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Optical Absorption Studies on Lithium Aluminosilicate Glasses Doped with Low Concentrations of WO_3

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Abstract: $Li_2O–Al_2O_3–SiO_2$ glasses mixed with low concentrations of WO_3 (0 to 1.0 mol %) have been synthesized. Lithium aluminosilicate glasses are known for their photochromic properties. The presence of tungsten ions in these glasses is expected to influence their physical properties to a large extent since these ions exist in different valence states. The optical absorption spectral studies have pointed out that a part of tungsten ions do exist in W^{5+} state in addition to W^{6+} state especially in the samples containing low concentration of WO_3. The W^{5+} ions are expected to participate in the depolymerisation of the glass network and create more bonding defects and non-bridging oxygens. The results of Optical absorption spectra indicates the decrease of redox ratio or decreasing proportions of W^{5+} ions that act as modifiers in the glass network.
Key words: Aluminosilicate glasses, Tungsten ions, Spectroscopic properties.

Introduction:

Lithium aluminosilicate glasses were considered as excellent materials for integrated optics and photonic applications because of their high physical, thermo, chemical and mechanical stability [1]. The presence of aluminum ions in silicate glasses will decrease the phonon energies for broadening the spectral range of transparency and to enhance the refractive indices of the glasses. Tungsten ions are known to influence the optical properties of glasses due to the reason that the oxides of it will participate in different tetrahedral and octahedral structural units because of its different valance states [2]. The influence of different structural groups of tungsten ions with different oxidation states at a given temperature depends on the properties of the modifier ion in the glass network. The presence of tungsten in lithium aluminosilicate glasses makes them suitable for optoelectronic devices since they exhibit photo-chromism and electro-chromism properties [3-7].The structural probing of tungsten ions in $Li_2O–Al_2O_3–SiO_2$ glass network is expected to be highly interesting and useful for the practical applications of these glasses. Thus the objective of present study is to investigate the structural changes that take place with the varied oxidation states of tungsten ions in $Li_2O–Al_2O_3–SiO_2$ glass network and the influence of modifier ions in this process by optical absorption spectral studies.

Experimental:

The detailed compositions of the glasses used in the present study are given in Table-1. The samples are prepared by melt quenching method and optical polished. The density of the glasses was determined by the principle of Archimedes' using o–xylene as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.0001 g using Ohaus digital balance Model AR2140 for evaluating the density. The optical absorption spectra of the glasses were recorded to a resolution of 1 nm at room temperature in the spectral wavelength range covering 300–1000 nm using JASCO Model V-670 UV–VIS–NIR spectrophotometer.

Table-1: Chemical composition of $Li_2O–Al_2O_3–SiO_2$: WO_3 glasses

Glass	Li_2O (mol%)	Al_2O_3(mol%)	SiO_2(mol%)	WO_3(mol%)
W_0	30.0	10.0	60.0	0.0
W_2	29.8	10.0	60.0	0.2
W_4	29.6	10.0	60.0	0.4
W_6	29.4	10.0	60.0	0.6
W_8	29.2	10.0	60.0	0.8
W_{10}	29.0	10.0	60.0	1.0

Results and Discussion:

By using the measured values of density and average molecular weight the physical parameters such as tungsten ion concentration N_i, mean tungsten ion separation molar volume are evaluated. Fig. 1(a) presents optical absorption spectra for $Li_2O–Al_2O_3–SiO_2$: WO_3 glass samples recorded at room temperature in the wavelength region 300-1200 nm. The absorption edge observed at 340 nm for the glass sample W_2 exhibited blue shift with increase in the concentration of WO_3. The spectra of all glasses exhibited a broad absorption band centered at about 854 nm. As the concentration of WO_3 is continued to increase, the intensity of these bands is observed to decrease with a slight shift in the peak position towards lower wavelength. The summary of the data on optical absorption spectra of these glasses is furnished in Table-2.

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these samples by drawing tauc plots (Fig. 2) between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ as per the equation.

$$\alpha(\omega)\hbar\omega = c(\hbar\omega - E_o)^2 \quad \text{-------------------------} \quad (1)$$

$\alpha(\omega)$ is the absorption coefficient, $\hbar\omega$ is the photon energy and c is a constant.

From the extrapolation of the linear portions of the curves of Fig. 2, the values of optical band gap (E_o) are determined and are presented in Table-3.

Tungsten ion is a transition metal ion and exists in +6 and +5 valence states and its W−O bond in hexavalent oxide is covalent as of Si–O bond [8]. The octahedral tungsten ions were also observed to be as stable as those of tetrahedral silicate ions, although the octahedral are distorted due to Jahn-Teller effect.

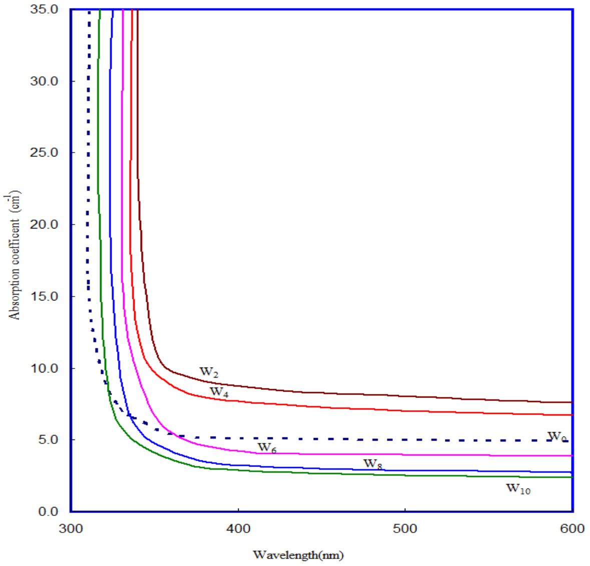

Fig. 1(a) Optical absorption spectra of $Li_2O–Al_2O_3–SiO_2$: WO_3 glasses (300-600 nm)

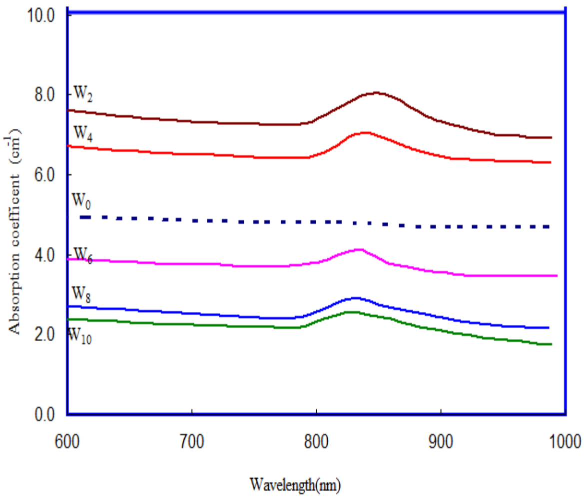

Fig. 1(b) Optical absorption spectra of $Li_2O–Al_2O_3–SiO_2$: WO_3 glasses (600-1000 nm)

Table-2: Physical parameters of $Li_2O–Al_2O_3–SiO_2$: WO_3 glasses

Glass	Density(g/cm^3)	N_i (10^{21}, ions/cm^3)	r_i (Å)	r_p (Å)	Mol.vol (cm^3/mol)
W_0	2.5880				
W_2	2.5983	0.59	11.93	4.81	1.30
W_4	2.6086	1.17	9.48	3.82	2.06
W_6	2.6189	1.75	8.29	3.34	2.69
W_8	2.6292	2.33	7.54	3.04	3.25
W_{10}	2.6395	2.91	7.01	2.82	3.76

Table-3: Data on optical absorption spectra $Li_2O–Al_2O_3–SiO_2$:WO_3 glasses

Glass	Cut-off wavelength (nm)	Optical band gap (eV) (± 0.01)	Band Position (nm)
W_0	311	4.05	---
W_2	340	3.65	852
W_4	337	3.70	841
W_6	331	3.75	836
W_8	324	3.85	832
W_{10}	316	3.92	830

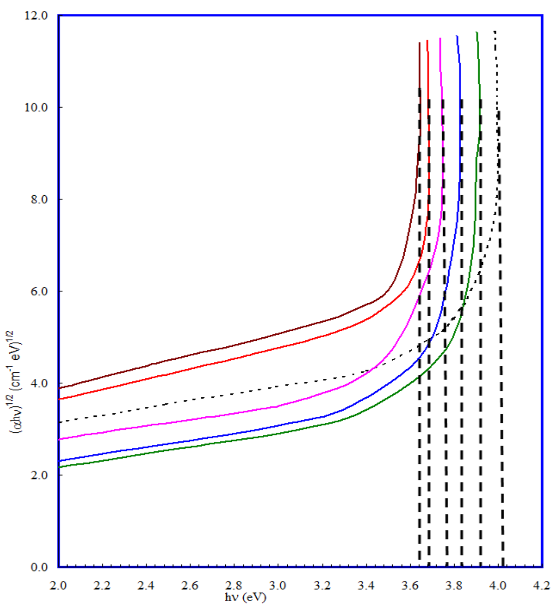

Fig. 2 Tauc plots of $Li_2O–Al_2O_3–SiO_2$: WO_3 glasses

The W^{5+} ions are expected to participate in the depolymerisation of the glass network similar to Li^{+} ions, create more bonding defects and non-bridging oxygens (NBOs) as mentioned earlier [2]. Lower concentration of these ions in the glass network means a lower number of donor centers are created, as a consequence, the degree of overlapping of the excited states of localized electrons originally trapped on W^{5+} sites with the empty 3d states on the neighboring W^{6+} sites decreases, the impurity or polaron band becomes less extended into the main band gap. The broad band observed in the optical absorption spectra of Li_2O–Al_2O_3–SiO_2: WO_3 glasses are identified due to $d_{xy} \rightarrow d_{x^2-y^2}$ transition of W^{5+} ions [6, 9]. The electron delivered by the impurity atom at the W^{6+} site converts this into a lower valence state W^{5+} and at the next stage, the trapped electron at this W^{5+} site is transferred to the neighboring new W^{6+} site by absorbing a photon energy. Thus the optical absorption in the glass samples is dominated by polaronic transfer between the W^{5+} and W^{6+} species especially in the samples containing low content of WO_3.

Conclusions:

The results have also suggested that the tungsten ions occupy octahedral and tetrahedral positions in the glass network. The analysis of these results further pointed out that there is an increasing rigidity of the glass network with increase in the concentration of WO_3. The optical absorption spectra of Li_2O–Al_2O_3–SiO_2: WO_3 glasses exhibited bands due to the transitions of W^{5+} ions, indicating the presence of a part of tungsten ions in the pentavalent state in addition to the hexavalent state in these glass samples. So the Li_2O–Al_2O_3–SiO_2 glasses doped with low concentration of WO_3 are better candidates for exhibiting photochromism since they contain higher proportions of W^{5+} ions.

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