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Research Article

Study of $PbTiO_3$-Based Glass Ceramics Containing SiO_2

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Glass samples with composition 50PbO : 25TiO_2 : (25-X) B_2O_3 : $XSiO_2$ (with X = 0, 1.5, 2.5, 3.5, and 5 mol%) were prepared by conventional quenching technique. These glass samples were converted to glass ceramics by the two-stage heat treatment schedule. Formation of ferroelectric lead titanate phase in the glass ceramics was confirmed from the XRD. The density, CTE, and dielectric constant of the glass and glass-ceramic samples were measured. The glass-ceramic sample containing 2.5 mol% SiO_2 exhibited the highest dielectric constant. The SEMs of glass-ceramic samples were studied. The P-E hysteresis loop studies also revealed the highest remnant polarization for this sample, which has a potential for being developed for practical applications.

1. Introduction

Lead titanate was reported to be ferroelectric in year 1950 on the basis of its structural analogy with $BaTiO_3$. The high transition temperature around 490°C [1] exhibited by $PbTiO_3$ was important from high temperature application point of view. Pore-free fine-grained microstructure and better properties can be achieved through controlled crystallization [2]. The glass crystallization method by thermal treatments is attractive because it can be conducted at lower temperatures and allows greater control over phase separation and crystallization [3]. The controlled crystallization of the perovskite $PbTiO_3$ was reported by Herczog [4]. Undoped perovskite titanate such as $PbTiO_3$ has been extensively studied [5]. A lot of work in the field of glass ceramics has been done on the electrical and thermal properties. However, few investigations have been reported on the high-permittivity glass ceramics containing $PbTiO_3$. Kokubo and Tashiro [6] have reported the studies on glass-forming regions, dielectric properties, and the spontaneous distortion in crystal grains of transparent glass ceramics based on $PbTiO_3$. These glasses got crystallization when subjected to heat treatment between 620°C and 740°C. Mandal et al. [7] have studied the dielectric properties in the glass and glass ceramics in BaO–PbO–TiO_2–B_2O_3–SiO_2 system. They have reported that the dielectric constant was in the range 15–25 at room temperature (RT) and 1 kHz.

The lead titanate-based glass ceramics containing B_2O_3 are vulnerable to moisture, and the problem can be addressed by the addition of SiO_2. Hence, the present work is aimed at the study of synthesis and characterization of $PbTiO_3$ glass ceramics, containing SiO_2.

2. Experimental

Glasses with composition 50PbO : 25TiO_2 : (25-X)B_2O_3 : $XSiO_2$ (where X = 0, 1.5, 2.5, 3.5, and 5 mol%) were prepared from high purity ingredients. The raw materials taken in appropriate proportions were mixed thoroughly and heated in alumina crucibles up to a temperature 40°C above the melting point which was in the range 1100°C 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 520°C all the glass samples were heat treated for 28 hrs (14 h nucleation + 14 h crystallization). The density of glass and glass-ceramics was measured by Archimedes principle with toluene as an immersion liquid. The coefficient of thermal expansion (CTE) of glass and glass-ceramic samples was measured using Orton dilatometer. The dielectric constant of glass and glass-ceramic samples was measured as a function of temperature at different frequencies using high-resolution dielectric analyser (Novocontrol system). The microstructure analysis was carried out by scanning electron microscope (JSM-7600F). The XRDs of 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 density, CTE of glass and glass-ceramics, and T_g values have been tabulated in Table 1. The density of glass-ceramic samples was observed to be higher than those of corresponding glasses. The variation in density of glass as well as glass-ceramics with SiO_2 content was not much significant. The maximum value of density was obtained for 2.5 mol% SiO_2 containing glass-ceramic sample. This was due to the higher volume fraction of lead titanate phase in glass matrix as confirmed from XRD. The coefficient of thermal expansion (CTE) for glass-ceramic samples had lower value than the corresponding glass samples, which may be attributed to the rigidity of the structure. Similar results have been reported for lead titanate glass-ceramics [8]. The lower values of CTE for glass-ceramics compared to glasses support the density results. Table 1 also shows the T_g values for all the glass samples. The variation in T_g with the addition of SiO_2 was not much significant. It was observed that the T_g values for all the glass samples were less than the curie temperature (T_c = 490°C) of lead titanate. This was of great advantage since according to Lynch and Shelby [9], to avoid the crystal clamping in glass-ceramics it was essential that the glass transition temperature (T_g) of the residual glass must be less than that of curie temperature of the ferroelectric crystal. This helps to prevent the large stresses at crystal glass interface.

The XRD patterns of a glass and all glass-ceramic samples have been shown in Figure 1. The XRD pattern of the as-quenched glass sample showed a broad hump with the absence of any sharp peaks, which confirmed the amorphous nature. All the glass-ceramic samples were found to have lead titanate as the major crystalline phase. All the major peaks matched very well with the tetragonal lead titanate phase (JCPDS-78-0298). Some low intensity lines were observed which were assigned to the lead borate phase (JCPDS-70-1389). The values of volume fraction of lead titanate phase, average crystallite size for glass-ceramic samples along with

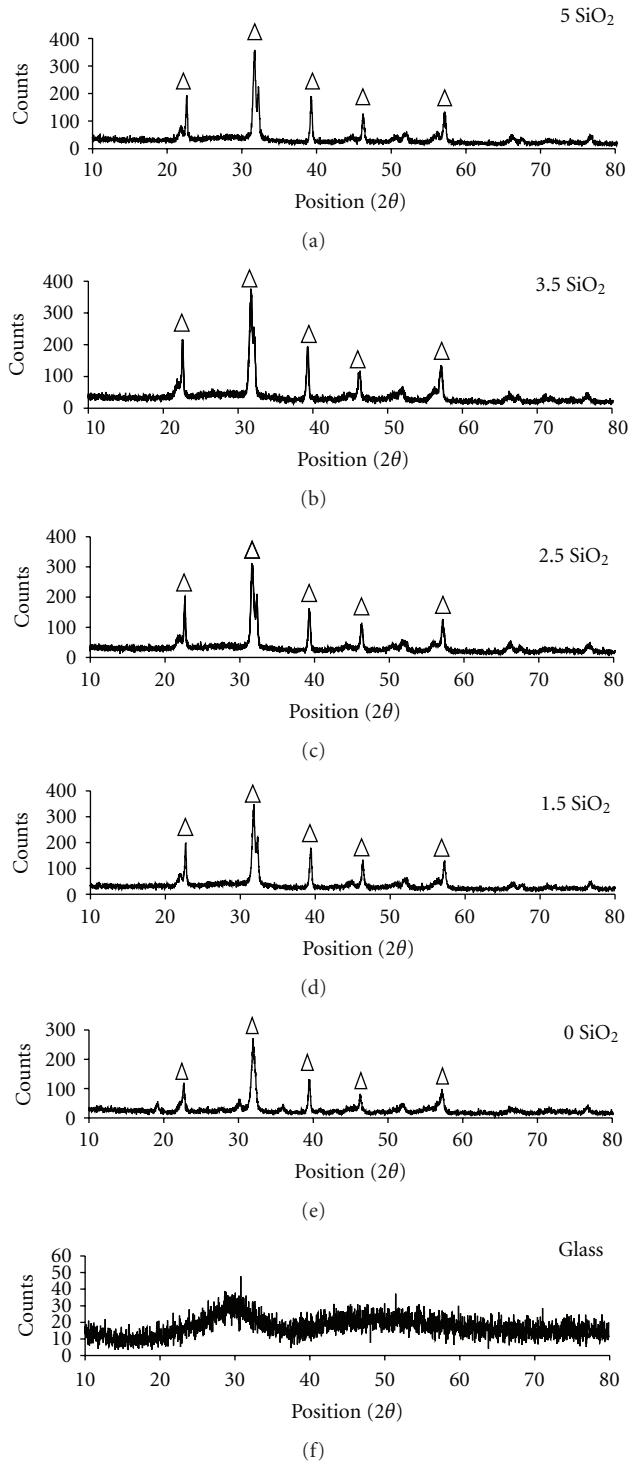


Figure 1: XRD patterns of the glass and glass-ceramic samples.

the room temperature dielectric constant for glass and glass-ceramics samples have been tabulated in Table 2. The volume fraction of lead titanate crystalline phase was calculated by comparison of integral intensities from X-ray diffraction patterns of amorphous and completely crystalline samples as per the method reported by Ilinsky et al. [10]. The volume

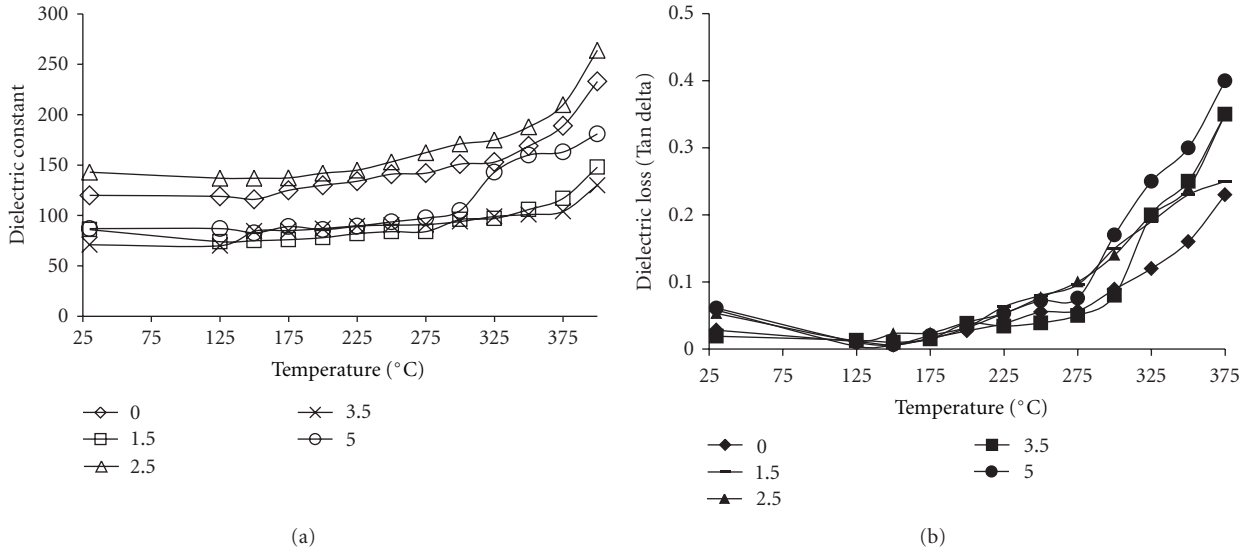


Figure 2: (a) Variation of dielectric constant with temperature at 1 kHz for glass-ceramic samples. (b) Variation of dielectric loss (Tan delta) with temperature at 1 kHz for glass-ceramic samples.

Table 1: Density and CTE for glass and glass-ceramic samples along with T_g values for glasses.

SiO_2 (mol %)	Density of glass (g/cm^3)	Density of glass ceramic (g/cm^3)	CTE for glass (10^{-6}/K)	CTE for glass ceramics (10^{-6}/K)	T_g (°C)
0	5.67	6.2	9.13	6.23	430
1.5	5.73	6.09	8.7	6.13	430
2.5	5.76	6.14	8.89	5.6	443
3.5	5.8	6.08	9.54	5.42	446
5	5.81	6.12	8.15	4.84	449

fraction of the $PbTiO_3$ in 2.5 mol% SiO_2 containing glass-ceramic sample was found to be 57.47%. The average particle size was calculated using Scherrer's formula, which was observed to be in the range of 57–69 nm, for all the glass-ceramic samples.

The room temperature dielectric constant of glass-ceramic samples was higher than those of corresponding glasses. The values of room temperature dielectric constant for glass and glass-ceramics were observed to be in the range of 51–66 and 71–143, respectively. The glass-ceramic sample with 2.5 mol% SiO_2 has shown maximum value of dielectric constant which may be due to the formation of optimum perovskite lead titanate phase in the glass-ceramics as confirmed from XRD. The variation of dielectric constant and dielectric loss (Tanδ) as a function of temperature for glass-ceramic samples has been depicted in Figures 2(a) and 2(b), respectively. The dielectric constant was observed to be nearly constant up to 300°C and showed sudden increase beyond this temperature. Similar variation was observed for dielectric loss. This may be attributed to space charge polarization [8].

The SEM micrographs for glass-ceramic samples have been shown in Figures 3(a), 3(b), 3(c), 3(d), and 3(e). The SEM images of 0, 1.5, and 2.5 mol% SiO_2 containing glass-ceramic samples showed the presence of fine rounded crystals of $PbTiO_3$ surrounded by the residual glass phase. The average crystallite size was found to be highest for glass-ceramic sample containing 2.5 mol% SiO_2, which supported the dielectric constant and volume fraction results. SEM images for 3.5 and 5 mol% SiO_2 containing glass-ceramic samples revealed the presence of voids and cracks, which may be responsible for the decrease in dielectric constant. Thus it is observed that the value of dielectric constant of glass ceramics is governed by the volume fraction of $PbTiO_3$ crystallized and the average particle size.

Due to the presence of fine $PbTiO_3$ crystallites in the glass-ceramic samples as confirmed from XRD and SEM results, the ferroelectric studies of these samples were carried out. The representative hysteresis loops for 0 and 2.5 mol% SiO_2 added to glass-ceramic samples are shown in Figures 4(a) and 4(b), respectively. The saturated loops were observed for these samples. This can be understood on the basis of presence of $PbTiO_3$ crystals in the glass-ceramic samples. The values of P_r and E_c at room temperature have been tabulated in Table 3. These are preliminary results, and further enhancement in the values of P_r and E_c can be obtained by optimizing the processing parameters of the glass ceramics.

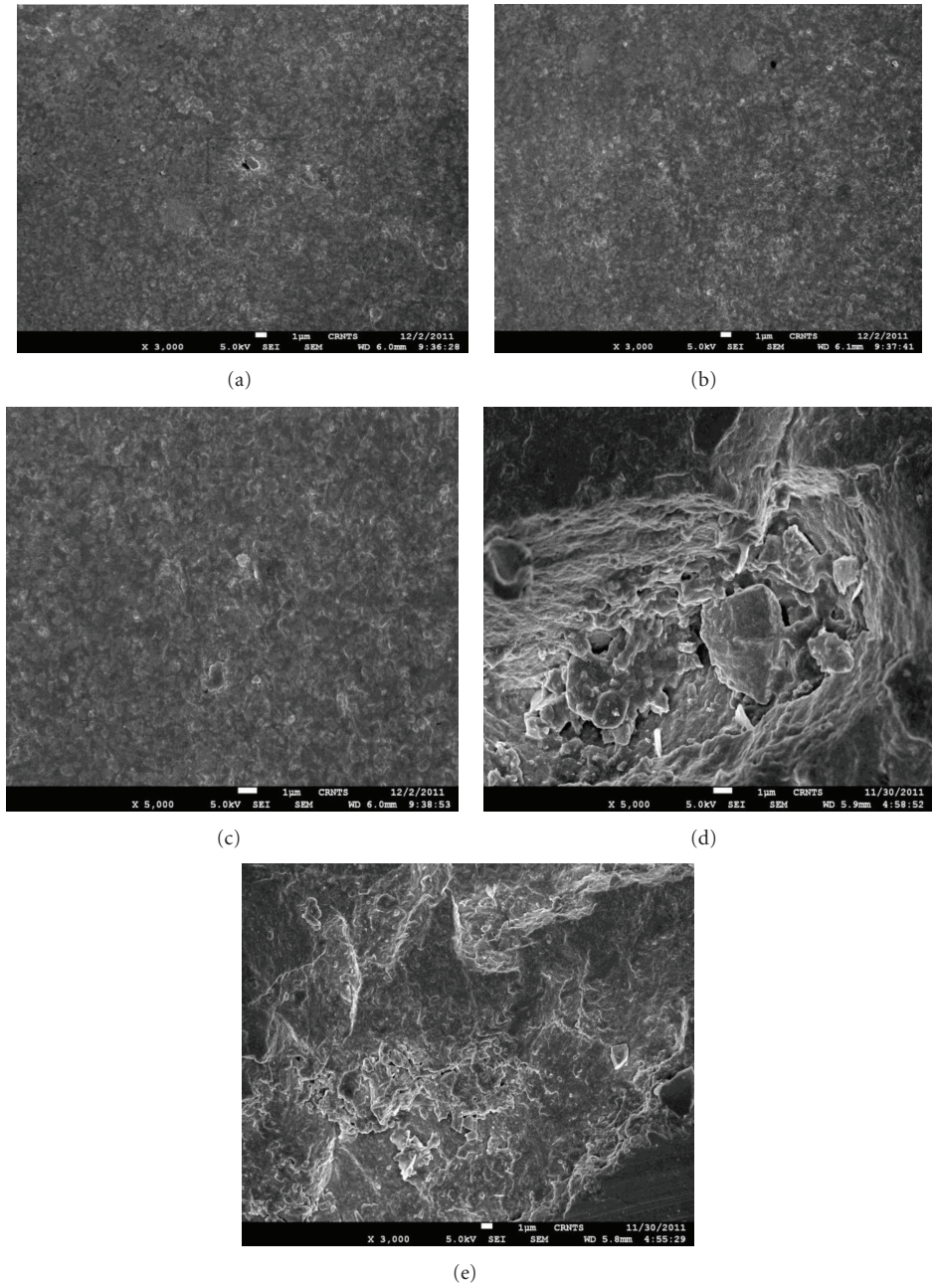
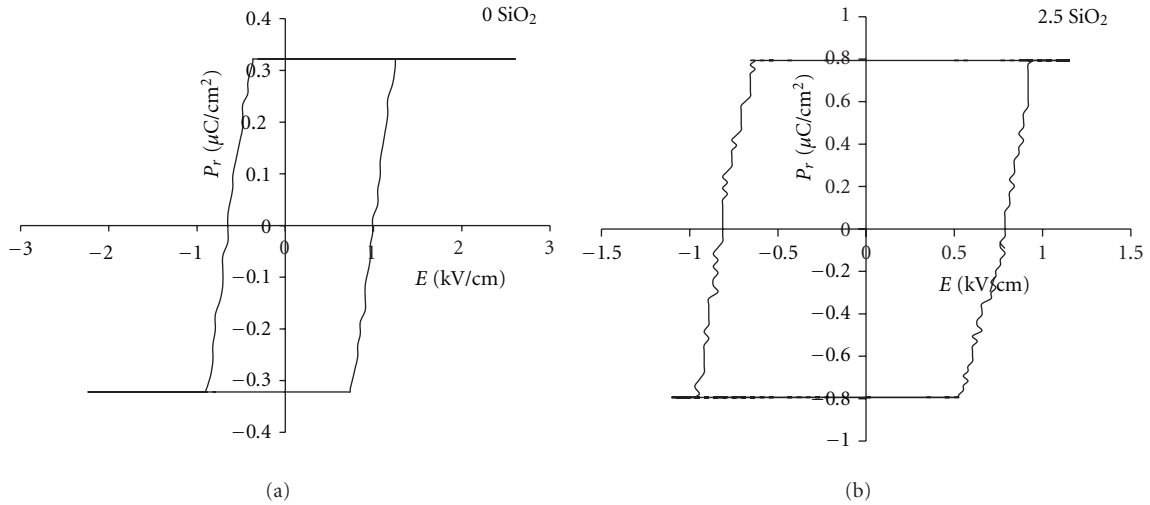


Figure 3: SEM of glass-ceramic samples: (a) 0 mol% SiO_2, (b) 1.5 mol% SiO_2, (c) 2.5 mol% SiO_2, (d) 3.5 mol% SiO_2, and (e) 5 mol% SiO_2.

Table 2: Volume fraction of $PbTiO_3$, average particle size, and RT dielectric constant for glass and glass ceramics.

SiO_2 (mol %)	Volume fraction of $PbTiO_3$	Average particle size (nm)	RT dielectric constant of glasses at 1 kHz	RT dielectric constant of glass ceramics at 1 kHz
0	55.64	69.57	66	120
1.5	52.26	69.44	51	86
2.5	57.47	69.57	54	143
3.5	40.58	57.53	65	71
5	44.78	58.69	60	87



(a) (b)

Figure 4: Hysteresis loops for glass-ceramic samples: (a) 0 mol% SiO_2 and (b) 2.5 mol% SiO_2.

Table 3: Remnant polarization (P_r) and coercive field (E_c) for glass-ceramics samples.

SiO_2 (mol %)	P_r (μC/cm^2)	E_c (kV/cm)
0	0.32	0.85
1.5	0.31	1.92
2.5	0.79	0.81
3.5	0.03	7.17
5	0.04	7.16

4. Conclusion

From the present study it can be concluded that the glass-ceramic sample with 2.5 mol% SiO_2 exhibited optimum density, dielectric constant, and remnant polarization in the entire series. This sample has a potential for developing it further for practical applications. The dielectric constant of the glass-ceramics is governed by the volume fraction of $PbTiO_3$ crystallized in them.

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