

## Dielectric behaviour of glasses and glass ceramics in the system BaO-PbO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

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**Abstract.** Glasses with varying molar ratios of PbO/BaO in the system BaO-PbO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> were prepared keeping (BaO + PbO)/TiO<sub>2</sub> ratio equal to one. The glasses were ceramized by two-stage heat treatment. X-ray diffraction indicates that PbTiO<sub>3</sub> crystallizes in lead-rich glasses while BaTiO<sub>3</sub> precipitates in barium-rich compositions. Solid solution (Ba, Pb)TiO<sub>3</sub> does not seem to crystallize over the entire range of compositions. Simultaneous presence of PbO and BaO in the initial glass composition reduces the yield of ferroelectric phase. Dielectric properties have been interpreted in terms of microstructural features.

**Keywords.** Glass ceramics; ferroelectric; dielectric constant.

### 1. Introduction

Glass ceramic processing provides an efficient way of producing uniform fine grains of a crystalline phase in a pore-free glassy matrix (McMillan 1979). These microstructural features, being highly desirable in ferroelectric ceramics, attracted the attention of many workers in the sixties to study ferroelectric glass ceramics (Bergeron 1961; Herczog 1964; Grossman and Isard 1969a). The amount of ferroelectric phase and its microstructure can be precisely controlled by choosing a suitable initial glass composition and a heat treatment schedule. Since ferroelectric ceramics possess useful properties in the solid solution form, efforts were made to precipitate the ferroelectric phase in the solid solution form in the glass ceramics. Herczog (1964) attempted to replace Ba in BaTiO<sub>3</sub> by various ions such as Ca<sup>2+</sup>, Sr<sup>2+</sup> and Pb<sup>2+</sup> etc by incorporating oxides of these ions in the initial glass composition. It was reported that only a limited amount of substitution was possible and the effects of such substitutions were similar to that in the polycrystalline materials. However, a recent publication by Herczog (1984) indicates that the substitution of Ba by Sr or of Ti by Zr is ineffective in modifying the properties as they crystallize in a different phase. Various glass ceramics containing ferroelectric phases have been reviewed recently by Om Parkash *et al* (1986b).

Grossman and Isard (1969b) reported the formation of PbTiO<sub>3</sub> during ceramization of glass in the system PbO-BaO-TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> using X-ray diffraction (XRD). Lynch and Shelby (1984) studied the same compositions as studied by Grossman and Isard (1969a, b) and confirmed the precipitation of PbTiO<sub>3</sub> using dilatometry. Om Parkash *et al* (1986a) studied the ceramization of a glass composition 21 BaO-21 PbO-42 TiO<sub>2</sub>-10 B<sub>2</sub>O<sub>3</sub>-6 SiO<sub>2</sub> (mole %) and confirmed the formation of BaTiO<sub>3</sub> on heat treatment. As is clear from this glass composition, an adequate amount of TiO<sub>2</sub> was used to react with both BaO and PbO while glass compositions studied by earlier workers did not contain requisite amount of TiO<sub>2</sub> i.e. the (BaO + PbO)/TiO<sub>2</sub>

ratio was  $< 1$ . This led us to the conjecture that ferroelectric phase crystallizing out during heat treatment depends on the  $(\text{BaO} + \text{PbO})/\text{TiO}_2$  and  $\text{BaO}/\text{PbO}$  molar ratios. In this paper we report the dielectric behaviour of glasses and glass ceramics in the system  $\text{BaO-PbO-TiO}_2\text{-B}_2\text{O}_3\text{-SiO}_2$  where the  $(\text{BaO} + \text{PbO})/\text{TiO}_2$  ratio is kept equal to one while the  $\text{BaO}/\text{PbO}$  ratio is varied.

## 2. Experimental

Glasses were prepared using AR grade  $\text{PbO}$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{H}_3\text{BO}_3$ . Batches weighing 25 g were mixed in an agate mortar using acetone. The dry powders were transferred to high alumina crucibles. The crucibles were heated to a temperature in the range 1350–1550 K depending on the composition to melt the mass. The molten mass was held at this temperature for about half an hour with intermittent stirring to homogenize the melt. The melt was quenched by pouring into an aluminium mould and pressing with a thick aluminium plate. The transparent glass discs were quickly transferred to another pre-heated furnace maintained at 500–600 K for annealing. The annealed samples were furnace-cooled after half an hour. The compositions of various glasses are given in table 1.

The amorphisity of glasses was confirmed by X-ray diffraction. The samples were given two-stage heat treatment based on DTA studies and earlier results (Om Parkash *et al* 1986a). The two stages correspond to the nucleation and growth of ferroelectric crystalline phase. All the glass samples were heated at 860 K for 30 min (nucleation stage) and 960 K for 3 hr (growth stage).

X-ray diffraction patterns were recorded using an X-ray diffractometer (JEOL) using  $\text{Cu-K}\alpha$  radiation. For microstructural studies, samples were polished, ground and etched using 10% boiling  $\text{HCl}$ . Surface was coated with  $\text{Au-Pd}$  alloy and the microstructures were observed using a scanning electron microscope (Philips PSEM 500). For dielectric measurements, samples were ground to a thickness of 0.5–1.0 mm and air-dried silver paint was applied on both the faces. Dielectric measurements were made using an impedance analyzer (HP 4192A LF) as a function of temperature and frequency in the temperature range 300–760 K. Temperature was stabilized within  $\pm 1^\circ\text{C}$  before each measurement.

## 3. Results and discussion

Plots of dielectric constant,  $\epsilon$ , and  $\tan \delta$  at 1 kHz, 10 kHz and 100 kHz as a function of temperature for glass sample no. 2 are shown in figure 1. All the glasses listed in

**Table 1.** Composition of various glasses.

Glass No.	Composition (mol %)				
	PbO	BaO	TiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
1	42	0	42	10	6
2	31.5	10.5	42	10	6
3	10.5	31.5	42	16	0
4	10.5	31.5	42	13	3
5	10.5	31.5	42	10	6
6	0	42	42	10	6

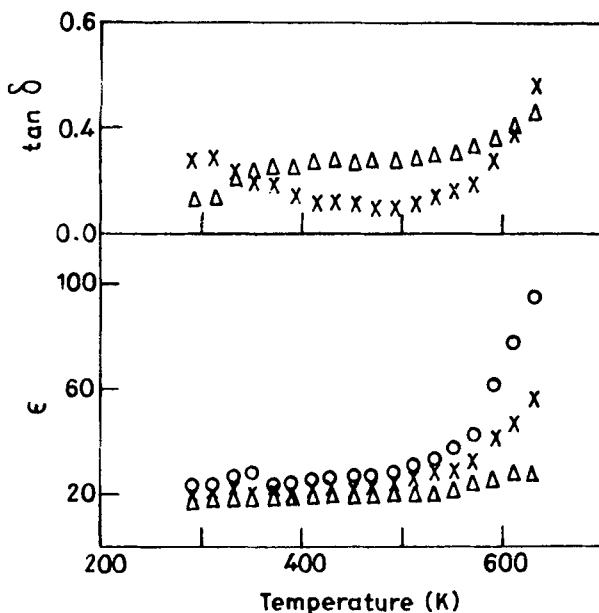


Figure 1. Variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) with temperature of glass no. 2 at 1 kHz ( $\circ$ ), 10 kHz ( $\times$ ) and 100 kHz ( $\triangle$ )

table 1 have a value of dielectric constant in the range 15–25 at 300 K and 1 kHz. These values agree with the results reported earlier (Skanavi and Kashtanova 1957). Values of dielectric constant change very little up to a particular temperature,  $T_a$ , above which they increase very sharply. Lead-rich glasses (1 and 2) show this rapid increase at lower temperature as compared to barium-rich glasses (3 to 6). Values of  $\tan \delta$  are in the range 0.10–0.20 for these glasses which seem to be high in alkali-free glasses. But this may be attributed to space charge polarization. Variation of  $\tan \delta$  with temperature is similar to that of  $\epsilon$ . Both  $\epsilon$  and  $\tan \delta$  show little frequency dispersion below  $T_a$  which become quite pronounced above it.

Figures 2 and 3 show the variation of dielectric constant,  $\epsilon$  and  $\tan \delta$  with temperature at 1 kHz, 10 kHz and 100 kHz of glass ceramics 2C and 3C respectively. It is interesting to note that the dielectric constant of glass ceramics 1C and 2C (figure 2) is not much higher than that of the parent glasses while barium-rich compositions show significant enhancement of dielectric constant over the parent glasses (figure 3). This can be understood in terms of different crystalline phases which develop during ceramization. Lead-rich compositions contain  $\text{PbTiO}_3$  and Ba-rich compositions contain  $\text{BaTiO}_3$  crystalline phase. This is supported by the X-ray diffraction data of these samples. Due to the higher dielectric constant of  $\text{BaTiO}_3$ , Ba-rich compositions show higher values of  $\epsilon$ . Variation of  $\epsilon$  with temperature is similar to the parent glasses i.e.  $\epsilon$  changes very little with temperature below a particular temperature and thereafter rises very rapidly. A similar trend is observed in  $\tan \delta$  vs  $T$  plots.

Variation of  $\epsilon$  with frequency at a few selected temperatures is shown in figure 4 for glass ceramic nos. 2C and 5C respectively. Stronger dispersion is observed in the range 1 kHz–100 kHz beyond which  $\epsilon$  seems to level off with frequency in these as

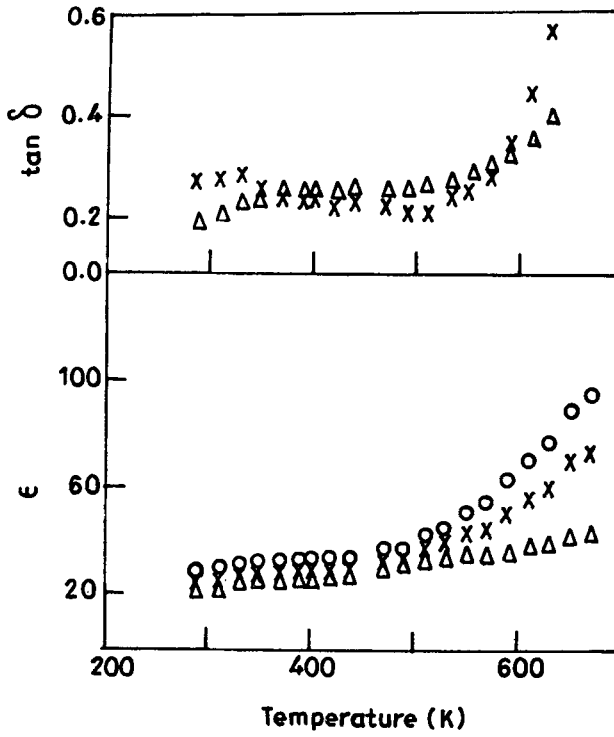


Figure 2. Variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) with temperature of glass ceramic 2C at 1 kHz ( $\circ$ ), 10 kHz ( $\times$ ) and 100 kHz ( $\Delta$ )

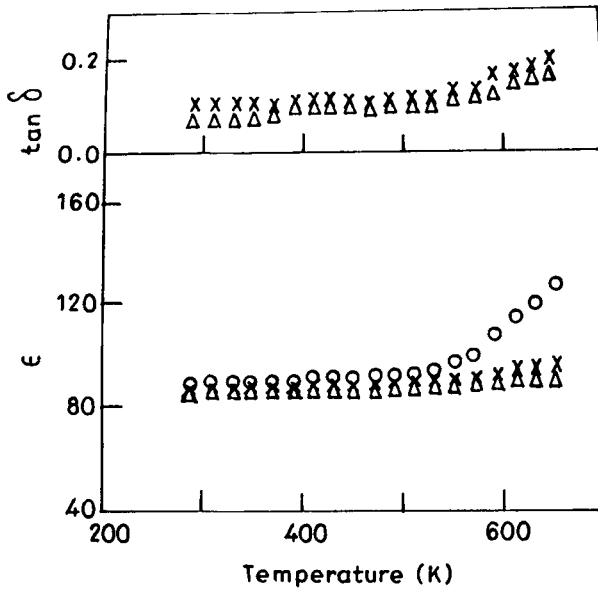


Figure 3. Variation of dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan \delta$ ) with temperature of glass ceramic 3C at 1 kHz ( $\circ$ ), 10 kHz ( $\times$ ) and 100 kHz ( $\Delta$ ).

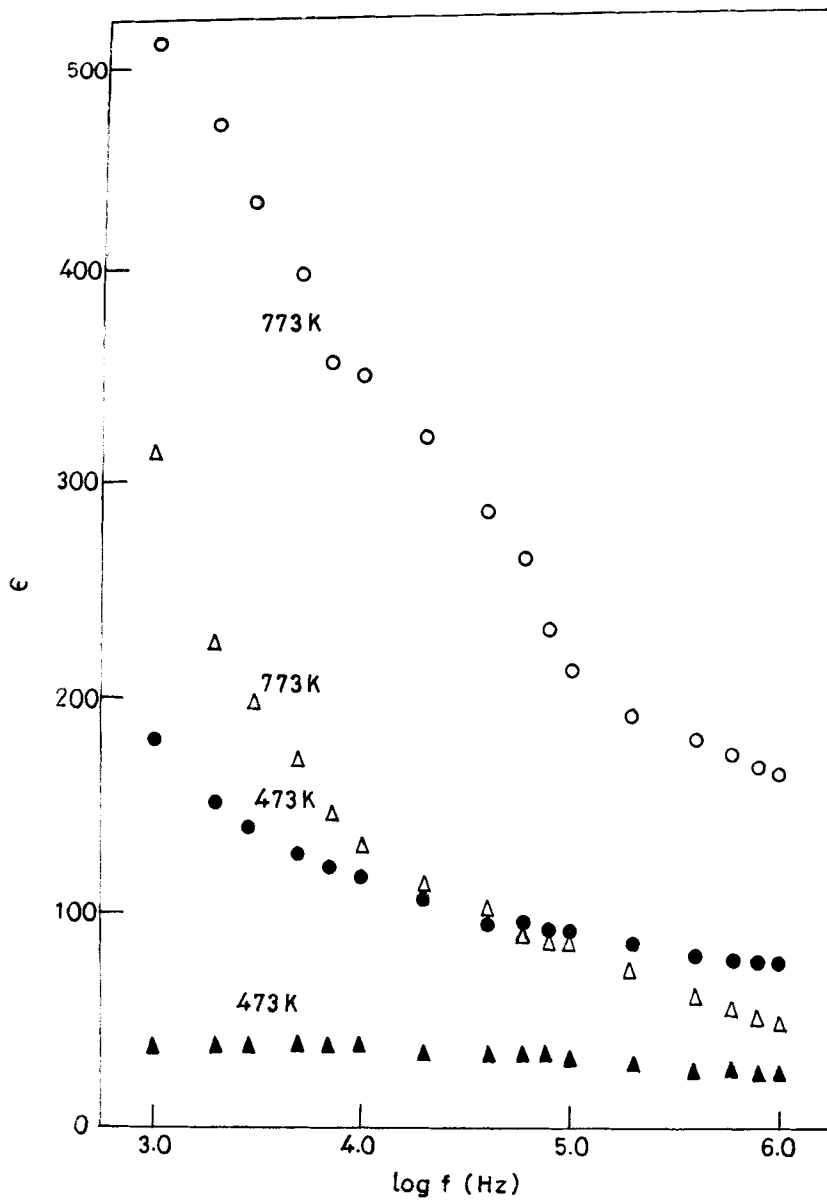
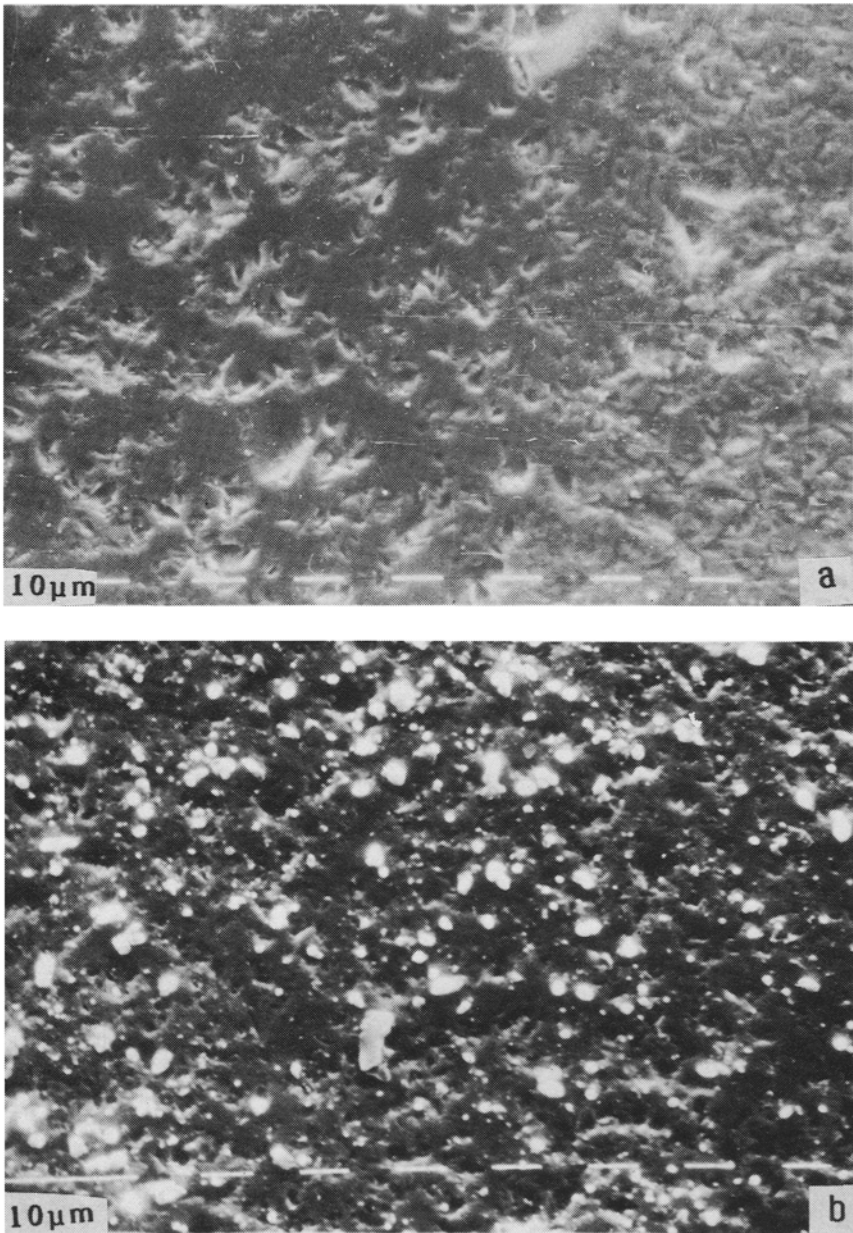


Figure 4. Variation of dielectric constant ( $\epsilon$ ) with frequency at few selected temperatures of glass ceramics 2C ( $\blacktriangle$ ,  $\triangle$ ) and 5C ( $\bullet$ ,  $\circ$ )

well as in other compositions. The frequency dependence becomes stronger with increasing temperature. Strong dispersion in the 1 kHz–100 kHz range indicates contribution of space charge and orientational polarization to the observed dielectric constant.

Figures 5(a) and 5(b) show the scanning electron micrographs of the glass ceramic samples 2C and 5C respectively. Particle size is in the range (0.8–10  $\mu\text{m}$ ) for sample 2C and (0.8–6  $\mu\text{m}$ ) for sample 5C. Distribution of particles is uniform in 5C as



**Figure 5.** Scanning electron micrograph of glass ceramic. a. 2C b. 5C

compared to 2C. Volume fraction of ferroelectric crystalline phase is smaller in 2C compared to 5C.

The observed dielectric behaviour of various glass ceramics can be understood on the basis of their microstructure. Those samples with uniform distribution of fine particles show very little variation in the dielectric constant upto quite high temperatures whereas samples with very non-uniform distribution of irregular size particles

show significant variation of  $\epsilon$ . The absence of peak in  $\epsilon$  vs  $T$  plots is due to the clamping of fine crystallites in rigid glassy matrix (Lynch and Shelby 1984). Samples with a few large crystallites, 3C and 4C do show small anomalies around 400 K which is close to the Curie temperature of  $\text{BaTiO}_3$ . It is observed from microstructural studies that the volume fraction of ferroelectric phase is quite small (less than 20 volume %). This is in conformity with the results reported earlier in an attempt to precipitate  $(\text{Ba-Sr})\text{TiO}_3$  in the glassy matrix (Herczog 1984). Attempts to produce a solid solution resulted in precipitation of a different phase lowering the yield of ferroelectric phase.

The absence of peak in  $\epsilon$  vs  $T$  plots of lead-rich samples can be understood as follows: On ceramization, two or more phases develop. The dielectric constant of these glass ceramics is not much higher than that of parent glass. This, as well as the microstructural studies, indicate that the volume fraction of  $\text{PbTiO}_3$  is quite small. As these samples are heated, dielectric constant changes very little up to  $\sim 600$  K and thereafter it increases rapidly due to space charge polarization effects. The contribution of these effects seems to dominate over that due to  $\text{PbTiO}_3$  beyond this temperature and hence masks the normal anomaly observed in  $\text{PbTiO}_3$ .

#### 4. Conclusions

The main conclusions of these investigations are:

- (i) The ferroelectric phase crystallising out during ceramization of glasses in the system  $\text{PbO-BaO-TiO}_2\text{-B}_2\text{O}_3\text{-SiO}_2$  depends on the  $\text{PbO/BaO}$  ratio if the  $(\text{PbO} + \text{BaO})/\text{TiO}_2$  ratio is 1:1. For  $\text{PbO/BaO} > 1$ ,  $\text{PbTiO}_3$  crystallizes out while for  $\text{PbO/BaO} \leq 1$ ,  $\text{BaTiO}_3$  separates out during heat treatment.
- (ii) Crystallization of solid solution  $(\text{Ba,Pb})\text{TiO}_3$  does not occur during ceramization. Reasons for this are not clear at the moment. Such attempts on the other hand reduce the yield of the ferroelectric phase. Further, the distribution of the crystallites is non-uniform and they are of varying sizes and shapes. These microstructural features impair the properties of resulting glass ceramics.

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