanofibers [180], or nanoplates [178]/graphene, nanofibers/Au [182]. For example, Bi₆Fe₂Ti₃O₁₈ (BFTO-5) nanosheet-BiOX (X = Cl, Br) heterojunctions were synthesized by a facile in-situ ion exchange chemical transformation method [58]. The optimum photocatalytic activity for BFTO-6/BOBr with about seven times higher O₂ production rate than pure BFTO-6 under full spectrum irradiation, which was assigned to the higher efficient charge-carrier separation in the interface due to heterojunction band alignment and ferroelectric polarization.

4. Extraordinary Properties and Potential Applications

4.1. ME Coupling

ME coupling is one of the most appealing aspects of multiferroics, because it provides additional degrees of freedom for manipulating the polarization/magnetization in multifunctional devices, such as actuators, sensors, and data storage devices [4]. Coupling between electric and magnetic dipoles at RT was demonstrated by (i) measuring the effects of electric poling on magnetic hysteresis loop or vice versa [183]; (ii) directly measuring the value of ME voltage coefficient α_ME using a ME coupling test system [184]; (iii) visualization of magnetic/electric-field-induced FE/FM domains switching by piezoresponse force microscopy (PFM) [68]; (iv) measuring the change in dielectric constant under an applied magnetic field [131]. The BFTO-n materials were deemed as potential RT single-phase multiferroics, including large FE and FM properties, high FE and FM transition temperatures, and a ME coupling that occurs at or above the RT together with the ability to be driven as an external electric or magnetic field as possible.

ME coefficient of the BFTO-4 was ~17 mV Oe⁻¹ cm⁻¹ at 8 kOe, and the BFTO-5 was only ~3.2 mV Oe⁻¹ cm⁻¹ at 4 kOe. When n > 6, the ME interaction is very weak and nearly undetectable [184]. Moreover, the coupling coefficient in single-phase BiFeO₃, as reported firstly by Ismailzade’s group (1979), was rather small but measurable, only 0.064 mV Oe⁻¹ cm⁻¹ at 9.5 kOe [185]. This seems to mean that as the Fe content increases,
the ME interaction in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$-$\text{BiFeO}_3$ system decreases, thereby affecting the ME coefficient. Recently, some attempts were made to enhance the ME coupling in the BFTO-$n$ by: (i) chemical substitution with rare earth elements at A-site; (ii) construction of nanosized bulk composites or film heterostructures; and (iii) development of nanoparticle or nano-fibers via various chemical routes.

Table 2 shows some reported ME coefficients of the BFTO-$n$. A maximum $\alpha_{\text{ME}}$ as high as $\sim 400 \text{ mV Oe}^{-1} \text{ cm}^{-1}$ at RT was obtained in the BFTO-4 thin film [186], the BFTO-4/NBT composite thin films [66] or pseudo1-3 type FeGa/BFTO-4 hetero-structural films [187]. However, the ME coefficient of the BFTO-$n$ materials is still inferior, compared with the bulk ME composites with $\alpha_{\text{ME}}$ up to several $\text{VOe}^{-1} \text{ cm}^{-1}$ for technological application as the ME devices. Therefore, there is still a large scope to improve ME coefficient. Perhaps forming composite films or nanocomposites consisting of a strong magnetic phase and piezoelectric phase with high piezo-response, structural architecture, and layer or interface engineering, and so on, may lead to a high ME coefficient.

**Table 2.** Magnetolectric (ME) coupling coefficients of selected BFTO-$n$ in ceramics (C), thin films (F), and nanostructures (N). (Unit: $\text{mV Oe}^{-1} \text{ cm}^{-1}$).

| Materials                        | Form | $\alpha_{\text{ME}}$ | Applied H (kOe) | Ref. |
|----------------------------------|------|----------------------|-----------------|------|
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | C    | 25                   | 6               | 190  |
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | F    | 400                  | 0               | 186  |
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | N    | 14                   | 16              | 126  |
| $\text{Bi}_5\text{Fe}_{0.7}\text{Co}_{0.3}\text{Ti}_3\text{O}_{15}$ | C    | 11.5                 | 0.6             | 127  |
| $\text{La}_{0.75}\text{Bi}_{4.25}\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | F    | 36                   | 8               | 191  |
| $\text{SmBi}_2\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | F    | 41.2                 | 9               | 28   |
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$/BiFeO$_3$ | F    | 65.1                 | 4.5             | 148  |
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$/CoFeO$_4$ | F    | 78.9                 | 6               | 149  |
| $\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$/Na$_{0.5}\text{Bi}_5\text{Ti}_4\text{O}_{15}$ | F    | 410                  | 7.6             | 66   |
| $\text{FeGa}/\text{Bi}_5\text{Fe}_2\text{Ti}_3\text{O}_{15}$ | F    | 418                  | 5               | 187  |
| $\text{SrBi}_2\text{Fe}_{0.5}\text{Co}_{0.5}\text{Ti}_4\text{O}_{18}$ | C    | 0.27                 | 1               | 138  |
| $\text{Bi}_6\text{Fe}_{5.4}\text{Ti}_{2.6}\text{O}_{27}$ | C    | 0.14                 | 6               | 162  |

Although the ME coefficient matters, the deterministic control of FE domains by magnetic field or control of magnetic domains by electric field is perhaps more critical to realize the practical device applications. In BiFeO$_3$-based multiferroics, this research topic has attracted tremendous research interests over the past few years and most of relevant works focusing on $\text{BiFeO}_3$/La$_{0.3}$Sr$_{0.7}$MnO$_3$ [188] or BiFeO$_3$/Co$_{0.4}$Fe$_{0.6}$ [189] have been comprehensively summarized in some excellent review papers. For BFTO-$n$, a direct evidence of the ME coupling was sought by performing PFM under a variable magnetic field to locally image any coupled piezoelectric-magnetic switching [67–69]. Single-frequency PFM was performed on the $\text{Bi}_6\text{Ti}_{2.99}\text{Fe}_{1.46}\text{Mn}_{0.55}\text{O}_{18}$ thin film and the influence of a full magnetic field step cycle on the FE domains was investigated [68], see Figure 11a. Two distinct types of FE domains behavior could be observed as demonstrated by regions of the sample circled in green and yellow in amplitude and phase images. It is evident that field-dependent reversible ME coupling behavior is observed for the yellow circles. Its feature is as follow: the magnitude of piezo-response and the size of domain increases on an increase in magnetic field to $+2500 \text{ Oe}$ and disappears on reversal of the magnetic field to 0 Oe, then the domain is again generated on a decrease in magnetic field to $-2500 \text{ Oe}$ and disappears again on reversal of the magnetic field to 0 Oe. The irreversible domain switching is also observed for the green circles, which shows that the piezoelectric domain emerges and grows but does not disappear under a variable magnetic field. More importantly, Jia et al. [69] demonstrated the availability of the manipulation of magnetic domains by electric field in the BFTO-4 film at RT, see Figure 11b. A sharp contrast in the magnetic domains indicates magnetic domains in the BFTO-$n$ film can be switched by the electric field. After removing the electric field for 22 h, the switched magnetic pattern nearly fades.
away, suggesting the E-switched magnetic domains are coupled to ferroelastic domains, caused by a short-range magnetic ordering status and unstable magnetoelastic coupling.

Figure 11. (a) Control of electric domains by magnetic field. Representative images of the effect of a complete magnetic field cycle applied locally to the Bi$_6$Ti$_{2.99}$Fe$_{1.46}$Mn$_{0.55}$O$_{18}$ thin film on the in-situ in-plane lateral piezoresponse force microscopy measurements. The images demonstrate magnetic-field-induced irreversible (green circles) and reversible (yellow circles) ferroelectric domain nucleation and saturation under the magnetic field cycle. Reproduced with permission from Ref. [68]. Copyright 2016, the American Ceramic Society. (b) Control of magnetic domains by electric field. Magnetic force microscope (MFM) phase images of the Bi$_5$FeTi$_3$O$_{15}$ thin film before electric poling, electric poling by +20 V in the area of 7 × 7 µm$^2$, −20 V in 5 × 5 µm$^2$, and +20 V in 2 × 2 µm$^2$, with reading over 10 × 10 µm$^2$, and after removing the electric field for 1 and 22 h. Reproduced with permission from Ref. [69]. Copyright 2017, Nature Publishing Group.

In a nutshell, both FE and magnetic domain switching behavior in BFTO-‐n multiferroic materials show the coupling between electric dipoles and magnetic orderings, and provide the possibility of manipulating one physical parameter by using one of the external stimuli, such as magnetic field, electrical field, and so on, which could yield an additional degree of freedom in novel multi-functional device design. We believe that these findings will give a great push to realize the practical single-phase RT ME device applications.

4.2. Exchange Bias

Exchange bias (EB) generally manifests itself as a shift of the magnetization hysteresis loop along the magnetic field axis when the system is cooling down fully through its Neel temperature under an external magnetic field. This EB effect plays a crucial role in developing fundamental physics as well as applications of magnetic tunnel junctions and spintronics. The EB effect was usually observed in a variety of artificial materials, such as superlattices, heterogeneous, and core-shell nanoparticles consisting of FM and AFM components. However, the RT EB effect for most materials greatly hinders their potential applications as devices. As an early stage effort, recently, the research has been to focus on the single-phase EB materials [190,191]. Unfortunately, till now, the EB materials with single-phase are still rare and the observed single-phase EB behaviors were still limited by the small exchange-bias field and the low reachable operation temperatures.
In this BFTO-\(n\) system, those short-period compounds have paramagnetic ground state at RT, while those long-period compounds (\(n > 6\)) are mostly AFM materials with a weak FM at RT [102]. Appearance of this weak FM could trigger the formation of spin glassy magnetic states, based on the coexisted FM and AFM interactions, and may induce EB effect. It was found that there is good EB behavior in the BFTO-7 [192], BFTO-8 [98], and BFTO-9 [106]. However, the detected bias temperatures, usually at 10–250 K below freezing temperatures (\(T_f\)) of spin glass transition, are all below RT. Surynarayana et al. [193] found that the \(T_f\) in the BFTO-\(n\) increases with their layer number \(n\). If so, the BFTO-9 has a \(T_f\) \(\sim 280\) K [162] and the anticipated EB temperature for the BFTO-\(n\) with \(n \geq 10\) may be close to RT, but, in fact, it is very difficult to synthesize such oxides because of their almost identical formation energies and more fragile stacked structures. A new strategy instead of merely increasing the layer numbers was proposed by a simple Fe/Ti mole ratio modulation in the BFTO-9 [162]. Consequently, the Neel temperature and \(T_f\) of the samples can reach above RT (Figure 12a) and the RT EB behavior was successfully realized in Bi\(_{10}\)Fe\(_{6.4}\)Ti\(_{2.6}\)O\(_{33+\delta}\) with a maximum EB field (\(H_{EB}\)) of approximately \(\sim 38\) Oe. In addition, the anisotropy of the EB effect was found in bismuth-based layered oxyhalides, for example a 4-layer Bi\(_7\)Fe\(_2\)Ti\(_2\)O\(_{17}\)Cl [123]. The \(H_{EB}\) values of Bi\(_7\)Fe\(_2\)Ti\(_2\)O\(_{17}\)Cl measured in the in-plane and out-of-plane directions at 20–270 K are shown in Figure 12b. Because of the blocked spin glasses, the EB anisotropy of difference should be attributed to the parallel direction of the dominant spin glasses and in-plane applied field after the FC process (Figure 12c).

Figure 12. (a) Magnetic characterization of Bi\(_{10}\)Fe\(_{6.4}\)Ti\(_{2.6}\)O\(_{33+\delta}\) measured at FC-ZFC mode with 500 Oe. The inset shows the plot of \(dM/dT\) vs. T simulated from the FC data. Reproduced with permission from Ref. [162]. Copyright 2018, American Chemical Society. (b) Exchange field (\(H_{EB}\)) and related coercivity (\(H_C\)) of S-A type Bi\(_7\)Fe\(_2\)Ti\(_2\)O\(_{17}\)Cl measured in the in-plane and out-of-plane directions at various temperatures. I and II regions represent the AFM pinning domain and the spin glass (SG) domain, respectively. (c) The illustration of the anisotropy of EB effect in single-phase Bi\(_7\)Fe\(_2\)Ti\(_2\)O\(_{17}\)Cl. For the in-plane field cooling, the uncompensated AFM can couple with the SG; however, for the out-of-plane field cooling, it would be difficult for the AFM to freeze the out-of-plane-oriented SG. Reproduced with permission from Ref. [123]. Copyright 2019, Elsevier Ltd. (d) Schematic sketches of a FM/AFM bilayer with freezing fields (\(H_{g}, E_{g}\)), magnetic moments (\(S_{FM}, S_{AFM}\)), and order parameter (M), where the AFM layer is single domain after ME fields cooling process.
Normally, EB effect denotes the horizontal shift of the FM hysteresis loop after proper magnetic FC to below the ordering temperature of the AFM component. For a single-phase ME material with AFM property, the ME-based switching EB effect from the system consisting of a FM multilayer on top of this ME single crystal was reported [194]. The switching mechanism is based on the so-called ME field (e.g., electric field) cooling process, which favors the growth of a distinct AFM single domain and thus an efficient control of the AFM interface moment whose sign is decisive for that of $H_{EB}$ (Figure 12d). For example, Cr$_2$O$_3$ (0001) and a FM Co/Pd multilayer film [195]. In this EB system, a reversible and global electric switching of the EB field was realized isothermally at RT. If a simple single-phase ME material with good RT EB effect can add a new regulating factor for EB through the use of an electric field, it will promise applicability in future ME devices. Unfortunately, electrically controlling EB in BFTO-$n$ was barely reported until now. A great deal of research, therefore, is urgently needed. Further, it will be interesting and open new possibilities, if the electric control of EB effect in single-phase BFTO-$n$ at RT can be realized.

4.3. Microwave Absorption

Design and development of novel high efficiency microwave absorbing materials and bringing these materials into practical use, such as healthcare, signal protection, and national defense security, are always important. Magnetic ferrite and carbon-based nanocomposites have been widely explored as two attractive candidates for microwave absorption; however, complex fabrication, relatively low output capacity, high density, and so on, limit their applications [196,197]. In fact, both electric and magnetic dipoles are strong absorbers of microwave. Dielectric-magnetic compositing is an effective strategy to enhance microwave attenuation. Recently, single-phase RT multiferroics are increasingly studied as candidates for eliminating electromagnetic waves. Some types of multiferroics, e.g., BiFeO$_3$ [198], YIG [199], and hexaferrite [200], were developed as microwave absorbing materials. Wen et al. [201] reported a minimum reflection loss (RL) of BiFeO$_3$ as $-46$ dB at 11.2 GHz and the absorption bandwidth of the RL below $-10$ dB is about 3 GHz. However, the absorption capacity, bandwidth and thickness of such studied materials still need to be improved further to meet the demand of high efficiency and stabilization. Aurivillius BFTO-$n$ can present large dielectric, FE, and FM behaviors and electromagnetic interaction, thus they are likely to be a new type of microwave materials with excellent microwave absorption. Liu et al. [202] reported that La-modified La$_{0.5}$Bi$_{0.5-x}$Fe$_{0.5}$Co$_{0.5}$Ti$_3$O$_{15}$ materials have a microwave absorption. Specifically, the specimen with $x = 0.75$ delivered a minimum RL of $-15.8$ dB at a small thickness of 1.8 mm and a broadened absorption bandwidth ($\leq -10$ dB) of 3.0 GHz (9.5–12.5 GHz). In our early work [203], a larger absorbing intensity and broader absorbing bandwidth in Bi$_7$Fe$_{2.25}$Co$_{0.75}$Ti$_3$O$_{21}$ was found. The minimum RL surpasses $-30$ dB at different thick-nesses (1–5 mm) and absorption bandwidth ($\leq -20$ dB) was close to 12 GHz (5.7–17.7 GHz). Moreover, the microwave absorption property is sensitive to the sample thickness and the electro-magnetic tailor-ability can be manipulated through appropriately designed the thickness. These works highlighted the application of the Aurivillius-type multiferroic oxide materials as smart absorbers in microwave field.

4.4. Photo/Electro-Catalyst Activity

As potential candidates for highly active photo-catalysts, a lot of attention has been given to the BFTO-$n$ oxides. The main reasons are as follows: (i) the presence of Bi enhances the likelihood of visible-light absorption by pushing up the valence band edge due to the hybridization of Bi 6$s$ with O 2$p$ orbital; (ii) largely dispersed hybridized valence band favors the high mobility of the photo-generated holes and is beneficial to the oxidation reaction; (iii) materials have narrow and tunable band gaps; (iv) spontaneous polarizations may be effective in helping the separation of photon-generated electrons and holes; (v) ferromagnetism may be helpful in making recyclable catalysts. Better than
the selective TiO$_2$-based oxides utilizing mostly UV light, the BFTO-$n$ materials may act as excellent visible-light-driven photocatalysts, having wide applications not only in environmental remediation, water disinfection, pollutant degradation, air purification, and self-cleaning of surfaces, but also in the area of renewable energy generation in the form of hydrogen by water splitting [204]. Aurivillius-type BFTO-$n$ have been reported as a family of visible-light photocatalysts such as BFTO-4 microflowers [53], BFTO-5 nanofibers [182], and BFTO-6 nanoshelf [54]. While most of the studies have only focused on the degradation of a single dye as a pollutant. For example, Naresh et al. [205] synthesized La-doped BFTO-4 and found that such oxides exhibited efficient rhodamine B (RhB) degradation under sunlight irradiation. As the wastewater is contaminated with multiple dyes rather than a single dye, it is desirable to test the efficiency of a catalyst toward the collective removal of multiple dyes from a mixture. Naresh et al. [206] reported that a series of five-layer Bi$_5$AFeTi$_4$O$_{18}$ ($A$ = Ca, Sr, and Pb) compounds not only exhibited collective photocatalytic degradation of RhB-methylene blue and RhB-rhodamine 6G mixture at pH = 2, but also showed almost 100% photo-catalytic selective degradation of methylene blue from the RhB-methylene blue mixture at pH = 11 under natural solar irradiation. In addition, size, morphology, surface area, etc., of a catalyst may greatly affect its catalytic performance. The BFTO-$n$ nanostructures by morphology control were studied and the synergistic effect of different facets in the separation of electrons and holes and oxidation/reduction reaction were found [207]. Rare-earth ions $f$-orbitals can form complexes with various Lewis bases and affect catalytic performance. For example, Eu doped Bi$_5$Fe$_{0.95}$Co$_{0.05}$Ti$_3$O$_{15}$ presents enhanced visible catalytic efficiency [56]. Because of near-infrared light making up about 47% of solar spectrum, the extended utilization of sunlight from ultraviolet and visible light to near-infrared light is an attractive issue for developing photocatalysts. Near-infrared photoactivity of the BFTO-$n$ photocatalysts [55,208] were also reported.

Aurivillius-type BFTO-$n$ was recently explored as a kind of high-efficiency electrocatalyst for oxygen evolution reaction (OER). OER is the rate-determining step in the electrocatalytic water splitting and both electrical conductivity and absorption capability are the two key factors for its strength. Excitingly, the spontaneous polarization of the FE materials can be taken advantage of to separate the carriers, as well as produce an external screening effect absorbing charged ions and molecules from outside to neutralize their polarization inside [209–211]. Therefore, the BFTO-$n$ with large FE intrinsic polarization, can be considered as an excellent material matrix to enhance electrical conductivity and adsorption capacity, further to improve the OER efficiency. Two works about the OER efficiency of the BFTO-$n$ were recommend: one is that three oxides in Bi$_7$Fe$_3$−$_x$Co$_x$Ti$_3$O$_{21}$ [212], all Fe-based ($x$ = 0), half-half Fe-Co based ($x$ = 1.5), all Co-based ($x$ = 3), were prepared to investigate OER activity; The other work [176] presents a methodology by in-situ growth of a secondary phase on a FE Bi$_4$Ti$_3$O$_{12}$−$n$ (BiCoO$_3$) matrix and corona poling it afterward to improve the OER activity.

4.5. Photovoltaic Effect

Coupling of FE polarization with optical properties in ferroelectrics has received a renewed attention, triggered notably by low-band-gap FE materials suitable for sunlight spectrum absorption and original photovoltaic (PV) effect [213]. Different from the $p$-$n$ junction interfacial PV effect, the FE PV effect is a bulk phenomenon and has some out-standing advantages: (i) the photo-generated carriers are separated by the depolarization field, which exists in the entire FE material, therefore, the PV is not restricted by the bandgap; (ii) PV responses can be generated without forming complex junction structures; (iii) the photocurrent is proportional to the polarization magnitude and the PV response can be tuned by controlling the polarization. Several typical types of FE perovskite oxides have been extensively investigated, such as BaTiO$_3$, PbZr$_{1-x}$Ti$_x$O$_3$, and BiFeO$_3$-based materials [214–216]. Among them, although the depolarization field can effectively maintain the separation of the photo-generated carriers, wide bandgaps of >3 eV make some conven-
tional FE oxides absorb only ultraviolet light, which contains only 3.5% of solar radiation intensity. Therefore, a good FE PV material should have a narrow bandgap and a large internal electric field simultaneously, which will improve the absorption of photons and the efficiency of separating photo-generated carriers.

The band gaps of the BFTO-\(n\) have been determined to be about in the range of 1.28~3.1 eV, for instance, 1.28~2.12 eV in Bi\(_6\)Fe\(_{2-x}\)Ni\(_x\)Co\(_x\)Ti\(_3\)O\(_{18}\) [217], 2.04 eV in BFTO-6 [43], and 2.20~2.57 eV in Bi\(_6\)Fe\(_{2-x}\)Co\(_x\)Ti\(_3\)O\(_{18}\) [218]. To achieve high-efficiency PV effects in Aurivillius-phase FE oxides, the materials for BFTO-\(n\) with narrow bandgap, robust polarization and good conductivity will be of interest. However, lots of work about PV effect for BFTO-\(n\) has always focused on the BFTO-4 in recent years. Kooriyattil et al. [219] reported the PV effect of the BFTO-4 thin films sandwiched between ZnO:Al transparent top electrode and SrRuO\(_3\) bottom electrode fabricated by PLD. This device exhibited a switchable photo-response, which is sensitive to polarization field and polarization direction, and the short-circuit photocurrent density (\(J_{sc}\)) and open-circuit voltage (\(V_{oc}\)) values are \(-6\) µA and \(-0.14\) V, respectively. Many parameters of the FE and electrode materials can affect the PV output, including remnant polarization, band gap, electrical conductivity, material/electrode interface, crystallographic orientations, microstructure, domain walls, and so on. Some attempts: band gap/interface/domain engineering) can be made to enhance PV efficiency or tune PV response of the BFTO-\(n\)-based devices. Bai et al. [220] investigated the PV behaviors regulated by band-gap and bipolar electrical cycling in Ho-doped BFTO-4 ferroelectric films, prepared via a chemical solution deposition. It was found that the PV response peak of Ho-doped BFTO-4 films shifts toward the visible region and the \(J_{sc}\) as well as \(V_{oc}\) are improved compared with the pure BFTO-4 films.

Zhu et al. [157] showed the polarization-regulated PV effect in CuO/BFTO-4 films fabricated on fluorine-doped tin oxide (FTO) glass substrate. For the Au/BFTO-4/FTO and Au/CuO/BFTO-4/FTO devices, the PV effect and power conversion efficiency of the BFTO-4 was improved by the addition of the CuO buffer layer, resulted from the formed p-n junction at the CuO/BFTO-\(n\) interface (Figure 13a). By applying pulse poled bias voltages of \(\pm 10\) V (Figure 13b), the \(J_{sc}\) and \(V_{oc}\) values are markedly enhanced and the switchable PV responses were observed, mainly due to the FE depolarization field. Cao et al. [29] reported the PV effect for \(c\)-axis preferentially oriented Bi\(_4\)NdTi\(_3\)FeO\(_{15}\) ceramics. The Ag/randomly oriented ceramic/ITO device exhibits larger \(J_{sc}\) and smaller \(V_{oc}\) than those of the Ag/\(c\)-axis oriented ceramic/ITO device. Bai et al. [221] reported the PV effect in heterostructural TbFe\(_2\)/BFTO-4 films (Figure 13d). The PV performances were modulated by the in-situ stress driven by magnetostriction of TbFe\(_2\) clusters under external magnetic fields, and the \(J_{sc}\) and \(V_{oc}\) values increase with the in situ stress, reaching 0.026 mA/cm\(^2\) and 9.5 V, respectively, under a maximum in-stress of 0.075 GPa (Figure 13g). Unfortunately, to the best of our knowledge, the reported BFTO-\(n\)-based devices only achieve the PV efficiency of \(<1\%\). However, using a semiconductor-based model with a charge distribution in the FE material that includes polarization surface charges, Schottky-induced space charges and screening charges in the electrodes [222], it has been estimated that an extremely high power conversion efficiency can be reached up to 19.5\%. Tremendous efforts made to enhance the PV efficiency are needed. Besides this, the origins of PV effect in the BFTO-\(n\) FE materials have also attracted a lot of research enthusiasm. So far, some origins have been proposed, such as the bulk PV effect, depolarization field driven PV effect, and domain wall theory. They all deserve further studies undoubtedly.
Figure 13. Photovoltaic (PV) performance of Bi$_5$FeTi$_3$O$_{15}$ (BFTO-4)/CuO films: (a) J-V curves of BFTO-4 and BFTO-4/CuO films under the same intensity of purple light; (b) J-V curves of BFTO-4/CuO films-based PV devices before and after polarization; (c) the ON–OFF curves of virgin and poled BFTO-4/CuO films at different poling voltages. Reproduced with permission from Ref. [157]. Copyright 2017, AIP Publishing. PV performance of TbFe$_2$/BFTO-4 heterostructural films: (d) sketched diagram and (e) cross-sectional SEM image of the heterostructural films; (f) RT P-E loops, (g) J-V curves, and (h) photocurrent response with light ON and OFF for the heterostructural films under in-situ stress. Reproduced with permission from Ref. [221]. Copyright 2019, AIP Publishing.

5. Outlook and Challenges

In this review, we summarized recent progress in the field of the synthesis of the BFTO-\(n\) materials and the modifications of their properties, and highlighted promising applications in the electronic industry, quantum devices, capacitors, transducers, microwave absorbers, catalysts, and photoelectric devices. Compared to BiFeO$_3$ and BiFeO$_3$-based materials, the BFTO-\(n\) materials not only keep giant polarization, high Curie temperature, and RT ME coexistence in the same phase, but also exhibit unique advantages, such as diversified modifications, larger ME effect (~400 mV/\(\text{Oe}\) cm$^{-1}$ at RT), low bandgap (1.28–2.5 eV), RT single-phase EB effect, microwave absorption, and excellent photo/electrocatalyst activity.

Especially, considerable efforts have been made in the studies of the ME multiferroic responses in the BFTO-\(n\). Firstly, confirming the intrinsic multiferroic properties of the BFTO-\(n\) are very critical for boosting the performances and promoting the practical use in functional devices. Because of some controversies about the origin of magnetism, intrinsic characterizations in ceramic bulks, thin films, and nanoparticles were addressed by both experimental and theoretical methods, especially the choices of preparation techniques and the use of proper measurements. Secondly, there is expectation to promote FE and FM properties by substituting other cations into different sites as well as changing the number of perovskite units, because manipulations of crystal structure can induce octahedral tilts and distortions, which largely influence structural and physicochemical functionalities. The strain-induced distortions are an interest topic, where chemical modification is often used.
to tailor the layered structures. In addition, the control of ceramic or thin film orientation can promote the performances. Thirdly, interfaces can influence electrical, magnetic and structural functionalities of the perovskite oxides. Interface engineering, such as interface from heterojunctions, interface between substrate and film and interface inside Aurivillius-type layered structure, exhibit several new physical effects and some excellent properties, achieved by interfacial structural distortion due to different strain states.

Indeed, some of the BFTO-\(n\) have been demonstrated with significant enhancement in selected functional properties, such as dielectric, FE, magnetic, and ME properties. A giant 2\(P_r\), of >50 \(\mu\)C/cm\(^2\) was achieved in doped BFTO-\(n\) ceramics and films, and a maximum ME coefficient as high as 400 mV/\(\text{Oe}\) cm\(^{-1}\) at RT was reported in BFTO-based composite films. The available control of FE domains by magnetic field and control of magnetic domains by electric field were demonstrated on the BFTO-4 thin film at RT. On the other hand, there is a rapid increase of research into other novel aspects. For example, RT EB effect in high-layer BFTO-\(n\) would add a new regulating factor for future device operation. Due to a relatively low and tunable band gap, photo/electro-catalyst activity and PV effect in the BFTO-\(n\) is attractive and promising, because of strong absorption of photons as well as high efficiency of separating photo-generated carriers. As the electric and magnetic dipoles are absorbers of microwaves, BFTO-based materials have been considered as candidates for microwave absorption.

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

1. **New strategies to improve properties.** Manipulations of micro-nanostructures and composition, substitutions of different ion-sites, and modulations of interfaces or layers were developed with the ultimate aim to boost FE and FM performances. Nevertheless, each design strategy applied alone results in the limited enhancement of the performances. Therefore, developing new strategies is an important and significant subject. The possibility of extending BFTO-\(n\) homologous series will be stimulated by the search for new Aurivillius phases containing various perovskite slabs. In-situ control of the strain inside the layer-structure may be a new strategy to realize the objective. Simultaneous symmetry and strain controlling, other perovskite-based derivatives, and phase-structure relations may be considered as methods to maximize performance advantages to meet the present demands. The study of quasi-continuous compositional changes across the homologous series may also be a strategy.

2. **Developing ME coupling and ME devices.** Encouragingly, the BFTO-\(n\) materials have already been demonstrated to show promising ME coupling at or above RT together with the ability to be driven by an external electric field or magnetic field. However, the majority of the reports regarding the ME effect are mainly based on individual experimental observations. The in-depth insight into the relationship between the structure/layers and ME effect of BFTO-\(n\) has not yet been systematically achieved. The mechanisms, mathematical modeling, theoretical simulation and size effect of the ME response for the BFTO-\(n\) remain to be clarified in details. A critical control of the BFTO-\(n\) thin films with precise composition and interface and the proper ME device designs for applications are an urgent need to develop. In addition, the BFTO-based ME composites are also a significant subject [223].

3. **Novel phenomena and functional applications.** Some fascinating phenomena in the BFTO-\(n\), such as EB effect, microwave absorption and PV effect, have been discovered. However, there is a rather long way for BFTO-based materials to go in terms of being applied in microwave absorbing materials and photovoltaic devices, given the poor absorptive capacity and low PV efficiencies, respectively. Meanwhile, the BFTO-\(n\) materials need to be further studied for new phenomena or effects, such as local order [224], electro-caloric effect [225], Raman effect [226], etc., and functional properties in other areas, for example, oxide ion conductors [227], ultraviolet detectors [228], solid-oxide fuel cell [229], energy storage [230], drug carrier [231], and so on.
(4) Multiple catalytic activity. The BFTO-\textit{n} materials are considered as a class of reasonable visible-light photocatalysts. Yet, it has been difficult to attain a high photocatalytic activity and be suitable for catalytic applications. Construction of the BFTO-based heterojunction may be the most effective way to further promote the photocatalytic activity. Furthermore, due to electrocatalytic activity, the electrochemical reduction of oxygen on the BFTO-\textit{n} catalysts was found. But few studies are focused on the mechanisms of OER, the influence of catalyst characteristics and reaction rate, and corrosion resistance, fabrication cost, and long-term stability for catalysts. More importantly, given the rich spectrum of the properties, including FE polarization, piezoelectric activity, and pyroelectric effect, multiple catalytic activity may be taken into consideration in the future, especially synergetic thermo-photo-catalysis [232] and sono-photo-catalysis [233], which will provide a major boost for the relevant technologies towards their aspirated commercialization.

(5) Other perovskite-based derivatives. Perovskite-based derivation is a useful approach to induce remarkable properties or discover fascinating phenomena of layered perovskites. Given a rich variety of structures, can BFTO-\textit{n} have other perovskite-based derivatives besides S-A type bismuth-based layered oxyhalides? Layered structures exhibit the same basic perovskite motif but with different connecting layers. There are some disputes on the connecting layers among these derivatives. A clear and general relationship between layer-stacked interfaces and properties needs to be established. This is essential for the design of BFTO-based derivatives with tailored properties linked to different applications.

In summary, single-phase layered multiferroics is one of the focus areas in functional materials research community and this field is poised to make significant breakthroughs. In this review, we have visited the progress and prospects of the Aurivillius-type BFTO-\textit{n} layered materials, where thorough fundamental understandings in structures and key properties are shown. We hope to provide an updated overview on the understanding and also highlighting of the existing issues that hinder the further development of the BFTO-based materials. With sustained and dedicated research efforts, we believe that these intriguing BFTO-\textit{n} functional materials would offer a new avenue to make the attractive multi-purpose technologies commercially viable.

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