

Mixed alkali effect in $\text{Li}_2\text{O-Na}_2\text{O-WO}_3\text{-TeO}_2$ glasses : Optical Parameters

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ABSTRACT

Glasses with composition $x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-20\text{WO}_3-50\text{TeO}_2$ (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 modulated DSC studies. The density and glass transition temperature 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 (E_o) and Urbach energy (ΔE) have been evaluated. The values of E_o and ΔE vary non-linearly with composition parameter, showing the mixed alkali effect.

Keywords: Mixed Alkali Effect, Tungsten Based Glasses, Density, Glass Transition Temperature, Optical Absorption.

I. INTRODUCTION

Mixed alkali glasses are unique from the point of view that certain properties change much more than normally anticipated from what appears to be a structurally and compositionally simple substitution of one alkali oxide for another. Mixed alkali effect in different physical properties are observed in silica, borate and phosphate glasses[1]. When two types of alkali metal ions are introduced into a glassy network, a phenomenon known as mixed alkali effect (MAE) is observed. It represents the non-linear variations in many physical properties, when one type of alkali ion in an alkali glass is gradually replaced by another while total alkali content in the glass being constant. Models for MAE have been proposed in the literature and compiled in several reviews[2]. Recently, Belostotsky reported a new defect model for the mixed alkali effect. The essential physical concept involved is that simultaneous migration of two unlike alkali ions in mixed ionic glass is accompanied by an expansion or contraction of the guest-occupied sites with distortion of the surrounding glass matrix. Far infrared spectroscopy has been employed to probe the effect of alkali mixing on the interactions between alkali ions and local sites in mixed alkali glasses[3]. Mass et al. developed the dynamic

structural model to explain the mixed alkali effect. To study the mixed alkali phenomenon, borate glasses proved to be promising hosts to investigate the influence of chemical environments, structural diversity of legendary groups and spectroscopic properties of the materials[4].

Tungsten ion containing glasses has gained much importance due to their nonlinear optical absorption and electrical properties for technological applications [5]. Tungsten ions are predicted to have strong influence on the physical properties of compounds. 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 TeO_2 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 [6]. 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 [7].

Many investigations have been reported on ternary alkali tungstate in phosphate, borate, tellurite, bismuthate, and niobate glasses [8]. More recently, presented physical, structural, optical, and dielectric properties of $15\text{Li}_2\text{O}-(65-x)\text{Bi}_2\text{O}_3-20\text{GeO}_2-x\text{WO}_3$ glasses (where $x = 2, 5, 10$ mol%) [9]. To the best of our knowledge, there are no reports on mixed alkali borate tungsten glasses. A recent investigation of the electrical, glass transition temperature, and density properties in $\text{Li}_2\text{O}-\text{Na}_2\text{O}-\text{WO}_3(\text{MoO}_3)-\text{P}_2\text{O}_5$ system showed the mixed alkali effect [10].

The aim of the present work is to investigate the mixed alkali effect in $x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-20\text{WO}_3-50\text{TeO}_2$ ($0 \leq x \leq 30$ mol%) glasses by measuring the optical properties as a function of compositional parameter R_{Li} , which is defined as $R_{\text{Li}} = \text{Li}_2\text{O}(\text{mol}\%)/(\text{Li}_2\text{O} + \text{Na}_2\text{O})(\text{mol}\%)$. R_{Li} takes the values 0, 0.166, 0.33, 0.5, 0.66, 0.83 and 1. Further, optical absorption studies have also been performed on glass samples.

II. Experimental

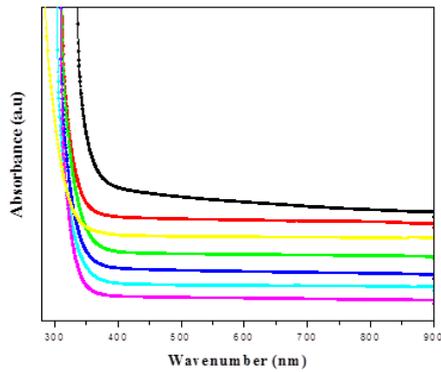
A batch of approximately 15 g of chemicals in powder form was weighed using a digital balance with an accuracy of $\pm 0.01\text{mg}$. The relative weights of the components were calculated according to the molar formula $x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-20\text{WO}_3-50\text{TeO}_2$, where x ranged between 0 and 30 mol%. The glass composition, compositional parameter and glass preparation temperature are listed in Table 1. Appropriate amounts of reagent grade Li_2CO_3 , Na_2CO_3 , TeO_2 , and WO_3 were well-mixed and melted in porcelain crucibles in the temperature range of $900-1000^\circ\text{C}$, depending on the glass composition, in an electrical muffle furnace for about 60 minutes. The porcelain crucibles containing glass melt was swirled frequently to insure the homogeneity. The clear liquid (free of bubbles) was quickly cast in a stainless steel mould kept at 200°C and pressed with another steel disc maintained at same temperature. Later, the samples were annealed 100°C below their respective glass transition temperature for about 24 hours and slowly cooled to laboratory temperature.

The amorphous nature of the glass samples was confirmed by X-ray diffraction study. An advance powder XRD (PANalytical X-pert PRO model with Cu-K Alpha radiation of wavelength 1.54048 \AA) was used. The room temperature optical absorption spectra of the polished glass samples were recorded using JASCO V670 spectrometer in the wavelength region $200-1000 \text{ nm}$.

III. Results and discussion

X-ray diffraction patterns of $x\text{Li}_2\text{O}-(30-x)\text{Na}_2\text{O}-20\text{WO}_3-50\text{TeO}_2$ glass samples shows no continuous or discrete sharp peaks but exhibit broad halo, which reflects the characteristics of amorphous glass structure.

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and 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. Fig. 1 shows the optical absorption spectra of the sample of the present glass system. There are two kinds of optical transitions at the fundamental edge of crystalline and non-crystalline semiconductors; direct transitions and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band, which is then raised across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band it is essential that the wave vector for the electron to be unchanged. In the case of indirect transitions the interactions with lattice vibrations (phonons) take place, thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons. In other words, if the minimum of the conduction band lies in a different part of k-space for the maximum of the valence band, a direct optical transition from the top of the valence band to the bottom of the conduction band is forbidden.



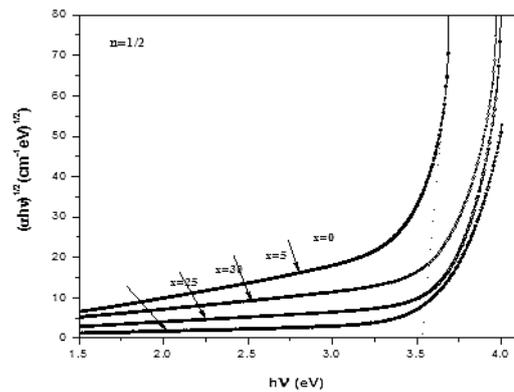
The optical absorption co-efficient $\alpha(\nu)$, near the fundamental absorption edge of the curve in the above figure was determined from the relation

$$\alpha(\nu) = 2.303(A/d)$$

Where I_0 and I_t is the intensities of the incident and transmitted beam, respectively, and d is the thickness of the glass sample. The factor $\log(I_0/I_t)$ corresponds to absorbance. Davis and Mott [11] and Tauc and Menth [12] relate this data to the optical band gap, E_{opt} through the following general relation proposed for amorphous materials.

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

where B is a constant related to the extent of the band tailing and $h\nu$ is incident photon energy. The index n determines the type of electronic transitions causing the absorption and takes the values $1/2$, 2 , $3/2$ and 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions. By plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of photon energy $h\nu$, one can find the optical energy band gap E_{opt} for indirect and direct transitions, respectively. The respective values of E_{opt} are obtained by extrapolating to $(\alpha h\nu)^{1/2} = 0$ for indirect transition and $(\alpha h\nu)^2 = 0$ for direct transition. Fig. 2 represents the Tauc's plots $\{(\alpha h\nu)^{1/2} \text{ vs } h\nu\}$ for different glass samples. Similar behavior was also observed by other workers [13, 14]. The values of the indirect optical energy gap, E_{opt} , thus obtained from the extrapolation of the linear region of



Tauc's plots are presented in Table 1. The values of the direct optical energy gap were also determined and are presented in Table 1. In the present glasses the indirect band gap energy varies from 3.41 to 3.835 eV and direct band gap energy vary between 3.66 to 3.977 eV respectively. Edukondalu et. al. [15,16] observed 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. In the present glasses, the compositional dependence of direct and indirect optical band gap energies. 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 $\alpha(\nu)$ with photon energy $h\nu$ and is given by Urbach rule [17-21]

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

where C is a constant and ΔE is the Urbach energy which is a measure of band tailing. Plots the variation of $\ln(\alpha)$ as function of photon energy $h\nu$. 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. Urbach energy is varying non-linearly with a compositional parameter indicating the existence of mixed alkali effect in present glasses.

IV. CONCLUSIONS

Mixed alkali tungsten borate glasses in the form of $xLi_2O-(30-x)Na_2O-20WO_3-50TeO_2$ ($0 \leq x \leq 30$) were prepared and their physical and optical properties have been studied. The following conclusions are made. The present glass system was prepared through conventional

melt quench technique. Amorphous nature of the samples is confirmed by the broad diffused haloes in XRD patterns. 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.

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