

# EFFECT OF LEAD CONTENT ON THE STRUCTURE AND PIEZOELECTRIC PROPERTIES OF HARD TYPE LEAD TITANATE-ZIRCONATE CERAMICS

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## 1. INTRODUCTION

Lead zirconate-lead titanate ceramics known as PZT become the most important materials in an increasing range of application. Their excellent electromechanical properties make them the key candidates for power ultrasonic transducers, actuators, piezoelectric motors, medical transducers. One problem encountered in obtaining high quality PZT materials is compositional control and stability since at high temperature PbO volatilizes and the stoichiometry of the final product is altered. One way to avoid PbO volatilization is to add small amounts of PbO in excess to the calcined powder before sintering this being the best approach to control the stoichiometry. PbO can be added before or after calcining step, as a means to find experimentally the optimum processing conditions for a given material with the highest parameters. In a previous paper we investigated the effect of small amount of lead oxide on the properties of soft type PZT ceramics. In the present investigation we extended the study regarding the effect of lack and excess PbO, compared to the stoichiometric formula, of a hard PZT ceramics.

## 2. OBJECTIVES

- To determine the effect of lack and excess PbO on the structure and properties of a hard type PZT material with the following chemical formula  $Pb_x(Mn_{0.017}Sb_{0.033}Zr_{0.48}Ti_{0.47})O_3$ ;
- To measure the properties as a function of composition that is as a function of the amount of PbO, as well as the processing temperature;
- To find out whether or not there exist an optimum amount of PbO in the basic composition for which the properties show maximum values.

## 3. EXPERIMENTAL

We have studied a hard type PZT material having the general chemical formula:  $Pb_x(Mn_{0.017}Sb_{0.033}Zr_{0.48}Ti_{0.47})O_3$  with  $0.96 \leq x \leq 1.04$ , that is we have 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  $x=1$ . Processing procedure was the conventional mixing oxide route. The specimens were sintered at temperatures between 1280 and 1340 °C for 4 h in sealed alumina crucibles being covered with a blanket of  $Pb(Zr_{0.5}Ti_{0.5})O_3$  powder already sintered at 1350 °C. The remnant polarization and Curie temperature were determined by charge integration method using a simple measuring device shown in figure 1a and an electronic circuitry shown in figure 1b. The pyroelectric charge at the sample surface was integrated between polarization P and the voltage being  $P(T) = V_{out}(T)C_oA^{-1}$  and the piezoelectric properties were determined by resonance spectroscopy using an HP4194A Impedance Analyzer.

## 4. RESULTS

The X ray diffractograms of the ceramic samples containing different amount of Pb are shown in figure 2. One observes that for lead deficient compositions, along with the known perovskite phase, another foreign phase appeared. This foreign phase was identified to be pyrochlore phase and it decreased with increasing lead content and completely disappeared for stoichiometric composition and for those containing excess lead. For excess lead compositions new peaks appeared, which were identified as belonging to PbO phase. SEM micrographs of the fracture surface for two significant ceramic samples are shown in figure 3. Thus for the deficient lead oxide samples ( $x=0.96$ ) the presence of the pyrochlore phase is evident (Fig 3a), while for those with excess lead oxide ( $x=1.04$ ) no trace of pyrochlore phase there exist but the presence of the PbO foreign phase, in small quantities is observed (Fig 3b). The formation of the pyrochlore phase for lead deficient compositions could be associated with the 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 octahedral. The perovskite phase consists of tetragonal and rhombohedral phases as indicated by the broad (200) peaks shown in the inset of figure 2 for the stoichiometric samples. Consequently, excess lead proved necessary to stabilize the perovskite structure, but too much lead oxide may induce the formation of undesired phases that may cause a decrease of the basic properties. But as we see there is an optimum amount of lead which stabilizes the structure and gives maximum values for the piezoelectric parameters. Figure 4 illustrates the densification degree of the samples as a function of lead content. 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 the optimum amount. Ferroelectric, dielectric and piezoelectric properties follow nearly the same trend as density. Thus figure 5 illustrates the behavior of remnant polarization against lead content. It increases for increasing lead content up to 2 at %. The Curie temperature shows a steady decrease with increasing lead content and a rather minimum value for 2 at % as can be seen in figure 6. The relative dielectric constant shows maximum values around 2 at % lead as shown in figure 7. The behavior of electromechanical planar coupling factor  $k_p$  and charge constant  $d_{33}$  with lead content is shown in figures 8 and 9. Both constants increases with increasing lead content and sintering temperature and show maximum values for 2 at % excess lead.

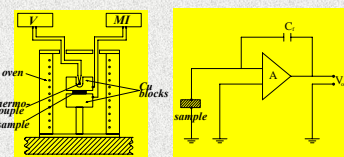


Figure 1a  
Experimental device for measuring remnant polarization and Curie temperature

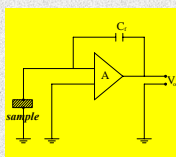


Figure 1b  
Electronic circuitry used to determine polarization

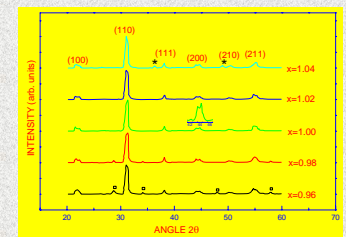


Figure 2  
XRD for hard PZT ceramic samples containing different amounts of lead: (hk) perovskite phase; (-) pyrochlore phase; (\*) PbO phase

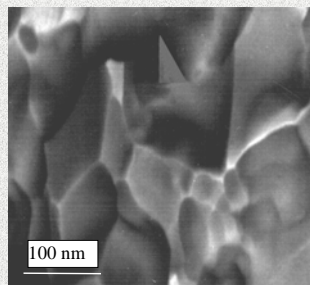


Figure 3a  
SEM image of the fracture surface of a deficient lead sample ( $x=0.96$ ). One observes a pyrochlore phase in the upper side of the image

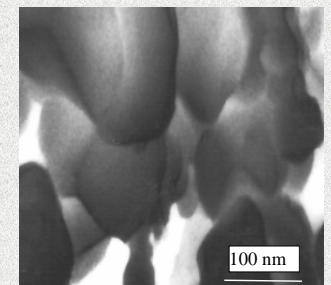


Figure 3b  
SEM image of the fracture surface of an excess lead sample ( $x=1.04$ ). One can observe the presence of PbO phase (white spots in the image)

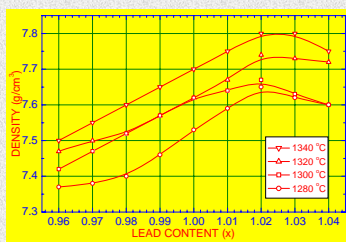


Figure 4  
Density versus lead content, for different sintering temperatures

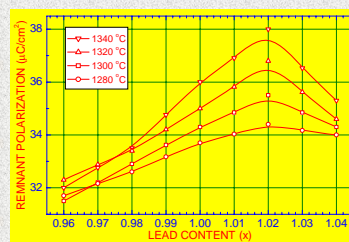


Figure 5  
Remnant polarization versus lead content, for different sintering temperatures

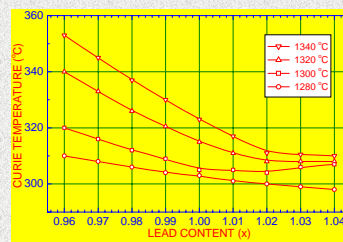


Figure 6  
Curie temperature versus lead content, for different sintering temperatures

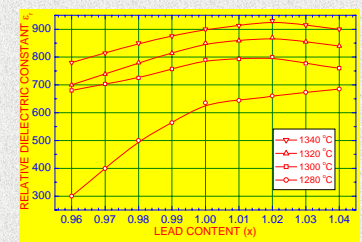


Figure 7  
Relative dielectric constant versus lead content, for different sintering temperatures

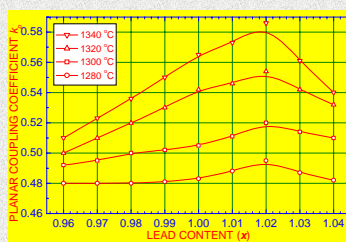


Figure 8  
Planar coupling coefficient versus lead content, for different sintering temperatures

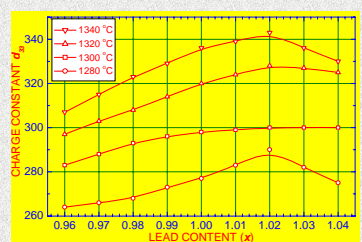


Figure 9  
Charge constant versus lead content, for different sintering temperatures

## 6. SUMMARY

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 to 4 % molar compositional range. The lead deficient samples show the presence of a pyrochlore type foreign phase while the excess lead samples show only the presence of 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 amount of lead in compositions, which is able to compensate for the PbO loss by evaporation at the sintering temperature of 1340 °C.