Exchange bias and *R3c* to *Pn2₁a* phase transition in single crystalline Gd-doped $BiFeO_3$ nanowires

Sandeep K.S. Patel*, Min-Kwan Kim, Miyoung Kim, Sang-Koog Kim
National Creative Research Initiative Center for Spin Dynamics and Spin-Wave Devices, Nanospinics Laboratory, Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, South Korea

1. Introduction

In recent years, the exchange bias effect has received considerable interest due to the intriguing physics and its importance in technological applications [1]. Exchange anisotropy appears in hybrid ferromagnetic–antiferromagnetic (FM/AFM) systems and manifests itself in the form of a shift of the magnetization hysteresis loop. The presence of uncompensated surface spins also leads to exchange bias anisotropy in the AFM nanostructured materials such as Co_3O_4 [2] and NiO [3]. Recently, the exchange bias effect has been observed in ABO_3 type AFM perovskite, such as $BiFeO_3$ [4].

Single phase $BiFeO_3$ (BFO) is the most promising multiferroic material because of its high ferroelectric Curie (T_C ~ 1103K) and Neel (T_N ~ 643K) temperatures [5,6]. Owing to its high T_C and T_N ordering temperatures, this material is expected to find potential applications in spintronics, data storage and electromagnetic devices [6-9]. It has G-type antiferromagnetic ordering with a spin cycloid with period of approximately 62 nm [10,11]. This spiral spin structure limits the observation of ferromagnetism in BFO. The limiting observation of ferromagnetism can be mitigate through the suppression of the spiral spin cycloid structure by reducing its size below 62 nm or by chemical substitution of Bi^{3+} or Fe^{3+} sites by suitable ions of comparable ionic sizes [12,13]. Recently, many authors have carried out rare-earth ions (R^{3+}) doping at Bi^{3+} sites to suppress the spin cycloid structure and enhance the magnetization in BFO [13,14]. In this study, we report the structural transformation and observation of exchange bias properties in one dimensional Gd-doped BFO nanowires (NWs). We provide an interpretation of the temperature dependence of exchange bias and coercivity, based on the uncoupled surface spins.

2. Results

Multiferroic one-dimensional single crystalline $Bi_{1-x}Gd_xFeO_3$ ($0 \leq x \geq 0.10$) nanowires of 50-60 nm diameters have been synthesized by hydrothermal technique. Addition of Gd^{3+} ions into the BFO NWs results in rhombohedral (*R3c*) to orthorhombic (*Pn2₁a*) phase transition and alters their magnetic properties. The improvement in the multiferroic properties could be due to the spin canted Dzyaloshinskii–Moriya (DM) interaction that were manifested by the suppression of cycloidal spin structure, since the sizes of the NWs are less than 62 nm. A distinct exchange bias phenomenon is also observed, which can be attributed to the exchange interaction at interface of AFM core–FM shell like structure.

3. Discussion

XRD pattern obtained for $Bi_{1-x}Gd_xFeO_3$ (x = 0) confirmed that the compound is single phase and possesses the rhombohedral lattice type with *R3c* space group and $Bi_{1-x}Gd_xFeO_3$ (x = 0.10) revealed an orthorhombic lattice type structure with P$n2_1a$ space group. The TEM images show that the particles have NWs shapes with diameter about 50–60 nm and a length from hundreds of nm to several microns. The enhancement in magnetic property of $Bi_{1-x}Gd_xFeO_3$ (x = 0.10) NWs can be attributed to the *R3c* to orthorhombic *Pn21a* structural transformation, which might cause a tilting of FeO_6 octahedrons due to the canting of Fe–O–Fe bond angles. Moreover, oxygen deficiency could also increase the magnetization by introducing Fe^{2+} through the double exchange mechanism across the Fe^{3+}–O^{2-}–Fe^{2+}, but the presence of Fe^{2+} rules out by the X-ray photoelectron spectroscopy measurements. The exchange coupling interactions between the AFM core and FM-like shell of the particles leads the exchange bias phenomenon.

4. Conclusions

$Bi_{1-x}Gd_xFeO_3$ NWs with rhombohedral (x = 0) and orthorhombic structure (x = 0.10) were successfully synthesized through a hydrothermal method. The decrease in intensity and broadening of Raman modes further confirms the structural changes. In addition to the antiferromagnetic behavior, the magnetization curves of the BFO nanowires also present a ferromagnetic response at 300 and 5 K. The $Bi_{1-x}Gd_xFeO_3$ (x = 0.10) nanowires exhibited significantly difference in exchange bias fields compared to BFO nanowires. This behavior is associated to the substitution induced suppression of cycloidal spins and AFM-core/FM-shell like structure in BFO. The existence of exchange bias makes BFO nanowires a potential candidate for spintronics and memory based devices.

5. References

[1] J. Nogues, J. Sort, V. Langlais, V. Skumryev, S. Surinach, J.S. Munoz, Phys. Rep. 422, 65 (2005).

[2] E. L. Salabas, A. Rumplecker, F. Kleitz, F. Radu, and F. Schuth, Nano Lett. 6, 2977 (2006).

[3] R. H. Kodama, S. A. Makhlouf, and A. E. Berkowitz, Phys. Rev. Lett. 79, 1393 (1997).

[4] S. K. Srivastav, N. S. Gajbhiye, and A. Banerjee, J. Appl. Phys. 113, 203917 (2013).

[5] S. V. Kiselev, R. P. Ozerov, and G. S. Zhdanov, *So*V. *Phys. Dokl 7*, 742 (1963).

[6] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, Phys. Rev. B. 76, 024116 (2007).

[7] H. Schmid, Ferroelectrics 162, 19 (1994).

[8] N. A. Hill, J. Phys. Chem. B, 104, 6694 (2000).

[9] J. F. Scott, J. Mater. Chem. 22, 4567 (2012).

[10] I. Sosnowska, T. P. Neumaier, and E. Steichele, J. Phys. C: Solid State Phys. 15, 4835 (1982).

[11] D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, Phys. Rev. B 76, 024116 (2007).

[12] D. C. Arnold, IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 62, 62 (2015).

[13] G. Catalan, and J. F. Scott, Adv. Mater. 21, 2463 (2009).

[14] P. Suresh, P. D. Babu, and S. Srinath, J. Appl. Phys. 115, 17D905 (2014).