

Homogeneous templated grain growth of $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.35\text{PbTiO}_3$ from nanocrystalline powders obtained by mechanochemical activation

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Abstract

The feasibility of a novel homogeneous templated grain growth approach for the processing of $0.65\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.35\text{PbTiO}_3$ ceramics is studied. Novelty rests on the use of a nanocrystalline powder synthesized by mechanochemical activation for the matrix, and also for obtaining the templates via conventional sintering. Templates are (1 0 0) faceted cube-shaped microcrystals with an average size of 12 μm . The role of processing parameters such as the presence of PbO excess, and a hot-pressing step previous to the final thermal treatment is studied. Extensive growth of the templates and nearly full densification are demonstrated. The approach used here involves only conventional ceramic technology from a single source powder, and can be used as a means of obtaining larger crystals.

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1. Introduction

The $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) relaxor-ferroelectric solid solution has attracted a great deal of attention due to the exceptional piezoelectric coefficients ($d_{33} > 2000$ pC/N) and large electromechanical coupling factors ($k_{33} > 90\%$) observed in single crystals with compositions around its morphotropic phase boundary (MPB) at $\sim 0.65\text{PMN-}0.35\text{PT}$,¹ making them promising materials for their use in more precise actuators and ultrasonic transducers for sonar and medical imaging applications. However, the introduction of the single crystals into the market is hindered by the high cost and long times of production, small crystal sizes, and difficulties in controlling the stoichiometry. The alternative, polycrystalline MPB PMN-PT ceramics, usually exhibit lower d_{33} -coefficient (~ 700 pC/N) than single crystals,² although they can be largely improved by inducing a preferential orientation. It has been demonstrated that enhanced piezoelectric properties can be attained in textured $\langle 001 \rangle$ ceramics ($d_{33} \sim 1500$ pC/N).^{3,4} This is perhaps the most promising approach to produce

domain engineered ferroelectrics for high-strain piezoelectric components.⁵

One of the most promising routes for obtaining controlled textures in ceramics is by using the so-called templated grain growth (TGG) process in combination with an appropriate forming technique.^{6,7} In this approach, texturing is achieved in two steps: firstly, a small amount of single crystals (templates) are dispersed and then aligned in a fine-grained matrix under a shear stress (e.g., by tape-casting or extrusion); and secondly, the green compacts are thermally treated under controlled conditions, resulting in densification and the growth of the templates at the expense of the surrounding matrix grains.⁸ The templates used in these processes usually possess anisometric morphology (platelets or whiskers) to facilitate their alignment during forming,⁶ and they are grown normally in the presence of a liquid phase to ensure a large volume fraction of template growth.^{8,9}

In the case of PMN-PT, anisometric particles of this relaxor-ferroelectric phase have not been obtained up to now, and textured PMN-PT ceramics with excellent piezoelectric properties have been prepared using alternative anisometric templates of isostructural phases such as SrTiO_3 and BaTiO_3 ,^{3,4,10} which is normally called heterogeneous-TGG. Nevertheless, the use of templates of the same phase is preferred, and recently textured PMN-PT ceramics were obtained by homogeneous-TGG

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for the first time by using PMN-PT cubic microcrystals grown in PbO flux at high temperatures as templates,^{11,12} showing that, with the appropriate processing parameters, cubic crystals can be successfully aligned during forming. However, the main drawback of homogeneous-TGG in this system resides in the complex preparation of the PMN-PT templates, that requires the use of an expensive and time consuming process of self-flux at high temperatures to grow single crystals, which makes the process unsuitable for industrial applications. Therefore, a study of homogeneous-TGG in this system as the one raised in this paper, must explore an alternative method to prepare the PMN-PT templates.

Another important element that must be considered in the TGG process besides the templates is the nature of the matrix they grow in. Since the driving force for the migration of the template boundary into the matrix is the difference in surface free energies between the moving crystal plane and the matrix grains,⁶ the smaller the starting matrix grain size the larger the driving force for TGG. In this sense, mechanochemical activation seems specially adequate for TGG matrices, because it is a powerful technique for synthesizing highly reactive powders with nanometric particle size, that has successfully been applied for the direct synthesis of relaxor ferroelectrics with perovskite structure.^{13,14} Therefore, mechanochemically activated powders are used in this paper to form the matrix in the homogeneous-TGG proposed.

In general, the templates and the matrix in TGG are prepared separately and come from different sources. This fact may be problematic for certain systems like PMN-PT, where small compositional variations from the MPB may lead to a degradation of the properties. In order to improve the quality of the ceramics obtained by TGG in this work we analyze the feasibility of a novel homogeneous-TGG approach to prepare 0.65PMN-0.35PT (PMN-35PT) by using a nanocrystalline powder obtained by mechanosynthesis and templates derived by conventional ceramic technology from the same mechanosynthesized powder. We focus on the processing of the templates, and in studying the TGG process itself, that is, in characterizing and optimizing the growth of the templates.

2. Experimental procedure

Perovskite PMN-35PT powders were prepared by mechanochemical activation in air by using a high-energy planetary mill and WC milling media. A complete study of the activation process that analyzes the perovskite formation was recently reported by Kuscer et al.¹⁵ The powder with the nominal composition and that containing a 2 wt.% (~1.7 vol.%) of PbO excess (for introducing a liquid phase during the TGG process) were both prepared by one-step direct mechanosynthesis from its constituent oxides in batches of ~200 g each time. The high-energy-milled powder consists of a major crystalline nanosized (~25 nm) PMN-35PT perovskite together with a 30 wt.% of amorphous phase depleted of MgO and traces of pyrochlore.¹⁵ Powders were formed by agglomerates with an average size of 0.8 µm.

PMN-35PT cubic templates were derived by conventional ceramic technology using as a precursor the mechanoactivated powder with the nominal composition. Firstly, the powder was uniaxially pressed into 12 mm diameter discs followed by a cold isostatic pressing at 200 MPa. The samples were then placed within a closed arrangement of two alumina crucibles, and then buried in PbZrO₃ (PZ) powder to create a PbO-rich atmosphere during the sintering. Conventional sintering was carried out at conditions that are known to result in a exaggerated grain growth and a degraded microstructure (<80% densification), those are, 1250 °C for 1 h in PZ packing powder with a heating rate of 3 °C/min.¹⁶

Cubic grains so obtained were separated by leaching the ceramic in acetic acid for 5 min, rinsing it in deionized water, and finally, putting it in ethanol and using a high-power ultrasonic processor (Sonics VCX 750) with a tapered microtip, which resulted in the complete disaggregation of the ceramic grains. The isolated particles were dried and sieved to pass through a 20 µm-mesh sieve. Its single crystal character was demonstrated by X-ray diffraction (XRD) using a Siemens D500 (Cu K α radiation) diffractometer. Previous to the experiment, the disaggregated particles were dispersed and put on a glass surface with a small shear force applied. The data were collected in the 2 θ range from 20° to 50° in steps of 0.05° with an integration time of 5 s/step. The shape of the particles was examined by optical microscopy, and their average size was determined via quantitative image analysis.¹⁷

The microcrystals so obtained were used as templates for the homogeneous-TGG experiments. Slurries for tape casting were prepared with 15 vol.% powder by ball-milling for 24 h in toluene with a polymeric dispersant (KD3), a binder (Polyvinyl Butyral, PVB) and a plasticizer (Benzyl Butyl Phthalate, BBP). Then, 5 wt.% of templates was added to the slurry and stirred for 4 h. Green tapes were cast with a blade height of 200 µm at 1 cm/s onto silicone-coated Mylar^{TD}, and dried under ambient conditions. The tapes were then cut, stacked and laminated using 50 MPa at 60 °C. The organics were burned out by heating in air to different temperatures (from 500 to 600 °C) for 0, 2 and 5 h, with heating and cooling rates of 0.5 °C/min, which are slow enough to prevent cracking and delamination.

For the template growth experiments, the green samples were placed within the two alumina crucibles closed arrangement, also buried in PZ powder. Thermal treatments were carried out between 1150 and 1250 °C for 1 and 10 h using heating and cooling rates of 3 °C/min. In some cases, a hot-pressing in air at 900 °C for 1 h under 60 MPa was carried out previously to the final thermal treatment, to separate the densification and TGG steps. Densification after the experiments was evaluated from weight and dimensions. XRD was carried out on the obtained ceramic samples for phase identification with the same diffractometer and conditions described for the templates. The ceramic bodies were polished and annealed at 600 °C for 5 h previously to their characterization. Microstructure was characterized by optical microscopy and scanning force microscopy (SFM). The samples were prepared by polishing with Al₂O₃ suspensions with decreasing sizes down to 0.05 µm and thermal etching for 1 h at and quenching from

800 °C to room temperature to reveal the template and matrix grain boundaries. Quantitative image analysis was also carried out to determine the final average template size after the TGG process.

3. Results and discussion

3.1. Preparation of PMN-35PT microcrystals from the mechanoactivated powder

Fig. 1a shows an optical micrograph of the polished and thermally etched/quenched surface of a PMN-35PT ceramic sintered at 1250 °C for 1 h in PZ powder. Large faceted grains with an average size of 12 μm are observed, indicating exaggerated grain growth (EGG), while the ceramic presents very low density <80% of the theoretical density (TD).¹⁶ It is known that exaggerated and abnormal grain growths in PMN-PT occur in the presence of a PbO-based liquid phase during long thermal treatment by increasing the grain boundary mobility, while limited growth resulted from samples without PbO excess.¹⁸ In our case, EGG was shown to depend strongly on the source of the PbO-rich atmosphere, since it was not observed in ceramics sintered at the same temperature and time but buried in PMN-PT packing powder, where high density values (~93% TD) and normal grain growth (~4 μm of grain size) were obtained. Therefore, the results indicate that the PbO-rich atmosphere created with the PZ packing powder produces a condensed PbO-based liquid phase inside the ceramic, which is responsible for the EGG observed during sintering. Fig. 2a shows the XRD pattern of this sample where single perovskite phase PMN-35PT is observed.

Fig. 1b shows an optical micrograph of the PMN-PT cubic grains that resulted after disaggregating the ceramic shown in Fig. 1a, following the procedure explained in the experimental section. The increase of the porosity with the development of large pores, typical of a deteriorated final stage of sintering at high temperatures,¹⁹ achieved in the ceramics after heating at 1250 °C for 1 h in PZ, made it possible to separate more easily the faceted cubic grains without breaking them. Their size distribution was found to follow a lognormal function (see inset in Fig. 1b), which is consistent with them being the result of a grain growth process. Cubic templates with an average size of 12 μm (standard deviation, S.D. = 2 μm) were obtained. Fig. 2b displays the XRD pattern of the PMN-PT cubic grains put on a glass holder with a small shear force applied. Only the 100 and 200 reflections are observed, thus indicating that the cube-shaped grains are single crystals whose faces correspond to {100} crystallographic planes. The splitting of the 200 reflection into three peaks is shown in detail in Fig. 2c, indicating a coexistence of monoclinic (*Pm* space group) and tetragonal phases, a finding that is characteristic of compositions at the MPB region.²⁰

Therefore, (100) faceted PMN-35PT cubic microcrystals (12 μm size) were obtained from ceramics by conventional sintering at 1250 °C for 1 h in PZ powder using a nanocrystalline precursor powder prepared by mechanochemical activation. Next, their use as templates for TGG of PMN-35PT by using the same nanocrystalline powder for the matrix is evaluated.

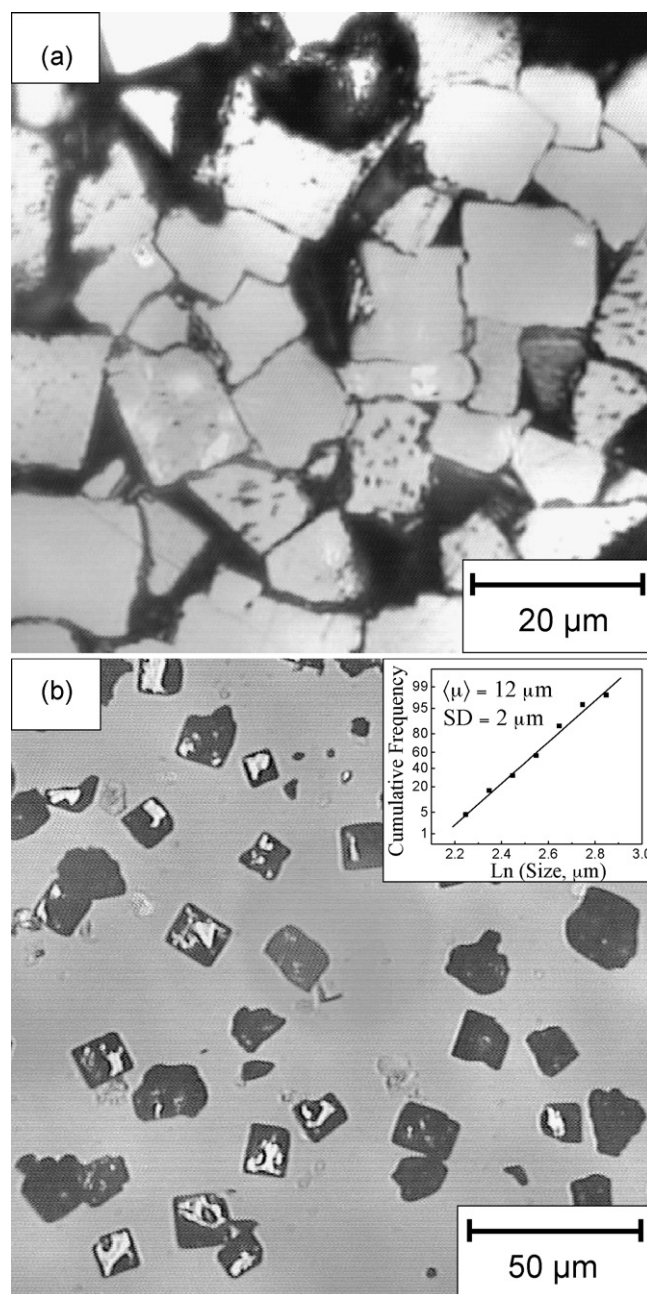


Fig. 1. Optical micrographs of (a) polished and thermally etched/quenched surface of a PMN-35PT ceramic without PbO excess sintered at 1250 °C for 1 h in PZ powder, and (b) PMN-35PT cubic microcrystals obtained from the ceramic and used as templates for homogeneous-TGG. (Inset) Probability plot of the microcrystals size distribution showing a lognormal character, $\langle \mu \rangle$ is the average size and S.D. is the standard deviation.

3.2. TGG in a matrix of the mechanoactivated powder with the nominal composition

Fig. 3 shows the XRD patterns of the green bodies obtained after pyrolysis of the tapes with the PMN-35PT powder of nominal composition at different temperatures and times, where a non negligible amount of pyrochlore is observed in all cases. The higher the pyrolysis temperature, the larger the amount of pyrochlore phase is, whereas no noticeable difference was

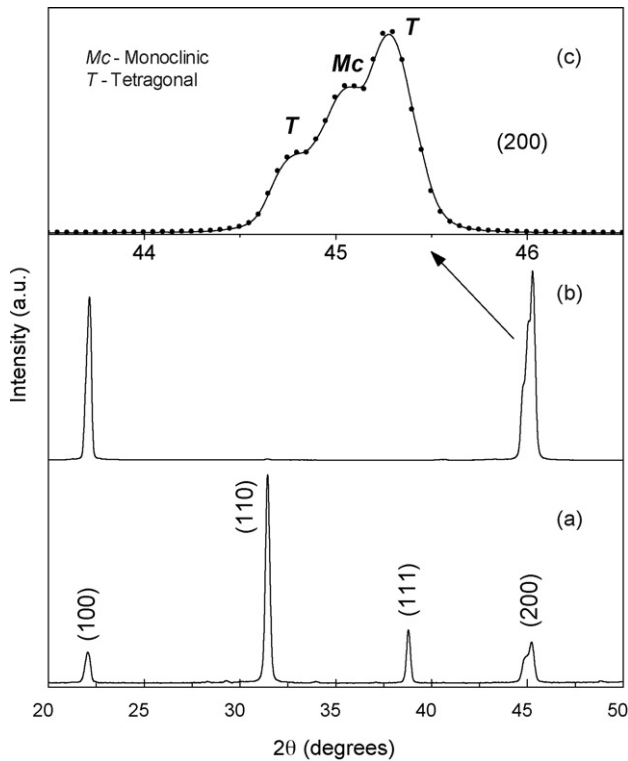


Fig. 2. XRD patterns for (a) the PMN-35PT ceramic without PbO excess sintered at 1250 °C for 1 h in PZ powder, and (b) the cube-shaped PMN-35PT microcrystals obtained from this ceramic. (c) Splitting of the 200 reflection into three peaks, indicating the coexistence of monoclinic and tetragonal phases.

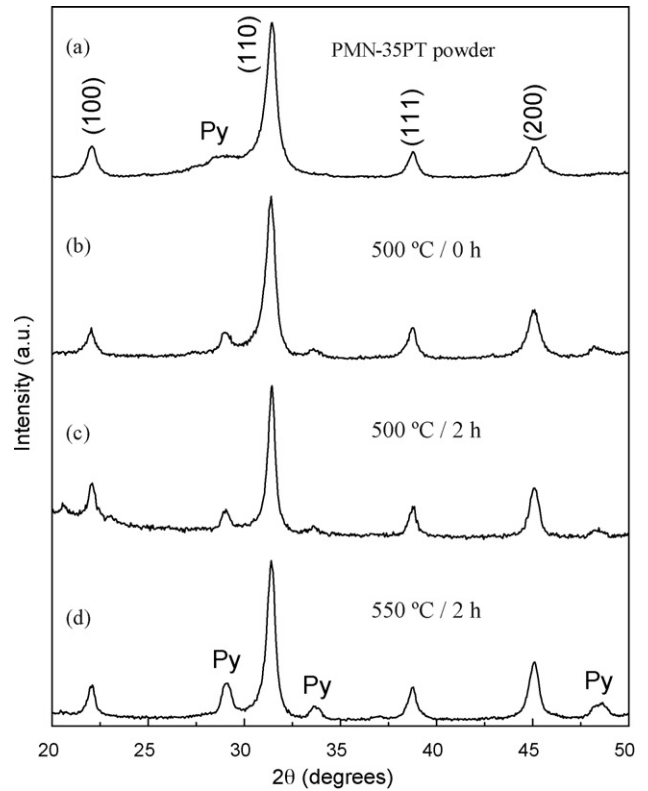


Fig. 3. XRD patterns for (a) the PMN-35PT powders with nominal composition obtained by mechanochemical activation, and (b–d) the green bodies after the pyrolysis of the tapes at different temperatures and times. Miller indexes refer to the perovskite. Py: pyrochlore.

observed for pyrolysis times between 0 and 2 h. On the other hand, pyrolysis at temperatures under 500 °C results in a poor compaction of the green bodies for subsequent sintering. This pyrochlore phase most probably arises from the fraction of amorphous phase present in the mechanoactivated powder (see Fig. 3a). Analogous results were obtained with the PMN-35PT powder containing a 2 wt.% of PbO excess, which indicate similar percentages of perovskite and amorphous phases for the powders with and without an excess of PbO. Attention had to be paid to the tailoring of the pyrolysis of the tapes in order to avoid the stabilization of the pyrochlore phase before the thermal treatment at higher temperatures for TGG. Pyrolysis was then carried out at 500 °C for 2 h in all cases, producing green bodies with densities of ~52–55% TD and a minimum amount of pyrochlore phase. This secondary phase remains in the samples without PbO excess after thermal treatments at different conditions, as shown in Fig. 4, whose final low densities (89–93% TD) can be partially attributed to the retarding effect on the sintering kinetics of this residual pyrochlore.

Fig. 5 shows optical micrographs of the cross-section of a templated PMN-35PT sample without PbO excess after a thermal treatment at 1200 °C for 10 h in PZ powder. Large templates embedded in a matrix of small grains (~4 μm size) are observed in Fig. 5a. A small amount of pull-outs produced during polishing can also be seen in the micrographs. A quantitative image analysis of the optical micrographs was carried out to determine the final average template size: 20 μm (S.D. = 2.8 μm), which is about twice the size of the initial templates. In fact, the grown

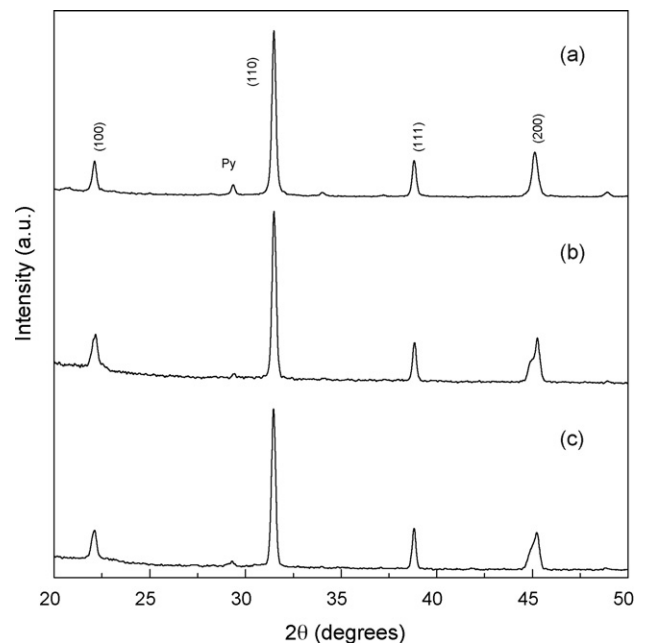


Fig. 4. XRD patterns for templated PMN-35PT without PbO excess: (a) after hot-pressing at 900 °C for 1 h, (b) after a thermal treatment at 1200 °C for 10 h in PZ powder, following the hot-pressing, and (c) after a direct thermal treatment at 1200 °C for 10 h in PZ powder. Miller indexes refer to the perovskite. Py: pyrochlore.

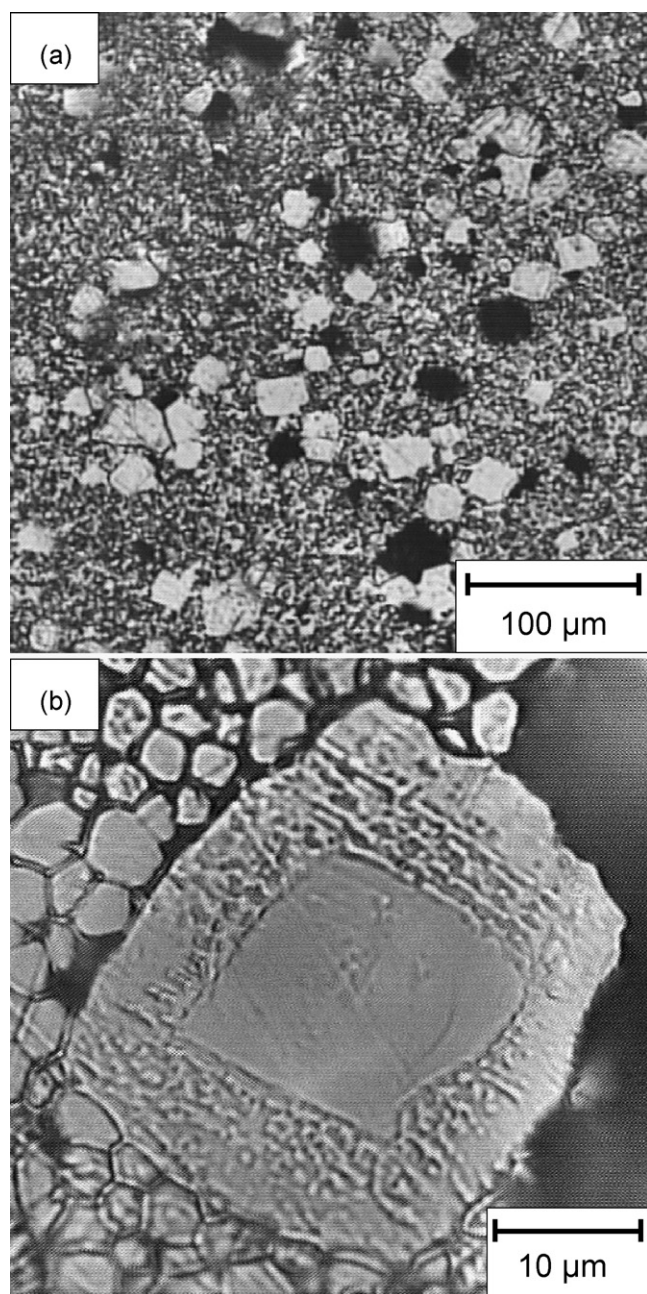


Fig. 5. Optical micrographs of the thermally etched/quenched cross-section of a templated PMN-35PT without PbO excess after a thermal treatment at 1200 °C for 10 h in PZ powder. Image (b) correspond to a magnification of image (a), showing a detail of the template growth achieved during the process.

area can be easily identified within the template in the images, as illustrated in Fig. 5b. TGG was thus confirmed in this sample obtained from a matrix without PbO excess. A final densification of 93% TD was achieved.

MacLaren et al.²¹ have suggested that the mobility of the grain boundaries in alumina is associated with the formation of thin disordered layers at the grain boundaries that increases their mobility, yielding to faster growth rates in some grains and subsequent abnormal grain growth. The absence of a large degree of disorder at the grain boundaries may explain the previous, very limited growth of the templates embedded in PMN-PT matrices

without PbO excess, as Gorzkowski et al. proposed.¹⁸ However, in our case, the use of a nanocrystalline powder synthesized by mechanochemical activation may explain the template growth observed without PbO excess. It is known that mechanochemical synthesized powders present large crystal strain,²² which most probably is accompanied with disordered regions at the grain boundaries that enhance their mobility. This feature together with the partial reactive character of the process, associated with the presence of an amorphous fraction along with traces of pyrochlore, and their transformation into perovskite during heating,¹⁵ enable the growth of the templates.

3.3. TGG in a matrix of the mechanoactivated powder with PbO excess

The role of incorporating PbO excess for promoting TGG of PMN-PT has been established, although a negative effect in the piezoelectric and dielectric properties is also recognized.^{23,24} Then, having a PbO excess as small as possible to enhance template growth is preferable. The influence of the PbO excess in the proposed novel TGG process of PMN-35PT was examined using a nanocrystalline powder containing a 2 wt.% of PbO excess added previously to the mechanochemical activation. Fig. 6a shows an optical micrograph of the cross-section of a templated PMN-35PT sample prepared with a matrix containing 2 wt.% of PbO excess after a thermal treatment at 1200 °C for 10 h in PZ powder. The final average template size increased up to 27 μm (S.D. = 3.8 μm). As mentioned before, the use of PbO excess should lead to the appearance of a liquid phase that enhances TGG by increasing template boundary migration into the matrix. It is believed that the PbO excess is located in the amorphous phase remaining after the mechanochemical synthesis, and that it is firstly crystallized, and subsequently transformed in the liquid phase during the thermal treatment.

A significant growth of the templates already occurs at 1150 °C, also in the presence of PbO, though it is more limited (a final average size of 19 μm with S.D. = 2.5 μm resulted in this case). This may be related to the decrease of the viscosity of the liquid phase with increasing the thermal treatment temperature, which favours grain rearrangement and mass transport.^{8,9} The effect of the PbO excess is significant not only for the final template size, but also for the final densification of the ceramic bodies and the pyrochlore stabilization after long times at high temperatures. The relative density of the templated PMN-35PT sample with a 2 wt.% of PbO excess thermally treated at 1200 °C is 98% TD, which is larger than that obtained with the matrix without PbO excess that presented traces of pyrochlore phase after the thermal treatment.

Fig. 7 shows the XRD patterns obtained on templated PMN-35PT containing a 2 wt.% of PbO excess after different thermal treatments. In this case, no pyrochlore phase is detected, which demonstrates the role of the PbO excess in promoting the reaction of the traces of pyrochlore and MgO to form the perovskite. It is also important to note that the PbO excess seems to modify the perovskite phases present in the ceramic samples after the prolonged thermal treatment at high temperature. A shift of the

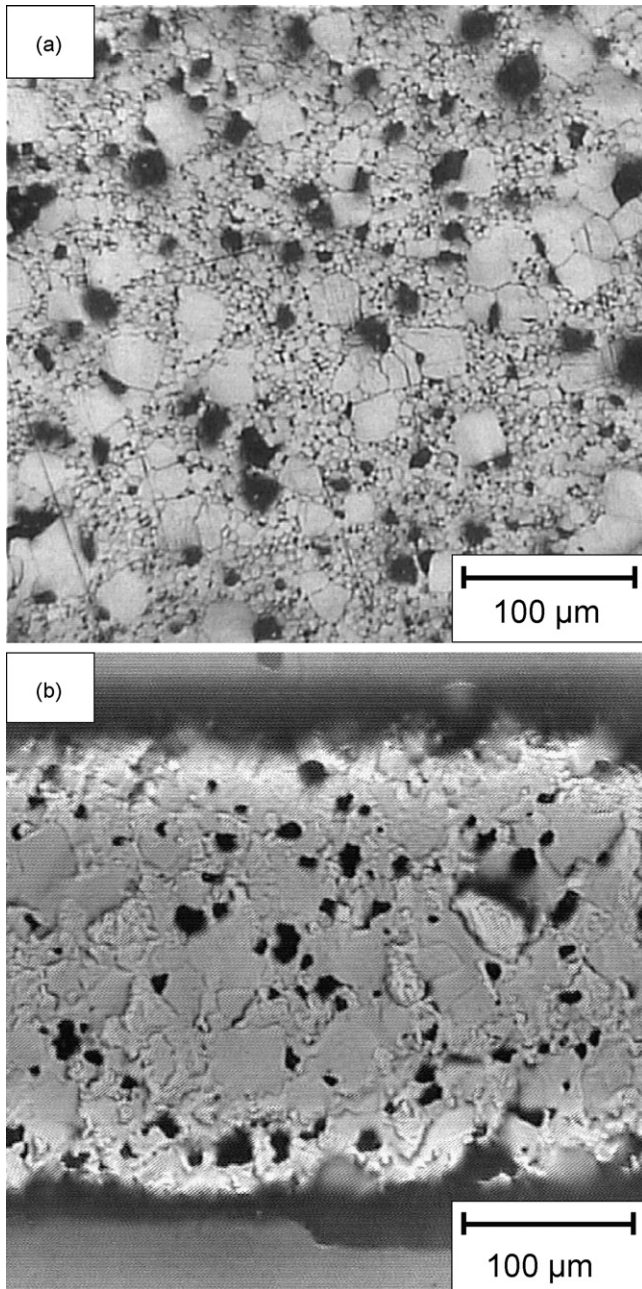


Fig. 6. Optical micrographs of the thermally etched/quenched cross-sections of templated PMN-35PT containing 2 wt.% PbO excess after a thermal treatment at 1200 °C for 10 h in PZ powder. The sample of image (b) was previously hot-pressed at 900 °C.

composition towards the PT-rich region of the phase diagram is indicated by the XRD results, since the contribution from the monoclinic phase to the splitting of the 200 reflection vanishes. This is consistent with the dynamic modification in the chemistry of the liquid phase during long thermal treatments in PMN-PT proposed by Gorzkowski et al.²⁵

3.4. Effect of separating the densification and TGG steps

In general, TGG is limited by the lack of grain connectivity due to limited densification, which hinders the close contact

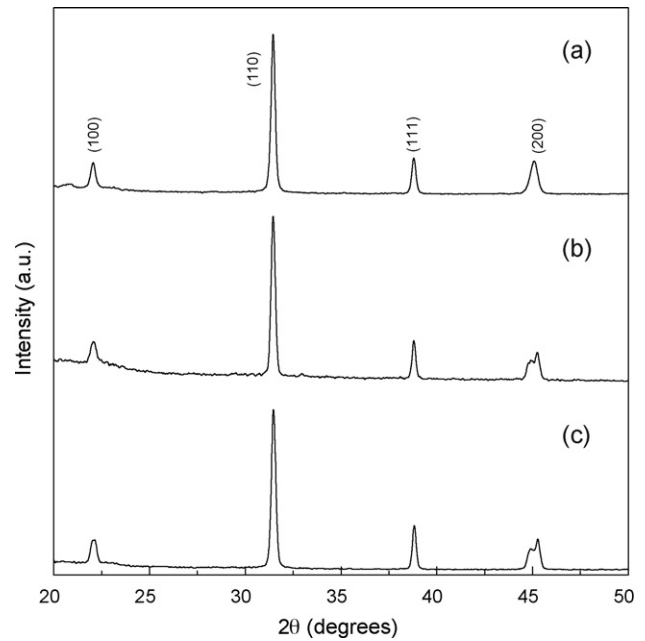


Fig. 7. XRD patterns for templated PMN-35PT containing 2 wt.% of PbO excess: (a) after a hot-pressing at 900 °C for 1 h, (b) after a thermal treatment at 1200 °C for 10 h in PZ powder, following the hot-pressing, and (c) after a direct thermal treatment at 1200 °C for 10 h in PZ powder.

between matrix grains and templates.⁹ It is known that growth is not triggered until a densification >90% TD is reached during the thermal treatment.^{26,27} Therefore, the matrix microstructure has to be as fine as possible after densification, prior to growth (the initial stage for TGG), since the smaller the matrix grain size the larger the driving force for TGG. Aiming at obtaining a more favorable initial stage for the TGG, the green bodies were hot-pressed at moderate temperatures into dense disks prior to the final thermal treatment at high temperature, thus separating the densification step from the TGG process. Fig. 8a shows an optical micrograph of the cross-section of a templated PMN-35PT sample prepared with a matrix containing 2 wt.% of PbO excess, subjected only to hot-pressing at 900 °C for 1 h under 60 MPa. These conditions are known to lead to high-density ceramics, but with limited grain growth.²⁸ Therefore, growth of the templates does not occur in this step, but a uniform distribution of templates in a very dense (>99% TD) matrix of fine grains of ~200 nm is achieved, according to the analysis of the SFM image of the surface of this ceramic, shown in Fig. 8b. The resultant microstructure can be regarded as an optimum initial stage for the TGG process.

Fig. 6b shows an optical micrograph of the cross-section of the same hot-pressed sample after a thermal treatment at 1200 °C for 10 h in PZ powder. Again, the apparent porosity is the result of grain pull-out during polishing, as the measurement of the relative density in this case gives a result of 99% TD. The average template size was increased up to 32 µm (S.D. = 4 µm), thus showing the beneficial effect of carrying out an intermediate hot-pressing step for improving the growth of the templates.

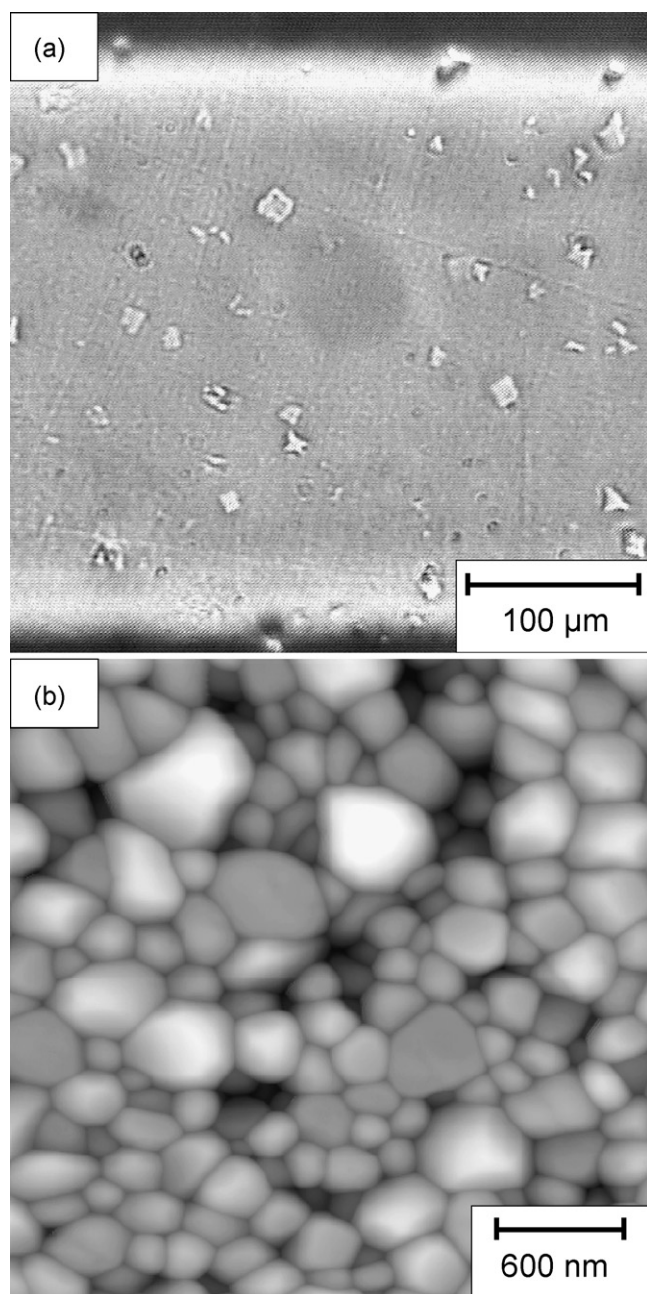


Fig. 8. (a) Optical micrograph of the thermally etched/quenched cross-section of templated PMN-35PT containing a 2 wt.% of PbO excess subjected only to hot-pressing at 900 °C for 1 h. (b) SFM image of the matrix grains structure.

Table 1 summarizes the final average template size and relative density of the templated PMN-35PT ceramic bodies after the thermal treatments. From this table we can conclude that the use of PbO excess allows higher densifications to be achieved, which can be further improved by the introduction of an intermediate hot-pressing step, and also promotes the growth of the templates. The relative density values obtained are very high, demonstrating the feasibility of using this novel TGG approach to produce high-quality piezoceramics. A comparison in terms of densification and template growth characteristics between our results and those previously reported in heterogeneous- and homogeneous-TGG can be found in Table 2. The final densifications and amount of growth of our templates is similar to that obtained in heterogeneous-TGG where SrTiO₃ single-crystal platelets were used.⁴ This significant growth of the templates ensures a large volume fraction of grown material in the final ceramic bodies, thus demonstrating the viability of the approach.

3.5. TGG as a means of obtaining larger microcrystals

This approach can also be used for the preparation of microcrystals with larger sizes. To this aim, the nanocrystalline PMN-35PT powder containing a 2 wt.% of PbO excess and a 5 wt.% of the cubic microcrystals with 12 μm size was thermally treated following the same procedure described in the Section 1, e.g., 1250 °C for 1 h in PZ powder. Fig. 9a shows an optical micrograph of the polished surface of the obtained sample, where large, cube-shaped grains with an average size of 27 μm (S.D. = 4 μm) are observed, this is more than twice the size of the initial templates. Once more, the faceted cubic grains were easily separated without breaking them. Fig. 9b shows an optical micrograph of the large PMN-PT cubic grains that resulted after disaggregating the ceramic. Also in this case, their size distribution was found to follow a lognormal function (see the inset in the figure). The XRD characterization demonstrated that the cubic grains are single crystals whose faces correspond to {1 0 0} crystallographic planes. The splitting of the 2 0 0 reflection into three peaks was also revealed, indicating the coexistence of monoclinic and tetragonal phases in the crystals. Therefore, (1 0 0) faceted PMN-35PT cubic crystals up to ~30 μm can be obtained by homogeneous-TGG of mechanoactivated powders by only ceramic technology.

Table 1

Results of the relative density and the final template size (average and standard deviation (S.D.)) of templated PMN-35PT containing a 2 wt.% and without PbO excess after thermal treatments at different temperatures for 10 h in PZ powder

| Hot-pressing | Sintering temperature (°C) | PbO excess (wt.%) | Relative density (%TD) ^a | Template size (μm) | S.D. (μm) |
|--------------|----------------------------|-------------------|-------------------------------------|--------------------|-----------|
| – | 1200 | 0 | 93 | 20 | 2.8 |
| 900 °C/1 h | – | 0 | 91 | 12 | 2.2 |
| 900 °C/1 h | 1200 | 0 | 89 | 22 | 3.2 |
| – | 1150 | 2 | 96 | 19 | 2.5 |
| – | 1200 | 2 | 98 | 27 | 3.8 |
| 900 °C/1 h | – | 2 | >99 | 12 | 2.1 |
| 900 °C/1 h | 1200 | 2 | 99 | 32 | 4.0 |

^a Density relative to the theoretical density (TD) of the PMN-PT, $\rho^{\text{Th}} = 8.1 \text{ g/cm}^3$.

Table 2

Review of results from previous studies on densification and template growth characteristics in homogeneous- and heterogeneous-TGG

| Templates | Sintering conditions | PbO excess (wt.%) | Relative density (%TD) ^a | Template size (μm) | |
|---------------------------------|----------------------|-------------------|-------------------------------------|--------------------|-------|
| | | | | Initial | Final |
| PMN-35PT ^b | 1150–1250 °C/10 h | 0–2 | 99 | 12 | ~30 |
| SrTiO ₃ ^c | 1150 °C/10 h | 0–3 | 98–99 | 10 × 2 | ~30 |
| PMN-25PT ^d | 1150–1200 °C/10 h | 2 | 95 | 25–50 | >100 |

^a Density relative to the theoretical density (TD) of the PMN-PT, $\rho^{\text{Th}} = 8.1 \text{ g/cm}^3$.

^b This work.

^c Kwon et al.⁴

^d Thi et al.^{11,12}

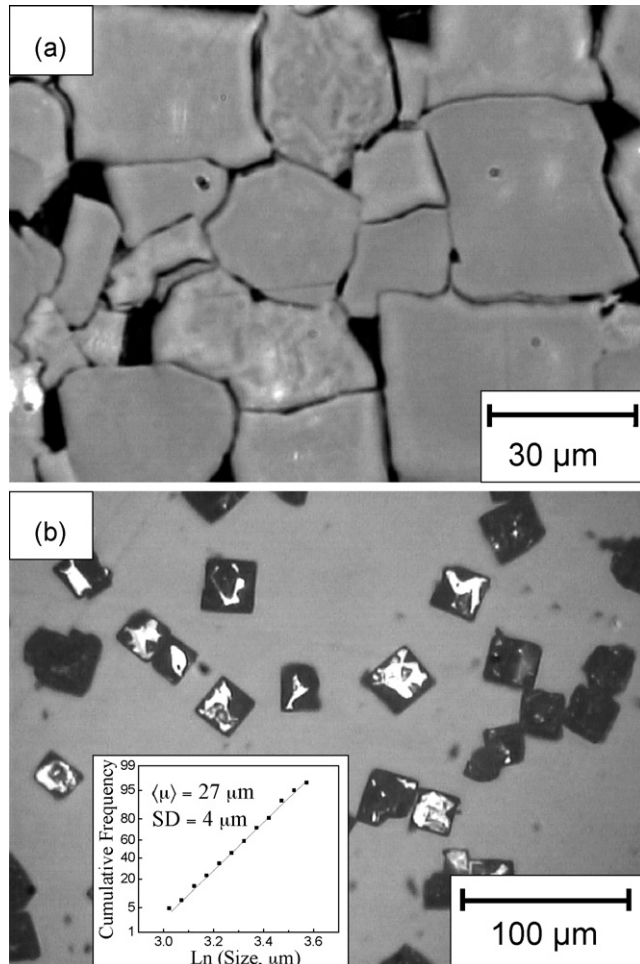


Fig. 9. Optical micrographs of (a) the polished surface of a 5 wt.% templated PMN-35PT containing a 2 wt.% of PbO excess after a thermal treatment at 1250 °C for 1 h in PZ powder, and (b) (100) faceted large PMN-35PT cube-shaped crystals obtained from the ceramic body. (Inset) Probability plot of the microcrystals size distribution showing a lognormal character, $\langle \mu \rangle$ is the average size and S.D. is the standard deviation.

4. Conclusions

(100) Faceted PMN-35PT cube-shaped microcrystals with coexistence of monoclinic and tetragonal phases and an average size of 12 μm were obtained by conventional sintering at 1250 °C for 1 h in PZ powder of a nanocrystalline powder synthesized by mechanochemical activation. These microcrystals

coming from the same source that the matrix they are embedded have grown by consuming the matrix grains during thermal treatments at high temperature. Template growth is further promoted by introducing a small PbO excess in the precursor powder to form a liquid phase during the thermal treatments. The contact between matrix grains and templates, which is already rather large thanks to the small size of the mechanoactivated powder, can be further improved by including an intermediate hot-pressing step previously to the thermal treatment, which separates the densification and the growth steps and results in an optimum initial microstructure for the templated grain growth. Template growth up to 32 μm and final densifications up to 99% TD were obtained under these tailored conditions. The process can be used as a means of obtaining larger (100) faceted PMN-35PT crystals with size up to ~30 μm.

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