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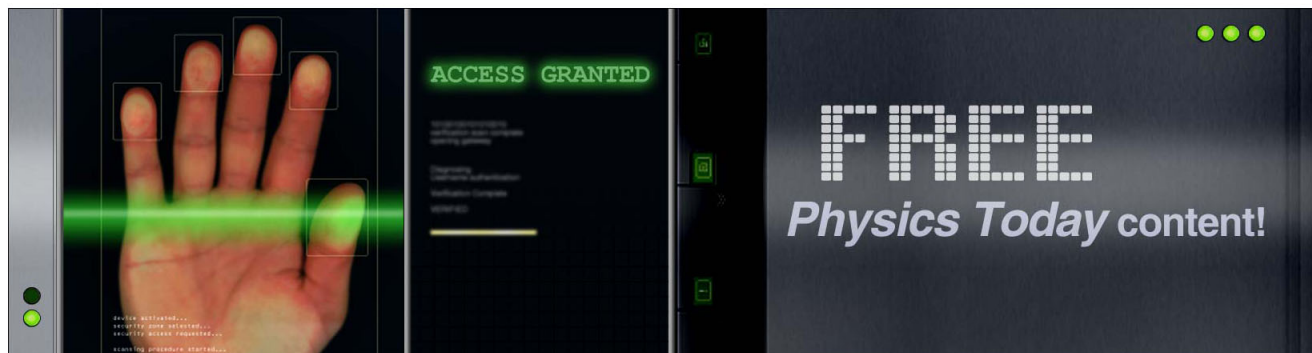
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## ADVERTISEMENT



# Dielectric relaxation and relaxor behavior in bilayered perovskites

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$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramics exhibit a complex dielectric behavior, showing typical relaxor behavior. The relaxation processes are described by the Cole–Cole model [K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941)]. At temperatures below 490 K, the dielectric relaxation is associated to the relaxorlike ferroelectric behavior, resulting from the inhomogeneous distribution of barium due to its preference for the bismuth site. Above that, the interaction between the dipoles, which form the microdomains above the relaxor ferroelectric peak and the electrons, which are due to the ionization of the oxygen vacancies are discussed as the probable origin of the relaxation.

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$\text{SrBi}_2\text{Nb}_2\text{O}_9$  is a member of the family of the bismuth layer-structured materials,<sup>1–6</sup> which are interesting ferroelectrics for technical devices. The crystal structure is composed of  $(\text{Bi}_2\text{O}_2)^{2+}$  layers interleaved with perovskite-type blocks  $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ . It has been suggested that the main contribution to its spontaneous polarization is due to displacement of the A cation in the perovskite block, which is quite different for the perovskite structure. An interesting feature of these materials is that some of them allow cation site mixing among atom positions,<sup>7</sup> especially between the bismuth and the A-site of the perovskite block.<sup>2</sup> Barium doping has showed its preference for the bismuth site, which occur to equilibrate the lattice dimensions between the  $(\text{Bi}_2\text{O}_2)^{2+}$  layers and the perovskite blocks.<sup>1</sup> On the other hand, for  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  the incorporation of barium to the structure promotes a complex dielectric spectrum showing a transition from a normal to a relaxor ferroelectric.<sup>3</sup> For these ceramics the analysis of the dielectric relaxation mechanisms could be complex but very interesting. The present paper shows the study, which have been made on the dielectric relaxation mechanisms in  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramics.

$\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ceramics were prepared by solid-state reaction method. The powders of the starting materials were mixed with approximately 4.5% excess weight of  $\text{Bi}_2\text{O}_3$  due to its high vapor pressure. The oxide mixtures were calcined in air atmosphere at 900 °C for 2 h; ground and again milled for 24 h. Then, these powders were pressed uniaxially by using 200 MPa and sintered in a closed alumina crucible at 1100 °C for 1 h. The relative density for the final ceramic was ~98%. The x-ray diffraction analysis showed a pure orthorhombic structure. Gold painted electrodes were applied to the opposite faces of sintered samples to make the dielectric analysis. The dielectric measurements were carried out by using a computer controlled Agilent 4284A LCR Meter over a wide frequency range ( $10^2$ – $10^6$  Hz) from room temperature up to 550 °C approximately, applying 200 mV ac to the samples.

Figure 1 shows the temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity, at various frequencies, as example of the observed behavior in the studied frequency range. For the real part  $\epsilon'$  it could be observed that its maximum value decreases with the increase in frequency and its corresponding temperature ( $T_m$ ) shifts up to higher temperatures, showing high frequency dispersion. The value of  $T_m$  is ~466 and ~529 K at 100 Hz and 1 MHz, respectively, showing a shift of temperature of approximately 63 K, which is in good agreement with previous reports,<sup>3</sup> but lower than that of other relaxor ceramics.<sup>8</sup> For  $\epsilon''$  the maximum values are observed at lower temperatures than that of  $T_m$  and the corresponding temperature again shows significant dispersion with the frequency. These features are typical of materials showing a relaxor behavior of

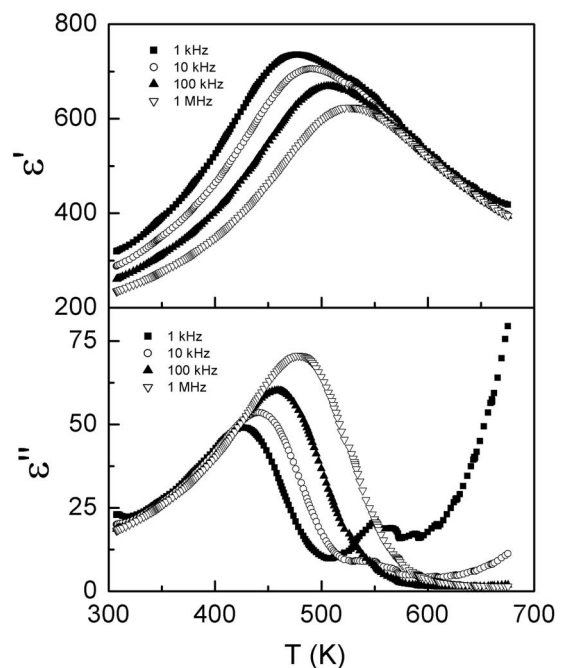


FIG. 1. Temperature dependence of the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric permittivity at various frequencies.

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the ferroelectric-paraelectric transition. At the higher temperature zone an abrupt increase of  $\varepsilon''$  is observed, especially in the low frequency range, which could be associated to the conductivity losses.

The origin of the relaxor behavior for these ceramics can be explained from a positional disorder of cations on A or B sites of the perovskite blocks that delay the evolution of long-range polar ordering.<sup>8</sup> It has been reported<sup>8</sup> that the incorporation of barium to the  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  system provides a higher frequency dependence of the dielectric parameters, showing a relaxorlike ferroelectric. This behavior could be explained by considering the incorporation of a bigger ion into the A site of the perovskite block.<sup>9</sup> The barium ions not only substitute the strontium ions in the A site perovskite block but enter the  $(\text{Bi}_2\text{O}_2)^{2+}$  layers leading to an inhomogeneous distribution of barium and local charge imbalance in the layered structure.<sup>1</sup>

From Fig. 1 it is evident that the dielectric parameters do not reflect the relaxation behavior described by the Debye model. The Cole–Cole model, which considers a distribution of the relaxation time,<sup>10</sup> is used to analyze the deviation from the ideal Debye model. In this model,  $\varepsilon'$  and  $\varepsilon''$  can be written as

$$\varepsilon'(\omega) = \varepsilon_\infty + \left( \frac{\Delta\varepsilon'}{2} \right) \left\{ 1 - \frac{\sinh(\beta z)}{\cosh(\beta z) + \cos\left(\beta \frac{\pi}{2}\right)} \right\}, \quad (1)$$

$$\varepsilon''(\omega) = \left( \frac{\Delta\varepsilon'}{2} \right) \frac{\sin\left(\beta \frac{\pi}{2}\right)}{\cosh(\beta z) + \cos\left(\beta \frac{\pi}{2}\right)}, \quad (2)$$

where  $z = \ln(\omega\tau)$ ,  $\Delta\varepsilon' = \varepsilon_s - \varepsilon_\infty$ ,  $\varepsilon_\infty$  is the permittivity at high frequency,  $\varepsilon_s$  is the static permittivity,  $\omega$  is the angular frequency,  $\tau$  is the mean relaxation time, and  $\beta = (1-\alpha)$ , where  $\alpha$  reflects the distribution width of the relaxation time.

For the studied ceramics the frequency dependence of  $\varepsilon'$  and  $\varepsilon''$  can be described by using Eqs. (1) and (2), respectively. Figure 2 shows the experimental data (solid points) and the corresponding theoretical results (solid lines) at a few representative temperatures, showing a good agreement between experimental and theoretical values. The analysis was made from 423 to 523 K approximately. For temperatures above 523 K the dielectric spectrum could not be described by using the Cole–Cole equations considering the behavior of  $\varepsilon''$  (Fig. 1).

Figure 3 shows the temperature dependence for the  $\alpha$  parameter, calculated from the  $\beta$  values, which were obtained from the fitting in Fig. 2. From  $\alpha$  values two characteristic regions could be considered from the break around 490 K, which were named as first (TR-1) and second (TR-2) temperature region, respectively. Below 490 K,  $\alpha$  decreases, being 0.86 and 0.67 for 433 and 488 K, respectively; showing a high dispersive relaxation. Above 490 K,  $\alpha$  is almost constant (between 0.57 and 0.53), showing a lower dispersive relaxation. The results for TR-1 have been obtained in the temperature range where a higher dispersion of the dielectric parameters is observed (Fig. 1), which is related to the relaxor ferroelectric behavior. Then, it could be consid-

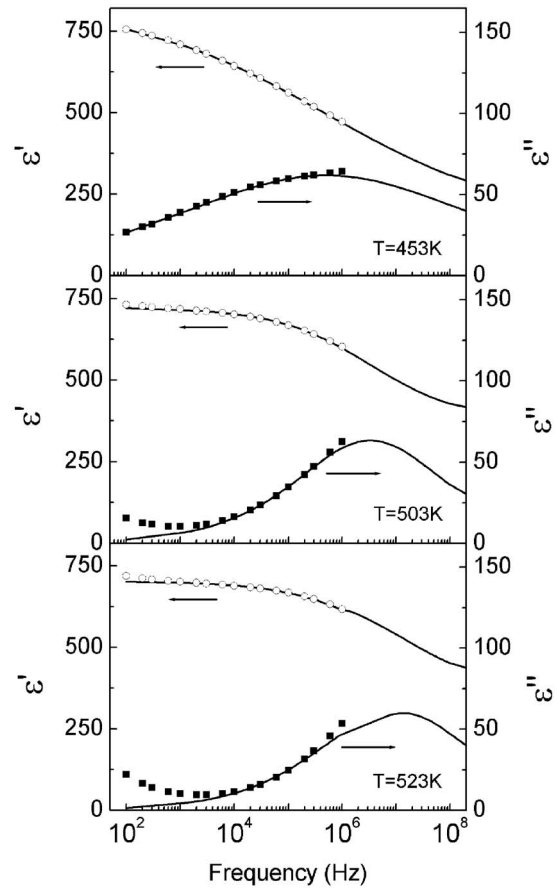


FIG. 2. Frequency dependence of the real  $\varepsilon'$  (○) and imaginary  $\varepsilon''$  (■) parts of the dielectric permittivity at a few representative temperatures. Solid lines represent the fitting by using Eqs. (1) and (2).

ered that the main origin of the dielectric relaxation process below 490 K could be associated to the relaxorlike ferroelectric behavior of the material.

It is known that the relaxation time ( $\tau$ ) of a relaxor behavior follows the empirical Vogel–Fulcher law, which could be written as  $\tau = \tau_0 \exp[U/k_B(T - T_{VF})]$ , where  $\tau_0$ ,  $U$ ,  $k_B$ , and  $T_{VF}$  are, respectively, the pre-exponential term, the activation energy, the Boltzmann's constant and the characteristic temperature. It is found that the temperature dependence of the relaxation time for TR-1 can be well fitted to the Vogel–

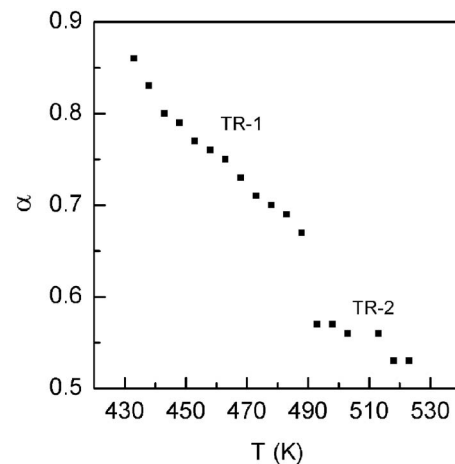


FIG. 3. Temperature dependence for the  $\alpha$  parameter, calculated from the  $\beta$  values, which were obtained from the fitting in Fig. 2.

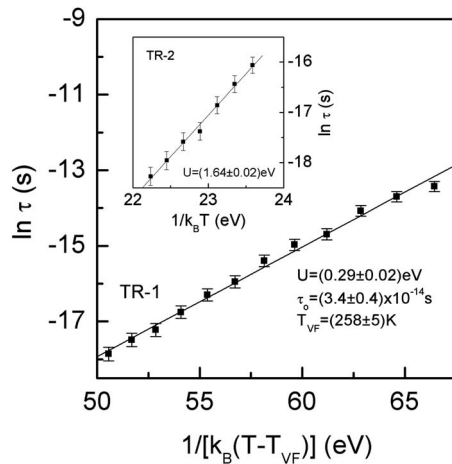


FIG. 4. Temperature dependence of the mean relaxation time ( $\tau$ ) for both characteristic temperature regions. The first one (TR-1) can be well fitted to the Vogel–Fulcher law and the second one (TR-2) follows the Arrhenius relation (inset of the figure), respectively.

Fulcher law, as shown in Fig. 4. On the other hand, it is found that the relaxation time for TR-2 follows the Arrhenius relation. Notice the temperature dependence of the mean relaxation time for TR-2 in the inset of Fig. 4. The corresponding activation energy value is quite different than that of the activation energy value obtained for TR-1. It is clear that the relaxorlike ferroelectric behavior cannot be the main cause of the second relaxation process. However, from Fig. 1 it could be assumed an important influence of the conductivity processes on the relaxation process above 490 K.

It is known that barium ions have preference for the bismuth site in the barium doped  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ceramics.<sup>1</sup> The electrical charge unbalance caused by the trivalent  $\text{Bi}^{3+}$  ion substitution for the divalent  $\text{Ba}^{2+}$  ions is compensated by the creation of oxygen vacancies. The activation energy value obtained for TR-2 is in the same order than those previous reports, which have been associated to ionized oxygen vacancies.<sup>11,12</sup> Hence, it is reasonable to assume that the hopping of the electrons, which appears due to the ionization of the oxygen vacancies, could contribute to the dielectric relaxation and its long-distance movement contributes to the electrical conduction.

On the other hand, the second relaxation process (above 490 K) occurs at higher-temperature side of the relaxor peak.

For a relaxor ferroelectric, microdomains can be observed even at higher temperature far from the temperature of the relaxor behavior peak.<sup>13</sup> From this point of view, the authors suggest that the second relaxation process could result from the contribution of the interaction between the dipoles, which forms the microdomains existing at higher-temperature side of the relaxor peak, and the electrons that are due to the ionization of the oxygen vacancies.

As summary, two dielectric relaxation processes have been analyzed in  $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramics. The first one has been associated to the relaxorlike ferroelectric behavior as the main cause. The other one has been associated to the interaction between the dipoles, which form the microdomains that exist above the relaxor ferroelectric peak, and the electrons, which are due to the ionization of the oxygen vacancies. Further analysis is required concerning the electrical conductivity behavior to archive a better understanding.

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<sup>1</sup>M. S. Haluska and S. T. Mixture, *J. Solid State Chem.* **177**, 1965 (2004).

<sup>2</sup>S. M. Blake, M. J. Falconer, M. McCreedy, and P. Lightfoot, *J. Mater. Chem.* **7**, 1609 (1997).

<sup>3</sup>S. Huang, Ch. Feng, L. Chen, and Q. Wang, *J. Am. Ceram. Soc.* **89**, 328 (2006).

<sup>4</sup>B. Wachsmuth, E. Zschech, N. W. Thomas, S. G. Brodie, S. J. Gurman, S. Baker, and S. C. Bayliss, *Phys. Status Solidi A* **135**, 59 (1993).

<sup>5</sup>D. Nelis, D. Mondelaers, G. Vanhoyland, A. Hardy, K. Van Werde, H. Van den Rul, M. K. Van Bael, J. Mullens, L. C. Van Poucke, and J. D'Haen, *Thermochim. Acta* **426**, 39 (2005).

<sup>6</sup>B. J. Kennedy, and Ismunandar, *J. Mater. Chem.* **9**, 541 (1999).

<sup>7</sup>M. Mahesh Kumar and Z.-G. Ye, *J. Appl. Phys.* **90**, 934 (2001).

<sup>8</sup>C. Miranda, M. E. V. Costa, M. Avdeev, A. L. Kholkin, and J. L. Baptista, *J. Eur. Ceram. Soc.* **21**, 1303 (2001).

<sup>9</sup>Y. Wu, M. J. Forbess, S. Seraji, S. J. Limmer, T. P. Chou, C. Nguyen, and G. Z. Cao, *J. Appl. Phys.* **90**, 5296 (2001).

<sup>10</sup>K. S. Cole and R. H. Cole, *J. Chem. Phys.* **9**, 341 (1941).

<sup>11</sup>S. A. Long and R. N. Blumenthal, *J. Am. Ceram. Soc.* **54**, 577 (1971).

<sup>12</sup>R. Waser, *J. Am. Ceram. Soc.* **74**, 1934 (1991).

<sup>13</sup>G. Burns, *Phase Transitions* **5**, 261 (1985).