

A spectroscopic study of some sodium tetraborate glasses containing lead and copper

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Optical absorption, infra-red absorption spectra and differential scanning calorimetry of amorphous $(\text{Na}_2\text{B}_4\text{O}_7)_{80-x}(\text{Pb}_3\text{O}_4)_{20-x}(\text{CuO})_x$ systems were studied as functions of copper content up to 10 mol%. When the Pb_3O_4 in the glasses is gradually replaced by CuO , a pronounced decrease in the optical energy gap and an increase in the optical absorption at 750 nm due to the Cu^{2+} ions is observed. The change in the optical absorption may be attributed to the concentration variation of the Cu^{2+} ions in the glasses as a consequence of changing the lead content.

1. Introduction

In recent years the properties of glasses have been interpreted in electronic rather than chemical terms. One of the first detailed investigations of glassy materials incorporating transition metal ions was undertaken by Sands [1] on the soda-lime-silicate glass-based system. Many transition metal oxides, when melted with glass-forming substances such as GeO_2 , SiO_2 and B_2O_3 , form glasses on quenching the melt. The change in the oxidation state in the melt produces lower valency transition metal ions and indeed the electronic conduction in these glasses is associated with a hopping of electrons from reduced to the normal valency ions as discussed in detail by Mott [2].

A survey of the literature shows that there are many studies which have been carried out on glass systems based on B_2O_3 [3-5]. Paul and Douglas [6] studied the cerous-ceric equilibrium in binary alkali borate and alkali silicate glasses. A spectroscopic study of some borate and vanadate glasses has been reported by Ahmed and Hogarth [7].

2. Sample preparation and experimental details

Glasses in the system having the composition in mol% $(\text{Na}_2\text{B}_4\text{O}_7)_{80-x}(\text{Pb}_3\text{O}_4)_{20-x}(\text{CuO})_x$ where x varies from 0 to 10 mol% (Table I) were prepared

from chemically pure grades of material according to their molar compositions in an alumina crucible. A typical melt containing some 20 g of material was stirred from time to time using an alumina rod and was melted at 900°C for 1 h. By slow heating it was hoped to reduce mechanical and volatilization losses. The molten glass was cast on to a stainless steel plate in the form of a circular disc of 2 cm diameter and 2 mm thickness. The disc was immediately transferred to another furnace which was already maintained at 300°C. The furnace was kept at this temperature for about 1 h and then switched off to cool down to room temperature. X-ray diffraction examination of the glass samples showed no discrete lines or structure and confirmed that our samples were essentially non-crystalline. Table I shows the composition of the glasses reported in this paper.

The glass samples used for ultraviolet and visible spectroscopy were polished to about 1 mm thick. The measurements were carried out at room temperature in the wavelength range 200 to 900 nm using an LKB Biochrom Ultrospec 4050 spectrophotometer.

For infra-red measurements, samples were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with a large quantity of KBr. KBr pellets transparent to infra-red were formed by pressing the mixture at 10 tons for a few minutes. The infra-red absorption spectra of these

TABLE I Composition data and some derived parameters for sodium tetraborate glasses containing lead and copper

Notation	Composition (mol %)	Optical gap E_{opt} (eV)	DSC phase transition temperature (°C)
(a)	$(\text{Na}_2\text{B}_4\text{O}_7)_{80}(\text{Pb}_3\text{O}_4)_{20}(\text{CuO})_0$	3.45	400
(b)	$(\text{Na}_2\text{B}_4\text{O}_7)_{80}(\text{Pb}_3\text{O}_4)_{17.5}(\text{CuO})_{2.5}$	3.25	405
(c)	$(\text{Na}_2\text{B}_4\text{O}_7)_{80}(\text{Pb}_3\text{O}_4)_{15}(\text{CuO})_5$	3.10	410
(d)	$(\text{Na}_2\text{B}_4\text{O}_7)_{80}(\text{Pb}_3\text{O}_4)_{12.5}(\text{CuO})_{7.5}$	2.9	418
(e)	$(\text{Na}_2\text{B}_4\text{O}_7)_{80}(\text{Pb}_3\text{O}_4)_{10}(\text{CuO})_{10}$	2.7	425

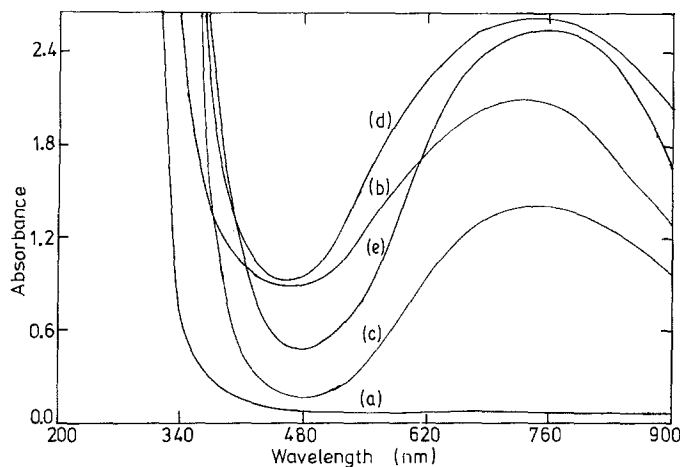


Figure 1 Absorbance as a function of wavelength for sodium tetraborate glass samples containing lead and copper. (a) 0.85 mm thick; (b) 1.08 mm thick; (c) 0.64 mm thick; (d) 0.98 mm thick and (e) 0.63 mm thick.

samples were determined by using a Unicam SP3-300 double beam recording infra-red spectrophotometer in the range 200 to 4000 cm^{-1} .

The thermal stability of the glasses was studied in a Mettler TA 3000 thermal analysis system. The differential scanning calorimetry (DSC) technique was applied in the temperature ranges 303–873 K. The heat flow to the sample was measured under thermally controlled conditions. The sample was well ground into a powder of 12.0 mg and contained in an aluminium crucible for measurement. The DSC pattern was then measured in relation to an empty aluminium crucible which served as a reference.

3. Results and discussion

3.1. Optical absorption

The measurements of the optical absorption coefficient particularly near the fundamental absorption edge provide a standard method for investigation of optically-induced electronic transitions and provide some ideas about the band structure and energy gap in

both crystalline and amorphous materials. Fig. 1 shows the variation of absorbance, A , with wavelength for the glass samples. A is given by $\log_{10}(I_0/I_t)$ where I_0 and I_t are the intensities of the incident and transmitted beams and A is related to the absorption coefficient α by the equation

$$\alpha = \frac{2.303A}{d} \quad (1)$$

where d is the sample thickness. The following facts emerge from these curves.

1. The fundamental optical absorption edge of the glass is fairly sharp, as has also been observed for different glass compositions [7, 8].

2. There is a broad absorption tail for glass sample (a) ($\text{Na}_2\text{B}_4\text{O}_7\text{-Pb}_3\text{O}_4$) without CuO , which extends from about 400 to 900 nm.

3. There is a broad absorption band, at around 750 nm, for glasses doped with CuO and there is an increase in absorption as the CuO content is increased. Bamford [9] has reported that the cupric (Cu^{2+}) absorption band in copper–sodium borate glasses is centred at 790 nm, and in copper–lead silicate glasses is centred at 755 nm. Haddon *et al.* [10] found an absorption band at 852 nm for copper–sodium phosphate glasses and attributed to Cu^{2+} ions in an octahedral field with strong tetragonal distortion. Harani *et al.* [11] observed an absorption band at 830 nm due to Cu^{2+} in $\text{CuO-CoO-P}_2\text{O}_5$ glass compositions.

4. The absorption edge seems to move to longer wavelengths as the CuO content is increased. The optical absorption coefficient $\alpha(\omega)$ may be displayed in a number of ways as a function of photon energy $\hbar\omega$. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ as suggested by Tauc *et al.* [12] and discussed fully by Davis and Mott [13]. The coefficient $\alpha(\omega)$ for many amorphous and glassy materials in which the optical transitions are indirect is found to obey the relation

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^2/\hbar\omega \quad (2)$$

where E_{opt} is the optical energy gap and B is a constant.

Fig. 2 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for the glass samples and the values of E_{opt} determined by extrapolating the linear parts of the curves to

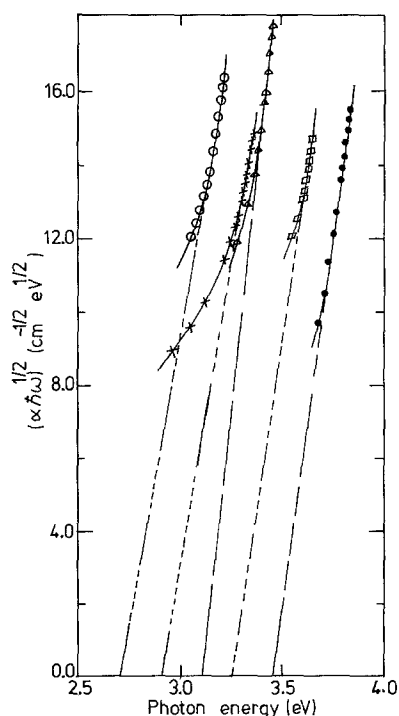


Figure 2 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy of glass samples. ●, Sample (a); □, (b); △, (c); ×, (d); ○, (e).

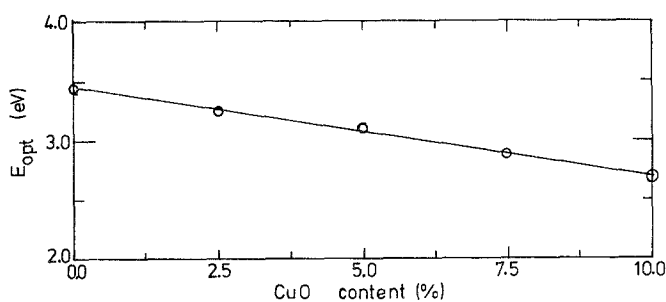


Figure 3 Variation of E_{opt} values with CuO content of glass samples.

$(\alpha\hbar\omega)^{1/2} = 0$ are listed in Table I. All plots show straight lines with some deviations from linearity at the lower values of α which were suggested by Redfield and Afromowitz [14] as possibly due to imperfections in the material, but this region of the curve is still not fully understood. However the extrapolation has generally been accepted as giving a reliable value for the optical gap as shown in Fig. 3 and Table I. It is clear from Table I that the values of E_{opt} of the glass samples are decreased following an increase in CuO content. This could possibly be explained by a change in the ratio of Cu^{2+}/Cu^{+} content in the glass with a decrease in lead oxide. Similar results have been reported by other workers in the copper-sodium phosphate glasses [15] and in the $V_2O_5-B_2O_3$ glasses [7]. The absorption characteristic in these glasses may be described by the generally accepted qualitative understanding that the absorption edge is determined by the oxygen bond strength in the glass-forming network. Any change of oxygen bonding in the glass network, for instance the formation of non-bonding oxygens, changes the absorption characteristics [16]. In the present work, by increasing the CuO content, the absorption edges shift towards lower energies which range from 3.45 to 2.70 eV. Such a change has been reported by others for different glass compositions [7, 15].

3.2. Infra-red absorption spectroscopy

The infra-red absorption spectra of glass samples given in Table I together with the spectrum of $Na_2B_4O_7$ are shown in Fig. 4.

The absorption peaks observed in all glasses are at 200, 470, 700, 830, 950, 1100, 1240 and 3400 cm^{-1} . Comparing the infra-red spectrum of $Na_2B_4O_7$ with that of lead-doped glass (Sample a) and copper-doped glasses containing 2.5, 5, 7.5 and 10 mol % of CuO, it

appears that all glasses show a great similarity in the general shape of their absorption spectra, without the appearance of any new peaks, with exception that the peaks are weakened and broadened with the CuO content. The observed peaks could be due to a number of causes such as bridging and non-bridging oxygen ions which are doubly or singly bonded, to the high BO_4 groups and low-state BO_3 groups, to sodium and lead ions and possibly due to some combination of these.

It seems that Pb_3O_4 or CuO can easily give the oxygen required for the formation of BO_4 groups, hence the maximum BO_4/BO_3 ratio will depend on the amount and the nature of Pb^{2+} and Cu^{2+} ions. It may be that the non-bridging oxygen present in $(Na_2O \cdot 2B_2O_3)$ glasses remains almost unchanged upon addition of lead or copper in small quantities, but leads to a reduction in vibrating bond concentration.

The absorption band at 3400 cm^{-1} is believed to be associated with water trapped in glasses during the experiment.

3.3. DSC measurements

The DSC patterns for different glass samples are obtained and shown in Fig. 5 for a heating rate of 20 K min^{-1} . It was found that all samples showed an endothermic peak around 400°C and are dependent on the CuO content. The glass sample undoped with CuO (Sample a) showed also an exothermic peak at around 565°C . It seems that the sample undoped with CuO shows two phase transitions at 400 and 565°C . With the addition of a small amount of CuO (2.5 mol %) the phase transition at 565°C disappeared or may have been shifted to higher temperature, and the phase transition at around 400°C is dependent on CuO, as shown in Fig. 6. In this temperature range the network begins to acquire a degree of mobility which

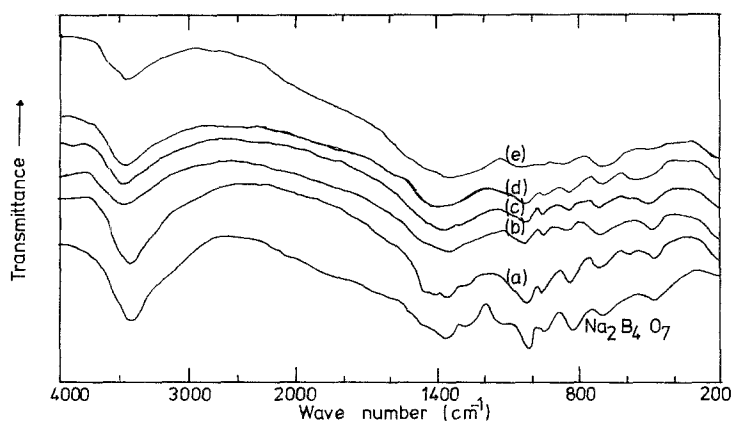


Figure 4 The infra-red absorption spectra of glass samples.

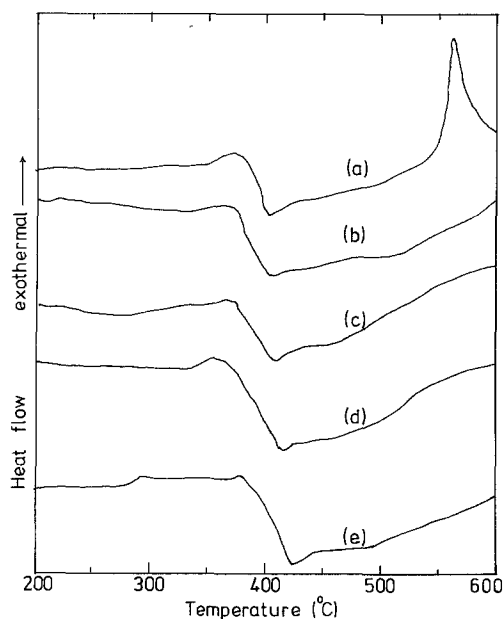


Figure 5 DSC curves of glass samples taken at a heating rate of 20 K min^{-1} .

increases the temperature as the CuO content is increased and Pb_3O_4 content is decreased. A process of bond switching or transfer of bonds occurs, whereby segments of the network can become detached and able to move relative to the rest of the network.

According to Ray [17] the glass transition temperature is strictly linked to the density of cross linking rather than to bond strength. When the samples were cooled down to room temperature, the DSC curves were again measured and the same endothermic peak reappeared for all glass samples while the exothermic peak at 565°C for Sample (a) disappeared. This indicates that the first phase transition in the first measurement was not permanent and reversible, while the second glass transition for Sample (a) obtained in the first measurement was permanent and irreversible. No significant change in the weight of the samples was

observed during the glass transition as this was checked by accurate weighing of the sample before and after measurements.

Limb and Davis [18] found that the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5\text{-B}_2\text{O}_3$ glass has a two-phase separation and subsequent crystallization of V_2O_5 at 290 and 410°C .

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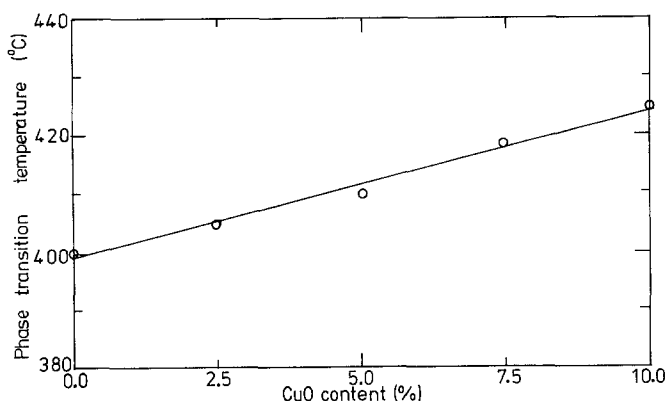


Figure 6 Variation of endothermal phase transition temperature with CuO content of glass samples.