

Microcharacterisation of grain-oriented ceramics based on $\text{Bi}_3\text{TiNbO}_9$ obtained from mechanochemically activated precursors

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Abstract

Hot pressing was applied to a novel powder, synthesised by the mechanochemical activation of starting oxides, in order to obtain dense ceramics of $\text{Bi}_3\text{TiNbO}_9$ for use as piezoelectric material at high temperatures. Since these compositions belong to the family of layered perovskites, hot pressing produces a preferential orientation of the grains. An assessment of the degree of orientation achieved was carried out by quantitative texture analysis using experimental X-ray pole figures. Although texture could be considered as the most influential factor on the final properties, other microstructural features were studied by transmission electron microscopy including grain boundaries and ferroelectric domains. The results of the microcharacterisation of these ceramics are discussed in order to understand the process involved in the development of preferential orientation in these ceramics. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The family of Aurivillius compounds, generally formulated $[\text{Bi}_2\text{O}_2][\text{A}_{n-1}\text{B}_n\text{O}_{3n+1}]$, are built up by the intergrowth of Bi–O and pseudo-perovskite layers.¹ The anisotropy of this crystal structure results in a characteristic lamella-like growth habit, where the shortest dimension corresponds to the $\langle 001 \rangle$ crystallographic direction. As a consequence, the processing of highly dense ceramics is not an easy task. In order to overcome this problem, alternative synthesis routes have been explored, and the use of mechanochemically activated precursors has recently been proved successful for a series of compositions. Mechanochemical activation of inorganic compound mixtures has been traditionally applied to obtain amorphous materials, nanocrystals and intermetallic compounds, although its application to obtain piezoelectric ceramics is very recent and scarce.^{2–6} Dense ceramics can be prepared by natural sintering, i.e. without any pressure applied, from amorphous mechanochemically activated powder, when conventional

synthesis and sintering present difficulties. Final porosity can be further reduced by the application of hot pressing.

Traditionally, hot pressing, and more frequently hot forging,^{7,8} have been used with this family of compounds to obtain grain-oriented ceramics. Other methods have also been developed, such as molten-salt synthesis or two-stage sintering processes.^{9,10} All of these methods start with crystalline precursors. If the starting materials are amorphous, like the ones obtained from mechanochemical activation, then during the hot pressing, the synthesis, sintering and grain growth take place simultaneously, allowing more control of the degree of texture and of the final microstructure of the ceramic.

In this work, ceramics of the Aurivillius family with the composition $\text{Bi}_3\text{TiNbO}_9$ (BTN) with controlled microstructure and texture are obtained from mechanochemically activated powder uniaxially hot pressed at different temperatures, and characterised in order to study the effect of the hot-pressing process on the material. Quantitative texture analysis, a method still not widely used in ferroelectrics in spite of the large amount of useful information that it provides regarding preferential orientations, is used to monitor the degree of orientation obtained, and transmission electron microscopy allows us to observe the grain structure.

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2. Experimental procedure

Ceramics of composition $\text{Bi}_3\text{TiNbO}_9$ were prepared from stoichiometric mixtures of analytical grade Bi_2O_3 , Nb_2O_5 and TiO_2 , manually homogenised in an agate mortar for 3 min. The mixture was then placed in a stainless-steel pot with one 5 cm diameter steel ball and mechanochemically activated for 336 h. The resulting mixture was amorphous according to X-ray diffraction data.² Powders were pressed as thin disks of approximately 10 mm diameter and 2 mm thickness first by uniaxial pressing at 300 kg cm^{-2} and then by isostatic pressing at $\sim 2000 \text{ kg cm}^{-2}$. The disks were then hot pressed in alumina dies, surrounded by alumina powder, at $\sim 200 \text{ kg cm}^{-2}$ and at temperatures ranging from 700 to 1050°C for 1 h.

The degree of orientation achieved with the hot pressing was measured by quantitative texture analysis of the experimental pole figures obtained with an X-ray diffractometer equipped with a four-circle goniometer and a position-sensitive detector.¹¹ The pole figures are normalised into distribution densities, which are expressed as a multiple of a random distribution (mrd). A sample without any preferred orientation has pole figures with constant density values of 1 mrd. The incidence angle used in the experiments was 18° , in order to obtain as much information as possible from the important 0 0 10 pole figure. We also used other figures for the calculations. These are (indicating the overlapping reflections): 115; 220/218; 2 0 10/0 2 10; and 135/315. The result of this analysis is the orientation distribution (OD), a function that describes the amount of crystallites in the material being in a specific range of orientation. The quality of the refinement is assessed by the reliability factors (RP0 and RP1, for global values above 1 mrd, respectively) and by comparing the experimental and the recalculated pole figures. The strength of the texture is estimated by a parameter obtained from the OD: the texture index F^2 , which is equal to 1 mrd^2 for random materials, and the direction of texture components is studied from calculated inverse pole figures.¹¹

Specimens for transmission electron microscopy were prepared by mechanical grinding and polishing up to $\sim 20 \mu\text{m}$, and then mounted onto Cu “7 HEX” (Pelco) TEM grids. This was followed by further thinning to electron transparency by Ar^+ ion milling at 5 kV and 2.5 mA at 10° first, and 5° for the final step. TEM observations were carried out in a JEOL-2000FX microscope working at 200 kV.

3. Microstructural results

The quantitative texture analysis of hot-pressed BTN ceramics provides us with complete information on the texture of the materials, some of which is summarised in

Table 1. While the ceramics hot pressed at 700°C present an almost random distribution of crystallites, with a texture index close to 1 mrd^2 , those treated at 1050°C present a strong preferential orientation ($F^2 = 3.3 \text{ mrd}^2$), with the crystallographic direction $\langle 001 \rangle$ parallel to the pressing direction. The low values of the reliability factors RP0 and RP1 show the good quality of the refinement. The recalculated 001 pole figures (Fig. 1) show this situation clearly. It can be observed that the highest density values for the textured ceramic are not in the centre of the pole figure, but displaced around 15° with respect to the normal to the sample surface. This can be attributed to some small mechanical mismatch of the press, which is applying the pressure not exactly perpendicular to the sample surface. This is also reflected in the recalculated 100 pole figure. As the $\langle 001 \rangle$ preferential orientation is normal to the sample surface, parallel to it we will have a reinforcement of the density of $\langle 100 \rangle$ and $\langle 010 \rangle$. This means that we will find high-density values close to the edge of the 100 and 010 pole figures. In the case of a fibre texture, i.e. texture with an axial symmetry, these density maxima will form a continuous circle in the edge. This is the case for our textured ceramic as it can be seen in the recalculated 100

Table 1
Results of the quantitative texture analysis of BTN ceramics

HP temperature ($^\circ\text{C}$)	Texture components	F^2 (mrd^2)	RP0 (%)	RP1 (%)
700	–	1.2	5.2	4.8
1050	$\langle 001 \rangle$	3.3	16	14

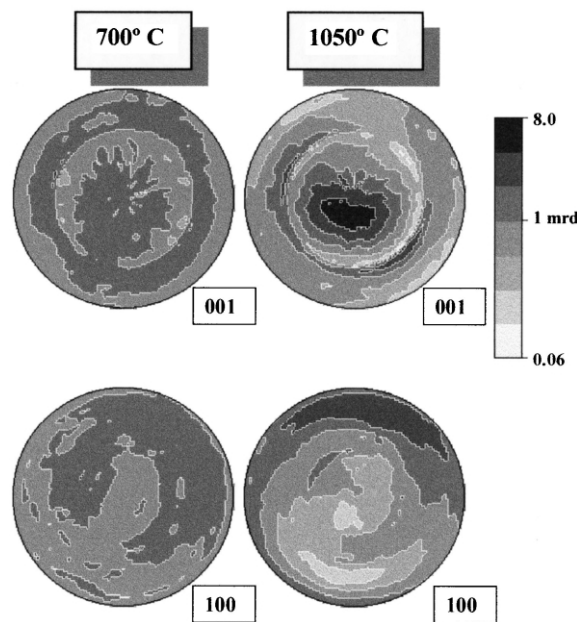


Fig. 1. 001 and 100 recalculated pole figures of two BTN ceramics hot pressed at different temperatures: (a) 700°C , (b) 1050°C . Equal-area projection and logarithmic density scale.

pole figure, although the circle is not complete and it is displaced, due to the fact that the preferential orientation is not exactly perpendicular to the film surface, but inclined by $\sim 15^\circ$. It has to be noted as well that the analysis of the inverse pole figure corresponding to the normal of the film surface does not reveal the existence of any other significant contribution to the global texture of these ceramics.

The evolution of the grain configuration with the hot-pressing temperature has been studied by TEM. The corresponding micrographs are shown in Fig. 2. The first observation is the increase of the grain size with increasing temperature. At 700°C , the grain size ranges from 75 to 200 nm; this increases at 850°C with a range of sizes between 100 and 800 nm. The shape of the grains is not the expected lamella-like shape in both cases. A further increase of the hot-pressing temperature to 1050°C results in the typical lamella-like grains with sizes of approximately $3\ \mu\text{m}$ in the long direction and

$0.5\ \mu\text{m}$ in the short direction. A more detailed study of the grain size distribution of this ceramic by optical microscopy shows a bimodal distribution,¹² whose smallest grains correspond to the ones observed here by TEM.

Segregation at the grain boundaries was not observed. As an example, the detail of the triple junction presented in the micrograph of Fig. 3 shows the absence of any second phase. It should also be noted that the low porosity achieved with the hot-pressing method ($< 1\%$)¹² can also be observed by the dense packing of the grains in the ceramics studied. Another important observation is that ferroelectric domains are not observed in the ceramics hot pressed at 700 or 850°C , and are difficult to identify in the material hot pressed at 1050°C . Observations in similar ceramics produced only by natural sintering reveal, very easily, the existence of a ferroelectric domain configuration, which is not the case here. It seems that hot pressing introduces a large number of defects in the crystallites, which can be observed

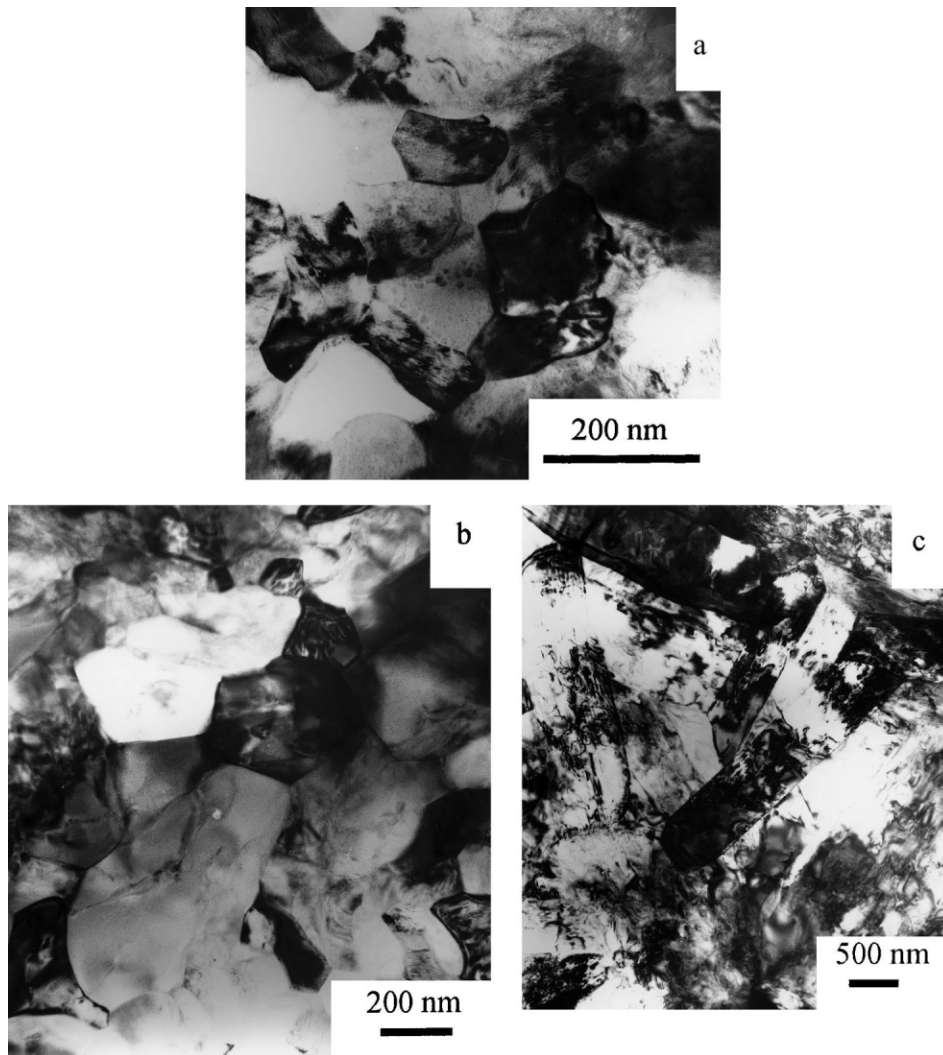


Fig. 2. TEM micrographs of BTN ceramics hot pressed at different temperatures: (a) 700°C , (b) 850°C and (c) 1050°C . The evolution of the grain configuration can be observed.

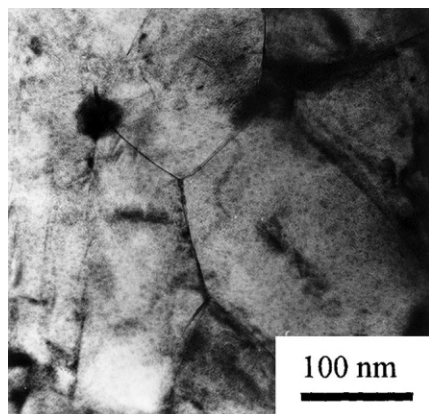


Fig. 3. TEM micrograph showing the detail of a triple junction in BTN ceramics hot pressed at 850°C.

in the TEM images. Usually defects intercept the domain boundaries, making their observation by TEM difficult. Further study is in progress in order to clarify this aspect, which can be important for the final properties of the material.

4. Discussion

Hot pressing of $\text{Bi}_3\text{TiNbO}_9$ ceramics results in textured materials along $\langle 001 \rangle$ in the direction of the applied pressure, but only when a certain temperature is reached. Below that temperature grains do not show the typical lamella shape characteristic of the Aurivillius crystals [Fig. 2(a) and (b)]. Although the material has reached the final structure at these low processing temperatures, confirmed by X ray diffraction,¹² the process of anisotropic grain growth seems not yet to have started. An increase in the processing temperature to 1050°C, and, therefore, to the energy supplied to the system, produces a process of grain growth, which due to the particular growth habit of Aurivillius compounds, results in lamella-shaped grains as observed in Fig. 2(c).

This evolution of the grain configuration is directly related to the appearance of preferential orientation in the hot-pressed ceramics, which is only developed for those with lamella-shaped grains [hot pressed at 1050°C, Fig. 2(c)]. Logically, an external pressure applied during the formation of isotropic crystals will only have consequences for the radical reduction of the final porosity, not producing any texture. This is the case for the ceramics hot pressed at low temperatures, which do not develop any preferential orientation. However, if the same pressure is applied to crystallites with the shape of thin plates, they will tend to be stacked one on top of another, with their largest faces normal to the pressure direction. As in the Aurivillius crystals the shortest dimension corresponds to the $\langle 001 \rangle$ crystallographic direction, this ordering generates a preferential orientation in that direction, as our results show. There is no

reason for any ordering in the other two perpendicular directions ($\langle 010 \rangle$ and $\langle 100 \rangle$), which results in an axial symmetry of the texture, i.e. the fibre texture observed in this ceramic.

Other effects of the hot pressing, important for the final properties of BTN ceramics, have been also observed. Firstly, there are no traces of second phases segregated at the grain boundaries, which prevent possible conduction problems. And secondly, grains of the textured ceramics seems to have a large amount of defects, most probably due to the large stresses produced by the hot pressing. Although this subject requires further study, we can point out that the appearance of these kinds of defects in ferroelectrics usually leads to domain-boundary pinning, which can determine the ferroelectric behaviour of the ceramic.

To sum up, hot pressing of mechanically activated powder of $\text{Bi}_3\text{TiNbO}_9$ results either in fine-grained non-textured ceramics or in large lamella grains $\langle 001 \rangle$ oriented along the pressing direction. This depends on whether the processing temperature is below or above the threshold when grain growth starts to be significant.

5. Conclusions

Mechanically activated powder of $\text{Bi}_3\text{TiNbO}_9$ has been hot pressed at different temperatures. The characterisation of the microstructure of the ceramics produced by this processing method, where synthesis, sintering and grain growth take place simultaneously, leads to the following conclusions:

1. Hot pressing ceramics of this composition at low temperatures ($< 1050^\circ\text{C}$) leads to fine-grained ceramics without texture. An increase of the processing temperature results in the activation of the grain growth process, which produces lamella-shaped crystals that are oriented along the $\langle 001 \rangle$ in the direction of the applied pressure.
2. Low porosity and the absence of second phases segregated at the grain boundaries are achieved by this method, regardless of the texture of the resulting ceramic.
3. In the case of textured ceramics, large stresses seem to be introduced in the material that lead to the appearance of a large number of defects in the grains.

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