Magnetic and Dielectric Properties of Multiferroic Bi$_{1-x}$Gd$_x$FeO$_3$


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Abstract

Bi$_{1-x}$Gd$_x$FeO$_3$ (0≤x≤1.0) nanoparticles with an average diameter of 18 to 47 nm were synthesized by a wet chemical method. The annealing temperatures were controlled to obtain single-phase Bi$_{1-x}$Gd$_x$FeO$_3$ nanoparticles. The crystal structures changed from rhombohedral to orthorhombic as Gd ions increased to around x=0.2. The behavior of magnetization curves of x=0.1 suggested canted antiferromagnetism and magnetization drastically increased compared with x=0 (BiFeO$_3$). This suggests that the canting angle increased with the increase of Gd ion. The dielectric properties of x=0.1 showed that dielectric loss (tan δ) has been improved compared with that of x=0 (BiFeO$_3$) to about 90%, while real dielectric constant ε’ decreased about 15%. The reason is considered to be that impurities are restrained and leakage current decreased.

Key Words: Nanoparticles, Multiferroics, Spintronics, Ferrimagnetism

I. INTRODUCTION

Multiferroic materials have various electric and magnetic properties, and have abilities for potential applications in the field of spintronics. A novel method to synthesize several types of magnetic nanoparticles encapsulated in amorphous SiO$_2$ was developed and their magnetic and thermal properties were reported [1-6]. BiFeO$_3$ (BFO) is a multiferroics that has antiferromagnetic ($T_N$=664 K) and ferroelectric ($T_C$=1103 K) ordering, so, BFO is expected to have magnetic and electric applications such as new device materials and green device materials. However, the conventional synthesis methods of BFO involve complex and massive steps [7-9]. For example, high-pressure hydrothermal synthesis and spark plasma sintering at 70 MPa had to be performed to obtain BFO. We have developed a novel synthesis method of BFO by a wet chemical method [10], however it was difficult to obtain single phase BFO because BFO tend to be more sensitive to heating treatment. Furthermore, BFO is antiferromagnetic material at room temperature and magnetic parameters such as remnant magnetization ($M_r$) could not be expected. In order to improve magnetic parameter of BFO; in this study, we prepared large magnetic moment Gd ion (7.9 $\mu_B$) doped BFO, Bi$_{1-x}$Gd$_x$FeO$_3$ and magnetic properties were reported.

II. EXPERIMENTS

Bi$_{1-x}$Gd$_x$FeO$_3$ nanoparticles were synthesized by mixing aqueous solutions of BiCl$_3$, GdCl$_3$·6H$_2$O, FeCl$_3$·6H$_2$O and NaOH. The mole ratio of the aforementioned mixture Bi:Gd:Fe:Na was 1-x:x:1:8. The obtained precipitates were washed several times with distilled water and then dried at approximately 320 K in a thermostat. The as-prepared samples were subjected to heat treatment in an air environment in a furnace at annealing temperatures of 1053 K to 1093 K. The annealing time was 10 hours. Each sample was examined by Cu Ka X-ray powder diffraction (XRD; $\lambda$=0.154 nm). The crystal size of these samples is estimated using Williamson-Hall’s plot method from [110] (rhombohedral structure) and [112] (orthorhombic structure) miller index peaks [11]. Lattice constants of samples were estimated by Bragg’s equation and miller indexes. DC magnetization of the samples in $H=50$ kOe magnetic field from 5 K to 300 K was measured using a SQUID magnetometer (Quantum Design, MPMS). The dielectric properties of samples that are dielectric constant ε’ and dielectric loss (tan δ) were measured by Material Analyzer (Agilent, E4991A).

II. RESULTS AND DISCUSSION

A. X-ray diffraction patterns

The most appropriate conditions for preparing Bi$_{1-x}$Gd$_x$FeO$_3$ (0≤x≤1.0) were determined by adjusting the annealing temperature. The annealing temperature was 1053 K for $x=0$, 1068 K for $x=0.05$ and 0.1, 1093 K for $x=0.15$, and 1073 K for $x=0.2-1.0$, respectively. The XRD patterns of samples are shown in Fig. 1. Single phase perovskite structure could
be observed in \( x = 0, 0.1, 0.6, 0.8, 1.0 \). Figure 2 shows lattice volume which exhibits the volume of the unit cell estimated from lattice constants. From this figure, lattice volumes obviously decreased as the amount of Gd ion increased. This result supports that the Gd ions were replaced in BiFeO\(_3\) because the radius of Gd ion (1.05 Å) is smaller than that of Bi ion (1.17 Å). XRD patterns also show that the structure changes from rhombohedral perovskite (\( R3c \)) to orthorhombic perovskite (\( Pbnm \)). It was found that BiFeO\(_3\) structure exhibited in the region of \( x = 0, 0.05, 0.1, \) and GdFeO\(_3\) structure above \( x = 0.6 \). Coexistence of both BiFeO\(_3\) and GdFeO\(_3\) structure would be suggested between \( x = 0.2 \) and 0.4. The crystal size of these samples is estimated to be 18 to 47 nm (Table 1). Magnetic and dielectric properties of the samples \( x = 0 \) and 0.1, which are expected to have high dielectric properties, were measured.

### B. Magnetization measurements

The magnetization curves for the samples of \( x = 0 \) and 0.1 is shown in Fig. 3. The \( M_r \) increased from \( 1.24 \times 10^{-3} \) emu/g to \( 2.20 \times 10^{-1} \) emu/g and coercive force \( H_c \) increased from 70 Oe to 870 Oe as the amount of Gd ion increased. These behaviors could also be explained by the increase of spin-canting angle of Fe ions. Simultaneously, this spin-canting angle is introduced the increase of the magnetic anisotropy, as the coercive force of this Gd doped BFO system increased. The larger coercive force appeared from the canted antiferromagnetism caused by Dzyaloshinskii-Moriya (DM) interaction. The magnetic field dependence of magnetization supports the increase in canting angle of the magnetic moment of Fe ion. Doped Gd ion causes distortion of the crystal structure. DM interaction works stronger as the crystal structure distorted, as the result, the spin canting angle increased.

Figure 4 shows the temperature dependence of the field-cooling (FC) and zero-field-cooling (ZFC) magnetization of \( x = 0 \) (BFO) and 0.1 (Bi rich region). This figure shows that the magnetization of \( x = 0.1 \) at room temperature increased approximately 5.4 times compared with pure BFO. The temperature dependence of magnetization for the sample of \( x = 0.1 \), namely Bi rich sample with slightly doped Gd ion, shows that the magnetization value increased drastically as the temperature decreased. The behavior of magnetization increase of \( x = 0.1 \) compared with BFO can be explained by the two reasons. First, the total paramagnetic moment increased with doping Gd ions, which have a large magnetic moment (7.9\( \mu_B \)). The second reason is that BiFeO\(_3\) is known for canted-antiferromagnetism, therefore the spin-canting angle of the Fe ions increased according to the doping amount of Gd ion; as a result, total magnetic moment increased.

![Fig. 1 XRD patterns of Bi\(_{1-x}\)Gd\(_x\)FeO\(_3\).](image)

![Fig. 2 Lattice volume versus amount of Gd ion](image)
C. Dielectric Properties

Figure 5 shows the frequency dependence of dielectric constant. The dielectric permittivity $\varepsilon'$ of $x = 0.1$ exhibited only 46% of that of BFO. In order to analyze this phenomenon, we noticed that crystal structure of BFO is totally different from that of GFO. The B-site of BFO, where FeO$_6$ composites tetragonal structure, is asymmetry against the center axis, in contrast, Fe ion in GFO forms symmetry. Therefore, this phenomenon explained that the symmetry of B-site of rhombohedral perovskite structure was improved, and local polarization was released. The symmetry of B-site improved with increasing Gd, leading to a reduction in the dielectric permittivity. On the other hand, dielectric loss ($\tan \delta$) decreased as the amount of Gd ion increased. This could explain that the generation of those impurities which cause leakage current were restrained, as the result, leakage current throughout the sample decreased. The doping effect of Gd ions caused not only improvement of magnetic properties, but also suppression of the impurity in the BiFeO$_3$. Dielectric properties at low frequency were also measured and a decrease tendency according to doping of Gd ions was observed, however, the difference was very small.
III. CONCLUSION
Multiferroic Bi$_{1-x}$Gd$_x$FeO$_3$ ($x = 0$ to 1.0) nanoparticles were synthesized by a novel and effective method. The most appropriate conditions were determined by annealing temperatures between 1053 K and 1093 K. The diameters of nanoparticles were between 18 nm and 47 nm. The magnetization measurements for the samples of $x = 0$ and 0.1 suggested canted-antiferromagnetism. Magnetization at room temperature and remnant magnetization increased drastically with the increase of Gd ion. It could be explained by the increase of the spin-canting angle of magnetic moment of Fe spins. The dielectric permittivity $\varepsilon'$ of $x = 0.1$ decreased 54 % compared with pure BFO. It could be explained by the improving symmetry of B-site. However, dielectric loss (tan $\delta$) decreases with the increase of Gd ion. This suggests that impurities are restrained and leakage current decreased.

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REFERENCES