Multiferroic properties of Bi 1 ∕ 2 Sr 1 ∕ 2 Fe O 3

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Multiferroic properties of $Bi_{1/2}Sr_{1/2}FeO_3$

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Polycrystalline $Bi_{1/2}Sr_{1/2}FeO_3$ was synthesized by solid state reaction method. Powder x-ray diffraction pattern of the sample was fitted using a noncentrosymmetric rhombohedral crystal system of space group $R3c$. The sample was found to be free from any secondary phases. This single phase material exhibits simultaneously ferrimagnetism and ferroelectricity with magnetic and electrical Curie transitions at $T_{CM} = 745$ K and $T_{CE} = 465$ K, respectively. Origin of this spontaneous magnetic order is discussed using the superexchange interaction between Fe ions. The observed ferroelectric polarization is explained based on the spontaneous ordering of $6s^2$ lone pair electrons of Bi^{3+} ions and a possible coexistence of charge-ordering of site- and bond-centered types. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3061746]

I. INTRODUCTION

Recently, there has been intense search for single phase materials exhibiting two or all the three ferroic (ferromagnetic, ferroelectric, and ferroelastic) properties simultaneously, known as multiferroics.[1] However the definition of multiferroics is flexible to adapt antiferroic order as well.[2] The attracting feature of the multiferroic materials is the coupling between their order parameters. This enables manipulation of the magnetic and electric polarizations by electric and magnetic fields, respectively. This is known as the magnetoelectric (ME) effect.[3] However, most of the existing single-phase ME multiferroics, e.g., $BiMnO_3$,[4] do not exhibit ME effect at room temperature. Bismuth ferrite ($BiFeO_3$) is a ferroelectric with relatively high ferroelectric Curie temperature ($T_{CE} \sim 1103$ K) and an antiferromagnet with high Néel temperature ($T_N \sim 643$ K). Ferroelectricity in this compound is due to the spontaneous ordering of $6s^2$ lone pair electrons of Bi^{3+} ions. Its G-type antiferromagnetic ordering is modulated by spiral spin structure of long wavelength of ~ 620 Å. Hence, it possess a weak ferromagnetism;[5,6] but its linear ME effect is inhibited. Due to its high transition temperature and the possibility to suppress this spiral spin structure many solid solutions based on $BiFeO_3$ have been investigated.[7–9] For example, Das *et al.*[10] observed enhanced ferroelectric and ferromagnetic properties in La modified $BiFeO_3$ ceramics.

We investigated the possibility of multiferroism at room temperature in 50% Sr substituted $BiFeO_3$. In this bismuth strontium ferrite, $Bi_{1/2}Sr_{1/2}FeO_3$, the Fe ions take two mixed valence states that might lead to a possible charge ordering (CO) similar to the one observed in $Bi_{1/2}Sr_{1/2}MnO_3$.[11] In this paper we present the structural, magnetic, and ferroelectric properties of polycrystalline $Bi_{1/2}Sr_{1/2}FeO_3$. This material exhibits simultaneously ferrimagnetism and ferroelectricity at room temperature. To our knowledge, this is the first report on the multiferroism of $Bi_{1/2}Sr_{1/2}FeO_3$.

II. EXPERIMENTAL DETAILS

Polycrystalline $Bi_{1/2}Sr_{1/2}FeO_3$ powder sample was prepared using the reagents (all from Sigma-Aldrich) Bi_2O_3 (99.999%), $SrCO_3$ (99.9+%), and Fe_3O_4 (99.99%) by standard solid state reaction method. An excess quantity of Bi_2O_3 (5 wt %) was added to the stoichiometric proportion of these starting materials in order to compensate the Bi evaporation during heat treatment of the mixed reagents.[12] This mixture was heated first at 873 K for 12 h. Final heat treatment was performed at 1123 K for 24 h with intermediate grinding to get good homogeneity. The pellet used for ferroelectric studies was sintered at 1123 K for 12 h. The powder x-ray diffraction (XRD) data of the sample were collected using (PANalytical X'Pert Pro) x-ray diffractometer with Cu $K\alpha$ radiation. Crystal structure refinements were carried out using General Structure Analysis System (GSAS).[13] Magnetization data were collected using a vibrating sample magnetometer. Morphology and element analysis, of the pellet used to study the ferroelectric properties of the sample, were carried out using scanning electron microscope (SEM) and energy dispersive x-ray (EDX) analysis, respectively. Ferroelectric hysteresis loops at different temperatures were recorded using a homemade setup based on Sawyer–Tower circuit.[14]

III. RESULTS AND DISCUSSION

A. Crystal structure analysis

Figure 1(a) shows the results of the Rietveld refinements of the XRD data of $Bi_{1/2}Sr_{1/2}FeO_3$. The refinements were carried out using the rhombohedral crystal system with noncentrosymmetric $R3c$ space group. The difference profile (Diff.) between the observed (Obs.) and calculated (Calc.) diffraction patterns is shown at the bottom of the plot. A good fit was obtained with R factors $R_{wp} = 3.51\%$, $R_p = 2.66\%$, and $\chi^2 = 1.764$. The refined lattice constants and volume of the unit cell are $a = 5.5833$ Å, $c = 13.6837$ Å, and $V = 369.42$ Å^3, respectively. The point group $3m$ of $R3c$ is noncentrosymmetric which allows the existence ferroelec-
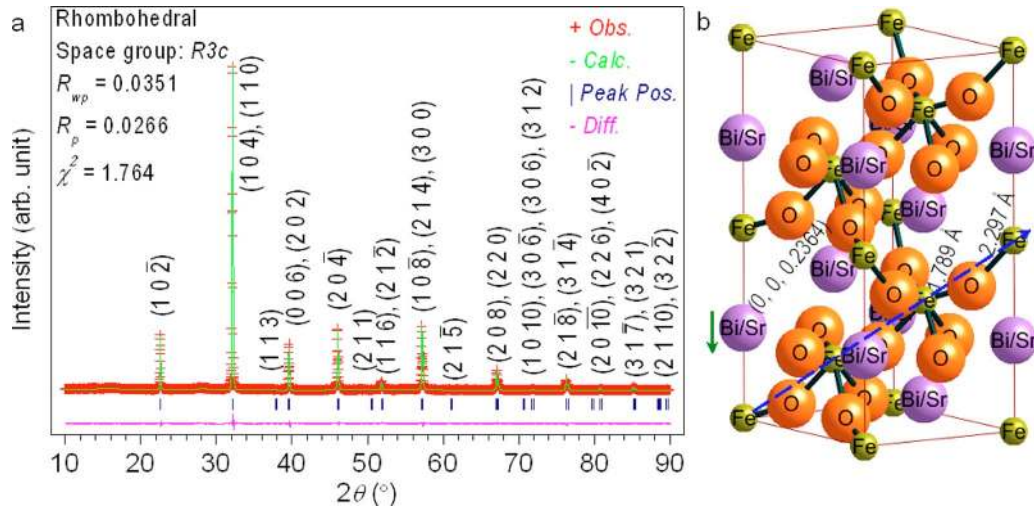
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FIG. 1. (Color online) (a) Results of this Rietveld analysis of the XRD pattern of $Bi_{1/2}Sr_{1/2}FeO_3$. The difference between the observed pattern (Obs.) and the calculated pattern (Calc.) is shown below these Obs. and Calc. patterns. Peak positions (Peak Pos.) are marked by small vertical lines. (b) Crystal structure of $Bi_{1/2}Sr_{1/2}FeO_3$. The dashed arrow mark indicate the [1−1 0.5] direction. The solid arrow indicates a typical downward displacement of Bi^{3+} ions along the c axis.

tricity in the sample as in the case of its parent compound $BiFeO_3$. Figure 1(b) shows the unit cell of $Bi_{1/2}Sr_{1/2}FeO_3$ which was plotted by CRYSTALMAKER 2.0 using a crystallographic information file (.cif) created by GSAS. There are two kinds of Fe–O bonds with bond lengths of 1.789 and 2.297 Å [which appear alternatively along the [1−1 0.5] direction as indicated by a dashed arrow in Fig. 1(b)]. Comparing these values with the calculated bond lengths of 1.855 and 2.180 Å of Fe–O bonds of 5+ and 2+ ionic states of Fe using Shannon's table of effective ionic radii,[15] we find that the Fe ions in this compound are in the Fe^{2+} and Fe^{5+} states. This is compatible with the 50% replacement of Bi^{3+} by Sr^{2+}. That is, instead of 50% Fe^{3+} and 50% Fe^{4+} as one would normally expect we have 50% Fe^{2+} and 50% Fe^{5+} ions. It is noteworthy here that the existence Fe ions in 5+ oxidation state had been confirmed using Mössbauer spectra in $La_{0.5}Ca_{0.5}FeO_{3-\delta}$ at temperatures ⩽175 K by Liang *et al.*[16] and at room temperature in $La_{1-x}Sr_{1-x}FeO_{3-\delta}$ by Dann *et al.*[17]

B. Morphology and element analysis

A well polished pellet sample was used for morphology and element analysis. Figure 2 shows EDX data collected from this sample, which indicate the presence of the elements Bi, Sr, Fe, and O. The inset of Fig. 2 (table) shows the elemental composition of the pellet. The elemental composition or atomic percentage (at. %) obtained from the EDX analysis is consistent with the stoichiometry 0.5:0.5:1:3 of the elements Bi, Sr, Fe, and O. From the color contrast of the SEM images taken at various regions with different magnifications, EDX analysis, and results of Rietveld analysis of the XRD data, we find that the sample is free from secondary phases.

C. Magnetic properties

The field dependent magnetization of $Bi_{1/2}Sr_{1/2}FeO_3$ exhibits a clear hysteresis loop as shown in Fig. 3. The magnetization shows a maximum magnetization value of ∼1.32 emu/g and no tendency to saturate up to the maximum applied filed of 1.5 T. We find a remanent magnetization of M_r=0.534 emu/g and a coercivity of H_c=0.21 T. The inset of Fig. 4 shows the temperature dependent magnetization for the applied field of 0.1 T. As the temperature is
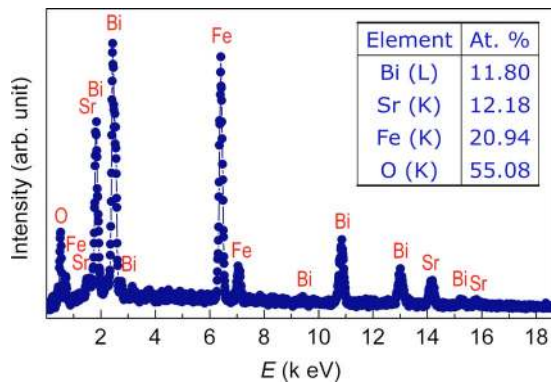

FIG. 2. (Color online) EDX data indicating the elements present in the sample. Inset: the elemental composition (table) of the polished pellet.
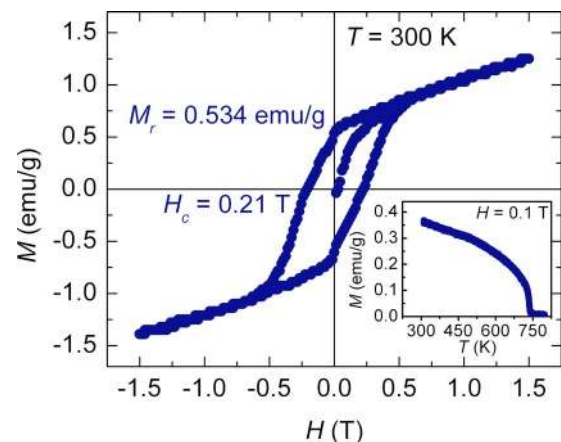

FIG. 3. (Color online) Field dependent magnetization at 300 K. Inset: temperature dependent magnetization, indicating magnetic Curie transition at T_{CM}=745 K of $Bi_{1/2}Sr_{1/2}FeO_3$.
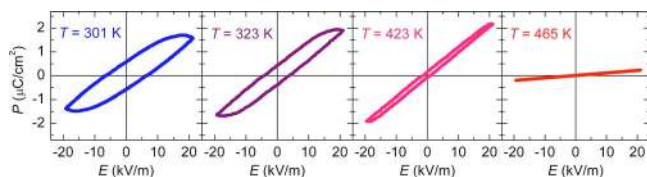
FIG. 4. (Color online) Ferroelectric hysteresis loop of $Bi_{1/2}Sr_{1/2}FeO_3$ at different temperatures recorded using a triangle wave with $V_{p.p}$=20.5 V. At T=465 K the hysteresis loop disappears and the sample becomes paraelectric.

increased the magnetization decreases gradually followed by a sudden drop at 745 K and the sample becomes a paramagnet. This magnetic order in this sample is expected due to the superexchange interaction between Fe^{2+} and Fe^{5+} ions supported by the Fe–O bond lengths which were discussed in Sec. III A. Therefore, the sample is a ferrimagnet with magnetic Curie temperature T_{CM}=745 K.

D. Ferroelectric properties

The possible hopping of electrons from one Fe ion to the next nearest neighbors [as shown by the dashed arrow in Fig. 1(a)] is prevented by their antiparallel alignment of the spin. Hence, the sample offers relatively large electrical resistivity of $\sim 1.23 \times 10^6$ Ω cm when compared to that of $Bi_{1/2}Sr_{1/2}MnO_3$, at room temperature.[18] A 50 Hz triangular wave (Ref. 14) of peak to peak voltage $V_{p.p}$=20.5 V was used to trace the ferroelectric hysteresis loops. Figure 4 shows the hysteresis loops traced at different temperatures. At 301 K the sample exhibited a maximum of 1.69 μC/cm^2 polarization corresponding to the applied electric field of 18.28 kV/m. As the temperature of the sample was raised the area enclosed by the loop decreased. At 465 K this hysteresis loop disappeared completely and the polarization became linear with the electric field; essentially that is the ferroelectric Curie temperature (T_{CE}). The observed ferroelectric character of the sample is expected to originate from the spontaneous ordering of the $6s^2$ lone pair electrons of Bi^{3+} ions as in the case of $BiFeO_3$,[19] $BiMnO_3$,[20] and a possible CO of the Fe ions.[21,22] The former mechanism is evident from the downward displacement of Bi by 0.1623 Å [as shown by a solid arrow in Fig. 1(b)] along the c axis of the crystal structure. That is none of the Bi ions in the structure sit exactly at the middle point of two successive Fe ions along the c axis; this is evident from the fractional coordinates (0, 0, 0.2364) of Bi. In addition to this, a ferrimagnetic structure with G-type antiparallel spin coupling is possible when there is a CO of Fe^{2+} and Fe^{5+} ions associated with it. Also, the bond lengths are varying to a large extent from the calculated lengths of Fe^{2+}–O^{2-} and Fe^{5+}–O^{2-} bonds. This implies that the CO cannot be mere site-centered ordering (SCO). Rather it is, possibly, a combination of SCO and bond-centered ordering which give raise to a net electric dipole moment and hence the ferroelectric polarization as proposed by Efremov et al.[23] Thus, $Bi_{1/2}Sr_{1/2}FeO_3$ is a ferroelectric with T_{CE}=465 K.

IV. CONCLUSION

Single-phase, polycrystalline $Bi_{1/2}Sr_{1/2}FeO_3$ prepared by solid state reaction method was found to crystallize in rhombohedral crystal system of noncentrosymmetric space group $R3c$. This sample is ferrimagnetic with T_{CM}=745 K and ferroelectric with T_{CE}=465 K. While the ferrimagnetism is due to the super-exchange interaction between Fe^{2+} and Fe^{5+} ions, the ferroelectricity originates from the spontaneous ordering of $6s^2$ lone pair electrons of Bi^{3+} ions and a combined site- and bond-centered charge-ordering of Fe^{2+} and Fe^{5+} ions. Thus, $Bi_{1/2}Sr_{1/2}FeO_3$ is a material exhibiting multiferroism at room temperature.

[1]N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[2]W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[3]M. Fiebig, J. Phys. D **38**, R123 (2005).
[4]T. Kimura, S. Kawamoto, I. Yamada, M. Azuma, M. Takano, and Y. Tokura, Phys. Rev. B **67**, 180401(R) (2003).
[5]I. Sosnowskat, T. Peterlin-Neumaier, and E. Steichele, J. Phys. C **15**, 4835 (1982).
[6]S. T. Zhang, M. H. Lu, D. Wu, Y. F. Chen, and N. B. Ming, Appl. Phys. Lett. **87**, 262907 (2005).
[7]D. Kothari, V. Raghavendra Reddy, A. Gupta, V. Sathe, A. Banerjee, S. M. Gupta, and A. M. Awasthi, Appl. Phys. Lett. **91**, 202505 (2007).
[8]V. A. Khomchenko, D. A. Kiselev, J. M. Vieira, Li Jian, A. L. Kholkin, A. M. L. Lopes, Y. G. Pogorelov, J. P. Araujo, and M. Maglione, J. Appl. Phys. **103**, 024105 (2008).
[9]D. H. Wang, W. C. Goh, M. Ning, and C. K. Ong, Appl. Phys. Lett. **88**, 212907 (2006).
[10]S. R. Das, R. N. P. Choudhary, P. Bhattacharya, R. S. Katiyar, P. Dutta, A. Manivannan, and M. S. Seehra, J. Appl. Phys. **101**, 034104 (2007).
[11]J. L. García-Muñoz, C. Frontera, M. A. G. Aranda, A. Llobet, and C. Ritter, Phys. Rev. B **63**, 064415 (2001).
[12]S.-T. Zhang, H.-W. Cheng, Y.-F. Chen, C.-H. Song, J. Wang, Y.-D. Xia, X.-N. Zhao, Z.-G. Liu, and N.-B. Ming, Solid State Commun. **130**, 235 (2004).
[13]A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748, 1994.
[14]A. M. Glazer, P. Groves, and D. T. Smith, J. Phys. E **17**, 95 (1984).
[15]R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).
[16]Y.-Q. Liang, N.-L. Di, and Z.-H. Cheng, Phys. Rev. B **72**, 134416 (2005).
[17]S. E. Dann, D. B. Currie, M. T. Weller, M. F. Thomas, and A. D. Al-Rawws, J. Solid State Chem. **109**, 134 (1994).
[18]C. Frontera, J. L. García-Muñoz, A. Llobet, M. A. G. Aranda, C. Ritter, M. Respaud, and J. Vanacken, J. Phys.: Condens. Matter **13**, 1071 (2001).
[19]P. Baettig, C. Ederer, and N. A. Spaldin, Phys. Rev. B **72**, 214105 (2005).
[20]T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Syono, J. Solid State Chem. **145**, 639 (1999).
[21]C. Ederer and N. A. Spaldin, Nature Mater. **3**, 849 (2004).
[22]S. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007).
[23]D. V. Efremov, J. van den Brink, and D. Khomskii, Nature Mater. **3**, 853 (2004).