Optical Properties of LiF–Li₂O –WO₃–B₂O₃ Glasses

M. Srinivasa Reddy^{1*}, S. Shankaraiah²

¹Department of Physics, Anurag Group of institutions, Hyderabad, Telangana, India

²Department of Chemistry, Anurag Group of institutions, Hyderabad, Telangana, India

*Corresponding author e-mail : msreddy@gmail.com

ABSTRACT

Article Info

Volume 7, Issue 6

Page Number: 344-348

Publication Issue :

November-December-2020

Article History

Submission : 02 Feb 2020

Accepted : 02 Nov 2020

Published : 10 Dec 2020

Glass with compositions $x\text{LiF}-(30-x)\text{Li}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ for $5 \leq x \leq 25$ mol% have been prepared using the normal melt quenching technique. The optical absorption and reflection spectra were recorded at room temperature in the wavelength range 300-800 nm. From the absorption edge studies, the values of the optical band gap (E_{opt}) and Urbach energy (ΔE) have been evaluated. The values of E_{opt} and ΔE vary non-linearly with composition parameter, showing the mixed alkali effect.

Keywords: Borate Glass, Mixed Alkali Effect, Optical Absorption, Band Gap Energy, Urbach Energy

I. INTRODUCTION

Glasses obtained from a variety of non-linear materials are widely used for multi-facets applications in modern technology due to their unusual optical properties. A glass exhibits non-linear variation in its properties which include density, viscosity, glass transition temperature and conductivity when one alkali component in a multi component glass is systematically replaced by another alkali species. This phenomenon is referred to as the mixed alkali effect (MAE) and is useful in manufacturing low loss electrical glass. Models for MAE have been proposed in the literature and compiled in several reviews . Recently, Sivakumar reported a new defect model for the mixed alkali effect[1-3].

Transition metal ion containing glasses is the subject of a great deal due to their important non-linear

optical absorption and electrical properties for technological applications. Tungsten ion containing glasses are the subject of a great deal due to their important non-linear optical absorption and electrical properties for technological applications [4]. Tungsten ions are predicted to have reflective influence on physical properties of compounds. In oxide glasses, tungsten ions are generally assumed to attain multiple oxidation states, such as hexavalent W^{6+} , pentavalent W^{5+} and also tetravalent W^{4+} , regardless of the oxidation state of the tungsten ion in the starting glass batch . W^{6+} ions participate in the glass network with different structural units, like WO_4 (T_d) and WO_6 (O_h) structural units and W^{5+} ions participate in the form of $\text{W}^{5+}\text{O}_3^-$, and occupy octahedral positions. Thus the concentration of different structural groups of tungsten ions with different oxidation states present in the glass matrix at a given temperature depends on the quantitative

properties of modifiers, glass formers, size of ions in the glass structure, mobility of the modifier cation etc. W^{5+} ions are well known paramagnetic ions. The presence of tungsten in borate glasses, further, makes these glasses suitable for optoelectronic devices since they exhibit photochromism, electrochromism and thermochromism properties, which are known for provoking a color change due to the action of electromagnetic radiation, electric field, and heat respectively. These glasses have several advantages over crystalline counterparts, such as easy formability over wide ranges of composition, isotropicity, absence of grain boundaries and ease of fabrication in complex shapes, which make them particularly attractive in practical applications [5].

Many investigations have been reported on ternary alkali tungsten in phosphate, borate, tellurite, bismuthate and niobate glasses. Recently, Samee *et al* presented physical, structural, optical and dielectric properties of tungsten based germanate glasses. More recently, Edukondalu *et al* studied and correlated the physical, optical and structural properties of transition metal ions doped WO_3 - Li_2O - Na_2O - B_2O_3 glasses. To the best of our knowledge, there are no reports on optical absorption studies of mixed alkali borate tungsten glasses[6,7].

The present investigation is a part of an ongoing program to study the MAE in lithium potassium tungsten borate glasses. Therefore, in this work we have concentrated on the influence of mixed alkalis on optical studies of $xLiF-(30-x)Li_2O-10WO_3-60B_2O_3$ ($5 \leq x \leq 25$ mol%) glasses. The optical properties of the glasses have also been determined with respect to glass compositional parameter R_{Li} defined as $R_{Li} = Li_2O \text{ (mol\%)} / (Li_2O + LiF) \text{ (mol\%)}$.

II. EXPERIMENTAL

In the present study, the glass, samples of composition $xLiF-(30-x) Li_2O-10WO_3-60B_2O_3$ ($x = 5, 10, 15, 20$ and 25 mol%) were prepared by melt quench technique. High purity (99.99%) Li_2CO_3 , LiF , H_3BO_3 and WO_3 (all Sigma Aldrich) were used as starting materials. A batch of 15gms of the above high purity chemicals in powder form was weighed, well mixed and melted in a porcelain crucible in the temperature range of $850-900^\circ C$ depending on the glass composition in an electrical muffle furnace for about 60 minutes. The melt was swirled frequently to insure the homogeneity. The melt was then quenched in between a couple of brass plates, pre-heated around $200^\circ C$. Later, the samples were annealed below their respective glass transition temperature for about 24 hours and slowly cooling them to laboratory temperature.

The room temperature optical absorption spectra of the polished glass samples were recorded using JASCO V670 spectrometer in the wavelength region 200-1000 nm.

III. RESULTS AND DISCUSSIONS

The Study of The Fundamental absorption edge in the UV region is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and the energy gap in both crystalline and non-crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed.

The room temperature optical absorption spectra of $(30-x) Li_2O-xLiF-10WO_3-60B_2O_3$ glass system is shown in Fig. 1. The non-sharp absorption edges in figure give a clear indication of the amorphous nature of the glasses. The UV absorption edge or the cut-off

wavelength of all glasses in the present study were determined and are presented in Table 1. The variation of the cut-off wavelength as a function of compositional parameter in the present glass system. It is reported that the fundamental absorption edge shifts towards longer wavelengths in single alkali borate glasses with an increase in alkali content^{33, 34}. In the present mixed alkali glasses, from the above it is clear that the cut-off wavelength varies non-linearly when Li₂O is replaced with LiF. This non-linear variation in cut-off wavelength is a consequence of mixed alkali effect.

Figure 1. The room temperature optical absorption spectra of (30-x) Li₂O-xLiF-10WO₃-60B₂O₃ glass system

The optical absorption co-efficient $\alpha(\nu)$, near the fundamental absorption edge was determined from the relation

$$\alpha(\nu) = (1/d) \ln(I_0/I_t) = 2.303A/d \quad (1)$$

where I_0 and I_t are the intensities of the incident and transmitted beam, respectively, and d is the thickness of the glass sample. The factor $\ln(I_0/I_t)$ corresponds to absorbance. Davis and Mott³⁵ and Tauc and Menth relate this data to the optical band gap, E_{opt} through the following general relation proposed for amorphous materials.

$$\alpha(\nu) = B (h\nu - E_{opt})^n / h\nu \quad (2)$$

where B is an energy-independent constant, $h\nu$ is incident photon energy. The index n is a constant which determines the type of the optical transitions and can have different values, namely 1/2, 2, 3/2 and 3 corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively. According to the theory of electronic structure of amorphous materials³⁷ the absorption edge in the amorphous material is in terms of indirect allowed transitions. By plotting $(\alpha h\nu)^n$ as a function of photon energy $h\nu$ (Tauc plots), one can find the optical energy band gap for all transitions. The values of optical band gap energy E_{opt} can be obtained by extrapolating the absorption co-efficient to zero absorption in the $(\alpha h\nu)^n$ against photon energy $h\nu$ as shown in Fig.3. The values of optical energy gap, E_{opt} , thus evaluated for the glass samples at different values of n are listed in Table 1. In the present glasses, the allowed indirect and direct band gap energy varies from 3.536 to 3.835 eV and 3.847 to 3.932 eV, respectively. Since the obtained values of the optical band gap (E_{opt}) are varying according to the selected value of the exponent n , one cannot really decide which value of n is better to be selected. Therefore, the Eq. 2 may be rather used only for the determination of the type of conduction mechanism, and E_{opt} it should be determined using another parameter the imaginary part of the dielectric constant, ϵ_2 by which the exact value of the exponent can be selected.

Literature on optical properties of mixed alkali glasses support the notion of defect formation in glass matrix caused by simultaneous movement of two unlike mobile ions. Agarwal et al have reported the existence of a mixed alkali effect in an optical band gap in lithium-potassium borate glasses from the existence of a minimum in the optical band gap at equimolar concentrations of alkali cations. The mixed alkali effect in indirect optical band gap energy is attributed to the formation of a large number of non-bridging oxygens (NBOs). The mixed alkali effect

in optical band gap energy was also reported by several other workers [8-10].

The main feature of the absorption edge of amorphous materials is an exponential increase of absorption coefficient $\alpha(\nu)$ with photon energy $h\nu$, which is given by the Urbach rule

$$\alpha(\nu) = C \exp(h\nu/\Delta E) \quad (3)$$

Where C is a constant, ΔE is the Urbach energy which indicates the width of the band tails of the localized states and (ν) is the frequency of the radiation. The exponential absorption tails, i.e., Urbach energy depend on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds and on average photon energies. The main factor contributing to edge broadening in crystalline materials is excitation-phonon coupling (dynamic disorder). In amorphous,

an additional broadening due to static disordered exists. The optical absorption coefficient just below the absorption edge shows the exponential variation with photon energy indicating the presence of an Urbach's tail. The values of Urbach energy (ΔE) were determined by taking the reciprocals of the slopes of the linear portion of $\ln(\alpha)$ vs $h\nu$ curves. The Urbach energy values of the present glass samples are presented in Table 1. The exponential dependence of the optical absorption coefficient with photon energy may arise from electronic transitions between the localized states. The density of these states falls off exponentially with energy, which is consistent with the theory of Tauc. However, the exponential dependence of the optical absorption coefficient of energy might arise from the random fluctuations of the internal fields associated with the structural disorder in many materials. The compositional dependence of Urbach energy ΔE is

Table 1. Optical parameters of the $x\text{LiF}-(30-x)\text{Li}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glass system.

Parameter	x=5	x=10	x=15	x=20	x=25
$\lambda_c(\text{nm})(\pm 1)$	319	317	322	308	316
Optical band gap energies (E_o) (eV) (± 0.05)					
Indirect allowed	2.757	2.825	2.748	2.814	2.717
Indirect forbidden	2.767	2.798	2.667	2.754	2.696
Direct allowed	2.856	2.968	2.837	2.932	2.848
Direct forbidden	2.976	2.992	2.829	2.898	2.851
ΔE (eV) (± 0.002)	0.219	0.221	0.216	0.220	0.227

illustrated. Urbach energy is varying non-linearly with a compositional parameter indicating the existence of a mixed alkali effect in present glasses[11-15].

IV. CONCLUSION

The following conclusions are drawn from the study of optical properties on $x\text{K}_2\text{O}-(30-x)\text{Li}_2\text{O}-10\text{WO}_3-60\text{B}_2\text{O}_3$ glasses: The non-sharp absorption edges in the

present study gives a clear indication of the amorphous nature of the glasses. The refractive index decreases with an increasing wavelength (low wavelength region) of the incident photon energy until a constant value is reached at longer wavelengths. From optical absorption edges the direct and indirect optical band gap energies and Urbach energies were evaluated and their non-linear behavior confirms the mixed alkali effect.

V. REFERENCES

- [1]. M. Purnima, Salavadi Stalin, Avula Edukondalu, M.A. Samee, Shaik Kareem Ahmmad, Syed Rahman, Chin. J. Phys. 66 (2020) 517 -526.
- [2]. B. Kalyani, Navaneetha Pujari, Avula Edukondalu, Potharaju Krishna, J. Chinna Babu, C. P. Vardhani, J. Aust. Ceram. Soc. 56 (2020) 1147–1154.
- [3]. Navaneetha Pujari, B. Kalyani, Avula Edukondalu, C. P. Vardhani, J. Phys. Chem. Solids 148(2021)109627.
- [4]. A. Edukondalu, Syed Rahman, K. Siva Kumar, D. Sreenivasu, Vib. Spectrosc. 71 (2014) 91–97.
- [5]. B. Kalyania, Navaneetha Pujari, Potharaju Krishna, J. Chinna Babu, Avula Edukondalu, C.P. Vardhani, AIP Conf. Proc. 2269 (2020) 030083.
- [6]. Salavadi Stalin, Avula Edukondalu, M.A. Samee, Shaik Kareem Ahmmad, Sair Md. Taqiullah, Syed Rahman, AIP Conf. Proc. 2269 (2020) 030102.
- [7]. M. Purnima, Avula Edukondalu, K. Siva Kumar, Syed Rahman, Mat. Res. 20(1) (2017)46-52.
- [8]. A. Edukondalu, V. Sathe, Syed Rahman, K. Siva Kumar, Physica B 438 (2014) 120–126.
- [9]. A. Edukondalu, B. Kavitha, M. A. Samee, Shaik Kareem Ahmmad, Syed Rahman, K. Siva Kumar, J. Alloys Compd. 552 (2013) 157-165.
- [10]. Avula Edukondalu, T. Sripathi, ShaikKareem Ahmmad, S Rahman, K. Sivakumar, J. Elect. Mater. 46(2) (2017) 808 – 816.
- [11]. Ch. Srinivasu, M.A. Samee, A. Edukondalu, Syed Rahman, Int. J. Mod. Phys: conf. series 22 (2013)284-291.
- [12]. A. Edukondalu, M. Purnima, Ch. Srinivasu, T. Sripathi, A.M. Awasthi, Syed Rahman, K. Siva Kumar, J. Non-Cryst. Solids 358 (2012) 2581.
- [13]. Shaik Kareem Ahmmad, M.A. Samee, A. Edukondalu, Syed Rahman Results in Physics 2 (2012) 175–181
- [14]. M.A.Samee, Shaikh Kareem Ahmmad, A.Edukondalu, Syed Rahman J. Elect. Mater. 42 (2013) 2516.
- [15]. A.Edukondalu, M.A.Samee, Shaikh Kareem Ahmmad, Sair Md. Taqiullah, International Journal of Modern Physics: conference series 22 (2013) 278-283.

Cite this article as :

M. Srinivasa Reddy, S. Shankaraiah, "Optical Properties of LiF–Li₂O –WO₃–B₂O₃ Glasses", International Journal of Scientific Research in Science and Technology (IJSRST), Online ISSN : 2395-602X, Print ISSN : 2395-6011, Volume 7 Issue 6, pp. 344-348, November-December 2020. Available at doi : <https://doi.org/10.32628/IJSRST207652>
Journal URL : <http://ijsrst.com/IJSRST207652>