

Dielectric and Ferroelectric Behaviour of PbO-TiO₂-ZrO₂-B₂O₃-SiO₂ Glass-Ceramics**Dr. V. U. Rahangdale**

Assistant Professor

Department of Physics,

Jagat Arts, Commerce and I.H.P. Science College,

Goregaon-441801, District Gondia, India

Abstract:

Glass samples were prepared by conventional melt quenching technique. Based on the DTA results, these glasses were converted to glass-ceramics by the two stage heat treatment schedule. Amorphous nature of glass and formation of ferroelectric lead titanate phase in the glass-ceramic samples was confirmed from the XRD. The density of the glass and glass-ceramic samples was measured by Archimedes principle and observed to be increasing with SiO₂ addition. Volume fraction of tetragonal lead titanate phase in glass-ceramic samples was calculated from XRD which show the good correlation with observed density. Dielectric properties of glass and glass-ceramic samples were studied. Ferroelectric hysteresis measurement was carried out at room temperature. The dielectric & ferroelectric properties were improved with SiO₂ addition.

Keywords: Glass; Two Stage Heat Treatment; Glass-ceramics

Introduction

Lead titanate (PbTiO₃) is a perovskite-type ferroelectric material with high Curie temperature of 490 °C which make them attractive for high-temperature and high-frequency piezoelectric applications [1, 2]. However, pure lead titanate ceramics are very difficult to be sintered because of its large lattice anisotropy of $c/a=1.063$. PbTiO₃ ceramics when prepared by conventional route generally have microcracks and fracture on cooling below T_c as a result of the large spontaneous strain generated when the structure changes from cubic to tetragonal. This has restricted the applications of undoped PT ceramics. The glass-ceramic route therefore offers the possibility of fabricating PT without cracking [3,4].

Ferroelectric glass-ceramics with a fine-grained structure have attracted much attention and exhibited potential in many important applications since the 1960s. [5, 18]. Kokubo et al [11] have reported the studies on glass forming regions, dielectric properties and the spontaneous distortion in crystal grains of transparent glass-ceramics based on PbTiO₃. These glasses got crystallization when subjected to heat treatment between 620 °C and 740 °C. R. K. Mandal et al. [19] have studied the dielectric properties in the glass and glass-ceramics

in BaO-PbO-TiO₂-B₂O₃-SiO₂ system. They have reported that the dielectric constant was in the range 15-25 at room temperature (RT) and 1 kHz. From the literature it is observed that the lot of study has been carried out in different glass-ceramic system. But the effect of SiO₂ addition on the dielectric and ferroelectric properties has not been fully explored in lead titanate based glass-ceramics.

The idea of adding SiO₂ is to reduce the hygroscopic nature, to improve the dielectric properties and mechanical strength of the samples. Hence the present work deals with the study of dielectric and ferroelectric properties of 50 PbO : 11.75TiO₂ : 13.25 ZrO₂ : (22.5-X) B₂O₃ : (2.5+X) SiO₂ glass-ceramics.

2. Experimental

Glasses with composition 50PbO : 11.75TiO₂ : 13.25 ZrO₂ : (22.5-X) B₂O₃ : (2.5+X)SiO₂

(where X= 0, 2.5, 5, 7.5 and 10 mol %) were prepared from high purity ingredients. The raw materials taken in appropriate proportions were mixed thoroughly and heated in an alumina crucible up to a temperature range 1100 to 1200 °C. The melt was homogenized by stirring and then quenched into aluminium mould at room temperature. The resultant glass samples were annealed at 380 °C for 3 hours to remove residual stresses. The glass transition temperature (T_g) and crystallization temperature (T_c)

for all the glass samples were determined from DTA (Perkin Elmer). To develop the crystalline phases, the glass samples were subjected to two stage heat treatment schedule. For this purpose, the temperatures (490 °C and 520 °C) were considered. Keeping the temperatures fixed at 490 °C and 590 °C all the glass samples were heat treated for 28 hour. The density of glass and glass-ceramics was measured by Archimedes principle with toluene as an immersion liquid. The dielectric constant of glass and glass-ceramic samples was measured as a function of temperature using high resolution dielectric analyser (novocontrol system). The XRD for glass and glass-ceramics were recorded with Xpert PANalytical diffractometer. The ferroelectric hysteresis loop measurements were performed using Automatic PE Loop Tracer (Marine India). The values of remnant polarization (P_r) and coercive field (E_c) were determined from the hysteresis loop.

3. Results and Discussion

The glass transition temperature (T_g) and crystallization temperature (T_c) for glasses, density and room temperature dielectric constant of glass and glass-ceramics are tabulated in Table1. The T_g and T_c values are found to increase with X mol %. The addition of SiO_2 may alter the network (BO_3 to BO_4), increasing the rigidity of the glass which enhances the T_g .

Table 1: T_g , T_c , of glass, density and room temperature dielectric constant of glass and glass-ceramics and volume fraction of lead titanate (PT).

X (mol %)	T_g (°C)	T_c (°C)	ρ_{glass} (g/cm ³)	$\rho_{glass-ceramic}$ (g/cm ³)	ϵ_R	ϵ_{RT} glass-ceramic	Volume % of PT
0	440	533	5.46	5.65	36	70	26.58
2.5	448	532	5.58	5.89	44	82	34.82
5	460	546	5.59	5.97	42	84	38.02
7.5	476	559	5.63	6.02	45	98	41.52
10	480	576	5.61	6.1	67	100	44.44

T_g values for all glass samples are less than the Curie temperature ($T_c = 490$ °C) of lead titanate. This is of great advantage, since according to Lynch and Shelby [20], to avoid the crystal clamping in glass-ceramics it is essential that the T_g of the residual glass must be less than that of Curie temperature of crystal. This helps to prevent the formation of large stress at crystal glass interface. The variation of density of glass & glass-ceramic samples is shown in Fig. 1. The density values for glass-ceramic samples are observed to be higher than those of corresponding glasses and increase with SiO_2 addition.

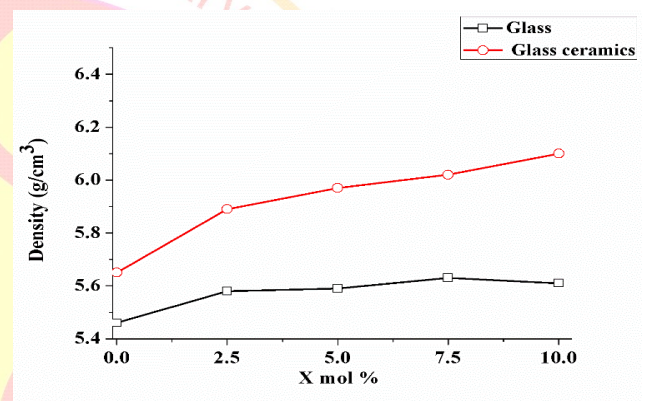


Fig. 1. Variation of density for glass & glass-ceramic samples

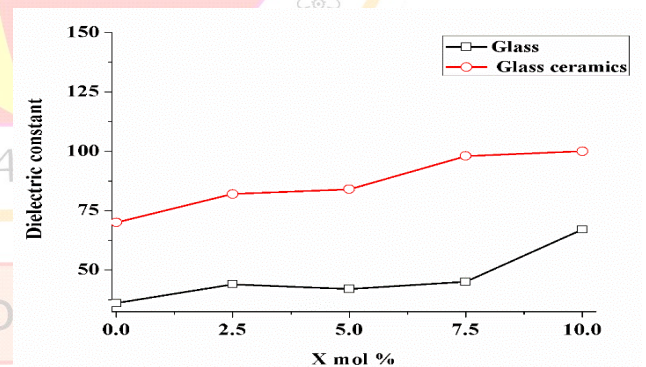


Fig. 2. Variation of room temperature dielectric constant for glass & glass-ceramic samples measured at 1 kHz

Fig.2 shows the values of room temperature dielectric constant for glass and glass-ceramic samples from which it is observed that the glass-ceramic samples have higher dielectric constant than that of corresponding glasses and increase with SiO_2 addition. This may be attributed to rigidity of structure which is in good correlation with the observed density variation.

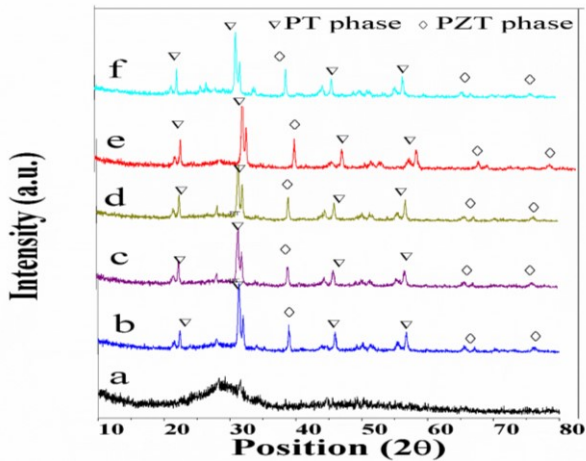


Fig. 3. XRD patterns for (a) glass, (b) 0 mol %, (c) 2.5 mol %, (d) 5 mol %, (e) 7.5 mol %, & (f) 10 mol % glass-ceramic samples

Fig.3 (a) The XRD pattern of the as quenched glass sample shows a broad hump lacking any sharp peaks, which confirm the amorphous nature. The XRD patterns of all the glass-ceramic samples are depicted in Fig.3 (b)-(f) for 0, 2.5, 5, 7.5 & 10 mol % respectively. All the major peaks matched very well with the tetragonal lead titanate phase (JCPDS-78-0298) and tetragonal lead zirconate titanium oxide phase (JCPDS-33-0784). The volume fraction of tetragonal lead titanate phase precipitate in the glass-ceramic samples is calculated from XRD patterns by comparison of integral intensities from X-ray diffraction patterns of amorphous and completely crystalline samples as per the method reported by A. G. Ilinsky et al. [20], using following equation:-

$$X_c = \frac{I(s) - I_a(s)}{I_c(s) - I_a(s)}$$

Where, $I(s)$, $I_c(s)$, $I_a(s)$ are accordingly intensities of scattering from the investigated amorphous-crystalline, completely crystalline and amorphous samples. The values of volume fraction of lead titanate phase are tabulated in Table 1. It is observed that the volume fraction of lead titanate phase is increased with the SiO_2 addition. Similar variation is observed in earlier work [22]. The observed room temperature dielectric constant shows the good correlation with the volume fraction of lead titanate as confirmed from XRD.

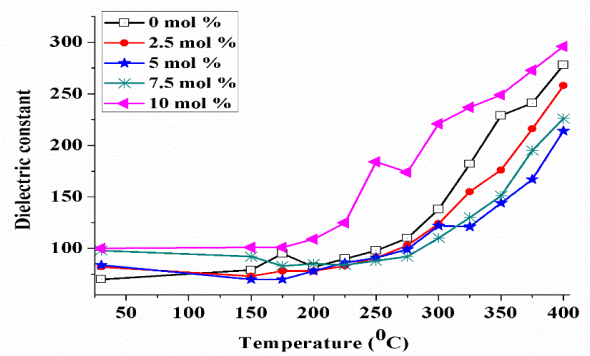


Fig. 4 (a). Variation of dielectric constant with temperature for glass-ceramic samples measured at 1 kHz

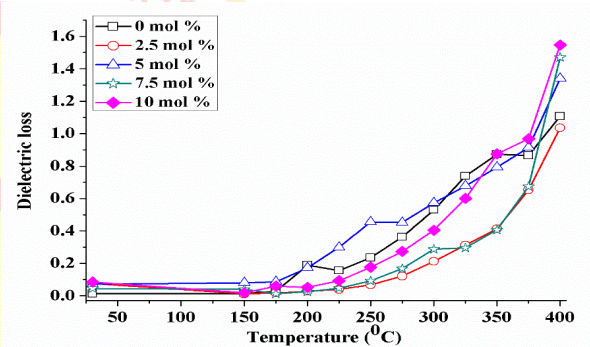
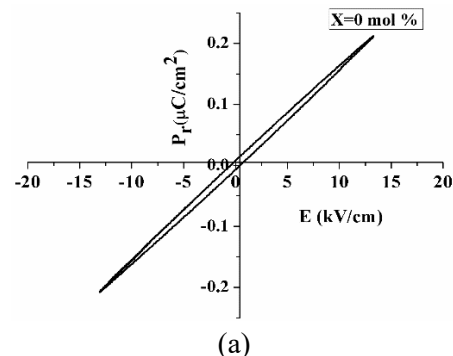


Fig. 4 (b). Variation of dielectric loss (tan δ) with temperature for glass-ceramic samples measured at 1 kHz

The variation of dielectric constant and dielectric loss with temperature for glass-ceramic samples are shown in Fig. 4 (a) and (b) respectively. The variation in dielectric constant is observed to be nearly constant up to 250 °C and showed sudden increase beyond this temperature. Similar variation is observed for dielectric loss. This may be attributed to space charge polarization. Up to 250 °C the polarization remains small as the dipoles cannot respond easily to the applied external electric field. After this temperature, the dipoles start responding to the external electric field giving high values of dielectric constant and dielectric loss. [10].



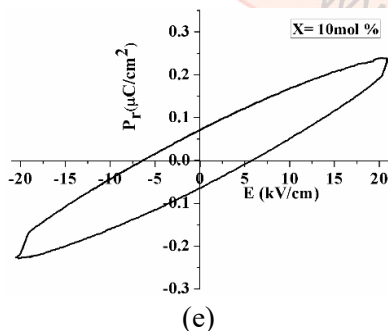
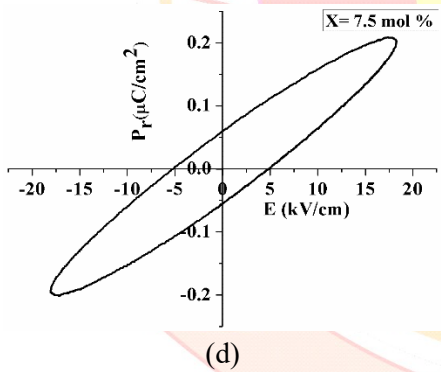
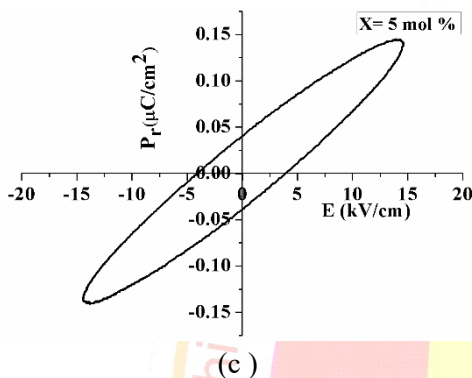
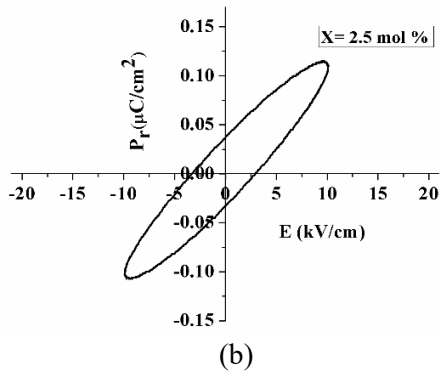


Fig. 5. Ferroelectric hysteresis loops for (a) 0,(b) 2.5, (c) 5, (d) 7.5 & (e)10 mol % glass-ceramic samples measured at room temperature

Due to the presence of tetragonal $PbTiO_3$ and PZT phase in the glass-ceramics samples as confirmed from XRD, the ferroelectric studies of these samples were carried out. The samples were poled at 5kV/cm at room temperature. The P-E measurement is carried out at room temperature. The hysteresis loops for glass-ceramic samples for 0, 2.5, 5, 7.5 and 10 mol % are shown in Fig. 5 (a) to (e) respectively. The nonsaturated loops observed for these glass-ceramic samples are may be due to the presence of residual glassy phase [23].

Table 2: Remnant polarization (P_r), maximum polarization (P_s), coercive field (E_c) and maximum field (E_{max}) for glass-ceramic samples

X (mol %)	P_r ($\mu C/cm^2$)	P_s ($\mu C/cm^2$)	E_c (kV/cm)	E_{max} (kV/cm)
0	0.008	0.21	0.45	3.19
2.5	0.034	0.11	3.09	10.01
5	0.04	0.14	3.98	14.53
7.5	0.059	0.18	5.07	17.60
10	0.075	0.13	5.16	9.24

The values of P_r , P_s , E_c and E_{max} for glass-ceramic samples are shown in Table 2. The remnant polarization is observed to increase with the mol % SiO_2 addition. This is due to the presence of tetragonal lead titanate and lead zirconate titanate phase in the glass-ceramic samples [24] Fig.7 shows the variation of remnant polarization & coercive field with the X mol % addition & found to increase with SiO_2 addition.

Conclusion:

Formation of ferroelectric phases in above prepared glass-ceramics is confirmed from XRD. The presence of SiO_2 and appropriate ratio (53:47) of the Zr:Ti helped in increasing the ferroelectric and dielectric properties of above prepared glass-ceramics. The presence of ferroelectricity would be very useful for developing these glass-ceramics for transducer materials.

Acknowledgment:

Author thanks Visvesvaraya National Institute of Technology, Nagpur (INDIA) for providing the fellowship during Ph. D.

References:

- | | |
|---|---|
| <p>[1] Ikegami S, Ueda I, Nagata T, <i>J Acoust Soc Am</i> 50 (1971) 1060.</p> <p>[2] Takahashi T, <i>Am Soc Ceram. Bull</i> 69 (1990) 691.</p> <p>[3] Palkar V R, Purandare S C, Pinto R, <i>Materials Letters</i> 43 (2000) 329.</p> <p>[4] Rahangdale V U and Deshpande V K, <i>Ferroelectrics</i> 467 (2014) 85.</p> <p>[5] Herzog A, <i>J. Am. Ceram. Soc.</i>, 47 (1964) 107.</p> <p>[6] Borrelli N F, <i>J. Appl. Phys.</i>, 38 (1967) 4243.</p> <p>[7] Layton M M and Herzog A, <i>J. Am. Ceram. Soc.</i>, 50 (1967) 369.</p> <p>[8] Borrelli N F and Layton M M, <i>IEEE Trans Electron Devices</i>, 16 (1969) 511.</p> <p>[9] Layton M M and Herzog A, <i>Glass Technol</i>, 10 (1969) 50.</p> <p>[10] Rahangdale V U and Deshpande V K, <i>Trans Indian Inst Met</i> 67, (2014) 701.</p> <p>[11] Kokubo T and Tashiro M, <i>J. Non-Cryst. Solids</i>, 13, (1973) 328.</p> | <p>[12] Tummala R R, <i>J. Mater. Sci.</i>, 11, (1976)125.</p> <p>[13] Ito S, Kokubo T, and Tashiro M, <i>J. Mater. Sci.</i>, 13 (1978) 930.</p> <p>[14] Herzog A, <i>J. Am. Ceram. Soc.</i>, 67 (1984) 484.</p> <p>[15] Wu M and Zhu P, <i>J. Non-Cryst. Solids</i>, 84 (1986) 344.</p> <p>[16] Banach U, Hubert T, Fellmuth B, and Hegenbarth E, <i>Ferroelectrics</i>, 100 (1989) 111.</p> <p>[17] Herzog A, <i>J. Am. Ceram. Soc.</i>, 73 (1990) 2743.</p> <p>[18] Kusumoto K and Sekiya T, <i>Mater. Res. Bull.</i>, 28, (1993) 885.</p> <p>[19] Mandal R K, Prasad C D, Parkash O and Kumar D, <i>Bull. Mater. Sci.</i> 9, (1987) 255.</p> <p>[20] Lynch S M, Shelby J E, <i>J Am Ceram Soc</i>, 67 (1984) 424.</p> <p>[21] Ilinsky A G, Maslov V V, Nozenko V K, Brovko A P, <i>J Mater Sci</i> 35 (2000) 4495.</p> <p>[22] Deshpande V K and Rahangdale V U, <i>ISRN Ceramics</i> 2012 (2012) 1.</p> <p>[23] Rahangdale V U, Gala D K, Acharya R M and Deshpande V K, <i>AIP Con Proc</i> 159 (2014) 705.</p> <p>[24] Rahangdale V U and Deshpande V K, <i>Materials Today: Proceedings</i> 29 (2020) 866.</p> |
|---|---|

