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The Influence of Vanadium Ions in Spectral Properties of $ZnO–Sb_2O_3–B_2O_3$ glasses

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ABSTRACT

Spectroscopic investigations of V_2O_5 doped $ZnO–Sb_2O_3–B_2O_3$glass system was prepared by melt-quenching technique. $ZnO–Sb_2O_3–B_2O_3$ glasses containing varying concentrations of V_2O_5 ranging from 0.1 to 1.0 mol% were prepared, here spectroscopic studies such as Optical absorption, IR and ESR spectra have been carried out as a function of vanadium ion concentration. The optical absorption spectrum of glasses has exhibited two broad absorption bands corresponding to ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions. The appearances of vibration bands in IR spectra are characteristic for B-O-B and V-O-V linkages, showing the network former role of V_2O_5.

Vanadium ions are believed to be present in two possible valence states, namely $V^{4+}$and V^{5+}. Here with increasing presence of V_2O_5 in the glass network, vanadium ions mostly exist in V^{4+}state and occupy modifying positions. Such increase obviously suggests most structural disorder in the network as the concentration of V_2O_5 is increased.

Keywords: *Borate glasses, Optical absorption, IR, ESR, Vanadium ions.*

INTRODUCTION

Transition metal ions are terribly fascinating ions to probe within the glass networks owing to their broad radial distribution of outer d-orbital lepton functions and their sensitive response to the encompassing actions [1]. Structural, optical, and nuclear magnetic resonance studies of V_2O_5-doped lead calcium titanate borosilicate glasses [2]. AC conductivity and polarization phenomenon of $Li_2O–MoO_3–B_2O_3:V_2O_5$ glasses [3]. Effect of vanadium oxide addition on thermo mechanical behaviours of borosilicate glasses: Toward development of high crack resistant glasses for nuclear waste disposal [4]. Optical properties of 3d transition metal ion-doped aluminophosphate glasses [5]. Intense pulsed light sintering of vanadium dioxide nanoparticle films and their optical properties for thermo chromic smart window [6].Among numerous conductive transition metal chemical compound glasses, the salt glasses notice applications in memory, change devices. V_2O_5 is thought to participate within the glass network with VO_5 pyramidal structural units.

many vandate glasses show conductive behaviour with the electrical physical phenomenon of 10^{-3} to 10^{-5} (□-cm)$^{-1}$, that is thought because of lepton hopping between V^{4+} to V^{5+} ions, existing within the glass network. The vanadium ions may additionally exist within the glass network in V^{2+} and V^{3+} states [7]. V_2O_5 is thought to participate within the glass network with VO_5 pyramidical structural units. Additionally, the vanadium oxide structural groups compound structural teams are expected to combine simply in ZnO-Sb_2O_3-B_2O_3 network as a result of a number of the infrared vibration bands of the structural groups of those ions lie identical region as those of SbO_3 and B_2O_3 structural units. The oxide, ZnO, generally could be a glass modifier and enters the glass network by calling it off the B-O-B, Sb-O-B bonds and introduces coordinate defects referred to as suspension bonds at the side of non-bridging oxygen ions. In a very salt network, the addition of a modifier chemical compound encompasses a positive result it will increase the degree of polymerization; the chemical element coordination changes from rhombohedral to tetrahedral, and a few of the fundamental units modification from BO_3 to BO_4 [8]. Metallic element salt glasses, as is that the case for several serious chemical compound containing glasses, have received attention owing to their potential nonlinear optical properties, this can be a consequence of the high polarizability of the serious metal ions and, within the case of Sb^{3+} the presence of a stereochemical active lone try of electrons. The Sb_2O_3–B_2O_3 system has been reportable to make glasses over the complete composition vary [9, 10].

2. EXPERIMENTAL METHODS

The glass samples of compositions used for the current study are ten ZnO – (20-x) Sb_2O_3–$70B_2O_3$: x V_2O_5 wherever x starting from 0 to 1.0 mol %. The glasses utilized in the current measurements are ready by the melting and conclusion techniques [11-13].

The chemical agent grade chemicals ZnO, Sb_2O_3, B_2O_3 and V_2O_5 were totally mixed in a very appropriate proportion and liquefied in a thick-walled platinum crucible within the temperature vary 950–1000 ^{0}C in a PID temperature-controlled chamber for regarding 30 min till a bubble free liquid was shaped. The resultant soften was then poured into a brass mould and after toughened at 300^{0}C with a cooling rate of 1°C/min. The samples ready were ground and optical polished to the scale of 1 cm x 1 cm x 0.2 cm. The amorphous nature of samples was verified by recording XRD mistreatment Rigaku D/Max ULTIMA III X-ray diffractometer with CuK□ radiation (Fig. 1).

The optical absorption spectra of the samples were recorded at temperature within the spectral wavelength vary covering 300–1200 nm to a spectral resolution of 0.1 nm victimisation JASCO Model V-670 UV–VIS–NIR photometer. The ESR spectra of fine powders of the samples were recorded at room temperature on E11Z Varian X–band (ν = 9.5 GHz) ESR mass spectrometer. Infrared transmission spectra were recorded on a Bruker IFS 66 V – IR photometer with a resolution of 0.1 cm^{-1} within the vary 400–2000 cm^{-1}using potassium bromide pellets (300 mg) containing pulverized glass (1.5 mg).

3. RESULTS

From the measured values of density and calculated average mass of the glasses numerous physical parameters like vanadium ion concentration N_i and mean vanadium ion separation R_i in these glasses are evaluated victimization the traditional formulae [14] and are conferred in Table 1.

Fig.2 represents the optical absorption spectra of ZnO-Sb_2O_3 -B_2O_3: V_2O_5 glasses recorded at room temperature within the wavelength region 300-1200 nm. The spectrum of pure glass doesn't exhibit any absorption bands as mentioned before. The spectrum of glass V_1 has exhibited two broad absorption bands at 635nm and 1005 nm such as $^2B_2 \rightarrow {}^2B_1$and $^2B_2 \rightarrow {}^2E$ transitions of VO^{2+} ions; with increase within the concentration of V_2O_5 from 0.1 to 1.0 %, the half width dimension and peak height of those bands are observed to increase. The small print of the optical absorption information of ZnO-Sb_2O_3 -B_2O_3: V_2O_5 glasses are given in Table 2. From the discovered absorption edges, we've got evaluated the optical band gaps (E_o) of those glasses by drawing Urbach plot between (□ $\hbar$ □) $^{1/2}$ and $\hbar$ □as per the equation:

□(□) $\hbar$ □ = C ($\hbar$ □ – E_o)^2. (1)

From the extrapolation of the linear portion of the curves of Fig. 3, the values of optical band gap (E_o) are determined and are conferred in Table 2. As the concentration of vanadium compound will increase the worth of E_o is found to decrease.

The ESR spectra of ZnO-Sb_2O_3-B_2O_3: V_2O_5 glasses are recorded at room temperature and are shown in Fig 4; spectra are discovered to be advanced created from resolved thin elements arising from un paired $3d^1$electron with ^{51}V isotope, because the concentration of V_2O_5 is redoubled, the intensity of signal is found to extend up to 1.0 mol %. The values of $g_\parallel$ and $g_\perp$ are obtained from these spectra. The spectra are discovered to be advanced created from resolved thin elements arising from unpaired$3d^1$electron with ^{51}V isotope whose spin is 7/2. As the concentration of V_2O_5 is increased, associate degree increasing degree of resolution and also the intensity of signal are discovered. The values of $g_\parallel$ and $g_\perp$ (obtained from these spectra) at the side of the opposite pertinent information are stocked with in Table 3.

The infrared transmission spectra of $ZnO\text{-}Sb_2O_3\text{-}B_2O_3$: V_2O_5 glasses (Fig.5) have exhibited two main teams of bands: (i) within the region 1300-1400 cm^{-1}, (ii) within the region 1100-1200 cm^{-1} and another band at regarding 710 cm^{-1}; these bands are known because of the standard stretching relaxation of B-O bond of the symmetrical BO_3 units, vibrations of BO_4 structural units and because of the bending vibrations of B-O-B linkages severally [15, 16]. Within the spectrum of this sample, the ν_1 undulation band of SbO_3 units is appeared at 910 cm^{-1} whereas the ν_3 vibrational band of SbO_3 units is appeared at 620 cm^{-1}. The ν_2 undulation bands united with the band because of bending vibrations of B-O-B linkages and will have shaped a typical vibrational band due to B-O-Sb linkages [17]. Within the region at regarding 1040 cm^{-1} band because of vibrations of isolated V=O teams in the VO_5 symmetrical bipyramids is additionally expected additional an intense optical phenomenon with a meta-center at regarding 780 cm^{-1} associated with V–O–V chains and a weak band at about 600 cm^{-1} resembling bending vibrations of the metal ions [18] have additionally been discovered. The outline of the info on the positions of assorted bands within the IR spectra of $ZnO\text{-}Sb_2O_3\text{-}B_2O_3$: V_2O_5 glasses are bestowed in the Table 4.

4. DISCUSSION

$ZnO–Sb_2O_3–B_2O_3:V_2O_5$ glasses network is an admixture of network formers, intermediate glass formers and modifiers. B_2O_3 may be a robust network former and participate within the glass network with BO_3 and BO_4 structural units. The compound viz., V_2O_5 standard modifiers, enters into the glass network by breaking B-O-B, Sb-O-B linkages; unremarkably the oxygens of those oxides break the native symmetry whereas cations occupy opening positions.

Sb_2O_3 is an inchoate glass network former and as such doesn't form glass however will thus within the presence of modifiers like ZnO, V_2O_5 with triangular SbO_3 pyramids. The coordination of metallic element within the glass network may be viewed as tetrahedrons with the gas at 3 corners (Sb-O distances as a pair of.023, 2.019 and 1.977 Å) and also the lone try of electrons of antimony (Sb^{3+}) at the fourth corner with the coordination number of Sb as 3.0. Sharing corners to create double infinite chains with the lone pairs mentioning from the chains joins the coordination polyhedral. These chains are command along by weak secondary Sb-O bonds with lengths larger than a pair of.6 Å. The third oxygen in every SbO_3 units should participate in linkages of kind Sb-O-B [19-22].

Vanadium ions are expected to exist in V^{5+} states within the $ZnO–Sb_2O_3–B_2O_3$ glass network. However, throughout the melting of the glasses at higher temperatures there is every possibility for the following redox equilibrium to take place:

$$2\,V^{5+} + O^{2-} \rightarrow 2\,V^{4+} + \frac{1}{2}\,O_2 \uparrow;$$

the V^{5+} ions participate network typing positions with VO_5 rhombohedral bipyramidal structural units wherever because the V^{4+} ions form VO^{2+} complexes, could act as modifiers and warp the glass network. With increase within the concentration of V_2O_5 up to 1.0 mol %, the manifestation of those results is that, with the increasing presence of V_2O_5 within the glass network, atomic number vanadium ions largely exist in V^{4+} state, occupy modifying positions. Such increase clearly suggests a high degree of disorder within the internet work of glass V_{10}.

The optical spectrum of V_2O_5 doped glass has exhibited two broad absorption bands at regarding 620 nm and 830 nm due to$^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2E$ transitions of VO^{2+} ions severally [23]; there's a clear shifting of the meta centers of those two bands towards lower wavelength aspect with a gradual hike within the intensity with increase in the concentration of V_2O_5. V^{4+} particle belongs to d^1 configuration with ^2D as the ground state. The presence of pure octahedral crystal field, ^2Dstate splits into $^2T_2$ and ^2E, whereas Associate in Nursing octahedral field with polygonal shape distortion any splits the $^2T_2$ level into ^2E and $^2B_2$; and ^2E level splits into $^2A_1$ and $^2B_1$. Among these, the $^2B_2$ are going to be the bottom state. So for the vanadyl particles we will expect three bands on the premise of energy theme for molecular orbital of VO^{2+} ion in a very matter field of C_{4v} symmetry provided by Bullhausen and grey [23] adore the transitions $^2B_2 \rightarrow ^2B_1$ (□ □), $^2B_2 \rightarrow ^2E$ □ □ □ □ □ □ □ and □ $^2B_2 \rightarrow ^2A_1$. However, within the spectra of the current glasses, solely the primary two bands are ascertained. The largest intensity and the half width of these bands for glass V_{10}, indicates the most important concentration of VO^{2+} (vanadyl) ions during this glass. Such VO^{2+} ions are expected to participate within the depolymerisation of the glass network, produce additional bonding defects and non-bridging oxygens (NBOs). As the concentration of atomic number vanadium compound will increase, the upper is that the concentration of NBOs within the glass matrix. This ends up in a rise within the degree of localization of electrons there by increasing the donor centers in the glass matrix. The presence of larger concentration of those donor canters decreases the optical band gap and shifts the absorption edge towards higher wavelength aspect as ascertained.

The well-resolved thin structure of the ESR spectra obtained for the glasses containing V_2O_5 (upto1.0 mol%), could be a typical of isolated V^{4+} ions in a very matter field of C_{4v} symmetry that are gift as VO^{2+} species. The variations of the resolution additionally the line dimension of ESR signal are clearly thanks to the variation within the concentration of V^{4+} ions and also due to structural and small structural modifications, which might turn out fluctuations of the degree of distortion or perhaps of the coordination pure mathematics of V^{4+} sites. The spectra indicate that VO^{2+} ions exist in the glass network in an octahedral site symmetry with tetragonal compression since $g_{\|}$ □ g□ □ □ge [24] (Table 3), the broadening of ESR signal with the con

Concentration of V_2O_5 is seemingly thanks to the presence of the larger concentration of V^{4+} ions and should even be due to exchange coupling between V^{3+} ions (if any) and V^{4+} ions [25]. The poor resolution of the ESR signal with low intensity within the spectra of the glasses containing low concentration of V_2O_5 additionally may be due to the presence of low concentration of V^{4+} ions or larger concentration of magnetic force V^{5+} ions that take network-forming positions and also due to magnetism exchange interaction existing between V^{4+} ions (since V^{5+} ion may be a diamagnetic and there's no proof for the existence of sizeable amounts of V^{3+} and V^{2+} ions) which can scale back the apparent concentration of V^{4+} ions.

Further, within the IR spectrum with the presence of Sb_2O_3 in the glass matrix, there's an occasion for the cross linking of a district of SbO_3 units with BO_4 units to make Sb-O-B bonds within the glass network. The presence of the common meta center of BO_4vibrational band and □$_1$ vibrational band of SbO_3 units within the IR spectra of the glass supports such a conclusion. When the concentration of Sb_2O_3 is magnified additional the intensity of common B-O-Sb vibrational band reduced step by step and resolved into separate bands; such an observation indicates that there's an increasing breaking of B-O-Sb linkages thanks to the increase within the modifying action of V_2O_5 glass network. The ascertained increase within the intensity of the band thanks to BO_3 structural units at the expense of band due to BO_4 units with the rise in the concentration of Sb_2O_3in the glass matrix conjointly supports such a read purpose.

5. CONCLUSIONS

Finally, the quantitative investigation on spectroscopic properties viz., optical absorption, ESR spectra and Infrared spectra of $ZnO–Sb_2O_3–B_2O_3$ glasses containing completely different concentrations of V_2O_5 were analyzed. The results indicate with increase within the concentration of V_2O_5 up to 1.0 mol %, there is an increasing presence of V_2O_5 within the glass network, vanadium ions largely exist in V^{4+} state and occupy modifying positions. Such increase clearly suggests a high degree of disorder within the glass network

Table 1

Summary of data on various physical parameters of $ZnO\text{-}Sb_2O_3\text{-}B_2O_3$: V_2O_5 glasses

Glass	Density d (g/cm^3)	Avg.Mol. weight($\overline{M}$)	Conc.of V^{5+} ions Ni (10^{20}/cm^3)	Inter ionic distance r_i(A^o)	Polaron radius r_p(A^o)
V_0	4.0513	140.96	-	-	-
V_2	4.1175	140.90	3.02	6.81	2.82
V_4	4.1974	140.82	4.91	5.19	2.43
V_6	4.2685	140.71	6.42	4.82	2.09
V_8	4.3860	140.63	8.46	4.03	1.90
V_{10}	4.5081	140.52	10.84	3.91	1.71

Table 2

Summary of data on optical absorption bands of ZnO-Sb_2O_3 -B_2O_3: V_2O_5 glasses

Glass	Cut-off wavelength (nm)	$^2B_2 \rightarrow ^2B_1$ (nm)	$^2B_2 \rightarrow 2_E$ (nm)	Optical band gap E_0 (eV)
V_2	451	615	982	2.74
V_4	460	622	993	2.69
V_6	472	625	998	2.62
V_8	485	630	1002	2.55
V_{10}	496	638	1007	2.5

Table 3

Summary of data on ESR spectra of ZnO-Sb_2O_3 -B_2O_3: V_2O_5 glasses

Glass	$g_\parallel$	$g_\perp$
V_2	1.90	1.991
V_4	1.912	1.992
V_6	1.914	1.993
V_8	1.917	1.995
V_{10}	1.919	1.997

Table 4

Summary of data on IR spectra of ZnO-Sb_2O_3 -B_2O_3: V_2O_5 glasses

Glass	BO_3 units /VO_5(cm^{-1})	BO_4 units (cm^{-1})	B-O-B / V-O-V (cm^{-1})	$SbO_3 \nu_3$ (cm^{-1})	$SbO_3 \nu_1$ (cm^{-1})
V_2	1384	1140	790	910	620
V_4	1373	1153	781	913	623
V_6	1361	1161	769	918	629
V_8	1352	1172	757	923	631
V_{10}	1340	1180	745	927	638

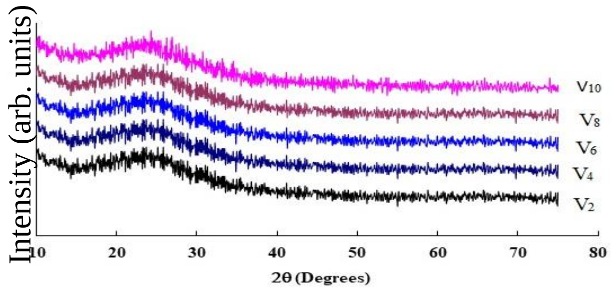


Fig.1. XRD pattern of ZnO–Sb_2O_3–B_2O_3: V_2O_5 glasses

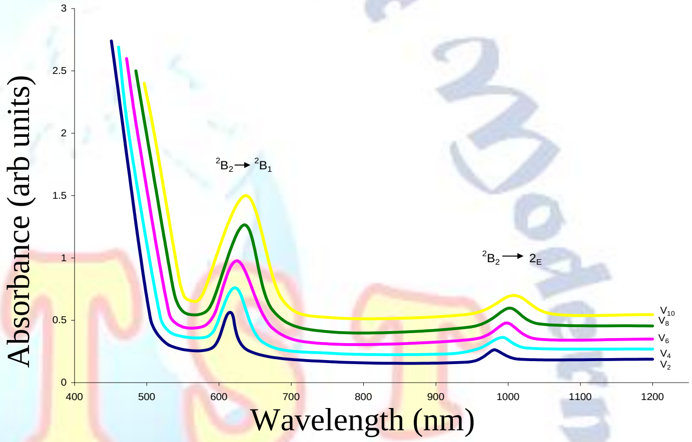
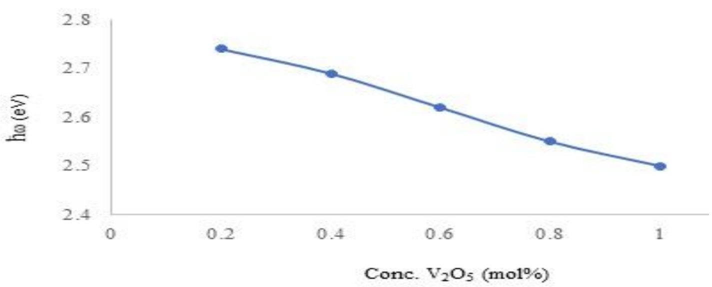


Fig. 2. Optical absorption spectra of ZnO–Sb_2O_3–B_2O_3: V_2O_5 glasses



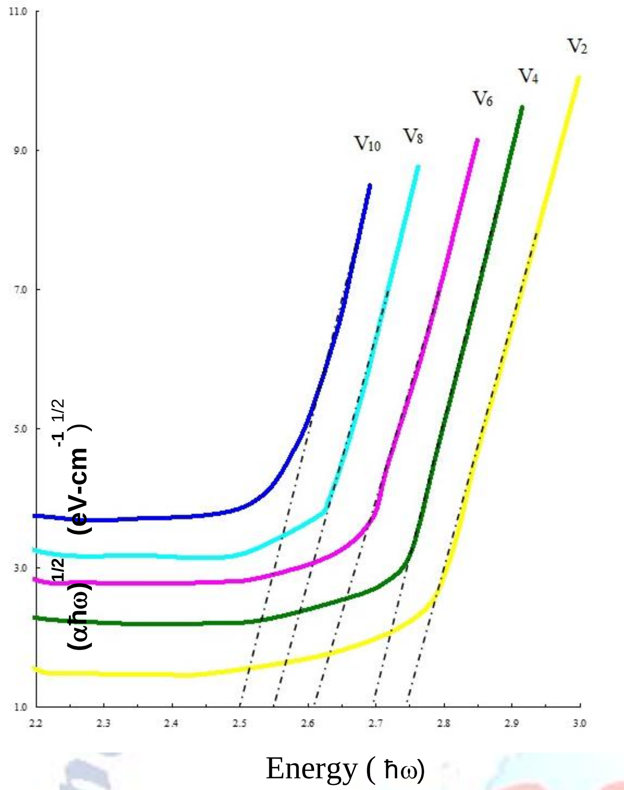
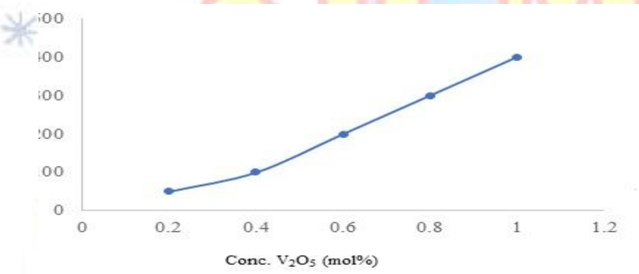


Fig 3. Urbach plots of $ZnO–Sb_2O_3–B_2O_3$: V_2O_5 glasses. Inset shows the variation of optical band gap with concentration of V_2O_5



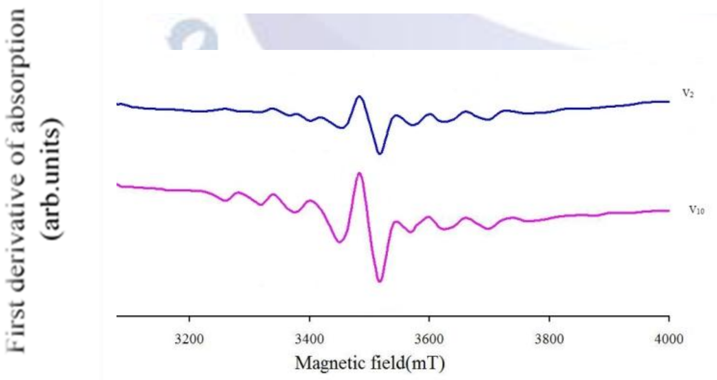


Fig .4. ESR spectra of $ZnO–Sb_2O_3–B_2O_3$: V_2O_5 glasses. Inset represents the variation of intensity with concentration of V_2O_5

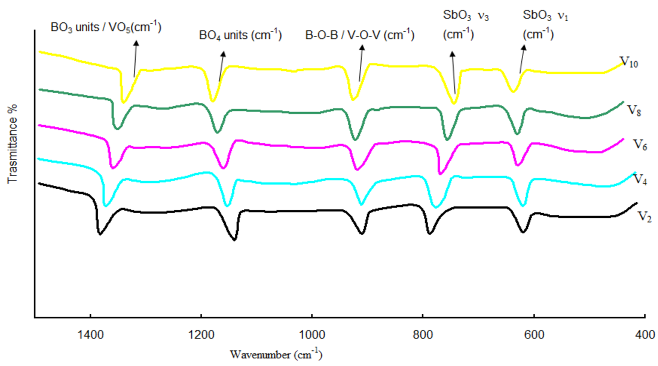


Fig. 5. IR spectra of $ZnO–Sb_2O_3–B_2O_3$: V_2O_5 glasses.

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