ENHANCED FERROELECTRICITY AND FERROMAGNETISM OF (Y, Ni) CO-DOPED BiFeO₃ MATERIALS

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ABSTRACT

Multiferroic Bi₁₋ₓYₓFe₀.₉₇₅Ni₀.₀₂₅O₃ (x = 0.00, 0.05, 0.10, and 0.15) called as (Y, Ni) co-doped BiFeO₃ materials were synthesized by a sol-gel method and characterized by X-ray diffraction (XRD), energy-dispersive X-ray (EDX) and vibrating sample magnetization (VSM) measurements. The result showed that all investigated materials present a single phase of the perovskite-type rhombohedral structure. Ferromagnetism and ferroelectricity of the materials have been affected by the (Y, Ni) co-doping, as a result the ferroelectric polarization and magnetization of the initial BiFeO₃ material were enhanced with increasing concentration of Y³⁺ ion. It is attributed to the difference of the magnetic moments of Ni²⁺ and Fe³⁺ ions, as well as the Y³⁺-Fe³⁺ and Y³⁺-Ni²⁺ super-exchange interactions. The characteristics of the investigated materials, such as remanent magnetization (Mᵣ), saturation magnetization (Mₛ), remanent polarization (2Pᵣ) and saturation polarization (2Pₛ) continuously increase in the range of x from 0.00 to 0.15. Origin of ferromagnetic and ferroelectric properties of Bi₁₋ₓYₓFe₀.₉₇₅Ni₀.₀₂₅O₃ materials will be discussed in this paper.

Keywords: multiferroic, ferromagnetism, ferroelectricity, co-doping.

1. INTRODUCTION

Multiferroic materials exhibit simultaneously both ferroelectric and ferromagnetic properties at room temperature. These materials are of high interest for the development of the next generation of micro-electromechanical devices such as magnetic recording media, spintronics and magneto-electric sensor devices [1-3]. Among all multiferroic materials studied so far, BiFeO₃ (BFO) is known as the only single-phase multiferroic material at room temperature. BFO material has simultaneously ferroelectric and antiferromagnetic properties with its Tc ~ 1103 K and TN ~ 643 K [4], which are appropriate for practical applications.
However, synthesis of a BFO single-phase material is hard due to some reasons: (i) large leakage current in BFO ceramics is induced by impurities; (ii) non-stoichiometry and oxygen vacancies, which made BFO material to be difficult to achieve good ferroelectric properties. So a chemical modification by doping rare-earth (RE) or transition metal (TM) ions into the BFO crystal was proposed [5-7]. Previous studies showed that the enhancement of magnetic properties of BFO material was obtained due to Bi-sites replaced by rare-earth or Fe-sites replaced by transition metal ions [8-10]. The substitution of RE ions at the Bi-sites is also effective way to decrease leakage current, to enhance ferromagnetic, meanwhile the substitution of TM ions at the Fe-sites contributes to improving ferroelectric properties. Therefore RE and TM co-doped BFO materials are expected to enhance both ferroelectric and ferromagnetic properties for application proposals [11, 12].

In this study, we report the synthesis of (Y, Ni) co-doped BFO materials with different doping contents by a sol-gel method. Structure, ferroelectric and ferromagnetic properties of BFO and Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ (x = 0.00, 0.05, 0.10, and 0.15) materials were investigated and discussed.

2. EXPERIMENTAL

Multiferroic BiFeO$_3$ and Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ (BYFNO) (x = 0.00, 0.05, 0.10, and 0.15) materials were synthesized by sol-gel method. The chemicals used in this work are iron (III) nitrate, bismuth nitrate, yttrium nitrate, nickel (II) nitrate, ethylene glycol and citric acid. In a typical procedure for the sample preparation, these chemicals were well mixed in correct weight contribution and an aqueous solution of citric acid:ethylene glycol of 7:3 volume ratio was prepared in distilled water. Then, the solution was added into the mixture in turn with continuous stirring at a temperature of 50 $\div$ 60 °C for an hour to avoid precipitation and obtain homogeneous solution. After that, water in the obtained solution was evaporated at temperature of 100 °C four three hours to obtain colloidal gel. The gel then was annealed at temperature of 800 °C for seven hours to remove organics and receive BFO/BYFNO powders.

Structure of the prepared powders was characterized by X-ray diffraction (XRD) using a D8-Advance diffractometer with CuK$\alpha$ radiation and scan step of 0.02°. Chemical composition of the BYFNO powders was determined by energy-dispersive X-ray (EDX) spectra. Vibrating sample magnetometer (7404_VSM) was used to measure the magnetization hysteresis ($M$-$H$) loops of samples. The polarization electric hysteresis ($P$-$E$) loops at room temperature were measured by a ferroelectricity tester (Radiant, Precision LC_10V).

For the investigation of ferroelectric property, BFO and BYFNO powders were compressed by 20 MPa pressure into round tablets of 6 mm in diameter and 1 mm thick and then sintered at temperature of 800 °C for five hours to obtain ceramics. The ceramic tablets were polished and measured accurate thickness and cross area. Finally, the samples were evenly covered with Pt glue as electrode and sintered at temperature of 500 °C for three hours.

3. RESULTS AND DISCUSSION

Figure 1 shows energy-dispersive X-ray spectra of Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ (x = 0.00, 0.05, 0.10, and 0.15) samples. It is clearly seen that all characteristic peaks of Bi, Y, Fe, Ni, and O are observed. The peaks characterized for Ni and Y can be seen in all EDX spectra. The intensity of Y-related peak increases as concentration of Y$^{3+}$ ion increased. This result presents the chemical
appropriateness in the investigated BYFNO samples. It is a basic understanding for the future research on properties of the BYFNO materials.

![Energy-dispersive X-ray spectra of Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$](image)

**Figure 1.** Energy-dispersive X-ray spectra of Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ ($x = 0.00, 0.05, 0.10, \text{and} 0.15$) samples.

![X-ray diffraction diagrams of BFO and BYFNO samples](image)

**Figure 2.** (a) X-ray diffraction diagrams of BFO and Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ ($x = 0.00, 0.05, 0.10, \text{and} 0.15$) samples; (b) The dependence of $a$ and $c$ lattice constants on the concentration of Y$^{3+}$ ion.

X-ray diffraction diagrams of BFO and BYFNO samples are presented in Fig. 2a. It shows that the XRD patterns are consistent with the JCPDS Card No. 71-2494 in crystalline perovskite-type rhombohedral structure ($R_{3c}$). As clearly seen, no secondary phase is found in the XRD diagram of the BFO material. In additional, XRD peaks tend to shift toward higher $2\theta$ values for all samples due to the substitution of the impurities. From the XRD diagrams of BFO and BYFNO samples, lattice constants were calculated by using UnitCell software and displayed in Fig. 2b. The lattice constants were determined to be $a = 5.580$ Å and $c = 13.860$ Å for the BFO sample. The result shows that (Y, Ni) co-doping makes slightly decrease in both $a$ and $c$ constants. Although the radius of Y$^{3+}$ ion (1.020 Å) and Ni$^{2+}$ (0.630 Å) ion are smaller than that of Bi$^{3+}$ ion (1.170 Å) and Fe$^{3+}$ ion (0.635 Å), respectively, the lattice constants $a$ increases from 5.566 Å to 5.575 Å and lattice constants $c$ increases from 13.810 Å to 13.821 Å with increasing in concentration of Y$^{3+}$ ion from 0 % to 15 % mol (Fig. 2b). It is due to the values of lattice constants do not only depend on atomic ion radius but also on the electronegativity of the elements [13].
Fig 3a shows magnetization hysteresis loops of BFO and BYFNO samples. The samples were measured by VSM with a maximum magnetic field of 10 kOe. It shows that all samples have weak ferromagnetic properties. The saturation magnetization ($M_s$) and remanent magnetization ($M_r$) are determined from data of $M$-$H$ loops of BFO and BYFNO samples. Fig. 3b presents the dependence of the values of $M_s$ and $M_r$ on the concentration of Y$^{3+}$ ion. For the BFO sample, the values of $M_s$ and $M_r$ are 0.133 emu/g and 0.036 emu/g, respectively, as shown. Both values increase as the concentration of Y$^{3+}$ ion increased. The value of $M_r$ is 0.794 emu/g when concentration of the Y$^{3+}$ ion is 15 % mol. So that, the magnetization of (Y, Ni) co-doped BFO samples is improved as presence of the impurities. The result could be explained by the destruction of an antiferromagnetic order resulting from the structural transition, the replacement of Ni$^{3+}$ ions at the Fe-sites and the oxygen vacancies created at these sites. The modification of the spiral spin structure of the (Y, Ni) co-doped BFO samples could also be a reason for the enhancement of the magnetization. It is caused by the decrease of Fe-O-Fe bond angles and associated the destruction in the structure. Because of the ion radius mismatch of Y$^{3+}$ and Bi$^{3+}$ions, the Fe-O bond length and the Fe-O-Fe bond angle decrease. A small amount of (Y, Ni) co-doping can bring new magnetic interactions, such as Y$^{3+}$-Y$^{3+}$, Y$^{3+}$-Fe$^{3+}$, Y$^{3+}$-Ni$^{2+}$, Fe$^{3+}$-Ni$^{2+}$, and Ni$^{2+}$-Ni$^{2+}$. The previous studies showed that RE substitution for Bi-sites created weak ferromagnetic order. That was attributed to partial destruction of spiral spin structure due to structural destruction and RE$^{3+}$-RE$^{3+}$ and/or RE$^{3+}$-Fe$^{3+}$ super-exchange interactions [14-16].
The polarization-electric field hysteresis ($P$-$E$) loops of BFO and BYFNO samples measured at room temperature are shown in Fig. 4a. All investigated samples exhibit the ferroelectric property. The shape of $P$-$E$ loops is much improved by the increase in concentration of $Y^{3+}$ ion. Hence, one can say the (Y, Ni) co-doping is effective to increase ferroelectricity of the BFO material. The reason is attributed to a presence of oxygen vacancies or a virtual hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions. In previous studies, it is shown that the ferroelectricity of $RE$, TM co-doped BFO materials was also improved. The enhancement of ferroelectric property in the co-doping materials is attributed to a reduction in the leakage current [17, 18]. Furthermore, ionic radius of $Y^{3+}$ (1.020 Å) and Ni$^{3+}$ (0.630 Å) ions are smaller than ionic radius of Bi$^{3+}$ (1.170 Å) and Fe$^{3+}$ (0.635 Å) ions, respectively, which may lead to a larger ion off-center in the Fe-O octahedral, so a larger ferroelectric polarization in the BFO unit cell could be obtained.

For the pure BFO material, very weak remanent polarization ($2P_r$) of 0.17 µC/cm$^2$ and saturation polarization ($2P_s$) of 0.38 µC/cm$^2$ are observed in the measurement under an applied field of 3 kV/cm. Both the $2P_r$ and $2P_s$ values of (Y, Ni) co-doped BFO samples are higher than that of the pure BFO sample. The $2P_s$ value increases from 1.79 µC/cm$^2$ to 16.58 µC/cm$^2$ and the $2P_r$ value increases from 4.79 µC/cm$^2$ to 27.99 µC/cm$^2$ as the concentration of $Y^{3+}$ ion increased from 0 % to 15 % mol. Fig. 4b shows the dependence of values of $2P_r$ and $2P_s$ on the concentration of $Y^{3+}$ ion. The result shows that ferroelectric property of BFO has been improved when Y and Ni impurities are co-doped into BFO material.

4. CONCLUSIONS

In summary, the effects of (Y, Ni) co-doping on the structure, ferroelectricity and ferromagnetism of the BiFeO$_3$ material are investigated. As a result, the Bi$_{1-x}$Y$_x$Fe$_{0.975}$Ni$_{0.025}$O$_3$ (BYFNO) ($x = 0.00, 0.05, 0.10, \text{and} 0.15$) materials behave a single phase of crystalline perovskite-type rhombohedral structure ($R_{3c}$). It is found that (Y, Ni) co-doping gives rise to the enhancement both ferromagnetic and ferroelectric properties of BiFeO$_3$ material. The ferroelectric and ferromagnetic properties of (Y, Ni) co-doped BiFeO$_3$ materials are improved when the concentration of $Y^{3+}$ ion is increased from 0 % to 15 % mol. The $M_s$ and $2P_s$ values increase up to 0.794 emu/g and 27.99 µC/cm$^2$, respectively. It is elucidated that Y and Ni are responsible for the improvement of ferromagnetic and ferroelectric properties of the BiFeO$_3$ material to be suitable for applications in multi-memory devices.

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