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Magnetoelectric effect in bilayer composites of Fe-doped BaTiO₃ and terfenol-D

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Abstract

Fe-doped BaTiO₃ has been synthesized with the doping level ranging from 0 to 0.02. Their transformation point from ferroelectric to paraelectric and the corresponding latent heat of phase transformation were observed to decrease with increasing doping level of the Fe³⁺. Bonded bilayers of Fe-doped BaTiO₃ and terfenol-D have been fabricated and their magnetoelectric (ME) effect has been investigated. The sample containing a layer of BaTi_{0.985}Fe_{0.015}O₃ was found to show a maximum transverse ME coupling in these bilayer composites. Analysis shows that the doped BaTiO₃ with a doping level of about 1.5% should have a largest piezoelectric coefficient in magnetoelectric coupling.

1. Introduction

There has been continual interest in the magnetoelectric (ME) effect in layered composite materials in recent years. Layered ME composites containing both magnetostrictive and piezoelectric phases have a simple structure, are easy to fabricate and often show high magnetoelectricity conversion coefficients [1, 2]. When such composites are placed in a magnetic field, they undergo deformation via interlayer mechanical stress due to the magnetostrictive effect and generate electric charge at the surface of the piezoelectrics due to the piezoelectric effect. The strength of the effect is generally expressed as the ME voltage coefficient $\alpha_E = \delta E / \delta H$ [3, 4].

PbZr_{1-x}Ti_xO₃ (PZT) is a typical piezoelectric used in layered ME composites, such as multilayer Ni(Co, Mn)Fe₂O₄-PZT [5-8], Tb_{1-x}Dy_xFe_{2-y}-PZT [9, 10], and La_{1-x}Sr_xMnO₃-PZT [11], since the manufacturing technology is mature and it has a relatively strong piezoelectric effect compared to that of BaTiO₃ (BTO), which is another typical piezoelectric. However, PZT is not an ideal ferroelectric due to it containing zirconium and lead, which are deleterious to the environment.

Recently, a very large reversible electro-strain effect in Fe(Mn)-doped BaTiO₃ crystal has been observed [12-16].

In the doped BaTiO₃, Fe³⁺(Mn³⁺) ions partly replace Ti⁴⁺ ions, leading to some oxygen vacancies in the crystal. The short-range order of the defect state consisting of the Fe³⁺ ion and an oxygen vacancy will follow the long-range order of the polar tetragonal symmetry of the perovskite in an electric field, resulting in a strong piezoelectric effect along the $\langle 100 \rangle$ direction of the crystal. It can show a huge reversible deformation of about 0.75%, which is 40 times larger than that for PZT [13, 14]. For this reason, a composite containing doped BTO should be a good choice for making new kinds of ME composites.

We have presented an investigation of the ME effect on layered BaTi_{0.99}Fe_{0.01}O_{3+ δ} and terfenol-D (Tb_{1-y}Dy_yFe_{2-z} (TDF)), which was used as the magnetostrictive phase. The transverse ME voltage coefficient for bilayer TDF-BaTi_{0.99}Fe_{0.01}O_{3+ δ} and trilayer TDF-BaTi_{0.99}Fe_{0.01}O_{3+ δ} -TDF can reach 578 and 2200 mV Oe⁻¹ cm⁻¹, respectively [17]. These values are about 50% larger than those observed in the layered composites formed by TDF and pure BTO, and can be comparable with those of the ME composites consisting of PZT [5-11]. Then, the next step should be to search a doped BTO with a more suitable doping level of Fe³⁺ (or other trivalent ions) in order to obtain better ME coupling. In this paper, we present a careful investigation of the influence of the

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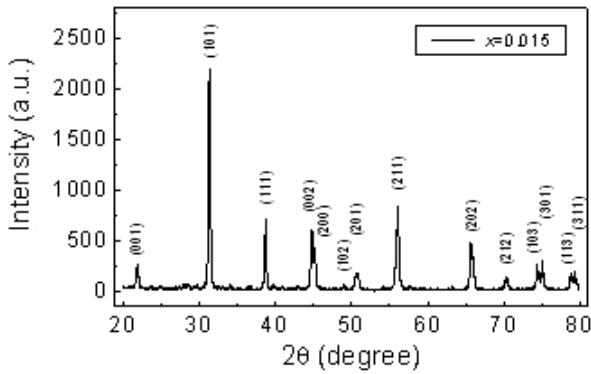


Figure 1. Pattern of x-ray diffraction of the fabricated $\text{BaTi}_{0.985}\text{Fe}_{0.015}\text{O}_3$.

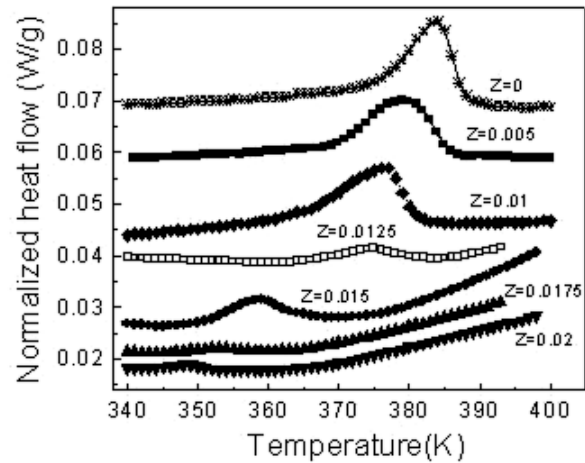


Figure 2. Results of differential scanning calorimetry tests for differently doped BTO.

doping effect in $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ (BTFO) on the ME coupling of BTFO–TDF.

2. Sample characterization

The $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ samples under investigation were synthesized using a sol–gel technique, as described previously [18]. The doping level x ranged from 0 to 0.02. The resultant powder was pressed into rods of 10 mm in diameter and 15 mm in length, and treated at 10 MPa and 900 °C for 10 h with a hot-pressing facility, then further sintered at 1300 °C for 10 h. The rods were cut into pellets with a thickness of 1 mm, and then aged for at least two weeks in order to let the oxygen vacancies generated due to doping diffuse sufficiently. The pellets of BTFO were painted with Ag to form electrodes, and then poled by heating to about 200 °C then cooled back to room temperature in an electric field of 8 kV cm⁻¹ perpendicular to the plane of the disc-shaped samples.

The fabricated BTFO are characterized by x-ray diffraction (XRD) in a rotating anode diffractometer (D/max-rC Rigaku) using Cu K α radiation, whose wavelength is $\lambda = 0.154\,505$ nm. The XRD pattern revealed the absence of any impurities except for tetragonal structure (with point group $4mm$), demonstrating that higher Fe-doped BTO, with a concentration of up to 0.02, is still in the perovskite structure, as shown in figure 1 [17].

3. Experimental results and discussion

Figure 2 shows the result of differential scanning calorimetry (DSC) tests for BTFO samples with doping levels ranging from 0 to 0.02. The transformation from ferroelectricity to paraelectricity in BTO is first order, accompanying by the apparent latent heat. The Curie point T_c of the transformation from ferroelectricity to paraelectricity and the corresponding latent heat ($|\Delta H|$) were observed to decrease with increasing doping level of Fe³⁺ ions. The concentration dependence of T_c and ΔH are shown in figure 3. These results suggest that doping increases the disorder in the structure and the distribution of electric dipoles in the perovskite.

The BTFO piezoelectrics have been bonded with TDF pellets and with epoxy resin, respectively. TDF is a

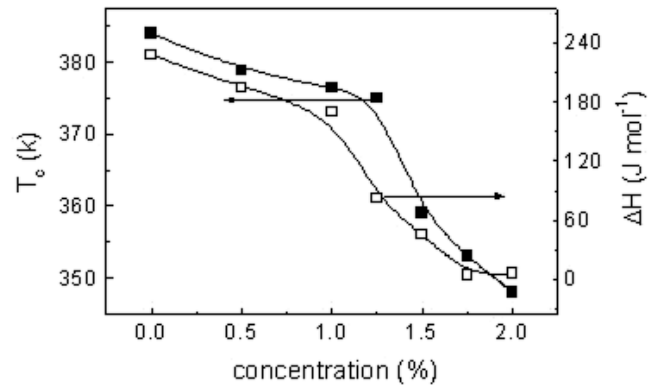


Figure 3. Concentration dependence of Curie temperature T_c and latent heat ΔH for BTFO samples. The points are measured data, and the lines are guides to the eye. The data points for the doping level 0 and 0.01 are taken from [17].

widely used magnetostrictive material with a magnetostrictive coefficient higher than 1000 ppm along a preferred orientation. The TDF used here is commercial and in a disc shape, 8 mm in diameter and 1.5 mm in thickness. The magnetic characterization of the TDF includes the Curie temperature T_c and the magnetostriction, as shown in figure 4. The former was obtained by applying a magnetic balance and the latter was measured by using the standard strain gage technique at room temperature. The T_c of the DTF is about 650 K. The measurement of magnetostriction shows that, with increasing magnetic field H , the magnetostrictive coefficient with the field along the direction of measurement, λ_{11} , increases first rapidly when $H \leq 750$ Oe, then slowly and approaches saturation at $H \approx 3000$ Oe. Its saturated magnetostriction can reach about 1470 ppm.

The laminate composites were placed in a measurement cell and subjected to a basis magnetic field H and an ac magnetic field $\delta H \approx 2$ Oe at a frequency of 100 Hz, which was produced by a couple of Helmholtz coils. Both were arranged to be parallel to each other. The electric voltage δV across the sample was amplified and measured for ME characterization

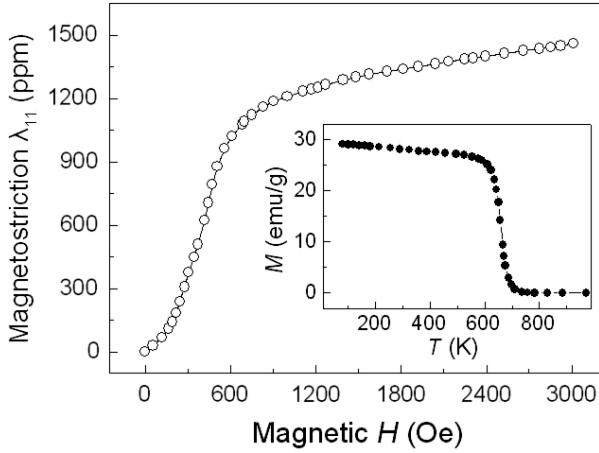


Figure 4. Magnetic field dependence of the magnetostriction for $Tb_{1-x}Dy_xFe_{2-y}$. Inset: temperature dependence of the magnetization for $Tb_{1-x}Dy_xFe_{2-y}$.

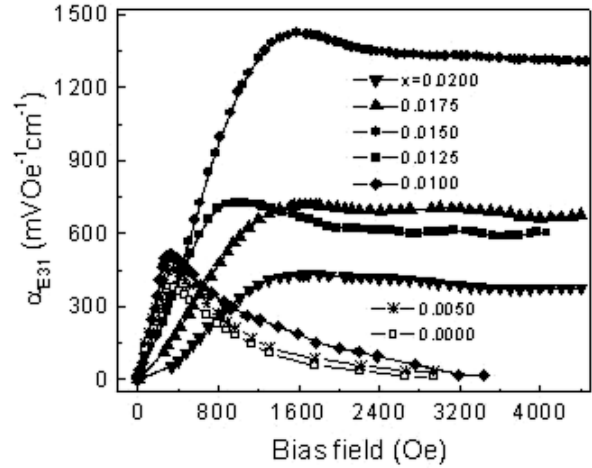


Figure 5. Bias magnetic field dependence of transverse ME voltage coefficient α_{E31} for bilayer composites BTFO–TDF at room temperature with an ac magnetic field at a frequency of 100 Hz. The data points for the doping level 0 and 0.01 are taken from [17].

with a multimeter. The ME voltage coefficient was estimated from $\alpha_E = \delta V / t \delta H$, where t is the thickness of the BTFO.

The measurements can be performed for two different field orientations, with magnetic fields H and δH along the direction parallel or perpendicular to the sample plane. The ME voltage coefficient for the former (transverse coefficient), denoted as α_{E31} , is often 3–10 times larger than that for the latter (longitude coefficient) [19]. So, here we discuss only the measured results of the latter, α_{E31} .

Figure 5 shows the α_{E31} as functions of bias field H for the bilayer composites BTFO–TDF at room temperature. It is found that the curves of α_{E31} versus H for the samples made of the doped BTO with a doping level from 0.0125 to 0.02 are quite different from those with a doping level from 0 to 0.01. For the latter, the α_{E31} first increases with increasing field H , a peak appears at the field of 350 Oe, and then decreases to zero when the field approaches 3000 Oe. But for the former, α_{E31} increases to a maximum with increasing field, then does not come down, but instead fluctuates slightly around the maximum. However, this phenomenon is not new. It has been reported in [20]. In addition, the maximum of the transverse ME voltage coefficient for the samples, $\alpha_{E31,max}$, is observed to change with increasing doping level x . The concentration dependence of $\alpha_{E31,max}$ undergoes a peak, which is located at about $x = 1.5\%$, as shown in figure 6.

A theoretical model for ME effects in bilayer structures was first proposed Harshe *et al* [21], then improved by Bichurin *et al* [23]. In this model, the composite is considered as a homogeneous medium with piezoelectric and magnetostrictive subsystems; any flexural deformations of the layers were ignored and an interface coupling parameter k was introduced. $k = 1$ means ideal interface coupling. According to the model, the transverse ME voltage coefficient is

$$\alpha_{E31} = \{-kv(v-1)^p d_{31} ({}^m q_{11} + {}^m q_{21})\} \times \{({}^m s_{11} + {}^m s_{12})^p \varepsilon_{33}^T kv + ({}^p s_{11} + {}^p s_{12})^p \varepsilon_{33}^T (1-v) - 2({}^p d_{31})^2 k(1-v)\}^{-1} \quad (1)$$

where $v = p_v / (p_v + m_v)$ and p_v and m_v denote the volume of the piezoelectric phase and the magnetostrictive phase,

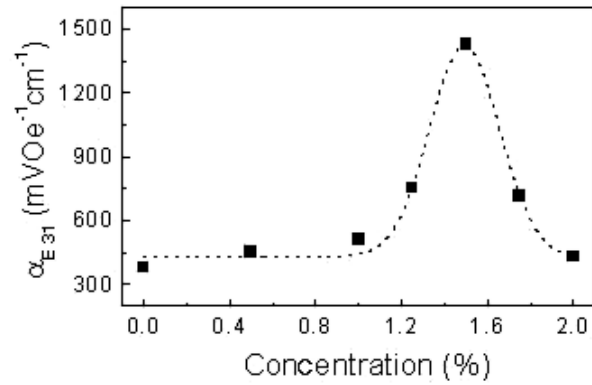


Figure 6. Concentration dependence of the maximum value of ME voltage coefficient $\alpha_{E31,max}$ for bilayer composites BTFO–TDF. The points are measured data, and the lines are guides to the eye.

${}^m S_{ij}$ and ${}^m q_{ki}$ are compliance and piezomagnetic coefficients; ${}^p S_{ij}$ and ${}^p d_{ki}$ are compliance and piezoelectric coefficients; and ${}^p \varepsilon_{kn}$ is the permittivity matrix. Generally, ${}^m S_{ij}$, ${}^p S_{ij}$ and ${}^p \varepsilon_{kn}$ are some constants for given ferromagnets and ferroelectrics. Thus α_{E31} mainly depends on the piezomagnetic and piezoelectric coefficients ${}^m q_{ki}$ and ${}^p d_{ki}$ from equation (1). Since the ferromagnet in all the bilayers above is TDF, α_{E31} should only be a function of the piezoelectric coefficient. Accordingly, we can reason that $BaTi_{0.985}Fe_{0.015}O_3$ has the largest piezoelectric coefficient in the magnetoelectric coupling discussed from the results shown in figures 5 or 6.

In addition, the volume fraction of the doped BTO in the present investigation was fixed at $v = p_v / (p_v + m_v) = 1 / (1 + 1.5) = 0.4$. The value taken here is based on the consideration below. According to equation (1), taking different values of v can yield different maxima of the ME voltage coefficient $\alpha_{E31,max}$. The theoretical estimation of the dependence of $\alpha_{E31,max}$ on the volume fraction v with different k values for the TDF–BTFO bilayer is shown in figure 7. The material parameters used in the calculation are

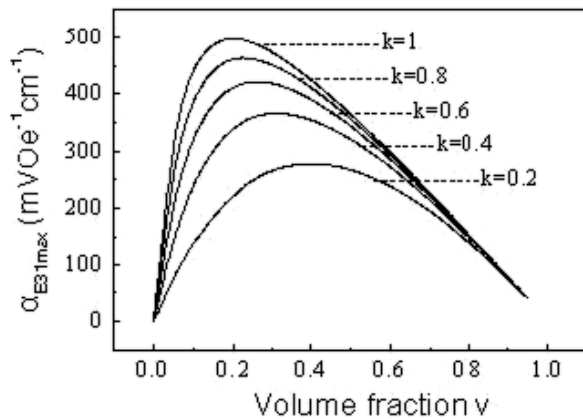


Figure 7. Calculated maximum value of ME voltage coefficient $\alpha_{E31,max}$ for bilayer composites BTFO–TDF as a function of the volume fraction of BTO with different values of the interface coupling parameter k .

$m_{s11} = 125 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ and $m_{s12} = -17 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$ for TDF [24], and $p_{s11} = 7.3 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$, $p_{s12} = -3.2 \times 10^{-12} \text{ m}^2 \text{ N}^{-1}$, $p_{e33} = 1345\epsilon_0$ and $p_{d31} = -78 \times 10^{-12} \text{ mV}^{-1}$ for BTO [25]. From figure 7, $\alpha_{E31,max}$ undergoes a gentle peak with increasing v . Ordinarily, the k value for most ME bilayers reported is in the range 20–40% [22]. Thus, the optimal value of v is about 0.4, as can be seen in figure 7.

4. Conclusion

$\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3$ as a ‘green’ ferroelectric can be a good choice for use as the piezoelectric phase in laminate ME composites. The transformation point from ferroelectric to paraelectric and the corresponding latent heat of the phase transformation decrease with increasing doping level x . The transverse ME voltage coefficient can become a maximum when x is about 1.5% for the bilayers $\text{BaTi}_{1-x}\text{Fe}_x\text{O}_3\text{--Tb}_{1-y}\text{Dy}_y\text{Fe}_{2-z}$. The maximum value can reach about $1420 \text{ mV Oe}^{-1} \text{ cm}^{-1}$. This suggests that Fe-doped BaTiO_3 with a doping level of about 1.5% has the largest piezoelectric coefficient in these doped BaTiO_3 samples.

Acknowledgment

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