Optical absorption and FTIR studies of Cu$^{2+}$ ion doped in 25Li$_2$O-15BaO-(60-x) B$_2$O$_3$ glasses

Ashok Bhogi,*a R. Vijaya Kumar,b and P. Kistaiah,c

*aVNR Vignana Jyothi Institute of Engineering and Technology, Hyderabad, Telangana, India
bSchool of Physics, University of Hyderabad, Hyderabad, Telangana, India
cDepartment of Physics, Osmania University, Hyderabad, Telangana, India

E-mail: ashokbhogi82@gmail.com

Abstract. Glasses with composition 25Li$_2$O-15BaO-(60-x) B$_2$O$_3$: x CuO (where x=0, 0.2, 0.4, 0.6, 0.8 and 1 mol %) were prepared using the conventional melt quench technique. The optical absorption spectra of studied glass samples show only one absorption band which is attributed to the $2B_{1g} \rightarrow 2B_{2g}$ characteristic transition of Cu$^{2+}$ ions in the distorted octahedral sites. The cut-off wavelength ($\lambda_c$), optical band gap ($E_{opt}$) and Urbach energy ($\Delta E$) were determined. The FTIR studies show different stretching and bending vibrations of alkaline earth lithium borate glasses. The relative variations in the intensities of BO$_3$ and BO$_4$ units in IR spectra with the concentration of CuO indicate that the copper ions mostly occupy modifying positions in the glass network when the concentration of CuO $\leq$ 0.8mol%.

1. Introduction

Oxide glasses incorporated with transition metal ions have attracted a great deal of attention, because of their potential applications as lasers, photo-conducting devices, magnetic materials, especially for tunable solid state lasers, efficient phosphors etc. [1]. Among the oxide glasses, borate glasses have attractive considerable scientific interest because of their potential applications such as electro-optic switches, electro-optic modulators, solid state laser material and non-linear optical parametric converters. In addition, they are often used as dielectric and insulating materials and it is known that borate glass constitutes a good shield against IR radiation [2]. Incorporation of Alkaline earth cations in the structure of these glasses are responsible for decrease of expansion coefficient, the glass transition temperature increases, strengthen the glass structure and may raise the chemical resistance of the glass [3]. The alkaline earths have been added to borate glasses were found to be good stabilizers of borate glasses. Copper oxide is used as a significant colorant in glasses for optical applications, Copper ions exist in various valence state in glass matrix such as monovalent Cu$^{1+}$ and divalent Cu$^{2+}$ and that it can also represent as CuO$_4$ and CuO$_6$ in the glass network. The co-existence of copper ions in more than one valance state i.e., Cu$^{2+}$ and Cu$^{1+}$ is a general condition for semiconducting and super paramagnetic behavior of borate glasses [4].

The fact that the addition of copper ions in glass matrix helps to bring significant changes in its structural, magnetic, electric, thermal and optical behavior, a careful optical and structural survey of glasses doped with CuO becomes quite. The present work is taken up with an objective to characterize the glass system with higher B$_2$O$_3$ content and constant BaO concentration by means of Optical absorption and Infrared studies and to understand the structural details of the Li$_2$O-BaO-B$_2$O$_3$ glasses containing copper ions.
2. Experimental

A series of glass samples with chemical formula 25Li$_2$O-15BaO-(60-x)B$_2$O$_3$:xCuO (where x = 0, 0.2, 0.4, 0.6, 0.8 and 1 mol%) have been prepared using conventional melt quenching technique. The requisite mixture of pure reagent grade chemicals, i.e. BaCO$_3$, Li$_2$CO$_3$, H$_3$BO$_3$ and CuO is grinded to obtain a fine powder and is melted in a porcelain crucible at a temperature of 1050°C for 2h and stirred frequently to ensure homogeneity. Then the melt is quenched by pouring on to a steel mould plate maintained at 200°C and pressing immediately with another steel plate in air. The prepared glasses were immediately transferred to another furnace maintained at 300°C for 3 hours, for annealing to obtain strain free glasses.

3. Results and discussion

Optical absorption

The optical absorption spectrum of prepared glass system in the wavelength region 300-1000 nm is shown in Fig. 1. LBBC0 pure glass sample has not shown any peak in the observed region and introduction of Cu$^{2+}$ ions into glass matrix a single broad absorption band has been observed at around 764 nm which is due to the characteristic transition of $2B_{1g} \rightarrow 2B_{2g}$ in a distorted octahedral site. Further increase of CuO concentration the broadness and intensity of the characteristic band of Cu$^{2+}$ ions has been increased up to 0.8 mol% and beyond this concentration the intensity of the characteristic band is found to decrease.

The non-sharp edge in the absorption spectra of these glass samples gives a clear indication of the amorphous nature of the prepared samples. The main feature of absorption edge of the amorphous materials at the lower values of absorption co-efficient is an exponential behavior of the absorption coefficient $a(\nu)$ with the photon energy $h\nu$ as shown in figure 3 and it usually follows the Urbach rule [5].

$$a(\nu)=C\exp(h\nu/\Delta E)$$

where $C$ is a constant and $\Delta E$ is measure of the band tailing and is also known as Urbach energy.

The absorption co-efficient $a(\nu)$ near the fundamental absorption edge can be determined at different wavelengths by using the formula

$$a(\nu)=(1/d)\ln(I_0/I)$$

where $A$ is absorbance at frequency $\nu$ and $d$ is the thickness of the sample.

For the amorphous materials, the variation of absorption coefficient $a(\nu)$ with photon energy $h\nu$ was given by the equation [3]

$$a(\nu)=[B(h\nu-E_{opt})^n]/[h\nu]$$

where $B$ is an energy independent constant and $n$ is an index.

According to Tauc’s relation, for most of the amorphous materials indirect transitions ($n=2$) are valid [6]. The values of indirect optical band gap energy $E_{opt}$ can be measured from the linear regions of the curves by extrapolating them to meet the hv axis at $(ahv)^{1/2}$=0 as shown in figure 2. From the plots $(ahv)^{1/2}$ vs $h\nu$, the slopes are calculated. The optical band gaps values obtained in the present work are given in Table 1. From Table 1, it has been observed that the absorption edge observed at 378 nm for LBBC0 (pure glass) is observed to shift slightly towards higher wavelength with increase in the concentration of CuO up to 0.8 mol% and beyond this concentration the edge is shifted towards lower wavelength. The value of $E_{opt}$ is found to decrease with the increase in concentration of CuO up to 0.8mol%. Beyond this concentration the value is however observed to increase.
When the concentration of CuO is increased beyond 0.8 mol%, a gradual decrease in the intensity of optical absorption band has been observed. This observation indicates a gradual decrease in the concentration of Cu$^{2+}$ ions that take modifying positions in the glass network. The lower concentration of modifying Cu$^{2+}$ ions, the lower is the concentration of NBO’s in the glass matrix. This leads to decrease in the degree of localization of electrons thereby decreasing the donor centers in the glass matrix. The presence of smaller concentration of these donor centers increases the optical band gap and shifts the absorption edge towards the lower wavelength side as observed for the glass LBBC10 [7].

**FTIR**

The FTIR is used to study the local structural modes in inorganic glassy materials. FTIR spectra in the glasses provide significant information of various bonds present between different ions in the glass network and these are identified by comparing the experimental data of glasses with those
of crystalline compounds. Fig. 4 shows the FTIR spectra of Cu$^{2+}$ ion doped in 25Li$_2$O-15BaO-(60-x) B$_2$O$_3$ glasses in the wavenumber region 400-1600 cm$^{-1}$ at room temperature. The addition of alkaline earth oxides (BaO) to the borate glass network is accompanied by a change in the co-ordination number from 3 to 4. The vibrational peak around ~460 cm$^{-1}$ is assigned to the angles modification of B-O-B linkages / specific vibrations of Ba-O bonds [8]. The position of this peak is observed to shift towards the higher frequencies up to 0.8 mol% of CuO and after that is found to shift towards the lower frequencies. Another absorption band around ~704 cm$^{-1}$ is assigned to the B-O-B bending vibrations. This band is found to shift towards the lower frequency up to 0.8 mol% of CuO and beyond this concentration it is found to shift towards the higher frequency. The absorption band around ~775 cm$^{-1}$ is due to the O$_2$B-O-BO$_4$ bending vibrations. The position of this band is remained in the same position. The intensity of this peak is observed to increase with increase in the concentration of CuO up to 0.8 mol% and later it is found to decrease. An absorption band around ~873 cm$^{-1}$ is present in all the prepared glass samples and is assigned to the stretching vibrations of B-O bonds in BO$_4$ units from diborate groups. The position of this peak is moved towards the higher frequencies till 0.8 mol% of CuO and later it is moved towards the lower frequencies. The absorption band around ~1010 cm$^{-1}$ which is attributed to the B-O symmetric stretching vibrations of BO$_4$ units. The area of this band is found to decrease up to 0.8 mol% of CuO and later it is found to increase. This band is observed to shift towards the higher frequencies up to x=0.8 mol% and later it is observed to shift towards the lower frequencies. The absorption band around ~1364 cm$^{-1}$ is present in all the prepared glass samples and is attributed to the asymmetric stretching vibrations of the B-O of triangle (BO$_3$)$_3^-$ units in meta-, pyro- and ortho-borate units. The intensity of this peak is observed to increase with increase in the concentration of CuO up to 0.8 mol% and later it is found to decrease. The another absorption band around ~1390 cm$^{-1}$ is attributed to the B-O stretch in BO$_3$O units from varied types of borate groups.

**Figure 4.** FTIR spectra of LBBC series glass system.

| Glass Composition | X=0 LBBC0 | X=0.2 LBBC2 | X=0 LBBC4 | X=0 LBBC6 | X=0 LBBC8 | X=0 LBBC10 |
|-------------------|-----------|-------------|-----------|-----------|-----------|------------|
| Cut-off wavelength(nm) | 378 | 385 | 391 | 397 | 407 | 404 |
| Indirect Optical bandgap(eV) | 3.324 | 3.225 | 3.203 | 3.141 | 3.101 | 3.163 |
| Urbach energy(ΔE) | 0.560 | 0.539 | 0.496 | 0.406 | 0.384 | 0.421 |

**Table 1.** Optical parameters of LBBC glass system.
4. Conclusion

The optical absorption studies of these glasses indicate the presence of copper ions mostly in tetragonally distorted octahedral positions. The FTIR study shows that the glass network consists of BO$_3$ and BO$_4$ units.

Acknowledgments

One of the authors Ashok Bhogi thanks the management of VNR Vignana Jyothi Institute of Engineering and Technology, Hyderabad for their constant encouragement and support.

References

1. N. J. Kreidl, J. Non-Cryst. Solids 123 (1990) 377.
2. R. P. S. Chakradhar, A. Murali, J.L. Rao, J. Alloys and Compd. 265 (1998) 121.
3. H.F. Shermer, J. Res. Nat. Bur. Stand. (US) 56 (2) (1956) 73.
4. Ashok Bhogi, R. Vijaya Kumar, P. Kistaiah, J. Non-Cryst. Solids 426 (2015) 47-54.
5. F. Urbach, Phys.Rev. 92(1953) 1324.
6. J. Tauc, Amorphous and Liquid Semiconductors, Plenum Press, New York 1974.
7. G. Naga Raju, M. Srinivasa Reddy, N. Veeraiah, Opt. Mater. 29 (2007) 1467-1474.
8. G.E. Walrafen, S.R. Samanta, P.N. Krishnan, J. Phys. Chem. 72 (1980) 113.