INFLUENCE OF CERAMIC TECHNOLOGY ON THE
MICROSTRUCTURE AND FERROELECTRIC
PROPERTIES OF TRANSPARENT PLZT CERAMICS

M. Kosec, D. Kolar

To cite this version:
M. Kosec, D. Kolar. INFLUENCE OF CERAMIC TECHNOLOGY ON THE
MICROSTRUCTURE AND FERROELECTRIC PROPERTIES OF TRANSPARENT
<10.1051/jphyscol:1986156>. <jpa-00225586>

HAL Id: jpa-00225586
https://hal.archives-ouvertes.fr/jpa-00225586
Submitted on 1 Jan 1986

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
INFLUENCE OF CERAMIC TECHNOLOGY ON THE MICROSTRUCTURE AND FERROELECTRIC PROPERTIES OF TRANSPARENT PLZT CERAMICS

M. KOSEC and D. KOLAR

"Jožef Stefan" Institute, E. Kardelj University of Ljubljana, Jamova 39, 61000 Ljubljana, Yugoslavia

Abstract - Mixed-oxides and the coprecipitation procedure were used to prepare PLZT x/65/35 powders. Transparent samples were obtained by hot-pressing. The influence of processing parameters on the microstructure and electrical properties was studied.

I - INTRODUCTION

Properties of the transparent PLZT ceramics can be substantially altered by the fabrication process. The synthesis of homogeneous PLZT powders and the sintering process leading to pore free, controlled grain size ceramics seem to be the most critical operations during PLZT fabrication. The PLZT solid solutions can be synthetized by a high temperature solid state reaction between the PbO, La₂O₃, ZrO₂ and TiO₂ oxides [1,2]. The semi-wet [3] and the wet chemical [4,5,6,7] methods seem to take advantage of the mixed-oxide technique, giving a chemically more homogeneous samples. The PLZT ceramics can be sintered with or without pressure. Some methods used are hot-pressing in oxygen [1,2,8], hot-pressing in vacuum [9], atmosphere sintering in oxygen [10,11,12], two stage sintering combining vacuum and atmosphere sintering [13], two-stage sintering combining vacuum hot-pressing and atmosphere sintering [14], and two-stage sintering combining normal sintering and isostatic hot-pressing [15].

It is well known that the following experimental conditions have to be fulfilled in order to obtain the highest optical quality PLZT ceramics using hot-pressing. The sintering procedure has to be performed for rather a long time in an oxygen atmosphere and an excess of PbO has to be present in an initial batch composition [8]. Wolfram [16] explained hot-pressing of PLZT with an excess of PbO as a transient liquid phase sintering, accelerated by the pressure applied. The influence of the atmosphere during the hot-pressing of PLZT on its final porosity and the other properties was discussed by Haertling and Land [3]. They suggested that the remaining porosity is removed by oxygen diffusion through the lattice and along the grain boundaries, which does not occur when nitrogen from air stays in the pores. Therefore the hot-pressing cycle must be conducted in such a manner that oxygen can replace the nitrogen while the pores are still open. This procedure requires gas-tight hot-pressing equipment.
If the role of oxygen is as suggested then the same effect can be expected by sintering PLZT to closed porosity in oxygen followed by hot-pressing in air. Realizing this, the hot-press apparatus can be significantly simplified. This approach was verified using mixed-oxide as well as coprecipitated PLZT powders. The microstructural, optical and dielectric properties of prefired and air hot-pressed samples were examined and compared with those of normal oxygen hot-pressed PLZT ceramics.

II – EXPERIMENTAL WORK

Fine particle size oxides, p.a. grade (Ventron, Fluka) were mixed together according to the formula

\[ \text{Pb}_{0.905}\text{La}_{0.095}(\text{Zr}_{0.65}\text{Ti}_{0.35})_1-\frac{0.095}{4} \text{O}_3 + 3 \text{ w/o PbO}. \]

The powder mixture was calcinated at 850°C, ball milled, and heated again at the same temperature (MO-samples).

A coprecipitated (CP) mixture was prepared according to the procedure of Haertling and Land [3] using lead oxide and lanthanum acetate powders and zirconium and titanium alkoxide solutions (Ventron). Only one calcination step at 500°C and 1 hour of milling were performed. The particle size of MO and CP synthesized powders were estimated by SEM and the crystal phases were determined by XRD. The MO powder contained at least two phases whereas the CP powder was a single perovskite. Both powders differed in particle size too. SEM pictures of the MO sample showed a rather agglomerated powder with the primary crystallite sizes from 0.5 – 1 μm, whereas the SEM pictures of CP powder revealed a particle size of some microns, which were presumably very strongly bonded agglomerates.

After synthesis, both powders were treated identically. They were cold pressed (100 MPa) into pellets of about 15 mm in height and 25 mm in diameter, placed into alumina crucibles and covered with powdered PLZT. Finally the crucible was closed with an alumina cover. The samples were heated in vacuum up to 700°C and in oxygen up to 1200°C, where they were held for 2 hours. After cooling, they were arranged for hot-pressing according to the reported data [8], hot-pressed for 2 and 24 hours under the pressure of 15 MPa in an air atmosphere.

For comparison PLZT samples were prefired at 1200°C and hot-pressed in oxygen as well as directly hot-pressed in oxygen under 15 MPa for 24 hours. After hot-pressing the samples were core drilled and sliced into 0.5 mm thick disks.

For microstructural analysis the samples were diamond polished and etched thermally at 1100°C for 1/2 hour in a PbO rich atmosphere or chemically using an aqueous solution of HF and HCl. The mean intercept length and its standard deviation were estimated from photomicrographs of the samples using linear methods (MOP/AMO2 Kontron Messgeräte). Crystal phases were identified by XRD.

Optical transmittance measurements were made on 0.4 mm thick polished samples in the 350 nm to 800 nm wavelength range using a spectrophotometer (Beckmann 5240).

Samples 12 mm in diameter were lapped to a thickness of 0.2 – 0.3 mm and silvered with Du Pont 7095 paste at 590°C for dielectric and hysteresis property measurements. Dielectric properties were measured with an impedance bridge at 1 KHz. The D–E hysteresis loop was determined with a Sawyer–Tower circuit by applying a maximum field of 10 kV/cm at 50 Hz.

III – RESULTS AND DISCUSSION

The hot-pressing technique is especially indicated if the grain growth has to be adjusted. Therefore it is of primary interest to compare the microstructures of prefired air hot-pressed, prefired oxygen hot-pressed and direct oxygen hot-pressed PLZT ceramics. The mean intercept length and its standard deviation of these samples are given in Table I. From Table I (1) it can be seen that the samples prefired in oxygen and then hot-pressed have a somewhat larger grain size and
broader distribution of the grain size than the samples directly hot-pressed in oxygen, independent of the powder preparation technique used. (2) The difference is not a consequence of the different atmospheres during hot-pressing, since the microstructural parameters of the samples which were prefired and hot-pressed in oxygen are closer to the microstructural parameters of the PLZT samples which were prefired and hot-pressed in air than to those which were hot-pressed directly in oxygen. (3) The powder preparation technique has only a minor influence on the microstructural parameters, such as mean intercept length and intercept length distribution, especially if direct O₂ hot-pressing is applied. This is rather surprising taking into consideration the very different powder characteristics of the CP and MO solid solutions.

To get a better insight into the combined sintering process, the microstructural and XRD examinations of prefired and 2 hour hot-pressed samples were carried out. In Fig. 1 the microphotographs of PLZT ceramics after prefiring, 2 hour hot-pressing and 24 hour hot-pressing are presented whereas Fig. 2 shows the XRD spectra of prefired and 2 hour hot-pressed samples.

![Microphotographs of MO samples](image)

From Figure 1 and 2 it can be seen that prefiring takes place in the presence of a liquid phase. The dark regions in Fig. 1.a are partly pores as well as solidified liquid phase which was determined as a PbO based solid solution by XRD (Fig. 2a), as proposed by the other investigators [12,16]. In less than two hours of hot-pressing the porosity as well as the liquid phase (Fig. 1b, 2b) were almost completely eliminated with only minor grain growth but with a change in the

<table>
<thead>
<tr>
<th>Preparation conditions</th>
<th>Mean intercept length ( \bar{L}_3 ) (( \mu \text{m} ))</th>
<th>Standard deviation ( \sigma ) (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO, prefired, HP (air)</td>
<td>7.1</td>
<td>3.8</td>
</tr>
<tr>
<td>MO, prefired, HP (O₂)</td>
<td>7.7</td>
<td>3.9</td>
</tr>
<tr>
<td>MO, HP (O₂)</td>
<td>6.5</td>
<td>3.0</td>
</tr>
<tr>
<td>CP, prefired, HP (air)</td>
<td>8.5</td>
<td>4.0</td>
</tr>
<tr>
<td>CP, HP (O₂)</td>
<td>6.4</td>
<td>3.3</td>
</tr>
</tbody>
</table>

HP - hot-pressed
grains from the rather spheroidal into the angular shape. The next step was hot-pressing of single phase PLZT giving a completely dense microstructure (Fig. 1c).

![XRD spectra of PLZT ceramics](image)

**Fig. 2:**
XRD spectra of PLZT ceramics

- a) after prefiring,
- b) after hot-pressing for 2 hours in air

It seems to be that more mechanisms take part in the early stage of hot-pressing. It is quite probable that larger pores are removed through the rearrangement of particles in the presence of the liquid phase, as it was proposed for the HIP process of PZT ceramics [17]. Then, the liquid phase can be removed through squeezing due to external pressure. The angular shape of the particles suggested transport of materials during sintering into neck areas, consequently reducing the intersticies at three grain junctions and causing the flow of the liquid phase through the network of channels lying along the three grain junctions on the sample surface [18].

The sintering process was conducted at a rather high temperature and for a long time in order to obtain the coarse grain ceramics. Since the pronounced grain growth occurs during the hot-pressing stage of the combined sintering process, it could be expected that fine grain ceramics could also be obtained by the adjustment of the hot-pressing temperature and time. This means that the combined sintering process retains the primary advantage of the hot-pressing procedure.

In Fig. 3 optical transmission of samples was plotted as a function of wavelength.

![Optical transmission of PLZT samples](image)

**Fig. 3:**
Optical transmission of PLZT samples

The transmissions of all samples were practically identical for wavelengths above 500 nm. Results differ less than 1 %, giving an impression of comparable homogeneity of samples besides the comparable microstructure already discussed. For a $\lambda$ less than 500 nm, direct $O_2$ hot-pressed
samples have a somewhat higher absorption than prefired, hot-pressed samples. Following the tentative explanation, that adsorption in this wavelength range is influenced by the small amount of free PbO in PLZT samples [2], it may be concluded that PbO, initially present in an excess of 3 weight % in all samples, is more completely eliminated from prefired hot-pressed samples than from directly O2 hot-pressed samples.

There are no essential differences in dielectric ($\varepsilon$, $\tan \delta$) and hysteresis properties ($P_r$, $P$ at 10 KV/cm) (Table II). The results could be explained on the basis that these properties are more sensitive to microstructural characteristics which are not very different than the chemical non-homogeneity on the particle size scale eventually existing in MO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\varepsilon$</th>
<th>$\tan \delta$</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$P$ ($\mu$C/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO, prefired, HP (air)</td>
<td>4800</td>
<td>0.025</td>
<td>0.4</td>
<td>7.1</td>
</tr>
<tr>
<td>MO, HP (O$_2$)</td>
<td>4500</td>
<td>0.023</td>
<td>0.4</td>
<td>7.2</td>
</tr>
<tr>
<td>CP, prefired, HP (air)</td>
<td>4500</td>
<td>0.024</td>
<td>0.7</td>
<td>7.5</td>
</tr>
<tr>
<td>CP, HP (O$_2$)</td>
<td>4100</td>
<td>0.024</td>
<td>0.5</td>
<td>6.7</td>
</tr>
</tbody>
</table>

IV – CONCLUSIONS

We conclude that the oxygen hot-press procedure can be successfully replaced by the process of prefiring in oxygen in the presence of PbO rich liquid phase followed by air-hot-pressing. This process, as well as oxygen hot-pressing, essentially eliminates the influence of the different powder characteristics arising from different powder preparation techniques.

REFERENCES

[2] Haertling, G.H., ibid, 303