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Comparison of two molten flux process for the elaboration of textured PZT thin plates

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Abstract

In this paper, we describe a new protocol for the elaboration of textured PZT thin plates. This protocol is based on three steps: (i) powder synthesis, (ii) tape casting/lamination in green state and (iii) sintering/densification.

Powder synthesis is operated through a specific molten flux method, which in optimised conditions allows the crystallisation of coarse and cubic shape grains of PZT. The powder is extracted from the flux by acidic attack, washing and filtration. It is used as raw material to elaborate a slip with organic media in order to achieve thick tapes that exhibit preferred orientations of the PZT phase. The crystallographic textures are measured on a four-circle X-ray diffractometer and determined using the so-called "combined approach" that uses Rietveld and orientation distribution function refinements.

Keywords: PZT; Microstructure prefiring; Flux synthesis

1. Introduction

Lead zirconium titanate (PZT) ceramics are piezoelectric polycrystalline materials largely used for sensing and actuating applications. Their success is mainly based on their good piezoelectric properties that can be largely modulated by the addition of doping agents. These properties can be optimised if the ceramic exhibits crystallographic preferred orientation in order to benefit of anisotropic properties of the crystals. For that, one way consists in favouring directional grain growth during sintering. If a template grain growth procedure is used, the precondition is the synthesis of crystal seeds.

The PZT solid solution presents congruent melting points only for the end-terms of the PT and PZ phase diagrams. For other compositions, and particularly near the morphotropic phase boundary (MPB), melting is incongruent and results in some segregation of compounds. It is then impossible to elaborate the needed seeds using crystal-pulling techniques. Many works have been carried out to overcome this drawback by using flux growth or molten salt methods for the synthesis of as large as possible PZT single-crystals.[1] If flux growth is used, this melting behaviour results in different dissolution ratio of Zr and Ti in the PbO melt. However, large PT seeds are easily obtained. These ones have mainly been used for the synthesis of PT–PMN or PT–PZT textured mixtures by templating grain growth methods (TGG).[2,3] Considering the Zr-rich PZT solid solution, flux growth gives rise to precipitation of zirconia prior to PZT. Finally, a mixture consisting of zirconia and Zr-deficient PZT grains is obtained.[4]

The problem here is to overcome the preferential precipitation of Ti-enriched perovskite due to the lower Zr solubility in the PbO melt. This solubility difference is also at the origin of the PZT decomposition mechanism observed during the sintering of PZT: as a PbO loss occurs, free zirconia precipitates appear.[5] Modified lead flux should favour the precipitation of larger grains, potentially polluted. However, the use of a pure lead flux might result in the precipitation of smaller and pure grains. We investigate in this work, the modified flux and the pure PbO routes. In the first case, flux growth parameters are optimised in order to limit preferential precipitation of zirconia

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and zirconium deficit in PZT. In the second case, pure Pb flux is used to precipitate large, cubic-like shaped grains with a sharp size distribution and controlled stoichiometry.

2. Experimental procedure

The flux synthesis of PZT cubic shape grains uses ZrO_2 (Baddeleyite, HUELS AG, >95%), TiO_2 (Anatase, LABOSI, >99%), PbO (Massicot, MERCK) raw materials, weighted, mixed and put in a closed platinum crucible. In some cases, a ZrO_2, TiO_2, PbO mixture is previously reacted by thermal treatment at 900 °C for 6 h. For the modified flux, $PbCl_2$ (FISHER), B_2O_3 (FISHER), KF (ACROS ORGANICS, >99%) are added in various amounts. Flux growth thermal treatment consists of a rapid heating to 1200 °C, followed by several steps of decreasing temperature. Seeds are extracted by a slight crushing followed by a 70 wt% nitric or acetic acid attack at 60 °C for 5 h.

The tape casting and sintering steps are carried out by means of a doctor blade apparatus. The slip is elaborated in an organic medium with 70 wt% PZT of dry powder. The solvent is an azeotropic (ratio 34/66 vol%) ethanol/methyl-ethyl-ketone solution. The binder (4 wt% with respect to the powder) is polyvinyl butyral plasticized at 100% in dibutyl phthalate. The thickness can be adapted between approximately 40 and 300 μm. All samples were sintered at 1100 °C for 6 h in a PZT powder bed.

Crystallisation quality was assessed by the sharp X-ray diffraction peaks (not shown here), of broadening close to the instrument resolution. Scanning electron micrographs of our powders are obtained on a Hitachi S-3500N microscope. The crystallographic textures are measured on green tapes and after sintering on a four-circles X-ray diffractometer,[6] and determined using the so-called "combined approach" that uses Rietveld and orientation distribution function refinements.[7]

3. Results

3.1. Modified PbO flux synthesis

Modified flux methods have been used for the synthesis of zirconia polluted PZT large grains.[4] In this work, we modified the flux/PZT ratio in order to improve the powder purity after synthesis. Using a target composition of Zr/Ti = 1, flux/PZT = 36/64 and 53/47 and a flux composition of $PbO:KF:PbCl_2:B_2O_3 = 2:1:2:0.5$, large and well faceted cubic-

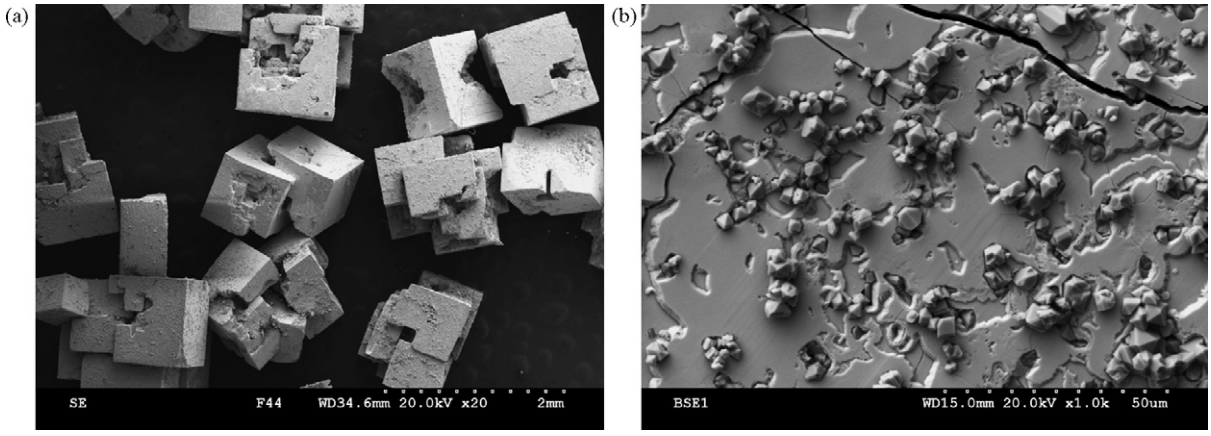

Fig. 1. SEM image of modified flux synthesised PZT grains: (a) general view and (b) surface details.

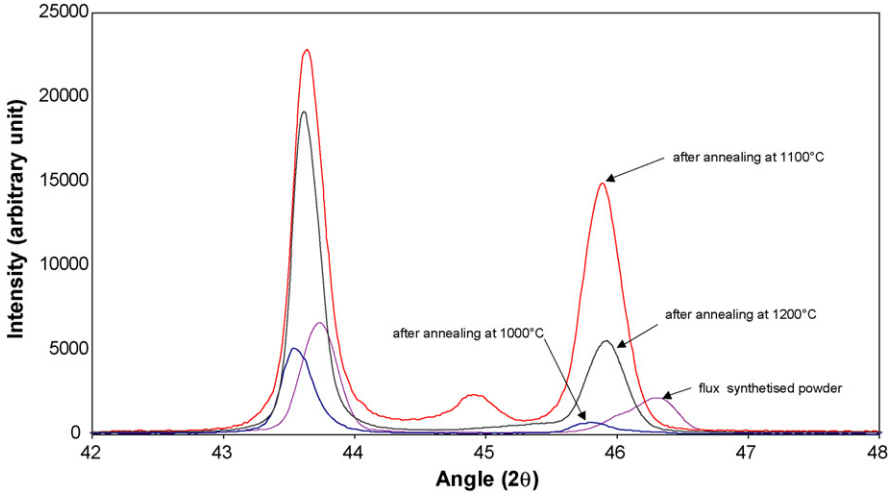

Fig. 2. X-ray diffractogram of a modified flux PZT powder. As synthesised (black), after 1000, 1100 and 1200 °C annealing in air.

Table 1
Modified flux synthesis conditions, operated with PbO(flux)/PZT = 60/40

Starting powders	Raw oxides	Raw oxides	Raw oxides	Planetary milled (2 h, 320 rpm)
Treatment label	1	2	3	4
Ramp 1	1200 °C/300 °C/h	1200 °C/300 °C/h	1200 °C/300 °C/h	1200 °C/300 °C/h
Dwell 1	1 h	1 h	2 h	2 h
Ramp 2	900 °C/60 °C/h	900 °C/60 °C/h	900 °C/60 °C/h	900 °C/60 °C/h
Dwell 2	900 °C, 10 h	900 °C, 10 h	900 °C, 10 h	900 °C, 10 h
Ramp 3	20 °C/10 °C/h	750 °C/5 °C/h	750 °C/5 °C/h	750 °C/5 °C/h

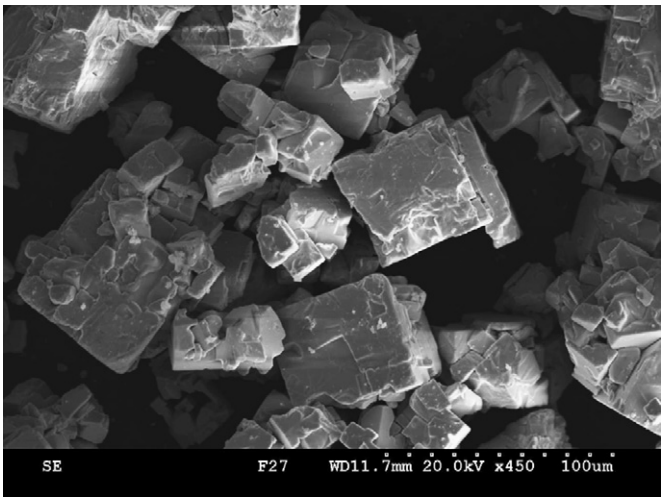

Fig. 3. SEM image of optimised pure PbO flux PZT powder.

like grains of about 1 mm edges are observed (Fig. 1). No significant differences in size are observed by changing initial flux ratio. However, an increase of flux invariably allowed easier grain extraction. SEM observation (Fig. 1) shows the presence of smaller and slightly embedded grains on the faces of the previous ones. These small grains have been identified as zirconia using X-EDS. We have not found any condition to directly avoid the precipitation of zirconia. However, a post-thermal homogenisation treatment of the cubes, consisting of an annealing in air buffered on a small PZT layer at 1000, 1100 and 1200 °C for 6 h, changes the powder composition and microstructure (Fig. 2). A quantitative phase analysis using the Rietveld approach shows that before annealing the major phase consists of tetragonal PT. Any attempt of declaring Zr in the PT structure gives rise to negative Zr occupation sites, indicating that Zr is absent or at a very low level in the grain structure. But the monoclinic zirconia peaks are detected to around 9 vol%. Since the initial Zr/Ti ratio introduced in the crucible was 50/50, we conclude that the majority of zirconia precipitates as a fine powder embedded in

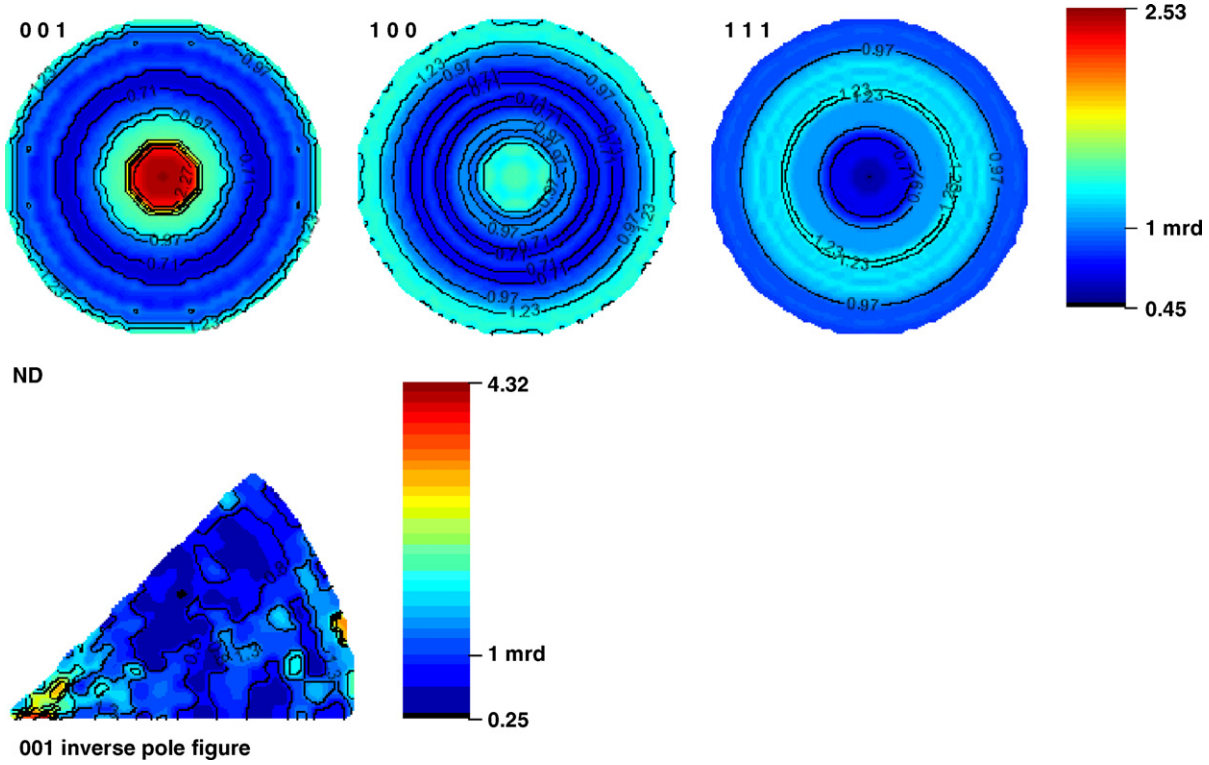

Fig. 4. {0 0 1}, {1 0 0} and {1 1 1} pole figures recalculated from the ODF refined by combined analysis, for the as-cast PZT sample synthesised by the PbO flux route.

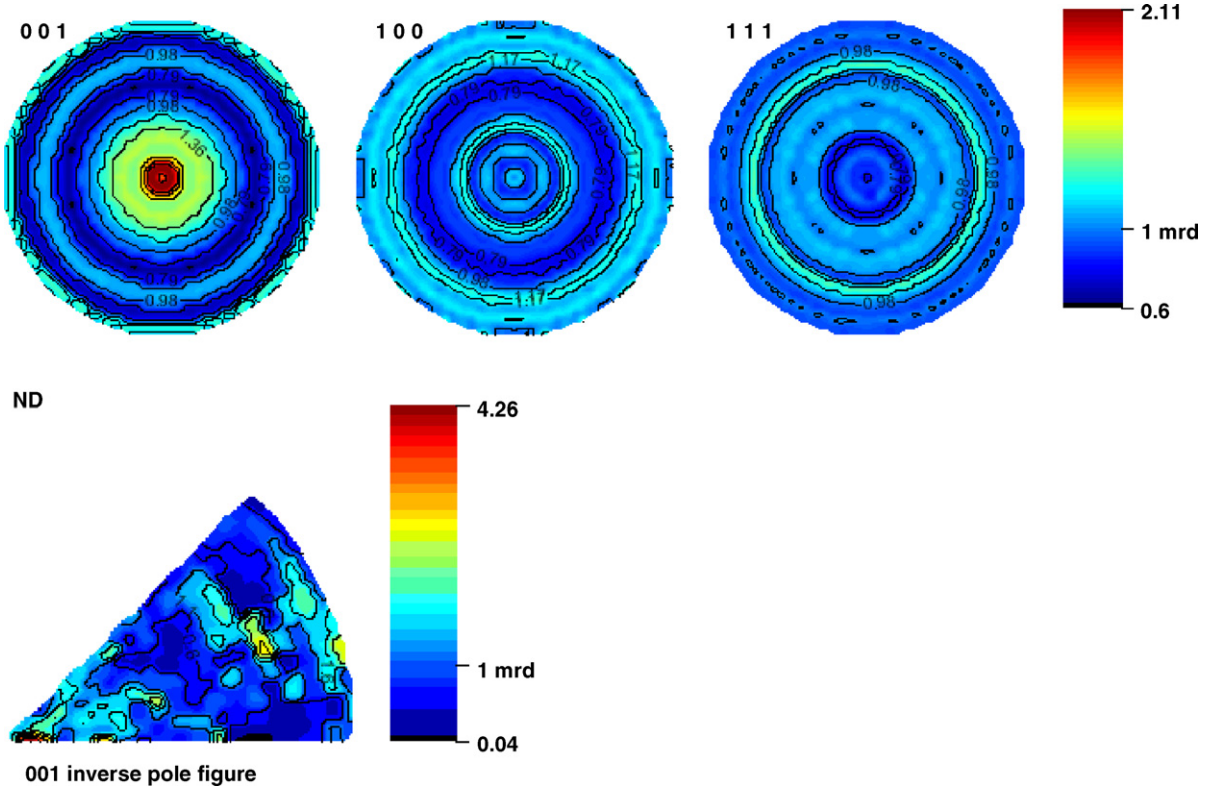

Fig. 5. {0 0 1}, {1 0 0} and {1 1 1} pole figures recalculated from the ODF refined by combined analysis, for the cast and sintered PZT sample synthesised by the PbO flux route.

PbO melt and is likely eliminated during the different sieving and washing steps. Nevertheless, after the first treatment some slight peak modification are observed (Fig. 2). After treatment at 1100 °C, rhombohedral peaks appear, which proves Zr incorporation in the grain structure. Annealing at a higher temperature (1200 °C) makes the rhombohedral PZT peaks disappearing.

3.2. PbO flux synthesis

The pure PbO flux route, initially used by Clarke and Whatmore,[1] is used here for the elaboration of large PZT grains, in the conditions listed in Table 1. With a flux/PZT ratio fixed to 60/40 mol%, a first attempt using a morphotropic composition resulted in poorly shaped grains, while working in the tetragonal area of the phase diagram, the obtained grains are cubic, well faceted and larger. For the following, the composition was fixed to Ti/Zr = 56/44. SEM observations (Fig. 3) for the optimised conditions number 4 reveal large cubic-like grains with sizes ranging from 10 to 70 μm edges. The EDS analysis reveals a Zr content of 0.47 ± 0.05.

This optimised powder was tape cast and sintered. The texture (Fig. 4) of the as-cast tetragonal PZT sinter exhibits a maximum density for the {0 0 1} pole figure of around 2.5 times the value of a perfectly randomly oriented powder. This ⟨0 0 1⟩ fibre texture component is moderate compared to texture strengths achieved in the literature, and one should not expect large anisotropy of the piezoelectric properties in our samples, as synthesised. However, the inverse pole figure calculated for the direction normal to the sample plane shows that the only texture component is the ⟨0 0 1⟩ fibre. The sintered sample (Fig. 5) does not show a large modification of the texture except for a larger inverse pole figure graininess, probably due to partial recrystallisation of PZT grains during sintering.

4. Conclusion

Two routes were tested for the production of large PZT grains usable as primary particles for the development of a preferentially oriented microstructure after tape casting and sintering. The first route consisting in a modified flux method gives rise to zirconia polluted PZT grains, and to incorporation of some Zr in PZT after annealing at 1100 °C. However, this integration is accompanied by PbO loss. Nevertheless, the produced grains are very large, cubic-like and well faceted. The second route tested is a pure PbO flux method, resulting in closely cubic grains of smaller sizes (10–50 μm), but of better composition control. Well faceted grains are only obtained for the tetragonal side of the morphotropic phase boundary. The use of these grains in tape casting and sintering allows the achievement of ⟨0 0 1⟩ fibre textured ceramics, with moderate texture strengths.

References

1. Clarke, R. and Whatmore, R. W., The growth and characteristics of $PbZr_xTi_{1-x}O_3$ single crystals. *J. Cryst. Growth*, 1976, **33**, 29–38.
2. Suchicital, C. T. A. and Payne, D. A., Flux growth of single crystal lead titanate. *J. Cryst. Growth*, 1990, **104**, 211–217.
3. Kakuta, K., Tsurumi, T. and Fukunaga, O., Dielectric properties of flux-grown $PbTiO_3$ single crystals. *Jpn. J. Appl. Phys.*, 1995, **34**, 5341–5345.

4. Hatanaka, T. and Hasegawa, H., Dielectric properties of $Pb(Zr_xTi_{1-x})O_3$ single crystals including monoclinic zirconia. *Jpn. J. Appl. Phys.*, 1995, **34**, 5346–5348.
5. Fernandez, J. F., Moure, C., Villegas, M., Duran, P., Kosec, M. and Drazic, G., Compositional fluctuations and properties of fine-grained acceptor-doped PZT ceramics. *J. Eur. Ceram. Soc.*, 1998, **18**, 1695–1705.
6. Ricote, J. and Chategnier, D., Quantitative microstructural and texture characterisation by X-ray diffraction of polycrystalline ferroelectric thin films. *J. Appl. Crystallogr.*, 2004, **37**, 91–95.
7. Chategnier, D., Combined Analysis: structure-texture-microstructure-phase-stresses-reflectivity determination by X-ray and neutron scattering, 2004, p. 147. http://www.ecole.ensicaen.fr/~chateign/texture/combined.pdf.