

The properties of SBFTi-x ferroelectric ceramics

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BFO(BiFeO₃)-SBTi(Sr₂Bi₄Ti₅O₁₈) composite ferroelectric ceramics(referred to as SBFTi-x) were prepared by Sr₂Bi₄Ti₅O₁₈ and BiFeO₃, with the increasing of BFO content, compared to SBTi ceramics, Bi³⁺ and Fe³⁺ co-doped in A and B site cause the lattice distortion, which make SBFTi-x ceramics show the higher the remanent polarization and low leakage current density at room temperature. SBFTi-0.3 ceramic exhibits excellent ferroelectric properties at the electric field of 85kV/cm, the remanent polarization 2Pr and coercive field 2Ec is 18.66μC/cm² and 77.7kV/cm respectively, the lowest leakage current density $J = 2.34 \times 10^{-6}$ A/cm². In addition, with the increase BFO content, the changes of oxygen concentration and built-in electric field make the leakage current mechanism of SBFTi-x ceramics turn into the Ohms transmission mechanism-based from the Space-charge limit for leading.

Key words: SBFTi-x, Solid solution, Ferroelectric.

Introduction

Sr₂Bi₄Ti₅O₁₈ (SBTi) is the typical Bismuth layer-structured perovskite ferroelectrics (BLSFs). It has been reported that SBTi films have natural fatigue-free properties on Pt electrodes, but there are many deficiencies, such as smaller residual polarization (2Pr=10μC/cm²) and lower Curie temperature and so on, which limits its practical application [1]. Element doping, combining with other ferroelectric or multi-ferrous material to form composite ceramic are main way to improve the performance of BLSFs ferroelectric [2-4].

It is also an effective mean to improve the property of BLSFs by means of two kinds of different bismuth layered structure or perovskite structure material which can be complementary to each other and form solid solution [5]. The SBTi ceramic can be understood as a composite ceramic structure with five-layer perovskite formed by inserting SrTiO₃ perovskite layer into Bi₄Ti₃O₁₂ ceramic with three-layer perovskite. So it is feasible to form a solid solution between the SBTi material and the perovskite structure material. In the process of solid solution with BLSFs In many perovskite materials, if choose perovskite structure material containing magnetic ions (such as BiFeO₃, referred to as BFO) to form solid solution with BLSFs material, the formation of solid solution will show multi-ferrous, which is also known as the magnetic

layer insert method. More importantly, the (Bi₂O₂)²⁺ layers in BLSFs play the key role as both space-charge compensation and insulation, with an expectation able to further reduce the leakage [6]. The study of BFO-SBTi solid solution materials [7-12] show this solid solution system has high ferrous properties at room temperature, and therefore has a magnetoelectric coupling effect, with very wide range of research prospects in many applications such as magnetic sensors, information storage and spin electronics.

At present, the research of SBFTi solid solution ceramics concentrate on the molar ratio of BFO and SBTi to 1 : 1, while the solid solution ceramics with different composition ratio are less studied. There are many reports about synthesis and electrical characterization of five-layered Aurivillius SrBi₃FeTi₄O₁₈ ceramics [8-10]. Motivated by these results and looking for a material where ferroelectric and magnetic orders coexist, we choose Sr₂Bi₄Ti₅O₁₈ with five-layer structure, compounded it with BiFeO₃. And we report here the crystal structure and ferroelectric properties of xBFO-(1-x)SBTi composite ceramics for four compositions (x = 0, 0.1, 0.3 and 0.5). To our knowledge, there are few reports about these compounds.

Experimental

xBFO-(1-x)SBTi(SBFTi-x, x = 0, 0.1, 0.3 and 0.5) composite ceramics were prepared by sol-gel with self-propagating combustion method. The Sr₂Bi₄Ti₅O₁₈ (SBTi) and BiFeO₃ (BFO) precursor solutions were prepared by dissolving strontium acetate, bismuth nitrate, tetrabutyl

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titanate and ferric nitrate in ethylene glycol at room temperature. Acetylacetone was added to stabilize the solution. 10 mol% excessive bismuth was used to compensate the evaporation of bismuth during the sintering process. The precursor solutions of SBFTi-*x* were dried in a drying oven at 60 °C ~ 80 °C for 10 hrs and finally the fluffy precursor powders were obtained. The obtained powders were calcined at 500 °C for 2 hrs to remove a large amount of organic matter. The pre-calcined powders were thoroughly mixed with ethanol in a ball mill for 15 hrs, and then pressed into pellets with diameter of 10mm, the thickness of about 1mm disc (pressure 160MPa). Then the pellets were sintered in air at 1060 °C~1120 °C for 8 hrs and followed by furnace cooling. The crystal structures of the ceramics were determined by X-ray diffraction (XRD) method using D8-Advanced X-ray diffraction with Cu K α radiation ($k = 0.54184$ nm) at a tube voltage of 40 kV and a tube current of 40 mA with scanning range from 20 degree to 60 degree. The ceramic surface morphology were tested by the Japanese production of high-resolution field emission scanning electron microscope SU8010 with working voltage 3.0 kV. The SBFTi-*x* ceramics were subjected to Raman spectroscopy in a range of 50 to 1200 cm⁻¹ using NEXUS670 Fourier transform infrared-Raman spectrometer manufactured by Thermo Nicolet Corporation of the United States. The pellets were filed and polished to a thickness of about 0.5 mm and then electroded with silver for ferroelectric and leakage property measurements.

Results and Discussion

The XRD analysis of SBFTi-*x* ceramics

Fig. 1(a) show the XRD patterns of the SBFTi-*x* ($x = 0, 0.1, 0.3, 0.5$) composite ceramics. These compounds are found to consist of a pure bismuth layer perovskite structure and their patterns can be matched well with the six-layered Aurivillius structure Bi₇Fe₃Ti₃O₂₁ (Space group Fmm2, JCPDS:54-1044). However, with *x* increasing, the second phase which was reported as cubic structure appears [13]. This is consistent with the results found by Wang [14] et al. in strontium doped Bi₇Fe_{1.5}Co_{1.5}Ti₃O₂₁. The (1131) plane diffraction peaks shift to the lower angles with the substitution of Fe³⁺ for Ti⁴⁺ and Bi³⁺ for Sr²⁺ and then to the higher angles from Fig. 1(b), which due to the incorporation of ionic radii [15-17]. The deviation of the diffraction peak angle indicates lattice distortion and it is the largest in SBFTi-0.3 ceramic.

The microstructure study of SBFTi-*x* Ceramics

Fig. 2 shows SEM images of SBTi and SBFTi-*x* ($x = 0.1, 0.3, 0.5$) ceramics. It can be seen from the figure that the grains of each ceramic sample sintered are lamellar and conform to the typical characteristics of bismuth layered perovskite structure. Besides, the grain

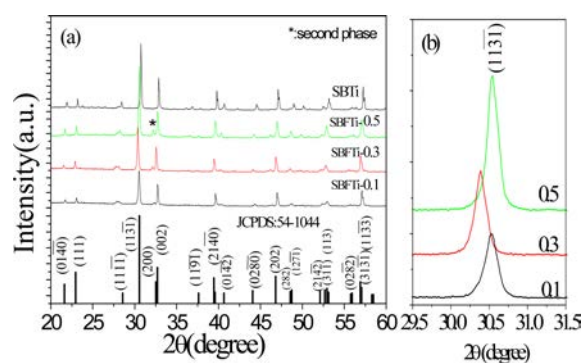


Fig. 1. XRD pattern of the SBFTi-*x* ceramics sintered at 1060 °C (a) 20 ° ~ 60 °; (b) 29.5 ° ~ 31.5 °.

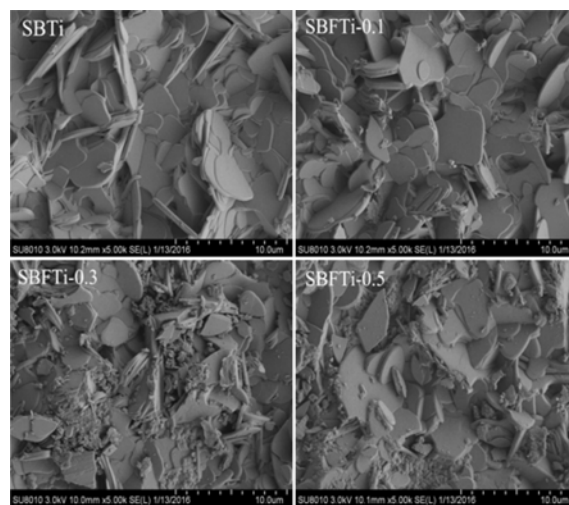


Fig. 2. SEM images of SBTi and SBFTi-*x* ($x = 0.1, 0.3, 0.5$) ceramics.

grows well and the grains are randomly oriented with low porosity. With the increase of the amount of BFO doping, the edge of the lamellar grains of SBFTi-*x* ceramics is gradually passivated when compared with the elliptical lamellar structure of SBTi ceramics, and meanwhile there comes out the second phase grains, which are consistent with the XRD results.

The Raman Spectra study of SBFTi-*x* Ceramics

Fig. 3 shows the Raman spectra of SBTi and SBFTi-*x* ($x = 0.1, 0.3, 0.5$) with Raman shift ν at 50~1000cm⁻¹ at room temperature. It can be seen from the figure that there are strong Raman phonon modes with the Raman frequency ν at 60 ~ 90 cm⁻¹, 110 ~ 160 cm⁻¹, 268 cm⁻¹, 560 cm⁻¹ and 872 cm⁻¹, respectively. Raman spectroscopy is very sensitive to the change of atomic position, and the change of phonon mode can reflect the substitution position of doping ions in composite ceramics [18-21]. In the high frequency, it corresponds to the twist die of TiO₆ when ν is 268 cm⁻¹ (at the C), while it corresponding to the TiO₆ tensile modulus when ν is 560 cm⁻¹ and 872 cm⁻¹ (D and D) [21]. It can be seen from the figure that with

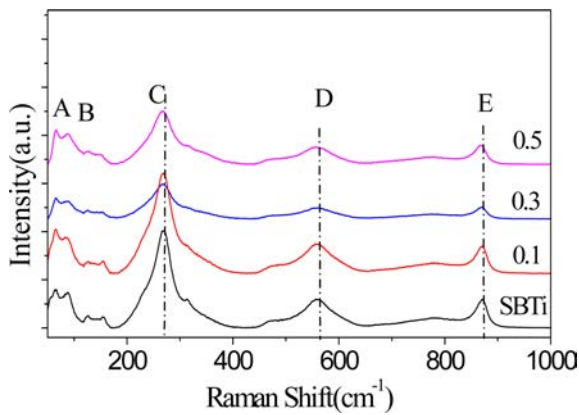


Fig. 3. Raman spectra of SBTi and SBFTi-x ($x = 0.1, 0.3, 0.5$) ceramics at room temperature.

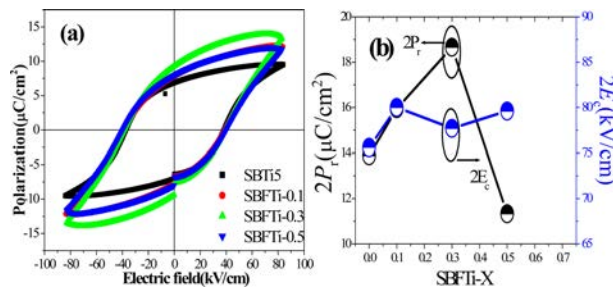


Fig. 4. (a) The hysteresis loops of SBTi and SBFTi-x ($x = 0.1, 0.3, 0.5$) ceramics; (b) $2P_r(2E_c)$ as function of x at room temperature.

the increase of x , the three high frequency phonon modes of the SBFTi ceramics at the C, D and E only change in strength while the shape is basically consistent. And that indicates the BFO doping does not have significant effect on the bismuth layer perovskite structure. The strength is gradually weakened mainly because Fe^{3+} gradually replaced Ti^{4+} ions to form Fe/TiO_6 octahedron, which result tilt in the original TiO_6 octahedron.

The ferroelectric properties study of SBFTi-x Ceramics

The hysteresis loops of the ceramic sample under 85 kV/cm were obtained in Fig. 4(a) and (b). From the figures, we can see that the hysteresis loop of each ceramic sample is saturated. The residual polarization intensity of SBFTi-x ceramics is improved first and then decreased while the coercive field $2E_c$ has been rising with the BFO content increased. When $x = 0.3$, the SBFTi-0.3 ceramic sample show the best ferroelectricity and its residual polarization intensity is $2P_r = 18.66 \mu\text{C}/\text{cm}^2$ and coercive field $2E_c = 77.7 \text{ kV}/\text{cm}$. There are many factors that will affect the ferroelectric properties of the bismuth layer perovskite material such as the internal defects of the material, the oxygen vacancy concentration and the degree of lattice distortion. From the XRD analysis above, the lattice distortion of SBFTi-0.3 ceramics is the largest and exhibits excellent

ferroelectric properties with the highest residual polarization intensity.

The leakage performance study of SBFTi-x ceramics

Fig. 5 shows the leakage current density curves of SBTi and SBFTi-x ($x = 0.1, 0.3, 0.5$) ceramics. It can be seen from the figure that the leakage current density of the ceramic samples increases with the increase of the test electric field. The leakage current density curve tends to be gentle when the test electric field is higher than 40 kV/cm. The leakage current density of SBTi ceramics is $2.66 \times 10^{-6} \text{ A}/\text{cm}^2$ under the electric field of 70 kV/cm, while the leakage of SBFTi-x ceramics increases and then decreases with the increase of BFO. The minimum leakage current density of SBFTi-0.3 is $2.34 \times 10^{-6} \text{ A}/\text{cm}^2$, which also ensures that the high electric field of breakdown, the high degree of residual polarization and other excellent ferroelectric properties.

In order to analyze the leakage current mechanism of SBTi and SBFTi-x ceramics, the leakage current density curve is fitted as shown in Fig. 6. The leakage mechanism inside the ceramic material can be determined according to the slope (s) in the different electric field range obtained after the fitting. It's important to note that with

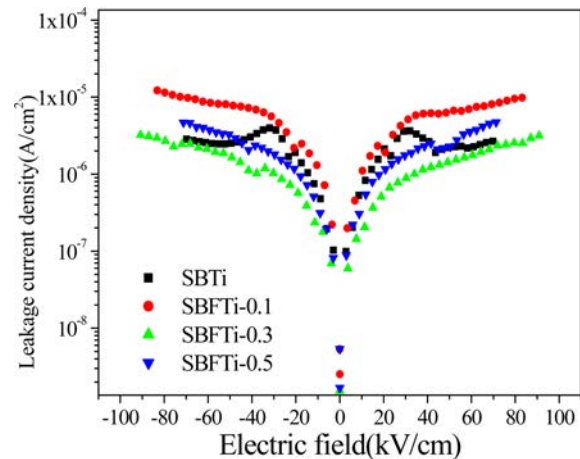


Fig. 5. Leakage current density of SBTi and SBFTi-x ($x = 0.1, 0.3, 0.5$).

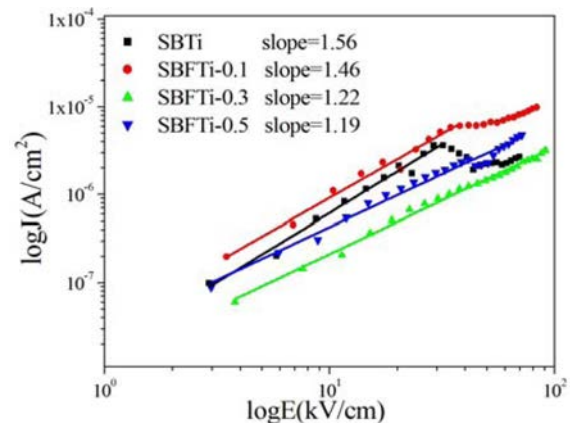


Fig. 6. $\log J$ - $\log E$ curve of SBTi and BFTi-x ($x = 0.1, 0.3, 0.5$) ceramics

the increase of BFO, the slope of $\log J$ - $\log E$ curve of SBFTi ceramics decreases gradually from 1.56 of SBTi ceramic to 1.19 of SBFTi-0.5 ceramic, which indicates that the leakage mechanism is closer to the ohmic conduction and in the meanwhile the effect of limiting the charge is reduced. The reason for this phenomenon is that: (1) Since the breakdown electric field of SBFTi ceramic is higher than the SBTi ceramic, the necessary electric fields of the internal potential well filled with carrier charge is also increased gradually. The formation of the carrier charge in the potential of the same electric field is gradually weakened, resulting in the internal electric field weakened and the role of space current decreases. (2) The migration of oxygen vacancies under the action of the electric field can affect the interfacial barrier to change the leakage mechanism [22]. SBFTi ceramics can be regarded as Bi^{3+} and Fe^{3+} co-doped SBTi ceramics, which reduces the oxygen vacancy concentration caused by the volatilization of Bi elements and leads to the decrease of carrier concentration. In the meanwhile the effect of space limiting current is weakened.

Conclusions

In this paper, SBFTi- x ($x = 0 \sim 0.5$) system ceramics were prepared by sol-gel method. The crystal structure and ferroelectric properties were studied and the following conclusions were obtained:

1) The SBFTi- x ($x = 0 \sim 0.5$) ceramics prepared at 1060°C for 2hrs were all bismuth layered perovskite structure. with the increasing of BFO content, compared to SBTi ceramics, Bi^{3+} and Fe^{3+} co-doped in A and B site cause the lattice distortion Fe^{3+} enters the perovskite layer. The phonon mode intensity of TiO_6 decreased at high frequency and the lattice distortion of SBFTi-0.3 ceramic was largest.

2) SBFTi-0.3 ceramic exhibits excellent ferroelectric properties due to large lattice distortion and the remanent polarization $2P_r$ and coercive field $2E_c$ at the electric field of 85 kV/cm was 18.66 $\mu\text{C}/\text{cm}^2$ and 77.7kV/cm respectively, and the lowest leakage current density $J = 2.34 \times 10^{-6} \text{ A}/\text{cm}^2$. In addition, with the increase BFO content, the changes of oxygen concentration and built-in electric field make the leakage current mechanism of SBFTi- x ceramics turn into the Ohms transmission mechanism-based from the Space-charge limit for leading.

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