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Some effects of the addition of iron oxide and of annealing on the optical and infrared absorption spectra of sodium tetraborate glasses

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The optical and infrared absorption spectra of sodium tetraborate glasses containing iron oxide have been studied as a function of iron content. It was found that the addition of iron oxide shifts the optical absorption edges towards lower energies and introduces a new absorption band as compared with the optical absorption spectrum of pure sodium tetraborate glass. The addition of iron does not introduce any new absorption band in the infrared spectrum of pure sodium tetraborate glass. The measurements were made on unannealed samples and samples annealed at different temperatures.

1. Introduction

Studies of the 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.

One of the first detailed investigation 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 substance such as SiO_2, P_2O_5, GeO_2, TeO_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 semiconductor glasses based on the borate system [3–6].

Spectroscopic studies have been reported on glass systems based on sodium borate [7–14].

Hakamatsuka *et al.* [15] studied the magnetic and electrical properties of borate glasses containing transition metal ions such as nickel oxide. Sanad and co-workers [16, 17] studied the effect of heat treatment and irradiation on some properties of barium borate glasses containing iron oxide. Park and Chen [18] studied the infrared spectra of crystallization in sodium disilicate glasses containing iron oxide. Khawaja *et al.* [19] studied the spectroscopic and electrical properties of sodium digermanate glasses containing iron oxide.

In this work we have studied the effects of the addition of iron oxide on the optical and infrared absorption of sodium tetraborate.

2. Experimental work

The glass samples were prepared for this study by mixing appropriate amounts of sodium tetraborate ($Na_2B_4O_7$) with Fe_2O_3 in an alumina crucible as shown in Table I. Before weighing, the borates were placed in a drying oven at 400° C for 1 h and then transferred to a vacuum desiccator and allowed to cool. The crucible containing the mixture was placed into a closed high-temperature furnace where it was held for 1 h under atmospheric conditions at a temperature of about 1000° C. During this time the melt was occasionally stirred with an alumina rod. By slow heating it was hoped to reduce mechanical and volatilization losses. 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 4 μm were obtained.

Bulk samples were prepared by pouring the melt onto a massive stainless steel plate and casting into a disc of 1.5 cm diameter and about 2 to 3 mm thickness.

Two discs of each composition were cast, one on a stainless steel plate which was at room temperature (unannealed sample) and the other cast on a stainless steel plate maintained at a temperature of 400° C, and introduced into a furnace which was already at this

TABLE I Composition data for sodium tetraborate glasses containing iron oxide.

Glass sample	Composition (mol %)	
	$Na_2B_4O_7$	Fe_2O_3
1	100.0	0.0
2	99.5	0.5
3	98.0	2.0
4	97.0	3.0
5	95.0	5.0

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temperature. The furnace was maintained at this temperature for 1 h and then switched off to cool down to room temperature. The bulk glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. Samples having thickness in the range 0.95 to 1.30 mm were used for optical absorption measurements.

The optical absorption measurements for thin film and bulk glasses were carried out at room temperature in the wavelength range from 185 to 2500 nm using a Varian model Cary 2390 spectrophotometer. In the low absorption region ($\alpha < 10^4\,\text{cm}^{-1}$) 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 of thin-film glasses was measured at room temperature in the range from 600 to 4000 cm^{-1} using an SP3-100 Pye Unicam double-beam recording infrared spectrophotometer. Also, for comparison, infrared measurements were made for powdered glass samples. The glass samples were ground in a clean mortar to a fine powder. A few milligrams of 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 12 tons (12.2 tonnes) for a few minutes.

3. Results and discussion

3.1. Optical absorption spectra

Complete optical absorption spectra were made at room temperature for unannealed thin blown glass films (thickness ranging from 1 to 4 μm) of the ($Na_2B_4O_7$–Fe_2O_3) glass system as indicated in Table I. Fig. 1 shows the absorption as a function of wavelength ranging from 185 to 2500 nm. Fig 2. shows the variation of the absorption coefficient α as a function of the photon energy. It is clear from these figures that in the high-energy region there appears an absorption band centred at about 186 nm (6.66 eV).

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The position of this band seems to be independent of the iron content in the glasses. Therefore this band cannot be due to transitions which involve iron. The charge-transfer band centred at about 216 nm (5.74 eV) increases slightly with iron content in the glass and is absent in the glass which does not contain iron, indicating the band to be associated with transitions that involve iron. Khawaja *et al.* [19] observed an absorption band at 5.7 eV in the high-energy region and a charge-transfer band at about 4.75 eV for sodium digermanate glasses containing Fe_2O_3. Beyond 3.6 eV (Fig. 2) the absorption tail extends to 2500 nm without showing any peak.

The optical absorption measurements were also made for unannealed bulk glass samples as indicated in Table I (thickness ranging from 1.2 to 1.50 mm). Fig. 3 shows absorption in arbitrary units as a function of wavelength for unannealed bulk glass samples. The following points may be noted:

1. The fundamental optical absorption edge of glasses doped with Fe_2O_3 is fairly sharp, as has been observed for other borate glasses, for example

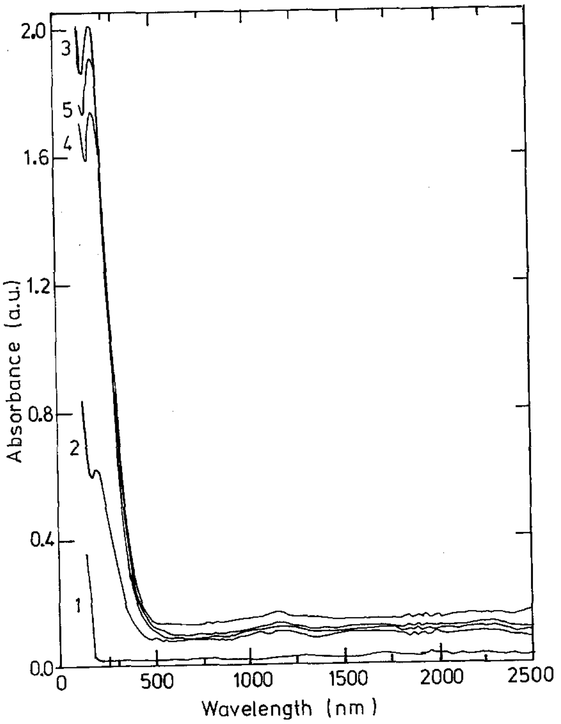


Figure 1 Absorption as a function of wavelength for unannealed thin blown glass films (a.u. = arbitrary units). Numbers by curves refer to Table I.

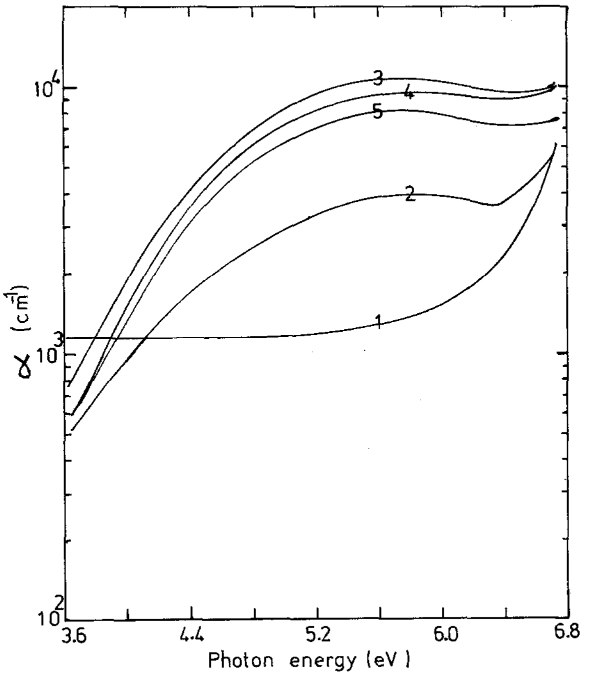


Figure 2 The optical absorption coefficient $\alpha(\omega)$ of various thin blown glass films (Table I) as a function of photon energy.

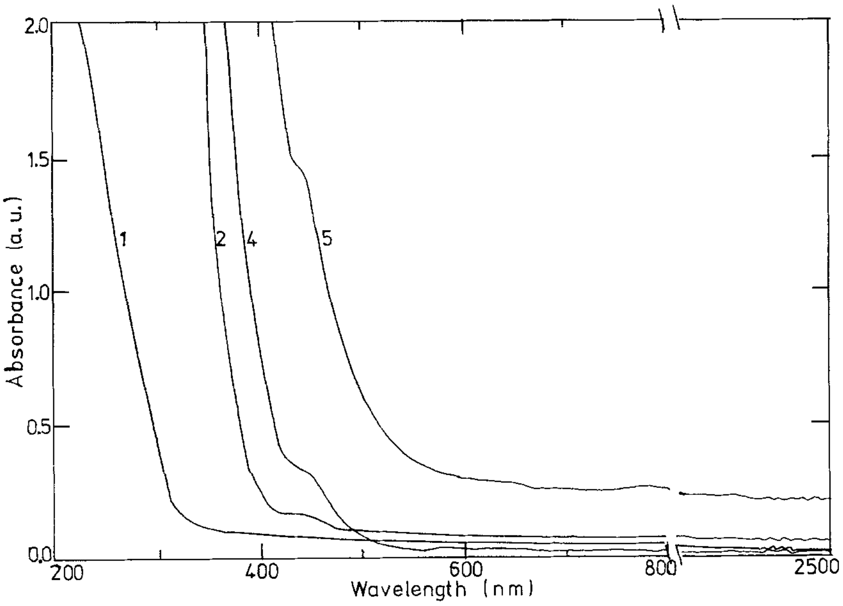


Figure 3 Absorption as a function wavelength for unannealed bulk glass samples (Table I).

$Na_2B_4O_7$–NiO glasses [12], $Na_2B_4O_7$–Pb_3O_4–CuO glasses [14] and ZnO–B_2O_3 glass system [20] rather than the usual $Na_2B_4O_7$ glass.

2. The absorption band at around 446 nm is observed for all glasses doped with Fe_2O_3 and there is an increase in absorption as the Fe_2O_3 content is increased. The same band is also observed in zirconium fluoride glasses doped with Fe_2O_3 [21]. Haddon *et al.* [22] attributed the absorption bands at 374, 425 and 440 nm in Na_2O–P_2O_5–Fe_2O_3 glasses to Fe^{3+} ions in the glasses and suggest that the Fe^{3+} ions are octahedrally or tetrahedrally coordinated. An absorption band at 430 nm has been observed for an unannealed $Na_2B_4O_7$ glass containing NiO [12].

3. There is a broad absorption tail for all glass samples that extends from about 600 to 2500 nm without showing any peak in this region.

4. By increasing the Fe_2O_3 content, the fundamental absorption edges shift towards lower energies which range from 5.5 to 3.0 eV. Such a change has been reported by others for different glass compositions [12, 23, 24].

Figs 4 and 5 show the absorption as a function of wavelength for bulk glass samples annealed at 400° C for 1 and 3 h, respectively. The thickness of these samples is the same as for the unannealed samples. It is clear from these figures that the absorption is generally decreased following annealing. The possible effects responsible for this change may be (a) valency changes in iron ions, (b) microstructure formation, or (c) a combination of both, which take place on annealing.

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-bonding oxygens, changes the absorption characteristics [23].

3. 2. Infrared absorption spectra

The spectral curves for the 4000 to 600 cm^{-1} region obtained from thin blown films of pure sodium tetraborate system and glasses containing various amount of Fe_2O_3 are shown in Fig. 6. The spectra of the same glass compositions obtained on KBr discs annealed at 400° C for 1 h are presented in Fig. 7 for the same spectral region. Fig. 8 shows the spectra obtained on KBr discs annealed at 600° C for 3 h.

The infrared spectra for various iron-doped glasses

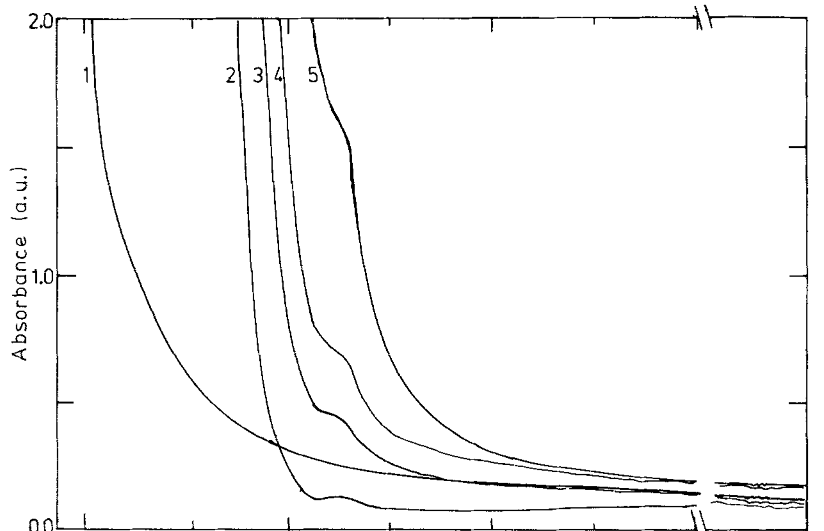


Figure 4 Absorption as a function of wavelength for bulk glass samples (Table I) annealed at 400° C for 1 h.

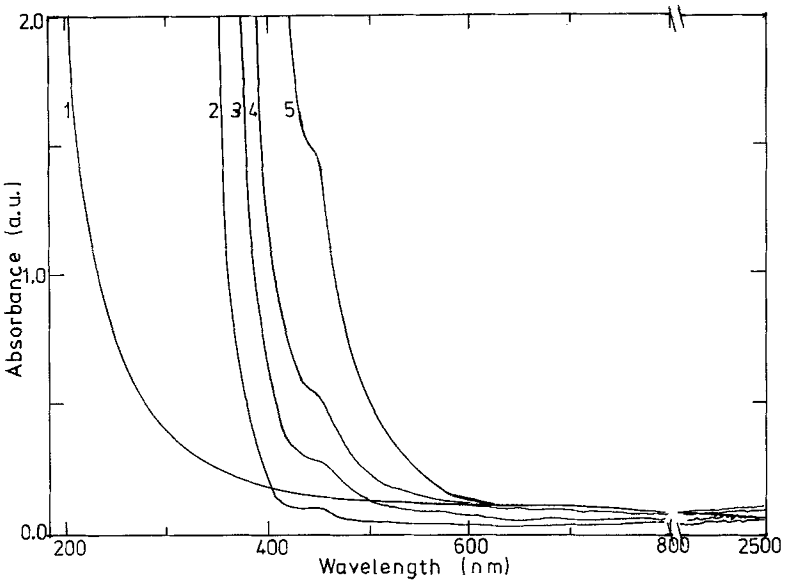
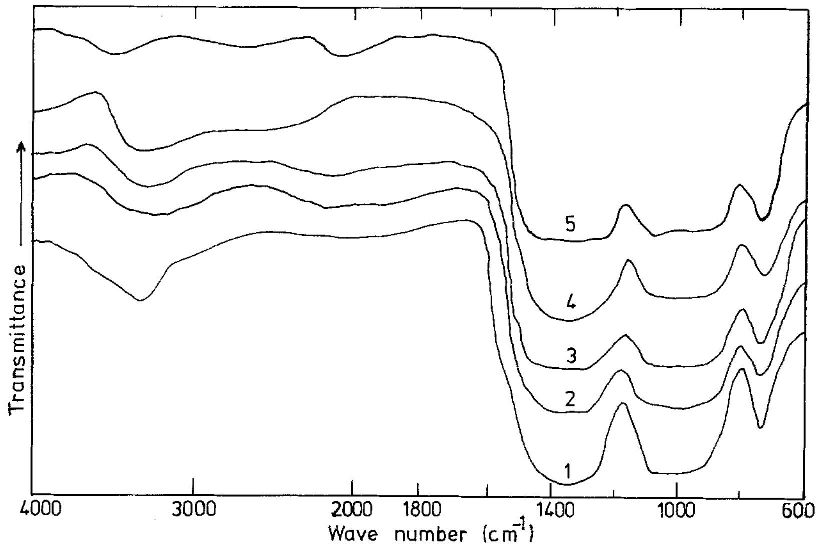


Figure 5 Absorption as a function of wavelength for bulk glass samples (Table I) annealed at 400° C for 3 h.

Figure 6 The infrared absorption spectra of sodium tetraborate glasses (Table I) containing Fe_2O_3, taken with thin blown films.



are quite similar in shape to the spectrum of undoped sodium tetraborate glass, without the appearance of any new peaks. These are in agreement with the spectra of Fe_2O_3-Na_2O-$2GeO_2$ [19] and of Fe_2O_3-Na_2O-$2SiO$ [18] glasses. The absorption peaks observed in all glasses are at 720, 850 to 1060, 1350 and 3400 cm^{-1}.

Comparing the spectra of thin blown films with KBr discs of the same composition, it appears that all the glasses show a great similarity in the general shape of the absorption spectra, with the exception that in the blown thin films the peaks become sharper and better defined.

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 BO_4 and BO_3 groups, to sodium and iron ions, and possibly to some combination of these. It seems that Fe_2O_3 can easily give the oxygen required for the formation of

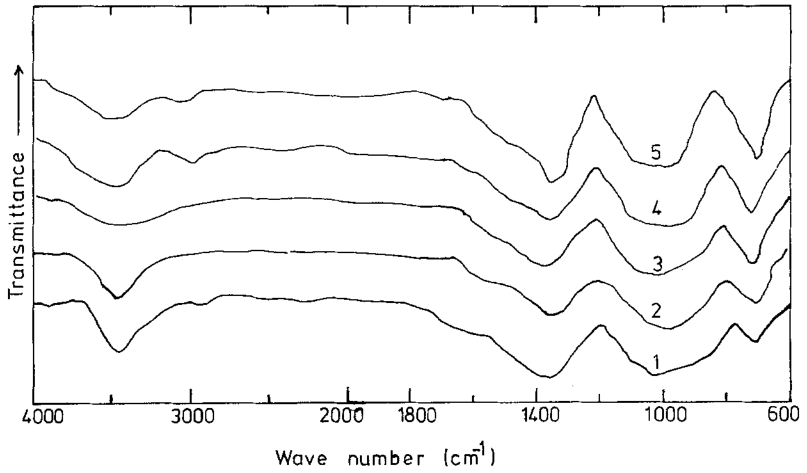


Figure 7 The infrared absorption spectra taken on KBr discs of glass samples (Table I) annealed at 400° C for 1 h.

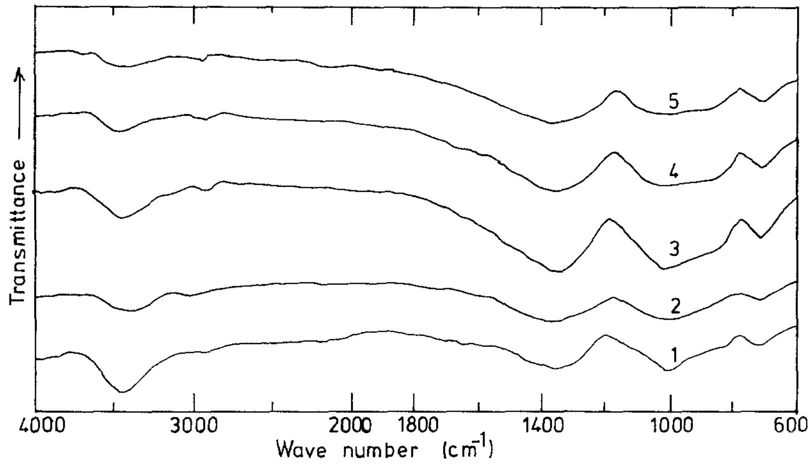


Figure 8 The infrared absorption spectra taken on KBr discs of glass samples (Table I) annealed at 600° C for 3 h.

BO_4 groups. Hence the maximum BO_4/BO_3 ratio will depend on the concentration and nature of the Fe^{3+} ions.

It may be that the non-bridging oxygen present in $Na_2O.2\,B_2O_3$ glasses remains almost unchanged upon the addition of iron in small quantities.

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

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