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Effect of Niobioum oxide in borate glasses

Physics

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ABSTRACT

- Glasses with composition xNb_2O_5.(30-x)MO.$70B_2O_3$ [where M = Ca, Sr, Ba] have been prepared by using normal melt-quench technique. The structure and optical properties have been investigated in order to understand the role of Nb_2O_5 in these glasses. The analysis of Infrared transmission (IR) spectra reveals the presence of NbO4 and NbO6 units in these glasses. The band gap energy (Eg) of the present glasses is found to decrease with increase in Nb_2O_5 content.

INTRODUCTION

The boric oxide, B_2O_3, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to formation of glasses [1]. Recently, considerable efforts have been devoted to materials and design for optical fibers, waveguide devices and fiber amplifiers to meet demands of present and future communication systems and other data transmitting services [2-3]. It has been reported that niobium borate glasses have large chemical resistance, surface hardness, high refractive indices, excellent transparency in the visible – IR region and intense UV absorption [4]. The structural role of Nb_2O_5 in different silicate-, borate-, germanate- and gallate-, glasses was investigated using Infrared (IR) and Raman spectroscopy [5]. Most of these studies had pointed out the presence of NbO_6 groups in the glass network. However, the role played by Nb_2O_5 in forming the glass structure and the coordination state of Nb^{5+} which in turn affects the thermal and electrical properties of glass system has still not been sufficiently elucidated. In the present work, the influence of Nb_2O_5 on the structure and optical properties of alkaline niobium borate glasses has been reported.

EXPERIMENTAL

The glass system xNb_2O_5•(30–x)MO•$70B_2O_3$ where M = Ca (NC glasses), Sr (NS glasses) and Ba (NB glasses) with $0 \le x \le 12$ mol% was prepared using AR grade chemicals: Nb_2O_5, $CaCO_3$, $SrCO_3$, $BaCO_3$, and H_3BO_3. Well – mixed batches were melted in a porcelain crucible at 1473 K for 1h to yield 10g of the glass. On quenching, the coin shaped glass samples were obtained. IR spectra were recorded (using KBr pellet technique) at RT on a FTIR spectrophotometer (Perkin-Elmer PC spectrophotometer) over the range 400-4000 cm^{-1}. Glass samples were polished to optical quality for optical measurements. The optical absorption spectra of all the glasses were recorded at RT using UV/VIS/NIR spectrophotometer (Cary 5000) in the wavelength range 200-3300 nm. The E_g was calculated from the observed absorption spectra.

RESULTS & DISCUSSION

The IR spectrum for NC, NB ans NS glasses is shown in Figs. 1 & 2 in the spectral range 400–1600 cm^{-1}. The IR spectra of the present glasses (Figs. 1 & 2) exhibit three groups of bands. The first group of bands (1200–1600 cm^{-1}) arises from borate units in which boron atom is connected to three oxygens (both bridging and nonbridging types). The second group of bands (800–1200 cm^{-1}) is attributed to the BO_4 units and the band between 600 and 800 cm^{-1} is due to the bending vibrations of B–O–B linkages in the borate network. It has been reported that in IR spectra the band for NbO_6 lies in between 600-700 cm^{-1} [4] and the bending vibrations of B-O-B linkages also manifest in this region. Fragoso et al [4] have observed that with the increase of Nb_2O_5 content the intensities of the BO_4 group stretching vibrational frequencies (800-1200cm^{-1}) decrease and the intensities of the band lying in between 600-800 cm^{-1} increase due to the presence of distorted NbO_6 octahedra groups in niobium borate glasses. The similar results obtained in the present glass systems (Figs. 1 & 2) confirm the presence of distorted NbO_6 octahedra groups in these glasses. It is observed that in NC and NS glasses up to $x \le 8$ mol% the intensities of the two bands (600-800 cm^{-1} and 800-1200 cm^{-1}) are nearly equal. It is expected that in these glass systems at lower concentration of Nb_2O_5, the NbO_4 units are present; however no band is observed in IR spectra for the confirmation of NbO_4 units. In NS4 glass the intensity of the band lying in between 600-800 cm^{-1} is higher than the intensities for 800-1200 cm^{-1} which indicates that the NbO_6 octahedra groups replace the BO_4 tetrahedral groups and give rise to non-bridging oxygen atoms. Earlier, it has been mentioned that Nb_2O_5 plays dual role in the glass matrix as modifier with NbO_6 and as glass former with NbO_4 structural units [5,6].

TABLE – 1

Cut-off wavelength ($\lambda_{cut\text{-}off}$), band gap (Eg), band tailing parameter (B), Urbach energy (ΔE) for xNb_2O_5•(30–x)MO•$70B_2O_3$ (M = Ca, Sr, Ba) glasses.

Glass No.	$\lambda_{cut\text{-}off}$ (nm)	Eg (eV)	B (cm eV)$^{-1/2}$	Eg (eV)	B (cm eV)$^{-1/3}$	ΔE (eV)
		$r = 2$		$r = 3$		
NC1	400	2.77	38.00	2.56	9.86	0.22
NC2	420	2.69	38.90	2.44	9.44	0.21
NS1	396	2.87	41.05	2.71	11.37	0.19
NS2	410	2.73	33.49	2.49	8.78	0.22
NS3	420	2.62	34.63	2.42	9.46	0.25
NS4	494	2.30	26.47	2.05	7.36	-
NB1	384	2.97	42.46	2.83	12.20	0.16
NB2	396	2.90	42.51	2.66	10.10	0.17
NB3	420	2.64	29.58	2.42	8.27	0.21
NB4	440	2.53	32.27	2.36	9.46	0.22

In NB glasses [Fig. 2] it can be seen that with the addition of Nb_2O_5 content in the glass matrix the intensity of the band lying in between 600-800 cm-1 increase and that of in between 800-1200 cm-1 decreases, indicating the presence of NbO_6 octahedra structural units in the glass network.

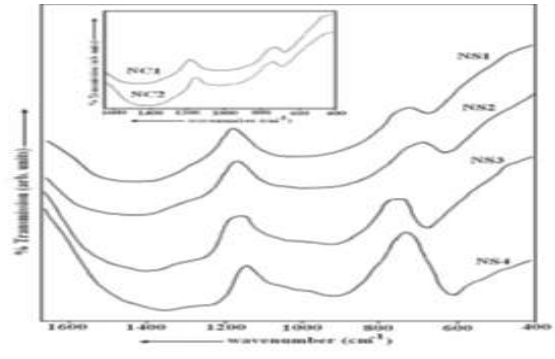

Figure 1: IR spectra of NS glasses. Insert: IR spectra for NC glasses.

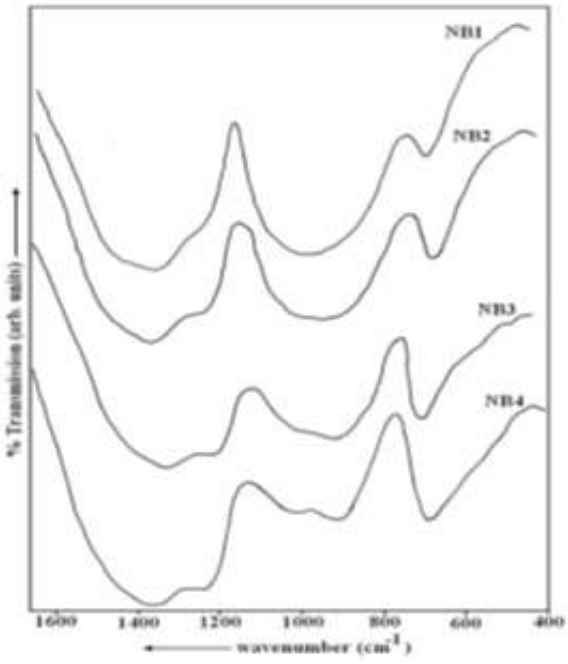

Figure 2: IR spectra of NB glasses.

The optical absorption spectra of the glasses under study are separately shown in Fig. 3 for the three glass systems. From these figures it can be seen that the absorption edge (λ cut-off) shifts towards longer wavelengths with increase in Nb_2O_5 content in the glass matrix (Table 1). The edges are not sharply defined, signifying the glassy nature of the samples

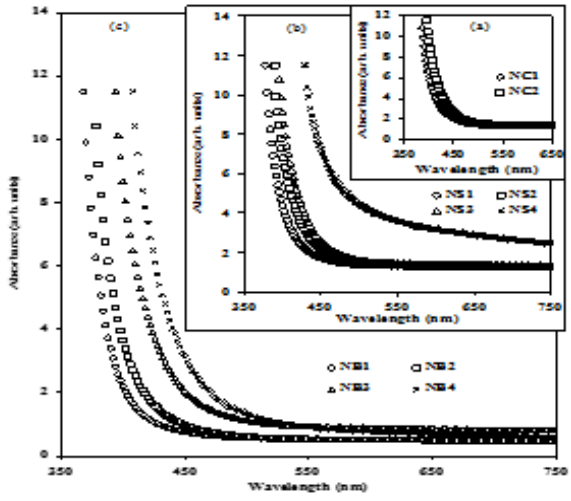

Figure 3: Optical absorption spectra for NC, NS and NB glasses.

For amorphous materials the optical absorption at higher value of $\alpha(\nu)$ (≥104 cm–1) above the exponential tail follows a power law given by Davis and Mott [6] which in the most general form is given by

$$\alpha(\nu) = \frac{B(h\nu - E_g)^r}{h\nu} \qquad (1)$$

The values of Eg are obtained [using Eq. (1)] by extrapolating the linear region of the curves are given in Table 1. The values of 'B' (Band tailing parameter) calculated from the linear portion of the Tauc's plot for r (index parameter) = 2 and 3 are also presented in Table 1 for all the glasses. The decreasing values of Eg on increasing the Nb_2O_5 content can be understood in terms of the structural changes that are taking place in the glasses under study. This feature is concurrent with the red shift in λ cut-off with increase in Nb_2O_5 content. This suggests that the non-bridging oxygen ions are increasing with increase in niobium oxide. This may be due to in metal oxides, the valance band maximum (VBM) mainly consists of O(2p) orbital and the conduction band minimum (CBM) mainly consists of M (nS) orbital. The NBO ions contribute to VBM. When a metal-oxygen bond is broken, the bond energy is released. The non-bridging orbitals have higher energies than bonding orbitals [3]. Increase in concentrations of the NBO ions results in the shifting of VBM to higher energies and reduces the band gap energy. Urbach energy (ΔE), which corresponds to the width of localized states, is used to characterize the degree of disorder in amorphous and crystalline systems. Materials with larger ΔE would have greater tendency to convert weak bonds into defects. The values of ΔE of the present glass system lie in the range 0.16 – 0.25 eV (Table 1) for all the glasses.

CONCLUSIONS

Analysis of IR spectra reveals the presence of NbO_4 and NbO_6 units in NC and NS glasses and NbO_6 units in NB glasses. The E_g of the present glasses is reducing with increasing content of Nb_2O_5

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