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STRUCTURAL STUDIES OF V_2O_5 DOPED Li_2CO_3-ZnO-Al_2O_3-H_3BO_3 GLASSES

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ABSTRACT

In this study, to synthesize various glasses for the system (20-x) Li_2CO_3-10 ZnO -5Al_2O_3 - 65H_3BO_3 – xV_2O_5 with (x = 0, 0.2, 0.4, 0.6 and 0.8 mol%) the melt-quenching technique was used. Fourier transform infrared (FT-IR), Electron paramagnetic resonance (EPR) and Ultraviolet-visible (UV-Vis) spectroscopy characterizations are analyzed for the prepared glass samples. The FTIR analyses indicated the presence of various bonds comprising V-O-V, B-O-B, and B-OH, which were attributed to different vibrations. The presence of VO^{2+} species was observed in the place of isolated V^{4+} ions in a ligand field of C_{4v} symmetry from the EPR spectra of these glass samples.From UV–Vis absorption spectra two characteristics bands related to $^2B_2 \rightarrow ^2E_1$ and $^2B_2 \rightarrow ^2B_1$ transitions of VO^{2+} are observed in the prepared glass samples.

Keywords: Borate Glasses, FT-IR, EPR and UV-Visible Spectroscopy.

INTRODUCTION

Among all types of glasses, borate glasses have the benefit of having the highest glass-forming ability. B_2O_3 is a strong glass former because of higher bond strength, lower cationic size and smaller heat of fusion[1-2]. Alkali metal ions like Li^+ at low concentrations in the borate glasses containing to pure borate glasses is accredited to convert the triangular borate units into the tetrahedrally coordinated borate units without the creation of NBOs, unlike their silicate counter parts[3]. Lithium is the most significant alkaline nature compound and it improves the thermal stability of the borate glasses [4]. The advantages with ZnO is that it easily makes the coordination with numerous metal ions and substituting ZnO to oxide glasses is also important due to their non-toxicity, non-hygroscopic nature, lower cost of production, higher polarizability. [5-8] The additions of alkalies to these zinc borate(ZnB) glasses are accountable for the non-linear variation of properties. This is really a remarkable change in the properties and has future key applications in optoelectronic and photonic devices.[9-10]

Transition metal ions are incorporated into these glasses in order to characterize their optical behaviors. Glasses containing vanadium oxide (V_2O_5) have become the subject of interest owing to their potential applications. Vanadium Oxide (V_2O_5) can act either as a network former or a network modifier in the same glassy network depending on its concentration [11]. Vanadium (V) can exist in various valence states. The main purpose of this present work is to study the Fourier transform infrared (FT-IR), Electron paramagnetic resonance (EPR) and UV–visible spectra of V_2O_5 doped Zinc Alumino Lithium borate glasses (Zn-Al-Li-B). This work will facilitate us to specify the existing valencies of vanadium ions in such glass system.

EXPERIMENTAL

The present glass samples (20-x) Li_2CO_3-10 ZnO -5Al_2O_3 - 65H_3BO_3 - xV_2O_5 with x = 0, 0.2, 0.4, 0.6 and 0.8 mol% were prepared by the melt quenching method. AnalaR grade chemicals Li_2CO_3, ZnO, Al_2O_3, H_3BO_3 and V_2O_5 were taken as preparatory materials and required amounts were weighed in a

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digital balance. The powders were mixed thoroughly to obtain a fine powder in an agate mortar and pestle. The mixtures were taken in a porcelain crucible and placed in an electrically heated furnace. The ingredients were heated at about 950°C for 40 min to get homogeneous melt. The melts were rapidly quenched on a brass plate by pressing it with another brass plate. The glasses so obtained were annealed at temperature 300°C below the glass transition temperature to relieve mechanical strains.

The Fourier Transform Infrared spectra of V_2O_5 doped zinc alumino lithium borate glasses were recorded on SHIMADZU 8201 PC FT-IR Spectrophotometer in the range 4000-400 cm^{-1} using KBr pellets. Electron Paramagnetic Resonance spectra were made at room temperature through BRUKER-ER073 series of EPR spectrometer which operates in the X-band frequency (9.4 GHz) at 100 kHz field modulation. The magnetic field was scanned from 0 to 800 mT and the microwave power used was 1mW. The UV-Vis absorption spectra of the present glasses were recorded using JASCO model V-670 UV-Vis-NIR spectrophotometer with a resolution of 0.1 nm at room temperature in the spectral wavelength range covering of 200-900nm.

RESULTS AND DISCUSSION

Figure-1 showed clearly FT-IR spectra of present glass samples. Meanwhile, the literature and are interrelated to various borate glass structures were indicated the assignment of different vibrational modes. Borate glasses are mostly composed of BO_3 triangle and BO_4 pyramidal groups and it depends on the additive to borate glass. A band at 450 cm^{-1} is attributed to vibration of the Zn^{+2} metal cations[12-13]. A band at 480 cm^{-1} is a reliable proof of the presence of vibrations of Li^+ cations against their network sites[14] and band at 710 cm^{-1} is due to the bending of B–O–B linkage[15]. Band at 1040 cm^{-1} may be due to B–O stretching vibration in BO_4 units which present in different borate groups[16]. The observed band at about 1410 cm^{-1} will be attributed to the B–O stretching vibration of BO_3 in pentaborate, pyroborate, orthoborate groups[17]. The absorption bands around 1640-3950 cm^{-1} in the spectra glasses are due to the water, O-H stretching vibrations, or BOH groups[18-19]. Due to the incorporation of moisture during sample preparation for FT-IR spectroscopy, the OH^- groups may be present. Only minor variations in the intensity of some bands are identified with an increment of vanadium concentration by the careful inspection on the FT-IR spectra. The observed results can thus be interpreted by assuming that vanadium concentration causes some limited variations in the bond angles and/or bond lengths within the structural groups.

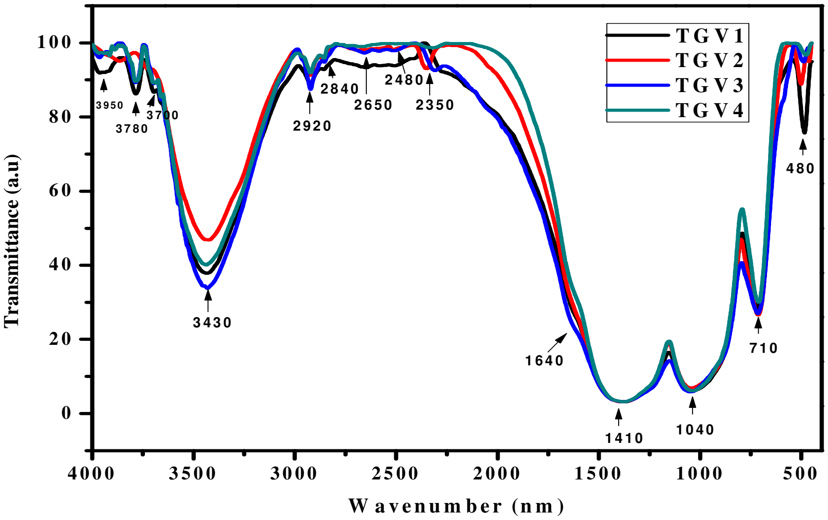

Fig.-1: FT-IR Spectra of Vanadium Doped Zinc Alumino Lithium Borate Glasses

The EPR spectra of VO^{2+} ions in the present glass system clearly showed in Fig.-2. The EPR signal is of three types. (a) Is due to the high concentration of vanadium. If the vanadium content in the compound is high, it gives a broad resonance line. As a result, the hyperfine line from ^{51}V cannot be resolved. The g value for this resonance is less than 2. (b) VO^{2+} ion has s= ½ and I = 7/2. The EPR spectrum shows a hyperfine pattern of eight equidistant lines. In C_{4v} symmetry, two sets of eight lines are expected, whereas in C_{2v} symmetry three sets of eight lines are expected. Further in tetragonal distortion, $g_{\parallel} < g_{\perp} < g_e$ which shows the presence of an unpaired electron in the d_{xy} orbital. This is a characteristic feature of a tetragonally compressed complex. The EPR spectra were analyzed by using the spin-Hamiltonian equation[20], is given below

$$H=\beta[g_{\parallel}H_zS_z+g_{\perp}(H_xS_x+H_yS_y)]+A_{\parallel}S_zI_z+A_{\perp}(S_xI_x+S_yI_y)$$

where β is the Bohr magneton, $g_{\parallel}$ and $g_{\perp}$ are the parallel and perpendicular principal components of the g tensor, $A_{\parallel}$ and $A_{\perp}$ are the parallel and perpendicular principal components of the hyperfine coupling tensors, H_x, H_y and H_z are the components of the magnetic field, S_x, S_y and S_z and I_x, I_y and I_z are the components of the spin operators of the electron and nucleus respectively. The spin-Hamiltonian parameters of VO^{2+} ions were determined and are given in Table-1. The g_{iso} values $[g_{iso} = (g_{\parallel} + 2g_{\perp})/3]$ and A_{iso} values $[A_{iso} = (A_{\parallel} + A_{\perp})/3]$ were also calculated and are presented in Table-1.

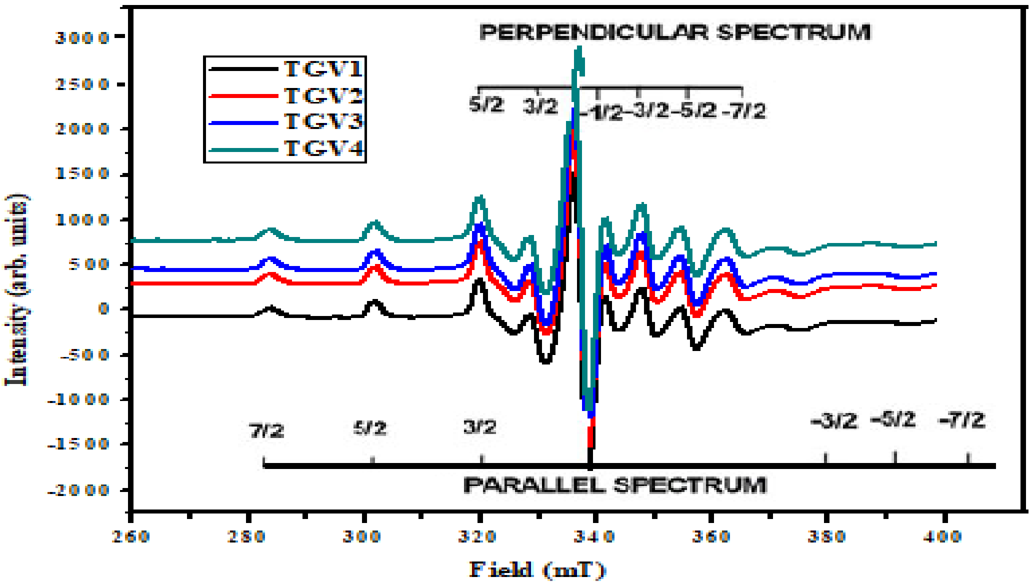

Fig.-2: EPR Spectra of Vanadium Doped Zinc Alumino Lithium Borate Glasses

With the increase of concentration of V_2O_5 concentration the intensity and resolution of EPR spectra increases and it is attributed to increasing in the concentration of V^{4+} ions and also due to structural and micro structural modifications, which produce fluctuations of the degree of deformation or even of the coordination geometry of V^{4+} sites[21-22]. It is also concluded that V^{4+} ions exist as VO^{2+} ions in octahedral coordination with a tetragonal compression with C_{4V} symmetry and that the ground state is d_{xy} orbital from the values presented in Table-1.

Table-1: Spin-Hamiltonian Parameters of Vanadium Doped Zinc Alumino Lithium Borate Glasses

Glass	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	g_{iso}	A_{iso}
TGV1	1.9281	1.9639	178.1951	63.1507	1.9519	80.4486
TGV2	1.9263	1.9632	179.1886	63.2011	1.9509	80.7965
TGV3	1.9252	1.9618	179.1843	63.5308	1.9496	80.9050
TGV4	1.9264	1.9627	179.1250	63.5127	1.9506	80.8792

The Optical absorption spectra of present glasses are shown in Fig.-3. Pure glass did not exhibit any visible bands. The visible absorption bands are observed to be more intensified with the increase of V_2O_5 content.

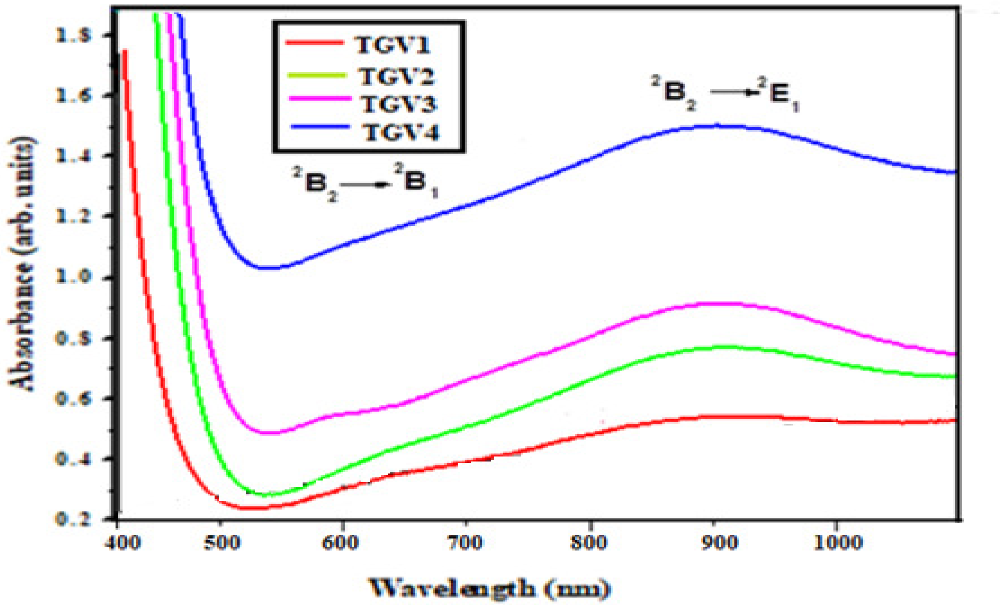

Fig.-3: Optical Absorption Spectra of Vanadium Doped Zinc Alumino Lithium Borate Glasses

The spectra of all glasses exhibited a small broad band centered at about 520 nm and with a resolution of a new broad band centered at about 908 nm, corresponding to $^2B_2 \rightarrow {}^2E_1$ and $^2B_2 \rightarrow {}^2B_1$ transitions of VO^{2+}. The width and peak height of these bands are observed to increases, with gradual increment in the concentration of V_2O_5. Therefore these bands are observed to take a red shift. These absorption peaks are characteristic of V^{4+} ions with a distorted octahedral site. Assignment of the absorption bands are made in the light of energy level scheme for molecular orbitals of the VO^{2+} ions in a ligand field of C_{4v} symmetry.[23]

CONCLUSION

In this study, analyses based on FT-IR, EPR, and UV-Vis spectra were conducted for all of the synthesized glass samples in order to determine their structural and optical properties. FTIR spectra showed that the increment of vanadium oxide caused the breaking of B-O-B bonds. EPR spectra were influenced by the variation of concentration of V_2O_5. It concluded that V^{4+} ions exist as VO^{2+} ions in octahedral coordination with a tetragonal compression with C_{4V} symmetry and that the ground state is d_{xy} orbital.

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