

## EFFECT OF SMALL AMOUNTS OF LEAD OXIDE ON THE PIEZOELECTRIC PROPERTIES OF SOFT-TYPE PZT CERAMICS

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*Soft type piezoceramics with stoichiometric composition  $Pb(Nb_{0.02}Li_{0.007}Zr_{0.51}Ti_{0.463})O_3$  were prepared by the usual ceramic technique. Several samples with lead oxide in excess of up to 4 % wt. were prepared. Careful measurements of the density of the sintered disc-shaped materials and the piezoelectric properties (piezoelectric voltage constant,  $g_{31}$ , piezoelectric strain constant,  $d_{31}$ , dielectric permittivity,  $\epsilon_r$ , electromechanical planar coupling coefficient,  $k_p$ , mechanical quality factor,  $Q_m$ ) were carried out. All piezoelectric properties were spectacularly enhanced by addition of small amount of lead oxide. The maximum values were reached for samples containing 2-3 wt.% PbO, regardless the sintering temperature. The experimental results were discussed in terms of the two competitive processes: structural rearrangement and dissolution-reprecipitation, which are active in the sintering process in the presence on the excess PbO liquid phase. The last process seems to be dominant and explains the improvement on the piezoelectric properties of PZT materials.*

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*Keywords:* PZT ceramics, Lead oxide, Piezoelectric properties.

### 1. Introduction

Lead titanate - lead zirconate solid solutions, currently named PZT ceramics, are extensively used as piezoelectric transducers in various industries [1,2]. The performances of such transducers depend to a great extent on the quality and properties of ceramic materials used. Consequently, efforts are being made towards improving the quality of the sintered ceramics for optimum piezoelectric properties.

Sinterability is a major step in the fabrication process of such ceramic bodies, since during it a high density body can be formed. Sintering takes place at high temperatures where the loss of the more volatile components (such as PbO) cannot be avoided. This leads, to some extent, to the degradation of the piezoelectric properties. Therefore a careful control of sintering temperature and PbO loss, becomes important in obtaining high quality piezoelectric ceramics.

The PbO loss during sintering can be controlled by using either powders of the same composition as the sintered material [3,4], or low melting substances that allow for the diminishing of the sintering temperature [5,11] and, consequently, the limitation of the volatilization process.

Both densification and PbO loss in PZT ceramic bodies can be controlled by adding PbO in excess [12-16] which, at high temperatures, forms a liquid phase that enhances the densification and improves the piezoelectric properties. Nevertheless, in some cases, it may affect, uncontrollably, the stoichiometry of the material. Kakegawa et al. [17] found that the solubility of  $TiO_2$  in liquid PbO is much higher than that of  $ZrO_2$  and this causes changes in composition of the perovskite phase. To study this process they used high amounts of PbO (up to 20 at.%) [18-20]. Scarce information exists

about the effect of small amounts of excess PbO on the piezoelectric properties [21-22]. Small amounts of lead oxide could have a beneficial effect, because it cannot drastically change the composition and also it may form the necessary liquid phase that could enhance the densification and the piezoelectric properties.

The present study reports on the results of the effect of small amounts (up to 4 wt.%) of excess PbO on the main piezoelectric properties of a soft type PZT ceramic.

## 2. Experimental procedure

### 2.1. Sample preparation

Reagent grade oxides with purities of 99.9 % were used to prepare a soft type piezoelectric material with the stoichiometric formula  $\text{Pb}(\text{Nb}_{0.02}\text{Li}_{0.007}\text{Zr}_{0.51}\text{Ti}_{0.463})\text{O}_3$  by the usual ceramic technique. The raw materials were wet mixed (with methanol) in a planetary ball mill in agate vessels with agate balls, for 2 hours and the slurries were dried at 80-100 °C with continuous mechanical stirring to prevent the separation of the heavy components. The powders were calcined at 850 °C and 900 °C for 2 hours in air, in high density alumina crucibles with an intermediate milling for 2 hours.

Portions of this powder were mixed with 1,2,3 and 4 wt.% PbO, respectively, and wet milled for 6 hours. The average grain size of these powders, as measured by means of an optical microscope was less than 1 µm. The mixed powders were uniaxially pressed into discs of 15 mm diameter and about 2 mm thick, in a steel die, at pressures of ~75 MPa. The discs were buried in powder of the same composition and sintered in lidded alumina saggars at various temperatures between 1150-1350 °C for 3 hours.

The sintered samples were mechanically processed to a final size of 10 mm diameter and 1 mm thickness on a special lapping machine using SiC abrasive. The diameter-to-thickness ratio of 10:1 was used to fulfill the requirements of the IRE Standards [23,24] for a correct measurement of the piezoelectric properties. After ultrasonically cleaning and heating at 700 °C for 1 hour, the samples were chemically electroded with Ni and poled in a silicone oil bath at 240 °C under an electric field of 3 kV/mm.

### 2.2. Measurements

The piezoelectric properties were determined by means of resonance-antiresonance method using a Hewlett Packard HP 4194A Impedance Gain/Phase Analyser. The densities were estimated both by Archimedes method and geometrical measurements. The sample microstructure was characterized by means of an optical microscope. The surfaces were prepared by polishing and lapping with alumina powders (3000 to 200 Å particle size) and then thermally etched at 1200 °C for 5 minutes.

The X-Ray diffraction analyses were performed in a Siemens Kristalloflex IV diffractometer provided with a copper target tube and a graphite monochromator in the diffracted beam. A water cooled scintillation counter was used in the detection of the X-ray quanta.

## 3. Results and discussion

Fig. 1 shows the effect of excess PbO on the bulk density of the samples sintered at three different temperatures for 3 hours. One may simply observe an increase of the density with increasing amount of PbO until 2 %, followed by a plateau and a slight tendency of decreasing (less than 0.1 %) for the largest addition: 4 % PbO. The increase is more pronounced for lower sintering temperatures as expected in the case of using sintering aid additives [8-11, 25]. The maximum of the density obtained for each sintering temperature is centred between 2 and 3 % PbO and the maximum increasing ratio for each sintering temperature against the samples without PbO ranged between 2.3 % and 1.4 % respectively. The highest density was obtained for the sample with 3 % PbO sintered

at 1250 °C for 3 hours. The increase was 2.3 % and the maximum density represents about 98 % from the theoretical density (taken as 8 g/cm<sup>3</sup>).

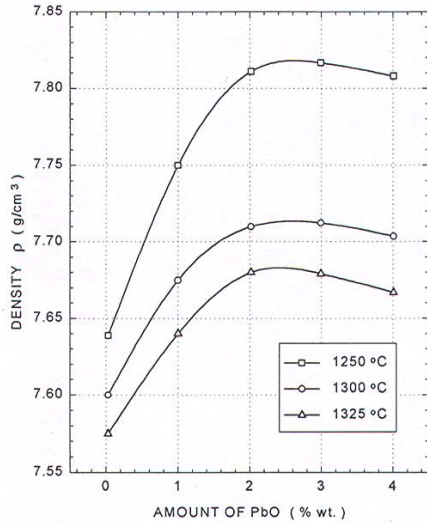


Fig. 1 Density as a function of the amount of excess PbO for samples sintered at three temperatures (specified in the insert) for 3 hours.

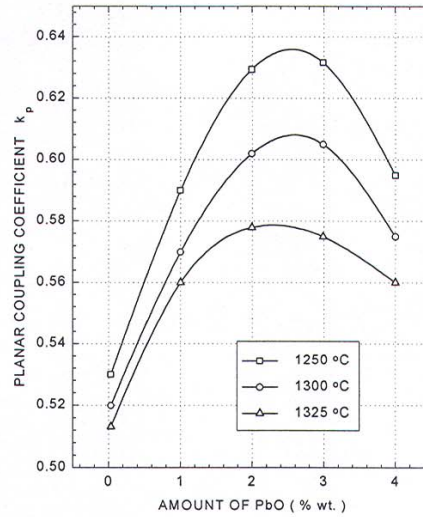


Fig. 2 The behaviour of the electromechanical planar coupling coefficient  $k_p$  against the amount of excess PbO for samples sintered at three different temperatures.

The most interesting fact brought about by this rather slight enhancement of the density, of only 1.5-2% for an excess PbO of 2-3% is the spectacular improvement of the main piezoelectric properties of materials. Fig. 2 shows the behaviour of the electromechanical coupling factor  $k_p$  as a function of PbO content. One can see that for samples sintered at 1250°C,  $k_p$  reaches a maximum value of ~0.64, the increase being about 20% compared with samples without PbO.

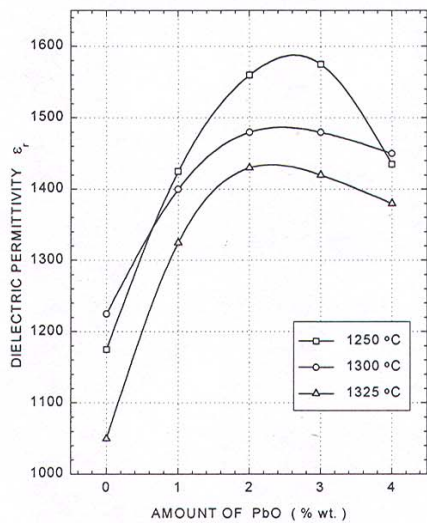


Fig. 3 Relative dielectric permittivity,  $\epsilon_r$ , as a function of excess PbO for samples sintered at three different temperatures.

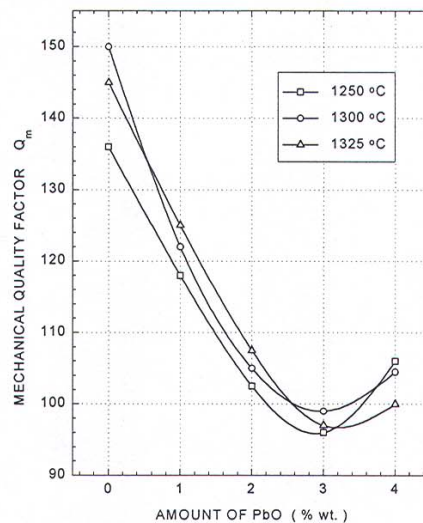


Fig. 4 Mechanical quality factor  $Q_m$  versus excess PbO for samples sintered at three different temperatures.

The relative dielectric constant  $\epsilon_r$ , shown in Fig. 3, increases with 35-37 % for samples containing 2-3 % PbO. A similar improvement of mechanical quality factor  $Q_m$  is shown in Fig. 4; it decreases from about 150 for stoichiometric samples to less than 100 when PbO is added.

Finally, both, voltage,  $g_{31}$  and strain,  $d_{31}$ , constants increase with about 20 % (Fig. 5) and 50 % (Fig. 6) respectively, for samples containing 2-3% PbO.

The enhancement of the piezoelectric properties of the PZT samples doped with such a small amount of PbO, added to the calcined powder, seems to be very interesting and it cannot be explained by the simple mechanism of densification only, especially due to the fact that all these properties show a rather pronounced extremum centred around 2-3 % PbO, followed by an important decrease for higher amounts of PbO, while the density seems to reach a saturation above 2 % PbO, followed by a decrease of less than 0.1 %.

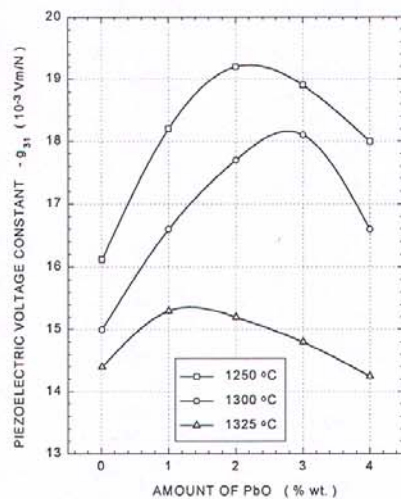


Fig. 5 Piezoelectric voltage constant  $g_{31}$  as a function of excess PbO for samples sintered at three different temperatures.

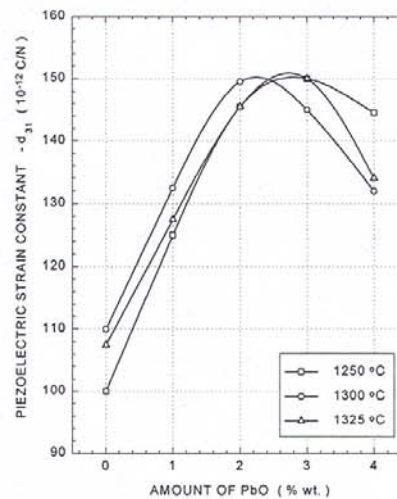


Fig. 6 Piezoelectric strain constant  $d_{31}$  versus excess PbO for samples sintered at three different temperatures.

The effect of excess PbO on the densification process was so far reported by several authors but no special attention was paid to the effect of small doping on the dielectric properties. Thus, Kingon and Clark [15] studied the densification kinetics on PZT type materials doped with PbO up to 19 at.%, but they did not mention how the piezoelectric properties change as a function of PbO amount or sintering temperature. More recently Kakegawa et al. [17] studied the possible compositional changes produced by the excess PbO, as high as 30 % mol but no mention was made concerning the properties modification brought about by this excess PbO. Ohtaka [11] used an eutectic composition of nearly equal amounts of PbO and PbF<sub>2</sub> as additive to enhance the sintering properties and to lower the sintering temperature of a PZT type materials and found that about 3 wt.% of this additive makes the density reach a maximum value representing 98 % of the theoretical density but again they did not report on the modification of the piezoelectric properties due to the presence of these additives.

It is commonly accepted that any excess PbO added to a PZT powder forms a liquid phase above 884 °C (the melting point of PbO [26]) in the process of sintering. This liquid phase enhances the densification process of the PZT material by a number of known mechanisms such as rearrangement, dissolution reprecipitation and coalescence [27]. The contribution of each mechanism depends on time and temperature of sintering as well as on the material composition and particle shape, but mostly, on the amount of liquid PbO. Low liquid content cannot fill in the pore volume and does not wet enough the particles to allow their rearrangement. For higher amounts of liquid, in turn, the liquid structure is continuous, the wetting can be complete, and both the particles arrangement and the accompanying processes take place easier.

Now, let us pay attention to two of the main densification processes: rearrangement and dissolution-precipitation involved in the initial and intermediate stage of sintering. It is easy to assume that as soon as the PbO phase melts, the rearrangement of the particles takes place rapidly in several minutes [15], this process being more intense if enough liquid is present. Therefore, the densification must be proportional with the amount of PbO added and this is clearly shown in Fig. 1. The saturation above 2 %, remains unclear because 2-3 % PbO or even more is not enough to fill in the whole pore volume of the sample so as to allow the particles to move on easily. Indeed, an estimation of the pore volume in the green, pressed samples gives a value of about  $7 \text{ cm}^3$  per 100 grams of material. Two or three percent of PbO added represent a volume of only  $0.22$  or  $0.33 \text{ cm}^3$ , respectively which is by far not enough to fill in the pores volume present in the sample. Anyhow, the presence of the liquid phase may undoubtedly help a rearrangement of the particles but such a mechanism alone cannot be responsible for the densification process.

The second mechanism, i.e. solution-precipitation, allows for the growth of solid grains and a better packing by selective dissolution of small grains at the contact point of the surfaces followed by reprecipitation at points in the microstructure removed from the grain contacts [27]. This makes possible the release of the available liquid into remaining pores, followed by a new rearrangement and new contact points on which the dissolution-precipitation starts again. Since the small grains exhibits greater solubility in the liquid, the general grain size increases as far as large size grains increase on the expenses of small size grains that disappear in this process, even though the volume fraction of solid remains constant and the solid-liquid interfacial area decreases. It appears that a peak density would be expected at a certain amount of PbO liquid phase when an equilibrium between the amount of liquid phase, pore volume and dissolution-precipitation, which allows a better shape accommodation, would be attained. This equilibrium seems to be, in our case, at an excess PbO of 3%. Higher amounts of liquid PbO cannot significantly change the density and this is experimentally observed. Such a behaviour was also observed in [11].

The most interesting finding in these PZT materials is the optimum peak of all the piezoelectric properties around 2-3 % PbO. One assumption that can be made is that this peak is related to the dissolution-precipitation mechanism. Lower amounts of PbO are not enough even for the rearrangement of the particles to give a high enough density, regardless the sintering temperature, as can be seen from Fig. 1. For higher PbO amounts the rearrangement is supposed to be completed but a selective dissolution (as already observed in [17]), of Ti rich tetragonal phase is very probable. The effect of this process could be a shift of the PZT phase to the rhombohedral side of the morphotropic phase boundary (MPB) and thus a modification of the properties should be expected. Such a slight tetragonal to rhombohedral shift was observed by X-ray diffraction patterns and it is illustrated in Fig.7. In the figure are shown the tetragonal (200) T and (002)T X-ray diffraction peaks and the rhombohedral (200)R peak. One observes that the intensity of the (002) T and (200) T peaks slightly decreases while the intensity of the (002) R peak increases for the samples containing 4 % PbO, which is a strong proof for the assumed T→R partial transformation.

The local compositional change is possible due to the compositional inhomogeneity brought about by the mechanical mixing technique of the raw material. It is naturally to assume that within the morphotropic phase region, where our compositions are situated, the distribution of T and R phases is not uniform and there should be large regions containing titanium only (say rich titanium zones, T-zones) and zirconium only (rich zirconium zones, R-zones). Therefore, the liquid PbO phase helps preferentially in the dissolving of the Ti rich zones, which, by transport through the liquid surrounding the grains and by reprecipitation improve the compositional stoichiometry of the sample with the final effect of improving the piezoelectric properties. This is observed, indeed, for samples containing 3 % PbO. For higher amounts of PbO it is possible that T→R shift to be more advanced and the composition could get out of the morphotropic phase boundary (MPB) with the effect of decreasing the piezoelectric parameters.

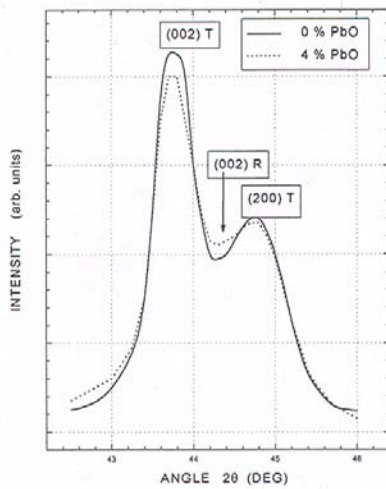


Fig. 7 X-Ray diffraction diagram for two samples containing 0 % and 4 % excess PbO, respectively.

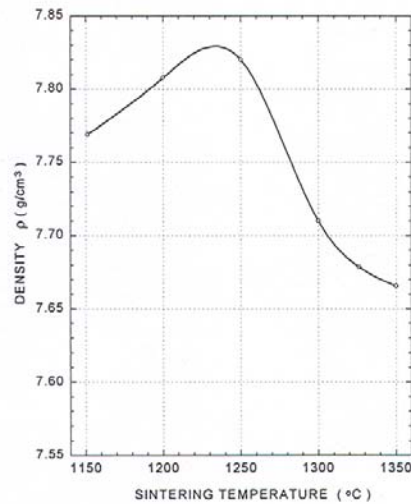


Fig. 8 Density as a function of the sintering temperatures for samples doped with 3 wt.% excess PbO. Sintering time was 3 hours.

As concerns the effect of sintering temperature one may say that lower temperatures cannot promote the mechanisms described but, at higher temperatures, a new effect appears, namely PbO loss by evaporation, which can deteriorate the stoichiometry and, consequently, can lower the properties: thus an optimum sintering temperature has to be expected and this was indeed the case for 1250 °C as can be easily observed in Fig. 8, where the density is shown as a function of sintering temperature. This phenomenon can be observed more or less in all figures presented and it is very pronounced for the piezoelectric voltage constant,  $g_{31}$  (Fig. 5), and electromechanical coupling coefficient,  $k_p$  (Fig. 2), while it is faint for the dielectric permittivity  $\epsilon_r$  (Fig. 3), mechanical quality factor,  $Q_m$  (Fig. 4), and strain constant,  $d_{31}$  (Fig. 6).

The mechanisms described so far can, at least qualitatively, explain the behaviour of the piezoelectric properties as a function of the excess PbO and sintering temperature. The role of each mechanism and its preponderance along the whole sintering process cannot yet be estimated. Further X-ray studies, to be made on samples clearly situated within or out of MPB, i.e. having T, R and a mixture of T and R structures, correlated with microstructural studies, would possible bring about more light on this matter.

#### 4. Conclusions

There was found that the properties of soft piezoelectric samples with chemical composition situated within MPB were improved by the addition of excess lead oxide. The optimum excess PbO to be introduced in PZT composition is around 2-3 wt.%. The improvement of the properties was explained by the presence, during the sintering process, of the liquid PbO phase, which may help the rearrangement of the powder particles, with the effect of increasing the density. At the same time a selective dissolution of the tetragonal (titanium rich) phase was followed by a homogenisation of the composition whose effect is the increasing of the piezoelectric parameters. Higher amounts of excess PbO, deteriorate the properties, due probably to the unfavourable change of composition with a more pronounced shift of the tetragonal phase towards the rhombohedral one.

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