Evidence of Magnetoelectric coupling in Bi$_{2(1-x)}$Ho$_{2x}$Fe$_4$O$_9$ (x=0, 0.01) multiferroic ceramics

S R Mohapatra$^1$, A K Singh$^1$, S D Kaushik$^2$

$^1$Department of Physics and Astronomy, National Institute of Technology, Rourkela-769008, Odisha, India.

$^2$UGC-DAE Consortium for Scientific Research Mumbai Centre, R-5 Shed, BARC, Mumbai-400085, India.

Corresponding author Email : singhanil@nitrkl.ac.in

Abstract: We report structural, magnetic, dielectric and magnetoelectric properties of orthorhombic Bi$_{2(1-x)}$Ho$_{2x}$Fe$_4$O$_9$ (x=0, 0.01) ceramics (space group ‘Pbam’) synthesized by conventional solid state reaction route. Rietveld refined X-ray diffraction (XRD) shows phase formation of the samples along with reduction in lattice parameters and cell volume due to lower ionic radii substitution of Ho$^{3+}$ at Bi$^{3+}$-site. DC magnetization study revealed antiferromagnetic transition (T$_N$) of the parent (BFO = 250 K) as well as 1% Ho substituted sample (BHFO1 = 253 K) along with increase in magnetization. Opening of hysteresis was observed for BHFO1 sample implying onset of weak ferromagnetism with dominating antiferromagnetic behaviour. Moreover, temperature dependent dielectric (ε’) study and its derivative (dε’/dT) for both the samples show significant anomaly around the antiferromagnetic transition (T$_N$) thus, implying a plausible magnetoelectric coupling between the magnetic as well as the electric order parameters in the studied samples. Magnetoelectric coupling was also confirmed from temperature and magnetic field (1.3 T) dependant tan loss plots.

Keywords: Rietveld refinement, Dielectric, Magnetization, Magnetodielectric.

1. Introduction
The quest for developing near room temperature magnetoelectric materials draws a considerable attention in the research community because of its rich technological applicability in developing pioneering devices [1-4]. These magnetoelectric materials exhibits magnetoelectric (ME) coupling usually defined as the coupling between the (ferro) magnetic and electrical ordering [4]. However, near room temperature ME materials are very rare in nature due to the incompatibility between these order parameters [3]. The compound of our interest is Bi$_2$Fe$_4$O$_9$ (BFO), a well-known near room temperature ME material has gained substantial interest in the past few years owing to its rich potential applications [5-7]. Ressouche et al. [8] has reported that a unit cell of BFO contains tetrahedrally and octahedrally coordinated Fe$^{3+}$ ions where the competing exchange interaction among various Fe$^{3+}$ ions generates rarely observed peculiar pancake spin frustration. Also, BFO shows antiferromagnetic (AFM) transition at T$_N$ ~260 K and displays ferroelectric hysteresis loop along with novel ME coupling in the vicinity of T$_N$. Further, urge for improving its multiferroicity and tune its ME coupling, several chemical substitution has been done at A and B-site of BFO [9].

In the present work, for the first time we introduce Ho$^{3+}$ substituted BFO sample using solid state route. Here, we report the effect of Ho$^{3+}$ (1.01 Å) substitution at Bi$^{3+}$ (1.17 Å) site of BFO in context to its crystal structure, magnetic and dielectric properties. Moreover, enhanced magnetization along with
evidence of possible ME coupling that extends close to room temperature has been explored due to 1% Ho$^{3+}$ substitution in BFO.

2. Materials and methods
The polycrystalline $\text{Bi}_2(1-x)\text{Ho}_x\text{Fe}_4\text{O}_9$ ($x = 0, 0.01$) samples were prepared using high purity chemicals namely $\text{Bi}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$ and $\text{Ho}_2\text{O}_3$ using solid state reaction route (SSR). The raw materials were calcined at 800 °C for 12 h followed by sintering at 850 °C for 10 h. The phase formation was confirmed by room temperature X-ray diffraction (XRD) study, RIGAKU, JAPAN using Cu-Kα radiation ($\lambda = 1.5405$ Å). Temperature dependant dielectric measurement was done using High precession impedance analyzer (Wayne Kerr 6500B) coupled with closed cycle refrigerator (Cryo-Industries of America, USA). Finally, magnetization measurement was carried out using 9T reliquefier based Physical Property Measurement System (PPMS)-Vibrating Sample Magnetometer (Quantum Design).

3. Result and Discussion
Rietveld refined XRD pattern of BFO (parent) and 1% Ho doped BFO (BHFO1) is shown in figure 1. All the major diffracted peaks are found to crystallize in orthorhombic structure with space group ‘Pbam’. The diffracted peaks are also consistent with the standard data (JCPDS no. 25-0090). The lattice parameters obtained using FULLPROF refinement are as follows: $a = 7.9735(2)$ Å, $b = 8.4414(4)$ Å, $c = 6.0028(5)$ Å, volume = 404.033(4) Å$^3$ for BFO and $a = 7.9733(5)$ Å, $b = 8.4412(2)$ Å, $c = 6.0027(2)$ Å, volume = 404.007(4) Å$^3$ for BHFO1. However, we observe decrease in lattice parameters due to 1% Ho doping along with the shifting of (002) and (220) peaks to higher angles (not shown here). This feature can be explained on the basis of lower ionic radii Ho$^{3+}$ (1.01 Å) substitution at the higher ionic radii Bi$^{3+}$ ions (1.17 Å).

Figure 1. Room temperature Rietveld refined XRD pattern of (a) BFO and (b) BHFO1

Figure 2 depicts the temperature dependant DC magnetic susceptibility of BFO and BHFO1 samples under an external field of 1 kOe. It is observed that both the samples show no signature of irreversibility in ZFC-FCW plot clearly signifying no signature of cluster or spin glass in the samples. A broad cusp around 250 K is noticed in the BFO typically revealing the antiferromagnetic (AFM) behaviour and is similar to our previous reported data [10]. Contrastingly, a much broader shoulder is observed in case of BHFO1 with a very small hump around 253 K (inset of figure 2 (b)). Further, on studying the isothermal magnetization (M-H) plots of parent and substituted sample, the M-H plot shows contrasting behaviour as illustrated in figure 2 (c, d). The M-H plot for both the samples were carried out at 240 K, 280 K and 320 K up to a maximum field of ±20 kOe. BFO shows a linear behaviour of magnetization relating its AFM characteristics as discussed above. Instead, BHFO1 shows opening of a small hysteresis curve at low field region which later follows a linear path on increasing the field. This is a
typical characteristic feature of superposition of AFM and weak ferromagnetism (FM) where the later has a substantial effect on the enhanced magnetic properties. At 320 K, the values of remnant magnetization (Mr) and coercive field (Hc) are 0.0117 emu/gm and 90 Oe respectively for BHFO1, subsequently confirming onset of weak FM even at room temperature.

![Figure 2. ZFC-FCW magnetization of (a) BFO and (b) BHFO1 at 1 kOe. Inset shows M-H plot of (c) BFO and (d) BHFO1 at selected temperatures](image)

Now, we try to explore the existence of any coupling between magnetic and electric order parameters. This fact can be proved by observing any anomalies in the dielectric data in the vicinity of magnetic transitions ($T_N$), often defined as the magnetoelectric (ME) coupling [1]. Figure 3 shows the temperature dependant real part of dielectric constant ($\varepsilon'$) of BFO and BHFO1 along with the derivative plot of the same at 12 kHz. Here, we observe a change in slope or a concomitant anomaly in $\varepsilon'$ for both the samples which exactly matches with the peak obtained in the $d\varepsilon'/dT$ plot of the same. Interestingly, this anomaly happens to be at same temperature matching with $T_N$. This demonstrates a plausible coupling of both magnetic as well as (di)electric order parameters. The peak for BFO is obtained at 250 K whereas BHFO1 shows the peak at 253 K (shown in figure 3 with dotted circle). Thus, slight Ho substitution (1%)has a substantial effect of enhancing magnetization as well as magnetic transition temperature ($T_N$) along with a clear evidence of ME coupling.

![Figure 3. Temperature dependence of dielectric constant (a) BFO and (b) BHFO1 at 12 kHz](image)
Figure 3. Temperature dependant $\varepsilon'$ study of (a) BFO and (b) BHFO1 sample at 12 kHz and $d\varepsilon'/dT$ versus T (K) plot of (c) BFO and (d) BHFO1

Furthermore, the existence of ME coupling in the material is confirmed from the temperature (150 K-310 K) and magnetic field (1.3 T) dependant tan loss plot as shown in figure 4. An S-shape anomaly is seen in both the cases along with distinguished separation of peaks (broad shoulder) due to application of 1.3 T field which clearly reveals the evidence of strong coupling in the sample. Also, the change in slope (marked by a black arrow) due to 1.3 T field is seen near the vicinity of magnetic transition as well as the peaks obtained in $d\varepsilon'/dT$ plot. For comprehensive understanding of ME coupling or magnetodielectric (MD) effect and their variation due to substitution, one needs to probe field and temperature dependant ME/MD study, which we shall study in near future.

Figure 4. Variation of temperature dependant tan loss at zero external field and 1.3 T for (a) BFO and (b) BHFO1

4. Conclusion

In summary, we have synthesized polycrystalline $\text{Bi}_{2(1-x)}\text{Ho}_{2x}\text{Fe}_4\text{O}_9$ (x=0, 0.01) using SSR and subsequently investigated its crystal structure, magnetic and dielectric properties. Enhanced magnetization along with a weak FM is observed in the modified sample from M-H study. Slight substitution (1%) induced $T_N$ to increase from 250 K (BFO) to 253 K (BHFO1). Significant anomalies in $\varepsilon'$ and tan loss around $T_N$ unambiguously establishes the existence of ME coupling between the electric and magnetic order parameters in this material. Future study of magnetic field dependant dielectric behavior and temperature dependent neutron diffraction will further enable us to understand the microscopic origin of magnetoelectric coupling in a much better way.

5. Acknowledgement

We acknowledge Board of Research in Nuclear Science (BRNS), Mumbai (Sanction No: 2012/37P/40/BRNS/2145), Department of Science and Technology (DST), New Delhi (Sanction No: SR/FTP/PS-187/2011) and UGC-DAE-CSRMumbai (Sanction No: CRS-M-187,225) for funding. SRM is thankful to BRNS for financial assistance.

Reference

[1] Erenstein W, Mathur ND, Scott JF 2006 Nature442 759.
[2] Khomskii D 2009 Physics2 20.
[3] Hill NA 2000 J. Phys. Chem. B 104 6694.
[4] Fiebig M 2005 J. Phys. D: Appl. Phy.38 R123.
[5] Mohapatra SR, Sahu B, Badapanda T, Pattanaik MS, Kaushik SD, Singh AK 2016 *J Mater Sci: Mater Electron* **27** 3645.

[6] Singh AK, Kaushik SD, Kumar Brijesh, Mishra PK, Venimadhav A, Siruguri V, Patnaik S 2008 *Appl. Phys. Lett.* **92** 132910.

[7] Shamir N, Gurewitz E 1978 *Acta Crystallogr. Sect. A* **34** 662.

[8] Ressouche E, Simonet V, Canals B, Gospodinov M, Skumryev V 2009 *Phys. Rev. Lett.* **103** 267204.

[9] Mohapatra SR, Sahu B, Chandrasekhar M, Kumar P, Kaushik SD, Rath S, Singh AK 2016 *Ceram. Int.* **42** 12352.

[10] Mohapatra SR, Swain A, Yadav CS, Kaushik SD, Singh AK 2016 *RSC Adv.* **6** 112282.