Enhanced ferromagnetic properties and high temperature dielectric anomalies in Bi$_{0.9}$Ca$_{0.05}$Sm$_{0.05}$FeO$_3$ prepared by hydrothermal method

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Abstract

Enhanced ferromagnetic properties and high temperature dielectric anomalies in the temperature range of 300–873 K in Bi$_{0.9}$Ca$_{0.05}$Sm$_{0.05}$FeO$_3$ (BCSFO) prepared by hydrothermal method are reported. BiFeO$_3$ is seen to crystallize in rhombohedrally distorted perovskite structure without any impurity phase. Substitution of small amount of Ca and Sm (Bi$_{0.9}$Ca$_{0.05}$Sm$_{0.05}$FeO$_3$) leads to increase in the lattice constant values and formation of small amount of secondary phase. Magnetization curve of pure BFO indicates very weak ferromagnetism combined with antiferromagnetic nature of the samples. Whereas, BCSFO sample shows very clear and enhanced ferromagnetic nature. Saturation magnetization and Neel’s temperature values are found to be 4.36 emu/g and 664 K, respectively. X-ray photoelectron spectroscopy indicates the creation of oxygen vacancies upon Ca substitution in Bi site. Dielectric anomalies at 420 and 540 K were observed for Bi$_{0.9}$Ca$_{0.05}$Sm$_{0.05}$FeO$_3$ from the temperature variation of dielectric constant and specific heat capacity measurements. Observation of dielectric anomalies in pure BiFeO$_3$ sample reveals that the origin of dielectric peaks is purely from the primary phase. Raman spectroscopy study indicates a clear shift and broadening of A modes (between 100 and 200 cm$^{-1}$) at the dielectric anomaly temperatures supporting the observed dielectric anomalies.

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1. Introduction

BiFeO$_3$ (BFO) is a multifunctional material, which simultaneously shows magnetic, ferroelastic and ferroelectric (FE) characteristics at room temperature (RT) [1–5]. Its antiferromagnetic Neel temperature ($T_N$) is 643 K and ferroelectric Curie temperature ($T_c$) is 1103 K [6]. In addition to the promising magnetoelectric applications, BFO finds applications as photovoltaic and photocatalytic materials due to its narrow bandgap of 2.67 eV [7–10].

Partial substitution of Bi$^{3+}$ ions by rare earth ions (R$^{3+}$) has been reported to enhance the ferroelectricity and saturation magnetization [11–14]. Structural changes, elimination of impurity phases and enhanced magnetization by destroying the cycloidal spin structure have been achieved by substitution of Sm, Nd, La and Gd ions on Bi site [11–14]. Oxygen vacancy ($V_{O}^{\cdots}$) concentration and its distribution play an important role in determining the ferroelectric properties of BFO material and its applications [15,16]. Amount of leakage current and strain relaxation in BFO thin films are mainly affected by oxygen vacancy concentration [15,16]. Recently, we have demonstrated that the substitution of calcium ions (Ca$^{2+}$) into Bi site causes the spontaneous formation of highly concentrated oxygen vacancies that compensate the Ca acceptors and maintain a stable Fe valence state in BFO thin film [17]. With the application of electric field, positively charged oxygen vacancies can be migrated and accumulated near the negatively biased electrode and subsequently the opposite side becomes p type, leading to the formation of a n–p junction across the film surface. C. H. Yang et al. [18], have demonstrated that the conductor–insulator transition takes place in a Ca doped BFO through band filling upon the application of electric field [18].

In the present work, we demonstrate a pathway to enhance the magnetic properties and the effect of oxygen vacancies on dielectric properties by substitution of Ca and Sm simultaneously at Bi site in BFO bulk material. The present work was performed on the controlled growth with faceted morphology and manipulation of structural changes, enhanced magnetic and dielectric properties of BFO and Bi$_{0.9}$Ca$_{0.05}$Sm$_{0.05}$FeO$_3$ (BCSFO) bulk material prepared by hydrothermal method. Interestingly, we found dielectric anomalies.
at high temperatures in BFO and BCSFO bulk material. In addition, specific heat capacity measurement and the temperature variation of Raman studies are seen to support the observed dielectric anomalies. The results obtained are presented and discussed in this paper.

2. Experimental details

2.1. Material synthesis

The BFO and BCSFO materials were prepared by a hydrothermal method. The starting materials used for hydrothermal reactions are Bi(NO₃)₃·5H₂O, Ca(NO₃)₂·4H₂O, Fe(NO₃)₃·9H₂O, Sm(NO₃)₃·6H₂O and KOH with 99.99% pure analytical grade. 0.09 M Bi(NO₃)₃·5H₂O, 0.005 M Ca(NO₃)₂·4H₂O, 0.005 M Sm(NO₃)₃·6H₂O were dissolved in 30 ml of deionized (DI) water and mixed using a magnetic stirrer to get a clear solution. 0.1 M Fe(NO₃)₃·9H₂O was dissolved in 30 ml of DI water and mixed well in a separate beaker. The above-mentioned solutions were slowly added into a 12 M KOH solution and stirred for 20 min to form a well mixed solution. The suspension solution was transferred to a 100 ml Teflon-lined container with 75% filling the volume of the autoclaves for hydrothermal reaction. The autoclaves were sealed and maintained at 200 °C for 24 h in a heating oven. After the reaction was complete, the autoclave was cooled down to room temperature. The final material was collected and washed with ethanol and DI water several times to wash out the impurity ions, and then dried in an oven at 80 °C for few hours.

2.2. Characterization

The synthesized BFO and BCSFO powders were characterized employing an X-ray diffractometer (XRD, Rigaku, D/MAX-IIIC X-ray diffractometer, Tokyo, Japan) with Cu Kα radiation (λ = 0.15406 nm at 40 kV and 40 mA). The size and shape of the particles were characterized employing a field emission scanning electron microscope (FE-SEM Hitachi S-4800, Japan). Elemental analysis was carried out employing a sigma probe multifunction X-ray photoelectron spectrometer (XPS), working with micro focused monochromatic X-ray source having an energy resolution of 0.47 eV FWHM. The pressure in the chamber during the experiments was maintained at 4.5 × 10⁻¹⁰ Torr. The Raman spectra of BCSFO powders were recorded employing a HR 800 Raman spectrophotometer (Jobin Yvon-Horiba, France) using monochromatic He–Ne LASER (632.8 nm), operating at 20 mW. For dielectric measurements, silver paste was applied on both sides of the pellets and dried before the pellet was kept in a sandwich geometry between two electrode terminals of a parallel plate capacitor set up connected to the impedance analyzer (HP 4192A). Magnetization measurement was carried out (0–15 T) at RT employing a vibrating sample magnetometer (VSM, LakeShore 7407, Westervill, OH, USA). Specific heat capacity (C_p) measurement was carried out from 350 to 700 K employing differential scanning calorimetry (DSC) setup (NETZSCH DSC 404C, Selb, Germany) with a heating rate of 10 K per minute.

3. Results and discussion

3.1. Structural characteristics and surface morphology

Fig. 1 shows the Rietveld refined XRD patterns of the pure BFO powders recorded at RT. BFO is found to crystallize in rhombohedrally distorted perovskite structure belonging to R3c space group without any impurity phase. Rietveld refinement was carried out on the XRD data obtained at RT using the GSAS program. The wp (weighted refined parameter) and the χ² (goodness of the fit) values of the fitting are 4% and 1.00, respectively. The calculated lattice constants a, b and c values at RT are 5.573, 5.573 and 13.854 Å (±0.002 Å), respectively, which agrees well with the reported values [19–22]. Fig. 2 shows the XRD patterns of the BCSFO powders recorded at various temperatures (RT to 600 °C). BCSFO is found to crystallize in rhombohedrally distorted perovskite structure belonging to R3c space group. The structure of the material is not seen to change in the temperature interval RT–600 °C. In addition to the primary phase, very small amount of Bi₂Fe₄O₉/Bi₂FeO₄ phase was identified as an impurity phase [20]. In order to eliminate the formation of impurity phases, pH value of KOH and the amount of precursors were varied during the hydrothermal process. All the processes resulted in the formation of BCSFO sample with small amount of secondary phase. BCSFO sample with least amount of secondary phase was considered for all the characterization in the present work. Contribution of
secondary phases to the physical properties in BFO is reported to be negligibly small [20,21]. Therefore, in the present case, the observed physical properties are mainly due to the parent BCSFO phase. The sharp diffraction peaks at RT indicate that the present hydrothermal process can easily achieve the well-crystallized BCSFO material. The calculated lattice constants \(a\), \(b\) and \(c\) values at RT are 5.578, 5.578 and 13.871 Å (\(\pm 0.002\) Å), respectively, which agrees well with the reported values [19–22]. Substitution of small amount of Ca and Sm leads to increase in the lattice constant values due to the larger ionic size of Sm and Ca. Amount of secondary phase was calculated from the ratio between the intensities of 100% peak of both the phases.

\[ Q = \frac{I_1}{I_2} = 8.6\% \]

where \(Q\), \(I_1\) and \(I_2\) are amount of secondary phase, intensity of the secondary phase and the intensity of parent phase, respectively. Fig. 3(a) and (b) shows the SEM images of pure BFO and BCSFO particles. SEM images indicate that the morphology of pure BFO is a combination of nanorods and particles with random shape. Morphology of BCSFO particles is seen to be faceted polygon surface with the average particle size of \(\sim 7–8\) μm. Presence of secondary phase in the BCSFO sample affects the growth dynamics and leads to form the sample with different morphology compared to that of BFO.

Figs. 4 and 5 show the XPS spectra of Fe, O and Bi. XPS spectra confirm the presence of all the elements in the BCSFO powder. The Fe 2p core level splits into two components namely 2P\(_{1/2}\) and 2P\(_{3/2}\) due to the spin–orbit coupling [23,24]. For Fe\(^{3+}\) and Fe\(^{2+}\) ions, the 2P\(_{3/2}\) core level appears at 710.8 and 709.4 eV, respectively. Fig. 4(a) shows the XPS spectrum covering 707–714 eV. An asymmetric broad-band at \(\sim 710\) eV indicates the existence of both Fe\(^{2+}\) and Fe\(^{3+}\) in the sample. Two Gaussian fitting was carried out on the broad peak, one centered at 709.4 and other at 710.8 eV, respectively. The decoupled two sub bands corresponding to the 2P\(_{3/2}\) core levels of Fe\(^{3+}\) and Fe\(^{2+}\), ion, respectively. Observation of both Fe\(^{2+}\) and Fe\(^{3+}\) in BCSFO sample could be due to the low synthesis temperature employed in the hydrothermal process, which might not be sufficient to reduce all the Fe ions into 3+ state. Fig. 4(b) shows the O 1s XPS spectra of BCSFO powders showing a slightly asymmetric peak at \(\sim 530\) eV. In addition to that, small additional peak near 532 eV is also observed in the spectra. Both curves were Gaussian fitted by two symmetrical peaks one centered at 529.7 and another at 531.6 eV, respectively. The low binding energy peak can be ascribed to the O 1s band of the BCSFO powders and the high binding energy peak of O 1s is in general related with the loss of oxygen (oxygen vacancy) in the sample [25]. The decoupled small sub band at 531.6 eV confirms the presence of small amount of oxygen vacancy present in the sample. Doping of Ca in BiFeO\(_3\) leads to the creation of oxygen vacancies to compensate Ca acceptors and maintain a highly stable Fe\(^{3+}\) valence state, as reported by several authors [17–20]. Oxygen vacancy \([V_0^\circ]\) transfers two electrons from oxygen atom to the conduction band in order to maintain charge equilibrium. Formation of oxygen vacancies in BCSFO can be represented as [26]:

\[O_0 = V_0^\circ + 1/2 O_2 + 2e^-\]  \(\text{(1)}\)

In this notation, the main symbol corresponds to the defect species which may be an ion indicated by the atomic symbol or a vacant site denoted by “V”. The subscript indicates the site occupied by the
Therefore, ferromagnetic zeration undergoes calculated perovskite BFO 3.2.

According to the previous equations, 1 mole of Ca atom introduced in the material is able to produce half a mole of oxygen vacancies. Fig. 5(a) shows the XPS spectra of Bi 4f having two bands as a result of Bi—O bonds. Bi 4f doublet consisting of two peaks centered at 157.3 and 162.5 eV were observed, consistent with the previous reports [24,29,30]. Binding energy of the valance band was determined using the XPS spectra in the range −5 to 20 eV and is shown in Fig. 5(b). The separation between valance band energy (E_v) and the Fermi energy (E_F) is found to be 1.23 eV.

3.2. Magnetic properties

Fig. 6(a) and (b) shows the magnetization curves (MH curve) of pure BFO and BCSFO powders at RT, respectively. Magnetization curve of pure BFO indicates the very weak ferromagnetism combined with antiferromagnetic nature of the samples through very narrow hysteresis with a linear curve at high fields. Whereas, MH curve of BCSFO sample shows very clear and enhanced ferromagnetic nature. The coercivity (H_c) and remanent magnetization (M_r) values of BCSFO was found to be 133 Oe and 1.02 emu/g, respectively. Saturation magnetization value of BSCFO was calculated to be 4.36 emu/g, employing Honda plot (1/H vs M, inset of Fig. 6(b)). Substitution of small amount of Sm at Bi site in BFO possibly leads to the straightening of Fe—O—Fe bond angle in perovskite structure and enhances the net ferromagnetism [31,32]. Bi₂Fe₄O₉ has been reported to be paramagnetic at RT and undergoes an antiferromagnetic transition below 250 K [33]. Therefore, the contribution from the Bi₂Fe₄O₉ phase to the observed enhanced magnetic properties can be neglected.

3.3. Dielectric properties

The temperature variation of real part of the dielectric constant ε′ (320–570 K) at different frequencies is shown in Fig. 7(a). It is evident that ε′ increases gradually with increasing temperature up to 370 K and then started increasing rapidly. Gradual increase of ε′ with temperature can be explained as follows. Thermal energies at low temperatures are not sufficient enough to free the localized dipoles to orient them in the field direction. This behavior is clearly observed at low temperatures as shown in Fig. 7(a). At sufficiently higher temperatures, the thermal energy liberates more localized

Fig. 5. (a) XPS spectra of Bi 4f and (b) valance band of BCSFO material.

Fig. 6. (a) Magnetization curve of pure BFO powders recorded at RT. (b) Magnetization curve of BCSFO powders recorded at RT. Enhanced ferromagnetic nature of the sample is clearly observed. Inset shows the Honda plot (1/H vs M).

Fig. 7. (a) Temperature variation of dielectric constant of BCSFO at various frequencies. (b) C_p curve as a function of temperature. Dielectric anomalies are observed at 420 and 540 K, confirmed from C_p measurements. Neel’s temperature is found to be 664 K.
diodes and aligns to the field direction leading to an increase of the polarization as well as of $\varepsilon'$. Dielectric constant of Bi$_2$Fe$_4$O$_9$ at RT is reported to be in the order of $10^4$ [34]. In the present case, observation of very large value of dielectric constant can be attributed to the contribution from both parent and secondary phases. Two broad peaks are observed around 420 and 540 K at all the frequencies. Maximum value of $\varepsilon'_\text{max} = 8.0 \times 10^3$ and $2.5 \times 10^3$ is observed at 420 and 540 K (3162 Hz), respectively. The $\varepsilon'_\text{max}$ value is seen to shift toward high temperature with increasing frequency. Dielectric anomalies in BFO material at low temperatures (temperatures below RT) is reported by several authors [29,30]. The anomalies close to RT (281 K) and at 25 K is generally attributed to the disorders produced by oxygen vacancies and the magnetic glassy transition, respectively. There is no report on dielectric anomalies at high temperatures in BFO or doped BFO bulk materials. In the present case, there was no structural change observed in the temperature range RT–873 K through high temperature XRD studies (Fig. 2). Changes in the amount of oxygen content, changes in the oxidation state of Fe$^{3+}$/Fe$^{2+}$, the magnetic glassy transitions and free charge polarization might have caused the disorder in the structure and lead to the present dielectric anomalies at high temperatures. High temperature magnetic studies on BCSFO material might throw some light on the physics behind the dielectric anomalies and the coupling between the ferromagnetic and ferroelectric order parameters in the present case. Detailed high temperature magnetic studies will be carried out as an extension of the present work. Larger value of $\varepsilon'$ at lower frequencies can be explained as follows. High mobility oxygen vacancies can move easily with externally applied electric field, resulting in a little space charge effect at low temperature. In addition, atomic, electronic, ionic and interfacial polarizations along with the grain-boundary contributions lead to the larger value of $\varepsilon'$ at lower frequencies. In order to confirm the dielectric anomalies, specific heat capacity ($C_p$) measurements were carried out from 350 to 700 K on BCSFO powders. Fig. 7(b) shows the specific heat capacity curves as a function of temperature. The peaks at 420 and 540 K are consistent with the dielectric anomalies and support the occurrence of disorders at these temperatures. The peak at 664 K in the $C_p$ curve is due to the antiferromagnetic Neel's temperature $T_N$. The $T_N$ value for pure BFO is reported to be 643 K [1–6] and a small increase in the $T_N$ in the present case could be due to the combined effects of enhanced superexchange interaction between Fe ions with the Sm substitution at Bi site and oxygen vacancy formation due to Ca substitution. In order to confirm the possibilities of contribution of secondary phase to the observed dielectric anomaly, the temperature variation of real part of the dielectric constant $\varepsilon'$ (300–550 K) at different frequencies for pure BFO was carried out and the plots are shown in Fig. 8. Two broad peaks are observed around 440 and 537 K at all the frequencies for pure BFO as well. Maximum value of $\varepsilon'_\text{max} = 3.7 \times 10^3$ and $6.3 \times 10^3$ is observed at 420 and 540 K (1 kHz), respectively. The $\varepsilon'_\text{max}$ value is seen to shift toward high temperature with increasing frequency. The above observation clearly suggests that the dielectric anomalies observed in BSCFO samples are from the primary phase and not due any impurity phase present in the sample.

The temperature variation of dielectric loss $\varepsilon''$ at selected frequencies is also shown in Fig. 9. $\varepsilon''$ was calculated using the relation [35]

$$\varepsilon'' = \varepsilon' \tan \delta$$

(3)

$\varepsilon''$ is found to decrease gradually with increasing temperature and then start to increase rapidly around 490 K. Small peak at 420 K for the frequency 3162 Hz is observed. With increasing frequency, the small peak at 420 K is seen to disappear.

3.4. Raman studies

Fig. 10 shows the Raman spectra for BCSFO powders measured at various temperatures ranging from RT to 673 K. The peaks can be
assigned to E and A modes [36,37]. The peaks appear at 270, 295, 348, 371, 440, and 524 cm\(^{-1}\) are assigned to the E modes. The A mode peaks have the positions of 124, 144, 173 and 210 cm\(^{-1}\). The A mode peak positioned at 124 cm\(^{-1}\) can be assigned to the Bi–O vibration mode. The E mode around 270 cm\(^{-1}\) is ascribed to the motion of oxygen atoms and the A mode around 152 cm\(^{-1}\) is a result of Fe–O vibration mode. The A mode around 144 cm\(^{-1}\) is generally considered as a result of coupling between magnetic and electric order parameters (dipoles). Clear shift and broadening of A modes (between 100 and 200 cm\(^{-1}\)) at the dielectric anomaly temperatures is observed in BCSFO sample. Structural distortion without structural phase change due to an increased disorder in the oxygen vacancy rich BCSFO leads to the observed broadening and shifts at 420 and 540 K dielectric anomalies. Peaks corresponding to the secondary phase is not observed in the Raman spectra.

4. Conclusions

In summary, substitution of small amount of Ca and Sm in BFO (Bi\(_{0.9}\)Ca\(_{0.05}\)Sm\(_{0.05}\)FeO\(_{3}\)) leads to the enhancement in ferromagnetic properties and high temperature dielectric anomalies. Bi\(_{0.9}\)Ca\(_{0.05}\)Sm\(_{0.05}\)FeO\(_{3}\) bulk material prepared by hydrothermal method was found to form in rhombohedrally distorted perovskite structure with faceted polygon morphology. Canted antiferromagnetic BFO is seen to become ferromagnetic upon the substitution of small amount of Sm at Bi site in BiFeO\(_3\) and its saturation magnetization and Neel's temperature values were found to be 4.36 emu/g and 664 K, respectively. XPS studies indicate the creation of oxygen vacancies upon the substitution of small amount of Ca in Bi site. Enhanced dielectric constant due to the space charge polarization effect and high temperature dielectric anomalies were observed from temperature variation of dielectric constant measurements. Specific heat capacity and temperature variation of Raman studies confirm the structural disorders present in the BCSFO sample.

References