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Enhancement of ferromagnetic properties in Ni-doped $BiFeO_3$

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Ni-doped $BiFeO_3$ samples were successfully synthesized by a hydrothermal method. The as-prepared samples were characterized by X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS). It was found that the magnetization can be controlled by the Ni doping concentration. The magnetization of Ni-doped $BiFeO_3$ was greatly enhanced when the Ni doping concentration was 0.5%. Therefore, it would be interesting to fabricate thin films with similar composition and study their properties with the aim of identifying new device applications.

Key words: *Ni-doped $BiFeO_3$; ferromagnetic property; hydrothermal method*

1. Introduction

Multiferroic materials exhibiting simultaneously ferroelectricity and ferromagnetism gain much attention due to their promising multifunctional device applications [1–4]. Besides the potential applications, the fundamental physics of multiferroic materials is also fascinating. However, there is a scarcity of materials showing multiferroic behaviour because the usual atomic level mechanisms driving ferromagnetism and ferroelectricity are mutually exclusive [5]. Bismuth ferrite ($BiFeO_3$) which shows ferroelectric (T_C = 1103 K) and antiferromagnetic properties (T_N = 643 K) at room temperature, has attracted great attention since its discovery in 1960 [6].

Recently, enhancement of the ferroelectric property in $BiFeO_3$ film has been realized [7] making it attractive from the point of view of possible applications. However, $BiFeO_3$ (BFO) shows the presence of a weak magnetic moment at room temperature

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because of the canting of the Fe sublattice moment [8]. Therefore, if the material is to be exploited in device applications, it is essential that its magnetic properties be improved. Several groups have enhanced the magnetic properties of BFO by ion substitutions [9–11] such as Mn substituting for Fe ions. To our knowledge, there is no report on the substitution of Ni for Fe ions. In this paper, the magnetization of BFO has been noticeably enhanced by the substitution of Ni for Fe ions. The doping concentration of Ni was set as the molar ratio of Ni/(Ni +Fe) (in the form of Ni^{2+} ions).

2. Experimental

The chemical reagents were bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), and potassium hydroxide (KOH). All the chemicals were of analytical grade and were used as received without further purification. Stoichiometric proportions of $Bi(NO_3)_3$, $Fe(NO_3)_3$ and $Ni(NO_3)_2$ were dissolved in diluted HNO_3 to form aqueous solutions. Then, the KOH solution was slowly added to the above solution to coprecipitate Fe^{3+}, Ni^{2+} and Bi^{3+} ions by constant stirring and a brown precipitate was formed. The precipitate was filtered, and washed with distilled water to remove NO_3^- and K^+ ions. Then, the precipitate was mixed with KOH solutions under constant magnetic stirring for 5 min. The suspension was poured into a stainless-steel Teflon-lined autoclave for hydrothermal treatment. The autoclave was sealed and maintained at 200 °C for 9 h. Finally, it was cooled down naturally to room temperature. The products were filtered, washed several times with distilled water and absolute ethanol, and then dried at 70 °C for 4 h for characterization. X-ray diffraction was performed on an ARL XTRA X-ray diffractometer with high-intensity CuK_α radiation. The EDS spectroscopy pattern was performed by X-ray energy dispersion spectroscopy using a GENENIS4000 spectrometer. Magnetic measurements were carried out using a Quantum Design superconducting quantum interference device (SQUID, MPMS XL-5).

3. Results and discussion

Figure 1 shows XRD patterns of the BFO samples doped with Ni of various concentrations. The XRD results showed that the obtained Ni-doped BFO samples were single phase with perovskite structure when the Ni doping concentration varied from 0% to 1%. However, an impurity phase ($Bi_{12}NiO_{19}$) can be detected in the case of the 1.5% Ni doping concentration, which is an indication of the saturation level of Ni substitution in BFO. An expanded view on the location of (110) diffraction peaks in the range of 30°–35° (Fig. 2) shows that the peak position of the sample obviously shifts toward a lower 2θ value in the case of Ni doping. Energy dispersive X-ray (EDS) patterns checked from the obtained products clearly demonstrate the presence

of Ni in the prepared products (Fig. 3). According to the above results, it is evident that Ni ions have been effectively incorporated into the crystal structure of $BiFeO_3$ and the lattice parameter *a* of $BiFeO_3$ is enlarged because of the larger radius of Ni^{2+} cations relative to that of Fe^{3+} cations.

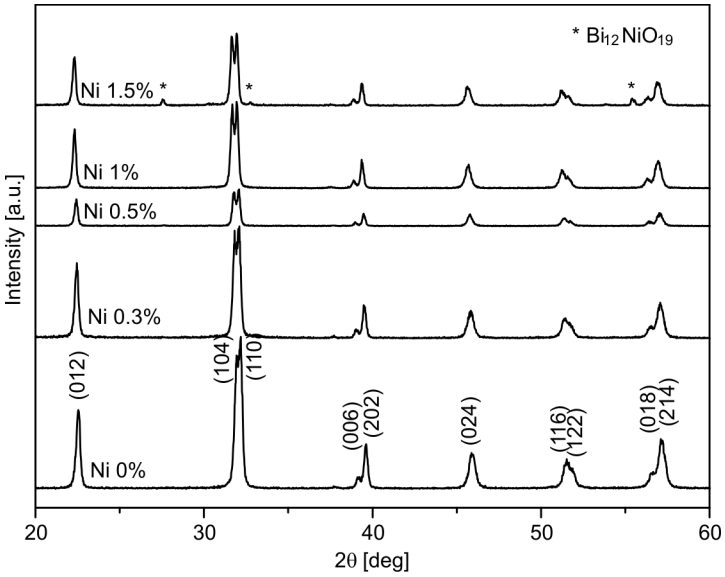

Fig. 1. XRD patterns of the Ni-doped BFO samples
with Ni doping concentrations ranging from 0% to 1.5%,

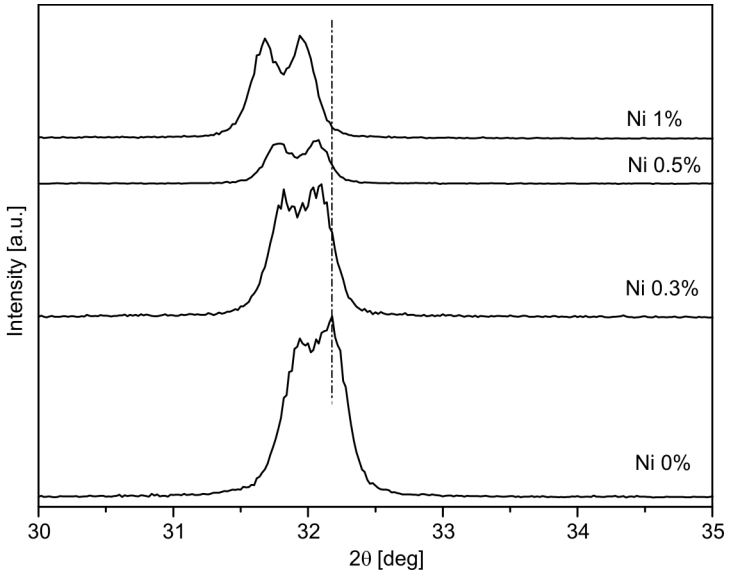

Fig. 2. Dependence of the (110) diffraction
peak positions in the patterns on Ni concentration

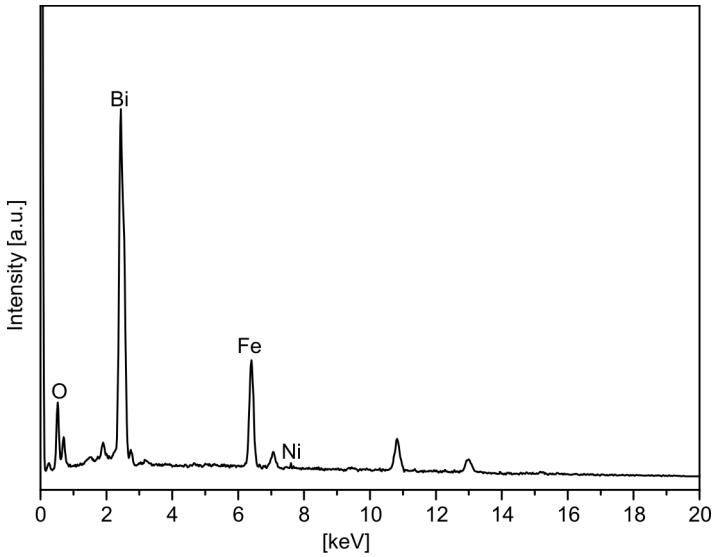

Fig. 3. The EDS spectroscopy pattern for the as-obtained Ni-doped BFO sample with a 0.5% Ni doping concentration

The lattice parameters of Ni-doped BFO samples are given in Table 1. It is clear that with the increase in Ni doping concentration there is an increase in both, *a* and *c* parameters of the unit cell. This is as expected, since the ionic radius of Ni^{2+} is slightly larger than that of Fe^{3+}. Since there is an increase in both, *a* and *c* parameters, the ratio *c*/*a* remains more or less unaffected, which is important for maintaining the ferroelectric properties in Ni-doped BFO samples.

Table 1. Lattice parameters of Ni-doped BFO samples

Ni doping concentration [%]	*a* [Å]	*c* [Å]	*v* [Å]^3	*c*/*a* ratio
0	5.571	6.911	185.78	1.241
0.3	5.577	6.914	186.28	1.240
0.5	5.578	6.926	186.68	1.241
1	5.586	6.937	187.46	1.242

Magnetic properties of the obtained Ni-doped BFO samples of various doping concentrations have been determined (Fig. 4). In pure BFO, the magnetization varies linearly with the applied magnetic field up to 20 kOe, similar to that of La-doped BFO powders [9]. There is no obvious increase of magnetization in the case of a 0.3% Ni doping concentration, but magnetization is greatly enhanced when the Ni doping concentration increases to 0.5%. Compared with the method to enhance ferromagnetic properties in BFO ceramic by La doping [10], Ni-doped BFO samples (with Ni doping

concentration 0.5%) show larger magnetization at room temperature. In addition, magnetization decreases when the Ni doping concentration is further increased to 1%. This indicates that the ferromagnetism of Ni-doped BFO does not increase with the increase of the Ni doping concentration.

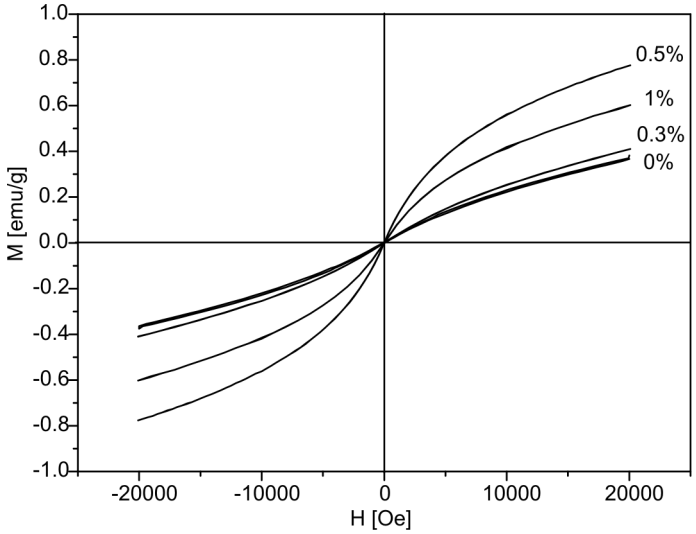

Fig. 4. *M–H* recorded at room temperature for the as-prepared Ni-doped BFO samples with Ni doping concentrations ranging from 0 % to 1 %

The dependence of the magnetization on the Ni doping concentration provides strong evidence that the noticeable enhancement in the ferromagnetism is not due to any precipitating secondary phase, such as nickel oxides. If nickel oxides are responsible for the enhancement of ferromagnetic behaviour, a stronger Ni concentration increasing up to 1% would presumably improve the corresponding magnetization. Instead, the opposite behaviour is observed.

4. Conclusions

In Ni substituted $BiFeO_3$, the magnetization varies with Ni doping concentration and the magnetization of Ni-doped $BiFeO_3$ is greatly enhanced when the Ni doping concentration is 0.5%. Therefore, it is an important task to produce thin films with similar compositions and to study their properties, in order to identify new applications in devices. Such investigations are in progress and will be reported elsewhere.

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