

Research Article

Dielectric Properties of La_2O_3 Doped Composite $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ Borosilicate Glass Ceramic

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Ferroelectric $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ (PST) perovskite phase has been crystallized in borosilicate glassy matrix with a suitable choice of composition and heat treatment schedule. La_2O_3 is a donor dopant for PST and can make it semiconducting. Dispersion of semiconducting perovskite phase in insulating glassy matrix in glass-ceramic samples may lead to the formation of space charge polarization around crystal-glass interface, leading to a high value of effective dielectric constant, ϵ_r . Therefore, with the aim of the developing glass ceramics with high dielectric constant, glasses in the system $64[(\text{Pb}_x\text{Sr}_{1-x})\text{O}\cdot\text{TiO}_2]-25[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-5[\text{K}_2\text{O}]-5[\text{BaO}]-1[\text{La}_2\text{O}_3]$ have been prepared ($0.5 \leq x \leq 1$). It is found that the addition of La_2O_3 strongly affected the crystallization and dielectric behavior of glass-ceramic with PST perovskite phase. All glass ceramic samples show a diffuse broad Curie peak in their ϵ_r versus T plots. Curie peak temperature, T_c , depends on compositions of the glass-ceramic samples as well as frequency of measurements.

1. Introduction

Lead titanate is a ferroelectric material having a cubic crystal structure similar to BaTiO_3 with a high Curie point (490°C). On decreasing the temperature through the Curie point a phase transition from paraelectric cubic phase to ferroelectric tetragonal phase takes place [1]. In recent years a considerable amount of work has been done on the ferroelectric properties of BaTiO_3 . In addition to BaTiO_3 , there are other different perovskites which have been reported as ferroelectrics [2]. On heating, BaTiO_3 undergoes a ferroelectric/paraelectric phase transition to the cubic polymorphism at a Curie temperature, T_C , of $\sim 130^\circ\text{C}$, at which high value of dielectric constant is 10,000 in undoped ceramic samples. The phase transition is first order, and the peak in ϵ_r is correspondingly sharp [3]. PbTiO_3 shows higher temperature applications, since its Curie temperature, T_C , has been reported to lie in the neighborhood of 500°C (490°C). Moreover the axial ratio c/a for PbTiO_3 in the tetragonal phase is 1.063, markedly larger than that in BaTiO_3 . Hence it is expected that PbTiO_3 should possess outstanding ferroelectric properties. PbTiO_3 and SrTiO_3 ceramics are well known to form solid solution

$(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ (PT-ST) with each other over the entire range of composition, that is, for $0.0 \leq x \leq 1.0$. Curie temperature, T_C , is one parameter, which is very sensitive to the composition, x . T_C , of PT-ST solid solution series that has been reported to vary linearly with composition “ x ” [4]. These ceramics with donor doping have high-value dielectric constant due to space charge polarization at semiconducting grains and insulating grain boundary or phases and show relaxer like behavior [5]. Various studies on the crystallization behavior and dielectric properties of glass-ceramics containing crystalline phase such as PbTiO_3 [6–14] and SrTiO_3 have been reported [15–22]. Studies on crystallization and dielectric behavior of solid solution lead strontium titanate glass-ceramics have been carried out by Sahu et al. [23–26]. Strontium rich glass-ceramics have cubic crystal phases and are nonferroelectric, whereas lead rich glass-ceramics are ferroelectric and Curie temperature linearly decreases with increasing strontium. No report is available on the very high value of dielectric constant in PT and ST or PST glass-ceramic system in the literature. While exploring the possibility of crystallization of perovskite SrTiO_3 phase in borosilicate

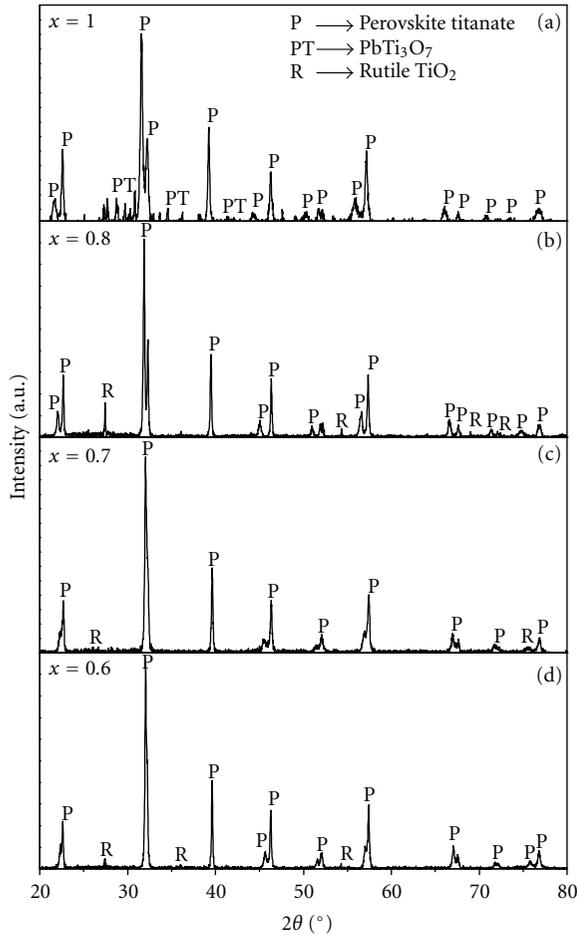


FIGURE 1: X-ray diffraction patterns of different glass-ceramic samples (a) PTL5B700T, (b) 8PL5B726T, (c) 7PL5B739T, and (d) 6PL5B730T.

glass, Thakur et al. also considered it worthwhile to study the effect of different rare earth and transition metal oxide additives on crystallization, a microstructural and dielectric behavior of SrTiO_3 -based glass-ceramics. It was reported that these additives also act as dopants for SrTiO_3 phase and change its electrical characteristics, resulting in a high value of dielectric constant due to space charge polarization at semiconducting crystal and insulating glass interface.

In the present paper efforts have been made to achieve a high value of dielectric constant in the PST borosilicate glass-ceramic system using a rare earth La_2O_3 as a dopant. The value of dielectric constant mainly depends on the crystallization behavior of the glasses and also on the doping. Perovskite PST solid solution phase has crystallized in borosilicate glassy matrix successfully. To see the effect of holding time on the dielectric properties of the glass-ceramic samples, all the glasses were crystallized for 3 hours. The determination of T_C , of glass-ceramic samples, may provide information regarding the composition of the perovskite ferroelectric phase crystallized in various compositions.

2. Materials and Methods

Glasses in the present system $64[(\text{Pb}_x\text{Sr}_{1-x})\text{O}\cdot\text{TiO}_2]-25[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-5[\text{K}_2\text{O}]-5[\text{BaO}]-1[\text{La}_2\text{O}_3]$ ($0.5 \leq x \leq 1$) were prepared by conventional melt quench method. Well mixed, dried powders containing appropriate amount of reagent grade PbO , SrCO_3 , TiO_2 , SiO_2 , H_3BO_3 , K_2CO_3 , BaCO_3 , and La_2O_3 were melted in pure alumina crucibles for an hour in the temperature range $1120\text{--}1240^\circ\text{C}$ under normal atmospheric conditions. The melt was quenched by pouring it in an aluminum mould and pressing with a thick aluminum plate. The glasses were then annealed at 400°C for 4 hr. Glass-ceramic samples were prepared by subjecting glasses to various heat treatment schedules based on their DTA results. Phases were identified using powder X-ray diffraction (XRD) analysis. Diffraction patterns were recorded employing a Rigaku ID 3000 diffractometer using Cu K_α radiation. The crystalline phase in each glass-ceramic sample was identified by comparing its XRD pattern with standard patterns of various crystalline phases which might have formed from different constituent oxides of the glass. The glass-ceramic samples were polished, etched with of 30 and 20 percent of HNO_3 and HF solution for 60 seconds. Etched glass-ceramic samples were coated with a thin film of gold for SEM. Observations were taken by using model number JSM-840.

For dielectric measurement of glass-ceramic samples, both the surfaces of these samples were ground and polished using SiC powders for attaining smooth surfaces to a thickness of 0.5 to 1 mm. The electrodes were made by applying silver paint (code Number 1337—A, Elteck Corporation, India) on both sides of the specimen and curing at 700°C for 5 minutes. The capacitance, C , measurements were made in a locally fabricated sample holder using an automated measurement system during heating. The sample was mounted in the sample holder, which was kept in a programmable heating chamber. The leads from the sample holder were connected to HP 4284 A, Precision LCR meter through scanner relay boards, and HPIB bus, which in turn was connected to a computer and printer. Measurement operational controls and data recording are done through the computer. The sample was heated in the heating chamber to the required temperature at a rate of $2^\circ\text{C}/\text{min}$. C and dissipation factor, D , of the glass-ceramic samples were recorded with 0.1, 1, 10, 100 KHz, and 1 MHz at equal intervals of time during heating in the temperature range $RT \sim 27\text{--}500^\circ\text{C}$. Dielectric constant, ϵ_r , was calculated from the measured C , using the following equation:

$$\epsilon_r = \frac{C \times d}{\epsilon_0 A}, \quad (1)$$

where C is the capacitance in farad, F , ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ F/m}$), d is the thickness (m), and A is the area (m^2) of the samples. The ϵ_r and D were plotted as a function of T , at a few selected frequencies to show the variation of ϵ_r , with T , and frequency of applied electric field.

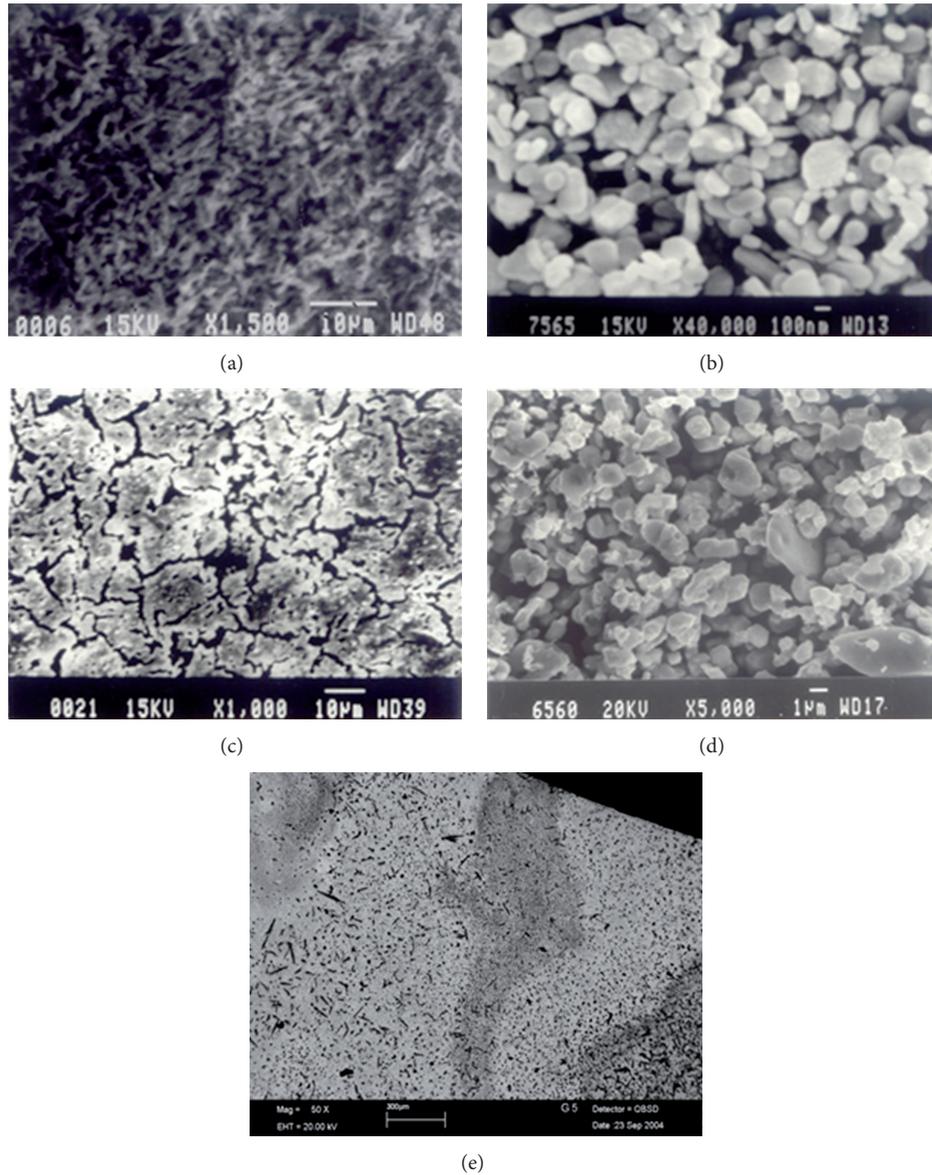


FIGURE 2: Scanning electron micrographs of glass-ceramic samples (a) PTL5B700T, (b) 9PL5B695T, (c) 8PL5B726T, (d) 7PL5B739T, and (e) 5PL5B806T.

Dissipation factor was noted directly or calculated by using the following relation:

$$D = \frac{G}{\omega C}, \quad (2)$$

where $\omega = 2\pi f$, f -is the frequency, and G is the conductance.

Five letters glass code represents the composition of the glass. First two letters PT, 9P, and so forth designate the fraction of lead, Pb, that is, x in the glass. PT refers to $x = 1.0$, that is, 100 percent Pb. 9P, 8P, and so forth refer to $x = 0.9, 0.8$ and so forth, respectively. The third letter L indicates that La_2O_3 is used as an additive. The last two letters 5B indicate to fraction of BaO. For the nomenclature of the glass-ceramic samples the first five letters in the code samples are similar to the code of their parent glass. Next three digits

indicate the crystallization temperature. The last letter T refers to 3 hours holding time at crystallization temperature. For example the glass-ceramic code PTL5B700T represents the glass-ceramic sample prepared from the parent glass PTL5B heat treated at 700°C for 3 hours. Similar coding processes have been adopted for the other glass-ceramic samples as shown in the Table 1.

3. Results

3.1. XRD Analysis. XRD patterns for glass-ceramic samples PTL5B700T, 8PL5B726T, 7PL5B739T, and 6PL5B730T, respectively, are shown in Figure 1. It is observed from the XRD patterns that perovskite PbTiO_3 (P) or $(\text{PbSr})\text{TiO}_3$ (PST) is the major crystalline phase, PbTi_3O_7 (PT), and

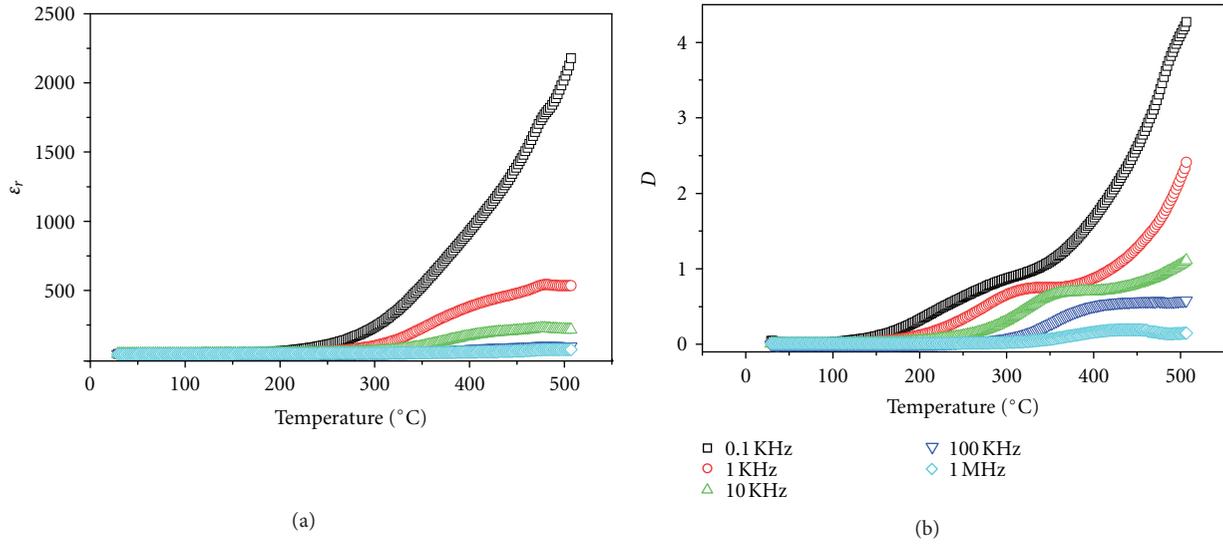


FIGURE 3: Variation of (a) dielectric constant, ϵ_r , and (b) dissipation factor, D , with temperature at different frequencies for the glass-ceramic sample PTL5B700T.

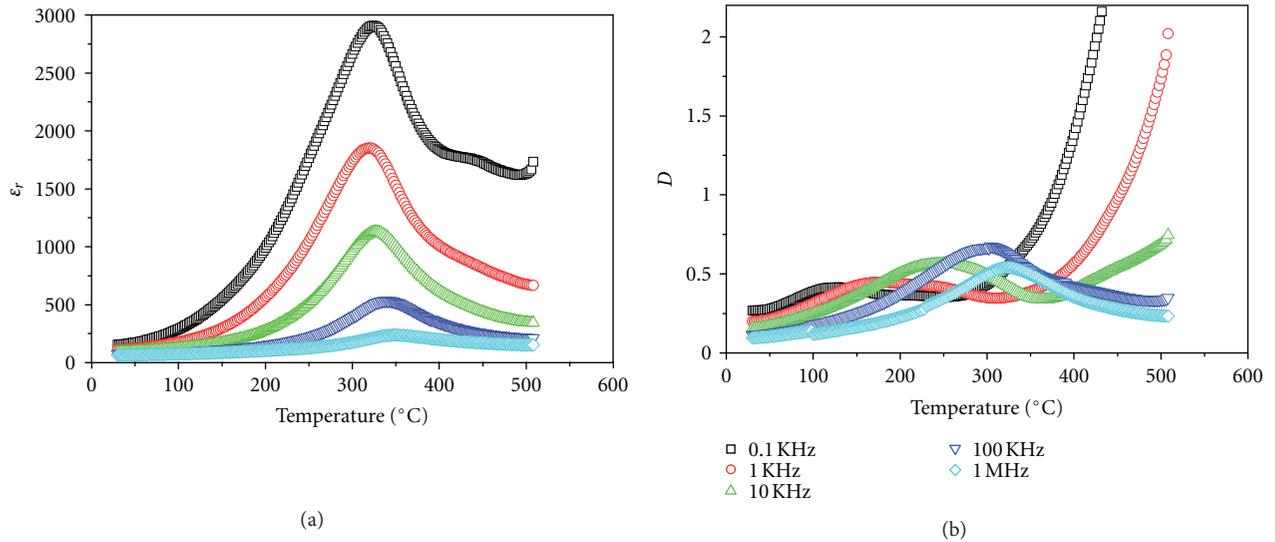


FIGURE 4: Variation of (a) dielectric constant, ϵ_r , and (b) dissipation factor, D , with temperature at different frequencies for the glass-ceramic sample 8PL5B726T.

TABLE 1: Dielectric characteristics of various glass-ceramic samples in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{O}\cdot\text{TiO}_2]-[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-[\text{K}_2\text{O}]-[\text{BaO}]-\text{La}_2\text{O}_3$.

Glass ceramic codes	Grain size (μm)	T_c at 1 KHz ($^{\circ}\text{C}$)	ϵ_r at 1 KHz at RT	Dissipation factor D at 1 KHz at RT	ϵ_r at T_c	T_c of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ ceramics [4]
PTL5B700T	2.25	481	40	0.0102	542	495
8PL5B726T	3.01	320	114	0.1990	1852	323
7PL5B739T	1.05	250	275	0.2706	2158	283
6PL5B730T	0.80	219	726	0.0877	8260	211
5PL5B806T	2.22	140	494	0.6636	1921	120

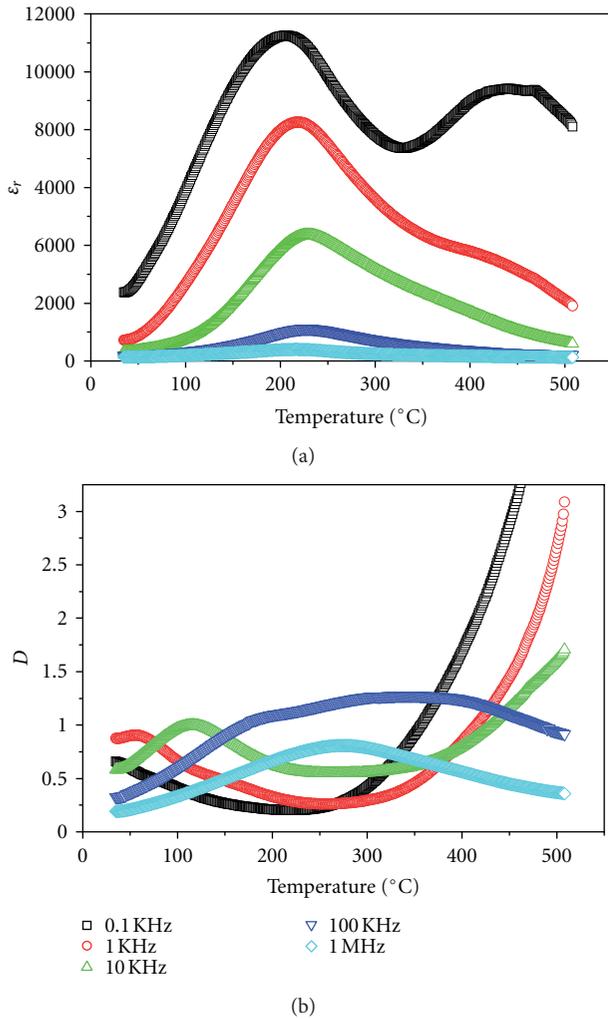


FIGURE 5: Variation of (a) dielectric constant, ϵ_r , and (b) dissipation factor, D , with temperature at different frequencies for the glass-ceramic sample 6PL5B730T.

TiO₂ (R) are the secondary minor phases in these glass-ceramics. The nature as well as amount of the minor phases depend on the initial compositions, x , of the glass and heat treatment schedule. The structure of major crystalline phase is tetragonal similar to PbTiO₃, and its lattice parameters, “ a ” and “ c ,” depend on the composition of the glass-ceramics, and the crystallization temperature. The axial ratio, c/a , decreases with increasing Sr content similar to (PbSr)TiO₃ solid solution ceramics. More results on lattice parameters and crystal structure are discussed in earlier published research paper [27].

3.2. Scanning Electron-Microscopic Analysis. Figures 2(a)–2(e) show scanning electron micrographs of a few selected glass-ceramic samples PTL5B700T, 9PL5B695T, 8PL5B726T, 7PL5B739T, and 5PL5B806T, respectively. The SEM micrographs show that submicrometer crystallites are uniformly distributed in the glassy matrix. The volume fraction of crystallites is large in comparison to the volume fraction of

the residual glass. It indicates that La₂O₃ acts as a nucleating agent and promotes the crystallization of perovskite phase [28]. Figure 2(c) shows dispersion and clear phase separation of the major perovskite phase in the glassy matrix. Well-developed interconnected and randomly distributed grains of the major crystalline phase have been clearly observed in the scanning electron micrograph of glass-ceramic sample 7PL5B739T (Figure 2(d)). Figure 2(e) depicts the SEM image of glass-ceramic sample 5PL5B806T crystallized at 739°C for 3 hr heat treatment schedule of the parent glass. The crystallized major phase of (PbSr)TiO₃ along with pyrochlore phase of rutile, R, distributed randomly inside the residual glassy matrix. The pyrochlore phase of R is also confirmed from XRD analysis for the same glass-ceramic sample. The shift in XRD peak positions of PbTiO₃ in the glass-ceramic samples as compared with the standard PbTiO₃ is reflected in the values of their lattice parameters. It may be due to the formation of lead titanate perovskite phase of solid solution of crystallites [27].

3.3. Dielectric Properties. The variation of dielectric constant, ϵ_r , and dissipation factor, D , for different glass-ceramic samples in the present system are shown in Figures 3–5. Figure 3 shows the dielectric behavior for the glass-ceramic sample PTL5B700T obtained by crystallizing glass at 700°C. Dielectric behavior of this glass-ceramic sample show very small temperature dependence of dielectric constant up to 200°C at all frequencies. Beyond this temperature, the magnitude of ϵ_r increases with increasing temperature, T , at 0.1, 1.0, and 10 KHz. The increase in the ϵ_r is higher at smaller frequencies. These glass-ceramics contain alkali ions, which are having high mobility. Increase in ϵ_r and D may be due to increase in electrical conduction with increasing T . Broad peak can be associated with ferroelectric to paraelectric phase transitions in PbTiO₃, crystallites present in the ϵ_r versus T as well as D versus T plots for this glass-ceramic sample. The temperature is very close to the Curie temperature, T_C of PbTiO₃ glass-ceramics (Table 1). Variation of D versus T shows almost similar behaviors except that broad peaks are observed within the same temperature range. These peaks are shifted toward higher-temperature side with increasing frequency, f , and show relaxor like behavior. In relaxor ferroelectrics a peak in ϵ_r versus T plots is observed at different frequencies. Since the ϵ_r increases rapidly with increasing T , around this temperature, this peak seems to be hidden by rapidly rising in ϵ_r due to rapidly increasing space charge polarization with T . Figures 4 and 5 depict variation of ϵ_r and D versus T , for the glass-ceramic samples 8PL5B726T and 6PL5B730T. The variation of ϵ_r with T , for both glass-ceramic samples, is almost similar while the variation of D with T is different. A broad peak is observed there ϵ_r versus T plots. The broadening in the ϵ_r peaks of 6PL5B730T with increasing frequency is more in comparison to the glass-ceramic sample 8PL5B726T [29]. This is due to increasing concentration of Sr. It is also observed that the position of the peak shifts to higher temperature with increasing f , in both ϵ_r plots as well as in D versus T plots. After this peak, the dielectric loss, D , again increases rapidly with

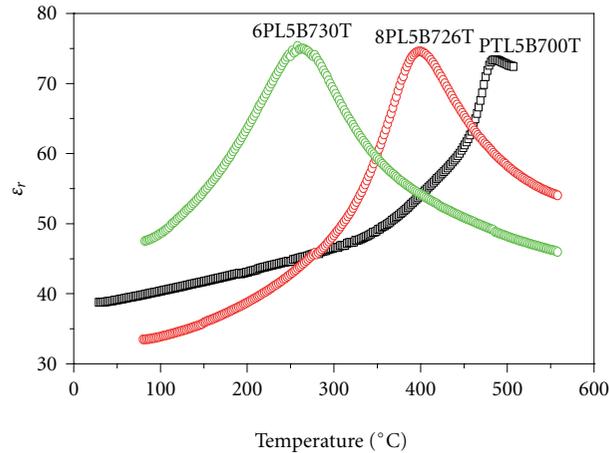


FIGURE 6: Variation of dielectric constant, ϵ_r , (at 1 MHz) with temperature for the crystalline phases developed in different glass-ceramic samples.

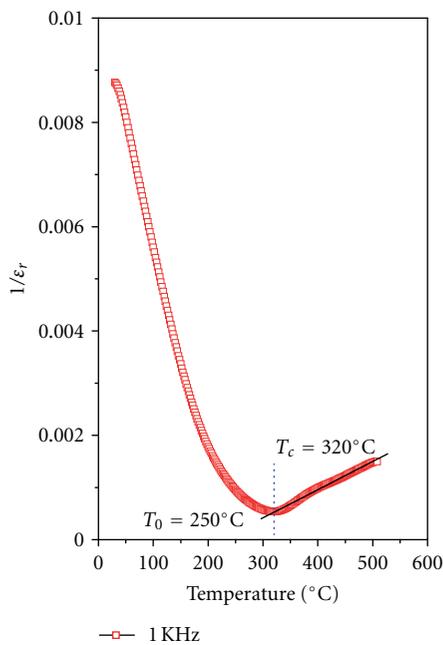


FIGURE 7: Temperature dependence of inverse of relative dielectric constant in the vicinity of transition temperature of glass-ceramic sample 8PL5B726T measured at 1 kHz.

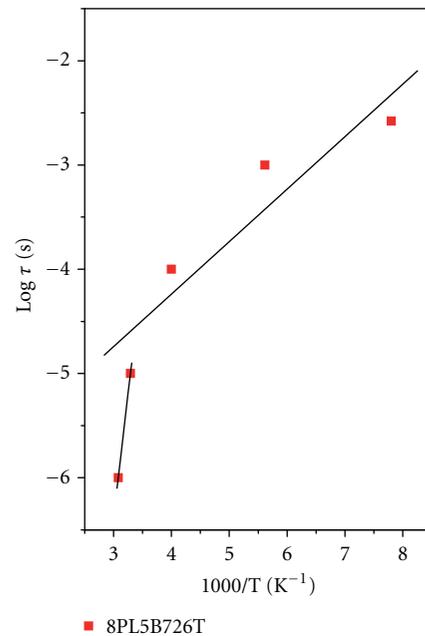


FIGURE 8: Variation of relaxation time, τ , with inverse of temperature for glass-ceramic sample 8PL5B726T.

increasing T . The dielectric constant, ϵ_r , strongly depends on the T (Figure 5). It is observed from the ϵ_r plot of this glass-ceramic sample that the value of ϵ_r rapidly increases with increasing, T , peaks and then decreases followed by another increase with temperature at 0.1 KHz. Two peaks are observed at a frequency of 0.1 KHz at temperatures 206 and 440°C, respectively. The first peak may be due to ferroelectric to paraelectric phase transition while the second peak may be due to relaxation polarization. ϵ_r is strongly dependent on T , around Curie temperature, T_C . The peak temperatures at 0.1, 1, 10, and 100 KHz frequencies are found to be 206, 219, 228, and 229°C, respectively. The various dielectric

parameters such as grain size, ϵ_r at 1 KHz, ϵ_r at T_C and T_C of $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ Pb-rich glass-ceramics studied in the present investigation are presented in Table 1.

A broad peak is observed in ϵ_r versus T plots whose position is dependent on frequency. $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ($x = 0.8$) ceramic composition shows peak due to ferroelectric to paraelectric transformation at Curie temperature $\sim 320^\circ\text{C}$. The presence of similar peak in ϵ_r versus T plots for these glass-ceramic samples is attributed to ferroelectric to paraelectric phase transformation of the crystallites embedded in the glassy matrix. The dissipation factor, D versus T plots for these glass-ceramic samples shows a peak (Figure 4) whose position shifts to higher-temperature side with

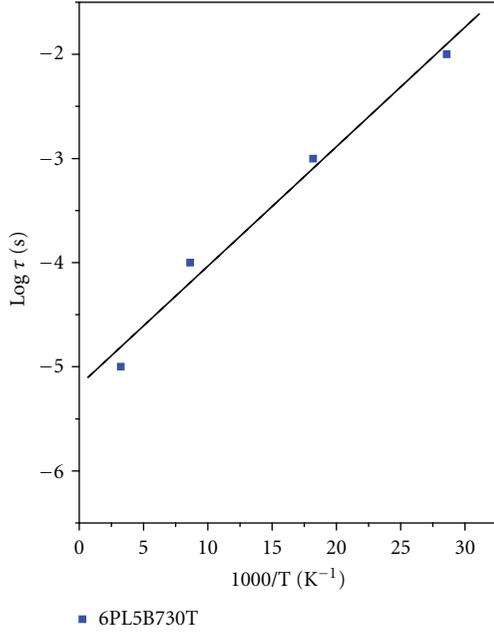


FIGURE 9: Variation of relaxation time, τ , with inverse of temperature for glass-ceramic sample 6PL5B730T.

increasing frequency. This indicates the presence of some relaxation polarization phenomena at around T_C values. The ferroelectric-to-paraelectric transformation and relaxation polarization increases the broadness of ϵ_r versus T peak with increased peak height. The dielectric characteristics of these glass-ceramic samples are very much closer to ferroelectric relaxor like ceramic materials. The increase of dielectric loss and dielectric constant beyond T_C may be attributed to space charge polarization present at crystallites-glass interface due to increase in conduction losses [30]. Figure 6 shows variation of ϵ_r with, T , at 1 MHz for the various glass-ceramic samples PTL5B700T, 8PL5B726T, and 6PL5B730T. The shift of Curie temperature to a lower value from that of PbTiO_3 may be a result of the formation of $(\text{PbSr})\text{TiO}_3$ solid solution crystallized in glassy matrix. The shift may also be related to the strain due to crystal clamping [9] and to the effect of particle size [31–33]. Crystal clamping can shift T_C by a few degrees only. Particle size comes into play only for particles smaller than $0.02 \mu\text{m}$, and the ferroelectric to paraelectric phase transition is less susceptible to particle size effects. Only particle size has a significant effect on the nature of the peak, and not transition temperature. In all glass-ceramic samples, the crystallites are in the micrometer size range [34]. Thus the continuation of particle size to shifting the Curie temperature is also ruled out.

3.4. Ferroelectric Behavior. In most ferroelectrics, the temperature dependence of the relative permittivity above the T_C (in paraelectric phase regime) can be described accurately by a simple relationship called the Curie-Weiss law [35]. Consider

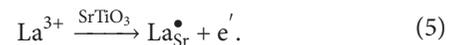
$$\epsilon = \epsilon_0 + \frac{C}{T - T_0}, \quad (3)$$

where ϵ is the permittivity of the material, ϵ_0 is the permittivity of vacuum, C is the Curie constant and T_0 is the Curie temperature. The Curie temperature T_0 is different from the Curie point T_c . T_0 is a formula constant obtained by extrapolation, while T_c is the actual temperature where the crystal structure changes. For first-order transitions $T_0 < T_c$ while for second-order phase transitions $T_0 = T_c$ [36]. Figure 7 shows the variation of inverse of ϵ_r with T , in the vicinity of transition temperature for $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ ceramics crystallized at 726°C . The dielectric data show clearly first-order phase transition and excellent Curie-Weiss behavior. The Curie constant, C , obtained for this sample is $1.1 \times 10^{5^\circ}\text{C}$.

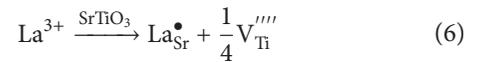
3.5. Discussion. D versus T plots for the glass-ceramic samples PTL5B700T and 8PL5B726T show a peak (Figures 8 and 9). The position of the peak shifts to higher temperature with increasing frequency. After this peak, D again increases rapidly with increasing temperature. It indicates that some relaxation polarization mechanism is operative in these glass-ceramics. The inverse of frequency of measurement represents the relaxation time, τ , of the polarization process at the peak temperature. Plots of $\log \tau$ versus $1/T$ for the glass-ceramic samples PTL5B700T and 8PL5B726T are shown in Figures 8 and 9. The plots are linear and obey Arrhenius relationship. Consider

$$\tau = \tau_0 \text{EXP} \left(-\frac{E_A}{kT} \right), \quad (4)$$

where E_A is the activation energy for the relaxation process. Value of E_A for the glass-ceramic samples 8PL5B726T, and 6PL5B730T is 1.27, 0.92 and 0.011 eV respectively. In these glass-ceramics, the peak in their ϵ_r versus T plots occurs close to T_C for the corresponding $\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$ solid solution ceramic composition (Table 1). The peaks in ϵ_r versus T plots for these glass-ceramic samples correspond to T_c of the crystallites embedded in the glassy matrix. D versus T plots indicate the presence of some relaxation polarization processes. The simultaneous presence of ferroelectric to paraelectric transition and relaxation polarization increases the broadness of ϵ_r versus T peaks with increased peak height. Dielectric characteristics of these glass-ceramic samples are very much similar to ferroelectric relaxor materials. Small concentration of donor dopants such as La^{3+} in perovskite ceramics is known to induce an n-type semiconductivity by electronic compensation [37]. Consider



At higher concentration, titanium vacancies form for compensating La^{3+} doping



The overall effect of La_2O_3 doping in perovskite ceramics (e.g., BaTiO_3) is described by the combination of above two mechanisms contributing to increase in broadness of Curie peak exhibiting ferroelectric relaxor like behavior [37]. More recently similar dielectric relaxation and effect of donor-doped Nb_2O_5 and La_2O_3 were reported [38, 39].

4. Conclusions

Differential thermal analysis (DTA) plots show more than one peak in the Pb-rich compositions. These peaks are sharp. Doping of La_2O_3 affects the crystallization behavior and dielectric properties of the glass-ceramic samples. The addition of La_2O_3 promotes nucleation and crystal growth of major phase and retards the crystallization of minor phases. XRD of Pb-rich glass-ceramic samples show that major phase of P or perovskite PST and secondary phases of PbTi_3O_7 (PT), rutile, R. ϵ_r versus T plots show high value of ϵ_r for 3-hour heat treatment due to better crystallization of the parent glass. It has been observed that the dielectric constant of these glass-ceramics is very high (of the order of thousands) unlike that of glass-ceramics obtained from glasses without the addition of La_2O_3 . A broad peak similar to relaxor ferroelectrics whose position shifts to lower temperature with increasing Sr content in the glass-ceramic samples is observed. The dielectric behavior of these glass-ceramic samples is attributed to space charge polarization associated with ferroelectric to paraelectric phase transition similar to relaxor-like materials. Glass-ceramic samples 8PL5B726T, and 6PL5B730T shows high value of dielectric constant with small temperature dependence. These may be used for ceramic capacitor applications.

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