Size Dependent Magnetic and Optical Properties of Mn Doped Bi$_{0.9}$Ho$_{0.1}$FeO$_3$ Nanoparticles

Fabia Farlin Athena$^1$, Tilottoma Saha$^1$, Md Rafiqul Islam$^1$, M. A. Matin$^2$ and Ahmed Sharif$^1$

$^1$Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh
$^2$Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Abstract. In this work, Bi$_{0.9}$Ho$_{0.1}$Fe$_{1-x}$MnxO$_3$ (x=0.0, 0.05, 0.10, 0.15) nanoparticles have been successfully synthesized by sol–gel technique and subsequent annealing process. The variation of Mn doping in Bi$_{0.9}$Ho$_{0.1}$FeO$_3$ (BHFO) on the properties such as morphological, structural, magnetic, and optical have been investigated in this study. X-ray diffraction (XRD) patterns demonstrated that Mn substitution in BHFO led to a structural transition from rhombohedral (R3c) to orthorhombic (Pn21a) phase. The field emission scanning electron microscope (FESEM) showed that Mn doping decreased particle size and consequently higher percentages of Mn resulted in agglomeration of particles severely. In this case particle sizes reduced from 60 nm to 30 nm. For Mn doping up to 5% in BHFO nanoparticles, the saturation magnetization (Ms) was enhanced, implying suppression of space modulated spin structure by structural transition. However, for a further increase of doping up to 15%, the Ms was started to decrease again. UV–Visible absorption spectra revealed that Mn substitution in BHFO led to strong reduction of band gap energy significantly. Band gap decreased from 2.9 to 2.38 eV on Mn doping, which allows the absorption of light extended to visible range.

Keywords: Nano-particles, X-ray diffraction, Orthorhombic, Magnetization.

1. Introduction

Perovskite based bismuth ferrite BiFeO$_3$ (BFO), is one of the most promising multiferroic materials and has received special attention in recent years because of its simultaneous ferro-electricity and antiferromagnetism above room temperature ($T_c$=1102K and $T_n$=643K) [1-3]. The limitation of miniaturization and speed which is being faced in conventional devices can be solved by its benchmark properties. These materials with their multi properties can successfully terminate the “Si Age” with next generation miniature high speed devices. For next generation devices including nonvolatile memories, spintronics, high density microactuators and piezoelectric sensors etc. these outstanding properties have aroused superior candidate [4,5]. However, it is very difficult to observe the ferromagnetic loop of a bulk BiFeO$_3$ sample at room temperature due to its low spiral spin modulation which is caused by defects and nonstoichiometry in the bulk BiFeO$_3$ sample. Hence, it is essential to
improve the ferromagnetic properties of BiFeO$_3$ without much disturbing its ferroelectric properties before its actual use in device application. The weak magnetization is attributed to the superimposition of a spiral spin structure on BFO antiferromagnetic order. In this spiral spin structure, the antiferromagnetic axis rotates through the crystal with an incommensurate long wavelength period of 62nm [6], which cancel the macroscopic magnetization and also inhibit the observation of the linear magnetic effect in bulk BiFeO$_3$.

To overcome the problems of BFO many techniques have been followed (eg. doping). A-site substitution by lanthanide ions (Gd, Sm, La, Dy, Ho, Sm) is known to be an effect way to overcome these obstacles [7]. These lanthanide ion substitutions would effectively suppress the formation of impure phases and oxygen vacancies. Suppression of spiral modulated spin structure occurred by substitution due to different ion radii between lanthanide and Bi$^{3+}$ ion. Kang et al. reported Ho$^{3+}$ substitution for Bi site is an effective way to increase the magnetization. Transitional metal doped at Fe site are thought to be an effective way to improve the ferromagnetic properties at room temperature. BFO may find application as photo catalytic material due to its small bandgap. It allows carrier excitation by laser pulse, hence enables the researcher to develop optoelectronic devices. Moreover, bandgap value of pure BFO can be tuned by substitution of heterovalent ion [8]. Therefore, it is widely expected that the strategies based on nanotechnology and aliovalent ion doping will have a great impact on their magnetic, optical properties as a result of the suppression of the helical order and quantum confinement effect [8].

2. Methodology

Modified pechini sol-gel method was used to synthesize 0, 5, 10, 15% Mn doped BHFO to make the co-doped bismuth ferrite nanoparticles using citric acid as the chelating agent. The reagents used in the present work were analytical grade bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), citric acid (C$_6$H$_8$O$_7$), ethylene glycol (C$_2$H$_6$O$_2$) and glacial acetic acid (CH$_3$COOH) (purity>99.98%). The final product was obtained by auto-combustion. Further the gel was dried at 120°C for 24 hrs. in a drier to obtain fluffy green xerogel. The xerogel samples were then ground into powders and annealed with 3°C/min at 500°C for 2 hrs. to get BiFeO$_3$ nanoparticles. Subsequently these samples were structurally characterized by XRD. Field emission scanning electron microscopy (FESEM) was used to determine surface texture and nanoparticles size. Magnetic property was measured using a vibrating sample magnetometer (VSM). Finally, the optical property was measured using a UV/Vis spectroscopy.

3. Results and Discussion

3.1 Structural and micro structural characteristics

Powder diffraction (PXRD) patterns of the samples BHFO, Bi$_{0.9}$Ho$_{0.1}$Fe$_{0.95}$Mn$_{0.05}$O$_3$ (BHFMO-5), Bi$_{0.9}$Ho$_{0.1}$Fe$_{0.85}$Mn$_{0.15}$O$_3$ (BHFMO-10), and Bi$_{0.9}$Ho$_{0.1}$Fe$_{0.85}$Mn$_{0.15}$O$_3$ (BHFMO-15) were recorded at room temperature and are shown in Figure 1(a) According to literature pure BFO structure possess rhombohedral (R3c) symmetry. Although observed patterns are slightly different but in agreement with the pattern of literature suggested BFO, so observed pattern confirms the peaks of doped BFO nanoparticle and shows polycrystalline behavior with good crystallinity.

According to the literature some impurity peaks are observed in pure BFO but in this XRD pattern impurity peaks are scarcely observed due to some reactions. In pure BFO:

\[
2\text{Bi}^{3+} + 3\text{O}_{2} \rightarrow \text{Bi}_2\text{O}_3 \quad (\text{evp}) + 2\text{V}_{\text{Bi}} + 3\text{V}_{\text{O}} \quad (1)
\]

\[
2\text{Fe}^{3+} + 2\text{O}_{2} \rightarrow 2\text{Fe}^{2+} + 0.5\text{O}_2 \quad (\text{gas}) + 2\text{V}_{\text{O}}^{-} \quad (2)
\]
When Bi$^{3+}$ is partially replaced by Ho$^{3+}$ which will suppress the Bi$^{3+}$ volatile because melting point of H$_3$O$_7$(2367°C) is much higher than Bi$_2$O$_3$(820°C). Vacancies become smaller amount for BHFO than BFO. When Mn is added then co-doping completely hinders the formation of impurity phase [9].

Figure 1(b), 1(c) shows magnified graph from 20(31-33$^\circ$) ranges for BHFO having slightly valley of dual peak which was merged later due to Mn substitution. This transition suggests a structural transformation from the rhombohedral structure (pure BFO) toward coexistence of tetragonal and orthorhombic symmetry structure. Due to slighter ionic radii difference between host ions (Bi$^{3+}$1.17Å and Fe$^{3+}$0.645Å) and dopant ions (Ho$^{3+}$1.015Å and Mn$^{2+}$0.58Å) [10], which makes it easier that Ho$^{3+}$ (or Mn$^{2+}$) enters the lattice to replace Bi$^{3+}$ (or Fe$^{3+}$) respectively. Structural transformation of nanoparticles can be explained using the Goldschmidt tolerance factor (t).

\[
t = \frac{(\langle r_A \rangle + r_O)}{(\sqrt{2} (\langle r_B \rangle + r_O))}
\]

where, $(r_A)$ and $(r_B)$ are the average ionic radii of A and B site cations, respectively; and $r_O$ is the ionic radius of oxygen. By substituting the dopants RA, and RB into the modified t is shown:

\[
t = \frac{(1-x)R_{Bi} + xR_{Ho} + R_O}{\sqrt{2} (0.95R_{Fe} + 0.05R_{Mn} + R_O)}
\]

Where, $R_{Bi}$, $R_{Ho}$, $R_{Fe}$, $R_{Mn}$, $R_O$ are 1.17, 1.015, 0.645, 0.58, 1.38 Å, respectively. Calculated t values of NP’s for BFO 0.8904, for BHFMO 0.8864 (Bi$_{0.9}$Ho$_{0.1}$Fe$_{0.95}$Mn$_{0.05}$O$_3$) [11]. The slight decrease of t proves the lattice distance of these planes gradually decreased leading to crystal distortion of the samples takes place. Further increase of Mn content causes more changes of Fe-O-Fe bond angle and Fe-O bond length so ratio of rhombohedral to orthorhombic (Pn21a phase) is changed [12].

Figure 2 shows the FESEM micrographs of Bi$_{0.9}$Ho$_{0.1}$F$_{1-x}$Mn$_x$O powders annealed at temperature 500°C for 2 hrs. Particle sizes are average 60, 45-50, 45, 30nm for $x = 0.0, 0.5, 0.10, 0.15$ respectively. Substitution of B-site Fe$^{3+}$(0.645 Å) with Mn leads to smaller particle size. Mn can present in Mn$^{2+}$ (0.83), Mn$^{3+}$ (0.645 Å), Mn$^{4+}$ (0.53 Å) ions which lead to a lattice distortion and hinder crystallite nucleation and thereby reduces particle size [13]. Grain size is also related to oxygen vacancies which is a source of Bi losing and the transformations of Fe$^{3+}$to Fe$^{2+}$. Mainly co-doping causes suppression of oxygen vacancies hence slower oxygen ion motion and slower grain growth rate. When 15% Mn was used then particle sizes have been reduced greatly to 30nm which has higher surface area and higher
energy, hence highly reactive [14] and the ultra-fine BFO nanocrystals due to high surface energy form neck by solid state diffusion and evaporation-condensation process which leads to agglomeration and particle growth [15]. Thus, severe agglomeration was observed.

![Figure 2: SEM micrographs of BiHo$_{0.1}$Fe$_{1-x}$Mn$_x$O$_3$ (x=0.00,0.05,0.10,0.15) samples (50,000x).]

3.2 Magnetic characteristics

The magnetization vs. applied field (M-H) measurements of the BHFO and BHFMO powders was carried out at 300K in order to investigate the magnetic behavior and M–H loops are presented in Figure 3. From the plotted graphs, it can be seen that magnetization value is higher than pure BFO from literature. According to literature BFO nanoparticles have weak ferromagnetic behavior because no spin canting is considered due to spin compensation into its two sublattices. However, here the SEM micrographs reveal that nanoparticles (NP’s) size decreased with doping. Enhancement of the magnetization of doped BFO occurred because of the uncompensated surface spins induced by the size effect of the NP’s. The magnetic parameters extracted from the magnetic hysteresis loops measured at 300K are presented in Table 1.

**Table 1:** Magnetic property analysis results.

| Sample   | Remnant magnetization, Mr(emu/gm) | Average Coercive Field, Hc(Oe) | Maximum Magnetization, Ms(emu/gm) |
|----------|-----------------------------------|---------------------------------|----------------------------------|
| BHFO     | 0.0898                            | 64.676                          | 1.08                             |
| BHFMO-5  | 0.0177                            | 12.476                          | 1.77                             |
| BHFMO-10 | 0.02277                           | 20.966                          | 1.06                             |
| BHFMO-15 | 0.0043                            | 115.305                         | 0.304                            |

BHFO exhibits a narrower hysteresis loop (Mr 0.089emu/g and Hc (64.6 Oe) in Figure 3, which reflects weak ferromagnetic behavior arising from canting of the antiferromagnetic sublattices. These features can be accounted due to the difference in ionic radius, (Ho$^{3+}$-0.901Å, Bi$^{3+}$-1.03Å) it is also expected that this distortion improves the magnetic properties[16]. Also, Ho causes increase magnetism by modifying exchange interaction due to decreasing of Fe-O-Fe bond angle that is the result from the distortion of lattice and destruction of spiral modulated spin structure (SMSS) due to tilting of FeO$_6$ octahedra or structural phase transition [16]. The substitution of non-magnetic...
Bi\textsuperscript{3+}([Xe]4f\textsuperscript{14}5d\textsuperscript{10}6s\textsuperscript{2}6p\textsuperscript{0}) ion by magnetic Ho\textsuperscript{3+}([Xe] 4f\textsuperscript{10}, theoretical magnetic moment 7.5µB) ion may be another reason of this increased Ms.

Among all, BHFMO-5 showed the maximum remnant magnetization and coercive field (Hc). There are many possible factors such as decrease in the average particle size as observed due to codoping. Destruction of spin arrangement has occurred due to structural transition, Mn\textsuperscript{3+}(0.46Å) is smaller than Fe\textsuperscript{3+}(0.645Å) hence structural transition is accelerated this change in bond angle and bond length hence tilting angle of FeO\textsubscript{6} octahedron and thereby suppress SMSS\textsuperscript{[17,18]}. By Dzyaloshinskye Moriya interaction in the orthorhombic phases the spin canting can originated which may introduce magnetization\textsuperscript{[19,20]}. In addition, Mn generally stays at multivalent (+2,+3and+4) states in BFO and the substitution of Fe\textsuperscript{3+}([Ar] 3d\textsuperscript{5},5µB) by Mn\textsuperscript{2+}([Ar] 3d\textsuperscript{5},5µB), Mn\textsuperscript{3+}([Ar] 3d\textsuperscript{6},4µB) and Mn\textsuperscript{4+} ([Ar] 3d\textsuperscript{3},3µB) may causes incomplete compensation of SMSS. Also, the redox coupling between Fe and Mn ions or may be due to incorporation Mn\textsuperscript{3+} (4.89 µB) at Fe site (5.92 µB) that develops local ferromagnetic spin structure \textsuperscript{[21,22]}. Increase of %Mn to higher level causes a decrease of saturation magnetization this may be due to thermal effects. Saturation magnetization is inversely proportional to coercivity as:

\[
H_c = \frac{\sigma-K}{M_s}
\]

Where, K=anisotropy constant, \(\sigma\) is constant which depends upon crystal structure and degree of alignment. The reason for the decrease in saturation magnetization for 10% Mn doping might be due to Fe\textsuperscript{2+} ion that act as inhibitor and weakens the super-exchange interaction existing between Fe\textsuperscript{3+}-O-Fe\textsuperscript{3+}[23]. Differences in coercive field values on either side of x-axis which signify the occurrence of both ferromagnetism and anti-ferromagnetism simultaneously and hence might result in unidirectional anisotropy shift. Also due to substitution of Mn\textsuperscript{3+}(4.89µB) on Fe\textsuperscript{3+}(5.92µB) site I increased and Ho content remain the same thus lower Bohr magnetron and increase of anisotropy constant nullify the effect of Ho as a result saturation magnetization value is decreased. Another reason is the Fe-O-Mn super exchanges is of antiferromagnetic nature and Ho Mn exchange interaction may compete with the ferromagnetic interaction resulting from co-doping and hence further reduced magnetization in BHMFO samples has been observed\textsuperscript{[12]}. 

![Figure 3: Comparison of magnetic moment of BHFO and after various % Mn doping where compositions are BiHo\textsubscript{0.1}Fe\textsubscript{1-x}MnxO\textsubscript{3} (x = 0.00, 0.05, 0.10, 0.15).](image-url)
3.3 Optical property analysis

3.3.1 Spectral analysis: Figure 4 shows absorbance vs. wavelength plot of BHFO and BHFMO samples derived from diffuse reflectance data. BHFO shows absorption peak at 430 nm. In addition of Mn, the absorbance of BHFO increases and change in peak position occurs for 5% Mn. As %Mn is increased to 10%, absorption peak of BHFO is gradually suppressed and absorption peak of Mn appears.

![Figure 4: UV-Vis (a) absorption (b) reflectance spectra of different percentage Mn doped BHFO.](image)

The Mn addition causes an increment of absorbance value. On the addition of Mn on BHFO, the absorption peak shifts towards right or higher wavelength position around 520 nm. Since visible light ranges from 400-700 nm, it can absorb visible light. Another peak occurs towards lower wavelength below 300 nm. UV light have wavelengths ranges from 200-400nm. So, the Mn and Ho doped structure can absorb visible as well as wave that pure BHFO alone can’t do. So, Mn and Ho codoping increases visible light response and narrower bandgap which has a great application as photocatalyst.

3.3.2 Band Gap Measurement: To determine $E_g$ (band gap energy), $[F(R)*h\nu]^2$ vs. $h\nu$ graph has been plotted for the synthesized powders. Here the intersection of the tangent line with $[F(R)*h\nu]^2=0$ represents the optical band gap energy, $E_g$. Here, $F(R)$ is given by Kubelka–Munk function:

$$F(R) = \frac{(1-R)^2}{2R}$$

Where, $R$=diffused reflectance value. This absorption can correspond to the electronic transition from the top of the valance band, which is mainly composed of O-2p hybridized with Bi-6s, to the bottom of the conduction band composed of Fe-3d. Figure 5 demonstrates that Ho single doping has bandgap of 2.9eV and for Mn doping percentages of 5%, 10% and 15% band gap values are 2.8, 2.47 and 2.4 eV respectively. This is due to reduced degree of hybridization associated with a stable electronic configuration (half occupation 4f10 5d0 6s0) of Ho3+ ion, in between Fe 3d and O 2p a unique energy level is formed and which causes this effective band gap of Ho doped BFO[24]. Cation doping changes the Fe-O and Fe-O-Fe bond angle which plays a critical role in modifying one-electron bandwidth (W) and resulting change in bandgap energy [25]. The empirical formula relating electron bandwidth with bond length and angle is:
\[ W \approx \frac{c o s \omega}{d_{Fe-O}} \] (7)

where, \( \omega = \frac{1}{2} [(\pi)-(Fe-O-Fe)] \) and \( d_{Fe-O} \) = Fe-O bond length. The band gap is related with \( W \) as follows: \( E_g = \Delta - W \). where \( \Delta \) is the charge-transfer energy [27,28].

\[ \text{Figure 5: } [F(R)h\nu]^2 \text{ vs. } h\nu \text{ plot for band gap calculation of BHFO and after various } \% \text{ Mn doping.} \]

As the Fe-O bond length of rhombohedral phase is larger than orthorhombic phase [28], Mn-doping decreases the Fe-O bond lengths hence increases orthorhombic phase, which results in an increase of the value of \( W \) and decrease of effective band gap energy. In addition, the 3d conduction band-edge (\( E_{cb} \)) of Mn\(^{4+}\)(\( E_{cb} = 5.83 \text{ eV} \)) is lower than Fe\(^{3+}\)(\( E_{cb} = 4.78 \text{ eV} \)) state [25] and brings the holes in the d band [26] which may reduce the effective energy gap between 3b conduction band and O2p valence band and resulting decrease in nanoparticles optical band gap.

4. Conclusion
The sol-gel method followed by thermal treatment has been used to prepare \( \text{Bi}_{0.9}\text{Ho}_{0.1}\text{Fe}_{1-x}\text{Mn}_{x}\text{O}_3(x=0, 0.05, 0.10, 0.15) \) NP’s system and their structural, magnetic and optical properties have been studied using standard experimental techniques. Studies of basic structural parameters using XRD reveals that all samples were crystallized perovskite form. Structural transition occurred toward orthorhombic and tetragonal biphasic form. Mn has smaller ionic radius than Fe, so decrease in bond length, bond angle and distortion of structure is confirmed by peak merging. Very small amount of \( \text{Bi}_2\text{FeO}_9 \) impurity phase is observed in BHFO. A highly dense SEM microstructure recorded on the sample has confirmed that NP’s size was decreased significantly therefore finally found to be around 30nm. Using VSM studies of magnetic property reveals that maximum magnetization \( M_s \) increased on 5\% Mn addition in BHFO, due to tilting of octahedral. However, increasing Mn\% to 15 \% causes a decrease of magnetization value due to anisotropy. Still all the samples showed greater than literature value of pure BiFeO\(_3\). The UV-vis exhibits that all samples has lower bandgap energy. Normally TiO\(_2\) based photo catalysts have a bandgap energy of 3.2eV while we have found values decreasing from 2.9 to
2.38eV. Also, from absorption spectra it is clear that photocatalytic activity under visible light, 48% of total solar energy, is prominent and TiO$_2$ based photocatalyst is only active for UV light, 4% of solar energy, is not very efficient. Therefore, this Mn doped BHFO can serve as a promising photocatalyst either for water splitted hydrogen generation or for degradation of organic pollutants.

5. Reference

[1] Charkrabarti K, Das K, Sarkar B and De S K 2011 Enhanced magnetic and dielectric properties of Eu and Co co-doped BiFeO$_3$ nanoparticles J APPL. Phy.110, 1035-5

[2] Ye W, Tan G Q, Dong G H, Ren H J, Xia A 2016 The effects of grain size on electrical properties and domain structure of BiFeO$_3$ thin films by sol–gel method. J Matter sci. Matter electronCeram.Int.41 (2015) 4668-4674

[3] Bai Y, Chen J, Zhao S, and Lu Q 2016 Magnetoelectric and magneto electric anisotropies of CoFe$_2$O$_4$/Bi$_2$Ti$_3$FeO$_{15}$ bilayer composite hetero structural films RSC Adv. 6(57), 52353–52359

[4] Raghavan C M, Kim J W and Kim S S 2014 Effects of Ho and Ti doping on structural and electrical properties of BiFeO$_3$ thin films J. Am. Ceram.soc, 97235-240

[5] Pradhan S K, Roul B K, Sahu D R 2012 Enhancement of ferromagnetism and multiferroicity in Ho doped Fe rich BiFeO$_3$ Solid State Commum.1521176-1180

[6] Chauhan S, Kumar M, Chhoker S, Katyal S C, Singh H, Jewariya M and Yadav K L 2012 Multiferroic, magnetoelectric and optical properties of Mn doped BiFeO$_3$ nanoparticles. Solid State Commum, pp152255-529

[7] Song G L, Song Y C, Su J, Song X H, Zhang N, Wang T X and Chang F G, 2017 Crystal structure refinement, ferroelectric and ferromagnetic properties of Ho modified BiFeO$_3$ multiferroic material. J. Alloys and Compound.503-509

[8] Chauhan S, Kumar M, and Katyal S C 2016 Band-gap tuning and magnetic properties of heterovalent ions (Ba, Sr and Ca) substituted BiFeO$_3$ nanoparticles AIP Conference Proceedings 1731, 130029

[9] Hongfeng, Guoqiang H, Li B C, Zhu Y, Yang J and Pradhan S K 2010 Effect of Ho, Mn co-doping on the structural, optical and ferroelectric properties of BiFeO$_3$ Journal of Physics and Chemistry of Solids 71 1557–156.

[10] Hasan M, Basith M A, Zubair M A, Hossain M S, Mahbub R, Hakim M A, and Islam M F, 2016 Saturation magnetization and band gaptuning in BiFeO$_3$ nanoparticles via co-substitution of Gd and Mn. Alloys Compd. 687, 701–706.

[11] Zhang Z, Wu P, Chen L and Wang J, 2010 Systematic variations in structural and electronic properties of BiFeO$_3$ by A-site substitution, Appl. Phys. Lett. 96 012905.

[12] Hasan M, Islam M F, Mahbub R, Hossain M S and Hakim M A, 2016 A soft chemical route to the synthesis of BiFeO$_3$ nanoparticles with enhanced magnetization, Mater. Res. 179e186.

[13] Hernandez B A, Chang K S, Fisher E R and Dorhout P K 2002 Solgel template synthesis and characterization of BaTiO$_3$ and PbTiO$_3$ nanotubes, Chem. Mater. 14, 480

[14] Lobo R, Moreira R L, Lebeugle D and Colson D 2007 Infrared phonon dynamics of a multiferroic BiFeO$_3$ single crystal Physics Review B, Vol. 76, pp. 172105.

[15] Kumar P, Shankhwar N, Srinivasan A and Kar M 2015 Oxygen octahedra distortion induced structural and magnetic phase transitions in Bi$_{1-x}$Ca$_x$Fe$_1$Mn$_x$O$_3$ ceramics J. Appl. Phys. 117 194103

[16] Kumar P and Kar M 2014 Tuning of net magnetic moment in BiFeO$_3$ multiferroics by co-substitution of Nd and Mn, Phys. B Condens. Matter 44890e95.
[17] Khomchenko V A, Pereira L C J and Paix~ao J A 2011 Substitution-driven structural and magnetic phase transitions in Bi0.86(La, Sm) 0.14FeO3 system, J. Phys. D Appl. Phys. 44185406.

[18] Sergienko I A and Dagotto E 2006 Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites, Phys. Rev. B 7.

[19] Majetich S A, Artman J O, and Tanaka C 1994 Calculation of magnetic moments in Ho2C3 nanocrystal J. Appl. Phys. 76, 10

[20] Kittel C, 1967 Introduction to solid state physics American Journal of Physics, Vol.35, pp547-548

[21] Fiebig M 2005 Revival of the magnetoelectric effect, Journal of Physics D: Applied Physics, Vol 38, pp. R123.

[22] Gao N, Chen W, Zhang R, Zhang J, Wu Z, Mao W, Yang J, Li X A and Huang W, 2016 First principles investigation on the electronic, magnetic and optical properties of Bi0.8M0.2Fe0.9Co0.1O3 Com. Theor. Chem. 108436e42.

[23] Zhang Z, Wu P, Chen L and Wang J, 2010 Systematic variations in structural and electronic properties of BiFeO3 by A-site substitution Appl. Phys. Lett. 96 012905.

[24] Xu Y, and Schoonen M A A, 2000 The absolute energy positions of conduction and valence bands of selected semiconducting minerals Am. Mineral. 85 543556.

[25] Rodríguez-Carvajal J, Hennion M, Moussa F, Moudden A H, Pinsard L and Revcolevschi A 1998 Neutron-diffraction study of the Jahn-Teller transition in stoichiometric LaMnO3 Phys. Rev. B 57 R3189eR3192.

[26] Medarde M, Mesot J, Lacorre P, Rosenkranz S, Fischer P and Gobrecht K 1995 High pressure neutron-diffraction study of the metallization process in PrNiO3 Phys. Rev. B 52

[27] Radaelli P G, Iannone G, Marezio M, Hwang H Y, Cheong S W, Jorgensen J D and Argyriou D N 1997 Structural effects on the magnetic and transport properties of perovskite A1,A0,MnO3 (x½0.25, 0.30) Phys. Rev. B 56

[28] Tütüncü H M and Srivastava G P 2008 Electronic structure and lattice dynamical properties of different tetragonal phases of BiFeO3 Phys. Rev. B 78 235.

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