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journal homepage: www.elsevier.com/locate/jmmmStructural and magnetic properties in $\text{Bi}_{1-x}\text{R}_x\text{FeO}_3$ ($x=0-1$, $R=\text{La, Nd, Sm, Eu}$ and Tb) polycrystalline ceramicsYu-jie Zhang^{a,b}, Hong-guo Zhang^a, Jin-hua Yin^{a,c}, Hong-wei Zhang^{a,*}, Jing-lan Chen^a, Wen-quan Wang^b, Guang-heng Wu^a^a State Key Laboratory for Magnetism, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, China^b Department of Physics, Jilin University, Changchun 130023, China^c Department of Physics, University of Science and Technology Beijing, Beijing 100083, China

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ABSTRACT

A series of rare-earth doped BiFeO_3 samples, $\text{Bi}_{1-x}\text{R}_x\text{FeO}_3$ ($x=0-1$, $R=\text{La, Nd, Sm, Eu}$ and Tb), were prepared in this work. X-ray diffraction analysis showed that the structure of rare-earth doped BiFeO_3 was transformed from rhombohedral lattice to orthorhombic one by increasing x . The lattice constants and unit-cell volume decreased with the increasing of the doping content, while both the Néel temperature and magnetization were enhanced. A magnetic phase transition was observed at about 35 K for BiFeO_3 . The variation of the magnetization with temperature depended on applied field strength and magnetizing history, which was explained according to the antiferromagnetic exchange interaction between Fe and R sites in $\text{Bi}_{1-x}\text{R}_x\text{FeO}_3$ ($x > 0$). The magnetocrystalline anisotropy contributed by Fe sublattice gave rise to a large coercivity in $\text{Bi}_x\text{Nd}_{1-x}\text{FeO}_3$ with an orthorhombic structure.

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1. Introduction

Multiferroics in a single material, especially exhibiting ferroelectricity and ferromagnetism simultaneously, have been investigated extensively, due to the potential application for new device functions [1]. Up to now, the single-phase BiFeO_3 (BFO), crystallized in ABO_3 -typed perovskite structure with $R3c$ space group at room temperature, shows the highest ferroelectric Curie temperature and antiferromagnetic Néel temperature in the family of multiferroic materials [1–4]. Therefore, much effort has been made to understand the linear coupling behavior between magnetization and electric polarization in BFO. On the other hand, it is found that the magnetism and ferroelectricity in BFO can be improved by substituting A-site ion with rare-earth [5–15] or alkaline-earth [16,17] ions or replacing B-site ion with transition-metal and rare-earth ones [18–27]. Although BFO has been extensively studied in recent years, some difficulties have limited its development. One of them is how to derive ferromagnetism in the canted G-type antiferromagnetic order with the space-modulated spin structure [13,28]. Mathe et al. [29] proposed to obtain ferromagnetic BFO by A-site substitution of a smaller Nd^{3+} ion for Bi^{3+} ion, and Yuan et al. [13] observed the weak ferromagnetism in single-phase $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x=0-0.2$)

multiferroic ceramics. Very few works on the structural and ferromagnetic properties of full scale rare-earth (R) doped BFO compounds have been reported.

In this paper, the phase composition, crystal structure and magnetization properties of $\text{Bi}_{1-x}\text{R}_x\text{FeO}_3$ ($x=0-1$, $R=\text{La, Nd, Sm, Eu}$ and Tb , abbreviated as BRFO) bulk ceramic samples are investigated.

2. Experiments

BRFO ceramics were synthesized by the conventional solid state reaction sintering at atmospheric pressure. Stoichiometric amounts of Bi_2O_3 , Fe_2O_3 and Nd_2O_3 (or other rare-earth oxides) (purity > 99.5%) were thoroughly mixed and ground in agate mortar (a 5 mol% excess bismuth was added to the mixture to compensate the bismuth loss during the process). The powder was pressed into disk specimen with a diameter of 10 mm and a thickness of 2 mm at a pressure of 10 MPa. The samples were calcined at 700–1200 °C for 2 days with several intermediate grindings.

The crystal structure of BRFO samples was examined by X-ray diffractometer (XRD). The magnetic properties were evaluated using a vibrating sample magnetometer (VSM) and superconducting quantum interference device (SQUID).

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3. Results and discussion

Fig. 1 shows powder X-ray diffraction patterns of $\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x=0-1$, BNFO) which are the typical samples in the series. It can be seen that the sample with $x=0$ is single-phase with the BFO structure, namely, the rhombohedral structure with $R3c$ space group at room temperature [30–32]. Small amount of second phase, might be $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$, shows up while $x=0.2$ and almost disappear when $x=0.4$ or $x \geq 0.4$, all the peaks match up to the orthorhombic structure with $Pnma$ space group and no impurity phase. The content of the impurity phase, given in 1 is determined using the Rietveld refinement [33–35]. As a representative, the calculated and the difference patterns of NdFeO_3 are shown in Fig. 1. Based on the above analysis, it can be concluded that the samples are of the rhombohedral structure until $x=0.2$ and show a structural transition to the orthorhombic type between $x=0.2$ and 0.4 , and then remain the orthorhombic structure up to $x=1$. XRD results of the samples doped with $R=\text{La}$, Sm , Eu and Tb show the same trend of structural transformation.

For $x \geq 0.4$, the samples doped with rare-earth elements show the orthorhombic structure; the lattice constants a , b , c and the unit-cell volumes of them are calculated by Jade. Fig. 2 shows the lattice constants as a function of x . It can be seen that the lattice constants decrease slowly with x increasing, so does

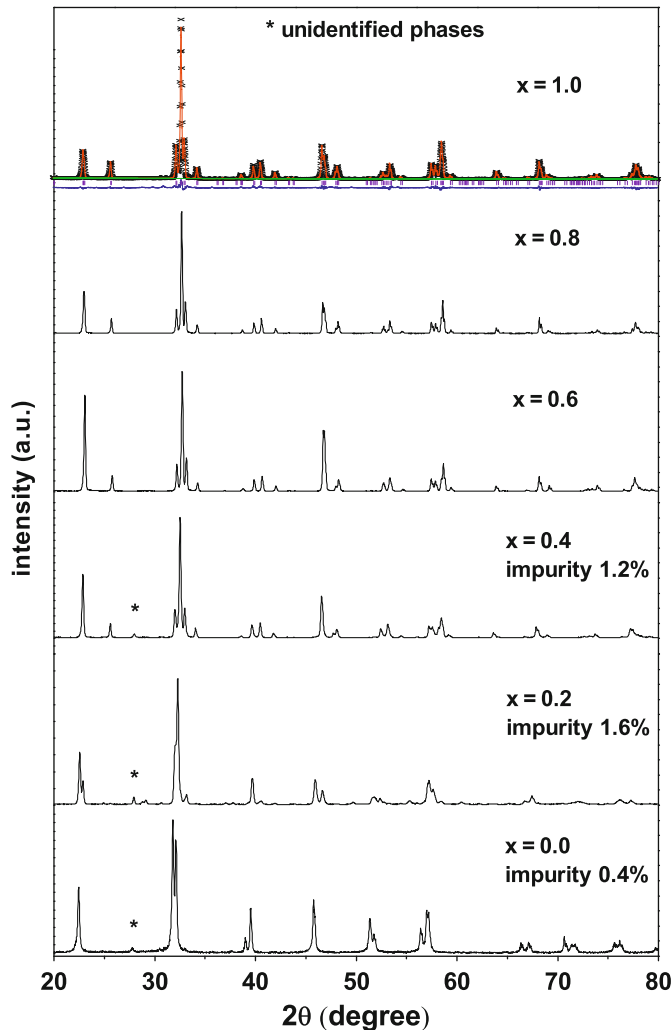


Fig. 1. X-ray diffraction patterns of BNFO ($x=0-1.0$) at room temperature. As a representative, the calculated XRD pattern is shown for NFO.

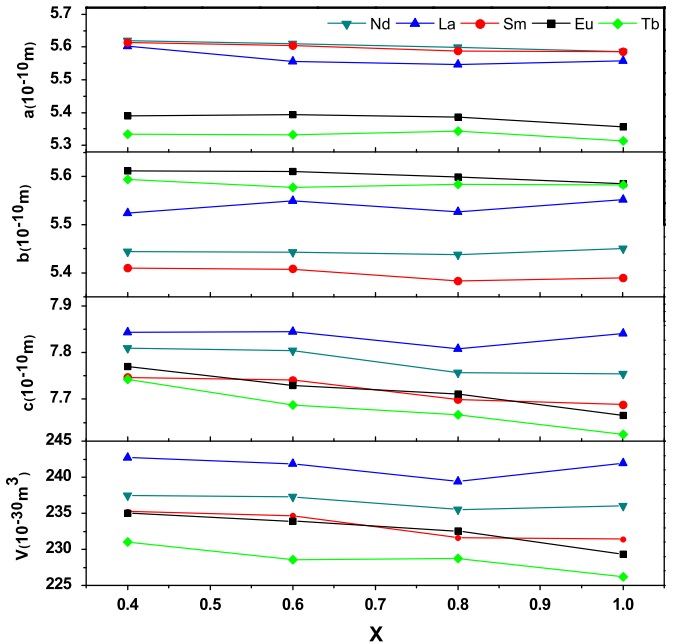


Fig. 2. Comparison of the lattice constants a , b , c and the unit-cell volumes of BRFO ($R=\text{Nd}$, La , Sm , Eu and Tb ; $x=0.4-1.0$).

the volume of unit-cell. The unit-cell volumes of BRFO are smaller than that of BFO, which might be due to the larger radius of Bi^{3+} than R^{3+} .

Fig. 3(a) presents room temperature magnetic hysteresis loops of BNFO ceramics with a maximum field of 50 kOe. All the samples cannot be saturated even with an applied field of 130 kOe, indicating the antiferromagnetic structure with the spiral magnetic ordering [36–39]. With the exception of $0.2 < x < 0.4$, which is the very structural transition area mentioned above, from Fig. 3(b), one can find that the magnetization (M) under the field of 50 kOe increases monotonically from $x=0$ to 1.0 . The origin of enhanced M might be caused by the distorted spiral magnetic ordering by the doping of rare-earth element. With the increasing Nd concentration, both the $R\text{-O}$ and Fe-O distances become shorter, which enhances exchange interaction between $R\text{-R}$ and Fe-R and leads to the increase of the magnetization. This behavior can also be observed in BRFO with $R=\text{La}$, Sm , Eu and Tb , and the enhancement of M for heavy rare-earth doping is larger than that for light rare-earth doping. Therefore, the magnetization shows a close relationship with the unit-cell volumes of BRFO. Fig. 3(c) shows the composition dependence of the Néel temperature (T_N), determined from the high temperature $M-T$ curve measured at 10 kOe using VSM, for the BNFO samples. T_N increases with the Nd content in the BNFO samples, which indicates that the antiferromagnetic interaction is enhanced by Nd doping. Because T_N mainly depends on the antiferromagnetic interaction between Fe sublattice magnetic moments, the enhancement of T_N is a result of the reduction of Fe-O distance.

Fig. 4(a) presents the field cooling (FC) and zero field cooling (ZFC) magnetization as a function of temperature at 1 and 50 kOe for NdFeO_3 sample with $x=1$. NdFeO_3 has two magnetic sublattices, Fe magnetic sublattice and Nd ones, which are coupled through a negative exchange interaction. The Fe sublattice is antiferromagnetism, while the magnetic moments of Nd ions have negative temperature coefficient [40,41]. Below 35 K, the magnitude of Nd moments is larger than that of Fe cations, and a ferromagnetic-like situation which reveals by ZFC curve as shown in Fig. 4(a) may occur. However, moments of Nd

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