# Effect of Excess PbO on Phase Formation, Microstructure and Dielectric Properties of (Pb<sub>0.975</sub>Ba<sub>0.025</sub>)ZrO<sub>3</sub> Ceramics

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### ABSTRACT

Polycrystalline samples of (Pb<sub>0.975</sub>Ba<sub>0.025</sub>)ZrO<sub>3</sub> (PBZ2.5). were prepared by a mixed oxide, solid-state reaction method. Excess PbO (1,3, 5 or 10 wt.%) was introduced prior to powder calcination to compensate for any PbO that may have been lost from the samples due to volatilsation during heat treatments. The phase structure was analyzed by XRD.A pure PBZ2.5 phase was observed in all of the ceramic samples. Microstructurally, excess PbO produced an increase in average grain size, from ~ 0.5  $\mu$ m for no excess to ~0.8  $\mu$ m for excess PbO. Dielectric constant-temperature plots showed a maximum peak value of 8070, for the 1 wt.% sample which was also the densest sample.

Keywords: lead barium zirconate, dielectric properties, excess lead oxide, phase transition

### **INTRODUCTION**

The effect of Ba<sup>2+</sup> ion substitution on physical properties and phase transitions behavior of  $(Pb_{1-x}Ba_x)ZrO_3$  (PBZ) has been investigated by many authors (Roberts, 1953; Shirane, 1952; Pokharel et al., 1999). The first one was Roberts but he did not get any evidence for the antiferroelectric (AFE) to ferroelectric (FE) phase transition (Roberts, 1953). Later, Shirane investigated the phase transformation behavior of  $(Pb_{1-x}Ba_x)ZrO_3$  for  $0 \le x \le 0.30$  and reported that the ferroelectric intermediate phase does not appear until the Ba<sup>2+</sup> concentration exceeds the threshold value at about 5 mol% (Shirane, 1952). The temperature range of this intermediate phase increases with the  $Ba^{2+}$  concentration. On the contrary, Ujma et al. reported the FE phase existence in PBZ containing up to 5 mol%  $Ba^{2+}$ , with dielectric properties different from the previous papers (Ujma et al., 1992). Recently, Pokharel et al.(1999) found unusually wide thermal hysteresis in the AFE-FE phase transition measured by dielectric measurement during heating and cooling cycles (e.g., nearly 100 °C for x = 0.05 in contrast to about 11 °C for pure PZ) and an irreversibility of the AFE to FE transformation temperature during the cooling cycle for x = 0.10 (Pokharel and Pandey, 1999). Different research groups reported the different results of AFE-FE phase transition (Yoon et al., 1997; Pokharel and Pandey, 2001; Pokharel and Pandey, 1999; Ujma et al., 1992; Pokharel and Pandey, 2000). Pokharel et al.(1999) proposed that the processing method used to prepare the PBZ powders may be important in influencing phase formation. Moreover, another factor to consider is also the possible effect of PbO loss due to evaporation during high temperature processing. The PbO vapour-pressure may be sufficient to create compositional changes in the powders. Moreover, any variation in Pb and O ion vacancy concentrations may be important in terms of phase stability.

Hence, the present work studied the effect of PbO contained on the phase formation and properties of PBZ2.5 which prepared via solid state reaction method. Structural phase formations, microstructure and densification of PBZ2.5 ceramics are investigated. Dielectric measurements are used for studies the details of AFE-FE and FE-paraelectric (PE) phase transitions

### **EXPERIMENTAL PROCEDURE**

The (Pb<sub>0.975</sub>Ba<sub>0.025</sub>)ZrO<sub>3</sub> (PBZ2.5) ceramics were prepared by using a conventional mixed oxide method. The raw materials of PbO (purity 99.9%, supplied by Johnson Matthey GmbH, UK), ZrO<sub>2</sub> (purity 99%, supplied by Aldrich, UK) and BaCO<sub>3</sub> (purity 99.9%, supplied by Johnson Matthey GmbH, UK) were weighed and mixed. Each mixture of the starting powders was milled and mixed in a ball mill, as well as wet-homogenized with acetone for 24 h using zirconia grinding media. The suspensions were dried and the powders were ground using an agate mortar and sieved (300  $\mu$ m) in to fine powder. All obtained powders were calcined at 1000 °C for 1 h. An excess of PbO, equivalent to 0, 1, 3, 5 or 10 wt.%, was applied prior to ball milling before calcination. The calcined powders were reground by wet ball-milling with 1wt.% binder (B-5 supplied by Rohn-Haas, Germany) for 24 h. The calcined powders with binder were dried, crushed and sieved again. The powder mixtures were isostatically pressed at 80 MPa into a pellet of 15 mm in diameter.

Finally, the pellets were fired in an alumina crucible and sintered at 1200 °C for 4 h. In order to minimize the loss of lead due to vaporization, the PbO atmosphere for the sintering was maintained using PbZrO<sub>3</sub> as the spacer powder. The phase evolution of the calcined powder and sintered pellets was determined using a diffractometer (Philips ADP1700). The density of the sintered samples was measured by Archimedes' method with distilled water as the fluid medium. The microstructure developments of the sintered samples were examined using scanning electron microscopy (JEOL, JSM5910). The sintered samples were prepared for electrical property measurements by first polishing and then gold sputtering on to the clean pellet faces. The dielectric measurements were carried out at 1 kHz using a HIOKI 3532-50 impedance analyzer, from room temperature to 300 °C with a heating rate of 0.5 °C/min was controlled by a computer.

### **RESULTS AND DISCUSSTION**

Figure 1 show XRD patterns of calcined powders made from starting mixtures containing different levels of PbO. For the sample made with no excess PbO, only the PBZ phase was observed (Pokharel *et al.*, 1999). On the other hand, small amounts of PbO (JCPDS no. 76-1796, 2000; JCPDS no. 85-1287, 2000) were

clearly present in the 10 wt.% excess PbO sample, and there was also some evidence of these phases being present, in the 5 wt.%, and to a much lesser extent, in the 3 wt.% samples.



Figure 1 XRD patterns of calcined powders of PBZ2.5 made from starting powders containing different amounts of excess PbO: (x) PbO (orthorhombic phase) and (\*) PbO (tetragonal phase).



**Figure 2** XRD patterns of sintered pellets of PBZ2.5 made from starting powders containing different amounts of excess PbO.

The presence of 'free' PbO is expected in the higher excess samples. The XRD data for sintered samples revealed that no PbO was present in any sample, indicating that the excess PbO beyond that required to maintain compositional control (assumed) in the PBZ2.5 powder was eliminated from the sample by volatilization during sintering at 1200 °C (Figure 2).

The density of PBZ2.5 ceramics as a function of amount of PbO content is shown in Table 1. The maximum density was 7.90 g/cm<sup>3</sup> for the sample containing PbO 1 wt.%. At the higher PbO contained, the density decreased with increasing the excess PbO. The results could be caused of loss of PbO from the compact pellet which increases its porosity. The presence of PbO rich liquid phase usually helps higher densification in sintering. However, the large amount of PbO liquid phase can produce an initial rapid densification but a low final density as a result of void formation due to the PbO evaporation. As a consequence the porosity of the pellet increase and this is not removed by solid state sintering (Kingon and Clark, 1983). Figure 3 shows SEM micrographs of the surface for the PBZ2.5 ceramics at various PbO contents. By using the linear intercept method, the average grain sizes were 0.5, 0.7, 0.8, 0.7 and 0.7 µm for samples with the excess PbO of 0, 1, 3, 5 and 10 wt.%, respectively. The grain size of the excess PbO was larger than the base composition. Moreover, the grain size distribution at the lower PbO content is more uniform than that of the samples contained at the higher PbO. Similar results were found in many lead base ceramics (Garg and Agrawal, 1999; Zhou et al., 2004).

Amount of PbO Excess (wt.%)	Density (g/cm <sup>3</sup> )	Maximum dielectric constant at the	Transition temperature (°C)	
		FE:PE phase	AFE:FE	FE:PE
		transition		
0	7.88	7485	184.1	223.6
1	7.90	8070	189.8	223.6
3	7.89	7960	189.9	223.5
5	7.81	7025	190.8	224.4
10	7.77	6420	189.6	224.1

**Table 1** Density, values of peak dielectric constant and transitions temperature.



Figure 3 SEM micrographs of as-sintered of sintered PBZ2.5 pellets made from starting powders with different PbO contents: (a) 0 wt.%, (b) 1 wt.%, (c) 3 wt.% and (d) 10 wt.%.

The dielectric constant of various excess PbO as a function temperature is shown in Figure 4. The FE-PE phase transition occurred at ~ 223-224 °C for all samples, Table 1. There was however an increase in peak dielectric constant from 7485 for the 0% sample to 8070 for the 1 wt.% sample, followed by reductions for the 3, 5 and 10 wt.% samples, Table 1. This trend matches that of the sintered densities, i.e. the lower density samples gave lower measured dielectric constants. There have been observation reported that compositions with excess PbO additions greater than 2.8 mol% results in degraded electrical properties (Swartz *et al.*, 2004). Furthermore, the amounts of excess PbO were found to have a significant effect on the AFE-FE phase transition. The AFE-FE phase transition temperature was increased from ~184 °C to ~190 °C with adding excess PbO (Table 1). Combined with density result, dielectric constant, the optimum electrical properties were obtained by adding a 1 wt.% excess lead content to the system.

#### CONCLUSION

The  $(Pb_{0.975}Ba_{0.025})ZrO_3$  ceramics were fabricated with various excess PbO contents. The effect of lead excess on the properties of the ceramics was studied. The pure perovskite orthorhombic phase was observed for all size in the sintered samples, from an average of ~0.5 µm for the unmodified composition to ~ 0.8 µm for the excess PbO compositions. The results indicate that ~ 1 wt.% excess PbO produced the highest density ceramics, exhibiting the maximum value of the dielectric constant.



**Figure 4** Dielectric constant versus temperature for PBZ2.5 ceramics made from powders with different amounts of starting excess PbO.

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#### REFERENCES

- Garg, A. and Agrawal, D.C. (1999). Effect of Net PbO Content on Mechanical and Electromechanical Properties of Lead Zirconate Titanate Ceramics. *Mat. Sci. Eng B-Solid.*, *56*, 46.
- Hagimura, A. and Uchino, K. (1989). Impurity Doping Effect on Electrostrictive Properties of (Pb,Ba)(Zr,Ti)O<sub>3</sub>. *Ferroelectrics.*, 93, 373.
- Kingon, A.I. and Clark, J.B. (1983). Sintering of PZT Ceramics: I, Atmosphere Control. J. Am. Ceram. Soc., 66, 253.
- Kingon, A.I. and Clark, J.B. (1983). Sintering of PZT Ceramics: II, Effect of PbO Content on Densification Kinetics. J. Am. Ceram. Soc., 66, 256.
- Pokharel, B. P., Datta, M. K. and Pandey, D. (1999). Influence of Calcination and Sintering Temperatures on the Structure of (Pb<sub>1-x</sub>Ba<sub>x</sub>)ZrO<sub>3</sub>. J. Mater. Sci., 34, 691.
- Pokharel, B. P. and Pandey, D. (1999). Irreversibility of the Antiferroelectric to Ferroelectric Phase Transition (Pb<sub>0.90</sub>Ba<sub>0.10</sub>)ZrO<sub>3</sub> Ceramics. J. Appl. Phys., 86, 3327.
- Pokharel, B. P. and Pandey, D. (2000). Dielectric Studies of Phase Transitions in (Pb<sub>1,x</sub>Ba<sub>x</sub>)ZrO<sub>3</sub>. J. Appl. Phys., 88, 5364.
- Pokharel, B. P. and Pandey, D. (2001). High Temperature X-ray Diffractometer Studies on Antiferroelelectric and Ferroelectric Phase Transitions in (Pb<sub>1-x</sub>Ba<sub>x</sub>)ZrO<sub>3</sub> (x=0.05, 0.10). J. Appl. Phys., 90, 2985.
- Pokharel, B. P., Ranjan, R. and Pandey, D. (1999). Rhombohedral Superlattice Structure and Relaxor Ferroelectric Behavior of (Pb<sub>0.70</sub>Ba<sub>0.30</sub>)ZrO<sub>3</sub> Ceamics. *Appl. Phys. Lett.*, 74, 756.
- Powder Diffraction File no.76-1796. (2000). International Centre for Diffraction Data, Newton Square, PA,.
- Powder Diffraction File no.85-1287. (2000). International Centre for Diffraction Data, Newton Square, PA.
- Roberts, S. 1953. Dielectric Properties of Lead Zirconate and Barium-Lead Zirconate. J. Am. Ceram. Soc., 33, 63.
- Swartz, S.L., Shrout, T.R., Schulze, W.A. and Cross, L.E. (1984). Dielectric Properties of Lead-Magnesium Niobate Ceramics. J. Am. Ceram. Soc. 67: 311.
- Shirane, G. 1952. Ferroelectricity and Antiferroelectricity in Ceramics PbZrO<sub>3</sub> Containing Ba or Sr. *Phys. Rev.*, *86*, 219.
- Shirane, G. and Hoshino, S. (1953). X-ray Study of Phase Transitions in PbZrO<sub>3</sub> Containing Ba or Sr. *Acta Cryst.*, *5*, 530.
- Ujma, Z., Handerek, J., Pawelczyk, M. and Dmytrow, D. (1992). Phase Composition and Dielectric Properties of Lead Barium Zirconate Solid Solutions. *Ferroelectrics.*, *129*, 127.
- Yoon, K. H., Hwang, S. C. and Kang, D. H. (1997). Dielectric and Field-induced Strain Behavior of (Pb<sub>1-x</sub>Ba<sub>x</sub>)ZrO<sub>3</sub> Ceramics. *J. Mater. Sci.*, *32*, 17.
- Zhou, L., Zimmermann, A., Zeng, Y. and Aldinger, F. J. (2004). Bipolar Electric Fatigue Behavior as a Function of Field Strength in Antiferroelectric (Pb,Ba,La)(Zr,Sn,Ti)O<sub>3</sub>. *Mater. Sci.: Mat. Elec.* 15, 145.