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Microstructural design of PZT ceramics

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Abstract

PZT ceramics, $Pb(Zr_{1-x}Ti_x)O_3$, are good dielectrics and piezoelectric materials. 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 [1][Soares, M. R., Senos, A. M. R. and Mantas, P. Q., Phase coexistence region and dielectric properties of PZT ceramics. *J. Eur. Ceram. Soc.*, 2000, **20**, 321–334].[1] In turn, a shorter coexistence region means a higher dielectric permittivity in compositions near the MPB zone [1][Soares, M. R., Senos, A. M. R. and Mantas, P. Q., Phase coexistence region and dielectric properties of PZT ceramics. *J. Eur. Ceram. Soc.*, 2000, **20**, 321–334][1] 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 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, high densities are already observed at 800 °C, 82–85%. Above 950 °C, the higher the 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 12 h of sintering time.

Keywords: PZT; Sintering; Microstructure

1. Introduction

The solid solutions between $PbZrO_3$ and $PbTiO_3$, $PbZr_xTi_{1-x}O_3$ or PZT, are widely used as piezoelectric materials, particularly those near the boundary between the tetragonal (Ti-rich side of the pseudo-binary system) and the rhombohedral (Zr-rich) phases, called the morphotropic phase boundary (MPB), because these compositions show higher piezoelectric performances. PZT materials with composition near the MPB are therefore very studied.[2]

One of the problems of the processing of these ceramics is the uncontrolled weight loss during sintering. Weight loss is caused by the volatilization of PbO and this problem is normally dissimulated by adding an equal amount of PbO prior to sintering or by controlling the PbO partial pressure in the atmosphere by sintering in the presence of, for example, $PbZrO_3$.[3] An excess of PbO in the compositions brings another benefit: at least at lower temperatures, sintering proceeds in the presence of a liquid phase. Liquid phase sintering affects both the densification and the grain growth processes and therefore it is difficult to predict the microstructural trajectory during sintering. The published work on the effect of liquid phase sintering using various additives in PZT ceramics is vast[4–10] but an uniformly dense material with large grains and controlled stoichiometry is hard to achieve with the previous studied additives.

In this work it was tried another approach for the use of a liquid phase sintering aid: it was deliberately introduced a glassy phase in the PZT composition. These glassy phases were based on the PbO–SiO_2 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 phases are formed at temperatures as low as 720 °C with a

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low SiO_2 content, ~8 wt% (Fig. 1). 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 had the composition of $Pb(Zr_{0.525}Ti_{0.475})O_3$, corresponding to the MPB. The following compositions (Fig. 1) were used to promote a liquid phase sintering in the material: 96%PbO + 4%SiO_2 and 92%PbO + 8%SiO_2 (w/w). The amount of glassy phase were 3% and 5% (w/w). The glassy phases were prepared from reagent-grade PbO (Alfa-Aesar 99.9%) and SiO_2 (BDH 99.9%). The powders were mixed for 3 h in a planetary ball milling (Restch, USA) using Teflon jars with alcohol medium and zirconia balls. The slurries were dried in an oven at 100 °C for 24 h. After drying, the mixtures were placed in an alumina crucible and melted at 900 °C during 30 min in an electric furnace. Once the melting was complete, the crucible was removed from the furnace and the molten glass was poured into cold distillated water. After drying, the glass was grounded in an agate mortar and then sieved through a 230 mesh screen.

The PZT powder was prepared using the reagents $PbCO_3$ (Merck), TiO_2 (Merck), and ZrO_2 (Aldrich), with high purity grade, >99%. The powders were mixed for 3 h in the planetary ball milling, in Teflon jars with alcohol medium and zirconia balls. The slurry was dried in an oven at 100 °C for 24 h, calcined at 900 °C for 2 h and grounded in an agate mortar. The glassy phase was then added, and all together was mixed and grounded for 16 h. The powder was uniaxially 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, for different sintering times from 1 h to 12 h. The atmosphere was enriched in PbO vapor using $PbZrO_3$ powder with 3 wt% excess of PbO.

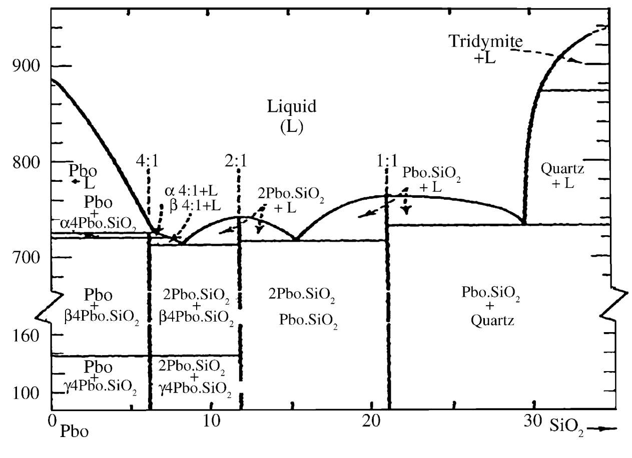

Fig. 1. PbO–SiO_2 phase diagram.[11]

The calcined powders and the sintered samples were analyzed by X-ray diffraction analysis (XRD) using a Rikagu/New diffractometer (Cu Kα radiation). A Hitachi-S4100 scanning electron microscope (SEM) was used to observe the microstructure of the sintered ceramics. The density of the green compacts was calculated by their weight and geometry. For sintered samples, the density was determined by the Archimedes' method. The results of the density will be expressed in terms of their relative values to $\rho = 8.0\ g/cm^3$, the theoretical density of the used PZT composition, in order to have an idea about the porosity of the system. The compacts had 63 ± 1% of relative green density, 2 μm of average particle size and no other crystalline phases besides PZT were detected by XRD.

3. Results and discussion

Fig. 2a shows the variation of the relative density of the PZT samples with 3% of glassy phase with sintering temperature, for each of the glassy phase composition. It is observed that an appreciable densification occurs at 800 °C (ρ = 82–86%), for both compositions, which is attributed to

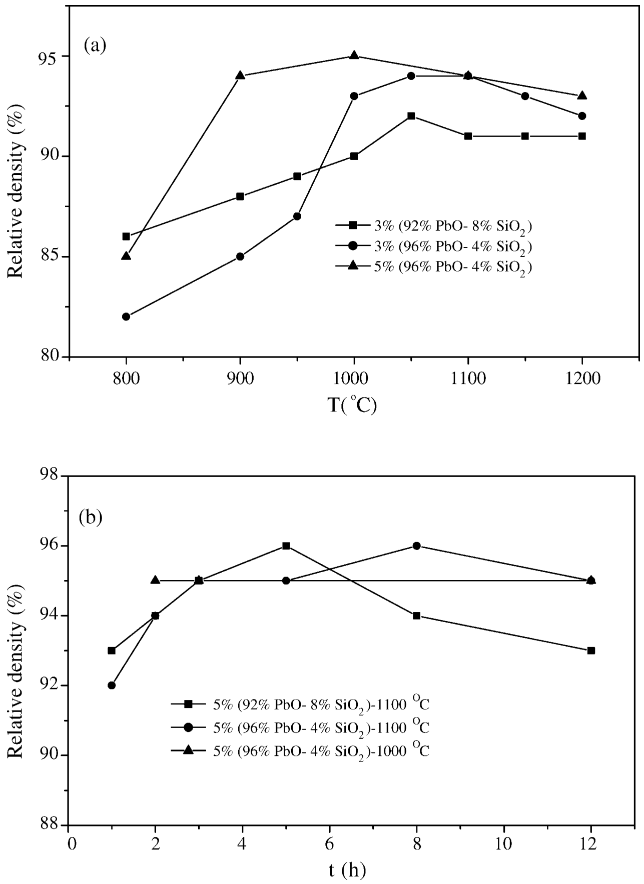

Fig. 2. Variation of the relative density of the sintered samples as a function of: (a) the sintering temperature for 2 h of holding time; (b) the holding time at constant temperature.

the effect of the glassy phases since, for pure PZT, higher temperatures, ∼1200 °C, are necessary to attain this level of relative density.[12,13]

A good wettability of 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 to make the materials dense. The densification is higher for the glass composition with a higher content of SiO_2, up to 950 °C, but the maximum attained density, ρ_{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 corresponds to those temperatures of the PbO–SiO_2 diagram. Looking for in the diagram, one concludes that for $T \geq 800\,^{\circ}$C both glass compositions are in the liquid state and therefore equivalent liquid amounts must be present in the PZT. 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 ∼950 °C with increasing the amount of SiO_2. For higher temperatures large weight losses occurred for the glass composition richer in SiO_2 (Fig. 3a).

Taking the case of the higher achieved density, which was observed for the 4% of SiO_2 glassy phase, we have observed the effect of the amount of the phase on the density, in Fig. 2a. As expected, the higher the amount of the glassy phase, the higher the densities of the samples. It is again observed a maximum in density, ρ_{max}, but now at lower temperatures.

The variation of the relative density with time, in Fig. 2b, shows that at 1000 °C a constant value of the density is attained for the glassy composition with the lowest SiO_2 content whereas at 1100 °C the density slightly increases up to 8 h. For the 8% SiO_2 content the density at 1100 °C increases up to 5 h and decreases for longer times. Again, large weight losses are observed after 5 h (Fig. 3b) for the samples with the richer SiO_2 glassy phase which may account for the observed decreasing in the corresponding density. The work of Purwasasmita and Kimura[14] also shows that the reactivity between PZT and PbO–SiO_2 glasses with higher contents of SiO_2 (40–60 mol%) is largely affected by the amount of SiO_2 in the glass composition.

The microstructures of the samples with 5% of the glassy phase with the lower SiO_2 content, sintered at 1100 °C, for 2 h and for 12 h, are presented in Fig. 4a and b, respectively. Both samples show very uniform microstructures with well developed grains. The grain growth occurred without pore separa-

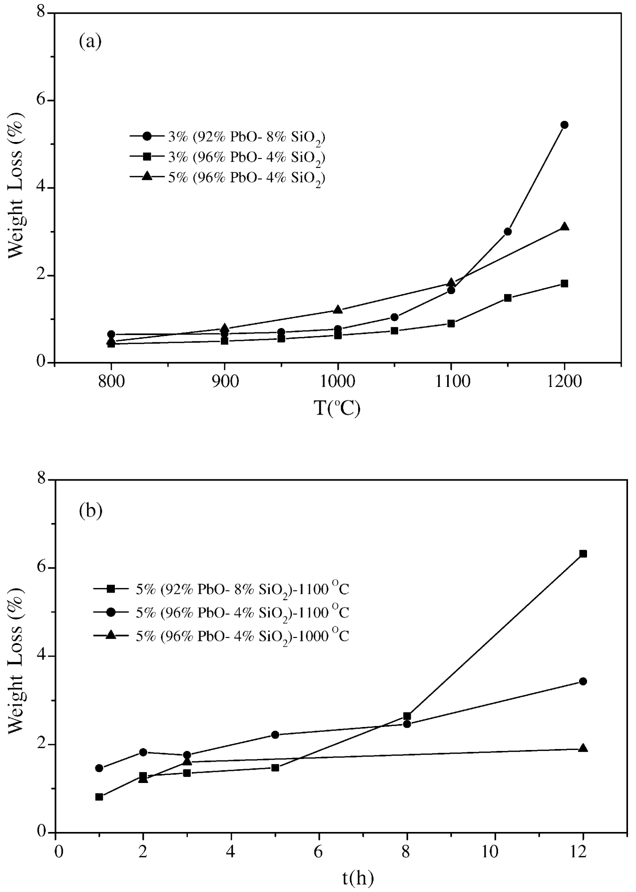

Fig. 3. Variation of the weight losses as a function of: (a) the sintering temperature for 2 h of holding time; (b) the holding time at a constant temperature.

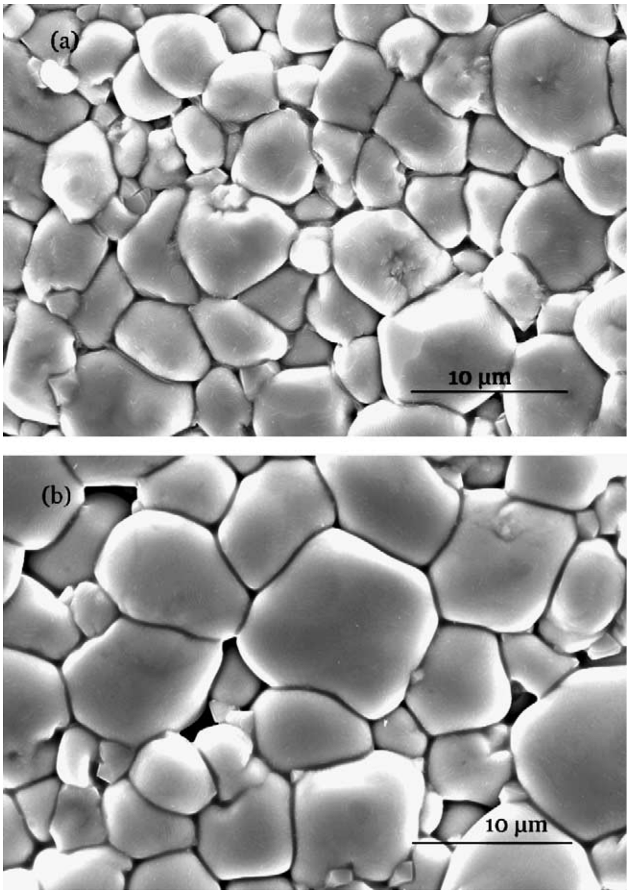

Fig. 4. SEM micrographs of fracture surfaces of PZT with 5% of glassy phase (92%PbO + 4% SiO_2) samples sintered at 1100 °C during: (a) 2 h; (b) 12 h.

tion 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., for $T \geq 1200\,^{\circ}\mathrm{C}$. However, the use of additives which lower the sintering temperature lead either to finer microstructures, as is the case of PbO–WO_3,[7] V_2O_5,[8] and CuO[9] additives, or to non-uniform compacts with large residual pores, like in the case of PbO in excess.[10]

It can be also observed in Fig. 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 Fig. 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 (Fig. 3b).

4. Conclusions

It has been shown that PbO–SiO_2 glassy phases with a low SiO_2 content (4–8 wt%) are very efficient in the promotion of the densification of PZT, leading to dense samples at lower temperatures than those used for pure PZT. The increase of the amount of SiO_2 from 4% to 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 wt% 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.

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