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Editorial

Functional Ferroic Materials, Films and Devices

Pengfei Guan [1] and Ming Zheng [1,2,*]

[1] School of Materials Science and Physics, China University of Mining and Technology, Xuzhou 221116, China
[2] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
* Correspondence: zhengm@mail.ustc.edu.cn

Ferroic materials (e.g., ferroelectrics, ferromagnetics and multiferroics) have been extensively investigated due to their interesting physical properties. The ferroelectric and ferromagnetic properties of ferroic materials can be tuned by external stimuli (e.g., electric field, magnetic field, strain field), which are indispensable for applications in microelectronic devices. Ferroic materials and their coupling interactions can generate many physical phenomena, such as charge ordering, magnetoelectric coupling, etc. We can convert one of their properties into another form and develop materials with multifunctionalities. Therefore, systematical exploration of and summarization of knowledge regarding ferroic materials are crucial for the development and application of functional oxide materials [1]. This article's objective is to provide an inventory of novel research in this field of functional oxide materials, focusing in particular on the preparation and properties of ferroelectric, ferromagnetic and multiferroic materials.

Ferroelectric materials are functional materials with spontaneous polarization, and spontaneous polarization is switchable and can be reversed by an external electric field. Therefore, these materials are technologically important for many applications (e.g., ferroelectric memory, sensor and energy storage devices), and they have thus received continuous attention [2]. For example, Hsu et al. found that the ferroelectric capacitor can dominate the transfer characteristics of a p-type SnO thin-film transistor through the modulation of series capacitance in the gate stack based on a one-transistor one-capacitor series configuration [3].

Lead-based ceramics such as $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ and $Pb_{0.97}La_{0.02}(Zr_{0.97}Ti_{0.03})O_3$ have been widely used in industry due to their suitable performance, such as piezoelectric and energy storage properties. However, as lead is harmful to the environment and to humans, lead-free materials have been studied in the last decade to substitute lead-based materials. For example, Li et al. prepared Bi_2O_3-doped $(K_{0.5}Na_{0.5})NbO_3$ (KNN) lead-free ceramics and found that Bi_2O_3 doping not only enhanced remanent polarization(Pr) from 8 $\mu C/cm^2$ for KNN to 18 $\mu C/cm^2$ for KNN-0.3%Bi_2O_3 due to the creation of an orthogonal–tripartite phase at room temperature but also reduced the grain size and improved the grain size uniformity of ceramics [4]. Li et al. found that piezoelectric constant d_{33} = 678 pC/N and electromechanical coupling coefficient K_p = 0.583 of $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ ferroelectric ceramics could be achieved by the co-doping of CeO_2 and Y_2O_3 [5].

Although three-dimensional (3D) ferroelectric materials have been proposed for different applications and can be easily fabricated using various methods at the laboratory level, their practical applications are still limited by certain problems, such as their deep thickness, uneven grain size and their many crystal defects. Therefore, two-dimensional (2D) ferroelectric thin films with smooth surfaces and stable polarization are promising for the development of electronic applications. For example, Griesiute et al. obtained La-substituted $BiFe_{0.5}Sc_{0.5}O_3$ perovskite thin films with different crystal structures and roughness through fabricating films on different substrates [6]. Similarly, Magalhaes

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et al. grew $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based epitaxial films on different single crystalline substrates and found that the films showed excellent ferroelectric and dielectric properties (Pr = 1.2 μC/cm^2, Ec = 58 kV/cm for 1 μm-NBT-BT films), and the roughness of films strongly was found to depend on film thickness [7]. Tkach et al. proved that variation of ferroelectric and dielectric properties of KNN-based thin films can be obtained by controlling the strain/stress level on the films by changing the substrates [8]. Furthermore, ferroelectric film/silicon carbide ($Ba_{0.4}Sr_{0.6}TiO_3$/SiC) structures were prepared and obtained a combination of high tenability, low losses and high dissipated power density of 125 W/mm^2 at microwaves [9].

Ferromagnetic materials, referring to the magnetic domain direction, can be controlled by an external magnetic field and have a certain level of hysteresis after the magnetic field is removed. Ferromagnetic materials have been widely applied for a long time, such as in ancient compasses and modern memories and sensors. Similar to ferroelectric materials, through the ages, it has been easy for 3D and nanocrystalline ferromagnetic materials with high Tc and magnetic intensity to be achieved [10]. For example, Ahmad et al. synthesized Ce^{3+}-doped $Ni_{0.5}Cd_{0.5}Fe_2O_4$ nanoparticles using the sol–gel auto-combustion method, and the nanoparticles showed a nonlinear decrease in saturation magnetization (from 40.7 emu/g for $Ni_{0.5}Cd_{0.5}Fe_2O_4$ to 26.5 emu/g for $Ni_{0.5}Cd_{0.5}Ce_{0.16}Fe_{1.84}O_4$) and coercivity (from 227 Oe for $Ni_{0.5}Cd_{0.5}Fe_2O_4$ to 170 Oe for $Ni_{0.5}Cd_{0.5}Ce_{0.16}Fe_{1.84}O_4$) with the increase in Ce concentration [11]. In addition, nanograined $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) and $Nd_{0.7}Sr_{0.3}MnO_3$ (NSMO) were produced using various methods. Sol–gel-synthesized NSMO was revealed to be a sample with single crystallite grains and exhibited excellent magnetic and electrical transport properties. The LSMO synthesized via solid-state reaction exhibited a magnetic hysteresis loop, and the NSMO exhibited a paramagnetic curve [12].

However, the absence of 2D ferromagnetics has always been a problem. In order to obtain a long-range magnetic order in 2D ferromagnetism materials at suitable temperature, researchers have established some theories, such as shape anisotropy, exchange anisotropy and magnetoelastic anisotropy, and many 2D ferromagnetic materials have also been successfully synthesized. For example, Albargi et al. prepared FeO, Fe_2O_3 and Fe_3O_4 doped In_2O_3 films under different oxygen pressures via pulsed laser deposition, and the effects of temperature on the magnetic properties of films were explored. FeO doped In_2O_3 films exhibited the largest Ms and Hc at H = 10,000 Oe compared with Fe_2O_3 and Fe_3O_4 doped In_2O_3 films due to the oxygen vacancies, and Fe^{2+} ions were necessary for ferromagnetism. With the increase in oxygen pressure, the number of oxygen vacancies was reduced, leading to a decrease in ferromagnetism. Furthermore, the separation of the zero-field cooled and the field cooled curves was observed due to the increase in the anisotropy field to a size comparable or larger than that of the measuring field.

Multiferroic materials, referring to multifunctional materials with multiple ferroic orders in a single phase, are quite crucial in both basic research and applications (e.g., actuators, nonvolatile memory and transducers). The unique properties of multiferroics have stimulated research interest for their use in mutual cross-coupling between ferroic orders by magnetoelectric and piezoelectric interactions [13]. $BiFeO_3$ (BFO) is a is a typical multiferroic material at room temperature and has two main ferroic orders, ferroelectricity and antiferromagnetism. Lin et al. explored the influence of Gd^{3+} doping on the ferroelectric and magnetic properties of BFO films. A Pr of 133.5 μC/cm^2 was achieved for $Bi_{0.9}Gd_{0.1}FeO_3$, and saturation magnetization (Ms) was enhanced from 4.9 emu/cm^3 for BFO to 23.9 emu/cm^3 for $Bi_{0.85}Gd_{0.15}FeO_3$. [14]. Wu et al. grew a $(Ba_{0.65}Sr_{0.35})TiO_3$(BST)/$(Bi_{0.875}Nd_{0.125})FeO_3$(BNF)/BST sandwich structured thin film on Pt-coated Si (100) substrates. Due to the coupling between BST and BNF thin films, the Pr values were enhanced from 3.77 μC/cm^2 for Au/BNF/Pt to 18.5 μC/cm^2 for Au/BST/BNF/BST/Pt thin-film capacitors. Furthermore, the BST/BNF/BST films had a higher Ms (10.1 emu/cm^3) and lower Hc field (351 Oe) compared with single-layer BNF films [15]. Similarly, Hu et al. prepared multilayer $BiFeO_3/BaTiO_3$ samples and systemically studied their magneto-electric effect. With the increase in the magnetic field from

0 to 1200 Oe, the Pr of pure 100 nm BFO films was almost stable, but that of multilayer $BiFeO_3/BaTiO_3$ samples increased from 66 μC/cm^2 to 97 μC/cm^2 due to the interfacial effects and multiferroic coupling [16].

However, due to the limited number of multiferroic materials and low coupling strength, recent studies have focused on controlling the various magnetic properties of materials through electric fields in multiferroic heterostructures via a strain-driven magnetoelectric coupling effect, such as tunneling anisotropic magnetoresistance, magnetic domain wall motion and perpendicular magnetic as well as magnetoresistance properties [17]. For example, $Fe_{50}Pt_{50}$ thin films were fabricated on (011)-oriented $0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$(PMN-PT) single crystal substrates. The Ms and Hc of the $Fe_{50}Pt_{50}$ film could be tuned by changing the electric fields. With the increase in the electric field, the magnetic properties of the $Fe_{50}Pt_{50}$ film along the in-plane [100] direction became harder and displayed a reduction in squareness ratio (M/Ms), but for the magnetic properties of the [1] direction, the change is the opposite. Furthermore, the magnetization changing rate $(M_E - M_0)/M_0$ is approximately +190% and −41% for the magnetic properties of the [100] and [1] directions, respectively. Simultaneously, Hc also shows an obvious response in the form of an increase in the electric field, and the change rate of (Hc(E)-Hc(0))/Hc(0) is approximately +137% for the magnetic properties of the [1] direction, while the change rate along the [100] direction is approximately −52%. Furthermore, the magnetic properties could be dynamically regulated by alternating the electric fields with the magnetic fields along the [1] direction, which indicates that the $Fe_{50}Pt_{50}$/PMN-PT structure is a promising method for developing magnetoelectric devices with lower power consumption [18]. The $LaMnO_{3-x}$ thin film (~40 nm thick) was deposited on (001)-oriented PMN-PT single crystal substrates by Ni et al. By applying electric fields to PMN-PT single crystal substrates, they determined the resistance and photoresistance (enhanced by ~4.1%) of the $LaMnO_{3-x}$ thin films. Under the action of a cycling electric field, the change curve of photoresistance shows a butterfly shape, which indicates the change induced by the piezoelectric strain effect. Furthermore, the resistance of the $LaMnO_{3-x}$ film is suppressed under light irradiation, with an increase in E from 0 to +4.8 kV/cm, whereas ΔPR/PR gradually increased by ~4.1% and the falling time increased from 3.1 to 4 s. It is apparent that the electric-field-induced ferroelastic (in-plane compressive) strain significantly increases photoresistance. Both the electric-field-induced strain effect and the photoelectric effect are coupled to each other, which can change the magnetic and electrical transport properties of $LaMnO_{3-x}$. This method that exerts electric-field-tunable effects on electric properties in ferromagnetic/ferroelectric heterostructures provides opportunities for designing multifunctional devices by external stimuli [19].

This article presents a significant, interesting topic. It provides an update on current research in the field of ferroic materials, films and devices. I am convinced that all these studies will be a source of inspiration for the development of new multifunctional materials. However, more experimental and theoretical studies should be carried out to explore the fundamental physical and chemical properties of such materials in future.

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