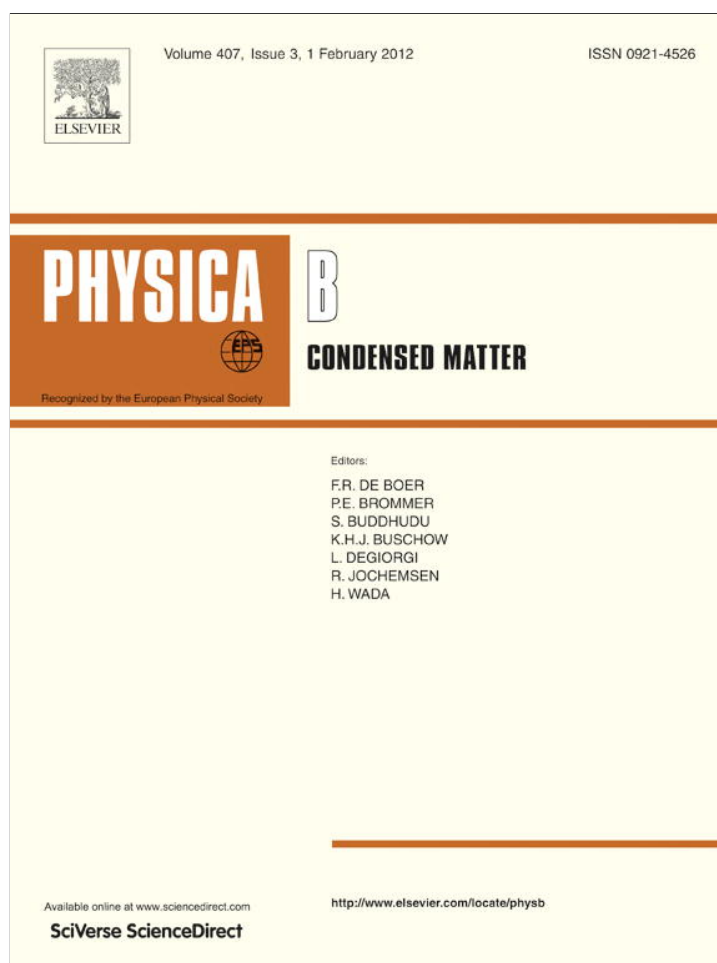


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Magnetic properties of Ni-substituted BiFeO₃

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ABSTRACT

BiFe_{1-x}Ni_xO₃ ceramic powders with x up to 0.10 have been prepared by the sol–gel technique. The band gap of BiFeO₃ is 2.23 eV, and decreases to 2.09 eV for BiFe_{0.95}Ni_{0.05}O₃ and BiFe_{0.90}Ni_{0.10}O₃. The Mössbauer spectra show sextet at room temperature, indicating the magnetic ordering and the presence of only Fe³⁺ ions. Superparamagnetism with blocking temperature of 31 K for BiFe_{0.95}Ni_{0.05}O₃ and 100 K for BiFe_{0.90}Ni_{0.10}O₃ was observed. Enhanced magnetization at room temperature have been observed (1.0 emu/g for BiFe_{0.95}Ni_{0.05}O₃ and 2.9 emu/g for BiFe_{0.90}Ni_{0.10}O₃ under magnetic field of 10,000 Oe), which is one order larger than that of BiFeO₃ (0.1 emu/g under magnetic field of 10,000 Oe). The enhanced magnetization was attributed to the suppression of the cycloidal spin structure by Ni³⁺ substitution and the ferrimagnetic interaction between Fe³⁺ and Ni³⁺ ions.

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1. Introduction

BiFeO₃ is the most widely studied multiferroic material, due to its above room temperature antiferromagnetic Neel temperature ($T_N \sim 643$ K) and ferroelectric Curie temperature ($T_C \sim 1100$ K), which provides the potential mutual manipulation of the magnetization and polarization by the magnetic and electric fields [1]. Large ferroelectric polarization with remnant polarization P_r of over 60 $\mu\text{C}/\text{cm}^2$ has been reported in high quality epitaxial BiFeO₃ films, single crystals and even polycrystalline films [2–4]. However, BiFeO₃ has canted G-type antiferromagnetic spin structure with a weak ferromagnetic moment ($\sim 0.02 \mu_B/\text{Fe}$) [5], and there is a superimposed cycloidal modulation with a period of about 62 nm, thus the macroscopic magnetization has been averaged to zero [6]. The magnetization is very weak, which inhibits the observation of linear magnetoelectric effect [7].

Much work has been done to suppress the cycloidal spin structure and enhance the room temperature ferromagnetism, such as thin-film heterostructure or mixtures of grains, the action of finite-size effect and the imposition of structure modifications by cation substitution [8]. Among them, cation substitution is the widely used method. For BiFeO₃, two cation sites (Bi site and Fe site) can be substituted. Compared with Bi-site substitution, Fe-site substitution by 3d transition metal (TM) ions might not only induce structure modifications to suppress the cycloidal spin structure, but also the ferrimagnetic interaction between Fe and 3d TM ions might further enhance the room temperature ferromagnetism. Enhanced room temperature has been reported in Y, Sm, Dy and 3d TM ions substituted BiFeO₃ ceramics and films [9–15], however, till now, detailed structural and magnetic investigation on Ni substituted

BiFeO₃ is still lacking. Here we report Ni substituted BiFeO₃, magnetization has been enhanced one order compared with that of BiFeO₃ at room temperature, which has been attributed to the suppressed cycloidal spin structure and ferrimagnetic interaction between Fe³⁺ and Ni³⁺ ions.

2. Experimental details

BiFe_{1-x}Ni_xO₃ ($x=0, 0.05, 0.10$) ceramic powders were prepared by a tartaric acid modified sol–gel technique [16]. Appropriate amounts of Bi(NO₃)₃·5H₂O, Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in diluted HNO₃ solution. Tartaric acid in 1:1 M ratio with respect to metal nitrates was added to the solution. The obtained solutions were dried at 80 °C, and heat treated in air at 600 °C for 2 h. As impurity phase of Bi₂₅FeO₃₉ was observed in the as-prepared BiFe_{0.90}Ni_{0.10}O₃ powders, the products were leached in diluted HNO₃ solution to remove the impurity of Bi₂₅FeO₃₉ [3], and then washed in deionized water and ethanol repeatedly, the final products were dried at 160 °C. The structures of samples were studied by X-ray diffraction (XRD) with Cu K α radiation. The optical properties were studied by diffuse reflectance technique. ⁵⁷Fe Mössbauer spectrum was recorded in a transmission geometry using a stand constant acceleration spectrometer with a ⁵⁷Co/Pd source, and the spectra were calibrated by the natural α -Fe foil at room temperature. The magnetization was measured by a physical property measurement system (PPMS-9, Quantum Design).

3. Results and discussion

Fig. 1 shows the XRD patterns of BiFe_{1-x}Ni_xO₃ ($x=0, 0.05, 0.10$) ceramic powders. From the XRD patterns, we can conclude that all three samples have R3c structure without other impurity

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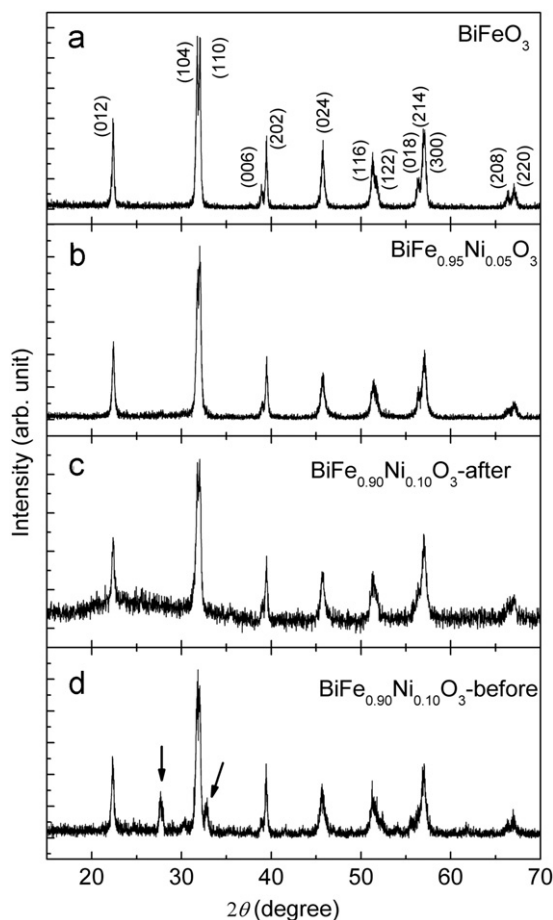


Fig. 1. XRD patterns of $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ceramic powders with $x =$ (a) 0, (b) 0.05, (c) 0.10. For comparison, the XRD pattern of $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ ceramic powders before leaching is shown in (d). The arrows mark the impurity phase of $\text{Bi}_{25}\text{FeO}_{39}$.

phases. It should be noted that impurity of $\text{Bi}_{25}\text{FeO}_{39}$ can be observed in the as-prepared $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ (shown in Fig. 1(d)). After leaching in diluted HNO_3 solution, the impurity phase can be completely removed (shown in Fig. 1(c)). As the as-prepared BiFeO_3 and $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ have pure R3c structure, no further leaching was performed. The intensity of some diffraction peaks, for example, (0 0 6), (0 1 8), was suppressed with increasing Ni substitution concentration, which might be due to distortion of the R3c structure [17]. The lattice constants a , c and unit-cell volume were calculated, and are 5.580 Å, 13.857 Å and 373.64 Å³ for BiFeO_3 , 5.575 Å, 13.882 Å and 373.65 Å³ for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$, 5.579 Å, 13.884 Å and 374.24 Å³ for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$. As the ion radius of Ni^{3+} (0.70 Å) is a little larger than that of Fe^{3+} (0.69 Å) [18], the increase of the lattice constant c and unit-cell volume confirms the substitution of Fe^{3+} by Ni^{3+} .

Fig. 2 shows the UV–visible optical diffuse reflectance spectra of $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ powders. It is clearly seen that the reflectance significantly decreased near the excitonic absorption edge for all samples, which is related to the optical band gap. For analysis purpose, the diffuse reflectance, R , of the sample can be related to the Kubelka–Munk function $F(R) = (1 - R)^2 / 2R$. The energy band gap can be obtained by plotting the $F(R)^2$ versus energy and extrapolating the linear part of the curve to $F(R)^2 = 0$ [19], as shown in the inset of Fig. 2. The band gap of BiFeO_3 is 2.23 eV, close to the previous reported band gap of BiFeO_3 microcrystals in submicrocube shape [20]. The band gap decreases to 2.09 eV for both $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$. The decrease of band gap might be explained by the suppressed tilt angle of the oxygen

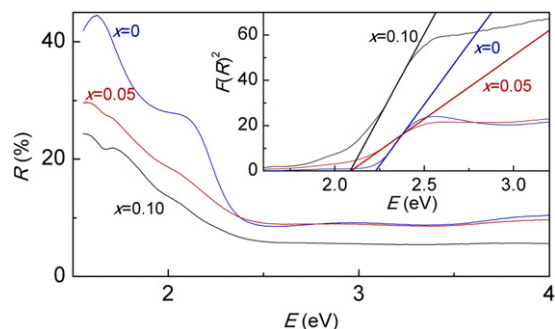


Fig. 2. Room temperature diffuse reflectance spectra of $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ceramic powders with $x = 0, 0.05, 0.10$. The inset shows the plot of $F(R)^2$ vs. E , and the thicker lines are the linear fitting to get the energy band gap.

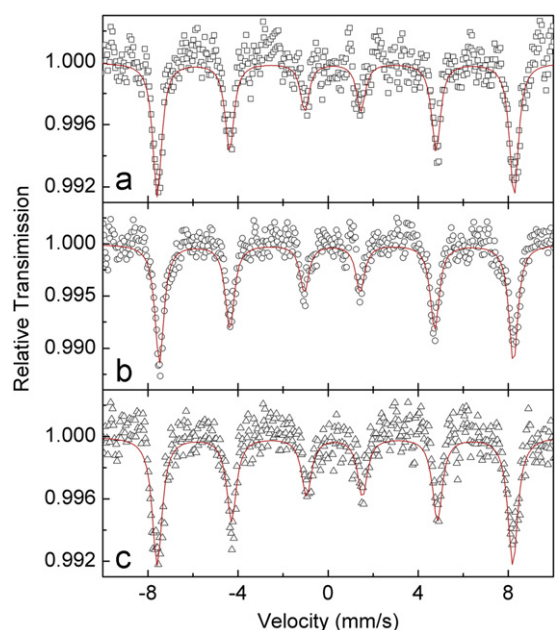


Fig. 3. Room temperature Mössbauer spectra of $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ceramic powders with (a) $x = 0$, (b) 0.05, (c) 0.10. The solid lines represent the best fit to the data.

octahedral due to Ni substitution, and increase the bandwidth of occupied and unoccupied bands, reducing the band gap [21].

To confirm the valence state of Fe ions, Mössbauer spectra were taken at room temperature, as shown in Fig. 3. The sextet in all three spectra can be attributed to the magnetically-ordered phase [22]. After fitting the curves, the obtained hyperfine parameters, isomer shift (IS), quadrupole splitting (QS) and internal field (BHF) are 0.272 ± 0.014 mm/s, 0.063 ± 0.009 mm/s and 49.4 T for BiFeO_3 , 0.277 ± 0.010 mm/s, 0.093 ± 0.007 mm/s and 49.0 T for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$, 0.295 ± 0.015 mm/s, 0.012 ± 0.009 mm/s and 49.2 T for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$. The IS, QS and BHF values are consistent with those of BiFeO_3 ceramics [22–24], which confirms the Fe^{3+} ions and excludes the possibility of Fe ions in other valence state.

Fig. 4(a) shows the $M-H$ curves for $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ powders at 300 K. As can be seen, with increasing Ni concentration, the magnetization increases drastically. However, within the measuring accuracy, only negligible hysteresis loop can be observed. Fig. 4(b) shows the $M-H$ curves at 5 K, and clear hysteresis loop can be observed for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$, suggesting the superparamagnetism at room temperature. To confirm this, the zero field cooled (ZFC) and field cooled (FC) temperature dependent magnetization was measured under magnetic field of

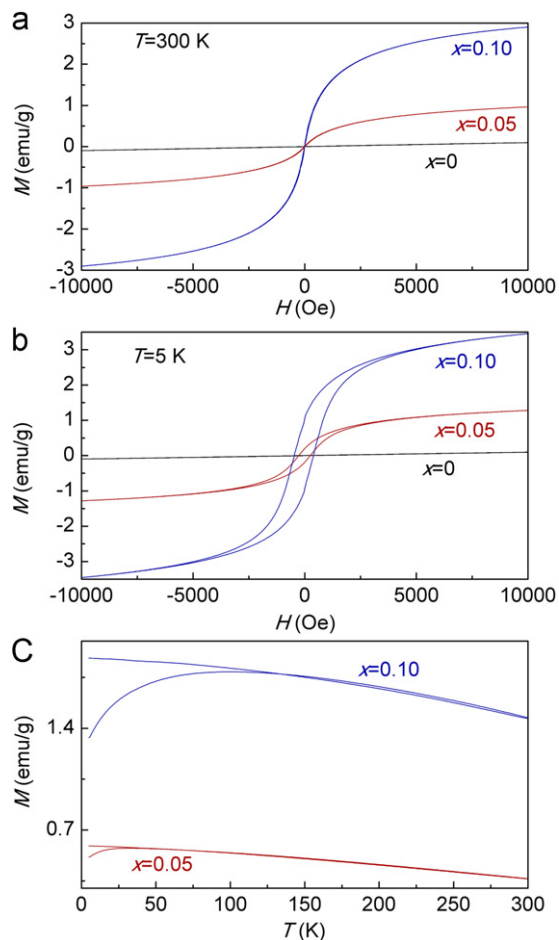


Fig. 4. M - H curves for $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ceramic powders with $x=0, 0.05, 0.10$ at (a) 300 K and (b) 5 K. The ZFC and FC M - T curves for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ measured under magnetic field of 1000 Oe.

1000 Oe, which is shown in Fig. 4(c). The ZFC and FC M - T curves bifurcate and a peak related to blocking temperature (T_B) can be observed in the ZFC curves. The T_B is 31 K for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and 100 K for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$, above which magnetic moments of the superparamagnetic particles move freely owing to thermal fluctuations, while they undergo a transition to a blocked state when $T \leq T_B$ [5]. As can be seen, the applied field of 1000 Oe is larger than the coercivity of $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ (430 Oe) and $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ (265 Oe) at 5 K, the ZFC/FC splitting does not disappear, which is a clear evidence of superparamagnetism [5]. The magnetization under magnetic field of 10,000 Oe is 1.0 emu/g at 300 K and 1.3 emu/g at 5 K for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$, 2.9 emu/g at 300 K and 3.5 emu/g at 5 K for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$, which is strongly enhanced compared with that of BiFeO_3 (0.1 emu/g at 300 K and 5 K).

It has been demonstrated that the valence state of Fe is only +3, thus the enhanced magnetization through the carrier mediated local ferromagnetic order across the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{2+}$ can be excluded [5]. With moment of $0.02 \mu_B/\text{Fe}$, the macroscopic magnetization is calculated to be about 0.4 emu/g, which is much smaller than the magnetization of $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$. Thus the weak magnetization owing to antisymmetric Dzyaloshinskii–Moriya (DM) exchange is not the only origin of the observed ferromagnetism. We consider another possible origin, the ferrimagnetic spin structure between the neighboring Fe^{3+} and Ni^{3+} ions [15], and the net magnetic moment between the neighboring Fe^{3+} and Ni^{3+} ions is $2 \mu_B$. Taking into account the ferrimagnetic ordering in $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$, the magnetization is

calculated to be 1.8 emu/g for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and 3.6 emu/g for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$, which is very consistent with our experimental results. Thus we conclude that besides the weak magnetization due to the DM exchange, the ferrimagnetic exchange between the neighboring Fe^{3+} and Ni^{3+} ions contributes mainly to the enhanced magnetization.

4. Conclusion

In summary, $\text{BiFe}_{1-x}\text{Ni}_x\text{O}_3$ ceramic powders have been prepared by a tartaric acid modified sol–gel technique. The band gap of BiFeO_3 is 2.23 eV, and decreases to 2.09 eV with Ni substitution concentration up to 0.10. The Mössbauer spectra show sextet at room temperature, indicating the magnetic ordering and the valence state of Fe ions is +3. Superparamagnetism with blocking temperature of 31 K for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and 100 K for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ was observed. Enhanced magnetization at room temperature have been observed (1.0 emu/g at 300 K and 1.3 emu/g at 5 K for $\text{BiFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ and 2.9 emu/g at 300 K and 3.5 emu/g at 5 K for $\text{BiFe}_{0.90}\text{Ni}_{0.10}\text{O}_3$ under magnetic field of 10000 Oe), which is one order larger than that of BiFeO_3 (0.1 emu/g at 300 K and 5 K under magnetic field of 10,000 Oe). The enhanced magnetization was attributed to the suppression of the cycloidal spin structure by Ni substitution and the ferrimagnetic exchange interaction between the neighboring Fe^{3+} and Ni^{3+} ions.

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