

## Microstructural design of PZT ceramics

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### Abstract

PZT ceramics,  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ , are good dielectrics and piezoelectrics. These properties reach a maximum in the morphotropic phase boundary (MPB), where phase coexistence occurs. The width of this coexistence region was found to be dependent on the size of the ferroelectric domain, through the size of the grains, within the relation that the larger the domain size, the shorter the coexistence region<sup>1</sup>. In turn, a shorter coexistence region means higher dielectric permittivities in compositions near the MPB one<sup>1</sup> and therefore, PZT ceramics with high densities and large mean grain size are necessary to obtain materials with better electrical properties. Here, a sintering additive of  $\text{PbO-SiO}_2$  was investigated to produce high dense materials with a good microstructural development, i.e., large grain sizes, at low sintering temperatures. Using 3 wt% of glassy phases, very high densities are already observed at 800°C, 82-85%. Above 950°C, the higher the  $\text{SiO}_2$  content in the glassy phase, the lower the densities. Larger amounts of the glassy phase increases the density at low temperatures and the microstructures are uniform, even after 12h of sintering time.

### 1. Introduction

The solid solutions between  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$ ,  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  or PZT, are widely used as piezoelectric material, particularly those near the boundary between the tetragonal (Ti-rich side of the pseudobinary system) and the rhombohedral (Zr-rich) phases, called the morphotropic phase boundary (MPB), because these composition show higher piezoelectric performances. PZT materials with composition near the MPB are therefore very studied<sup>1</sup>. One of the problems of the processing of these ceramics is the uncontrolled weight loss during sintering<sup>2</sup>. Weight loss is caused by the volatilization of  $\text{PbO}$  and this problem is normally dissimulated by adding an equal amount of  $\text{PbO}$  prior to sintering or by controlling the  $\text{PbO}$  partial pressure in the atmosphere by sintering in the presence of, for example,  $\text{PbZrO}_3$ <sup>3</sup>. An excess of  $\text{PbO}$  in the composition brings another benefit: at least at lower temperatures, sintering proceeds in presence of a liquid phase. Liquid phase sintering

enhances both the densification and the grain growth and therefore it is difficult to predict the final result (the enhancement of the grain growth hinders the densification process). The published work on the effect of liquid phase sintering in PZT ceramics is vast<sup>4-9</sup>, and the addition of impurities to this phase is necessary if a reduction of the grain growth is sought.

In this work it was tried another approach for the use of liquid phase sintering aid: it was deliberately introduced a glassy phase in the PZT composition. These glassy phases were based on the PbO-SiO<sub>2</sub> binary system, since they could present the following advantages: they are PbO-rich, which in principle could compensate losses of PbO from the PZT phase; it has never been reported that silica is dissolved in the PZT lattices, which is important to maintain the efficiency of this additive during all the sintering process and to keep the original electrical characteristics; and liquid phase are formed at temperatures as low as 760°C (figure1). The results presented here are those of the ceramic processing only; those of the electrical measurements will be published in a forthcoming paper.

## 2. Experimental procedure

The PZT ceramics studied in this work have the composition of Pb(Zr<sub>0.525</sub>Ti<sub>0.475</sub>)O<sub>3</sub> (PZT525), corresponding to the morphotropic phase transition between the rhombohedral Zr-rich phase and the tetragonal Ti-rich phase. In order to investigate the effect of SiO<sub>2</sub> additives on the densification of the sintered PZT ceramics, 3 and 5 wt% of (96 wt% PbO + 4 wt% SiO<sub>2</sub>) and (92 wt% PbO + 8 wt% SiO<sub>2</sub>) liquid phase compositions were added to the initial PZT content. First, a glass was prepared using the raw materials with reagent-grade PbO (Alfa-Aesar 99.9%) and SiO<sub>2</sub> (BDH 99.9%). The powder was mixed for 3 hours in a planetary ball milling (Restch, USA) using Teflon jars with alcohol medium and zirconia balls. The slurry was dried in an oven at 100°C for 24 hours? After mixing, the mixture was placed in an alumina crucible and melted in an electric furnace. The glass melted very rapidly at 900 °C during 30 min. Once the melting was complete, the crucible was removed from the furnace and the molten glass was poured into cold distilled water. After drying, the glass was grounded in an agate mortar and then sieved through a 230 mesh screen.

The samples were prepared by traditional ceramic technique, starting from >99% of pure reagent-grade PbCO<sub>3</sub> (Merck), TiO<sub>2</sub> (Merck), ZrO<sub>2</sub> (Aldrich). A mixture of the starting powders prepared for 3 hours in the planetary ball mill in teflon jars and zirconia balls. The

slurry was dried in an oven at 100 °C for 24 hours, and then calcined at 900 °C for 2 hours. The calcined mixture was grounded in an agate mortar and the glass was added, after was mixed and grounded for 12 hours. The fine powder was pressed into disks of 10 mm diameter at 460 MPa. Finally, the disks were fired in covered alumina crucibles at various sintering temperatures between 800 °C and 1250 °C and different sintering times from 1 to 12 hours. The atmosphere was enriched in PbO vapor using PbZrO<sub>3</sub> powder with 3 wt% excess of PbO.

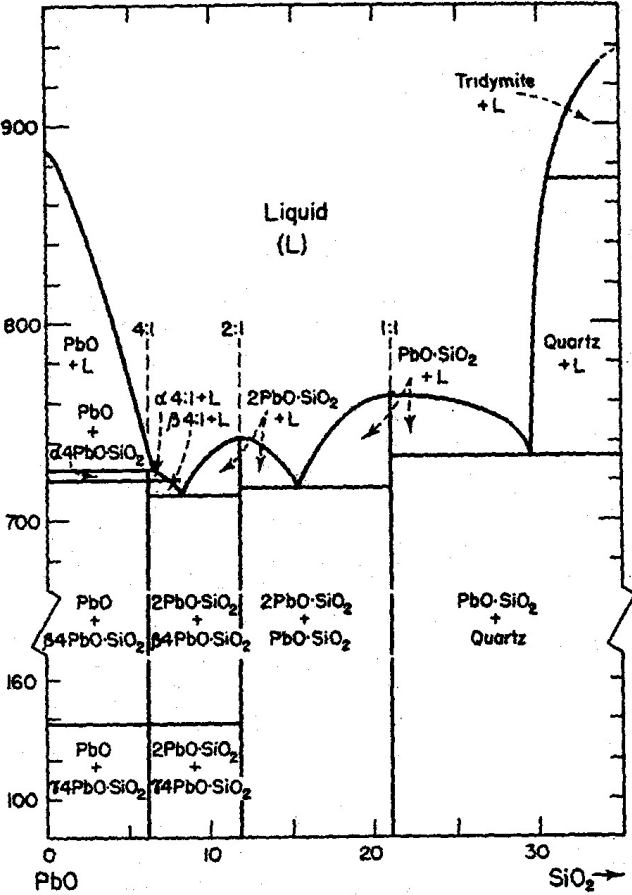


Fig.1. PbO-SiO<sub>2</sub> phase diagram.

The calcined powder and sintered ceramics were analyzed by X-ray diffraction analysis (XRD) using a Rigaku/New diffractometer (CuK<sub>α</sub> radiation), to verify the present phases. A Hitachi-S4100 scanning electron microscope (SEM) was employed to study the morphology and the grain size of the sintered ceramics. The density of the green compacts was measured by geometric (diameter and thickness) method. For sintered samples, the density was measured from Arquimede's method. The loss weight loss due to PbO volatilization were also **countervailed** by mass determination.

### 3. Results and Discussion

Figure 2a) shows the variation of the relative density of the PZT samples with 3% of glassy phase with sintering temperature, for each one of the glassy phase composition. It is observed that an appreciable densification occurs at 800°C ( $\rho=82-86\%$ ), for both compositions, which is attributed to the effect of the glassy phases since for pure PZT, higher temperatures,  $\sim 1200^\circ\text{C}$ , are needed to attain this level of relative density<sup>10, 11</sup>.

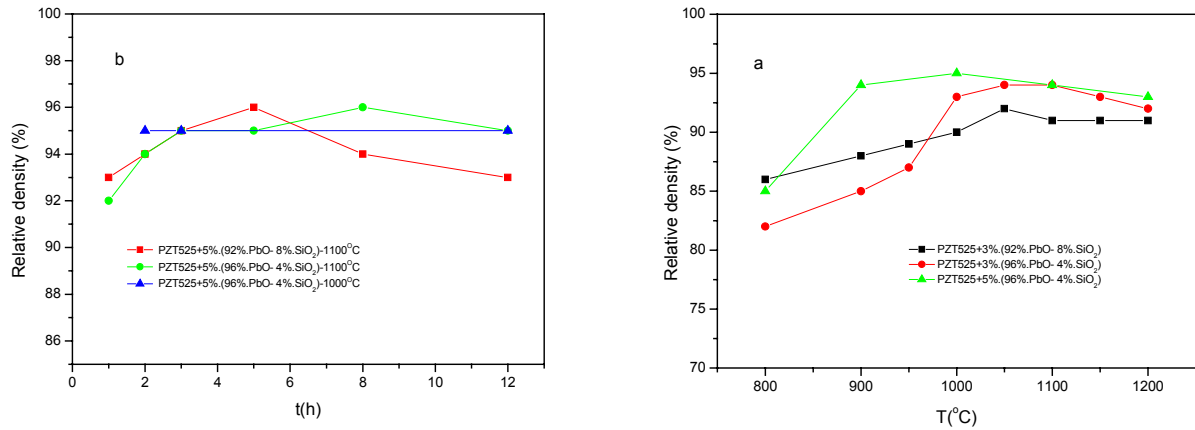


Figure 2. Variation of the relative density of the sintered samples as a function of: a) the sintering temperature for 2h of holding time; b) the holding time at a constant temperature.

A good wettability for the glassy phase and a high solubility of the solid phase in the liquid, may be presumed from the high efficiency of the glassy phase on the densification process. The densification is higher for the glassy composition with a higher content of SiO<sub>2</sub>, up to 950°C, but the maximum attained density,  $\rho_{\text{max}}$ , is lower. Since the systems are not in chemical equilibrium before sintering, it is reasonable to assume that the appearance of the liquid phases correspond to those temperatures of the PbO-SiO<sub>2</sub> diagram. Looking for in the diagram one concludes that for  $T \geq 800^\circ\text{C}$  both glassy phase compositions are in the liquid state and therefore equivalent liquid amounts must be present. A decrease of the viscosity of the liquid phase or an increase of the solubility of the solid phase could account for the observed higher densification up to  $\sim 950^\circ\text{C}$  with increasing the amount of SiO<sub>2</sub>. For higher temperatures large weight losses occurred for the glassy composition richer in SiO<sub>2</sub> (figure 3a)).

Taking the case of the higher achieved density, which was observed for the 4% of SiO<sub>2</sub> glassy phase, we have observed the effect of the amount of the phase on the density, in figure 2a). As expected, the higher the amount of the glassy phase, the higher the densities of the samples. It is again observed a maximum density,  $\rho_{max}$ , but now at lower temperatures.

The variation of the relative density with the time in figure 2b), shows that at 1000°C a constant value of the density is attained for the glassy composition with a lowest SiO<sub>2</sub> content whereas at 1100°C the density slightly increases up to 8 h. For the 8% SiO<sub>2</sub> content of glassy phase the density at 1100°C increases up to 5 h and decreases for longer times. Again, large weight losses are observed after 5 h, figure 3b), for the samples with the richer SiO<sub>2</sub> glassy phase which may account for the observed decreasing in the correspondent density.

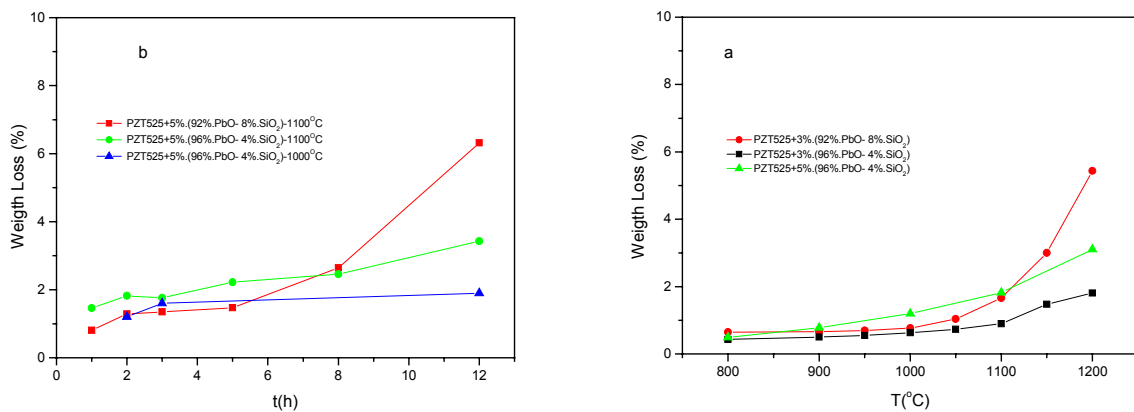


Figure 3. Variation of the weight losses as a function of: a) the sintering temperature for 2 h of holding time; b) the holding time at a constant temperature.

The microstructures of the samples with 5% of the glassy phase with the lower SiO<sub>2</sub> content, sintered at 1100 °C, for 2 h and for 12 h, are presented in figure 4a) and b), respectively. Both samples show very uniform microstructures with well developed grains. The grain growth occurred without pore separation and residual pores are situated in the junction of three or more grains. Uniform microstructures, like the ones here obtained, with well developed grains and reduced porosity, can be obtained in pure PZT sintered at higher temperature, i. e.  $T \geq 1200^\circ\text{C}$ . However, the use of additives which lower the sintering temperature lead either to finer microstructures, as is the case of PbO-WO<sub>3</sub><sup>12</sup>, V<sub>2</sub>O<sub>5</sub><sup>13</sup>, and CuO<sup>14</sup> additives, a result in non-uniform compacts with large residual pores, like in the case of PbO in excess<sup>15</sup>.

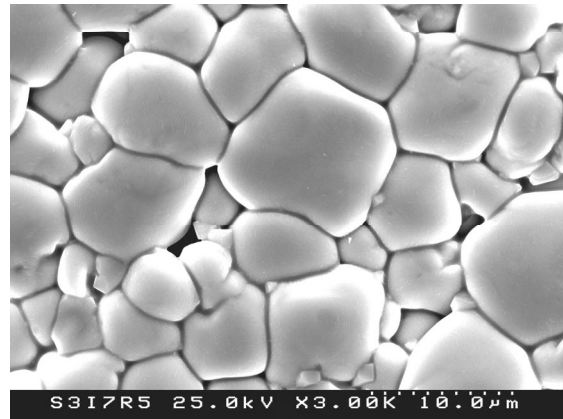
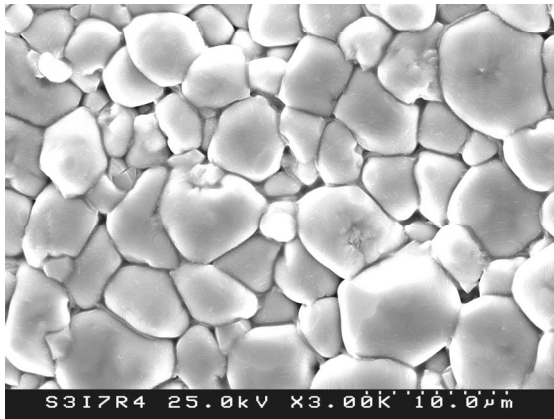


Figure 4. SEM micrographs of fracture surfaces of PZT with 5 % of glassy phase (92%PbO+ 4% SiO<sub>2</sub>) samples sintered at 1100°C during: a) 2 h; b)12 h.

It can be also observed in figure 4a) that the grains are surrounded by a viscous phase, well infiltrated in the grain junctions and showing a good adaptation to the grain surfaces as expected in face of its good efficiency in the promotion of the densification. In figure 4b), for 12 h, larger grains and a reduction in the amount of the viscous phase are observed in accordance with the determined larger weight losses for longer sintering times (figure 3b).

#### 4. Conclusions

It has been shown that PbO-SiO<sub>2</sub> glassy phases with a low SiO<sub>2</sub> content (4-8 wt%) are very efficient in the promotion of the densification of PZT, leading to densified samples at lower temperatures than those used for pure PZT. The increase of the amount of SiO<sub>2</sub> from 4-8% increases the densification up to ~950°C but reduces the maximum attained density due to large weight losses at higher temperatures or longer times. Increasing the amount of glassy phase from 3 to 5 wt% improves the density and reduces the sintering temperature. The sintered samples present very uniform microstructures with well-developed grains, without the occurrence of abnormal grain growth, pore separation or the formation of large pores.

#### References

1. M.RSoares, A.M.R.Senos, P.Q.Mantas, J.Eur.Ceram. Soc., 20,321-34 (2000).
2. R.L.Holman, and R.M.Fulrath, J.Appl.Phys, 44(12) 5227 (1973)
3. A.I.Kingon, and B.Clark, J.Am.Ceram.Soc.66(4) 253 (1982).part.I.
4. BS. Purwasasmita, T.Kimura, J.Ceram.Soc.Jpn., 109(1) 4 (2001)

5. BS. Purwasasmita, T.Kimura, J.Ceram.Soc.Jpn., 108(11) 966 (2000)
6. SF.Wang, TCK.Yang, YR.Wang, Y.Kuromitsu, Ceram Intern., 27(2) 157 (2001)
7. CH.Wang, and L.Wu, Jpn.J.Appl.Phys.**32(7)** 3209 (1993) part.I.
8. S.Takahashi, Jpn.J.Appl.Phys.**19(4)** 771 (1980)
9. G.Zhilun, L.Longtu, G.Suhua, and Z.Xiaowen, J.Am.Ceram.Soc., **72(3)** 486 (1989)
10. Z.He, J.Ma, J.Phys.Chem.Soc.64 177 (2003)
11. S.Kim, G.S.Lee, T.R.Shrouf, S.Venkataramani, J.Mater.Sci, 26 4411 (1991)
12. E.R.Nielsen, E.Ringgaard, and M.Kosec, J.Eur.Ceram. Soc., 22 1847 (2002)
13. D.E.Wittmer and R.C.Buchanan. J.Am.Ceram.Soc., **64(8)** 485 (1981)
14. D.L.Corker, R.W.Whatmore, E.Ringgaard, and W.W.Wolny, J.Eur.Ceram. Soc., 20 3039 (2000).
15. A.I.Kingon, and B.Clark, J.Am.Ceram.Soc.66(4) 256 (1982).part.II.