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Optical and differential scanning calorimetry studies of the $(Na_2B_4O_7)$–(CuO)–(CeO_2) glass system

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A series of glass samples was prepared from an admixture of sodium tetraborate, copper and cerium based on the system $(Na_2B_4O_7)_{98}$–$(CuO)_{2-x}$–$(CeO_2)_x$, where $x = 0.5$, 1 and 1.5 mol%, and results of optical absorption, infrared absorption spectra and differential scanning calorimetry are reported as a function of copper and cerium contents. It was found that increasing the CuO content and decreasing the CeO_2 content shifted the fundamental absorption edge to longer wavelengths. It was also found that the incorporation of CuO and CeO_2 did not affect the limits of the ultraviolet absorption edge of the base glass.

1. Introduction

During the last decade or so, there has been considerable activity in the field of semiconducting oxide glasses containing a single transition metal oxide. Transition metal ions can remain in two or more valence states in glasses, and charge transfer is due to electron hopping from lower to higher valence states. The properties of semiconducting glasses have been of increasing interest since their discovery in 1954 by Denton *et al.* [1]. Studies of optical properties of transition metal ions in glass have made it possible not only to interpret the energy levels involved in the observed transitions, but also to comment on the chemical and structural environment about the metal ion centre.

Traditional spectroscopic studies of lanthanide salts have been reported [2, 3] and traditional glasses doped with small quantities of rare earth oxides have been investigated [4–7]. The difference in the spectral behaviour from that shown by ions of the d-block transition elements, is due to the fact that electrons responsible for the spectral properties of rare-earth ions are 4f electrons, and the 4f orbitals are very effectively shielded from the effect of external forces by the overlying $5s^2$ and $5p^6$ shells.

The states arising from the 4f configurations are only slightly affected by the surroundings of the ions and remain particularly invariant for a given ion in various compounds.

The spectroscopic studies of a glass system containing transition and rare-earth oxides together have rarely been investigated. Ohishi *et al.* [8] studied the optical absorption of 3d transition metal and rare-earth elements in zirconium fluoride glasses. The optical properties of copper phosphate glasses containing some rare-earth oxide have been reported [9, 10].

In previous work we have investigated the spectroscopic studies of sodium tetraborate glasses containing CeO_2 [7] and sodium tetraborate glasses containing CuO [11]. In the present work we report the optical absorption, infrared absorption and differential scanning calorimetry (DSC) measurements on sodium tetraborate glasses with low concentrations of CuO and CeO_2 together. The absorption data are analysed in the light of existing theories on optical absorption in amorphous semiconductors.

2. Experimental procedure

2.1. Glass preparation

The glasses were prepared with the base glass composition of $[Na_2B_4O_7]$ with CuO and CeO_2 according to their molar composition in an alumina crucible (Table I).

A typical melt contained some 30 g material. To reduce the tendency to volatilization, the crucible was initially heated for 1 h at 350 °C and then transferred to another furnace maintained at a temperature which ranged from 1100–1200 °C for 2 h.

The melt was stirred from time to time using an alumina rod. The melt was finally poured on to a clean stainless steel plate and cast into a disc shape of 2 cm diameter and about 1.5 mm thick, maintained at 400 °C and introduced into a furnace which was already at this temperature. The furnace was maintained at this temperature for 1 h and 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

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TABLE I Composition data of glass in the system ($Na_2B_4O_7$–CuO–CeO_2)

Glass sample	Composition (mol %)			Optical gap, E_{opt} (eV)
	$Na_2B_4O_7$	CuO	CeO_2	
a	98	0.50	1.50	5.4
b	98	1.00	1.00	5.3
c	98	1.50	0.50	5.1

a small amount of glass melt on the end of the tube, and blowing it into the air. Films ranging in thickness from 2–6 μm were obtained.

2.2. Optical measurements

Optical measurements for thin films and bulky glasses were carried out at room temperature in the wavelength range 185–800 nm using a Varian model Cary 2390 spectrophotometer. In the absorption region ($\alpha < 10^4\ cm^{-1}$) for these film glasses, multiple interference effects were very pronounced and use of this was made in determining the thickness of the films.

The infrared absorption of thin-film glasses was measured at room temperature in the range 400–4000 cm^{-1} using an IR-460 Shimadzu double-beam recording infrared spectrophotometer.

2.3. DSC measurements

Thermal stability of the glasses was studied at atmospheric pressure in a Mettler TA-3000 thermal analysis system. The differential scanning calorimetry (DSC) technique was applied in the temperature range 303–873 K, where the heat flow to the sample is measured under thermally controlled conditions. The sample was ground well to a powder form and about 20 mg were contained in an aluminium crucible for measurement. The DSC pattern was then measured relative to an empty 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 ternary glass system ($Na_2B_4O_7$–CuO–CeO_2) indicated in Table I. Fig. 1 shows the absorbance as a function of wavelength for the glass films of different compositions. High absorption is observed at wavelengths in the ultraviolet region. This absorption region seems to move towards longer wavelengths as the CuO content is increased and the CeO_2 content is decreased. Absorption peaks around $\lambda = 245$ nm were observed for all samples, where the absorbance increases as the content of CeO_2 decreased and the content of CuO increased.

It is worth mentioning that the same absorption peaks have been reported in the binary glass system ($Na_2B_4O_7$–CeO_2) [7]. It is clear that Fig. 1 shows no absorption peaks that could be attributed to CuO in this ternary glass system. This may be due to the low concentration of copper, as was previously observed in the binary glass system of ($Na_2B_4O_7$–CuO) [11], and ternary glass system of (P_2O_5–V_2O_5–CuO) [12].

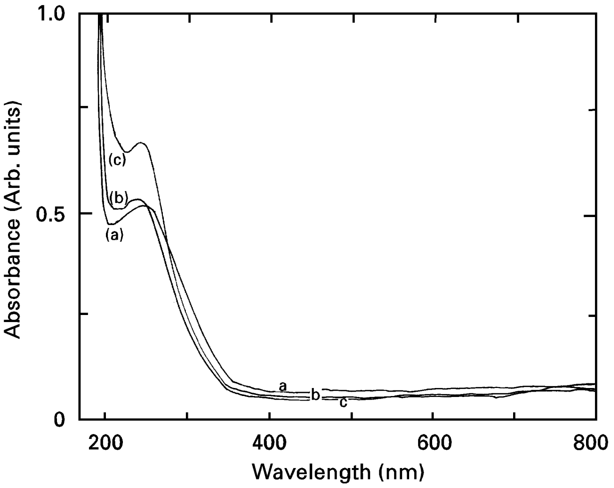

Figure 1 Absorption as a function of wavelength for the unannealed thin blown films listed in Table I.

The absorption peak observed around 245 nm may be attributed to the electron transition from the 4f-orbital to the 5d-level in the Ce^{3+} spectrum.

The absorption in the ultraviolet wavelength region is considered here to be due to the charge transfer between the Ce^{4+} ions and the surrounding oxygens. Similar observations have been reported on phosphate glasses and Al_2O_3–B_2O_3–K_2O doped with cerium oxide [4, 13].

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.

Many amorphous and glassy materials in which the optical transitions are indirect are found to obey the relation suggested by Davis and Mott [14]

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

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

It is clear from Table I that the values of E_{opt} of the glass samples decrease with increase in CuO and decrease in CeO_2 concentrations. It is also evident that the position of the absorption edge and the values of E_{opt} are not particularly sensitive to the incorporation of rare-earth oxides. This may be ascribed to the unusual electronic configuration in these materials, i.e. the shielding of the 4f electrons from external forces by overlying $5s^2$ and $5p^6$ shells. It is expected that the states arising from the various $4f^n$ configurations will remain invariant for a given ion in various compounds, including oxide glasses. Additional evidence

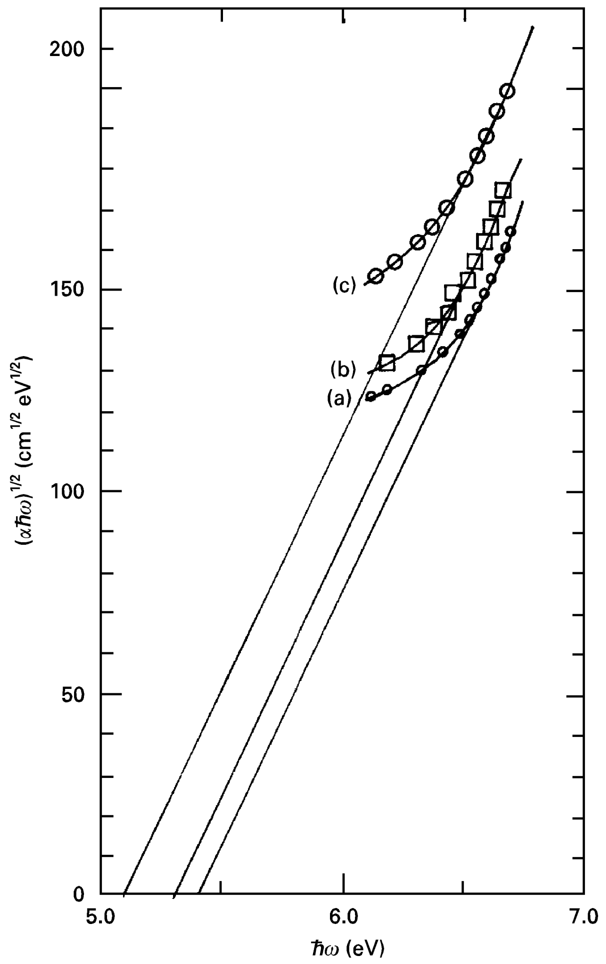

Figure 2 $(\alpha\hbar\omega)^{1/2}$ a function of photon energy for ($Na_2B_4O_7$)–(CuO)–(CeO_2) glass samples (see Table I).

for these phenomena has been presented by Smith and Cohen [5] and others [9, 15]. The high values of E_{opt} measured for higher doping of cerium in ($Na_2B_4O_7$)–(CuO)–(CeO_2) are almost certainly related to the high values of glass-formation temperature which is generally higher than that for ($Na_2B_4O_7$)–(CuO) glass. Optical absorption measurements were also made for annealed bulk glass samples as indicated in Table I (thickness ranging from 1.0–1.4 mm). Fig. 3 shows absorption in arbitrary units as a function of wavelength for annealed bulk glass samples in the wavelength range 200–900 nm. 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 compositions [4, 9, 16].
2. There are no absorption peaks just beyond the edge for all bulk glass samples.
3. A broad absorption band at about 780 nm due to Cu^{2+} is observed for glass sample (C) doped with 1.5 mol % CuO and 0.5 mol % CeO_2. It disappears as the content of CuO is decreased and the content of CeO_2 is increased (sample a, b). This could possibly be explained by a change in the ratio of Cu^{2+}/Cu^{+} content in the glass composition.

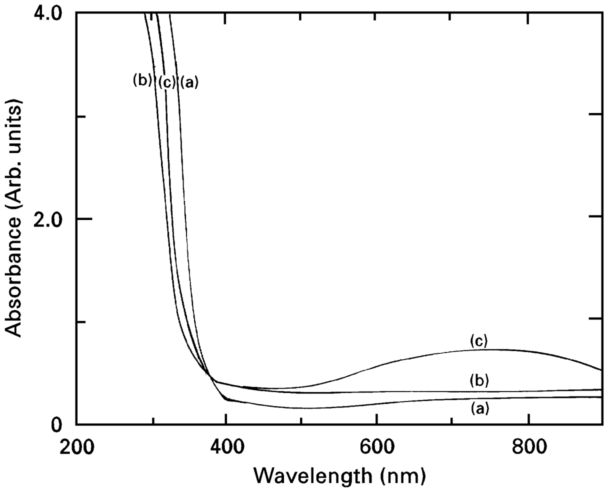

Figure 3 Absorption as a function of wavelength for bulk glass samples (Table I).

Haddon *et al.* [17] 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. Bamford [18] has reported that the cupric (Cu^{2+}) absorption band in copper–sodium borate glasses is centred at 755 nm.

The reason for this different spectral behaviour in cerium glasses lies in the 4f electrons of cerium, as has been discussed earlier.

3.2. Infrared absorption spectroscopy

The infrared absorption spectra of unannealed ($Na_2B_4O_7$)–(CuO)–(CeO_2) glasses given in Table I are shown in Fig. 4 in the range 400–4000 cm^{-1}.

It appears that all the glasses show a great similarity in the general shape of absorption spectra with the exception that for glass sample (a) containing 0.5 mol % CuO and 1.5 mol % CeO_2, well-defined peaks appeared at 950 and 1100 cm^{-1} instead of the broad peak at 900–1150 in the spectra with the low concentration of CeO_2 in the glass (samples b, c). It has been reported [11] that ($Na_2B_4O_7$) glass doped with CuO only showed peaks at 690, 810, 990, 1350 and 3400 cm^{-1} while ($Na_2B_4O_7$) glass doped with CeO_2 [7] showed peaks at 750, 950, 1100, 1250–1500 and 3400 cm^{-1}. It seems that CeO_2 makes some contribution to the formation of the new peaks observed at 950 and 1100 cm^{-1}.

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, copper and cerium ions and possibly to some combinations of these.

It seems that CuO can easily provide 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 the 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 cerium in small quantities, but leads to a reduction in vibrating bond concentration.

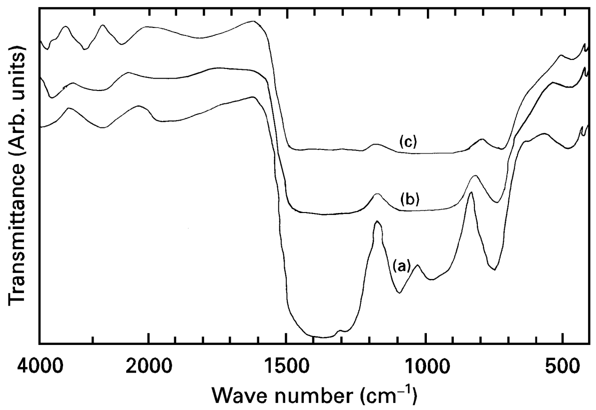

Figure 4 The infrared absorption spectra of sodium tetraborate glasses containing CuO and CeO_2 (Table I) taken with thin blown films.

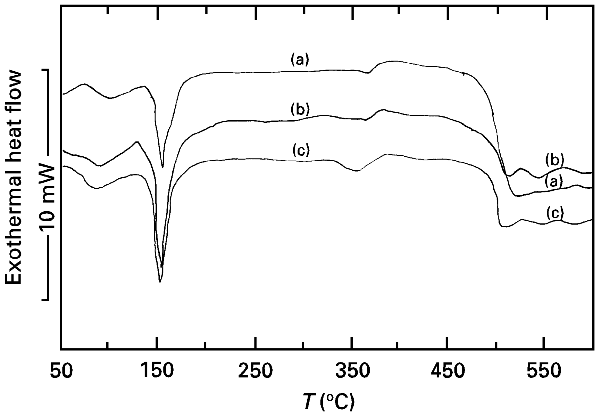

Figure 5 DSC curves of glass samples (Table I) taken at a heating rate of 20 K min^{-1}.

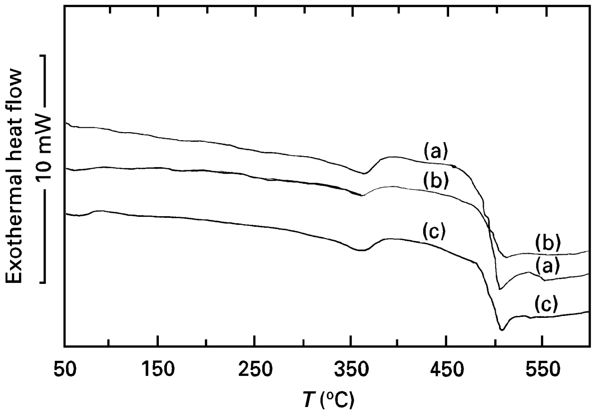

Figure 6 Re-measurements of DSC curves of the glass samples from Fig. 5, after cooling down to room temperature.

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 obtained for different glass samples are shown in Fig. 5 for a heating rate of 20 K min^{-1}. It is clear that all samples show three endothermal peaks at about 150, 360, and 510 °C. Similar results have been reported for ($Ba_2Cu_3O_{7-\delta}$) containing different rare-earth oxides [19].

In our previous works, ($Na_2B_4O_7$) doped with 0.5 mol % CuO [11] showed an endothermal peak about 485 °C while ($Na_2B_4O_7$) doped with 0.02 mol % CeO_2 showed an endothermal peak at 472 °C [7].

Lin *et al.* [19] related the endothermal peak at 510 °C, for the composition ($Ba_2Cu_3O_{7-\delta}$) containing different rare-earth oxides, to the phase transition from an orthorhombic to tetragonal which was confirmed by X-ray diffraction studies.

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.

According to Ray [20], 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 re-measured for all glass samples, and the DSC pattern is shown in Fig. 6.

It is clear from this figure that the endothermal peak at 150 °C disappeared while the endothermal peaks at 360 and 510 °C reappeared. This indicates that the first phase transition at 150 °C in the first measurement was permanent and irreversible, while the second glass transitions at 360 and 510 °C obtained in the earlier measurement were not permanent and reversible.

No significant change in the weight of the samples was observed during the glass transition, as this was checked carefully by accurately weighing the sample before and after measurements.

El-Bayoumi and Subramanian [21] reported that lead borate glasses containing CeO_2 exhibited endotherms over the temperature range 400–515 °C. They also observed a broad weak exothermic maximum at 600 °C in the base glass (lead borate glass) which was attributed to crystallization. This maximum disappeared upon the addition of CeO_2.

4. Conclusion

It was possible to study the optical absorption of sodium tetraborate glasses containing low concentrations of CuO and CeO_2 in the wavelength range from 200–900 nm. An absorption peak around 245 nm was observed for all samples, where the absorbance increased as the content of CeO_2 decreased and the content of CuO increased.

The infrared absorption spectra of unannealed glasses show a great similarity in the general shape of absorption spectra.

The DSC patterns obtained showed three endothermal peaks at about 150, 360 and 510 °C. When the samples were cooled down to room temperature, the DSC curves were remeasured, the endothermal peak at 150 °C disappeared while the endothermal peaks at 360 and 510 °C reappeared.

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