

Relaxor behavior of (Sr, Ba, Bi)TiO₃ ferroelectric ceramic

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Abstract

The dielectric behavior of (Sr_{0.4}Ba_{0.6})_{0.925}Bi_{0.05}TiO₃ (SBBT) ceramic was investigated in the temperature range from 100 K to 450 K. Broad dielectric maxima, which shift to higher temperature with increasing frequency, and the value of the relaxation parameter $\gamma = 1.6\text{--}2$ estimated from the linear fit of the modified Curie–Weiss law, indicated the relaxor nature of the SBBT ceramic. The dielectric relaxation which follows the Vogel–Fulcher relationship with $T_{VF} = 188$ K, $E_a = 0.0392$ eV, and $\nu_0 = 2.98 \times 10^{11}$ Hz, further supports such a relaxor nature. The P – E hysteresis loop at different temperatures and ‘butterfly’ shape dc bias field dependence of permittivity at $T > T_m$ (the temperature of permittivity maximum) signifies the occurrence of nanopolar clusters, which is the typical characteristic of relaxor ferroelectrics. At 300 K and 10 kHz, the dielectric constant and loss $\tan\delta$ are ~ 2210 and 0.00118, respectively. The tunability (28%) and figure of merit (237) at room temperature show that the SBBT ceramic could be a promising candidate for tunable capacitor applications.

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1. Introduction

Barium strontium titanate (Sr, Ba)TiO₃ with high dielectric constant value combined with low dissipation factor makes SBT one of the promising candidates for dynamic random access memory (DRAM) applications. The (Sr, Ba)TiO₃ system is well known for its strong response to the applied dc electric field. This property is very attractive and has been used to develop devices operating in the microwave and millimeter range such as phase shifters, frequency agile filters, and tunable capacitors [1].

Recently, the effect of substitution on dielectric relaxation, ferroelectric phase transition and electrical properties of (Sr, Ba)TiO₃ has been extensively studied [2,3]. On partial substitution of dopants like Pb, Zr, Mg, Hf [4–8], the variation of ϵ around T_c gets broadened out in both ceramics and single crystal samples. Broadening increases with increasing concentration of the dopants, as also does the deviation from Curie–Weiss behavior at temperatures

above the peak temperature (T_m) of the ϵ – T variation. The observed broadening in ϵ – T variation has been attributed to the presence of nano-regions resulting from local composition variation. Different nano-regions in a macroscopic sample transform at different temperatures giving rise to a range of transformation temperature, the so-called ‘Curie range’. Thus the compositional fluctuation [9,10] in an otherwise compositionally homogeneous system leads to a diffuse phase transition (DPT). In compositionally homogeneous systems quenched random disorder breaks the long range polar order at unit cell level, leading to broad ϵ – T response [11]. Such materials exhibit slow enough relaxation dynamics and hence have been termed as ferroelectric relaxors [9–11]. All of a series of impurity doped (Sr, Ba)TiO₃ systems such as Mg, Zr, Pb, etc., show ferroelectric relaxor behavior.

In the present investigation, we have studied the ferroelectric relaxor behavior in Bi substituted (Sr_{0.4}Ba_{0.6})TiO₃. There are several reports on the dielectric properties of (Sr, Ba)_{1–1.5x}Bi_xTiO₃ bulk ceramics [12–14], however, the detailed descriptions on the relaxor behavior have not been found in the literature. We report detailed dielectric studies and structure description of the sample, the relaxor behavior of (Sr_{0.4}Ba_{0.6})_{1–1.5x}Bi_xTiO₃ ($x = 0.05$) ferroelectric ceramic

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was studied chiefly, and nanopolar clusters were attributed to it. Meanwhile, the data has been quantitatively analyzed in terms of parameters characterizing the relaxor behavior. It was a good example for studying other doped perovskite systems.

2. Experimental

The $(\text{Sr}_{0.4}\text{Ba}_{0.6})_{1-1.5x}\text{Bi}_x\text{TiO}_3$ ($x = 0.05$, abbreviated as SBBT) ceramic was prepared following the conventional solid-state reaction technique. High purity (99.99%) powders of SrCO_3 , BaCO_3 , TiO_2 and Bi_2O_3 were weighed in stoichiometric proportions and wet-mixed, taking alcohol as the mixing medium. After mixing and drying, the powder was calcined at 1100°C for 6 h. The calcined powder was remixed, dried, and then pelletized at 25 MPa pressure into a 12 mm dia. pellet using polyvinyl alcohol as binder. The pellets were then sintered at 1260°C for 4 h and cooled naturally to room temperature.

The pellets of SBBT were subjected to structural and phase purity characterization employing powder X-ray diffraction (XRD) and scanning electron microscopy (SEM-JSM-5800). The XRD analysis was carried out using $\text{Cu K}\alpha$ X-rays employing a Rigaku goniometer and rotating anode X-ray generator working at 4 kW output power. Electroding of the pellets for dielectric measurement was then done by painting their flat surfaces with high temperature silver paint and then keeping them at 850°C for 30 min. The dielectric constant and loss $\text{tg}\delta$ of the samples were measured using an HP4284 LCR meter from 0.1 to 1000 kHz in the temperature range of 100–450 K. The polarization–electric field (P – E) hysteresis loop was obtained by TF analyzer 2000 FE-module system (AIXACCT). The tunability was measured using a dc power source (PS350/5000V-25W) and multi-frequency LCR meter (TH2816) at room temperatures.

3. Results and discussion

3.1. Dielectric behavior and diffuse phase transition of SBBT ceramics

Fig. 1 shows the dielectric constant (ϵ) and loss $\text{tg}\delta$ of the SBBT ceramic as a function of temperature at different frequencies (0.1–1000 kHz). From Fig. 1(a), the temperature dependences of dielectric constant depict a typical relaxor behavior with strong dispersion of the $\epsilon(T)$ peak at $T < T_m$ (T_m , the temperature of permittivity maximum). The broad dielectric maxima shifting towards higher temperature with increasing frequency signify the relaxor-type behavior of the ceramic. The loss tangent (Fig. 1(b)) peak is also found shifting to higher temperature with increasing frequency. At room temperature (300 K), the ϵ is ~ 2210 with a low loss $\text{tg}\delta$ of 0.00118 at 10 kHz.

It is known that the dielectric constant ϵ of a normal ferroelectric, above the Curie temperature, follows the Curie–Weiss law described by:

$$1/\epsilon = (T - T_c)/C \quad (T > T_c) \quad (1)$$

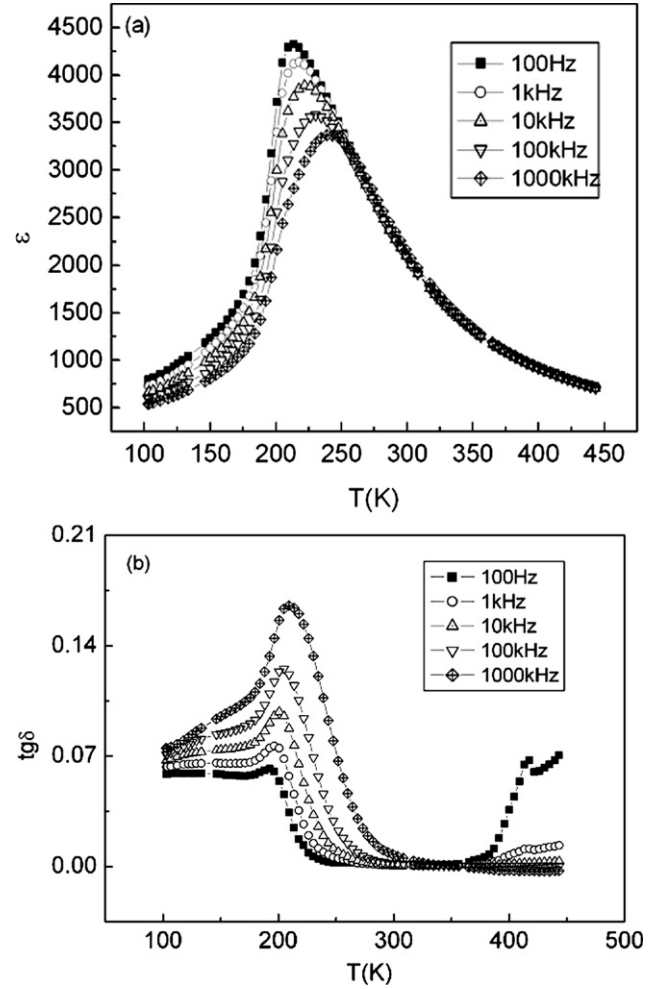


Fig. 1. Temperature dependence of ϵ and $\text{tg}\delta$ of SBBT ceramic at different frequency.

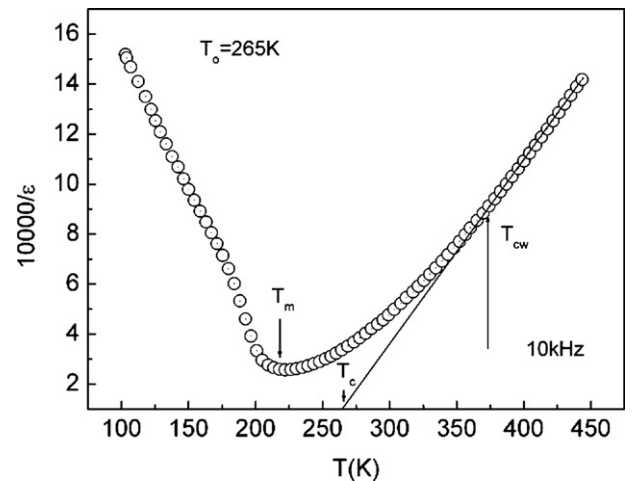


Fig. 2. The inverse dielectric constant ($1/\epsilon$) as a function of temperature at 10 kHz. (Symbols, experimental data; solid line, fitting to the Curie–Weiss law).

where T_c is the Curie–Weiss temperature and C is the Curie–Weiss constant. Fig. 2 shows the plots of temperature versus inverse dielectric constant (at 10 kHz) fitting to the Curie–Weiss law for SBBT ceramic.

Table 1
The maximum dielectric constant (ϵ_m), the temperature of the maximum dielectric constant (T_m), Curie–Weiss temperature (T_c), the temperature above which the dielectric constant (ϵ) follows the Curie–Weiss law (T_{cw}), $\Delta T_m = T_{cw} - T_m$ and the critical parameter γ for SBBT ceramic at different frequencies

Frequency (kHz)	ϵ_m	T_m (K)	T_c (K)	T_{cw} (K)	ΔT_m (K)	γ
0.1	4325	214	263	370	156	1.599
1	4137	218	264	371	153	1.620
10	3890	222	265	372	150	1.746
100	3576	230	266	375	145	1.699
1000	3367	239	272	377	138	1.929

The parameter ΔT_m , to illustrate the degree of the deviation from the Curie–Weiss law, was defined as

$$\Delta T_m = T_{cw} - T_m \quad (2)$$

where T_{cw} denotes the temperature from which the permittivity starts to deviate from the Curie–Weiss law, and T_m represents the temperature of the dielectric constant maximum. At 10 kHz, $\Delta T_m = 150$ K. It can be seen from Table 1 that ΔT_m decreases slightly with increasing frequency.

The dielectric characteristics of relaxor ferroelectrics are known to deviate from the typical Curie–Weiss behavior and can be described by a modified Curie–Weiss relationship [15, 16]:

$$1/\epsilon - 1/\epsilon_m = (T - T_m)^\gamma / C_1, \quad 1 \leq \gamma \leq 2 \quad (3)$$

where γ and C_1 are assumed to be constant, with $1 \leq \gamma \leq 2$. The parameter gives the information on the character of the phase transition. Its limiting values are $\gamma = 1$ and $\gamma = 2$ in expression (3) of the Curie–Weiss law, $\gamma = 1$ is for the case of a normal ferroelectric and the quadratic dependence is valid for an ideal ferroelectric relaxor respectively [17,18]. Thus the value of γ can also characterize the relaxor behavior. The plot of $\log(1/\epsilon - 1/\epsilon_m)$ as a function of $\log(T - T_m)$ is shown in Fig. 3 by fitting with Eq. (3): the exponent γ , determining the degree of the diffuseness of the phase transition, is obtained from the slope of $\log(1/\epsilon - 1/\epsilon_m)$ -vs- $\log(T - T_m)$ plot. We obtained the value of the parameter γ to be 1.6–1.92, which is close to 2, suggesting that the prepared ceramic is a relaxor ferroelectric [18,19]. Yet another parameter, which is used to characterize the degree of relaxation behavior in the frequency range of 100 Hz to 100 kHz, is described [8] as

$$\Delta T_{\text{relax}} = T_{\epsilon_m(100 \text{ kHz})} - T_{\epsilon_m(100 \text{ Hz})}. \quad (4)$$

The value of ΔT_{relax} was determined to be 29.9 K for the present sample. The above characterization done on the basis of Curie–Weiss law and the value of empirical parameters like ΔT_m , γ , and ΔT_{relax} suggest that the permittivity of SBBT ceramic follows the Curie–Weiss law only at temperatures much higher than T_m . Thus the large deviation from the Curie–Weiss behavior, large relaxation temperature T_{relax} , and γ close to 2 all suggest that SBBT is a relaxor ferroelectric.

3.2. Vogel–Fulcher relationship

In relaxor materials, an empirical Vogel–Fulcher (VF) relationship can be used to account for the dielectric relaxation nature [20,21]. The dielectric relaxation appears as a result

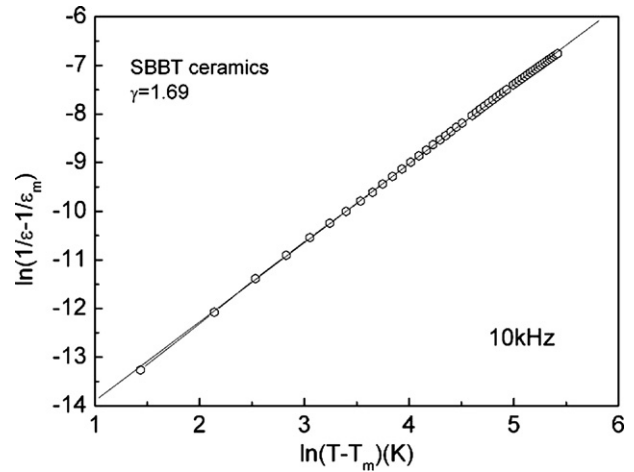


Fig. 3. Plot of $\log(1/\epsilon - 1/\epsilon_m)$ as a function of $\log(T - T_m)$ for SBBT ceramics measured at 10 kHz. The solid line is the fit using Eq. (3).

from thermally activated polarization reversals between two equivalent variants. Based on this model, the polarization flipping frequency ν_o is related to the activation energy E_a (the barrier between two equivalent polarization states) as follows:

$$\nu = \nu_o \exp[-E_a/k_B(T - T_{VF})] \quad (5)$$

where ν_o is the attempt frequency, k_B is Boltzmann's constant, and T_{VF} is the static freezing temperature. Fig. 4 shows the temperature dependence of the relaxation frequency, plotted as T vs $\ln \nu$, and the best of Eq. (5) to the experimental data. Our analysis based on the VF model yielded $T_{VF} = 188$ K, $E_a = 0.0392$ eV, and $\nu_o = 2.98 \times 10^{11}$ Hz, which provides the evidence of the relaxor behavior in SBBT ceramic.

The relaxor behavior can be induced by many reasons such as microscopic composition fluctuation, the merging of micropolar regions into macropolar regions, or a coupling of order parameter and local disorder mode through the local strain, or the randomly distributed electrical field [9,10,13,22]. However, the occurrence of relaxation in Bi substituted barium strontium titanate should be attributed to the existence of a nano-polar region due to Bi doping. The replacements of Sr^{2+} by Bi^{3+} ions is known in the reports [13,23,24] as the size of the Bi^{3+} ionic radius being close to that of Sr^{2+} ions, which leads to the formation of dipolar impurities and defects that have a profound influence on the static and dynamic properties of this material. In SBBT ceramic, the dipolar entities form polar nanodomains and these domains can interact leading to complex relaxational behavior. The quantitative characterization and comparison of the relaxor behavior based on empirical parameters (ΔT_m , γ , ΔT_{relax}) confirm this.

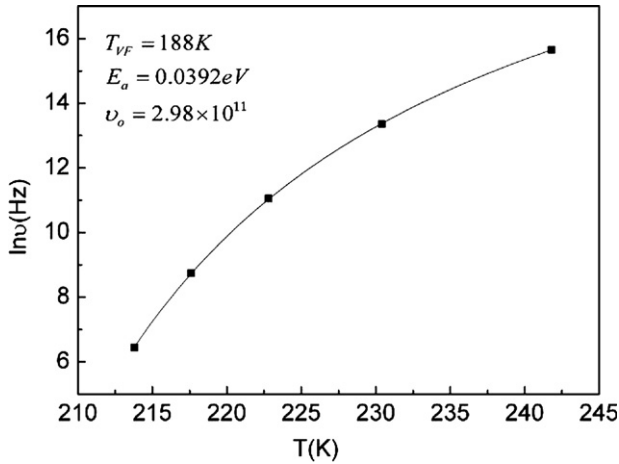


Fig. 4. Temperature as a function of relaxation frequency for SBBT ceramic, plotted in the form of T_m versus $\ln \nu$. The solid line is the fit using the Vogel–Fulcher model, as expressed in Eq. (5).

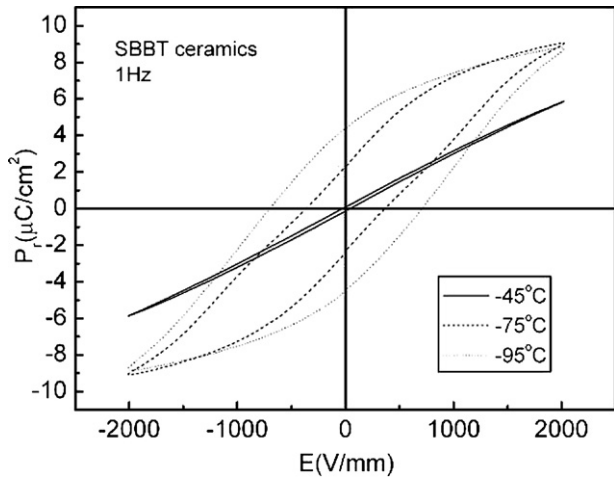


Fig. 5. P – E hysteresis loops of SBBT ceramics measured at different temperatures.

3.3. Electrical properties of SBBT ceramics

The P – E hysteresis loop of the SBBT ceramics measured at different temperatures and 1 Hz is shown in Fig. 5. It was found that the slim hysteresis loop was becoming the broad one with decreasing temperature, and remnant polarization P_r also increased gradually with decreasing temperature, which signifies the forming process of polar nanodomains in this temperature range. That is a typical behavior of ferroelectric relaxor [9,21,24].

Fig. 6 shows the dc field dependence of the ϵ and $tg\delta$ for the SBBT ceramic, which was measured at 10 kHz. The electric field dependence of dielectric permittivity (tunability) is defined as

$$k = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0)} \quad (6)$$

where $\epsilon(0)$ and $\epsilon(E)$ represent the ϵ without and with a certain field E , respectively. The ‘butterfly’ shape field dependence of dielectric permittivity further supports the appearance of nanopolar clusters of a ferroelectric relaxor. The tunability of

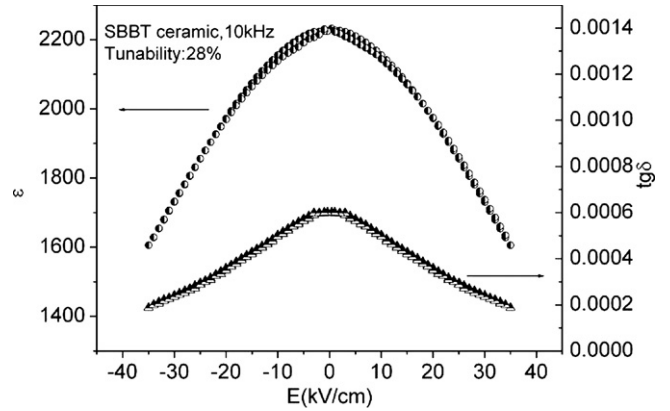


Fig. 6. DC electric field dependence of ϵ and $tg\delta$ for SBBT ceramic at room temperature.

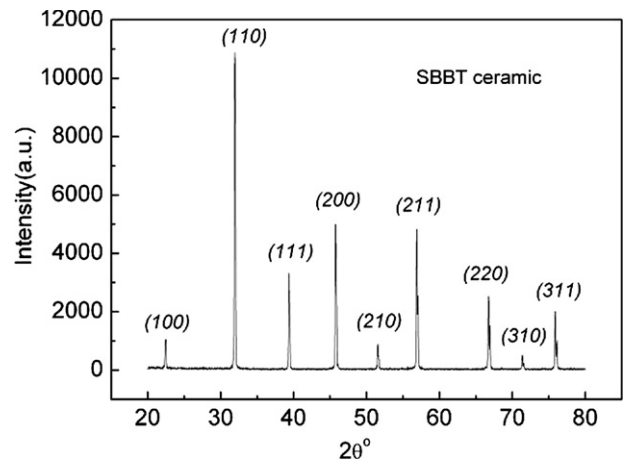


Fig. 7. The XRD pattern of SBBT ceramic at room temperature.

the SBBT ceramic is about 28%. The ϵ and loss $tg\delta$ were found to decrease from 2230 to 1605, and from 0.0006 to 0.0002 with increasing electric fields from 0 to 35 kV/cm, respectively. The calculated figure of merit FOM ($k/tg\delta$) is 237 [5], implies the SBBT ceramic could be a promising candidate for microwave applications.

These values are competitive to all the currently studied tunable materials, such as $(\text{Sr}, \text{Pb})\text{TiO}_3$ and $(\text{Ba}, \text{Sr})\text{TiO}_3$, etc. [4,25]. In addition, the high ϵ value permits much space in further decreasing $tg\delta$. It is expected that the properties, in particular the loss $tg\delta$, can be further improved by adding additives to this solid solution and the ϵ can be tailored to suitable values for tunable capacitor applications.

3.4. Structure descriptions

It can be seen from Fig. 7 that SBBT was pure cubic perovskite phase structure at room temperature. It suggested that Bi ions dissolved into A-site absolutely.

We also can learn from Fig. 8 that SBBT ceramic was symmetrical and regular and grain size ranged from 1 to 2 μm . It signified more that this ceramic was feasible for the applications.

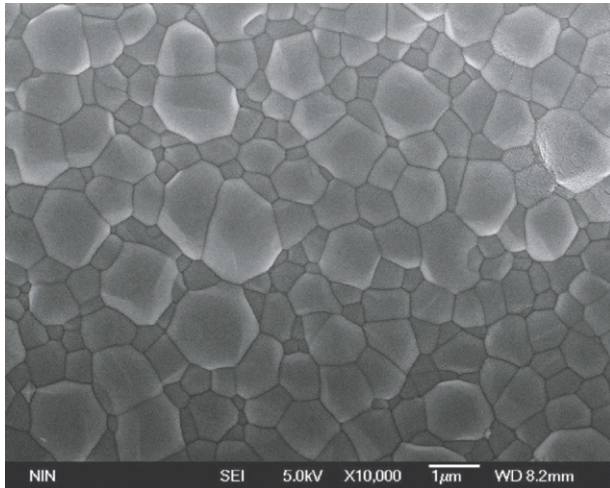


Fig. 8. Scanning electron micrograph of SBBT ceramic.

4. Conclusions

In summary, the ferroelectric relaxor behavior of SBBT ceramic are studied in the temperature range from 100 K to 450 K at various frequencies. A broad dielectric peak with frequency dispersion was observed. The occurrence of diffused phase transition and strong frequency dispersion of maxima in the permittivity versus temperature strongly indicates the relaxor behavior for this SBBT ceramic. The quantitative characterization and comparison of the relaxor behavior based on empirical parameters (ΔT_m , γ , ΔT_{relax}) confirms its relaxor behavior. It was a good example for studying other doped perovskite systems. Meanwhile, the high dielectric constant, low loss tangent, high tunability, high figure of merit and compact structure at room temperature, indicates the ceramic is promising for tunable capacitor applications.

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