CHAPTER-7

OVERALL CONCLUSIONS AND FUTURE PROSPECTS

This chapter summarizes the work carried out in this thesis and presents the important findings along with future scope of the work.

7.1 Conclusions

In this thesis the structural, thermal and optical properties of borate glasses and glass ceramics modified with barium titanate have been studied. Dielectric relaxation spectroscopy of \((70\text{B}_2\text{O}_3\text{-29Li}_2\text{O}\text{-1Dy}_2\text{O}_3-x\text{BT})\) glass and glass ceramics has also been studied in the framework of dielectric permittivity, electric modulus and ac conductivity formalisms. The entire experimental observations and discussion done in chapters 3 to 6, lead to the following conclusions:

The glass samples with composition \((70\text{B}_2\text{O}_3\text{-29Li}_2\text{O}\text{-1Dy}_2\text{O}_3-x\text{BT})\); \(x = 0, 5, 10, 15 \) and 20 weight percent, were subjected to XRD, DSC, FTIR, Raman and UV-Vis spectroscopic studies. The results of these studies were found to be in good correlation with each other. XRD patterns revealed the glassy nature of the samples. The analysis of DSC curves showed an increase in glass transition temperature \((T_g)\) with increasing BT content which can be due to the increasing number of strongly bonded BO\(_4\) units upon addition of BT. The thermal stability of the glass samples is also found to be enhanced with the introduction of BT into the glass matrix. The transformation of BO\(_3\)→BO\(_4\) units with an increase in the concentration of BT is concluded from the FTIR and Raman spectroscopy studies, suggesting the modifier role of barium titanate in the glass network. Since, BO\(_4\) units are more dense and rigid, hence they provide stability to the system. The direct and indirect optical band gap energies have been calculated from Tauc’s plots. The calculated values of indirect band gap energies have been found to lie in the range 4.38-3.56 eV and that of direct band gap energies lie between 4.45-3.71 eV. The observed decrease in the values of these energies could be related to the compaction of glass network due to the formation of four coordinated BO\(_4\) units. The dielectric permittivity of the samples has been found to increase with an increase in the
temperature and BT content. Non exponential Kohlrausch-Williams-Watts (KWW) function has been invoked to fit the experimental data of the imaginary part of the electric modulus (M''). The values of stretched exponent (β) obtained from the fitting data have been found to lie between 0.48-0.52, suggesting the presence of non-Debye type relaxation processes in the studied glass system. Scaling of M'' plots resulted in perfect overlap of M'' curves into a single master curve signifying temperature independence of the relaxation dynamics. The frequency dependent ac conductivity has been analyzed using Jonscher’s universal power law. The decrease in values of power exponent n with an increase in temperature further suggested that the ac conduction mechanism of the studied samples follows the correlated barrier hopping (CBH) model. Values of activation energy determined from electric modulus (E_R) and that from dc conductivity (E_{dc}) have been found to be quite close to each other suggesting that the same type of charge carriers are involved in the relaxation and the conduction mechanisms.

The glass ceramics with composition (70B_2O_3-29Li_2O-1Dy_2O_3)-xBT were prepared by heat treating their corresponding glass samples at 585 °C temperature for 18 h. XRD patterns recorded for the samples showed sharp peaks confirming the crystalline nature of these samples. Its analysis revealed the presence of tetragonal Li_2B_4O_7 and monoclinic Ba_2Ti_6O_13 phases in the studied samples. The analysis of FTIR and Raman spectra of prepared glass-ceramics showed the presence of various structural units like BO_3, BO_4, TiO_4, TiO_6 etc. along with the vibrations of Li^+ and Ba^{2+} ions. Also, it is found that the TiO_4 tetrahedrons enter the glass network and alternate with borate structural units forming B-O-Ti linkages. FTIR spectra of these samples depicted an increment in the number of BO_3 structural units along with the nonbridging oxygens (NBO’s) in the presently studied system. The dielectric measurements carried out on these samples, as a function of temperature, in frequency range 1 Hz-10^6 Hz, showed an increase in real (ε') and imaginary (ε'') parts of dielectric constants, both, with increasing temperature and BT content. Experimental data of imaginary part of the electric modulus has been fitted to nonexponential Kohlrausch-Williams-Watts (KWW) function and the values of β obtained from the fitting 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 all the curves into a single master curve indicated that the relaxation processes occurring at different frequencies has same thermal activation energy. ac conductivity has been analyzed using Jonscher’s universal power law. The behavior of exponent $n$ for $x = 10$ and $x = 20$ suggested that the conduction mechanism in these samples more or less follows overlapping large polaron tunneling (OLPT) model. A close agreement in the values of activation energy determined from electric modulus ($E_r$) and dc conductivity ($E_{dc}$) indicated the involvement of similar type of charge carriers in both relaxation and conduction processes. The observed decrease in the activation energy could be associated with the increasing number of NBO’s (as depicted from FTIR) which in turn facilitates the easy movement of cation in the glass network.

Glass samples with composition $(70B_2O_3-29Bi_2O_3-1Dy_2O_3)\times$BT, where BT is added in different successive weight percent, have been synthesized by conventional melt quenching technique. The X-ray diffraction studies confirmed the amorphous nature of these samples. Detailed analysis of FTIR and Raman spectra of the samples depicted that the glass network to be built up of mainly BiO$_6$, BiO$_3$, BO$_3$ and BO$_4$ units. Bi$_2$O$_3$ has been found to exist as BiO$_6$ octahedral and BiO$_3$ pyramidal units in all the glass network except for $x = 0$ glass sample where it existed only as BiO$_6$ octahedral units, thus, suggesting the modifier role of BT in the glass network. Introduction of BT into the glass matrix also found to lead to the conversion of BO$_3$ trigonal units into BO$_4$ tetrahedral units, which resulted in a decrease in the degree of disorder in the glass network and made the glass system more stable. The optical absorption measurements carried out for well-polished samples showed a decrease in optical band gap energy with an increase in BT content, which could be related to the compaction of the borate network due to the formation of four coordinated BO$_4$ units. The calculated values for the indirect and direct transitions were found to lie between 3.20-2.82 eV and 3.39-3.07 eV respectively.

Glass-ceramics with composition $(70B_2O_3-29Bi_2O_3-1Dy_2O_3)\times$BT were obtained by subjecting the glasses with same composition to a suitable heat treatment at 570°C for 24 h. X-ray diffraction studies revealed that the heat treated glasses gave rise to a
crystalline phase of $\text{Ba}_2\text{Ti}_6\text{O}_{13}$ embedded in the host glass matrix. FTIR and Raman study showed that the glass ceramic network consists of $\text{BiO}_3$, $\text{BiO}_6$, $\text{BO}_3$ and $\text{BO}_4$ units. From the analysis of FTIR spectra it is also observed that the increasing BT content in the glass ceramic samples favors the formation of $\text{BO}_4$ and $\text{BiO}_6$ units. Thus, it is concluded that barium titanate acts as a structural modifier in the studied glass ceramics. Also, it is observed that the introduction of BT into the glass matrix and the crystallization process, leads to the breakage of B-O-B linkages and results in B-O-Ti bond formation. The optical absorption measurements carried out on the well-polished samples show a decrease in the optical band gap energy with an increase in BT content and the values were found to lie in the range 3.18-2.68 eV and 3.30-2.70 eV for indirect and direct band gap energies respectively.

7.2 Future Prospects

1. The temperature dependence of dielectric properties of (70$\text{B}_2\text{O}_3$-29$\text{Bi}_2\text{O}_3$-1$\text{Dy}_2\text{O}_3$)-$x$BT glasses and glass-ceramics can be studied to understand their relaxation dynamics and conduction mechanism.

2. The prepared samples can further be heat treated at different temperatures, above their glass transition temperature ($T_g$), in order to see the effect of grain size on their various properties, as, the heat treatment processes are considered to have a significant influence on the amount and size of nano/micro crystallites formed.

3. In order to have an insight of the microstructural properties such as morphology, grain size etc. of the glass ceramics, microscopy techniques such as Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) can be used.

4. In recent years, there has been an increasing interest in materials having high optical nonlinearity because of their important applications in fabricating the optical devices including optical switching, optical modulation, optical computing, optical storage and devices for advanced telecommunication system. The knowledge of nonlinear optical properties of the materials is quite important.
Overall Conclusions and Future Prospects

to assess their capability for the development of optical devices. Keeping this in view, nonlinear optical properties of these samples can also be studied.

5. Since, presently studied samples didn’t show any ferroelectric behavior which could be due to low BT content. New samples with increased BT content can be fabricated to enhance their polarization and hence to find ferroelectricity.