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DSC, ESR AND IR SPECTRAL STUDIES ON Li_2O–WO_3–B_2O_3 GLASS SYSTEM DOPED WITH VANADIUM IONS

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With in glass forming region of Li_2O–WO_3–B_2O_3 glass system, a particular composition $40Li_2O$–$5WO_3$–$(55–x)$ B_2O_3: xV_2O_5 (with x ranging from 0.2 to 0.8, all are in mol.%) is chosen. The DSC traces are obtained to identify the glass transition temperature (T_g) and the glass forming ability of all the glass samples. The ESR and IR spectra portray the local structure of the glass system and valance states of the vanadium ions in the glass matrix. As the content of V_2O_5 increases up to 0.6 mol.% in the glass system, a gradual conversion of vanadium ions from V^{5+} state to V^{4+} state is observed, causing the depolymerization in the glass matrix by the transformation of several glass forming units $BO_4 \rightarrow BO_3$ and $WO_4 \rightarrow WO_6$.

Keywords: Glasses; differential scanning calorimetry; electron spin resonance and infrared spectra.

Electron spin resonance (ESR) and Infrared (IR) spectral studies on glasses containing transition metal ions enhance the information about the structural aspects of the glass matrix. The valance states of the transition metal ions as a function of their concentration provide the local environment in the glasses. The transition metal ions like tungsten and vanadium ions are very useful to investigate the characteristics of the glass network because of their modifying and/or networking action in the glass matrix.[1–3] The addition of lithium oxide into the borate glass network is accompanied by a change in the boron coordination from three to four or vice versa depending on its concentration, and also on other ingredients of the glass matrix. Lithium-borate glasses play a vital role in science and technology as electrolytic materials, laser hosts, and fiber optic substances.[4–6] The present work concerns the comprehensive study on the ESR and IR spectra of Li_2O–WO_3–B_2O_3 glass system to identify the local structure and valance states of the tungsten and vanadium ions.

Reagent grades of Li_2CO_3, WO_3, H_3BO_3 and V_2O_5 powders were used as raw materials to prepare a particular composition $40Li_2O$–$5WO_3$–$(55–x)B_2O_3$: xV_2O_5 (with x ranging from 0.2 to 0.8, mol.%) by melt-quenching technique. The particulars of the composition of various glass samples and their labels are:

V_2: $40Li_2O$–$5WO_3$–$54.8B_2O_3$: $0.2V_2O_5$
V_4: $40Li_2O$–$5WO_3$–$54.6B_2O_3$: $0.4V_2O_5$
V_6: $40Li_2O$–$5WO_3$–$54.4B_2O_3$: $0.6V_2O_5$
V_8: $40Li_2O$–$5WO_3$–$54.2B_2O_3$: $0.8V_2O_5$

Appropriate amounts of all the chemicals were thoroughly mixed in an agate mortar and melted in a porcelain crucible in the temperature range 950–1050°C in an electric furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then quenched at room temperature in air by pouring it into a brass mould and subsequently annealed from 300°C with a cooling rate of 1°C/min. The amorphous nature of the glasses was checked by X-ray diffraction studies by X-ray diffraction spectrometer (X'pert Graphics & Identify). The density d of the samples was determined to an accuracy of 0.001 by standard Archimedes principle using o-Xylene (99.99% pure) as the buoyant liquid. The glass transition temperature and the glass forming ability of the glasses were determined by differential scanning calorimetry (DSC) traces recorded using Universal V2.6DTA instrument with programmed heating rate of 20°C/min in the temperature range of 30–600°C to an accuracy ±1°C. The ESR spectra of the fine powders of the glass samples were recorded at room

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temperature on ESR spectrometer (JES-FA SERIES) operating in the X-band ($\nu \sim 9.16$ GHz) with modulation frequency of 100 kHz. Infrared transmission spectra of the glass samples in KBr matrices were recorded on JASCO-FTIR-5300 Fourier Transform Infrared Spectrophotometer in the range 400–4000 cm^{-1}.

From the measured values of density d and computed average molecular weight M, various physical parameters such as vanadium ion concentration N_i and mean vanadium ion separation r_i of these glasses are evaluated using the conventional formulae and are presented in Table 1.

Figure 1 shows the differential scanning calorimetry (DSC) traces of the glass samples under investigation. The DSC traces exhibit an endothermic effect due to the glass transition temperature T_g between 449–453°C, followed by an exothermic peak T_c due to crystal growth.[7] From the measured values of T_g and T_c, the parameter $(T_c–T_g)$ gives the information on the stability of the glass against devitrification is evaluated and presented in Table 2. It has been reported that T_g is strictly dependent on the intensity of covalent cross-linking and the coordination of the network formers.[8,9] As V_2O_5 content increases up to 0.6 mol.%, the values of T_g, T_c and $(T_c–T_g)$ are observed to decrease. Therefore, we may predict the coordination changes in the glass matrix by replacement of boron-oxygen bonds by vanadium-oxygen bonds[10,11] due to the modifying action of vanadium ions in V^{4+} state which reduces the cross-link density and mean bond strength.[12] Among all the glasses, the glass sample V_6 (glass containing 0.6 mol.% of V_2O_5), exhibited the lowest value of T_g and $(T_c–T_g)$. This implies glass forming ability is lower for the glass sample V_6.

The ESR spectra recorded at room temperature for Li_2O–WO_3–B_2O_3: V_2O_5 glasses are shown in Fig. 2. The values of $g_\parallel$ and $g_\perp$ (obtained from these spectra) along with the other pertinent data are furnished in Table 3. The spectra have structures that are characteristic of a resolved hyperfine interaction[2,13,14] arising from unpaired $3d^1$ electron with ^{51}V nucleus whose spin is 7/2. At higher temperatures, the molten V_2O_5 dissociates according to $V_2O_5 \leftrightarrow V_2O_{5-p}+(p/2)O_2\uparrow$, where p increases with temperature.[15] Thus, vanadium ions subsist in V^{4+} state ($3d^1$ paramagnetic) along with V^{5+} state ($3d^0$ non-magnetic).

Table 1. Various physical parameters of Li_2O–WO_3–B_2O_3 glasses doped with V_2O_5.

Glass sample	Density d (g/cm^3)	Avg. Mol. weight (M)	Conc. of V^{5+} ions N_i (10^{20}/cm^3)	Inter ionic distance r_i (Å)	Polaron radius r_p (Å)
V_2	2.538	62.060	49.280	5.876	2.368
V_4	2.546	62.284	98.514	4.665	1.880
V_6	2.559	62.511	147.987	4.073	1.642
V_8	2.617	62.734	201.070	3.678	1.482

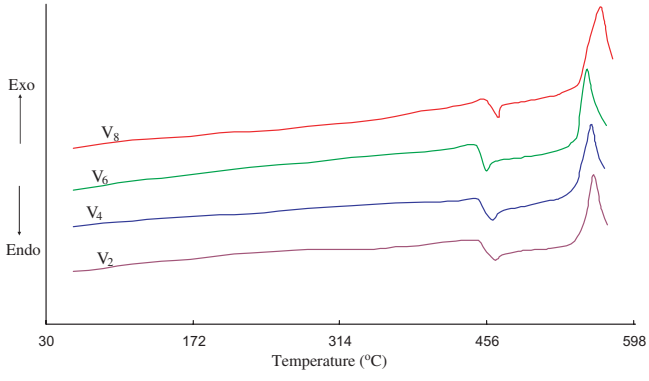

Fig. 1. DSC plots of Li_2O–WO_3–B_2O_3: V_2O_5 glasses.

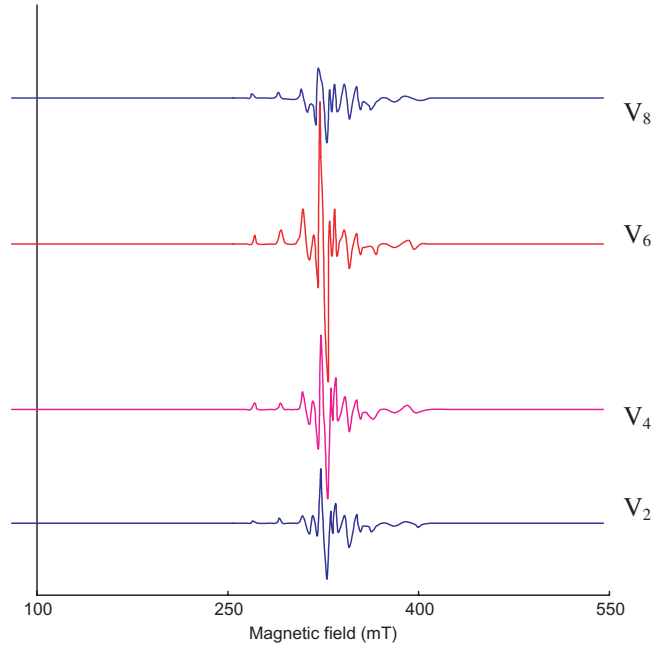

Fig. 2. ESR spectra of Li_2O–WO_3–B_2O_3: V_2O_5 glasses recorded at room temperature.

Table 2. Data on DSC traces of Li_2O–WO_3–B_2O_3: V_2O_5 glasses.

Glass sample	T_g(°C)	T_c(°C)	$(T_c–T_g)$
V_2	449	559	110
V_4	448	557	109
V_6	446	553	107
V_8	453	566	113

Table 3. Data on ESR spectra of Li_2O–WO_3–B_2O_3: V_2O_5 glasses.

Glass sample	$g_\parallel$	$g_\perp$	$\Delta g_\parallel/\Delta g_\perp$
V_2	1.962	1.992	3.913
V_4	1.959	1.991	3.832
V_6	1.956	1.989	3.481
V_8	1.964	1.993	4.118

As the concentration of V_2O_5 is increased up to 0.6 mol.% in the glass system, an increasing degree of resolution and intensity of signal have been observed, since the vanadium ions mostly exist in V^{4+} state and form the ligand environment of VO^{2+} complexes in octahedral coordination with tetragonal distortion[16,17] (ligand field of C_{4v} symmetry) as $g_{\parallel} < g_{\perp} < g_e$. The value of $\Delta g_{\parallel}/\Delta g_{\perp}$ gives the tetragonal nature of the $V^{4+}O_6$ octahedra in the glass matrix. As the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ decreases with increase in the concentration of V_2O_5 up to 0.6 mol.%, a gradual conversion of vanadium ions V^{5+} state to V^{4+} state takes place; these vanadium ions in V^{4+} state in the form of VO^{2+} species are expected to distort the glass network by creating bonding defects and non-bridging oxygens (NBOs). This leads to an increase in the localization of electrons, thereby donor centers in the glass matrix.

When the concentration of V_2O_5 exceeds 0.6 mol.% in the glass system (for the glass sample V_8), suppression in the hyperfine spectra has been observed. Thus, we may expect the conversion of vanadium ions from V^{4+} state to V^{5+} state that take network forming positions with VO_5 trigonal bipyramidal structural units.[18] As $(g_e - g_{\perp})$ decreases and simultaneously $\Delta g_{\parallel}/\Delta g_{\perp}$ increases when $V_2O_5 > 0.6$ mol.%, the strength of V=O bond in isolated VO_5 polyhedra increases. In other words, the covalent bonding between the vanadium ions and the surrounding ligands increases as the tetragonal nature of the $V^{4+}O_6$ octahedra increases.[19] Thus, when $V_2O_5 > 0.6$ mol.%, the decrease in redox ratio (V^{4+}/V^{5+}) takes place by the hopping of mobile electrons from V^{4+} sites to V^{5+} sites that may decrease degree of disorder in the glass network. Thus, one may presume the electronic conduction in these glasses by means of super exchange of mobile electron along V^{4+}–O–V^{5+} bond.[20]

The ESR studies on the glasses containing two types of transition metal ions undergo the dipole-dipole type interactions between the redox pairs like {V^{4+}–V^{5+} and Mo^{5+}–Mo^{6+}}[12,19] and {V^{4+}–V^{5+} and Mn^{2+}–Mn^{3+}}[21]; such interactions are responsible to the derivation of asymmetric ESR signal and/or superposition of the signals. However, no signal is observed in the ESR spectra of the present glasses (containing the two types of redox pairs V^{4+}–V^{5+} and W^{5+}–W^{6+}) due to the tungsten ions in W^{5+} state, and the signal due to VO^{2+} species is unaffected and quite symmetric; since the tungsten ions may exist in the W^{6+} state and take network forming positions with tetrahedral units WO_4. The redox potentials of the two redox pairs V^{5+}–V^{4+} and W^{6+}–W^{5+} are 1 V and −0.03 V respectively, indicating that the V^{4+} should be the more easily reducible species too.[22,23]

Infrared spectra of Li_2O–WO_3–B_2O_3: V_2O_5 glasses are shown in Fig. 3; the various band positions in the spectra and their assignments of functional groups in the glass matrix are presented in Table 4. Intense bands at 3450, 2750, 2340 and 1550 cm^{-1} are obtained due to the stretching vibrations O–H

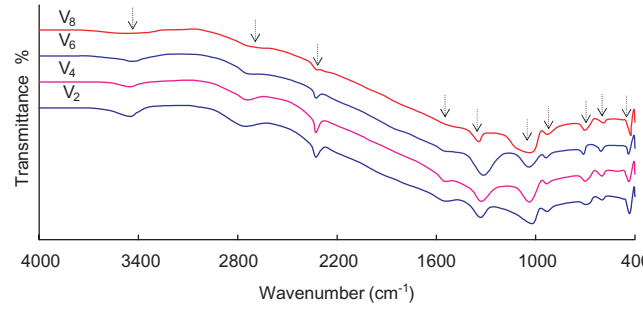

Fig. 3. IR spectra of Li_2O–WO_3–B_2O_3: V_2O_5 glasses.

Table 4. Assignment of absorption band positions (in cm^{-1}) in IR spectra of Li_2O–WO_3–B_2O_3: V_2O_5 glasses.

Glass sample				Assignment
V_2	V_4	V_6	V_8	
1334	1329	1318	1345	B–O stretching vibrations of BO_3 units
1019	1035	1041	1014	V=O stretching vibrations of VO_5 polyhedra/B–O stretching vibrations of BO_4 units
929	934	936	926	ν_1 vibrations of WO_4 units/ν_3 vibrations of WO_6 units
702	704	710	704	Bending vibrations of B–O–B linkages
597	599	605	590	Bending vibrations of V–O–V chains
430	433	437	426	Doubly degenerate bending (ν_4) vibrations of WO_4

bonds of water.[3,10,24] The amplitude of such bands gradually decreases as the concentration of V_2O_5 in the glass system increases. It may be concluded safely that these glasses are hygroscopic at the lower content of V_2O_5.

The spectra have exhibited conventional bands due to BO_3, BO_4 and B–O–B units.[25] With the introduction of V_2O_5 into the glass network, the band at 1025 cm^{-1} identified due to stretching vibrations of V=O bonds in isolated VO_5 polyhedron is observed to merge with the BO_4 units.[26] This suggests the formation of B–O–V chains in the glass network. As the concentration of V_2O_5 increases up to 0.6 mol.%, the decrease in the intensity of BO_4 units and increase in the intensity of BO_3 units is observed; further, the band due to B–O asymmetric stretching vibrations of tetrahedral BO_4 shift towards higher wave number region. A weak absorption band at about 600 cm^{-1} corresponding to bending vibration of vanadium ions of V–O–V chains is also observed[27] with growing intensity from V_2 to V_6. The addition of WO_3 yields the vibrational bands located in the region ~930 cm^{-1} and ~430 cm^{-1} respectively due to ν_1 (symmetric stretching) and ν_4 (doubly degenerate bending) vibrations of WO_4 groups.[28] In the region of ~930 cm^{-1}, a band ascribed to ν_3 (doubly generate stretching) vibrations of WO_6 units is also expected[29]; this band may be overlapped with the ν_1 (symmetric stretching) vibrations of WO_4 groups. As the concentration of V_2O_5 increases up to

0.6 mol.%, these two bands ν_1 and ν_3 of WO_4 tetrahedron shift towards the high frequencies with reducing intensity. Therefore, from the glass sample V_2 to V_6, the degree of disorder of the glass system increases as the vanadium ions act as network modifiers by transforming $BO_4 \rightarrow BO_3$ and $WO_4 \rightarrow WO_6$.

The presence of larger concentration of Li_2O in the glass system, executes the Li^+ ions such that they act as modifiers[30] similar to V^{4+} ions and W^{5+} ions (if any), generate bonding defects and NBOs by breaking the B–O–B, B–O–V, B–O–W bonds etc., and depolymerize the glass matrix. The DSC studies also give support for this analysis as T_g deceases from the glass sample V_2 to V_6 because of three factors: (i) the decreasing of coordination of boron from four fold to three fold,[31] (ii) the substitution of strong B-O bonds (3 dimensional) of BO_4 and/or BO_3 units by weak V–O–V chains (2 dimensional),[32] and (iii) modifying action of Li^+, V^{4+}, W^{5+} and octahedron of WO_6 which create bonding defects and are responsible for the growing degree of disorder in the glass matrix. When $V_2O_5 > 0.6$ mol.% in the glass system (for the glass sample V_8), the intensity of BO_3 units decreases with simultaneous increase in BO_4 units ($BO_3 \rightarrow BO_4$). Additionally, the intensity of the bands $\sim$930 cm^{-1}, 1025 cm^{-1} increases by shifting to lower wavelength number side. The tungsten ions take network forming positions with the transformations $WO_6 \rightarrow WO_4$. The presence of borate and tungsten tetrahedral units facilitate the formation of homogeneous solid solution of the glass system.

In summary, the results on the study of Li_2O–WO_3–B_2O_3: V_2O_5 glasses are as follows:

(1) The glass forming ability gradually decreases on increasing concentration of V_2O_5 up to 0.6 mol.% in the glass system. The glass forming ability is lower for the glass sample V_6.
(2) ESR spectra indicates that the vanadium ions exist in two stable states viz., V^{4+} and V^{5+}; the tungsten ions mostly exist in W^{6+} state in the glass system. When $V_2O_5 <$ 0.6 mol.% in the glass system, the vanadium ions mostly exist in V^{4+} state that act as network modifiers; when $V_2O_5 > 0.6$ mol.%, the vanadium ions mostly exist in the V^{5+} state, acting as network formers in the glass matrix.
(3) The IR spectra show that the transformation of several glass forming units $BO_4 \rightarrow BO_3$ and $WO_4 \rightarrow WO_6$ from the glass sample V_2 to V_6.

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