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Vanadium doped Lithium Borate glasses: PL and Optical absorption studies

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Abstract

$20Li_2O – 10Na_2O – (70-x)B_2O_3$ doped with xV_2O_5 glass systems were prepared by melt quenching technique and well characterized with XRD, FTIR and DSC techniques. XRD study confirmed glassy nature, Optical absorption spectra showed a broad band in the range 800 to 850nm. The photo luminescence spectra of these samples excited with the wavelength 254nm have been recorded at room temperature. The spectra exhibited an emission band in the wavelength region 370 – 470 nm .

Keywords: Lithium Borates glasses, Optical absorption and Photoluminescence

1.0 INTRODUCTION

Glasses have many technological applications due to their electrical and optical properties. The aim of the authors is to prepare $20Li_2O – 10\ Na_2O – (70\text{-}x)\ B_2O_5$ (PLNB) glasses doped with xV_2O_5 and characterize by techniques like XRD, FTIR and DSC and analyze optical properties such as optical absorption and photoluminescence. As is well described in literature, vanadium doped glasses are known to exhibit semiconductor properties. Investigations on borate glasses are the focus of interest due to their typical structures and properties.

2.0 EXPERIMENTAL

The sample with the general formula $20Li_2O – 10\ Na_2O – (70\text{-}x)\ B_2O_5$ doped with xV_2O_5 glasses were prepared by melt quenching technique. The mixtures were heated in an electric furnace at 1225 K for 20 min. The melt was then quenched at 250ºC to remove internal stress and slowly cooled to room temperature.

3.0 RESULTS AND DISCUSSIONS

XRD [Fig1] spectra of LNB glasses confirmed the amorphous phase of the samples with two humps at $2\Theta = 25º$ and $2\Theta = 45º$ that are characteristic of borate glasses[1].

FTIR study [Fig2] revealed that V_2O_5 doping acted differently in PLNB glass matrix and produced small variations in the glass structure. The observed absorption band, observed at 692-694 cm^{-1}, is due to the bending vibration B–O–B. The bands at 448 and 548 cm^{-1} are specific to the vibrations of Li–O bonds in Li_2O octahedral units[2],whereas the band at 1018 – 1020 cm^{-1} is due to asymmetric stretching vibration of the B–O bonds in BO_4 units. The broad band at 1334-1337 cm^{-1} is attributed to the B–O bonds due to stretching vibration in BO_3 and BO_4 tetrahedral units in the borate B_2O_3 – glass structure. The bands at 3437-3434 cm^{-1} are assigned to OH stretching vibration.

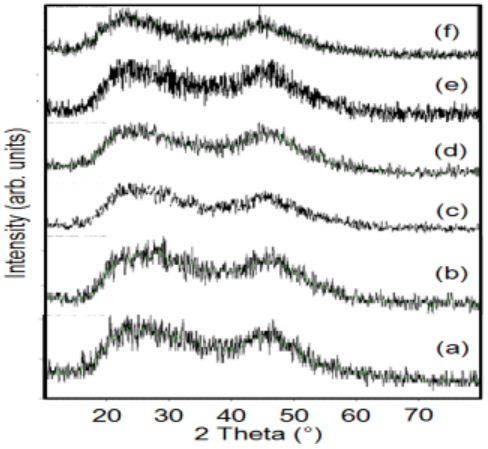

Fig.1: XRD spectra for (a) undoped PLNB and vanadium doped (b-f) LNBV glasses

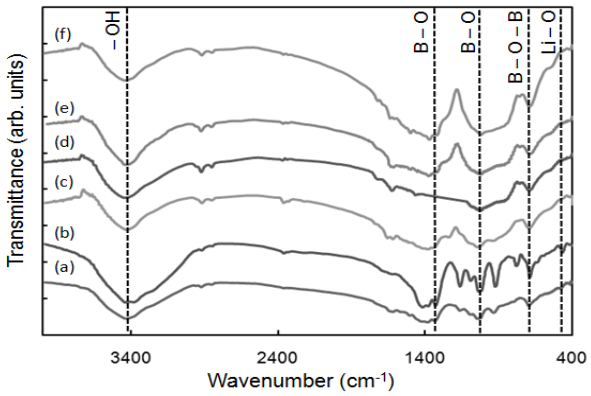

Fig. 2 FT-IR spectrum of PLNB and LNBV series of glass system

DSC has been shown to be a simple and useful technique to obtain information about the cross-link density of glass systems. The DSC thermograms Fig3 for all the glasses were recorded in the temperature range 50–550 °C with a heating rate of 10 °C/min.

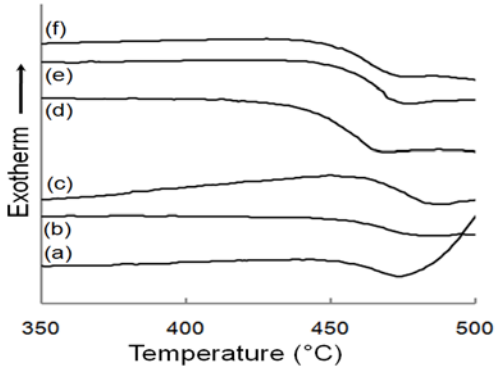

Fig 3: DSC thermograms of (a) PLNB and vanadium doped (b-f) LNBV glasses

Table1: Glass transition temperatures of (a) PLNB and vanadium doped (b-f) LNBV glasses

Glass	T_g (°C)
PLNB(a)	452.74
LNBV-0.2(b)	452.81
LNBV-0.4(c)	459.82
LNBV-0.6(d)	464.33
LNBV-0.8(e)	466.83
LNBV-1.0(f)	469.91

The obtained glass transition temperatures T_g obtained for the various undoped and vanadium doped PLNB glasses are listed in Table 1. The increase in T_g with increasing content of vanadium is due to (i) increase in density (ii) increase in bond length of B-O groups formation of BO_4 units (iii) increase in mass of the glass network former B_2O_3 and (iv) increase in the mass of the alkaline earth atom. Hence, the observed increase in T_g can be attributed to increase in boron–oxygen connectivity.

Various physical parameters of the prepared glasses such as density, molar volume, inter ionic distance and polaron radius have been evaluated and are presented in Table 2.

Table 2: Various physical parameters of PLNB and LNBV series of glasses

GLASS	DENSITY (g/cm^3)	MOLAR VOLUME, V_m (cm^3)	INTER IONIC DISTANCE, r_i (Å)	POLARON RADIUS, r_p(Å)
PLNB	3.0590	19.9111	-	-
LNBV-0.2	3.1489	19.4581	4.4568	0.9040
LNBV-0.4	3.8375	15.9887	3.5949	0.6725
LNBV-0.6	3.3453	15.4551	3.2914	0.6157
LNBV-0.8	4.0459	14.7553	2.9905	0.5595
LNBV-1.0	4.3136	10.6191	2.5568	0.4783

3.1OPTICAL ABSORPTION

Optical absorption spectra [Fig.(4a)], of all the glasses were recorded in the range of 300-900 nm at room temperature and cutoff wavelength, optical band gap energy and Urbach energies were calculated. Plots of optical band gap energies and Urbach energies were drawn with $\ln(\alpha)$ against $h\nu$ for the mixed alkali borate glasses [Fig.4 (b and c)].

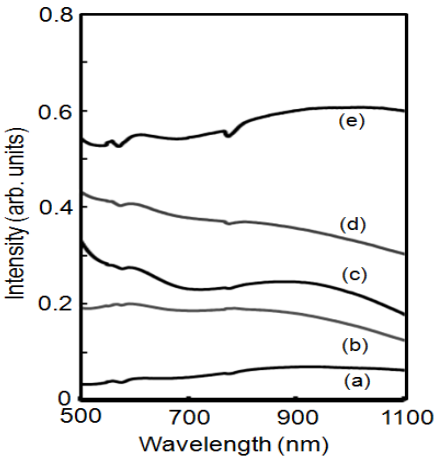

Fig.4(a):Optical absorption spectra of vanadium doped LNBV glasses.

The observed absorption peaks [**Table 3**] at ~ 600 nm and 860 nm can be attributed to $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2E$ transitions, respectively.

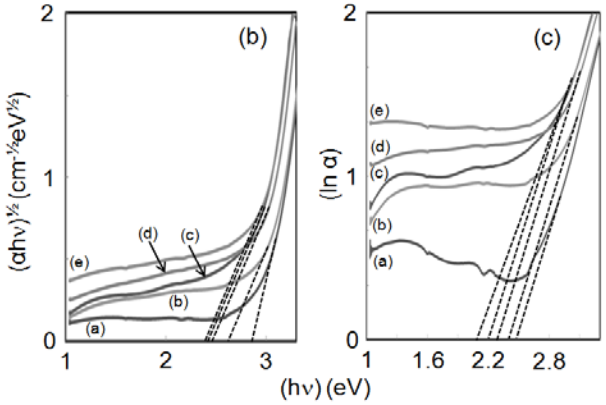

Fig.4(b) Optical band gap (c) Urbach energies of vanadium doped LNBV glasses

The values of Urbach energy were calculated by determining the slopes of the linear regions of the curves and taking their reciprocals.

Table3: Optical absorption spectral data of vanadium doped LNBV glasses.

Glass	Cutoff wavelength (nm)	$^2B_2 \rightarrow {}^2B_1$ (nm)	$^2B_2 \rightarrow {}^2E$ (nm)	Optical band gap E_0 (eV)	Urbach energies (eV)
LNBV0.2(a)	410	640	940	2.90	2.50
LNBV0.4(b)	450	620	900	2.75	2.40
LNBV0.6(c)	480	615	920	2.60	2.25
LNBV0.8(d)	515	600	860	2.45	2.20
LNBV1.0(e)	570	560	820	2.30	2.15

Optical band gap energies vary from 2.9eV to 2.3eV which is of the same order as expected for borate glasses [3].Optical band gaps and Urbach energies are decreasing with increase in vanadium concentration as can be seen in Table 4.

3.2 PHOTOLUMINESCENCE

Photoluminescence emission spectra [Fig.5] of glasses $20Li_2O$ – 10 Na_2O – (70-X) B_2O_5 doped with different concentrations of V_2O_5 were recorded at 254nm excitation wavelength at room temperature. The luminescence spectra Fig.(5)shows two sharp peaks at 370nm and 470nm. These results show the wavelengths corresponding to their absorption edge. The peaks observed shows that the luminescence of octahedral complexes is found to be much higher than tetrahedral complexes [4].This could be due to the reason that Stokes shift is smaller in the case of octahedral complexes

The PL spectra exhibited gradual shift in the intensity maxima with increase of concentration towards higher wavelength while the full width at half maximum decreases.

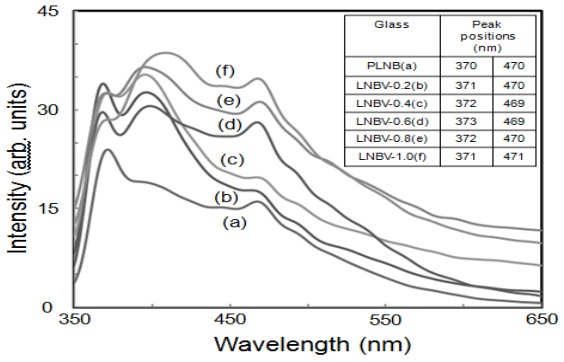

Fig.5: Photoluminescence spectra of Glasses excited at 250nm wavelength and their peak positions in Table4(inset)

4.0 CONCLUSION

The XRD results showed the amorphous nature of the glass system. From FTIR spectra a considerable shift in the intensity values are observed. The compositional dependence of *Tg* of Lithium borate glasses doped with vanadium is established by DSC technique. The optical absorption showed a large broad band at ≈ 800 -950 nm, which was observed to increase with increasing V_2O_5 concentration. Studies on Physical properties of the system revealed structural changes.There is a gradual shift in the peak position towards higher wavelength.

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