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Effect of lead content on the structure and piezoelectric properties of hard type lead titanate–zirconate ceramics

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Abstract

In the present investigation we studied the effect of lead content on a hard type ceramics starting from lack to excess PbO. Specimens of $Pb_x(Mn_{0.017}Sb_{0.033}Zr_{0.48}Ti_{0.47})O_3$ with $0.96 \leq x \leq 1.06$ were prepared by conventional oxide mixing technique and sintered at temperatures between 1280 and 1350 °C. In samples with lower Pb concentration the pyrochlore phase appeared, while in those with higher Pb an excess of PbO phase was detected. These phases proved detrimental for the properties of sintered ceramics. The highest values of piezoelectric properties were observed only for samples with an excess lead of about 2% sintered at 1340 °C, indicating that it represents the optimum amount of PbO. For such samples, the density ρ was 7.77 g/cm^3, the remnant polarization P_r was 37 μC/cm^3 the planar coupling coefficient k_p was 0.57 and the charge constant d_{33} was 340 pC/N.
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Keywords: PZT; PbO loss; Sintering; Piezoelectric properties; Dielectric properties

1. Introduction

Solid solution of lead zirconate–lead titanate ceramics, known as PZT ($Pb(Zr,Ti)O_3$ compounds modified with izo or aliovalent ions, in order to improve their basic properties, have become the most important materials in an increasing range of application as sensors and transducers. Their excellent electromechanical properties make them the key candidates for power ultrasonic transducers, actuators for fine displacements systems, piezoelectric motors, medical transducers for diagnosis and ultrasonic imaging.[1] The performance requirements for transducers implies similar requirements for piezoelectric materials. Hence high care must be taken in controlling the material properties by a careful control of processing factors such as composition, structure and heat treatment. One of the problem encountered in obtaining high quality PZT materials is the compositional control and stability due to the fact that at high temperature, one of the basic component, PbO, volatilizes in a uncontrollably manner and so the stoichiometry of the final product is altered.[2] Some studies regarding the effect of compositional fluctuations due to the PbO loss on material properties were already reported.[3,4] More recently Fernandez et al.[5] studied in details the origin of the decomposition mechanism and its relationship with compositional fluctuations and the final properties of an iron-doped PZT material. They suggested that the dopant incorporation into the crystalline lattice of the material represents the main phenomenon which controls the nature and evolution of foreign phases formed by PbO loss and the change of the properties of iron-doped PZT. This process is temperature dependent, being more intense at high temperature. Unfortunately, there is not yet known a relationship between temperature and PbO loss in PZT type ceramics, because there are many other factors of influence such as the nature and amount of other additives used,[6] the samples environments (sintering atmosphere) during sintering. There are a few ways to avoid as much as possible the PbO volatilization. The usual practice is to protect the samples during sintering either by covering them with a blanket of a similar presintered powder able to create a rich PbO atmosphere during sintering[7] or by tightly sealing the crucibles in which the samples are sintered. Another way is to add small amounts of PbO in excess to the basic composition[8–12] or to use sintering aids to lower, to some extent, the sintering temperature.[13–22] Unfortunately, though helpful, neither way can provide a satisfactory solution to the problem but from the

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practical point of view the best approach still remains the control of stoichiometry by adding a certain amount of PbO before or after calcining, as a means to find experimentally the optimum processing conditions for a given material.

In a previous paper[9] we investigated the effect of small amount of lead oxide on the properties of a soft type PZT ceramics. In the present investigation we extended the study regarding the effect of lack and excess of PbO, compared to the stoichiometric formula, on the properties of a hard type PZT ceramics.

2. Experimental

The PZT material investigated has the general chemical formula: $Pb_x(Mn_{0.017}Sb_{0.033}Zr_{0.48}Ti_{0.47})O_3$ with $0.96 \leq x \leq 1.04$. We prepared samples with 4%, 3%, 2% and 1% lack of Pb and 1%, 2%, 3% and 4% excess Pb, respectively, with respect to the stoichiometric composition with $x = 1$. The processing procedure was the conventional mixing oxide route, using p.a. purity raw oxides. The weighted amounts of oxides were mixed for 2 h in a planetary ball mill using agate jars and methanol as wetting media. The balls/powder weight ratio was 2/1. The dried mixtures were double calcined in alumina crucibles at 850 °C for 3 h and at 880 °C for 4 h, respectively, with an intermediate manually dry crushing and sieving, followed by a final ball milling of 6 h in methanol. The dried milled powders were moistened by spraying with about 5 wt.% distilled water and uniaxially pressed into discs of 12 mm diameter and 1.5 mm thick at pressures of about 50 MPa. The pressed specimens were sintered at temperatures between 1280 and 1340 °C for 4 h in alumina crucibles being covered with a blanket of $Pb(Zr_{0.5}Ti_{0.5})O_3$ powder, already sintered at 1350 °C. The sintered discs were next mechanically processed by abrasion, ultrasonically cleaned, dried and electroded with a silver paste burned out at 650 °C for 10 min. The polling was carried out in a silicon oil bath at 220 °C under an electric field of 3 kV/mm and cooled down to room temperature still being under the influence of the electric field.

The charge integration method was used to determine the remnant polarization as well as the Curie temperature, using a ROB74 type amplifier with an offset voltage lower than 5 mV and polarizing currents lower than 100 pA. The pyroelectric charge generated on the sample with a area A was integrated by the amplifier and the polarization P was determined by the following relationship: $P(T) = V_{\mathrm{out}}(T)C_0\mathrm{A}^{-1}$ where V_{out} represents the difference between the voltages at transition temperature, where polarization become zero, and at temperature T. C_0 represents the capacitance of the reaction circuitry and it was fixed at a constant value of 14 μF. An automatic acquisition data unit made from a 288 AT PC and an IEEE 488 interface was used in the experiment.

The dielectric constants were determined by measuring the capacitance of the samples by means of an impedance analyzer HP 4194A. The same impedance analyzer was used to determine the piezoelectric properties by resonance spectroscopy. X-ray diffraction analysis was carried out by means of a Siemens Kristalloflex IV diffractometer provided with a copper target tube.

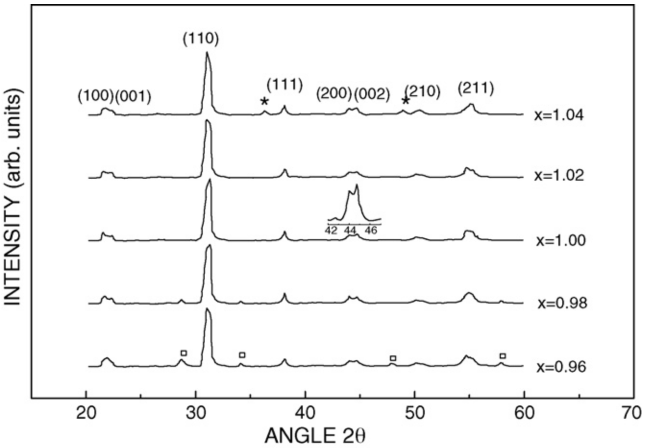

Fig. 1. XRD for hard PZT ceramic samples containing different amounts of lead: (*h k l*) perovskite phase; (✻) yirochlore phase; (✻) PbO phase.

3. Results and discussion

The X-ray diffractograms of the ceramic samples, containing different amount of Pb, are shown in Fig. 1. One observes that for lead-deficient compositions, along with the known perovskite phase, another foreign phase appeared. This foreign phase may possible be pyrochlore phase. This phase decreased with increasing lead content and completely disappeared for stoichiometric composition and for those containing excess lead. In turn for excess lead compositions new peaks appeared, which were identified as belonging to PbO phase. This is because too much lead may cause the formation of a lead rich liquid phase that crystallize as PbO at the grain surfaces during cooling from the sintering temperature. Two SEM micrographs of the fracture surface of ceramic samples are shown in Fig. 2. In Fig. 2a for the deficient lead oxide sample ($x = 0.96$) one can observe a triangular-shaped phase which we have associated with a pyrochlore phase, as indicated by the small peaks in the X-ray patterns from Fig. 1. For the samples with excess lead oxide ($x = 1.04$) one can see the presence of PbO foreign phase, in small quantities (Fig. 2b). We believe that the formation of a pyrochlore phase for lead-deficient compositions could be possible associated with some modification of the coordination number due to the A vacancies, produced by the lack of Pb. They may provoke a supplementary lattice distortion which make the coordination number of the A cation to decrease to eight instead of twelve now being located within scalenohedra. At the same time the B cations change their coordination number from eight to six, being located within trigonal antiprism due to the distortion of the octahedra.[23] This is only an assumption. To verify it we need to check the lattice parameters of the samples in order to determine the distorsion degree of the lattice based on the possible modifications produced by the lead vacancies which may change the electrical interaction between the neighborhood ions of A sites. The perovskite phase consists of tetragonal and rhombohedral phases as indicated by the broad (2 0 0) peaks shown in the inset of Fig. 1 for the stoichiometric samples.

The excess lead proved necessary to stabilize the perovskite structure, by catalyzing the decomposition of PZT as suggested

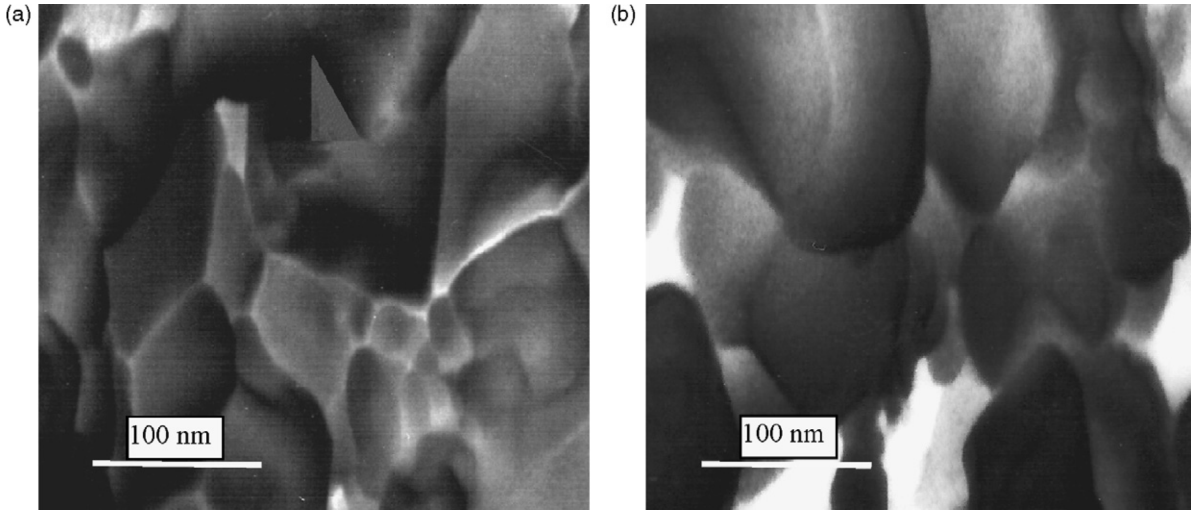

Fig. 2. (a) SEM images of the fracture surface of a deficient lead sample ($x = 0.96$). One observes a pyrochlore phase in the upper side of the image. (b) SEM images of the fracture surface of an excess lead sample ($x = 1.04$). One observes the presence of PbO phase (white spots in the image).

in Ref.[5]; but too much lead oxide may induce the formation of undesired phases that may cause a decrease of the basic properties. But as we shall see further there is an optimum amount of lead which stabilizes the structure and gives maximum values for the piezoelectric parameters.

Fig. 3 illustrates the densification degree of the samples as a function of lead content for different sintering temperatures. One can see a rather steady increase of the density with increasing lead content and sintering temperature up to maximum values with 3–4% higher for an excess lead of about 2% and a sintering temperature of 1340 °C. This fact indicated that an excess lead of 2% represents indeed the optimum amount for such compositions.

This forms the liquid phase which help the initial stage of sintering (rearrangement) and the second stage (dissolution) without reprecipitation, i.e., it replace the amount of lead that volatilized during sintering. Higher amounts of lead cannot enter the lattice to compensate for the volatilized lead and form the undesired secondary phase of PbO, as detected by XRD. Due to this the density decreased as can be seen in Fig. 3 for samples with $x > 1.02$.

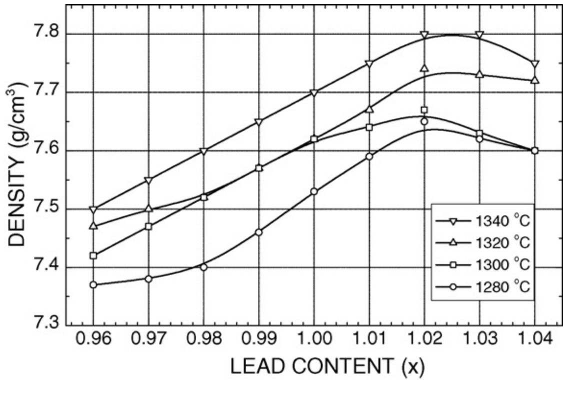

Fig. 3. Density vs. lead content, for different sintering temperatures.

Ferroelectric, dielectric and piezoelectric properties follow nearly the same trend as density. Thus Fig. 4 illustrates the behavior of remnant polarization against lead content. It increases with about 15% for increasing lead content up to 2 at% and then

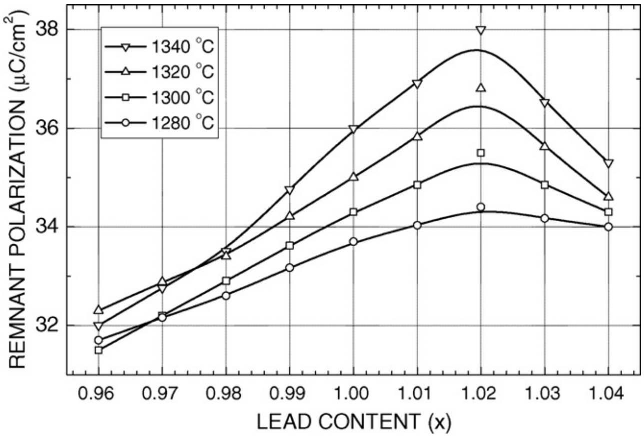

Fig. 4. Remnant polarization vs. lead content, for different sintering temperatures.

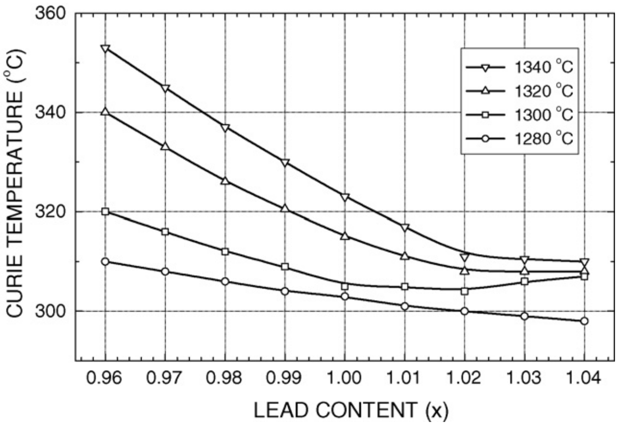

Fig. 5. Curie temperature vs. lead content, for different sintering temperatures.

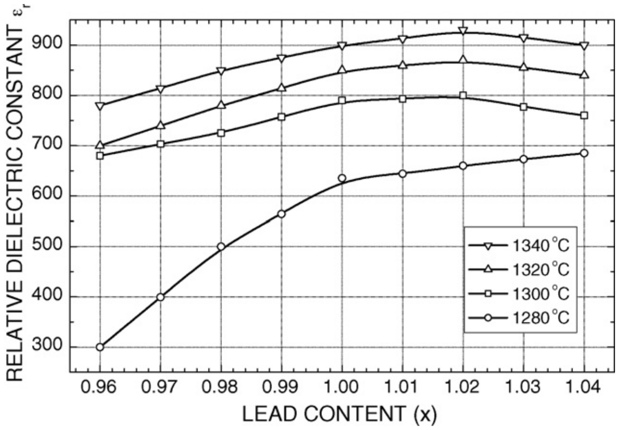

Fig. 6. Relative dielectric constant vs. lead content, for different sintering temperatures.

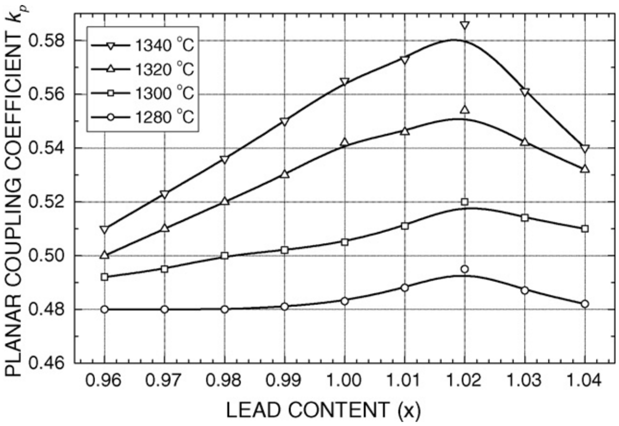

Fig. 7. Planar coupling coefficient vs. lead content, for different sintering temperatures.

decreases. This behavior is more pronounced for the sintering temperature of 1340 °C. The Curie temperature as a function of lead content shows a steady decrease with increasing lead content and a rather minimum value for 2 at% lead as can be seen in Fig. 5. The relative dielectric constant does not change significantly with lead content, but still shows maximum values around 2 at% lead as shown in Fig. 6.

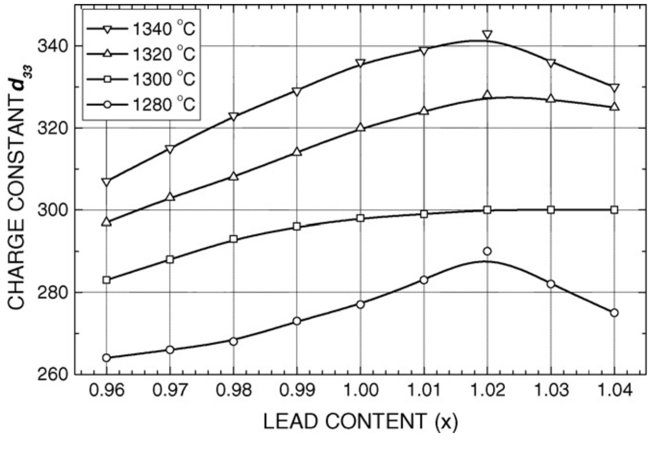

Fig. 8. Charge constant vs. lead content, for different sintering temperatures.

The behavior of electromechanical planar coupling factor k_p and charge constant d_{33} with lead content is shown in Figs. 7 and 8.

Both constants increase with increasing lead content and sintering temperature and show maximum values for 2 at% excess lead. This seems naturally as long as foreign phases are formed for both deficient and excess lead samples.

4. Conclusion

The structure, ferroelectric, dielectric and piezoelectric properties of a hard type piezoceramic material were determined as a function of the lack and excess lead oxide within −4 up to 4% molar compositional range. The lead-deficient samples showed the presence of a pyrochlore type foreign phase while the excess lead ones showed only the PbO foreign phase. Maximum values for all materials parameters were recorded in all samples containing 2 mol% excess lead, which means that this amount of lead, in excess, represents an optimum, able to compensate for the PbO loss by evaporation at sintering temperature of 1340 °C.

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