Structural and magnetic properties in Bi$_{1-x}$R$_x$FeO$_3$ ($x=0$–1, $R=$La, Nd, Sm, Eu and Tb) polycrystalline ceramics

Yu-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

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 Bi$_{1-x}$Nd$_x$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 Bi$_{1-x}$R$_x$FeO$_3$ ($x=0$–1, $R=$La, Nd, Sm, Eu and Tb), abbreviated as BRFO, were investigated.

2. Experiments

BRFO ceramics were synthesized by the conventional solid state reaction sintering at atmospheric pressure. Stoichiometric amounts of Bi$_2$O$_3$, Fe$_2$O$_3$ and Nd$_2$O$_3$ (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).
3. Results and discussion

Fig. 1 shows powder X-ray diffraction patterns of Bi$_{1-x}$Nd$_x$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 Bi$_{36}$Fe$_{2}$O$_{57}$, shows up while $x=0.2$ and almost disappear when $x=0.4$ or $x=0.4$, 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 $R=$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 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 $R$–O and Fe–O distances become shorter, which enhances exchange interaction between $R$–$R$ and Fe–$R$ and leads to the increase of the magnetization. This behavior can also be observed in BRFO with $R=$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

![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.](image-url)
ions decrease with the increasing $T$, which induces the monotonical drop in magnetization up to 35 K. Consequently, the antiferromagnetism of Fe sublattice becomes prominent and ZFC curve tends to increases from 35 to 100 K. Above 100 K, the magnetization becomes almost unchanged. For FC, the moments of Fe will align along the external field, and the moments Nd sublattice will be opposite to those of Fe. Due to the characteristic of Nd moments as mentioned above, the total magnetic moment will reach a maximum at 35 K, then decline with decreasing temperature [41]. Under a field larger than the local field that is suffered by the Nd sublattice and is produced by the Fe sublattice, the moments of Nd will drive to be parallel to that of Fe, which results in the magnetization behavior as shown by the 50 kOe FC curve in Fig. 4(a).

ZFC and FC curves of BNFO with $x=0.4$ are showed in Fig. 4(b). It is quite different from those of NdFeO$_3$ sample. The Nd concentration is much lower in BNFO with $x=0.4$ compared to NdFeO$_3$. Thus, the mentioned antiferromagnetic interaction between the Nd and Fe sublattices is neglected, and the Nd sublattice can be considered as paramagnetic i.e. the moments of Nd align along the applied field. Due to the [40] temperature dependence of Nd moments, the macroscopic magnetization increases slowly as temperature is decreasing to 100 K, and then sharply rises up with further decreasing temperature.

Fig. 4(c) exhibits the ZFC and FC curves of BFO under 1 kOe. Both the FC and ZFC curves drop slightly with decreasing temperature from 300 to 100 K, which is consistent with the temperature-dependent magnetization of antiferromagnetic magnetic structure. As temperature goes down further from 100 to 5 K, the magnetization increases rapidly, confirming that there is a magnetic phase transition. The magnetic phase transition is suggested to be a transformation of Fe sublattice from antiferromagnetic to weak ferromagnetic at low temperature [38,42,43]. No superposition of FC and ZFC in Figs. 4(b),(c) indicates that the magnetic phase transition is sensitive to the magnetizing history.

At room temperature, a large coercivity is observed in the samples doped with R. In order to investigate the rare-earth element contribution to the magnetic crystalline anisotropy of BNFO samples, the coercivity (examined by VSM) of BRFO ($R=$Nd, La, Sm, Eu and Tb) with the similar crystalline structure as a function of rare-earth content is shown in Fig. 5. For BFO, the modulated wave length, [1] 62 nm, is far larger than crystal constants. So the contribution of Fe sublattice to magnetocrystalline anisotropy can be neglected. As a result, zero coercivity is found in BFO. On the other hand, the rare-earth content dependences of the coercivity for BRFO are similar to each other, indicating the common coercivity origin. However, since La could not provide the magnetic crystalline anisotropy, the large coercivities of BNFO should not stem from the magnetic crystalline anisotropy provided by Nd cations. According to Refs. [44–46], the doping of Nd ions may cause deformation of the ligands of Fe ions,
which will lead to a reduction of the degree of symmetry of the crystal field. Consequently, the perturbation of Coulomb repulsion and crystal field will make a contribution to a uniaxial anisotropy by the excited terms of single Fe$^{3+}$ ions. Although the anisotropy constant of Fe$^{3+}$ ion is small, it cannot be ignored in this low symmetry system. The magnetic structure of Fe sublattice in RFeO$_3$ is different from that in BFO.$^{22}$

Shape anisotropy and magnetoelastic anisotropy are usually considered to be the main sources of the coercivity of magnetic materials in addition to magnetocrystalline anisotropy.$^{47}$ As shown in Fig. 5, the highest coercivity is found at the middle area of $X$ range ($x=0.4, 0.6, 0.4, 0.2$ and $0.2$ for $R=$Nd, Sm, Eu and Tb, respectively) instead of $x=1.0$, which means that there should be contributions from shape and magnetoelastic anisotropy for the highest coercivity. The shape anisotropy is proportional to the magnetization. However, the magnetization of the samples is significantly smaller than the typical magnetization of ferromagnetic materials. Therefore, the contribution of shape anisotropy can be neglected. The highest coercivity found here might be contributed by the magnetoelastic anisotropy in addition to magnetocrystalline anisotropy.

4. Conclusions

The crystalline structure of BFO transforms from rhombohedral lattice to orthorhombic one by doping different rare-earth content. The lattice constants and unit-cell volume decrease with the increasing of rare-earth doping content. Both $T_N$ and magnetization are increased with $R$ content, which might be due to the enhanced exchange interactions between $R$–$R$, $T$–$R$ and $T$–$T$. The enhanced exchange interactions are caused by the drops in $R$–$O$ and $T$–$O$ distances. The temperature dependence of magnetization for NdFeO$_3$ is explained by the magnetic coupling between Nd and Fe moments. A magnetic phase transition is observed at 20–35 K. The main source of the large coercivity might be the magnetocrystalline anisotropy offered by Fe sublattice.

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References