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XRD and Mössbauer spectroscopy study of Ho doped $BiFeO_3$

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Abstract The structural and magnetic properties of Ho substituted $BiFeO_3$ (BHFO) have been investigated using ^{57}Fe Mössbauer spectroscopy and X-Ray diffraction (XRD) as a function of temperature. The Mössbauer spectrum obtained at room temperature for the as-synthesized BHFO sample exhibits broadened features due to the hyperfine field distributions related to the local variation of the neighbourhood of Fe and the magnetic hyperfine splitting patterns are indicative of magnetic ordering, mostly probably screwed or slightly antiferromagnetic. The spectrum was fitted with two superimposed asymmetric sextets, with similar hyperfine magnetic fields of $B_{hf1} = 48.0(1)$ T and $B_{hf2} = 49.0(1)$ T, corresponding to rhombohedral BFO. The hyperfine fields of the magnetic components decreased systematically with increasing temperature to a 'field distribution' just below the Néel temperature, $T_N \sim 600$ K. At temperatures above 600 K, the spectral line associated with the $Bi_{25}FeO_{40}$ impurity phase dominates the spectra. This phase is confirmed by XRD measurements. From

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the temperature dependence of the site populations of the spectral components an average Debye temperature of $\theta_D = 240(80)$ K has been estimated.

Keywords Mössbauer spectroscopy · X-ray diffraction · Ferromagnetic · Paramagnetic

1 Introduction

$BiFeO_3$ (BFO) has been reported to have a rhombohedral distorted perovskite structure [1] corresponding to the $R3c$ group with unit cell parameters of $\mathbf{a} = 3.96$ Å and $\alpha = 89°28'$, with Fe^{3+} and Bi^{3+} ions displaced along the (111) direction. The space group $R3c$ allows for both ferroelectric atomic displacements [2] and weak ferromagnetism below the Néel temperature (T_N), which has been observed to be around 640 K. The doping of BFO with lanthanide elements like Ho with a radius smaller than Bi can result in structural distortions of the lattice that can enhance the ferroelectric and magnetic properties of BFO [3]. Here we report on the temperature dependence of the structural and magnetic properties of BHFO which has been investigated by Mössbauer spectroscopy and X-Ray diffraction.

2 Experimental

BHFO bulk ceramics ($Bi_{1.15}Ho_{0.05}FeO$) were synthesized by the solid state reaction method at the Institute of Material Science, Acharya Vihar, India [4]. Cylindrical pellets of 13 mm diameter and 2 mm thickness were prepared under a pressure of 9.8×10^8 Pa, and then slowly heated (50 °C/h) to 200 °C and maintained for 4 h to release the PVA binder from the pellets using a high temperature programmable controller (EuroTherm 2204) vacuum furnace.

Transmission ^{57}Fe Mössbauer measurements were carried out with a 50 mCi ^{57}Co (Rh) source. Measurements were performed on the BHFO sample sandwiched between two concentric Boron nitride (BN) discs sample holders in a MBF-100 furnace at temperatures up to 750 K.

X-Ray Diffraction (XRD) measurements were conducted on the as-synthesized sample using a Bruker D2 Phaser desktop diffractometer, which employs a sealed tube Cu Kα X-ray source and equipped with a Bruker Lynxeye PSD detector using 2.5° primary and secondary beam radial Soller slits. The sample was loaded by pressing on a zero background silicon single crystal disk supported in a polymer circular sample holder. The XRD patterns were obtained in the 2θ range (10°–90°) at scan steps of $0.020° \text{ min}^{-1}$.

3 Results and discussion

A series of selected Mössbauer spectra obtained on a Ho doped BFO sample as a function of temperature is shown below in Fig. 1. Mössbauer spectrum for the as-synthesized (303 K) BHFO sample was analysed with two broadened sextets, an asymmetric Lorentzian doublet and a single line. The magnetic phase was analysed in terms of two sextets due to line broadening which is a result of the distribution

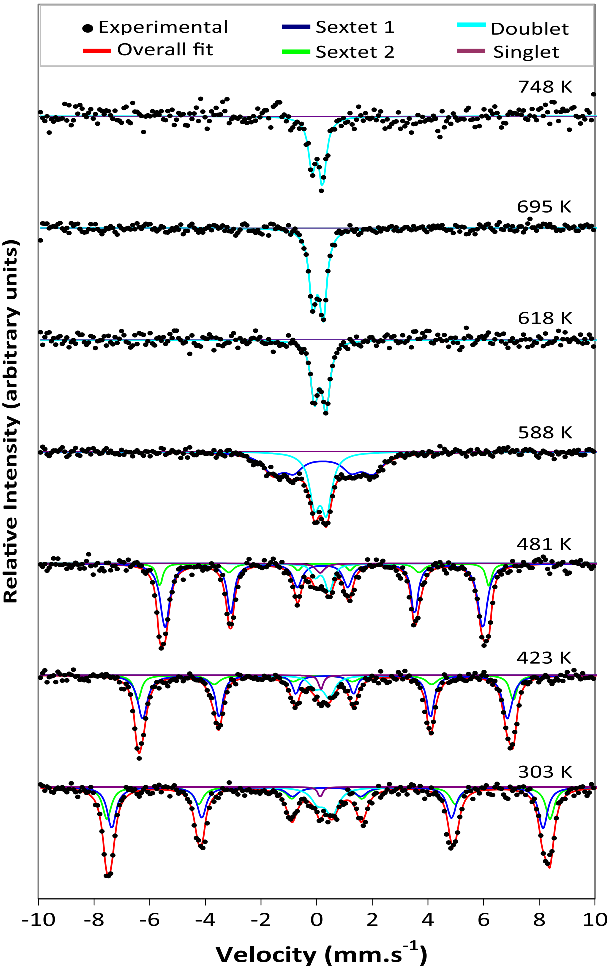


Fig. 1 Selected ^{57}Fe Mössbauer spectra for BHFO observed at the temperatures indicated

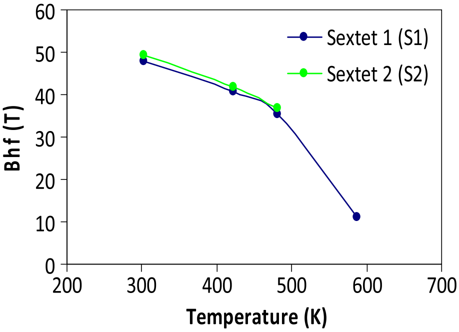
of hyperfine fields. In the initial analysis the isomer shifts for all spectral components showed a linear decrease with temperature, which closely followed the second order Doppler shift, while the quadrupole splitting displayed a $T^{3/2}$ temperature dependence. In the final, simultaneous analysis of the spectra using the software program Vinda (Gunnlaugsson, H.P., 2008–2009, personal communication) both hyperfine parameters were restricted to follow their respective behaviours with increasing temperature. Minor observed misfits to the data can be ascribed to poor statistics which could be attributed to the fact that Bi has a very high absorption coefficient for 14.4 keV Mössbauer gamma-rays.

In the temperature range 300–481 K, the Mössbauer spectra are characterized by inhomogeneous line broadenings which can be accounted for by the magnetic structure of $BiFeO_3$. Table 1 gives a summary of the hyperfine parameters obtained from the Mössbauer measurements for the as-synthesized BHFO sample. The extracted hyperfine parameters of sextet S1 ($B_{\mathrm{hf}} = 48.0(1)$ T, $\delta = 0.37(1)$ mm.s^{-1} and $\Delta E_{\mathrm{Q}} =$

Table 1 Hyperfine parameters obtained from Mössbauer measurements for the as-synthesized BHFO sample

	Sextet 1 (S1)	Sextet 2 (S2)	Doublet (D)	Singlet (SL)
B_{hf} (T)	48.0(1)	49.0(1)	–	–
δ (mm.s^{-1})	0.37(1)	0.40(1)	0.29(4)	0.13(4)
ΔE_Q(mm.s^{-1})	0.03(2)	0.06(2)	0.52(4)	–

Fig. 2 The hyperfine magnetic fields of sextets 1 and 2 as a function of temperature



0.03(2) mm.s^{-1}) are consistent with those of rhombohedral $BiFeO_3$ determined from other studies [1, 5].

The magnetic fields of spectral components S1 and S2 shows a systematic decrease with increasing temperature as shown in Fig. 2, to a ‘field distribution’ from just below 600 K.

Above 600 K, the magnetic components disappear completely from the spectra, and this behaviour is consistent with the results published by Blaauw and Van der Woude [1]. Above the Néel temperature (T_N = 643 K), their spectra were characterized by a quadrupole split doublet, with ΔE_Q = 0.44 to 0.41 mm.s^{-1} in the temperature range 657–788 K.

These results are in good agreement with our data, where at $T > 600$ K, the paramagnetic doublet with hyperfine parameters of δ = 0.14 mm.s^{-1} and ΔE_Q = 0.43 mm.s^{-1} becomes dominant in the spectra. This spectral feature is attributed to the $Bi_{25}FeO_{40}$ impurity phase [6]. The hyperfine parameters of the S1 component are characteristic of magnetically ordered Fe^{3+} due to the presence of hyperfine fields B_{hf} acting on the nuclear spin. The magnetic pattern of S2 component (B_{hf} = 49.0(1) T, δ = 0.40(1) mm.s^{-1} and ΔE_Q = 0.06(2) mm.s^{-1}) is characteristic of an undoped BFO spectrum which is typical of the Fe^{3+} oxidation state. De Sitter et al. [7] performed ^{57}Fe Mössbauer measurements on BFO and fitted the spectra with two superimposed sextets with hyperfine magnetic fields of B_{hf1} = 50.1 T, and B_{hf2} = 49.8 T. These two sites were distinguished from each other by the different ΔE_Q values, which were attributed to the different trigonal distortions of the octahedral environment of both the Fe-sites which results in different q-values.

XRD measurements were performed to identify the various phases in the BHFO sample and also to confirm the Mössbauer findings. The XRD data revealed the presence of the $R3m$ phase, with lattice parameters of a_{rh} = 3.962 Å and α_{rh} = 89.4°. Figure 3 shows a representative XRD pattern obtained for the as-synthesized BHFO sample that reflects contributions from the rhombohedral impurity phase of BFO, a

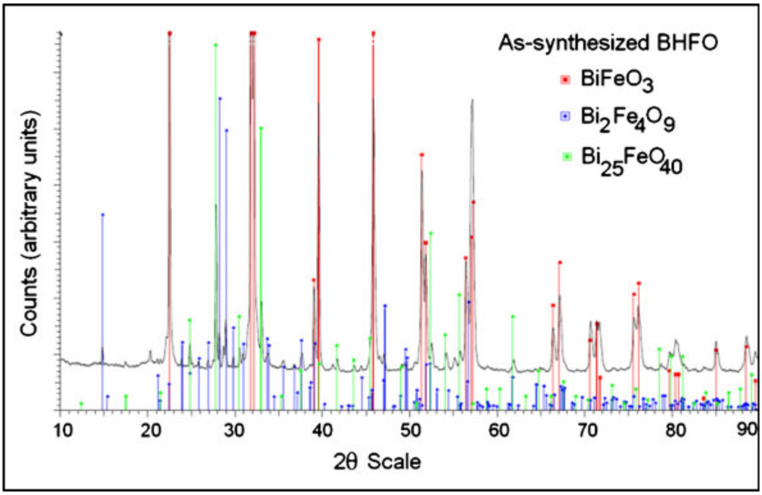


Fig. 3 The fingerprint of different phases for the as-synthesized BHFO sample measured at room temperature. The red lines correspond to the $BiFeO_3$ phase, the blue and green lines to the $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{40}$ impurity phases, respectively

major $Bi_{25}FeO_{40}$ [4, 8, 9] (JCPDS 72–1832) and a minor $Bi_2Fe_4O_9$ phase [10]. The XRD spectrum has been analysed using the finger printing process with a Bruker DiffracPLUS EVA software [11].

Pradhan et al. [4] performed Rietvield analysis on a similar BHFO sample and proposed that these non-perovskite impurity phases are a consequence of the local stoichiometry fluctuations in BFO and were attributed to insufficient reactions between the Bi_2O_3 and Fe_2O_3 powders during the synthesis process.

Previous Mössbauer studies of $BiFeO_3$ and doped systems [6, 8, 12] have shown that the origin of the paramagnetic doublet D is attributed to the $Bi_{25}FeO_{40}$ phase which indicates a disordered and amorphized system [5] and the singlet SL (present at $T < 588$ K) to the $Bi_2Fe_4O_9$ phase. Kothari et al. [13] observed an increasing fraction of the paramagnetic component with increasing Eu doping, but ruled out any contribution from the $Bi_2Fe_4O_9$ phase. The isomer shift and quadrupole splitting values of the paramagnetic doublet D ($\Delta E_Q \sim 0.52$ mm.s^{-1}, $\delta \sim 0.29$ mm.s^{-1}) and SL, ($\delta \sim 0.13$ mm.s^{-1}) determined at RT corresponds to Fe with an oxidation state of 3+. From the measured data, we estimate a Néel temperature for BHFO to be in the range 598–617 K. Our results are in good agreement with neutron diffraction studies performed by Fischer et al. [2], where they determined the Néel temperature of BFO as 595(10) K. A Debye temperature of $\theta_D = 240(80)$ K has been estimated from the site population of spectral components for BFHO, which is lower than the value of 340(50) K that has been previously cited for $BiFeO_3$ [1]. This value has been determined from the temperature dependent resonance area (A) of a given component i according to:

$$A_i(T) = A_0 \cdot p_i(T) \cdot f\left(T, \theta_{D,i}\right)$$

where p_i is the site population $\left(\sum_i p_i(T) = 1\right)$ and f is the Debye-Waller factor, depending on the temperature and Debye temperature of the component. The parameter A_0 depends on the experimental setup and the detector and is not often constant, which varies with the behaviour of the detector. The difference in the Debye temperatures is attributed to the fact that different crystallographic sites in the same solid have different f-factors [14], and if the sample is not homogenously mixed, discrepancies are bound to occur.

4 Conclusions

We have employed X-Ray Diffraction and ^{57}Fe Mössbauer spectroscopy measurements to investigate the structural and magnetic properties of Ho substituted $BiFeO_3$. Both techniques have revealed, in addition to the rhombohedral $BiFeO_3$ phase, the presence of two non-perovskite impurity phases attributed to $Bi_{25}FeO_{40}$ and $Bi_2Fe_4O_9$. At temperatures below 500 K, the Mössbauer spectra are characterized by broadened magnetic hyperfine splitting patterns due to hyperfine field distributions, indicative of magnetic ordering most probably screwed or slightly antiferromagnetic. The magnetic hyperfine fields decreased systematically with increasing temperature to a field distribution just below the Néel temperature ($\sim$ 600 K) after which the spectral line assigned to the $Bi_{25}FeO_{40}$ impurity phase dominates the spectra. An average Debye temperature, $\theta_D = 240(80)$ K, has been estimated from the dependence of the relative site populations of spectral components on temperature.

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