Room-Temperature Ferromagnetism in Nickel-Doped Wide Band Gap Ferroelectric $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ Nanocrystals

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We report the effect of nickel doping on the structural, optical, and magnetic properties of $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ nanocrystal. The X-ray diffraction results indicated that Ni was substituted into the Ti sites in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ and the NiTiO_3 phase was formed when Ni concentration was higher than 3 mol%. The band gap value decreased from 3.31 eV to 2.96 eV when the Ni concentration changed from 0 to 3 mol% and then increased with higher Ni concentration. Both weak-ferromagnetism and diamagnetism coexisted in un-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples. The ferromagnetic signal strongly influenced the paramagnetic signal for Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples at room temperature. The room-temperature ferromagnetism in Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples could be contributed by intrinsic reason due to presence of Ni ion in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ crystal and by extrinsic reason due to segregation of NiTiO_3 clusters when Ni concentration was over 3 mol% threshold. This method may provide a useful way to get both single-phase multiferroics and composite multiferroics materials. [doi:10.2320/matertrans.MA201548]

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1. Introduction

One of the promising approaches to create novel materials is to combine different physical properties in one material to achieve rich functionality. The ideal to combine both ferromagnetic and ferroelectric properties in one system started in 1960s by Smolenskii and Venevtsev.^{1,2)} However, there is a scarcity of multiferroic material in nature because the conditions for being simultaneously ferroelectric and ferromagnetic are difficult to achieve due to the usual atomic-level mechanism.^{3,4)} Therefore, it remains a major challenge to obtain new multiferroic materials at room temperature. There are four ways to obtain and to develop the multiferroic materials: i) enhancing the performances of natural multiferroic materials such as BiFeO_3 ,⁵⁾ ii) synthesis of new multiferroic materials such as KBiFe_2O_5 ,⁶⁾ iii) combining ferromagnetic materials with ferroelectric materials as composite or multilayer such as $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ or NiFe/BiFeO_3 , etc.,^{7,8)} and iv) introducing the transition metal to ferroelectric material as dopants such as Fe-doped BaTiO_3 .⁹⁾

Recently, the ferromagnetism at room temperature was obtained in transition metal Mn- and Fe-doped PbTiO_3 and $\text{PbTiO}_3\text{-CoFe}_2\text{O}_4$ composite,^{10–12)} However, since Pb in lead-based material pollutes environment and harmful to human, considerable effort has been devoted towards the development of lead-free multiferroic materials.¹³⁾ Among lead-free ferroelectric materials, the $\text{Bi}_{0.5}\text{A}_{0.5}\text{TiO}_3$ ($\text{A} = \text{Na}, \text{K}$) are widely studied.¹⁴⁾ Recently, the room temperature ferromagnetism was obtained in transition metal (Co, Fe)-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ferroelectric materials.^{15,16)} However, the effects of transition metal in transition metal-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT) ferroelectric materials has not been deeply investigated.

In this work, the Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ nanocrystalline materials were fabricated by using sol-gel technique. The Ni strongly influenced the band structure of $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$; reduction of band gap. The Ni had low solid solution in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ crystal and the NiTiO_3 clusters were formed when Ni concentration dopants are over 3 mol%. The Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples exhibited ferromagnetism at room temperature. The saturation magnetization was found to be $\sim 0.875 \text{ Am}^2/\text{kg}$ at 5 K for $\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_{0.99}\text{Ni}_{0.01}\text{O}_3$ sample.

2. Experimental Procedures

The Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples were synthesized by using the sol-gel technique. The raw materials used consist of bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), potassium nitrate (KNO_3), tetraisopropoxytitanium (IV) ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$), and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). The acetic acid (CH_3COOH) and acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) were selected as solvents. The experimental procedure for the Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ was as follows. Firstly, bismuth nitrate pentahydrate and potassium nitrate were dissolved in acetic acid and CO_2 -free distilled water (10 ml $\text{DI-H}_2\text{O}$:1 ml acetic acid). After stirring vigorously for 1 h, a transparent homogeneous sol was formed. Then, the acetylacetone was introduced into a prepared solution after adding the tetraisopropoxytitanium (IV). After stirring vigorously for 2 h, a thin yellow homogeneous sol was formed. Then, the amounts of nickel nitrate were added. The solutions were stirred around one day at room temperature. Then, the sol was heated at 100°C to prepare dry gels. The dry gels were ground and calcined at 400°C for 2 h and sintered at 700°C for 3 h. The white potassium bismuth titanate and green nickel-doped potassium titanate powders were obtained. The crystalline structures of the samples were characterized by X-ray diffraction (XRD, Bruker D8 Advance) in range 2θ from 20 to 60° . The optical properties were studied by UV-

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Fig. 1 (a) X-ray diffraction patterns of Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples as a function of Ni doping concentration, (b) a comparison of (111) diffraction peak positions.

Vis spectroscopy (Jasco V-670) in wavelength range from 200 to 800 nm. The magnetic properties were characterized by using superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc.) at 5 K and vibration sample magnetometer (Lakeshore 7400) at room temperature.

3. Results and Discussion

Figure 1(a) shows the XRD patterns of the Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples. The peaks in θ - 2θ XRD patterns were indexed as tetragonal phase in perovskite structure. The NiTiO_3 phases were found in the logarithmically scaled θ - 2θ XRD pattern when Ni concentration dopant was over 3 mol%, indicating that Ni solutes in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ with low concentration. The (111) peak position in the range of 35–43 slightly shifted toward a higher 2θ values with Ni doping, as shown in Fig. 1(b). The diffraction peak shifted due to transition metal presence at Ti-site and different ionic radii between them.^{9,10,16,17} Note that the ionic radius of Ni depends on the coordination number charge and spin states, etc. The ionic radii of Ni^{2+} , Ni^{3+} , Ni^{4+} and Ti^{4+} with six coordination are 0.069, 0.056, 0.048, and 0.061 nm, respectively.¹⁸ The extended X-ray absorption fine structure and X-ray absorption near-edge structure results indicated that the Ni charge state is close to 4+ in Ni-doped SrTiO_3 , while the X-ray photoelectron spectroscopy result indicated that the Ni charge state is 2+ in Ni-doped BaTiO_3 .^{19,20} However, Niishiro *et al.* reported that both Ni^{3+} and Ni^{2+} are present in SrTiO_3 .²¹ Our result indicate that the peaks position shift to higher angle for doped samples suggests that the average ionic radius of Ni dopant is smaller than that of ionic Ti^{4+} .

The optical absorption spectra of $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples with various Ni concentrations are shown in Fig. 2(a). Clearly, the Ni doping into $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ below solubility limit makes the spectra red-shift, indicating the reduced band gap (E_g). In addition, the appearance of absorbance peaks at around 440 and 710 nm suggest multi-charge-states of Ni. Our results are in accordance with the previous report for Ni-doped SrTiO_3 .²² The results were further evidence for Ni

cations incorporation into $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$. The E_g values were calculated by using the plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$, as shown in Fig. 2(b), where α is absorbance coefficient, h the Planck constant, and ν the frequency. Inset of Fig. 2(b) shows the band gap values as function of Ni doping concentration. The optical band gap is calculated to be 3.31 eV for pure $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ and 2.96 eV for 3 mol% Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ and it decreased with further addition of Ni. The reduction of E_g values was recently reported in transition metal-doped ferroelectric perovskite structure. Oanh *et al.* obtained the reduction of band gap from 2.98 to 1.50 eV in 3 mol% Mn-doped PbTiO_3 .¹¹ Hu *et al.* reported the band gap values of 3.4 and 3.2 eV in pure PbTiO_3 film and 2 mol% Fe-doped PbTiO_3 film, respectively.²³ Xie *et al.* reported that the absorption tail is partly attributed to the electron excitation from Fe impurities levels to the conduction band of SrTiO_3 .²⁴ However, the E_g values increased from 2.96 (3% mol Ni-doped BKT) to 3.21 eV (9% mol Ni-doped BKT) with additional Ni over solubility limit of Ni in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$. The presentation of low solid solution of Ni in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ results in phase separation as NiTiO_3 .

Figure 3 shows the magnetic hysteresis (M - H) loops of the un-doped and Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples at room temperature. The S-shape at low field and anti-S-shape at high field were observed in un-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples, indicating the strong diamagnetic contribution, as shown in Fig. 3(a). The clear magnetic hysteresis loop was achieved after subtracting the diamagnetic contribution, as shown in inset of Fig. 3(a). The coercive field (H_C) and remanence magnetization (M_r) was estimated about 0.012 T and 0.2 mAm²/kg for un-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples, respectively, which were solid evidence for ferromagnetism at room temperature. The unexpected room temperature ferromagnetism for un-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples was attributed to O- and/or Ti-vacancies,^{11,25–27} or the exchange interactions between localized electron spin moments and oxygen vacancies at the surface of nanoparticles.²⁸ Whereas, the M - H curve becomes S-type shape with the Ni concentration at 3 mol%, indicating the appearance of ferromagnetic long-range ordering, as shown in Fig. 3(c). The non-zero H_C and

Fig. 2 (a) UV-Vis absorption spectra of the Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ and (b) The $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) of the $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples for various Ni dopants. The inset of (b) shows the band gap E_g of the $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples as function of Ni dopant.

Fig. 3 The as-obtained M - H curve of $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples for various Ni dopants at room temperature; (a) un-doped, (b) 2 mol% Ni-doped, (c) 3 mol% Ni-doped, (d) 5 mol% Ni-doped, (e) 7 mol% Ni-doped, and (f) 9 mol% Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples. The inset of (a) shows the M - H curve of the un-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples after subtraction of the diamagnetic signal.

M_r values were obtained; 0.017 T and 0.41 Am^2/kg of 2 mol% Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples, which were solid evidence for ferromagnetic ordering at room temperature. At higher amount of Ni dopant, the M - H curve exhibited no saturation. This phenomenon is well known in transition metal-doped wide band gap ferroelectric materials such as Fe-doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ or PbTiO_3 , etc., which results from the contribution of paramagnetic isolated magnetic ion.^{9,10,15,16} Thus, the observed magnetism in Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples is attributed to the competition between ferromagnetism and paramagnetism. For higher Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples, e.g. 9 mol% Ni-doped in this experiment, the volume fraction of Ni ions increases. It is known that the super-exchange interactions between neighboring Ni ions are antiferromagnetic. As a result, the

enhanced Ni-Ni antiferromagnetic associations suppress the ferromagnetic coupling, resulting in a rapid decrease in the magnetic moment as shown in Fig. 3(f). In addition, there are some contribution of NiTiO_3 phases, when the amount of Ni dopant was over 3 mol%. Note that the NiTiO_3 is antiferromagnetic with Neel temperature ($T_N \sim 23$ K) in bulk.²⁹ However, it exhibited weak-ferromagnetism below 250 K in thin film or room temperature ferromagnetism in nanoparticles.^{30,31} Thus, we suggest that room temperature ferromagnetism in Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ nanocrystals may be originated from both intrinsic reason caused by the Ni ion solution in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ crystal and extrinsic reason caused by segregation of NiTiO_3 phase.

Figure 4(a) shows the temperature dependence of magnetization in $\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_{0.99}\text{Ni}_{0.01}\text{O}_3$ under an applied field of

Fig. 4 (a) The M - T curve for the $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples at 0.1 T magnetic field with 1 mol% Ni doping concentration and (b) M - H curve of the $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples with 1 mol% Ni doping concentration at 5 K.

0.1 T. Figure 4(b) shows the M - H curve of $\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_{0.99}\text{Fe}_{0.01}\text{O}_3$ samples up to 7 T at 5 K. The $\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_{0.99}\text{Ni}_{0.01}\text{O}_3$ samples exhibited no saturation even at very high magnetic field. The magnetization was found to be $\sim 0.875 \text{ Am}^2/\text{kg}$ at applied magnetic field of 7 T. The average magnetic moment per formula unit in Bohr magneton (μ_B) was calculated using the following equation $\mu_B = (M \times M_S) / 5585$ where M is the molecular weight of the sample and M_S is the saturation magnetization.³²⁾ Here, we note that the magnetic signal of $\text{Bi}_{0.5}\text{K}_{0.5}\text{Ti}_{0.99}\text{Ni}_{0.01}\text{O}_3$ samples was not saturated and it was strong competition between paramagnetism and ferromagnetism. However, we can use this equation to roughly estimate the magnetic moment of samples. The average magnetic moment per Ni atom is $3.44 \mu_B/\text{Ni}$. When in octahedral coordination, Ni^{2+} has a spin configuration of $t_{2g}[\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow]e_g[\uparrow\uparrow]$ ($M_{\text{spin}} = 2 \mu_B/\text{Ni}$). Assuming a low spin state, the spin configurations of Ni^{3+} and Ni^{4+} are $t_{2g}[\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow]e_g[\uparrow]$ ($M_{\text{spin}} = 1 \mu_B/\text{Ni}$) and $t_{2g}[\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow]$ ($M_{\text{spin}} = 0 \mu_B/\text{Ni}$), respectively. Thus, Ni^{2+} and Ni^{3+} are magnetic but Ni^{4+} is non-magnetic. Therefore, it is worthwhile to make a remark on the value of the measured strength of magnetization in Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples in comparison with the expected spin moments of $M_{\text{spin}} = 2 \mu_B/\text{Ni}$ for Ni^{2+} and $1 \mu_B/\text{Ni}$ for Ni^{3+} ions, which is rather small compared to the experimental value. Ogale *et al.* and Hong *et al.* reported that the possibility of an additional orbital contribution to the magnetic moment of an ion through a relaxation of orbital angular momentum quenching.^{33,34)} This assumption seems to be convincing because, when the Ni-added amount is increased, the magnetic moment decreased due to an enhancement of quenching through an increase in dopant-dopant associations and/or due to an increase in the antiferromagnetic super-exchange coupling strength between two neighboring magnetic impurity ions via a nearly O^{2-} ions.³⁵⁾ In addition, it is possible to enhance magnetization due to contribution of magnetism rising from O- and/or Ti-vacancies.

4. Conclusion

The room-temperature ferromagnetism was obtained from introduction of Ni ions to lead-free $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ferroelectric

materials. The low solid solution of Ni in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ structure resulted in NiTiO_3 phase when Ni concentration was added over 3 mol%. The room-temperature ferromagnetism in Ni-doped $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ samples could be contributed by intrinsic reason due to presence of Ni ion in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ crystal and by extrinsic reason due to segregation of NiTiO_3 clusters when Ni concentration was over 3 mol% threshold. The replacement of Ti cations at octahedral site by Ni cations of $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ nanocrystalline resulted in the reduction of band gap. The pristine $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ had a band gap of 3.31 eV and it decreased to 2.96 eV for 3 mol% Ni-dopant. We expect that this way can be further developed new lead-free multiferroics materials.

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