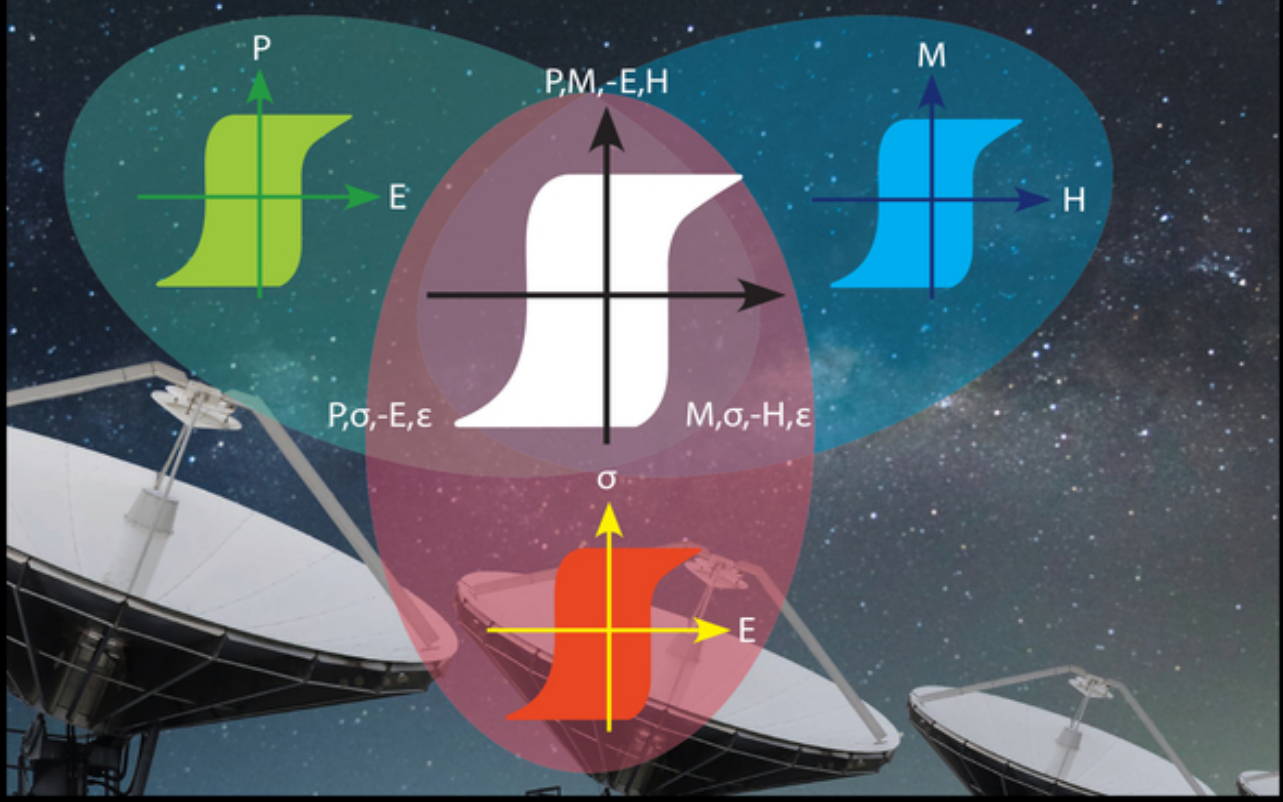


Edited by  
Ming Liu and Ziyao Zhou

# Integrated Multiferroic Heterostructures and Applications





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*Edited by Ming Liu and Ziyao Zhou*

**WILEY-VCH**

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## Preface

Multiferroic materials exhibit significant potential applications in the fields of novel multifunctional magnetic-electric devices, spintronics devices, and high performance information storage and processing, etc. Besides, multiferroic has become a hot topic due to its rich connotation in condensed matter physics concerning charge, spin, orbital, and lattice.

The possibility of an intrinsic magnetoelectric (ME) effect in some crystals had been predicted by Pierre Curie in 1894. The research on magnetoelectric physics and materials was quite slow in the whole twentieth century due to the rare of magnetoelectric materials and the poor magnetoelectric performance. Schmid coined a new terminology of multiferroics in 1994, which denotes the coexistence of multiple ferroic (ferroelectric, ferromagnetic and ferroelastic) orders in a single-phase material. The research on multiferroic materials resurged because of the two unexpected breakthroughs (epitaxy  $\text{BiFeO}_3$  thin films and  $\text{TbMnO}_3$ ) in 2003. It stimulated numerous subsequent investigations on single-phase multiferroic, multiferroic composites, and multiferroic heterostructures (oxides and metallic/ferroelectric).

### What is this Book?

The book presents a unified summary of multiferroic materials, multiferroic simulations and multiferroic prototype devices. Specifically, it covers a broad variety of multiferroic materials, including single phase multiferroic, oxides and metallic/ferroelectric multiferroic heterostructures, bulk, thin film and nanostructure multiferroic materials. And for each family of materials, their magnetoelectric coupling mechanisms and multiferroic simulations (first-principle calculation, phase simulation and theoretical modes of ME coupling in multiferroic heterostructures) are also extensively discussed. Some prototype devices, including tunable RF/microwave devices (antenna, inductor, bandpass/stop filters and phase shifter), multiferroic memories, multiferroic sensors and integration of multiferroics on chip were presented. Novel multiferroic composites and devices were also prospected. Given these rich contents, it provides readers an introductory overview of multiferroic materials and devices, both beneficial for beginner and experienced researchers. I believe that such a book will invaluable reference for the multiferroic community.

Meanwhile, there are numerous reviews on single-phase multiferroic, multiferroic composites, or multiferroic heterostructures, respectively. Theoretical

modes and prototype devices were briefly mentioned in these reviews. Books introducing widespread multiferroic materials and prototype devices together with the required basics and theory are rare. With this book, we fill this gap.

## Why this Book?

The book is aimed at advanced undergraduate and graduate students of the materials science, electronic devices design and physics. Since these are usually recruited from most natural sciences, i.e. physics, materials, electronic devices, we addressed the book to this readership. Readers would definitely profit from a sound knowledge of materials and physics. However, all authors are engaged in materials science, physics and electronic devices for many years and achieved outstanding achievements in these field. Hopefully, you will find that they came upon good solutions. In case you see room for improvement, please let me know.

## Is this Book for You?

Students, who require an in-depth knowledge, should begin at their level of knowledge, either in Chapters 1 (Introduction to multiferroics and its application) or 2 (Multiferroics materials). To deeply understand the physical mechanism of magnetoelectric coupling effect and simulations of multiferroic materials. Then, they should proceed through Chapters 3 (Mechanisms of multiferroic material) and 4 (Multiferroic simulations). Chapters 5–8 introduce the application and prototype devices of multiferroic materials and Chapter 9 prospects the novel multiferroic composites and devices. They should be studied according to interest and requirement.

## Acknowledgments

Finally, I would like to thank some people that contributed directly and indirectly to this book. First of all, I would like to name Prof. Dr. Nian X. Sun, Prof. Dr. Gopalan Srinivasan, Prof. Dr. Gail Brandon, Prof. Dr. Cewen Nan, and Prof. Dr. Shuxiang Dong. As mentioned, they encouraged me to write this book and given many valuable opinions during this project. Furthermore, I would like to thank all authors, including Dr. Bing Peng, Dr. Jing Ma, Prof. Dr. Chungang Duan, Dr. Xi Yang, Dr. Brandon Howe, Prof. Dr. Zhongqiang Hu, Prof. Dr. Zhiguang Wang, Dr. Menghui, Dr. Tianxiang Nan, Dr. Yuan Gao, and Dr. Qu Yang, who invested their expertise, time and energy in writing, correcting and finalizing their respective chapters. All are very respected colleagues, and some of them became friends during this project. Also, I acknowledge the project-editors responsible at Wiley-VCH for this project, Dr. Andreas Sendtko and Dr. Zai Yu, who sincerely supported this project and showed a very professional patience, when yet another delay occurred, but also pushed, when required.

## 1

## Introduction to Multiferroics and Its Application

Qu Yang, Bin Peng, Ziyao Zhou, and Ming Liu

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This chapter gives an introduction to multiferroics including the concept, characteristics, advantages, and existing researches toward potential applications. Voltage-controlled ferromagnetism based on multiferroic heterostructures is focused here because of the capacity for low energy dissipation, high signal-to-noise ratio, etc. We discuss the basic understanding and potential applications.

### 1.1 Concept of Multiferroics and the Existing Magnetization Manipulation Methods for Practical Applications

Of late, multiferroic materials have been very popular in spintronics [1]. They simultaneously occupy ferromagnetic (FM) and ferroelectric (FE) orders, enabling magnetism to be manipulated by an electric field ( $E$ -field) or vice versa [2–19]. Therefore, multiferroic materials are very promising in producing multifunctional, miniature, high-speed devices [1]. So far, several methods (e.g. electric currents, voltages, thickness, or temperature) based on multiferroic materials have been well established to manipulate magnetization to realize applications like sensors, magnetic random access memories (MRAMs), radiofrequency (RF)/microwave systems, and so on [20–22]. Methods like electric currents manage to control high-anisotropy magnetic cells through the current-induced spin/strain-transfer torque (STT), thus holding out prospects for magnetic devices like information storage devices [23]. Multiferroic devices with voltage controlling techniques have low energy dissipation and high signal-to-noise ratio due to the absence of electromagnets [18, 22]. These methods can largely reduce the accumulation of heat as well as increase the integrated quality by substitutional magnetoelectric (ME) coupling [18, 20]. Meanwhile, accompanied by increasing memory density and decreasing mass,

the voltage modulation is preferred for satellite, radar, and portable electronic devices where volume, mass, and energy consumption are precious [22].

## 1.2 Typical Multiferroic Heterostructures and Their Characteristics

Although extensive work has been carried out in single-phase multiferroic compounds like  $\text{BiFeO}_3$ , they are still limited in achieving controllable modulation with ME coupling while at room temperature [24]. On the contrary, multiferroic heterostructures that integrate individual magnetic and FE materials have strong room-temperature ME effects, and are more likely to be utilized in ME devices in the near future [24]. Besides, they are also favored for the flexibility of material choices and device designs [24]. Multiferroic heterostructures, like  $\text{Fe}_3\text{O}_4/\text{PMN-PT}$  (lead magnesium niobate–lead titanate),  $\text{FeGaB/Si/PMN-PT}$ , and YIG (yttrium iron garnet)/PMN–PT, have been explored on the basis of particular FE crystal material (PMN–PT) with a large piezoelectric coefficient [1, 5]. With the external electric field (E-field) applied along the PMN–PT substrates, these heterostructures should obtain strains and charge accumulations [1, 20]. It provides a great opportunity for the adjacent magnetic layers to achieve magnetic anisotropy and, eventually, to obtain a large change of ferromagnetic resonance (FMR) through the inverse magnetoelastic coupling [1, 20]. What is more, it is also demonstrated that FM/FE heterostructures are exceptionally useful in the applications of STT random access memory due to the strain-induced magnetostatic surface spin waves as well as the strain-controlled repeatable and nonvolatile magnetic anisotropy reorientation [20]. Here, we mainly focus on the voltage-controlled ferromagnetism based on multiferroic heterostructures and discuss recent progress in the fundamental understanding and the potential applications.

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## 2

## Multiferroic Materials

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### 2.1 Introduction

Ferromagnets, generated by the spontaneous, uniform orientation of atomic or molecular magnetic moments, have been investigated for more than 2500 years and just unfolding [1]. Ferroelectricity, named so based on the likeness to ferromagnetism, was discovered merely a century ago. Multiferroic materials [2] with the coexistence of at least two ferroic orders have recently aroused ever-growing attention because of their potential for significantly broadening applications. On the one hand, they combine the performances of two materials that were formerly separate from different fields. On the other hand, the coupling interaction between the various states can produce added functionalities not present in either state alone, such as the magnetoelectric (ME) effect discovered more than a century ago [3, 4].

The ME response can be divided into two categories. One is the direct ME effect, which produces an electric polarization  $P$  by applying a magnetic field  $H$ :

$$\Delta P = \alpha \Delta H \text{ or } \Delta E = \alpha_E \Delta H \quad (2.1)$$

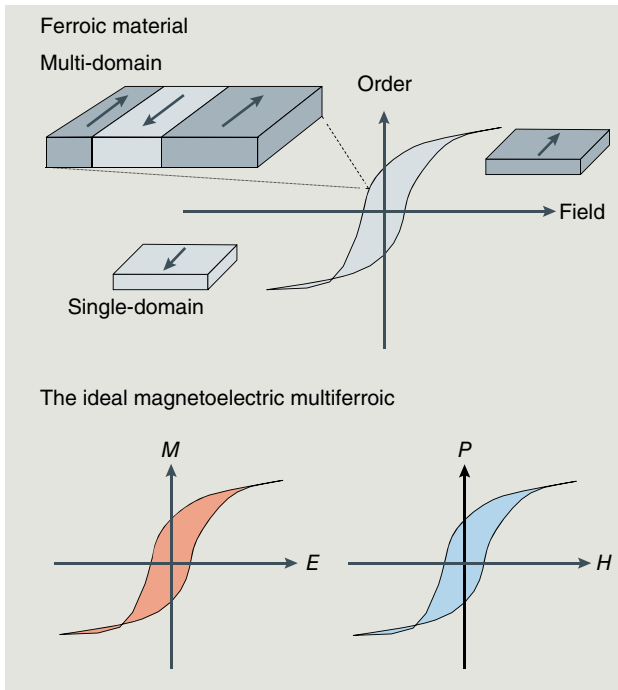
where  $E$  denotes the electric field and  $\alpha(\alpha_E)$  is the ME (ME voltage) coefficient.

The other is the simultaneously converse ME effect, that is, the emergence of magnetization  $M$  upon applying an electric field  $E$ :

$$\Delta M = \alpha \Delta E \quad (2.2)$$

In a multiferroic material, where ferroelectric, ferromagnetic, as well as a strong enough ME coupling coexist ideally, the electric (magnetic) polarization–magnetic (electric) field curves ( $P$ – $H$  or  $M$ – $E$  curves) would show a hysteresis response, as schematically demonstrated in Figure 2.1, which resemble the celebrated ferroelectric or ferromagnetic hysteresis loops.

From the viewpoint of physical architectures, multiferroic materials can be classified into two types: single phase and composite. The intrinsic ME coupling exists in some natural monophasic substances and has been found in more than 10 compounds so far such as BiFeO<sub>3</sub> (BFO) and rare earth manganates.



**Figure 2.1** Schematic illustration of an ideal case of the multiferroics [1]. There is a  $P$ - $H$  or  $M$ - $E$  hysteresis loop similar to the celebrated ferroelectric or ferromagnetic hysteresis loops.

However, the applications of most single-phase compounds are strictly limited due to the low Curie temperatures (below room temperature) and a weak inherent ME coupling (especially above room temperature).

Alternatively, multiferroic ME composites [5–7] combining ferroelectric and ferromagnetic phases have been gradually coming into view and have become “hot.” In ME composites, remarkable ME coupling can be produced because of the cross-interaction between the phases although neither of the constituent phases has ME effect, which was first proposed by Van Suchtelen as a product tensor property [7]. Generally, the composite ME coupling is the product effect of the magnetostrictive effect (magnetic/mechanical effect) in the ferromagnetic phase and the piezoelectric effect (mechanical/electrical force) in the ferroelectric one, namely [8],

$$\begin{aligned}
 \text{Direct ME effect} &= \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electric}} \\
 \text{Converse ME effect} &= \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}
 \end{aligned} \tag{2.3}$$

Overall, ME composites have much larger ME effect at room temperature than single-phase compounds, which makes the practical application of multiferroic

materials a significant step forward. Thus, various ME composites have been investigated recently, from bulk ME composites to thin films.

However, the research history of ME materials is not smooth sailing. In 1894, Curie pointed out through symmetry analysis that there might be intrinsic ME coupling effect in some crystals. In 1961, American scientists first reported the essential ME effects observed in  $\text{Cr}_2\text{O}_3$  at low temperatures, which led to a small climax in the early studies of ME effects in the 1970s. At the same time, the concept and materials of ME composite appeared for the first time. However, due to the lack of practical applications, the limitation of low-temperature conditions, and the complexity of the coupling mechanism involved, all related studies entered a low glacial period of nearly 30 years. In the recent 10 years, with the tremendous progress of material preparation technology, characterization means, and theoretical calculation, as well as the urgent need for new information functional devices in the modern information society, research on multiferroic materials and methods has witnessed unprecedented rapid development [9].

## 2.2 Single-Phase Multiferroics

According to the mechanism of formation, we can divide many magnetoelectric multiferroic materials into four main categories [10]:

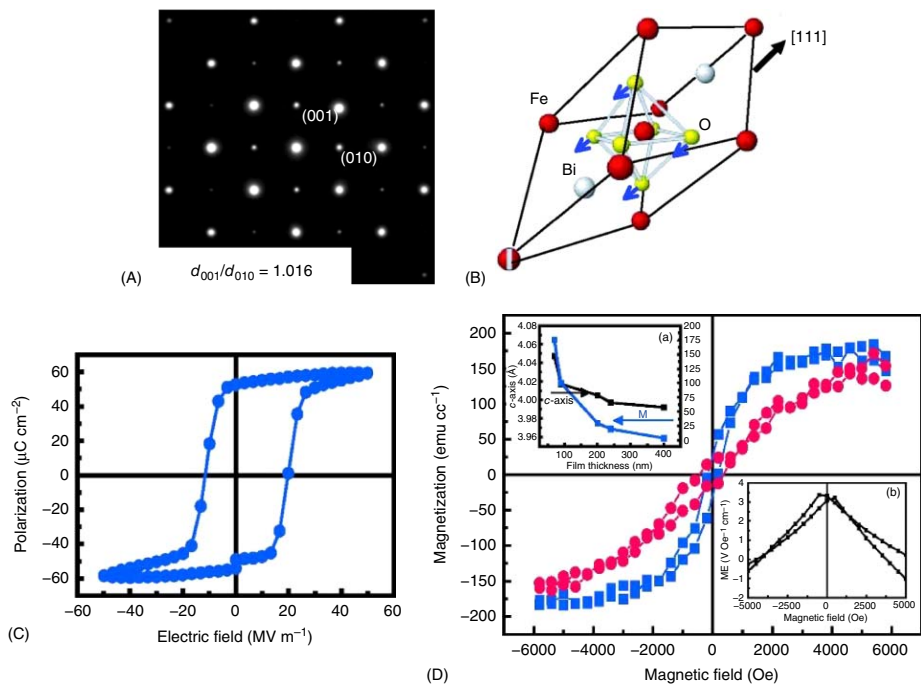
- (1) Perovskite-type compounds such as BFO,  $\text{BiMnO}_3$  (BMO), and  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ . In these materials, the only pair of 6s electrons of Bi ions at A site of perovskite provides a ferroelectric order, while the 3d transition metal electrons at B site provide a spin order. In general, the ferroelectric properties of these materials are first-order order parameters, which make the electric field actively interact with the spin.
- (2) Structural dislocation materials, commonly known as rare earth manganites such as  $\text{RMnO}_3$  ( $R = \text{Sc}, \text{Y}, \text{etc.}$ ) and  $\text{RMn}_2\text{O}_5$  ( $R = \text{Y}, \text{Tb}, \text{etc.}$ ). In this kind of material, the ferroelectric polarization temperature is usually higher than room temperature, but the ME coupling can be formed at antiferromagnetic Neel temperature ( $\sim 70 \text{ K}$ ).
- (3) Magnetic charge ordered materials, represented by  $\text{LuFe}_2\text{O}_4$ . The ionic non-centrosymmetry in such materials leads to ferroelectric polarization.
- (4) Multiferroic bulk materials, represented by  $\text{TbMnO}_3$  and  $\text{DyMnO}_3$ . Their ferroelectricity is based on the long-range order of spin in magnetic materials.

Undoubtedly, the most widely studied single-phase ferroelectric material is  $\text{ABO}_3$ -type perovskite oxide. In ferroelectric materials with this structure, most of the ferroelectricity originates from B-position ions located in the center of the oxygen octahedron, which deviates from the center of the oxygen octahedron below Curie temperature, reducing the symmetry of crystal structure and separating the positive and negative charge centers to form electric dipole

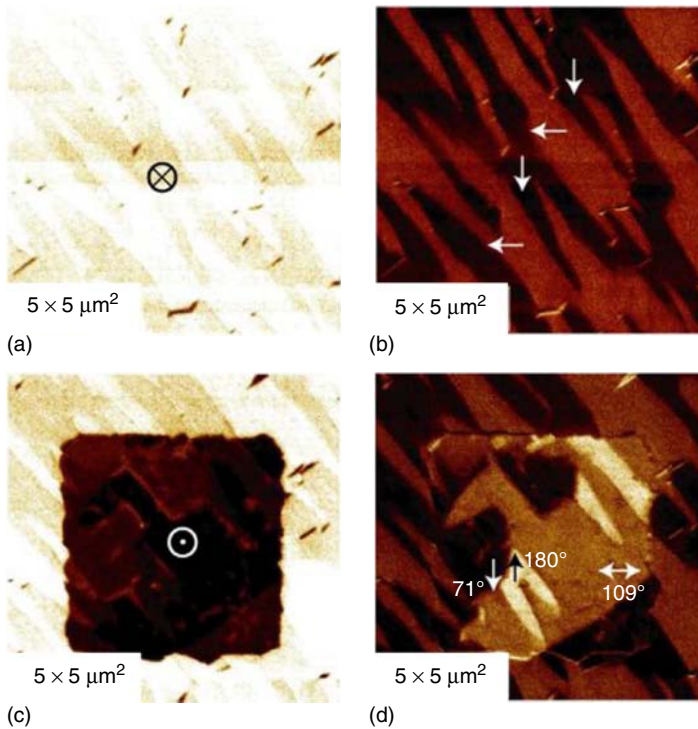
moments. Generally,  $ABO_3$ -type perovskite ferroelectrics have no electron occupation in the d orbit of B ions and behave as  $d_0$  states. On the contrary, it is impossible to produce any magnetic order because of the absence of local magnetic moments resulting from vacancies in electrons in the d orbit, which indicates that the mechanisms of conventional ferroelectric and magnetic orders are mutually exclusive at the atomic scale. Therefore, an additional driving force that satisfies both the structural symmetry condition of ferroelectric crystals and the electronic shell structure condition of magnetic crystals is vital.

From past research, there is no doubt that the most striking single-phase multiferroic is BFO, in bulk, nanoparticles, or in thin films [11]. BFO is the only material with ferroelectric Curie temperature and antiferromagnetic Néel transition temperature much higher than room temperature (which can realize ferroelectricity at room temperature and coexist with antiferromagnetism), and also with strong ME coupling characteristics, which thus can achieve field-controlled magnetization. The research upsurge originated from the study of BFO thin films epitaxially grown on (001)  $SrTiO_3$  (STO) single crystal substrates by pulsed laser deposition (PLD) reported by Ramesh's group [12] in 2003, as shown in Figure 2.2. In this study, for the first time, they observed remarkable ferroelectric properties with full electrochemical strength  $P_s = 50\text{--}60 \mu\text{C cm}^{-2}$  and magnetization  $M_s = 150 \text{ emu cm}^{-3}$ . It is understood that the ferroelectric order and magnetic order in BFO originate from the contributions of different ions, namely, Bi ions and Fe ions, which leads to weak intrinsic coupling. For example, the ME coefficient of La-doped BFO thin films calculated by Jang et al. [13] is about  $10 \text{ mV cm}^{-1}$ . Subsequently, Zhao et al. [14] succeeded in observing one-to-one correlations and coupling relationships between ferroelectric and antiferromagnetic orders in BFO by piezoelectric force microscopy (PFM) and X-ray magnetic circular dichroism–X-ray photoemission electric microscopy (XMCD–PEEM), as shown in Figure 2.3. On this basis, ME coupling is only found at specific polarization reversal (e.g.  $109^\circ$  and  $71^\circ$ ) [15]. Eom and coworkers [16] realized selective polarization reversal on nanoscale by scanning electric probe field, which laid the foundation for electrical field control of the antiferromagnetic direction in rhombic phase BFO. In addition, since the tetragonal BFO epitaxial crystals were synthesized, the ME effect has attracted widespread attention. Yang and coworkers [17] found that the ferroelectric Curie point and antiferromagnetic Néel temperature in tetragonal BFO occur at about 380 K at the same time through permeability measurement. This temperature is above the ferroelectric phase transition temperature, at which the antiferromagnetic structure will be destroyed, which means that the two order parameters have a strong interaction.

Although the application potential of BFO is universally acknowledged, it suffers from limitations due to some inherent problems, such as a narrow temperature range of phase stabilization, formation of impurity phase ( $Bi_2Fe_4O_9$ ,  $Bi_{25}FeO_{39}$ , etc.) during processing, and leakage problems [18]. Hence, various measures, such as (i) introducing some suitable elements of the Bi/Fe sites, (ii) fabricating robust solutions or composites with polar and nonpolar structure,



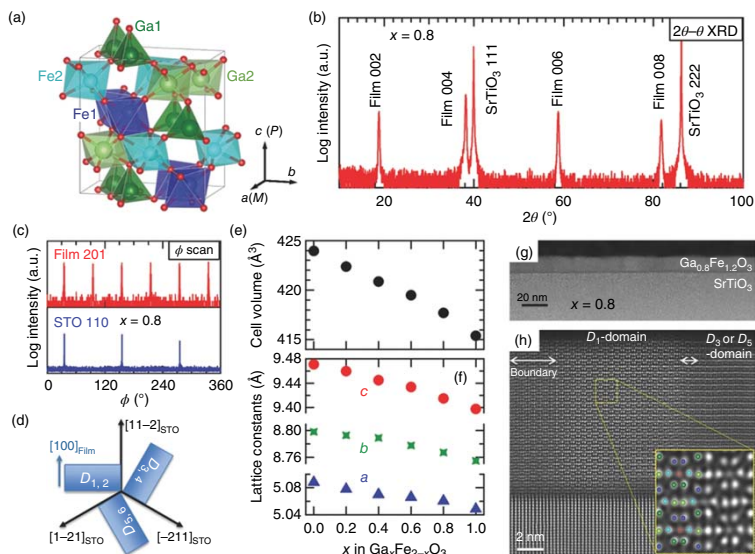
**Figure 2.2** (A) The selected area electron diffraction pattern confirms the structure distortion. (B) Schematic of the prototypical rhombohedral BFO unit cells. (C) A ferroelectric hysteresis loop measured at a frequency of 15 kHz. (D) The in-plane (blue) and out-of-plane (red) magnetic hysteresis loops measured by vibrating sample magnetometry for a 70-nm-thick BFO film. Inset (a) shows the thickness dependence of saturation magnetization. Inset (b) is a preliminary ME measurement result [12].



**Figure 2.3** (a) and (b) Out-of-plane (a) and in-plane (b) PFM images of the BFO film.  $\otimes$  and the arrows represent the directions of out-of-plane and in-plane ferroelectric polarization components, respectively. (c, d) Out-of-plane (c) and in-plane (d) PFM images taken after applying an electric field perpendicular to the film in the same area as in (a, b).  $\odot$  Indicates that the out-of-plane polarization component was switched by the applied electric field. The arrows in (d) indicate new in-plane polarization directions after ferroelectric switching. Different polarization switching mechanisms are labeled in (d) [14].

(iii) developing new processing techniques, and (iv) introducing tetragonal ferroelectric phase have been undertaken [19–26]. Multiferroic  $\text{Ga}_x\text{Fe}_{2-x}\text{O}_3$  ( $x = 0-1$ ) epitaxial thin films with ferroelectric and magnetic properties at room temperature have been fabricated. Room-temperature out-of-plane ferroelectricity at  $x = 0-1$ , in-plane ferrimagnetism with a Curie temperature  $>350$  K at  $x = 0-0.6$ , and room-temperature magnetocapacitance effects have been observed, as shown in Figure 2.4 [27]. A  $0.85 \text{ BiTi}_{0.1}\text{Fe}_{0.8}\text{Mg}_{0.1}\text{O}_3-0.15 \text{ CaTiO}_3$  solid solution thin film deposited by PLD showed both ferroelectricity and magnetism at room temperature with ME coupling. Note that ferroelectric domains and magnetic domains could be switched by a magnetic field, electric field, and mechanical force, indicating the existence of cross-coupling [28].

To date, added single-phase compounds have been proposed continuously through first-principles calculations and fine experiments, including boracite such as  $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$  ( $\text{M} = \text{Cr}, \text{Mn}, \text{etc.}, \text{X} = \text{Cl}, \text{Br}$ ) as well as  $\text{BaMF}_4$  compounds ( $\text{M} = \text{Mg}, \text{Mn}, \text{etc.}$ ).



**Figure 2.4** (a) Crystal structure of the  $\text{GaFeO}_3$  unit cell ( $Pna2_1$ ). Spontaneous polarization ( $P$ ) and magnetization ( $M$ ) appear parallel to the  $c$ - and  $a$ -axes below 1368 and 200 K, respectively. (b) XRD  $2\theta$ - $\theta$  pattern. (c)  $\phi$  scan for the  $\text{Ga}_{0.8}\text{Fe}_{1.2}\text{O}_3$  film deposited on the STO (111) substrate. (d) Schematic image of (f) the domain structure in the film viewed by the  $c$ -axis. (e) Cell volume and (f) lattice are constant for the  $\text{Ga}_x\text{Fe}_{2-x}\text{O}_3$  films as a function of  $x$ . (g) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the  $\text{Ga}_{0.8}\text{Fe}_{1.2}\text{O}_3$  film with  $[11-2]_{\text{STO}}$  zone axis. (h) Expanded HAADF-STEM image around the interface between the film and substrate. The inset shows the magnified image. Green, light green, light blue, and blue points show atoms at the Ga1, Ga2, Fe1, and Fe2 sites, respectively [27].

## 2.3 Bulk Composites

Since Van Suchtelen first proposed the concept of the composite ME effect in 1972, the bulk ME composites have undergone tremendous development [5]. Before 2000, scientists did not pay much attention to the particulate ceramic composites [29] of ferrites and BaTiO<sub>3</sub> (BTO) or Pb(ZrTi)O<sub>3</sub> (PZT). Therefore, most of the research in that period was based on theoretical analysis, and there was little progress in experimental research. But these academic studies provide a qualitative understanding of the ME coupling of bulk composite materials. The turning point appeared in the early 2000s. The landmark event was the discovery of the rare earth iron alloy Tb<sub>1-x</sub>Dy<sub>x</sub>Fe<sub>2</sub> (Terfenol-D) containing the giant magnetostrictive in 2001, which led to the appearance of the Terfenol-D-based bulk composites exhibiting giant magnetoelectric (GME) response (with an ME voltage coefficient of larger than 1 V cm<sup>-1</sup> Oe<sup>-1</sup>) both in theoretical [30] and experimental works [31, 32]. It was widely believed to have great potential in the application of ME devices. To date, all kinds of bulk composites with various connectivity schemes (e.g. 0-3 type particulate composites, 2-2 type laminate composites, and 1-3 type fiber/rod composites) have been explored. Some current ME bulk composites were summarized as shown in Table 2.1[60].

**Table 2.1** Some ME bulk composites and their ME coefficients[60].

ME composite <sup>a)</sup>	ME coefficient (mV cm <sup>-1</sup> Oe <sup>-1</sup> ) <sup>b)</sup>	References
<i>Ceramic composites</i>		
(0-3) CFO/BTO	50@ $f_r$	[29]
(0-3) NZFO/PZT	155@1 kHz	[33]
(2-2) NCZF/PZT/NCZF	782@1 kHz	[34]
<i>Ceramic-alloy composites</i>		
(2-2) Terfenol-D/PMT-PT	10.3 × 10 <sup>3</sup> @1 kHz	[35]
(2-2) Terfenol-D/PVDF	1.43 × 10 <sup>3</sup>	[36]
(2-1) FeBSiC/PZT-fiber	22 × 10 <sup>3</sup> @1 Hz and 750 × 10 <sup>3</sup> @ $f_r$	[37, 38]
(2-2) FeBSiC/PVDF	21.46 × 10 <sup>3</sup> @20 Hz	[39]
(2-2) FeCoSiB/AlN	3.1 × 10 <sup>3</sup> @1 Hz and 737 × 10 <sup>3</sup> @ $f_r$	[40]
<i>Polymer-based composites</i>		
(2-2) PZT in PVDF/Terfenol-D in PVDF	80@1 kHz and 3 × 10 <sup>3</sup> @ $f_r$	[41]
(1-3) Terfenol-D in epoxy/PZT	500@100 Hz and 18.2 × 10 <sup>3</sup> @ $f_r$	[42]
(0-3) CFO/P(VDF-TrFE)	40@5 kHz	[43]

a) CFO, CoFe<sub>2</sub>O<sub>4</sub>; NZFO, Ni<sub>0.8</sub>Zn<sub>0.2</sub>Fe<sub>2</sub>O<sub>4</sub>; NCZF, Ni<sub>0.6</sub>Cu<sub>0.2</sub>Zn<sub>0.2</sub>Fe<sub>2</sub>O<sub>4</sub>; PMN-PT, Pb(Mg,Nb)O<sub>3</sub>-PbTiO<sub>3</sub>; PVDF, polyvinylidene-fluoride; P(VDF-TrFE), poly(vinylidene fluoride-trifluoroethylene).

b)  $f_r$ , electromechanical resonance frequency.

### 2.3.1 Ceramic Composites

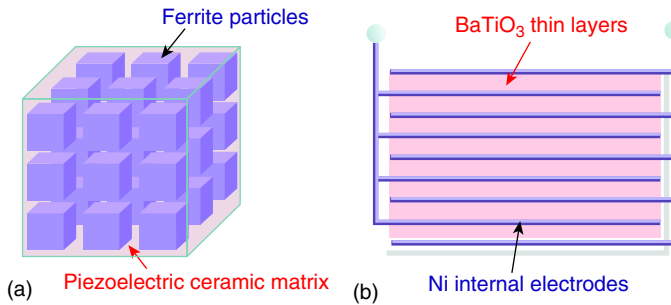
Work on the in situ synthesis of ME composite ceramics started in Philips Laboratories [29, 44–46]. It was a eutectic composition of the quinary system Fe-Co-Ti-Ba-O prepared by unidirectional solidification. The results showed that the composite exhibited a very high ME voltage coefficient, namely  $\alpha_E = 50 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ , because of the excess of  $\text{TiO}_2$  (1.5 wt%). Subsequently, a more simple and economic sintering process makes ceramic composites combined with widely different crystal structures appear because the presence of eutectic or eutectoid transformations is not required, and thus becomes a widely used preparation process.

In general, a bulk ME ceramic composite can be obtained by selecting combinations of ferroelectric oxides and magnetic oxides (mainly ferrites) via co-sintering at high temperatures. The ME effect so far observed in such composites is around 10 times or lower than predicted, however, attributed mostly to atomic interfacial interdiffusion and/or reaction problems as well as thermal expansion mismatch between two ceramic phases during the co-sintering process. Until recently, the focus has been on ways to reduce the sintering temperature of ceramics to alleviate this problem. Nevertheless, lower sintering temperature would lead to incomplete sintering and low density, which would also affect the properties of materials. Accordingly, novel sintering technologies, which can avoid element interdiffusion while increasing sintering density, such as spark plasma sintering (SPS) [47, 48] and microwave sintering [49], are taken advantage of to prepare composite ceramics. Nan et al. [5] took the lead in preparing granular composite ceramics by SPS method. The ME voltage coefficient of the ceramics is increased by about 25% compared with that of the ceramics sintered by conventional method because no reaction and obvious mutual diffusion occur between the two phases by adjusting the sintering process.

Generally speaking, composite ceramics are divided into two types, namely, 0-3 type particulate ceramic composites and 2-2 type laminate composite ceramics.

For the 0-3 type particulate ceramic composites, ceramic composites obtained by conventional sintering process had minimal ME coupling (about  $1 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ ) [50–56] in the early days. Until the 2000s, higher ME coefficients of about  $10\text{--}100 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ , mostly attributed to a homogeneous and well-dispersed microstructure as well as the large grain size of the matrix phase, have been obtained by carefully controlling the sintering processing and composition. For example, Ryu et al. [57] found a high ME voltage coefficient of  $115 \text{ mV cm}^{-1} \text{ Oe}^{-1}$  at 1 kHz for the 0-3 particulate Ni-ferrite/lead zirconate titanate (NFO/PZT) composites. However, these experimental values are still lower than the calculated values, as described above. SPS is an efficient solution. Besides, the core-structured shell particles with ferrite core and piezoelectric shell [58, 59] are often adopted to avoid direct contact of ferrite particles during high-temperature process because of the leakage problems resulting from ferrites' conductivity and semiconducting, as shown in Figure 2.5a.

By comparison, the 2-2 type laminate composite ceramics featuring metagenic ferrite and piezoelectric oxide layers possess high ME coefficients on account of



**Figure 2.5** Schematic illustrations of (a) an ideal 0-3 type ME bulk composite with a high concentration of magnetic (ferrites) particles well dispersed into a piezoelectric matrix. (b) A 2-2 type ME bulk composite: commercialized MLCC with alternating BaTiO<sub>3</sub> ferroelectric layers and ferromagnetic Ni internal electrodes [60].

elimination of the leakage problem and much larger anisotropy than the particulate ones. For instance, a high ME voltage coefficient of up to  $0.4 \text{ V cm}^{-1} \text{ Oe}^{-1}$  was observed on a laminate NFO/PZT multilayer stack [61–64]. However, a loss of the direct ME output signal exists in the laminate composite ceramics due to the low conductivity of the ferrite layer as the conductive electrode. Thus, internal electrodes (e.g. Ag, Ni, and Ag–Pd) can be introduced between the piezoelectric and magnetic layers. Islam et al. [34] reported that the introduction of Ag–Pd inner electrode into the three-layer composite ceramics of nickel ferrite/PZT/nickel ferrite resulted in a significant increase in the magnetoelectric voltage output of the ceramics. Well-commercialized multilayer ceramic capacitors (MLCCs) are well-designed ME sensors [65], consisting of BTO thin layers and ferromagnetic Ni internal electrodes (Figure 2.5b). Their laminar structure simplifies strain fields, thus enhancing ME coupling; their large capacitance is in favor of generation of sizeable magnetically induced output charges. The mass-produced cheap MLCC-ME sensor can be operated at room temperature with highly reproducible cross-field cycles and temperature cycles [65]. By wiring the capacitor plates in series, the direct ME sensitivity could be significantly improved. Thus, MLCCs could be used as magnetic-field sensors in a variety of fields, due to their very low cost.

Interface control during high-temperature sintering is also important, which is similar to the 0-3 type particulate composites; thus, low-temperature processing and deposition techniques of films have recently been employed instead of high-temperature co-sintering [34, 66, 67]. Ferroelectric films (e.g. BTO and PZT) can be directly grown on the dense ferrite ceramics by PLD or low-cost solution spin-coating method, which only needs to be annealed at low temperatures (e.g. around  $600\text{--}700^\circ\text{C}$ ), much lower than co-sintering temperatures. Nan and coworkers [67] proposed an idea of directly growing another ceramic film on a compact ceramic substrate at low temperature to prepare laminated ceramic magnetoelectronic composites. For example, the PZT ceramic membrane was directly grown on ferrite ceramic substrate by a sol–gel method, by which rapid annealing at  $650^\circ\text{C}$  was carried out, thus achieving the low-temperature preparation of laminated composite ceramics, which is far below the traditional co-firing temperature above  $1200^\circ\text{C}$ .