Research Article

Rare Earth-Doped BiFeO$_3$ Thin Films: Relationship between Structural and Magnetic Properties

Ngo Thu Huong,[1,2] Seunghun Lee,[3] Timur Sh. Atabaev,[1] Makio Kurisu,[4] and Nguyen Hoa Hong[1]

[1]*Nanomagnetism Laboratory, Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea*
[2]*Faculty of Physics, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam*
[3]*Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA*
[4]*Department of Physics, Graduate School of Science and Engineering, Ehime University, Matsuyama 790-8577, Japan*

Correspondence should be addressed to Nguyen Hoa Hong; nguyenhong@snu.ac.kr

Rare Earth- (RE-) doped BiFeO$_3$ (BFO) thin films were grown on LaAlO$_3$ substrates by using pulsed laser deposition technique. All of BFO films doped with 10% of RE show a single phase of rhombohedral structure. The saturated magnetization in the Ho- and Sm-doped films is much larger than those reported in literature and was observed at a quite low field as of 0.2 T. As for Pr- and Nd-doped BFO films, Fe^{2+} amount is not dominant; thus, ferromagnetism is not favored. As the RE concentration goes up to 20%, all compounds have drastically gone through a structural transition. The RE-doped BFO films have changed from rhombohedral to either pure orthorhombic phase (for Ho, Sm), or a mixed phase of orthorhombic and tetragonal (for Pr, Nd), or pure tetragonal (for Eu). We observed magnetic properties of RE-doped BFO films have significantly changed. While 20% Ho/Sm-doped BFO films have ferromagnetism degraded in comparison with the 10% doping case, the 20% Pr/Nd-doped BFO thin films, whose structure is a mixed phase, have magnetic ordering improved due to the fact that the Fe^{2+} amount has become greater. It seems that one can control the magnetic properties of BFO films by using appropriate RE dopants and concentrations.

1. Introduction

BiFeO$_3$ (BFO) is a promising multiferroic material due to its high ferroelectric and antiferromagnetic ordering temperatures. Generally, BiFeO$_3$ has G-type antiferromagnetic due to the local spin ordering of Fe^{3+} that basically forms a cycloidal spiral spin structure. In order to make BFO be room temperature ferromagnetic to be used in industrial applications, people have tried to suppress the spiral magnetic ordering by applying a very high magnetic field, or making them nanostructured, or by replacing Bi^{3+} or Fe^{3+} by other ions of comparable ionic sizes [1, 2]. Dimension reduction is likely to be a good way to improve the magnetization in BFO [3, 4]. Some groups have reported about the increase of magnetization in the bulk, thin films, and nanoparticles of BFO, by substituting either on the Bi-site by trivalent rare earth and divalent ions or on the Fe-site by transition metal ions [5, 6]. Some groups had showed that the magnetic moment of the nanoparticles could be increased three times by substituting Bi by Sr, or Ho. However, the reported saturated magnetization is found only at very high fields as of 5 T [2] and 6 T [1], respectively.

Our study focuses on tailoring the magnetic properties of BiFeO$_3$ by choosing the appropriate RE ion for substitution and selecting the appropriate concentration, in order to obtain the largest magnetization possible at room temperature, at relatively low fields. Understanding the structure dependence of magnetic properties of RE-doped BFO films is of utmost importance in order to tune the magnetism of this type of materials to match up the requirements of applications.

2. Experiment

RE$_x$Bi$_{1-x}$FeO$_3$ ceramic targets (where RE = Ho, Sm, Pr, Nd, and Eu; x = 0, 0.1, and 0.2) were prepared by a sol-gel

Table 1: List of structural phases, lattice parameters, and $Fe^{2+}:Fe^{3+}$ ratio for $RE_xBi_{1-x}FeO_3$ films (RE = Ho, Sm, Eu, Pr, and Nd; $x = 0.1$ and 0.2).

Compound		Structure	Lattice parameters	$Fe^{2+}:Fe^{3+}$
$Pr_xBi_{1-x}FeO_3$	$x = 0.1$	Rhombohedral	3.933 Å	40 : 60
	$x = 0.2$	Phase 1: orthorhombic	$a = 4.9817$ Å $b = 5.5108$ Å $c = 7.1725$ Å	51.8 : 48.2
		Phase 2: tetragonal	$a = b = 4.622$ Å $c = 6.5936$ Å	
$Nd_xBi_{1-x}FeO_3$	$x = 0.1$	Rhombohedral	3.9329 Å	40 : 60
	$x = 0.2$	Phase 1: orthorhombic	$a = 4.7412$ Å $b = 5.1102$ Å $c = 7.7901$ Å	48.5 : 51.5
		Phase 2: tetragonal	$a = b = 4.4879$ Å $c = 6.5117$ Å	
$Ho_xBi_{1-x}FeO_3$	$x = 0.1$	Rhombohedral	3.925 Å	50 : 50
	$x = 0.2$	Orthorhombic	$a = 4.9761$ Å $b = 5.6361$ Å $c = 8.6088$ Å	45.6 : 54.4
$Sm_xBi_{1-x}FeO_3$	$x = 0.1$	Rhombohedral	3.925 Å	50 : 50
	$x = 0.2$	Orthorhombic	$a = 5.96573$ Å $b = 5.17858$ Å $c = 2.85499$ Å	43.7 : 56.3
$Eu_xBi_{1-x}FeO_3$	$x = 0.1$	Rhombohedral	4.5875 Å	48.6 : 51.4
	$x = 0.2$	Tetragonal	$a = b = 4.6314$ Å $c = 6.5968$ Å	48.7 : 51.3

method. Rare earth- (RE-) doped $BiFeO_3$ (RBFO) thin films have been fabricated by pulsed laser deposition (PLD) technique (excimer KrF laser with $\lambda = 248$ nm; the repetition rate was 13 Hz and the energy density was 2.1 J/cm^2), with typical thicknesses as of 200 nm. All the films were grown on (001) $LaAlO_3$ (LAO) substrates. During deposition, the substrate temperature was kept at 700°C and the oxygen partial pressure (P_{O_2}) was 1.4×10^{-3} Torr. After deposition, the sample was kept in the chamber at 500°C with the same oxygen partial pressure as during deposition for 30 min and then finally cooled down slowly to room temperature.

The structural analysis was done by high resolution X-ray diffraction (HRXRD) with Cu K_α radiation. The magnetic measurements were performed by a Quantum Design Superconducting Quantum Interference Device (SQUID) system under magnetic field (H) from 0 up to 0.5 T under a range of temperatures (T) from 350 K down to 5 K.

The surface chemistry and composition of RE-doped BFO thin films were characterized by X-ray photoelectron spectroscopy (XPS, KRATOS, and AXIS-HSi). XPS measurements were performed with an Mg/Al X-ray source. The energy calibrations were made against the C 1s peak and the Shirley background subtraction was used.

3. Results and Discussion

Concerning structure, for the case of 10% of RE substituted for Bi in BFO, there is no significant change in comparison to the pristine $BiFeO_3$ [7]. Our laser ablated $RE_{0.1}Bi_{0.9}O_3$ films

are single phase rhombohedral $R3c$. Doping with different RE elements only causes some shift of the BFO peak positions, indicating some change in lattice parameters. The out-of-plane parameters are 3.925, 3.925, 3.9329, 3.933, and 4.585 Å for Sm, Ho, Nd, Pr, and Eu doping, respectively. One can notice here that the Eu doping distorts the structure the most (see details in Table 1), if we compare with parameters of the undoped $BiFeO_3$ [8].

When the RE doping concentration increases up to 20%, a structural transition has occurred. When doping Ho and Sm up to 20%, the structure has become single phase orthorhombic, while for Pr and Nd, it has turned to be a mixture of orthorhombic and tetragonal phases. For Eu doping case, it is single phase tetragonal. A representative feature of X-ray patterns for RE-doped BFO films is shown in Figure 1. In order to make it easier to have an overall picture, we list the structure types as well as parameters for all of $RE_xFe_{1-x}O_3$ thin films in Table 1. It is known that changing dopant concentration can lead to a structural transition, as reported in [5, 6, 9]. Normally for concentration of RE greater than 0.2, the orthorhombic phase is likely favored [5, 9, 10].

Magnetization versus magnetic field taken at 300 K for $RE_{0.1}Bi_{0.9}O_3$ film was reported in [7]. Our new result for Eu-doped BFO films (shown in Figure 2) reveals a strong ferromagnetic behavior that is quite similar to those of Sm-doped and Ho-doped BFO films. Previously, some ferromagnetic ordering in Ho-doped BFO was reported, however, with a much smaller magnitude, and M_s was obtained at much larger field (as of 6 T) [1], while ours has a larger M_s, but
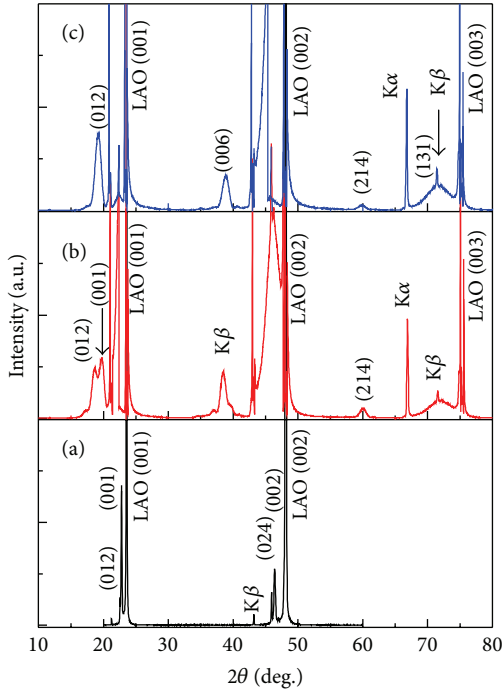
FIGURE 1: X-ray diffraction patterns for 200 nm-thick films grown on LaAlO$_3$ substrates of (a) Nd$_{0.1}$Bi$_{0.9}$FeO$_3$, (b) Nd$_{0.2}$Bi$_{0.8}$FeO$_3$, and (c) Eu$_{0.2}$Bi$_{0.9}$FeO$_3$.
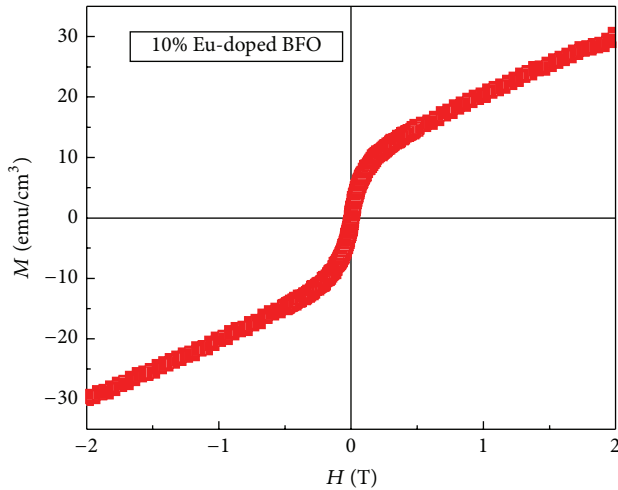

FIGURE 2: Magnetization versus magnetic field taken at 300 K (field applied parallel to the film plane) for 200 nm-thick films of Eu$_{0.1}$Bi$_{0.9}$FeO$_3$.

at a much lower field (as of 0.2 T), as seen in Figure 3(a). While other groups reported paramagnetic behavior for Eu-doped BFO ceramics [10], as seen in Figure 2, our Eu-doped BFO film is room temperature ferromagnetic at 0.2 T. This should be quite advantageous for applications. Comparing to Ho-, Sm-, and Eu-doped BFO films, then the Pr- and Nd-doped BFO films show much smaller magnetic moments. As seen in Figure 3(b), the typical M-H curves of Pr-doped BFO (10%) taken at room temperature are almost linear, showing

a paramagnetic behavior. In Figures 3(a) and 3(b), one can also see the obvious difference in magnetic properties for samples of 10% and 20% doping of RE. As for Ho, when doping 10%, because the Fe^{2+} : Fe^{3+} ratio is 50% : 50% (see Table 1), the ferromagnetic phase is more favored. When doping 20% of Ho, the Fe^{2+} amount is decreased (45.6%, shown in Table 1); then, the ferromagnetic phase is a bit degraded. One can see from Figure 3(a) that the M-H curve of the Ho$_{0.2}$Bi$_{0.8}$FeO$_3$ film shows that it has a different slope in comparison with that of the Ho$_{0.1}$Bi$_{0.9}$FeO$_3$ film. A very similar feature is found for Sm and Eu doping cases. This remark is consistent with our comments earlier about structural transition. Changing from rhombohedral to orthorhombic phases would be the main reason for the difference in observed magnetic behaviors. This remark is in accordance with previous reports about RE-doped BFO ceramics, or powders [5, 9].

As mentioned earlier, as for doping Pr and Nd case, when the concentration is up to 20%, the structure is a mixed phase of orthorhombic and tetragonal. Then, as a consequence, the samples have changed from paramagnetic to be a mixture of paramagnetic and ferromagnetic phases (data for Pr case is shown in Figure 3(b)). The inset of Figure 3(b) shows a clear hysteresis loop confirming the existence of the ferromagnetic phase. However, from the shape of the M-H curve, one can see that it is accumulated by two phases, paramagnetic and ferromagnetic. Even though the 20% Nd-doped BFO film has a much weaker magnetic moment (see Figure 3(c)), the behavior is quite similar to the Pr doping case. One can see from Table 1 that, in Pr (then Nd) case, when doping 10%, the Fe^{2+} amount was less than 50%, so that ferromagnetic ordering was not favored. However, when doping up to 20%, then Fe^{2+} has become 51.8% for Pr doping case and 48.5% for Nd doping case. Thus, in the Pr case, it helps to improve the ferromagnetism, while for Nd doping, it also made Fe^{3+} less dominant.

An example of scan of the Fe 2p line from XPS data for RE$_{0.2}$Bi$_{0.8}$FeO$_3$ films is shown in Figure 4. One can see that the peak of Fe 2p could be observed at 711 eV for Fe^{3+} and at 709.5 eV for Fe^{2+}. From the shape of the peaks, it is shown that both Fe^{2+} and Fe^{3+} exist in all doping cases (Ho, Sm, Nd, Pr, and Eu). The oxidation states of Fe in our films are listed in Table 1. One can see that, for the 10% doping of Ho and Sm, Fe^{2+} : Fe^{3+} ratio is about 50% : 50%; for Eu doping, it is similar; however, it is only about 40% : 60% for the 10% doping of Pr and Nd (refer also to [7]). This is in agreement with a previous report on BFO films made by sol-gel method [11]. The coexistence of Fe^{2+} and Fe^{3+} is supposed to be in favor of the ferromagnetic ordering in BFO films [11, 12]. When the amount of Fe^{3+} is more favored, the ferromagnetism gets weaker due to the fact that the Fe^{3+}-Fe^{3+} interaction is in favor of antiferromagnetic ordering [11]. This explains why, from the corresponding SQUID data shown in Figures 3(b) and 3(c) for the 10% doping case, we see that the ferromagnetic phase is not favored in Pr- and Nd-doped BFO films.

When RE concentration is 20%, the Fe^{2+} : Fe^{3+} ratio has changed as a result of structural transition. It is obvious from Table 1 that, for Pr- and Nd-doped BFO, there is
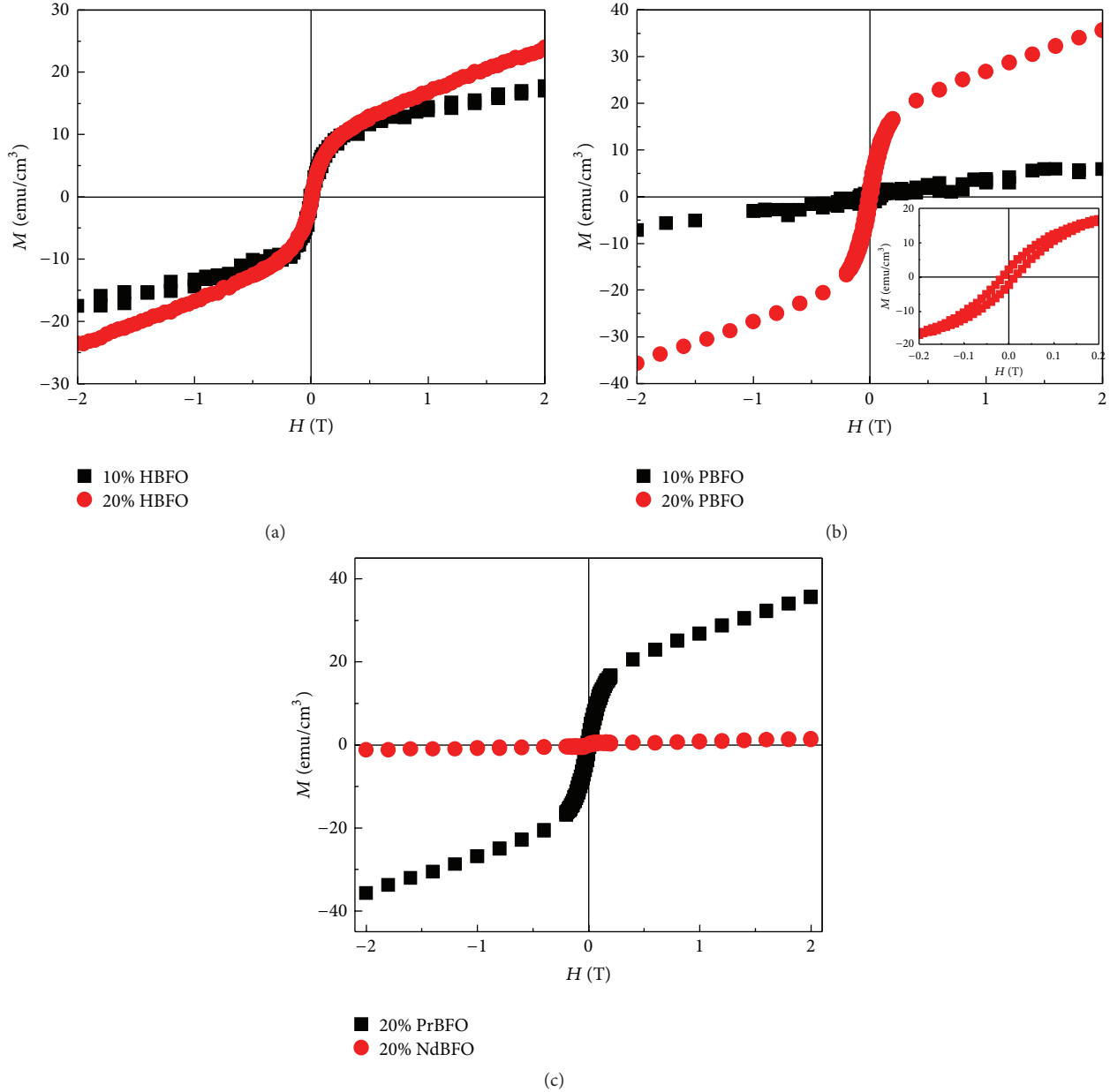
(a)

(b)

(c)

FIGURE 3: Magnetization versus magnetic field taken at $300\,K$ (field applied parallel to the film plane) for $200\,nm$-thick films of (a) $Ho_{0.1}Bi_{0.9}FeO_3$ and $Ho_{0.2}Bi_{0.8}FeO_3$, (b) $Pr_{0.1}Bi_{0.9}FeO_3$ and $Pr_{0.2}Bi_{0.8}FeO_3$, and (c) $Pr_{0.2}Bi_{0.8}FeO_3$ and $Nd_{0.2}Bi_{0.8}FeO_3$. The inset in (b) shows the zoom of M-H curve of $Pr_{0.2}Bi_{0.8}FeO_3$ film to see the hysteresis loop.

a significant increase of Fe^{2+} amount, leading to a favor of the ferromagnetic ordering. On the other hand, as for Ho, Sm, and Eu doping cases, Fe^{2+} seems to be decreased, relating to the weakening of ferromagnetic phase. It is obvious that once the structure has gone through a transition, it changes the $Fe^{2+}:Fe^{3+}$ ratio, and as a consequence, the magnetic properties have changed. It appears that one can use all these factors to completely manipulate the magnetic properties of the BFO system. Our experimental findings were further completed by performing density functional theory calculations to explore the effect of RE doping in BFO for the considered three phases. Details could be seen in [13].

4. Conclusion

All the $RE_{0.1}Bi_{0.9}FeO_3$ films show a single phase of rhombohedral structure. The saturated magnetization for Ho-, Sm-, and Eu-doped BFO films is much larger than those reported elsewhere and was observed at a much lower field as of $0.2\,T$. The observed ferromagnetism in our RE-doped BFO films was likely due to the coexistence of Fe^{2+} and Fe^{3+}. When the RE concentration is increased up to 20%, there is a big change in structure: while Ho-, Sm-, and Eu-doped BFO films have become orthorhombic (and as a result, the Fe^{2+} amount is reduced), the Pr- and Nd-doped BFO films

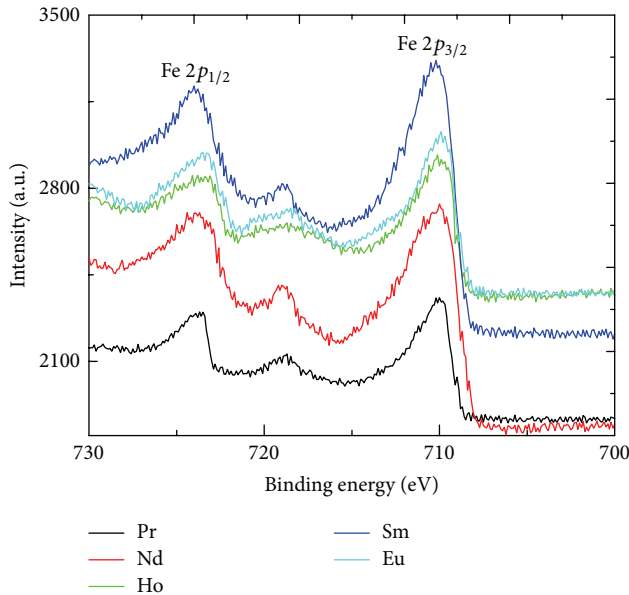Figure 4: XPS spectra of the Fe ions for the 200 nm-thick $RE_{0.2}Bi_{0.8}FeO_3$ films (where RE = Sm, Ho, Pr, Nd, and Eu).

have turned to be a mixture of orthorhombic and tetragonal phases, leading to Fe^{2+} amount increased, thus, favoring the ferromagnetic phase. Our results show that there is a strong relationship between structural and magnetic properties in RE-doped BFO films. It is found that, by choosing correctly the type and concentration of dopant, one can tailor the magnetism of $BiFeO_3$ films with expectation to satisfy the needs of industrial applications. It should be important to guide the materials search.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
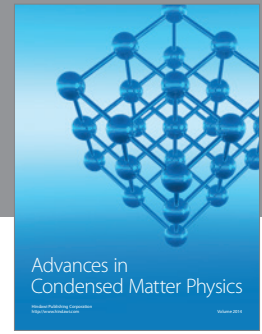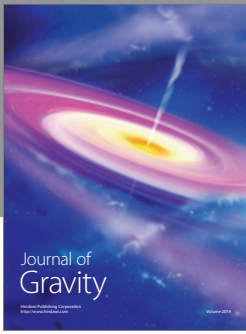
Acknowledgments

References

[1] P. Thakuria and P. A. Joy, "High room temperature ferromagnetic moment of Ho substituted nanocrystalline $BiFeO_3$," *Applied Physics Letters*, vol. 97, no. 16, Article ID 162504, 2010.

[2] T. Hussain, S. A. Siddiquia, S. Atiq, and M. S. Awan, "Induced modifications in the properties of Sr doped $BiFeO_3$ multiferroics," *Progress in Natural Science: Materials International*, vol. 23, no. 5, pp. 487–492, 2013.

[3] J. Wang, J. B. Neaton, H. Zheng et al., "Epitaxial $BiFeO_3$ multiferroic thin film heterostructures," *Science*, vol. 299, no. 5613, pp. 1719–1722, 2003.

[4] A. T. Raghavender, N. H. Hong, C. Park, M.-H. Jung, K. J. Lee, and D. Lee, "Thickness dependent magnetic properties of $BiFeO_3$ thin films prepared by pulsed laser deposition," *Materials Letters*, vol. 65, no. 17-18, pp. 2786–2788, 2011.

[5] Z. C. Cheng, A. H. Li, X. L. Wang et al., "Structure, ferroelectric properties, and magnetic properties of the La-doped bismuth ferrite," *Journal of Applied Physics*, vol. 103, Article ID 07E507, 2008.

[6] V. V. Lazenka, G. Zhang, J. Vanacken, I. I. Makoeced, A. F. Ravinski, and V. V. Moshchalkov, "Structural transformation and magnetoelectric behaviour in $Bi_{1-x}Gd_xFeO_3$ multiferroics," *Journal of Physics D: Applied Physics*, vol. 45, no. 12, Article ID 125002, 2012.

[7] T.-Y. Kim, N. H. Hong, T. Sugawara, A. T. Raghavender, and M. Kurisu, "Room temperature ferromagnetism with large magnetic moment at low field in rare-earth-doped $BiFeO_3$ thin films," *Journal of Physics: Condensed Matter*, vol. 25, no. 20, Article ID 206003, 2013.

[8] J. G. Speight, Ed., *Lange's Handbook of Chemistry*, McGraw-Hill, 16th edition, 2005.

[9] S. Pattanayak, R. N. P. Choudhary, and P. R. Das, "Effect of Sm-substitution on structural, electrical and magnetic properties of $BiFeO_3$," *Electronic Materials Letters*, vol. 10, no. 1, pp. 165–172, 2014.

[10] X. Zhang, Y. Sui, X. Wang, Y. Wang, and Z. Wang, "Effect of Eu substitution on the crystal structure and multiferroic properties of $BiFeO_3$," *Journal of Alloys & Compounds*, vol. 507, no. 1, pp. 157–161, 2010.

[11] Y. Wang, Q. H. Jiang, H. C. He, and C. W. Nan, "Multiferroic $BiFeO_3$ thin films prepared via a simple sol-gel method," *Applied Physics Letters*, vol. 88, no. 14, article 142503, 2006.

[12] T. Schedel-Niedrig, W. Weiss, and R. Schlögl, "Electronic structure of ultrathin ordered iron oxide films grown onto Pt(111)," *Physical Review B*, vol. 52, no. 24, pp. 17449–17460, 1995.

[13] N. H. Hong, N. T. Huong, T.-Y. Kim, S. Goumri-Said, and M. B. Kanoun, "Tuning magnetic properties of $BiFeO_3$ thin films by controlling rare-earth doping: experimental and first-principles studies," *The Journal of Physical Chemistry C*, vol. 119, no. 25, pp. 14351–14357, 2015.