

## Evidence of improved ferroelectric phase stabilization in Nd and Sc co-substituted BiFeO<sub>3</sub>

T. Durga Rao and Saket Asthana

Citation: [Journal of Applied Physics](#) **116**, 164102 (2014); doi: 10.1063/1.4898805

View online: <http://dx.doi.org/10.1063/1.4898805>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/116/16?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Enhanced magnetization and improved insulating character in Eu substituted BiFeO<sub>3</sub>](#)

J. Appl. Phys. **115**, 124110 (2014); 10.1063/1.4869775

[Mn substitution-modified polar phase in the Bi<sub>1-x</sub>NdxFeO<sub>3</sub> multiferroics](#)

J. Appl. Phys. **113**, 214112 (2013); 10.1063/1.4810764

[Polarization fatigue of Pr and Mn co-substituted BiFeO<sub>3</sub> thin films](#)

Appl. Phys. Lett. **99**, 012903 (2011); 10.1063/1.3609246

[Sol-gel derived multiferroic Bi Fe O<sub>3</sub> ceramics with large polarization and weak ferromagnetism](#)

Appl. Phys. Lett. **89**, 092910 (2006); 10.1063/1.2345603

[Structural and multiferroic properties of BiFeO<sub>3</sub> thin films at room temperature](#)

J. Appl. Phys. **96**, 3399 (2004); 10.1063/1.1775045

---



## Evidence of improved ferroelectric phase stabilization in Nd and Sc co-substituted BiFeO<sub>3</sub>

T. Durga Rao and Saket Asthana<sup>a)</sup>

Advanced Functional Materials Laboratory, Department of Physics, Indian Institute of Technology Hyderabad, Telangana 502205, India

(Received 7 July 2014; accepted 9 October 2014; published online 24 October 2014)

Polycrystalline BiFeO<sub>3</sub> and Bi<sub>0.9</sub>Nd<sub>0.1</sub>Fe<sub>1-x</sub>Sc<sub>x</sub>O<sub>3</sub> ( $x = 0, 0.05, \text{ and } 0.10$ ) multiferroic compounds were prepared using conventional solid-state route. X-ray diffraction studies and Raman measurements indicated that the compounds were crystallized in rhombohedral structure with  $R3c$  space group. Weak ferromagnetism was induced due to the suppression of canted spin structure in the substituted compounds. Both remanent magnetization ( $M_r$ ) and coercive field ( $H_c$ ) were enhanced in Nd and Sc substituted compounds. Further, Néel temperature  $T_N$  was decreased from 644 K for BiFeO<sub>3</sub> to 550 K for Bi<sub>0.9</sub>Nd<sub>0.1</sub>Fe<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>3</sub> compound due to weakening of magnetic exchange interactions between  $B$ -site cations in the substituted compounds. Enhanced and nearly well saturated electrical polarizations were observed in Sc substituted compounds, which are attributed to the strengthening of covalent hybridization between Bi and O ions and reduction in oxygen vacancies. The remnant polarization was enhanced to  $12.5 \mu\text{C}/\text{cm}^2$  in Bi<sub>0.9</sub>Nd<sub>0.1</sub>Fe<sub>0.9</sub>Sc<sub>0.1</sub>O<sub>3</sub> compound. Impedance studies revealed that insulating character of substituted compounds is enhanced and electrical relaxations are of non-Debye type. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4898805>]

### INTRODUCTION

Multiferroics are the materials, which simultaneously exhibit ferroelectric and (anti) ferromagnetic orders in the same phase. These materials have attracted considerable research attention because of interesting physics involved and technological applications such as spintronics, data storage devices, sensors, etc.<sup>1,2</sup> In multiferroics, electric polarization can be switched with the application of magnetic field and vice versa due to the existence of coupling between the ferro orders. Among all the perovskite type single phase multiferroics, BiFeO<sub>3</sub> (BFO) is fascinating and well-studied due to its excellent ferroelectric properties at room temperature. Bulk BFO crystallizes in rhombohedral crystal structure with  $R3c$  space group. BFO shows  $G$ -type antiferromagnetic ordering below  $T_N = 643$  K and ferroelectricity below  $T_C = 1103$  K.<sup>3</sup> Ferroelectricity is resulted due to the hybridization of stereochemically active Bi  $6s^2$  lone pair electrons with the empty  $6p^0$  orbital of Bi<sup>3+</sup> ion and  $2p^6$  orbital of O<sup>2-</sup> ions. Theoretical calculations envisaged that the displacements of cations lead to the large spontaneous polarization.<sup>4</sup> Due to active lone pair electrons, Bi ions show relatively larger displacements compared to Fe ions. On the other hand, spin moments of Fe<sup>3+</sup> ions are arranged in  $G$ -type antiferromagnetic order superimposed with a long range space modulated spin structure (SMSS) of incommensurate wave length of 620 Å. The presence of long range SMSS inhibits the observation of linear magnetoelectric effect. And also the combination of superexchange interaction between the half-filled orbital of Fe<sup>3+</sup> ions and spin-orbit coupling leads to antisymmetric Dzyaloshinskii-Moriya (DM)

exchange interactions, which, in turn, produce a weak ferromagnetic moment ( $\sim 0.02 \mu_B/\text{Fe}$ ).<sup>5,6</sup> However, the potential of BFO in device applications is greatly hindered mainly due to the presence of leakage currents, formation of secondary phases such as Bi<sub>2</sub>Fe<sub>4</sub>O<sub>9</sub>, Bi<sub>25</sub>Fe<sub>40</sub> and long range spiral spin arrangement.<sup>7</sup> Persistent attempts have been made to minimize leakage currents and secondary phases and to induce weak ferromagnetism in BFO. Substitution of lanthanides or alkaline earth elements (La, Nd, Gd, Ca, Ba, etc.) at  $A$ -site<sup>8-11</sup> and transition metal elements (Mn, Ti, Cr, etc.) at  $B$ -site<sup>12,13</sup> can effectively tune the multiferroic properties of BFO. As  $A$ -site and  $B$ -site are mainly responsible for ferroelectric and magnetic properties, respectively, it is a scientific approach to tune the multiferroic properties by simultaneous substitution of elements at the both sites. Recently, enhanced magnetization, reduced leakage current, and improved dielectric properties were observed in Y and Zr,<sup>7</sup> La and Ti,<sup>14</sup> Ho and Ni,<sup>15</sup> Gd and Ti,<sup>16</sup> and Ca and Ti<sup>17</sup> co-substituted BFO compounds.

In this paper, Nd and Sc have been chosen to substitute at  $A$ -site and  $B$ -site, respectively. Nd and Sc are chosen because; (i) the valence state of Nd<sup>3+</sup> and Sc<sup>3+</sup> ions are more stable. Substitution of these ions minimizes the Fe<sup>2+</sup> ions and improves insulating character, which is essential for the potential applications. (ii) substitution of Sc<sup>3+</sup> for Fe<sup>3+</sup> suppresses the space modulated spin structure and changes Fe-O-Fe bond angles and Fe-O bond distances, which in turn improve the physical properties of BFO, and (iii) as the bond enthalpies of Nd-O ( $703 \pm 13$  kJ/mol) and Sc-O ( $681.6 \pm 11.3$  kJ/mol) bonds are, respectively, stronger than that of Bi-O ( $337 \pm 12.6$  kJ/mol) and Fe-O ( $390.4 \pm 17.2$  kJ/mol) bond enthalpies,<sup>18</sup> substitution of Nd and Sc for Bi and Fe would recover the oxygen vacancies caused by volatilization of Bi atoms, which in turn improve electrical insulating

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: [asthanas@iith.ac.in](mailto:asthanas@iith.ac.in)

character by minimizing  $\text{Fe}^{2+}$  and oxygen vacancies. In the present work, structural, magnetic, and electrical properties of Nd and Sc co-substituted compounds have been investigated.

## EXPERIMENTAL DETAILS

Polycrystalline  $\text{BiFeO}_3$  (BFO),  $\text{Bi}_{0.9}\text{Nd}_{0.1}\text{FeO}_3$  (BNFO), and  $\text{Bi}_{0.9}\text{Nd}_{0.1}\text{Fe}_{1-x}\text{Sc}_x\text{O}_3$  (BNFSO) [ $x = 0.05$  (BNFSO5) and  $0.10$  (BNFSO10)] compounds were synthesized by conventional solid-state route. The detailed experimental procedure could be found elsewhere.<sup>19</sup> Phase analysis of the compounds was confirmed by using X-ray diffractometer (Panalytical X'pert Pro) with  $\text{Cu-K}_\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) over the angular range  $20^\circ \leq 2\theta \leq 90^\circ$ . Microstructural characterization and energy dispersive X-ray analysis (EDX) were carried out using field emission scanning electron microscope (FE-SEM, Carl Zeiss, Supra 40). Raman scattering measurements were performed on sintered and polished pellets using a laser micro Raman spectrometer (Bruker, Senterra) with an excitation laser source of  $785 \text{ nm}$  wave length. The magnetic properties were measured using the physical property measurement system (PPMS) with a vibrating sample magnetometer (VSM) assembly (Quantum Design, USA). Room temperature polarization ( $P$ )-electric field ( $E$ ) loop measurements were carried out using aixACCT TF 2000 analyzer. The Impedance measurements were performed using Wayne Kerr 6500B impedance analyzer.

## RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of BFO, BNFO, and BNFSO compounds are shown in Fig. 1. A trace amount of impurity phases such as  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{40}$  are observed along with rhombohedral phase (which are designated as  $\blacklozenge$  and  $*$ , respectively). These phases are always formed along with the bulk BFO phase.<sup>20</sup> Rietveld refinement<sup>21</sup> is carried out to analyse the crystal structure of the

compounds. From the refinement, it is evident that all compounds stabilized in rhombohedral structure with  $R3c$  space group. Compared to BFO, XRD pattern of BNFO compound is shifted towards the higher  $2\theta$  side due to the substitution of smaller size  $\text{Nd}^{3+}$  ( $1.27 \text{ \AA}$ ) ions at  $\text{Bi}^{3+}$  ( $1.33 \text{ \AA}$ ) ion positions. On the other hand, Sc substitution in BNFO compound shifts the XRD pattern towards lower  $2\theta$  side. Shifting the XRD pattern towards lower  $2\theta$  side is expected due to the substitution of larger ionic size of  $\text{Sc}^{3+}$  ( $0.745 \text{ \AA}$ ) ion at  $\text{Fe}^{3+}$  ( $0.645 \text{ \AA}$ ) ion positions (as shown in Fig. 1(b)).

It is worth to mention here from the above discussion that Nd and Sc substitutions replace Bi and Fe ions, respectively, from their host sites and hence the corresponding changes observed in the XRD patterns. Moreover, partial merging and broadening of the doubly split peaks such as (104) & (110), (116) & (122), and (018) & (214) in vicinity of  $2\theta = 32^\circ$ ,  $51^\circ$ , and  $57^\circ$ , respectively, are observed with the substitution of Nd and Sc ions (a typical behaviour at  $2\theta = 51^\circ$  is shown in Fig. 1(c)). Further, no additional evolution or peaks splitting is observed, which indicates the absence of any structural transition in the studied compounds. The lattice parameters  $a$ ,  $c$  and volume of unit cell decrease in BNFO compound, whereas the same increase in BNFSO compounds, which is consistent with ionic size considerations. Fig. 1(b) shows the XRD peak around  $22^\circ$  for BFO, BNFO, and BNFSO compounds. From the figure, it is revealed that the full width at half maximum (FWHM) of the peak increases from  $0.100^\circ$  in BFO to  $0.134^\circ$  in BNFO, which further increases to  $0.151^\circ$  in BNFSO10 compound. Increase in FWHM indicates decrease in crystallite size. Structural parameters estimated from the refinement are given in Table I.

FE-SEM micrographs of BFO, BNFO, and BNFSO compounds are shown in Fig. 2. The average grain sizes of BFO, BNFO, BNFSO5, and BNFSO10 compounds are  $9 \mu\text{m}$ ,  $2 \mu\text{m}$ ,  $1.75 \mu\text{m}$ , and  $1.5 \mu\text{m}$ , respectively, which are also reflected in terms of increase in FWHM of XRD peaks. BFO

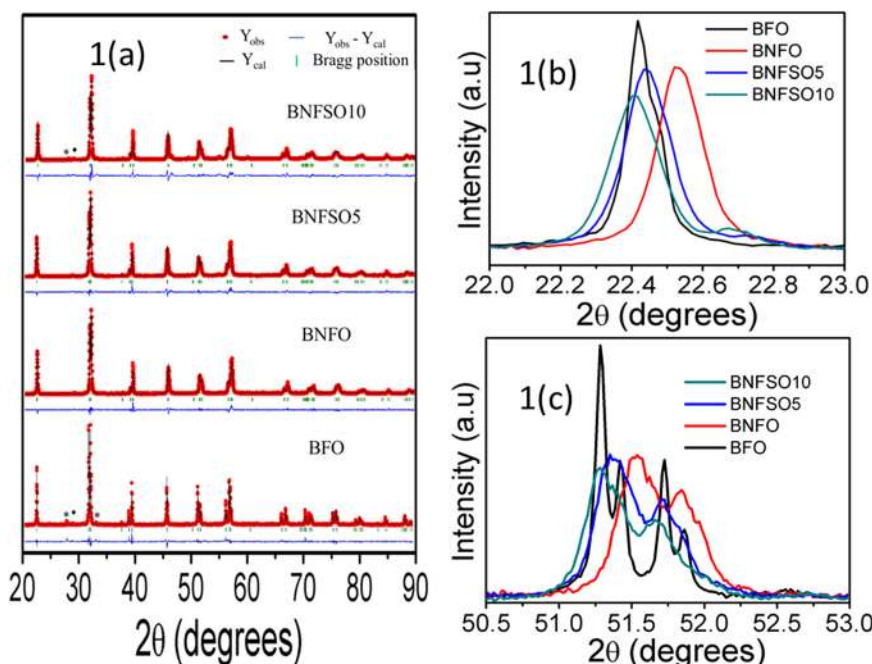


FIG. 1. (a) XRD patterns of BFO, BNFO, and BNFSO compounds. The asterisks  $\blacklozenge$  and  $*$  represent impurity phases corresponding to  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{40}$ , respectively. (b) A typical shifting behaviour in  $2\theta$  at around  $22^\circ$  and (c) XRD peak around  $51^\circ$  to show only the partial merging for BFO, BNFO, and BNFSO compounds.



TABLE I. Lattice parameters, volume of the unit cell, bond angle, and bond distance of BFO, BNFO, BNFSO5, and BNFSO10 compounds.

	BFO	BNFO	BNFSO5	BNFSO10
$a$ (Å)	5.5794(4)	5.5756(6)	5.5846(2)	5.5915(6)
$c$ (Å)	13.8709 (6)	13.8154(4)	13.8478(9)	13.8706(2)
Volume (Å) <sup>3</sup>	373.9	372.0	374.0	375.6
Bi				
$x$	0	0	0	0
$y$	0	0	0	0
$z$	0	0	0	0
Fe				
$x$	0	0	0	0
$y$	0	0	0	0
$z$	0.2207	0.2239	0.2239	0.2256
O				
$x$	0.4312	0.4474	0.4581	0.4786
$y$	0.0018	0.0181	0.0271	0.0364
$z$	0.9476	0.9522	0.9534	0.9508
Bi-O	2.310(2)	2.266(11)	2.247(11)	2.185(14)
Fe-O1	2.215(16)	2.131(8)	2.088(8)	2.087(14)
Fe-O2	1.860(17)	1.930(10)	1.972(10)	1.978(15)
Fe-O-Fe	153.2(7)	154.1(4)	155.1(4)	155.3(6)
$\chi^2$	2.53	1.79	3.63	7.28

has average grain size of 9  $\mu\text{m}$  with a few distinct pores due to presence of oxygen vacancies formed during the synthesis at high temperatures. Larger grains are resulted due to easy diffusion of mobile oxygen vacancies. It has been observed that average grain size of BFO decreases with the substitution of Nd, which is further decreased with Sc substitution.

The reduction in oxygen vacancies in the substituted compounds could be expected as the substituted elements Nd and Sc are more stable in 3+ states and have stronger bond enthalpies. The decrease in grain size could be due to lower grain growth rate, which may be presumably due to the reduction in oxygen vacancies.<sup>22</sup> Elemental analysis studies using EDX (not shown here) are carried out and observed the atomic percentage ratio Bi (Nd):Fe (/Sc):O is nearly close to 1:1:3 in all compounds, which confirms the stoichiometry in our compounds.

The normalized Raman spectra of BFO, BNFO, and BNFSO compounds are shown in Fig. 3. The natural

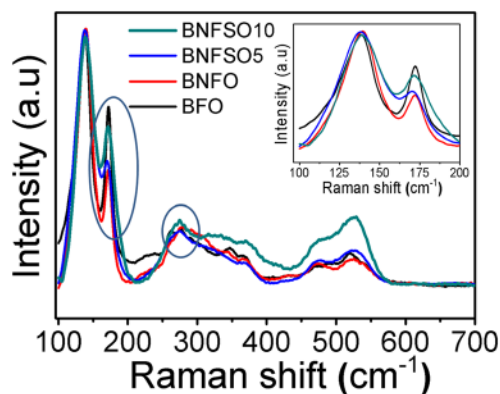


FIG. 3. Raman spectra of BFO, BNFO, BNFSO5, and BNFSO10 compounds. Inset shows the Raman spectra between 100–200  $\text{cm}^{-1}$  for all compounds.

frequency of each Raman active mode is obtained by fitting the measured spectra and deconvoluting the fitted spectra into individual Lorentzian components. For BFO, out of the thirteen possible Raman modes,<sup>23,24</sup> which can be summarized using the following irreducible representation:  $\Gamma = 4A_1 + 9E$ , three  $A_1$  modes at 139, 172, and 231  $\text{cm}^{-1}$  (can be assigned as  $A_1-1$ ,  $A_1-2$ , and  $A_1-3$ , respectively) and nine  $E$  modes at 129, 261, 276, 303, 346, 369, 432, 480, and 524  $\text{cm}^{-1}$  are observed. The  $A_1-1$ ,  $A_1-2$ , and  $A_1-3$  and  $E$  modes with frequencies less than 400  $\text{cm}^{-1}$  are corresponding to Bi-O bonds, whereas the  $E$  modes with frequencies greater than 400  $\text{cm}^{-1}$  are corresponding to Fe-O bonds.<sup>25</sup> Nd substitution at A-site shows much weaker scattering intensities of  $A_1-2$  mode (172  $\text{cm}^{-1}$ ) and  $E$  mode (261  $\text{cm}^{-1}$ ) as compared to BFO (as shown in the circles in Fig. 3). This could be due to the decline in stereochemical activity of  $6s^2$  lone pair electrons of Bi, which in turn affects the ferroelectric ordering.<sup>26</sup> The intensity of above mentioned modes increases with Sc- substitution in BNFO compounds, which suggests an enhancement in the ferroelectric ordering. Also Nd substitution causes A-site disorder and hence weakens the intensity and broadens the modes (i.e., increases the

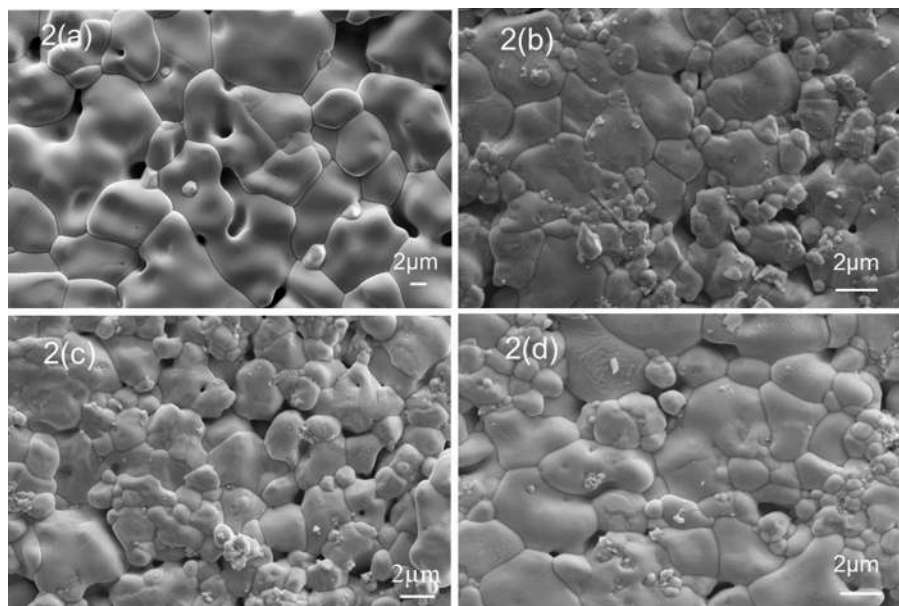


FIG. 2. FE-SEM micrographs of (a) BFO, (b) BNFO, (c) BNFSO5, and (d) BNFSO10 compounds.

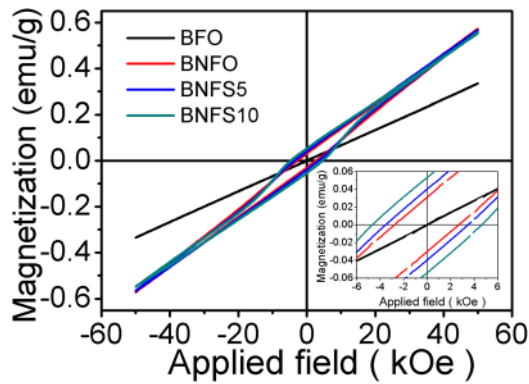


FIG. 4. Room temperature magnetization plots of BFO, BNFO, and BNFSO compounds. Inset shows the enlarged view near origin.

FWHM of the modes as shown in the inset of Fig. 3). The broadening is more pronounced with the Sc substitution. The life times of phonons in real crystals are reduced due to the scatterings from defects, disorder, strain, etc. As the FWHM is inversely proportional to life times, decrease in life times of phonons leads to increase in FWHM.<sup>19,27</sup> From the above discussion, it can be concluded that substitution of Nd and Sc replaces Bi and Fe, respectively, which is also well supported from XRD measurement.

Fig. 4 shows the room temperature magnetization ( $M$ ) – field ( $H$ ) hysteresis loops of BFO, BNFO, and BNFSO compounds at 300K up to the magnetic field of 50kOe. BFO shows a linear field dependent narrow hysteresis loop with insignificant remnant magnetization. It has been reported that in BFO,  $G$ -type antiferromagnetic structure is superimposed with a spiral spin structure of incommensurate wave length of 620 Å.<sup>20</sup> Substitution of Nd at  $A$ - site distorts the crystal structure, which in turn change Fe-O distances and Fe-O-Fe bond angles and leads to enhancement in magnetization and coercive field in BNFO compound. Remanent magnetization and coercive field are further increased with the substitution of Sc in BNFO compound. The contribution of impurity phases

such as  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{40}$  to magnetization is ruled out as these phases are paramagnetic at room temperature.<sup>9,19</sup> Remanent magnetization values are 0.6 memu/g for BFO, 30 memu/g for BNFO, 40 memu/g for BNFSO5, and 54 memu/g for BNFSO10 compounds. The improved magnetic properties in terms of increase in remanent magnetization result from the suppression of SMSS with the substitution.

Since in BFO, SMSS of incommensurate wave length is 620 Å, which is far larger than the lattice constants, the contribution from Fe magnetic sublattice to the magnetocrystalline anisotropy is negligible. Hence the small coercive field (235 Oe) is observed in BFO. However, the coercive field is enhanced in BNFO compound to 2.75 kOe, which is one order greater than that of BFO. Coercive field is further increased to 3.5 kOe in BNFSO5 and to 4.7 kOe in BNFSO10 compounds.

Such high coercive fields cannot be due to pinning of magnetic domain walls alone, because the typical coercive field for such pinning is less than 0.3 kOe.<sup>28</sup> High coercive fields in the substituted compounds may be due to change in magnetic anisotropy. Also, it has been reported that in case of La and Nb co-substituted BFO<sup>29</sup> and Pr and Zr co-substituted BFO compounds,<sup>30</sup> increase in coercive field with the substitution is attributed to decrease in grain size, which is also consistency with our findings. The non-saturating behaviour (up to applied field of 50 kOe) with significant loop opening in substituted compounds suggests the possibility of competing antiferromagnetic and ferromagnetic interactions. It is interesting to note that the magnetization at 50 kOe is enhanced in BNFO compound compared to that of BFO. However, substantial change in magnetization has not been observed with Sc-substitution, which could be due to its diamagnetic nature.

Zero field cooled (ZFC) and FC magnetization measurements are carried out under a magnetic field of 1000 Oe for BFO, BNFO, and BNFSO compounds as shown in Fig. 5. A small anomaly has been observed near 270 K in BFO compound, indicating spin glass-like transition similar to as

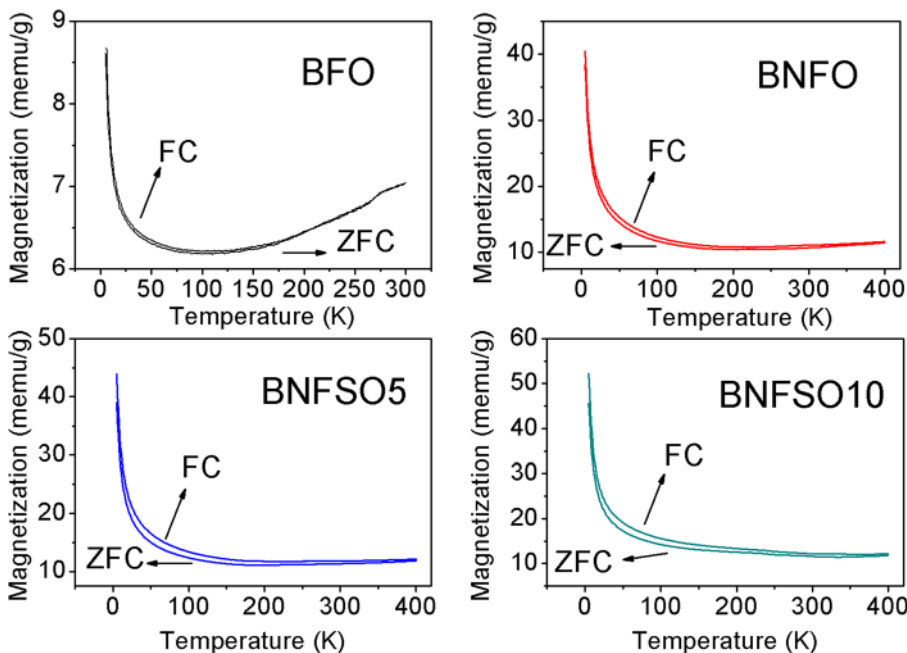


FIG. 5. ZFC and FC curves of BFO, BNFO, BNFSO5, and BNFSO10 compounds under the magnetic field of 1000 Oe.

observed by Singh *et al.*,<sup>31</sup> which disappears in Nd and Sc co-substituted compounds. These anomalies may originate from domain wall pinning effects, which are caused by random distribution of oxygen vacancies.<sup>31</sup> The magnetization (in BFO) decreases with the temperature from 300 K to 100 K suggesting the antiferromagnetic nature of the compounds up to 100 K. An abrupt increase in magnetization has been observed, especially, in the low temperature below 25 K, which reveals the development of incommensurate magnetic structure in all compounds.<sup>32</sup> The large jump in magnetization in BNFO compound compared to that of BFO could be due to the contribution from magnetic sublattice of Nd- along with Fe sublattice. Also, the thermomagnetic irreversibility between ZFC and FC curves at 170 K increases in the BNFO compound, which further increases with the Sc content. This indicates an enhancement in weak ferromagnetism in the substituted compounds, which is also confirmed from *M-H* discussion.

Fig. 6 shows the temperature variation (300 K–750 K) of magnetization for BFO, BNFO, and BNFSO compounds under the magnetic field of 1000 Oe. BFO shows antiferromagnetic to paramagnetic transition temperature ( $T_N$ ) at 644 K, which is well consistent the existing literature. Substitution of Nd at A-site affects bond distances and bond angles, which in turn change the transition temperature  $T_N$  to 633 K. Small or insignificant changes in  $T_N$  due to the substitution of rare earth elements at A-site has also been reported.<sup>10,33,34</sup> However, Sc substitution at B-site weakens the magnetic interaction strength and reduces  $T_N$  to 565 K in BNFSO5 and to 550 K in BNFSO10 compounds.

The decrease in  $T_N$  with Sc content can also be explained using the following equation:<sup>35</sup>

$$T_N = JZS(S + 1) \cos \theta, \quad (1)$$

where  $J$  is the magnetic exchange constant,  $S$  is the spin of  $\text{Fe}^{3+}$ ,  $Z$  is the average number of linkages per  $\text{Fe}^{3+}$  ions, and  $\theta$  is  $\langle \text{Fe} - \text{O} - \text{Fe} \rangle$  bond angle.

An increase in  $T_N$  is expected with the substitution of Nd and Sc due to the variation in Fe-O-Fe bond angles towards  $180^\circ$  as also confirmed from Rietveld refinement analysis, however, decrease in  $T_N$  is observed here. The factor, which strongly influences the reduction in  $T_N$  could be possibly due to the weakening of magnetic interactions rather than bond angle variation. Weakening in magnetic interaction is due to the presence of larger ionic size of diamagnetic  $\text{Sc}^{3+}$  ions at Fe-site. Substitution with Sc leads to existence of different types of exchange constant  $J$  such as  $J_{\text{Fe-Fe}}$ ,  $J_{\text{Fe-Sc}}$ , and  $J_{\text{Sc-Sc}}$  between the B-sites. The strength of  $J_{\text{Fe-Sc}}$  and  $J_{\text{Sc-Sc}}$  will be weaker than  $J_{\text{Fe-Fe}}$ , which presumably suppresses the overall  $J$ . As a result of weakening of  $J$  leads to reduction in Néel temperature.

Polarization ( $P$ ) – Electric field ( $E$ ) hysteresis loops of BFO, BNFO, and BNFSO compounds are shown in Fig. 7. BFO shows a leaky and rounded hysteresis loop, which is due to the leakage currents. The leakage currents are generated due the presence of oxygen vacancies and mixed valence states of B-site cations, which are likely to exist in  $\text{ABO}_3$  perovskite ferroelectric materials.<sup>36</sup> However, these vacancies are suppressed with the substitution of Nd and Sc, which results well shaped and nearly saturated hysteresis polarization loops. In BFO, there exists a strong hybridization of lone pair  $6s^2$  electrons of  $\text{Bi}^{3+}$  ions with  $6p^0$  orbital of  $\text{Bi}^{3+}$  ion and  $2p^6$  orbital of  $\text{O}^{2-}$  ion to form Bi-O covalent bonds, which result the non-centrosymmetric distortions and hence ferroelectric order.<sup>37</sup> In the case of BNFO compound, remanent polarization ( $P_r = 5.4 \mu\text{C}/\text{cm}^2$ ) is lower than that of BFO ( $P_r = 9 \mu\text{C}/\text{cm}^2$ ). This can be expected as Nd substitution declines the stereochemical activity and hence the reduction in remanent polarization.<sup>38</sup> The corresponding feature is also observed in terms of suppression of the intensity of  $A_{1-2}$  ( $172 \text{ cm}^{-1}$ ) and  $E$  ( $261 \text{ cm}^{-1}$ ) modes in the normalized Raman spectra as these modes are corresponding to Bi-O modes.<sup>26</sup> The substitution of Sc in BNFO compound further decreases the Bi-O bond length due to the structural distortions. The shortening of the Bi-O bonds strengthens

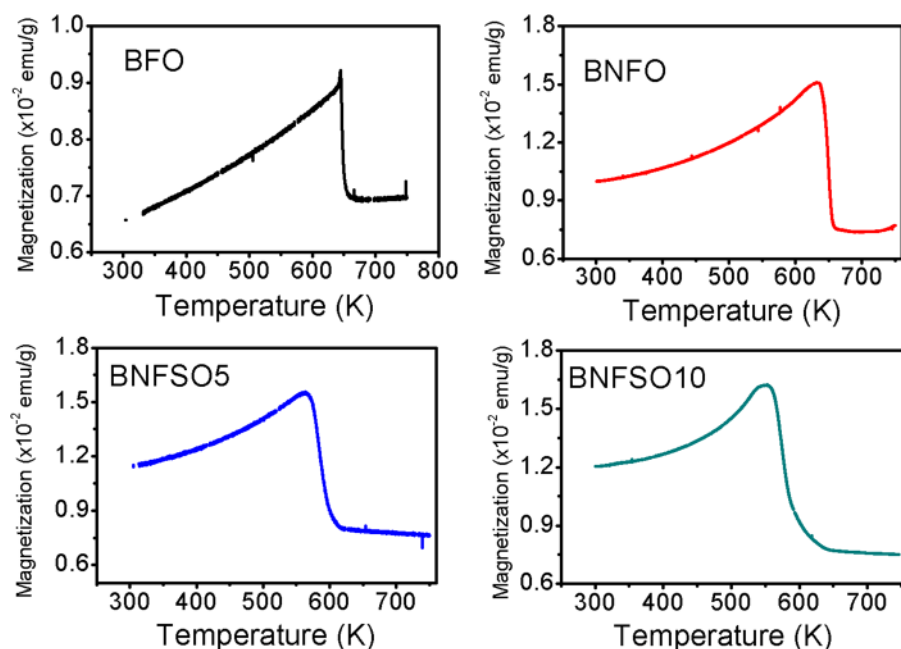


FIG. 6. Temperature dependence of magnetization for BFO, BNFO, BNFSO5, and BNFSO10 compounds under the magnetic field of 1000 Oe.

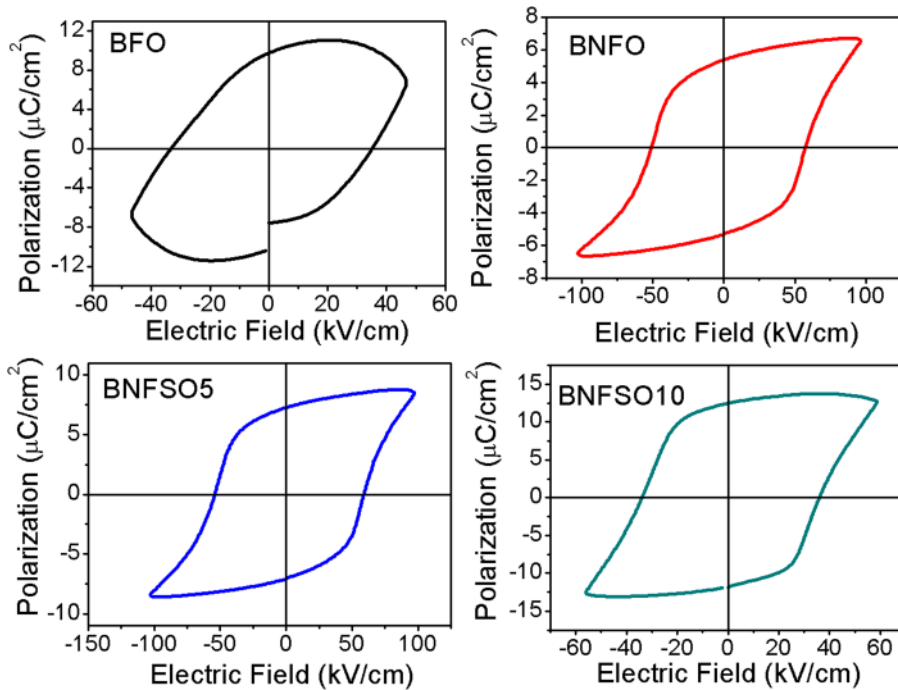


FIG. 7.  $P$ - $E$  loops of BFO, BNFO, BNFSO5, and BNFSO10 compounds.

covalent Bi-O hybridizations and causes non-centrosymmetric distortions to displace  $\text{Bi}^{3+}$  ions along  $[111]_c$  direction and improves the polarizations in BNFSO compounds.<sup>39,40</sup> Increase in remanent polarization to  $7.3 \mu\text{C}/\text{cm}^2$  in BNFSO5 compound and to  $12.5 \mu\text{C}/\text{cm}^2$  in BNFSO10 compound is observed from the polarization measurements. The strengthening of stereochemical activity of the Bi lone pair electrons is also observed in terms of increase in the intensities of  $A_{1-2}$  ( $172 \text{ cm}^{-1}$ ) and  $E$  ( $261 \text{ cm}^{-1}$ ) modes with Sc content, which support the observed polarizations in BNFSO compounds. Hence, Sc substitution improves the polarizations further due to strengthening in hybridization.

The insulating character of BFO, BNFO, and BNFSO compounds can be studied using impedance spectroscopy (IS). IS spectroscopy is a non-destructive method<sup>41</sup> to analyse the microstructural and electrical properties of material. It provides information regarding the grain and grain boundary contributions to the electrical resistivity of BFO, BNFO, and BNFSO compounds. The variation of imaginary part of complex impedance ( $Z''$ ) with the real part of complex impedance ( $Z'$ ) (Nyquist plots) for BFO in the temperature range  $30^\circ\text{C}$  to  $210^\circ\text{C}$  is shown in Fig. 8(a). At low temperatures ( $\leq 100^\circ\text{C}$ ), the impedance of these compounds is very high and hence the

semi-circular arcs in Nyquist plots are more inclined towards  $Z''$  axis. Appearance of single semi-circular arc indicates that electrical process are attributed to bulk (grain) in the compounds. As the temperature increases (above  $100^\circ\text{C}$ ), the semi-circular arc deviates towards  $Z'$  axis due to increase in the conductivity of compounds, which indicates the negative temperature coefficient of resistance (NTCR) character. Further, above  $150^\circ\text{C}$ , evolution of second semi-circular arc in the low frequency region is attributed to beginning of intergranular activities (grain boundary effects) in the compounds. Hence, both grain and grain boundary effects can be separated in all compounds above  $150^\circ\text{C}$ . Similar behaviour has been observed for other compounds. The impedance of resultant circuit in terms of grain resistance  $R_g$ , grain boundary resistance  $R_{gb}$ , grain capacitance  $C_g$ , and grain boundary capacitance  $C_{gb}$  can be expressed as<sup>42</sup>

$$Z^* = \frac{R_g}{1 + (j\omega R_g C_g)^{n_g}} + \frac{R_{gb}}{1 + (j\omega R_{gb} C_{gb})^{n_{gb}}}, \quad (2)$$

where  $n_g$  and  $n_{gb}$  are grain and grain boundary relaxation time distribution functions, respectively. The value of  $n$  ranges from zero to unity and represents the magnitude of deviation of

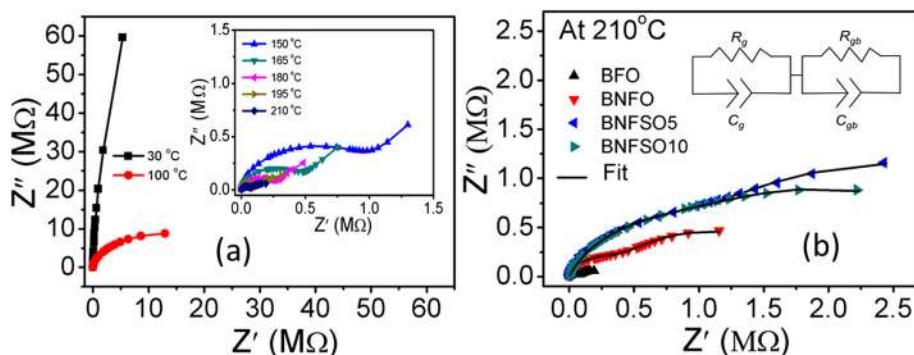


FIG. 8. (a) Nyquist plots for BFO at  $30^\circ\text{C}$  and  $100^\circ\text{C}$ . Insets show Nyquist plots for BFO between  $150^\circ\text{C}$  to  $210^\circ\text{C}$  and (b) Nyquist plots for BFO, BNFO, BNFSO5, and BNFSO10 compounds at  $210^\circ\text{C}$ .



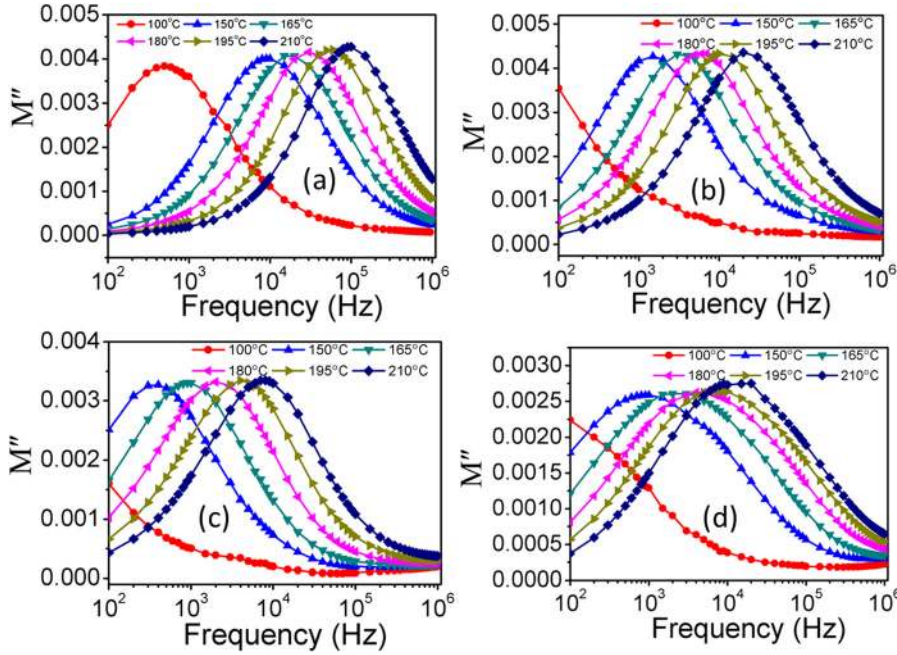


FIG. 9. Frequency variation of imaginary part of complex electric modulus ( $M''$ ) plots for (a) BFO, (b) BNFO, (c) BNFSO5, and (d) BNFSO10 compounds.

electrical responses from the ideal conditions. The centre of these depressed semi-circular arcs in the Nyquist plots lies below the real axis, which indicates the presence of Non-Debye type relaxations. Also, the intercept of semi-circular arc on the real  $Z'$ -axis decreases due to decrease in resistivity of the compounds (NTCR character). Each semi-circular arc can be modelled in terms of electrical equivalent circuit consisting of a parallel combination of resistor  $R$  and capacitor (or constant phase element CPE)  $C$  as shown in inset of Fig. 8(b). Both grain and grain boundary resistances of BFO increase with the substitution of Nd at  $A$ - site, which further increase with the Sc content at  $B$ -site. This indicates that Nd and Sc co-substitution enhances the electrical resistivity of BFO, which could be due to improved barrier properties for the flow of charge carriers with the substitutions.<sup>19</sup> However, there is a slight decrease in grain and grain boundary resistances of BNFSO10 compound compared to grain and grain boundary resistances of BNFSO5 compound. Both  $R_{gb}$  and  $R_g$  are extracted by fitting the observed data with Eq. (2) in the temperature range from 165°C to 225°C in all compounds. The values of  $R_{gb}$  and  $R_g$  decrease, respectively, from 8.4 M $\Omega$  to 1 M $\Omega$  and 0.9 M $\Omega$  to 42 k $\Omega$  for BFO, 13 M $\Omega$  to 0.50 M $\Omega$  and 2.24 M $\Omega$  to 0.12 M $\Omega$  for BNFO, 22.3 M $\Omega$  to 1.43 M $\Omega$  and 5.76 M $\Omega$  to 0.36 M $\Omega$  for BNFSO5, and 18 M $\Omega$  to 1.17 M $\Omega$  and 4.27 M $\Omega$  to 0.37 M $\Omega$  for BNFSO10 compounds in the above mentioned temperature range.

Electric modulus formalism can also be used to study the electrical response of the material. In case of impedance formalism, intensity of relaxation peaks is corresponding to the most resistive components in the compounds whereas in modulus formalism, intensity of relaxation peaks is inversely proportional to capacitance of the compounds.

The electric modulus ( $M^*$ ) is expressed as

$$\begin{aligned} M^* &= M' + iM'' = i\omega C_o Z^* \\ &= i\omega C_o (Z' - iZ'') = \omega C_o Z'' + i\omega C_o Z', \end{aligned} \quad (3)$$

where  $\omega$  is the frequency of applied electric field and  $C_o$  is the capacitance in vacuum. Frequency variation of imaginary part of electric modulus ( $M''$ ) plots of BFO, BNFO, and BNFSO compounds at different temperatures are shown in Fig. 9.

The value of electric modulus ( $M''$ ) is calculated using the formula

$$M'' = \omega C_o Z'. \quad (4)$$

At low frequency region,  $M''$  shows very small values due to the high value of capacitance and exhibits a peak in the high frequency region. These peaks are not observed in the frequency dependent dielectric data (not shown here), but are clearly seen in the modulus data. These peaks are generally characterized by significant broadening and shifting of peak position towards high frequency region with the rise of temperature. Broadening in the peak indicates the presence of distribution of relaxation times and hence the relaxation is of non-Debye type. The shifting of peak position indicates that the relaxation process is thermally activated.

The frequency region below the peak value of  $M''$  ( $M''_{\max}$ ) indicates the range of frequencies for the charge carriers to perform long range hopping from one site to another site, where as frequencies above  $M''_{\max}$ , charge carriers perform short range hopping and the charged particles are confined to their potential wells and execute only localized motions. The frequency ( $\omega_{\max}$ ) corresponding to the  $M''_{\max}$  gives the most probable relaxation time ( $\tau_{\max}$ ) for the charge carriers and follows the Arrhenius law

$$\omega_{\max} = \omega_o e^{-E/kT}, \quad (5)$$

where  $\omega_o$  is the pre exponential factor and  $E$  is the activation energy. The activation energies are calculated from the slope of the plot (shown in Fig. 10) drawn between  $\ln(\omega_{\max})$  and  $1000/T$ . The obtained activation energies for BFO, BNFO, BNFSO5, and BNFSO10 compounds are  $0.69 \pm 0.04$ ,



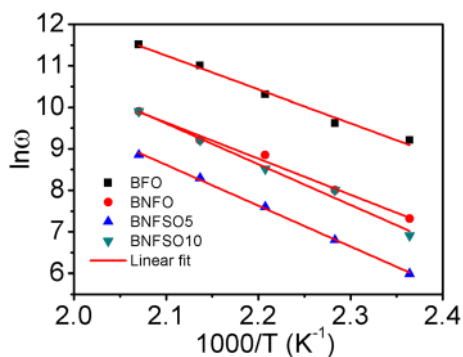


FIG. 10. Arrhenius plot of  $\ln\omega$  versus  $1000/T$  for (a) BFO, (b) BNFO, (c) BNFSO5, and (d) BNFSO10 compounds.

$0.75 \pm 0.04$ ,  $0.85 \pm 0.02$ ,  $0.85 \pm 0.05$  eV, respectively. The typical activation energy values associated for singly ionised oxygen vacancies are in the range 0.3–0.5 eV, whereas for doubly ionised oxygen vacancies, activation energies are in the range 0.6–1.2 eV for a perovskite based oxide materials.<sup>43</sup> The observed activation energies indicate that doubly ionised oxygen vacancies are responsible for the relaxation process. Overall, impedance analysis confirms an improvement in insulating character in Sc-substituted compounds, which is also consistent with the observation of near to saturation  $P$ - $E$  loops as well as improved ferroelectric ordering.

## CONCLUSIONS

Polycrystalline  $\text{BiFeO}_3$  and  $\text{Bi}_{0.9}\text{Nd}_{0.1}\text{Fe}_{1-x}\text{Sc}_x\text{O}_3$  ( $x = 0, 0.05$ , and  $0.10$ ) compounds were prepared using solid state reaction technique. Room temperature XRD and Raman studies revealed that compounds crystallized in rhombohedral structure with  $R3c$  space group. Induced weak ferromagnetism in the substituted compounds was mainly attributed to suppression of modulated spin structure. Reduced Néel temperature in BNFSO5 and BNFSO10 compounds could be due to weakening of magnetic exchange interactions due to the presence of larger diamagnetic  $\text{Sc}^{3+}$  ions in place of  $\text{Fe}^{3+}$  ions. Improved ferroelectric properties in the substituted compounds were attributed to the strengthening of covalent hybridization between Bi and O ions and reduction in oxygen vacancies. Improved insulating character in terms of improved grain and grain boundary resistances were observed in the substituted compounds due to structural distortions. Doubly ionised oxygen vacancies were responsible for the dielectric relaxation process. Reduced Néel temperature down towards room temperature and enhancement of magnetic and electrical properties demonstrate its potential use in device applications.

## ACKNOWLEDGMENTS

Authors 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.

<sup>1</sup>K. M. Song, Y. A. Park, K. D. Lee, B. K. Yun, M. H. Jung, J. Cho, J. H. Jung, and N. Hur, *Phys. Rev. B* **83**, 012404 (2011).

<sup>2</sup>W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* **442**, 759 (2006).

- <sup>3</sup>J. B. Neaton, C. Ederer, U. V. Waghmare, N. A. Spaldin, and K. M. Rabe, *Phys. Rev. B* **71**, 014113 (2005).
- <sup>4</sup>J. R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* **8**, 1073 (1970).
- <sup>5</sup>J. M. Moreau, C. Michel, R. Gerson, and W. J. James, *J. Phys. Chem. Solids* **32**, 1315 (1971).
- <sup>6</sup>C. Michel, J.-M. Moreau, G. D. Achenbach, R. Gerson, and W. J. James, *Solid State Commun.* **7**, 701 (1969).
- <sup>7</sup>J. L. Xu, D. Xie, C. Yin, T. T. Feng, X. O. Zhang, G. Li, H. Zhao, Y. F. Zhao, S. Ma, T. L. Ren, Y. J. Guan, X. S. Gao, and Y. G. Zhao, *J. Appl. Phys.* **114**, 154103 (2013).
- <sup>8</sup>J. K. Kim, S. S. Kim, W. J. Kim, A. S. Bhalla, and R. Guo, *Appl. Phys. Lett.* **88**, 132901 (2006).
- <sup>9</sup>T. D. Rao, T. Karthik, and S. Asthana, *J. Rare Earths* **31**(4), 370 (2013).
- <sup>10</sup>T. D. Rao, T. Karthik, A. Srinivas, and S. Asthana, *Solid State Commun.* **152**, 2071 (2012).
- <sup>11</sup>W. Weia, H. C. Xuan, L. Wang, Y. Zhang, K. Shen, D. H. Wang, T. Qiu, and Q. Xu, *Physica B* **407**, 2243 (2012).
- <sup>12</sup>T. D. Rao, A. Kumari, M. K. Niranjan, and S. Asthana, *Physica B* **448**, 267 (2014).
- <sup>13</sup>S. Yasui, H. Uchida, H. Nakai, K. Nishida, H. Funakubo, and S. Koda, *Appl. Phys. Lett.* **91**, 022906 (2007).
- <sup>14</sup>Y. F. Cui, Y. G. Zhao, L. B. Luo, J. J. Yang, H. Chang, M. H. Zhu, D. Xie, and T. L. Ren, *Appl. Phys. Lett.* **97**, 222904 (2010).
- <sup>15</sup>J. S. Park, Y. J. Yoo, J. S. Hwang, J.-H. Kang, B. W. Lee, and Y. P. Lee, *J. Appl. Phys.* **115**, 013904 (2014).
- <sup>16</sup>M. A. Basith, O. Kurni, M. S. Alam, B. L. Sinha, and B. Ahmmad, *J. Appl. Phys.* **115**, 024102 (2014).
- <sup>17</sup>Reetu, A. Agarwal, S. Sanghi, Ashima, and N. Ahlawat, *J. Appl. Phys.* **113**, 023908 (2013).
- <sup>18</sup>J. A. Kerr, in *CRC Handbook of Chemistry and Physics*, 81st ed. (CRC Press, Boca Raton, Florida, USA, 2000).
- <sup>19</sup>T. D. Rao, R. Ranjith, and S. Asthana, *J. Appl. Phys.* **115**, 124110 (2014).
- <sup>20</sup>I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, *Phys. C* **15**, 4835 (1982).
- <sup>21</sup>J. Rodrigues-Carvajal, FULLPROF: A Rietveld Refinement and Pattern Matching Analysis Program, Laboratoire Leon Brillouin, CEA-CNRS, France, 2000.
- <sup>22</sup>C. F. Chung, J. P. Lin, and J. M. Wu, *Appl. Phys. Lett.* **88**, 242909 (2006).
- <sup>23</sup>R. Haumont, J. Kreisel, P. Bouvier, and F. Hippert, *Phys. Rev. B* **73**, 132101 (2006).
- <sup>24</sup>H. Fukumura, H. Harima, K. Kisoda, M. Tamada, Y. Noguchi, and M. Miyayama, *J. Magn. Magn. Mater.* **310**, 367 (2007).
- <sup>25</sup>M. K. Singh, S. Ryu, and H. M. Jang, *Phys. Rev. B* **72**, 132101 (2005).
- <sup>26</sup>G. L. Yuan, S. W. Or, and H. L. W. Chan, *J. Appl. Phys.* **101**, 064101 (2007).
- <sup>27</sup>Z. Quan, W. Liu, H. Hu, S. Xu, B. Sebo, G. Fang, M. Li, and X. Z. Zhao, *J. Appl. Phys.* **104**, 084106 (2008).
- <sup>28</sup>E. C. Stoner, *Rep. Prog. Phys.* **13**, 83 (1950).
- <sup>29</sup>L. Zhai, Y. G. Shi, S. L. Tang, L. Y. Lv, and Y. W. Du, *J. Phys. D: Appl. Phys.* **42**, 165004 (2009).
- <sup>30</sup>P. C. Sati, M. Arora, S. Chauhan, S. Chhoker, and M. Kumar, *J. Appl. Phys.* **112**, 094102 (2012).
- <sup>31</sup>M. K. Singh, W. Prellier, M. P. Singh, R. S. Katiyar, and J. F. Scott, *Phys. Rev. B* **77**, 144403 (2008).
- <sup>32</sup>Z. P. Chen, C. Wang, T. Li, J. H. Hao, and J. C. Zhang, *J. Supercond. Novel Magn.* **23**, 527 (2010).
- <sup>33</sup>D. Kothari, V. Raghavendra Reddy, A. Gupta, V. Sathe, A. Banerjee, S. M. Gupta, and A. M. Awasthi, *Appl. Phys. Lett.* **91**, 202505 (2007).
- <sup>34</sup>S. Saxin and C. S. Knee, *J. Solid State Chem.* **184**, 1576 (2011).
- <sup>35</sup>M. A. Ahmed and S. I. El-Dek, *Mater. Lett.* **60**, 1437 (2006).
- <sup>36</sup>O. D. Jayakumar, S. N. Achary, K. G. Girija, A. K. Tyagi, C. Sudakar, G. Lawes, R. Naik, J. Nisar, X. Peng, and R. Ahuja, *Appl. Phys. Lett.* **96**, 032903 (2010).
- <sup>37</sup>G. L. Yuan, S. W. Or, J. M. Liu, and Z. G. Liu, *Appl. Phys. Lett.* **89**, 052905 (2006).
- <sup>38</sup>A. Kumar and D. Varshney, *Ceram. Int.* **38**, 3935 (2012).
- <sup>39</sup>K. Fujii, H. Kato, K. Omoto, M. Yashima, J. Chen, and X. R. Xing, *Phys. Chem. Chem. Phys.* **15**, 6779 (2013).
- <sup>40</sup>J.-B. Li, G. H. Rao, Y. Xiao, J. K. Liang, J. Luo, G. Y. Liu, and J. R. Chen, *Acta Mater.* **58**, 3701 (2010).
- <sup>41</sup>J. R. Macdonald, *Impedance Spectroscopy: Emphasizing Solid-State Material and Systems* (Wiley, New York, 1987), chap. 2 and 4.
- <sup>42</sup>A. Singh, R. Chatterjee, S. K. Mishra, P. S. R. Krishna, and S. L. Chaplot, *J. Appl. Phys.* **111**, 014113 (2012).
- <sup>43</sup>S. Sarangi, T. Badapanda, B. Behera, and S. Anwar, *J. Mater. Sci. - Mater. Electron.* **24**, 4033 (2013).