Research Article

Study of Impedance Spectroscopy of Ferroelectric (Pb Sr)TiO₃ Glass Ceramic System with Addition of La₂O₃

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Various composition of glasses were prepared by melt-quenched method in the glass ceramic system 64[(Pb_xSr_{1-x})·OTiO₂]-25[(2SiO₂·B₂O₃)]-7[BaO]-3[K₂O] doped with 1 mole % La₂O₃ (0.0 ≤ *x* ≤ 0.4). Solid solution of perovskite lead strontium titanate (PST) phase was crystallized in borosilicate glassy matrix with controlled heat treatment schedule. X-ray diffraction analysis of these glass ceramic samples revealed that major crystalline phase of the entire glass ceramic samples bears cubic structure similar to SrTiO₃ ceramic. Impedance spectroscopy studies were done in the frequency range 0.01 Hz to 3.0 MHz and in the temperature range 50 to 275°C. Impedance and complex modulus spectroscopic techniques were used to find out the various contributions to the polarization process. Resistive and capacitive contributions of the processes relaxing in the highest frequency range were found to have low values in comparison to the resistive and capacitive contributions for the processes relaxing in lower and intermediate frequencies ranges.

1. Introduction

Glass ceramics are polycrystalline materials prepared by controlled crystallization of glass whose mechanical properties are superior to those of their parent glasses. Glass ceramics are frequently used to develop new materials with pore-free, fine-grained microstructure. This type of microstructure is highly desirable in ferroelectric ceramic products. The fabrication of such type materials shows a significant improvement over traditional ones [1]. Crystallization, microstructure, and dielectric properties of strontium titanate glass ceramics have been widely investigated because of their technological importance [2–7]. Glass ceramics containing perovskite titanate phases such as BaTiO₃ [8–10], PbTiO₃ [11–13], and SrTiO₃ [14] have been extensively investigated for various dielectric applications. These studies reveal that the dielectric properties of glass ceramics are controlled by various factors such as the nature and content of crystalline phases, crystal clamping, and content of the doping. Since the nature and composition of crystalline

phases and the microstructure of glass ceramics can be controlled by heat treatment conditions, the dielectric properties of glass ceramics can thus be tailored to suit a particular application. (Pb/Sr)TiO₃ are known to form solid solutions over the entire composition range [15]. However, in case of electrically active materials, impedance spectroscopic techniques provide information that is not accessible by electron microscopy alone [16]. Impedance spectroscopy has attracted the great attention of several materials scientists and has undergone major development in recent years with the availability of automated equipment [17–20]. In the recent publication by our group [21], we have reported dielectric characterization of ferroelectric glass ceramic system [(Pb_xSr_{1-x})O·TiO₂]-[2SiO₂·B₂O₃]-[K₂O]-[BaO]-[La₂O₃] (0.5 ≤ *x* ≤ 1). The dielectric properties of glass ceramics are affected by the microstructural elements present in system. Different microstructural elements can be characterized by employing electron microscopic technique. Our results showed improved crystallization and remarkable increase in dielectric constant value. Doping of La₂O₃

FIGURE 1: DTA pattern of glass sample 4PL7B in the system $64[(\text{Pb}_{1-x}\text{Sr}_x)\text{O} \cdot \text{TiO}_2] - 25[2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - [7\text{BaO} \cdot 3\text{K}_2\text{O}] - 1[\text{La}_2\text{O}_3]$.

influenced dielectric constant value causing a considerable enhancement in its value. In view of the interesting results of $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ glass ceramics doped with La_2O_3 , it was considered worthwhile to probe the electrical and dielectric properties for the system $64[(\text{Pb}_x\text{Sr}_{1-x}) \cdot \text{OTiO}_2] - 25[(2\text{SiO}_2 \cdot \text{B}_2\text{O}_3)] - 7[\text{BaO}] - 3[\text{K}_2\text{O}]$ doped with 1 mole % La_2O_3 for relatively low concentration of substituents, that is, $0.0 \leq x \leq 0.4$. More recently, work has been done by Gautam et al. [22, 23] on crystallization behavior and microstructural analysis of lead and strontium-rich $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ glass ceramic containing 1 mole percent La_2O_3 and found very interesting results for the crystallization of major phase of PT/PST in the glassy matrix.

In this paper, we report the effect of one mole percent addition of La_2O_3 on the electrical and dielectric properties of the lead strontium titanate borosilicate glass ceramic system and also the significant result of impedance and modulus spectroscopic analysis to find out the various contributions to the observed dielectric relaxation behavior. The objective of the present investigation is to study the electrical/dielectric properties of ferroelectric $(\text{Pb},\text{Sr})\text{TiO}_3$ glass ceramic system with addition of La_2O_3 by using impedance spectroscopy.

2. Experimental Procedures

A series of glasses were prepared in the glass ceramic system $64[(\text{Pb}_x\text{Sr}_{1-x})\text{O} \cdot \text{TiO}_2] - 25[2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - 7[\text{BaO}] - 3[\text{K}_2\text{O}] - 1[\text{La}_2\text{O}_3]$ by conventional melt-quenched method. Well-mixed, dried powders containing appropriate amount of high-purity 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 – 1240°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 3 hours. Glass ceramic samples were prepared by subjecting glasses to various heat treatment schedules based on their DTA results. DTA measurements were recorded by using an NETZSCH simultaneous (STA-409) from room temperature ($\sim 27^\circ\text{C}$) to 1400°C employing

a heating rate of $10^\circ\text{C}/\text{min}$ to determine T_g and T_c . The XRD patterns for the identification of different crystalline phases in the resulting glass ceramics were recorded by X-ray diffractometer (Rigaku X-ray) using $\text{Cu K}\alpha$ radiation. Capacitance (C) and dissipation factor (D) were recorded as a function of temperature between 25°C and 500°C at 0.1, 1, 10, 100 kHz, and 1 MHz using an HP 4284A precision LCR meter. Measurement for impedance analysis was performed using a Novo Control α -S high-resolution impedance analyzer. Data were taken in the frequency range 0.01 Hz to 3 MHz and in the temperatures range 50 – 275°C .

The nomenclature of glass and glass ceramic samples are listed in Table 1. Five-letter glass code refers to the composition of the glass. The First two letters 4P, 3P, and so forth designate the fraction of lead in the glass. The third letter L indicates that La_2O_3 is used as an additive. The last two letters 7B refer to fraction of modifier oxides BaO in the parent glass compositions. For the nomenclature of the glass ceramic samples, following methodology has been adopted: The first five letters in the code for the glass ceramic samples are similar to the code of their parent glass and refer to the composition of glass, and the next three digits indicate the crystallization temperature. The last letter T or S refers to holding time at crystallization temperature, 3 and 6 hours, respectively. For example, the glass ceramic code 4PL7B850T represents the glass ceramic sample which has been prepared from the glass 4PL7B containing 40% lead, 1% La_2O_3 , and BaO/ K_2O ratio of 7/3 heat treated at 850°C for 3 hours.

3. Results and Discussion

3.1. DTA Studies. The DTA pattern of the glass sample 4PL7B in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{O} \cdot \text{TiO}_2] - [(2\text{SiO}_2 \cdot \text{B}_2\text{O}_3)] - [\text{BaO} \cdot \text{K}_2\text{O}] - \text{La}_2\text{O}_3$ is shown in Figure 1. A shift in the base line is observed in the DTA pattern of this glass sample. This shift in the base line representing a change in the specific heat may be attributed to the glass transition temperature, T_g . The T_g of the glass sample was found to be 625°C . Two exothermic peaks (T_{c1} and T_{c2}) are observed in the DTA pattern of this glass sample at temperatures 850 and 941°C . The first T_{c1} peak arises due to the crystallization of different secondary phase, while the second exothermic peak arises due the major phase formation of PST.

3.2. X-Ray Diffraction Studies. The heat treatment schedule and nomenclature of glass ceramic samples are listed in Table 1. All compositions (x) show a cubic crystal structure at room temperature [24]. All glass ceramic samples were obtained by crystallization of their parent glasses 4PL7B, 3PL7B, and 2PL7B by heat treatment for 3 and 6 hours. Figures 2(a), 2(b), 2(c), and 2(d) depicts X-ray diffraction patterns of various glass ceramic samples 4PL7B850S, 3PL7B941T, 3PL7B941S, and 2PL7B840T with $x = 0.4$, 0.3, and 0.2, respectively. Perovskite PST is crystallized as a major phase with secondary phase of TiO_2 for the first three glass ceramic samples, while for remaining glass ceramic samples, perovskite PST crystallized as a major phase with trace amount of secondary phase of $\text{Sr}_2\text{B}_2\text{O}_3$ (SB).

TABLE 1: Glass and glass ceramic codes heat treatment schedules (heating rate 5°C/min), crystalline phases, crystal structure, and lattice parameters of different glass ceramic samples.

Glass code	Glass ceramic code	Heat treatment schedules		Crystalline phases	Crystal structure	Lattice parameters a (Å)	(PbSr)TiO ₃ ceramic*, a (Å)
		Holding time (hrs)	Holding temp (°C)				
4PL7B	4PL7B850T	3.0	850	P + R	Cubic	3.926 ± 0.004	3.927
	4PL7B850S	6.0	850	P + R	Cubic	3.910 ± 0.001	
3PL7B	3PL7B941T	3.0	941	P + R	Cubic	3.907 ± 0.001	3.943
	3PL7B941S	6.0	941	P + R	Cubic	3.906 ± 0.001	
2PL7B	2PL7B840T	3.0	840	P + SB	Cubic	3.914 ± 0.001	3.880
	2PL7B840S	6.0	840	P + R	Cubic	3.907 ± 0.0002	
1PL7B	1PL7B842T	3.0	842	P + SB	Cubic	3.905 ± 0.0003	3.880
	1PL7B842S	6.0	842	P + R	Cubic	3.893 ± 0.003	
STL7B	STL7B905T	3.0	905	P + SB	Cubic	3.902 ± 0.0003	3.904
	STL7B905S	6.0	905	P + R + SB	Cubic	3.904 ± 0.001	

* Reference [16].

Heat treatment schedules, lattice parameters, and crystalline phase constitutions of all glass ceramic samples are listed in Table 1. XRD patterns of glass ceramic samples 4PL7B850S, 3PL7B941T, and 3PL7B941S indicate the same perovskite phase (P) and rutile phase (R). The lattice parameters of these glass ceramic samples are matched very closed to standard lattice parameters.

3.3. Scanning Electron Microscopy Studies. Figures 3(a), 3(b), 3(c), and 3(d) show scanning electron microscopic (SEM) image of some representative glass ceramic samples 4PL7B850S, 3PL7B941T, 3PL7B941S, and 2PL7B840T, respectively. These figures reveal that micrometer or sub-micrometer fine grains of perovskite PST phase are formed during the crystallization of the glass samples. In most of the cases, these crystallites show agglomeration and dense microstructure regions with some glassy regions in between. This type of microstructure is normally observed for those glass ceramics, which show initial phase separation before crystallization. Two regions show different tendency of crystallization during heat treatment of the glass samples. The region with higher tendency of crystallization occupies greater volume with respect to the region, which does not crystallize and remains in glassy matrix. The crystallization of 4PL7B850S shows well-interconnected fine crystallites of major phase of PST embedded in the residual glassy matrix. Microstructure becomes fine indicating very large nucleation rate [25]. The agglomeration of the major phase of PST crystallites was observed along with the secondary phase of TiO₂ (rutile, R) heat treated at 941°C for 3 hours (Figure 3(b)). Again, glass sample is crystallized at 941°C for 6 hours holding time, and the morphology of the crystallites is marked to be changed. The agglomeration of major phase of PST crystallites is disappeared, but the secondary phase of R remains the same. Secondary phase formation of R is also confirmed by the XRD studies. SEM of the Sr-rich composition $x = 0.2$, for the glass ceramic samples 2PL7B840T heat treated for 3 hours, is shown in Figure 3(d).

Directional growth of perovskite PST phase is observed with uniform and well connectivity to one another.

3.4. Dielectric Behaviours. Dielectric constant, ϵ_r , and dissipation factor, D , were measured as a function of temperatures within the temperature range from 25°C to 500°C at a few selected frequencies such as 0.1, 1, 10, 100 kHz, and 1.0 MHz for various glass ceramic samples. A representative glass ceramic sample 4PL7B850S has been chosen to study the ferroelectric relaxor like dielectric behavior. Figures 4(a) and 4(b) show the variation of ϵ_r and D , with temperature for glass ceramic sample 4PL7B850S. The value of ϵ_r increases with T , at all the frequencies. The values of dielectric constant and D at room temperature and at 1 kHz have been found to be 6265 and 0.3294, respectively. ϵ_r rapidly decreases with increasing T , at 0.1, 1, 10, and 100 kHz and then remains constant for this glass ceramic sample. A broad peak is observed at all frequencies near room temperature. The broadening in the peaks increases with increasing frequency. Due to the difference in conductivity, interfacial polarization arises at crystal to glass interface and attributing to high value of ϵ_r . The relaxor-like peaks in the dielectric behavior for this glass ceramic sample are similar to those glass ceramic samples, which are rich in Pb content. The increase in the broadening of peaks with increasing temperature at 0.1 and 1 kHz for this glass ceramic sample might be due to the increasing concentration of Sr²⁺ in the parent glass compositions. Shifting in peaks is also observed towards higher temperature side which is marked by a vertical line in ϵ_r versus T plot as shown in Figure 4(a). The presence of similar peak in ϵ_r versus T plot for these glass ceramic samples is attributed to ferroelectric and paraelectric phase transformation. The addition of donor dopant La₂O₃ makes the semiconducting nature to these glass ceramic samples, because during the crystallization of these glass ceramics, La is associated with major phase of ferroelectric perovskite PST. Inside these glass ceramic samples; there are semiconduction crystallites of PST and minor amount

FIGURE 2: X-ray diffraction patterns of different glass ceramic samples: (a) 4PL7B850S, (b) 3PL7B941T, (c) 3PL7B941S, and (d) 2PL7B840T in the system.

of residual glass which is insulating in nature; therefore, a conductivity difference is produced between them. This causes the effective value of ϵ_r of the order of 12000.

3.5. Impedance Spectroscopic Data Analysis. Immittance spectroscopy plots Z'' versus $\log f$ and M'' versus $\log f$ of glass ceramic sample 4PL7B850S ($x = 0.4$) in the glass ceramic system $64[(\text{Pb}_x\text{Sr}_{1-x})\text{OTiO}_2]-25[(2\text{SiO}_2 \cdot \text{B}_2\text{O}_3)]-7[\text{BaO}]-3[\text{K}_2\text{O}]-1[\text{La}_2\text{O}_3]$ at a few selected temperatures in the range $50-275^\circ\text{C}$ are shown in Figures 5(a) and 5(b). This glass ceramic sample shows anomalous behavior, and Z'' plots show a peak in the low frequency range. Generally,

Z'' plots do not show a peak. Only at high temperature, a peak is observed. It appears that the peak at lower temperatures is beyond the lowest frequency of measurement. With increasing temperature, this peak initially shifts towards lower frequency up to a particular temperature, 100°C . The peak height also initially increases with T , and after a particular temperature, the peak height decreases. The large peaks in the high-frequency regions exhibit an opposite trend, while the peaks in the low-frequency region do not show such trend. In M'' versus $\log f$ plots, one small, and one large peak appear within the range of frequency measurements. These peaks shift to higher frequency side with increasing T . In Z'' versus $\log f$ and M'' versus $\log f$ spectroscopic plots, a peak is observed at a frequency where a polarization process shows a relaxation. The height of Z'' peak is proportional to resistance, R , of the equivalent circuit corresponding to the polarization process. The height of the M'' peak is proportional to the modulus, that is, inverse of ϵ_r . Hence, Z'' plots show the most resistive contribution of the equivalent circuit model, and M'' plots highlight the least capacitive contribution of the equivalent circuit. Steeply rising Z'' curves or a peak in the low-frequency region for all the glass ceramic samples in this system indicates large contribution of space charge polarization at highly resistive interface. In these glass ceramic samples, La_2O_3 has been added as an additive. La ions can diffuse into the solid solution crystallites of PST phase and make them semiconducting during the crystallization. La_2O_3 doping in SrTiO_3 leads to the formation of electronic defects and/or vacancies of titanium cation, depending on the doping level and processing condition. The interface between semiconducting crystalline phases of PST and insulating glassy matrix is highly resistive, and space charge polarization develops at this interface. The highly resistive circuit element is highlighted in Z'' versus $\log f$ plots (Figure 5(a)). M'' versus $\log f$ plots highlight the least capacitive circuit element of the equivalent circuit representing the glass ceramic samples. The prominent peak in all the M'' plots of different glass ceramic samples represents such type of contributions (Figure 5(b)).

3.6. Complex Plane Impedance and Modulus Data Analysis. The relationship among these can be explained with the help of lossy dielectric, which can be expressed as a parallel RC circuit. The four functions broadly called immittance functions are given below:

$$\text{complex impedance } Z^* = Z' - jZ'',$$

$$\text{complex permittivity } \epsilon^* = \epsilon' - j\epsilon'',$$

$$\text{complex admittance } Y^* = Y' + jY'' = j\omega C_0 \epsilon^*, \quad (1)$$

$$\text{complex modulus } M^* = M' + jM'',$$

where $\tan \delta = \epsilon''/\epsilon' = M'/M'' = Z'/Z'' = Y''/Y'$ and

$$Z^* = \frac{1}{Y^*} = \frac{1}{\tau\omega\epsilon_0\epsilon_r}, \quad M^* = \frac{1}{\epsilon^*}, \quad (2)$$

where $\omega (= 2\pi f)$ is the angular frequency. $j = \sqrt{-1}$ and C_0 are the capacitance of a capacitor with similar dimensions

FIGURE 3: Scanning electron micrographs of polished and chemically etched surfaces of glass ceramic samples: (a) 4PL7B850S, (b) 3PL7B941T, (c) 3PL7B941S, and (d) 2PL7B840T.

FIGURE 4: Variation of (a) dielectric constant, ϵ_r , and (b) dissipation factor, D , with temperature at different frequencies for the glass ceramic sample 4PL7B850S.

and vacuum between the electrodes, that is, geometrical capacitance

$$C_0 = \frac{(\epsilon_0 \cdot A)}{t}, \quad (3)$$

where t and A are the thickness and area of the sample and $\epsilon_0 = 8.854 \times 10^{-12}$ F/m.

The impedance measurements were carried out as a function of frequency from 0.01 Hz to 3 MHz. The values of C , D and conductance G , Z' and Z'' were measured with

FIGURE 5: Variation of (a) Z'' and (b) M'' with $\log f$ at some steady temperatures for the glass ceramic sample 4PL7B850S.

varying frequencies ω for different glass ceramic samples with this instrument. Based on the value of frequency ω , C and G of various immittance data were calculated using the following formulae:

$$Z' = \frac{1}{[G(1 + 1/D^2)]}, \quad (4)$$

$$Z'' = \frac{Z'}{D}.$$

Using these values of Z' and Z'' , the real and imaginary components of modulus (M' and M'') were calculated as

$$M' = \omega C_0 Z'', \quad (5)$$

$$M'' = \omega C_0 Z' = M' D.$$

Complex plane impedance (Z'' versus Z') and modulus (M'' versus M') plots at some steady temperatures for glass ceramic sample 4PL7B850S in the temperature range from 50°C–275°C are shown in Figures 5 and 6, respectively. At lower temperature, one circular arc is observed. On close examination of the higher frequency side of the circular arc (insets of Figure 6), we find that there is another very small arc near the origin. A third arc also starts appearing in the lower frequency range at high temperatures. Complex plane modulus plots (M'' versus M') for glass ceramic sample 4PL7B850S are shown in Figure 7 and indicate the presence of three semicircular arcs. Two circular arcs in the high-frequency region and one circular arc in the low-frequency region are observed. The low-frequency arc near the origin being small represents the high-capacitive contribution of polarization processes at crystal to glass interface and in the glassy region. The insets of the complex plane modulus plots of Figure 7 also indicate that the relaxation processes, which are not separable at high temperature, are separable in the intermediate temperature range (125–200°C). The

ϵ_r of this glass ceramic sample is very high (of the order of 12000, Figure 4) and has anomalous Z'' and M'' versus $\log f$ spectroscopic plots (Figure 5). The values of R 's, and C 's contributions for different polarization processes determined from these complex plane impedance plots at different temperatures for this glass ceramic sample are given in Table 2. As shown by the spectroscopic plot of this glass ceramic sample containing cubic crystallites of Sr-rich PST, perovskite phase dispersed in the glassy matrix and has three contributions of the polarization processes. The R 's and C 's contributions for different polarization processes were determined from the manually fitted arcs. It is noted from Table 2 that R 's and C 's contributions of interfacial processes relaxing in the lower frequency range are higher as compared to the corresponding contributions from the bulk crystalline phases relaxing in the higher frequency range. The equivalent circuit for Figures 6 and 7 has been given in Figure 8 and can be modeled as combinations of three parallel RC elements (R_2C_2 , R_3C_3 , and R_4C_4) connected in series based on their complex plane and spectroscopic plots. The resistive and capacitive element of the three parallel RC circuits represents the contribution of grains, grain boundaries, and glass to glass ceramic interface to the overall resistance and capacitance of the sample. It is observed from Table 2 that the resistance of the grains is smaller as compared to resistance of grain boundary, and it is much higher for glass to glass ceramic interfaces.

4. Discussions

The polarization contributions are relaxing at high-frequency side which is divided into three parts and representing the contributions of the major crystalline phase and minor crystalline phase. It has been reported that La doping in ferroelectric ceramics changes the Curie temperature. Curie temperature decreases with increasing La doping [26].

FIGURE 6: Complex impedance, Z'' versus Z' , plots at a few selected temperatures for the glass ceramic sample 4PL7B850S.

FIGURE 7: Complex modulus, M'' versus M' , plots at a few selected temperatures for the glass ceramic sample 4PL7B850S.

TABLE 2: Resistive, capacitive contribution for different model equivalent circuit elements for the glass ceramic sample 4PL7B850S along with the relaxation time at different temperatures calculated from complex modulus plots.

Temp (°C)	C_1 (pF)	R_1 (ohm)	τ_1 (Sec)	C_2 (pF)	R_2 (ohm)	τ_2 (Sec)	C_3 (pF)	R_3 (ohm)	τ_3 (Sec)	C_4 (pF)	R_4 (ohm)	τ_4 (Sec)
50	—	—	—	—	—	—	272	1.48×10^3	4.03×10^{-7}	5.82×10^3	3.42×10^8	1.99
100	—	—	—	—	—	—	248	2.44×10^3	6.04×10^{-7}	10.6×10^3	2.89×10^8	3.00
150	—	—	—	251	5.42×10^3	1.36×10^{-6}	6.12×10^3	2.49×10^6	1.53×10^{-2}	8.74×10^3	5.20×10^8	4.54
200	—	—	—	232	8.79×10^3	2.04×10^{-6}	6.12×10^3	1.11×10^6	6.01×10^{-3}	8.74×10^3	1.99×10^7	0.17
250	—	—	—	—	—	—	201	1.02×10^4	2.04×10^{-6}	2.04×10^3	9.85×10^5	2×10^{-3}
275	—	—	—	—	—	—	194	1.05×10^4	2.04×10^{-6}	2.91×10^3	3.07×10^5	8.94×10^{-4}

FIGURE 8: Equivalent circuit used to represent the impedance response of PST borosilicate glass ceramic sample with addition of La_2O_3 .

In these glass ceramics, La_2O_3 addition enhances the crystallization of perovskite phase and hence serves as a nucleating agent. La ions might not be distributed homogeneously inside the glass ceramic sample because of nonuniform distribution of La ions of different regions of the crystallites. Glass ceramic samples may have different Curie temperature, T_c , and also different conductivity. This may lead to different polarization processes in different regions of crystallites, which can give rise to relaxor-like behavior with high value of ϵ_r in these glass ceramic samples. The contributions of the polarization process relaxing in the low-frequency region are due to polarizations at the crystal to glass interface and the glassy region. The model equivalent RC circuit element representing the polarization process relaxing in the low-frequency region can be subdivided into two RC elements. The glass ceramic sample also contains alkali K_2O and alkaline earth oxide BaO . It has been reported that these modifier elements are necessary for the crystallization of the perovskite phase in major amount in the glass ceramics.

5. Conclusions

From the present study, it is concluded that bulk transparent glasses were successfully prepared in the glass ceramic system $64[(\text{Pb}_x\text{Sr}_{1-x})\text{O} \cdot \text{TiO}_2] - 25[2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - 7[\text{BaO}] - 3[\text{K}_2\text{O}]$ with addition of 1 mole % La_2O_3 . Perovskite PST is crystallized as major phase for all the glass ceramic samples. SEM images show very fine crystallites uniformly distributed in the glassy matrix. Addition of La_2O_3 serves as a nucleating agent for this glass ceramic system. Glass ceramic sample 4PL7B850S showing high value of ϵ_r with temperature dependence may be used for ceramic capacitor applications. The high value of ϵ_r is attributed to space charge polarization. According to modulus spectroscopic study, there are three

semicircular arcs in M'' versus M' plots, two circular arcs in the high-frequency region and one circular arc in the low-frequency region.

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