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Piezoelectric ceramics based on Bi_3TiNbO_9 from mechanochemically activated precursors

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Abstract

Ceramics based on the Aurivillius type structure compound Bi_3TiNbO_9 were processed by natural sintering and hot pressing of amorphous precursors obtained by mechanochemical activation of oxides and carbonates mixtures. Synthesis, grain growth and sintering take place in a single thermal treatment at moderate temperatures in comparison with ceramics processed from crystalline precursors. The influence of the processing parameters on the ceramic texture and microstructure at mesoscopic scale were studied by XRD and quantitative optical microscopy. It was possible to obtain both isotropic and textured ceramics. The occurrence of abnormal grain growth was observed under some conditions. An ample electrical characterisation of the ceramics was carried out comprising dielectric, ferroelectric and piezoelectric properties. The influence of the microstructure on the properties and the interest of the materials as high temperature piezoelectrics are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hot pressing; Microstructure-final; Milling; Niobates; Piezoelectric properties

1. Introduction

Aurivillius compounds, named after the researcher that first synthesised oxides with such structure and determined it in 1949,[1] have a general formula $[Bi_2O_2][A_{n-1}B_nO_{3n+1}]$ and their crystal structure alternates layers of bismuth–oxygen and n pseudo-perovskite layers.

Many of these compounds are ferro-piezoelectrics, since structures with oxygen octahedra and a light ion with high charge in the centre (e.g. Ti^{4+}, Nb^{5+}, Ta^{5+}) favour the appearance of spontaneous reversible polarisation. This spontaneous polarisation, arising 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 [100] direction, a-axis, of the perovskite-like layers. These types of compounds are characterised by high ferro-paraelectric transition temperatures and are good candidates for use as high temperature ($>300°C$) piezoelectrics.

As a consequence of the anisotropic crystallographic structure of these compounds, their crystals have a lamellae-like shape. The processing of dense ceramics from crystallised precursor powder is not easy, there are difficulties in compacting such powder particles and sintering, due to lack of mass diffusion. Alternative processing routes have to be considered. Here, ceramics of composition $(Bi_3TiNbO_9)_x(SrBi_2Nb_2O_9)_{1-x}$, hereinafter called $(BTN)_x(SBN)_{1-x}$, and controlled texture and microstructure have been prepared from mechanochemically activated precursors powders. The ceramics were characterised and a discussion of the results is made based on their microstructure.

2. Experimental

Ceramics of composition $(BTN)_x(SBN)_{1-x}$, with $x=1.00$, 0.65 and 0.35, were prepared from stoichiometric mixtures of analytical grade Bi_2O_3, Nb_2O_5, TiO_2 and $SrCO_3$, homogenised in an agate mortar for 3 min by hand. Then, the mixture was placed in an stainless-steel pot with a 5 cm diameter steel ball and mechanochemically activated during 336 h in a vibrating mill Fritsch Pulverisette 0, obtaining an amorphous mixture, according to X-ray diffraction examination.[2] For the sake of comparison, crystallised precursors were also

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obtained by conventional method of solid state reaction at 1050°C, as reported elsewhere.[2] Powders were shaped by uniaxial pressing at 300 kg cm^{-2} as thin disks of approximately 10 mm diameter and 2 mm thickness. Disks were isostatically pressed at 2000 kg cm^{-2} and then natural sintering was carried out on a Pt foil at temperatures from 1000 to 1150°C for times from 1 to 2 h. Some of the disks were hot-pressed in alumina dies and surrounded by alumina powder at temperatures from 700 to 1050°C and ~200 kg/cm^{-2} for 1 h.

A Siemens D500 powder diffractometer with a Cu anode was used to obtain the ceramic diffraction patterns, with Bragg-Brentano geometry, 1° min^{-1} rate and 0.05° 2θ step.

Scanning electron and optical microscopy were used to examine the precursor powder morphology and the polished ceramic surfaces, respectively. Ceramic surfaces were analysed before and after thermal etching in order to examine porosity and grain morphology, respectively. Quantitative characterisation of the ceramic microstructures was carried out with the aid of computerised image analysis (IMCO10-KAT386 system, Kontron Elektronic GMBH, 1990) and measurement system by a procedure explained elsewhere.[3] Hardness was determined with a Vickers indentor Leco V100-A2.

Sintered disks were lapped to a ratio thickness/diameter of less than 1/10. The samples with painted Pt electrodes were poled in a silicon oil bath at 200°C with fields of ~80 kV cm^{-1}. The piezoelectric d_{33} coefficient was measured in a Berlincourt meter by the direct piezoelectric effect at 100 Hz, at room temperature and after successive thermal annealing at temperatures between 200 and 900°C during 15 min. Dielectric, elastic and piezoelectric constants and electromechanical coupling factors corresponding to the thickness and radial (planar) extensional vibration modes of the thin disk shaped ceramic resonators were calculated by an automatic iterative method described elsewhere.[4] Two types of measurements at resonance from complex impedance at the appropriated frequencies with a HP4192A impedance analyser were carried out: (a) from room temperature to 200°C in a modified HP16085B terminal adapter, and (b) at room temperature after annealing.

3. Results and discusion

3.1. Precursor morphology

Fig. 1(a) shows the aspect of a particle in Bi_3TiNbO_9 (BTN) crystalline precursor powder conventionally synthesised at 1050°C. The particles in this type of powder are clusters of large (~2 μm) lamellae-like crystals, difficult to close pack in the moulding of the green pellet. Fig. 1(b) shows the aspect of the particles of the BTN mechanochemically activated precursor powder by milling at 336 h. It is remarkable the much lower particle size of this type of powder than greatly facilitates the moulding of the green pellets. There is not a defined morphology in the particles of the mechanochemically activated powder. When this powder is annealed at 600°C, the synthesis of the Aurivillius structure takes place as was previously reported.[2] Fig. 1(c) shows the change in the particle morphology and the appearance of the tiny (~900 nm) clusters of incipient anisotropic crystallites already at this low temperature.

3.2. Texture and microstructure

As reported previously,[5] the main difference between sintered ceramics from crystalline and mechanochemically activated precursors is the microstructure. The latter have much lower porosity (see Table 1) and present lower grain size than the former. As Table 1 shows, the porosity of sintered BTN ceramics from mechanochemically activated precursors is of the order of 10%, compared with the 20% for crystalline precursors, for a sintering temperature of 1050°C, and reduces slightly as the temperature or the sintering time increases. The effect of hot pressing on the porosity of BTN ceramics from mechanochemically activated precursors is remarkable. These can be prepared even at 700°C with a porosity lower than 1%.

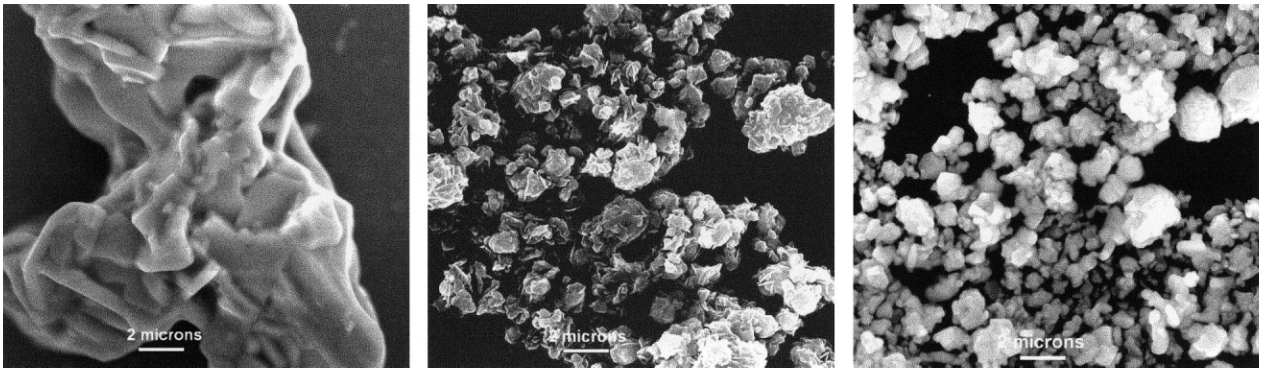

Fig. 1. Particle aspect of: (a) BTN crystallised precursor powder synthesised at 1050°C; (b) BTN mechanochemically activated precursor powder by milling at 336 h; and (c) BTN mechanochemically activated precursor powder after annealing at 600°C.

Table 1
Characteristics of the microstructure of BTN ceramics from mechanochemically activated precursors

Processing conditions	Pore size distributions			Grain size distributions						H_v (GPa)
	Area (μm^2)	σ_A (μm^2)	Porosity (%)	Area (μm^2)		σ_A (μm^2)		D_{max}/D_{min}		
BTN sintered ceramics										
1000°C 1 h	–	–	> 25	1.4		1.9		1.56		1.9
1050°C 1 h	5.3	5.9	10.9	2.3		2.5		1.69		3.9
1050°C 2 h	2.7	4.7	13.9	2.6		2.6		1.69		3.1
1100°C 1 h	6.2	6.7	9.8	4.1		4.5		1.72		3.4
1100°C 2 h	9.0	9.8	8.5	fine	coarse	fine	coarse	fine	coarse	2.1–2.7
				5.7	2253	7.5	7896	1.85	2.40	
BTN hot-pressed ceramics										
700°C 1 h	7.1	4.5	0.5	< < 1		–		–		6.3
850°C 1 h	7.3	7.6	0.4	< < 1		–		–		5.9
900°C 1 h	2.6	1.3	0.4	< < 1		–		–		5.8
1000°C 1 h										
⊥	1.9	2.4	0.5	1.6		2.1		1.9		5.8
‖				1.4		1.6		2.0		
1050°C 1 h				fine	coarse	fine	coarse	fine	coarse	
⊥	4.3	3.2	1.2	2.4	35.6	3.5	73.1	2.3	2.4	3.3
‖				2.0	29.0	3.3	56.9	2.7	2.4	

Similar porosity and an increase in grain size are observed when the hot-pressing temperature is increased.

The values of Vickers hardness shows that all the ceramics are mechanically stable, being harder the hot-pressed ones, as corresponds to their lower porosity.

Anisotropic microstructure is presented in the ceramic processed at 1050°C, as is revealed by the difference in grain size distributions when measured in perpendicular or parallel direction to the applied pressure. These differences, compared with the very similar distributions when measured for the hot-pressed ceramic at 1000°C, are much higher. Average grain area is larger when measured perpendicularly to the pressure. The grains have an anisotropic morphology with an aspect ratio D_{max}/D_{min} from 2.3 to 2.7 (Table 1), smaller when measured perpendicularly to the pressure, revealing the lamella morphology. This anisotropic microstructure corresponds to an inconvenient texture detrimental for the simultaneous occurrence of good ferroelectric and mechanical properties.

The texture of the hot-pressed BTN ceramic at 1050°C is also revealed by the high intensity of the 0010 peak in the XRD pattern, shown in Fig. 2. However the fine grained hot-pressed ceramic prepared at 700 to 1000°C presents a XRD pattern, also shown in Fig. 2, corresponding to randomly oriented grains, which most probably have a much lower aspect ratio, thus preventing the occurrence of a texture. These grains have a lower aspect ratio.[6]

The dielectric permittivity increases in BTN ceramics, which present one of the highest ferro-paraelectric transition temperatures known among Aurivillius ferroelectrics, ca. 900°C, when are prepared by hot pressing, due to the lower porosity. The texture of the hot-pressed BTN ceramic at 1050°C is also revealed by the different permittivity measured for samples parallel and perpendicular to the applied pressure, being higher for the measurement in the a axis direction (parallel cut).[7]

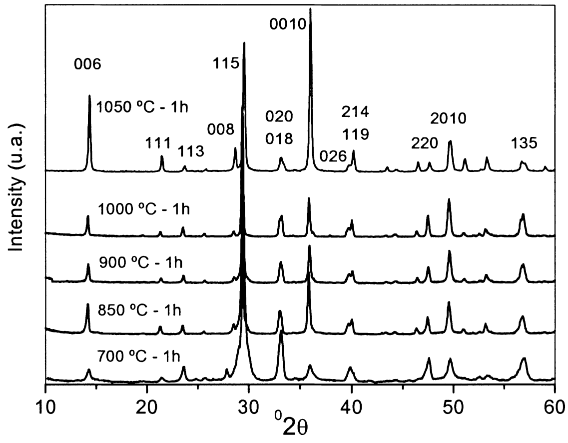

Fig. 2. XRD patterns of hot-pressed BTN ceramics from mechanochemically activated precursors.

Figs 3 and 4 show the evolution with temperature of the planar electromechanical coefficient, K_p, for BTN and $(BTN)_x(SBN)_{1-x}$ ceramics sintered from amorphous precursors. No significant changes occur until 200°C except for BTN ceramic sintered at 1050°C. The values are higher for solid solution than for BTN ceramics at each temperature. The reduction of the transition temperature as x decreases gives place to a reduction of the coercive field at the poling temperature. Consequently, the piezoelectric coefficients and electromechanical coupling factors are increased.

Figs. 3 and 4 also show K_p and d_{33} values measured at room temperature after thermal annealing at temperatures well above 200°C, up to the transition temperature. Except

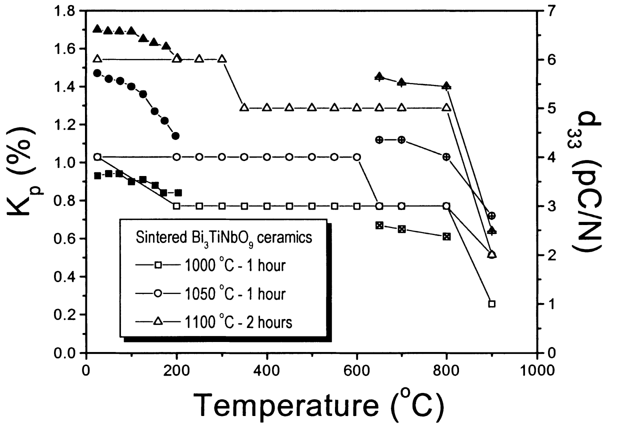

Fig. 3. Temperature evolution of planar electromechanical coupling factor K_p (solid symbols) and piezoelectric coefficient d_{33} (open symbols) and K_p (centred symbols) measured at room temperature after annealing at several temperatures for BTN ceramics.

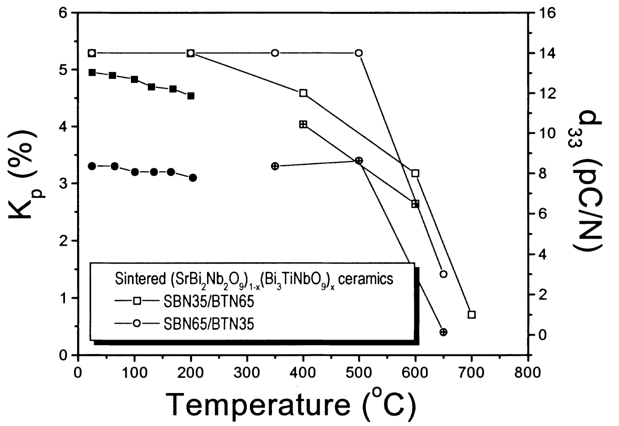

Fig. 4. Temperature evolution of planar electromechanical coupling factor K_p (solid symbols) and piezoelectric coefficient d_{33} (open symbols) and K_p (centred symbols) measured at room temperature after annealing at several temperatures for $(SBN)_{1-x}(BTN)_x$ ceramics.

for BTN and $(BTN)_{0.65}(SBN)_{0.35}$ ceramics, values are stable until each T_c, indicating that no depoling process occurs until near the phase ferro-paraelectric phase transition. Again, values for solid solution are higher at all temperatures.

4. Conclusions

Mechanochemical activation provides $(Bi_3NbTiO_9)_x(SrBi_2Nb_2O_9)_{1-x}$ ceramic precursors of high reactivity. BTN piezoceramics from amorphous precursors obtained by mechanochemical activation can be processed by a single thermal treatment in which synthesis, grain growth and sintering takes place at as low temperatures as 1000°C for natural sintering and 700°C for hot-pressing. Hot-pressing from amorphous precursors provides highly densified BTN ceramics with controlled texture: isotropic and fine grained at low temperatures, 700–1000°C, and textured and coarse grained at 1050°C for 1 h.

The dielectric and piezoelectric properties of BTN ceramics from mechanochemically activated precursors, improved in comparison to ceramics from crystalline precursors, are related to their porosity and texture, and which is furthermore directly related to grain size and, thus, can be tailored.

Isotropic piezoceramics of $(Bi_3NbTiO_9)_x(SrBi_2Nb_2O_9)_{1-x}$ can also be prepared by natural sintering from mechanochemically activated precursors and their piezoelectric performance remarkably improved from BTN ceramics, due to their better polarizability, caused by a reduction of the ferro-paraelectric transition temperature and coercive field.

Ceramics with $x=0.65$ and 0.35 were prepared from amorphous precursors and their piezoelectric properties were measured. They do not show remarkable reductions of electromechanical coupling factors and piezoelectric coefficients below 500°C. Ceramics of this system, with ferro-paraelectric transition temperatures in the range from 420 to ca. 900°C, have been proved suitable candidates for use as high temperature piezoelectrics.

Acknowledgements

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