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## Debye's temperature and heat capacity for $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$ relaxor ferroelectric ceramic

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A lead-free relaxor ferroelectric,  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$ , was synthesized via solid-state reaction and the temperature-dependence of the heat capacity was measured in a wide temperature range. The dielectric permittivity was also measured between 500 Hz and 5 MHz in the same temperature range. No anomaly has been detected in the heat capacity curve for the whole temperature range covered in the present experiments, while broad peaks have been observed in the dielectric permittivity with high frequency dispersion. A typical relaxor behavior has been observed from the dielectric analysis. The Debye's temperature has showed a minimum value near the freezing temperature. The results are discussed considering the spin-glass model and the high frequency dispersion, which has been observed for the studied relaxor system.

**Keywords:** Relaxors; ferroelectrics; heat capacity; ceramics.

### 1. Introduction

It is known that normal ferroelectric materials go through a phase transition into the ferroelectric phase at the Curie temperature ( $T_C$ ), which is accompanied by a sharp dielectric permittivity peak without any frequency-dependence. On the other hand, relaxor ferroelectric systems show a broad maximum peak dielectric permittivity and a frequency-dependence on its corresponding temperature; the temperature of the corresponding maximum for the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) components of the dielectric permittivity appears at different values.

An important number of researches have been developed on relaxor ferroelectrics.<sup>1-5</sup> However, despite their very attractive physical properties, the identification of the nature of the dielectric response in relaxor systems still remains open and requires additional theoretical and experimental information, which can be very interesting to contribute to the explanation of the origin of the observed anomalies.

In order to understand the nature of the relaxor behavior, the thermodynamic information is very important and for that specific heat measurements over wide temperature ranges are indispensable. Heat-capacity experiments on relaxor ferroelectrics have showed different behaviors for typical relaxors such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (see Ref. 6) than that of  $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$  relaxor ferroelectric.<sup>7,8</sup> For the lead-based systems, the results have been associated to the formation of the ferroelectric polar nanoregions (PNRs)

showing an order-disorder type mechanism.<sup>6</sup> A displacive type mechanism has been associated to the behavior which was observed for the lead-free ferroelectric relaxor.<sup>8</sup>

$\text{SrBi}_2\text{Nb}_2\text{O}_9$  system, which belongs to the Aurivillius family, shows a normal ferroelectric behavior in the ferroelectric-paraelectric phase transition.<sup>9,10</sup> Dielectric studies in  $\text{Sr}_{1-x}\text{A}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  system, with  $A = \text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $0 \leq x \leq 30$  at.%, have also showed a normal ferroelectric behavior.<sup>11</sup> However, relaxor ferroelectric behavior has been reported for  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  when  $x \geq 50$  at.%.<sup>5,12</sup> The increase of the compositional disorder has been analyzed as the main cause for the relaxor behavior.<sup>5</sup> It has been shown by using the refined atomic data that there is a mixing of different elements into A sites and bismuth sites in the layered structure. An increase of the frequency dispersion degree has also been observed with the increasing of the barium concentration.<sup>5</sup>

The present paper shows the heat capacity measurement results, which has been carried out on  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  relaxor ferroelectric ceramic in order to study thermodynamic properties of this lead-free ferroelectric system.

### 2. Experimental Procedure

$\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic was prepared by the solid-state reaction method. The powders of the starting materials were mixed with a desired weight ratio. The oxide

mixtures were calcined, in air atmosphere, at 950°C for 2 h in a closed alumina crucible and ball-milled again. The powders were pressed uniaxially by using 200 MPa and sintered in a closed alumina crucible at 1100°C for 1 h. A density value higher than 97% of the theoretical density values was obtained. The structural analysis by using X-ray diffraction<sup>5</sup> has showed an orthorhombic structure with the space group  $A2_1am$ . The refined atomic data, which was obtained from using the X-ray diffraction pattern, has showed the mixing of different elements into  $A$  sites of the perovskite blocks and bismuth sites in the layered structure.<sup>5</sup> The studied system has also been evaluated concerning dielectric, piezoelectric, pyroelectric and ferroelectric properties.<sup>5,13,14</sup>

The differential scanning calorimetry (DSC) measurements were performed between 40°C and 500°C in argon atmosphere (Netzsch 404C with TASC 414/4 controller). Silver painted electrodes were applied to the opposite faces of disk-like samples by a heat treatment at 590°C. The dielectric measurements were carried out by using a computer controlled HIOKI 3532-50 LCR HiTESTER over a wide frequency range (50 Hz–1 MHz) from room temperature up to 500°C, approximately, by applying 200 mV AC to the samples.

### 3. Results and Discussion

Figure 1 shows the temperature-dependence of the specific heat ( $C_p$ ) and also the dielectric permittivity ( $\epsilon'$ ). It is known that relaxor ferroelectrics do not exhibit thermodynamic anomalies in  $C_p$  versus  $T$ . However, the corresponding Debye's temperature ( $T_D$ ) curves, which can be obtained by

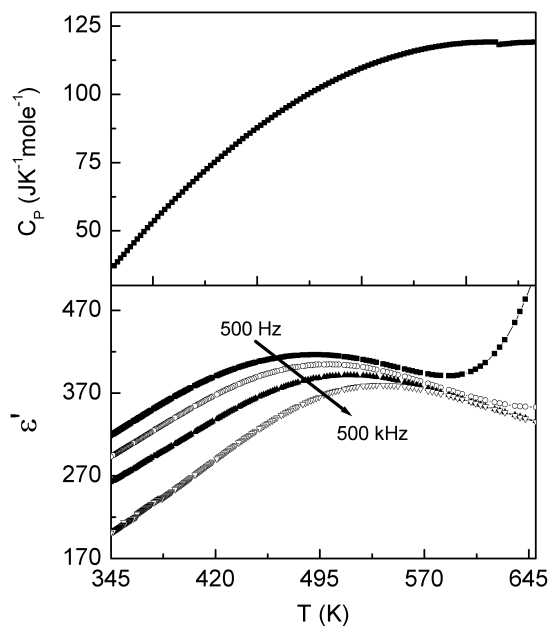


Fig. 1. Temperature-dependence of the heat capacity ( $C_p$ ) and the dielectric permittivity ( $\epsilon'$ ) for  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic system.

using differential scanning calorimetric measurements, exhibit other kinds of anomalies for some relaxors.<sup>6,8</sup>  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  have showed a minimum value for  $T_D$  at high temperatures, which has been associated to the formation of the ferroelectric PNRs showing an order–disorder type mechanism.<sup>6</sup> On the other hand, no anomalous behavior for  $T_D$  has been reported for  $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ , where a displacive type mechanism has been considered to explain the results.<sup>8</sup> Even though DSC measurement is a poor technique to analyze the relaxor ferroelectric materials,  $T_D$  versus  $T$  curves can provide elements to analyze the mechanisms, which are associated to the relaxor behavior and the formation of PNRs. All previous reports were obtained under adiabatic conditions, which are not our case, and  $C_p$  versus  $T$  curves did not show any anomaly. Under our conditions, no anomaly has been found in  $C_p$  versus  $T$  for the studied relaxor system (Fig. 1).

The results for  $\epsilon'$  show typical behavior of relaxor ferroelectrics; (i) wide peaks in  $\epsilon'$  vs  $T$  curves, (ii) the temperature for its corresponding maximum increases with frequency. The dielectric losses factor ( $\epsilon''$ ) also shows relaxor behavior characteristics.<sup>5</sup>

It is known that the relaxor behavior can be described by using two characteristic temperatures, the Burn's temperature ( $T_B$ ) (see Ref. 15) and the freezing temperature ( $T_F$ ).<sup>5</sup> PNRs are formed below  $T_B$ , whose volume, and also their interactions, increase when the temperature decreases. Then, the dielectric permittivity also increases on cooling from  $T_B$ . However, its increasing takes care until the relaxation frequency of the dipole fluctuation becomes lower than the measurement frequency. After that the dielectric permittivity decreases on cooling. The size and the interaction between PNRs become negligible below the freezing temperature ( $T_F$ ). For  $T < T_F$ , the applied electric field is not strong enough to break such interactions and only the smallest regions can switch with the electric field, that is to say, there is a frustration of the cooperative effect.

In order to carry out a better analysis of the heat capacity behavior, the Debye's temperature ( $T_D$ ) was calculated<sup>8</sup> by using Eq. (1), where  $n = 8$  (number of atoms in the unit cell for the Aurivillius family with  $m = 2$ ) and  $R$  is the gas constant. Figure 2 shows the results for the studied temperature range. The minimum values can be observed at 388 K.

$$C_p = 3nR \left( \frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (1)$$

The study of the dielectric behavior for the present system has been previously made in a wide temperature and frequency ranges.<sup>5</sup> The dynamics of the PNRs and the spin-glass model have been considered to analyze the relaxor behavior. By using the Vogel–Fulcher equation, the freezing temperature has been obtained ( $T_F = 378$  K).<sup>5</sup> Thus, the minimum value for  $T_D$  occurs near  $T_F$ .

Previous study<sup>16</sup> on  $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$  relaxor system has showed two anomalies in  $C_p(T)$ , one around 250–350 K and

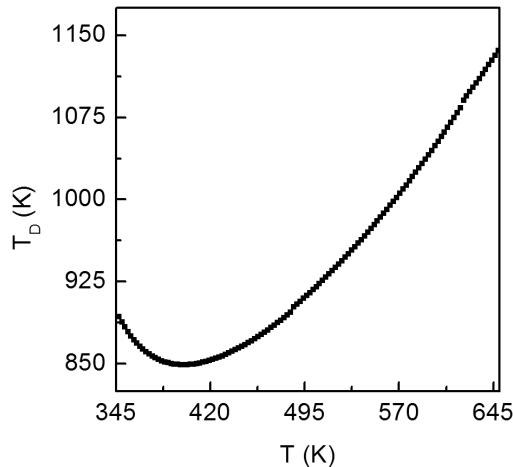


Fig. 2. Debye's temperature ( $T_D$ ) for  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic system.

the other one around 150–200 K. The former occurs in the same region where the dielectric permittivity starts to deviate from the Curie–Weiss law ( $T_B$ ). The second one appears in the  $T_m$  region (where the dielectric permittivity shows a maximum value, which depends on frequency).

On the other hand, no obvious anomalies have been reported in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  relaxor system for the temperature-dependence of the heat capacity.<sup>6</sup> However, the temperature-dependence for  $T_D$  has showed a minimum around 320 K, a region where the nucleation and growth of PNRs occur.

For the present studied system, no anomalies have been found in  $C_p(T)$  like in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  relaxor system but  $T_D$  shows a minimum value near  $T_F$ , which is quite different from previous reports.<sup>6,16</sup>

The freezing temperature is determined by the random-field effects and the random intercluster interactions, which influence the PNRs' size distribution. A high frequency dispersion degree has been obtained for  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  ( $\Delta T = 54^\circ\text{C}$ ), which is higher than that for  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ .<sup>5</sup> A higher frequency dispersion degree suggests a higher size distribution of PNRs. Then, a quite different distribution of  $T_m$  values could be expected concerning  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  system.

Considering the spin-glass model, which has been previously applied to the present system,<sup>5</sup> if there are strong dipolar interactions among PNRs, an anomalous relaxation and/or hysteresis must be observed in  $C_p$  versus  $T$  around the freezing temperature. It has not been observed, suggesting that the dipolar interactions among PNRs are not strong enough to be thermally detected relative to the inside of PNRs. It could be associated to the high frequency dispersion around  $T_F$  for the studied system in any frequency range. However,  $T_D$  has exhibited a minimum near  $T_F$ , which has not been previously reported for other relaxor systems with lower frequency dispersion.

#### 4. Summary

As summary, the heat capacity and the dielectric behavior were analyzed for  $\text{Sr}_{0.15}\text{Ba}_{0.85}\text{Bi}_2\text{Nb}_2\text{O}_9$  lead-free relaxor ferroelectric in a wide temperature range. No anomaly was detected in the heat capacity while broad peaks were observed in the dielectric permittivity showing high frequency dispersion. The Debye's temperature showed a minimum value near the freezing temperature. The results were discussed considering the spin-glass model and the high frequency dispersion, which was observed for the studied relaxor system.

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