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Magnetoelectric effects on ferromagnetic and ferroelectric phase transitions in multiferroic materials

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Abstract

The magnetoelectric effects on ferromagnetic and ferroelectric phase transitions in multiferroic materials were researched experimentally and theoretically. Shifts of the ferroelectric/ferromagnetic Curie temperature under magnetic/electric fields were observed due to the magnetoelectric coupling in magnetoelectric composites. We employed the Landau method with a Gibbs free energy function including ferroelectric, ferromagnetic and magnetoelectric items to understand our experimental results and some recent reports. The numerical simulations presented some important conclusions, including the jump of magnetization/polarization near the ferroelectric/ferromagnetic phase transition, the shifts of Curie temperature under external fields and the enhancement of magnetoelectric susceptibility near the Curie temperatures. These calculations coincide very closely with the experimental results. The magnetoelectric limitation ($\chi_{me}^2 < \chi_m \cdot \chi_p$) was also proved with this simple method. The results indicate that parameters such as Curie temperature, polarization, magnetization and susceptibilities can be adjusted by the magnetic or electric field.

Keywords: Multiferroics; Phase transition; Magnetization; Polarization; Susceptibility

1. Introduction

The coupling between magnetic and electric orders in solids is currently one of the hottest topics in condensed matter physics and materials science [1–3]. This coupling exhibits direct magnetoelectric and converse magnetoelectric effects [4], also generally called the magnetoelectric (ME) effect. The ME coupling is not only of great theoretical interest, but also of great practical importance for next-generation novel multifunctional devices. The direct ME effect is usually quantified in terms of the change $\delta \boldsymbol{P}$ in electric polarization or the associated output voltage δV induced by an applied magnetic field $\delta \boldsymbol{H}$. Since the direct ME effect impacts the dielectric properties of multiferroic materials as well, additional important information is provided by the magnetodielectric (MDE) coefficients, which can be easily evaluated experimentally by measuring the dependence of capacitance C on magnetic-field intensity. Many efforts have been devoted to finding proper materials with a large MDE effect, especially in single-phase materials. Giant MDE effects have been found in $DyMn_2O_5$, $TbMn_2O_5$ and antiferromagnetic $HgCd_2S_4$ because their phase transition is affected by a magnetic field [5,6] or strong magnetic frustration under a strong magnetic field and low temperature [7]. Large MDE effects were observed in $GdFeO_3$, $GaFeO_3$ and $TbMnO_3$ resulting from the shift of dielectric peak under a magnetic field [8,9]. The dielectric anomalies near the phase transition result from the strong competition and interplay among the charge, orbital and spin degrees of freedom [10]. However, the natural MDE materials in single phases are known to be extremely rare

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[1,11] and the MDE effects usually appear at a lower temperature and under a strong magnetic field as high as several Teslas [5–7,9,10]. These lead to many difficulties for practical applications.

Alternatively, ME composites, integrating the piezoelectric and magnetostrictive parts, enjoy much stronger ME coupling above room temperature, resulting from the strain transferring between the two parts in comparison with the single phase [3]. Analogously, the MDE effect is strong in the ME composites. It should be noted that in some cases the MDE effect can be achieved without the intrinsic ME coupling; for example, through the combination of magnetoresistance and the Maxwell–Wagner effect [12], and through a strain from the magnetostrictive part under a magnetic field [13,14]. In both of these cases the direct ME effect is weak [15]. Fortunately, the ME coupling always brings a high MDE effect in the ME composites [16,17]. On the other hand, the converse ME effect is usually characterized as the change $\delta \boldsymbol{M}$ in magnetization induced by an applied electric field $\delta \boldsymbol{E}$. The converse ME effect influences the magnetic permeability of ME composites as well. As a result, electric-field-induced magnetic permeability is induced, and was evaluated experimentally by the dependence of inductance on the electric field [16]. However, research on the electric-field-induced magnetic permeability is very scarce. This is unfavorable for understanding the ME coupling completely.

The dielectric peak shifts towards a lower temperature under a high magnetic field in single-phase multiferroics due to the magnetic phase transition [7–9]. Similarly in the ME composites, the ferroelectric phase transition will be affected by the magnetic field and, conversely, ferromagnetic phase transition will be influenced by the electric field due to the ME coupling. Unfortunately, this has not been reported so far. In fact, the magnetic moment abruptly changes near the $BaTiO_3$ structural phase transition temperature [18–21], exhibiting the effect of ferroelectric phase transition on the magnetic properties. In this work, we discussed the ME effects on the ferromagnetic and ferroelectric phase transitions in detail. Section 2 introduces the experimental details for the ME composite preparation and measurements. Section 3 presents the experimental results for the effects of a magnetic field on the ferroelectric phase transition and the electric polarization on the ferromagnetic phase transition. Then, we develop the Landau phenomenological theory to understand our experimental results and some recent reports in Section 4. Finally, the conclusions are summarized in Section 5.

2. Experimental details

We selected ferrites and ferroelectrics with different Curie temperatures to research the effects of magnetic field and electric polarization on the phase transitions. The Curie temperature of $Ni_{(1-x)}Zn_xFe_2O_4$ ferrites decreases linearly with the Zn content [22]. This lets us easily tailor a ferrite with a suitable Curie point. In this study, $Ni_{0.37}Zn_{0.63}Fe_2O_4$, $Ni_{0.5}Zn_{0.5}Fe_2O_4$ and $NiFe_2O_4$ were selected as the magnetic part for their different Curie points ($T_{C,m}$) of 125, 250 and 570 °C. The oxide powder NiO (purity 99%), ZnO (purity 99%) and Fe_2O_3 (purity 99%) were used as starting materials, mixed with a planetary mill and preheated at 970 °C for 5 h to synthesize the ferrite powders. $BaTiO_3$ and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) were selected as the ferroelectric part for their high piezoelectric constant. $BaTiO_3$ is known to have a structural phase transition at 120 °C. The raw materials – $BaCO_3$ (purity 99%) and TiO_2 (purity 99.99%) – were mixed with the planetary mill and preheated at 1200 °C for 6 h to synthesize the $BaTiO_3$ powder. PZT powder with a Curie point ($T_{C,p}$) of 165 °C was brought from Zibo Yunhai Electronic Ceramic Co. Ltd [23]. Then, ME composite powders $(1-x)BaTiO_3 + xNiFe_2O_4$ (designated as CG-I-1, 2, 3 and 4, with $T_{C,p} < T_{C,m}$), $(1-x)PZT + xNi_{0.5}Zn_{0.5}Fe_2O_4$ (designated as CG-II-1, 2, 3 and 4, with $T_{C,p} < T_{C,m}$) and $(1-x)PZT + xNi_{0.37}Zn_{0.63}Fe_2O_4$ (designated as CG-III-1, 2, 3 and 4, with $T_{C,p} > T_{C,m}$) with $x = 10\%$, 20%, 30% and 40% were mixed completely with the planetary mill, respectively. After drying, the composite powders were pressed into tablets and toroids for the dielectric and magnetic measurements. Finally, the CG-I samples were sintered at 1200 °C while the CG-II and CG-III samples were sintered at 1140 °C to obtain better properties [23].

The toroids were wrapped with 10 turn copper wire for testing the magnetic permeability. The samples were placed in a furnace with a heating rate of 3 °C min^{-1}. The inductance was measured with an Agilent E4980A complex impedance analyzer at 100 kHz to obtain the temperature dependence of magnetic permeability. Then, the toroids were coated with silver electrode on both parallel surfaces, polarized then polished to remove the silver electrode and the magnetic permeability was remeasured to investigate the effect of electric polarization on the magnetic phase transition. The tablets were polished and coated with silver electrode for the dielectric test. The temperature dependence of the dielectric constant was also measured by the Agilent E4980A at 100 kHz in a furnace with a heating rate of 3 °C min^{-1}. Then, the sample was measured repeatedly under a magnetic field of 300 Oe to investigate the magnetic effect on the ferroelectric phase transition.

3. Experimental results

The X-ray diffraction patterns show only two phases of ferrite and perovskite ($BaTiO_3$ or PZT) in the composite ceramics without any other foreign phase formed [23–26]. The scanning electron microscopy morphologies exhibit dense ceramics with two kinds of particles: the smaller ferrite particles and the larger ferroelectric particles. The ferrite grains are embedded in the ferroelectric particles randomly [23]. The dense composite ceramics allow us to research the dielectric and magnetic properties in depth.

Fig. 1 demonstrates the variation of piezoelectric constant for the CG-II and CG-III ceramics sintered at 1140 °C. The piezoelectric constant of the composites