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## Polarization and Thermally Stimulated Processes in Lead-Free Ferroelectric Ceramics

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Aimé Peláiz-Barranco, Yuslín González Abreu,  
José de los Santos Guerra, Jinfei Wang,  
Tongqing Yang and Pierre Saint-Grégoire

Additional information is available at the end of the chapter

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### Abstract

Over the last 20 years there has been an enormous effort in developing lead-free ferroelectric ceramics in order to obtain good dielectric, ferroelectric, piezoelectric and pyroelectric properties than those the conventional ferroelectric ceramics based on lead, such as lead zirconate titanate. An important group of lead free ferroelectric materials belong to the Aurivillius family, compounds which are layered bismuth  $[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$ .  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  is a member of this family where the ferroelectric properties can be affected by the crystallographic orientation due to their anisotropic crystal structure. The divalent Sr cation located between the corner-sharing octahedra can be totally or partially replaced by other cations, most commonly barium. The chapter presents the analysis of the thermally stimulated current in  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic system with  $x = 0, 15, 30, 50, 70, 85, 100$  at%. A numerical method is used to separate the real pyroelectric current from the other thermally stimulated processes. The remanent polarization is evaluated considering the hysteresis ferroelectric loops; the pyroelectric coefficient and the merit figure are evaluated too.  $\text{Sr}_{0.70}\text{Ba}_{0.30}\text{Bi}_2\text{Nb}_2\text{O}_9$  shows better ferroelectric and pyroelectric properties.

**Keywords:** Ferroelectrics, Aurivillius, Ceramics, Polarization, Pyroelectricity

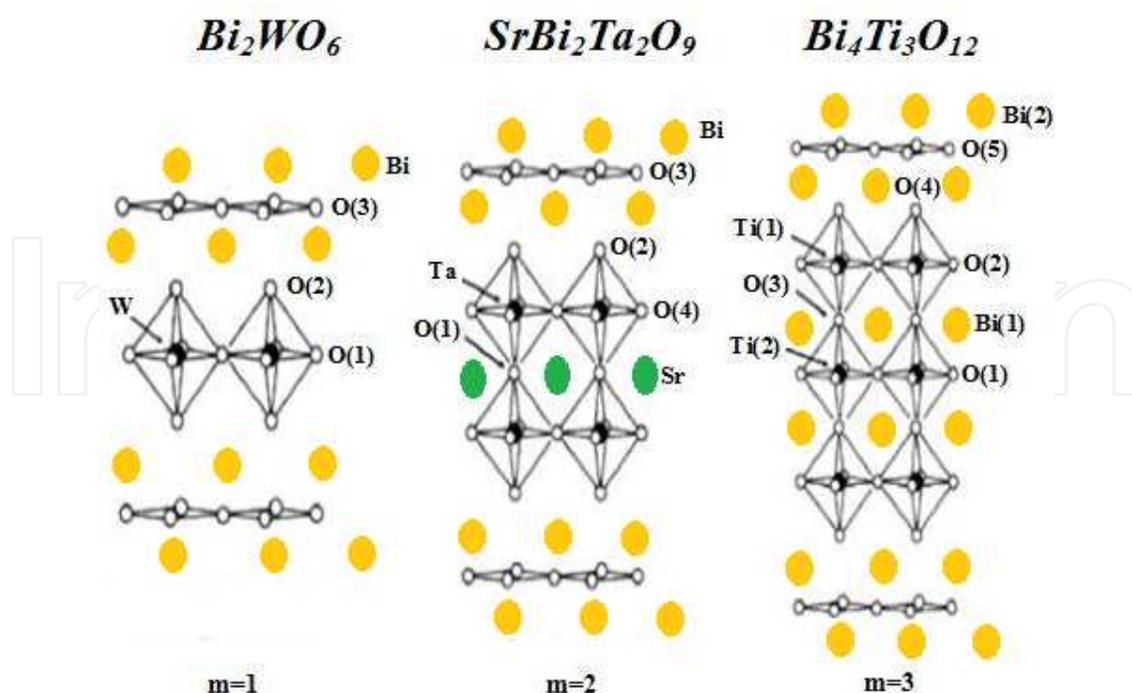
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## 1. Introduction

It is known that lead-based ferroelectric systems exhibit very good properties for different kinds of applications [1-6] and also that high-level ferroelectric and piezoelectric activities have remained confined to these materials. The only drawback in the technology as a whole has been the environmentalist's nightmare of its dependence on a high lead-containing family of materials [7]. Therefore, over the last 20 years there has been an enormous effort made in developing lead-free ferroelectric systems in order to obtain better dielectric, ferroelectric, piezoelectric and pyroelectric properties than those of conventional ferroelectric ceramics based on lead, such as lead zirconate titanate (PZT) [8-10].

An important group of lead-free ferroelectric materials belong to the Aurivillius family  $\{[\text{Bi}_2\text{O}_2]^{2+}[\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-}\}$ , which was discovered by Bent Aurivillius in 1949 [11]. These compounds have a complex structure, which is composed of perovskite blocks  $([\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}]^{2-})$  interleaved between bismuth and oxygen layers  $([\text{Bi}_2\text{O}_2]^{2+})$ , where  $m$  is the number of perovskite blocks in the structure. The  $A$  sites of the structure are typically occupied by elements such as  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Bi}^{3+}$ , with low valence; the  $B$  sites are typically occupied by elements with high valence such as  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$  and  $\text{W}^{6+}$  [12-16]. These materials have received great attention due to their large remanent polarization, low real dielectric permittivity at room temperature, lead-free nature, relatively low processing temperatures, high Curie temperatures, high electromechanical anisotropy and coercive fields, and excellent piezoelectric properties [8-9], which have suggested them as good candidates for high-temperature piezoelectric applications and memory storage. The bismuth layers  $[\text{Bi}_2\text{O}_2]^{2+}$  constrain the size of perovskite blocks establishing a limit for the incorporation of elements into them and providing the mixing of different elements between  $A$  sites and bismuth sites in the layered structure [17]. The ferroelectricity depends strongly on the crystallographic orientation of these materials, which is the subject of continuing researches. The main contribution to its spontaneous polarization comes from the displacement of the  $A$  cation in the perovskite block, which is quite different for the perovskite structure. It is well known that these have the majority polarization vector along the  $a$ -axis in a unit cell and that the oxygen vacancies prefer to stay in the  $\text{Bi}_2\text{O}_2$  layers, where their effect upon the polarization is thought to be small, and not in the octahedral site that controls polarization [18].

Figure 1 shows the structure for some Aurivillius systems with  $m=1$ ,  $m=2$  and  $m=3$ , at the paraelectric phase, as examples. The structural studies on these materials have shown a relation between the number of perovskite blocks and the symmetry of the cell, i.e., the number of perovskite blocks is related to the crystallographic orientation and to the plane of polarization in these materials [12-16, 18-19]. The polarization vector has also shown a relation to the number of perovskite blocks [18]. For even-layered systems, it has been reported to be a restriction on the polarization to the  $a$ - $b$  plane of the cell and an orthorhombic symmetry with  $A2_1am$  space group [18]. For odd-layered systems, the polarization has shown a component in  $c$  and orthorhombic phase with  $B2cb$  space group [18]. Other results have shown a strong relation between the elements in  $A$  sites of the structure and the symmetry of the cell [13-14, 17].



**Figure 1.** Structure of some Aurivillius materials with  $m=1$ ,  $m=2$  and  $m=3$ , at the paraelectric phase.

$SrBi_2Nb_2O_9$  (SBN) is a member of the Aurivillius family in which the ferroelectric properties can be affected by the crystallographic orientation due to their anisotropic crystal structure [13-14]. This system has received particular attention due to its large fatigue resistance, which has been associated with the migration of oxygen vacancies in the material [20]. The  $Sr^{2+}$  cation, which is located between the corner-sharing octahedral, can be totally or partially replaced by other cations, as barium is an important element for improving fatigue resistance [20]. The studies on the barium-modified  $SrBi_2Nb_2O_9$  system have shown interesting results from the structural and dielectric point of view [13-14, 20-25]. Structural studies have shown an orthorhombic symmetry with  $A2_1am$  space group for pure and doped SBN samples [22]. The mixing of different elements between  $A$  sites and bismuth sites, which occurs to equilibrate the lattice dimensions between the  $(Bi_2O_2)^{2+}$  layers and the perovskite blocks, has been also analysed [22]. The oxygen vacancies, which are the results of  $Bi^{3+}$  for  $Ba^{2+}/Sr^{2+}$  substitution, could have an important influence in the properties of these compositions [22].

For the  $Sr_{1-x}Ba_xBi_2Nb_2O_9$  system ( $x= 0, 15, 30, 50, 70, 85, 100$  at%), the barium concentration dependence of  $T_m$  as well as the temperature of the corresponding maximum for the real part of the dielectric permittivity, has suggested a cation site mixing among atomic positions, which has been supported by structural analysis [22]. For compositions with  $x \leq 30$  at%,  $T_m$  increased with the barium concentration; for  $x \geq 50$  at%, a decrease of  $T_m$  and a widening of the curves was observed with the increase of the barium concentration. The structural studies have shown the mixing of  $Sr^{2+}$ ,  $Ba^{2+}$  and  $Bi^{2+}$  into  $A$  sites and the bismuth sites of the structure [22]. For lower barium concentrations ( $x \leq 30$  at%), the presence of bismuth into  $A$  sites and the increasing of the strontium concentration into this site, has been discussed as the principal reason for the

increase of the  $T_m$  value. The higher barium concentration into  $A$  sites was obtained for the compositions with  $x \geq 50$  at% [22], supporting the decreasing of  $T_m$  [22].

On the other hand, a change from normal ferroelectric-paraelectric phase transition to relaxor behaviour has been observed when the barium concentration is increased [22]. For the compositions showing relaxor behaviour, an increase of the frequency dispersion degree was also observed with the increase of barium concentration. The relaxor behaviour is typical of materials with a disorder distribution of different ions in equivalent sites of the structure, which is called compositional disorder. For the studied materials, the relaxor behaviour has been explained with reference to the positional disordering of cations at  $A$  sites of the structure, which delays the evolution of long-range polar ordering [23, 26].

### 1.1. Ferroelectric behaviour and pyroelectricity in ferroelectric materials

It is known that ferroelectric materials present a spontaneous polarization in the absence of an electrical field ( $E$ ), for temperatures below the temperature of the phase transition from the ferroelectric to the paraelectric phase [1]. These materials have regions with uniform polarization, which are called ferroelectric domains. If an electrical field is applied to the material, the structure of domains changes due to the reorientation of the dipoles with  $E$ . In ferroelectrics with normal ferroelectric-paraelectric phase transitions, if the electrical field is strong enough the system can reach a saturated state, showing a high percentage of oriented domains in the  $E$  direction, which depends on the structure of the system. When the electrical field is removed, the system exhibits a remanent polarization ( $P_r$ ), which corresponds to the configuration of the minimal energy. On the other hand, for relaxor ferroelectrics, typical slim loops suggest that most of the aligned dipole moments switch back to a randomly oriented state upon removal of the field.

Ferroelectric materials, good isolators by their nature, exhibit temperature-dependent polarization, i.e., when the sample is heated the polarization changes and an electrical current is produced (pyroelectric current) which disappears at a certain temperature [1]. For normal ferroelectrics, the pyroelectric current ( $i_p$ ) achieves a maximum value when the temperature ( $T$ ) increases, and then decreases until zero at the ferroelectric-paraelectric phase transition temperature. For relaxor ferroelectrics, the pyroelectric current is different from zero even at higher temperatures than  $T_m$ , as well as the temperature of the corresponding maximum for the real part of the dielectric permittivity [27].

However, the study of the pyroelectric behaviour and its corresponding physical parameters may be quite difficult in many ferroelectric systems because, apart from the localized dipolar species, free charges can also exist in the material. The decay of the electrical polarization could be due to dipolar reorientation, the motion of the real charges stored in the material and its ohmic conductivity. The first of these is induced by thermal excitation, which leads to decay of the resultant dipole polarization, and the second is related to the drift of the charges stored in the internal field of the system and their thermal diffusion. During the temperature rise, the dipoles tend to be disordered gradually owing to the increasing thermal motion, and the space charges trapped at different depths are gradually set free. Therefore the pyroelectric behaviour is usually overlapped by other thermally stimulated processes, and a detailed analysis of this

phenomenon is very important in order to separate the different components of the electrical current during the heating of the material ( $i$ - $T$  dependences), to then make a real pyroelectric characterization of any system.

The thermally stimulated discharge current method is a typical technique for this analysis, which has been applied with very good results to ferroelectric materials [28-30]. By using this method, the pyroelectric current can be separated from other stimulated processes (including the electrical conductivity mechanisms), providing better knowledge of the material response in a wide temperature range.

Several analytical methods have been developed to analyse the thermally stimulated processes [30-33]. Among these can be mentioned the initial rise method, the peak shape method and the numerical method using Gaussians [30-33].

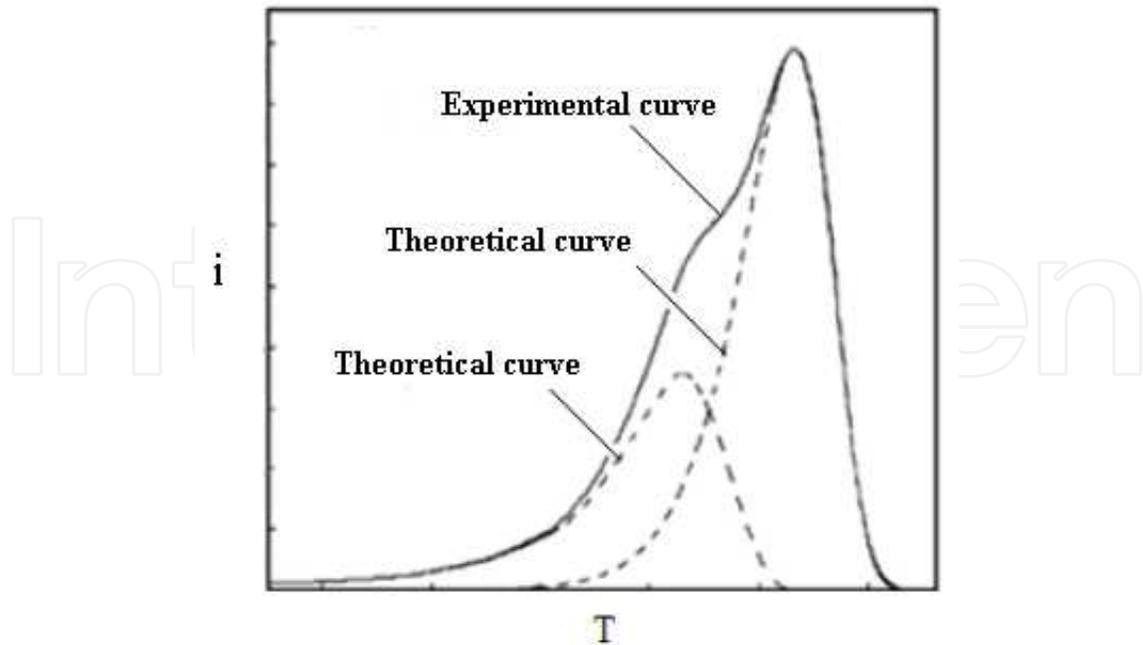
For the initial rise method, it is considered that measurements do not depend on the heating rate in the initial rise region [33]. Then, a slow heating rate can be used, reducing the problems related to the difference of temperature between the samples and the thermocouple or gradients of temperature in the sample. The peak shape methods [34] depend on the constant heating rate, but consider more experimental points concerning the initial rise method. However, these methods do not consider the overlapping of several peaks in the material response, as the Gaussian method does. This method considers the overlapping of several peaks in  $i$ - $T$  dependences, which is very useful for a better understanding of the material response.

The Gaussian method was proposed by Faubert and Sánchez [32]. It consists of fitting the rightmost part (highest temperatures) of the curve with a single time relaxation theoretical curve (Gaussians), and then a new spectrum is obtained by subtracting the theoretical curve from the experimental one (Figure 2). The operation is repeated until the resulting spectrum is smaller than a fixed limit. The final test is carried out summing all the theoretical curves, which may offer the experimental spectrum.

From the so-called area method given by equation (1), where  $T_f$  is the final temperature and  $\beta$  is the constant heating rate, which is constant, the relaxation times ( $\tau$ ) can be calculated for each theoretical curve (single curves). On the other hand, it is known that the relaxation times usually show a temperature dependence which can be expressed by the Arrhenius law (equation 2, where  $k_B$  and  $\tau_0$  are constants). Then, the activation energy value ( $U$ ) for each process can be obtained from the  $\ln \tau$  vs  $1/T$  dependence.

$$\tau(T) = \frac{\int_T^{T_f} i(T) dT}{\beta \cdot i(T)} \quad (1)$$

$$\tau(T) = \tau_0 e^{\frac{U}{k_B T}} \quad (2)$$



**Figure 2.** Theoretical decomposition of the  $i$ - $T$  dependence using the Gaussian method.

The remanent polarization ( $P_r$ ) can be obtained from the pyroelectric current  $i_p(T)$  using equation 3, where  $A$  is the area of the samples. The integration is made from the operation temperature  $T$  (usually room temperature) until  $T_m$  (or a higher temperature in the case of relaxor ferroelectrics).

$$P_r = -\frac{1}{A\beta} \int_T^{T_m} i_p dT \quad (3)$$

Other parameters can be evaluated from the  $i_p(T)$  dependence, such as the pyroelectric coefficient ( $p$ ) and several merit figures. The pyroelectric coefficient is related to the variation of  $P_r$  (equation 4). The current response parameter ( $R_v$ ) is one of the important merit figures which are associated with pyroelectric behaviour, and can be obtained using equation 5.

$$p = \frac{dP_r}{dT} \quad (4)$$

$$R_v = \frac{p}{\epsilon'} \quad (5)$$

There are not many reports concerning the pyroelectric behaviour of ferroelectric systems from the Aurivillius family. Most of the studies have been carried out on pure and modified bismuth

titanate [35-36]. For niobium- and thallium-modified bismuth titanate, it has been reported that there is a pyroelectric coefficient of  $12 \mu\text{C}/\text{m}^2\text{K}$  at room temperature [36], which is better than that for pure bismuth titanate ceramics [35]. The  $P$ - $E$  hysteresis loops have showed a remanent polarization of  $3.49 \mu\text{C}/\text{cm}^2$  at room temperature [36].

The chapter presents studies on ferroelectric properties and thermally stimulated processes which have been carried out on the  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic system with  $x = 0, 15, 30, 50, 70, 85$  and  $100$  at%. The dependence of the polarization on the applied electric field is discussed at room temperature, for normal and relaxor ferroelectrics compositions. For the thermally stimulated current, the Gaussian method is used to separate the pyroelectric contribution from the other contributions to the total  $i(T)$  response in the studied samples. The remanent polarization is evaluated, at room temperature, considering the hysteresis ferroelectric loops and the pyroelectric current dependence  $i_p(T)$ . The pyroelectric coefficient and the current response merit figure are also evaluated.

## 2. Experimental Procedure

### 2.1. Sample preparation

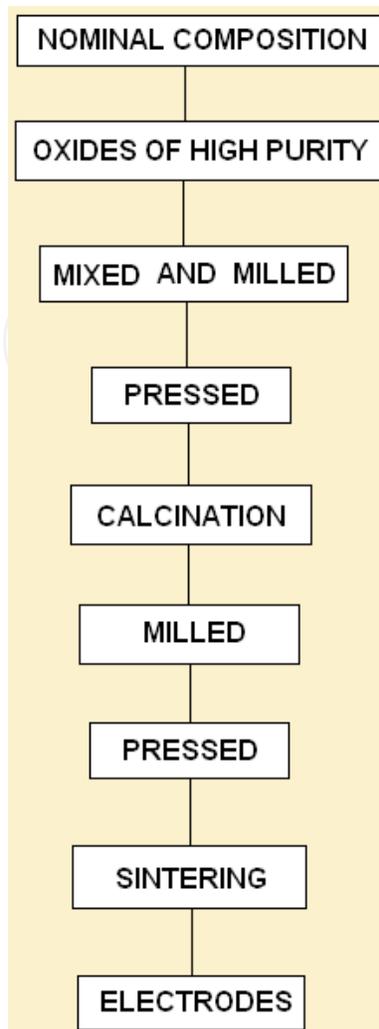
$\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ( $x = 0, 15, 30, 50, 70, 85, 100$  at%) ferroelectric ceramic samples were prepared by solid-state reaction method (Figure 3).

The powders of the starting materials  $\text{SrO}$ ,  $\text{BaO}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were mixed with a desired weight ratio. The mixture of oxides was milled with alcohol for two hours, dried and pressed by applying  $100 \text{ MPa}$ . The pressed samples were calcined in air atmosphere at  $950 \text{ }^\circ\text{C}$  for two hours. After calcination the samples were milled again for one hour, dried and pressed by applying  $200 \text{ MPa}$ . The sintering process was made in a sealed alumina crucible at  $1100 \text{ }^\circ\text{C}$  for one hour. Samples with density values higher than  $90 \%$  of the theoretical density values were obtained. Silver electrodes were deposited on the opposite faces of the disk-like samples by using a heat treatment at  $590 \text{ }^\circ\text{C}$ . The samples were named SBN ( $x=0$ ), SBBN- $x$  ( $x=15-85$  at%) and BBN ( $x=100$  at%), respectively.

### 2.2. Ferroelectric measurements and thermally stimulated discharge current experiments

Polarization-electric field ( $P$ - $E$ ) loops were obtained at room temperature for  $10 \text{ Hz}$  by using a precision ferroelectric analyser (Premier II, Radiant Technologies Inc.), which is combined with a high-voltage power supply (TReK Model 663A). The highest applied electric field was  $90 \text{ kV}/\text{cm}$  for the studied samples.

The study of thermally stimulated depolarization currents was carried out in sequential thermal cycles as follows: (i) zero-field heating - heating from room temperature to  $60 \text{ }^\circ\text{C}$  under zero electrical field; (ii) field cooling - cooling to room temperature while a polarizing electrical field is applied ( $E_p = 2 \text{ kV}/\text{mm}$ ); (iii) zero-field heating - heating from room temperature to temperatures higher than  $T_m$  under zero electrical field. The thermal discharge current was



**Figure 3.** Solid-state reaction method for the sample preparation.

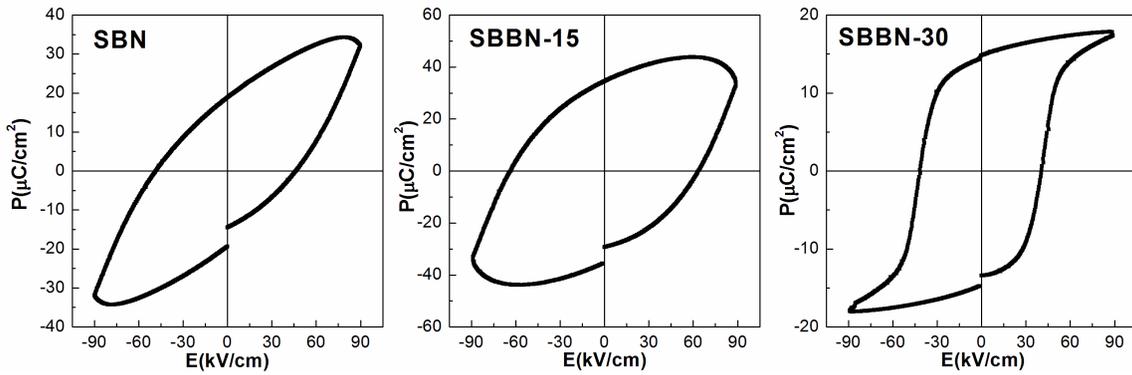
measured (during the third step) using a Keithley 6485 Electrometer, while keeping a temperature rate of about 5 K/min.

### 3. Results and discussion

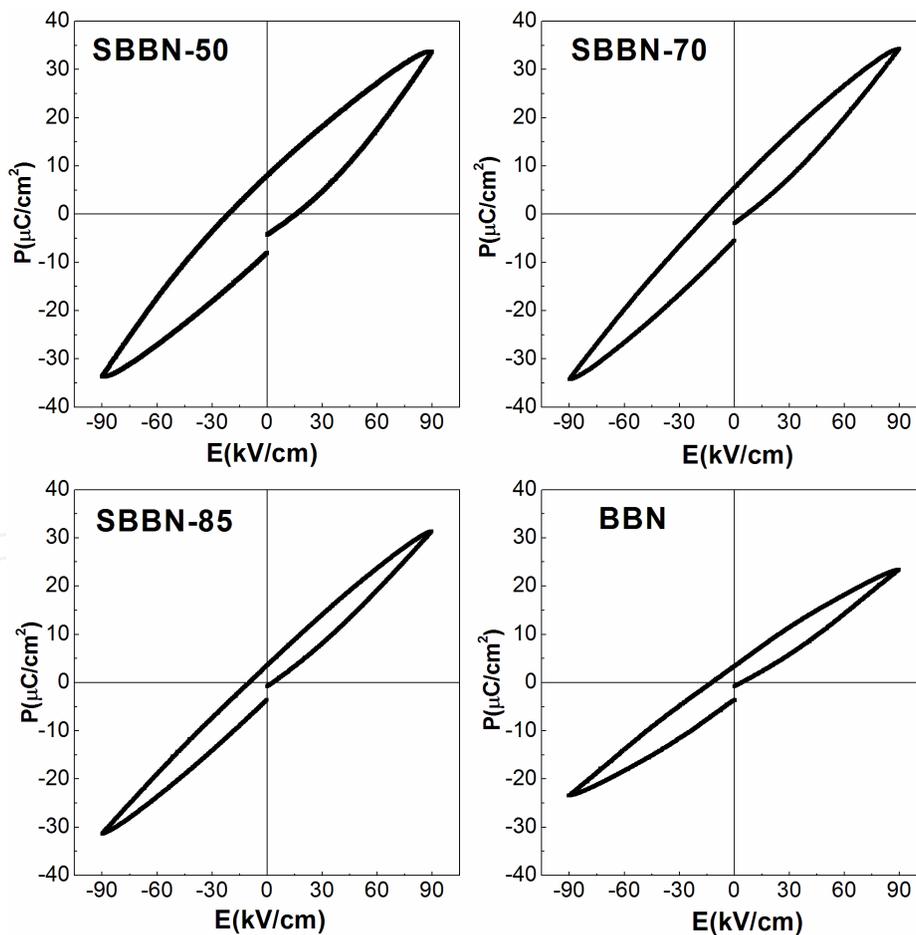
#### 3.1. Ferroelectric properties

The hysteresis loops at room temperature are shown in Figure 4 and Figure 5 for the studied samples. The compositions with  $x \leq 30$  at% show polarization-electrical field ( $P$ - $E$ ) loops typical of normal ferroelectric materials. The compositions of SBN and SBBN-15 show wide loops at room temperature. This behaviour could be associated with high dielectric losses in these samples. The composition with 30 at% of barium shows the better response with a clear tendency to saturation with the applied electric field. The samples with  $x \geq 50$  at% show thin hysteresis loops, which are typical of relaxor ferroelectric systems. These compositions have

shown relaxor behaviour in the corresponding dielectric analysis [22]; relaxor ferroelectrics do not show a tendency to saturation in the  $P$ - $E$  dependence even in a very high electric field.



**Figure 4.** Polarization ( $P$ ) dependence on the applied electric field ( $E$ ), at room temperature, for samples with  $x \leq 30$  at %.



**Figure 5.** Polarization ( $P$ ) dependence with the applied electric field ( $E$ ), at room temperature, for samples with  $x \geq 50$  at %.

Composition	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$P_r/P_{max}$	$E_c$ (kV/cm)
SBN	18.96	0.55	45
SBBN-15	34.48	0.80	63
SBBN-30	13.45	0.75	42
SBBN-50	8.10	0.24	22
SBBN-70	5.44	0.16	14
SBBN-85	3.68	0.11	12
BBN	3.55	0.14	13

**Table 1.** Values of the remanent polarization ( $P_r$ ),  $P_r/P_{max}$  relationship and the coercive field ( $E_c$ ) for the studied samples at room temperature.

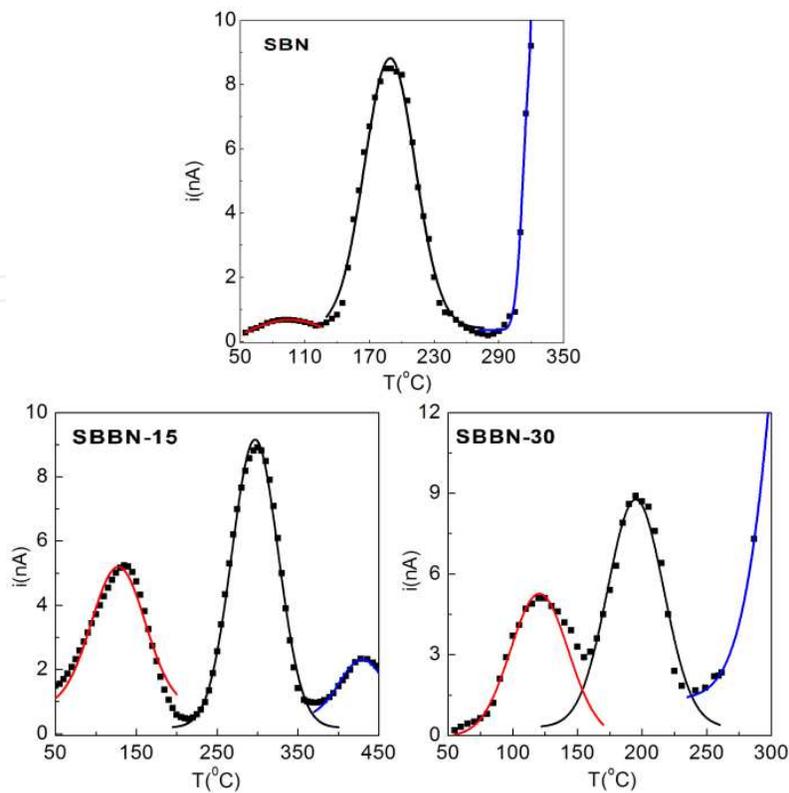
Table 1 shows the values of the remanent polarization ( $P_r$ ), the  $P_r/P_{max}$  relationship and the coercive electric field ( $E_c$ ), at room temperature, for the studied compositions.  $P_{max}$  is the polarization at the highest applied electric field. The SBN and SBBN-15 samples show the highest  $P_r$  values. This is associated with higher dielectric losses for these samples. The compositions with  $x \geq 50$  at% show the lower  $P_r$  values. These ceramics have also presented lower piezoelectric activity [37]. The sample with 30 at% of barium shows the better ferroelectric response with a high  $P_r$  value and a  $P_r/P_{max}$  relation, showing a good saturation. For this composition, a better piezoelectric response has been reported [37]. The  $E_c$  values tend to decrease with the increase of barium concentration. For compositions with  $x \leq 50$  at%, the  $E_c$  values are higher than those for other ferroelectrics materials from the Aurivillius family [35].

### 3.2. Thermally stimulated processes and pyroelectricity

Figure 6 and Figure 7 show the dependence of the thermally stimulated current ( $i$ ) on the temperature in the studied samples. The black points represent the experimental curve and the lines represent the fitting, which was carried out using the Gaussian method.

For the compositions with  $x \leq 30$  at% (Figure 6), three different contributions were observed below the transition temperature ( $T_m$ ). The contribution at higher temperatures (blue line) is observed from the increase of  $i$  at temperatures near to and higher than the transition temperature. The pyroelectric contribution is characterized by an increase to a maximum value, when the temperature ( $T$ ) increases, and then a decrease to zero at the ferroelectric-paraelectric phase transition temperature. From this point of view, the third contribution is not the pyroelectric contribution.

The dielectric analysis of the studied samples has shown a strong influence of the electric conductivity on the dielectric parameters at the higher temperature range [22]. The third contribution could be associated with the electric conductivity processes in this temperature range. The influence of this contribution on the second (black line) is remarkable; this second contribution must be associated with the pyroelectric response. The first contribution (red line)



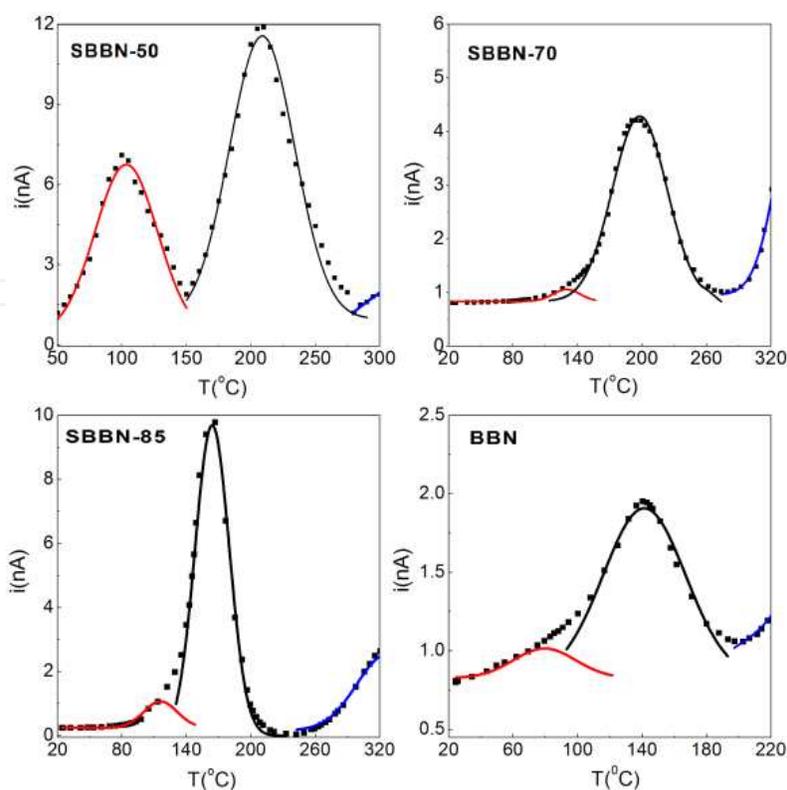
**Figure 6.** Thermally stimulated current curves ( $i$ ) in a wide temperature range for the SBN, SBBN-15 and SBBN-30 samples. The black points show the experimental data and the red line (first contribution), black line (second contribution) and blue line (third contribution) represent the fitting using the Gaussian method.

is observed at the lower temperature range; it could not be associated with the pyroelectric response or electrical conductivity processes.

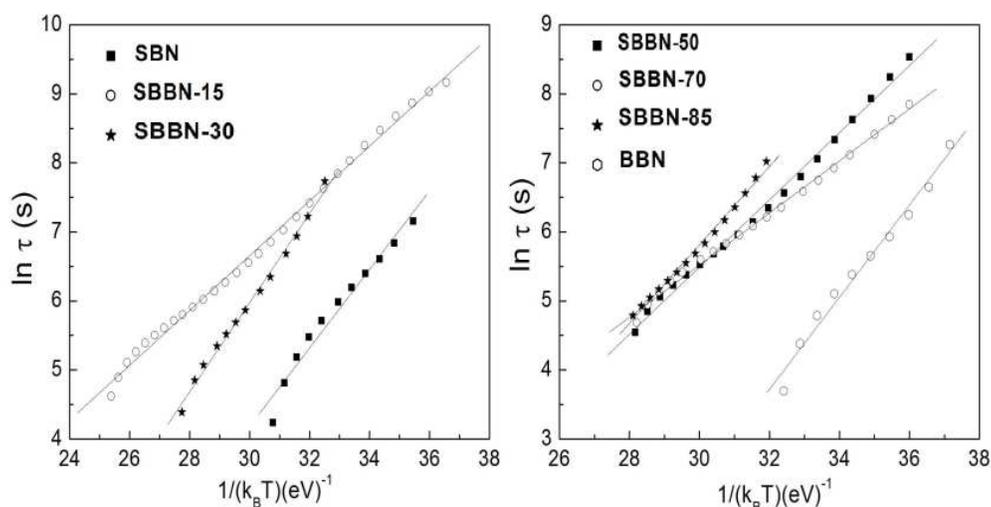
The compositions with  $x > 30$  at% show the three contributions for temperatures lower than  $T_m$  as well (Figure 7).

From the theoretical curves  $i(T)$ , which were obtained by using the Gaussian method, the values of the relaxation time ( $\tau$ ) were calculated (equation 1). The temperature dependence for  $\tau$  (Figures 8 and 9) was obtained for the first and second contributions, showing a typical Arrhenius dependence (equation 2). The values of  $\ln \tau$  are represented by points and the lines represent the fitting using equation 2. From the fitting, the corresponding activation energy values ( $U$ ) for each contribution were obtained, and are shown in Table 2.

The activation energy values for the first contribution are between 0.40 and 0.60 eV. This contribution is observed in the lower temperature range, showing lower current values than those obtained for the second contribution. The first contribution could be related to space charge, which is injected during the polarization process. For the second contribution, which is associated with the pyroelectric current, the activation energy values tend to increase with the increase of the barium concentration until 30 at%; above that concentration, this parameter decreases.

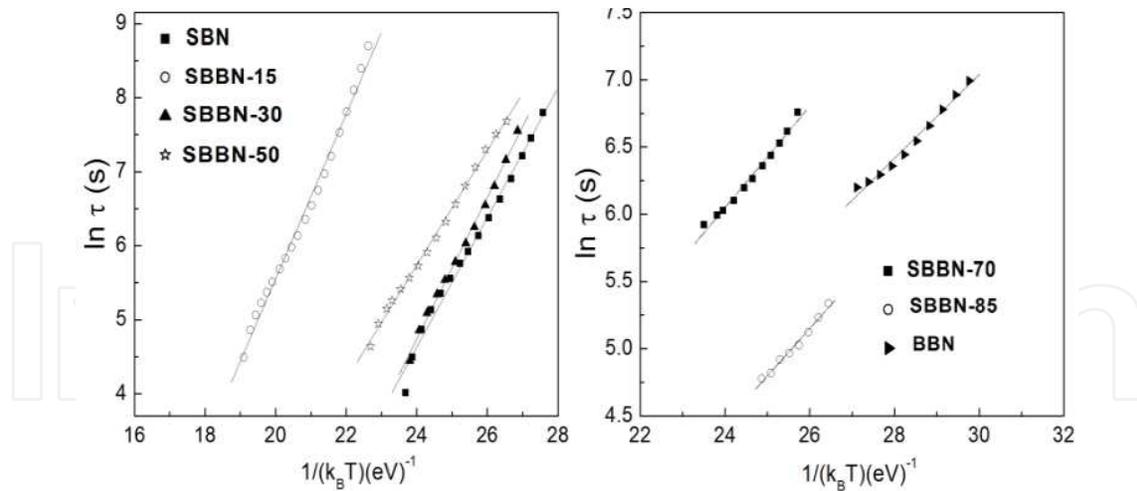


**Figure 7.** Thermally stimulated current curves ( $i$ ) in a wide temperature range for the compositions with  $x > 30$  at%. The black points show the experimental data and the red line (first contribution), black line (second contribution) and blue line (third contribution) represent the fitting using the Gaussian method.



**Figure 8.** Arrhenius dependence of the first contribution on the  $i$ - $T$  dependence. The solid points correspond to the relaxation time values, which were obtained using equation 1; the solid lines correspond to the fitting using equation 2.

For materials from the Aurivillius family, the major contribution to the spontaneous polarization comes from the motion of the  $A$  cation in the perovskite blocks [20, 23, 26]. The analysis of the dielectric behaviour for the studied samples has shown a lower ferroelectric-paraelectric



**Figure 9.** Arrhenius dependence of the second contribution on the  $i$ - $T$  dependence. The solid points correspond to the relaxation time values, which were obtained using equation 1; the solid lines correspond to the fitting using equation 2.

transition temperature for the SBN sample [22] than that of the previous report [20]. This result suggests a decrease of the thermal energy, which is necessary to transition from a ferroelectric phase to a paraelectric phase. The structural study for this composition has also shown a higher occupancy of  $\text{Bi}^{3+}$  in  $A$  sites of the structure [22] than previous reports [14], which can explain the lower  $T_m$  value considering the lower radii ionic of the  $\text{Bi}^{3+}$  than that of the  $\text{Sr}^{2+}$ . Therefore, a lower activation energy value is necessary for the thermal depoling (pyroelectric contribution) of the studied SBN sample compared to previous reports. The SBBN-15 and SBBN-30 samples show an increase of the activation energy value with respect to the SBN composition, which is in agreement with the  $T_m$  behaviour from 0 to 30 at% [22].

Composition	First contribution U (eV)	Second contribution U (eV)
SBN	0.57	0.88
SBBN-15	0.40	1.11
SBBN-30	0.51	0.98
SBBN-50	0.49	0.82
SBBN-70	0.37	0.38
SBBN-85	0.57	0.35
BBN	0.60	0.33

**Table 2.** Activation energy values, which were obtained from the fitting shown in Figures 8 and 9.

For compositions with  $x > 30$  at%, the activation energy values for the pyroelectric contribution have shown a decrease with the increase of the barium concentration in the structure. These results are in agreement with the dielectric behaviour of these compositions, which is shown

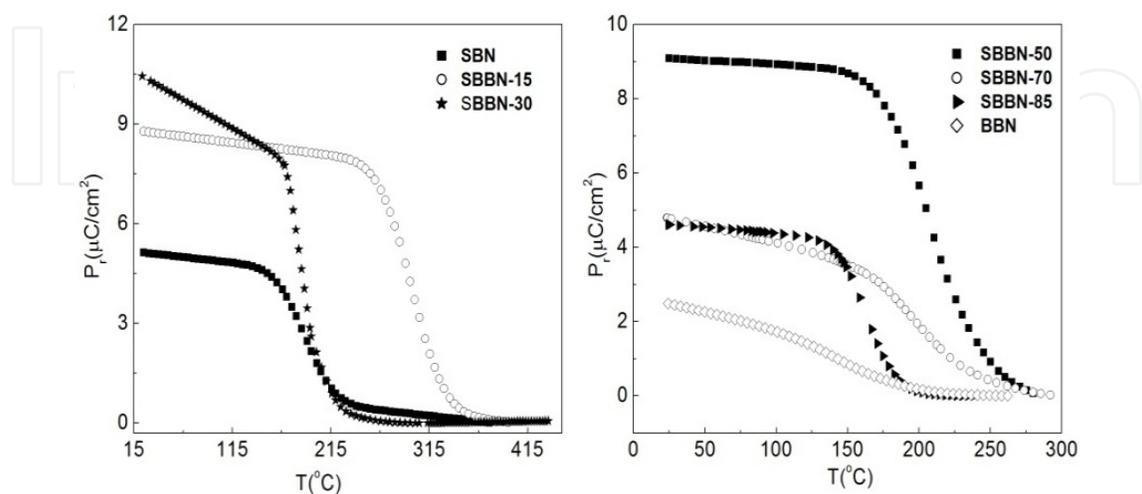
in a decrease of the  $T_m$  values when the barium concentration increases [22]. The SBBN-50 and SBBN-70 samples have shown a greater increase in the occupancy of  $\text{Ba}^{2+}$  and  $\text{Bi}^{3+}$  in  $A$  sites than was observed in the SBBN-30, since the concentration of  $\text{Ba}^{2+}$  is higher than that of  $\text{Bi}^{3+}$ , which explains the decrease of  $T_m$  from 30 to 70 at% of barium and then by extension the lower activation energy values for the pyroelectric contribution.

For SBBN-85 and BBN, a greater decrease of the  $\text{Ba}^{2+}$  occupancy in  $A$  sites is observed than in SBBN-70 [22], but the  $T_m$  values are lower. For both compositions, it has also been reported that there is a higher  $\text{Ba}^{2+}$  occupancy in  $\text{Bi}^{3+}$  sites than in the other compositions [22]. A higher  $\text{Ba}^{2+}$  occupancy in  $\text{Bi}^{3+}$  sites and the corresponding generated oxygen vacancies would distort the ionic dipoles due to the  $A$  sites' ions. Then, the decay of the spontaneous polarization could be affected, providing a decrease of the  $T_m$  values and the activation energy values for the thermal depoling process (pyroelectric response).

For the third contribution, there were not enough experimental points in some compositions. Thus, the activation energy was only estimated for the studied samples, showing values between 0.7 and 1.50 eV. These values are related to electrical conductivity processes, which are governed by double ionized oxygen vacancies [21, 24]. The oxygen vacancies in the structure of the studied samples are generated to compensate the electrical charge unbalance, which is caused by the substitution of trivalent  $\text{Bi}^{3+}$  ion for divalent  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions.

### 3.3. Ferroelectric and pyroelectric parameters

Figure 10 shows the temperature dependence of the remanent polarization ( $P_r$ ), which has been obtained from the pyroelectric current dependence  $i_p(T)$  using equation 3. It can be noted that there is an important influence of the barium concentration on the  $P_r$  values. At room temperature, an increase of  $P_r$  is observed for the lower barium concentration ( $x \leq 30$  at%); above 30 at%,  $P_r$  decreases. These results are in agreement with the  $P_r$  behaviour, which has previously been discussed in relation to the hysteresis loops ( $P$ - $E$  dependence).



**Figure 10.** Temperature dependence of the remanent polarization ( $P_r$ ) for the studied compositions.

Composition	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$p$ ( $\mu\text{C}/\text{m}^2 \text{ }^\circ\text{C}$ )	$R_V$ ( $\mu\text{C}/\text{m}^2 \text{ }^\circ\text{C}$ )
SBN	5.03	34	0.12
SBBN-15	8.63	38	0.16
SBBN-30	10.4	73	0.62
SBBN-50	9.02	20	0.07
SBBN-70	4.79	4	0.01
SBBN-85	4.61	10	0.04
BBN	2.49	4	0.02

**Table 3.** Values of the remanent polarization ( $P_r$ ), the pyroelectric coefficient ( $p$ ) and the current response parameter ( $R_V$ ).

Table 3 shows the values for the remanent polarization ( $P_r$ ), the pyroelectric coefficient ( $p$ ) and the current response parameter ( $R_V$ ), at room temperature, for the studied samples. The last two parameters were obtained using equations 4 and 5, respectively. The SBBN-30 sample shows the better pyroelectric parameter. The values for the pyroelectric parameters are analogous to previous reports in other Aurivillius materials [24]. However, these are lower than those for conventional lead-based ferroelectric systems [38-39]. Further researches are in progress.

## 4. Conclusions

The ferroelectric properties and thermally stimulated processes were studied in the  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ferroelectric ceramic system with  $x = 0, 15, 30, 50, 70, 85, 100$  at%. The dependence of the polarization on the applied electric field was discussed, at room temperature, for normal and relaxor ferroelectric compositions. The Gaussian method was used to separate the pyroelectric contribution from the other contributions to the total  $i(T)$  response in the studied samples. Three different contributions were obtained in the studied temperature range. The first contribution was associated with space charge, the second with the pyroelectric current and the third with the electric conductivity processes. The remanent polarization, the pyroelectric coefficient and the current response merit figure were evaluated at room temperature. The SBBN-30 showed better ferroelectric and pyroelectric properties.

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## Author details

Aimé Peláiz-Barranco<sup>1\*</sup>, Yuslín González Abreu<sup>1</sup>, José de los Santos Guerra<sup>2</sup>, Jinfei Wang<sup>3,4</sup>, Tongqing Yang<sup>3</sup> and Pierre Saint-Grégoire<sup>5</sup>

\*Address all correspondence to: [pelaiz@fisica.uh.cu](mailto:pelaiz@fisica.uh.cu)

1 Facultad de Física - Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana. San Lázaro y L, Vedado. La Habana, Cuba

2 Grupo de Ferroelétricos e Materiais Multifuncionais, Instituto de Física, Universidade Federal de Uberlândia. Uberlândia – M G, Brazil

3 Functional Materials Research Laboratory, College for Materials Science and Engineering, Tongji University, Caoan, Shanghai, China

4 Dwo Chemical (China) Investment, LTD. Pudong district, Shanghai, China

5 University of Nîmes, Department of Sciences and Arts, Nimes cedex, France

## References

- [1] Xu Y. *Ferroelectric Materials and Their Applications*. The Netherlands: Elsevier Science Publishers B.V.; 1991.
- [2] Haertling GH. Ferroelectric ceramics: History and technology. *Journal of the American Ceramic Society* 1999; 82(4) 797-818.
- [3] Ivan IA, Rakotondrabe M, Agnus J, Bourquin R, Chaillet N, Lutz P, Poncot J, Duffait R, Bauer O. Comparative material study between PZT ceramic and newer crystalline PMN-PT and PZN-PT materials for composite bimorph actuators. *Advanced Materials Science* 2010; 24(15-16) 1-9.
- [4] Rauls MB, Dong W, Huber JE, Lynch CH. The effect of temperature on the large field electromechanical response of relaxor ferroelectric 8/65/35 PLZT. *Acta Materialia* 2011; 59(7) 2713-2722.

- [5] Li F, Zhang S, Xu Z, Wei X, Luo J, Shrout TR. Temperature independent shear piezoelectric response in relaxor-PbTiO<sub>3</sub> based crystals. *Applied Physics Letters* 2010; 97(25) 252903.
- [6] Li F, Zhang S, Lin D, Luo J, Xu Z, Wei X, Shrout TR. Electromechanical properties of PbIn<sub>1/2</sub>Nb<sub>1/2</sub>O<sub>3</sub>-PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>-PbTiO<sub>3</sub> single crystals. *Journal of Applied Physics* 2011; 109(1) 014108.
- [7] Wang H, Ren MF. Characteristics of Ag/Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub>/p-Si heterostructure prepared by sol-gel processing. *Journal of Sol-Gel Science and Technology* 2007; 42(3) 247-250.
- [8] Zhang H, Yan H, Reece MJ. Microstructure and electrical properties of Aurivillius phase (CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>)<sub>1-x</sub>(BaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>)<sub>x</sub> solid solution. *Journal of Applied Physics* 2010; 108(1) 014109.
- [9] Yi ZG, Li YX, Liu Y. Ferroelectric and piezoelectric properties of Aurivillius phase intergrowth ferroelectrics and the underlying materials design. *Physica Status Solidi A* 2011; 208(5) 1035-1040.
- [10] Cui Y, Fu X, Yan K. Effects of Mn-doping on the properties of BaBi<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> bismuth layer structured ceramics. *Journal of Inorganic and Organometallic Polymers and Materials* 2012; 22(1) 82-85.
- [11] Aurivillius B. Mixed bismuth oxides with layered lattice. I. *Ark. Kemi* 1949; 1(54) 463-480.
- [12] Wachsmuth B, Zschech E, Thomas N, Brodie S, Gurman S, Baker S, Bayliss S. Structure model of Aurivillius compounds. *Physica Status Solidi A* 1993; 135(1) 59-71.
- [13] Ismunandar, KB. Structure of ABi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (A = Sr, Ba): Refinement of powder neutron diffraction data. *Journal of Solid State Chemistry* 1996; 126 136-141.
- [14] Blake S, Falconer M, McCreedy M, Lightfoot P. Cation disorder in ferroelectric Aurivillius phases of the type Bi<sub>2</sub>ANb<sub>2</sub>O<sub>9</sub> (A=Ba, Sr, Ca). *Journal of Materials Chemistry* 1997; 7(8) 1609-1613.
- [15] Mercurio D, Troliarda G, Hansen T, Mercurio J. Crystal structure of the ferroelectric mixed Aurivillius phase Bi<sub>7</sub>Ti<sub>4</sub>NbO<sub>21</sub>. *International Journal of Inorganic Materials* 2000; 2(5) 397-406.
- [16] Perez-Mato J, Aroyo M, García A, Blaha P, Schwarz K, Schweifer J, Parlinski K. Competing structural instabilities in the ferroelectric Aurivillius compound SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. *Physics Review B* 2004; 70(21) 214111.
- [17] Haluska M, Misture S. Crystal structure refinements of the three-layer Aurivillius ceramics Bi<sub>2</sub>Sr<sub>2-x</sub>A<sub>x</sub>Nb<sub>2</sub>TiO<sub>12</sub> (A=Ca, Ba; x= 0, 0.5, 1) using combined x-ray and neutron powder diffraction. *Journal of Solid State Chemistry* 2004; 177(6) 1965-1975.

- [18] Newnham R, Wolfe R, Dorrian J. Structural basis of ferroelectricity in the bismuth titanate family. *Materials Research Bulletin* 1971; 6 1029-1040.
- [19] Newnham R, Wolfe R, Horsey R, Diaz-Colon F. Crystal structure of  $(\text{Sr},\text{Ba})\text{Bi}_2\text{Ta}_2\text{O}_9$ . *Materials Research Bulletin* 1973; 8(10) 1183-1195.
- [20] Huang S, Feng Ch, Chen L, Wang Q. Relaxor behavior of  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  ceramics. *Journal of the American Ceramic Society* 2006; 89(1) 328-331.
- [21] Wu Y, Forbess MJ, Seraji S, Limmer SJ, Chou TP, Nguyen C, Cao GZ. Doping effect in layer structured  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  ferroelectric. *Journal of Applied Physics* 2001; 90 5296-6002.
- [22] González-Abreu Y, Peláiz-Barranco A, Guerra JDS, Gagou Y, Saint-Grégoire P. From normal ferroelectric transition to relaxor behavior in Aurivillius ferroelectric ceramic. *Journal of Materials Science* 2014; 49(21) 7437-7444.
- [23] Peláiz-Barranco A, González-Abreu Y. Dielectric relaxation mechanisms in relaxor bi-layered perovskites. *Ferroelectrics* 2012; 426(1) 122-131.
- [24] Peláiz-Barranco A, González-Abreu Y. Ferroelectric ceramic materials of the Aurivillius family. *Journal of Advanced Dielectrics* 2013; 3(4) 1330003.
- [25] Ismunandar, Kennedy BJ. Effect of temperature on cation disorder in  $\text{ABi}_2\text{Nb}_2\text{O}_9$  ( $\text{A}=\text{Sr}, \text{Ba}$ ). *Journal of Materials Chemistry* 1999; 9(2) 541-544.
- [26] González-Abreu Y, Peláiz-Barranco A, Araújo EB, Franco Júnior A. Dielectric relaxation and relaxor behavior in bilayered perovskites. *Applied Physics Letters* 2009; 94(26) 262903.
- [27] Cross LE. Relaxor ferroelectrics: An overview. *Ferroelectrics* 1994; 151(1) 305-320.
- [28] Liu W, Randall CA. Thermally stimulated relaxation in Fe-doped  $\text{SrTiO}_3$  systems: II. Degradation of  $\text{SrTiO}_3$  dielectrics. *Journal of the American Ceramic Society* 2008; 91(10) 3251-3257.
- [29] Almeida A, Correia TM, Chaves MR, Vilarinho PM, Kholkin AL, Costa AM. Study of polar relaxation processes in  $\text{Sr}_{(1-1.5x)}\text{La}_x\text{TiO}_3$  ceramics by using field-induced thermally stimulated currents. *Journal of the European Ceramic Society* 2008; 27(13) 3701-3703.
- [30] Peláiz Barranco A, Calderón Piñar F, Pérez Martínez O. Pyroelectricity and mechanisms of conductivity in  $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3 + 2.5 \text{ mol\% La}_2\text{O}_3$  ferroelectric ceramics. *Journal of Material Science Letters* 2001; 20(15) 1439-1441.
- [31] Chen R, Krish Y. *Analysis of Thermally Stimulated Processes*. Oxford: Pergamon Press; 1981.

- [32] Faubert F, Sánchez M. Numerical decomposition of a complex thermostimulated depolarization current spectrum in single time relaxation peaks. *Journal of Applied Physics* 1998; 84(3) 1541-1545.
- [33] Chen R, Haber G. Calculation of glow curves activation energies by numerical initial rise method. *Chemistry Physics Letters* 1968; 2(7) 483-485.
- [34] Grossweiner LI. A note on the analysis of first-order glow curves. *Journal of Applied Physics* 1953; 24(10) 1306-1307.
- [35] Kong LB, Ma J, Zhu W, Tan OK. Preparation of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ceramics via a high-energy ball milling process. *Material Letters* 2001; 51(2) 108-114.
- [36] Hou J, Vaish R, Ou Y, Krsmanovic D, Varma KBR, Kumar RV. Dielectric, pyroelectric and ferroelectric properties of  $\text{Bi}_4\text{Ti}_{2.98}\text{Nb}_{0.01}\text{Ta}_{0.01}\text{O}_{12}$  Ceramics. *Materials Chemistry Physics* 2010; 121(1-2) 32-36.
- [37] González-Abreu Y, Peláiz-Barranco A, Guerra JDS, Saint-Grégoire P. Piezoelectric behavior in  $\text{Sr}_{1-x}\text{Ba}_x\text{Bi}_2\text{Nb}_2\text{O}_9$  Aurivillius-type structure ferroelectric ceramics. *Physica Status Solidi B* 2013; 250(8) 1-5.
- [38] Zhang MF, Wang Y, Wang KF, Zhu JS, Liu J-M. Characterization of oxygen vacancies and their migration in Ba-doped  $\text{P}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  ferroelectrics. *Journal of Applied Physics* 2009; 105(6) 061639.
- [39] Peláiz-Barranco A, García-Wong AC, González-Abreu Y, Gagou T, Saint-Grégoire P. Thermally stimulated processes in samarium-modified lead titanate ferroelectric ceramics. *Applied Physics A* 2013; 112(2) 419-423.

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