



Dielectric properties of BaBi₄Ti₄O₁₅ ceramics produced by cost-effective chemical method

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ABSTRACT

BaBi₄Ti₄O₁₅, an Aurivillius compound, was synthesized by a cost-effective soft chemical route. The precursor was prepared by precipitating Bi- and Ba-oxalates inside a TiO₂ powder suspension. A phase pure orthorhombic BaBi₄Ti₄O₁₅ was synthesized by heating the precursor powder at 1000 °C. The phase formation behavior was investigated using TG-DSC and XRD. Densification behavior of the powder and microstructure development in sintered pellet was examined. Temperature dependent dielectric study of the ceramic has been investigated in the temperature range 300–780 K and frequency range of 1 kHz–1 MHz. The broad dielectric constant peaks at temperature T_m was frequency dependent. The dielectric relaxation rate follows the Vogel–Fulcher relation with activation energy = 0.2639 eV, relaxation frequency = 4.95×10^{21} Hz, and freezing temperature = 620 K. All these parameters indicate that BaBi₄Ti₄O₁₅ is a relaxor ferroelectric.

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1. Introduction

Bi-based Aurivillius family of compounds have received considerable attention as the materials for ferroelectric random access memory (FRAM) because of their low operating voltage, fast switching speed, large remnant polarization, low coercive field, superior polarization fatigue resistant characteristics and high Curie temperature [1–7]. A large remnant polarization, low coercive field and high Curie temperature are required for better performance of FRAM devices.

Majority of Aurivillius oxides are normal ferroelectrics with fairly high Curie temperature, while only a few of them such as BaBi₂Nb₂O₉, BaBi₂Ta₂O₉, BaBi₄Ti₄O₁₅ (BBT) etc. exhibit relaxor behavior [3,8,9]. Relaxor ferroelectrics are attractive for a wide range of applications owing to their excellent high dielectric and piezoelectric responses over a wide range of temperatures [10,11].

Bi-based Aurivillius family of compounds is generalized as Bi₂A_{m-1}B_mO_{3m+3}. The crystal structure consists of 'm' number of (A_{m-1}B_mO_{3m+1})²⁻ slabs sandwiched between (Bi₂O₂)²⁺ layers, where 'A' represents monovalent, divalent or trivalent element and 'B' represents tetravalent, pentavalent or hexavalent metallic cations which are in 12-fold and 6-fold co-ordination, respectively

[4,10,11]. Our present work deals with the compound BBT with 'm' = 4 and structural formula as (Bi₂O₂)²⁺((BaBi₂)Ti₄O₁₃)²⁻, where the Ba- and Bi-ions occupies the A-site and Ti-ions resides in the B-site, respectively.

Although there are many reports on the dielectric properties, electrical properties or crystal structure of BBT, there are limited reports on its diffuse phase transition-relaxor behavior [2–4,12–16]. Recently Hou et al. [3] reported that though there is a shift of T_m (the temperature at which dielectric constant shows a maximum) with measuring frequency, BBT underwent a real paraelectric-ferroelectric phase transition on zero-field cooling. In some other works, the relaxor property of BBT has been explained through the crystallographic aspect [2,4,14]. Tellier et al. [4] reported a shearing-type defect and micro-twinning in BBT which arises from the existence of a compositional inhomogeneity and disorder at local scale. This paper reports a detailed analysis of dielectric dispersion and diffuseness behavior of BBT compound.

In this work, a cost-effective soft chemical route was used to synthesize BBT powders. There are many reports of the preparation of BBT powders by conventional solid-state method [2–4] and few reports using non-conventional methods like Pechini Method [5], sol-gel [6], templated grain growth [7], etc. Here a non-conventional method was used to get better homogeneous and reactive precursor powder compared to solid-state method. The precursor for BBT synthesis was prepared by precipitating Bi- and

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Ba-oxalates inside a TiO_2 powder suspension. Usually Ti-alkoxides and Ti-chlorides are used as the Ti-metal source in chemical routes. Since Ti-alkoxides/nitrates are relatively costlier and highly unstable/volatile than TiO_2 , use of TiO_2 powder can reduce the powder synthesis cost, compared to chemical synthesis process.

2. Experimental procedure

BBT powder was synthesized using reagent grade barium nitrate $\text{Ba}(\text{NO}_3)_2$ (Merck India Ltd., Assay >99%), bismuth nitrate $\text{Bi}_2(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Merck India Ltd., Assay >99%), titanium dioxide TiO_2 (Merck India Ltd., Assay >99%, particle size: $d_{10} = 0.27 \mu\text{m}$, $d_{50} = 0.35 \mu\text{m}$, $d_{90} = 0.48 \mu\text{m}$) and oxalic acid $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (Merck India Ltd., Assay >99%) as precursor. A 0.02 molar barium nitrate solution was prepared by dissolving $\text{Ba}(\text{NO}_3)_2$ in distilled water. Required amount of $\text{Bi}_2(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was separately dissolved using minimum quantity of concentrated nitric acid. Bismuth nitrate solution was then drop-wise added to the barium nitrate solution under constant stirring. A low concentration of barium nitrate solution (<0.03 M) must be used in order to avoid cations precipitation during this addition. A required amount of TiO_2 was dispersed in 0.4M oxalic acid solution in a separate vessel. The suspension was ultrasonicated for 15 min to break the soft agglomerates of TiO_2 . Now, the barium- and bismuth-nitrate mixed solution was added drop-wise into the TiO_2 -oxalic acid suspension under vigorous stirring. Barium- and bismuth-oxalate hydrates were precipitated inside the suspension by heterogeneous nucleation. Finally, the pH of the suspension was adjusted to 7 by adding ammonium hydroxide solution. The precipitated mixture of TiO_2 and barium- and bismuth-oxalates was separated by filtration and washed thoroughly using deionized water, followed by drying at 50°C for 24 h.

The decomposition behavior of the resulting dried powder was studied using thermo-gravimetric (TG) analysis and differential scanning calorimetry (DSC) using Netzsch STA 409C machine, at a heating rate of $10^\circ\text{C}/\text{min}$ in air from room temperature up to 1000°C . The powder was calcined at various temperatures at an interval of 100°C , in the temperature range 400 – 1000°C in air atmosphere to study the phase formation behavior. The phase identification in powders was performed at room temperature using a $\text{Cu K}\alpha$ X-ray Diffractometer (PW-1830, Philips, Netherlands). The synthesized BBT powder was pelletized at a pressure of 220 MPa using polyvinyl alcohol as a binder. Sintering kinetics of the BBT powder was studied on pellet sample using NETZSCH Thermal Analyzer (Model no DL 402C, Germany). The pellets were sintered at 1100°C for 1 h. The density of sintered pellet was determined by Archimedes' method. The microstructure of sintered specimen was studied using scanning electron microscopy (SEM) (JSM-6480LV). For dielectric measurement, the sintered pellet was electroded with silver conductive electrode paste (Alfa Aesar). The frequency dependence of the dielectric constant and loss tangent was obtained using an LCR meter (Hioki, Japan) in the temperature range from 300 to 780 K and in the frequency range from 1 kHz to 1 MHz. The temperature was controlled with a programmable oven. All the dielectric data were collected while heating at a rate of $1^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1. Phase formation behavior

Fig. 1 shows the decomposition behavior of the synthesized powder obtained by DSC/TG measurements. The decomposition

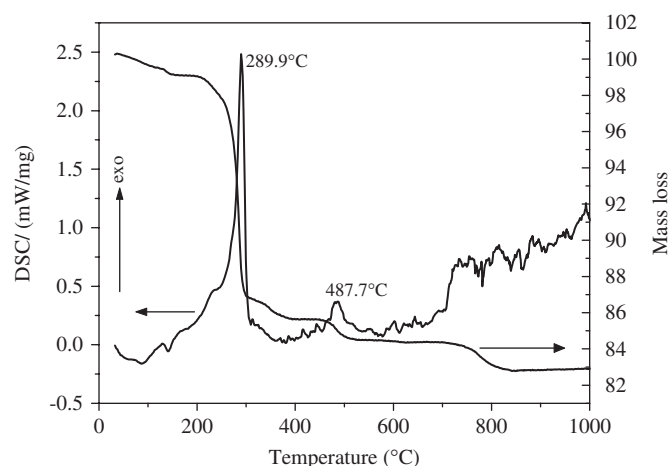


Fig. 1. DSC/TG plot of precursor powder for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics.

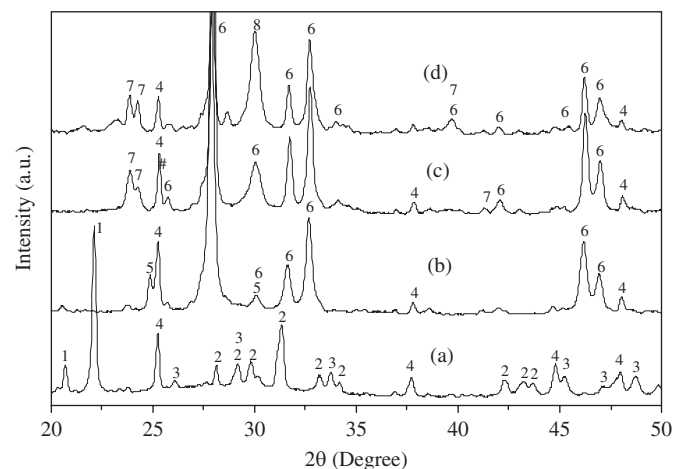


Fig. 2. Room temperature XRD pattern of raw precursor powder (a) and precursor powder calcined at 400°C (b), 500°C (c), and 600°C (d). Major phases identified are marked as: (1) $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$; (2) $\text{C}_2\text{BaO}_4 \cdot 0.5\text{H}_2\text{O}$; (3) $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$; (4) TiO_2 ; (5) BaC_2O_4 ; (6) Bi_2O_3 ; (7) BaCO_3 ; and (8) $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$.

reaction proceeds mainly in three steps. The initial TG weight loss ($\sim 0.92\%$) up to 150°C corresponds to the dehydration of the precursor. Next weight loss ($\sim 12.31\%$) in the temperature range 200 – 400°C corresponds to the decarboxylation of oxalates, which results in an exothermic peak in the DSC curve at 289.9°C . Further weight loss $\sim 2.30\%$ in the temperature range 400 – 600°C is due to the decomposition of residual Ba-oxalate with an exothermic peak at 487.7°C . Lastly, the decomposition of Ba-carbonate occurs with associated weight loss of about 1.59% in the temperature range 700 – 900°C .

To understand the phase formation behavior in BBT, the dried powder was heated in the temperature range 400 – 1000°C , at an interval of 100°C and each time the calcined powder was analyzed by XRD at room temperature. Fig. 2 shows the XRD patterns of precursor powder and the precursors calcined at 400 , 500 and 600°C . The XRD pattern reveals that the precursor powder contains bismuth-oxalate phase $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$, along with two different types of barium-oxalate phases ($\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$, and $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and TiO_2 phases. The XRD pattern of 400°C calcined sample (Fig. 2(b)) shows the presence of BaC_2O_4 and Bi_2O_3 phases along with TiO_2 . This indicates that upon calcination, $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$ decomposes to form Bi_2O_3 , and Ba-oxalate hydrates decompose to form anhydrous Ba-oxalate. These

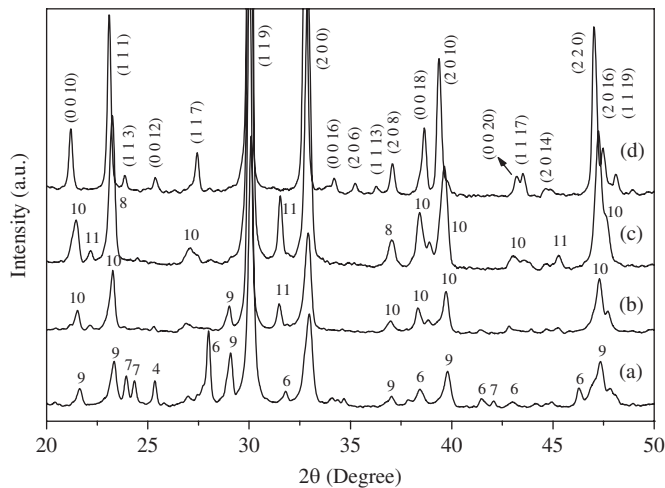
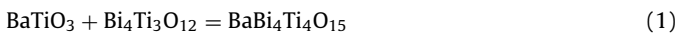


Fig. 3. Room temperature XRD pattern of precursor powder calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C with 4 h of heating. Major phases identified are marked as: (4) TiO₂; (6) Bi₂O₃; (7) BaCO₃; (8) BaBi₄Ti₄O₁₅; (9) BaBiO₃; (10) Bi₄Ti₃O₁₂; and (11) BaTiO₃.

decomposition reactions correspond to a weight loss of about 12.3% in TG curve (Fig. 1) as explained above. Fig. 2(c) shows the XRD pattern of sample calcined at 500 °C, where the BaC₂O₄ phase is absent and BaCO₃ phase appears. This is due to the exothermic de-carboxylation of anhydrous barium-oxalate to BaCO₃ with an associated DSC peak at 487.7 °C (Fig. 1). Fig. 2(d) shows the appearance of BBT phase in the specimen calcined at 600 °C with a decrease in the peak intensities of Bi₂O₃, TiO₂ and BaCO₃ phases in comparison with Fig. 2(c).

The precursor powder was also calcined at 700, 800, 900 and 1000 °C to study the intermediate phase formation and reaction mechanism. Fig. 3 shows the XRD patterns of precursors calcined at 700, 800, 900 and 1000 °C. There are evidences of the formation of few intermediate phases during heat treatment of the precursor. In the temperature range of 600–700 °C, Bi₂O₃ react with BaCO₃ resulting in the formation of an intermediate phase BaBiO₃ along with BBT as shown in Fig. 3(a). The two new intermediate phases Bi₄Ti₃O₁₂ and BaTiO₃ were observed in the specimen that was calcined at 800 °C (Fig. 3(b)). The 900 °C calcined specimen contained mainly Bi₄Ti₃O₁₂, BaTiO₃ and BBT phases as shown in Fig. 3(c).

Finally, a pure phase of BBT was found in the specimen after calcination at 1000 °C for 4 h as shown in Fig. 3(d). Hence, it can be concluded that the main mechanism of BBT formation is



BBT phase was indexed in orthorhombic symmetry with A2₁am (no. 36-cab) space group [14] and refined lattice parameters were $a = 5.4731 \text{ \AA}$, $b = 5.4676 \text{ \AA}$, and $c = 41.9381 \text{ \AA}$, respectively.

3.2. Densification behavior

Fig. 4 shows the non-isothermal shrinkage behavior of the BBT powder compact. It is evident that the shrinkage of the specimen starts at about 1040 °C and continues up to 1130 °C. Heating above 1130 °C causes the specimen to melt. So a sintering temperature of 1100 °C was selected. More than 94% dense ceramics was obtained by sintering pellet samples at 1100 °C for 1 h.

Microstructure of the as-sintered sample was obtained by SEM. Microstructure (Fig. 5) shows plate like grains with random orientation of plate faces. It is known that plate like grain formation is a typical characteristic of bismuth layer-structured ferroelectrics as they have highly anisotropic crystal structure. The

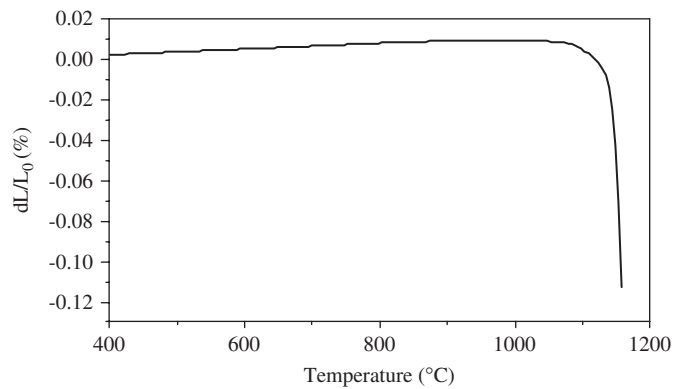


Fig. 4. Non-isothermal sintering behavior of BaBi₄Ti₄O₁₅ powder compact.

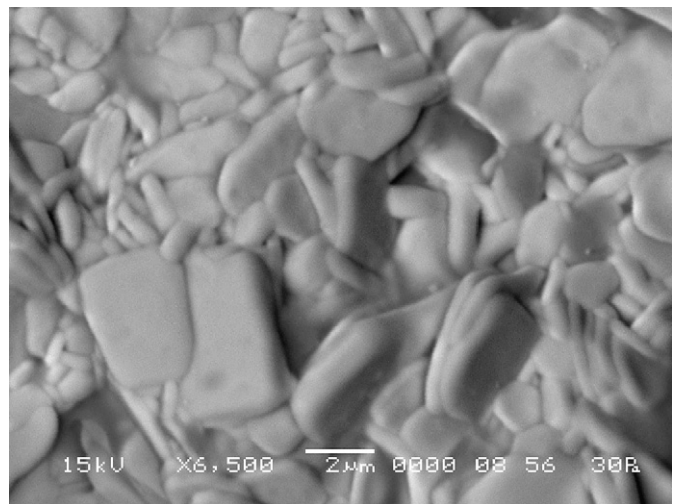


Fig. 5. Microstructure of as-sintered specimen surface of BaBi₄Ti₄O₁₅ ceramics.

plate like grains has an edge length between 2 and 5 µm and a thickness of about 0.3 µm.

3.3. Dielectric properties

Fig. 6 shows the temperature dependence of dielectric constant (ϵ') and loss factor (ϵ'') for BBT ceramics at various frequencies. Broad peaks are observed in the $\epsilon'(T)$ and $\epsilon''(T)$ plots. The temperature T_m corresponding to the maximum value (ϵ'_m) of ϵ' is shifted to higher temperatures and the value of ϵ'_m decreases with the increase of frequency. The T_m is 692 and 707 K at 1 kHz and 1 MHz, respectively. The temperature corresponding to ϵ'' -maximum also increases with the increase of frequency. The temperature variation of both ϵ' and ϵ'' at various frequencies supports the relaxor behavior of BBT as observed by earlier researchers [3,5]. The degree of relaxation behavior, obtained by $\Delta T_{\text{relaxor}} = T_{m(1 \text{ MHz})} - T_{m(1 \text{ kHz})}$ is found to be 15 K only which suggests the shift of T_m with frequency is not much distinct in BBT ceramics. Similar results are observed by Hou et al. [3].

The dielectric characteristics of relaxor ferroelectrics are known to deviate from the Curie–Weiss law. A modified Curie–Weiss relationship [17] is used to study the diffuseness behavior of a ferroelectric phase transition, given as

$$1/\epsilon' - 1/\epsilon'_m = (T - T_m)^\gamma / C \quad \text{for } (T > T_m) \quad (2)$$

where C is the modified Curie–Weiss constant and the value ($1 \leq \gamma \leq 2$) of γ indicates the degree of diffuseness of the material.

In case of normal ferroelectric, $\gamma = 1$ and for ideal relaxors, $\gamma = 2$. Fig. 7 shows a plot of $\ln(1/\epsilon' - 1/\epsilon'_m)$ as a function of $\ln(T - T_m)$ at 100 kHz. The value of γ calculated from the slope of the curve is found to be 1.88, which reveals the near-relaxor nature of BBT ceramics.

An empirical Vogel–Fülcher relationship [18] is used to account for the dielectric relaxation nature in relaxor ferroelectrics. The variation of frequency of ac field with T_m is given [18] as

$$v = v_0 \exp\{-E_a/k_B(T_m - T_f)\} \quad (3)$$

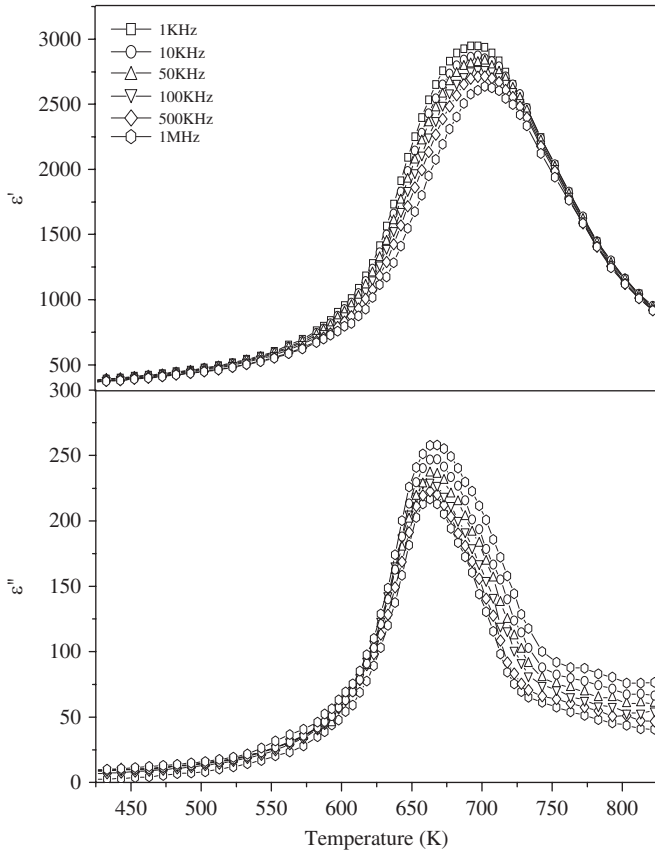


Fig. 6. Temperature dependence of ϵ' and ϵ'' of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics.

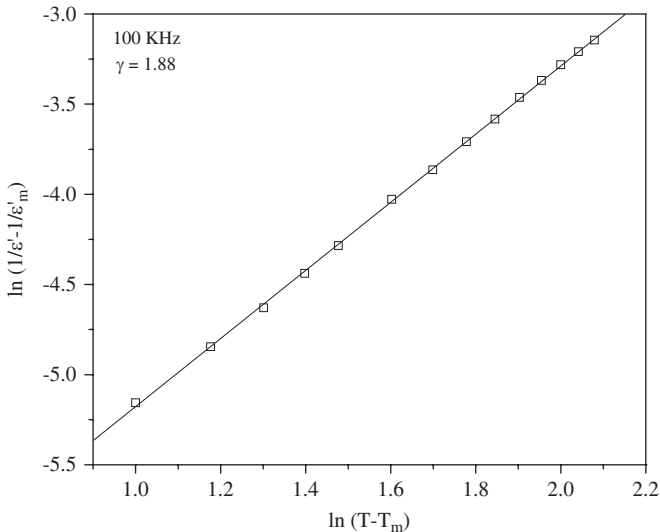


Fig. 7. Plot of $\ln(1/\epsilon' - 1/\epsilon'_m)$ versus $\ln(T - T_m)$.

where v_0 is the Debye frequency, E_a is the activation energy (i.e., the energy barrier between two equivalent polarization states), k_B is the Boltzmann's constant, T_f is the static freezing temperature (i.e., the temperature at which dynamic reorientation of the dipolar cluster polarization can no longer be thermally activated). Fig. 8 shows the plot of $\ln(v)$ as a function of $1000/T_m$ where the symbols represent the experimental data points and the continuous line is a fit to Eq. (3). The analysis of the Vogel–Fülcher model yielded $E_a = 0.2639$ eV, $v_0 = 4.95 \times 10^{21}$ Hz, and $T_f = 620$ K.

It is known that BBT possesses orthorhombic structure below T_m and has stable spontaneous polarization due to the displacement of atoms along polar a -axis [2]. The shifting of T_m with measuring frequency suggests the existence of polar cluster in BBT. Single crystal X-ray diffraction of BBT has suggested a cation re-distribution in the perovskite A- and bismuth-site in the $(\text{Bi}_2\text{O}_2)^{2+}$ layer [14]. The cation re-distribution might be related to the existence of shearing-defects. The random field caused by

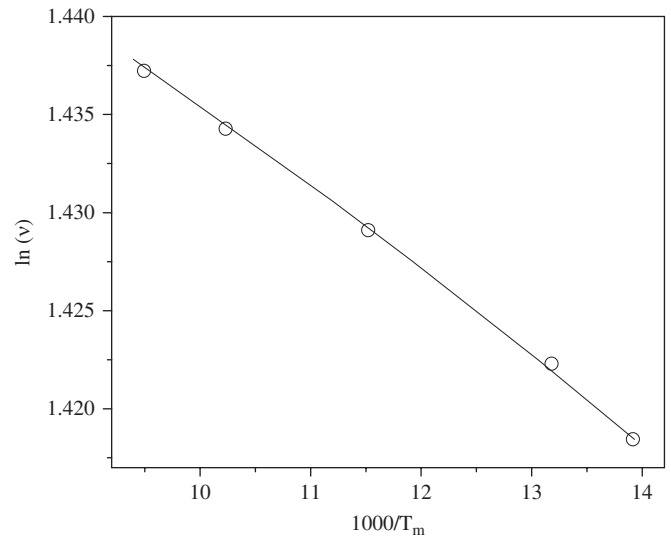


Fig. 8. Frequency dependence of T_m . The symbols and solid line indicate data points and fit to Vogel–Fülcher relationship, respectively.

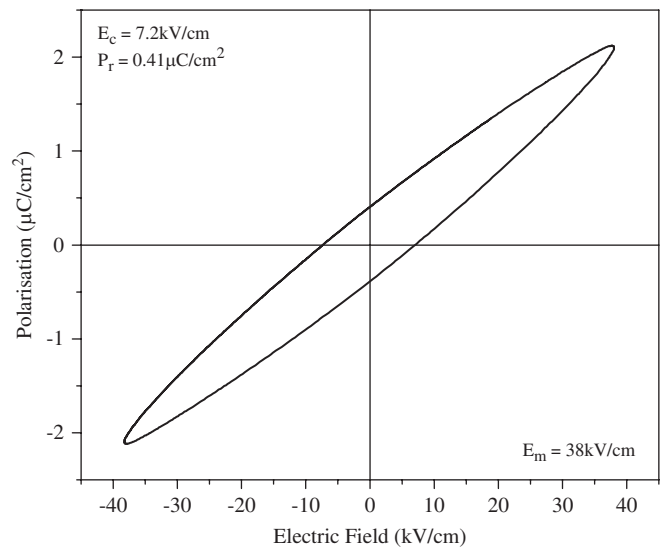


Fig. 9. Polarization–electric field (P–E) hysteresis loop recorded for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ceramics at room temperature.

cation redistribution can result in some polar clusters existing in the macrodomains of the material. But it is not strong enough, compared with the mean electric field, to destroy completely the long range electric ordering in the material [2]. That is why weak relaxor behavior can be found in BBT.

In order to establish the ferroelectric nature of the BBT ceramics, polarization versus electric field measurement on the ceramics was performed at room temperature. Fig. 9 shows the polarization versus electric field loop for BBT. A remnant polarization (P_r) of $0.41 \mu\text{C}/\text{cm}^2$ with a coercive field (E_c) of $7.2 \text{ kV}/\text{cm}$ was obtained under an applied field of $38 \text{ kV}/\text{cm}$. The saturation polarization curve was not achieved due to the limitation (field strength) of the equipment used. The P_r and E_c values were comparable to that reported in the literature for the polycrystalline material [5], although the P_r value was very low compared to single crystal BBT [19].

4. Conclusion

$\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBT) powder was synthesized by a cost-effective soft chemical route. The precursor powder, a mixture of Bi-, Ba-oxalates and TiO_2 was calcined at 1000°C to produce a pure phase BBT. Better homogeneity of the precursor and exothermic decomposition of oxalates had facilitated the formation of BBT phase at 600°C onwards. The microstructure of sintered specimen showed the formation of randomly oriented plate like grains in the ceramics. The temperature dependence of dielectric constant at various frequencies explained the relaxor behavior of the sample. The value of critical exponent γ ($= 1.88$) obtained from the modified Curie–Weiss law, confirmed the same. The frequency

dependence of T_m was modeled using Vogel–Fülcher relation. All these observations clearly suggest that BBT is a relaxor ferroelectric.

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