The doping effects of $BiFe_{1-x}Co_xO_3$ ($x = 0.0$–0.8) in layered perovskite $Bi_4Ti_3O_{12}$ ceramics*

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$Bi_5Fe_{1-x}Co_xTi_3O_{15}$ ($x = 0.0$, 0.2, 0.4, 0.5, 0.6, and 0.8) multiferroic ceramics are synthesized in two steps using the solid state reaction technique. X-ray diffraction patterns show that the samples have four-layer Aurivillius phases. At room temperature (RT), the samples each present a remarkable coexistence of ferromagnetism (FM) and ferroelectricity (FE). The remnant polarization ($2P_r$) reaches its greatest value of 14 μC/cm^2 at $x = 0.6$. Remnant magnetization ($2M_r$) first increases and then decreases, and the greatest $2M_r$ is 7.8 menu/g when $x = 0.5$. The magnetic properties for $x = 0.4$ are similar to those for $x = 0.6$, indicating that the magnetic properties originate mainly from the coupling between Fe^{3+} and Co^{3+} ions, rather than from their own magnetic moments.

Keywords: multiferroic, ferromagnetism, ferroelectricity

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1. Introduction

Bismuth-layered structure ferroelectrics (BLSFs) have been studied widely because of their stable structure, high ferroelectric Curie temperature and wide applications. These compounds have a general formula, $Bi_2A_{n-1}B_nO_{3n+3}$, whose structures are built up with the $(Bi_2O_2)^{2+}$ layers interleaved by $(A_{n-1}B_nO_{3n+1})^{2-}$ perovskite-like slabs, in which A and B are the sites that are occupied by the typical cations forming the perovskite slabs, and n refers to the number of perovskite-like layers between the $(Bi_2O_2)^{2+}$ layers. Bismuth titanate ($Bi_4Ti_3O_{12}$, BTO), as a typical bismuth layered perovskite material, is composed of three perovskite slabs sandwiched by two $(Bi_2O_2)^{2+}$ layers. The BTO compound has good ferroelectric properties and a relatively high Curie temperature. Nevertheless, it shows a relatively high anisotropic, electrical conductivity, which makes it very difficult to polarize the ceramic bodies based on this composition.[1]

In recent years, multiferroic materials have received much attention. These materials exhibit simultaneous ferroelectricity (FE) and ferromagnetism (FM) and may offer a wide scope of potential applications in functional devices that are able to convert signals from magnetic to electric and *vice versa*. The simultaneous presence of FM and FE in a single phase material is required. This coexistence at RT is also required for improving the full functionalities of such devices and reducing their operational cost. Unfortunately, multiferroic materials are rare in nature and none of them have been used yet in practical applications due to the fact that they either have too small a response to an external field or they have very small coupling between the electric or magnetic properties. Materials that are multiferroic at RT are even scarcer. Much effort has been devoted to preparing new materials with multiferroic properties or to discover the multiferroic properties in the known compounds. Until now, the most frequently investigated multiferroic compound has been $BiFeO_3$ (BFO).[2,3] BFO intrinsically shows G-type antiferromagnet (AFM) and FE at RT.[4] Although this compound is an AFM, the magnetic moment of the canted antiferromagnetically ordered spins gives rise to a weak FM. The FE, on the other hand, originates from a non-centrosymmetric crystal structure, in which the bismuth lone pair plays a crucial role in the large structural distortion.[5,6]

To achieve the coexistence of FM and FE, the latest method is to insert a magnetic octahedral group into the ferroelectric matrix. The octahedron must

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have ferroelectric properties and can stimulate the ferromagnetism. Based on this idea, the typical material, $Bi_5FeTi_3O_{15}$ (BFTO), was obtained and its structure, FM and FE studied,[7−11] but a major problem arose: BFTO takes on antiferromagnetism at RT. By inserting the same proportions of BFO and $BiCoO_3$ (BCO) into BTO, we prepared a $Bi_5Fe_{0.5}Co_{0.5}Ti_3O_{15}$ ceramic, and its electrical and magnetic properties are also reported.[12] In that study, we explain that the enhanced FM characteristic is the coupling of Fe–O–Co octahedral clusters.

In this paper, to further study the dependence of multiferroic property on the ratio between Fe and Co in four-layer perovskite structures, different proportions of magnetic unit $(1-x)$BFO and (x)BCO were incorporated into the BTO powder, and then the results in a composition of $Bi_5Fe_{1-x}Co_xTi_3O_{15}$ (BFCT-x, $x = 0.0 \sim 0.8$). The samples were synthesized by a multi-calcination procedure. The ceramic presents a remarkable coexistence of FM and FE at RT.

2. Experiment

The procedure to make BFCT-x ceramics is divided into two steps.[13] First, BTO powders were prepared. We selected Bi_2O_3 (analytically pure, with 15 wt% excess Bi_2O_3 to compensate for volatilization loss) and TiO_2 (spectrally pure) as the raw materials, and then weighted in stoichiometric ratios. These starting materials were finely ground by ball milling in ethanol liquid and calcined at 760, 780, and 800 °C for 8, 16, and 24 h, respectively. As-obtained BTO powders were further mixed with Fe_2O_3, Co_2O_3, and Bi_2O_3 according to the stoichiometry. Next, the mixtures were ball-milled together for 24 h in ethanol liquid, presintered at 640 °C for 8 h, and then ball milled again for 24 h. Finally, the pretreated powders were pressed into pellets and sintered at 780 °C–850 °C.

All the samples were characterized by X-ray diffraction (XRD) using Bruker D8 diffractometry with Cu Kα radiation. Micrographs of the fracture surfaces were obtained using a field emission scanning electron microscope (FESEM; Hitachi, S-4800). The magnetic properties of each sample were measured by a vibrating samples magnetometer (VSM) (EV-7, ADE Co, USA). The ferroelectric properties were measured on a Precision LC ferroelectric analyzer (Radiant Technology, USA). Raman spectra were measured in a backward micro-configuration using the 514.5 nm line from an Ar^+ laser ($\sim$ 300 mW) focused on a spot with a diameter of 1 mm–2 mm on the ceramics surface.

3. Results and discussion

The X-ray diffraction patterns of the BFCT-x ceramics are displayed in Fig. 1. The four-layer Aurivillius phase is formed in each of the samples, which contain no extra peaks from the impurity phases. The Co doping did not change the crystal structure of the BFTO phase.

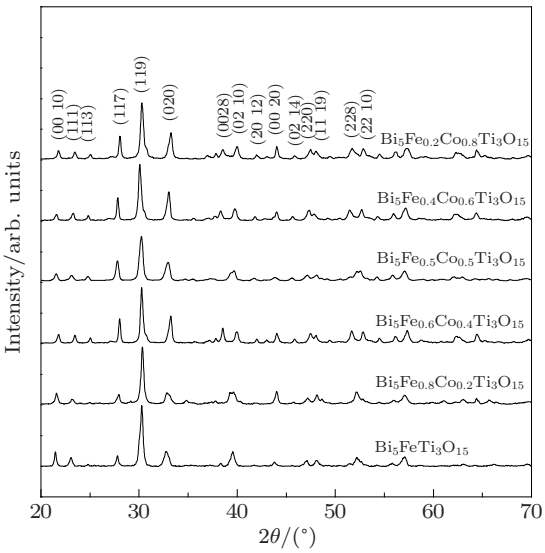


Fig. 1. XRD spectra of the BFCT-x ceramics.

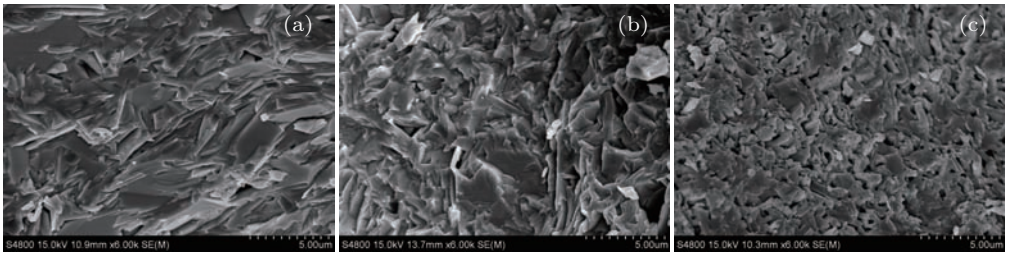


Fig. 2. FESEM micrographs of the BFCT-x samples: (a) $x = 0.2$, (b) $x = 0.5$, (c) $x = 0.8$.

In Fig. 2, the FESEM images of BFCT-x ($x = 0.2$, 0.5, 0.8) each show a slab-like structure. The grain growth is homogeneous, and the grains are small and randomly oriented. The grain sizes of the BFCT-x samples decrease regularly as the Co content increases.

Figure 3 shows magnetic hysteresis loops of BFCT-x at RT. The relationship between the magnetization and magnetic field of BFTO is almost linear. However, once Co doped, the hysteresis loop opens immediately and shows a typical ferromagnetic hysteresis loop. This result indicates that the samples have each been in a ferromagnetic state at RT. Figure 4 shows the variation in $2M_r$ with doping mole fraction x. As x increases, $2M_r$ first increases and then decreases, and the greatest $2M_r$ is 7.8 menu/g at $x = 0.5$, which is about 3000 times the value of BFTO. The magnetic properties for $x = 0.4$ are similar to those for $x = 0.6$. When the doping is excessive, the magnetic properties decrease significantly. The BFCT-0.8 sample is almost paramagnetic, however, small residual magnetization can be observed from the local amplification.

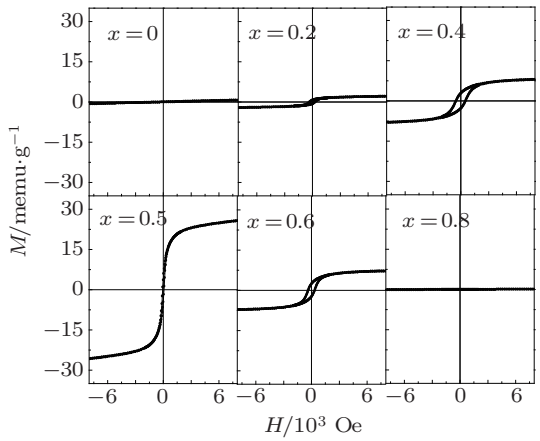


Fig. 3. Magnetic hysteresis loops of BFCT-x samples at RT (1 Oe=79.5755 A/m).

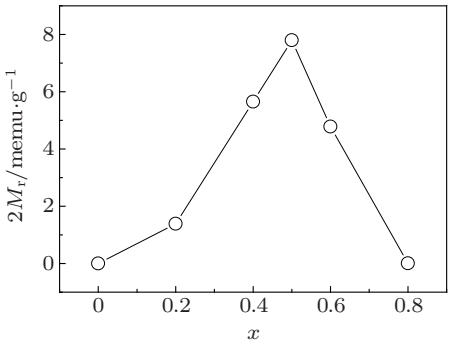


Fig. 4. The variation in $2M_r$ with doping x (Co).

The magnetic properties of layer-perovskite multiferroic materials are related to B-site ions. As is well known, Co^{3+} has a smaller magnetic moment than Fe^{3+}. Co doping can improve the magnetic properties of materials, indicating that the magnetization does not only originate from its own magnetic moment. BFTO shows the super-paramagnetic (SPM) behaviours with dominant AFM interaction background at low temperature.[10] Because the superexchange of the Fe–O–Fe clusters favours the local AFM interaction, Co doping results in local Co–O clusters. Fe–O clusters and Co–O clusters may appear at the adjacent positions, forming Fe–O–Co and Co–O–Co interactions.[14] Co–O–Co interaction favours a C-type AFM spin structure in BCO.[15] The substitution of Fe for Co in the BCO samples has been found to be effective in stimulating FM.[16] With the increase in Co doping, the chance in the adjacent appearance of Fe–O and Co–O octahedra becomes large, and Fe–O–Co coupling is also likely to increase. The chance of this coupling reaches a maximum when $x = 0.5$ (the ratio of Fe^{3+} to Co^{3+} is 1:1). In fact, the $2M_r$ of the BFCT-0.5 sample reaches a maximum value. Similarly, the Fe–O–Co coupling is likely to do so when $x = 0.4$ and $x = 0.6$, as they have similar magnetism.

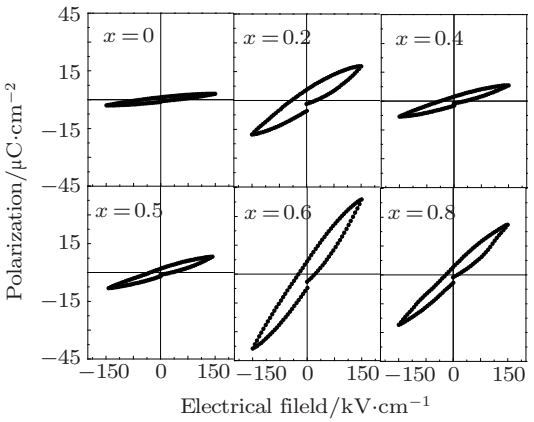


Fig. 5. P–E hysteresis loops of the BFCT-x ceramics at 150 kV/cm.

Figure 5 shows P–E hysteresis loops of BFCT-x at RT, each of which was measured at an electrical field of 150 kV/cm. A comparison between the $2P_r$ and $2M_r$ values of the BFCT-x ceramics are shown in Table 1. The $2P_r$ value increases with Co doping, because Co^{3+} is more stable than Fe^{3+}, which has a few transformations of Co^{3+}–Co^{2+}. From 0.2 to 0.6, $2P_r$ first decreases when $x \leq 0.5$, and then increases. The maximum polarization observed is around 14 $\mu C/cm^2$ at $x = 0.6$. Kroger and Vinik[17,18] have reported

that the random occupancy of Fe^{3+} and Ti^{4+} in the oxygen octahedral may lead to oxygen vacancies in the present bismuth oxide structure, which are expected to lose traces of oxygen during sintering at higher temperatures. The samples were synthesized using the solid-state reaction method in the experiment, and the sintering temperature was high. Therefore, the random occupancy of Fe^{3+}, Co^{3+}, and Ti^{4+} under the high sintering temperature leads to more oxygen vacancies, resulting in a decline of the ferroelectric properties. This may form a new Co and Ti ferroelectric ordered state when $x > 0.5$, so that the $2P_r$ values of the samples increase again. Overall, the changes in $2P_r$ and $2M_r$ are in the opposite directions. It seems that a modulation exists between FM and FE in BFCT ceramic.

Table 1. Variations in $2M_r$ and $2P_r$ with doping x (Co).

	$x = 0$	$x = 0.2$	$x = 0.4$	$x = 0.5$	$x = 0.6$	$x = 0.8$
$2M_r$/memu·g^{-1}	0.0027	1.3900	5.6500	7.8000	4.7800	0.0047
$2P_r$/μC·cm^{-2}	2.3901	10.5280	4.6385	3.9533	14.1174	8.2966

Figure 6 displays the Raman spectra of the BFCT-x sample at RT, which was investigated in a Raman frequency range of 200 cm^{-1}–1000 cm^{-1}. The high frequency modes above 200 cm^{-1} are known to result from the torsional bending and the stretching modes of the BO_6 octahedral,[19] which exactly corresponds to the B-doping of BFTO. The Raman spectra of BFCT-x exhibit intense phonon modes at around 270 cm^{-1}, 325 cm^{-1}, 544 cm^{-1}, 573 cm^{-1}, and 860 cm^{-1}. The whole characteristics of the observed Raman spectra of the BFCT-x samples are very similar to each other. These results demonstrate that the basic structure did not vary with Co doping. However, comparing with the nondoping case, a new peak appears at about 724 cm^{-1} and shifts toward higher frequency as Co content increases. This may be related to the vibration of CoO_6 octahedra. In fact, this mode can be observed in $LaCoO_3$.[20] This shows that Co occupies the B site.

The frequency mode from the torsional bending of TiO_6 octahedra appears at around 270 cm^{-1}. It is found to shift toward a higher frequency as Co content increases, which implies that Co doping may stabilize the oxygen octahedron. As Co ions are heavier than Ti ions, the peaks at around ~ 320 cm^{-1} and ~ 860 cm^{-1} shift toward a lower frequency as Co content increases. For BFTO, the 539 cm^{-1} mode originates from FeO_6 octahedra, whose intensity for the mode is found to increase as Co content increases to $x = 0.5$, and then decrease with a further increase of Co doping. The result can be explained by the following two kinds of conditions. Due to Co doping, the CoO_6 octahedra are formed, which probably induces overlapping of the torsional mode with FeO_6 octahedra, and the overlapping is reached to the greatest extent possible at $x = 0.5$. This corresponds to the result of the magnetic increase. With further doping, CoO_6 octahedra increase and FeO_6 octahedra decrease, the effect of overlapping is attenuated, and the torsional mode of CoO_6 octahedra becomes a main factor.

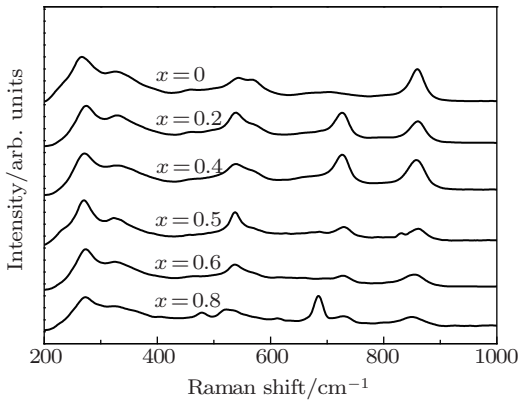


Fig. 6. Raman spectra of the BFTO-x ceramics at room temperature.

4. Conclusions

The BFCT-x ceramics are of single phase with a four-layer Aurivillius structure via a multicalcination procedure. At RT, BFTO shows a paramagnetic property, and BFCT-x ($x = 0.2 \sim 0.8$) shows a typical ferromagnetic behaviour. The doping of Co is effective in enhancing the ferromagnetic properties. The magnetic properties are similar between $x = 0.4$ and $x = 0.6$, further drawing a conclusion that coupling between Fe^{3+} and Co^{3+} is the main reason for the magnetic increase. Each of the samples shows a visible ferroelectric due to the fact that the coexistence of FM and FE is implemented in BFCT-x ceramics. The $2P_r$ values of the BFCT-x samples are obtained, and the greatest value is 14 μC/cm^2 when $x = 0.6$.

The comparison of $2P_r$ with $2M_r$ indicates that they change in opposite directions. They seem to have a modulation between them.

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