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TEXTURE AND MICROSTUCTURE CONTROL IN $(SrBi_2Nb_2O_9)_{1-x}$ $(Bi_3TiNbO_9)_x$ CERAMICS

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ABSTRACT
Texture and microstructure are determinant factors of the physical properties of piezoelectric ceramics. Among them we have those based on compositions $(SrBi_2Nb_2O_9)_{1-x}$ $(Bi_3TiNbO_9)_x$, with an Aurivillius-type structure. It has been shown that from mechanochemically activated precursors it is possible to obtain isotropic and highly densified (>99%) ceramics by hot uniaxial pressing at temperatures as low as 700 °C. The ceramics obtained are difficult to pole due to the submicron grain size. In order to promote grain growth without affecting the high density achieved, a combination of hot pressing and natural sintering is tested. The isotropic character of the ceramics, i.e., the absence of texture, is monitored by X-ray diffraction and pole figures. Dielectric strength and piezoelectric response are measured and correlated to the porosity content and grain size.

Keywords: $SrBi_2Nb_2O_9$, Bi_3TiNbO_9, hot pressing, microstructure, texture, piezoelectric properties

INTRODUCTION
Aurivillius compounds have as general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$, and are made from n pseudo-perovskite layers alternating with $[Bi_2O_2]^{2+}$ layers[1]. Many of these compounds are ferroelectrics with high ferro-paraelectric transition temperature, which makes them good candidates to be tested for its use as high temperature (>300 °C) piezoelectric ceramics[2].
Dense ceramics of these compounds are not easy to obtain from crystalline precursors powder. There are difficulties in compacting such powder particles and sintering, due to lack of mass diffusion. Hot-pressing has been used in order to obtain dense ceramics. Such ceramics develop an inconvenient texture detrimental for the simultaneous occurrence of good ferroelectric and mechanical properties. Alternative processing routes, as mechanochemical activation of the ceramics precursors, have to be considered[3].

It is possible to obtain highly dense Bi_3TINbO_9 ceramics (porosity <1%) by hot-pressing of mechanochemically activated precursors at moderate temperatures (700 °C-1000 °C). These ceramics are isotropic, because the grains do not develop the size and morphology needed for the appearance of texture. When the hot-pressing temperature increases (1050°C), the ceramics present a preferential orientation with the crystallographic direction <001> parallel to the direction of the applied pressure[4]. However, the small grain size of non-textured ceramics makes difficult the poling process needed to obtain a piezoelectric response. In order to promote the grain growth in highly dense and isotropic ceramic, a natural sintering process after hot-pressing is tested in this work.

EXPERIMENTAL PROCEDURE

Ceramics of composition $(SrBi_2Nb_2O_9)_{0.35}(Bi_3TiNbO_9)_{0.65}$, hereinafter called SBN/BTN (35/65), were prepared from amorphous precursors[5]. These precursors were prepared by energetic milling in vibrating mill from stoichiometric mixtures of analytical grade Bi_2O_3, Nb_2O_5, TiO_2 and $SrCO_3$. Mixtures were homogenised in an agate mortar for 5 minutes and then placed in a stainless-steel pot with a 5 cm steel ball in a vibrating mill (Fritsch Pulverisette 0). An amorphous precursor, according to X-ray diffraction, was obtained by mechanochemical activation of the mixture by milling during periods of 400 to 840 hours. The powder was shaped by uniaxial pressing at 300 Kg/cm^2 as disks of approximately 10 mm diameter and 2 mm thickness, which were then isostatically pressed at 2000 Kg/cm^2.

These disks were hot-pressed at 900 and 1000 °C during 1 hour under a pressure of ~200 Kg/cm^2 in alumina dies and surrounded by alumina powder. Ceramics obtained in this way were then naturally sintered in order to increase the grain size. 900 °C hot pressed ceramics were sintered at 1000 °C for 2 hours and 1050 and 1100 °C for 1 hour, whereas the 1000 °C hot-pressed ceramics were sintered at 1050 and 1100 °C for 1 hour.

The diffraction patterns of the ceramics were obtained with a Siemens D500 powder diffractometer with a Cu anode, using Bragg-Brentano geometry, $1°min^{-1}$ rate and 0.05° 2θ step.

The degree of orientation was obtained by quantitative texture analysis of experimental pole figures[6,7]. These are obtained with a Huber four-circle goniometer mounted on an INEL X-ray generator (Cu $K\alpha$) and an INEL CPS-120 curved position sensitive detector. The pole figures are normalised into distribution densities, which are expressed as multiples of a random distribution (m.r.d.). A sample without any preferred orientation has pole figures with constant values of 1 m.r.d. From several of the pole figures we calculated the orientation distribution function (OD), following an iterative method. The OD describes the amount of crystallites within a specific range of orientation. The quality of the refinement is assessed by the reliability factors RP0 and RP1. From the OD we can calculate relevant pole figures not available experimentally, and estimate the texture strength by the texture index F^2 (F^2 =1 m.r.d.^{2} for random

materials). The calculations to obtain and manipulate the OD have been carried out with the Berkeley Texture Package (BEARTEX).
Ceramics surfaces were polished and analysed by optical microscopy (Leitz Laborlux) before and after thermal etching, in order to examine the porosity and the grain morphology, respectively. Quantitative characterisation was carried out with the aid of computerised image analysis and measurement system (IMCO10-KAT386 system, Kontron Elektronic GMBH, 1990) by a procedure explained elsewhere[8].
Ceramics with a 0.4-0.6 mm thickness with Pt electrodes sintered at 900 °C were poled in a silicon oil bath at 200 °C with fields of ~100 kV/cm. The piezoelectric coefficient d_{33} was measured in a Belincourt meter (at room temperature) by the direct piezoelectric effect at 100 Hz.

RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction pattern of the ceramic hot-pressed at 900 °C and sintered at 1000 °C-1h, that shows the Aurivillius type structure corresponding to the solid solution, without the appearance of second phases. It seems to correspond to a randomly oriented ceramic, since the relatively low intensity of the 00 10 peak indicates that the texture usually developed by hot-pressing is not present. The rest of the ceramics studied here showed similar patterns than the one shown in Figure 1. A quantitative analysis of texture was carried out to further characterise the effectiveness of hot-pressing and subsequent sintering to obtain isotropic ceramics.

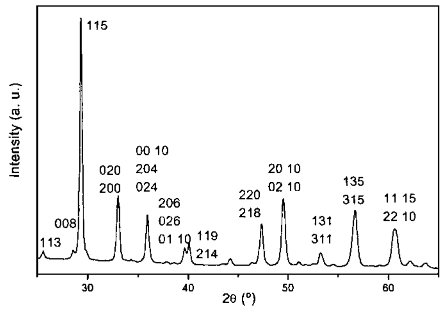

FIGURE 1. XRD of a ceramic hot-pressed at 900°C-1h and sintered at 1000°C-1h

Figure 2 shows the results of the quantitative texture analysis of the same ceramic. Pole figures recalculated from OD are represented. The OD gives a texture index F^2=1.04 mrd^2, with reliability factors RP0=6.6% and RP1=6.5%. These low values show the good quality of the refinement. Recalculated pole figure shows constant density values very close to 1 mrd, as corresponds to a ceramic without any preferred orientations. These results clearly indicate that this ceramic presents a random distribution of crystallites and that no texture is developed in the later sintering treatment.

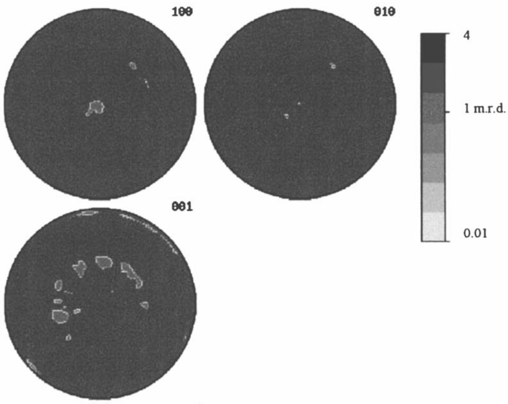

FIGURE 2 Quantitative texture analysis of a ceramic processed at 900°C-1h (HP)+1000°C-1h

Table I shows the characteristics of the microstructure of the ceramics hot-pressed and after sintering. All the ceramics have a porosity lower than 4% that increases as the grain size does in each of the series. Pore area also increases with the temperature.

Table I: Characteristics of microstructure of the SBN/BTN (35/65) ceramics obtained by hot-pressing and sintering (HP: hot-pressed).

Thermal treatment		Pore Area Distributions			Grain size Distributions			d_{33} (pC/N)
		Area (μm^2)	σ_A (μm^2)	Porosity (%)	Area (μm^2)	σ_A (μm^2)	$\frac{D_{máx}}{D_{min}}$	
HP at 900°C 1h +	as-HP	1.8	1.0	0.2	-	-	-	±7
	1000°C-2h	2.2	1.7	1.4	2.0	2.6	1.6	±12
	1050°C-1h	2.5	1.7	3.7	5.1	10.1	1.8	±7
	1100°C-1h	2.9	1.9	3.3	11.3	21.0	1.9	±14
HP at 1000°C 1h +	as-HP	2.5	1.6	0.5	-	-	-	±7
	1050°C-1h	2.8	1.6	1.0	3.3 4.9	3.3 5.0	1.4 1.5	+12, -13
	1100°C-1h	2.8	3.5	3.5	7.5	10.9	1.7	±12

Figure 3 shows the polished surface of the hot-pressed ceramics at 900ºC-1h before, (a), and after, (b) and (c), sintering at 1100ºC-1h. As it happens with Bi_3TiNbO_9 [9], SBN/BTN (35/65) ceramics with relative densities higher than 99% (Table I) of the theoretical one can be achieved by hot-pressing of mechanochemically activated precursors. Thus, a porosity is developed in the sintering process. The higher the sintering temperature with respect to the hot-pressing one, the more important is the developed porosity and the more deteriorated the final microstructure. The porosity is due to the appearance of new intergranular pores and a higher pore size is linked to the grain size increase.

As expected, the data in Table I shows that the grain size, as well as the aspect ratio increases with the sintering temperature. The hot pressed ceramics at 900 ºC present a single lognormal grain size distribution, indicating that the re-crystallization process taking place is still a normal grain growth one. The hot pressed ceramics at 1000 ºC and re-crystallized at 1050 ºC shows a bimodal distribution, which suggest an abnormal grain growth process in which some grains grow at expenses of the surrounded grains, which growth is inhibited. The reason could be a non-homogeneous stress distribution in the hot-pressed initial ceramic, which difficulties the grain growth in some parts of the ceramics, whereas this is promoted in others.

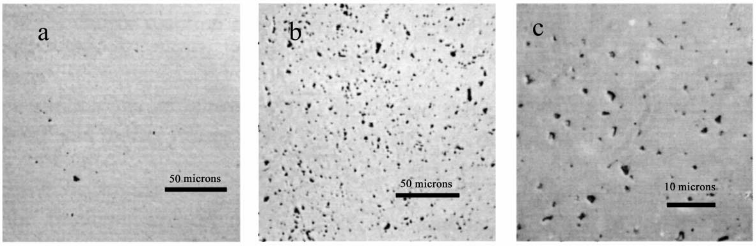

FIGURE 3. Polished surface of SBN/BTN (35/65) ceramics hot pressed at 900ºC before, (a) and after, (b) and (c) re-crystallization at 1100 ºC-1h

It is also remarkable the difference of grain distributions for ceramics re-crystallized at the same temperature from different initial microstructures. The samples re-crystallizated after hot-pressing at 900ºC-1h have a higher grain size and aspect ratio. TEM results have revealed [4] that grains in Bi_3TiNbO_9 ceramics hot-pressed at low temperatures (700-850ºC) have almost equiaxial shape and a submicron size. This is most probably the aspect of the grains in the hot-pressed ceramics, being larger when ceramics are pressed at 1000ºC. The additional re-crystallization of the hot-pressed ceramics makes differences not only in the size, but also in the shape of the ceramics grains. Ceramics with initial fine grains develop much easier the lamella shape characteristic of the Aurivillius-type structure ceramics. This is mostly due to the larger reaction area for the required mass diffusion linked to the small grain size.

Table I also shows the piezoelectric coefficient d_{33}. All the re-crystallized ceramics have coefficients around 12-14 pC/N, except the 900 ºC-1h (HP)+1050ºC-1h one. The coefficients increase with respect to the hot-pressed ceramics as a consequence of a better polarizability. While electric fields of ~120 kV/cm can be applied to the re-crystallized ceramics, dielectric breakdown occurs in the hot-pressed ceramics at fields lower than 100 kV/cm. Not only the grain size but also the aspect ratio and the porosity seems to have influence in the conductivity of the ceramics. This could have some influence in the poling process. Further studies are necessary to clarify this point.

CONCLUSIONS

Aurivillius type ceramics with $(SrBi_2Nb_2O_9)_{0.35}(Bi_3TiNbO_9)_{0.65}$ nominal composition have been prepared from mechanochemical activated precursors by hot-pressing and later re-crystallization by natural sintering at higher temperatures. The quantitative texture analysis of experimental XRD pole figures assesses the isotropic character of the ceramics obtained by this process.

Porosity, pore size and grain distributions are dependent on the initial microstructure. Grain growth from the initial virtually fully dense ceramic promotes the appearance of new intergranular pores. However, ceramics with porosity lower than 4% are obtained for all the conditions tested.

Due to the larger reaction area, ceramics re-crystallized from hot-pressed fine-grained ones, developed higher grain growth and aspect ratio of the grains increase.

Poling difficulties of hot-pressed ceramics are solved by the re-crystallization treatment and higher values of the d_{33} piezoelectric coefficient obtained.

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References.

[1]. B. Aurivillius. Archiv. Kemi. **1**, 463-480 (1949).
[2]. B. Jiménez, L. Pardo, A. Castro, P. Millán, R. Jiménez, M. Elaatmani and M. Oualla. Ferroelectrics, **241**, 279-286 (2000).
[3]. A. Castro, P. Millán, L. Pardo and B. Jiménez. J. Mater. Chem. **9**, 1313-1317 (1999).
[4]. J. Ricote, L. Pardo, A. Moure, A. Castro, P. Millán and D. Chateigner. J. Eur. Ceram. Soc. **21 (10-11)**, 1403-1407 (2001).
[5]. L. Pardo, A. Castro, P. Millán, C. Alemany, R. Jiménez and B. Jiménez. Acta Mater, **48**, 2421-2428 (2000).
[6]. J. Ricote, D. Chateigner, L. Pardo, M. Algueró, J. Mendiola and M.L. Calzada. Ferroelectrics, **241**, 167-174 (2000)
[7]. J. Ricote and D. Chateigner. Bol. Soc. Esp. Cerám. Vidrio, **38 (6)**, 587-591 (1999).
[8]. J. Ricote and L. Pardo. Acta Mater. **44(3)**, 1155-1167 (1996).
[9]. A. Moure, L. Pardo, C. Alemany, P. Millán and A. Castro. J. Eur. Ceram. Soc. **21 (10-11)**, 1399-1402 (2001).