FTIR and EPR studies of Vanadium ion doped in ZnO-Li2O-Na2O-K2O-B2O3 Glasses

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Abstract— EPR studies were made on xZnO-10Li2O-10Na2O-10K2O- (68-x) B2O3-2V2O5 glass system in which VO2+ is acting as paramagnetic probe while FTIR studies are conducted on Vanadium free glass samples of the composition xZnO-10Li2O-10Na2O-10K2O-(70-x) B2O3 . The glass samples are prepared by melt quenching method and the amorphous nature of the glass samples was confirmed by X-Ray diffraction studies. From the FTIR studies it was observed that the glass is made up of [BO3] and [BO4] units. From the EPR spectra the spin-Hamiltonian parameters were evaluated. It was observed that the vanadyl (V4+) ions exist as VO2+ ions in octahedral coordination with tetragonal compression and belong to C4v symmetry, with dxy ground state. The measure of tetragonality $\Delta E_{\parallel}/\Delta E_{\perp}$ vary in non-linear manner with glass composition. The covalency rates were estimated. The number of spins participating in the resonance (N) and susceptibility (χ) were evaluated.

Index Terms— FTIR, EPR, Borate Glasses, VO2+ ions, Paranagnetic susceptibility

1 INTRODUCTION

Glasses containing alkaline earth oxides along with ZnO, TeO2, PbO, Bi2O3 etc as glass modifiers are having the applications in the field of optical communications (optical fibers), photonic devices, ray absorbers, optical filters, laser hosts etc [1],[2],[3]. Glasses containing heavy metal oxides exhibits good non-linear optical properties and good chemical durability [3],[4]. Glasses doped with transition metal (TM) ions have attracted a great deal of attention because of their potential application in the development of new solid-state lasers, solar energy converters. Borate glasses are particularly interesting model systems as they exhibit a variety of structural changes with allali oxide borate glasses. Hence an attempt is made to study the FTIR and EPR studies on zinc oxide contained ternary alkali oxide glasses. In the present paper we reportinf FTIR and EPR studies on ternary alkali oxide glasses containing ZnO using VO2+ as spin probe.

2 EXPERIMENTAL

The glass samples in the present investigation are prepared with melt quenching method. The starting materials were analar grades boric acid (H3BO3), sodium carbonate (Na2CO3), lithium carbonate (Li2CO3), potassium carbonate (K2CO3), zinc oxide (ZnO), and vanadium pent oxide (V2O5). The materials were mixed in appropriate mole percent to get the required composition. Each batch was melted in a porcelain crucible around 30-40 minutes in an electrical furnace which is maintained at 1273 K. To obtain the homogeneity the melt was shaken frequently. The glasses were annealed for 24 hours at the same temperature to relieve the mechanical stress. The prepared glass samples are stored in paraffin liquid to avoid any degradation due to moisture. X-Ray diffractometer was used to confirm the glassy nature of the samples. KBr pellet method was used to record the FTIR spectra. FTIR spectra of xZnO-10Li2O-10Na2O-10K2O-(70-x) B2O3 (x = 0,2,4,6&8 mole%) samples recorded on Bruker optics (Tensor 27). The EPR spectra of xZnO-10Li2O-10Na2O-10K2O-(68-x) B2O3-2V2O5 (x = 0,2,4,6&8 mole%) the powdered glass sample (100 mg was taken in a quartz tube) in the present investigation were recorded on a JEOL (FE-1X) X-band EPR spectrometer, with 100 kHz field modulation at room temperature. The magnetic field was scanned from 220mT to 420mT. Table 1 shows the glass compositions prepared for EPR.

TABLE 1: COMPOSITION OF $xZnO\text{-}10Li_2O\text{-}10Na2O\text{-}10K_2O\text{-}(68\text{-}x)\ B_2O_3\text{-}2V_2O_5$ GLASS SYSTEM.

GLASS	COMPOSITION
ZLNKBV1	0ZnO-10Li2O-10Na2O-10K2O-68B2O3-2V2O5
ZLNKBV2	2ZnO-10Li2O-10 Na2O -10K2O-66B2O3-2V2O5
ZLNKBV3	4ZnO-10Li2O-10 Na2O -10K2O-64B2O3-2V2O5
ZLNKBV4	6ZnO-10Li2O-10 Na2O -10K2O-62B2O3-2V2O5
ZLNKBV5	8ZnO-10Li2O-10 Na2O -10K2O-60)B2O3-2V2O5

3 RESULTS AND DISCUSSIONS

3.1 Ftir spectra

The Infrared spectra of the glasses exhibited absorption peaks. The peaks are sharp, medium weak and broad. The vibrational mode of the borate network seems to be mainly active in three infrared regions which are similar to those reported by [5]. Figure 1 shows the FTIR spectra of xZnO-10Li2O-10Na2O-10K2O-(70-x) B2O3 (where x = 0, 2, 4, 6 & 8 mole %) glass system. The first group of bands which occur at 1200-1600 cm-1 are due to the asymmetric stretching relaxations of the B-O bond of trigonal BO3 units. The second group lying between 800-1200 cm-1 is due to the B-O bond stretching of the tetragonal BO4 units and the third group is

observed around 700 cm-1 and it is due to the bending of B-O-B linkages in the borate network. The shallow broad band around 3446 cm-1 can be assigned to hydroxyl group (-OH) or water group [6]. A shoulder around 1645 cm-1 observed in x = 0, 2,& 4 mole % ZnO glass sample may be due to OH bending mode of vibrations. Both these peaks may be due to the hygroscopic nature of grounded glass powdered sample. As the ZnO content is increased i.e. x= 6 and 8mole% the bands around 1645cm-1 are disappeared. Which indicates the absence of OH bending modes. A deep band around 1360-1240 cm-1 are assigned to the stretching vibrations B-O of trigonal (BO3)3- units in metaborate, pyroborate and orthoborates [7],[8]. A prominent shallow broad band around 990cm-1 are observed in x = 4,6 & 8 mole % of ZnO while in x= 0&2 mole % of ZnO this band is converted into two small shoulders appearing around 925 & 1024 cm-1. These bands are assigned to the stretching vibrations of BO4 tetrahedra [9].The strong band around 700 cm-1 are due to bending vibrations of B-O-B linkages of BO3 units.The small shoulders appearing around 530 & 450 cm-1 are due to the vibrations of Zn present in the glass system. The assignments are in good agreement with reported values of several workers [10].

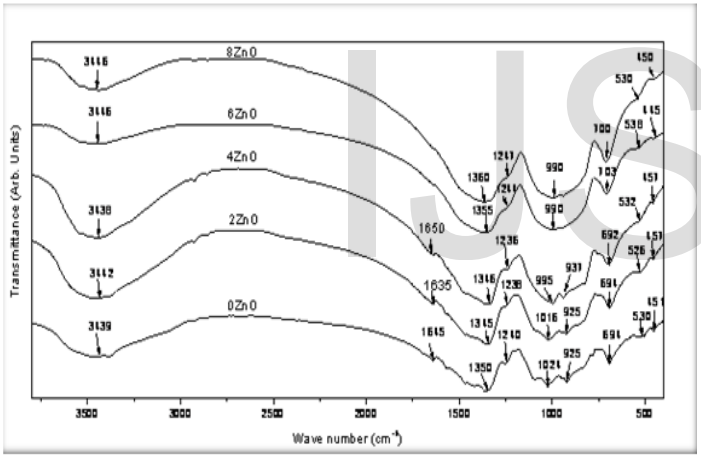

Fig 1. FTIR spectra of $xZnO\text{-}10Li_2O\text{-}10Na_2O\text{-}10K_2O\text{-}(70\text{-}x)\ B_2O_3$ (where x = 0, 2, 4, 6 & 8 mole %) glass system

3.2 EPR spectra of VO 2+ ions

The EPR spectra of VO2+ ions in xZnO-10Li2O-10Na2O-10K2O-(68-x) B2O3-2V2O5 glass system (x = 0,2,4,6 & 8 mole %) are shown in Figure 2. From this figure it is noticed that all the glass samples have similar spectral features. The spectra have structures which are characteristic of hyperfine interaction arising between an un-paired electron with the 51V nucleus whose spin is 7/2 and which is present in 99.75% abundance. The spectra consisted of two sets of hyperfine lines corresponding to the parallel and perpendicular components. The EPR spectra were analyzed by using spin –Hamiltonian assuming that the vanadium is present as vanadyl ion in ligand field of C4v symmetry. The solution of spin- Hamiltonian, for the parallel and perpendicular orientations are given by the following equations respectively.

$$H_{\parallel} = H_{\parallel}(0) - mA_{\parallel} - \left\{\left(\frac{63}{4}\right) - m^2\right\}\frac{}{2} \quad (1)$$

$$H_{\perp} = H_{\perp}(0) - mA_{\perp} - \left\{\left(\frac{63}{4}\right) - m^2\right\}\frac{A}{2} \quad (2)$$

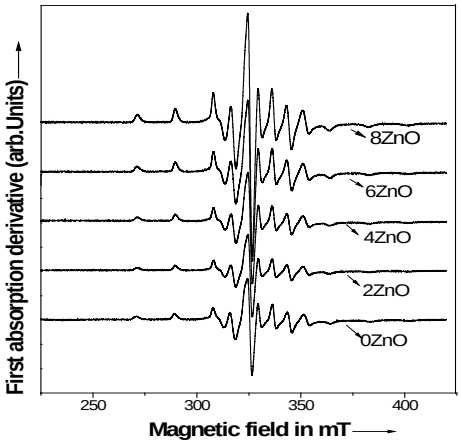

Fig 2. EPR spectra of xZnO-10Li2O-10Na2O-10K2O-(68-x) B2O3-2V2O5 glass system (where x = 0,2,4,6 & 8 mole %)

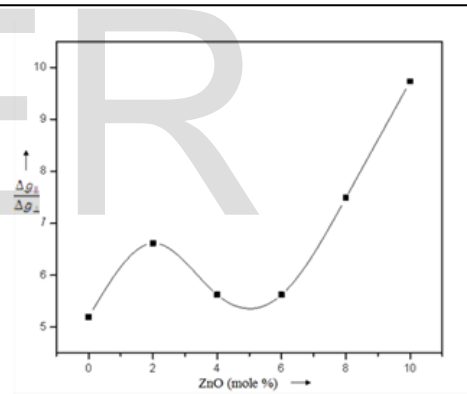

Fig3. Variation of $\frac{\Delta g_{\parallel}}{\Delta g_{\perp}}$ with ZnO content in xZnO-10Li2O-10Na2O-10K2O-(68-x) B2O3-2V2O5 glass system where x = 0,2,4,6,8 & 10 mole %)

where m is the magnetic quantum number of the vanadium nucleus having values $\pm\frac{}{}, \pm\frac{}{}, \pm\frac{}{}$ and ; $H_{\parallel}(0) = h\nu/$ and $H_{\perp}(0) = h\nu/$ where 'h' planks constant, is the frequency and is Bohr magneton. The spin-Hamiltonian parameters are calculated and are presented in Table 2. The crystal field of V4+ ions in glasses are described by either three fold or four fold symmetries [11]. The measured values of and critically depends on the local symmetry of this field. Generally V4+ ion is found in six fold co-ordination in vanadyl complexes, its local symmetry is distorted octahedron of oxygen ions, i.e. the length of the bond between vanadium and vanadyl oxygen is short compared with those of the other bonds. An octahedral site with tetragonal compression would give $g_{\parallel} < g_{\perp} <$ and > [12].The and values obtained in the present work agree with the relationship. It is therefore confirmed that the vanadyl ions in the present glasses exist as VO2+ molecular ions

in an octahedral co-ordination with tetragonal compression. The VO2+ion has C4v symmetry and the ground state of 3d1 is dxy. The values of $(\Delta g_{\parallel}/\Delta_{|}$ which measure the tetragonality [where $\Delta g_{\parallel} = g_e -$ and $\Delta g_{\perp} = g_e -$,] are calculated for the xZnO-10Li2O-10Na2O-10K2O-(68-x)B2O3-2V2O5 glass system and are presented in Table 2. It is observed that the values of $(\Delta g_{\parallel}/\Delta_{\perp}$ have shown a non-linear variation with the ZnO content. As the ZnO content is varied it is observed that the tetragonal distortion varies in a non-linear manner around the VO2+ ion i.e. the deviation from octahedral symmetry varies. The variation of $(\Delta g_{\parallel}/\Delta_{|}$ with the ZnO content is shown in the Figure 3. As the ZnO content is varied it is observed that the tetragonal distortion varies in a non-linear manner around the VO2+ ion i.e the deviation from octahedral symmetry varies. The variation of and values may be due to the change in the environment of V4+, i.e. in the ligand field at the site of V4+, which may be attributed to the structural changes in the glass. Thus the incorporation of ZnO in the glass will influence the field at the site of V4+, which in turn will reflect in the non-linear variation of the spin-Hamiltonian parameters as observed in the present case. The EPR data can be used to calculate the paramagnetic susceptibility of the sample using the formula.

TABLE 2: SPIN-HAMILTONIAN PARAMETERS, NUMBER OF SPINS (N) PER KG AND SUSCEPTIBILITY ( ) OF VO^{2+} IONS IN XZNO-10LI_2O-10NA_2O-10K_2O-(68-X) B_2O_3-2V_2O_5. (WHERE X = 0,2,4,6,8 & 10 MOLE %)

Glass system	$g_{\parallel}$	$g_{\perp}$	$\lvert A_{\parallel}\rvert$ $(\times 10^{-4} cm^{-1})$	$\lvert A_{\perp}\rvert$ $(\times 10^{-4} cm^{-1})$	N $(\times 10^{18} Kg^{-1})$	χ $(\times 10^{-9} m^3 Kg^{-1})$
ZLNKBV1	1.954	1.993	185	69	0.49	0.49
ZLNKBV2	1.954	1.995	185	73	7.35	7.41
ZLNKBV3	1.950	1.993	185	77	0.19	0.19
ZLNKBV4	1.950	1.993	181	77	1.71	1.72
ZLNKBV5	1.945	1.995	185	69	4.99	5.02

$$\chi = \frac{[\text{illegible}]}{[\text{illegible}]} \quad (3)$$

where N is the number of spins per m3, J is the total angular momentum quantum number, β is the Bohr magneton, KB is the Boltzman constant, T is the absolute temperature and 'g' $[g = g_{\parallel} + 2g_{\perp}/3]$ is the Lande g factor. The values of N and g are taken from EPR data.

The number of spins (N) participating in resonance and the paramagnetic susceptibility (χ) were calculated and are given in Table 3. N and χ values vary in a non-linear manner with ZnO content. The spin-Hamiltonian parameters and chemical bonding parameters are calculated [13] using the following equations

$$\Delta g_{\parallel} = g_e - g_{\parallel} = \frac{[\text{illegible}]}{[\text{illegible}]} \quad (4)$$

$$\Delta g_{\perp} = g_e - g_{\perp} = \frac{[\text{illegible}]}{[\text{illegible}]} \quad (5)$$

$$A_{\parallel} = -P\left|\beta^2\left(\frac{[\text{illegible}]}{[\text{illegible}]} + K\right) + \Delta g_{\parallel} + \left(\frac{[\text{illegible}]}{[\text{illegible}]}\right)\Delta g_{\perp}\right| \quad (6)$$

$$A_{\perp} = P\left|\beta^2\left(\frac{[\text{illegible}]}{[\text{illegible}]} - K\right) - \left(\frac{[\text{illegible}]}{[\text{illegible}]}\right)\Delta g_{\perp}\right| \quad (7)$$

In the above equations is a measure of the out-of-plane π bonding with the equatorial ligand and it is assumed to be unity in the calculations [13]. The dipolar hyperfine coupling parameter P, is proportional to the expectation value of in the 'd' orbital of free VO2+ ion which is given by $P = 2\gamma\beta\beta_N\langle r$, where is gyromagnetic ratio, the Bohr magneton, the nuclear magneton, K the contribution of the hyperfine coupling due to the isotropic Fermi contact interaction which represents the amount of unpaired electron density at the vanadium nucleus and and represents the $^2B_{2g} \rightarrow {}^2E_g$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ transitions respectively.

TABLE 3: TETRAGONALITY, COVALENCY RATES, P AND K VALUES OF V^{4+} IONS IN $xZnO\text{-}10Li_2O\text{-}10Na_2O\text{-}10K_2O\text{-}(68\text{-}x)\ B_2O_3\text{-}2V_2O_5$ GLASS SYSTEM. (WHERE X = 0,2,4,6,8 & 10 MOLE %)

Glass system	$\Delta g_{\parallel}/\Delta g_{\perp}$	$\lvert A_{\parallel}^{'}\rvert$ $(\times 10^{-4}cm^{-1})$	$\lvert A_{\perp}^{'}\rvert$ $(\times 10^{-4}cm^{-1})$	$(1-\alpha^2)$	$(1-\nu^2)$	P $(\times 10^{-4}cm^{-1})$	K
ZLNKBV1	5.19	76	40	0.612	0.766	142	0.765
ZLNKBV2	6.61	73	39	0.612	0.816	137	0.812
ZLNKBV3	5.62	71	37	0.580	0.766	133	0.855
ZLNKBV4	5.62	68	36	0.580	0.766	128	0.877
ZLNKBV5	7.48	75	40	0.540	0.816	144	0.761

4 CONCLUSIONS

From the infrared spectra it was observed that the bands in the region of 450 and 550 cm-1 which are due to vibrations of Zn present in all the glasses studied. The strong band around 700 cm-1 is due to the bending vibrations of B-O-B linkages of BO3 units. A prominent shallow broad band in the region (925-1024) cm-1 are attributed to the stretching vibrations of BO4 tetrahedra. A deep band around 1360-1240 cm-1 are assigned to the stretching vibrations B-O of trigonal (BO3)3- units in metaborate, pyroborate and orthoborates. A broad band around 3440 cm-1 can be assigned to hydroxyl group (-OH) or water group for the glass systems.

EPR spectra of all the glass systems studied reveled that the vanadium ions (V4+) exist as VO2+ ions in octahedral coordination with tetragonal compression and belong to C4v symmetry, with dxy ground state. The values of which measure the tetragonality of the V4+ sites vary in a non-linear manner with the glass composition. This non-linear variation indicates that the tetrgonal distortion of the V4+-O6 complex is non-linear. The covalency rates (1 – and (1 – indicated moderate covalency for the σ a bonds in all the complexe. The N and values vary in a non-linear manner with the glass composition.

REFERENCES

[1] Khattak.G. D. and Tabet.N, Structural properties of glasses in the series (SrO)x(V2O5)1−x,(SrO)0.5−y(B2O3)y (V2O5)0.5 and (SrO)0.2 (B2O3)z (V2O)0.8 "Physical Review", Vol.B72, 104203-14 (2005).

[2] Senthil Murugan.G., Fargin, E., Rodriguez.V, Adamirtz.F, Couzi.M., Buffeteau.T and Le Coustumer.P, Temperature-assisted electrical poling of TeO2–Bi2O3–ZnO glasses for non-linear optical applications, "J. Non-Cryst. Solids", 344 158-166, (2004).

[3] Dumbaugh. W.H and Lapp. J.C, "Heavy-Metal Oxide Glass", J. Am. Cer. Soc., 75 (1992) 2315

[4] Lin. J.J, Huang.W, Sun.Z, Ray.C.S and Day.D.E ,"Structure and non-linear optical performance of TeO2–Nb2O5–ZnO glasses", J. Non-Cryst. Solids, 336(3),189-194 , (2004).

[5] E.I Kamitsos, M.A. Karakassides and G.D. Chryssikos, "Vibrational spectra of magnesium-sodium-borate glasses. 2. Raman and mid-infrared investigation of the network structure", J.Phys.Chem.Glasses, 91 (1987) 1073.

[6] A.A.Abou Shama and F.H.El-Batal, "Structural Analysis of Glassy Lead Borate Containing MoO3 In Relation to Its Optical Properties" Egypt J. Solids, 29 (2006) 1.

[7] B.Karthikeyan, reji Philip and S.Mohan," Optical and Nonlinear optical properties of Nd3+-doped heavy metal borate glasses " Optics Communications"246 (2005) 153-162.

[8] Yasser B.Saddeek, Essam R.Shaaban, El Sayad Moustafa, Hesham M.Moustafa "Spectroscopic properties, electronic polarizability, and optical basicity of Bi2O3–Li2O–B2O3 glasses",Physica B, 403 (2008) 2399-2407.

[9] E.I. Kamitsos and G.D. Chryssikos, "Borate glass structure by Raman and infrared spectroscopies" J. Mol. Struct. 247 (1991) 1.

[10] S.G. Motke, S.P. Yawale, "Infrared spectra of zinc doped lead borate glasses",Bull.Mater. Sci. 25 (2002) 75.

[11] H. G. Hecht and T. S. Johnston, "Study of the Structure of Vanadium in Soda—Boric Oxide Glasses," Journal of Chemical Physics, Vol. 46, No. 1 (1967) 23-34.

[12] A.Abragam and B.Bleaney, "Electron Paramagnetic Resonance of Transition ions" (Clarendon Press, Oxford, 1970) 175.

[13] D. Kivelson and S.K. Lee, "ESR Studies and the Electronic Structure of Vanadyl Ion Complexes"J.Chem.Phys., 41 (1964)

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