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Lead-strontium titanate glass ceramics: II-dielectric behaviour

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Dielectric properties of glass ceramic samples prepared in the system $[(Pb_{1-x}Sr_x)O.TiO_2)]$-$[2SiO_2.B_2O_3]$-$[K_2O]$-$[BaO]$ have been studied. Dielectric constant vs temperature plots of lead rich glass ceramics samples show a peak similar to Curie peak in case of ceramic lead strontium titanate. The Curie temperature of tetragonal crystalline phase of various glass ceramics has been found to decrease with Pb/Sr ratio in the initial glass. This complements X-ray diffraction (XRD) studies carried out previously to establish that the crystallites in various glass ceramic samples are $(Pb_{1-x}Sr_x)TiO_3$ solid solutions. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Glass ceramics containing perovskite titanate phases such as $PbTiO_3$ [1–3] and $SrTiO_3$ [4–10] have been investigated for various dielectric applications. These studies concluded that the dielectric properties of glass ceramics are mainly controlled by the factors such as the nature of crystalline phases, crystallite size and morphology, secondary phases, crystal clamping, connectivity of high permittivity of perovskite crystals in low permittivity glassy matrix. Since the nature and composition of crystalline phases and 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.

Crystallization and microstructural characteristics of the glass ceramic samples in the system $[(Pb_{1-x}Sr_x)O\cdot TiO_2)]$-$[2SiO_2\cdot B_2O_3]$-$[K_2O]$-$[BaO]$ used in this investigation are reported in the previous paper [11]. For various glass ceramic samples a shift in X-ray diffraction (XRD) peak positions from that of undoped $PbTiO_3$ was observed. The magnitude of the shift was found to vary systematically with changing lead-to-strontium ratio in the initial glass. These and XRD intensity calculations provided information about the composition of crystallites. Lead titanate and strontium titanate are known to form solid solutions with each other over the entire composition range [12]. Curie temperature (T_C) is one parameter which is sensitive to composition of the solid solution. It is observed that the Curie temperature of $PbTiO_3$-$SrTiO_3$ ceramic solid solution series vary linearly with composition. Determination of Curie temperature of glass ceramic samples may provide information regarding the actual composition of the crystallites The present investigation was carried out to study the dielectric characteristics and the variation of Curie temperature of crystalline phase developed in the $[(Pb_{1-x}Sr_x)O.TiO_2)]$-$[2SiO_2\cdot B_2O_3]$-$[K_2O]$-$[BaO]$ system. These studies will further confirm the formation of solid solution lead strontium titanate perovskite phase in these glass ceramics.

2. Experimental

The glass ceramic samples studied for their dielectric behaviour are given in Table I. For dielectric measurement of glass ceramic samples, both the surfaces of glass ceramic samples were ground and polished using SiC powders for attaining smooth surfaces to a thickness of about 1 mm. The electrodes were made by applying silver paint (code No. 1337-A, Elteck Corporation, India) on both sides of the specimen and curing at 700°C for 5 min. The capacitance measurements were made in a locally fabricated sample holder using an automated measurement system

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TABLE I. Heat treatment schedules and crystalline phases of different glass ceramic samples in the system [(Pb$_{1-x}$Sr$_x$)O·TiO$_2$]-[2SiO$_2$·B$_2$O$_3$]-[K$_2$O]-[BaO]

	Heat treatment schedules				
Glass code	Heating rate (°C/min)	Holding temperature (°C)	Holding time (h)	Crystalline phase(s)	Glass ceramic code
8P5K	5	650	3	P + PT$_3$* + PB*	8P5K650
	5	700	3	P + PT$_3$*	8P5K700
	5	750	3	P + R* + SB*	8P5K750
	5	750	6	P	8P5K750S
	5	750	12	P + PT$_3$*	8P5K750T
7P5K	5	700	3	P + PT$_3$*	7P5K700
	5	750	3	P	7P5K750
	5	800	3	P + PT$_3$* + R*	7P5K800
6P5K	5	700	3	P + PT$_3$*	6P5K700
	5	750	3	P + PT$_3$* + R*	6P5K750
	5	750	6	P	6P5K750S
	5	750	12	P	6P5K750T
	5	800	3	P + R*	6P5K800
5P5K	5	700	3	P + PT$_3$*	5P5K700
	5	750	3	P + PT$_3$* + PB*	5P5K750
	5	800	3	P + R*	5P5K800
4P5K	5	750	3	P + PT$_3$* + PB*	4P5K750
	5	800	3	P + R*	4P5K800
	5	850	3	P	4P5K850
3P5K	5	800	3	P	3P5K800
	5	850	3	P + U*	3P5K850
2P5K	5	800	3	P + U*	2P5K800
	5	850	3	P + U*	2P5K850
1P5K	5	800	3	P + PT$_3$*	1P5K800
	5	850	3	P + U*	1P5K850
ST5K	5	850	3	ST + U*	ST5K850
	5	900	3	ST + R + U*	ST5K900

P = Perovskite Titanate; PT$_3$ = PbTi$_3$O$_7$; R = TiO$_2$ (Rutile); SB = Sr$_2$B$_2$O$_5$; PB = PbB$_2$O$_4$; ST = SrTiO$_3$; U = Unidentified Phase; *Trace amount

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°C/min. Capacitance and dissipation factor of the samples were recorded at 0.1, 1, 10, 100 KHz and 1 MHz at equal intervals of time during heating in the temperature range RT (~27°C)–500°C.

3. Results and discussion

Variation of dielectric constant, ε' and dissipation factor, D with temperature at a few selected frequencies, 0.1, 1, 10, 100 KHz and 1 MHz for the glass ceramic samples 8P5K650, 8P5K700 and 8P5K750 are presented in Figs. 1–3. The dielectric constant gradually increases with temperature at all frequencies and a peak is observed except at 0.1 KHz for the glass ceramic sample 8P5K650. The peak is masked at 0.1 KHz in ε' vs T plot for the glass ceramic sample 8P5K650 which may be due to the fact that dissipation factor rises rapidly before the Curie temperature. The Curie temperature is found to be 356, 366 and 357°C for the glass ceramics 8P5K650, 8P5K700 and 8P5K750 respectively (Table II). The small variation in Curie temperature may be due to a slight modification of chemical composition, crystal imperfections and deviation from stoichiometry as observed in the case of ceramics and glass ceramics [13]. Curie temperature is less than that of undoped PbTiO$_3$ ceramic (490°C). The decrease in Curie temperature may be due to crystal clamping and/or formation of solid solution (Pb,Sr)TiO$_3$ phase. It has been reported that magnitude of crystal clamping may be sufficient to shift the position of XRD peaks but not sufficient enough to decrease T_C to such an extent. Clamping produces a small decrease in T_C of the order of ~2°C [2] while composition may have a more significant effect. T_C of the corresponding ceramic phase i.e. (Pb$_{0.8}$Sr$_{0.2}$)TiO$_3$ is reported to be 323°C [12]. The observed T_C of glass ceramics is higher than that of corresponding ceramics. This may be due to the fact that a part of Sr^{2+}, added in form of SrO in initial glass remained in the residual glass after crystallization. Another possibility is that Ba^{2+} enters the lattice. If Ba^{2+} enters the lattice, the lattice parameter ‘a’ should increase. The lattice parameter ‘a’ did not change with composition and is very much similar to lead-

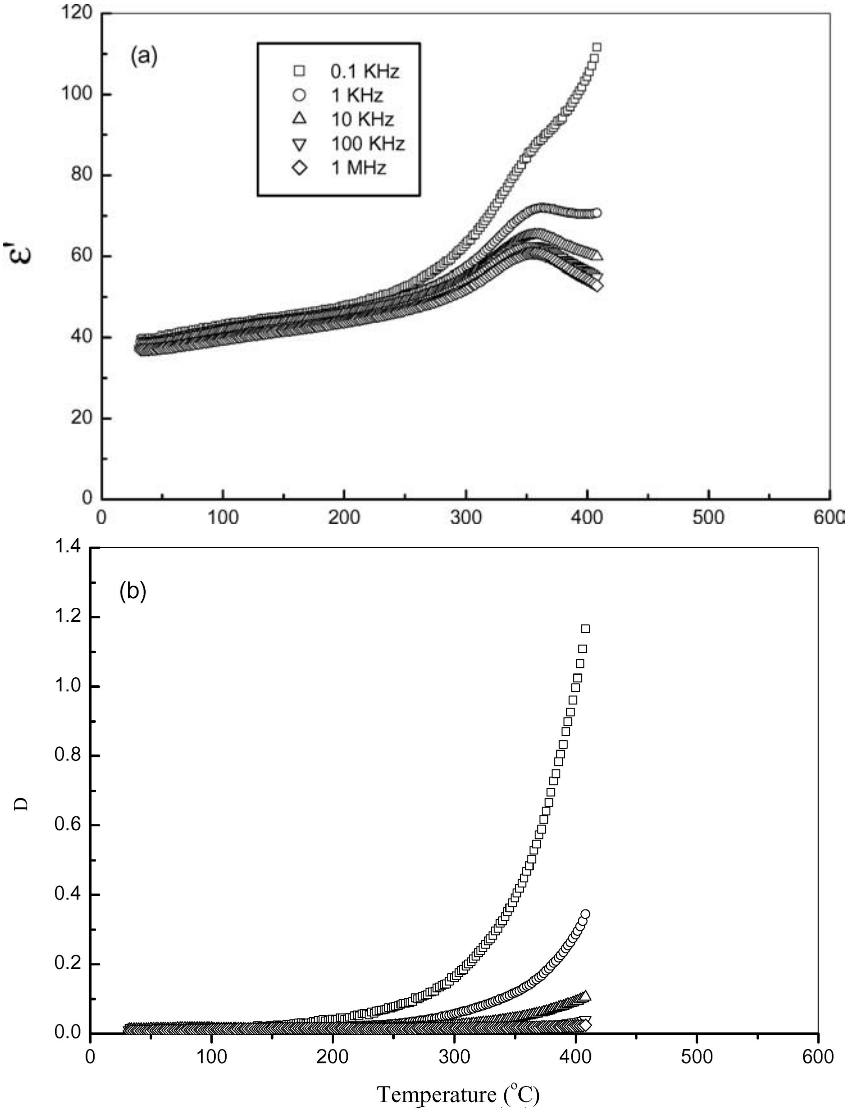


Figure 1 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 8P5K650.

strontium titanate solid solution ceramics. Difference in ionic radii of Ba^{2+} from that of Pb^{2+} and Sr^{2+} reduces the chances of formation of $(Pb,Ba)TiO_3$ and $(Sr,Ba)TiO_3$ solid solution. Increase in T_C of the perovskite titanate phase in glass ceramics than that reported for corresponding ceramics with same Pb^{2+}/Sr^{2+} ratio is also observed in glass ceramics of $10K_2O$ system where BaO is not present. Moreover, BaO concentration in glass is very small. So the possibility of Ba^{2+} entering the lattice is ruled out.

It is interesting to note that the dielectric constant at 0.1 KHz changes very little with temperature below a particular temperature and thereafter rises rapidly. The dissipation factor also increases sharply beyond this particular temperature at 0.1 KHz. Loss at higher temperature may be due to the movement of the alkali ions present in the residual glass. These samples exhibit very low value of dissipation factor (<0.0001) at around room temperature which is beyond the range of measuring instrument.

The dielectric behaviour of glass ceramic samples obtained by heat treating the glass 8P5K at 750°C for 6 h (8P5K750S) and 12 h (8P5K750T) was also studied. The behaviour of both these glass ceramics is similar to that observed for 8P5K750. In microstructural study, it has been mentioned that increase of holding time to 6 and 12 h increased the percentage crystallinity of these glass ceramic samples. As the dielectric constant of the crystalline phase is higher than that of the residual glass, the dielectric constant of 8P5K750S and 8P5K750T is expected to be higher than that of 8P5K750. No such change in dielectric constant is observed. Had the percentage crystallinity been the only factor responsible, the dielectric constant would have increased. But there are other factors such as size, distribution and interconnectivity of crystallites in the glassy matrix which also contribute to the value of dielectric constant. Moreover, the nature of minor phase also changed in the glass ceramic samples (Table II). The glass ceramic sample 8P5K750

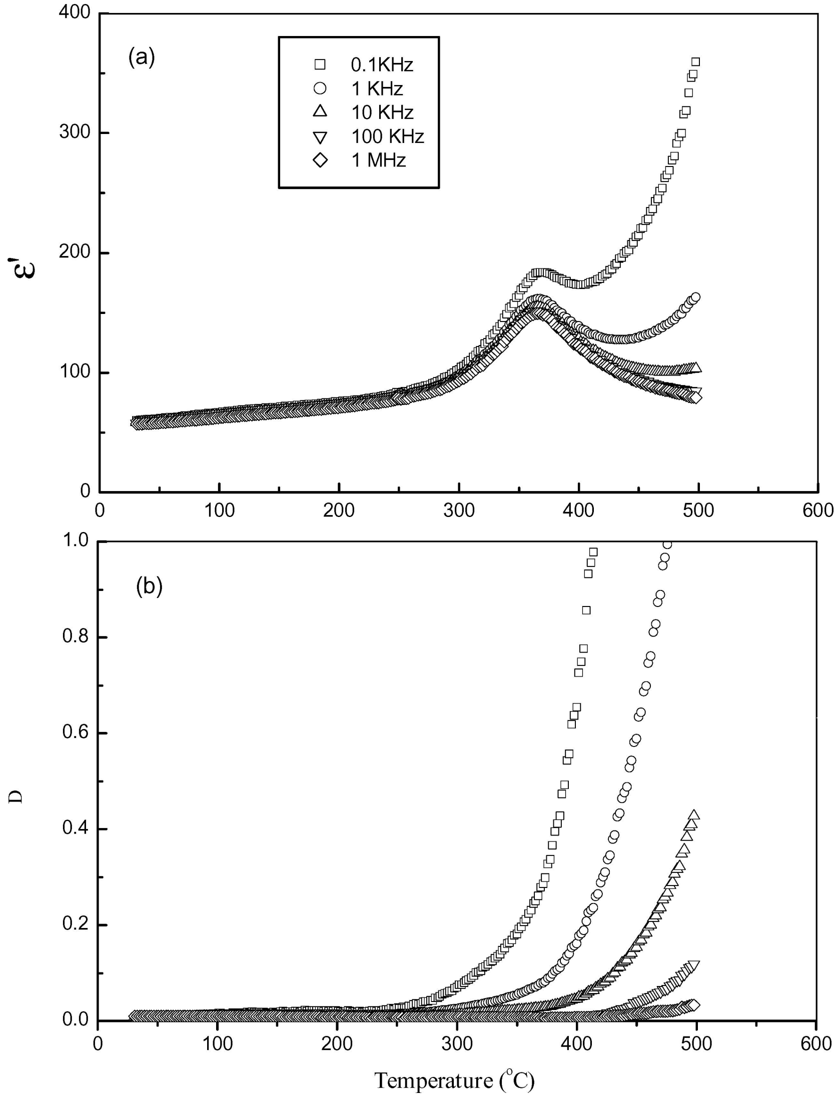


Figure 2 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 8P5K700.

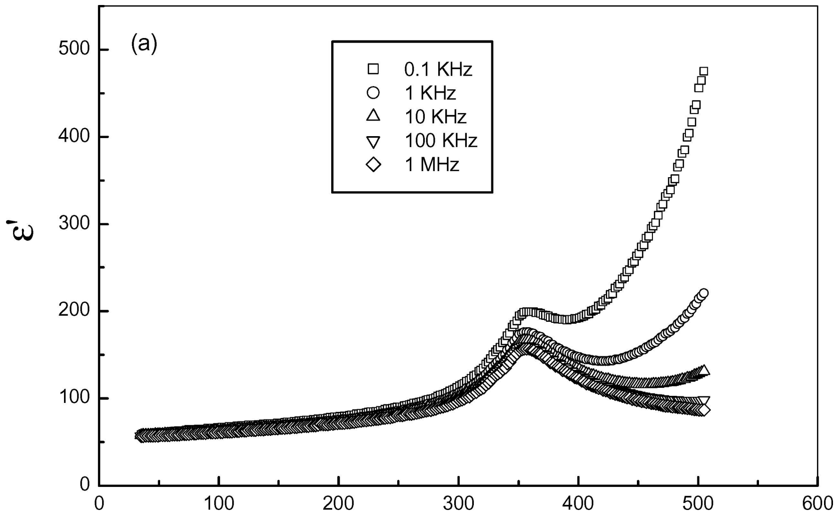


Figure 3 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 8P5K750. (*Continued*.)

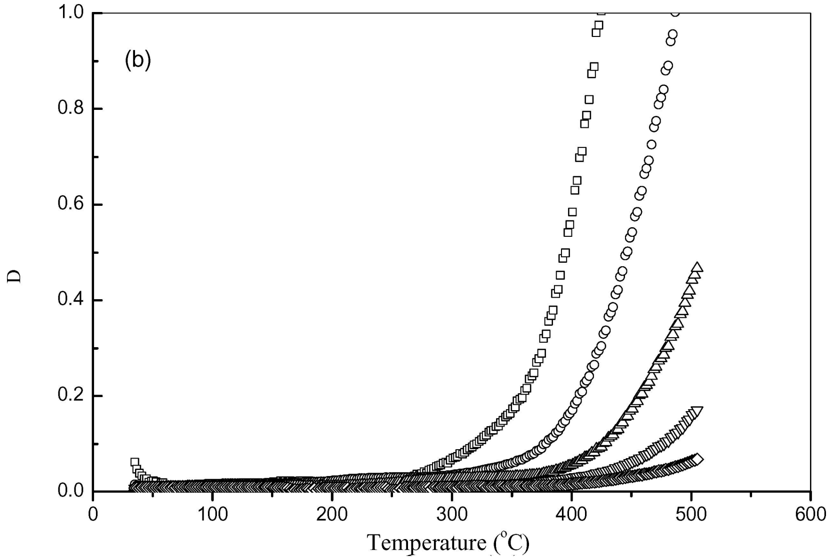


Figure 3 Continued.

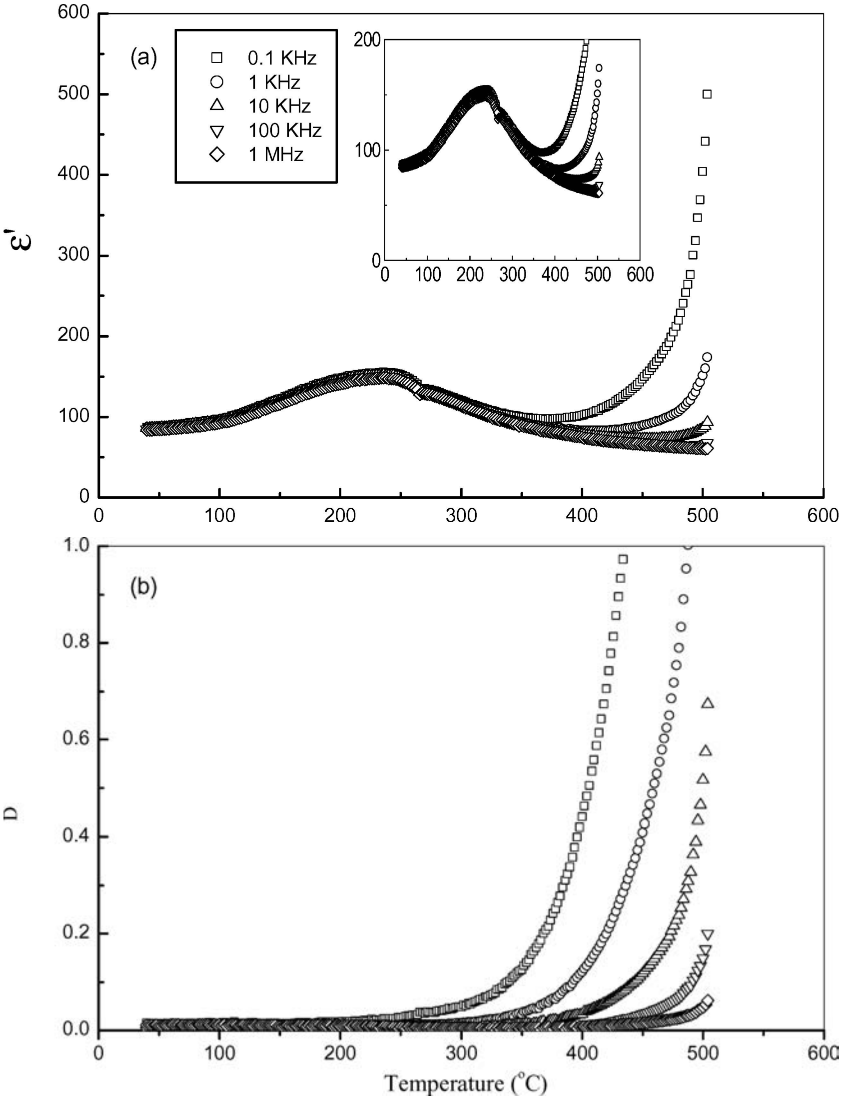


Figure 4 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 6P5K750.

TABLE II. Dielectric constant ε', Dissipation factor D, Curie temperature (T_C) and temperature coefficient of dielectric constant ($Tc\varepsilon$) of some representative glass ceramic samples.

Glass ceramic	ε' at 1 MHz at room temperature	D at 1 MHz at room temperature	Curie temperature (T_C) (°C)	$Tc\varepsilon$ at 1 MHz (ppm/°C)	
8P5K650	37	0.0075	356	+1277	RT–250+C
8P5K700	57	0.0098	366	+1742	
8P5K750	56	0.0075	357	+2040	
8P5K750S	37	0.0098	353	+1887	
8P5K750T	58	0.0036	356	+2030	
7P5K700	77	0.0094	302	+4927	
7P5K750	82	0.0101	299	+6780	
7P5K800	54	0.0082	288	+7543	
6P5K750	84	0.0105	236 (Diffuse)	+1906	RT–100+C
6P5K750S	79	0.0069	230	+4238	
6P5K750T	79	0.0043	232	+4270	
6P5K800	65	0.0089	219 (Diffuse)	+4343	
5P5K700	80	0.0079	136 (Diffuse)	+2104	
5P5K800	80	0.0100	146 (Diffuse)	+3743	
4P5K750	129	0.0140	71 (Diffuse)	−2271	150–250+C
4P5K850	133	0.0121	75 (Diffuse)	−2134	
3P5K800	90	0.0069	–	−1515	
2P5K800	35	0.0052	–	−1121	
1P5K800	22	0.0005	–		

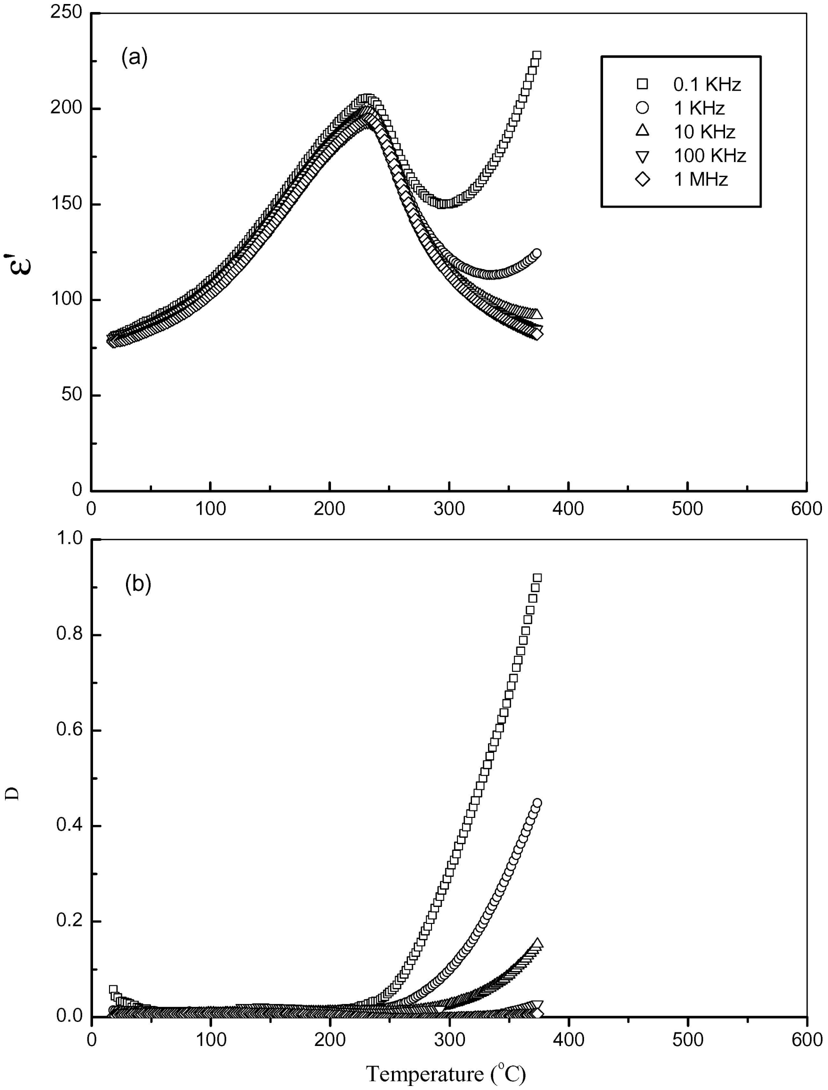


Figure 5 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 6P5K750T.

contains rutile (TiO_2), and $Sr_2B_2O_5$ (SB) as the minor phase whereas glass ceramic sample 8P5K750T has only one minor phase viz. $PbTi_3O_7$. No minor phase was observed for the glass ceramic sample 8P5K750S. For all the three glass ceramic samples 7P5K700, 7P5K750 and 7P5K800, the dielectric constant ε' is strongly dependent on temperature which is also reflected in their respective temperature coefficient of dielectric constant ($T c\varepsilon$) values (Table II). These glass ceramics show ferroelectric to paraelectric phase transition. Dielectric constant is strongly dependent on temperature around Curie temperature. The value of $T c\varepsilon$ was determined in a temperature range away from the Curie temperature. $T c\varepsilon$ was determined in any of the three temperature ranges RT-250°C, RT-100°C and 150–250°C depending on the Curie temperature of the crystalline phase of various glass ceramic samples. Curie temperature for these glass ceramic samples 7P5K700, 7P5K750 and 7P5K800 was found to be 302, 299 and 288°C respectively. The variation in the Curie temperature may be due to slight modification in the chemical composition of the crystalline phase, effect of particle size, crystal clamping, crystal imperfections and deviation from stoichiometry as reported for ceramics and glass ceramics [2, 13]. As expected, when Tc decreases, $T c\varepsilon$ increases. Curie temperature observed for these three glass ceramic samples was found to be higher than that of corresponding ceramics (283°C for $Pb_{0.7}Sr_{0.3}TiO_3$) [12]. This may be due to the presence of a few Sr^{2+} ions in the residual glass. Variation of dissipation factor, D with temperature was found to follow the same trend as that of the glass ceramic samples of glass 8P5K already discussed.

The variation of dielectric constant and dissipation factor with temperature at a few selected temperatures for the glass ceramic sample 6P5K750 is shown in Fig. 4. Unlike the glass ceramic samples of glasses 8P5K and 7P5K, the nature of ferroelectric to paraelectric phase transition is broad. When the holding time was increased

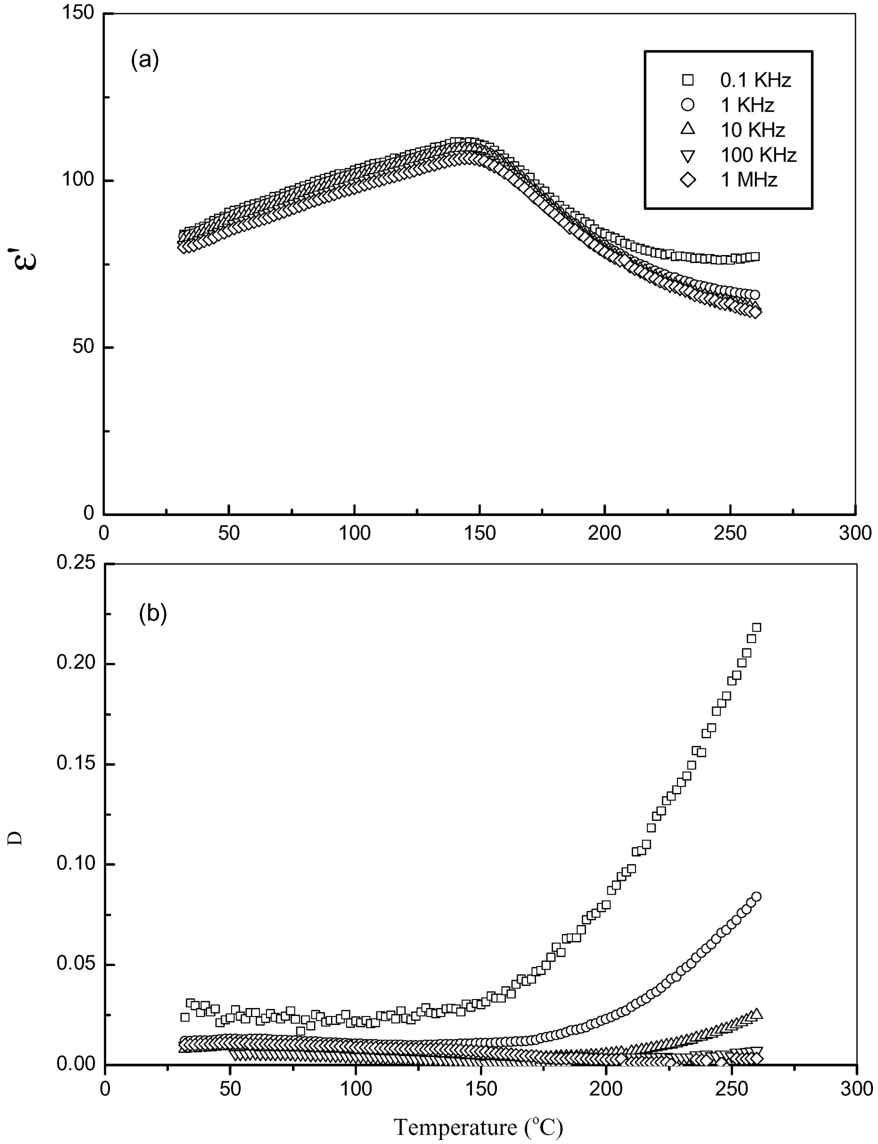


Figure 6 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 5P5K800. (Continued.)

to 6 h (6P5K750S) and 12 h (6P5K750T) (Fig. 5), the nature of phase transition becomes sharp. This is reflected in the value of Tcε (Table II). The dielectric properties of the sample 6P5K800 are similar to that of 6P5K750. Fig. 6 shows variation of dielectric constant and dissipation factor with temperature at 0.1, 1, 10, 100 KHz and 1 MHz for the glass ceramic sample 5P5K800. A broad peak is observed in ε' vs T plots of these samples. From XRD study, it has also been confirmed the crystalline phase developed in these two glass ceramic samples is found to have tetragonal crystal structure with very small tetragonality (~1.004) [11]. The dissipation factor, D is temperature independent at higher frequencies (100 KHz and 1 MHz). At low frequencies it is almost constant upto a certain temperature and thereafter it increases rapidly.

The variation of dielectric constant, ε' and dissipation factor, D for the glass ceramic samples 4P5K750 and 4P5K850 is given in Fig. 7. A broad peak in ε' vs T is observed similar to the glass ceramic samples 5P5K700 and 5P5K800 with the difference that the peak shifts to lower temperature with decreasing Pb^{2+} to Sr^{2+} ratio. The dielectric behaviour of 3P5K800 and 2P5K800 was found to be similar to that of the glass ceramic samples 4P5K750 and 4P5K850 with the difference that no broad peak is observed for these samples within the temperature range of measurement. It is possible that dielectric study below room temperature will provide information about the nature and position of peak in these samples, if any. The negative temperature coefficient of dielectric constant within the temperature range of measurement indicates that the perovskite titanate phase developed is rich in

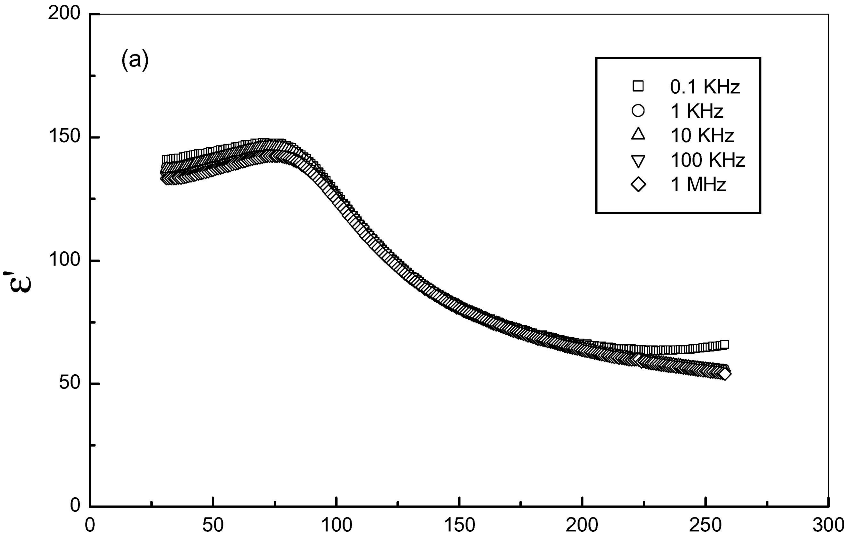
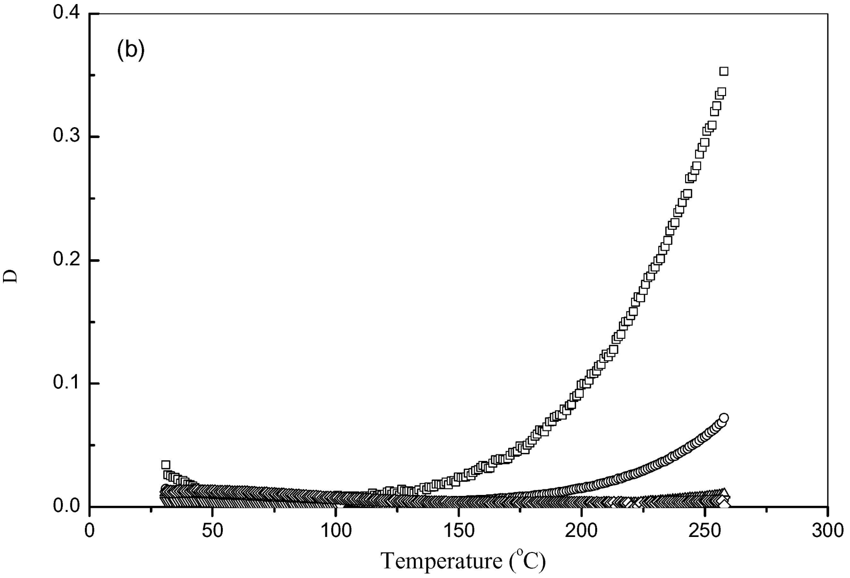


Figure 7 Variation of (a) Dielectric constant, ε' and (b) Dissipation factor, D with temperature at different frequencies for the glass ceramic sample 4P5K850. (Continued.)



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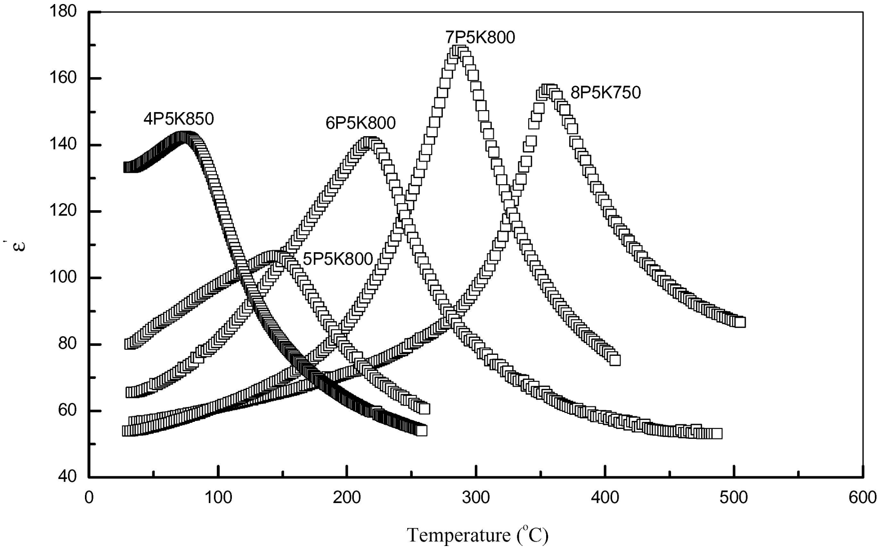

Figure 8 Variation of dielectric constant (at 1 MHz) with temperature for the crystalline phases developed in different glass ceramic samples.

strontium as $SrTiO_3$ ceramic has negative $T c\varepsilon$ in the same temperature range.

A comparative study of various glass ceramic samples has been made by plotting ε' against temperature at 1 MHz frequency for the glass ceramic samples 8P5K750, 7P5K800, 6P5K800, 5P5K800 and 4P5K850 (Fig. 8). Variation of Curie temperature of these samples with composition, × i.e. PbO to SrO ratio is shown in Fig. 9. A shift in Curie temperature to lower temperature from that of undoped $PbTiO_3$ is obtained for these glass ceramic samples. Systematic variation of Curie temperature with composition was observed which is very similar to the variation of Curie temperature of the corresponding ceramics. As it has already been discussed that the shift of Curie temperature may be due to solid solution formation with $SrTiO_3$ and/or strain due to crystal clamping or particle size effect [2, 14]. It has been reported that strain due to crystal clamping and effect of particle size is not significant and do not contribute solely to the large shift in T_C. Crystal clamping can alter the T_C by a few degrees only [2] whereas particle size effect becomes significant only for particles ≤ 0.02 μm [14]. Since, there is large shift in T_C and size of the crystallites are $\geq$0.5 μm [11], role of strain due to crystal clamping and particle size in shifting the T_C to lower temperature is ruled out. Hence the shift of T_C is due to formation of $(Pb_{1-x}Sr_x)TiO_3$ solid solution crystallites only.

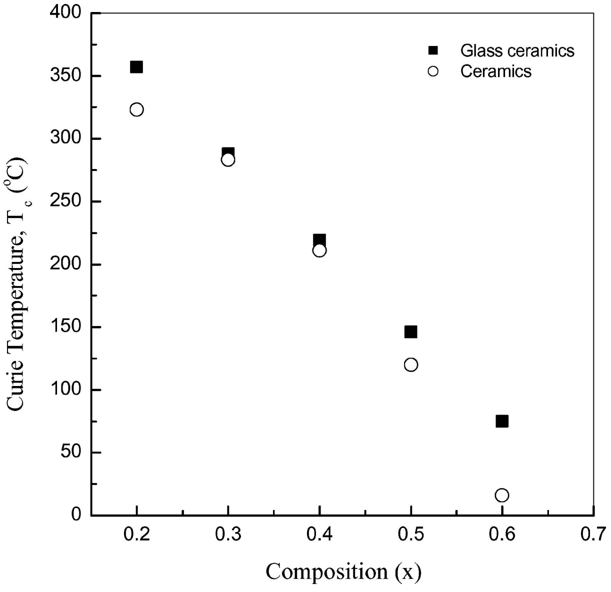

Figure 9 Variation of Curie Temperature (at 1 MHz) of the crystalline phases developed in the glass ceramics by crystallization of different glasses in the system $[(Pb_{1-x}Sr_x)O.TiO_2]$-$[2SiO_2{\cdot}B_2O_3]$-$[K_2O]$-$[BaO]$. Curie temperature of corresponding ceramics shown for comparison.

4. Conclusions

The Curie temperature (T_C) of tetragonal crystalline phases was found to be below 490°C. T_C was found to decrease systematically with decreasing lead/strontium ratio in the initial glass. Since strain due to crystal clamping and particle size has negligible effect on T_C, the variation in T_C was solely due to $(Pb_{1-x}Sr_x)TiO_3$ solid solution formation.

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