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The optical properties of some borate glasses

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The optical properties of potassium borate and sodium borate glasses are presented. The fundamental absorption edge for all the series of glasses were analysed in terms of the theory of Davis and Mott. The position of absorption edge and hence the value of the optical gap, was found to depend on the semiconducting glass composition, and the absorption in these glasses is believed to be associated with indirect transitions. The infrared spectra were recorded and appeared individually similar, which is consistent with the absence of significant structural change between the various glass specimens.

1. Introduction

The ultraviolet absorption is generally believed to involve the excitation of electrons associated with oxygen anions in glasses and Stevels [1, 2] was the first worker to discuss theoretically the UV absorption mechanism in glasses. The early investigation of the UV spectra of binary and ternary borate and silicate glasses containing Na_2O, K_2O, BaO, ZnO, Al_2O_3 and CaF_2 as network modifiers, was reported by Zschimmer [3]. Other workers such as McSwain *et al.* [4] studied the affect of composition on the UV spectra of some borate and silicate glasses and concluded that for both alkali silicate and borate glasses there is a shift of the UV transmission cut-off to longer wavelength as the alkali content increases. A spectroscopic study of some borate and vanadate glasses has also been reported by Ahmed and Hogarth [5].

The infrared spectra of glassy materials have been used to explain the structure of glass, and are involved with the type of bonding and arrangement of the atoms in the glassy network. One of the important IR studies of glassy boron oxide and alkali borate glasses has been reported by Krogh-Moe [6].

2. Glass preparation and experimental procedure

Two binary systems based on B_2O_3–K_2O and B_2O_3–Na_2O with 55 to 70 and 50 to 70 mol % B_2O_3, respectively, were prepared from chemically pure grades of material as shown in Table I. These oxides were mixed together in an alumina crucible using an alumina rod and then transferred to an electrically heated furnace for 1 h at 673 K to minimize losses by evaporation. Then it was transfered to a second furnace which was already at a temperature of the order of 1273 K and kept there for 3 h, and during this time the glass melts were stirred by an alumina rod several times in order to produce a homogeneous melt. At the end of the 3 h melting period some molten glass was gathered at the end of a hollow alumina tube in order to blow thin films for the ultraviolet spectroscopy. The optical measurements were carried out at room temperature in the wavelength range of 188 to 300 nm by using a Perkin–Elmer spectrometer. For infrared measurements, samples were ground in a clean mortar to a fine powder and were mixed with powdered KBr with a ratio of 1 to 10 respectively, and ground KBr pellets, transparent to light, were formed by pressing the mixture at 10 to 15 tonnes for a few minutes under vacuum. Infrared spectral measurements were carried out by using a Unicam SP2000 double beam infrared spectrometer at room temperature in the wave number range 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Optical absorption

The measurement of optical absorption and particularly the absorption edge is important especially in connection with the theory of the electronic structure of amorphous materials. The absorption edge in disordered materials at the higher levels of absorption coefficient ($> 10^4$ cm^{-1}) is usually interpreted in terms of indirect transitions across an optical gap. For absorption by indirect transitions the absorption coefficient $\alpha(\omega)$ is given [7] by

$$\alpha(\omega) = A(\hbar\omega - E_{opt})^2/\hbar\omega \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient, A a constant, E_{opt} the optical gap and $\hbar\omega$ the photon energy of the

TABLE I Optical energy gap for sodium and potassium borate glasses.

Glass	K_2O Content (mol %)	Na_2O Content (mol %)	B_2O_3 Content (mol %)	E_{opt} (eV)
b	30	—	70	5.67
c	35	—	65	5.59
d	40	—	60	5.51
e	45	—	55	5.46
g	—	35	65	6.01
h	—	40	60	5.90
i	—	45	55	5.79
j	—	50	50	5.72

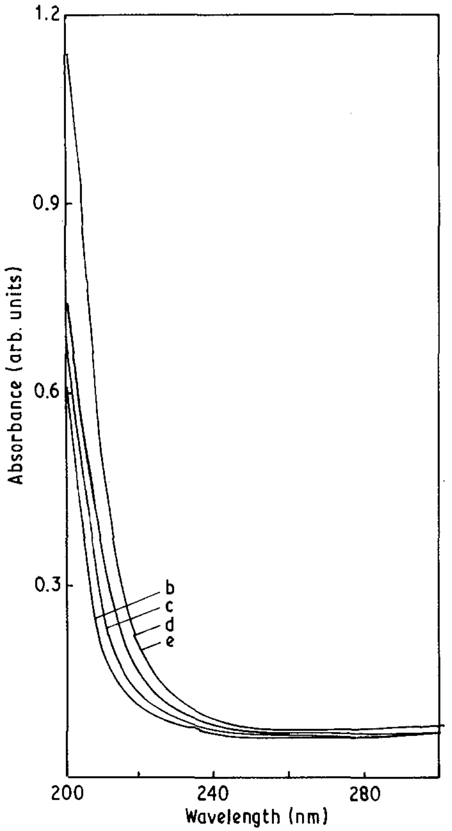

Figure 1 Optical absorption as a function of wavelength in the UV region for some K_2O–B_2O_3 glasses.

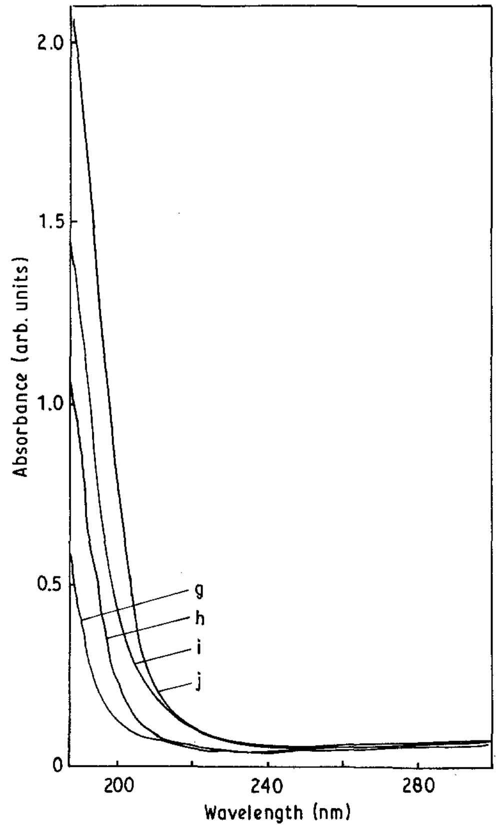

Figure 2 Optical absorption as a function of wavelength in the UV region for some Na_2O–B_2O_3 glasses.

incident radiation. Absorption at lower photon energy usually follows the Urbach rule [8], i.e.

$$\alpha(\omega) = C \exp \frac{\hbar\omega}{\Delta E} \qquad (2)$$

where C is a constant and ΔE the Urbach energy usually interpreted as the width of the tails of localized states in the band gap. ΔE is typically in the range of 0.006 to 0.14 eV [9] for various materials below and at room temperature, while above room temperature the value of ΔE increases with increasing temperature.

The optical absorption spectra for K_2O–B_2O_3 and Na_2O–B_2O_3 glasses as a function of wavelength are shown in Figs 1 and 2. It can be seen from these figures that the optical absorption edge is less sharp than those characteristic of crystalline semiconductors. It is also clear that the position of the fundamental absorption edge shifts to longer wavelengths with an increase of the content of glass modifier in the sample. The absorption coefficient $\alpha(\omega)$ can be determined near the edge from the relation $\alpha(\omega) = (1/d) \ln (I_0/I)$ [10] where d is the thickness of the sample; I_0 and I are the intensities of the incident and transmitted beams, respectively. Figs 3 and 4 represent $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy $\hbar\omega$ for K_2O–B_2O_3 and Na_2O–B_2O_3 glasses, respectively. The values of the optical energy gap are obtained by extrapolating from the linear region of the plots of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ to $(\alpha\hbar\omega)^{1/2} = 0$ and are given in Table I. It can be seen that the values of optical gap E_{opt} decrease with increasing K_2O or Na_2O content. The E_{opt} values have been plotted against K_2O and Na_2O content for both series of glasses as shown in Figs 5 and 6 for K_2O–B_2O_3 and Na_2O–B_2O_3, respectively. The equivalent Urbach plots are also presented in Figs 7 and 8 in which the absorption coefficients are plotted as logarithmic functions of $\hbar\omega$ for different compositions

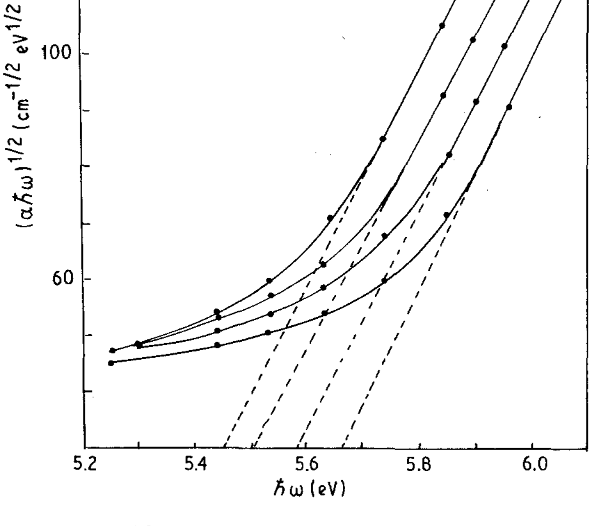

Figure 3 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for K_2O–B_2O_3 glasses.

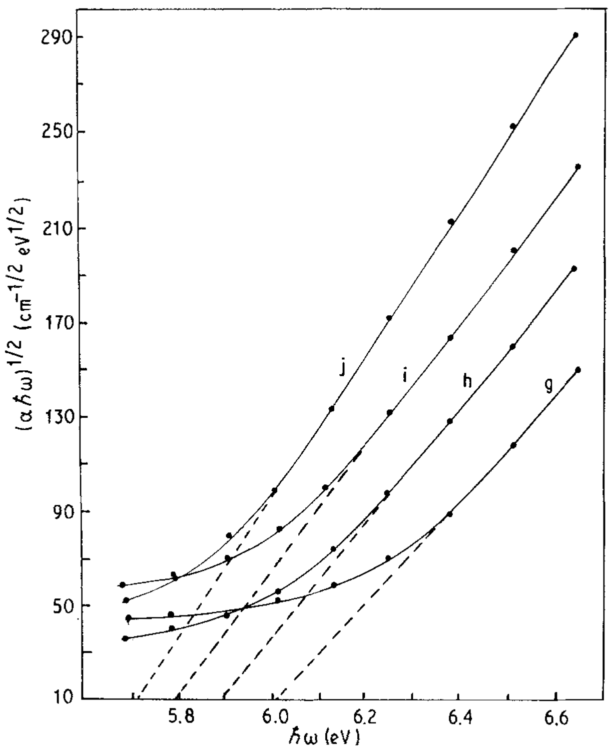

Figure 4 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for Na_2O–B_2O_3 glasses.

of K_2O–B_2O_3 and Na_2O–B_2O_3 glasses. The values of ΔE from Equation 2 were calculated from the slopes of the linear regions of these curves. The average value of ΔE was found to be 0.12 eV for K_2O–B_2O_3 glasses and 0.11 eV for Na_2O–B_2O_3 glasses.

In the present work the shift of the absorption edge to a longer wavelength and the decrease of E_{opt} to lower energies with increase in alkaline oxide content is probably related to the gradual increase in concentration of non-bridging oxygens. The linear variation of the $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ graphs with very good correlation for all the glasses prepared, shows the validity or Equation 1 for indirect transitions.

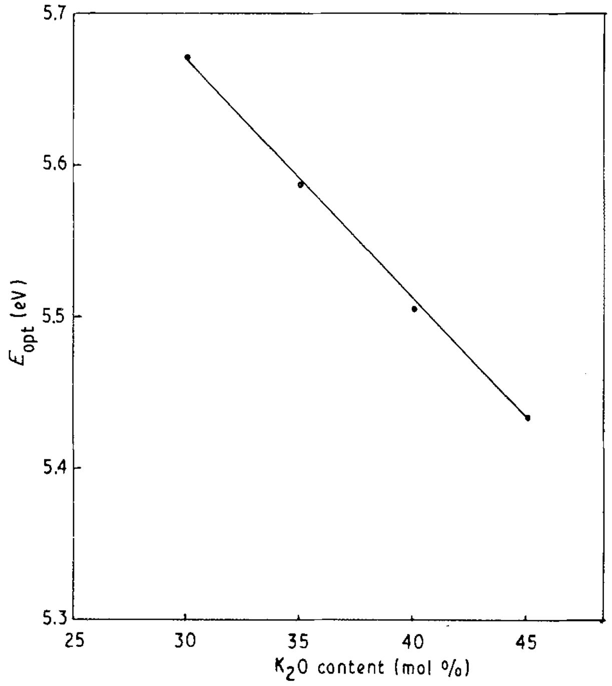

Figure 5 Optical energy gap as a function of K_2O content for a series of K_2O–B_2O_3 glasses.

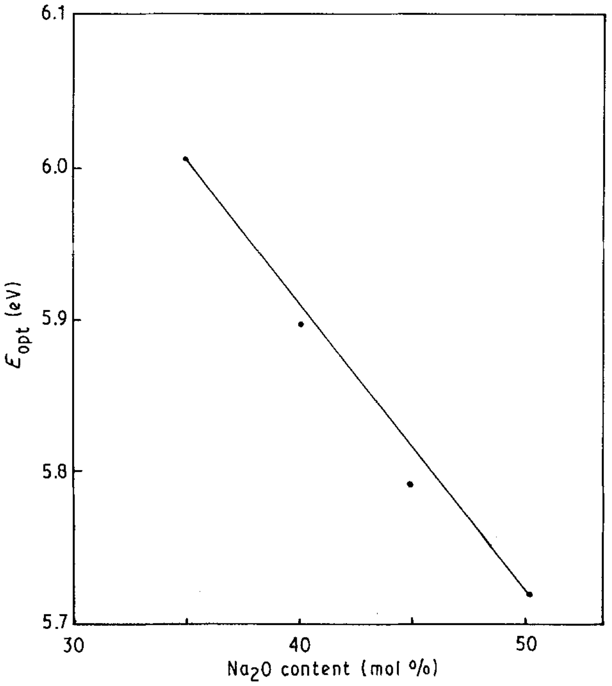

Figure 6 Optical energy gap as a function of Na_2O content for a series of Na_2O–B_2O_3 glasses.

3.2. Infrared absorption

The vibrational absorption spectra of the series of Na_2O–B_2O_3 and K_2O–B_2O_3 glasses are shown in

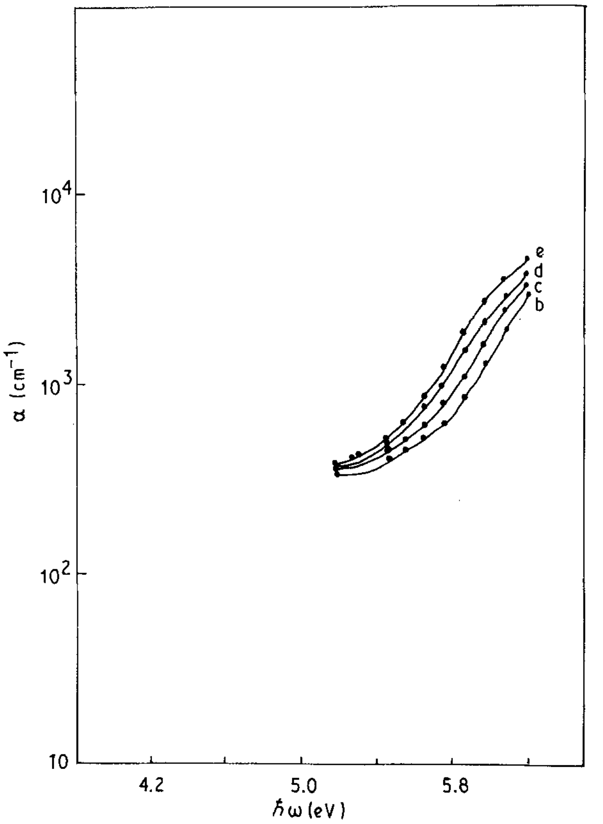

Figure 7 Optical absorption coefficient plotted against photon energy for K_2O–B_2O_3 glasses.

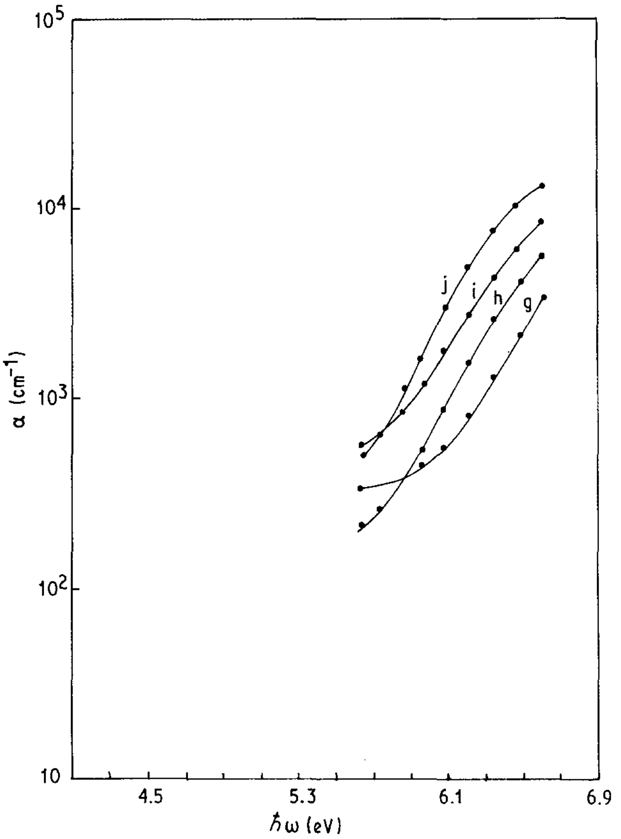

Figure 8 Optical absorption coefficient plotted against photon energy for $Na_2O–B_2O_3$ glasses.

Figs 9 and 10, respectively and the absorption spectrum of crystalline B_2O_3 is also shown in Fig. 11. The characteristic infrared absorption bands present in the glasses studied (Table II) show that there is no significant distinction between the glasses containing sodium compared with those containing potassium. Comparing the spectra of crystalline B_2O_3 with those of $Na_2O–B_2O_3$ and $K_2O–B_2O_3$, it appears that the alkaline oxides in these glasses make some contribution to the formation of fairly broad bands from 1250 to 1460, 870 to 1110 cm^{-1} for $Na_2O–B_2O_3$ and 1300 to 1480, 860 to 1120 cm^{-1} for $K_2O–B_2O_3$, respectively. The band positions at 1250 to 1460 cm^{-1} or 1300 to 1480 cm^{-1} for $Na_2O–B_2O_3$ and $K_2O–B_2O_3$, respectively, are characteristic of a $[=B–O–B\equiv]^-$ group in which one of the borons is tetrahedrally coordinated and the band starting from 860 cm^{-1} is also attributed to this grouping [11, 12]. Jellyman and Proctor [12] have shown that the band at 690 to 714 cm^{-1} is triangularly coordinated. In the present work the absorption bands appear at 730 and 740 cm^{-1} for $K_2O–B_2O_3$ and $Na_2O–B_2O_3$, respectively, and therefore they may be related to B–O–B linkages in which both boron atoms are triangularly coordinated. These glasses contain some water [11] and the bands at 3460 and 3500 cm^{-1} for $Na_2O–B_2O_3$, respectively, are associated with an OH group.

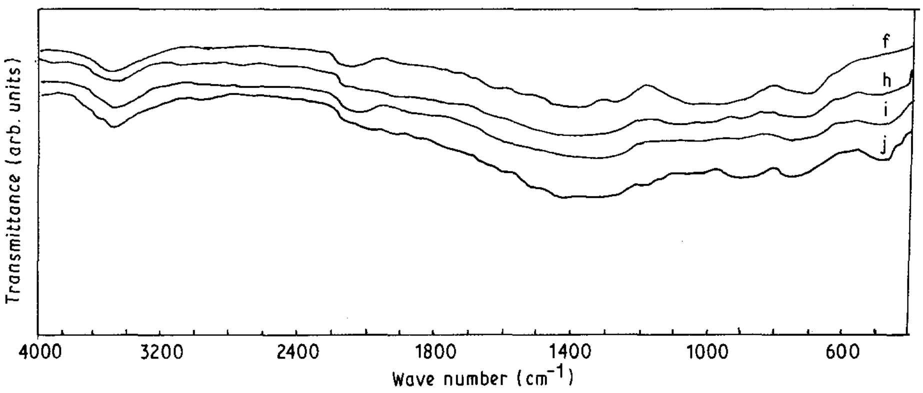

Figure 9 Infrared absorption spectra for a series of $Na_2O–B_2O_3$ glasses.

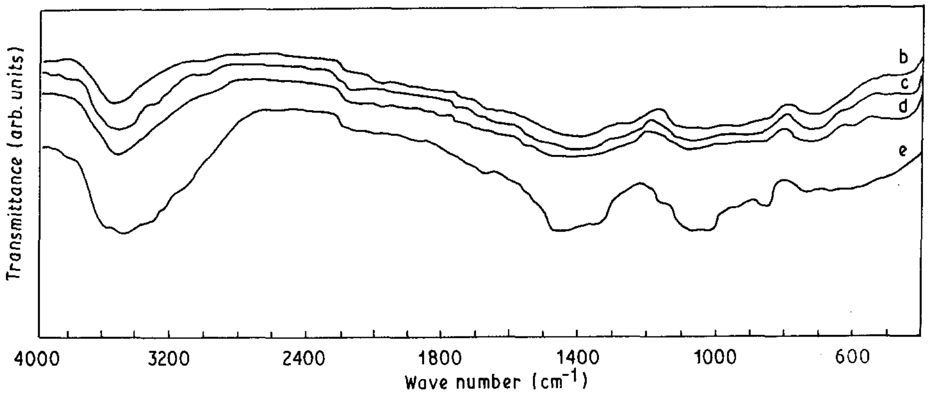

Figure 10 Infrared absorption spectra for a series of $K_2O–B_2O_3$ glasses.

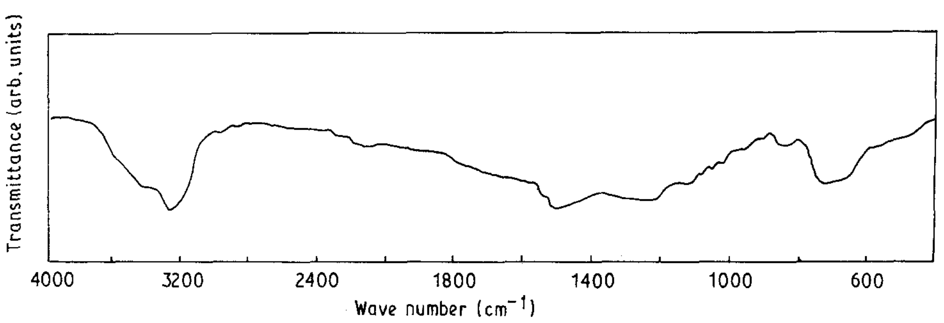

Figure 11 Infrared spectra of crystalline B_2O_3.

TABLE II Positions of infrared absorption bands for sodium and potassium borate glasses and for boric oxide.

Specimen	K_2O Content (mol%)	Na_2O Content (mol%)	B_2O_3 Content (mol%)	Infrared band positions (cm^{-1})					
b	30	—	70	730	860–1120		1300–1480	3500	
c	35	—	65	730	860–1120		1300–1480	3500	
d	40	—	60	730	860–1120		1300–1480	3500	
e	45	—	55	730	860–1120		1300–1480	3500	
f	—	30	70	740	870–1110		1250–1460	3460	
h	—	40	60	740	870–1110		1250–1460	3460	
i	—	45	55	740	870–1110		1250–1460	3460	
j	—	50	50	740	870–1110		1250–1460	3460	
B_2O_3				660–740	850	1120	1215	1400–1520	3220

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