CHAPTER-4
CHARACTERIZATION OF (70B₂O₃-29Li₂O-1Dy₂O₃)-xBT GLASS-CERAMICS

This chapter includes the structural analysis and electrical transport characteristics of (70B₂O₃-29Li₂O-1Dy₂O₃)-xBT glass-ceramics. XRD studies were performed to confirm the crystallinity of the samples and to detect the crystalline phases formed in the glass matrix upon heat treatment. FTIR and Raman studies were employed to infer the structural changes brought about by BT addition and heat treatment process in these samples. The investigation regarding the temperature and frequency dependence of dielectric relaxation of prepared glass-ceramic samples have also been made through the framework of dielectric permittivity, electric modulus and conductivity formalisms.

4.1 Introduction

Glass ceramics comprising nano/micro crystallites have attained a vast popularity among the glass researchers owing to their several functionalities, comparatively easy preparation methods and their potential applications in optical and electronics devices (Al-Assiri et al. 2009; Chen et al. 2010; Szreder et al. 2014; Al-Syadi et al. 2014; Abdel-Khalek and Ali 2014). The ceramic materials could be prepared by several methods such as solid reaction method, sol gel method, hydrothermal and aerosol methods etc. But there are certain drawbacks and difficulties associated with them such as high temperature requirement for preparation process or the long time of reaction (Dutta et al. 1994; Funakubo et al. 1997; Beck et al. 1998; Berbenni et al. 2001). Such difficulties are overcome in glass ceramics as they are prepared by the controlled crystallization of glass. Such materials possess the properties of both the constituents i.e. of the host glass matrix and the embedded ferroelectric material. Al-Assiri et al. (2014) reported the transport properties of vanadate glasses containing BaTiO₃ glass ceramics. Al-Syadi et al. (2014) studied the kinetic characterization of barium titanate-bismuth oxide-vanadium pentoxide glasses and Szreder et al. (2014) have reported the dielectric properties of BaTiO₃ substituted vanadate glasses. However, not much literature is found for barium titanate modified lithium borate glass ceramics. In the present work, the crystallites have been grown in

♦ Results of this chapter are Under Review in Journal of Alloys and Compounds.
Characterization of (70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-xBT Glass-Ceramics

(70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-xBT glass matrix by a controlled heat treatment process and the structural and temperature dependent electrical properties of these glass ceramics have been investigated using XRD, FTIR spectroscopy, Raman spectroscopy, electrical modulus and ac conductivity formulation.

4.2 Experimental

The glass samples with composition (70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-xBT; x = 0, 5, 10, 15 and 20 weight percent, were prepared by melt quench technique (as discussed in chapter 3). These prepared glass samples were further heated at 585 °C for 18 hours under a controlled heat treatment process so as to obtain glass ceramics. These glass ceramic samples were subjected to XRD, FTIR, Raman spectroscopy and dielectric measurements.

4.3 Results and Discussion

4.3.1 X-Ray Diffraction

Fig. 4.1 depicts the XRD patterns of the studied glass ceramic samples, thermally treated at 585 °C for 18 h. The presence of the peaks in the diffraction patterns confirmed the presence of crystalline phase in these samples. The Bragg’s peaks encountered in the XRD patterns could be indexed to tetragonal Li$_2$B$_4$O$_7$ phase [a = b = 9.477, c = 10.28] and monoclinic Ba$_2$Ti$_6$O$_{13}$ phase [a = 15.00, b = 3.953, c = 9.085] (JCPDS card no.84-2191 and 84-2211 resp.). The crystallinity of the samples was also found to increase with increasing BT content.

4.3.2 Fourier Transform Infrared Spectroscopy

Fig. 4.2 shows the Fourier transform infrared spectra of the studied glass ceramic samples. It is clear from the spectra that the bands between 400 and 1800 cm$^{-1}$ are broad and asymmetric and exhibit some shoulders. So, a deconvolution of the experimental data was necessary in order to have a better identification of the component peaks comprised in the bands of FTIR spectra. Each component peak is related to a certain type of vibration in a specific structural group and has its own characteristic parameters such as peak positions, amplitude and full width half maximum. These parameters of each deconvoluted peak are depicted in Table 4.1. The deconvoluted spectra for each sample of studied composition are shown in Fig. 4.3.
**Figure 4.1:** XRD patterns for the glass ceramic samples with composition (70B₂O₃-29Li₂O-1Dy₂O₃)-xBT.

**Figure 4.2:** FTIR spectra of glass ceramics with composition (70B₂O₃-29Li₂O-1Dy₂O₃)-xBT.
The first peak observed at 456 cm\(^{-1}\) may be assigned to the vibration of Li\(^+\) cations (Saddeek et al. 2008; Soliman et al. 2009). The peak at around 535 cm\(^{-1}\) can be attributed to the borate deformation modes, such as the in-plane bending of boron-oxygen triangles (Yawale et al. 1995). With addition of BT in the samples, this peak is found to be shifted to lower wavenumber at around 500 cm\(^{-1}\) and can be related to the vibrations of Ba\(^{2+}\) ions at their residing sites (ElBatal et al. 2014). The next peak at 690 cm\(^{-1}\), observed in all the samples, is the characteristic of the bending vibrations of B-O-B linkages of BO\(_3\) units (Pascuta et al. 2009; Doweidar and Saddeek 2009). A new peak found at near 700 cm\(^{-1}\) for all the samples except for \(x=0\), may be attributed to Ti-O-Ti symmetric stretching vibrations of TiO\(_6\) structural units (Rao et al. 2004). Also, the intensity of this peak increases with an increase in the BT content, indicating an increment in TiO\(_6\) units. The peak positioned at 765 cm\(^{-1}\) can be assigned to the vibrations of the symmetric mode of TiO\(_4\) tetrahedral units (Rajyasree and Rao 2012; Rao et al. 2004). Also, there is a possibility that the TiO\(_4\) tetrahedrons enter the glass network and alternate with borate structural units forming B-O-Ti linkages. The broad band extending from 860-1140 cm\(^{-1}\) is a typical vibrational range of tetrahedral BO\(_4\) units. After deconvolution, this broad band is found to be consisting of four component peaks positioned at 887 cm\(^{-1}\), 965 cm\(^{-1}\), 1003 cm\(^{-1}\) and 1092 cm\(^{-1}\). These peaks can be associated with the B-O stretching vibrations in BO\(_4\) units from di-borate, tri-, tetra- and penta borate groups respectively (Mansour 2012; Kundu et al. 2014). With increasing BT content, these peaks are found to be shifted to higher wavenumber. The end region of the spectrum extending from 1200-1650 cm\(^{-1}\) is the characteristic of trigonal BO\(_3\) units. This broad band is further found to be comprising of five component peaks positioned at 1252 cm\(^{-1}\), 1341 cm\(^{-1}\), 1475 cm\(^{-1}\), 1575 cm\(^{-1}\) and 1637 cm\(^{-1}\). However, the peak located near 1575 cm\(^{-1}\) is observed in \(x=0\) and \(x=5\) samples only and vanishes for higher compositions. The peak positioned at 1252 cm\(^{-1}\) has been assigned to the B-O stretching vibrations of trigonal BO\(_3\) units in boroxol rings (Mansour 2012; Pascuta et al. 2008), with increasing BT content this peak is found to be shifted to higher wavenumber and an increase in its intensity and peak width is also observed. The next peak at 1340 cm\(^{-1}\) can be related to the B-O stretching vibrations of trigonal BO\(_3\) units in meta-, pyro-, and ortho-borate groups (Saddeek et al. 2008; Gaafar et al. 2013;
Saddeek and Gaafar 2009). The third component peak at 1475 cm\(^{-1}\) may be attributed to the anti-symmetric stretching vibrations with three non bridging oxygens (NBO’s) of B-O-B groups (Saddeek et al. 2008; Gaafar et al. 2013; Saddeek and Gaafar 2009). The end peak near 1630 cm\(^{-1}\) is assigned to the asymmetric stretching of B-O bond of BO\(_3\) units (Kamitsos et al. 1987). It is observed that as we increase the amount of BT, the intensity and width of the peaks, occurring in region 1200-1600 cm\(^{-1}\), increases gradually. This indicates an increment in the number of BO\(_3\) structural units along with the NBO’s in the presently studied system. Hence, the various changes occurring in the spectra of the samples could be the result of the structural changes brought by the addition of BT into the glass matrix and the crystallization process.

**Figure 4.3:** Deconvoluted FTIR spectra of glass ceramic samples with composition \((70B_2O_3-29Li_2O-1Dy_2O_3)-x BT\).
Table 4.1: Peak position $x_c$ (cm$^{-1}$), amplitude A (a.u.) and full width at half maximum w (cm$^{-1}$) of deconvoluted peaks of FTIR spectra of glass ceramic samples with composition (70B$_2$O$_3$-29Li$_2$O-1Dy$_2$O$_3$)-xBT.

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4.3.3 **Raman Spectroscopy**

Fig. 4.4 depicts the Raman scattering spectra recorded for the prepared glass ceramic samples. The shoulder around 80 cm\(^{-1}\) can be related to the acoustic like vibrational modes of the ordered micro regions within the glass (Kundu *et al.* 2014). A small peak arising at 164 cm\(^{-1}\) may be assigned to the librational motion of cyclic borate groups containing tetrahedral borons (Rahman *et al.* 1993), also this peak becomes quite sharp with increasing content of BT. The peak at 254 cm\(^{-1}\) found in all the compositions except for \(x = 0\) may be correlated to the vibrations of Ba\(^{2+}\) cations (Thakur *et al.* 2015). The band at 490 cm\(^{-1}\) can be assigned to the symmetric stretching vibrations of BO\(_4\) units superimposed by Li-O bond vibrations (Padmaja and Kistaiah 2009; Griguta and Ardelean 2008). However, for compositions other than \(x=0\) this band is found to be splitted into three peaks positioned at around 413 cm\(^{-1}\), 485 cm\(^{-1}\) and 509 cm\(^{-1}\) and shifts to higher wavenumber for higher values of \(x\). For \(x = 15\) composition the only peak at 515 cm\(^{-1}\) is observed, other peaks may be suppressed due to their lower intensity.

**Figure 4.4:** Raman spectra for different compositions of presently studied glass-ceramic samples.
The peak arising at 660 cm\(^{-1}\) can be related to the ring type metaborate units (Dwivedi \textit{et al.} 1993) and the position of this peak is found to be shifted to higher wavenumber with increasing BT content. Two sharps peaks positioned at 714 cm\(^{-1}\) and 778 cm\(^{-1}\) are observed in all the compositions except for \(x=15\) where only peak at 778 cm\(^{-1}\) is observed. The peak appearing at 714 cm\(^{-1}\) may be attributed to the bending vibrations of B–O–B bridges in metaborate groups of BO\(_3\) triangular units (Majhi \textit{et al.} 2013; Osipov and Osipova 2013) and the next sharp peak at 778 cm\(^{-1}\) can be attributed to the symmetric breathing vibrations of a ring containing BO\(_3\) triangles replaced by BO\(_4\) tetrahedral and also superimposed by four coordinated Ti atoms in TiO\(_4\) units (Padmaja and Kistaiah 2009; Kundu \textit{et al.} 2014). The band positioned at 900 cm\(^{-1}\) indicates the presence of B-O-B and B-O vibrational modes in ortho borate groups of BO\(_3\) triangular units (Rajesh \textit{et al.} 2012; Majhi \textit{et al.} 2013). But it becomes negligible for the compositions with higher content of BT. The peaks in the range 1027-1160 cm\(^{-1}\) can be related to the symmetric stretching vibrations of B-O\(^-\) bonds in pyroborate groups (Griguta and Ardelean 2008; Rajesh \textit{et al.} 2012). The position of the peak at 1027 cm\(^{-1}\) is found to be almost constant for all the compositions. However, an increase in its intensity is observed. The bands in the range 1350-1432 cm\(^{-1}\) can be related to the B-O\(^-\) stretching vibrations involving non bridging oxygens (NBO’s) in various borate groups (Subhadra and Kistaiah 2012). Thus, all the changes in the Raman spectra such as the shifting of the peaks position towards lower/higher wavenumber alongwith the changes in the intensity of the peaks and the occurrence of new peaks in the samples with \(x\neq0\) can be related to the structural changes taking place in the glass system due to the introduction of BT and also due to the crystallization process.
4.3.4 **Dielectric Studies**

The frequency dependent real ($\varepsilon'$) and imaginary part ($\varepsilon''$) of dielectric constant of the sample with $x = 10$, at various temperatures are shown in figures 4.5 and 4.6 respectively. From the figures, we observe that the both the quantities are almost constant at low temperatures but with an increase in the temperature an abrupt increase in the dielectric constant and dielectric loss is observed in the low frequency regime. This increase is usually associated with the decrease in bond energies (Pereira *et al.* 2014). At a given temperature, $\varepsilon'$ becomes larger at lower frequencies, which is an expected behavior for the oxide glasses, also, it indicates the absence of spontaneous polarization in the glasses. At high temperatures, the hopping frequency of charge carriers is comparable to the frequency of the applied field. At lower frequency the charge carriers may easily hop out of the low energy sites and start accumulating at high energy barrier sites (Majhi and Varma 2010; Ali and Shaaban 2011; Thakur *et al.* 2015), resulting in an increased net polarization. This further leads to an increased dielectric constant and loss. However, at higher frequency region, the electric field changes so fast that the oscillations of charge carriers tend to lag behind the applied electric field thereby resulting in the decrease in $\varepsilon'$ and $\varepsilon''$ values. Both $\varepsilon'$ and $\varepsilon''$ have been found to increase with an increase in BT content and are shown in the inset of figures 4.5 and 4.6.

4.3.5 **Electric Modulus Formalism**

The complex electric modulus formalism is used in order to have an understanding of the bulk response of moderately conducting materials. Whenever the dielectric constant and the loss of a material tend to increase exponentially at lower frequency, with increasing temperature, there arises a difficulty of distinguishing the interfacial polarization and conductivity contributions from that of the intrinsic dipolar relaxation. Such a difficulty is overcome by representing the data in electric modulus formalism (Majhi and Varma 2010).

The complex electric modulus ($M^*$) is expressed as the inverse of the complex dielectric constant ($\varepsilon^*$) (Majhi *et al.* 2013) i.e.

$$ M^* = (\varepsilon^*)^{-1} $$

(4.1)

$$ M^* = M' + iM'' = \frac{\varepsilon'_r}{(\varepsilon'_r)^2 + (\varepsilon''_r)^2} + i \frac{\varepsilon''_r}{(\varepsilon'_r)^2 + (\varepsilon''_r)^2} $$

(4.2)
Figure 4.5: Variation of $\varepsilon'$ with frequency and temperature for glass ceramic sample with $x = 10$. Inset shows the variation of $\varepsilon'$ with frequency at 523 K for different concentrations of BT.

Figure 4.6: Variation of $\varepsilon''$ with frequency and temperature for glass ceramic sample with $x = 10$. Inset shows the variation of $\varepsilon''$ with frequency at 523 K for different concentrations of BT.
where $M'$, $M''$ are the real and imaginary parts of electric modulus and $\varepsilon'$, $\varepsilon''$ are the real and imaginary parts of the dielectric constant respectively. For the presently studied glass ceramic samples, the real and imaginary parts of electric modulus at different temperatures have been calculated using eqn. 4.2.

The frequency dependent real part of the electric modulus ($M'$) at different temperatures (433 K-643 K) is shown in Fig. 4.7. At lower frequencies, $M'$ is found to be approaching zero for all the given temperatures, which may be due to the suppression of electrode polarization (Dhankhar et al. 2015). But with an increase in the frequency, its value increases and at higher frequencies it reaches a maximum value corresponding to $(M_\infty) = (\varepsilon_\infty)^{-1}$ due to the relaxation processes. However, there is a decrease in the value of $M'$ with increasing temperature, suggesting that the conduction in present glass ceramic system may be due to the short range mobility of charge carriers.

Fig. 4.8 depicts the imaginary part of the electric modulus ($M''$) as a function of frequency at various temperatures. The plot is found to be exhibiting the characteristic peaks (at $f_{\text{max}}$) centered at the dispersion region of the real part of electric modulus ($M'$). The presence of these peaks in the modulus spectra is a clear indication of the conductivity relaxation processes, also, the relaxation peak tend to be shifted towards higher frequencies with increasing temperature, suggesting the temperature dependent relaxation process in presently studied glass ceramic system. This temperature dependent behavior can be explained on the basis that with an increase in temperature, the charge carriers get thermally activated and they acquire a rapid movement which leads to a decrease in the relaxation time and hence increases the relaxation frequency. This results in the shifting of relaxation peaks towards higher frequency with an increasing temperature. Fig. 4.8 describes two relaxation regions: the frequency region below this relaxation peak is associated with the hopping conduction due to mobile charge carriers over long distances whereas the region above this peak corresponds to the short range / localized motion of charge carriers as they are spatially confined to the potential wells. Thus, the peak frequency ($f_{\text{max}}$) is suggestive of the transition from long range to short range mobility of charge carriers (Vaish and Varma 2009; Kaur et al. 2013).
**Figure 4.7:** Frequency dependence of real part ($M'$) of electric modulus at various temperatures for $x = 10$ sample.

**Figure 4.8:** Frequency dependence of imaginary part ($M''$) of electric modulus at various temperatures for $x = 10$ sample.
$M^*$ could be expressed as Fourier transform of a relaxation function $\phi(t)$ (Macedo et al. 1972)

$$M^* = \frac{1}{\varepsilon_\infty} \left[ 1 - \int_0^\infty \exp(-\omega t) \left( \frac{d\phi}{dt} \right) dt \right] \tag{4.3}$$

where $\varepsilon_\infty$ is the high-frequency asymptotic value of the real part of the dielectric constant and the function $\phi(t)$ is the time evolution of the electric field within the materials, known as Kohlrausch-Williams-Watts (KWW) function and is given by (Kohlrausch 1854; Williams and Watts 1970)

$$\phi(t) = \exp \left[ -\left( \frac{t}{\tau_m} \right)^\beta \right] \quad 0 < \beta < 1 \tag{4.4}$$

where $\tau_m$ is the conductivity relaxation time. The exponent $\beta$ is the Kohlrausch stretched coefficient, which indicates the deviation from Debye type relaxation. The value of $\beta$ varies between 0 and 1. For ideal Debye type relaxation $\beta = 1$. Value of $\beta$ could be estimated by fitting of the experimental data in the above equations. The electric modulus behavior of presently studied glass ceramic samples has been rationalized by invoking the modified KWW function suggested by Bergman (2000). Accordingly, the imaginary part of electric modulus can be defined as

$$M'' = \frac{M''_{\text{max}}}{(1-\beta)+\frac{\beta}{1+\beta} \left[ \frac{\omega_{\text{max}}}{\omega} \right]^\beta} \tag{4.5}$$

where $M''_{\text{max}}$ is the maximum value of $M''$, $\omega_{\text{max}}$ is the corresponding maximum angular frequency and $\beta$ is the KWW parameter. The experimental data of $M''$ has been fitted theoretically using eqn. 5 and is depicted in Fig. 4.8. From the figure, it is clearly seen that the experimental data is well fitted to this model. Values of $\beta$ so obtained by fitting the frequency plots of $M''$ have been found to lie between 0.43-0.56. The values of $\beta$ obtained for the three studied compositions have been tabulated in Table 4.2.
Activation energy associated with the relaxation process has been determined from the temperature dependent relaxation frequency, which according to Arrhenius law is given by

\[ f_m = f_0 \exp \left( -\frac{E_R}{kT} \right) \quad (4.6) \]

where \( f_0 \) is a pre-exponential factor, \( E_R \) is the activation energy related to the relaxation process, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature in Kelvin.

Fig. 4.9 illustrates the plot of \( \ln(f_m) \) vs. \( 1000/T \), where solid lines are the best fits to the above equation. The values of activation energy (\( E_R \)) computed from above plot are given in Table 4.2.

**Figure 4.9:** Arrhenius plot of relaxation frequency for different compositions of studied glass-ceramic samples.

The scaling behavior of \( M'' \) has been analyzed so as to have a deeper understanding of the relaxation dynamics. Fig. 4.10 depicts the normalized plot of \( M'' \) for \( x = 10 \) composition at different temperatures, where the frequency axis has been scaled by peak frequency (\( f_{max} \)) and the \( M'' \) axis has been scaled by \( M''_{max} \). The perfect overlapping of all the curves into a single master curve indicates that the relaxation
Characterization of $(70\% \text{B}_2\text{O}_3-29\% \text{Li}_2\text{O}-1\% \text{Dy}_2\text{O}_3)_{-x} \text{B}_7\text{T}$ Glass-Ceramics

**Figure 4.10:** Normalized plots for the imaginary part ($M''$) of electric modulus for $x = 10$ glass ceramic sample at different temperatures.

**Figure 4.11:** Normalized plot for the imaginary part ($M''$) of electric modulus for the samples with $x = 0, 10$ and 20 at 523 K. Inset shows the frequency dependence of $M''$ for different compositions at a particular temperature.

process occurring at different frequencies has same thermal activation energy. Fig. 4.11 shows the modulus spectra of all the three samples scaled at 523 K and it shows a deviation from the single master curve indicating that in the presently studied system the relaxation process is composition dependent.

4.3.6 ac Conductivity Formalism

Fig. 4.12 depicts the frequency dependence of real part of the conductivity measured at selected temperatures for the sample with \( x = 10 \). Frequency dependent conductivity is found to be comprised of two regions: i) the plateau region, dominant in low frequency region and it is almost frequency independent. This region corresponds to the direct current (dc) part of conductivity. ii) the dispersion region, observed at higher frequencies. This region is strongly dependent on frequency and increases linearly with frequency. From the conductivity plot it is clearly observed that the width of dc part (the plateau region) increases with an increase in temperature and shifts towards higher frequency. This frequency dependent behavior of the conductivity is suggestive of the hopping conduction at high frequency between localized sites to another (Pike 1972).

Phenomenon of conductivity dispersion is analyzed using Jonscher’ power law (Jonscher 1999)

\[
\sigma_{ac} = \sigma_{dc} + A\omega^n
\]  

(4.7)

where \( \sigma_{ac} \) and \( \sigma_{dc} \) represent the \( ac \) and \( dc \) conductivities of the sample at given temperature, \( A \) is the temperature dependent parameter and \( n \) is known as the power law exponent and its value varies between 0 and 1 depending upon temperature.

The exponent \( n \) represents the degree of interaction between the mobile ions (with decreasing \( n \), interaction between mobile ions and lattice is expected to increase; \( n = 1 \) represents non-interacting Debye system) (Majhi and Varma 2010). The presently studied glass ceramic samples have been found to obey the above mentioned universal power law at all the temperatures and frequencies.
Figure 4.12: Frequency dependence of the electrical conductivity for $x = 10$ sample.

The theoretically fitted lines of eqn. (4.7) to the experimental data are depicted in Fig. 4.12 (solid lines). The values of exponent $n$ as obtained from the fitting of experimental data with eqn. (4.7) have been found to lie between 0.37-0.59 and are given in Table 4.2 for the three glass ceramic samples. It is well known that the conductivity mechanism in any material could be understood from the temperature dependent behavior of $n$. To ascertain the electrical conduction mechanism in the materials, various models such as quantum mechanical tunneling (QMT) model, the overlapping large-polaron tunneling (OLPT) model, and the correlated barrier hopping (CBH) model have been proposed, based on the variation of frequency exponent with temperature and frequency (Punia et al. 2012; Austin and Mott 1969; Elliot 1977; Elliot 1978; Elliot 1987; Mott and Davis 1979; Long 1982; Ghosh 1990; Ghosh et al. 2014). The temperature variation of exponent $n$ correlates the ac conductivity mechanism as discussed below (Dhankhar et al. 2015; Vaish and Varma 2009):

1. The conduction mechanism can be explained by the quantum mechanical tunneling model if the exponent $n$ depends upon frequency but is temperature independent.

2. If $n$ increases with an increase in the temperature, then the conduction process can be explained with the small polaron quantum mechanical tunneling theory.
Figure 4.13: Temperature dependence of \( n \) for different compositions of \((70B_2O_3-29Li_2O-1Dy_2O_3)-xBT\) glass ceramic samples. Inset shows the frequency dependence of the electrical conductivity for three different compositions of studied glass ceramic samples at 523 K.

Figure 4.14: Arrhenius plot of dc conductivity for three different compositions of \((70B_2O_3-29Li_2O-1Dy_2O_3)-xBT\) glass ceramic samples.
Howsoever, is $n$ decreases at first, reaching at minimum and increases thereafter with increase in temperature then it can be explained by large polaron quantum mechanical tunneling model.

3. If the exponent $n$ decreases with temperature then the conduction mechanism can be explained by the correlated barrier hopping (CBH) model.

The values of exponent $n$ obtained for the glass ceramics with $x = 10$ and $x = 20$ (shown in Fig. 4.13) at first decrease with temperature, attains a minima and then increases thereafter with temperature. Such behavior of $n$ is found to be consistent with overlapping large polarons tunneling (OLPT), suggesting that the conduction mechanism in these samples could be analyzed by OLPT model (Szreder et al. 2014; Dhankhar 2015). But for sample $x = 0$, temperature independent behavior is observed. Inset of Fig. 4.13 clearly shows that ac conductivity of the present samples increases with an increase in the temperature.

The activation energy for dc conductivity has been calculated from the plot of $\ln(\sigma_{dc})$ vs. $1000/T$ (Fig. 4.14). The plot has been found to be linear and fitted using the following Arrhenius equation:

$$\sigma_{dc}(T) = B \exp\left(\frac{-E_{dc}}{kT}\right)$$  \hspace{1cm} (4.8)

where $B$ is pre exponential factor and $E_{dc}$ is the activation energy for dc conduction.

**TABLE 4.2:** Activation energy ($E_R$) determined from the relaxation process, stretched exponent ($\beta$), the activation energy ($E_{dc}$) determined from dc conductivity and power law exponent ($n$) for glass ceramics with composition $(70\%B_2O_3-29\%Li_2O-1\%Dy_2O_3-x\%BT)$; $x = 0$, 10 and 20.

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</tbody>
</table>
Activation energy \((E_{dc})\) for the given samples have been estimated from the slope of the fitted line and are depicted in Table 4.2. This value shows a decreasing trend in the activation energy values and this indicates an increased conductivity. This behavior can be associated with the increase in the number of NBO’s in the presently studied system. As, is clear from the FTIR also that addition of BT into the glass matrix leads to the production of more NBO’s during the crystallization process. These NBO’s in turn facilitates the easy movement of cation in the glass network. Perusal of data in Table 4.2 shows a close agreement in the values of activation energy \((E_{dc})\) associated with conduction process and that associated with the relaxation process \((E_R)\). Thus, suggesting the involvement of similar type of charge carriers in both the relaxation and conduction processes.

### 4.4 Conclusions

The glass ceramics were prepared by heat treating the glass samples at 585 °C temperature for 18 h. XRD patterns recorded for the samples revealed the presence of tetragonal \(\text{Li}_2\text{B}_4\text{O}_7\) phase and monoclinic \(\text{Ba}_2\text{Ti}_6\text{O}_{13}\) phase. Analysis of FTIR and Raman spectra confirmed the presence of various structural units like \(\text{BO}_3\), \(\text{BO}_4\), \(\text{TiO}_4\), \(\text{TiO}_6\) along with the vibrations of \(\text{Li}^+\) and \(\text{Ba}^{2+}\) cations. The imaginary part of the electric modulus has been fitted to KWW function and the values of \(\beta\) have been found to lie between 0.43-0.56 suggesting the presence of non Debye relaxation in the presently studied system. The perfect overlapping of the \(M''\) curves into a single master curve suggested the temperature independence of the relaxation dynamics. Electrical transport properties investigated for the prepared samples have been found to obey Jonscher’s universal law. The behavior of exponent \(n\) for \(x = 10\) and \(x = 20\) suggested that the conduction mechanism in these samples more or less follows OLPT model. The activation energy associated with the dc conductivity and that with the relaxation process are found to be in close agreement with each other which leads us to conclude that the charge carriers in the present system are to cross the similar charge barriers in both the processes.