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Some effects of the addition of nickel oxide and of annealing on the optical absorption of sodium tetraborate glasses

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A range of sodium tetraborate glasses containing nickel oxide was prepared and the optical absorption spectra measured. The differential scanning calorimetry technique was used to study compositional features of the glass formation. It was found that the addition of nickel oxide decreases the optical energy gap and introduces new absorption bands as compared with the optical absorption spectrum of pure sodium tetraborate glass. The results revealed that the decrease in the optical energy gap and the disappearance of some absorption bands of the annealed samples could be attributed to an increase in the concentration of reduced valence states of nickel ions which accompanies the microstructure formation.

1. Introduction

Oxide glasses containing transition metal ions were first reported in 1954 [1]. Several transition metal oxides when heated with glass-forming substances such as SiO_2, P_2O_5, TeO_2, GeO_2 and B_2O_3, 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 [2]. A great deal of work has been carried out on many glass systems including a number of glasses based on B_2O_3. Spectroscopic studies have been reported earlier on glass systems based on sodium borate [3–8]. The investigation of the magnetic and electrical properties of borate glasses containing transition metal ions such as nickel oxide has been reported by Hakamatsuka *et al.* [9]. Mironova *et al.* [10] investigated the fine structure of the absorption spectrum of antiferromagnetic NiO, studied the d–d transition and analysed the role of various interactions influencing the absorption spectrum of NiO. Recently Mott [11] has given a full discussion of the role of nickel ions, and how these ions in a crystal can make the material an insulator or a metal. In this work we try to study the effects of annealing and the addition of NiO to sodium tetraborate glasses on both the optical absorption spectroscopy and the glass transition temperature, as studied by using the differential scanning calorimetry (DSC) technique.

2. Experimental procedure

High-purity $Na_2B_4O_7$ and $NiCO_3$ (as a source of NiO) were the materials used for glass preparation in the system having the composition, expressed in mol %, $(Na_2B_4O_7)_{100-x}(NiO)_x$ where x varied from 0 to 3 mol %. A typical melt contained 20 g of material which was carefully mixed in an alumina crucible and placed in a furnace maintained at 1050° C for 1 h. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was stirred from time to time using an alumina rod and was finally poured on to a clean stainless steel plate and cast into a disc 1.5 cm diameter and about 2 to 3 mm thick. Two discs of each composition were cast, one on a stainless steel plate which was at room temperature (unannealed samples) and the other disc was immediately transferred to another furnace which was already maintained at 400° C. The furnace was maintained at this temperature for 2 h and was then switched off to cool down 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 samples examined. The optical density of the samples was measured as a function of wavelength using a Perkin-Elmer 402 spectrophotometer in the spectral range from 190 to 900 nm. The unannealed and the annealed samples used for ultraviolet and visible spectroscopy were polished to about 2 mm thick. The thermal stability of the glass samples was studied in a Mettler TA 3000 thermal analysis system. The DSC technique was applied where the heat flow in air to the samples was measured under thermally controlled conditions. All samples used for this measurement were well ground into powder of 5 mg and contained in an aluminium crucible which served as a reference material.

3. Results and discussion

The optical absorption measurements were made for the pure ($Na_2B_4O_7$) glass system and for glasses containing 1 and 3 mol % of NiO. Figs 1 and 2 show

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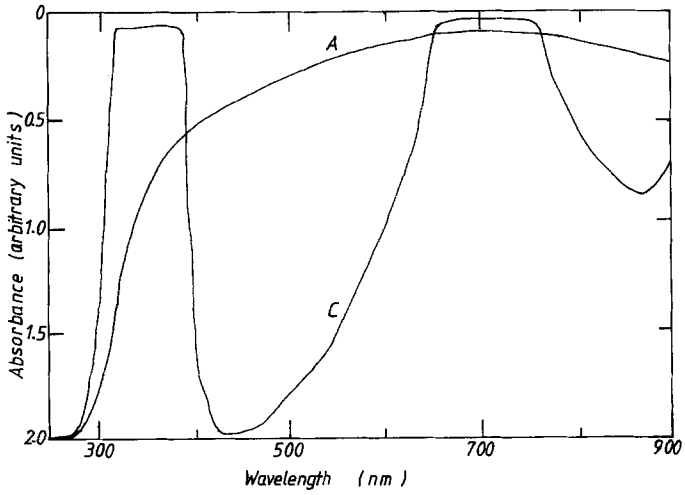

Figure 1 Absorption as a function of wavelength for unannealed glasses (see Table I): Al (2.7 mm thick) and Cl (2.3 mm thick).

the absorption in arbitrary units as a function of wavelength for unannealed and annealed glass samples, respectively. The following facts emerge from these results.

1. The fundamental optical absorption edge of glasses doped with NiO is fairly sharp, as has been observed for the other borate glasses, for example $ZnO–B_2O_3$ glasses [12], rather than the usual $Na_2B_4O_7$ glass.

2. There is a broad absorption tail that extends to longer wavelengths (say, from 600 to 900 nm).

3. The absorption bands at around 430 nm are observed for glasses doped with NiO as is also observed in copper phosphate glasses doped with NiO [13] and there is an increase in absorption as the NiO content is increased (Fig. 2). Haddon *et al.* [14] attribute the absorption band at 435 nm to Ni^{2+} ions in the glasses and suggest that the Ni^{2+} ions are octahedrally coordinated. A band at 870 nm is observed for an unannealed glass containing 3 mol % NiO.

4. The absorption edge seems to move to lower wavelengths as the NiO content is increased.

The effects of annealing on the optical absorption spectrum of the samples could be summarized as follows.

1. The absorption is generally decreased following annealing. The possible effects responsible for this change may be (a) microstructure formation, (b) valency changes in nickel ions, or (c) a combination of both, which take place on annealing.

2. The broad absorption band at about 430 nm for an unannealed 3 mol % NiO-doped sample (Fig. 1) became narrower and more like a peak at 430 nm (Fig. 2).

3. The weak absorption band at 870 nm for the unannealed 3 mol % NiO-doped sample (Fig. 1) disappeared and gave a broad absorption tail extending to longer wavelengths (Fig. 2).

The optical absorption coefficient $\alpha(\omega)$ may be displaced 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.* [15] and discussed fully by Davis and Mott [16]. The coefficient $\alpha(\omega)$ for many amorphous and glassy materials in which the optical transitions are indirect is found to obey the relation

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

where E_{opt} is the optical energy gap and B is a constant. Fig. 3 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for the unannealed and annealed 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. All plots show straight lines with some deviations from linearity at the lower values of α, which were suggested by Redfield and Afromowitz [17] as possibly due to imperfections in the material, but this region of the

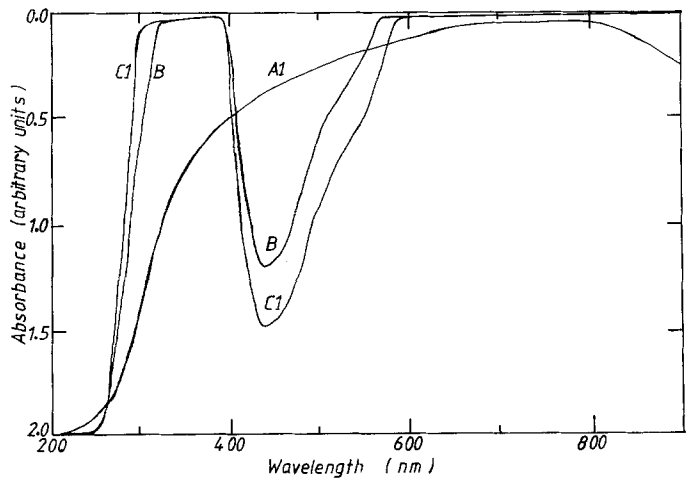

Figure 2 Absorption as a function of wavelength for annealed glasses (see Table I): Al (2.45 mm thick), B (1.35 mm thick), and Cl (2.00 mm thick).

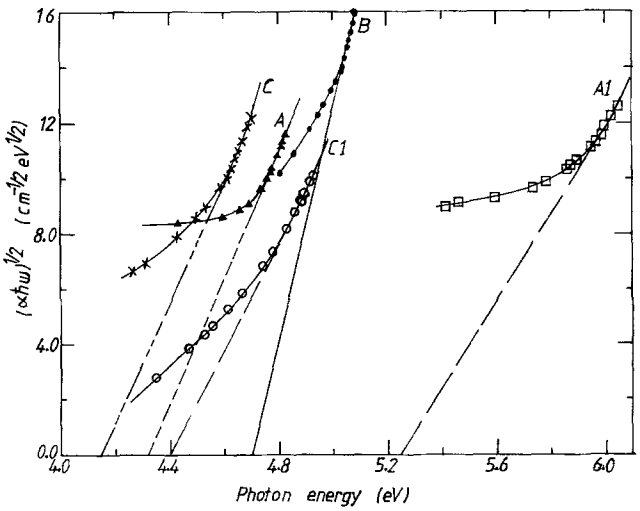

Figure 3 Absorption coefficient as a function of photon energy for unannealed and annealed glass samples (see Table I).

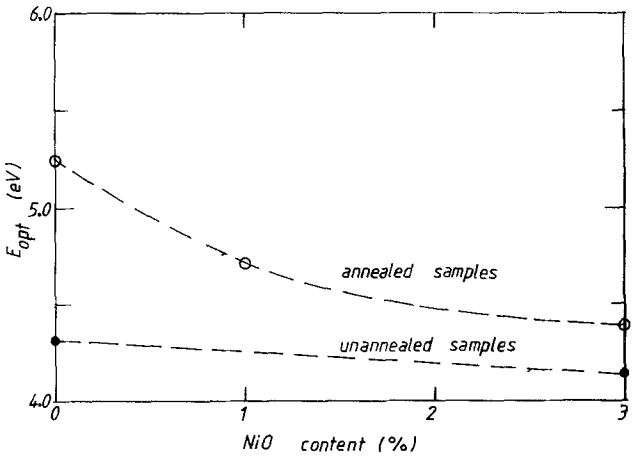

Figure 4 Variation of E_{opt} values with NiO content for unannealed and annealed glass samples.

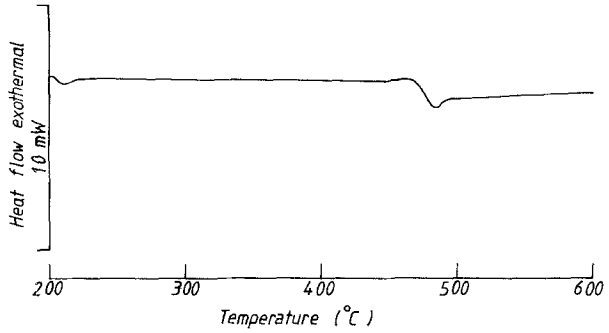

Figure 5 DSC curve of a sodium tetraborate glass sample doped with nickel oxide taken at a heating rate of 10 K min^{-1}.

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. 4 and Table I. It is clear from Table I that the values of E_{opt} of the glass samples are increased followed the annealing, which is consistent with a general reduction of disorder in the glass composition.

The absorption characteristic in these glasses may be described on 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-bridging oxygens, changes the absorption characteristics [18]. By increasing the NiO content, the absorption edges shift towards higher energies which range from 4.15 to 5.25 eV. Such a change has been reported by others for different glass compositions [12, 19–21].

Attempts to fit the data for lower values of absorption to an Urbach plot were not very successful. However, an estimate of the Urbach characteristic energy E_e, which is often taken as a measure of the extent of band tailing, suggests that E_e is of the order of 0.2 to 0.3 eV and decreases by a small amount on annealing. This is consistent with a general reduction of disorder in the system, i.e. the band tailing starts at higher energies and extends to a lesser extent following the annealing. Ahmed and Hogarth [12] calculated the value of E_e for $ZnO-B_2O_3$ glasses as 0.28 eV, which is in good agreement with the values for our glasses.

The DSC patterns were obtained for different unannealed and annealed glass samples. Fig. 5 shows a general DSC pattern for a heating rate of 10 K min^{-1}. It was found that the endothermal peak for the glass transition temperature is around 458° C and is independent of the NiO content or annealing effect. 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. When the sample was cooled down to room temperature, the DSC curve was again measured and the same peak reappeared. This indicates that the glass transition temperature in the first measurement was not permanent and reversible.

TABLE I Composition data and some derived characteristic energies for sodium tetraborate glasses doped with nickel oxide

Glass reference	NiO content (mol %)	E_{opt} (eV)
A	0 (unannealed)	4.32
Al	0 (annealed)	5.25
B	1 (annealed)	4.71
C	3 (unannealed)	4.15
Cl	3 (annealed)	4.40

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