

Ferroelectric and dielectric properties of nanocrystalline BiFeO₃ multiferroic ceramics synthesized by solution combustion method (SCM)

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Nanocrystalline multiferroic BiFeO₃ ceramics was prepared by a novel solution combustion method (SCM). The X-ray diffraction (XRD) studies on structural properties of the synthesized ceramics reveal that the BiFeO₃ ceramics has rhombohedral perovskite structure with an average crystallite size of 15 nm. The ferroelectric P-E hysteresis loop measurement at room temperature shows unsaturated behavior with a partial reversal of polarization. Investigations on temperature dependence of dielectric constant in BiFeO₃ demonstrate a clear dielectric anomaly at approximately around 380 °C, which corresponds to antiferromagnetic to paramagnetic phase transition (TN) and also evidences a possible coupling among the electric and magnetic dipoles of BiFeO₃. A room temperature variation of dielectric constant “ ϵ ” and dielectric loss “ $\tan \delta$ ” as a function of frequency in the range of 100 Hz – 1 MHz, confirms that both dielectric constant and loss are strong functions of frequency.

Keywords: *BiFeO₃ ceramics; solution combustion method; X-ray diffraction; ferroelectric properties; dielectric properties*

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1. Introduction

A multiferroic material exhibits an electric and magnetic nature simultaneously, which results in concurrent existence of ferroelectricity and magnetism in a single phase [1]. This distinctive coupling between electric and magnetic ordering parameters yields a unique phenomenon known as magnetoelectric effect (ME), in which magnetization can be switched under the influence of electric field and electric polarization can be switched by magnetic field. Mostly, it provides additional opportunities for the fabrication of microelectronic and spintronic devices [2–4]. These materials have acquired much interest in terms of their potential applications in several fields such as: information storage, spintronics, sensors [5], thin film capacitors,

nonvolatile memory devices, nonlinear optics, photo-electrochemical cells, magneto-electric sensor devices, multiple state memories, high density ferroelectric random access memory, electric field controlled ferromagnetic resonance devices, radio transmission, microwave, satellite communication, digital recording and permanent magnet applications [6–10]. The multifunctional BiFeO₃ has a rhombohedral perovskite structure having ferroelectric Curie temperature $T_c \sim 1103$ K and G-type antiferromagnetic Neel temperature $T_N \sim 643$ K [11, 12]. In BiFeO₃, the ferroelectricity is induced due to Bi 6s lone pair electrons whereas the partially filled d-orbitals of Fe are responsible for magnetic ordering [13].

Several workers have been engaged towards the enrichment of ferroelectric and dielectric properties of the ceramic material, investigating the ferroelectric and dielectric properties of BiFeO₃ ceramics. Among this, the dielectric properties

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of sol-gel BiFeO₃ powders synthesized by Jia et al [14], represent a dielectric anomaly around 330 °C, associated with antiferromagnetic to paramagnetic phase transition. The dielectric properties of BiFeO₃ ceramics synthesized by combustion route by Fruth et al. [15] showed that both dielectric constant and loss increased with increasing temperature. Dai et al. [16] reported room temperature frequency dependent dielectric properties of BiFeO₃ ceramics, which exhibited a low resistivity, higher dielectric constant and relatively lower dielectric loss. Jiang et al. [17] observed an unsaturated P-E hysteresis loop caused by higher conductivity and stable dielectric constant of BiFeO₃ ceramics whereas the dielectric loss showed distinct changes in the frequency range of 10² to 10⁴ Hz. Recently, Kumar et al. [18] observed the unsaturated P-E hysteresis loops in BiFeO₃ due to the higher conductivity of this ceramics.

The current study deals with synthesis of BiFeO₃ compound by solution combustion method and investigations on their ferroelectric as well as dielectric properties.

2. Experimental section

2.1. Materials

The preparation of BiFeO₃ ceramics was carried out using the precursors such as Bi(NO₃)₃·5H₂O (CDH, India) and Fe(NO₃)₃·9H₂O (Fischer Scientific) as oxidizers whereas glycine (NH₂CH₂COOH) (CDH, India) was used as a fuel.

2.2. Synthesis process of BiFeO₃

The nanocrystalline BiFeO₃ multiferroic powder was prepared by solution combustion method (SCM). For this, the oxidizer (O) to fuel (F) ratio was appropriately determined from oxidizing and reducing valences of the metal nitrates and fuel radicals respectively [19]. The metal nitrates and glycine were completely dissolved in distilled water in stoichiometric ratios. Afterwards, the mixture was heated in a Pyrex dish (150 mm x 50 mm) with a burner until the excess of

free water evaporated, with simultaneous triggering of spontaneous ignition, which led to formation of a combustion powder of BiFeO₃. Subsequently, the pure BiFeO₃ powder was grinded and calcined at 630 °C for 4 h. Furthermore, this powder was pelletized under uniaxial pressing with addition of polyvinyl alcohol as a binder. Finally, these pellets were sintered at high temperature of 650 °C for 30 min and used for further characterization and measurements.

2.3. Characterization

The sintered samples were characterized by X-ray diffraction (XRD) using CuK α radiation ($\lambda = 1.54178$) (Philips X-pert PRO) for phase identification in the 2θ range (20° – 75°). Dielectric measurement was done with H.P impedance analyzer (4192A LF) in the frequency range of 10 kHz – 1 MHz with temperature varying from 30 – 500 °C. The dielectric constant as a function of frequency was measured with a precise impedance analyzer (Agilent 4294 A) at room temperature. The ferroelectric measurement was carried at room temperature with a ferroelectric tester (Radiant Precision Premier II Technology). For electrical characterization, ohmic contacts of an Ag paste were imposed onto both sides of sintered pellets.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the room temperature X-ray diffraction pattern of BiFeO₃ sintered pellets. The XRD result reveals that the BiFeO₃ sample has a rhombohedral perovskite structure with the presence of an additional impurity phase which corresponds to Bi₁₂(Bi_{0.5}Fe_{0.5})O_{19.5} and can be observed in XRD pattern of the samples around 30° in 2θ range. The XRD results are in accord with results reported by Xu et al. [20]. The average crystallite size was calculated by using Scherrer's equation:

$$t = \frac{k\lambda}{\beta \cos(\theta)} \quad (1)$$

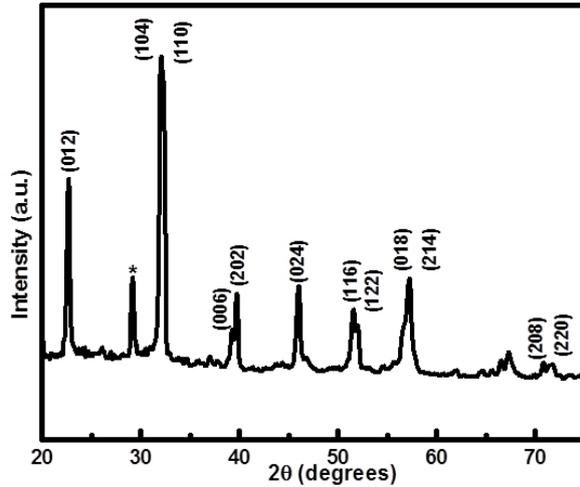


Fig. 1. X-ray diffraction (XRD) pattern of BiFeO₃ ceramics sintered at 650 °C for 30 min. (*represents an impurity phase).

where, t is the crystal size, λ is the wavelength of X-ray used, β is the angular line width of half maximum intensity, k is the Scherrer constant and ' θ ' is the Bragg's angle. The average crystallite size as determined from XRD pattern of BiFeO₃ ceramics was found to be 15 nm.

3.2. Ferroelectric P-E hysteresis loop

Fig. 2 illustrates the P-E hysteresis loop of BiFeO₃ sample sintered at 650 °C for 30 min. The ferroelectric (P-E) loop was measured at room temperature. The loop seems to exhibit unsaturated behavior, which is mainly due to lower resistivity of the BiFeO₃ sample. This results in higher leakage current and indicates partial reversal of polarization for BiFeO₃, showing magneto-electric behavior.

3.3. Dielectric measurement

Fig. 3 presents the temperature dependence of dielectric constant for the BiFeO₃ ceramics at different frequencies ranging from 10 kHz – 1 MHz. The dielectric constant shows a continuous increase with temperature for BiFeO₃ system. In our case, an apparent dielectric anomaly has been detected in the BiFeO₃ ceramics for all frequencies around 380 °C. This anomaly seems to be related with phase transformation from antiferromagnetic to paramagnetic phase and is

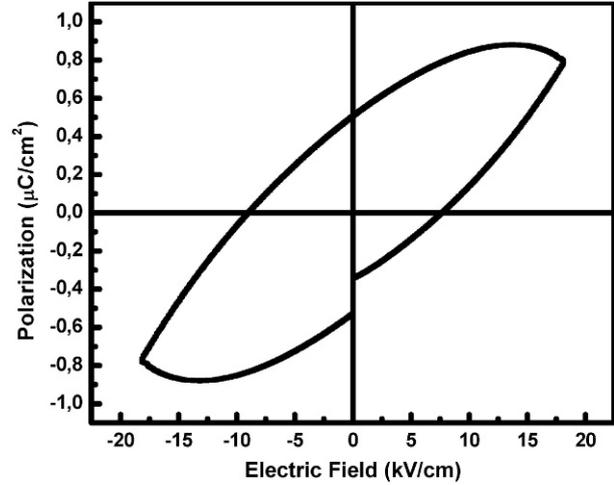


Fig. 2. Room temperature (RT) P-E hysteresis loop at $f = 10$ kHz for BiFeO₃ ceramics.

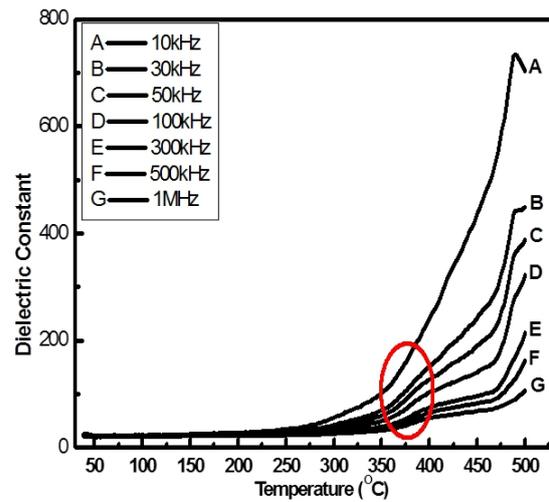


Fig. 3. Dielectric constant versus temperature in the frequency range of 10 kHz – 1 MHz for BiFeO₃ sample.

evidence of a possible coupling between electric and magnetic dipole moments in BiFeO₃, which is similar to the results reported by Chaudhari et al. [21]. The values of dielectric constant for the BiFeO₃ ceramics measured at room temperature were found to be 26 at 10 kHz.

The variation of dielectric loss with temperature at various frequencies for the BiFeO₃ ceramics is depicted in Fig. 4. The frequency was varied from 10 kHz – 1 MHz. The dielectric loss reveals a continuous increase with temperature for all

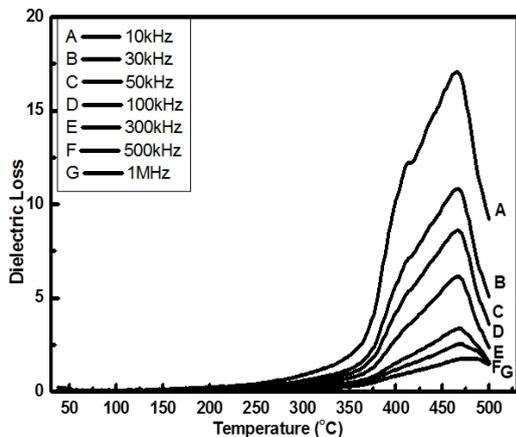


Fig. 4. Dielectric loss versus temperature in the frequency range of 10 kHz – 1 MHz for BiFeO₃ sample.

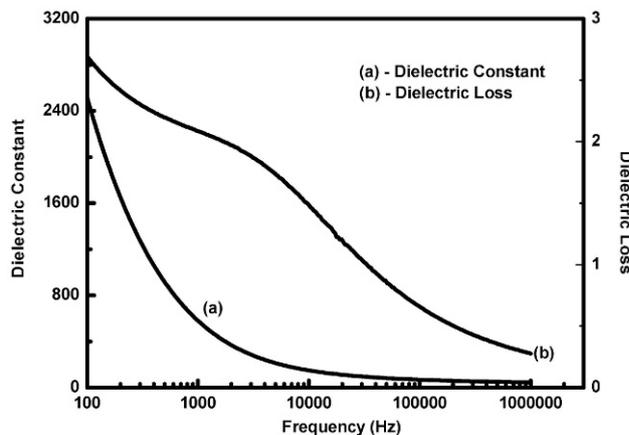


Fig. 5. Dielectric constant and loss versus frequency at RT of BiFeO₃ sample.

frequencies. The value of dielectric loss for the BiFeO₃ sample, measured at room temperature at 10 kHz, was 0.26.

The frequency dependence of dielectric constant (curve (a)) and loss (curve (b)) at room temperature for BiFeO₃ sample is shown in Fig. 5. The frequency was varied from 100 Hz – 1 MHz. It can be seen that in the low frequency range, both dielectric constant “ ϵ ” and dielectric loss “ $\tan \delta$ ” have very high values; also it is evident that both “ ϵ ” and “ $\tan \delta$ ” decrease gradually with the increase in frequency and are strong functions of frequency.

4. Conclusions

We have synthesized the BiFeO₃ bulk multiferroic ceramics by solution combustion method (SCM). The room temperature ferroelectric hysteresis loop of the BiFeO₃ ceramics was not saturated and indicated a partial reversal of polarization. The dielectric constant dependency on temperature for the BiFeO₃ showed an anomaly around 380 °C demonstrating an antiferromagnetic to paramagnetic phase transition (T_N) in this ceramics.

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