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Microstructure of organometallic derived PLZT ceramics

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Abstract

The PLZT powders with the formula $Pb_{0.905}La_{0.095}(Zr_{0.65}Ti_{0.35})_{0.976}O_3 + 3.5$ wt.% PbO were prepared by the organometallic precursor method (Pechini and partial oxalate processes). The microstructure of sintered 9.5/65/35 PLZT ceramics obtained from a partial oxalate procedure shows that the outstanding feature of this microstructure is its fairly uniform grains of about 1.8 μm. The microstructure of sintered PLZT ceramics obtained by the Pechini process consists of uniform small randomly-oriented grains tightly bonded together in the central part of the sample with a grain size of about 1.2 μm. Cubic and elongated grains are formed at the sample's border. The microstructures of hot pressed PLZT ceramics obtained from both processes are dense and rather uniform. After a double stage of hot pressing (2 plus 20 h) the microstructure of PLZT is fully dense, uniform and homogeneous with a grain size of approximately 2.5 μm.

Keywords: Hot-pressing; Microstructure-final; PLZT; Precursors: organic

1. Introduction

PLZT materials consist of a wide range of homogeneous ABO_3 compositions existing within the basic lead zirconate-lead titanate solid solution system.[1–3] Because of the complete miscibility between lead zirconate and lead titanate, and the substantial solubility (up to 40 at.% at the high $PbTiO_3$ end) of lanthanum oxide in the system, it is possible to custom-make various combinations of chemical compositions to get specific desirable properties. Although PLZT ceramics are constituted of a wide variety of compositions, ranging from those best suited for piezoelectric applications to those specifically designed for pyroelectric devices, they are unquestionably most widely known for their electro-optic properties.

It was shown that the satisfactory electro-optical properties of PLZT could be achieved only by a suitable procedure of PLZT synthesis. Initial work on the synthesis of PLZT was done using mixed oxides[1–3] or chemical coprecipitation methods. [4–7] Another very important area of the PLZT process is to obtain the fully dense ceramics using hot pressing in an oxygen atmosphere. This procedure is essential to obtain a uniform and homogeneous microstructure of PLZT.[8,9] Otherwise, the literature data are poorly reported about the hot pressing process from ceramic powders prepared by polymeric precursor method from organometallic complexes such as citrates.

The aim of this paper is concerned with the microstructure of 9.5/65/35 PLZT ceramics prepared by the Pechini process and partial oxalate procedure, sintered and hot pressed in oxygen atmosphere to yield dense PLZT ceramic materials. Since these methods have not been extensively used for PLZT powder synthesis to obtain dense ceramics by hot pressing, the influence of powder preparation on the obtained microstructure was investigated.

2. Experimental procedure

It is well known that precursor-prepared PLZT powders reach a high chemical homogeneity. On the basis of that, the PLZT ceramic powders were prepared according to the chemical formula $Pb_{0.905}La_{0.095}(Zr_{0.65}Ti_{0.35})_{0.976}O_3 +$ 3.5 wt.% PbO using the polymeric precursor process

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from organometallic complex such as citrates. An excess of 3.5 wt.% of PbO was added to the initial solutions to compensate the loss of PbO from evaporation during firing processes and to enhance the densification by forming a PbO-rich liquid phase during sintering.

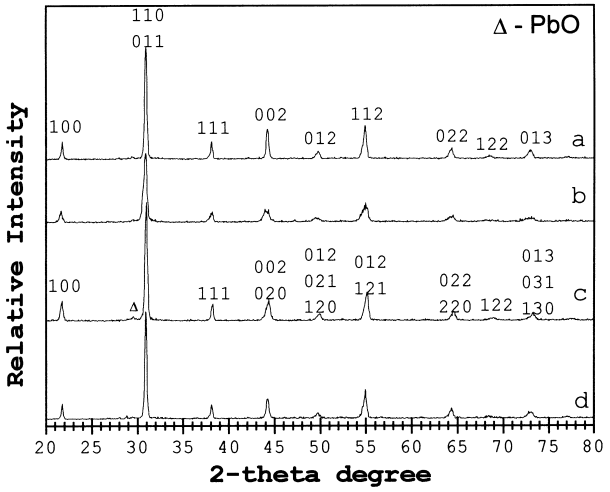

Fig. 1. The X-ray data for sintered (at 1200°C — 4 h) and hot pressed (at 1100°C — 2 h). (a) PLZT sintered (obtained by Pechini process); (b) PLZT hot pressed (obtained by Pechini process); (c) PLZT sintered (obtained by partial oxalate procedure); (d) PLZT hot pressed (obtained by partial oxalate procedure).

The method known as the Pechini process (PCP) was used in three-stages.[10] First, to prepare the polymeric precursor resin formed in a citric acid and ethylene glycol solution, secondly, to chelate the cations and finaly, to decompose it during thermal treatment. The organometallic complex was thermally treated in two steps (300 and 400°C) to release the organic materials of previous solutions. The same method was also used as an intermediate process to obtain PLZT, using a partial oxalate procedure (POP). A mixture of zirconium titanate (ZT) particles (obtained by PCP), lead nitrate and lanthanum oxides was dripped in ammonia solution of oxalic acid. The lead oxalate and lanthanum oxide were precipitated at the surface of the ZT particles and after that were decomposed during thermal treatment in three steps (300, 350 and 400°C). After calcination at 700°C for 4 h followed by milling, the powders were pressed at 175 MPa, into 10×2.5 mm^2 pellets, using a cold isostatic press. The particle size of PLZT powders obtained by both procedures were less then 50 nm [11] with green density of about 60% of theoretical density measured by a volumetric method. Sintering was performed at 1200°C

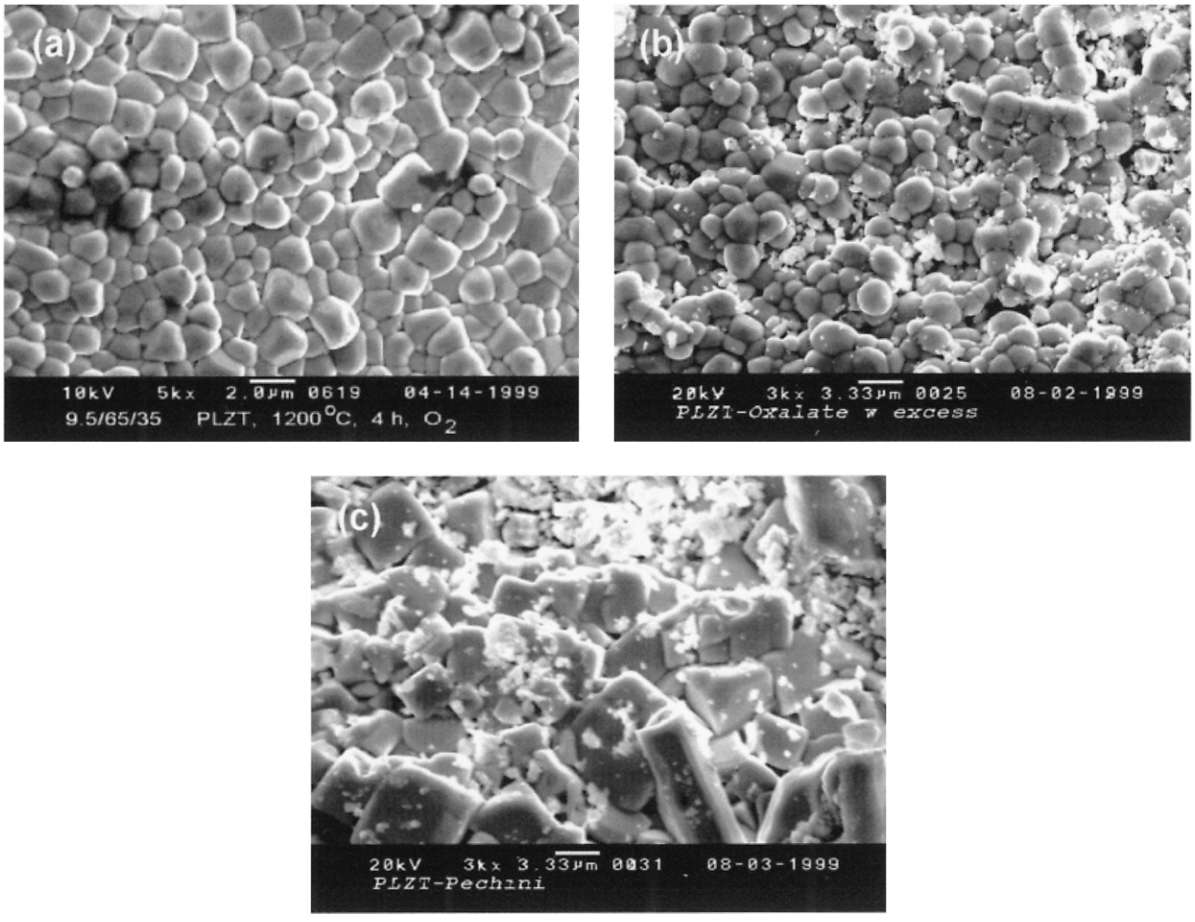

Fig. 2. The microstructure of 9.5/65/35 PLZT ceramics sintered at 1200°C in oxygen. (a) PLZT obtained by Pechini process (central part); (b) PLZT obtained by partial oxalate procedure; (c) PLZT obtained by Pechini process (at border's part).

for 4 h and hot pressing was carried out at the temperature of 1100°C for 2 h. After sintering in oxygen, PLZT densified to 92–95% of theoretical density, measured by Archimedes method. The PLZT ceramic obtained by the Pechini procedure was also double-stage hot pressed for 2 h plus 10 h and 2 h plus 20 h the same temperature. After hot pressing PLZT densified to 96–98% of TD, depending on hot pressing time. The temperature regime during sintering and hot pressing was adjusted for slow heating and cooling rates.[11,12] Applied pressure, during hot pressing, was 26 MPa at the sintering temperature and was performed in a dynamic oxygen flow into the furnace.

The characterisation of PLZT was done by XRD (Siemens D5000 diffractometer), TEM (Philips CM200) and SEM (Topcon SM-300). The samples for microstructural analysis were prepared by chemical etching for sintered pellets and by thermal etching for hot pressed pellets.

3. Results and discussion

The most obvious advantage offered by chemical solutions to prepare ceramic powders is that the reagents are mixed generally on an atomic rather than on a particulate scale. We have reported earlier herein[12] that the formation of PLZT phases occurred after thermal treatment at 400°C, with a small amount of PbO besides the PLZT phase. The PLZT cubic crystal phase was observed in calcined PLZT powders obtained from both processes. Otherwise, besides PLZT, a small amount of PbO and pyrochlore phases were observed in PLZT obtained by POP. After sintering the monophased crystal structure was obtained by both procedures (Fig. 1a and c). It was observed that after hot pressing the PLZT structure showed small lattice tetragonality (Fig. 1b and d), which was verified by the Rietveld method.[13]

The microstructures of the sintered 9.5/65/35 PLZT ceramics obtained by both methods exhibit generally a fairly uniform grain size and consist of small grains, approximately 1.2–1.8 μm (Fig. 2a and b). In PLZT ceramics obtained by PCP, the grains were bonded together in the central part of the sample (Fig. 2a) contrary to cubic and elongated grains at the sample's border (Fig. 2c). The structure consisted of PLZT grains and other phases rich with La and Zr, probably La_2O_3 or $La_2Zr_2TiO_7$.[9,11] The change in grain shape from a rounded to a cubic form of grain growth (PLZT phase) and appearance of elongated grains (second phases, such as La_2O_3 or $La_2Zr_2O_7$) during sintering at 1200°C was caused not only by PbO loss but also by the previous agglomeration

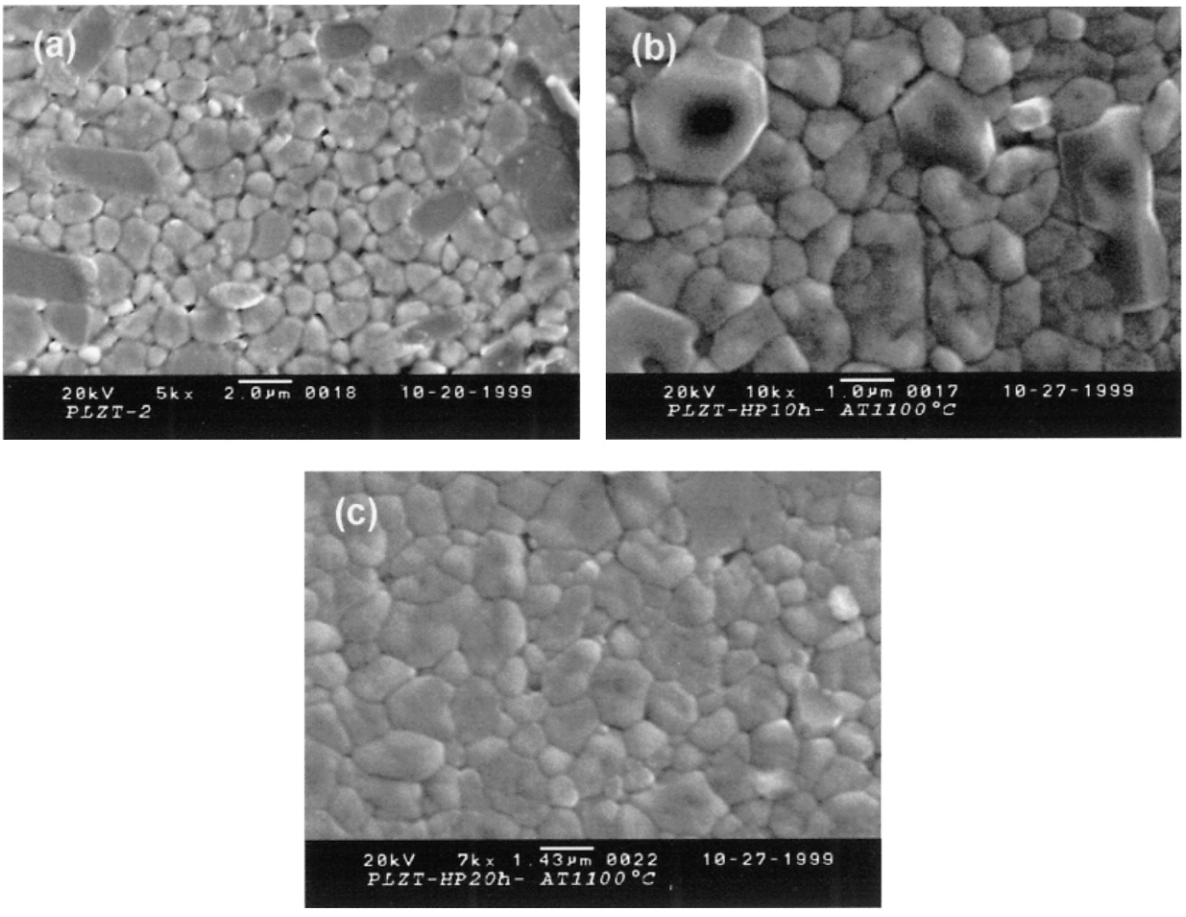

Fig. 3. The microstructure of 9.5/65/35 PLZT ceramics prepared by PCP process and hot pressed at 1100°C: (a) for 2 h; (b) for 2 plus 10 h; (c) for 2 plus 20 h.

of high reactive sub-micron grain size of PLZT powder particles. This resulted in a non-homogeneous microstructure at the sample's border.

After one stage of hot pressing for 2 h, the microstructure consists of randomly oriented grains tightly bonded together, with a grain size of 1.5 μm (by PCP) and 2.1 μm (by POP). The small grain size was affected by small initial particle size and by a short time of hot pressing (Fig. 3a). After two stages of hot pressing, the amount of secondary phases due to non-homogeneity was less significant than in the previous process. These results indicate that the densification of ceramics occurs in several stages. In the early stage of the hot pressing and densification process, the fine-grained ceramic material was usually not uniformly dense and there was evidence of specific zones of equal density, which could lead to non-homogeneity and to the appearance of second phases. Thus, further densification during the second stage of hot pressing leads to more than 98% dense ceramics with a uniform microstructure. After 2 plus 20 h the PLZT ceramics is fully dense, uniform and homogeneous with a grain size of approximately 2.5 μm (Fig. 3c). It can be assumed that after 2 plus 20 h, only a small amount of residual porosity is present. The density obtained for the hot pressed samples, i.e. over 98% of the theoretical density, justifies this assumption.

4. Conclusions

High reactive sub-micron grain size of PLZT powders prepared by the Pechini process and partial oxalate method were used to obtain hot pressed PLZT ceramics. The microstructure of sintered 9.5/65/35 PLZT ceramics exhibit generally a fairly uniform grain size and consists of small grains of 1.2–1.5 μm. The exaggerated grain growth observed at the border of PLZT obtained by the Pechini process was caused not only by PbO loss but also by the agglomeration of PLZT powder particles which resulted in a non-homogeneous microstructure on the sample's border. After hot pressing for 2 h, the microstructure consists of randomly oriented grains tightly bonded together with grain size approximately 1.8 μm. The microstructure of a typical 2 plus 20 h hot pressed PLZT composition is fully dense and rather uniform, with a grain size of approximately 2.5 μm. Following the above results the polymeric precursor process (PCP) has been shown, for the first time, to be a very effective approach for hot pressing production of PLZT ceramics with high density and fine grain size such as are normally required for most advanced electro-optical applications.

Acknowledgements

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