

Ferroelectric and Ferromagnetic Properties of $0.7\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3-0.3\text{BaTiO}_3$ Solid Solutions

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$0.7\text{Bi}(\text{Fe}_{1-x}\text{Cr}_x)\text{O}_3-0.3\text{BaTiO}_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2$) solid solutions were prepared by the traditional ceramic process. X-ray diffraction revealed that all samples with $x = 0-0.15$ showed pure rhombohedral perovskite structure. Frequency dependences of dielectric constants and dielectric loss were investigated. Proper amount of Cr could decrease the dielectric loss. Measurements of magnetic and ferroelectric hysteresis loops at room temperature indicated that the solid solutions showed ferroelectricity and ferromagnetism simultaneously. Magnetization of the solid solutions was with increasing content of Cr.

I. Introduction

FERROELECTROMAGNETIC materials possess ferromagnetism and ferroelectricity simultaneously as a result of the coexistence 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 Néel temperature ($T_N = 380^\circ\text{C}$) and ferroelectric with high $T_c = 810^\circ\text{C}$.² However, bulk BFO ceramic has several disadvantages. First, it is difficult to prepare single-phase BFO. Second, BFO ceramic has low electrical resistivity. This has prevented its practical applications as piezoelectric or magnetoelectric functional components. To date, several perovskites (such as PbTiO_3 , PZT, and BaTiO_3)³⁻⁵ have been used to form solid solution with BFO in order to enhance the electrical resistance and stabilize the perovskite structure. Although the 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 still weak due to the antiferromagnetic nature. Substantial work has been implemented on BFO-based materials to improve magnetization, such as doping on A sites^{6,7} or B sites,⁸ but the effect of improving magnetization of BFO-based materials is not remarkable.

Baettig and Spaldin⁹ performed first principle's calculations on $\text{BiFeO}_3-\text{BiCrO}_3$ system. Double-perovskite $\text{Bi}_2\text{FeCrO}_6$ was constructed hypothetically with a long-range $\text{Fe}^{3+}-\text{Cr}^{3+}$ order, and a magnetic moment of $2 \mu_B$ per formula unit and a polarization of $\sim 80 \mu\text{C}/\text{cm}^2$ were predicted. Therefore, it is worthwhile to investigate experimentally 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.*¹⁰ They found that the solubility of Cr in BFO is rather small and a second phase ($\text{Bi}_{25}\text{FeO}_{40}$) was observed in the thin films with 5 mol% Cr. Till date, no bulk Cr-doped BFO-based solid solution using solid-state reaction method has been reported in the literature. Because perovskite structure of BFO-based solid solution is stable with the content of BaTiO_3 over 20 mol%,¹¹ $0.7\text{BiFeO}_3-0.3\text{BaTiO}_3$ solution was selected in the present study. $0.7\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3-0.3\text{BaTiO}_3$ solid solutions with $x = 0-0.2$ were synthesized by the conventional solid-state reaction process. It is found that the substitution of Cr for Fe enhances the room temperature magnetization remarkably.

II. Experimental Procedure

$0.7\text{BiFe}_{1-x}\text{Cr}_x\text{O}_3-0.3\text{BaTiO}_3(\text{BFOC}_x\text{-BT}, \text{ with } x = 0-0.2)$ solid solutions were fabricated by the conventional solid-state reaction method. Analytical-grade raw materials, Bi_2O_3 , Fe_2O_3 , Cr_2O_3 , BaCO_3 , 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 $860^\circ-960^\circ\text{C}$ 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 $1060^\circ-1100^\circ\text{C}$ for 3 h in air. The specimens were polished and electroded with a postfire silver paste on both sides.

Phase compositions of the specimens were characterized using X-ray diffraction (XRD) (Rigaku D/MAX-2400, Rigaku, Tokyo, Japan, $\text{CuK}\alpha$ radiation). Microstructure of fresh fracture surfaces of sintered samples was examined using a scanning electron microscopy (SEM) (JSM-6360, JEOL, Tokyo, Japan). Electrical insulation resistance was measured using an HP4339A-HP16339A high resistance meter (Agilent, Palo Alto, CA). Frequency dependence of complex permittivity was measured using an HP4284 impedance analyzer (Agilent). Ferroelectric hysteresis loops were characterized by using a ferroelectric test system (TF Analyzer 2000, aixACCT, Aachen, Germany) and magnetic hysteresis loops were measured using an LakeShore 7307 vibrating sample magnetometer (VSM) (Lakeshore Cryotronic, Westerville, OH).

III. Results and Discussion

Figure 1 shows the XRD patterns for $\text{BFOC}_x\text{-BT}$ with $x = 0, 0.05, 0.1, 0.15,$ and 0.2 . All samples possess single phase of rhombohedral perovskite structure for $x = 0-0.15$. There were some nonperovskite phases in the sample with $x = 0.2$. 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 decrease with increasing content of Cr, which is because the radius of Cr^{3+} is smaller than that of Fe^{3+} .

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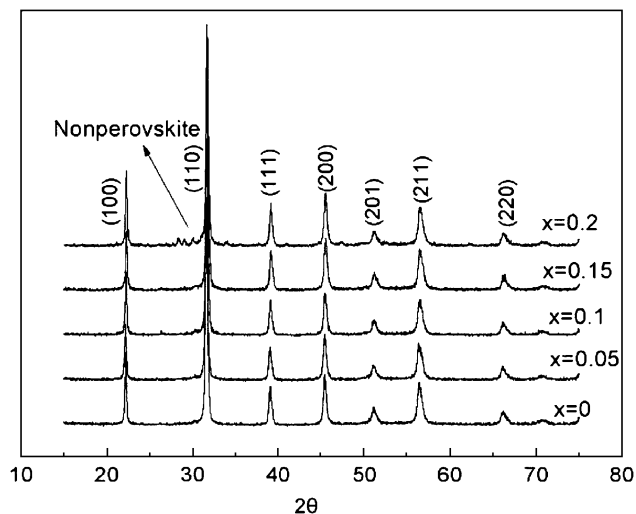


Fig. 1. X-ray diffraction patterns of the $\text{BFOCr}_x\text{-BT}$ ceramics with different Cr contents.

Figure 2 shows SEM images of $\text{BFOCr}_x\text{-BT}$. The ceramics were fully densified. The average grain size was about 2–4 μm , which slightly increased 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.

Figure 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 decreases first and then increases with increasing content of

Cr at a given frequency. The sample with $x = 0.2$ has the largest dielectric constant. The trend of dielectric loss at low frequencies correlates with the corresponding electrical resistivities. The resistivities were measured to be 3×10^{10} , 5×10^{12} , 6×10^{12} , 3×10^{12} , and $5 \times 10^{11} \Omega \cdot \text{cm}$ for $\text{BFOCr}_x\text{-BT}$ with $x = 0, 0.05, 0.1, 0.15,$ and 0.2 , respectively. For example, 10^3 Hz, and $\tan\delta$ values of $\text{BFOCr}_x\text{-BT}$ were 0.13, 0.084, 0.079, 0.088, and 0.115, respectively. This indicates that small amount of Cr could decrease the conductivity of the solid solutions, thus decreasing dielectric loss. This is due to the fact that the presence of Cr promoted densification of the samples. However, the dielectric losses of samples are still high, which might be attributed to relaxation polarization losses and conductive losses, especially the relaxation ones. Because $\tan\delta$ values of the samples show a peak as a function of frequency, such as the sample with $x = 0$. If the frequency measured increases, the other Cr-doped samples will also show similar peaks. Similar phenomena were also observed in other literatures.¹² They explained that this was relaxation polarization maybe due to the orientational polarization present in the bulk. In addition, as the content of Cr is increased to $x > 0.1$, the dielectric loss started to increase, which is because the dielectric relaxation mainly resulted from oxygen vacancies becomes more stronger with the content of Cr.

P - E curves of the samples are shown in Fig. 4. For the sample with $x = 0$, P - E loop rounded corners, indicating significant conductive losses. This is consistent with the observation of lower resistivities and higher dielectric losses for the sample. The samples with higher Cr content were less conductive. However, P - E saturation could not be reached at electric fields of < 70 kV/cm. Owing to their high dielectric strength, these materials have potential high-energy applications. Unfortunately, the coercive field of the $\text{BFOCr}_x\text{-BT}$ ceramics was too high to allow specimens to be completely poled, and hence the piezoelectric properties were not characterized.

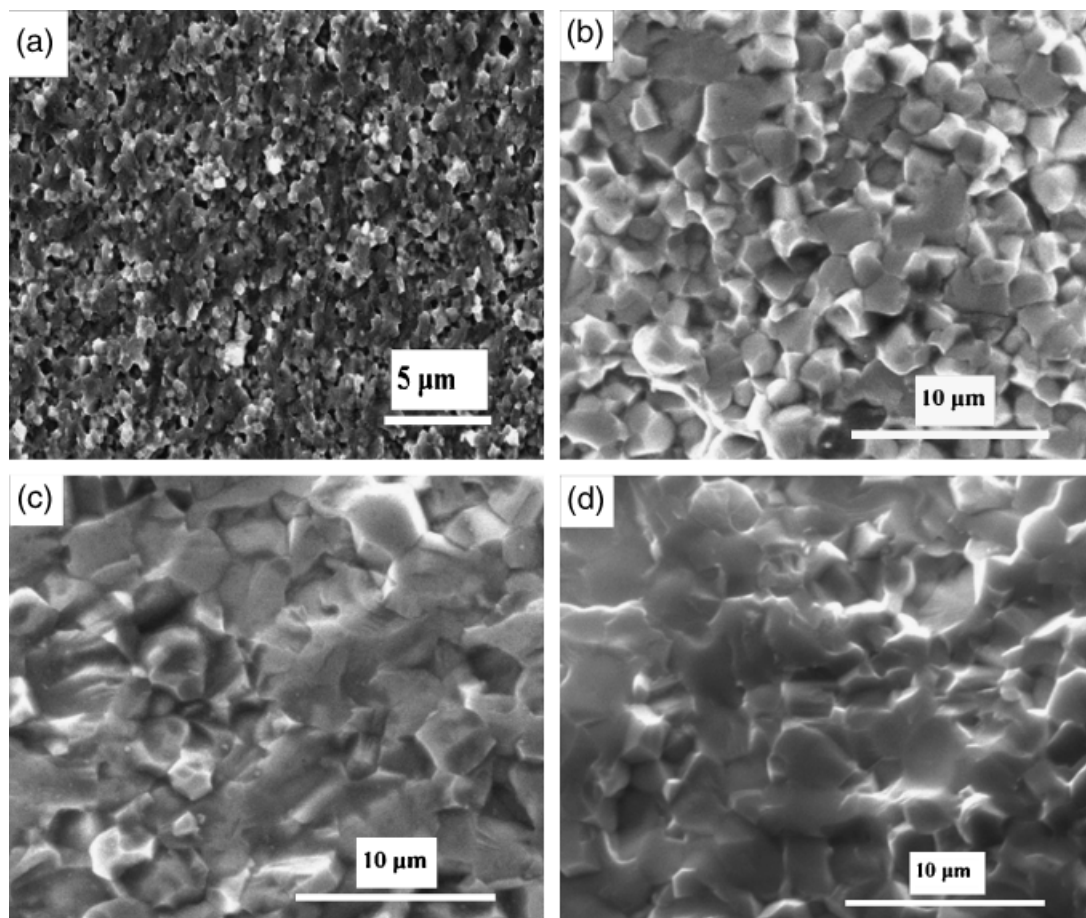


Fig. 2. SEM photos of fracture surfaces of the $\text{BFOCr}_x\text{-BT}$ samples with different Cr contents (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, and (d) $x = 0.15$.

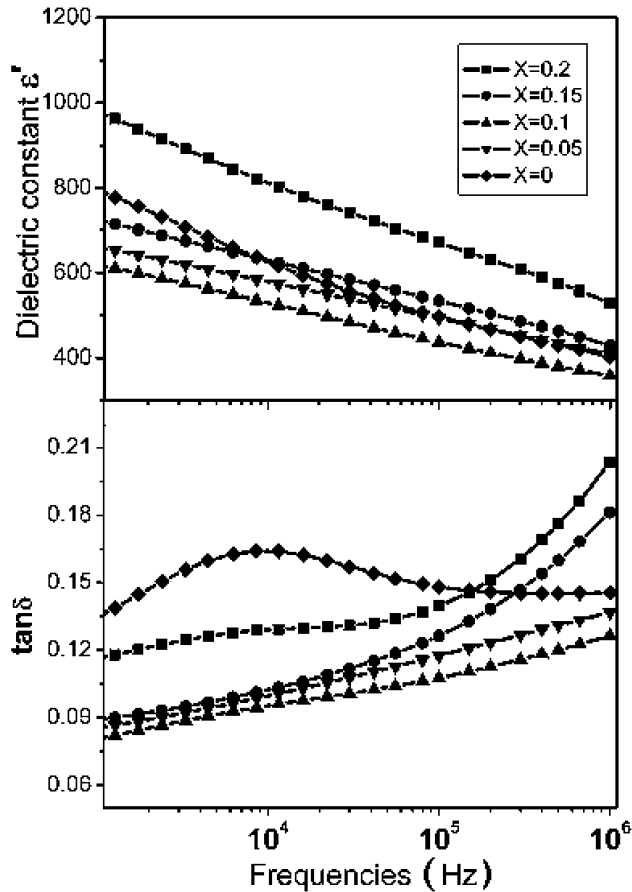


Fig. 3. Dielectric constant and loss of the BFOCr-BT ceramics as a function of frequency with different Cr contents.

Figure 5 shows $M-H$ curves of the BFOCr-BT samples with $x = 0, 0.05, 0.1,$ and $0.15,$ respectively, measured at room temperature. The BFOCr-BT solid solutions exhibit symmetric magnetic hysteresis loops, indicating that they are magnetically ordered materials. The remanent magnetizations of BFOCr-BT for $x = 0.05, 0.1,$ and 0.15 are about $0.02, 0.59,$ and 0.79 emu/g, respectively, showing an increase with the increasing Cr content. The remanent magnetizations were relatively small as compared with nominal ferromagnetic compounds. Small remanent magnetizations and unsaturated $M-H$ behavior of the solid solutions indicate that they are basically antiferromagnetic with weak ferromagnetism.¹³ In such a case, spontaneous magnetization M_s could be obtained by extrapolating the linear portion

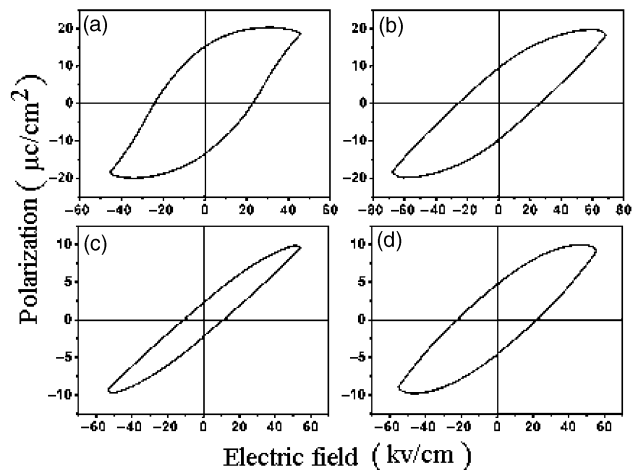


Fig. 4. Ferroelectric hysteresis loops of the BFOCr-BT samples with different Cr contents (a) $x = 0,$ (b) $x = 0.05,$ (c) $x = 0.1,$ and (d) $x = 0.15.$

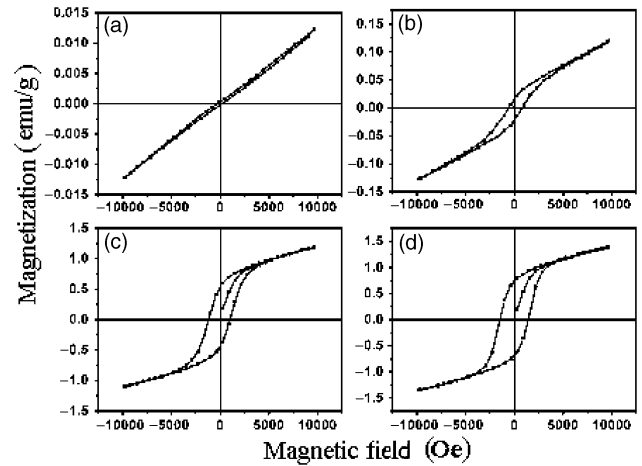


Fig. 5. Magnetic hysteresis loops of the BFOCr-BT samples with different Cr contents (a) $x = 0,$ (b) $x = 0.05,$ (c) $x = 0.1,$ and (d) $x = 0.15.$

of the $M-H$ curves to $H = 0.$ The estimated values of M_s increased with increasing $x,$ maximized at $x = 0.15,$ as shown in Table I, which is much higher than that of other BiFeO₃-based single-phase materials reported previously.^{13,14}

Physical properties of BFO-based solid solutions with simultaneously occurring magnetic and electric orderings are not yet understood. Remanent magnetizations observed in this investigation reveal ferromagnetism, but very weak compared with typical ferromagnetic compounds. However, the enhancements of net magnetization in these solid solutions relative to BiFeO₃ single crystal or other BiFeO₃-based solid solutions are enormous. With the addition of BaTiO₃, it has been possible to detect the spontaneous magnetic moment, as in the case of solid solutions with PbTiO₃ and PZT.⁴ Moreover, addition of Cr doping increased the magnetization more remarkably. We consider 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-Driscoll¹⁵ 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 BFOCr-BT solid solutions observed in our work might also be attributed to the canting of the magnetic moments arising from oxygen vacancies. This is also in agreement with the foregoing dielectric properties of BFOCr-BT solid solutions. The second possible reason for Cr to increase the magnetization of BFOCr-BT is that local ferromagnetic ordered structure might form between Fe³⁺ ions and Cr³⁺ ions, though the long-range Fe³⁺-Cr³⁺ order is impossible to form in BFOCr-BT solid solutions prepared by a solid-state reaction method. It is known that the strong ferromagnetic coupling exists between Fe³⁺ and Cr³⁺ via 180° superexchange interaction.¹⁶ Much more work is required to interpret the magnetization mechanism of the Cr³⁺-doped BFOCr-BT.

IV. Summary

In summary, pure perovskite BFOCr-BT solid solutions with $x \leq 0.15$ were synthesized using solid-state reaction method. Rel-

Table I. Remanent Magnetization and the Spontaneous Magnetization of BFOCr-BT (Room Temperature)

x	M_r (emu/g)	M_s (emu/g)
0.05	0.02	0.03
0.1	0.59	0.7
0.15	0.79	0.88

atively, large saturation magnetizations and well-developed hysteresis loops were observed in these materials, indicating that the addition of Cr enhance the magnetization remarkably. The synthesis of pure BFOC_x-BT solid solutions provides not only the opportunity to investigate the role of Cr in BFOC_x-BT compounds, but also shows the possibility to bring about significant magnetoelectric effect in BFO-based ceramics.

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