Physical and optical studies on Li₂O-Na₂O-WO₃-B₂O₃ glasses

Avula Edukondalu¹,³*, B. Kavitha¹,³, Abdul Hameed² and K. Siva Kumar¹,³

¹Department of Physics, Osmania University, Hyderabad, India.
²Department of Physics, Nizam College, Hyderabad, India.
³Department of Physics, Osmania University College for Women, Hyderabad, India.

E-mail: kondalou@gmail.com (Edukondalu)

Abstract. Glasses with composition xLi₂O-(30-x)Na₂O-10WO₃-60B₂O₃ (where x=0, 5, 10, 15, 20, 25 and 30 mol%) have been prepared using the melt quenching technique. In the present work, the mixed alkali effect (MAE) has been investigated in the above glass system through density and optical studies. The density of the present glasses varies non-linearly, exhibiting the mixed alkali effect. From the optical absorption studies, the values of direct optical band gap, indirect optical band gap energy (E₀) and Urbach energy (ΔE) have been evaluated. The values of E₀ and ΔE vary non-linearly with composition parameter, showing the mixed alkali effect.

1. Introduction

Optical absorption studies on amorphous materials yield important information regarding electronic and vibrational edges plus the contributions from impurities such as transition metal ions. Stevels [1] was the first to suggest that the intrinsic absorption edge of an oxide glass corresponded to the transition of valence electron of an oxygen ion in the glass network to an excited state. Although thermal vibrations are assumed to be responsible for the tail part of the optical absorption edge a number of glasses obeying Urbach rule for the absorption coefficient, whose physical origin is not well understood.

Tungsten oxide containing glasses is of great interest because they can exhibit unusual electrochromic or photosensitive properties related to the ability of tungsten atoms to exhibit various oxidation states (W⁴⁺, W⁵⁺ or W⁶⁺). The extent and ability of incorporating WO₃ in glasses strongly depends on the glass former, size of ions in the glass structure, mobility of the modifier cation, etc. Large amount of WO₃ is easily incorporated into germinate, tellurite, phosphate and borate glasses [2-5].

The present investigation is a part of an ongoing program to study the MAE in lithium sodium tungsten borate glasses. Therefore, in this work we have concentrated on the influence of mixed alkalis on physical and optical absorption properties of xLi₂O-(30-x)Na₂O-10WO₃-60B₂O₃ (0 ≤ x ≤ 30 mol%) glasses. The physical properties of the glasses have also been determined with respect to glass compositional parameter R_Li defined as R_Li = Li₂O (mol%)/(Li₂O+Na₂O) (mol%) which takes the values 0, 0.166, 0.332, 0.5, 0.666, 0.832 and 1.
2. Experimental

The xLi₂O–(30-x)Na₂O–10WO₃–60B₂O₃ (0 ≤ x ≤ 30 mol%) glass system was prepared through the standard melt quenching method. Details of the preparation and characterization of the glass specimens are given in ref. [6,7]. The optical absorption spectra of the glasses were recorded in the wavelength range 200–800 nm at room temperature using a Schimadzu 3100 UV-VIS-NIR spectrometer. The uncertainty in the observed wavelength was about ±1 nm.

3. Results and Discussion

3.1. Physical parameters

The molar volume (Vₘ) and oxygen packing density (O) are calculated using the measured values of density [8]. From Table 1 it can be observed that the variation of density, molar volume and oxygen packing density as a function of compositional parameter is non-linear. This non-linear variation can be taken as a signature of the mixed alkali effect. The change in the molar volume is a result of the creation of non-bridging oxygens (NBOs), which will break the bonds and increase space in the glass network. This result indicates that the glass structure becomes loosely packed.

![Figure 1. Variation of Vₘ and OPD as function of compositional parameter R_Li.](image)

![Figure 2. Optical absorption spectra of x = 15 glasses sample.](image)

3.2. Optical absorption

The optical absorption spectra of xLi₂O-(30-x)Na₂O–10WO₃–60B₂O₃ glass system is shown in Fig. 2. Other glass samples in the present series also show similar spectral behavior. The optical absorption co-efficient α(ν), near the fundamental absorption edge of the curves in the above figure was determined from the relation

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

where I₀ and Iₜ are the intensities of the incident and transmitted beams, respectively, and d is the thickness of the glass sample. The factor log(I₀/Iₜ) corresponds to absorbance. Davis and Mott and Tauc and Menth [9,10] relate this data to the optical band gap, Eᵦ through the following general relation proposed for amorphous materials.
(αhν)^n = B(hν-E_{opt}) \tag{2}

where B is a constant related to the extent of the band tailing and hν is incident photon energy.

The index n determines the type of electronic transitions causing the absorption, and takes the values 1/2, 2, 2/3 and 1/3 for indirect allowed, direct allowed, direct forbidden and indirect forbidden transitions, respectively. According to the theory of electronic structure of amorphous materials [11] the absorption edge of the amorphous material is interpreted in terms of indirect allowed transitions. The values of optical band gap energy E_{opt} can be obtained by extrapolating the absorption coefficient to zero absorption in the (αhν) against photon energy hν plots as shown in Fig 3. The optical band gap energy, 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 3.54 to 3.83 eV and 3.66 to 3.98 eV, respectively. Srinivasa Rao et al [12], and Huang et al [5]. Observed a large band gap energies around 3.25 eV and 4.18 eV in PbO-Bi_2O_3-As_2O_3-WO_3 and Li_2O-B_2O_3-WO_3 glasses, respectively. It is observed that the band gap energies vary non-linearly with compositional parameter, indicating the existence of a mixed alkali effect.

The main feature of the absorption edge of amorphous materials is an exponential increase of absorption coefficient α(ν) with photon energy hν, which is given by the Urbach rule [13]

α(ν) = C \exp(hν/ΔE) \tag{3}

where C is a constant, and ΔE is the Urbach energy which is a measure of band tailing.

Fig. 4 plots the variation of ln(α) as function of photon energy hν. The values of Urbach energy (ΔE) were determined by taking the reciprocals of the slopes of the linear portion of ln(α) vs hν curves. The Urbach energy values of the present glass samples are presented in Table 1. The compositional dependence of Urbach energy ΔE is illustrated in Fig. 4. Urbach energy is varying non-linearly with a compositional parameter indicating the existence of a mixed alkali effect in present glasses.

---

**Figure 3.** (αhν)^1/2 versus hν, Tauc’s plot for the present glass system.

**Figure 4.** lnα versus hν, Tauc’s plot for the present glass system.
Table 1. Density (ρ), Molar volume (V_m), Oxygen Packing Density and Optical parameters of the \(x\text{Li}_2\text{O-(30-x)Na}_2\text{O-10WO}_3-60\text{B}_2\text{O}_3\) glass system

| Parameters     | x=0  | x=5  | x=10 | x=15 | x=20 | x=25 | x=30 |
|----------------|------|------|------|------|------|------|------|
| ρ (g/cc) (±0.001) | 2.821| 2.918| 2.849| 2.851| 2.854| 2.805| 2.724|
| \(V_m\) (cc/mol)(±0.001) | 29.616| 28.082| 28.199| 27.616| 27.025| 26.925| 27.136|
| OPD (g-atm/l)(±0.001) | 81.037| 85.464| 85.109| 86.906| 88.807| 89.136| 88.443|
| \(\lambda_c\) (nm) (±1) | 338| 318| 287| 318| 313| 307| 313|
| Indirect \(E_0\) (eV) | 3.41| 3.80| 3.83| 3.62| 3.57| 3.72| 3.73|
| Direct \(E_0\) (eV) (±0.05) | 3.66| 3.93| 3.99| 3.77| 3.86| 3.85| 3.92|
| \(\Delta E\) (eV) (±0.001) | 0.285| 0.342| 0.394| 0.266| 0.288| 0.265| 0.235|

4. Conclusions

Mixed alkali tungsten borate glasses in the form of \(x\text{Li}_2\text{O-(30-x)Na}_2\text{O-10WO}_3-60\text{B}_2\text{O}_3\) \(0 \leq x \leq 30\) were prepared, and their physical and optical properties have been studied. The following conclusions were made: The physical properties like density, refractive Index and glass transition temperature were evaluated for the glass studied in the present work varies non-linearly with a compositional parameter which shows the MAE. 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.

References

[1] Bih L, Abbas L, Mohdachi S and Nadiri A 2008 J. Mol. Struct. 891 173.
[2] Bergman A G, Machavar Z N and Maltsev V T 1972 Russ. J. Inorg. Chem. 17 3106.
[3] Shaltout I, Tang Y, Braunstein R and Abu-Elazm A M 1995 J. Phys. Chem. Solids, 56 141.
[4] Carla C. de Araujo, Wenzel Strojek, Long Zhang, Hellmut Eckert, Gael Poirier, Sidney J. L. Ribeiro and Younes Messaddeq 2006 J. Mater. Chem. 16 3277.
[5] Huang P N, Huang X H and Gan F X 1990 Solid State Ionics 44 11.
[6] Edukondalu A, Purnima M, Srinivasu Ch, Sripathi T, Awasthi A M, Syed Rahman and Siva Kumar K 2012 J. Non-Cryst. Solids 358 2581–2588.
[7] Edukondalu A, Sathe V, Syed Rahman, Siva Kumar K and Sreenivasu D 2014 Vibrational Spectroscopy 71 91–97.
[8] Edukondalu A, Sathe V, Syed Rahman and Siva Kumar K 2014 Physica B 438 120.
[9] Davis E A and Mott N F 1970 Philos. Mag. 22 903.
[10] Tauc J and Menth A 1972 J. Non-Cryst. Solids 8 569.
[11] Edukondalu A, Kavitha B, Samee M A, Shaik Kareem ahmmad, Syed Rahman and Siva kumar k 2013 J. Alloys Compd. 322 324 -335.
[12] Rao N S, Ravi Kumar V and N. Veeraiah N 2011 Physica B 4064494.
[13] Urbach F1953 Phys. Rev. 92 1324.