JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Spectroscopic Properties VO^{2+} in Li_2O-SrO-CdO-B_2O_3 glasses

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ABSTRACT

Glasses made from Li2O−SrO−CdO−B2O3 with varying concentrations of V2O5 (from 0 to 1.0 mol %) were synthesized. The samples were analyzed using X-ray diffraction, scanning electron microscopy, and differential scanning calorimetry. Studies on optical absorption, ESR, photoluminescence, and IR were conducted on these glass materials. The optical absorption spectrum of the vanadium-doped glasses showed two broad absorption bands at 534 and 820 nm. These bands are associated with the transitions 2B2→2B1 (Δ⊥) and 2B2→2E (Δ||) of the 3d1 electron in the V4+ state. A significant shift of the peak positions of these bands toward longer wavelengths was observed, along with an increase in intensity as the concentration of V2O5 rose to 0.6 mol %. The highest intensity of these bands in the spectrum of V6 glass suggests a maximum concentration of VO2+ ions, which act as modifiers in the glasses. Analysis of the Li2O−SrO−CdO−B2O3: V2O5 glasses indicates that when V2O5 concentration is ≤ 0.6 mol%, vanadium ions are primarily in the VO2+ state, occupying modifier positions and weakening the glass network. Conversely, when the V2O5 concentration exceeds 0.6 mol%, some vanadium ions transition to the V5+ state, taking network-forming positions and reinforcing the glass structure.

1. INTRODUCTION

Alkali/alkali earth oxy borate glasses are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices. These glasses are relatively moisture resistant, posses high electrical insulating and mechanical strength when compared with the pure borate glasses. These glasses are transparent from the near UV to the middle infrared region. Addition of alkali-earth oxides like CaO, BaO, MgO, SrO etc., in to these glass matrices is expected to increase the resistance of the glasses to the moisture. Spectroscopic studies on alkali metal borate glasses have revealed that the structure of alkali metal borate

glasses is dependent not only upon the content of the alkali metal ion but also upon the difference in the alkali metal ions [1]. Among various alkali oxides, lithium oxide not only acts as a modifier but also makes the glasses as ionic conducting materials and makes them as promising electrolyte materials to use in solid state batteries [2]. Semiconducting transition metal oxide such as V_2O_5 based glass has gained much interest in solid state chemistry and material science with regard to their possible applications has memory and switching devices [3]. Vanadium-containing oxide glasses are known to be semiconductors and the transport mechanism involves the exchange of electrons between vanadium (IV) and vanadium (V) centers, e.g. [4].

$$V^{4+} - O \rightleftharpoons V^{5+} \qquad V^{5+} - O - V^{4+}$$

Vanadate glasses are identified as n-type semiconductors for low V^{4+}/V^{5+} ratio [5]. It is also known that V^{5+} in low ratios enter the amorphous structure as a modifier whereas when V^{5+} present in high ratios, these ions participate in the glass network as glass formers with VO_5 structural units [6]. The present study is devoted to spectroscopic studies that include optical absorption, photoluminescence and IR spectra of Li_2O-SrO-CdO-B_2O_3: V_2O_5 glasses.

1. EXPERIMENTAL

Glasses of the following composition are chosen for the present study:

(30-x) Li_2O- 5 SrO-5CdO- 60 B_2O_3: x V_2O_5 (with x = 0.2 (V_2), 0.4 (V_4), 0.6 (V_6) ,0.8 (V_8) and 1.0 (V_{10}) all in mol%) are chosen for the present study.

AR grade Li_2CO_3, SrO, B_2O_3 and V_2O_5 powders were thoroughly mixed in an agate mortar and melted in a thick-walled platinum crucible in the temperature range 900-950 $^{\circ}$C in an automatic temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed from 300 ^{o}C with a cooling rate of 1°C/min. The amorphous state of the glasses was checked by X- ray diffraction and scanning electron microscopy.

The samples were then ground and optically polished. The final dimensions of the samples used for optical absorption were about 1 cm x 1 cm x 0.2 cm. The density d of the glasses was determined to an accuracy of 0.001 by standard principle of Archimedes' using o-xylene (99.99 % pure) as the buoyant liquid. The optical absorption spectra of the glasses were recorded at room temperature in the wavelength range 300-1200 nm up to a resolution of 0.1 nm using CARY 100 (Varian) Spectrophotometer. Infrared transmission spectra were recorded on a Bruker IFS 66V – IR spectrophotometer with a resolution of 0.1 cm^{-1} in the range 400-2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized glass (1.5 mg). A thin coating of silver paint was applied (to the larger area faces) on either side of the glasses to serve as electrodes for dielectric measurements. The painted samples were then dried with a hot blower for about 10 minutes on either side.

2. RESULTS AND DISCUSSION

The optical absorption spectra of Li_2O-SrO-CdO-B_2O_3:V_2O_5 glasses recorded at room temperature in the wavelength region 300-1200 nm (Fig. 1). The spectrum of vanadium free glass does not exhibit any absorption bands. The absorption edge observed at 381 nm for glass V_0 (pure glass) is found to shift towards slightly higher wavelength side with increase in the concentration of V_2O_5 up to 0.6 mol %. The spectrum of glass V_2 exhibited two broad absorption bands at 620 and 992 nm corresponding to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions [7]; with increase in the concentration of V_2O_5 up to 0.6 mol%, the half width and peak height of these bands are observed to increase. For further increase of V_2O_5 concentration, the intensity of these bands is observed to decrease gradually. From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot between $(\alpha\, \hbar\omega)^{1/2}$ and $\hbar\omega$ as per the equation: $\alpha(\omega)\hbar\omega = X(\hbar\omega - E_o)^2$. (1)

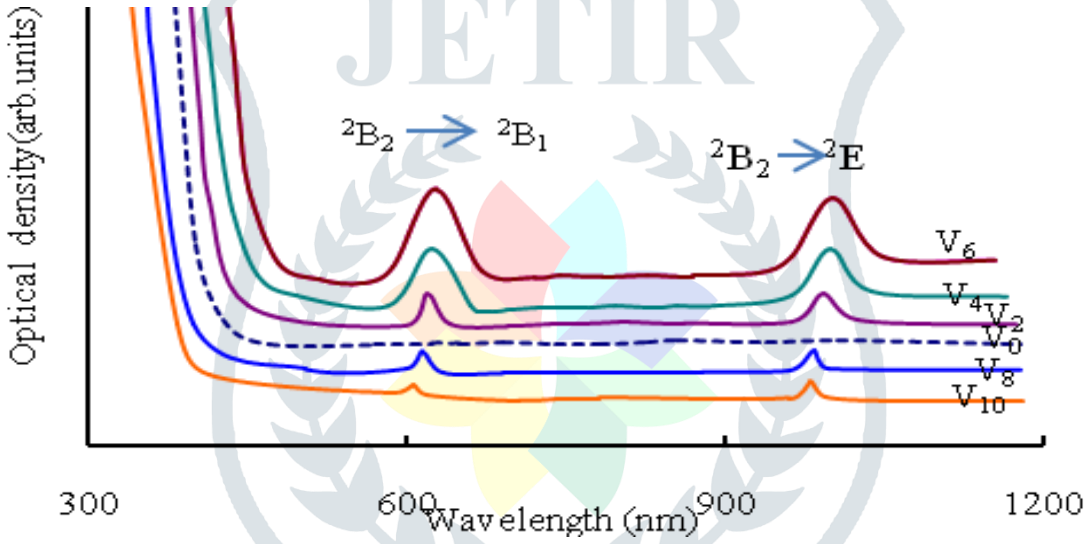

Fig.1 Optical absorption spectra of Li_2O-SrO-CdO-B_2O_3:V_2O_5 glasses

Fig. 2 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. These glasses doped with different concentrations of vanadium oxide recorded at room temperature in the spectral wavelength region 600-900 nm. The spectra of all the samples exhibited a broad emission band with the peak positions varying in the regions 760-768 nm, as the concentration of vanadium oxide is increased up to 0.6 mol%, the intensity of this band is observed to increase, beyond this concentration, the intensity of the band is found to decrease.

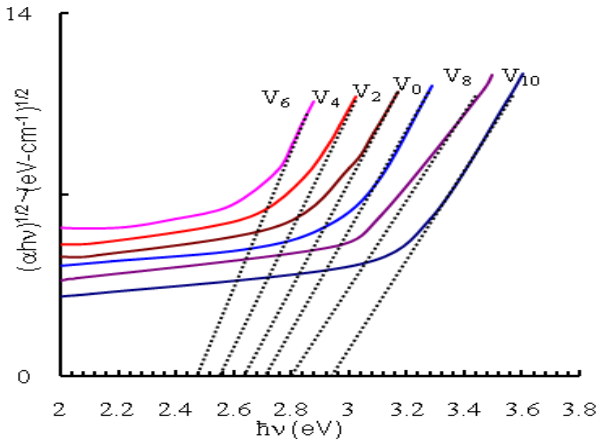

Fig. 2. Optical band gap for the Li_2O-SrO-B_2O_3:V_2O_5 glasses

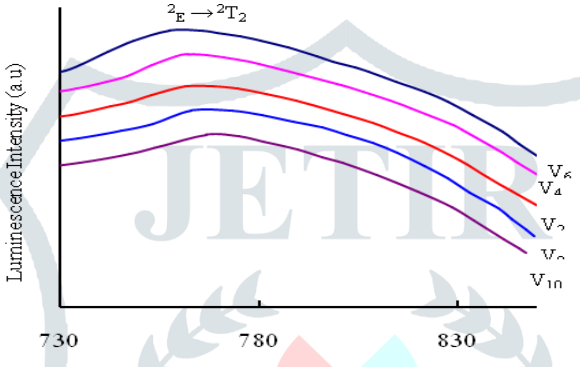

Fig. 3 Photoluminescnce spectra of Li_2O-SrO-B_2O_3:V_2O_5 glasses

The infrared transmission spectra of vanadium free Li_2O-SrO-CdO-B_2O_3 glasses (Fig. 4) exhibit two groups of bands: (i) in the region 1200-1300 cm^{-1}, (ii) in the region 1000-1100 cm^{-1} and another band at about 710 cm^{-1}. The second group of bands is attributed to the BO_4 units while the first group of bands is identified as due to the stretching relaxation of the B-O bond of the trigonal BO_3 units and the band at 710 cm^{-1} is due to the bending vibrations of B-O-B linkages in the borate network [8]. With the introduction V_2O_5 into the glass matrix, an additional band due to V-O-V bending vibrations is observed at about 600 cm^{-1} [9]. In the region of vibrations of BO_4 units (at about 1000 cm^{-1}) band due to vibrations of isolated V=O groups in VO_5 trigonal bipyramids is also expected [10]. As the concentration of V_2O_5 is increased up to 0.6 mol%, the intensity of the band due to BO_3 structural units is observed to increase where as that of BO_4 structural units is observed to decrease. When the concentration is increased beyond 0.6 mol%, the band due to BO_4 structural units is observed to grow at the expense of the band due to BO_3 structural units.

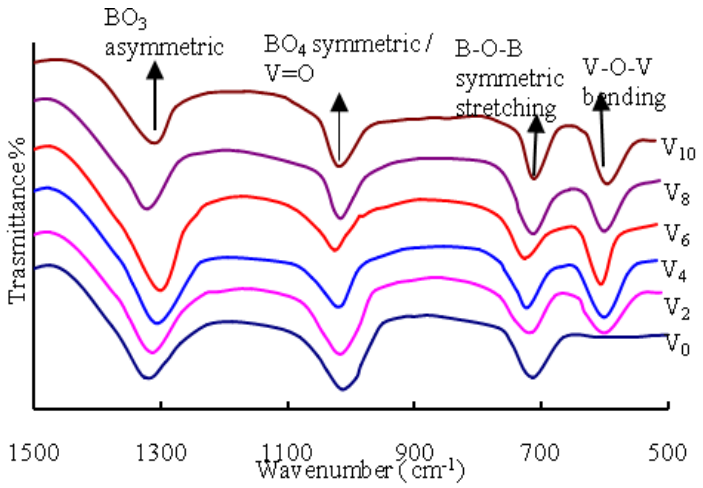

Fig. 4 IR spectra of Li_2O-SrO-B_2O_3:V_2O_5 glasses

In Li_2O-SrO-B_2O_3 glass network, the coordination geometry of boron atoms is expected to be strongly dependent on the composition of the glasses and on the nature of the network modifiers. The addition of lithium oxide and strontium oxide in to the borate glass network is accompanied by a change in the boron coordination from three to four or vice versa depending up on its concentration and also on other ingredients of the glass matrix. Vanadium ions are anticipated to subsist mainly in V^{5+} state in the present Li_2O-SrO-B_2O_3 glass network. However, during the melting of the glasses at higher temperatures there is every possibility to reduce a part of V^{5+} ions into V^{4+} ions as per the following redox equilibrium:$2\ V^{5+} + O^{2-} \rightarrow 2\ V^{4+} + 1/2\ O_2 \uparrow$ V^{5+} ions take part network forming positions with VO_5 trigonal bipyramidal structural units where as the V^{4+} ions form VO^{2+} complexes, may act as modifiers and distort the glass network. The Obsorption spectra of the present glasses exhibited only the two bands corresponding to the transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$. The intensity and the half width of these bands have been observed to be maximum in the spectrum of glass V_6; this observation indicates the presence of the largest concentration of VO^{2+} (vanadyl) ions in this glass. These VO^{2+} ions are expected to participate in the depolymerisation of the glass network, create more bonding defects and non-bridging oxygens (NBO's). The higher the concentration of such modifiers, the higher is the concentration of NBO's in the glass matrix. This leads to an increase in the degree of localization of electrons there by increasing the donor centres in the glass matrix. The presence of larger concentration of these donor centers decreases the optical band gap and shifts the absorption edge towards higher wavelength side as observed. Excitation of these glass samples with the wavelength corresponding to $^2B_2 \rightarrow {}^2B_1$, resulted a broad emission band as shown in Fig. 3. Since the wavelength of this band is close to the maximum of the band $^2B_2 \rightarrow {}^2E$, we attribute this band as the $^2E \rightarrow {}^2T_2$ transition of V^{4+} ions; the emission band is relatively broad and structures less. With increase in the concentration of vanadium metal oxide up to 0.6 mol %, the meta center of this peak is shifted towards higher wavelength with gradual hike in the intensity; beyond this concentration, the intensity of the peak is observed to decrease and shifted towards lower wavelength side. The shift of this PL peak, the shape and the structured nature of the PL emission band are a signature of shallow levels with an

electron–phonon coupling. [11]. The analysis of IR spectra also supports the view point that as the concentration of V_2O_5 is raised up to 0.6 mol %, there is a growing degree of disorder in the glass network. Thus the results of IR spectra also indicate that there is higher concentration of vanadyl ions that act as modifiers in the glass sample V_6.

CONCLUSIONS

Optical absorption, photoluminescence and IR studies of these glasses have indicated that vanadium ions exist in V^{4+} state in addition to V^{5+} state. From the analysis of these results it is evident that the highest concentration of vanadyl ions that act as modifiers in the glass doped with 0.6 mol% of V_2O_5.

ACKNOWLEDGEMENT

The author would like to thank the Principal, GDC Paloncha and CCE, Govt of Telangana for the academic support throughout this work..

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