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Dielectric and impedance spectroscopic studies of $(Sr_{1-x}Pb_x)TiO_2$ glass ceramics with addition of Nb_2O_5

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Abstract. Glasses were made by melt-quench method in the system $[(Sr_{1-x}Pb_x)O{\cdot}TiO_2]$–$[2SiO_2{\cdot}B_2O_3]$–5$[K_2O$–BaO] ($0{\cdot}0 \le x \le 0{\cdot}4$) with addition of 1 mol% Nb_2O_5. Perovskite strontium lead titanate in solid solution phase has been crystallized in borosilicate glassy matrix with suitable choice of composition and heat treatment schedule. Addition of 1 mol% of Nb_2O_5 enhances the crystallization of lead strontium titanate phase in the glassy matrix. Scanning electron microscopy (SEM) is performed to study the surface morphology of the crystallites and crystalline interface to the glass. Dielectric properties of these glass ceramics were studied by measuring capacitance and dissipation factor as a function of temperature at a few selected frequencies. Nb_2O_5 doped strontium lead titanate glass ceramic shows a high value of dielectric constant. It is of the order of 10,000 while the dielectric constant of undoped glass ceramic sample is of the order of 500. Complex impedance and modulus spectroscopic techniques were used to find out the contributions of polarization of crystallites and glass crystal interfaces to the resulting dielectric behaviour.

Keywords. Perovskite lead strontium titanate; dielectric properties; impedance spectroscopy.

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 and fine-grained microstructure. This type of microstructure is highly desirable in ferroelectric ceramic products. The fabrication of such type materials may prove to be a significant improvement over traditional ones. Glass ceramics containing perovskite titanate phases such as $BaTiO_3$ (Herczog 1964, 1984; Prakash *et al* 1986; Mandal *et al* 1987; McCauley *et al* 1998), $PbTiO_3$ (Kokubo *et al* 1973/1974; Lynch 1984) and $SrTiO_3$ (Swartz *et al* 1983, 1986, 1988a, b; Shyu *et al* 1995) have been extensively investigated for several dielectric applications. These studies reveal that the dielectric properties of glass ceramics are controlled by factors such as the nature and amount of crystalline phases, crystallite size and morphology, secondary phases and the connectivity of the high permittivity perovskite crystals in the low-permittivity glassy matrix (Thakur 1998). Thakur *et al* (1995, 1997, 2002) reported the crystallization behaviour of strontium titanate borosilicate glass ceramics and showed that the strontium titanate precipitates as the major phase with several secondary phases. Recently (Sahu *et al* 2003) investigated dielectric behaviour of glass ceramics in the system $[(Pb_{1-x}Sr_x)O{\cdot}TiO_2)] - [2SiO_2{\cdot}B_2O_3] - [K_2O]$ and also studied the variation of Curie temperature of the crystalline phase developed with composition and heat treatment schedule. $PbTiO_3$ was found to be the major phase in all the glass ceramics obtained from glass free of SrO. Perovskite titanate was found to be the major phase in the glass ceramics obtained from glasses containing SrO. A shift in X-ray diffraction (XRD) peak positions from that of undoped $PbTiO_3$ was observed. It has been concluded that lead strontium titanate solid solution crystallites can be developed in a glassy matrix with suitable choice of composition and heat treatment schedule.

In the present investigation strontium-rich glasses were made by melt and quench method in the system $[(Sr_{1-x}Pb_x)O{\cdot}TiO_2)] - [2SiO_2{\cdot}B_2O_3] - [K_2O{\cdot}BaO]$ Nb_2O_5, ($0{\cdot}0 \le x \le 0{\cdot}4$). The addition of 1 mol% of Nb_2O_5 by mol in the above-mentioned glass system shows very interesting dielectric properties. In this paper, we report the effect of 1 mol% addition of Nb_2O_5 on the dielectric properties of the lead strontium titanate borosilicate glass ceramic system and also the results of impedance and modulus spectroscopic analysis to find out the different contributions to the observed dielectric behaviour.

2. Experimental

Glasses were prepared using AR grade PbO, $SrCO_3$, TiO_2, H_3BO_3, K_2CO_3, $BaCO_3$ and Nb_2O_5 of purity better

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than 99%. Well-mixed, dried powders of appropriate amount of different components were melted in a high-grade alumina crucible for 1 h in the temperature range 1200–1300°C under normal atmospheric conditions. The melt was quenched by pouring it into an aluminum mould and pressing with a thick aluminum plate. Bulk glass was immediately kept in another furnace for annealing at 722 K for 4 h. Based on differential thermal analysis (DTA) results, glass ceramic samples were prepared by subjecting glasses to various heat treatment schedules. Density of the glass ceramic samples was determined using Archimedes principle (Hiremath *et al* 2001). Distilled water was used as the liquid medium. The following weights were taken and used in the density calculations:

W_1 = Weight of empty specific gravity bottle (g); W_2 = weight of specific gravity bottle with sample (g); W_3 = weight of specific gravity bottle with sample and distill water (g) and W_4 = weight of specific gravity bottle with distill water (g).

Density was calculated using the formula:

$$\text{Density} = \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)}.$$

The glass ceramic samples were ground and polished successively using SiC powders on a thick and flat glass plate. Finally polishing was carried out on a blazer cloth using diamond paste (1 μm). The polished glass ceramic samples were etched for 1 min with a suitable etchant (30% HNO_3 + 20% HF) solution. Etched surface of various glass ceramic samples were coated with gold by sputtering method for scanning electron microscopy (SEM) to study the morphology of different crystalline phases. 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. The electrodes were made by applying silver paint (code no. 1337 – A, Elteck Corporation, India) on both sides of the specimen and curing at 972 K for 10 min. The capacitance 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°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 of room temperature (~ 972 K) to 672 K. For impedance and modulus spectroscopic analysis, capacitance and dissipation factor of samples were measured at a few selected temperatures with respect to frequency in the range 0·01 Hz to 3 MHz. Immittance functions were determined from these values of capacitance and dissipation factor.

3. Results and discussion

3.1 *Scanning electron microscopic studies*

Figures 1a and b show the scanning electron micrographs for the glass ceramic samples 1PN5B898T and STN5B880T at high and low magnifications. At low magnification for 3 h, heat-treated glass samples show secondary phase of rutile in small fractions. The major phase of $SrTiO_3$ was observed for both the glass ceramic samples. Spherulitic crystal growth of major phase of strontium titanate is observed while the white tiny crystallites of secondary phase of rutile are observed. All spherulites comprise fibrous crystals radiating from a common centre. Most of these have a spherical shape but a few have a sheaf-like appearance (Keith and Padden

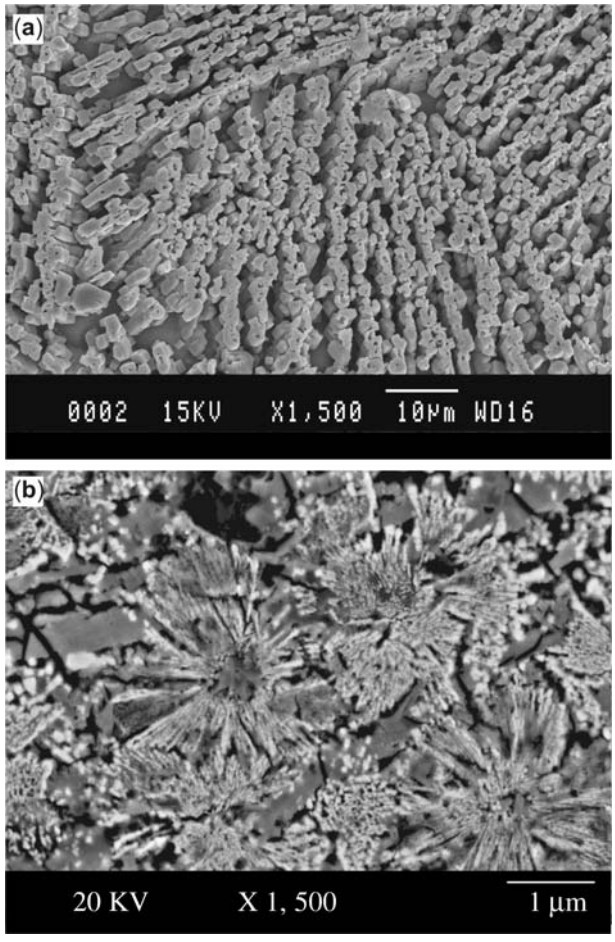

Figure 1. Scanning electron micrographs of polished and chemically etched surfaces of glass ceramic samples: (**a**) 1PN5B898T and (**b**) STN5B880T.

Table 1. Compositions, codes, heat treatment schedule, crystalline phases and density of different glass ceramic samples in the system $[(Sr_{1-x}Pb_x)O{\cdot}TiO_2] - [2SiO_2{\cdot}B_2O_3] - [5K_2O - 5BaO] - [Nb_2O_5]$.

Composition (x)	Glass ceramics code	Heat treatment schedule temperature (°C) and time (h)	Crystalline phases	Density (g/cc)
0·0	STN5B880T	880, 3	ST + SB + R + U*	2·572
0·1	1PN5B898T	898, 3	P + R	3·054
0·2	2PN5B896T	896, 3	P + SB + R*	3·271
0·3	3PN5B825T	825, 3	P + SB	3·342
0·4	4PN5B765T	765, 3	P + SB + U	3·427

P, Perovskite lead, strontium titanate; ST, strontium titanate; SB, strontium borate; U, unidentified; R, TiO_2 (rutile) and *minor phase.

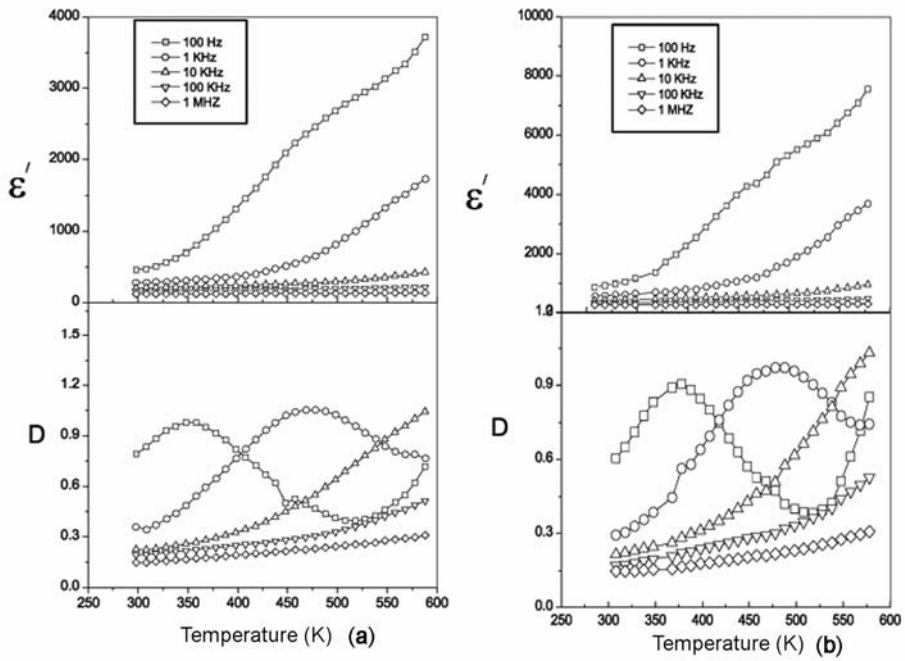

Figure 2. Variation of dielectric constant, ε' and dissipation factor, D with temperature at different frequencies for the glass ceramic samples: (**a**) STN5B880T and (**b**) 2PN5B896T.

1963). Good crystallization is observed for this glass ceramic sample.

3.2 *Density studies*

The compositions of various glass ceramic samples, with their codes, heat treatment schedule, the crystalline phases and density are shown in table 1. The density of glass ceramics depends on its chemical constituents, internal structure and crystallization behaviour and residual glass. The densities of glass ceramic samples were found to be in the range 2·572–3·427 g/cc. From the table 1, it is observed that the density of the glass ceramic samples for all the compositions increases with decreasing the concentration of strontium because the atomic weight of Sr (87·62) is comparatively less than the atomic weight of Pb (207·19). The density of the strontium-rich glass ceramic sample STN5B880T is lowest.

3.3 *Dielectric characteristics*

Figures 2a and b depict the variation of dielectric constant ε', and dissipation factor, D with temperature at five different frequencies 0·1, 1, 10, 100 KHz and 1 MHz for the glass ceramic samples STN5B880T ($x = 0{\cdot}0$) and 2PN5B896T ($x = 0{\cdot}2$), respectively. The dielectric constant of these glass ceramic samples increases as the temperature is raised from room temperature 297 K to 600 K at frequencies 0·1 and 100 KHz, while at other frequencies, the increase in the value of dielectric constant is insignificant. The dissipation factor, D shows a broad peak at frequencies 0·1 and 1 KHz while at other frequencies,

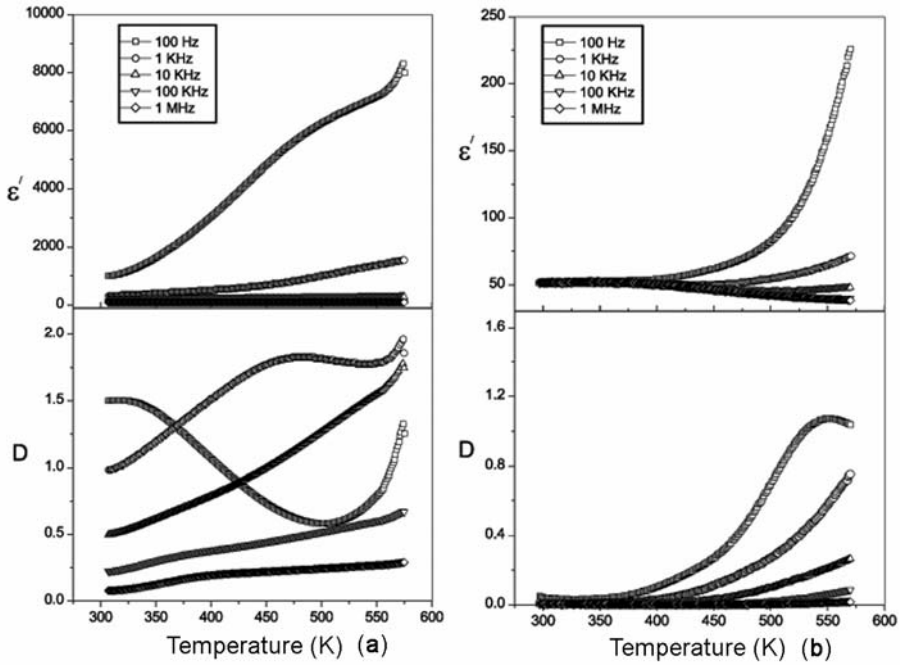

Figure 3. Variation of dielectric constant, ε' and dissipation factor, D with temperature at different frequencies for the glass ceramic samples: (**a**) 3PN5B825T and (**b**) 4PN5B765T.

it increases with increasing temperature. It appears that at these frequencies the dissipation factor, D will show a peak at high temperatures. Figure 3a shows the variation of dielectric constant, ε' and dissipation factor, D for the glass ceramic sample 3PN5B826T. The dielectric behaviour of glass ceramic sample 3PN5B826T is similar to that of STN5B880T and 2PN5B896T. The dielectric constant values for all these glass ceramic samples are also very high. It is of the order of a few thousands. The dielectric characteristics of glass ceramic sample 4PN5B765T (figure 3b) are somewhat different than those of other glass ceramic samples. The value of dielectric constant and dissipation factor are small. The dielectric constant initially decreases with increasing temperature. After a particular temperature it increases rapidly with increasing temperature. All the glass ceramic samples have similar crystalline phase constitution containing mainly $SrTiO_3$ (STN5B880T glass ceramic) or solid solution perovskite (Pb, Sr)TiO_3 (other glass ceramics) and trace amount of TiO_2 (rutile) and thus have similar dielectric behaviour except glass ceramic sample 4PN5B765T. The dielectric constant value for undoped glass ceramic samples containing solid solution lead strontium titanate phase is of the order of 500 (Sahu *et al* 2003). In these glass ceramics, the value of dielectric constant is not significantly affected by the change in ratio of K_2O/BaO while it is strongly affected by the addition of 1 mol% of Nb_2O_5.

The addition of Nb_2O_5 has a strong influence on the dielectric properties of these glass ceramics. Nb_2O_5 promotes the crystallization of the glass during heat treatment. Niobium acts as a donar dopant to perovskite lead strontium titanate. When these glass ceramics are crystallized at higher temperatures, Nb ions present in the glass diffuse in the crystalline perovskite phase and make them semiconducting. On the application of electric field, the glass ceramic samples STN5B880T, 2PN5B896T and 3PN5B825T show space charge polarization around semiconducting crystal and insulating glass interface with very high value of effective dielectric constant. The space charge polarization relaxes with increasing frequencies. The relaxation time decreases and relaxation frequencies increase with increasing temperature. Due to these space charge relaxation processes, a maxima is observed in their dissipation factor, D vs temperature plots, whose position shifts to higher temperature with increasing temperature. It is also observed that the value of dielectric constant is less for the glass ceramic sample 4PN5B765T. It may be that Nb ions could not diffuse into the crystalline perovskite phase in the glass ceramic sample because of its lower crystallization temperature (765°C) and do not make them semiconducting. Hence, the glass ceramic sample 4PN5B765T does not show space charge polarization and high value of effective dielectric constant. The rise in the value of dielectric constant at 0·1 KHz may be due to the movement of alkali and alkaline earth ions, which are present in the residual glass at high temperature in their glass ceramic samples.

3.4 *Complex plane impedance and modulus analysis*

Complex plane impedance and modulus spectroscopy has been extensively used for separation of resistive and

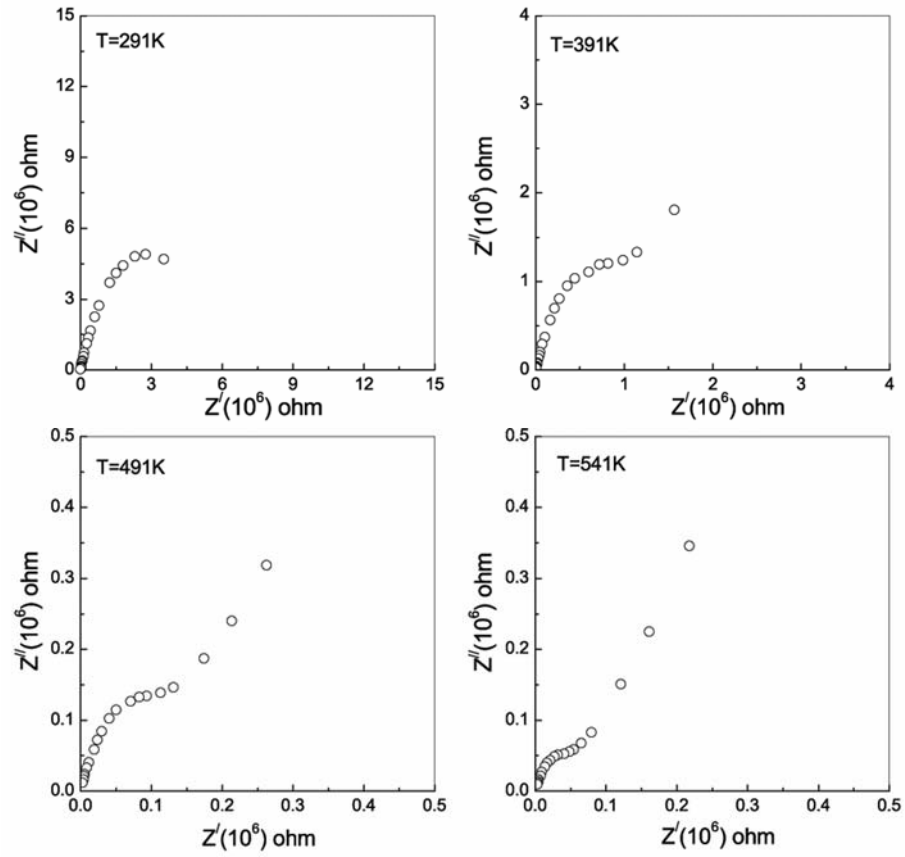

Figure 4. Complex plane impedance Z'' vs Z' plots at some steady temperatures in frequency range 100 Hz to 2 MHz for glass ceramic sample, 4PN5B765T.

capacitive contributions of different phases and interfaces of ceramics and glass ceramic materials. If these materials have two or more contributions with different relaxation times, then two or more circular arcs are observed in their complex plane impedance (Z'' vs Z') plots and complex plane modulus plots (M'' vs M') (MacDonald 1987; Sinclair and West 1988, 1989; Morrison *et al* 1999). In the present paper, the impedance and modulus spectroscopic data for only one glass ceramic sample 2PN5B896T with composition $x = 0{\cdot}2$ is presented. Complex plane impedance (Z'' vs Z') plots and complex plane modulus plots (M'' vs M') at a few selected temperatures in the temperature range 291–541 K for the glass ceramic sample 2PN5B896T are shown in figures 4 and 5, respectively. One circular arc appears in its Z'' vs Z' plots (figure 4) at low-temperature (291–391 K). With increasing temperatures, a second steeply rising arc appears in the low-frequency range. The M'' vs M' plots show only one steeply rising arc at all temperatures. A closer look of modulus arcs near the origin indicate that the steeply rising arc actually consists of a small depressed circular arc near the origin and a steeply rising arc. These plots indicate that there are at least two polarization processes, which are contributing to the resulting dielectric behaviour of glass ceramic sample 2PN5B896T. The equivalent circuit model may consist of two parallel RC circuits connected in series. The resistance and capacitance R_1, C_1 and R_2, C_2 of this model-equivalent circuit represents the resistive and capacitive contributions of crystal phase and glass to crystal interface, respectively.

The resistance R_1 values at different temperatures are obtained from the intercept of the arc on Z' axis corresponding to that element. Capacitance values are calculated by using the relation $\omega RC = 1$, where $\omega = 2\pi f_{max}$ and f_{max} the frequency corresponding to the maximum of each semicircular arc. The values of resistances of the crystallites at different steady temperatures vary between $0{\cdot}0114 \times 10^6$ and $4{\cdot}785 \times 10^6$ ohm. It is observed that the value of resistance decreases with increasing temperature. Furthermore, the capacitance values of these crystallites lies in the range 0·21–0·54 nF. The values of capacitance for crystal interface are obtained from the intercept of the small arc near the origin in the complex plane modulus plots in low-frequency region (figure 5). The value of interface capacitance lies in the range 2·16–17·29 nF. The value of interface capacitance increases with increasing temperature. It is due to decreasing resistance of the crystalline phase leading to increased charge accumulation at the interface. The contribution of capacitance and resistance of the crystal interface decreases with

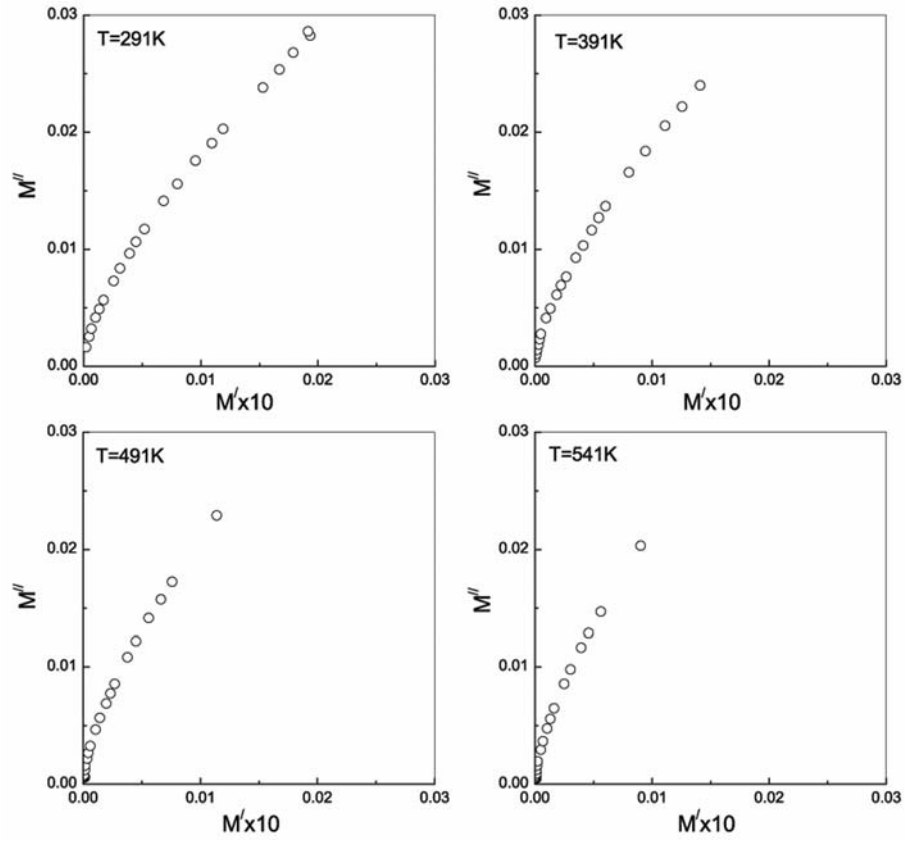

Figure 5. Complex plane modulus M'' vs M' plots at some steady temperatures in frequency range 100 Hz to 2 MHz for glass ceramic samples, 2PN5B896T.

increasing temperature. The values of resistance of the crystallites interface lie between $2{\cdot}45 \times 10^7$ and $2{\cdot}059 \times 10^9$ ohm. Thus the contribution of crystal interface resistance was found to be more in comparison to the resistance of the crystallites of the major phase.

4. Conclusions

Dielectric behaviour and impedance spectroscopy of various glass ceramic samples in the system $[(Sr_{1-x}Pb_x)O{\cdot}TiO_2] - [2SiO_2{\cdot}B_2O_3] - [5K_2O–5BaO]–[Nb_2O_5]$ are studied. The addition of 1 mol% Nb_2O_5 enhances the crystallization of lead strontium titanate perovskite phase and retards the crystallization of minor phases. The high value of dielectric constant is attributed to space charge polarization for these glass ceramic samples. Impedance spectroscopy shows that the value of resistance of the crystallites for all the glass ceramic samples decreases with increasing temperature.

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