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Microstructural and electrical characterization of La-doped PZT ceramics prepared by a precursor route

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Abstract

The effect of a powder processing route on the microstructure and electrical properties of 2 mol% La-doped PZT powders with tetragonal, rhombohedral and morphotropic compositions was investigated. Powders were prepared by using mixed-oxide and precursor methods, and different sintering regimes were used to control the grain size of the ceramics. It was shown that, by using the precursor method, ceramics with a submicrometer grain size and a narrow grain size distribution could be obtained. In addition, the precursor method results in ceramics with higher chemical homogeneity with respect to the Zr/Ti-distribution within the grains compared to the mixed-oxide route. In the case of the morphotropic composition, the chemical homogeneity affects the magnitude of the coercive field. The coercive field also increases with decreasing grain size, due to larger internal elastic stresses related to grain boundaries. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Ferroelectric properties; Grain size; Powder processing routes; PLZT

1. Introduction

Piezoelectric ceramics lead zirconate titanate, $Pb(Zr_x Ti_{1-x})O_3$ (PZT), is a material of high technological importance, due to its applications in solid state actuators, transducers and sensors. The present trend is to make such devices in smaller and smaller sizes, which requires fine grained ceramics with uniform microstructures. Therefore, recently there has been a strong interest in developing processing methods which would produce PZT powder with a fine particle size and high chemical homogeneity, since both features are important to obtain ceramics with a controlled microstructure. One of the methods of powder processing is the so-called precursor route, where PZT is formed in a two-stage reaction: first by forming a solid solution $Zr_xTi_{1-x}O_2$, which is subsequently reacted with PbO.[1] This method is comparatively simple and inexpensive, which makes it attractive for industrial application.

The objective of the present work is to investigate the effect of powder processing on the microstructure and ferroelectric properties of PZT ceramics by comparing the precursor and mixed-oxide routes.[2] The latter is a conventional industrial method to produce PZT.

2. Experimental

Several compositions with the general chemical formula $Pb_{0.97}La_{0.02}(Zr_xTi_{1-x})O_3$ were prepared by using two processing routes, with x corresponding to different crystalline modifications of the ferroelectric phase: tetragonal ($x = 0.45$), rhombohedral ($x = 0.60$) and at the morphotropic phase boundary ($x = 0.54$), which consists of a mixture of the rhombohedral and tetragonal modifications.[3] In the mixed-oxide method, the starting powders of PbO (Analytical pure, Merck KGaG, Germany), ZrO_2 (E101, MEL Chemicals, England), TiO_2 (Bayertitan A-Z, Bayer AG, Germany) and La_2O_3 (>99,99%, Ventron, Germany) were homogenized for 3 h in an attrition mill by using ZrO_2 balls and isopropyl alcohol as a milling media.[4] After drying in a rotation evaporator, the mixture of powders was calcined in air at 850°C for 2 h. In the precursor route, ZrO_2 and TiO_2 were first homogenized for 3 h by attrition milling, dried and heat treated at 1400°C for 2 h. The obtained precursor was

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subsequently mixed with PbO and La_2O_3, homogenized for 3 h by attrition milling and calcined at 800°C for 2 h. In both methods, the calcined PZT powders were ball-milled in isopropyl alcohol for 4 h to break up the agglomerates. In both methods, single perovskite phase of PZT was formed, which was verified by X-ray diffraction analysis using a standard laboratory diffractometer (D5000, Siemens, Germany). Particle size distribution in terms of the volume fraction of particles with a given diameter was measured using a laser granulometer (Helos, Sympatec).

Green bodies were formed by cold pressing of the obtained powders. To vary the median grain size of sintered ceramics, three sintering regimes were employed: 1050°C/2 h, 1225°C/2 h and 1300°C/10 h. Sintering was performed in an oxygen atmosphere. A $PbZrO_3 + 8$ wt.% ZrO_2 powder bed was placed into the crucible in order to establish a constant PbO vapor pressure during densification. Weight loss during sintering was determined for each sample, and was smaller than 1.9 wt.%, even for samples sintered at 1300°C/10 h. X-ray diffraction showed again that all sintered samples consisted of a single perovskite phase PZT. The sintered densities were determined by the Archimedes method and were greater than 98% of the theoretical density independent of the powder processing method, composition and sintering condition. Grain size distribution of sintered ceramics was determined from quantitative image analysis (Soft Imaging Software, Kontron, Germany) of micrographs obtained using SEM from polished and chemically etched surfaces of samples. Electrical characterization was performed at room temperature on samples with typical dimensions $10\times10\times1$ mm^3. Gold was sputtered on large polished surfaces to form electrodes. The electric field induced polarization was measured using a Sawyer–Tower circuit. The amplitude of the electric field was equal to 3 MV/m and the duration of one measurement cycle was equal to 100 s.

3. Results and discussion

3.1. Powder characterization

The particle size distribution of PZT powders obtained via the precursor method was unimodal for all studied compositions, with only small variations of the median diameter with composition: 0.50 μm ($x = 0.45$), 0.51 μm ($x = 0.54$) and 0.49 μm ($x = 0.60$). In comparison, PZT powders obtained from the mixed-oxide route showed slightly larger median particle sizes, for example 0.60 μm for the composition with $x = 0.54$. However, SEM observation of the studied powders revealed that the value of the median particle size measured by granulometer did not correspond to the true particle size, but it was affected by agglomerates which were not broken into separate particles by ultrasonic treatment during sample preparation. SEM images showed that powders consisted of very fine particles. The average particle size determined from SEM images was approximately equal to 400 nm for PZT powder with $x = 0.54$ derived using the precursor method and to 200 nm for the mixed-oxide powder ($x = 0.54$). In the case of powders issued from the precursor route, the particle size was homogeneous, whereas the powders obtained via the mixed-oxide route showed a broader particle size distribution.

3.2. Microstructure of sintered ceramics

Fig. 1 compares the microstructure of ceramic samples with a composition $x = 0.45$ made from powders obtained by using the two studied processing routes. Similar microstructures were observed for the other studied compositions. One can see in Fig. 1(a) that a large number of grains in the sample made via the mixed-oxide route exhibit an "etching hole" located in the center of the grain. These holes are due to the gradient of Zr/Ti

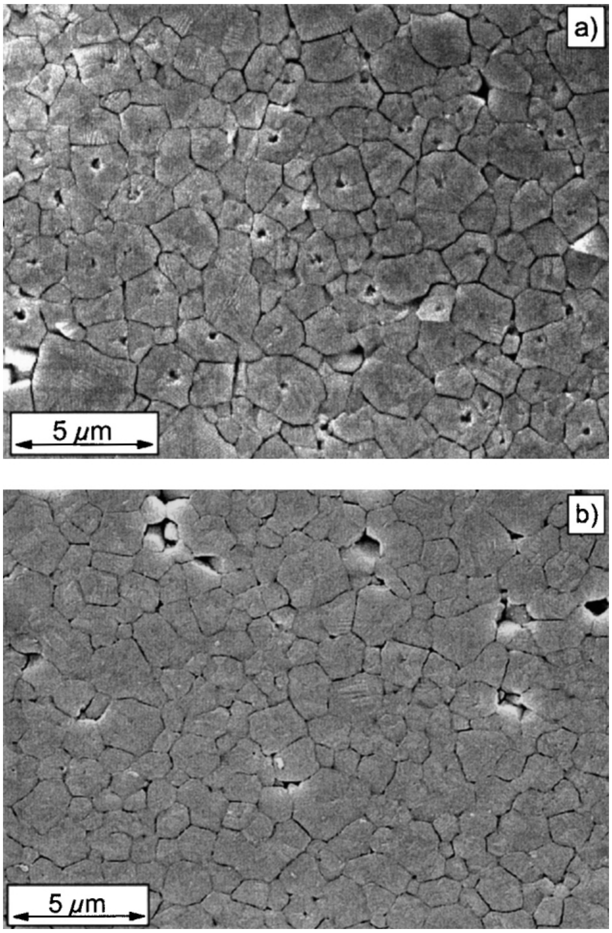

Fig. 1. SEM-micrographs of PZT ceramics ($x = 0.45$) sintered at 1225°C/2 h from powders prepared using (a) mixed-oxide and (b) precursor routes.

concentration across the grain which occurs during sintering because of different diffusion coefficients of Ti and Zr ions.[4] In the mixed-oxide route, lead titanate is the first reaction product to appear before the PZT solid solution is formed because of the higher diffusion coefficients of Pb^{2+} and Ti^{4+} in comparison to Zr^{4+}. Therefore, PZT grains show a gradient of Zr/Ti concentration from the core to the shell. Furthermore, a preferred La diffusion into Ti-rich compositions during sintering was observed.[4] La-doping leads to an increase of lead vacancies in the perovskite structure, and therefore, to a destabilization of the ceramic in the center of the grain, which is the origin of the formation of holes at the center of the grains during etching. In contrast, samples made via the precursor route do not exhibit such etching effect, Fig. 1(b), which indicates higher chemical homogeneity of these ceramics with respect to the Zr/Ti and also La-concentration within the grains.

Fig. 2 compares median grain size of ceramics for the two studied powders. One can see that at higher sintering temperatures, 1225 and 1300°C, the precursor method results in ceramics with a smaller grain size than the mixed-oxide route, for example 1.9 compared to 2.9 μm at 1300°C. In addition, the precursor route leads to a more uniform microstructure of sintered ceramics. For example, Fig. 3 compares the grain size distribution of ceramics with a composition $x=0.54$ sintered at 1050°C/2 h. One can see that although the median grain size of both samples is nearly the same, 0.70 μm, the width of the grain size distribution is narrower in the case of the precursor method.

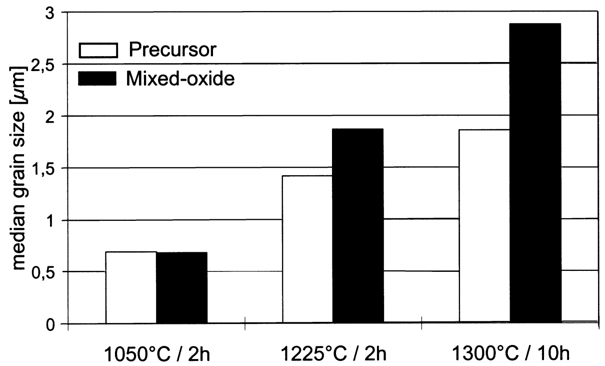

Fig. 2. Median grain size of PZT ceramics ($x=0.54$) sintered at different conditions. Powder was prepared using either precursor or mixed-oxide route.

3.3. Electrical measurements

Fig. 4 shows an example of polarization-versus-electric-field hysteresis loops for ceramics with a composition $x=0.54$ sintered from the powder obtained via precursor route. One can see that with decreasing grain size, the coercive field, necessary to switch the polarization, becomes larger. A similar trend was observed for other compositions investigated, and also for ceramics made from the mixed-oxide powder. Possible origin of the grain size effect is the presence of internal elastic stresses from grain boundaries and surrounding grains. The stresses hinder the motion of domain walls, which controls the polarization switching in ferroelectric ceramics.[5] These internal stresses are in fact residual stresses related with the development of the domain structure below the Curie temperature.[6] It is expected that the stresses should be higher in the fine grained ceramics, mainly because the domain structure cannot compensate completely the change of the shape of individual grains during phase transformation.[5,6] To verify the presence of internal stresses in our samples, we compared lattice parameters measured using X-ray diffraction from the bulk ceramics and from the free powder, which was obtained by crushing sintered ceramics. We found that as the grain size decreased, the spontaneous lattice distortion of ceramics reduced compared to that of the powder.[2] This reduction can be interpreted as the result of an increase in the internal stresses in the ceramics when the transition from the paraelectric to the ferroelectric phase occurs.[5] As the stresses hinder the motion of domain walls, one can expect that for smaller grain sizes, a larger electric field will be required to switch the polarization, which is observed in Fig. 4.

Another result of this study is the effect of chemical inhomogeneity of the material resulting from the powder

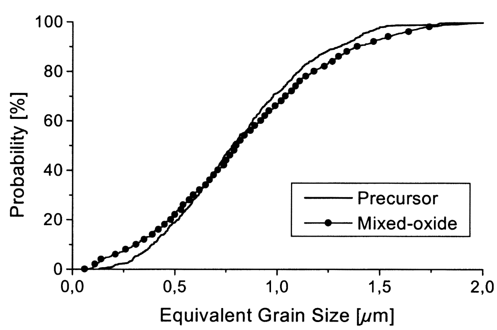

Fig. 3. Grain size distribution in ceramics with composition $x=0.54$ sintered at 1050°C/2 h from the precursor and mixed-oxide powders.

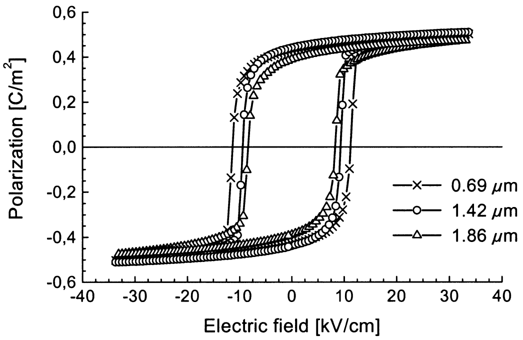

Fig. 4. Grain size effect on polarization loops of ceramics ($x=0.54$) sintered from the powder obtained via precursor route.

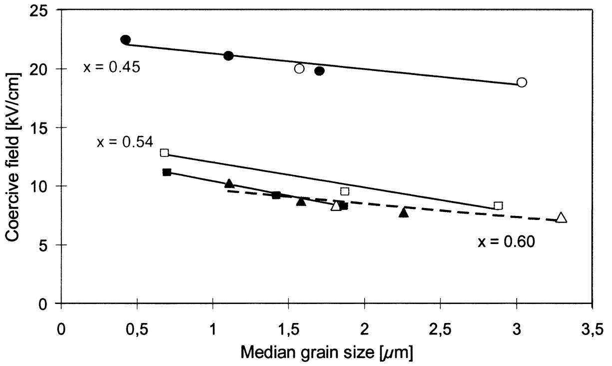

Fig. 5. Grain size dependence of the coercive field. Open symbols correspond to ceramics made from the mixed-oxide powder and closed symbols to the precursor powder.

processing route on the coercive field. It is illustrated in Fig. 5, where the coercive field is plotted as a function of grain size for ceramics made from the mixed-oxide powder (open symbols), and from the precursor powder (closed symbols). One can see that for the material consisting of a single phase, tetragonal ($x = 0.45$) or rhombohedral ($x = 0.60$), a small variation of composition related to the powder processing route, i.e. Zr/Ti concentration, within the grains does not affect the value of the coercive field. For both materials, the coercive field depends only on the grain size. At the same time, the material at the morphotropic phase boundary ($x = 0.54$) appears to be sensitive to the powder processing route. For the same grain size, ceramics sintered from the mixed-oxide powder exhibits higher values of the coercive field, Fig. 5. A possible reason for this result is that for the material consisting of a mixture of the tetragonal and rhombohedral phases, even a small variation of composition can lead to the phase separation across the grain, tetragonal in the Ti-rich core of the grain and rhombohedral in the Zr-rich shell.

4. Conclusions

In conclusion, we investigated the effect of the powder processing route on the microstructure and electrical properties of La-doped PZT ceramics, with compositions close to the morphotropic phase boundary. It was shown that by using the precursor method, a powder with uniformly shaped particles and an average particle size about 400 nm can be obtained. Ceramics made of this powder exhibits a smaller median grain size than samples made of mixed-oxide powder. By adjusting the sintering regime to 1050°C/2 h, ceramics with a median grain size smaller than 1 μm and with a narrow grain size distribution can be obtained by using powder from the precursor route. The precursor method also results in a higher chemical homogeneity of ceramics compared to the standard mixed-oxide route. It was shown that the chemical homogeneity affects the magnitude of the coercive field for composition at the morphotropic phase boundary ($x = 0.54$), most likely due to the phase separation related with a composition gradient across individual grains. At the same time, the chemical inhomogeneity does not influence the coercive field in the case of single-phased compositions ($x = 0.45$ and $x = 0.60$). The coercive field also depends upon the grain size, due to the presence of internal elastic stresses which are not compensated in fine grained ceramics by the development of domain structure at the ferroelectric phase transition.

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References

1. Shrout, T. R., Papet, R., Kim, S. and Lee, G.-S., Conventionaly prepared submicrometer lead-based perovskite powders by reactive calcination. *J. Am. Ceram. Soc.*, 1990, **73**, 1862–1867.
2. Schreiner, U., Herstellung von La-dotiertem Blei-Zirkonat-Titanat über die Precursorroute. Diploma thesis, University of Karlsruhe, 2000.
3. Jaffe, B., Cook, R. Jr. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, 1971.
4. Hammer, M. and Hoffmann, M. J., Sintering model for mixed-oxide-derived lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 3277–3284.
5. Randall, C. A., Kim, N., Kucera, J. P., Cao, W. and Shrout, T. R., Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics. *J. Am. Ceram. Soc.*, 1998, **81**, 677–688.
6. Arlt, G., The influence of microstructure on the properties of ferroelectric ceramics. *Ferroelectrics*, 1990, **104**, 217–227.