Magnetic and Dielectric Properties of BST/BF Multiferroic Ceramic Materials

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Abstract: The lead-free multiferroic ceramic of $(1-x)\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ (BST) + $x\text{BiFeO}_3$ (BFO) was synthesized by a conventional solid-state reaction method. The dielectric, ferroelectric and magnetic properties was studied. The X-ray diffractometry (XRD) revealed that the ceramic formed a single perovskite structure. The results suggested that the remanent magnetization (M_r) reached to maximum when the BFO content is up to 0.05. The powder of the samples $M_r = 70 \text{ memu/g}$ when $x = 0.05$. The change of the electrical resistance with magnetic field of the $(1-x)\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3 + x\text{BiFeO}_3$ samples reached 25.6% when $x = 0.03$. The relative dielectric constant was reduced under magnetic field compared with no magnetic field and the change is 13.1% as $x = 0.01$. It is indicated that the lead-free multiferroic ceramic of $(1-x)\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3 + x\text{BiFeO}_3$ exhibited both ferroelectric and magnetic at room temperature. The ferroelectric and magnetic properties are derived from the displacement of magnetic atom iron and the change of the atomic spin state.

Key words: Multiferroic, dielectric, ferroelectric, BST.

1. Introduction

Multiferroic magnetoelectrics are materials that both ferromagnetic/antiferromagnetic and ferroelectric/antiferroelectric properties exist in the same phase. These materials have a magnetoelectric effect that electric polarization can be induced in the material by an applied magnetic field and magnetization is induced by an applied electric effect, that is magnetoelectric coupling in the multiferroic materials [1]. This is difficult to be synthesized because ferroelectricity and ferromagnetism make a mutually exclusive group [2]. But the magnetoelectric coupling of magnetic and electrical properties is a more general and widespread phenomenon. As this new century unfolds, the study of materials possessing coupled magnetic and electrical order parameters has been revitalized [3, 4].

Barium strontium titanate $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ is a solid solution composed of barium strontium and strontium

titanate. When barium atoms are replaced by strontium atoms at A site in perovskite barium titanate matrix, the phase transition temperature of paraelectric to ferroelectric decreases and the phase transition behavior changes from sharp to diffuse [5-7]. Among the perovskites mixed systems, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) is an interesting series due to its unique ferroelectric properties which are suitable for various potential applications [8]. And that the BST system shows high permittivity which has a wide interest in the field of electrically controlled devices [9].

Bismuth ferrite (BiFeO_3) is one of the few known single-phase multiferroic materials which exhibits rhombohedrally distorted perovskite structure. The parameters of the hexagonal elementary cell are: $a = 5.5876 \text{ \AA}$ and $c = 13.867 \text{ \AA}$ at room temperature. It has antiferromagnetic ordering with $T_N \sim 370 \text{ }^\circ\text{C}$ and ferroelectric properties with a high Curie temperature of about $\sim 830 \text{ }^\circ\text{C}$ [10]. BiFeO_3 has showed magnetoelectric coupling. But there are some obstacles need to be overcome before to be applied. Firstly, it is also difficult to control oxygen

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stoichiometry and the evaporation of bismuth oxide in the sample. Secondly, the BiFeO₃ bulk material exists the large leakage current since the existence of the mixed valence Fe²⁺/Fe³⁺ ions and oxygen vacancies [11, 12]. Thirdly, the BiFeO₃ shows very weak even no ferromagnetism from a near-linear magnetization-magnetic field (M-H) relation [13]. So it is proposed that the compound of a solid solution with BST compositions.

It is said that the structure of Ba_{0.7}Sr_{0.3}TiO₃ is difficult to decide whether it is tetragonal or cubic because of the large uncertainties after final refinement [14], and we choose Ba_{0.7}Sr_{0.3}TiO₃ and BiFeO₃ as research object so that we could use the properties to study the magnetoelectric coupling.

In this work, it is studied that the magnetic and electrical properties of (1-x)BST + xBiFeO₃ system and the effect of BiFeO₃ doping on the formation of the (1-x)BST + xBiFeO₃ solid solution. It was found that the (1-x)BST + xBiFeO₃ series ceramic both have ferroelectric and ferromagnetic at room temperature. With the increase of BFO doping amount, ceramic remanent magnetization first increase then decrease. When x = 0.05, the remanent magnetization of the sample powder reached maximum that is Mr = 70 memu/g at this time. When x = 0.01, the largest of the remanent polarization is Pr = 11 $\mu\text{C}/\text{cm}^2$. And after applied magnetic field, the relative dielectric constant of ceramic material decreases, exhibiting obvious electro-magnetic coupling behavior.

2. Experimental Methods

The (1-x)Ba_{0.70}Sr_{0.30}TiO₃(BST) + xBiFeO₃ ceramic system was prepared by a conventional solid-state reaction process. The addition of BiFeO₃ is x = 0.01, 0.03, 0.05 and 0.07, respectively. Commercial BaCO₃, SrCO₃, TiO₂, Bi₂O₃ and Fe₂O₃ powders all were of purities greater than 99.9%. Raw powders according to the stoichiometric ratio were ball milled with ethylalcohol for 6 h. After the mixture was dried, it was calcined at 1,150 °C for 2h in air. Then after the

second ball milled, the calcined powders were mixed with 6% PVA binder and pressed into cylindrical pellets of 15mm diameter. Samples were sintered at 5 °C /min to 1260 °C, with a 2 h hold at 1,260 °C. Phase identification of these specimens was conducted by X-ray diffractometry (XRD) (D8 ADANCED XRD, BRUKER/AXS Co., Germany) with Cu Ka radiation. Data was collected from 20° to 80° of 2 θ . A scanning electron microscope (SEM) (JEOL-JSM-6460, Japan) was used to detect the micromorphology. Silver paste was deposited on the surface of the pellet. The ferroelectric properties were examined by p-e loop (MTI 2000). The magnetic properties of the samples were measured by VSM (Lakeshore 7400). The permittivity was investigated at 1 ~ 300 KHz by TH2818 Automatic Component Analyzer.

3. Results and Discussion

Fig. 1 shows the XRD spectra of (1-x)BST + xBFO (x = 0.01, 0.03, 0.05 and 0.07) ceramics were measured with a Cu Ka source at room-temperature. The sintering temperature is 1,260 °C. It is found that the samples have no other phase diffraction peak and exhibit single perovskite structure. BST and BFO formed a good solid solution and did not change the structure. Bi ions and Fe ions entered the lattice of BST, instead of Ba and Sr ions at A site. Because the ionic radius of Bi and Fe is smaller than Ba and Sr, the distance between the oxygen atoms is reduced, further the crystal lattice constant is reduced, and the d-spacing d decreases. According to Bragg equation:

$$2d\sin\theta = n\lambda \quad (1)$$

the diffraction Angle theta decreases with d decreases, and the intensity of the diffraction peakenhances. So the diffraction peak move slightly to the right.

Fig. 2 shows the magnetic hysteresis loops of (1-x)BST + xBFO (x = 0.01, 0.03, 0.05 and 0.07) powder at room temperature. The saturated magnetizing strength and the remanence firstly increased and then decreased with the increment of BFO.

Fig. 1 XRD spectra of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07).

Fig. 2 Magnetic hysteresis loops of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) powder.

The remanent magnetization (M_r) reached maximum when the doping amount of BFO is up to 0.05. The $M_r = 70 \text{ memu/g}$ when $x = 0.05$. It is indicated that the powder hold good ferromagnetic at room temperature. BiFeO_3 is perovskite materials with type G antiferromagnetic structure, and the relative displacement of Bi^{3+} causes uneven crystal structure, so that it arranged in spiral structure, and performance

weak ferromagnetic on a macro. Barium strontium titanate is perovskite ferroelectric materials, and Fe Bi ions can enter into oxygen octahedral structure of BST, destroyed the ferrite bismuth spiral magnetic structure.

Fig. 3 shows the electric hysteresis loops of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics. We can know the leakage current is too large from this image except $x = 0.03$. The remanent

polarization reached $12 \mu\text{C}/\text{cm}^2$ as $x = 0.01$. As we can see from the Fig. 3, these samples exhibited large leakage current. It is easy that Bi elements volatilized under thih temperature. In this case, it caused the crystal defect.

Fig. 4 shows the insulation resistance of $(1-x)\text{BST} +$

$x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics under the condition of magnetic field (the red line) and with no magnetic field (the black line). First the resistance decreased after add the magnetic field and then increased slightly. When $x = 0.03$, the change of the resistance is 25.6%. The magnetic field make the ceramic

Fig. 3 Electric hysteresis loops of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics.

Fig. 4 Resistance of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07).

grain oriented lead to the resistance drop at the beginning. When BiFeO_3 reaches a certain limit, the number of crystal orientation with different increase, the grain boundary changed a lot, the grain boundary resistance is bigger, the resistance of the charge movement increase.

Fig. 5 shows the contrast of the relative dielectric constant with frequency of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics. Compared with no magnetic field, the relative dielectric constant was reduced under magnetic field. When $x = 0.01$, the change is biggest. At this point, the change is about 13.1%. Under the condition of magnetic field, the magnetic field force acting on domain boundary make the mobility of domain boundary reduce and domain's

contribution on the dielectric constant decreases, and make the dielectric loss decrease.

Fig. 6 shows the contrast of the dielectric loss with frequency of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics. Compared with no magnetic field, the relative dielectric constant increased slightly under magnetic field. But it is reduced when $x = 0.03$. The change of the dielectric loss reached 28.2% at 20 KHz. The reasons for the results may be the structure of the material that in the vicinity of the phase boundary changed by a strong magnetic field, resulting in increase of the dielectric response. Moreover, the clamping action of magnetic make the contribution of domain boundaries of the domain of dielectric loss reduce, significantly reducing the dielectric loss.

Fig. 5 The relative dielectric constant with frequency of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05, 0.07$).

Fig. 6 The dielectric loss with frequency of $(1-x)\text{BST} + x\text{BFO}$ ($x = 0.01, 0.03, 0.05$ and 0.07) ceramics.

4. Conclusions

In general, the $(1-x)\text{BST} + x\text{BiFeO}_3$ ceramics exhibit single perovskites structure. The samples have both ferroelectricity and ferromagnetism at room temperature. The dielectric constant of ferroelectric materials change evidently at the phase temperature and arise the peak even reach the highest value at curie temperature (T_c). In this case, the structure relaxation leads to lower activation energy of ions. So the new domains can formed spontaneously as the ions have larger mobility. The domains turn easily under the added electric field. When it is magnetized by external magnetic field, makes the lattice deformation occur in each domain. The content of

BiFeO_3 from 1% to 3% can result in obvious magnetoelectric coupling effect, but when excess BiFeO_3 could easily produce the defects of iron clusters lead to make smaller dielectric response, and related research is underway. The results suggest that the lead-free material is important to new magnetoelectric coupling and multiferroic materials and it could be widely used in many fields in the future.

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