



Investigation of structural, magnetic and optical properties of rare earth substituted bismuth ferrite

T. Durga Rao ^a, T. Karthik ^{a, b}, Saket Asthana ^a,

^a Advanced Functional Materials Laboratory, Department of Physics, Indian Institute of Technology Hyderabad, Andhra Pradesh –502205, India

^b Department of Materials Science and Engineering, Indian Institute of Technology Hyderabad, Andhra Pradesh –502205, India

Journal of Rare Earths
Vol. 31 ; Issue 4 ; Pages 370-375 (2013)

[http://dx.doi.org/10.1016/S1002-0721\(12\)60288-9](http://dx.doi.org/10.1016/S1002-0721(12)60288-9)

This is author version post print archived in the official Institutional Repository of IIT-H
www.iith.ac.in

Investigation of Structural, magnetic and optical properties of rare earth substituted Bismuth Ferrite

T. Durga Rao^a, T. Karthik^{a, b}, Saket Asthana^a *

^a *Advanced Functional Materials Laboratory, Department of Physics,*

Indian Institute of Technology Hyderabad, Andhra Pradesh – 502205, India

^b *Department of Materials Science and Engineering, Indian Institute of Technology Hyderabad,
Andhra Pradesh – 502205, India*

* Author for Correspondence: asthanas@iith.ac.in

Abstract: Polycrystalline BiFeO₃ and Rare earth substituted Bi_{0.9}R_{0.1}FeO₃ (BRFO, R = Y, Ho and Er) compounds were prepared by rapid solid state sintering technique. Structural phase analysis indicates that all the compounds stabilized in rhombohedral structure (*R3c* space group) and a small orthorhombic phase fraction was observed in BRFO compounds. From the Raman spectra results, the changes in the phonon frequencies (*A₁*) and line widths suggest lattice distortion in the BRFO compounds as is evidenced in the XRD analysis. Compared to the linear variation of magnetization with magnetic field (*M-H*) shown by BFO, an obvious *M-H* loop was observed in BRFO compounds which could be due to the suppression of space modulated spin structure and explained on the basis of weak ferromagnetism and field induced spin reorientation. UV-Vis spectroscopy evidences a change in local FeO₆ environment due to shift in the ⁶A_{1g} → ⁴T_{2g} energy transition band. BRFO compounds with improved remnant magnetization and coercive field are applicable for magnetoelectric devices.

Key words: structural distortion, spin-reorientation, G-type antiferromagnet.

Introduction:

Materials which simultaneously exhibit more than one ferroic orders are called Multiferroics. These materials are not only interesting because of their ferroelectric and magnetic properties, but also due to the existence of coupling between the ferroics orders. In these materials, magnetization can be controlled with the application of electric field and vice versa. Existence of coupling of ferroelectric and (anti)ferromagnetic orders imparts a great value to these materials for device applications such as actuators, data storage and sensors [1-4]. In most of the single phase multiferroic materials, such as rare earth manganites [5, 6], have their magnetic / ferroelectric transition temperatures well below room temperature and their application is limited at room

temperature. Among all the multiferroics, BiFeO₃ is a unique material having its magnetic and ferroelectric transition temperatures well above room temperature. Its ferroelectric Curie temperature is 1103K and magnetic Neel temperature is 643K [7, 8]. In this compound, ferroelectricity is originated due to the relative displacement of cations resulting from the stereochemical activity of 6s² lone pair electrons of Bi³⁺-ions. Magnetic structure of BiFeO₃ is G-type antiferromagnetic. This G-type antiferromagnetic ordering is superimposed with the spiral spin structure leading to a zero net magnetization. Ferromagnetism can be induced by suppressing the space modulated spin structure (SMSS) [9, 10]. The SMSS can be suppressed by substitution of elements at A – site (Bi) or at B – site (Fe). Generally, rare earth elements (La, Nd, Eu, Dy, Gd, Ho, Y, etc.) or Alkaline earth elements (Ca, Ba, Sr, Pb, etc.) and transition metal elements (Sc, Cr, Mn, Co, etc.) will be substituted respectively at A – site and B – site [10-16]. With the partial substitution of elements at these sites, the crystal structure will be distorted due to the internal chemical pressure. This induced distortion helps in tailoring electric, magnetic and dielectric properties [13-16].

In this report, three elements Y, Ho and Er have been chosen to substitute at Bi-site of BiFeO₃. As these elements (in 3+ valence state) have their radii smaller than Bi³⁺, they can occupy Bi³⁺ positions and moreover their bond energies with O²⁻ are greater than that of Bi-O bond energy which may reduce oxygen vacancies during synthesis. In this present study, R substituted BiFeO₃ compounds were synthesized using Rapid solid state sintering technique which may minimize secondary phases and reduce oxygen vacancies [17-19]. In this technique, compounds are sintered at high temperatures in sufficiently small times. Since the melting temperature of Bi₂O₃ is 820°C, use of higher temperatures above 820°C leads to the formation of liquid phase. This liquid phase may accelerate the synthesis and minimize the secondary phases.

1. Experimental Details

BiFeO₃ (BFO) and Bi_{0.9}R_{0.1}FeO₃ (BRFO) [BHFO for R = Ho, BEFO for R = Er and BYFO for R = Y] polycrystalline compounds were synthesized by Rapid solid state sintering technique using the high purity Bi₂O₃, Fe₂O₃ and Ho₂O₃ (purity > 99.9%) as starting materials. These powders were mixed with their stoichiometric ratios and ground thoroughly for 6 hrs. The powders were made as pellets in the form of circular disc and sintered at 860°C for 300s in a tubular furnace and taken out immediately to room temperature. The sintered pellets were crushed into powders and used for characterizations. The Phase analysis of the compounds were examined by an X-ray diffractometer (Rigaku D/Max-2500) with Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$). Raman scattering spectra were measured at room temperature using a Laser Micro Raman spectrometer (Bruker, Senterra) with an excitation source of 785nm with power of 10mW. The magnetic properties of these compounds were measured using MPMS (Quantum design MPMS). Diffuse reflectance spectra (DRS) of the powders were recorded in the wavelength range from 200–900nm using (Shimadzu UV–3600) UV–Vis–NIR spectrophotometer having a wavelength accuracy of $\pm 1\text{nm}$ resolution.

2. Results and Discussion

XRD patterns of polycrystalline BFO and BRFO compounds shown in Fig. 1 depict that all the compounds crystallize in rhombohedral structure and the diffraction peaks are indexed with *R3c* space group. Along with the main phase BFO, a trace amount of secondary phases like Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ is observed which is unavoidable during the kinetics of formation of BFO [16]. In the 2θ range of 31 – 32°, partial overlap of doubly split peaks (104) and (110) of BFO is observed in the R – ion substituted BFO. This indicates that coexistence of small percentage of orthorhombic phase with the parent rhombohedral phase with R – ion substitution [20- 22]. Substitution of smaller radius R – ions at Bi positions will decrease the average A-site which can be accounted using tolerance factor *t*, defined as $t = (\langle r_A \rangle + r_O) / \sqrt{2}(r_B + r_O)$ where $\langle r_A \rangle$ is the average radius at A site and *r_B* and *r_O* are the radii of Fe³⁺ and O²⁻ respectively.

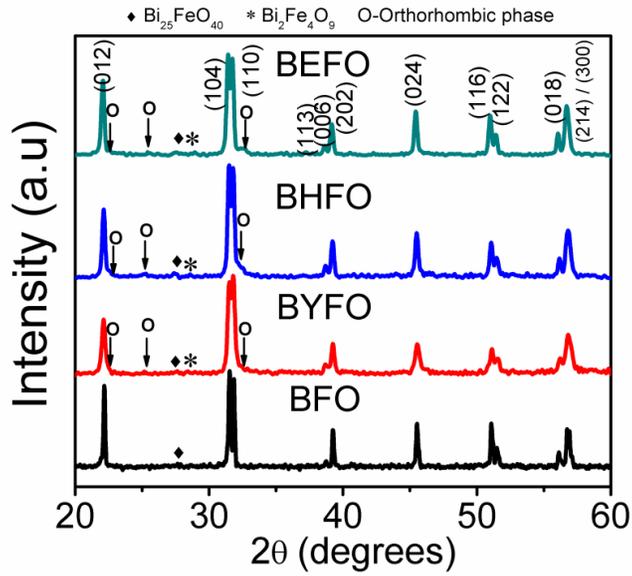


Fig.1. Room temperature powder X-ray diffraction patterns for BFO and BRFO (R = Er, Ho and Y) compounds.

When the tolerance factor decreases below unity, compression forces are acted upon Fe – O bonds and consequently $\text{Bi}^{3+} / \text{R}^{3+} - \text{O}$ bonds are under tension. Cooperative rotation of oxygen octahedral takes place in order to reduce the lattice stress [21]. This induced lattice distortion nominally suppresses the rhombohedral phase and leads to evolution of lower symmetric phases like orthorhombic or tetragonal with reduction in lattice parameters as well as volume of the unit cell. It is worth to mention here, the prominent phase in our compounds is found to be rhombohedral crystal structure with the weak signature of orthorhombic phase.

Raman spectra of BFO and BRFO polycrystalline compounds are shown in Fig. 2 (a). The measured spectra were fitted and deconvoluted in to individual Lorentzian components to obtain the peak position of the each component i.e., the natural frequency (cm^{-1}) of each Raman mode. For Rhombohedral ($R3c$) BiFeO_3 , the Raman active modes can be summarized using the following irreducible representation: $\Gamma = 4A_1 + 9E$ [23-25]. The phonon modes at lower frequencies 139.3, 171.1 and 224.6 cm^{-1} can be assigned as A_1-1 , A_1-2 and A_1-3 respectively. Nine other phonon modes at 128.2, 260.3, 275.2, 293.8, 347.3, 368.4, 432.2, 469.0 and 526.4 cm^{-1} are assigned as E_1 , E_2 , E_3 , E_4 , E_5 , E_6 , E_7 , E_8 and E_9 modes respectively. A_1 modes (139.3, 171.1 cm^{-1}) are attributed

to Bi – O covalent bonds [26]. In the present study, both the high intensity modes A_{1-1} and A_{1-2} shift to higher frequency side. Because with the partial substitution of these elements (Y, Ho and Er) at A – site, the average mass at A – site will be decreased. If k is the force constant and M is the reduced mass, then the frequency of the mode is proportional to $(k / M)^{1/2}$ provided it is governed by the local factors [27]. Since the masses of the elements Ho, Er and Y are approximately 21%, 21% and 57% respectively less than the mass of the element Bi, substitution of the relatively lighter element Y at A – site will increase more shift in the frequency of vibration of the modes than Ho and Er which is consistent with our observation as shown in Fig. 2(b). Individual Raman modes of each compound are given in table. 1. Decrease in the intensity of A_{1-1} and A_{1-2} modes in the R– ion substituted BFO indicates decline of stereochemical activity of Bi^{3+} lone pair electrons which in turn changes the Bi – O bonds [28].

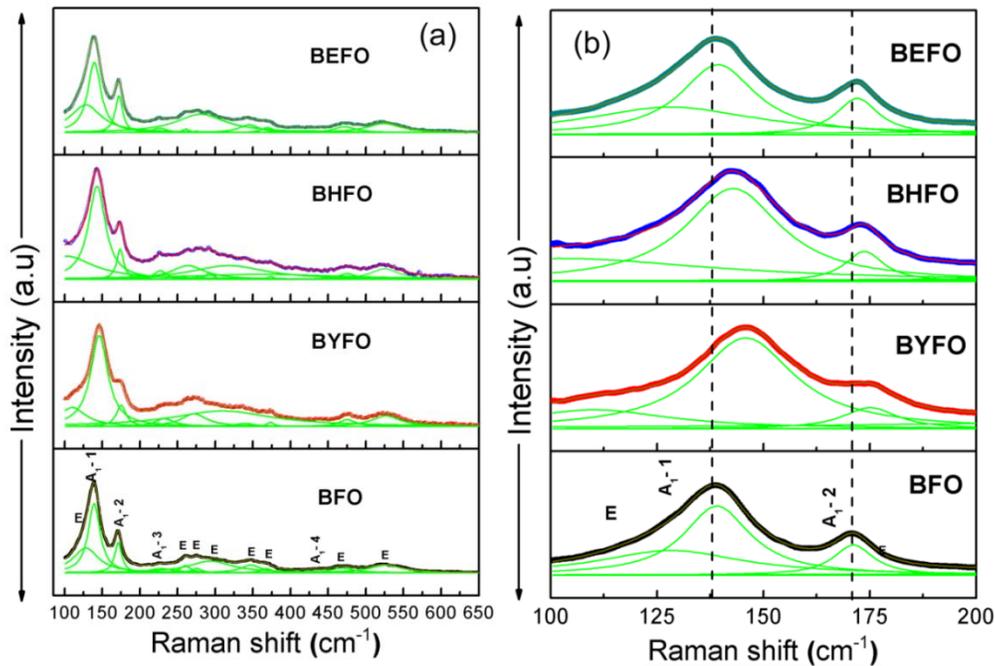


Fig. 2(a) Raman scattering spectra of BFO and BRFO compounds with their phonon modes deconvoluted into individual Lorentzian components. (b) Close observation of the A_{1-1} and A_{1-2} phonon modes indicating a clear blue shift in their peak positions due to A-site cation disorder in BRFO compounds.

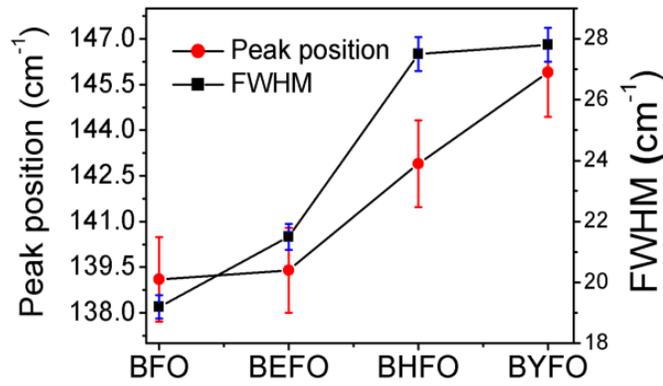


Fig. 3 Plots showing the increase in FWHM and blue shift in frequency of A₁₋₁ phonon mode due to R- ion substitution in BFO host lattice.

In addition to this, change in the intensity of low frequency E modes is observed in R – ion substituted BFO. This indicates that all the R – ions replace the host site (Bi site) and affecting the Bi – O bonds. Fig. 3 shows the variation in Full Width Half Maxima (FWHM) and peak position for A₁₋₁ phonon mode with the A-site substitution by R³⁺ ions. Similar trend is also observed for A₁₋₂ mode. This clearly indicates that decrease in average A-site radius in BRFO compounds affect the Bi – O bonds and creates disorder in the lattice.

Variation of magnetization with magnetic field at 300K for all the compounds is shown in Fig. 4. In BFO, magnetic moments of Fe³⁺ cations are coupled ferromagnetically in the pseudo cubic (111) planes, but antiferromagnetically between the adjacent planes. The superposition of SMSS with the G-type antiferromagnetic spin ordering prevents both the observation of net magnetization and the linear magnetoelectric effect. In BFO, Fe³⁺ ion is surrounded by six O²⁻ ions and O²⁻ ion is the common apex of two adjacent FeO₆ octahedra. The ionic size of Bi³⁺ is larger than that of substituted R³⁺ ions. Substitution of smaller ionic size elements, at Bi³⁺-site, decreases the average A-site ionic size which in turn decreases tolerance factor. This, in-turn increase the octahedral tilt and change in the Fe – O – Fe bond angles and Fe – O bond distances [29]. Variation in bond angles and bond distances affects superexchange interaction between the two antiferromagnetically aligned Fe³⁺-ions with possibility of canted structure which in turn

presumably suppresses the SMSS [28]. An appearance of weak ferromagnetism in BRFO is accounted due to the enhancement of Dzyaloshinskii–Moriya (DM) interactions [30]. Contribution of magnetization from the secondary phases is ruled out as these phases are paramagnetic at room temperature [31, 32]. In case of Y substituted BFO, a non linear variation of magnetization was observed (unlike Ho and Er-substituted BFO). There are three nearly closed loops in the M – H curve for this compound. A narrow loop symmetrically situated between ± 0.6 kOe arising from ferromagnetic interactions, and two loops lying between ± 0.6 kOe and ± 50 kOe in first and third quadrants arising from antiferromagnetic interactions. Presence of antiferromagnetic and ferromagnetic exchange interactions in the same phase leads to competition between the two interactions. These competing interaction may induce spin reorientation towards the field direction in Y substituted BFO. Similar behavior has been explained in terms of metamagnetism [33] which is directly related to spin orientation phenomenon [34]. These spin reorientation transitions mainly depend on R-Fe interactions. It has been observed in Lu substituted $YFeO_3$ that spin reorientation diminishes with Lu substitution [35]. It is reasonable to predict that the spin reorientation mechanism is more pronounced in BYFO as compared to that of BHFO and BEFO which is consistent with the observation. The remanent magnetization M_r and coercive field (H_c) of BFO and BRFO compounds are given in Table 1

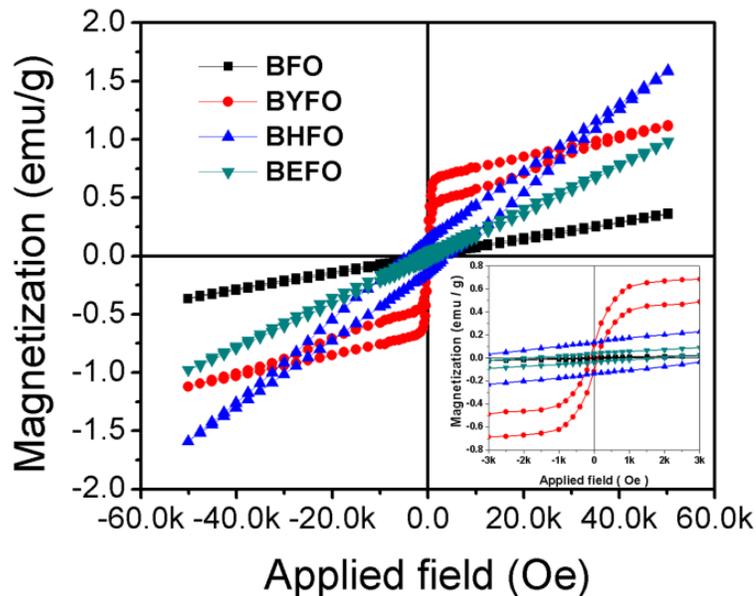


Fig. 4. Magnetization plots showing the evolution of weak ferromagnetic behavior in BRFO compounds measured at room temperature. Inset shows the non-zero coercivity (H_C) and remanent magnetization values (M_r).

Table 1 Remanent magnetization M_r and coercive field (H_c) of BFO and BRFO compounds

Compound	BFO	BYFO	BHFO	BEFO
Remnant Magnetization M_r (emu / g)	0.004	0.112	0.136	0.038
Coercive Field H_c (Oe)	460	116	3880	1924

Fig. 5 shows the room temperature UV–Visible absorption spectra of BFO and BFO-Er, BFO-Ho, BFO-Y compounds derived from the diffuse reflectance (R) spectrum using Kubelka–Munk function [34] $F(R) = (1-R)^2/2R$ which is plotted as a function of energy (eV). BFO has a distorted cubic structure, as a result there is a point group symmetry breaking from O_h to C_{3v} [40]. By considering C_{3v} local symmetry of Fe^{3+} ions ($3d^5$ – High spin configuration; $t_{2g}^3 e_g^2$) in BFO and using the correlation group and subgroup analysis for the symmetry breaking from O_h to C_{3v} , there expected to have six transitions between 0 and 3eV [37].

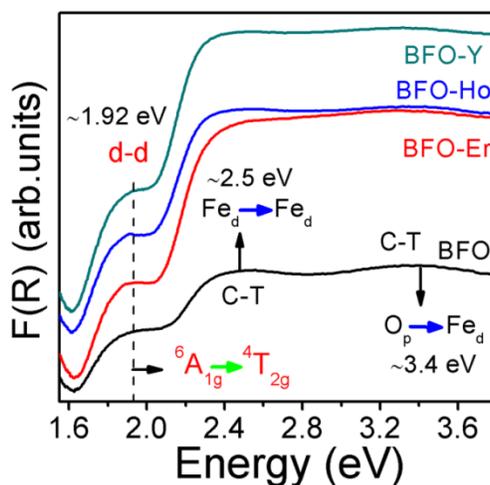


Fig. 5 Shows the UV-Visible absorption spectra of BFO and BRFO compounds with respect to $F(R) = (1-R)^2/2R$ as a function of energy (eV) derived from Diffuse Reflectance Spectrum measured at 300K.

In our case we observed three transitions corresponding to three anomalies which lies in the range between 1.6eV to 4 eV. However other authors reported a similar type of transitions

along with two more transitions, one observed below 1.6eV and other above 4 eV [37, 38]. In order to observe these we need to perform the experiment still in the higher energy regions. However the observed there transitions matched well with the previous reports. From the DRS spectrum of BFO as shown in Fig. 5 a shoulder centered around 1.92 eV corresponds to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ excitation which arises due to the d–d crystal field excitations of Fe^{3+} ions in BFO [37, 38]. Formally these excitations are forbidden because they change the total spin of Fe^{3+} from $S = 5/2$ to $S = 3/2$. However, spin orbit coupling relaxes the spin selection rule and gives rise to these transitions [39, 40]. Above 2 eV, absorption increases significantly with a small shoulder centered at ~2.5 eV and near ~3.4 eV. These two features were assigned to the charge transfer (CT) excitations [30]. Among these CT transitions the band centered at ~2.5 eV corresponds to two center CT transitions which is driven by $Fe_1 3d - Fe_2 3d$ intersite electron transfer. The other band around ~3.4 eV corresponds to one center CT transitions which is associated with the interatomic $O 2p - Fe 3d$ transition [39]. A similar kind of absorption bands as such in BFO were also observed for Er^{3+} , Ho^{3+} and Y^{3+} substituted BFO compounds, which indicates that their electronic energy level scheme looks similar. But on close observation, there appeared to be a slight redshift on the d–d and CT transition bands for BRFO compounds. A noticeable shift in this transition bands clearly indicates that substitution of Er^{3+} , Ho^{3+} , Y^{3+} in BFO increases the internal chemical pressure which arises as a result of the changes of FeO_6 local environment, as a consequence of contraction in unit cell volume. Our Raman spectroscopy results as discussed earlier also supports well in this context.

3. Conclusion:

Polycrystalline BFO and $Bi_{0.9}R_{0.1}FeO_3$ ($R = Y, Ho$ and Er) compounds were prepared by rapid solid state sintering technique. All the compounds stabilized in rhombohedral structure ($R3c$ space group). Structural distortion in the Rare earth substituted compounds evolve a weak orthorombic

phase at the expense of rhombohedral phase. A significant change in the phonon modes of R substituted BFO compounds indicates a clear local distortion in the crystal lattice and supports well with the x-ray analysis. Remnant magnetization is greatly enhanced in BRFO compounds due to the suppression of spiral modulated spin structure. UV-Vis spectroscopy evidences a change in local FeO_6 environment upon substitution.

Acknowledgement

Authors T. D, T. K and S. A are grateful to the Department of Science and Technology (DST), Government of India for their financial support under Fast Track scheme (SR/FTP/PS-065/2011) to carry out this work.

References:

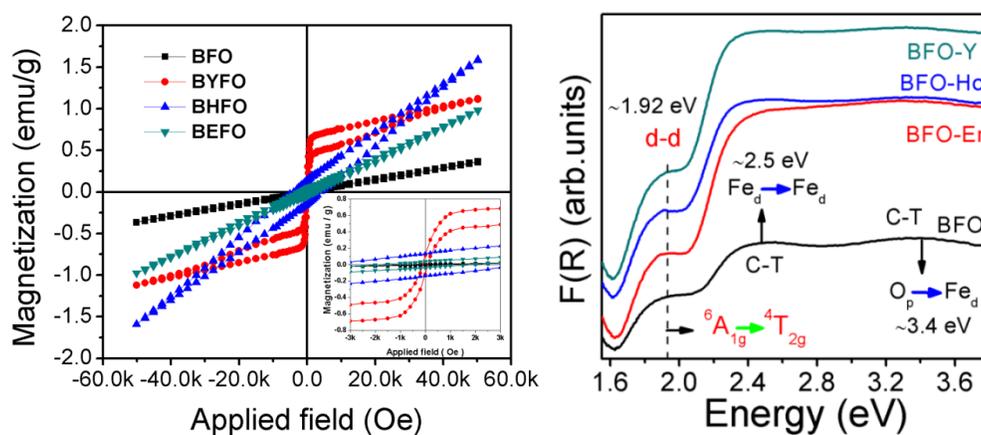
- [1] Eerenstein W, Mathur N D, and Scott J F. Multiferroic and magnetoelectric materials [J]. Nature (London), 2006, 442: 759.
- [2] Fiebig M. Revival of the magnetoelectric effect [J]. J. Phys. D, 2005, 38: R123.
- [3] Hur N, Park S, Sharma P A, et al. Electric polarization reversal and memory in a multiferroic material induced by magnetic fields [J]. Nature, 2004, 429: 392–395.
- [4] Dong S X, Zhai J Y, Li J F, et al. Magnetoelectric gyration effect in $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_{2-y}/\text{Pb}(\text{Zr,Ti})\text{O}_3$ laminated composites at the electromechanical resonance [J]. Appl.Phys. Lett., 2006, 89: 243512.
- [5] Kimura T, Goto T, Shintani H, et al. Magnetic control of ferroelectric Polarization [J]. Nature, 2003, 426: 55–58.
- [6] Goto T, Kimura T, Lawes G, et al. Electricity and giant magnetocapacitance in perovskite rare-earth manganites [J]. Phys. Rev. B, 2004, 92: 257201.
- [7] Teague J R, Gerson R, James W J. Dielectric hysteresis in single crystal BiFeO_3 [J], Solid State Commun, 1970, 8: 1073.
- [8] Cheng Z X, Wang X L, Kannan C V et al. Enhanced electrical polarization and ferromagnetic moment in a multiferroic $\text{BiFeO}_3/\text{Bi}_{3.25}\text{Sm}_{0.75}\text{Ti}_{2.98}\text{V}_{0.02}\text{O}_{12}$ double-layered thin film [J]. Appl Phys Lett., 2006, 88:132909.

- [9] Sosnowska I, Schäfer W, Kockelmann W et al. Crystal structure and spiral magnetic ordering of BiFeO₃ doped with manganese [J]. Appl. Phys. A, 2002, 74 [Suppl.]: S1040–S1042
- [10] Haiyang Dai, Zhenping Chen, Tao Li, Yong Li et al. Microstructure and properties of Sm-Substituted BiFeO₃ ceramics [J]. J. Rare. Earths, 2012, 30:1123.
- [11] Uchida H, Ueno R, Funakubo H, et al. Crystal structure and ferroelectric properties of rare-earth substituted BiFeO₃ thin films [J]. J. Appl. Phys., 2006, 100: 014106.
- [12] Qian F Z, Jiang J S, Guo S Z, et al. Multiferroic properties of Bi_{1-x}Dy_xFeO₃ nanoparticles [J]. J. Appl. Phys., 2009, 106: 084312.
- [13] Chang Fanggao, Song Guilin, Fang Kun, et al. Effect of Gadolinium Substitution on Dielectric Properties of Bismuth Ferrite [J]. J. Rare Earths, 2006, 24: 273.
- [14] Khomchenko V A, Kiselev D A, Vieira J M, et al. Effect of diamagnetic Ca, Sr, Pb, and Ba substitution on the crystal structure and multiferroic properties of the BiFeO₃ perovskite [J]. J. Appl. Phys., 2008, 108: 024105.
- [15] Chang F, Zhang N, Yang F, et al. Effect of Cr substitution on the structure and electrical properties of BiFeO₃ ceramics [J]. J. Phys. D: Appl. Phys., 2007, 40: 7799–7803.
- [16] Reddy V R, Kothari D, Gupta A, et al. Study of weak ferromagnetism in polycrystalline multiferroic Eu doped bismuth ferrite [J]. Appl. Phys. Lett., 2009, 94: 082505.
- [17] Wang Y P, Zhou L, Zhang M F, et al. Room-temperature saturated ferroelectric polarization in BiFeO₃ ceramics synthesized by rapid liquid phase sintering [J]. Appl. Phys. Lett., 2004, 84: 1731.
- [18] Manoj Kumar and Yadav K L, Rapid liquid phase sintered Mn doped BiFeO₃ ceramics with enhanced polarization and weak magnetization [J]. Appl. Phys. Lett., 2007, 91: 242901.
- [19] Pradhan A K, Kai Zhang, Hunter D, et al. Magnetic and electrical properties of single-phase multiferroic BiFeO₃ [J]. J. Appl. Phys., 2005, 97: 093903.
- [20] Ji-Zhou Huang, Yang Shen, Ming Li, et al. Structural transitions and enhanced ferroelectricity in Ca and Mn co-doped BiFeO₃ thin films [J]. J. Appl. Phys., 2011, 110: 094106.
- [21] Xingquan Zhang, Yu Sui, Xianjie Wang, et al. Effect of Eu substitution on the crystal structure and multiferroic properties of BiFeO₃ [J]. J. Alloys Compd., 2010, 507: 157.
- [22] Yan F, Zhu T J, Lai M O et al. Enhanced multiferroic properties and domain structure of La-doped BiFeO₃ thin films [J]. Scripta Materialia, 2010, 63: 780–783

- [23] Manoj K. Singh, Hyun M. Jang, Sangwoo Ryu, et al. Polarized Raman scattering of multiferroic BiFeO₃ epitaxial films with rhombohedral *R3c* symmetry [J]. Appl. Phys. Lett., 2006, 88: 042907.
- [24] Haumont R, Kreisel J, Bouvier P, et al. Phonon anomalies and the ferroelectric phase transition in multiferroic BiFeO₃ [J]. Phys. Rev. B, 2006, 73: 132101.
- [25] Fukumura H, Harima H, Kisoda K, et al. Raman scattering study of multiferroic BiFeO₃ single crystal [J]. J. Magn. Magn. Mater., 2007, 310: 367.
- [26] Lin J W, Teddy Tite, Tang Y H, et al. Correlation of spin and structure in doped bismuth ferrite nanoparticles [J]. J. Appl. Phys., 2012, 111: 07D910.
- [27] Wu D, Deng Y, Mak C L, et al. Raman scattering study of La-, Nd- and Sm-substituted Bi₄Ti₃O₁₂ [J]. Appl. Phys. A, 2005, 80: 607.
- [28] Yuan G L, Siu Wing Or, Helen Lai Wa, et al. Raman scattering spectra and ferroelectric properties of Bi_{1-x}Nd_xFeO₃ (x = 0–0.2) multiferroic ceramics [J]. J. Appl. Phys., 2007, 101, 064101.
- [29] Bellaki M B, Manivannan V, Madhu C, et al. Synthesis and Magnetic Properties of BiFeO₃ and Bi_{0.98}Y_{0.02}FeO₃ [J]. Materials Chemistry and Physics, 2009, 116: 599.
- [30] Mishra K. K, Satya A. T, Bharathi A, et al. Vibrational, magnetic, and dielectric behavior of La-substituted BiFeO₃-PbTiO₃ [J]. J. Appl. Phys., 2011, 110: 123529.
- [31] Iliev M N, Litvinchuk A P, Hadjiev V G, et al. Phonon and Magnon Scattering of Bi₂Fe₄O₉ [J]. Phys. Rev. B, 2010, 81: 024302.
- [32] Kanwar Singh Nalwa, Ashish Garg et. al. Phase evolution, electric and magnetic properties in Sm-doped Bismuth ferrite [J]. J. Appl. Phys. 2008, 103: 044101.
- [33] Mishra R K, Dillip K Pradhan, Choudhary R N P et al. Effect of yttrium on improvement of dielectric properties and magnetic switching behavior in BiFeO₃ [J]. J. Phys.: Condens. Matter., 2008, 20: 045218.
- [34] Durbin G. W, Johnson C. E, Thomas M. F, Direct observation of field-induced spin reorientation in YFeO₃ by the Mossbauer effect [J]. J. Phys. C : Solid State Phys., 1975, 8.
- [35] Xue-ping Yuan, Yan-kun Tang, Yue Sun, et al. Structure and magnetic properties of Y_{1-x}Lu_xFeO₃ (0≤x≤1) ceramics [J]. J. Appl. Phys., 2012, 111: 053911.
- [36] Ramachanran B, Dixit A, Naik R, et al. Charge transfer and electronic transitions in polycrystalline BiFeO₃ [J]. Phys. Rev. B, 2010, 82: 012102.

- [37] Ramirez M O, Kumar A, Denav S A, et al. Magnon sidebands and spin-charge coupling in bismuth ferrite probed by nonlinear optical spectroscopy[J]. Phys. Rev. B, 2009, 79: 224106.
- [38] Xu X S, Brinzari T V, Lee Set al. Optical properties and magnetochromism in multiferroic BiFeO₃ [J]. Phys. Rev. B. 2009, 79: 134425.
- [39] Pisarev R V, Moskvin A S, Kalashinkova A M, et al. Charge transfer transitions in multiferroic BiFeO₃ and related ferrite insulators [J]. Phys. Rev. B, 2009, 79: 235128.
- [40] Gerald F D, Magnetic Oxides [M], Newyork: Springer publications, 2009: 47–90.

Graphical Abstract



Highlights

- XRD pattern of R-BFO samples indicates a weak coexistence of orthorhombic phase along with the parent rhombohedral phase due to structural distortion in the BFO lattice.
- Shift and increased FWHM of the A_1-1 and A_1-2 phonon mode confirms the A-site cation disorder and change in covalency of the Bi-O bond due to Rare-earth ion substitution.
- Improved Magnetic properties (i.e., M_r and H_c) of R-BFO samples were attributed to the suppression of SMSS structure and spin- reorientation transitions.
- UV-Vis spectroscopy evidences a change in the local FeO_6 environment upon rare-earth ion substitution.