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Piezoelectric PMN-PT ceramics from mechanochemically activated precursors

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Abstract

Piezoelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) ceramics with 0.2 and 0.35 PT have been prepared from mechanochemically activated powders. Pressureless sintering in air and hot pressing were tested. $PbZrO_3$ packing was necessary to limit lead oxide losses and to avoid the formation of second phases at the surface when temperatures above 1000 °C were used. Ceramics sintered at 1200 °C presented densities of 90% and a grain size of 4 μm. Hot pressed ceramics hardly showed porosity and had submicron (0.1–0.5 μm) grain size, which make the mechanoactivated powders very suitable for templated grain growth matrices. Electrical and electromechanical characterisation was accomplished. The 0.2 PT composition combined relaxor dielectric behaviour with piezoelectricity after poling. The 0.35 PT ceramics presented a first order ferroelectric-paraelectric transition at 171 °C and a complex transverse piezoelectric coefficient of −(181.8-i3.6) pC N^{-1} at room temperature.

Keywords: A. Mechanochemical synthesis; A. Sintering; B. Microstructure-final; C. Piezoelectric properties; D. Perovskites

1. Introduction

Ultrahigh piezoelectricity and electric field induced strain have been found in relaxor ferroelectric $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PZN-PT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) rhombohedral single crystals with composition close to the rhombohedral-tetragonal morphotropic phase boundary (MPB).[1] Longitudinal piezoelectric coefficients and high field strains as high as 2500 pC N^{-1} and 1.7%, respectively, were observed along the <001> direction of the structure. These values are significantly higher than those provided by the best lead zirconate titanate (PZT) based piezoceramics (600–700 pC N^{-1} and 0.17%).[1] Textured PMN-PT ceramics have been prepared showing a piezoelectric coefficient of 1200 pC N^{-1} and a high field strain of 0.3%.[2] Texturing was achieved by heterogenous templated grain growth (TGG) from $BaTiO_3$ single crystal template particles and a highly reactive PMN-PT precursor mixture matrix. High densification and fine (submicron) grain size of the matrix prior the TGG thermal treatment are necessary for achieving high texture.[3]

Mechanochemical activation of precursors is a powerful technique for preparing highly reactive fine powders of ferroelectric oxides, which has been applied to the direct synthesis of electrostrictive 0.9 PMN–0.1 PT from the constituent oxides.[4] Piezoelectric PMN-PT ($\geqslant$0.2PT)[5] fine powders with different PT contents have been recently prepared by mechanochemical synthesis.[6] We report here on the microstructure and electromechanical properties of ceramics prepared by pressureless sintering and hot pressing of 0.2 PT (well below the MPB) and 0.35 PT (slightly above the MPB)[7] such powders. Emphasis is put on the microstructure resulting from hot pressing, and its suitability for TGG processes, and on the piezoelectric coefficients of the ceramics.

2. Experimental methods

Piezoelectric 0.8 PMN–0.2 PT and 0.65 PMN–0.35 PT fine powders were prepared by mechanochemical activation of PbO (Aldrich 99.9+% >10 μm), MgO (Aldrich 98% ignition loss 2%), Nb_2O_5 (Aldrich 99.9% 325 mesh) and TiO_2 (Fluka 99%). Details of the procedure will be given elsewhere.[6] X-ray diffraction (XRD) patterns of the two powders are shown in Fig. 1. They

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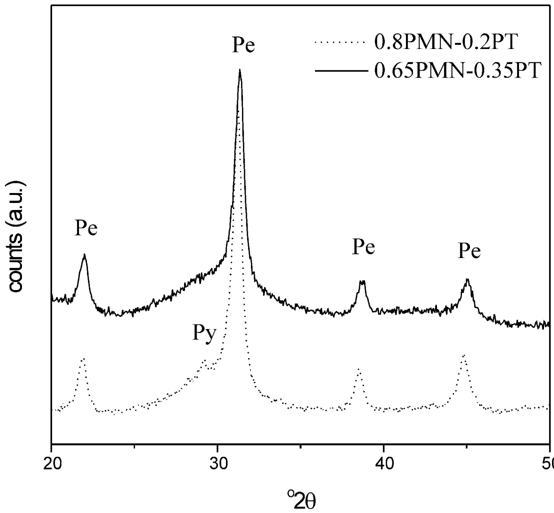

Fig. 1. XRD patterns of the mechanoactivated PMN-PT powders. Pe, perovskite, Py, pyrochlore.

consisted mainly of the perovskite phase, therefore, mechanochemical synthesis occurred during the high energy milling. A minor amount of second phase (note the small diffraction peak at $\sim 29°2\theta$ that could be a modified $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$ pyrochlore: JCPDF-ICDD file n° 33-0769) was also present in the 0.2 PT powder.

Powders (1.5 or 2 g) were uniaxially pressed into 12 mm diameter pellets, and further consolidated by isostatic pressing at 200 MPa. Pressureless sintering was accomplished in air at temperatures between 700 and 1200 °C for 1 h, with a heating rate of 3 °C min^{-1}. Hot pressing was accomplished at temperatures between 700 and 1000 °C with the same soaking time and heating rate, and at 25 MPa. A list of the prepared samples is given in Table 1.

Phases in the sintered discs were monitored by Bragg-Brentano X-ray diffraction (Siemens D500 powder diffractometer with Cu k_α radiation) Samples for microstructural characterisation were prepared by polishing one face up to 0.3 μm alumina. Grain boundaries were marked by quenching from a temperature 100 °C below the sintering temperature. Either an optical microscope or a scanning electron one (ISI DS-130C working at 20 kV) was used to characterise the porosity and grain size. Ag electrodes were painted on the disc faces and sintered at 650 °C for the electromechanical characterisation. The dependence of the dielectric permittivity on temperature at 100 Hz, 1 and 10 KHz was first measured with a HP4192A LF impedance analyser. Poling was then accomplished at fields between 2 and 4 kV mm^{-1} and temperatures between 50 and 150 °C. The piezoelectric radial resonance of the poled discs was recorded with the same analyser, and the material coefficients relevant to the mode (ϵ_{33}^T permittivity, s_{11}^E and s_{12}^E compliances and d_{31} piezoelectric coefficient) were obtained in complex form by an automatic iterative method.[8] The d_{33} coefficient was also measured with a Berlincourt meter.

3. Results and discussion

The XRD diffraction patterns of the 0.2 PT sintered ceramics are given in Fig. 2. The perovskite structure was the main phase after pressureless sintering at 700 and 800 °C, yet a minor amount of second phase, already present in the powder, remained in the ceramics. No second phase was found in the samples sintered at 900 and 1000 °C. Significant quantities of the second phase were present in the ceramic sintered at 1100 °C. The presence of six diffraction peaks allowed identifying it as $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$ pyrochlore (JCPDF-ICDD file n° 33-0769), yet a small shift of the peaks towards higher °2θ angles indicated a cell contraction, most probably related to a composition modification (Ti incorporation). No perovskite structure was found after sintering at 1200 °C, but a mixture of the pyrochlore

Table 1
Prepared PMN-PT ceramics, and some of their characteristics. $^+$after 100 μm thinning. *with PZ packing

PT content	Sintering type	Sintering temperature	Weight loss (%)	Density (%)	d_{31} pC N^{-1}	d_{33} pC N^{-1}
0.2 PT	Pressureless sintering	700 °C	1.3	63.3	–	–
		800 °C	1.2	64.8	–	–
		900 °C	1.4	67.2	–	–
		1000 °C	1.6	73.1	–	–
		1100 °C	2	86.2	–	–
		1200 °C	4.0	88.8$^+$	– (67.9-i1.2)$^+$	223
		1200 °C*	1.0	93.0	– (77.3-i1.8)	270
	Hot pressing	700 °C	–	91.9	–	–
		800 °C	–	94.7	–	–
		900 °C	–	98.6	– (31.6-i0.6)	80
		1000 °C	–	96.4	– (49.3-i0.5)	138
0.35 PT	Pressureless	1200 °C*	1.2	89.8	– (181.8-i3.6)	570
	Hot pressing	900 °C	–	98.0	– (142.8-i3.5)	373

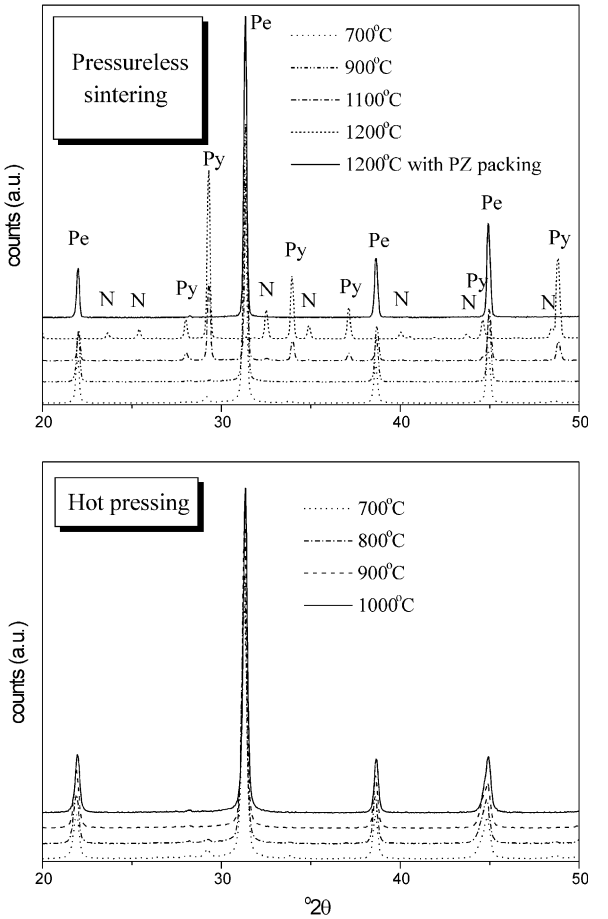

Fig. 2. XRD patterns of the PMN-PT ceramics. Pe, perovskite, Py, pyrochlore, N, tetramagnesium diniobate.

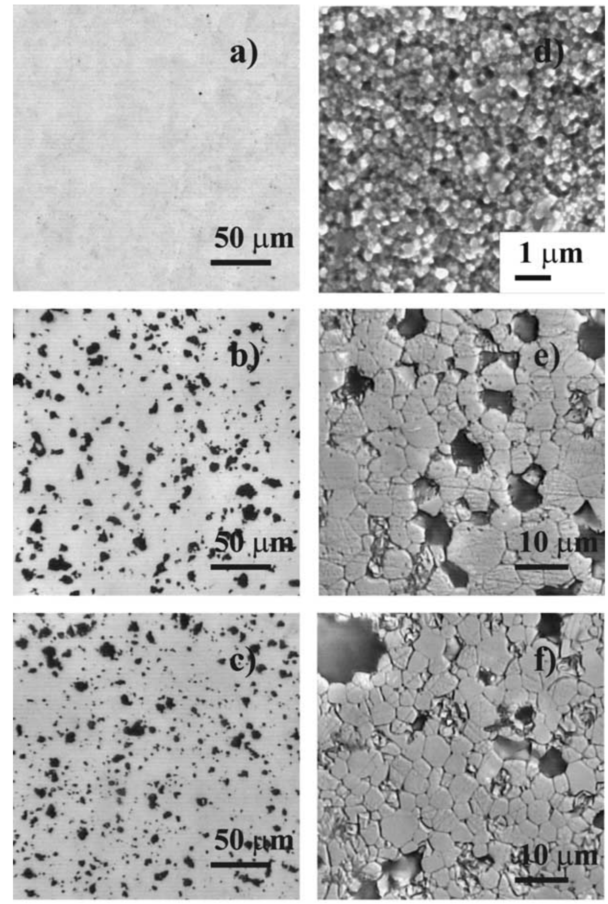

Fig. 3. Optical micrographs of polished surfaces for (a) 0.2 PT hot pressed at 900 °C, (b,c) 0.2, 0.35 PT sintered at 1200 °C with PZ packing, (d) SEM micrograph of a fracture surface for 0.2 PT hot pressed at 900 °C, (e,f) optical of thermally etched polished surfaces for 0.2, 0.35 PT sintered at 1200 °C with PZ packing.

and $Mg_4Nb_2O_9$ (JCPDF-ICDD file n° 38-1459). Weight loss data during pressureless sintering are given in Table 1. Note the increase above 1000 °C, temperatures at which second phases started appearing. The loss at 1200 °C was only of 4%, which seemed to indicate that it was a surface effect. The XRD pattern of a 100 μm thinned ceramic showed only the perovskite phase. In addition, new samples were prepared at 1200 °C with $PbZrO_3$ (PZ) packing and single phase perovskite ceramics were obtained. Analogous results were obtained for the 0.35 PT ceramics.

Optical micrographs of polished surfaces are shown in Fig. 3 for 0.2 PT ceramics hot pressed at 900 °C, and for pressureless sintering at 1200 °C with PZ packing for 0.2 PT and 0.35 PT ceramics. Sintered densities are given in Table 1. Porosity was hardly found for hot pressed samples at 700, 800 and 900 °C, the latter presenting the smallest value in good agreement with the density data. The porosity slightly increased to ~1.1% for the sample pressed at 1000 °C. Thermal etching did not reveal the grain boundaries for hot pressed ceramics and the grain size structure was studied in fracture surfaces. A secondary electron image of one such surface for the 0.2 PT sample hot pressed at 900 °C is shown in Fig. 3d. A homogenous submicron (0.1–0.5 μm) grain size distribution resulted. This combination of high density and fine grain size structure makes these mechanochemically derived powders very suitable for TGG matrices. Optical images of thermally etched surfaces for 0.2 PT and 0.35 PT samples pressureless sintered at 1200 °C with PZ packing are shown in Fig. 3e,f. A grain size of 4.0 ± 1.5 μm was obtained (equivalent diameter average and standard deviation over 100 grains).

The dielectric permittivity of the samples sintered at 1200 °C with PZ packing are shown in Fig. 4. The 0.2 PT ceramic showed typical relaxor behaviour, with a diffuse phase transition around 95 °C, and frequency dispersion of both the dielectric maximum and the permittivity at temperatures below the maximum. The 0.35 PT ceramic showed conventional ferroelectric behaviour, with a first order transition at 171 °C and a maximum dielectric permittivity of $36000\varepsilon_o$. These values compare well with those previously reported for ceramics prepared by the columbite route.[9]

The complex d_{31} and Berlincourt d_{33} values after poling are given in Table 1. Significant piezoelectricity was

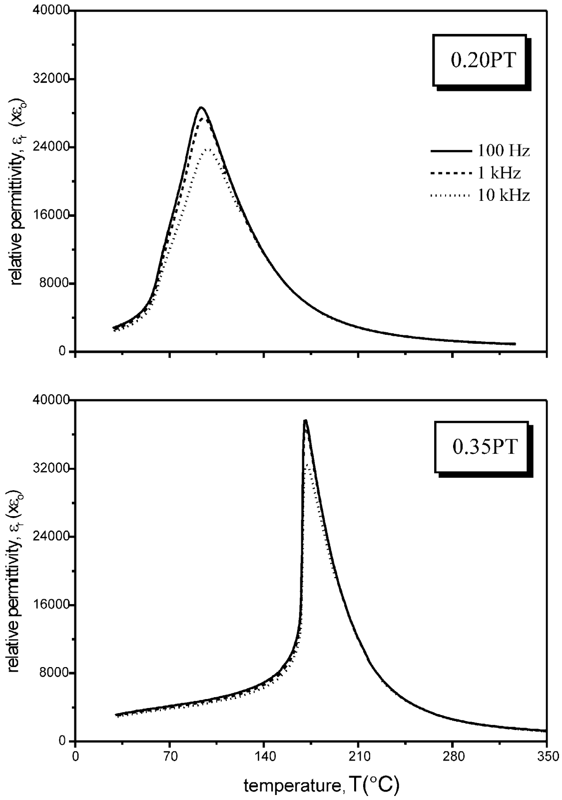

Fig. 4. Temperature dependence of the dielectric permittivity for the PMN-PT ceramics sintered at 1200 °C with PZ packing.

found for the 0.2 PT ceramics in spite of their relaxor dielectric characteristics. A Relaxor to conventional ferroelectric transition is known to be induced by the electric field in rhombohedral lanthanum modified lead zirconate titanate (PLZT).[10] The poling experiments suggested that the coercive field was significantly higher for the hot pressed ceramics (>3 kV mm^{-1} at 50 °C) than for the pressureless sintered ones (<2 kV mm^{-1}). A d_{31} of −(181.8-i3.6) pC N^{-1} and a d_{33} of 570 pC N^{-1} were found for the 0.35 PT ceramic, which is comparable with those of typical PZT soft piezoceramics.

4. Conclusions

Hot pressing of piezoelectric PMN-PT mechanoactivated powders allowed the obtaining of very dense ceramics with submicron grain size (0.1–0.5 μm). This makes the mechanoactivated powders very suitable for TGG matrices. $PbZrO_3$ packing was necessary for pressureless sintering over 1000 °C to limit weight losses and avoid the appearance of second phases at the surface. PZ packing sintering at 1200 °C resulted in ~90% dense ceramics with 4 μm grain size and good electrical and electromechanical properties. 0.8 PMN–0.2 PT ceramics presented a mixed relaxor ferroelectric character, with a diffuse phase transition around 95 °C and dielectric frequency dispersion below this temperature, but piezoelectricity after poling. 0.65 PMN–0.35 PT ceramics showed a clear first order phase transition at 171 °C, and complex d_{31} and Berlincourt d_{33} piezoelectric coefficients of − (181.8-i3.6) and 570 pC N^{-1}, respectively, at room temperature.

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