Recent progress in multiferroic materials

WU Liang, GAO Ya & MA Jing*

School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

Multiferroic materials, by definition, process two or more ferroic order parameters. For example, the coexistence of spontaneously polarization and spontaneous magnetization enables coupling between polarization and magnetic field (direct magnetoelectric effect), or between magnetization and electric field (converse magnetoelectric effect). Multiferroic materials have attracted increasing interest in the past decade. Such coupling effects in multiferroics can be exploited to implement additional functionalities on existing devices or to design some novel multifunctional devices, such as memory devices, tunable microwave devices, sensors, and spintronic devices [1,2]. Various single-phase and composite multiferroic materials respectively integrate magnetism and ferroelectricity intrinsically and artificially, and have been achieved by the developed materials synthesis methods. The rapid development of characterization techniques has led to deeper understanding in fundamental physics and applications. In this context, *Chinese Science Bulletin* provided a platform for materials and physics scientists to share their understanding on several hot topics in multiferroic materials research, and demonstrated their significant contributions to some specific questions of common interest.

The magnetoelectric (ME) effect has been observed as an intrinsic effect in some compounds, which have been under intensive study recently [3]. So far, over tens of different compound families have been widely investigated as multiferroic ME materials, such as BiFeO_3 (BFO) and rare-earth manganates. Although the intrinsic ME effect exists in the single-phase compounds, most multiferroic compounds exhibit low Curie temperatures (below room temperature), and a high inherent ME coupling (especially above room temperature) has not yet been found in the single-phase compounds. Among them, BFO, with the typical

ABO_3 perovskite structure, is unique with high Curie and Neel temperatures far above room temperature, and thus most widely investigated. The anti-ferromagnetism of BFO originates from the super-exchange effect of the magnetic transition metal ions Fe^{3+} with a 62 nm space-modulated spin spiral structure, and the ferroelectricity results from particular orientation of the lone pair electrons of Bi^{3+} . Even though the multiferroicity of BFO comes from different physical origins, the two orderings are able to couple through crystal and electrical structure. Thus, the anti-ferromagnetic order would be switched by electric field. In this scenario, BFO is expected to be a lead-free candidate in piezoelectric devices, ferroelectric random access memory (FeRAM) and voltage control of magnetic random access memory (MRAM) [4]. However, the practical applications of BFO are hindered by some drawbacks: the electrically induced breakdown, high leakage current density, relatively small remanent polarization, poor fatigue behavior, the easy transformation of Fe^{3+} and Fe^{2+} ions and the oxygen vacancies in BFO and BFO-based ceramics. Hussain et al. [5] summarized the progresses in improving the multiferroic properties of BFO-based ceramics by means of optimizing sintering method and doping with certain rare earth elements in pure BFO. They pointed out that the densities of oxygen vacancies and Fe^{2+} in BFO-based ceramics could be remarkably reduced by liquid-phase sintering method, thus a high breakdown electric field ($E > 150$ kV/cm) was achieved. In addition, the effects of rare earth ions doping of $\text{Bi}_{1-x}\text{A}_x\text{FeO}_3$ ($\text{A} = \text{Nd, La, Dy, Sm, Eu and Pr}$) were summarized in details. Appropriate doping can improve the piezoelectric properties by introducing the morphotropic phase boundaries (MPB), and destroying the space-modulated spin spiral structure. The weak ferromagnetism can be unlocked, and then it results in more significant ME coupling. Co-doping of La and Co has been employed to improve the electrical properties of BFO. Wu et al.

*Corresponding author (email: ma-jing@tsinghua.edu.cn)

[6] successfully prepared $\text{Bi}_{0.97}\text{La}_{0.03}\text{Fe}_{0.90}\text{Co}_{0.10}\text{O}_3$ thin films with improved electric properties, i.e., the remnant polarization $2P_r \sim 175.6 \mu\text{C}/\text{cm}^2$, coercive field $2E_c \sim 699.5 \text{ kV}/\text{mm}$, dielectric constant $\epsilon_r \sim 257$, $\tan\delta \sim 0.038$ and an enhanced fatigue behavior.

Besides BFO, some other Bi-containing systems, such as Aurivillius phase materials (layered structure containing Bi_2O_2 layers alternating with perovskite-type layers), have been considered as the candidates for single-phase multiferroics. Wang et al. [7] synthesized a new Aurivillius phase $\text{Bi}_9\text{Fe}_{4.7}\text{Me}_{0.3}\text{Ti}_3\text{O}_{27}$ (Me=Fe, Co, Ni, Mn) with an eight-layer structure by a citrate combustion method. Both ferromagnetic and ferroelectric properties can be enhanced by Co or Ni substitution, and depressed by Mn substitution. Among them, $\text{Bi}_9\text{Fe}_{4.7}\text{Co}_{0.3}\text{Ti}_3\text{O}_{27}$ exhibited the largest remnant polarization, and the largest remnant magnetization with a Curie temperature about 764 K, while $\text{Bi}_9\text{Fe}_{4.7}\text{Ni}_{0.3}\text{Ti}_3\text{O}_{27}$ had the largest spontaneous magnetization. In $\text{Bi}_9\text{Fe}_{4.7}\text{Co}_{0.3}\text{Ti}_3\text{O}_{27}$ and $\text{Bi}_9\text{Fe}_{4.7}\text{Ni}_{0.3}\text{Ti}_3\text{O}_{27}$ the enhancement of the ferromagnetic properties has been attributed to the spin canted moment arising from the Dzyaloshinskii-Moriya interaction and the magnetic ions exchanging interactions ($\text{Fe}^{3+}\text{-O-Co}^{3+}$ or $\text{Fe}^{3+}\text{-O-Ni}^{3+}$) in the magnetic ion-based sublattices.

Another flourishing candidate for single-phase multiferroic materials is the hexagonal manganite, which exhibits intriguing physical phenomena. In this series, hexagonal RMnO_3 , where R=Y, Nd, Ho, Tm, Lu, Yb, Tb, Dy, Gd, Sm, etc. (as well as element doping on the A site), has been intensively studied. Among them, YMnO_3 (YMO) is a typical prototype. Although the ferroelectricity and A-type anti-ferromagnetism were found in bulk YMO in early 1960s, the origin of ferroelectricity has not been clearly explained until 2004 [8], considering the combination action of the long range dipole-dipole interactions and oxygen rotations. Meanwhile, manipulating both the ferroelectricity and magnetism in YMO has been continually studied. For instance, substitution for Y with other metal elements was an effective and easily achievable method. Based on this understanding, Wang et al. [9] investigated the magnetic properties, ferroelectric polarization and domain structure of YMO with In substitution for Y ($\text{Y}_{1-x}\text{In}_x\text{MnO}_3$). The results indicated that low-temperature magnetic properties including magnetic transition could be significantly tuned by In substitution. Besides, the ferroelectric polarizations of $\text{Y}_{1-x}\text{In}_x\text{MnO}_3$ were suppressed with the increase of In content x along with the observably decrease of ferroelectric vortex domain size.

Besides optimizing properties of the above-mentioned BFO and hexagonal manganites, more multiferroic compounds containing rare earth and transition metal elements have been synthesized and demonstrated to exhibit very unusual structural and physical properties. Hu et al. [10] systematically summarized the rare earth orthoferrite crystals, rare earth titanate strained film, and rare earth-based

superlattices to provide a broad overview on their promising electric, magnetic, and structural properties. As an example, Tan et al. [11] observed unexpected ME coupling in $\text{BaFe}_{12}\text{O}_{19}$ ceramic by doping rare earth La element on Ba site. The doped sample $\text{La}_{0.1}\text{Ba}_{0.9}\text{Fe}_{12}\text{O}_{19}$ exhibited large ferroelectricity and strong ferromagnetism simultaneously. Furthermore, the ferroelectric polarization can be actuated by an applied magnetic field, indicating the existence of coupling effect which has not been observed in pure $\text{BaFe}_{12}\text{O}_{19}$.

Compared to single-phase multiferroic, multiferroic composites integrating individual magnetic and ferroelectric materials provide a new perspective of artificial material design. The robust room-temperature ME effects and flexibility for materials choices and device designs make them more likely to be utilized in ME devices in the near future. In particular, kinds of ME composites have been implemented in several laboratory device prototypes, based on both direct ME effect (e.g., magnetic sensors) and converse ME effect (e.g., electric field write magnetic recording and electrically tunable microwave devices) [12]. For example, ME composite based magnetic sensors, taking the advantages of low cost, high sensitivity, compact size, broad operating temperature range, are competitive in traditional sensors market. However, the noise would always limit the sensitivity in application. In a ME sensor, there are three main noise sources: thermal noise introduced via pyroelectric currents, vibration or acoustic noises introduced via the piezoelectric effect, and electric noises from the detecting circuits. The former two are intrinsic to constitution ferroelectric materials. In order to suppress the intrinsic vibration noise, Liu and Dong [13] designed a differential configuration with one pair of piezoelectric $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) fiber layers with multiple push-pull polarization units laminated between high-permeability metglas ribbon layers. This differential configuration was confirmed to reject vibration-induced noise from the magnetic signal and enhance the ME signal-to-noise ratio by a factor of 30 times. Additionally, a special design differential amplifier and signal processing circuit were proposed to further noise suppression.

In the view of converse ME effect, the principle of tunable microwave magnetic devices such as filters, resonators and phase shifters is based on the control of the effective magnetization by electric field. ME composites offer a way to create an effective magnetic field by an externally applied electric field, and then further change the ferromagnetic resonance frequency in the coupled ferromagnetic phases through ME coupling effect. The recent progress of ME composites' application in microwave devices was reviewed by Liu [14] in details. With creative material design as laminated heterostructures, strong ME coupling can be achieved through interfacial effect. This simple layered-structure is realizable on tunable microwave signal processors, and the microwave properties are manipulated by ferroelectric domain switching via ME coupling. Such

multiferroic materials devices provide a promising pathway towards the next generation of electrically tunable microwave applications in the field of ultra-low power electronics and spintronics.

Another fascinating potential application field of converse ME effect in multiferroic heterostructures is the memory devices. In commercial magnetic medium storage devices, a magnetic field (usually generated by electric current) is employed to perform the data writing process. With the development of semiconductor manufacture, the magnetic storage industry encounters the contradiction of higher thermal stability and lower power consumption. The magnetic medium requires possessing a high perpendicular anisotropy for the stability, and a high current is demanded to generate the sufficient magnetic field to write the information (magnetic-write technology, that leads to undesired overheating). The possibly ultimate method to solve this problem is electrical-write technology, i.e., reversing the magnetism directly by an applied electric field instead of current. The converse ME effect allows the modulation of magnetism using a non-power-dissipating electric field, and hence provides an extremely energy-efficient driving approach for most devices that rely on magnetic domain switching or magnetic domain wall motion. Several device prototypes were presented or proposed based on multiferroic heterostructures [15,16], but certain technical problems were not solved, especially the stability, reliability, and compatibility with the current IT manufacture.

Before reaching the ultimate goal, compromising technologies, such as heat-assisted magnetic recording (HAMR), bit-patterned media (BPM), etc., have been used in practices. Another possible method is voltage-assisted magnetic recording. The magnetic coercive field H_c of some multiferroic materials can be reduced by applying an assisting voltage during writing process. Definitely, the writing magnetic field can be reduced. Shu et al. [17] studied the electrically tunable coercive field of Co thin film in a Co/BaTiO₃ heterostructure. Under applied voltages, they observed reversible manipulation of H_c of the Co film using a magneto-optic Kerr effect (MOKE) measurement. MOKE is widely used to determine the converse ME effect in multiferroic materials. However, it is worth mentioning that the applied voltage can probably give rise to the electro-optical effect from the ferroelectric phase, which is an interference signal to MOKE measurement. Gao et al. [18] verified that the Kerr signal induced by voltage contained several origins, in which the ME effect dominated the Kerr signal change.

In conclusion, multiferroic materials are one of the most unique classes of materials systems that exhibit not only a rich variety of new physical phenomena, but also great technological potential in the near future. Many exciting results and new concepts have so far been reported, but

some important issues are still open for further studies: (1) exploring new single-phase multiferroic materials with both FM and FE above room temperature; (2) improving compatibility of multiferroic materials and Si-based semiconductor industry; (3) enhancing device reliability based on multiferroic materials. Undoubtedly, the original researches of Chinese materials and physics scientists will influence and contribute the overall direction of research in this attractive field.

This work was supported by the National Natural Science Foundation of China (Grant No. 51402164 and 51332001), and Tsinghua University Initiative Scientific Research Program (Grant No. 2014Z21010).

- 1 Eerenstein W, Mathur N D, Scott J F. Multiferroic and magnetoelectric materials. *Nature*, 2006, 442: 759–765
- 2 Nan C W, Bichurin M I, Dong S, et al. Multiferroic magnetoelectric composites: historical perspective, status, and future directions. *J Appl Phys*, 2008, 103: 031101
- 3 Spaldin N A, Cheong S W, Ramesh R. Multiferroic: past, present, and future. *Phys Today*, 2010, 63: 38–43
- 4 Sando D, Barthélémy A, Bibes M. BiFeO₃ epitaxial thin films and devices: past, present and future. *J Phys Condens Matter*, 2014, 26: 473201
- 5 Hussain V A, Xu X, Yuan G, et al. The development of BiFeO₃-based ceramics. *Chin Sci Bull*, 2014, 59: 5161–5169
- 6 Wu J, Xiao D, Zhu J. Effect of La and Co-doping on microstructure and electrical properties of BiFeO₃ thin films. *Chin Sci Bull*, 2014, 59: 5205–5211
- 7 Wang G, Sun S, Huang Y, et al. Ferromagnetic and ferroelectric properties of Aurivillius phase Bi₀Fe_{4.7}Me_{0.3}Ti₃O₂₇ (Me=Fe, Co, Ni, Mn). *Chin Sci Bull*, 2014, 59: 5199–5204
- 8 Van Aken B B, Palstra T T, Filippetti A, et al. The origin of ferroelectricity in magnetoelectric YMnO₃. *Nat Mater*, 2004, 3: 164–170
- 9 Wang L, Chiang F K, Li J, et al. Ferroelectric polarization, domains structures and magnetic property of Y_{1-x}In_xMnO₃. *Chin Sci Bull*, 2014, 59: 5194–5198
- 10 Hu S, Chen L, Wu Y, et al. Selected multiferroic perovskite oxides containing rare earth and transition metal elements. *Chin Sci Bull*, 2014, 59: 5170–5179
- 11 Tan G, Wang W, Li W, et al. Multiferroic and magnetoelectric properties of La_{0.1}Ba_{0.9}Fe₁₂O₁₉ ceramics. *Chin Sci Bull*, 2014, 59: 5212–5217
- 12 Ma J, Hu J, Li Z, et al. Recent progress in multiferroic magnetoelectric composites: from bulk to thin films. *Adv Mater*, 2011, 23: 1062–1087
- 13 Liu G, Dong S. A differential magnetoelectric laminated composite for vibration noise suppression. *Chin Sci Bull*, 2014, 59: 5223–5226
- 14 Liu M. Novel laminated multiferroic heterostructures for reconfigurable microwave devices. *Chin Sci Bull*, 2014, 59: 5180–5190
- 15 Heron J T, Bosse J L, He Q, et al. Deterministic switching of ferromagnetism at room temperature using an electric field. *Nature*, 2014, 516: 370
- 16 Wang J J, Hu J M, Ma J, et al. Full 180 degrees magnetization reversal with electric fields. *Sci Rep*, 2014, 4: 7507
- 17 Shu L, Gao Y, Nan C. Strain-induced modulation of magnetic anisotropy in Co/BaTiO₃ composite. *Chin Sci Bull*, 2014, 59: 5191–5193
- 18 Gao Y, Li Z, Shu L, et al. Voltage-controlled Kerr response in Ni/Pb(Zr_{0.52}Ti_{0.48})O₃ heterostructures. *Chin Sci Bull*, 2014, 59: 5218–5222