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# Optical, infrared and DSC studies of sodium tetraborate glasses containing copper oxide

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The optical absorption, density, DSC and infrared absorption spectra of a series of sodium tetraborate glasses are measured as a function of copper content up to 5 mol%. It is found that the addition of CuO shifts the fundamental absorption edges towards lower energies in the range from 6.17–3.48 eV. The addition of CuO does not seem to introduce any new absorption band as compared with the spectrum of a pure sodium tetraborate glass. DSC measurements showed endothermal peaks varying from 486–476 °C depending on the CuO content.

## 1. Introduction

As a part of a continuing study of transition metal ions in glasses [1–3], the results of a study of $Cu^{2+}$ ions in the sodium tetraborate glass system are reported here. Oxide glasses containing transition metal ions were first reported in 1954 [4]. Several transition metal oxides when heated with glass-forming substances such as $GeO_2$, $B_2O_3$, $SiO_2$, $TeO_2$ and $P_2O_5$, form glasses on quenching from the melt. The loss of oxygen from 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 normal valency ions as discussed in detail by Mott [5]. A great deal has been carried out on many glass systems including a number of glasses based on sodium tetraborate [6–10].

The present work reports results of optical, infrared absorption spectra and differential scanning calorimetry (DSC) measurements on sodium tetraborate glasses with low concentrations of copper. The absorption data were analysed in the light of existing theories on optical absorption in amorphous semiconductors.

## 2. Experimental procedure

### 2.1. Glass preparation

Homogeneous glass samples of the composition (mol%) $(Na_2B_4O_7)_{100-x}$-$(CuO)_x$ where $x$ varied from 0 to 5 mol% (Table I) were prepared from chemically pure grades of material according to their molar composition in an alumina crucible. A typical melt contained some 30 g of material. In order to reduce a tendency to volatilization the crucible was initially heated for 1 h at 300 °C and then transferred to another furnace maintained at 900 °C for 1 h. The melt was stirred frequently, using an alumina rod. The melt was finally poured on to a clean stainless steel plate and cast into a disc shape of diameter 1.5 cm and 2 mm thickness. The disc was immediately transferred to another furnace for annealing at 300 °C for 1 h. The furnace was then switched off to allow it to cool down gradually to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. X-ray diffraction measurements confirmed the glassy nature of all the glass samples examined. Thin blown films of the glasses were prepared by dipping an alumina tube into the molten material, collecting a small amount of glass melt on the end of the tube, and blowing it into the air. Films ranging in thickness from 1 to 10 μm were obtained.

The densities of the glass samples were measured at room temperature by the displacement method using xylene as the immersion liquid and a single pan balance of $10^{-4}$ g sensitivity.

### 2.2. Optical measurements

Optical measurements for thin films and bulky glasses were carried out at room temperature in the wavelength range 185–900 nm using a Varian model Cary 2390 spectrophotometer. In the low absorption region ($\alpha < 10^4\ cm^{-1}$) for thin film glasses, multiple interference effects were well pronounced and use of this was made in determining the thickness of the films.

The infrared absorption measurements were made for powdered glass samples using an SP3-100 Pye Unicam double-beam infrared spectrophotometer. The glass samples were ground in a clean mortar to a fine powder. A few milligrams of the glass powder were mixed and ground with a relatively large quantity of KBr. KBr pellets transparent to infrared were formed by pressing the mixture at 10 tons for a few minutes.

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

| Glass No. | CuO composition (mol %) | Relative density | Concentration of Cu ions $N$ ($10^{19}$ cm$^{-3}$) | Mean Cu–Cu spacing $R$ ($10^{-7}$ m) | Polaron radius $r_p$ ($10^{-7}$ m) | Optical gap $E_{opt}$ (eV) |
|---|---|---|---|---|---|---|
| a | 0.00 | 2.662 | – | – | – | 6.25 |
| b | 0.02 | 2.669 | 0.160 | 8.553 | 3.450 | 6.05 |
| c | 0.25 | 2.678 | 2.007 | 3.679 | 1.483 | 5.87 |
| d | 0.50 | 2.683 | 4.028 | 2.917 | 1.176 | 5.83 |
| e | 2.00 | 2.726 | 16.520 | 1.822 | 0.734 | 5.70 |
| f | 3.00 | 2.731 | 24.980 | 1.588 | 0.640 | – |
| g | 5.00 | 2.757 | 42.550 | 1.329 | 0.536 | – |

### 2.3. DSC measurements

The differential scanning calorimetry (DSC) measurement was carried out at atmospheric pressure in a Mettler TA 3000 thermal analysis system in the temperature range 303–873 K. The heat flow to the sample was measured under thermally controlled conditions. The sample was ground well to powder form and about 10 mg were contained in an aluminium crucible which served as a reference.

## 3. Results and discussion

### 3.1. Optical absorption spectroscopy

The optical absorption measurements were made at room temperature for the $Na_2B_4O_7$ glass system and for glasses containing CuO as indicated in Table I. Fig. 1 shows the absorbance as a function of the wavelength for the glass films of different compositions. It is clear from the optical absorption spectra that there are no absorption peaks due to CuO in $Na_2B_4O_7$ glasses. This may be due to the low concentration of copper in the glass compositions. The region of high absorption of all film glass samples in the ultraviolet range seems to move to longer wavelengths. Such a change has been reported for ($Na_2B_4O_7$–$Pb_3O_4$) [6] and for the ($V_2O_5$–$B_2O_3$) glass system [11]

The measurement of the 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 ($\alpha > 10^4$ cm$^{-1}$) is usually interpreted in terms of indirect transitions across an optical gap. For many amorphous and glassy materials in which the optical transitions are indirect is found to obey the relation suggested by Davis and Mott [12]

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

where $\alpha(\omega)$ is the absorption coefficient, $\beta$ is a constant, $E_{opt}$ the optical gap and $\hbar\omega$ the photon energy of the incident radiation. Fig. 2 shows the plot of $(\alpha\hbar\omega)^{\frac{1}{2}}$ against $\hbar\omega$ for the glass samples, and the values of $E_{opt}$ determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{\frac{1}{2}} = 0$, are listed in 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

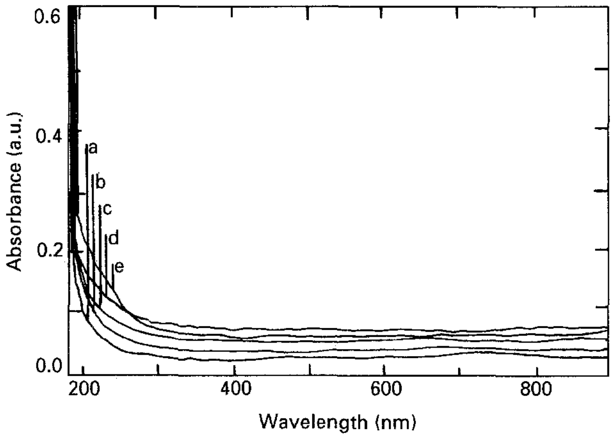

*Figure 1* Optical absorption as a function of wavelength for some $Na_2B_4O_7$–CuO thin film glasses (as listed in Table I).

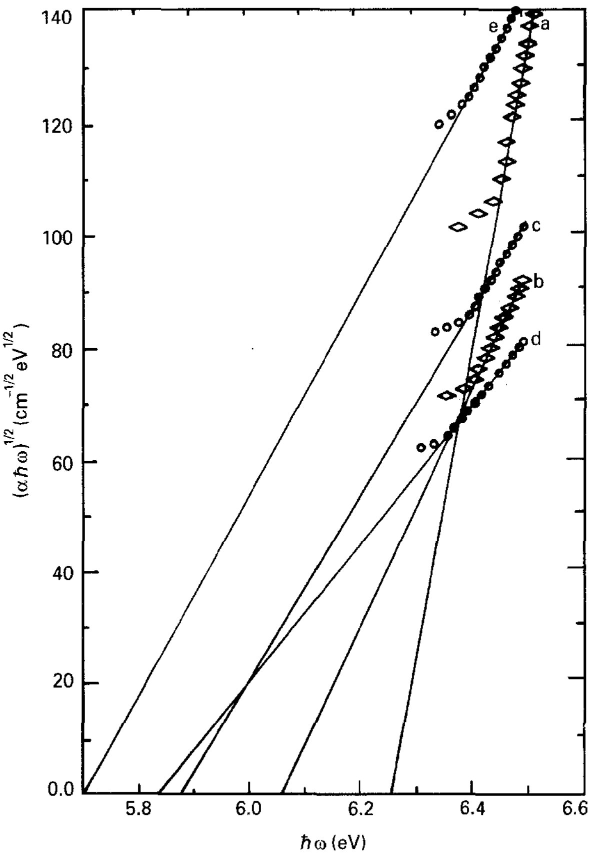

*Figure 2* $(\alpha\hbar\omega)^{\frac{1}{2}}$ as function of photon energy for $Na_2B_4O_7$–CuO glasses (as listed in Table I).

content. This could possibly be explained by a change in the ratio of $Cu^{2+}/Cu^{+}$ content in the glass composition. Similar results have been reported by other workers for the ($Na_2B_4O_7$–$CeO_2$) [7], ($Na_2B_4O_7$–$V_2O_5$) [8] and ($V_2O_5$–$B_2O_3$) [11].

The absorption characteristics of these glasses may be described with the generally accepted qualitative understanding that the absorption edge is determined by the oxygen bond strength in the glass-forming network; for instance, the formation of ion-bridging oxygen, changes the absorption characteristics.

Optical absorption measurements were also made for annealed bulk glass samples as indicated in Table I (thickness ranging from 1.1 to 1.4 mm). Figs 3 and 4 show absorption in arbitrary units as a function of wavelength for annealed bulk glass samples in the wavelength range 180 to 900 nm (Fig. 3) and 180–2500 nm (Fig. 4.).

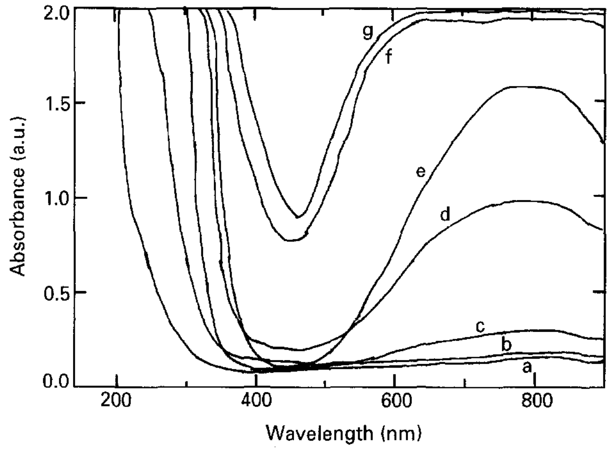

*Figure 3* Absorption as a function of wavelength for sodium tetraborate bulk glass samples containing copper (as listed in Table I).

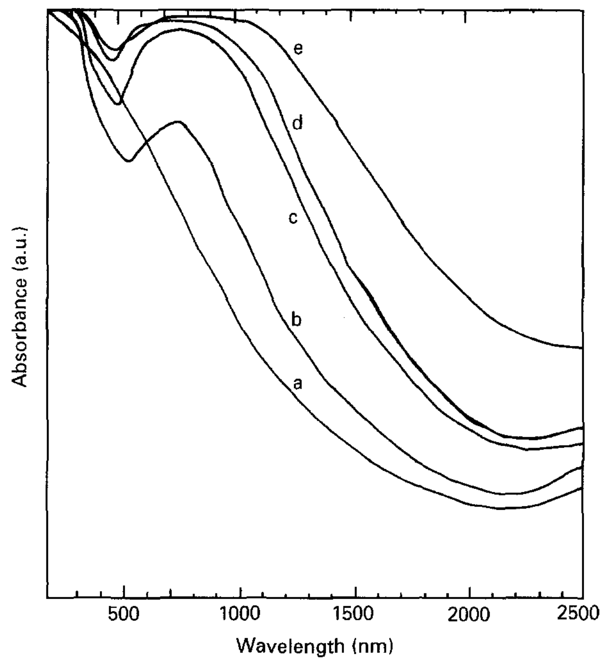

*Figure 4* Absorption as a function of wavelength for $Na_2B_4O_7$–CuO bulk glass samples (as listed in Table I).

The following facts emerge from Fig. 3:

1. The fundamental optical absorption edge of the glass is fairly sharp, as has been observed for different glass composition [9, 10].
2. There is a broad absorption tail for glass sample (a) ($Na_2B_4O_7$) without CuO, which extends from about 340 to 900 nm.
3. There is a broad absorption band at around 780 nm, for glasses doped with CuO and there is an increase in absorption as the CuO content is increased. Bamford [14] 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.* [15] found an absorption band at 852 nm for copper–sodium phosphate glasses attributed to $Cu^{2+}$ ions in an octahedral field with strong tetragonal distortion. It is also reported that an absorption band at 750 nm has been observed in $Na_2B_4O_7$–$Pb_3O_4$–CuO glasses [9] and at 830 nm due to $Cu^{2+}$ in CuO–CoO–$P_2O_5$ glass composition [16].
4. The region of high absorption of all annealed bulk glass samples is in the ultraviolet range and seems to move to longer wavelength, approaching the visible range as the CuO content is increased. By increasing the CuO content, the absorption edges shift towards lower energies which range from 6.17 to 3.48 eV. Such a change has been reported for different glass compositions [6, 10, 11, 17].

The density measurements enable us to calculate $N$, the concentration of copper ions in each composition. The polaron radius can be calculated from the relation

$$r_p = 0.5\,(\Pi/6N)^{\frac{1}{3}} \tag{2}$$

which was postulated by Bogomolov *et al.* [18]. The total copper ion concentration was calculated using the equation used by Nester *et al.* [19]

$$N = \rho N_A/\omega_a \tag{3}$$

where $\rho$ is the density of glass, $N_A$ is Avogadro's number and $\omega_a$ the atomic weight of Cu in the glass. The average Cu–Cu spacing in the glasses was calculated as

$$R = (1/N)^{\frac{1}{3}} \tag{4}$$

The calculated values of $r_p$, $N$ and $R$ are listed in Table I. It is clear from Table I that the polaron radius decreased as the CuO content increased The polaron radius $r_p$ in each composition is less than the corresponding Cu–Cu distance, which is in accordance with the usual prediction of polaron theory that the polaron radius should be smaller than the site separation and greater than the radius of the ion on which the electron is localized.

## 3.2. Infrared absorption spectroscopy

The infrared absorption spectra of glass samples given in Table I together with the spectrum of $Na_2B_4O_7$ are shown in Fig. 5. The absorption peaks observed in all glasses are at 690, 810, 990, 1350 and 3400 $cm^{-1}$

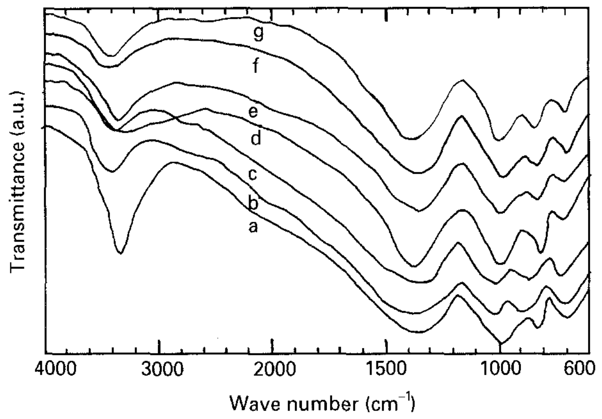

*Figure 5* The infrared absorption spectra taken on KBr discs of glass samples (as listed in Table I).

comparing the infrared spectrum of $Na_2B_4O_7$ with that of copper doped glasses. It appears that all glasses show a great similarity in the general shape of their absorption spectra, without the appearance of any new peaks. The observed peaks could be due to a number of causes such as bridging and non-bridging oxygen ions which are doubly or singly bounded, to the high $BO_4$ groups and low-state $BO_3$ groups, to sodium and copper ions and possibly to some combination of these.

It seems that 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 $Cu^{2+}$ ions.

It may be that the non-bridging oxygen present in ($Na_2O \cdot 2B_2O_3$) glasses remains almost unchanged upon addition of 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 pattern measured for different glass samples are shown in Fig. 6 for a heating rate of 10 K min$^{-1}$. All samples showed an endothermal peak which shifts to lower temperature as the CuO content is increased. Fig. 7 shows the variation of endothermal peak temperature with CuO content in the glass samples. It is obvious from this figure that the phase transition temperature changes from 486 °C in the undoped sample to 476 °C for the doped sample with 5 mol% CuO.

With the addition of a small amount of CuO (0.02 and 0.25 mol%) the shift to the lower temperature is greater than that noted with the addition of a large amount of CuO (3 and 5 mol%) (Fig. 7). Similar results have been reported for $Na_2B_4O_7$–$Fe_2O_3$ [20] and $Na_2B_4O_7$–$V_2O_5$ [10] glass systems.

A process of bond switching or transfer of bonds occurs, whereby segments of the network can become detached and able to move in relation to the rest of the network.

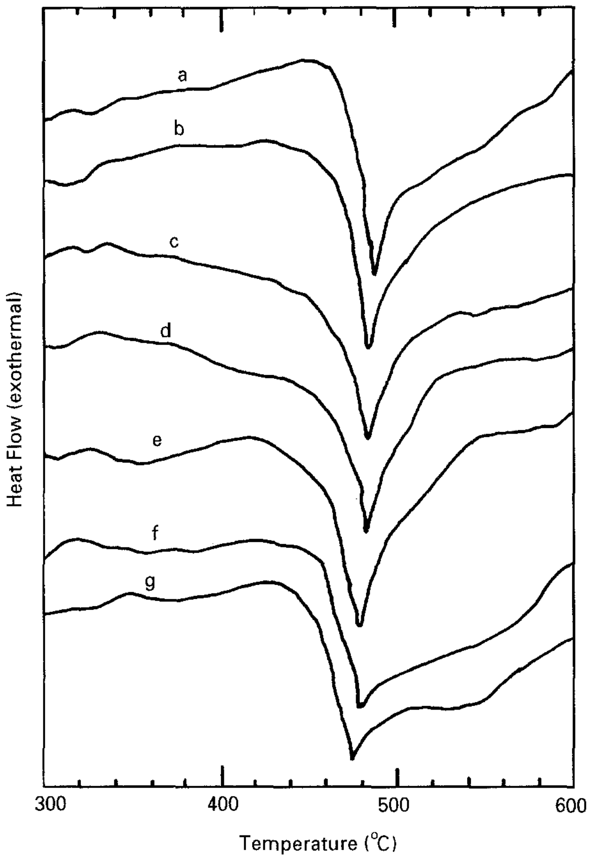

*Figure 6* DSC curves of glass samples (as listed in Table I) taken at a heating rate of 10 K min$^{-1}$.

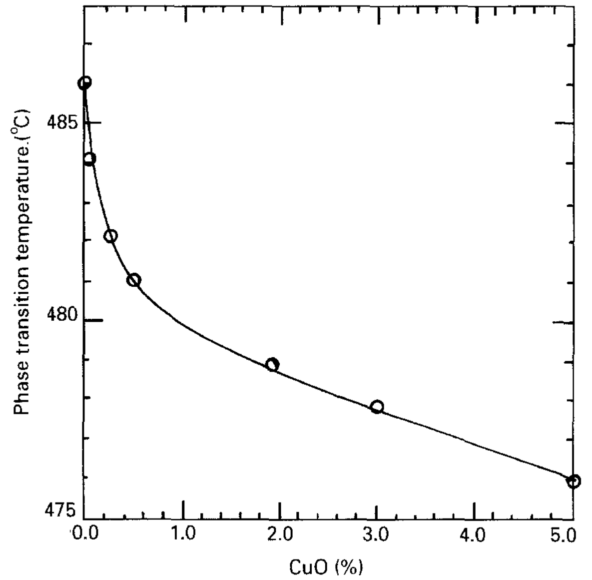

*Figure 7* Variation of endothermal phase transition temperature with CuO content of glass samples (as listed in Table I).

According to Ray [21] the glass-transition temperature is strictly linked to the density of cross-linking rather than to the bond strength. When the samples were cooled down to room temperature the DSC curves were remeasured for all glass samples. This indicates that the phase transition measurements were not permanent and were reversible. No significant change in the weight of the samples was noticed.

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