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Synthesis and characterization of $(Bi_{0.5}Ba_{0.5})$ $(Fe_{0.5}Ti_{0.5})$ O_3 ceramic

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ABSTRACT

The polycrystalline sample of $(Bi_{0.5}Ba_{0.5})$ $(Fe_{0.5}Ti_{0.5})$ O_3 (BF–BT) was prepared by a standard mixed oxide method. Analysis of room temperature XRD pattern and Raman/FTIR spectra of the compound does not exhibit any change in its crystal structure of $BaTiO_3$ on addition of $BiFeO_3$ in equal ratio. The surface morphology of the gold-plated sintered pellet sample recorded by SEM (scanning electron microscope) exhibits a uniform distribution of grains with less porosity. Detailed studies of nature and quantity of variation of dielectric constant, tangent loss, and polarization with temperature and frequency indicate the existence of ferroelectric phase transition at high-temperature. There is a low-temperature anti-ferromagnetic phase transition below 375 °C in the material. Detailed studies of electrical properties (impedance, modulus, etc.) of the material confirmed a strong correlation between micro-structure and properties.

1. Introduction

In the last few decades, material scientists have a plethora of interest on multi-ferroic materials which have ferroelectric/anti-ferroelectric and ferromagnetic/anti-ferromagnetic properties in the same crystal phase. This type of materials may also exhibits magneto-electric effect by virtue of which electric polarization is induced in the material on application of magnetic field and magnetization is induced on application of electric effect. Among all the multi-ferroics studied so far, $BiFeO_3$ (BFO) has both anti-ferromagnetic and ferroelectric properties much above the room temperature (i.e., anti-ferromagnetic Neel temperature $(T_N) \sim 350$–370 °C [1] and the ferroelectric–paraelectric transition temperature $(T_C) \sim 810$–830 °C [2,3]). Since the discovery of muliti-ferroicity in BFO, lots of research work on this material have been carried out on its bulk as well as thin film. This spate of interest is mostly due to the existence of multi-ferroic properties of the material useful for fabrication of devices in microelectronics, spintronics, pyroelectric detector, ferroelectric memory, piezo-electric sensor [4–9]. For the purpose, much attention has been paid on enhancement of device parameters by optimizing material processing and reducing leakage current and stabilizing crystal and

microstructure. According to the binary Bi_2O_3–Fe_2O_3 phase diagram, $BiFeO_3$ (BFO) is a linear compound [10], so that any deviation from stoichiometry should lead to the appearance of secondary phase such as $Bi_2Fe_4O_9$ (mullite phase), $Bi_{24}Fe_2O_{39}$, or a sillenite-type phase $(Bi_{25}FeO_{40})$. Though the synthesis of single BFO phase has been reported in the past, it is still under question. Lufaso et al. [11] have supported this observation by saying that BFO is formed readily with a small fraction of secondary phase, and hence no single phase of the material could be obtained. In order to overcome the technological shortcomings in BFO for applications, a number of investigations have been carried out on $CoFe_2O_4$–$BaTiO_3$ nanoparticles [12], $NiFe_2O_4$–$Pb(Zr_{0.52}Ti_{0.48})O_3$ nanowire arrays [13], $Ni_{0.75}Co_{0.25}Fe_2O_4$–$BiFeO_3$ nanocomposites [14], $0.71BiFe_{1-x}(Mg_{0.5}Ti_{0.5})_x$ O_3–$0.29BaTiO_3$ $(x = 0$–$0.12)$ [15], and Mn-modified $(1-x)BiFeO_3$–$xBaTiO_3$ [16]. Singh et al. [17] studied various properties of polycrystalline $(1-x)$ $BiFeO_3$–$xBaTiO_3$ $(x = 0.00, 0.10, 0.20,$ and $0.30)$, and reported that the systematic increase in net magnetization and dielectric constant and decrease in leakage current with increase in concentration of $BaTiO_3$.

In view of technological importance of $BaTiO_3$ modified BFO multiferroic, we have studied its structural, dielectric, and electric properties using standard synthesis and characterization techniques.

2. Experimental

The polycrystalline sample of $(Bi_{0.5}Ba_{0.5})$ $(Fe_{0.5}Ti_{0.5})O_3$ (BF–BT) was prepared by a mixed-oxide method using high-purity (AR

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grade) raw materials: Bi_2O_3, Fe_2O_3, Ba_2CO_3, and TiO_2. All these chemicals were procured from M/S LOBA Chemie Co. The oxides and carbonate were thoroughly mixed in dry (air) and wet (methanol) medium for 1 h using agate mortar. The calcination temperature was optimized (835 °C) using repeated firing and mixing for 4 h in alumina crucible. X-ray diffraction (XRD) pattern of calcined powder was recorded at room temperature using X-ray powder diffractometer (Rigaku Miniflex) with CuKα radiation (λ = 1.54060 Å) in a wide range of Bragg's angle (θ) ($20° \leq 2\theta \leq 80°$) at a scanning rate of 2°/min. The fourier transform infrared (FTIR) spectrum of the sample was recorded at room temperature in the spectral range of 400–4000 cm^{-1} using JASCO-FTIR/4100 infrared spectrophotometer. The room temperature Raman spectra of the powder sample was recorded out by NIR Raman spectrometer. The fine and homogenous powder was then cold pressed into pellets of diameter 10 mm and 1–2 mm thickness under uni-axial pressure of 4×10^6 N m^{-2} (using hydraulic press). Polyvinyl alcohol (PVA) was used as binder for preparation of pellets. The pellets were sintered at 855 °C in air atmosphere for 4 h. Before taking any electrical measurements the sintered pellets were coated with high-quality silver paste, and dried at 160 °C for 4 h in order to remove moisture. The microstructure of the pellet sample was recorded by ZEISS scanning electron microscope (SEM). Some electrical parameters (capacitance, dissipative factor, impedance, and inductance) of a sintered pellet were measured as a function of frequency (1–3 MHz) at different temperatures (25–525 °C) using a computer-controlled LCR meter (PSM LCR 4NL Model: 1735, UK) with a laboratory-designed sample holder and furnace. A chromel–alumel thermo-couple and KUSAM MECO 108 digital milli-voltmeter were used to measure the temperature. The polarization (hysteresis loop) of the material on the poled sample was obtained at different temperatures using loop tracer (M/S Marine India, New Delhi).

3. Results and discussion

3.1. Structural analysis

The room temperature X-ray diffraction (XRD) pattern of BF–BT powder is shown in Fig. 1. The diffraction pattern of the sample consists of sharp and single diffraction peaks. Most of the peaks match with $BaTiO_3$ of (JCPDS No. 01-075-0583) with slightly higher values of 2θ [18]. With addition of $BaTiO_3$ in $BiFeO_3$, the secondary phases like $Bi_2Fe_4O_9$ (mullite phase), $Bi_{24}Fe_2O_{39}$, or a sillenite-type phase ($Bi_{25}FeO_{40}$) are not observed. Absence of impurity phase/
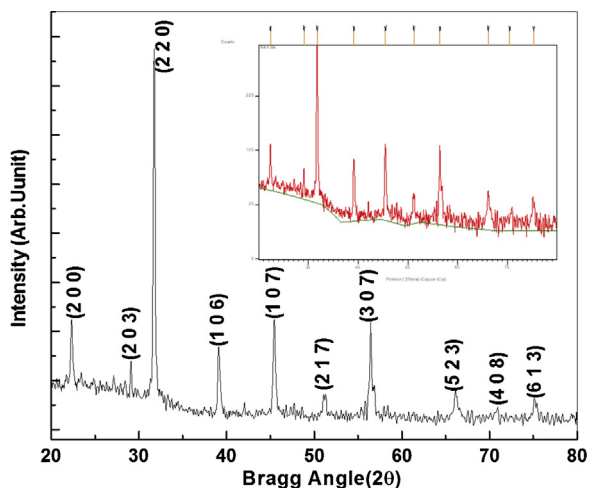
secondary phase with the addition of $BaTiO_3$, suggests the anti-ferromagnetic Neel temperature is above room temperature [17]. Again, all these peaks are different from those of the ingredients of the compound which suggests the formation of single-phase new compound [19]. Indexing of these peaks was attempted in different crystal systems and unit cell configurations using a standard computer program package "POWD" [20]. Based on the good agreement between observed ($d_{obs.}$) and calculated ($d_{cal.}$) inter-planar distance, tetragonal crystal system was selected. The selected unit cell/lattice parameters (a and c) were refined using least-squares refinement subroutine of POWD. The least-squares refined unit cell parameters are: $a = 7.9531(18)$ Å and $c = 14.4244$ (18) Å with c/a = 1.8137 and volume $V = 912.37$ Å^3. The number indicated in parenthesis is estimated standard deviation in unit cell parameters.

Besides XRD, FTIR spectroscopy is very important when analyzing multi-ferroic materials. In this technique, a beam of infrared light interacts with the sample. The molecule absorbs energy when the vibration frequency of a chemical bond matches the beam frequency. The wavelength whose absorption occurs is characteristic of each type of covalent bond, enabling material characterization. The FTIR spectra (transmittance T versus wave number) of the compound recorded at room temperature in the range of 4000–400 cm^{-1}. We have gone through Fig. 2. FTIR spectrum shows several types of vibration at 586 cm^{-1}, 860 cm^{-1}, 916 cm^{-1}, 968 cm^{-1}, 1029 cm^{-1}, 1546 cm^{-1}, 1743 cm^{-1}, 2931 cm^{-1}, and 3742 cm^{-1}. The 586 cm^{-1} is attributed to bending vibration of Fe—O bond in the FeO_6 octahedral unit in BiO_6 [21]. The other bands of the spectra (i.e., 860 cm^{-1}, 916 cm^{-1}, 968 cm^{-1}, 1029 cm^{-1}, 1546 cm^{-1}, 1743 cm^{-1} 2931 cm^{-1}, and 3742 cm^{-1}) related to Ti—O and Ba—O stretching [22].

As Raman spectroscopy analysis is a supplementary method, it was used to identify the products of BF–BT. Fig. 3 shows the Raman spectrum of the BF–BT sample. According to group theory, pure $BiFeO_3$ with rhombohedral R3c structure has 12 Raman active modes: $4A_1$ and 8E [23]. The Raman peaks located at 261, 506, and 701 cm^{-1} match well with the typical Raman peaks of $BaTiO_3$ [24]. The bands around 261 and 506 cm^{-1} are assigned to the transverse optical (TO) modes of A_1 symmetry. The peak at 701 cm^{-1} is related to the longitudinal optical mode (LO) with A_1 symmetry. Generally, A_1 mode related to the motion of A-site atoms, in particular Ba—O, Bi—O bond. Raman peak at 1366 cm^{-1} corresponds to bending and stretching of Fe—O [25] bond.

Fig. 3(inset) shows the room temperature scanning electron micrograph of BF–BT. The nature of the microstructure of the sample suggests that the different shape of grains are densely and uniformly distributed on the surface.

3.2. Dielectric study

Fig. 4(a and b) shows the variation of ε_r (relative dielectric constant) and $\tan \delta$ (tangent loss) as a function of temperature at three different frequencies (10 kHz, 100 kHz, and 1000 kHz). There is a dielectric anomaly in the vicinity of Neel temperature ($T_N \sim 375$ °C) attributing the magnetoelectric coupling in the BF–BT system. The values of ε_r increases on increasing temperature up to a particular temperature, usually referred as anti-ferromagnetic Neel temperature (T_N), and then decreases. The room temperature dielectric constant and tangent loss of the compound are 465 and 0.22, respectively. It is observed that ε_{max} (dielectric constant at $T_N = 375$ °C) at 10 kHz, 100 kHz, and 1000 kHz are 2646, 1876, and 405, respectively. The increase in ε_r with temperature can be ascribed to change of electric dipole ordering [26]. The decrease in dielectric constant after possible anti-ferromagnetic transitions may be due to reduction of dipole ordering in the paramagnetic phase. There is a peculiar behavior in shifting of T_N to higher

Fig. 1. Room temperature XRD pattern of BF–BT.