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Ferroelectricity in Aurivillius-Type Structure Ceramics with $n = 2$ and $(SrBi_2Nb_2O_9)_{0.35}(Bi_3TiNbO_9)_{0.65}$ Composition

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Abstract. Aurivillius-type structure compounds are good candidates for their use as high temperature piezoelectrics, due to their high ferro-paraelectric phase transition temperature. However, this characteristic correlates with a high coercive field that makes difficult the poling process, necessary to have piezoelectric activity. The electric properties, specially conductivity, limit the maximum poling field. On the other hand, piezoelectric properties are directly related to the ferroelectric remanent polarization. Thus, the study of both characteristics is towards improving the piezoelectric properties of these materials.

In this work, ceramics with nominal composition $(SrBi_2Nb_2O_9)_{0.35}(Bi_3TiNbO_9)_{0.65}$ (T_C ~760°C), prepared by hot pressing of mechanically activated precursors, have been studied. The electrical properties (permittivity, dielectric loss factor and d.c. conductivity) as a function of frequency and temperature have been measured, up to temperatures higher than the ferro-paraelectric phase transition, and their anisotropy explained in terms of the ceramic texture. Well-saturated ferroelectric hysteresis loops at 250°C have been obtained, with values of $P_r =$ 21.4 μC/cm^2 and $E_c = 70.4$ kV/cm.

Keywords: Bismuth Layered Structure Ferroelectrics (BLSF), Ferroelectricity, Texture

Introduction

The Aurivillius-type structure alternates n pseudo-perovskite $[A_{n-1}B_nO_{3n+1}]^{2-}$ blocks and $[Bi_2O_2]^{2+}$ layers, having as general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ [1]. Many of the compounds with such structure are ferroelectric, and the spontaneous polarisation, that arises from different modes of simultaneous rotation of the oxygen octahedra and displacements of the ions in the perovskite B-sites, has a major component in the a-b plane of the perovskite-like layers. In the last years, the interest in Bismuth Layered Structure Ferroelectrics (BLSF) has been mainly focused on two issues. One is their use as non-volatile ferroelectric memories when they are prepared as thin films [2], due to the large P_r, reduced fatigue and low leakage currents. The second is their use as high temperature piezoelectrics, due to the high ferro-paraelectric phase transition temperature [3].

In both cases, it is essential to determine the ferroelectric characteristics, namely remanent polarization P_r and coercive field E_c. Many works have focused on the improvement of the properties, by appropriate substitutions [4, 5], doping of the structures [6] or by non-stoichiometry [7]. During the last years, the combination of doping and the formation of intergrowth ferroelectrics, with two different bismuth layered structure materials ($Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$) has been also shown as a good method to increase P_r [8, 9].

Among Aurivillius compounds with relatively high values of remanent polarization, one with a very high ferro-paraelectric phase transition temperature (T_C) is to $Bi_4Ti_3O_{12}$-$SrBi_4Ti_4O_{15}$, [8] with $T_C = 610$°C and $2P_r = 30$ μC/cm^2. In applications as high temperature piezoelectrics, a large value of T_C is desirable to have a wide range of working temperatures. One of the highest T_C in Aurivillius-type structure compounds corresponds to Bi_3TiNbO_9 ($T_C = 915$°C [10]). However, this high T_C makes the ceramics of this composition very difficult to pole. In fact, no hysteresis loops can be obtained in ceramics of this composition [11], because the breakdown field is lower than the field necessary to obtain a well defined loop. It has been proved that the $(SrBi_2Nb_2O_9)_{1-x}(Bi_3TiNbO_9)_x$ solid solution provides a family of ferroelectrics with decreasing values of T_C as x decreases [12]. However, only incipient hysteresis loops of ceramics of this composition with $x = 0.60$ at 120°C and 0.01 Hz, and with $x = 0.25$ at 200°C and 70 Hz, have been previously published. They were measured on sintered isotropic ceramics with poor values of switchable polarization (P_r = 2.71 and 1.1 μC/cm^2, respectively [11, 13]). The study of these ferroelectric characteristics is determinant to improve the properties of the piezoceramics.

The increase in density improves the remanent polarization of Aurivillius-type structure ceramics [14]. A number of synthesis and ceramic processing techniques have been tested for this purpose [15–17]. Among them, the use of mechanochemically activated precursors has been successfully used to obtain dense ceramics [18, 19], which are further improved by the use of hot-pressing. The latter procedure allows ceramics with very small porosity (~1% or less [20]) to be processed. A characteristic of this processing route is that, below a certain temperature, isotropic ceramics with almost equiaxed grains are obtained. Above that temperature, ceramics with an increasing degree of texture, grains of increasing aspect ratio [21] and, consequently, anisotropic properties resulted. The grains are arranged with the *c*-axis of the structure aligned with the hot-pressing direction. As the ferroelectric axis lies in the *a-b* plane, the properties in a textured ceramic depend on the direction of the sample cut (Fig. 1).

In this work, electric measurements and ferroelectric hysteresis loops of high ferro-paraelectric phase transition temperature ($T_C \sim 760$°C) hot-pressed ceramics, with Aurivillius-type structure, are presented. The properties are compared with other Bismuth Layered Structure Ferroelectrics (BLSF).

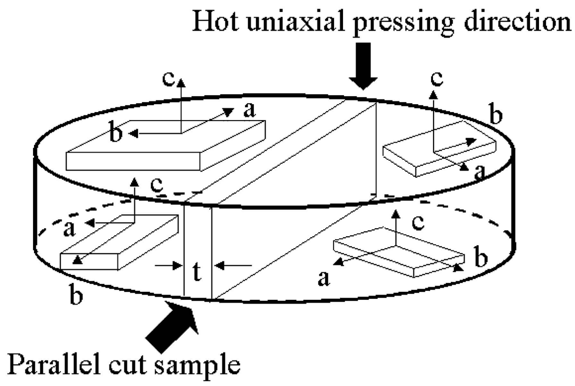

Fig. 1. Ideal arrangement of the lamellar grains under hot pressing of BLSF ceramic and scheme of parallel (to the applied pressure) cut sample.

Experimental Procedure

Ceramics of composition $(SrBi_2Nb_2O_9)_{0.35}(Bi_3TiNbO_9)_{0.65}$ (hereinafter called SBN/BTN 35/65) were prepared by hot pressing of mechanically activated precursors as explained elsewhere [20]. The precursor powder was shaped by uniaxial pressing at 300 Kg·cm^{-2} as disks of approximately 10 mm diameter and 2 mm thickness. Disks were then isostatically pressed at 2000 Kg·cm^{-2}. Ceramics were obtained by hot-pressing in alumina dies, at 1050°C with pressures of ~200 kg/cm^{-2} during 1 h. Coarse grained alumina powder was used as packing

Impedance measurements as a function of temperature at frequencies between 100 Hz and 5 MHz, were carried out with a HP4194A analyser on plane capacitor samples with painted Pt electrodes sintered at 700°C, in an experimental set-up for the temperature control described in [22]. The measurements were accomplished in both parallel and perpendicular cuts to the applied pressure (Fig. 1). The heating and cooling rates were 2°C/min, stabilising the temperature for 1 minute. From these experimental data, complex permittivity, $\varepsilon^* = \varepsilon - i\varepsilon''$, and dielectric losses, tan δs were obtained. The d. c. conductivity was calculated by fitting impedance arcs, Z′-Z″, using the EQUIVCRT program (B. A. Boukamp. AC Inmitance Data Analysis System Equivalent Circuit. Version 4.50. University of Twente. Twente. 1999). This program uses a processing of non-linear least squares fit technique that allows the simultaneous determination of all the parameters of the equivalent circuit, as it is described in detail in [23]. These equivalent circuits consist of two or three (depending on the temperature) RQC circuits in series, each one consisting of a resistance (R) in parallel to a capacitor (C) and to a constant phase element (Q). To start calculations, one needs to introduce some initial values. With this aim, the program calculates circles, with three experimental data in each one, to have the initial values of R and Q for each RQC sub-circuit. The value of C is taken as the capacitance at high frequencies, which is usually constant at frequencies higher than 10 KHz. From these initial data, the non-linear least squares fit is carried out by a iterative calculation. This process was repeated at each temperature. It allows the R values to be obtained with the minimum relative errors. The reciprocal values of R, multiplied by a geometric factor, give the d. c. conductivity of the ceramics.

The ferroelectric hysteresis loops were obtained on samples lapped to a ~60 μm thickness. To grind these samples to such thickness, the ceramics were mounted on a Si substrate and glued with silver paste, dried at room temperature, which also acts as the bottom electrode. After thinning the ceramic on the substrate, the top electrode was also prepared with the same silver paste. The loops were obtained with a commercial Radiant Technologies RT66A unit. A maximum signal of 20 V can be applied with this equipment. Electric fields higher than the coercive one cannot thus be reached. This was overcome by connecting a Kepco Power amplifier, model BOP 1000 M, in series with the RT66A unit. The voltage output from the Radiant set-up was multiplied by 1000 with the amplifier. Triangular voltage signals of 4 Hz were used to have the loops at temperatures of 200°C or higher.

Results

Figure 2 shows the X-ray diffraction pattern of the SBN/BTN 35/65 hot-pressed at 1050°C-1 h. It is remarkable the high relative intensity of the (00 10) peak, showing that certain level of the typical texture of Aurivillius-type structure ceramics has been developed. This results from the arrangement of the platelet-like grains perpendicular to the applied pressure. To quantify the degree of texture achieved, the Lotgering factor [24], f, was calculated from the expression: $f = (p - p_0)/(1 - P_0)$, where $p = \Sigma I(001)/ = \Sigma I(\text{hkl})$, and P_0 is the value of p for a randomly oriented powder material. It was calculated with the data of the intensity peaks (I) taken from JCPDF ICPD file no. 39-0233. The Lotgering factor calculated in our case was $f = 0.25$. It is far from the high values of ceramics obtained by hot-pressing ($f = 0.83$, [25] in $PbBi_2Nb_2O_9$) or hot-forging ($f = 0.52$, [26] in $SrBi_2Ta_2O_9$) of crystalline precursors, or by templated grain growth ($f = 0.93$, [27] in $Na_{0.475}Ca_{0.05}Bi_{4.475}O_{15}$).

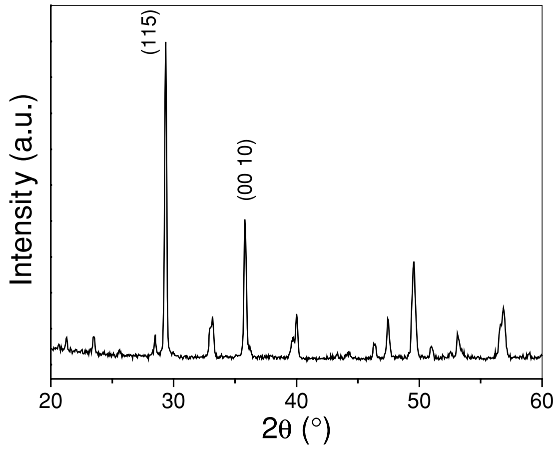

Fig. 2. XRD patterns of SBN/BTN 35/65 ceramics hot pressed at 1050°C-1 h from mechanically activated precursors.

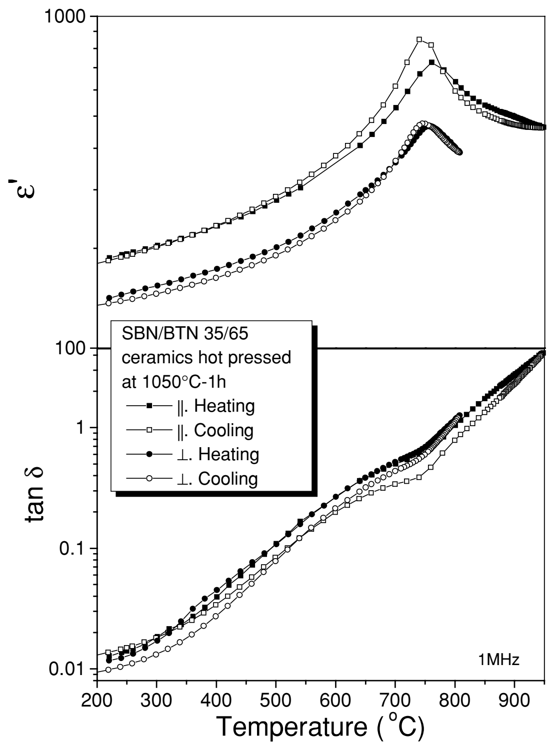

Fig. 3. Real part of the dielectric permittivity and loss factor at 1 MHz as a function of temperature for SBN/BTN 35/65 hot pressed ceramics (solid symbols: heating; open symbols: cooling).

Figure 3 shows the temperature dependence of the dielectric permittivity and the loss factor measured at 1 MHz for SBN/BTN 35/65 ceramics hot-pressed at 1050°C-1 h. Both the properties for the parallel and perpendicular to the hot pressing direction sample cuts (Fig. 1) are shown. The former cut has higher values than the latter one close to the ferro-paraelectric phase transition. The ferro-paraelectric phase transition, T_C, is slightly shifted to lower temperatures for the measurement on cooling for both sample cuts. The dielectric loss factor is very similar for the parallel and perpendicularly sample cuts on heating. During cooling, they are reduced for both cuts.

Figures 4 and 5 show the same features, measured at 100 and 1 KHz respectively. T_C does not shift with respect to the 1 MHz measurement (Fig. 3), as it corresponds to a non-relaxor ferroelectric material. An anomaly in the dielectric loss factor between 400 and 600°C, that is almost unappreciable at 1 MHz, is more visible, both during heating and cooling, and in both sample cuts at 100 KHz. The measurement at 1 KHz shows more clearly the anomaly in the dielectric permittivity, between 350–500°C. In the dielectric losses, the anomaly has now shifted to lower temperature (300–500°C). In all cases, they appear in both sample cuts and thermal runs.

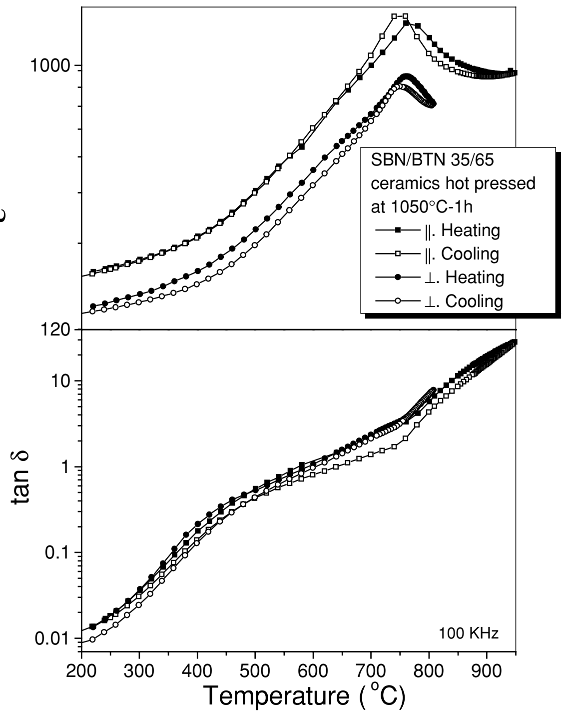

Fig. 4. Real part of the dielectric permittivity and loss factor at 100 KHz as a function of temperature for SBN/BTN 35/65 hot pressed ceramics (solid symbols: heating; open symbols: cooling).

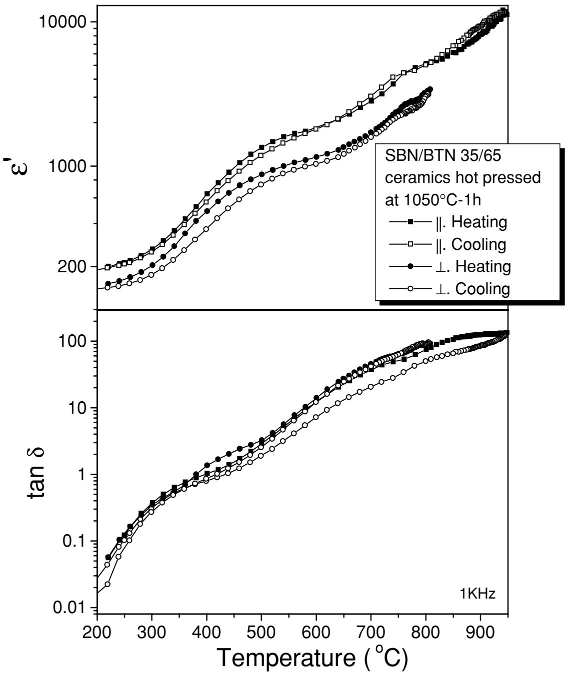

Fig. 5. Real part of the dielectric permittivity and loss factor at 1 KHz as a function of temperature for SBN/BTN 35/65 hot pressed ceramics (solid symbols: heating; open symbols: cooling).

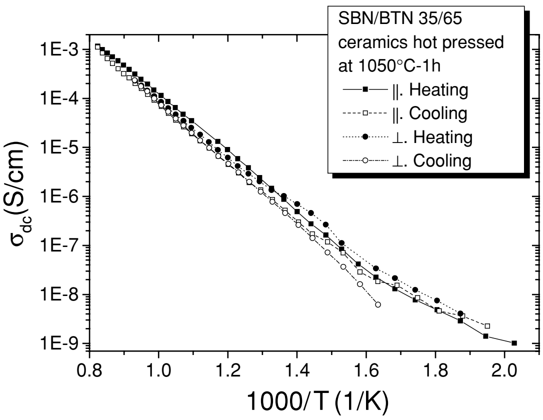

Fig. 6. Arrenhius plot of the d. c. conductivity for SBN/BTN 35/65 hot pressed ceramics (solid symbols: heating; open symbols: cooling).

Figure 6 shows the Arrhenius plot of the d.c conductivity of the ceramics, for both parallel and perpendicular (in relation to the applied pressure) sample cuts (Fig. 1). The differences observed in permittivity between both cuts are not so clearly seen in conductiv-

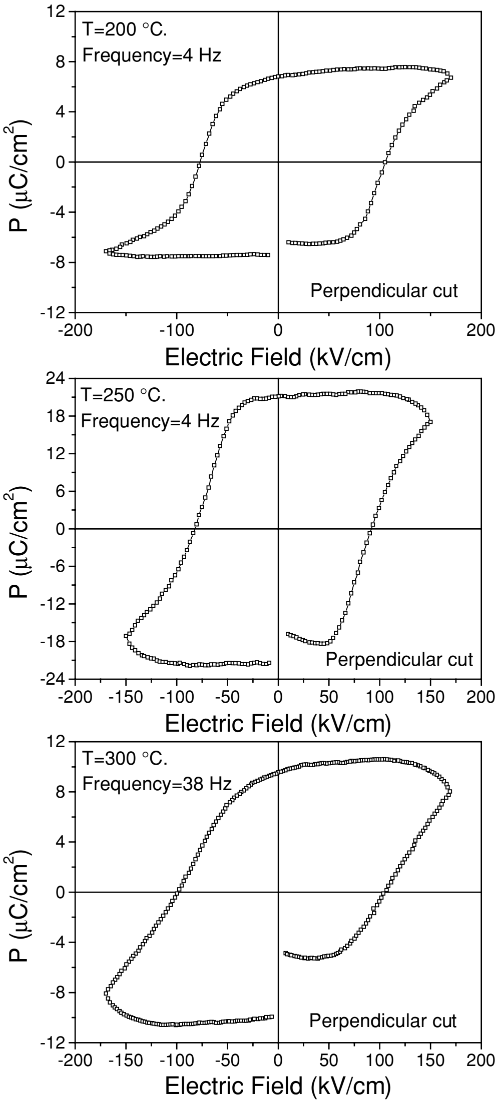

Fig. 7. Hysteresis loops in the perpendicular sample cut of SBN/BTN 35/65 hot pressed ceramics.

ity. The parallel cut seems to have higher conductivity at higher temperatures. There are two regimes in the plot, and conductivity is reduced during the cooling run.

Figure 7 shows the compensated hysteresis loop of the perpendicular to the applied pressure sample cut. With compensation, the ohmic and capacitive contributions to the integrated charge are eliminated, and thus only the ferroelectric polarisation contribution is represented. The measurement of the loops depends on the conditions of temperature and frequency. Close to room temperature, the applied field needed to obtain a ferroelectric loop is higher than the dielectric breakdown one. As temperature increases, coercive field decreases and it is possible to measure the hysteresis loop. For the perpendicular sample cut (Fig. 7), at 200°C and 4 Hz, a well defined loop is obtained, with values of $P_r = 7.1$ μC/cm^2 and $E_c = 90.1$ KV/cm. The same frequency of 4 Hz and a temperature of 250°C are the best conditions to have a well-saturated loop. Values of $P_r =$ 21.4 μC/cm^2 and $E_c = 70.4$ KV/cm are obtained under these conditions. At 300°C (and at a slightly higher frequency of 38 Hz) there is a decrease in the value of P_r (9.7 μC/cm^2) and an increase of E_c (86.6 KV/cm) with respect to those obtained at 250°C. A further increase of temperature increases the conductivity (Fig. 6), and the breakdown field is reduced. The maximum applicable field before breakdown is not enough to produce polarization switching at temperatures higher than 300°C. On the other hand, it is not possible to have a so well saturated loop for the parallel cut, as Fig. 7 shows.

Discussion

The degree of texture achieved, observed in Fig. 2, has an influence in the anisotropy of the dielectric and ferroelectric properties of the ceramics. This anisotropy in the dielectric permittivity and loss factor in Aurivillius-type structure textured ceramics is a well known phenomenon [25–28]. The parallel to the applied pressure sample cut has higher values of both parameters due to the anisotropy in the crystalline structure. In this cut, the a-b plane contribution to ε', which contains the ferroelectric axis, dominates the response. The difference between the properties of ceramics measured in both sample cuts indicates the degree of texture developed in the ceramics during the hot-pressing. Figs. 3–5 shows that the ratio $\varepsilon'_{||}/\varepsilon'_{\perp}$ at the maximum is $\sim$1.6. In single crystals of $Bi_4Ti_3O_{12}$ ($n = 3$), this ratio [29] is 10. In highly textured $Bi_4Ti_3O_{12}$ ceramics obtained by hot-forging, this parameter [30] is 4.3, and in other Aurivilliues-type structure hot-pressed ceramics with $n = 2$ ($PbBi_2Nb_2O_9$), as the one presented here, it is also $\sim$10 [25]. The lower value obtained for ε' in ceramics with respect to the one reported for single crystals is due to the spatial averaging for the polycrystal orientations, the presence of certain level of porosity (although very low) and the grain boundary effect. In any case, the relation shown in Figs. 3–5 indicates that the texture degree is not high.

The appearance of anomalies in both sample cuts is also representative of the low texture achieved. It has been proposed [31] that the anomalies in the permittivity and loss factor as those shown in Figs. 3–5, specially at lower frequencies, are due to a dipole relaxation produced by an ion-jump mechanism as that described for $Bi_4Ti_3O_{12}$. It does not promote significant d.c ionic conductivity, and it occurs in the a-b plane. It has been shown that the same effect is observed in SBN/BTN $1-x/x$, for different x values [13]. Since in hot-pressed highly textured ceramics, the perpendicular to the applied pressure cut is representative of the c-axis properties, the anomalies in the dielectric properties should not be observed [31]. This is opposite to the result found in this work, in agreement with the low texture degree achieved.

Anisotropy in the d.c. conductivity between both cuts should also appear in textured ceramics. Fouskova and Cross showed that conductivity for $Bi_4Ti_3O_{12}$ single crystals along the a-axis is 30 times higher than along the c-axis [32]. This ratio reduces to the half, approximately, in highly textured ceramics, due to the same influence of grain boundaries and porosity as in permittivity [33]. Similar results are found in other Aurivillius textured ceramics with $n = 2$ [25]. The differences in the conductivity between both cuts, shown in Fig. 6, are not so high as the reported ones. It indicates, once again, that the texture is not high in the SBN/BTN 35/65 ceramics hot-pressed at 1050°C-1 h. This fact has a major influence on the ferroelectric measurements.

The dielectric measurements were accomplished at low electric field, with a maximum voltage applied of 50 mV. However, the hysteresis loops are obtained at high electric fields, over 150 KV/cm when applying 900 V. As Figs. 7 and 8 show, the field has a different influence in both cuts of the ceramics. Well saturated loops are not measured in the parallel cut. This result is remarkable, since in textured ceramics the parallel to the applied pressure sample cut, which contains the a-b plane, should have better ferroelectric properties. This is consequence of the higher conductivity when a high electric field is applied along the perpendicular to the c-axis direction (a-b plane). The maximum applicable field before dielectric breakdown is just enough to produce polarisation switching, but saturation does not take place, and the hysteresis loop appears as in Fig. 8.

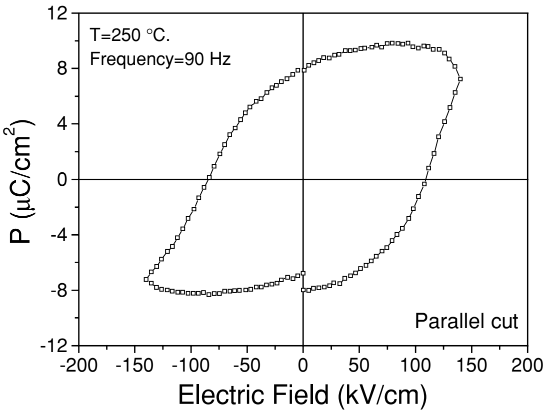

Fig. 8. Hysteresis loops in the parallel sample cut of SBN/BTN 35/65 hot pressed ceramics.

The perpendicular to the applied pressure sample cut has a larger fraction of grains arranged with the c-axis parallel to the direction of the applied field. It reduces conductivity, because $[Bi_2O_2]^{2+}$ planes in the oriented grains act as charge barriers [34]. Higher fields, enough to saturate the loop, are applicable at certain conditions of frequency and temperature (Fig. 7). Although it must be pointed out that the grains arrangement that allows obtaining well saturated loops also reduces the value of P_r, because the c-axis is not the ferroelectric one, values of $P_r = 21.4$ $\mu C/cm^2$ can be obtained at 250°C and 4 Hz. These values are higher than the highest reported for other hot-pressed $SrBi_2Nb_2O_9$-based composition ceramics, with $P_r = 10$–16 $\mu C/cm^2$ at 200°C [5]. The increase of Pr with temperature is due to the reduction of the coercive field, that allows increasing the switching at 250°C. An increase in conductivity at 300°C reduces the applicable field, decreasing in such way the switching, and a further increase of temperature produce the dielectric breakdown.

Most of the published works in BLSFs report the hysteresis loop at room temperature. As it is observed in Fig. 7, P_r depends on the measurement temperature, and it is not easy to compare with other BLSFs. In highly texture W-doped $Bi_4Ti_3O_{12}$ ($n = 3$) ceramics, values of up to $P_r = 20.5$ $\mu C/cm^2$ at room temperature (similar to those found here at 250°C) have been reported [35]. A comparison with similar compositions to the one here studied can be done. A highest value of $P_r = 14.4$ $\mu C/cm^2$ has been reported at room temperature for $(SrBi_2Ta_2O_9)_{1-x}(Bi_3TiNbO_9)_x$

sintered ceramics with $x = 0.2$ [36]. The limitation of the materials of this composition as high temperature piezoelectric is that $T_C \sim 400°C$. To the authors knowledge, the Aurivillius-type structure materials with the highest T_C in which ferroelectric hysteresis loops have been obtained (at 200°C) is Bi_3TiNbO_9-$BaBi_2Nb_2O_9$ ($P_r = 7.1\ \mu C/cm^2$ and $T_C \sim 800°C$ [37]).

The improvement in the ferroelectric properties correlates with the control of the microstructure (low porosity ~1%) and texture obtained by hot-pressing of mechanically activated precursors [19]. A processing at higher temperature would develop a higher level of texture, with the problems of conductivity explained above. A lower hot-pressing temperature produces isotropic ceramics, but with a fine grain size [20] that makes difficult the polarization as the low value of d_{33} shows [20]. The use of mechanical activation allows obtaining highly dense ceramics with a controlled texture in which the measurement of hysteresis loops is possible. The values of $P_r = 21.4\ \mu C/cm^2$ at 250°C and 4 Hz, together with the high $T_C \sim 760°C$ confirms these ceramics to be good candidates for uses as high temperature piezoelectric materials.

Conclusions

Ceramics of composition $(SrBi_2Nb_2O_9)_{0.35}$-$(Bi_3TiNbO_9)_{0.65}$ ($T_C \sim 760°C$), obtained by hot-pressing of mechanically activated precursors at 1050°C-1 h, have been studied. The calculated Lotgering factor was $f = 0.25$, which shows incipient ceramic texture.

The dielectric permittivity in parallel and perpendicular to the applied pressure sample cuts was measured. Anomalies at temperatures lower than the ferro-paraelectric phase transition were observed for both cuts. This fact and the lack of anisotropy in the d.c. conductivity at low field supports the fact that the texture degree is not very high.

The reduction in conductivity perpendicular to the applied pressure sample cut associated with the texture, allows the application of high electric fields at temperatures higher than 200°C and thereby obtain ferroelectric hysteresis loops. The values of remanent polarization achieved are higher ($P_r = 21.4\ \mu C/cm^2$ at 250°C) than those reported in ceramic materials of similar composition and with high T_C, which is desirable for applications as high temperature piezoelectrics.

Acknowledgments

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References

1. B. Aurivillius, *Arkiv Kemi*, **1**, 463 (1949).
2. C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, and J.F. Scott, *Nature*, **374**, 627 (1995).
3. E.C. Subbarao, *Phys. Chem. Solids*, **23**, 665 (1962).
4. A. Castro, P. Millán, M.J. Martinez-Lope, and J.B. Torrance, . *Solid State Ionics*, **63–65**, 897 (1993).
5. P. Durán-Martín, A. Castro, P. Millán, and B. Jiménez, *J. Mater. Res.*, **13**, 2565 (1998).
6. T. Takenaka and K. Sakata, *Ferroelectrics,* **38** (1–4), 769 (1981).
7. Y. Noguchi, T. Hase, and Y. Miyasaka, *Jpn. J. Appl. Phys,* **35**(9B), 4900 (1996).
8. Y. Noguchi, M. Miyayama, and T. Kudo, *Appl. Phys. Lett.*, **77**(22), 3639 (2000).
9. J. Zhu, X.B. Chen, W.P. Lu, X.Y. Mao, and R. Hui, *Appl. Phys. Lett.*, **83** (9), 1818 (2003).
10. L. Pardo, A. Moure, A. Castro, P. Millán, C. Alemany, and B. Jiménez, *Bol. Soc. Esp. Cerám. Vidrio*, **38**(6), 563 (1999).
11. L. Pardo, A. Castro, P. Millán, C. Alemany, R. Jiménez, and B. Jiménez, *Acta Mater.* **48**, 2421 (2000).
12. B. Jiménez, L. Pardo, A. Castro, P. Millan, R. Jimenez, M. Elaatmani, and M. Oualla, *Ferroelectrics*, **241**(1–4), 1923 (2000).
13. B. Jiménez, A. Castro, L. Pardo, P. Millán, and R. Jiménez, *J. Phys. Chem. Solids*, **62**, 951 (2001).
14. C. Jovalekic and S. Stevic, *Ferroelectrics*, **132**, 185 (1992).
15. Y. Shi, C. Cao, and S. Feng, *Mater. Lett.*, **46**, 270 (2000).
16. P. Durán, C. Moure, M. Villegas, J. Tartaj, A.C. Caballero, and J. F. Fernández, *J. Am. Ceram. Soc.*, **83**(5), 1029 (2000).
17. J.G. Lisoni, P. Millan, E. Vila, J.L.M. de Vidales, T. Hoffmann, and A. Castro, *Chem Mater*., **13**(6), 2084 (2001).
18. A. Castro, P. Millán, L. Pardo, and B. Jiménez, *J. Mater. Chem.*, **9**, 1313 (1999).
19. A. Moure, L. Pardo, C. Alemany, P. Millán, and A. Castro, *J. Eur. Ceram. Soc.*, **21**, 1399 (2001).
20. A. Moure, A. Castro, and L. Pardo, *Acta Mater.*, **54**(4), 945 (2004).
21. J. Ricote, L. Pardo, A. Moure, A. Castro, P. Millán, and D. Chateigner, *J. Eur. Ceram. Soc.,* **21**, 1403 (2001).
22. P. Durán-Martín. Tesis Doctoral UAM (1997).
23. B.A. Boukamp, *Solid State Ionics,* **20**, 31 (1986).
24. F.K. Lotgering, *J. Inorg. Nucl. Chem.*, **9**, 113 (1959).
25. H. Igarashi, K. Matsunaga, T. Taniai, and K. Okazaki, *Ceram. Bull.*, **57**(9), 815 (1978).
26. K. Shoji, M. Aikawa, Y. Uehara, and K. Sakata, *Jpn. J. Appl. Phys.*, **37**, 5273 (1998).

27. T. Takeuchi, T. Tani, and Y. Saito, *Jpn. J. Appl. Phys*., **38**, 5553 (1999).
28. J.P. Mercurio, *Bol. Soc. Esp. Ceram Vidrio*, **38** (6), 568 (1999).
29. S.K. Kim, M. Miyayama, and H. Yanagida, *Mater. Res. Bull*., **31**(1), 121 (1996).
30. T. Takenaka and K. Sakata, *Jpn. J. Appl. Phys*., **19**, 31 (1980).
31. H.S. Shulman, D. Damjanovic, and N. Setter, *J. Am. Ceram. Soc*., **83**(3), 528 (2000).
32. L. Fouskova and L.E. Cross, *J. Appl. Phys*., **41**, 2834 (1970).
33. S. Swartz, W.A. Schulza, and J.M. Biggers, *Ferroelectrics*, **38**, 765 (1981).
34. I.S. Yi and M. Miyayama, *Mater. Res. Bull*., **32**(10), 1349 (1997).
35. Y. Noguchi, I. Miwa, Y. Goshima, and M. Miyayama, *Jpn. J. Appl. Phys*., **39**, 1259 (2000).
36. Y. Zhu, X. Zhang, P. Gu, P.C. Joshi, and S.B. Desu, *J. Phys.: Condens. Matter*., **9** 10225 (1997).
37. M. Nanao, M. Hirose, and T. Tsukada, *Jpn. J. Appl. Phys*., **40**, 5727 (2000).