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Letter

Dielectric and magnetic properties of $0.7Bi(Fe_{1-x}Cr_x)O_3$–$0.1BaTiO_3$–$0.2PbTiO_3$ solid solutions

Xiao-hui Liu[a,*], Zhuo Xu[a], Xiao-yong Wei[a], Xi Yao[a], Xiao Yang[b]

[a] Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China
[b] School of Information Science and Technology, Jiujiang University, Jiujiang 332005, China

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ABSTRACT

$0.7Bi(Fe_{1-x}Cr_x)O_3$–$0.1BaTiO_3$–$0.2PbTiO_3$ ($x = 0$, 0.1, 0.2, 0.3) solid solutions were prepared by the traditional ceramic process. X-ray diffraction results revealed that the samples with $x = 0$–0.3 showed pure perovskite structure. Frequency and temperature dependences of dielectric constants and dielectric loss of the samples were investigated. Both dielectric constant and the loss tangent increased at given frequencies (100 Hz–1 MHz), while the Curie temperature of the solid solutions decreased with increasing Cr content. Room temperature magnetic hysteresis loops indicated that an appropriate amount of Cr could improve magnetization of the solid solutions.

1. Introduction

Ferroelectromagnetic materials possess ferromagnetism and ferroelectricity simultaneously as a result of the coexistence of electric and magnetic orders. In this case, magnetization can be induced by an electric field while electrical polarization can be induced by a magnetic field [1]. However, due to their low Néel temperature or negligible magnetoelectric effect in most ferroelectromagnetic materials, no practical application of ferroelectricity and ferromagnetism has been reported. $BiFeO_3$ (BFO) is a promising candidate as single phase ferroelectromagnetic material because it is antiferromagnetic with a relatively high Neel temperature ($T_N = 380\,^\circ C$) and ferroelectric with high $T_c = 810\,^\circ C$ [2]. Unfortunately, bulk BFO ceramic has several disadvantages. First, it is difficult to prepare single phase BFO. Second, BFO ceramic has low electrical resistivity. These have prevented its practical applications as piezoelectric or magnetoelectric functional components. To date, several perovskites (such as $PbTiO_3$ and $BaTiO_3$) [3,4] have been used to form solid solution with BFO so as to increase electrical resistance and stabilize the perovskite structure. Although perovskite structure of these solid solutions has been found to be stable and the spontaneous magnetic moment is increased at room temperature, their ferromagnetism is weak due to the antiferromagnetic nature. Substantial work has been implemented on BFO-based materials to improve magnetization, such as doping at A sites [5,6] or B sites [7], but the effect for such a purpose is not remarkable.

Baettig and Spaldin performed first principle calculations on $BiFeO_3$–$BiCrO_3$ system [8]. Double-perovskite Bi_2FeCrO_6 was hypothetically constructed with a long-range Fe^{3+}–Cr^{3+} order, and a magnetic moment of $2\mu_B$ per formula unit and a polarization of $\sim 80\,\mu C/cm^2$ were predicted. Therefore, it is worthwhile to experimentally investigate the effect of substitution of Cr for Fe on the physical properties of BFO-based materials. Recently, BFO thin films doped with 3 mol% Cr were prepared using a chemical solution deposition method by Kim et al. [9]. They found that the solubility of Cr in BFO is rather small and a second phase ($Bi_{25}FeO_{40}$) was observed in the thin films with 5 mol% Cr. $Bi(Fe_{1-x}Cr_x)O_3$ ($x \le 0.2$) were synthesized using a combustion method by Li et al. [10]. Up to now, bulk Cr-doped BFO-based solid solutions using solid-state reaction method have been seldom reported in the literature. In this letter, we report the preparation and characterization of $0.7Bi(Fe_{1-x}Cr_x)O_3$–$0.1BaTiO_3$–$0.2PbTiO_3$ (BFOC–BT–PT, $x \le 0.3$) solid solutions via the conventional solid-state reaction method. Magnetic and dielectric properties were investigated.

2. Experimental procedure

$0.7Bi(Fe_{1-x}Cr_x)O_3$–$0.1BaTiO_3$–$0.2PbTiO_3$ ($x = 0$, 0.1, 0.2, 0.3, 0.4) solid solutions were fabricated by the conventional solid-state reaction method. Analytical-grade

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* Corresponding author. Tel.: +86 29 82668679; fax: +86 29 82668794.
E-mail address: lxhui@mail.xjtu.edu.cn (X.-h. Liu).

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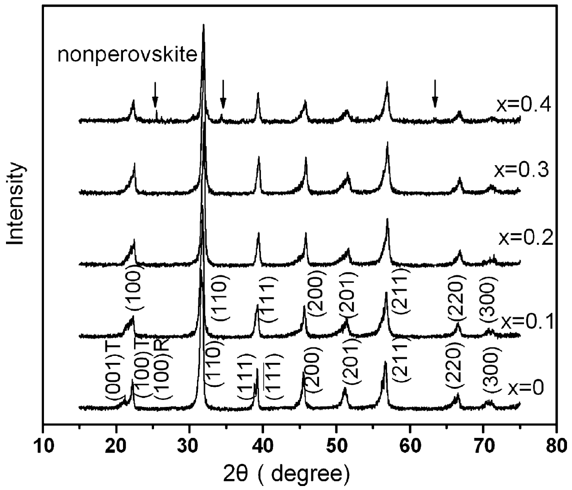

Fig. 1. XRD patterns of the BFOC–BT–PT ceramics with different Cr contents.

raw materials, Bi_2O_3, Fe_2O_3, Cr_2O_3, $BaCO_3$, PbO and TiO_2, were weighed and mixed in a ball mill for 12 h, using alcohol as media. After drying, the powders were calcined at 860–1000 °C for 2 h in air and ball milled for another 12 h. The resultant powders were pressed into disks of 10 mm in diameter and 1 mm in thickness using a hardened stainless steel die at a pressure of 400 MPa, with polyvinyl alcohol (PVA) as binder. After burning off PVA, the pellets were sintered at 1050–1130 °C for 3 h in air. The specimens were polished and electroded with a postfire silver paste on both sides to measure electric properties.

Phase compositions of the specimens were characterized by an X-ray diffraction (XRD) (Rigaku D/MAX-2400, CuK_α radiation). Microstructure of fresh fracture surfaces of sintered samples was examined by using a scanning electron microscopy (SEM) (JSM-6360). Frequency and temperature dependences of complex permittivity were measured by using an Aglient 4294A impedance analyzer and an HP4284 impedance analyzer. Magnetic hysteresis loops were measured by LakeShore 7307 vibrating sample magnetometer (VSM).

3. Results and discussion

Fig. 1 shows XRD patterns of the BFOC–BT–PT with $x = 0$, 0.1, 0.2, 0.3, and 0.4. The sample with $x = 0$ shows the presence of both rhombohedral and tetragonal phases. The tetragonal phase cannot be clearly resolved [3] but manifests itself as a peak adjacent to the (1 0 0) peak at lower angle. The samples with $x = 0.1$–0.3 possess single phase of rhombohedral structure. There were nonperovskite phases in the sample with $x = 0.4$. In addition, diffraction peaks of the samples shift toward higher angles with increasing content of Cr. This result indicates that lattice constant of the samples decreases with increasing content of Cr, which is because the radius of Cr^{3+} is smaller than that of Fe^{3+}.

Fig. 2 shows SEM images of the BFOC–BT–PT samples. The ceramics were fully densified, with an average grain size of about 2–3 μm, which slightly decreased with increasing concentration of Cr. It is noticed that transgranular fracture becomes more and more pronounced due to the increased crystalline stress. The intrinsic stress was superimposed on the external stress, which prevented the fracture from beginning along grain boundaries.

Fig. 3 shows the frequency dependence of dielectric response of the samples measured at room temperature (100 Hz–1 MHz). It can be seen that the dielectric constant and the loss tangent increase with increasing content of Cr at a given frequency. This can be attributed to the fact that the substitution of Cr^{3+} for Fe^{3+} ions produced more vacancies that improved charge space polarization, thus leading to an increase in dielectric constant and the loss tangent. The dielectric constant of the samples with $x > 0.1$ decreases

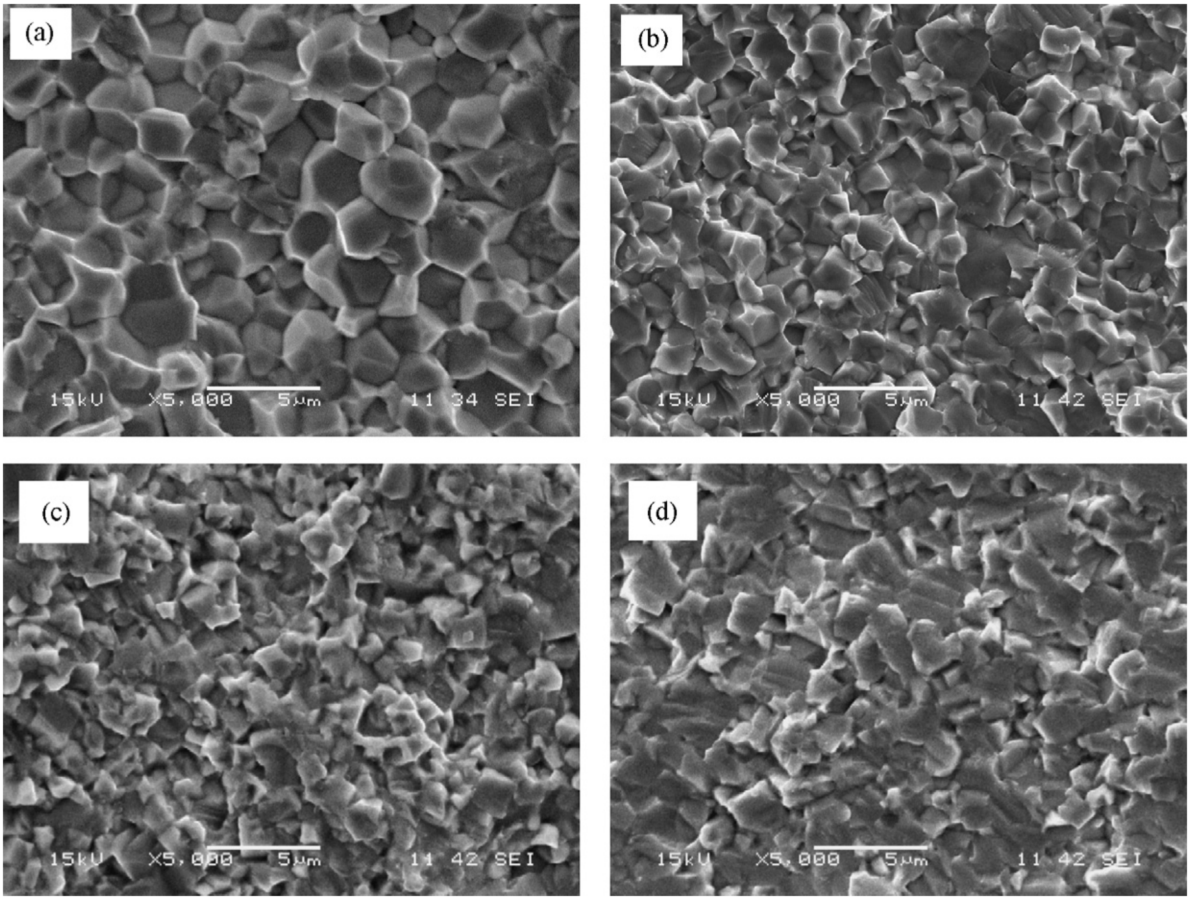

Fig. 2. SEM photos of fracture surfaces of the BFOC–BT–PT samples with different Cr contents. (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$.

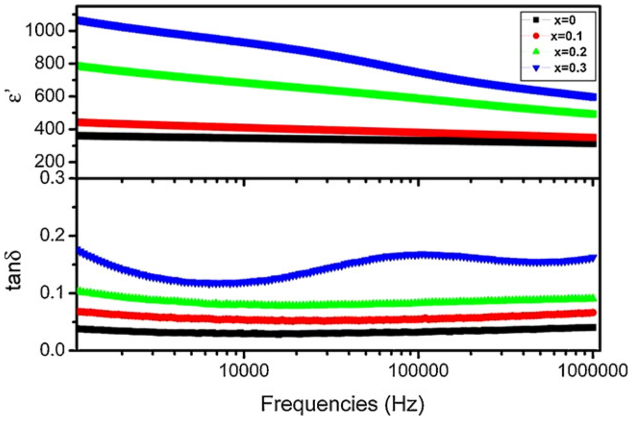

Fig. 3. Dielectric constant and loss of the BFOC–BT–PT ceramics as a function of frequency with different Cr contents.

more quickly with frequency, indicating their relaxor characteristics [11].

Fig. 4 shows dielectric constant and loss of the samples as a function of temperature at 10^6 Hz. Dielectric maximum can be observed, revealing the ferroelectric–paraelectric phase transition of the BFOC–BT–PT ceramics. A sharp dielectric peak of the samples with $x \leq 0.1$ reflects ferroelectric characteristics. However, the dielectric peaks of the samples with $x > 0.1$ become broad reflecting the diffuse characteristics of the phase transition [12]. The peak dielectric constant decreases initially with increasing Cr to $x = 0.2$, and then increases with further increase in Cr content. The temperature at the peak determines that the phase transition temperatures are about 637, 621, 589, and 545 °C for $x = 0$, 0.1, 0.2, and 0.3, respectively, decreasing with increase in Cr content. The structure disorder and compositional fluctuation produced in the arrangement of cation at B site with lattice vacancies lead to the microscopic heterogeneity in composition resulting in the distribution of different local Curie regions [13]. Therefore, the more Cr substitutions the higher degree of the structure and compositional disorder and thus more pronounced diffuse phase transition would be.

Fig. 5 shows *M*–*H* curves of the BFOC–BT–PT samples, measured at room temperature. The *M*–*H* behavior of the sample with $x = 0$ shows a typical antiferromagnetic character, but those of the other samples are of typical ferromagnetic (or ferrimagnetic) character, with remanent magnetizations being relatively small as compared to normal ferromagnetic compounds. Small remanent magnetizations and unsaturated *M*–*H* behavior of the solid solutions indicate that they are basically antiferromagnetic with weak ferromagnetism [14]. The remanent magnetizations of BFOC–BT–PT show a rise with the increase of Cr content when $x \leq 0.2$. Above $x = 0.2$, the remanent magnetization decreases.

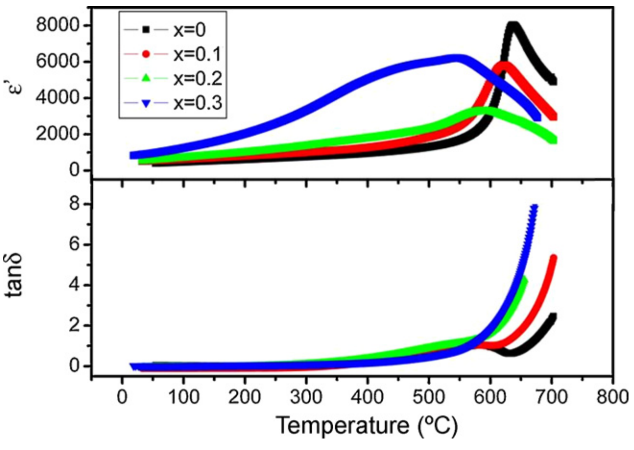

Fig. 4. Dielectric constant and loss of the BFOC–BT–PT ceramics as a function of temperature with different Cr contents.

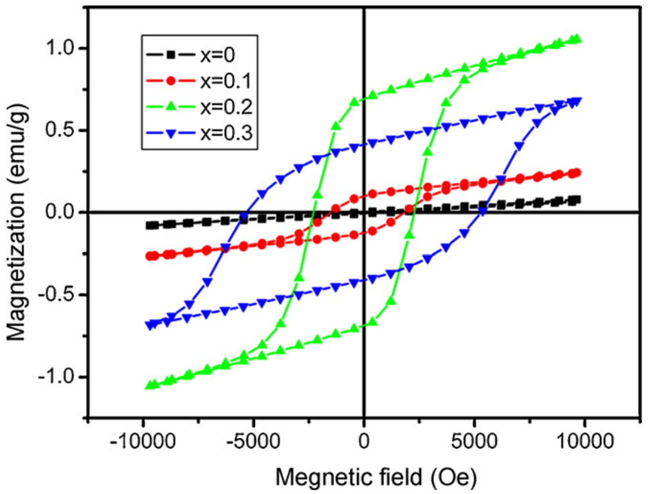

Fig. 5. Magnetic hysteresis loops of the BFOC–BT–PT samples with different Cr contents.

Physical properties of BFO-based solid solutions with simultaneously occurring magnetic and electric orderings are not yet understood. Remanent magnetizations observed in this letter reveal ferromagnetism, but very weak compared to typical ferromagnetic compounds. However, the enhancements of net magnetization in these solid solutions relative to $BiFeO_3$ single crystal and $BiFeO_3$-based solid solutions are enormous. With the addition of $BaTiO_3$ and $PbTiO_3$, it has been possible to detect the spontaneous magnetic moment, as in the case of solid solutions with $BaTiO_3$ [4]. Moreover, the magnetization increased remarkably by doping Cr at $x \leq 0.2$. We think that the driving force of weak ferromagnetism in antiferromagnets originates from two aspects. The first possible reason is the increase of oxygen vacancies. Li and MacManus-Driscoll [15] studied the effect of oxygen vacancies, using coulometric titration, on the magnetization of polycrystalline BFO and found that the magnetization of BFO increased with increasing content of oxygen vacancies. Thus, the relative large magnetization of the BFOC–BT–PT solid solutions observed in this work might also be attributed to the canting of the magnetic moments arising from oxygen vacancies. This is also in an agreement with their dielectric properties. The second possible reason is that local ferromagnetic ordered structure might form between Fe^{3+} ions and Cr^{3+} ions, though the long-range Fe^{3+}–Cr^{3+} order is impossible to form in the BFOC–BT–PT solid solutions prepared by the solid-state reaction method. It is known that the strong ferromagnetic coupling exists between Fe^{3+} and Cr^{3+} via 180° superexchange interaction [16]. With further doping Cr, the magnetic coercive field *Hc* increased obviously, and the remanent magnetizations *Mr* decreased. This is because the sintering temperature increases with the increase of Cr content, the volatilization of Pb^{2+} and Bi^{3+} in the solid solutions occurred more easily. Consequently, vacancies and stress would be produced [17]. Much more work is required to interpret the magnetization mechanism of the Cr^{3+}-doped $BiFeO_3$-based materials.

4. Conclusions

Single phase perovskite BFOC–BT–PT solid solutions with $x \leq 0.3$ were synthesized using solid-state reaction method. Magnetic hysteresis loops and ferroelectric response were observed in these materials, indicating that the addition of an appropriate amount of Cr enhances the magnetization remarkably. The synthesis of

BFOC–BT–PT solid solutions provides not only an opportunity to investigate the role of Cr in $BiFeO_3$-based compounds, but also shows a possibility to bring about significant magnetoelectric effect in BFO-based ceramics.

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