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Doping effect on crystal structure of $BaTiO_3$ and magnetoelectric coupling of layered composites $Tb_{1-x}Dy_xFe_{2-y}$–$BaTi_{0.99}M_{0.01}O_{3+\delta}$

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ABSTRACT

1.0 mol% Cr-, Mn- and Co-doped $BaTiO_3$ composites have been synthesized as a kind of "green" piezoelectrics. The lattice constants of the doped $BaTiO_3$ are calculated from their patterns of X-ray diffraction. The tetragonality (c/a) of these doped samples has been found to decrease in turn according to the order Cr-, Mn- and Co-doped $BaTiO_3$, and be lower than that of pure $BaTiO_3$. The transition temperature of ferroelectric to paraelectric phase and the accompanying latent heat of the transition have also been found to decrease in turn according to the order above for the doped $BaTiO_3$. Bonded bilayer composites $Tb_{1-x}Dy_xFe_{2-y}$ (TDF)–$BaTi_{0.99}M_{0.01}O_{3+\delta}$ (M = Cr, Mn and Co) have been fabricated. Their ME effect has been investigated. The maximum value of the transverse ME voltage coefficients for the bilayers were observed to decrease in turn, from 586 to 445 mV cm^{-1} Oe^{-1}, in the sequence of TDF–$BaTi_{0.99}Cr_{0.01}O_{3+\delta}$, TDF–$BaTi_{0.99}Mn_{0.01}O_{3+\delta}$ and TDF–$BaTi_{0.99}Co_{0.01}O_{3+\delta}$. It indicates that tetragonality of the structure is a key factor in determining both the physical property of the doped $BaTiO_3$ and the ME effect of the composite containing the doped $BaTiO_3$.

1. Introduction

Magnetoelectric (ME) effect is defined as magnetic field-induced change of polarization. As a potential magnetic field probe and transducer for magnetoelectric conversion [1], the ME effect has attracting continuous attention since it was first observed in antiferromagnetic Cr_2O_3 [2,3]. The primary requirement for the observation of ME effect is the coexistence of magnetic and electric orders. Materials exhibiting ME effect can be classified into two classes, single-phase materials and composites. The ME effect in a single-phase material was found too weak to be utilized for practical purpose, even at low temperature. The ME effect could also be realized in a composite consisting of ferroelectric and ferromagnetic phases using product effect [4], which can be expressed as [5]:

$$\text{ME effect} = \frac{\text{magnetic}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{electrical}}$$

It means that a mechanical deformation due to magnetostriction results in a dielectric polarization due to piezoelectric effects. Thus, in order to fabricate composites with enhanced ME effect, ferromagnet with large piezomagnetic effect and ferroelectrics with large piezoelectric effect should be needed. To data, many ME composites have been developed. Some works were devoted to bulk materials, such as $CoFe_2O_4$–$BaTiO_3$ [4], $Ni_{0.9}Zn_{0.1}Fe_2O_4$–PZT [6], $NiFe_2O_4$–$Ba_{0.7}Sr_{0.3}TiO_3$ [7], $Ni_{0.92}Co_{0.03}Mn_{0.05}Fe_2O_4$–$BaTiO_3$ [8] and $Ni_{0.8}Co_{0.1}Cu_{0.1}Fe_2O_4$–$PbZr_{0.5}Ti_{0.5}O_3$ [9]. But the ME effect in the bulks has proved to be much weak due to leakage current and low degree of polarization. In recent years, strong ME coupling has been reported in several layered ME composites containing magnetostrictive and piezoelectric layers, such as Terfenol-D–Pb(Zr,Ti)O_3 [10,11], $NiFe_2O_4$–Pb(Zr,Ti)O_3 [12], Terfenol-D/epoxy–PZT [13] and $Tb(Fe_{0.55}Co_{0.45})_{1.5}$–PZT [14], etc.

Barium titanate $BaTiO_3$ (BTO) and lead zirconate titanate Pb(Zr,Ti)O_3 (PZT) are some typical piezoelectrics. Historically, BTO was the first polycrystalline piezoelectrics, but soon replaced by PZT because the latter has much better piezoelectric performance and relatively mature preparation techniques. However, PZT is now facing a big challenge due to the environmental hazard by its toxic lead.

Recently, it is reported that a large recoverable electrostrain has been obtained in aged single crystal of Fe-doped $BaTiO_3$ [15–18]. It provides a choice to synthesize high performance lead-free piezoelectrics. For this reason, one can expect that a bilayer of

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transition-metal-doped BTO and $Tb_{1-x}Dy_xFe_{2-y}$ (TDF) may show a strong ME coupling. TDF or Terfenol-D is a newly developed rare-earth-iron alloy with desirable magnetostriction performance, high Curie temperature and low anisotropy in magnetic crystals. Those make it an ideal magnetostrictive material for preparation of ME composites. We have investigated layered composite $BaTi_{0.99}Fe_{0.01}O_{3+\delta}$–TDF. The transverse ME voltage coefficient of it can reach 578 $mVOe^{-1}\,cm^{-1}$. This value is about 50% larger than that observed in the bilayer of pure BTO and TDF [19]. In this work, polycrystals of 1.0 mol% Cr-, Mn- and Co-doped BTO samples were synthesized. Bonded bilayer composites of the doped BTO and TDF were fabricated. And the ME coupling in these bilayers were investigated.

2. Sample preparation and characterization

Samples of 1.0 mol% Cr-, Mn- and Co-doped BTO were prepared from nanoparticles obtained by a sol–gel technique [20]. The resultant powder was pressed into rods of 10 mm in diameter and 15 mm in length, hot-pressed at 10 MPa and 900 °C for 2 h with a hot-press facility and finally sintered at 1250 °C for 10 h to obtain compact samples. The rods were cut into pellets of 1 mm in thickness, and aged at room temperature for 2 weeks. The pellets were painted with Ag to form electrodes, then poled by heating to 200 °C and cooling back to room temperature in an electric field of 10 kV/cm perpendicular to the sample plane. The hot-pressing technique was employed in order to obtain samples with high compactness, which is necessary for realizing a good piezoelectric performance. The effect of hot-pressing can be seen from the scanning electronic microscopy (SEM) photos for both hot-pressed (HP) and not hot-pressed (NHP) Cr-doped BTO sintered at same temperature (1250 °C), as shown in Fig. 1. It can be seen that the compactness of the HP sample is much larger than that of the NPH one.

The doped BTO samples are characterized by X-ray diffraction (XRD) in a rotating anode diffractometer (Rigaku D/max-rC, Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å) and a scan step of 0.02° from $2\theta = 20°$ to 80°. The XRD patterns of the doped BTO revealed the absence of any impurities except tetragonal perovskite structure (with point group 4 mm) as that observed from pure BTO, as shown in Fig. 2. It demonstrates that doping does not change the structure of BTO.

Commercial TDF discs of 8 mm in diameter and 1 mm in thickness are used in this study. The characterization of its magnetostriction was performed by the standard strain gauge technique. The results are shown in Fig. 3. It is found that, with increasing magnetic field H, the magnetostrictive coefficient parallel to the field λ_{11} increases rapidly when $H \leq 750$ Oe, then slowly and approaches to saturation when $H \approx 3000$ Oe. The field dependence of λ_{12} shows a similar behavior with that of λ_{11}, but the absolute value of λ_{12} is much smaller than that of λ_{11}. Meanwhile, the corresponding piezomagnetic coefficient $d(\lambda_{11} + \lambda_{12})/dH = q_{11} + q_{12}$ is also given in Fig. 3. That will be used later for calculation. It is found that $(q_{11} + q_{12})$ undergoes a peak at about 350 Oe, and then decreases to zero with increasing the field. In addition, the temperature dependent magnetization of the TDF was measured with a magnetic balance. The Curie temperature of the TDF was found at about 656 K.

The doped BTO samples were bonded to the TDF using a slow-dry epoxy resin to obtain bilayers of $BaTi_{0.99}M_{0.01}O_{3+\delta}$–TDF (M = Cr, Mn and Co). Fig. 4 shows the SEM picture of the bilayer of TDF and Cr-doped BTO. It shows that the epoxy layer is in thickness of about 40 μm. And the TDF presents the topography of bulk alloy.

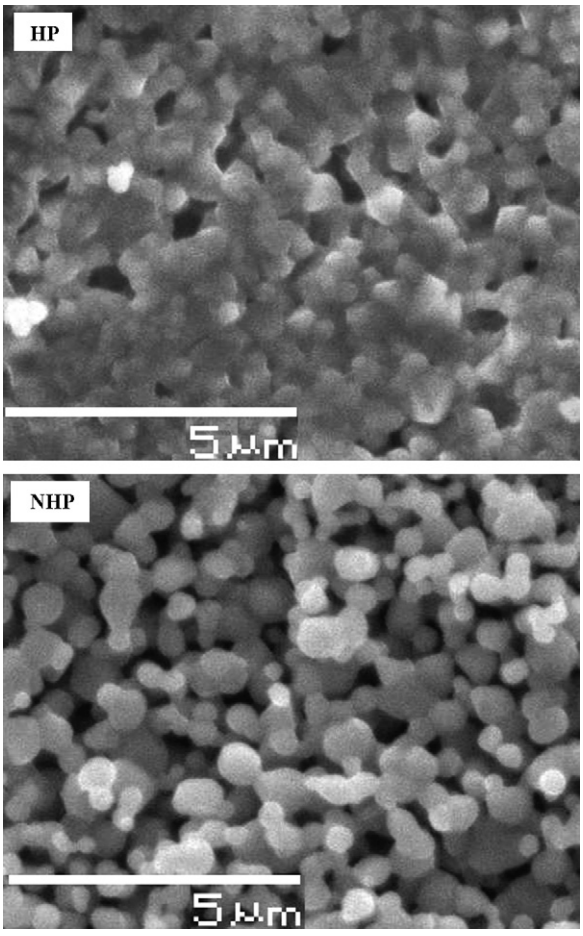

Fig. 1. Scanning electronic microscopy (SEM) photos for both hot-pressed (HP) (upper panel) and not hot-pressed (NHP) (lower panel) Cr-doped BTO sintered at same temperature (1250 °C).

3. Results and discussion

The transition of ferroelectrics to paraelectric phase of BTO is the first order and accompanies by apparent latent heat. Fig. 5 shows the results of differential scanning calorimetry (DSC) (PerkinElmer Diamond DSC, USA) test for Cr-, Mn- and Co-doped BTO. The initial purge gas is nitrogen and the samples are heated from 25 to 250 °C at a velocity of 10.00 °C/min. For comparison, the result of DSC test for Fe-doped BTO is also plotted in Fig. 5. As can be seen, the Curie

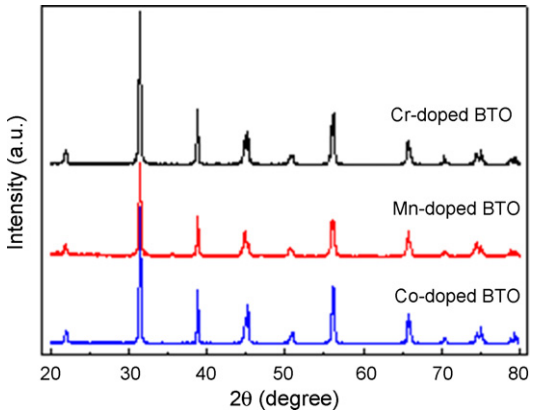

Fig. 2. X-ray diffraction (XRD) patterns of Mn-, Cr- and Co-doped BTO samples.