

Dielectrics of lead zirconate bonded with barium borate glass

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Abstract. Dielectric constant variation with temperature and frequency is reported for barium-borate glass-bonded lead zirconate. Lowering of the relative permittivity of the ceramic is attributed to the presence of the glass.

Keywords. Liquid phase sintering; dielectric constant; ceramics; lead zirconate; barium borate glass.

1. Introduction

Liquid phase sintering (LPS) technique plays a predominant role in the current technology of metallurgy and ceramics because it reduces the sintering temperature, modifies the properties of the material under preparation and provides better mechanical strength and higher reproducibility (Fukami 1974). Following LPS, lead zirconate was bonded with glass consisting mainly of oxides of heavy metals such as PbO and Bi₂O₃ with about 10% of glass formers (SiO₂, B₂O₃). Lead zirconate bonded with this glass was found to be suitable for energy storage with energy density as 2 J/cm³ (Burn 1971). It was reported that the energy density value of borosilicate with PbO, Bi₂O₃ glass-bonded barium titanate to be the same and 30% lower in the case of 4BaO·Al₂O₃·2B₂O₃ glass bonded SrTiO₃ (Burn and Smyth 1972). The glass used earlier was a multicomponent system and it was further reported that barium from the glass reacts with lead zirconate and forms lead-barium zirconate. In order to explore this possibility, a two-component BaO-B₂O₃ glass system was prepared. The glass was added in the ratio of 0.5 and 10 wt%. The dielectric constant was studied as a function of temperature and frequency.

2. Experimental details

Lead zirconate ceramic was prepared using the technique described earlier (Singh *et al* 1982). For bonding, the glass system chosen was BaO·B₂O₃ (10:90, 20:80 and 30:70 mol% respectively). The ingredients were ground thoroughly under acetone, dried and heated moderately in a controlled and thermally sensed electric furnace. The melting point ranged between 800 and 900°C. The melt was soaked at that temperature for 1 h to allow homogenization. Glass was then quenched in an aluminium mould at room temperature. In order to use it as a binder, quenched glass pieces were crushed to fine powder.

Finely crushed powder of lead zirconate and glass were passed through a sieve (450 mesh size) and weighed in the desired ratio and ground well. The process of mixing continued for a longer time to ensure perfect mixing of the ingredients. This

mixed and powdered mass was pressed isostatically in a steel die and punched at 10 tons/cm² resulting in pellets of 13 mm dia and 0.5 to 1 mm in thickness. These pellets were subjected to different heat treatments for a fixed duration of 1 h. The sintering temperatures mainly depended on the glass content and the melting point of the glass. Generally it was observed that as the glass content was increased the sintering temperature decreased. The optimized sintering temperature is given in table 1. The sintered pellets were silver-coated and baked at 150°C for 2 h to achieve perfect ohmic contact. Dielectric constant measurements are reported as a function of temperature and frequency with a input voltage of 1 volt by means of Hewlett–Packard multi-frequency inductance-capacitance resistance (LCR) meter 4261A and Hewlett–Packard impedance analyser 4192A with input voltage of 500 mV respectively. The measuring temperature and frequency ranged from room temperature to 300°C and 100 Hz to 100 kHz.

3. Results and discussion

The functional dependence of dielectric constant on temperature and frequency was studied experimentally for pure and glass-bonded lead zirconate at a fixed frequency of 1 kHz from room temperature to 300°C and at room temperature from 100 Hz to 100 kHz respectively.

Figure 1 depicts the dependence of dielectric constant for pure lead zirconate in the temperature range from room temperature to 300°C at 1 kHz. It is seen that for pure PbZrO₃ beyond 200°C, the increase in ϵ is very rapid till 230°C at which it reaches a maximum value of 3200 and then decreases. The value of Curie constant was found to be 6×10^4 °C and the Curie–Weiss temperature T_0 was 207°C.

Figures 2–4 illustrate the relative permittivity variation vs temperature of 0.5 and 10 wt% of PbZrO₃ bonded with glasses I–III. Table 2 gives the data regarding the peak value of the dielectric constant ϵ_{peak} , T_c , T_0 and C for all the samples.

Figure 5 depicts the frequency variation of the dielectric constant for pure and glass-bonded samples. In the frequency range studied, the dielectric constant is independent of frequency and hence did not merit further attention. For 0.5 wt% glass addition the value of ϵ_{peak} for PbZrO₃ bonded with glass systems I, II and III are found to be 670, 3238 and 703 respectively and that for 10 wt% glass addition it is 150, 2992 and 669 respectively.

In the present case, the peak value of the dielectric constant is understandably lower than that for high purity material (Roberts 1950; Shirane *et al* 1951;

Table 1. Optimized sintering temperatures.

Glass No.	Glass composition BaO-B ₂ O ₃	Weight % of added glass	Optimized sintering temperature(°C)
I	10:90	0.5	950
		10	875
II	20:80	0.5	900
		10	800
III	30:70	0.5	800
		10	725

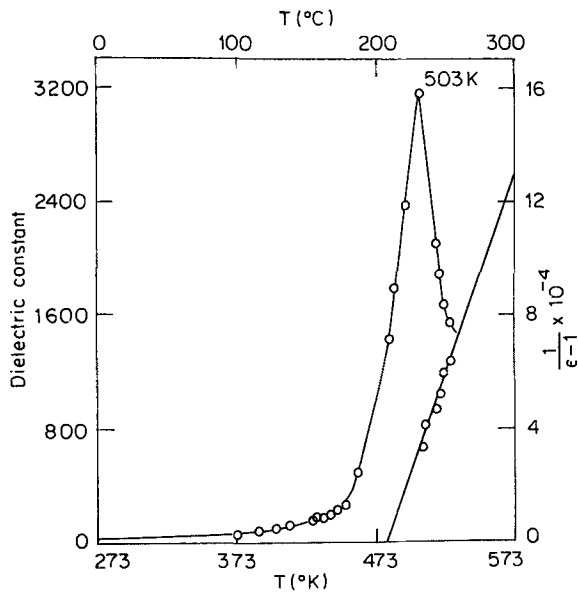


Figure 1. Dielectric constant variation with temperature for pure lead zirconate.

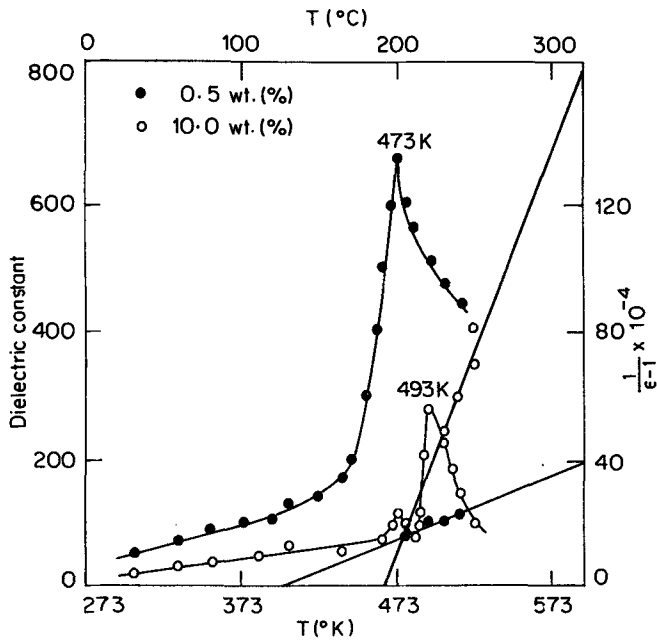


Figure 2. Dielectric constant variation with temperature for lead zirconate bonded with glass I.

Weirauch and Tennery 1970). Burn (1971) reasoned that the permittivity of the ceramic gets diluted by the addition of the glass and an extra peak appears in the PbZrO_3 matrix. It has been attributed to the reaction of the glass with ceramic.

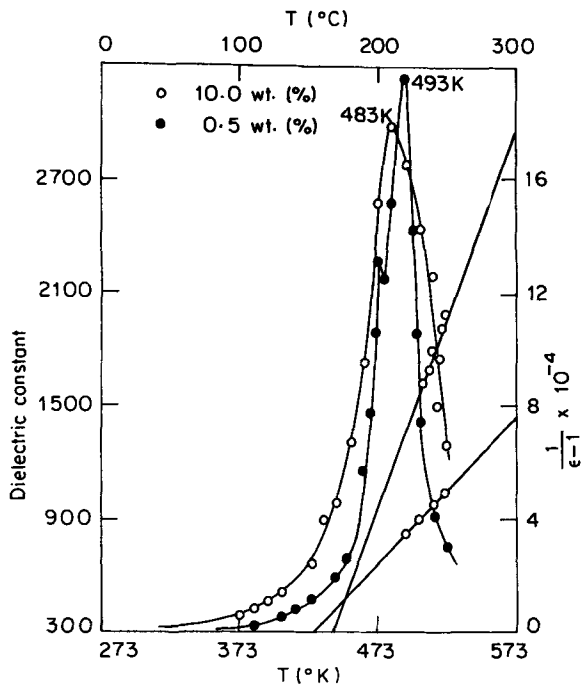


Figure 3. Dielectric constant variation with temperature for lead zirconate bonded with glass II.

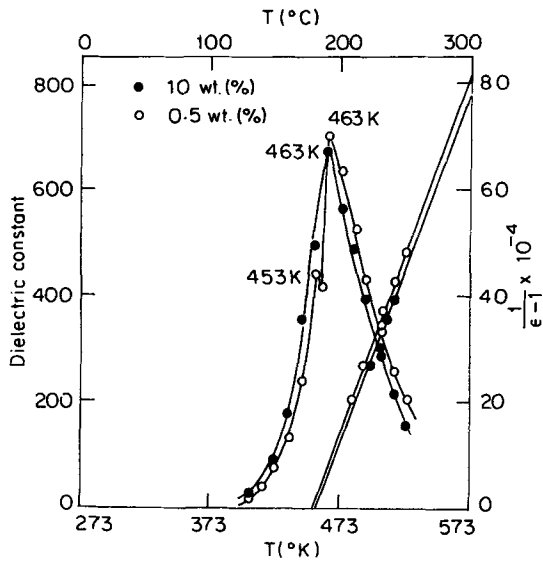
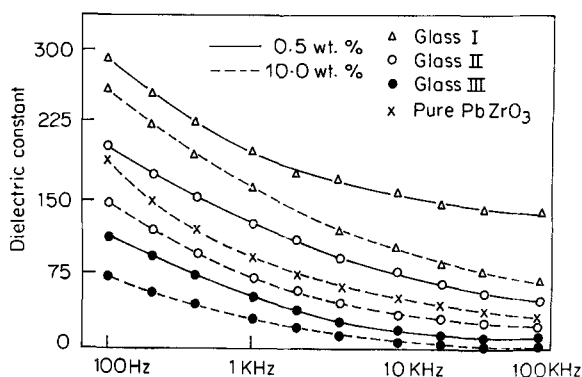


Figure 4. Dielectric constant variation with temperature for lead zirconate bonded with glass III.

Table 2. Compositional dependence of ϵ_{peak} , T_c , T_0 , C .

	Pure PbZrO ₃	Glasses					
		I		II		III	
% of glass doping	—	0.5	10	0.5	10	0.5	10
ϵ_{peak}	3200	670	280	3238	2992	703	669
Transition temperature (°C)	230	200	220	220	210	190	190
C (°C)	6×10^4	5×10^4	0.83×10^4	1.35×10^5	0.5×10^5	6.2×10^5	6.5×10^5
T_0 (°C)	207	124	190	166	154	178	181
Width of ferroelectric region (°C)	—	—	20	18	—	10	—
Density g/cm ³	90	90	80	81	80	76	74

**Figure 5.** Frequency variation of dielectric constant for unbonded and barium borate glass-bonded lead zirconate.

In the present study, the barium-borate glass was found to be a viscous glass. With the increase of BaO from 10 mol% to 30 mol%, the amount of the viscous flow during sintering increases. According to Subbarao (1979) the liquidous flow should have minimum viscosity at the sintering temperature so that the amount of liquid is kept to a minimum. The barium-borate glass being very viscous, it might not be getting creaped across the grain boundaries of whole of the pellet, since after the sintering the pellet is suddenly quenched to room temperature. Because of the collection of the glassy phase on some parts of the pellet, there might be an overall decrease in the value of ϵ_r .

SEM photographs of pure and glass-bonded lead zirconate (figure 6) indicate that due to the addition of glass there is a change in the packing density of the material and an increase in the grain size. Further work in this direction is in progress.

Table 2 indicates that the density of the lower glass (0.5 wt%) added sample is greater than that of the higher glass (10 wt%) added sample. Theoretical considerations of the model bearing on the influence of the quantity of liquid on the degree of densification conclude that the density of the samples sintered in the presence of liquid depends on its amount (Kingery 1959). In the case of spinels it has been

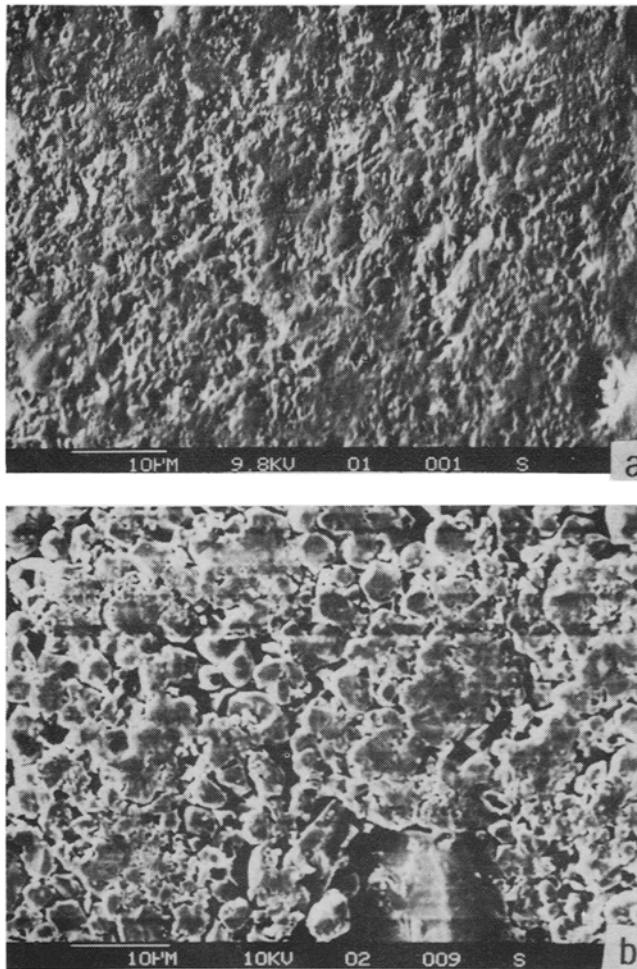


Figure 6. SEM photographs of pure and glass-bonded lead zirconate.

shown that by the presence of greater quantity of additives (i.e. amount of liquid) above the optimal one, a decrease in density is observed. This behaviour was explained by setting up the repulsion forces between particles in samples when the amount of liquid is greater than the optimal quantity for densification (Eremenko *et al* 1968). It is further reported that the microstructural analysis of the samples sintered in the presence of different quantity of additives showed that the quantity of liquid within the samples affected the grain growth as well as the open porosity. Table 2 illustrates that for lower glass additions, the density and ϵ_r are higher than that of 10 wt% glass addition. This factor is reasonable because higher packing density would result in a larger value of ϵ_r .

4. Conclusion

The present study shows that there is an overall decrement in the value of dielectric

constant of lead zirconate after the glass addition. The glass addition needs to be tried over the entire range, i.e. between 0.5 and 10 wt%.

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