



DIELECTRIC BEHAVIOUR IN THE GLASS CERAMIC SYSTEM [(Pb_{1-x}Sr_x)O.TiO₂] - [2SiO₂.B₂O₃] -[3K₂O-7BaO] WITH ADDITION OF La₂O₃(0.0≤x≤0.5)

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ABSTRACT

The high temperature dielectric properties of lead strontium titanate borosilicate glass ceramics, in which perovskite PbTiO₃ is the major crystalline phase, have been investigated. These glass ceramics exhibit high values of dielectric constant and low value of dissipation factor in comparison to the undoped glass ceramic samples. The dielectric properties are strongly dependant on the crystallization behavior. The addition of one mole percent of La₂O₃ enhances the crystallization of lead strontium titanate solid solution perovskite phase dispersed in the glassy matrix and retards the crystallization of minor phases. Results of the dielectric studies on this glass ceramic system [(Pb_{1-x}Sr_x)O.TiO₂]-[2SiO₂.B₂O₃]-[7BaO]-[3K₂O] show relaxor like behavior with very high value of dielectric constant. Scanning electron micrographs of different glass ceramic samples show uniform morphology of fine crystallites, which are dispersed in the glassy matrix. The high value of dielectric constant is attributed to space charge polarization at crystal - glass interface. La₂O₃ diffuses into the crystalline phase and make it to semiconducting during the crystallization of the different glass samples at high temperature.

Keywords: Glass ceramics; Perovskite lead strontium titanate; Scanning electron micrographs and Dielectric constant.

1. INTRODUCTION

Glass ceramics have become established as commercially important materials in fields such as consumer products, vacuum tube envelopes, telescope mirror blanks, radomes for the aerospace industry and protective coating for metals¹. Lot of work has been done on various glass ceramic systems. Recently a series of perovskite glass ceramic are investigated. The glass ceramics of these systems were developed with the objective of producing materials for the electronic industry with high dielectric constants or optoelectronic effects. The controlled crystallization of the perovskite type lead titanate, PbTiO₃, was first reported by Herczog and Stookey in the SiO₂-Al₂O₃-TiO₂-PbO system². Glass ceramics containing undoped perovskite titanate such as PbTiO₃³⁻¹⁰ have been extensively investigated. High dielectric constant were achieved that allowed application as capacitor dielectric materials. The crystallization process of PbTiO₃ in glasses was studied by Russell and Bergeron¹¹. They discovered that nucleation proceeded via glass-in-glass phase separation. Kokubo et al¹² studied glass formation and the subsequent controlled crystallization in the SiO₂-Al₂O₃-TiO₂-PbO system in the range of 15-45 mol% SiO₂, 0-26 mol% Al₂O₃, 16-33 mol%

TiO₂, 27-52 mol% PbO. They determined that glass formation without secondary crystallization could occur during the cooling of glasses. Furthermore, if these glasses were subjected to heat treatment in a second step, crystallization took place between 620°C and 740°C. In the processes, it was possible to precipitate PbTiO₃ of the perovskite type, of the pyrochlore type PbTi₃O₇, or both as the primary crystals. Kokubo et al¹³, also conducted an in-depth study of the nucleation process that led to formation of this primary phase. In the course of this study, they made an important discovery. Kokubo and Tashiro¹⁴ outlined the issue of controlling the dielectric properties of PbTiO₃ glass ceramics for special requirements. In this publication, they presented a glass ceramic containing large amount of PbO as well as TiO₂, with which they achieved a high PbTiO₃ crystallites content and a high dielectric constant. Recently Sahu et al investigated dielectric behavior of glass ceramics in the system [(Pb_{1-x}Sr_x)O.TiO₂] – [2SiO₂.B₂O₃] – [K₂O] and also studied the variation of Curie temperature of the crystalline phase developed with composition and heat treatment schedule¹⁵. PbTiO₃ was found to be the major phase in all the glass ceramics obtained from glass free of SrO. Perovskite titanate solid solution was found to be the major phase in the glass ceramics obtained from glasses containing SrO.

In this investigation, we studied the dielectric properties of lead rich glass ceramic samples. The glasses were made by melt and quench method in the system [(Pb_{1-x}Sr_x)O.TiO₂] – [2SiO₂.B₂O₃] – [K₂O.BaO], (0.0 ≤ x ≤ 0.5). The addition of one mole percent La₂O₃ in the above mentioned glass system shows the quite high dielectric constant.

2. EXPERIMENTAL PROCEDURE

Well mixed, dried powders containing appropriate amounts of Analytical Reagent (AR) grade PbO, SiO₂, SrCO₃, TiO₂, H₃BO₃, K₂CO₃, BaCO₃ and La₂O₃ were melted in an alumina crucible for an hour at 1100 °C and then quenched by pouring onto a aluminium mould and immediately pressing with a thick aluminium plate. The glass was then annealed at 400°C for 3 hours and then furnace cooled to room temperature. The annealed glasses were cut by diamond cutter to get the desired shape. The amorphosity of glasses was confirmed by x-ray diffraction. Differential thermal analysis (DTA) was done using NETZSCH Simultaneous Thermal Analyzer 409 to find the glass transition, T_g, nucleation and growth temperature of various crystalline phases which are formed during crystallization. One set of heat treatment conditions were used to convert glass into glass ceramics. These glass samples were heated at their crystallization temperatures on the basis of differential thermal analysis (DTA) for 3 hours with 5°C /min heating rate. X-ray diffraction patterns were taken using Rigaku Diffractometer employing Cu Kα radiation over a 2θ range of 20° - 80° at a scan rate of 4° 2θ/min. to determine the primary and secondary phases. For dielectric measurements, glass ceramic samples were polished with 200, 400, 600 and 1000 grit SiC powder slurry respectively. Silver paint was applied on both sides of the glass ceramic samples to ensure good electrical contact and then cured at 700°C for 10 minutes. A multifrequency impedance-capacitance-resistance (LCR) meter (Model 4284A, Hewlett-Packard Precision) recorded at five frequencies (0.1, 1, 10, 100 KHz and 1 MHz) over a temperature range of 25 to 500°C using a locally made furnace. For microstructural studies the samples were polished and etched using 30% nitric acid and 20% hydrofluoric acid (30%HNO₃+20%HF) solution for 30 seconds to 1 minute. After they were etched, the samples were cleaned by distilled water for 2 minutes to remove unwanted debris from the surface prior to gold coating.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

On the basis of the DTA results, various glass ceramic samples were prepared in the temperature range 663-796⁰C. Representative x-ray diffraction patterns for the glass ceramic samples P663T7B and 5P781T7B heat treated at 663⁰C and 781⁰C for 3 hours are shown in Fig. 1. These patterns indicate that the formation of perovskite phase of PbTiO₃ in major amount with small amount of some secondary phases of PbTi₃O₇ and TiO₂ during the crystallization of the glass samples with composition x=0 and 0.5 respectively. A few unidentified peaks with very low intensity are observed in these XRD patterns. The structure of major perovskite crystalline phase is tetragonal similar to PbTiO₃. Compositions, glass ceramic codes, observed phases and lattice parameters are listed in the Table 1.

The lattice parameters of PbTiO₃ phase in various glass ceramic samples closely match those reported for PbTiO₃ ceramic phase. The variation in 'c' value of the perovskite lead titanate phase with crystallization temperature is large in comparison with variation in 'a' value.

The observed lattice parameters were found to be influenced by crystallization temperature, value of 'c' parameter was found to be decrease initially with crystallization temperature while 'a' was less affected. It is also observed that 'c' value was found to decrease with increasing concentration of SrO except for glass ceramic sample 5P781T7B, whereas a little bit change was observed in 'a' values.

3.2 Scanning electron microscopy

Fig. 2 shows the scanning electron micrographs of representative glass ceramic samples P663T7B and 5P781T7B heat treated at 663⁰C and 781⁰C for 3 hours respectively. The white portion inside the micrographs show the major phase of the lead strontium titanate perovskite, which are so called fine crystallites of order of micron size (1-2 μm), while black portion shows the residual glass embodied around the fine crystallites of the major phase. These fine crystallites are interconnected and uniformly distributed in the glassy matrix. It is also observed that the secondary phase of rutile (TiO₂) agglomerated at surfaces of the crystallites and appears more white. This secondary phase is more for the glass ceramic sample P663T7B while it is less for the glass ceramic sample 5P781T7B.

3.3 Dielectric Studies

Fig. 3 (a and b) shows the variation of dielectric constant, ϵ' and dissipation factor, D with temperature at 0.1, 1, 10, 100 KHz and 1 MHz for the glass ceramic sample P663T7B with (x=0) and 9P680T7B (x=0.1) respectively. The dielectric constant, ϵ' remains constant upto a certain temperature thereafter it increases rapidly. Dielectric constant and dissipation factor at room temperature and at 1 KHz for glass ceramic sample P663T7B have been found to be 36 and 0.0176 respectively. A peak in ϵ' vs. T is observed at all frequencies. Since the dielectric constant increases rapidly with increasing temperature around this temperature, these peaks seems to be shifted towards the higher temperature side followed by rapidly rising dielectric constant due to increasing space charge polarization. Later on we will explain in detail why the dielectric constant is increasing. The variation of dissipation factor with temperature also shows a peak. The position of the peak in the plots of dissipation factor D vs. T shifts to higher temperature with increasing frequency. After this peak the dielectric loss again increases rapidly with increasing temperature.

Fig. 4 (a and b) depict the variation of dielectric constant ϵ' and dissipation factor D with temperature for glass ceramic samples 8P775T7B and 7P790T7B (glass with 20 % strontium heat treated at 775⁰C and 790⁰C respectively for 3 hrs. A broad dielectric peak is observed whose position is dependent on frequency. Lead strontium solid solution ceramic $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ composition shows ferroelectric to Para electric transformation Curie peak at $\sim 323^0\text{C}$ ¹⁶. XRD studies show the presence of solid solution lead strontium titanate phase in these glass ceramics. The presence of similar peak in ϵ' vs. T plot for these glass ceramic samples is attributed to ferroelectric to paraelectric transformation Curie peak of the crystallites embedded in the glassy matrix.

The dissipation factor D vs. T plot for these glass ceramic samples shows a dielectric relaxation peak Fig4 (a) and (b) whose position shifts to higher temperature with frequency. This indicates the presence of some relaxation polarization phenomena around the Curie temperature. The ferroelectric to paraelectric transformation and relaxation polarization increases the broadness of ϵ' vs. T peak with increasing peak height. The dielectric characteristics of these glass ceramic samples are very much closer to ferroelectric relaxor ceramic materials. The increase of dielectric loss and dielectric constant beyond Curie peak may be attributed to space charge polarization at crystallite glass interface¹⁷.

Fig. 5 (b) shows dielectric behavior of the glass ceramic samples 5P781T7B. The dielectric behavior is quite different from that of other glass ceramic samples. The dielectric characteristic for this glass ceramic sample 5P781T7B shows broad peaks at all frequencies. The broadening in the peaks increases with increasing frequency¹⁸. Dielectric constants for all the glass ceramic samples were found to be strongly frequency dependent. The high value of dielectric constant for these glass ceramic samples can be explained as follows.

The addition of the La_2O_3 promotes the crystallization of the different glasses during the heat treatment of the glass samples. At higher temperature La^{3+} ions present in the glasses diffuse into the crystalline phase and make these glass ceramic samples semiconducting. On the application of the electric field these glass ceramic samples shows space charge polarization around semiconducting crystal and insulating glass interface with very high value of effective dielectric constant. The relaxation time decreases and relaxation frequencies increases with increasing the temperature¹⁹. The space charge polarization is arising from the differences amongst conductivity of various phases which are present in the glass ceramic samples. If phases of different conductivity are present, motion of charge carriers occurs readily through one phase but it interrupted when it reaches a phase boundary of other high resistivity phase. This cause a build up of effective dielectric constant. Higher dielectric constant at lower frequencies is also caused by ion displacement and hopping mechanism²⁰.

It is also observed that the value of dielectric constant is less for the glass ceramic samples 7P790T7B and 6P796T7B respectively. It may be that La^{3+} could not diffuse properly in to the crystalline perovskite phase in the glass ceramic samples and do not make them semiconducting. Therefore, the glass ceramic samples 7P790T7B and 6P796T7B does not show space charge polarization and high value of dielectric constant.

5. CONCLUSIONS

Dielectric behavior of various glass ceramic samples in the system $[(\text{Pb}_{1-x}\text{Sr}_x)\text{O} \cdot \text{TiO}_2] - [\text{2SiO}_2 \cdot \text{B}_2\text{O}_3] - [\text{7BaO}] - [\text{3K}_2\text{O}] [\text{La}_2\text{O}_3]$ have been studied. The addition of one mole percent La_2O_3 promotes the crystallization of lead strontium titanate perovskite phase and retards the minor phases. The high value of effective dielectric constant is due to the space charge polarization which is indicated by the relaxation peaks in their respective dissipation factor vs. temperature plots. Glass ceramic sample 5P781T7B show high value of the effective dielectric constant with relatively smaller dielectric loss.

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TABLE

Table1: Compositions, glass ceramic codes, crystal structure, lattice parameters and axial ratio in the glass ceramic system $[(\text{Pb}_{1-x}\text{Sr}_x)\text{O} \cdot \text{TiO}_2] - [2\text{SiO}_2 \cdot \text{B}_2\text{O}_3] - [7\text{BaO} \cdot 3\text{K}_2\text{O}][\text{La}_2\text{O}_3]$

x ↓	Glass Ceramic Code	Crystalline phases	Crystal Structure	Lattice Parameters		Axial Ratio (c/a)
				c(Å)	a(Å)	
00	P663T7B	P+PT+R+U*	Tetragonal	4.082±0.001	3.908±0.001	1.043
0.1	9P680T7B	P+PT	Tetragonal	4.059±0.002	3.912±0.002	1.037
0.2	8P775T7B	P+PT+U*	Tetragonal	4.030±0.001	3.912±0.001	1.030
0.3	7P790T7B	P+PT	Tetragonal	4.012±0.003	3.915±0.003	1.024
0.4	6P796T7B	P+PT	Tetragonal	3.975±0.001	3.914±0.001	1.041
0.5	5P781T7B	P+PT+U*	Tetragonal	4.174±0.008	3.902±0.008	1.069

P-Perovskite Titanate

PT-PbTi₃O₇R-Rutile (TiO₂)

U-Unidentified

*-Trace amount

FIGURES

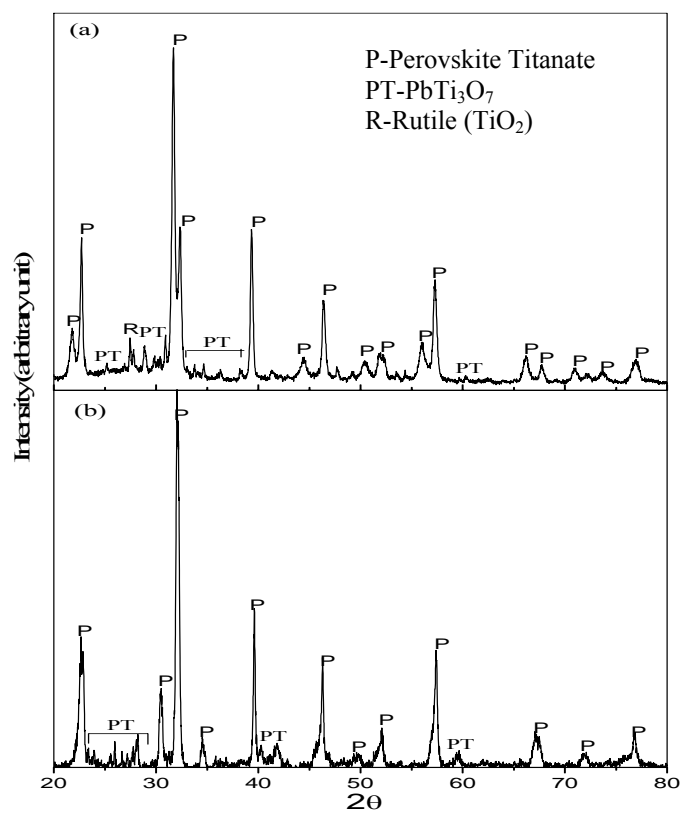


Fig. 1 XRD patterns of glass ceramic samples (a) P663T7B and (b) 5P781T7B

2θ⁰

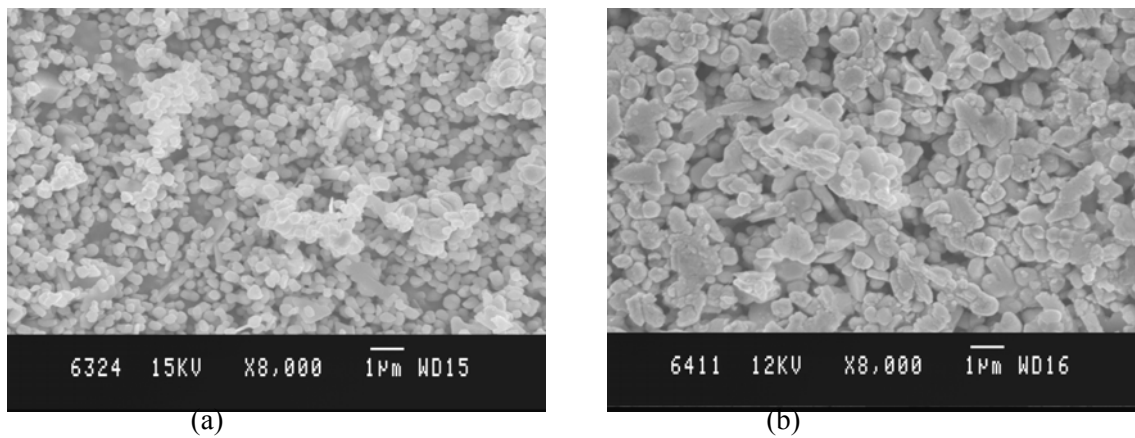


Fig. 2 Scanning electron micrographs of glass ceramic samples (a) P663T7B and (b) 5P781T7B

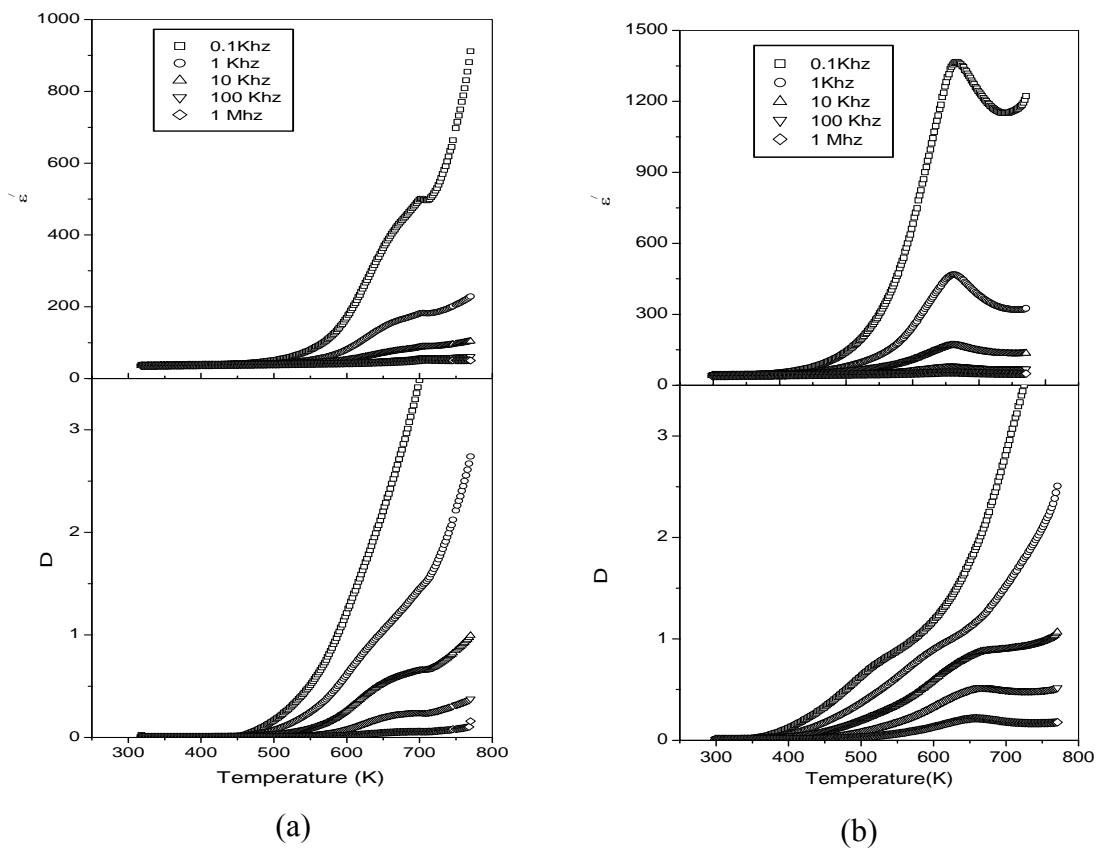
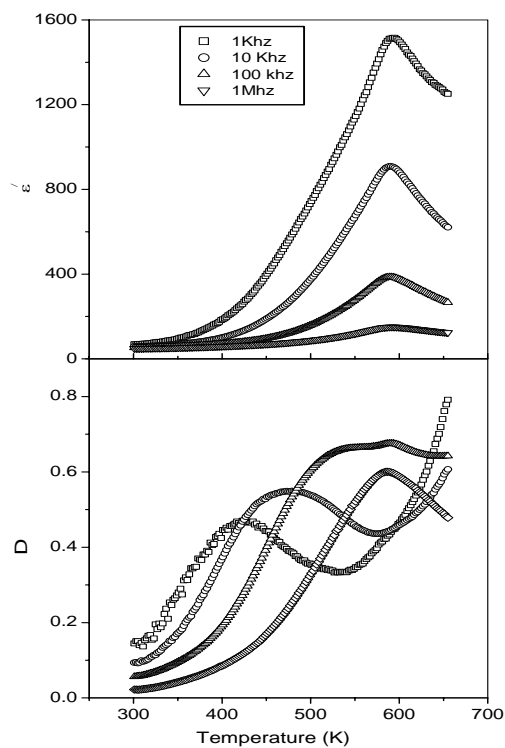
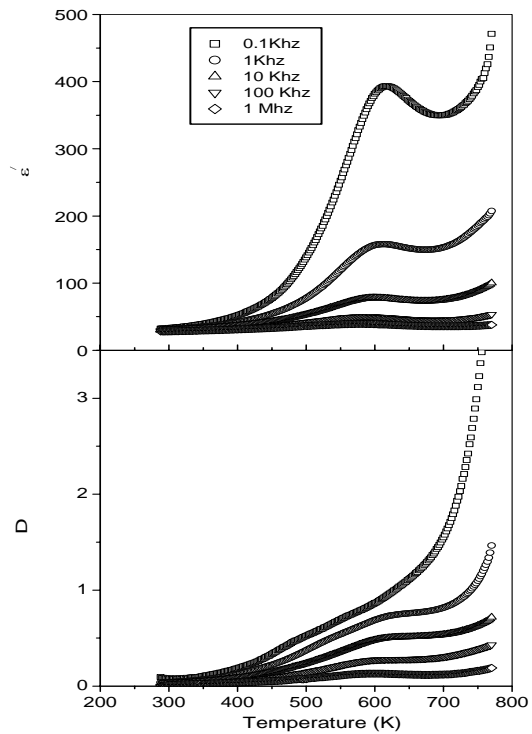


Fig.3 Variation of Dielectric constant, ϵ' and Dissipation factor, D with temperature at different frequencies for the glass ceramic samples (a) P663T7B and (b) 9P680T7B respectively

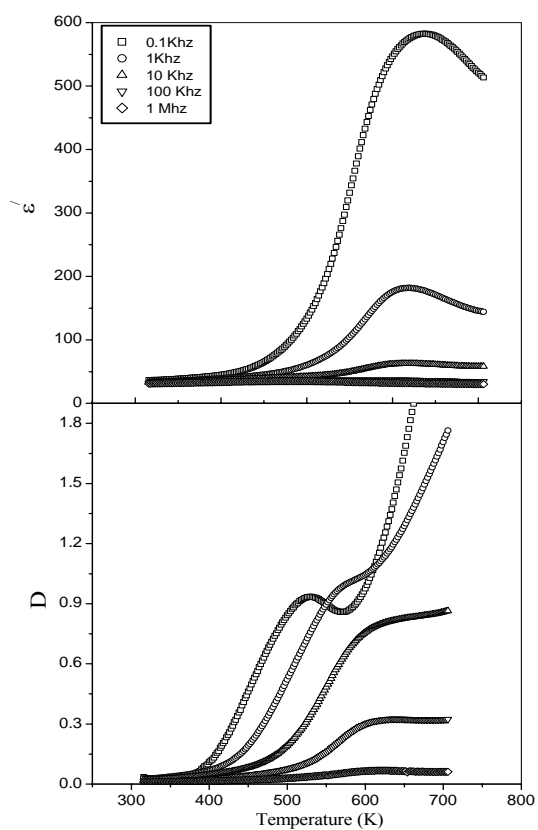


(a)

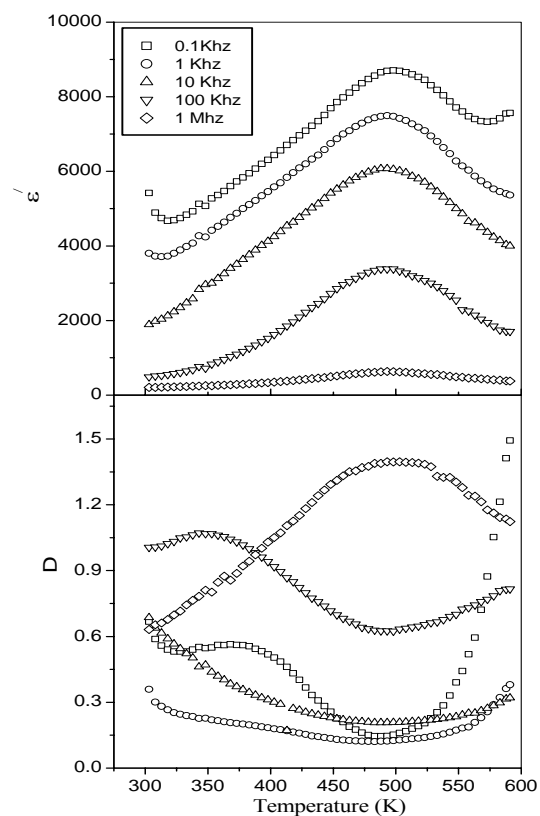


(b)

Fig.4 Variation of Dielectric constant, ϵ' and Dissipation factor, D with temperature at different frequencies for the glass ceramic samples (a) 8 P775T7B and (b) 7P790T7B respectively.



(a)



(b)

Fig. 5 Variation of Dielectric constant, ϵ' and Dissipation factor, D with temperature at different frequencies for the glass ceramic samples (a) 6P796T7B and (b) 5P781T7B respectively.