Structural and magnetic properties of $BiFe_{1-x}Cr_xO_3$ synthesized samples

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Chromium doping effects on the structure and the magnetic properties of bismuth ferrite $BiFe_{1-x}Cr_xO_3$ ($x = 0$–0.3) (BFC_xO) polycrystalline samples are examined. The Perovskite-type oxide samples are synthesized by the conventional solid state reaction at a high pressure of 7 GPa and a temperature of 1273 K. The X-ray powder diffraction patterns at room temperature show that all the samples with $x = 0.0$–0.3 are described by the rhombohedral structure. In the meantime, it is revealed that the doping of Cr can induce noticeable lattice distortions in the doping samples, and the largest distortion is observed in the case $x = 0.1$. The magnetic hysteresis loops measured at room temperature exhibit week ferromagnetic behaviors of the samples and the magnetization is found to increase with the increase in Cr concentration. The temperature-dependent magnetization curves indicate antiferromagnetic features in samples. Moreover, Cr-doping tends to reduce the ordering temperature.

Keywords: X-ray diffraction, magnetic properties

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1. Introduction

Multiferroic magnetoelectric materials could exhibit both ferromagnetic or antiferromagnetic and ferroelectric or antiferroelectric features in the same phase. As a result, these materials each have a spontaneous magnetization which can be switched by an applied magnetic field or exhibit a switched spontaneous polarization by an applied electric field, and often the some coupling can occur between the two. Such a material has generated a revived interest in research studies.[1–5]

Although the work in this area can be traced back to the pioneering research in the 1950s and 1960s, there has been a recent resurgence of interest driven by long-term technological aspirations. Also, there is significant attention because of the potential for use in technological applications and the field of electro–optic transducers controlled by magnetism and microwave devices.[6,7] This kind of material has been studied for the purpose of finding a new type of memory application using a combination of ferroelectric and ferromagnetic properties.[8]

Among the materials studied so far, $BiFeO_3$ is known to be one of several compounds that exhibit ferroelectromagnetism at room temperature. It has a rhombohedral structure with lattice parameters $a = 5.581$ Å and $c = 13.86$ Å.[9,10] $BiFeO_3$ was reported to show G-type antiferromagnetic ordering with a relatively high Nèel temperature ($T_N \sim 643$ K),[11] and a ferroelectric ordering with high Curie temperature ($T_C \sim 1143$ K),[12] which make it very fascinating for possible applications.

In order to improve and increase the magnetic and ferroelectric properties of $BiFeO_3$, several research groups have reported on the results of Bi-site substitution by using a rare-earth element (La, Nd, etc.) or Fe-site substitution by using a transition element (Mn, Ti, Cr, etc.).[13–20]

Essentially, Fe-site doping changes the Fe–O–Fe super-exchange interactions and thus affects the structure and magnetic property of $BiFeO_3$. Among them, Cr-doping $BiFeO_3$ is of immense interest as Baetting and Spaldin predicted that alternating Fe^{3+} and Cr^{3+} cations may improve the magnetic properties due to the interaction between Fe^{3+} and Cr^{3+}.[21] Therefore, in the present study, we plan to dope $BiFeO_3$ at Fe site by Cr to enhance its magnetic properties.

In this work, $BiFe_{1-x}Cr_xO_3$ (BFC_xO), $x = 0.0$, 0.1, 0.2, 0.3 samples each with a Perovkite-type structure are synthesized under a high pressure 7 GPa and at a temperature of 1273 K. The structural and magnetization characteristics of the prepared samples were investigated.

2. Experiment

Polycrystalline samples of $BiFe_{1-x}Cr_xO_3$ ($x = 0$, 0.1, 0.2 and 0.3) (BFC_xO), were synthesized by the solid state reaction technique under a high pressure 7 GPa. A powder of Bi_2O_3 (99.9%), Fe_2O_3 (99.9%), and Cr_2O_3 (99.9%) with a stoichiometric 1:1 mole ratio was mixed in an agent mortar for half an hour, then packed into a gold capsule (≈ 4 mm $\times$ 6 mm) and heated in a cubic anvil-type apparatus under 7-GPa pressure and at 1273 K for 1 hour.

X-ray diffractions (XRD) were carried out using a diffractometer with Cu–K_α source. The X-ray pattern was collected in intervals of 0.01°. The structural parameters were refined by Rietveld analysis of diffraction data in a 2θ range of 20°–70°.

The dc magnetic susceptibility measurements were performed using a superconducting quantum interference device

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magnetometer (SQUID Quantum Design). The data were collected while heating up from 300 K to 800 K below and above the Neel temperature.

3. Results and discussion

3.1. Structural analysis

Figures 1(a)–1(c) each show the XRD patterns for the BFC_xO ($x = 0.0$, 0.1, 0.2, and 0.3) ceramics at room temperature (RT) which include strong and sharp peaks indicating good crystallization of the samples. Although calcination is performed, there are some impurity phases of $Bi_2Fe_4O_9$ and Bi_2O_3 emerging at a diffraction angle range of $2\theta = 25.5°$–$30.1°$ for all samples. It has been reported by several authors[22,23] that impurity phases are usually formed along with a $BiFeO_3$ phase in the solid state reaction process. Moreover, when $x = 0.3$, there appears an additional impurity phase corresponding to $Bi_{25}FeO_{40}$ at $2\theta = 44.3°$.[24]

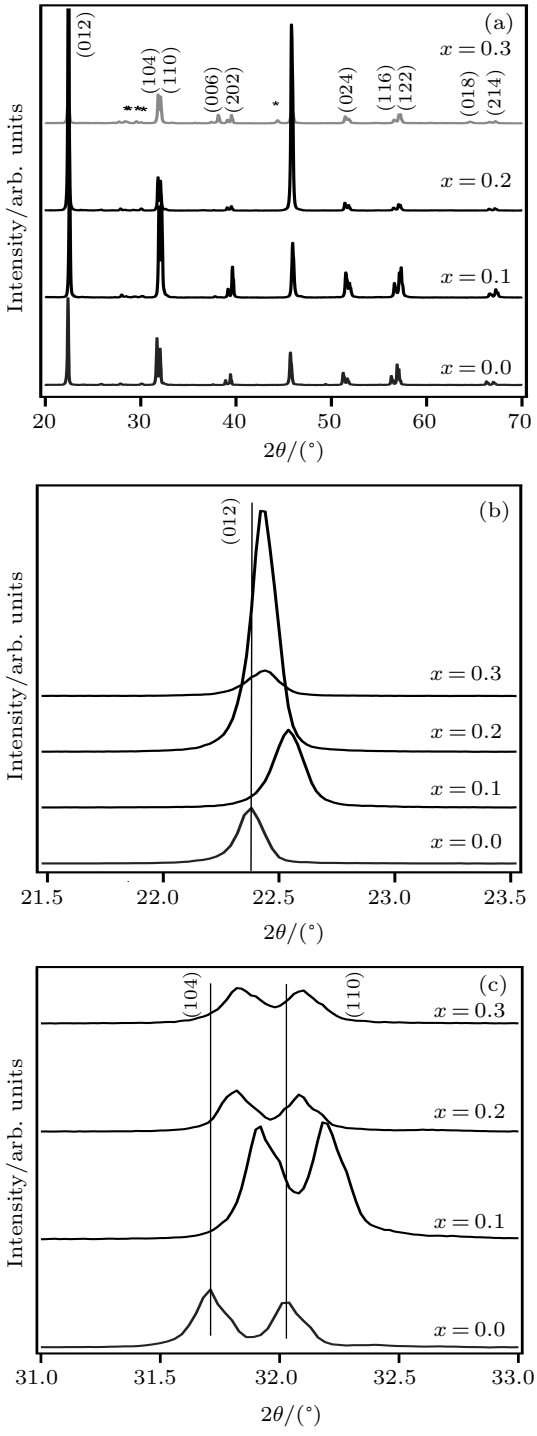


Fig. 1. XRD patterns at room temperature for BFC_xO, $x = 0$–0.3.

In order to investigate the influence of Cr^{+3} doping on the structure, we obtain subtle XRD patterns of 2θ near 22.5° and 32°, as shown in Figs. 1(b) and 1(c). It can be clearly seen that the (012), (104), and (110) diffraction peaks shifted gradually toward high diffraction angles for $x = 0.1$, indicating a decrease of the lattice parameter. However, with further doping Cr^{+3} ($x > 0.1$), the peaks shift towards the lower angle instead, which means that the lattice parameters are increased alternately, as shown in Table 1. The change in the lattice parameter at $x = 0.1$ may be attributed to the lattice distortion of the sample due to the variation of the Cr+^{3} content value and the difference in ionic radius between ions Cr^{3+} (0.615 Å) and Fe^{3+} (0.645 Å).[25] For $x \geq 0.2$ the change in the lattice parameter and the shifting of peaks towards a lower angle may be due to the occurrence of impurity phases.[26] This means that lattice expansion in the doped ceramics with the largest distortion occurs at $x = 0.1$. Each crystallized sample exhibits a rhombohedral structure with the *R3C* spacing group and can be indexed as a hexagonal unit cell.

Table 1. Lattice parameters of $BiFe_{1-x}Cr_xO_3$ ($x = 0.0$–0.3) ceramics.

Sample	a/Å	c/Å	c/a	V/Å^3
$x = 0.0$	5.580	13.876	2.486	374.15
$x = 0.1$	5.563	13.794	2.479	369.69
$x = 0.2$	5.576	13.841	2.482	372.68
$x = 0.3$	5.571	13.812	2.479	371.23

3.2. Magnetic measurements

Figure 2 shows the plots of magnetization versus field (M–H) of BFC_xO with $x = 0$, 0.1, 0.2, and 0.3 measured at 300 K with applied magnetic fields ranging from −10 kOe (1 Oe = 79.5775 A·m^{-1}) to 10 kOe. Magnetization is found to increase as the concentration of Cr^{+3} increases. All the samples show nonlinear magnetization loops representing a weak ferromagnetic behavior. $BiFeO_3$ is reported to be G-type antiferromagnetic at room temperature.[11] The substitution of Cr^{+3} at Fe^{+3} sites can enhance the magnetization by two possibilities. One is due to the ferromagnetism accompanied with antiferromagnetic coupling. In this case, with the addition of Cr^{+3}, local ferromagnetic super-cells may be formed due to the size difference between Fe^{+3} and Cr^{+3}, which is characterized by a strong ferromagnetic coupling between Fe^{3+} and Cr^{3+} under 180° super-exchange interaction.[21] The other possibility is due to a structure distortion upon the introduction of Cr^{+3}. Obviously, the structure distortion can change the Fe–O–Fe bond angle or spin order and thus would evoke the transition from a spatially modulated spin structure to a homogeneous canted one.[27] Moreover, the crystal structure of

$BiFeO_3$ allows the appearance of weak ferromagnetic (see the inset of Fig. 2) arising from the canting of the antiferromagnetic sublattices.[11] The magnetization curves are not really saturated even at 10 kOe, indicating the basic antiferromagnetic nature of the sample. The magnetization was found to increase with the increase of Cr^{+3}.

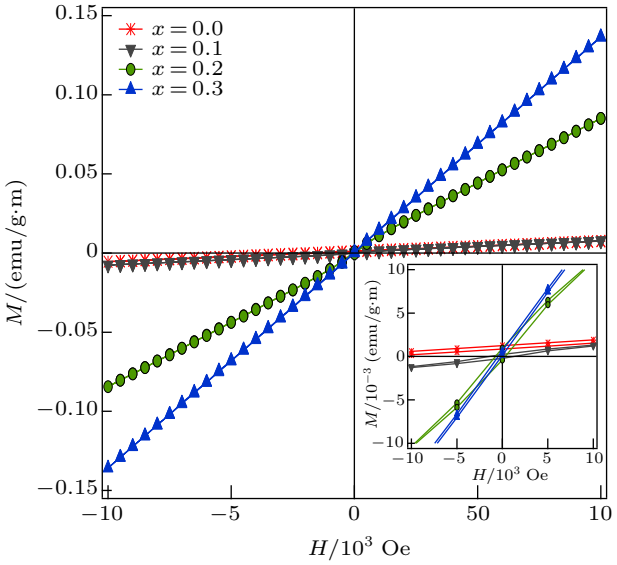


Fig. 2. (color online) Plots of M–H for BFC_xO, $x = 0$–0.3.

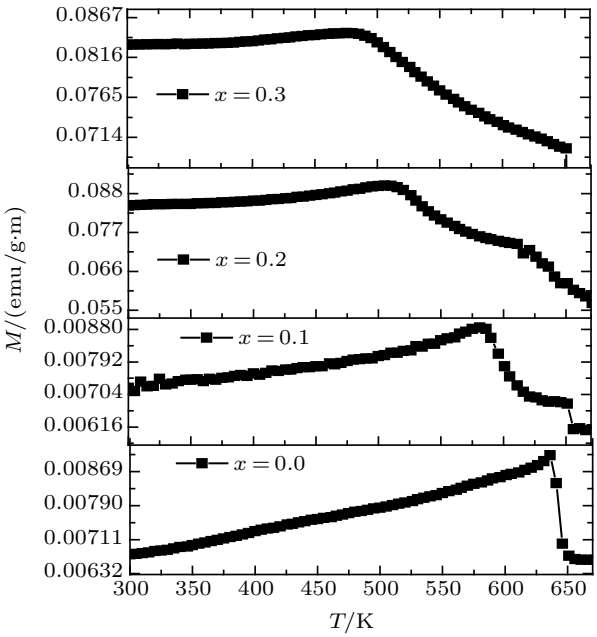


Fig. 3. Plots of M–T for BFC_xO, $x = 0$–0.3.

The magnetization against temperature (M–T) measurements of the samples at a magnetic field of 10 kOe from room temperature up to 670 K are shown in Fig. 3 in order to determine the magnetic ordering. The magnetization for each sample shows a sharp decrease, which is considered to be the magnetic transition. The magnetic transition temperature (Nèel temperature) T_N decreases with the increase of Cr^{+3} doping concentration, which are found to be 640, 580, 510, and 475 K for samples $x = 0$, 0.1, 0.2, and 0.3, respectively. The reductions in the T_N value for Cr^{+3}-doped samples may be due to their particle sizes decreasing with the increase of Cr^{+3} concentration. The reduction in particle size is an intrinsic finite size effect causing a reduction in the magnetic ordering temperature.[13]

4. Conclusion

The X-ray studies at room temperature for BFC_xO ($x =$ 0.0, 0.1, 0.2, and 0.3) reveal that the crystal structures are rhombohedral with a space group $R3C$. It is found that the doping of Cr^{+3} can cause noticeable lattice distortion of the doping sample, and the greatest distortion appears at $x = 0.1$. The M–H hysteresis loops at room temperature each exhibit a weak ferromagnetic behavior of the samples. Each of the M–T measurements exhibits an antiferromagnetic transition for the samples. However, the Nèel temperature (T_N) decreases as the concentration of Cr^{+3} doping increases. In conclusion, the increase of Cr^{+3} substituting for Fe^{+3} in $BiFe_{1-x}Cr_xO_3$ can augment the magnetization and magnetic transition temperature.

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