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Hot-pressed 9.5/65/35 PLZT prepared by the polymeric precursor method

B.D. Stojanovic [a,c], M.A. Zaghete [a], C.O. Paiva-Santos [a], M. Cilense [a], R. Magnani [b], E. Longo [b], J.A. Varela [a,*]

[a] Institute of Chemistry, Universidade Estadual Paulista (UNESP), Caixa Postal 355, 14800 Sao Paulo, Brazil
[b] Department of Chemistry, UFSCar, São Carlos, SP, Brazil
[c] Center for Multidisciplinary Studies, University of Belgrade, Yugoslavia

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Abstract

A 9.5/65/35 PLZT ceramic with a $Pb_{0.905}$ $La_{0.095}$ $(Zr_{0.65}$ $Ti_{0.35})_{0.976}$ $O_3 + 3.5$ w% PbO formula was prepared using the Pechini method for powder preparation and two-step sintering in an oxygen atmosphere. The first step consisted of sintering at 1200°C for 4 h with slow heating and cooling rates. The second step consisted of hot pressing at 1200°C for 4 h, with slow heating and cooling rates and pressing pressures of 20 MPa (initial pressure) and 40 MPa (at sintering temperature). Investigations were made of the powder phase formation and powder morphology, i.e. the structure of sintered and hot-pressed PLZT ceramics. SEM microstructural analyses were carried out on the sintering and hot-pressing processes. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Ceramics are traditionally prepared using powders obtained from oxides or compounds, such as carbonates, acetates or nitrates that decompose into oxides at high temperatures. Initial work on PLZT was also done using mixed oxides [1–3]; however, this method eventually proved to be inadequate from the standpoint of chemical and optical uniformity [3,4]. Today there are numerous publications on both mixed oxide and chemical coprecipitation methods [5–7]. Thus, coprecipitation methods were designed for PLZT materials, using liquid and oxide precursor materials developed and subsequently implemented into production processes [2,8].

Haertling and Land's [2,9] process for the preparation and production of PLZT materials is a useful method that employs lead oxide, zirconium and titanium alkoxide and lanthamum acetate solutions. The process calls for a mixture of tetrabutyl zirconate, tetrabutyl titanate and lead oxide precipitated into a finely dispersed slurry in isopropyl alcohol and acetic acid. Freshly hydrolysed precipitates react with lead oxide and lanthanum acetate to produce a final product consisting of oxides and hydroxides.

Although this process has proved to be successful in the production of PLZT, there are other methods to prepare powder for PLZT materials. Haertling and Land [10] used chemical coprecipitation in alcohol solutions of all alkoxides in the presence of PbO, and Brown and Mazdiyashi [11] employed the same method using water. Thomson started with an aqueous solution of nitrates and organometallic Ti precipitated in a NH_4OH bath or processed directly [12], Murata et al. [13] used chemical precipitation from a clear aqueous solution of nitrates and chlorides precipitate in NH_4OH, while Yin [14] used chemical dehydration, i.e. alcohol dehydration of a citrate solution.

One of the most convenient methods to synthesize PLZT powders is a polymeric precursor method [14]. In 1967, Pechini [15] developed a three-stage process for the preparation of a polymeric precursor resin: first, a mixture of cations is formed in a citric acid and ethylene glycol solution; second, the cations become chelated,

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* Corresponding author. Tel.: +55-16-222-0015; Fax: +55-16-222-7932.
E-mail address: varela@iq.unesp.br (J.A. Varela).

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and third, a polymeric resin is formed which can become decomposed during thermal treatment. Some authors have used this method as an intermediate process to obtain PZT and PLZT. This method was used in combination with part of the oxalate method, i.e. starting from a mixture of ZT particles (obtained by the Pechini method), lead nitrate and lanthanum oxides were dripped into an ammoniac solution of oxalic acid [16], leading to the precipitation of lead oxalate and lanthanum oxide onto the ZT particle surface [17].

Another very important area of PLZT processing is sintering into fully dense ceramics, a process that is critically important to achieve optical transparency. To date, hot processing has been widely employed, whereby pressure is applied to the material during sintering at elevated temperatures. However, hot pressing alone proved to be insufficient to consistently yield high quality material, for which reason an oxygen atmosphere was subsequently added to produce satisfactory results [18–20].

In view of the above, this paper reports on work carried out on 9.5/65/35 PLZT ceramic materials in bulk form prepared by the Pechini and the hot-pressing process. The influence of powder preparation and heat treatment on the PLZT stoichiometry, crystal structure and microstructure is analyzed.

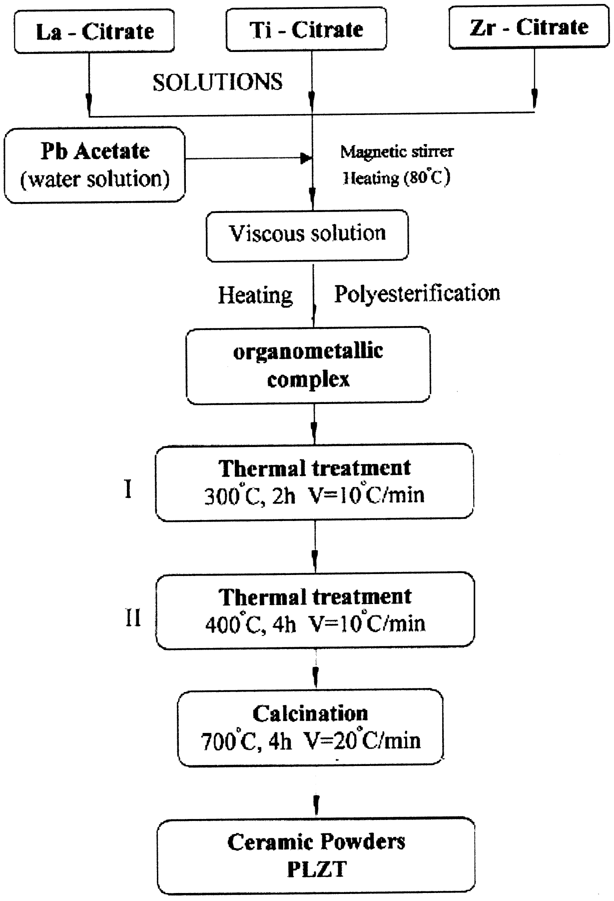


Fig. 1. Block scheme for PLZT powder preparation by polymeric precursor method.

2. Experimental procedure

2.1. Powder synthesis and sintering

In this study, PLZT ceramic powders were prepared according to the chemical formula $Pb_{0.905}(Zr_{0.65}Ti_{0.35})_{0.976}O_3 + 3.5$ w% PbO and the block diagrams of the process presented in Figs. 1 and 2.

The methods are based on the polyesterification of La-, Ti, and Zr- acetate solutions and a Pb-acetate water solution. The organometallic complex obtained was thermally treated in two steps to rid it of organic materials remaining from previous solutions. After calcination at 700°C for 4 h, the powders were milled, sieved and pressed into pellets using a cold isostatic press.

The sintering process was carried out by two-step sintering. The first step consisted of conventional sintering in oxygen atmosphere, while the hot-pressing process, also in an oxygen atmosphere, was used in the second step. During sintering and hot pressing, the pellets were covered by pre-sintered powders (coarse and fine-grained powders in two layers underneath and on top of pellets placed in a covered aluminum crucible). The temperature during conventional sintering and hot-pressing was adjusted to slow heating and cooling rates of 250°C/h to 700°C, followed by 100°C/h up to 1200°C for heating and 120°C/h for the cooling process in first sintering step. The heating rate employed during the hot

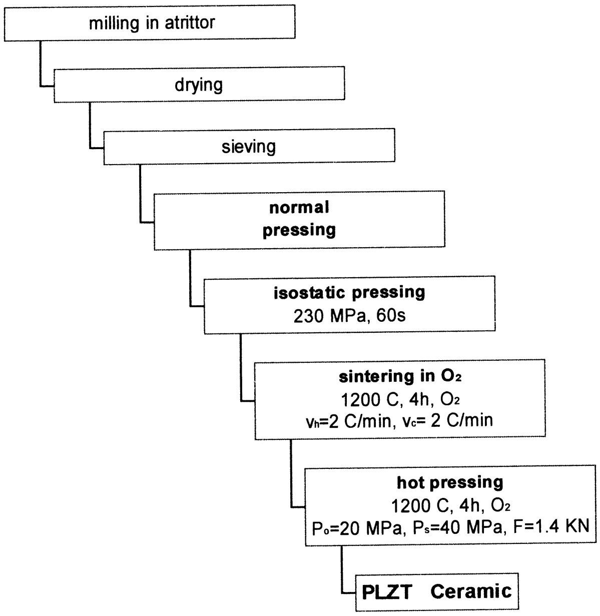


Fig. 2. Block scheme for preparation of PLZT ceramics from powders obtained by polymeric precursor method.

pressing process was 60 and 30°C/h during the cooling process. Applied pressing pressure was 20 MPa (initial pressure), and 40 MPa at the sintering temperature for 4 h. Hot-pressing was performed in a dynamic oxygen flow into the furnace.

2.2. Characterization of PLZT powders and ceramics

The X-ray diffraction data for PLZT powders, and sintered and hot-pressed PLZT ceramics were collected using a Siemens D 5000 diffractometer under the following experimental conditions: 40 kV, $20° < 2\theta < 80°$, $2\theta = 0.02°$, monochromatized by a graphite crystal. Specific surface area measurements were taken with the B.E.T. method, using N_2 as adsorbate. SEM observations were made to identify the sintered and hot-pressed PLZT sample microstructures (Topcon SM-300).

A simultaneous DTA-TG analysis (Netzsch STA 409, TASC 414/2) was made at a 10°C/min heating rate in dry air and a nitrogen atmosphere for characterization of the PLZT powders.

3. Results and discussion

3.1. Phase formation

The most obvious advantage offered by solutions used in the preparation of ceramic powders is that the reagents are mixed on an atomic rather than on a particulate scale. Consequently, the chemical homogeneity is high, but how well this homogeneity is maintained depends on the technique used to convert the solutions from a liquid into a solid state. It is well known that precursor-prepared PLZT powders reach a high chemical homogeneity. In this study, which was based on the Pechini method, a three-stage process was employed to prepare the precursor polymeric resin, the 9.5/65/35 PLZT powder composition. An excess of 3.5 wt% PbO was added in the initial solutions for two main reasons. First, PbO was added to compensate the loss of PbO from evaporation during the calcination and sintering processes. Without this excess of PbO, the high vapor pressure of PbO can result in PbO-deficient phases after sintering. Second, it was necessary to enhance densification by forming a PbO-rich liquid phase during sintering. In this regard, the addition of excess PbO is essential to keep an initial stoichiometry and to achieve densification and the desired properties of PLZT ceramics.

The formation of the PLZT phase is shown in Fig. 3. The powder diffraction data showed that the formation occurred after thermal treatment at 400°C when, besides PLZT, a small amount of PbO phase was observed (Fig. 3a). Only the presence of a PLZT crystal phase was observed in the calcined powders (Fig. 3b). These results are in agreement with the conclusion of Kakegawa [21] and Cerqueira et al. [17], and also relate to the results of Braga and Zaghete [22].

With regard to PLZT powder morphology, the specific surface area of the powders was determined. After thermal treatment at 400°C, the surface area was 34.20 m^2/g while for calcined, milled and sieved powders it was 19.80 m^2/g. Thus, the fairly high specific area values indicated that the PLZT powders had a fine sub-micron grained structure.

3.2. PLZT sintering and hot-pressing

An analysis of the X-ray data after the first sintering step indicated the formation of a monophase PLZT system (Fig. 4). Keeping in mind the mass losses during sintering (~1.25%), it should be emphasized that the PLZT stoichiometry did not undergo any noticeable change during the sintering due to evaporation of lead oxide. Indeed, the production of a heterogeneous PLZT, $La_2Zr_2O_7$ and $La_2Ti_2O_7$ phase formed by the evaporation of lead oxide within the regions of homogeneous solid solubility [10], as suggested in the literature, was not confirmed in this study.

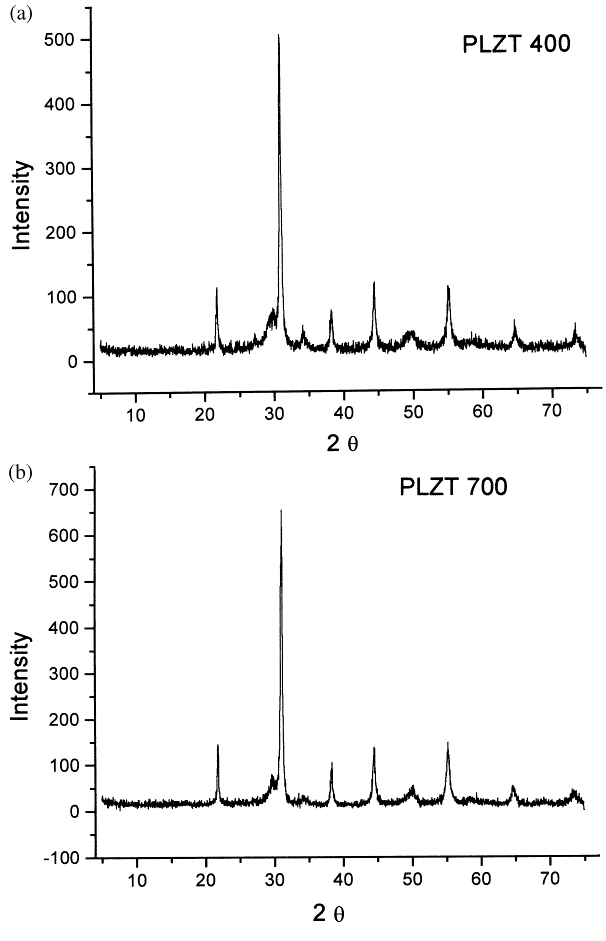


Fig. 3. The X-ray data for PLZT phase formation (a) after thermal treatment at 400°C and (b) calcinated at 700°C.

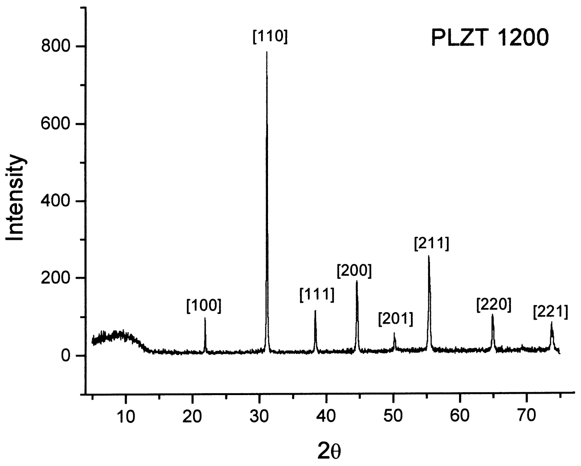


Fig. 4. The X-ray data for PLZT ceramics sintered at 1200°C in oxygen atmosphere.

The average sintered density value of 96% of the theoretical one obtained in this study strongly suggests dense PLZT ceramic materials. Accordingly, a fully dense ceramic material after hot pressing can be expected. Thus, during hot pressing of PLZT ceramics, the oxygen atmosphere exerts a strong influence since the remaining porosity is removed by oxygen diffusion through the lattice along the grain boundaries. This does not occur when nitrogen from the air remains in the pores, causing lower densification.

The results obtained with hot-pressed 9.5/65/35 ceramics indicate that the densification of ceramics occurs in several stages. Densification begins in those areas of the material where pressure is at the maximum and most of the material has already become rearranged. In fact, 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. Indeed, during the early stage of densification in an initial stage of the pressing pressure, the appearance of cracks in the ceramic material caused by high pressure and non-uniform density, as was observed in some cases, can favor the preferential plane orientation during the crystal growth process. In fact, as shown in Fig. 5, the PLZT diffraction peaks are preferentially oriented in the {111} direction. The cubic crystal structure parameters were as follows: $a=4.0522$ A and $V=66.538$ A^3.

On the other hand, increasing the hot-pressing temperature may cause the phase composition to become lead-rich and a liquid phase sintering may occur (similar to the process in PZT ceramics), leading to homogenization of PLZT ceramics and to grain growth. The calculation of lattice parameters demonstrated that the PLZT ceramics structure obtained shows a small lattice tetragonalness ($a=4.0712$ Å, $c=4.0703$ Å, $V=67.783$ Å^3) with an a/c ratio of 1.00135 similar to a pseudocubic structure (Fig. 6).

3.3. Microstructure

Ceramic compositions in the PLZT system characteristically exhibit a highly uniform microstructure consisting of randomly oriented equiaxial grains (crystallites). The microstructure of the 9.5/65/35 system according to the literature, generally has small grain sizes that may vary from 1.5 to 15 μm [4].

A distinctive feature of the PLZT materials (especially after hot pressing) is their fully dense pore-free microstructure which is devoid of any second phase. This is reflected in measured bulk densities, which routinely exceed 99.9% of the theoretical density. The existence of pores or second phases in the grain volume or the grain boundaries is undesirable since both increase light scattering and reduce optical transparency [5].

Chemical etching of the microstructure of the investigated 9.5/65/35 PLZT ceramics shows its outstanding feature to be a fairly uniform grain size after conventional

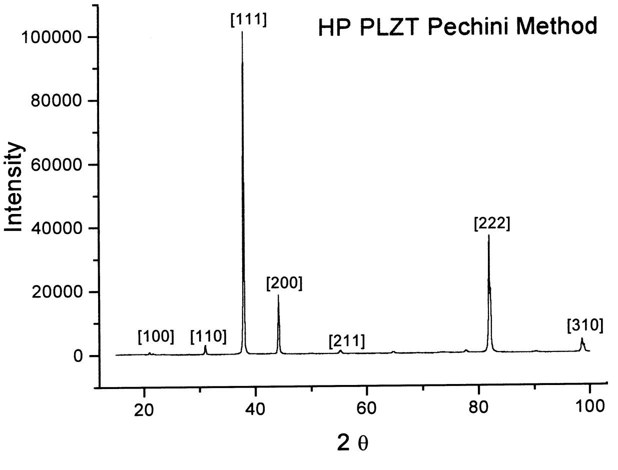


Fig. 5. The X-ray data for PLZT hot pressed at 1200°C in oxygen atmosphere and with preferential orientation.

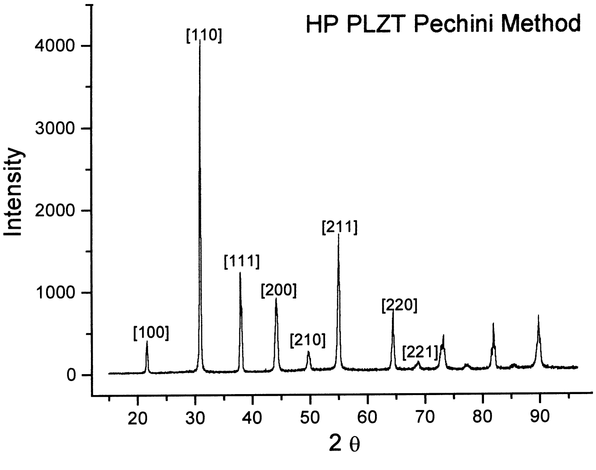


Fig. 6. The X-ray data for hot pressed 9.5/65/35 PLZT ceramics with cubic structure.

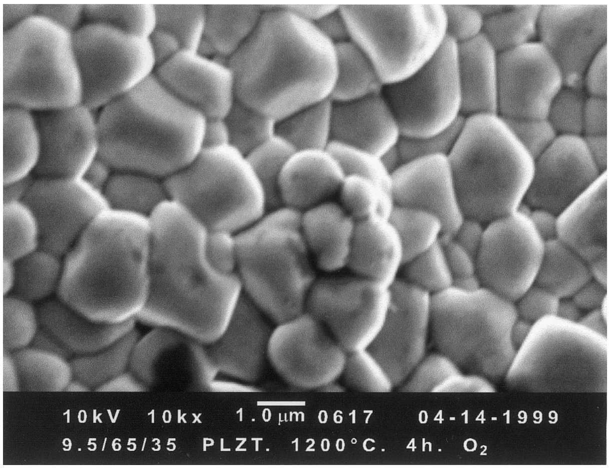
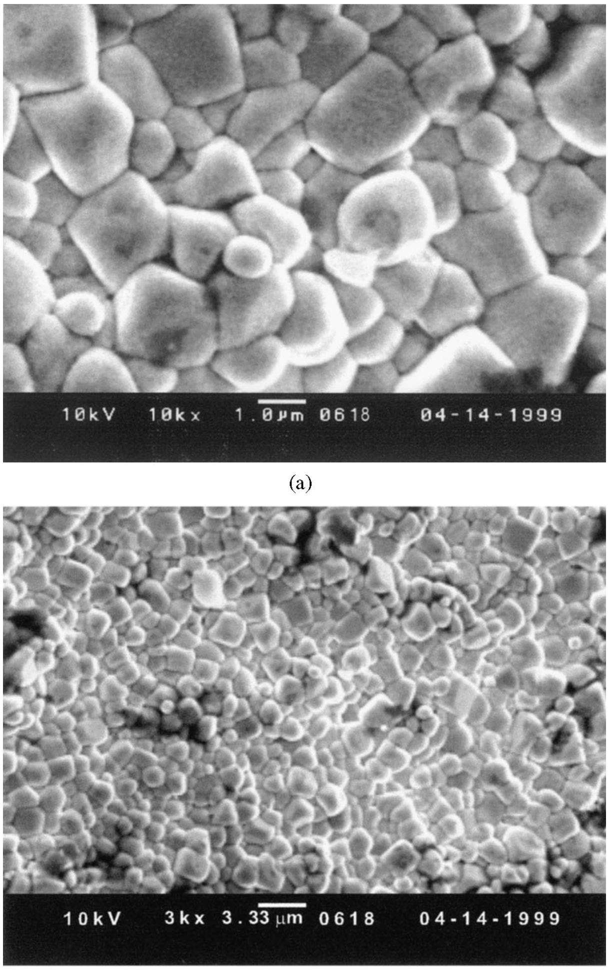


Fig. 7. The microstructure of 9.5/65/35 PLZT ceramics sintered at 1200°C.

sintering and hot pressing. After conventional sintering, the microstructure of PLZT ceramics obtained by the Pechini procedure consisted of small grains. The intercept length and its standard deviation were estimated for microstructural analysis and grain size was approximately 1.5 µm (Fig. 7). Otherwise, the change in grain size, which was approximately 1.8 µm after hot pressing, was insignificant (Fig. 8a). Moreover, the microstructure was uniform and devoid of regions that might indicate the presence of pores (Fig. 8b). Keeping in mind that the density of hot pressed PLZT ceramics was more than 98% of the theoretical density, the microstructure observed was in agreement with this. The main reason for the minor grain growth may be attributed to the fairly short time of hot pressing. Taking the above into consideration, it should be emphasized that, although the time of hot pressing was insufficient, the porosity and the liquid phase could be eliminated during the densification process. However, the hot pressing time was insufficient for grain growth.

4. Conclusion

The formation of 9.5/65/35 PLZT powders prepared with a 3.5 w% excess of PbO is obtained by the organic polymeric precursor method (Pechini process) at 700°C. The X-ray diffraction pattern shows that the paraelectric cubic phase of PLZT is formed during the first stage of sintering in an oxygen atmosphere at 1200°C for 4 h. After hot-pressing at 1200°C for 4 h in an oxygen atmosphere and at a 40 MPa pressing pressure, the PLZT structure changes from cubic to pseudo-cubic, with a tetragonalness parameter of $a/c = 1.00135$. The preferential orientation of the cubic lattice after hot pressing, observed in some cases, was favored by the appearance of internal cracks in the ceramic material caused by non-uniform density. After sintering, a uniform microstructure was obtained with an average grain size of about 1.8 µm. The minor grain growth observed after hot pressing was caused by insufficient hot pressing process time.



(a)

(b)

Fig. 8. The microstructure of 9.5/65/35 PLZT ceramics hot pressed at 1200°C (a) magn. 10 Kx, (b) magn.3 Kx.

Acknowledgements

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