

# ELECTROMECHANICAL PROPERTIES OF SBN/BTN AURIVILLIUS-TYPE CERAMICS UP TO THE TRANSITION TEMPERATURE

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## **Abstract**

An increasing interest on ceramics with Aurivillius-type structure has developed during the last years due to their high ferro-paraelectric transition temperatures, which make them good candidates for use as high temperature piezoelectrics. However, there are not many works in the literature that study the evolution of their piezoelectric activity with temperature.

An automatic iterative procedure has been used in this work to characterise the piezoelectric, mechanical and dielectric properties at resonance of the  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{1-x}(\text{Bi}_3\text{TiNbO}_9)_x$  solid solution, with  $x=0.35$  and  $0.65$ , from room temperature up to the ferro-paraelectric phase transition temperatures, at  $T_c=580^\circ\text{C}$  and  $790^\circ\text{C}$  respectively. In order to study the influence of the microstructure on the properties, sintered and re-crystallized after hot pressing ceramics were prepared. Mechanochemically activated precursors were used to prepare the ceramics with moderate processing temperature and time. Re-crystallization was successfully tested to obtain a range of microstructures with low porosity and variable grain size. In general, it is observed that low porosity and large grain size enhances the piezoelectric properties. Ceramics with  $x=0.65$  present piezoelectric activity at temperatures as high as  $500^\circ\text{C}$ , with  $k_p=2.9\%$

**Keywords:** Piezoelectric properties, Aurivillius phases, recrystallization, hot-pressing, microstructure-final

## **1. Introduction**

Aurivillius-type structure compounds<sup>1</sup> have as general formula  $[\text{Bi}_2\text{O}_2][\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$  and they are built up by  $n$  pseudo-perovskite  $[\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]^{2-}$  layers alternating with  $[\text{Bi}_2\text{O}_2]^{2+}$  layers. In the last years, an increased interest has been developed by their possible use as non-volatile ferroelectric memories when they are prepared as thin films<sup>2</sup>, due to their large  $P_r$ , reduced fatigue and low leakage currents. Another characteristic of the materials with this structure is their high ferro-paraelectric transition temperature, which makes them good candidates as high temperature

piezoelectrics. Among Aurivillius compounds, the most studied ones are  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT, with  $n=3$ ) and  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT, with  $n=2$ ), and modifications of them to improve their properties, i. e., to reduce the conductivity (doping BIT with  $\text{Nb}^3$  or  $\text{W}^4$ ) or to modify their stoichiometry to obtain better ferroelectric properties<sup>5,2</sup>. Despite their potential application in different fields, there are not many works on Aurivillius ceramics that study the piezoelectric activity throughout the temperature range up to their ferro-paraelectric phase transition.

One of the biggest difficulties in the processing of this kind of ceramics is to obtain a microstructure with the right porosity and grain size<sup>6</sup>. The particles of the precursor powder develop a lamella shape, resembling the anisotropic crystallographic structure. This occurs when they are prepared by solid state reaction, in difficulties in the shaping of the green body and in the later sintering, due to the lack of mass diffusion. During the last years, mechanochemical activation has been applied to obtain piezoceramic precursor powders<sup>7,8</sup>, as it was used before in alloys. Activation is carried out by highly energetic milling of a stoichiometric mixture of oxides and carbonates. A precursor with two important characteristics is obtained in this way: reduced particle size, that allows a better shaping of the green body, and an increased reactivity that enhances sintering. Mechanochemical activation allows to synthesise the compound by milling<sup>8</sup> or gives place to an amorphous<sup>9</sup> powder that reduces the sintering temperature. This fact prevents the loss of volatile elements (Pb or Bi) and controls the grain growth that is produced when a high temperature is needed to obtain dense ceramics.

In this work, sintered and re-crystallized after hot-pressing ceramics were prepared to study the influence of the microstructure on the piezoelectric properties of the Aurivillius-type structure compounds under study. It is well known that hot-pressing is an alternative to obtain highly dense ceramics. However, when it is applied to

lamella-shape compounds, as the Aurivillius phases, it induces texture, with the grains piled-up with their c-axis (which is perpendicular to the major faces of the lamella) in parallel to the applied pressure<sup>10</sup>. This texture is detrimental for the simultaneous appearance of good ferroelectric and mechanical properties. When highly reactive precursors, as the mechanochemically activated ones, are hot-pressed, lower temperatures and hot-pressing times are used. This allows to have highly dense ceramics (>99%<sup>6</sup>) with fine and almost equiaxial grains<sup>11</sup> that prevent the appearance of texture. These fine-grains are difficult to pole<sup>12</sup>. In order to obtain isotropic ceramics with controlled microstructure, re-crystallization after hot-pressing was successfully tested<sup>12</sup>. Quantitative texture analysis from XRD pole figures confirms that isotropic ceramics can be obtained by natural sintering and re-crystallization after hot-pressing. Highly dense ceramics with a wide range of grain sizes can be obtained by this method, as quantitative microscopy shows.

The influence of all of these factors on the elastic, piezoelectric, electromechanical and dielectric properties of the solid solution of Aurivillius-type ceramics of composition  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{1-x}(\text{Bi}_3\text{TiNbO}_9)_x$  ( $n=2$ ), with  $x=0.35$  and  $0.65$  was studied here, from room temperature up to the ferro-paraelectric phase transition of each composition. It had been shown previously that for solid solutions of these compounds, the change of  $T_c$  has a linear relation with  $x$ <sup>13</sup>. For the compositions studied here, the ferro-paraelectric phase transition temperatures are  $\sim 580^\circ\text{C}$  and  $\sim 760^\circ\text{C}$ <sup>14</sup>.

## **2. Experimental**

Ceramics of nominal composition  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{1-x}(\text{Bi}_3\text{TiNbO}_9)_x$ , hereafter called SBN/BTN  $1-x/x$ , with  $x=0.35$  and  $0.65$  were prepared from stoichiometric mixtures of analytical grade  $\text{Bi}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$  and  $\text{SrCO}_3$ , that were mechanochemically

activated. To do this, the mixtures were placed in a vibrating mill (Fritsch, model Pulverisette 0) in a pot and with 5-cm diameter ball, made both of stainless steel, and milled during 400 to 800 hours. This precursor powder was shaped by uniaxial pressing as disks of ~10 mm diameter and ~2 mm thickness. These disks were isostatically pressed at 2000 Kg/cm<sup>2</sup>. Some of them were naturally sintered at 1150 and 1200°C during 2 or 3 hours. Others were hot-pressed in an alumina die, surrounded by alumina powder to avoid contact with the die, at 900 and 1000°C during 1 hour, and with a pressure of 200 Kg/cm<sup>2</sup>. Some of the latter ceramics were re-crystallized at 1050, 1100 and 1150°C during 1 hour. The density of the ceramics was measured by Archimedes method, using distilled water. In both sintered and re-crystallized ceramics thickness was reduced by lapping to have a diameter/thickness ratio higher than 10/1. After polished with a finishing of 5 µm alumina powder, Pt electrodes were painted and sintered at 900°C. Then ceramics were poled to saturation in a silicon oil bath at 200°C, with fields of 120 kV/cm before dielectric breakdown.

For the piezoelectric characterisation with temperature, an automatic iterative method for the planar resonance mode, developed by C. Alemany et al.<sup>15</sup> was used. The original programs were modified to allow calculations from the stored files of complex impedance as a function of the frequency for each temperature. During measurement, the displacement of the resonance frequency with temperature has to be taken into account. To do this, an acquisition of a impedance-frequency file with just 200 points is first done in a wide frequency interval, from which the resonance is located, and then a new file with 400 data points in a narrower interval around the resonance is collected. The main modification with respect to the original method<sup>15</sup> comes when choosing the auxiliary frequencies ( $f_1$ ,  $f_2$ ) used for the measurements of  $Z$  during a step of the iterative process. In the method described in that work, the program demands these

measurements from the impedance analyser. When data acquisition and calculations are separated the auxiliary frequencies and the corresponding values of the absolute electrical admittance,  $|Y|$ , and its phase angles  $\theta$ , are taken by lineal interpolation of the acquired data during measurements.

The data acquisition was made with an impedance analyser HP-4194 with the experimental set-up for the temperature control described in<sup>16</sup>.

### **3. Results and discussion**

Table I shows the density of the studied ceramics. For  $x=0.65$ , the increase in sintering temperature from 1150°C to 1200°C produces an increase in the density of the ceramics as expected. However, ceramics re-crystallized after hot-pressing have higher density than the sintered ones even through final processing temperatures are always lower. For  $x=0.35$  it is clearly seen that sintering time for this composition is an important factor controlling the ceramic density. The highest densities correspond to ceramics sintered for 3 hours. The increase in sintering temperature from 1150°C to 1200°C for 3h produces a decrease in density, probably due to a degradation of the microstructure from grain growth.

Figure 1 shows the evolution of the planar electromechanical coupling factor,  $k_p$ , with temperature, for (a) SBN/BTN 35/65 and (b) 65/35. The  $k_p$  values are higher in the whole temperature range for the  $x=0.65$ , which is the composition with the highest ferro-paraelectric transition temperature. Due to the relation  $k_p \sim P_r^{17}$ ,

$$k_p = 2 \left( \frac{2\varepsilon_{33}^T}{(1-\sigma) s_{11}^E q_{31}} \right)^{1/2} P_r, \text{ the planar electromechanical coupling factor decreases as}$$

$P_r$  does. From  $\sim 650^\circ\text{C}$ , close to  $T_c \sim 760^\circ\text{C}$  but below it,  $k_p=0$ . The resonance was also

observed from 650°C, but calculus was not possible, because the increase of the dielectric losses makes the data acquisition with enough quality difficult.

The results for the ceramic sintered at 1150°C-2h (with  $x=0.35$ ) are shown in the heating and cooling measurement. Heating values fit with cooling ones, indicating the lack of depolarization at 600°C in the first thermal cycle. In fact, this is observed in all the ceramics. The rest of the data shown here, measured up to depoling temperatures allow to know the whole temperature range in which piezoelectric activity exists.

For  $x=0.65$  ceramics the differences in  $k_p$  values among the studied ceramics decrease as the temperature increases (Figure 1a). Differences among the  $k_p$  values are not noticeable and seem to depend on other microstructural characteristics in addition to the density, since no direct relationship between this and  $k_p$  values was found. At 450°C all ceramics exhibit  $k_p \approx 3\%$ . The differences in frequency number (Figure 2a) and elastic stiffness (Figure 3a) among the  $x=0.65$  ceramics remain similar in the whole temperature range studied. They directly depend on the density values, being higher for higher ceramic density. In all the studied ceramics there is a slightly decrease of  $N_p$  and  $s_{11}^E$  as the temperature increases, and no large changes occur near the ferro-paraelectric phase transition. The stiffness decreases in the whole temperature range, indicating that the ceramics become continuously softer as the temperature increases.

Figure 1b shows similar features for  $x=0.35$  as those commented for  $x=0.65$  ceramics, but more enhanced since differences in density are higher among the  $x=0.35$  (~12%) than among  $x=0.65$  ceramics (~6%). At 450°C only the two ceramics sintered for 3h have a  $k_p > 2\%$ . In addition to the fact that  $x=0.35$  ceramics have lower transition temperature other factors are influencing this lower piezoelectric activity.

When the amount of  $\text{SrBi}_2\text{Nb}_2\text{O}_9$  increases in the ceramic composition, longer time is needed to obtain dense ceramics. It is due to the use of  $\text{SrCO}_3$  to obtain the

precursor, while only oxides are needed for  $\text{Bi}_3\text{TiNbO}_9$ . During the one-step synthesis and sintering, volatile  $\text{CO}_2$  is produced that retards the densification process. In  $x=0.35$  ceramics, more  $\text{SrCO}_3$  is used, and longer time rather than high temperature are needed to obtain denser ceramics. Figures 2b and 3b show that the comparatively lower density values for  $x=0.35$  ceramics also lead to lower values of the frequency number and elastic stiffness in these ceramics.

#### **4. Conclusions**

Ceramics of nominal composition  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{1-x}(\text{Bi}_3\text{TiNbO}_9)_x$ , with  $x=0.35$  and 0.65 have been obtained by sintering or re-crystallization after hot-pressing of mechanochemically activated precursors. These ceramics present piezoelectric activity at temperatures higher than  $600^\circ\text{C}$ , and no thermal hysteresis is observed in the first thermal cycle, if temperatures well above the maximum in permittivity are not reached.

The ceramics with  $x=0.65$  have higher  $k_p$  than those with  $x=0.35$  in the whole temperature range with piezoelectric activity, both the lower ferro-paraelectric transition temperature and the ceramic processing influence this result.

Re-crystallization after hot-pressing allows to have the highest  $k_p$  values and elastic properties.

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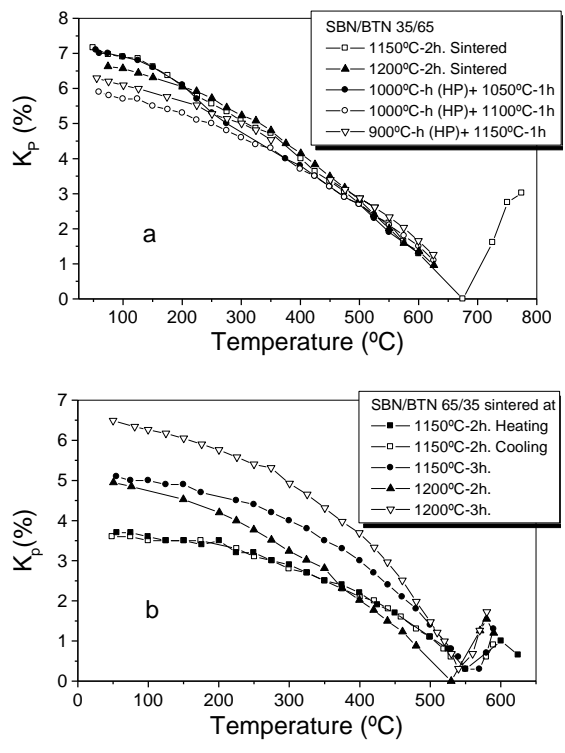


Figure 1.

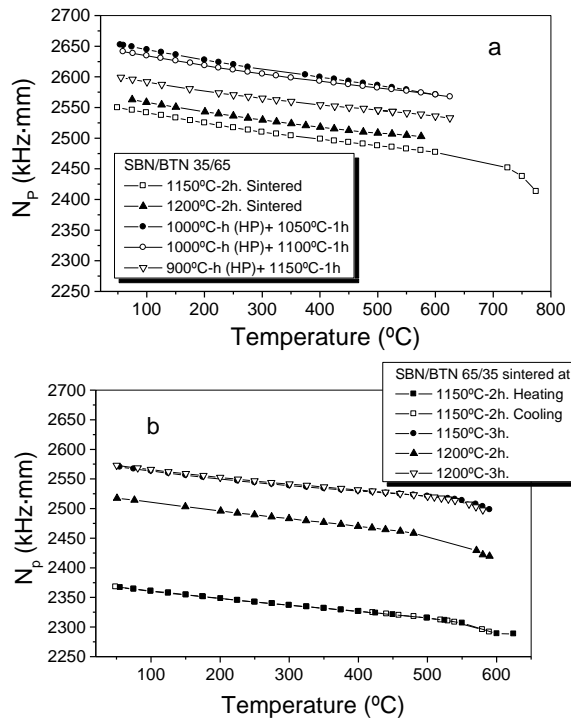


Figure 2

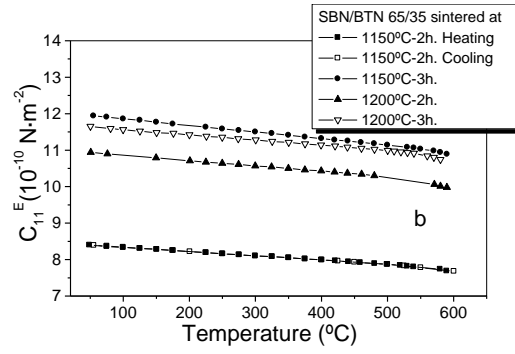
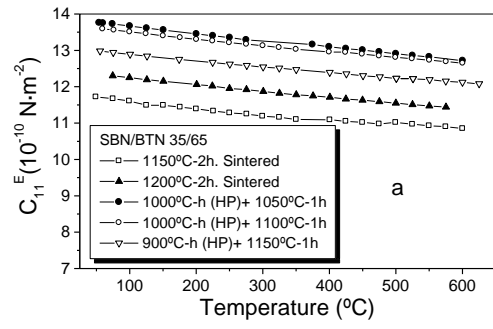


Figure 3

**Table I**

Composition	Ceramic processing conditions	Density (gr/cm <sup>3</sup> )
x=0.65	1150°C-2h sintered	7.44
	1200°C-2h sintered	7.50
	1000°C-1h HP + 1050°C-1h recrystallized	7.90
	1000°C-1h HP + 1100°C-1h recrystallized	7.83
	900°C-1h HP + 1150°C-1h recrystallized	7.70
x=0.35	1150°C-2h sintered	6.28
	1150°C-3h sintered	7.30
	1200°C-2h sintered	6.94
	1200°C-3h sintered	7.13

## Figure captions

Figure 1. Temperature evolution of the planar electromechanical coupling factor for:  
(a)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.35}(\text{Bi}_3\text{TiNbO}_9)_{0.65}$  and (b)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.65}(\text{Bi}_3\text{TiNbO}_9)_{0.35}$  ceramics.

Figure 2. Temperature evolution of the planar frequency number for:  
(a)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.35}(\text{Bi}_3\text{TiNbO}_9)_{0.65}$  and (b)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.65}(\text{Bi}_3\text{TiNbO}_9)_{0.35}$  ceramics.

Figure 3a. Temperature evolution of the elastic stiffness coefficient for:  
(a)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.35}(\text{Bi}_3\text{TiNbO}_9)_{0.65}$  and (b)  $(\text{SrBi}_2\text{Nb}_2\text{O}_9)_{0.65}(\text{Bi}_3\text{TiNbO}_9)_{0.35}$  ceramics.