Catalyzed crystallization and some physical properties of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses

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Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses were crystallized at three different temperatures. The samples were characterized by scanning electron microscopy and differential scanning calorimetry. Various physical properties viz., optical (optical absorption, IR spectra and thermoluminescence), magnetic (magnetic susceptibility and ESR spectra) have been studied as a function of temperature of crystallization. The investigation is further extended to the dielectric properties viz., dielectric constant, loss and a.c. conductivity over a moderately wide range of frequency and temperature. The analysis of these results indicated a considerable increase in the electrical insulating strength of the samples due to crystallization.

Keywords: Glasses, Crystallization, Optical absorption, IR spectra, Thermoluminescence
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1 Introduction

Alkali/alkaline-earth borate glasses like Li$_2$O-MgO-B$_2$O$_3$ glasses doped with different transition metal ions are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices$^{1-6}$. Recently, a detailed study on the influence of various modifier oxides on certain important physical properties of Li$_2$O-MO-B$_2$O$_3$ glasses doped with vanadium ions$^{7,8}$ has been reported. These studies have yielded valuable information regarding optical and electrical properties, which are helpful to consider these materials for the practical applications. Among various transition metal, oxide-doped glasses and the titanium oxide-doped glasses have gained much importance in recent years due to their potential applications in non-linear optical devices such as ultrafast switch and power limiters$^{9-11}$. The crystalline glass materials have a fine-grained uniform structure consisting of small crystals of irregular, distorted form often aggregated into sphenulites with residual glass inter layers cementing crystalline glass-ceramic concretion; such effects hinder the crack growth in the material. Intensive research on production and characterization of these materials is being carried out by a number of researchers$^{12-16}$. In general, titanium oxide is considered as a nucleating agent for crystallization in silicate glasses. However, there are certain recent studies where titanium ions were used as nucleating agents in other glass systems$^{17-19}$ like P$_2$O$_5$, GeO$_2$. TiO$_2$ is easily miscible in the glassy network at high temperatures but induces phase separation during the cooling of the melt.

In addition to the conventional X-ray/electron microscopic methods, it is also quite possible to understand the structure of the glass ceramics by investigating various physical properties viz., optical, magnetic, electrical and elastic properties depending upon their chemical composition. For the present study, we have selected Li$_2$O-MgO-B$_2$O$_3$ glass system with TiO$_2$ as nucleating agent or catalyst for the crystallization.

The current investigation is aimed at understanding the catalyst action of the titanium ion on the crystallization of Li$_2$O-MgO-B$_2$O$_3$ glass system by means of multiple analysis technique that includes differential scanning calorimetry, electron microscopy, spectroscopic, magnetic and dielectric properties.

2 Experimental Details

For the present study, the following composition is chosen: 30 Li$_2$O-10 MgO-59.8B$_2$O$_3$:0.2 TiO$_2$. Appropriate amounts of Analar grade reagents of Li$_2$CO$_3$, MgCO$_3$, H$_3$BO$_3$ and TiO$_2$ were thoroughly mixed in an agate mortar and melted in a platinum crucible at 950 ± 10°C for about 1 hr until a bubble free liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 200°C. The differential scanning calorimetric studies (for determining glass transition temperature $T_g$) on these samples was carried out using TA instruments.
DSC 2010 Differential Scanning Calorimeter with a programmed heating rate of 20°C/min in the temperature range 30-550°C to an accuracy of ±0.1°C.

The specimens were heat treated (both below and above $T_g$) in a furnace at 200°C ($G_2$), 400°C ($G_4$) and 600°C ($G_6$) for 5 hr. After heat treatment in the furnace at specified temperature, the samples were quenched in air at room temperature. Automatic controlling furnace was used for raising the temperature to the required level and for maintaining it for the specified duration. The density $d$ of these glasses was determined by the standard principle of Archimedes' using $o$-xylene (99.99% pure) as the buoyant liquid to an accuracy of ±0.001. The scanning electron microscopic pictures (SEM) of the glasses were taken with a LEICA S440I microscope.

The IR transmission spectra of these glasses in KBr matrices were recorded using Perkin-Elmer 283B spectrophotometer in the frequency range 400-4000 cm$^{-1}$. The samples were then ground and optically polished. The final dimensions of the samples used for the dielectric measurements, optical absorption and thermoluminescence were about 1 cm x 1 cm x 0.2 cm. The optical absorption spectra of these glasses were recorded on Shimadzu-3101 pc UV-VIS-NIR spectrophotometer in the wavelength range 300-800 nm. For recording thermoluminescence emission, the samples were irradiated with X-rays for ½ hr with Norelco X-ray unit operated at 35 kV, 10 mA; thermoluminescence output of these glasses was recorded with a rate of heating of 1°C/s, on a computerized Nucleonix-TL set-up (Nucleonix Pvt., Ltd., Hyderabad). The glow peak temperature was determined to an accuracy of ±1°C.

A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for dielectric measurements. The dielectric measurements were made using LCR Meter (Hewlett-Packard Model-4263 B and at higher frequencies, a Radart Q-meter); the accuracy in the measurement of dielectric constant is ~0.001 and that in loss is ~10$^{-4}$. The dielectric breakdown strength of all the glasses was determined at room temperature in air medium using a high ac voltage breakdown tester (ITL Model AAH-55, Hyderabad) operated with an input voltage of 250 V at a frequency of 50 Hz; it was ensured that all the glasses used for this study were of nearly identical thicknesses. Magnetic susceptibility measurements were made by Guoy's method using fine powder of these samples to an accuracy of 10$^{-4}$ emu. The ESR spectra of the fine powders of the samples were recorded at room temperature on JES SA 200 ($v = 9.234$ GHz) ESR spectrometer with 100 kHz field modulation.

3 Results and Discussion

Figure 1 shows scanning electron microscopic pictures (SEM) of the glasses subjected to heat treatment at different temperatures; the pictures clearly show an increasing crystallinity with increase in the temperature of heat treatment.

The density of the virgin glass is measured to be 2.872 g/cm$^3$, as the temperature of crystallization increases the density is found to increase gradually. From the measured values of density ($d$) and the average molecular weight $M$ (57.97 g/mol) of the sample various other physical parameters such as titanium ion concentration $N_i$, mean titanium ion separation are calculated and presented in Table 1.

Figure 2 shows typical DSC traces obtained for the present samples. The trace of virgin glass ($G_0$) exhibits an endothermic change at 530°C corresponding to the glass transition temperature $T_g$, an exothermic peak attributed to the crystallization temperature range (where its maximum corresponds to the crystallization temperature, $T_c$). The appearance of a single peak corresponding to $T_g$ for virgin glass indicates that the prepared glass is highly homogeneous. As the temperature of the crystallization increases, the parameter, $T_c - T_g$, which is directly proportional to the stability of the glass against devitrification, is found to decrease (Table 2).

The infrared transmission spectra of Li$_2$O-MgO-B$_2$O$_3$: TiO$_2$ glasses exhibit two groups of bands in the region: (i) 1200-1600 cm$^{-1}$, (ii) 800-1200 cm$^{-1}$ and (iii) a band at about 710 cm$^{-1}$ (Fig. 3). It is well known that the effect of introduction of alkali oxides into B$_2$O$_3$ glass is the conversion of sp$^3$ planar BO$_3$ units into more stable sp$^3$ tetrahedral BO$_4$ units. Each BO$_4$ unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long tetrahedron chains. The second group of bands is attributed to such BO$_4$ units whereas the first group of bands is identified as due to the stretching relaxation of the B-O bond of the trigonal BO$_3$ units and the band at 710 cm$^{-1}$ is due to the bending of B-O linkages in the borate network. It may be worth mentioning here that the earlier studies on the IR spectra of various other glasses containing TiO$_2$ indicate the presence of a vibrational band at about 720 cm$^{-1}$ due to vibrations.
Table 1—Physical parameters of Li₂O·MgO·B₂O₃·TiO₂ glass-ceramics

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cryst. temp (°C)</th>
<th>Density (g/cm³)</th>
<th>N_i (×10²¹ ions/cm³)</th>
<th>r_i (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₀</td>
<td>—</td>
<td>2.872</td>
<td>6.30</td>
<td>5.42</td>
</tr>
<tr>
<td>G₂</td>
<td>200</td>
<td>2.893</td>
<td>6.34</td>
<td>5.40</td>
</tr>
<tr>
<td>G₄</td>
<td>400</td>
<td>2.914</td>
<td>6.38</td>
<td>5.39</td>
</tr>
<tr>
<td>G₆</td>
<td>600</td>
<td>2.926</td>
<td>6.41</td>
<td>5.38</td>
</tr>
</tbody>
</table>

Table 2—Data on DSC studies of Li₂O·MgO·B₂O₃·TiO₂ glass ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_g (°C)</th>
<th>T_c (°C)</th>
<th>T_c − T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₀</td>
<td>530</td>
<td>610</td>
<td>80</td>
</tr>
<tr>
<td>G₂</td>
<td>535</td>
<td>600</td>
<td>65</td>
</tr>
<tr>
<td>G₄</td>
<td>540</td>
<td>592</td>
<td>52</td>
</tr>
<tr>
<td>G₆</td>
<td>545</td>
<td>580</td>
<td>35</td>
</tr>
</tbody>
</table>

of TiO₄ groups²³. Hence, there is a possibility for the formation of single boron-oxygen-titanium framework in the glass network. Additionally, a band at 650 cm⁻¹, identified due to Ti-O-Ti symmetric stretching vibrations of TiO₆ structural units²⁴ is also observed in the spectra of virgin glass; with increase in the temperature of crystallization, the intensity of
band due to B-O-Ti linkages is observed to increase with the shifting of meta-center towards lower wavenumber whereas the intensity of the band due to TiO$_6$ structural units is observed to decrease (Table 3). These observations suggest that as the temperature of crystallization increases there is an increase in the concentration of linkages of type B-O-Ti and the structure becomes more rigid.

Figure 4 shows the optical absorption spectra of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses recorded at room temperature in the wavelength region 450-800 nm; the spectrum of the virgin glass (G$_0$) has exhibited two conventional absorption bands at 512 and 674 nm. The bands are attributed to $^2B_{2g} \rightarrow ^2B_{1g}$ (512 nm) and $^2B_{2g} \rightarrow ^2A_{1g}$ (674 nm) transitions of 3d$^1$ electron of the Ti$^{3+}$ ions in tetragonal distorted octahedral sites$^{25-27}$; with the increase in the temperature of crystallization, the half width and intensity of these two bands decrease. The lowest intensity of these bands observed in the spectrum of crystalline glass G$_6$ indicates the lowest concentration of Ti$^{3+}$ ions that take modifying positions in the glass network.

The ESR spectra, recorded at room temperature for Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses under investigation are shown in Fig. 5; the spectrum of virgin glass G$_0$ exhibits a weak asymmetric signal with $g$ =1.93 due
to 3d¹ unpaired electron of Ti³⁺ ions in a tetragonally distorted octahedral field. A considerable decrease in the intensity of the signal is observed as the temperature of crystallization increases. Such an observation indicates a gradual decrease in the concentration of Ti³⁺ ions in the glass network. Further, the process Ti⁴⁺ → Ti³⁺ takes place, with $E^o = 0.2V$ only; hence it is quite likely to take place such oxidation and reduction reaction during the heat treatment of the samples. The increasing presence of such Ti⁴⁺ ions may be taken as the manifestation of increase in the rigidity of the ceramic material. The weak intensity of the signal observed in the ESR spectrum of sample G₆ clearly indicates the presence of very low concentration of Ti³⁺ ions in this glass.

The value of the magnetic susceptibility of the virgin glass measured at room temperature is observed to decrease with increase in the temperature of crystallization (Table 4). From the values of magnetic susceptibilities, the concentration of Ti³⁺ ions (N') and the redox ratio (N'/Ni) are also evaluated and presented in Table 4. For the calculation of the concentration of Ti³⁺ ions, the value of the effective magnetic moment of Ti³⁺ (3d¹) ion is taken as 1.75 μB. The magnetic susceptibility for these glasses arises due to paramagnetic Ti³⁺ (3d¹) ions. The gradual decrease in the concentration of redox ratio, (N'/Ni) with the temperature of crystallization from the sample G₀ to G₆ obviously suggests a decreasing concentration of Ti³⁺ ions that act as modifiers in the glass network.

It is now certain that titanium ions exist in both Ti⁴⁺ (situated in both tetrahedral and octahedral positions) and in Ti³⁺ (positioned octahedral sites) state present glasses.

Figure 6 represents the thermoluminescence (TL) glow curves of crystallized Li₂O–MgO-B₂O₃:TiO₂ glasses. The virgin glass exhibits a TL peak at 473 K. The crystallization of glasses caused a drastic reduction in the TL light output. Inset of Fig. 6 (a) represents the variation of TL light output with the temperature of crystallization. The activation energies associated with the glow peak are computed using Chen's formula:  

$$E_c = 1.52 \left( \frac{KT_M^2}{\tau} \right) - 1.58(2KT_M) \quad \ldots (1)$$

<table>
<thead>
<tr>
<th>Glass</th>
<th>Temp. (°C)</th>
<th>Magnetic susceptibility (χ10⁻⁶ emu)</th>
<th>Ti³⁺ ion concentration (N' (10²¹ ions/cm³))</th>
<th>(N'/Ni) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₀</td>
<td>—</td>
<td>1.10</td>
<td>0.50</td>
<td>8.0</td>
</tr>
<tr>
<td>G₂</td>
<td>200</td>
<td>0.95</td>
<td>0.45</td>
<td>7.1</td>
</tr>
<tr>
<td>G₄</td>
<td>400</td>
<td>0.84</td>
<td>0.39</td>
<td>6.3</td>
</tr>
<tr>
<td>G₆</td>
<td>600</td>
<td>0.74</td>
<td>0.36</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Fig. 6(a)—Thermoluminescence recordings of X-ray irradiated Li₂O-MgO-B₂O₃:TiO₂ glass ceramics. Inset gives variation of TL light output with temperature of crystallization.
for the first order kinetics. In the above equations $K$ is the Boltzmann constant, $\beta$ is the rate of heating, $\tau = T_m - T_1$, $\delta = T_2 - T_m$, where $T_m$ is the glow peak temperature and $T_1$ (rising end) and $T_2$ (falling end) are the temperatures at the half widths of the glow peaks. A summary of the data on thermoluminescence peaks and corresponding trap-depth parameters of the present glasses is furnished in Table 5.

It may be noted here that prior to TL measurements we have recorded the optical absorption spectrum of all the samples before and after X-ray irradiation. The X-ray irradiation does not produce any significant changes of the pattern and the intensity of the existing absorption bands. These observations indicate X-ray irradiation does not produce any changes in the concentration of existing oxidation states of titanium ions in these samples due to X-ray irradiation.

In the Li$_2$O-MgO-B$_2$O$_3$ glass ceramic samples the Li$^+$ ions have closed structure, do not have energy levels within 10 eV of the ground state and hence these ions do not participate directly in luminescence but may act as activator ions. The magnesium ions occur as Mg$^{2+}$ ions; in the activation process, the Li$^+$ replaced by doubly charged Mg$^{2+}$ ions. As a result, the energy levels of the surrounding oxygen ions will be slightly lifted up in comparison with the normal Li$^+$ ions due to charge imbalance. This process gives rise to occupied energy levels close to the top of the valence band. These levels form the ground state of the luminescence.

The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming colour centres. The trapping sites may be the metal cations that constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. Thus, this process leads to

The formation of (1) boron electron centres, (2) non-bridging oxygen hole centres and (3) boron oxygen hole centres.

Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron centre) and an anti-bonding molecular orbital of the nearest of the oxygen hole centres. However, the TL emission due to such recombination process is possible only at low temperatures. Alternatively, the TL emission in these glasses may be explained as follows. During the heating process the electrons that were captured by metal ions are liberated and later trapped by holes in the recombination centers giving out TL light output. This process inhibits the radiative recombination of electron and hole centres causing a reduction in the TL light output (Fig. 6b).

In the absence of Ti$^{4+}$ ion in the glass network, each electron released by heating from electron centres would be caught by an anti-bonding molecular orbital of the nearest of the oxygen hole centre giving out maximum TL light output. The near invariance of the optical absorption spectrum of the crystallized glasses even after X-ray irradiation indicates that the titanium ions in these glasses exist in the same valence states with more or less same concentrations.

Let us assume that these ions are uniformly distributed throughout the glass; electrons released by heating from electron centres would be trapped at Ti$^{4+}$ ions thereby reducing these ions to Ti$^{3+}$ state. This process inhibits the radiative recombination of electron and hole centres causing a reduction in the TL light output. The maximum quenching in the TL light output of glass G$_6$ obviously suggests the presence of larger concentration of titanium ions in Ti$^{4+}$ state in this glass. The dielectric constant $\varepsilon'$ and loss tan$\delta$ at room temperature (30°C) of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ (G$_0$) glass at 100 kHz is measured to be

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_m$ (K)</th>
<th>$\tau$ (K)</th>
<th>$\delta$ (K)</th>
<th>$E_\tau$ (eV)</th>
<th>$E_\delta$ (eV)</th>
<th>area (arb. units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G$_0$</td>
<td>521</td>
<td>78</td>
<td>37</td>
<td>0.31</td>
<td>0.61</td>
<td>360</td>
</tr>
<tr>
<td>G$_2$</td>
<td>492</td>
<td>54</td>
<td>51</td>
<td>0.45</td>
<td>0.40</td>
<td>179</td>
</tr>
<tr>
<td>G$_4$</td>
<td>484</td>
<td>51</td>
<td>54</td>
<td>0.46</td>
<td>0.36</td>
<td>115</td>
</tr>
<tr>
<td>G$_6$</td>
<td>471</td>
<td>43</td>
<td>56</td>
<td>0.54</td>
<td>0.33</td>
<td>94</td>
</tr>
</tbody>
</table>

Fig. 6(b) — Proposed TL mechanism for TiO$_2$ doped glass ceramics
5.72 and 0.0095 respectively; these values are found to increase with the decrease in frequency.

Figure 7 presents the variation of $\varepsilon'$ with temperature at different frequencies for the glass crystallized at 200°C whereas Fig. 8 presents a comparison plot of variation of $\varepsilon'$ with temperature at 1 kHz for the glasses crystallized at different temperatures. $\varepsilon'$ is found to exhibit a considerable increase at high temperatures especially at lower frequencies. As the temperature of crystallization increases, the dielectric constant $\varepsilon'$ is found to decrease gradually at any temperature and frequency. The summary of the data on the variation of $\varepsilon'$ with the crystallization temperature of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glass-ceramics are presented in Table 6.

The temperature dependence of tan$\delta$ of sample G$_4$ (crystallized at 400°C) measured at different frequencies is shown in Fig. 9 and the comparison plot of tan$\delta$ with temperature at a frequency of 10 kHz is presented in Fig. 10. The loss curves have exhibited distinct maxima and with increasing frequency the temperature maximum shifts towards higher temperature, indicating the dielectric relaxation character of dielectric losses in Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glass-ceramics. The comparison of dielectric loss variation with temperature at a particular frequency for different glass-ceramics indicates a gradual decrease of relaxation intensity with increase in the temperature of crystallization. The summary of the data on the relaxation effects of tan$\delta$ with crystallization temperature is presented in Table 7.
Using the relation:

\[ f = f_0 \exp\left(-\frac{W_d}{kT}\right) \]  \hspace{1cm} \ldots (3)

the effective activation energy, \( W_d \), for the dipoles is calculated for different glass-ceramics and presented in Table 7; the activation energy is found to increase with increase in the temperature of crystallization.

The ac conductivity \( \sigma \) is calculated at different temperatures using the equation:

\[ \sigma = \omega \varepsilon_0 \varepsilon' \tan\delta \]  \hspace{1cm} \ldots (4)

(where \( \varepsilon_0 \) is the vacuum dielectric constant) at different frequencies and plots of \( \log(\sigma) \) against \( 1/T \) are shown in Fig. 11 or glass \( G_6 \) for different frequencies and for all samples at 100 kHz in Fig. 12. From these plots, the activation energy for conduction in the high

### Table 7—Data on dielectric loss of Li₂O-MgO-B₂O₃:TiO₂ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>(( \tan\delta_{\text{max}} ))avg</th>
<th>Temp. region of relaxation (°C)</th>
<th>AE (eV) for dipoles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_0 )</td>
<td>0.016</td>
<td>95-108</td>
<td>2.71</td>
</tr>
<tr>
<td>( G_2 )</td>
<td>0.012</td>
<td>99-124</td>
<td>2.82</td>
</tr>
<tr>
<td>( G_4 )</td>
<td>0.010</td>
<td>102-136</td>
<td>2.85</td>
</tr>
<tr>
<td>( G_6 )</td>
<td>0.008</td>
<td>104-141</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Fig. 9—Temperature dependence of \( \tan\delta \) at different frequencies for glass \( G_4 \)

Fig. 10—A comparison plot of \( \tan\delta \) with temperature of Li₂O-MgO-B₂O₃:TiO₂ glass ceramics at 10 KHz frequency

Fig.11—Conductivity \( \sigma_{ac} \) against \( 1/T \) at different frequencies for glass \( G_6 \)
temperature region over which a linear dependence of \( \log \sigma \) with \( 1/T \) could be observed, is calculated and is found to be the highest for the glass \( G_6 \) (Table 7). The activation energy varies linearly with the conductivity as shown in Fig. 13. The variation of conductivity measured at 200°C with the temperature of crystallization and at a frequency of 100 kHz is shown in the inset of Fig. 13. The conductivity is observed to decrease with the temperature of crystallization. The dielectric breakdown strength for glass \( G_0 \) is determined to be 11.10 kV/cm. With the increase in the temperature of crystallization the value of the breakdown strength is increased to a value of 13.41 kV/cm for the sample \( G_6 \) (Table 6).

In general, TiO\(_2\) (when present on octahedral positions) acts as modifier similar to Li\(_2\)O and enters the glass network by breaking up B-O-B bonds and introduces, coordinated defects known as dangling bonds. The bonding defects thus produced create easy pathways for the migration of charges that would build up space charge polarization\(^{35-37}\) leading to the increase in the dielectric parameters with increase in temperature of measurement for any sample as observed in Figs 7-12.

As the temperature of crystallization increases, \( \varepsilon' \), \( \tan \delta \) and \( \sigma_{ac} \) are found to decrease at any frequency and temperature and the values of dielectric
breakdown strength and activation energy for ac conduction are observed to increase with respect to the values of virgin glass. Such a decrease can be understood if there is an increase in the concentration of Ti$^{4+}$ ions with increase in the temperature of crystallization. The increase of concentration of Ti$^{4+}$ ions is in fact evidenced from optical absorption, ESR spectra and magnetic susceptibility data. As mentioned before, it is quite likely that these Ti$^{4+}$ ions to take network-forming positions by forming a single B–O–Ti framework strengthen its structure and decrease the space charge effects causing a reduction in the dielectric parameters.

In general, the dielectric relaxation effects are observed only when the metal ions present, are in the divalent state as mentioned before. Our earlier investigation$^{38}$ on the dielectric properties of Li$_2$O-MgO-B$_2$O$_3$ glasses indicates that these glasses have also exhibited the relaxation effects and those were attributed to the divalent ions of magnesium together with a pair of any cationic vacancies. When the glasses are crystallized, we have observed a decreasing relaxation character of dielectric loss; this may be due to a decreasing freedom of dipoles to orient in the field direction due to increase in the rigidity of the sample.

Though variety of models have been put forward for explaining the conduction mechanism in mixed alkali and alkaline earth materials, the defect model suggested by Ingram$^{38}$ seems to be more appropriate for the present Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glass-ceramics. The near linearity between the conductivity and the activation energy in the high temperature region suggests the conductivity enhancement with the temperature of measurement is directly related to the increasing mobility of the charge carriers. Since the alkaline earth ions are much less mobile than the alkali ions in the mixed alkali and alkaline earth glasses (like the present Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses) the alkaline earth ions (Mg$^{2+}$ ions) can be regarded as virtually immobile within the time window of hopping processes of the alkali (Li$^+$) ions$^{39}$. Therefore, the contribution to the conduction for the present glasses in the high temperature region can be mainly considered due to Li$^+$ ions. As it appears, due to decreasing modifying action of titanium ions with the temperature of crystallization, easy paths for the movement of the charge carriers are reduced and hence a decrease in the conductivity is resulted. In other words, as the temperature of crystallization increases, there is a gradual increase in the concentration of tetragonally positioned Ti$^{4+}$ ions in the present glass ceramics; if the least rigidly bound Li$^+$ ions are replaced by Ti$^{4+}$ ions, the remaining Li$^+$ ions are more tightly bound so that (if the Ti$^{4+}$ ions are not able to move) the conductivity falls. The low temperature part of the conductivity (a near temperature independent part, as in the case of present glasses up to nearly (373 K) can be explained on the basis of quantum mechanical model as reported elsewhere$^{40,41}$.

When the dielectric is placed in the electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss i.e., the loss per unit volume of the dielectric is given by$^{42}$,

$$\rho_l = E^2 \omega \varepsilon' \varepsilon \tan \delta \text{ W/m}^3 \quad \ldots (7)$$

Eq. (7) indicates that the higher the values of ($\varepsilon' \tan \delta$) of the glass at a given frequency, higher are the values of $\rho_l$. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then raises and the specific dielectric loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by Eq. (7).

Our observations on breakdown strengths of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glass-ceramics, indicate the rate of increase of $\varepsilon' \tan \delta$ with temperature is the lowest for the sample G$_6$. Though the breakdown strengths are actually determined at room temperature, the heat liberated during the breakdown raises the temperature of the sample and hence raises the $\varepsilon' \tan \delta$ value. Since the rate of increase of $\varepsilon' \tan \delta$ with temperature is the lowest for sample G$_6$, the breakdown strength (which is inversely proportional to $\rho_l$) is the highest when compared with the other glasses. Thus, the experiments on the dielectric breakdown strength of Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses reveal that there is an increase in the insulating strength of the sample with increase in the temperature of crystallization.

4 Conclusions
Li$_2$O-MgO-B$_2$O$_3$:TiO$_2$ glasses were crystallized at three different temperatures viz., 200, 400 and 600°C. The scanning electron microscope pictures and differential scanning calorimetric analysis indicate a gradual increase in the crystallinity in the samples. Optical absorption, IR spectral investigations and magnetic susceptibility measurements indicate a gradual increase in the concentration of tetragonally
positioned Ti$^{4+}$ ions, which increase the rigidity of the network. Thermoluminescence measurements on these samples show a gradual quenching of TL light output of the single glow peak observed with the increase in the temperature of crystallization indicating Ti$^{4+}$ ions act as TL killers. The dielectric measurements and breakdown strength show a gradual increase in the electrical insulating strength of these materials with increase in the temperature of crystallization.

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References