Optical and DSC studies of the $Na_2B_4O_7$–Pb_3O_4 glass system

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A series of glass samples were prepared from admixtures of $Na_2B_4O_7$ and Pb_3O_4 and results are reported for optical absorption, infrared absorption spectra and differential scanning calorimetry (DSC) as a function of lead content up to 40 mol%. It is found that the addition of lead oxide decreases the optical energy gap and shifts the optical absorption edges towards lower energies in the range from 4.96 to 3.29 eV. The addition of lead oxide does not seem to introduce any new absorption band as compared with the infrared spectrum of pure sodium tetraborate glass.

1. Introduction
In recent years the properties of glasses have been interpreted in electronic terms rather than simply from the chemical point of view. Much of the state of the art is included in a book written by Mott and Davis [1], and in particular the relationships between structure and properties has led to an increase in the potential application of glasses and glassy complex materials in electronic systems, for example.

Several papers have appeared recently reporting the properties of glassy and amorphous semiconductors based on the borate glass system [2–6].

Spectroscopic studies have been reported earlier on glass systems based on sodium tetraborate [7–13]. Worrell and Henshall [14] studied the vibrational spectroscopy of some lead silicate glasses. Qualitative studies of the nucleation and crystallization of lead borate glass containing CeO_2 have been reported by El-Bayoumi and Subramanian [15].

In previous papers we have studied the optical [16] and electrical [17] properties of some sodium tetraborate glasses containing lead and copper. In the present work we report some optical and differential scanning calorimetry measurements with a view to study the effect of Pb_3O_4 addition to sodium tetraborate glasses.

2. Experimental procedure
Homogeneous glass samples of the composition (mol %) $(Na_2B_4O_7)_{100-x} - (Pb_3O_4)_x$, where x varied from 0 to 40 mol % (Table I), were prepared from chemically pure grades of material. The basic materials were placed in an electrical furnace, gradually heated and kept at 900° C for one hour. The melt was stirred frequently, using an alumina rod. By slow heating it was intended to reduce mechanical and volatilization losses. 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. The furnace was maintained at this temperature for 1 h and was then switched off to allow it to cool off 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 samples examined.

The optical density of the samples was measured as a function of wavelength at room temperature using an LKB Biochrom Ultrospec 4050 spectrophotometer in the spectral range from 200 to 900 nm. The glass samples used for ultraviolet and visible spectroscopy were polished to about 1 mm thickness. For infrared 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 infrared, were formed by pressing the mixture at 10 tons (10.16 Mg) for a few minutes. The infrared absorption spectra of these samples were determined, using a Unicam SP3-300 double-beam recording infrared 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 technique was applied in the temperature range 303 to 873 K. The heat flow to the sample was measured under thermally controlled conditions. The sample was well ground into a powder and about 10 mg was contained in an aluminium crucible for measurement.

The differential scanning calorimetry (DSC) pattern was then measured relative to an empty alumina crucible which served as a reference.

3. Results and discussion
3.1. Optical absorption
The optical absorption measurements were made at room temperature for the pure $Na_2B_4O_7$ glass system and for glasses containing Pb_3O_4 as indicated in
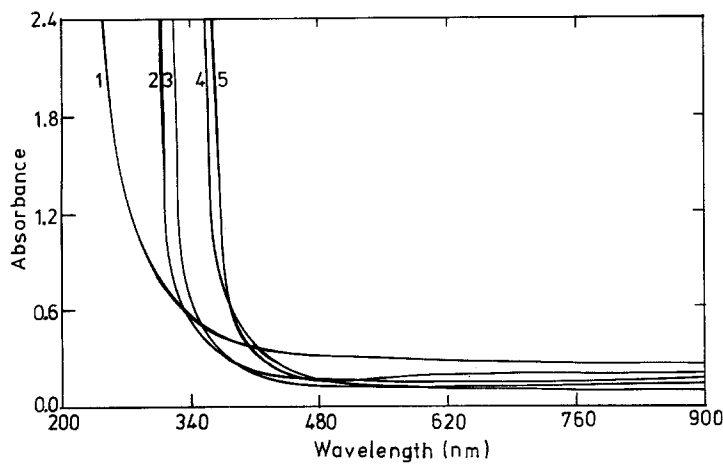
Figure 1 Absorption as a function of wavelength for $Na_2B_4O_7$–Pb_3O_4 glass samples (numbered as in Table I): 1 (1.21 mm thick), 2 (0.92 mm thick), 3 (0.85 mm thick), 4 (1.89 mm thick), 5 (1.02 mm thick).

Table I. Fig. 1 shows the absorption as a function of wavelength. It is clear from this figure that the region of high absorption of all glass samples is in the ultra-violet range and seems to move to longer wavelength, approaching the visible range, as the Pb_3O_4 content is increased. Furthermore, it is noted that the fundamental optical absorption edge of glass samples doped with Pb_3O_4 is fairly sharp, as has been observed for other borate glasses, for example, nickel-doped sodium tetraborate glasses [13] and ZnO–B_2O_3 glasses [18], rather than the usual $Na_2B_4O_7$ glass. By increasing the Pb_3O_4 content, the absorption edges shift towards lower energies which range from 4.96 and 3.29 eV. Such a change has been reported for nickel-doped sodium tetraborate glasses [8, 13] and for the V_2O_5–B_2O_3 glass system [18].

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.* [19] and discussed fully by Davis and Mott [20]. The coefficient $\alpha(\omega)$ for many amorphous and glassy materials in which the optical transitions are indirect is found to obey the relation

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

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 $(\alpha\hbar\omega)^{1/2} = 0$, are listed in Table I. 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 decrease following the increase in the Pb_3O_4

content. Similar results have been reported by other workers for the V_2O_5–B_2O_3 glass system [18].

The absorption characteristics of 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 oxygen, changes the absorption characteristics [21].

3.2. Infrared absorption spectroscopy

The infrared absorption spectra of glass samples given in Table I are shown in Fig. 4. The absorption peaks observed in all glasses are at 470, 710, 820, 940, 1010, 1130, 1340 and 3400 cm^{-1}. Comparing the infrared spectrum of $Na_2B_4O_7$ with those lead-doped glasses containing 10, 20, 30 and 40 mol% respectively of Pb_3O_4, it appears that all glasses show great similarity in their general shape of absorption spectra without the appearance of any new peaks, with the exception that the peaks are weakened and broadened with increasing Pb_3O_4 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

TABLE I Chemical composition and derived optical energy gap for the $Na_2B_4O_7$–Pb_3O_4 glass system

Sample No.	Composition (mol %)		Optical gap, E_{opt} (eV)
	$Na_2B_4O_7$	Pb_3O_4	
1	100	0	3.85
2	90	10	3.58
3	80	20	3.45
4	70	30	3.05
5	60	40	2.70
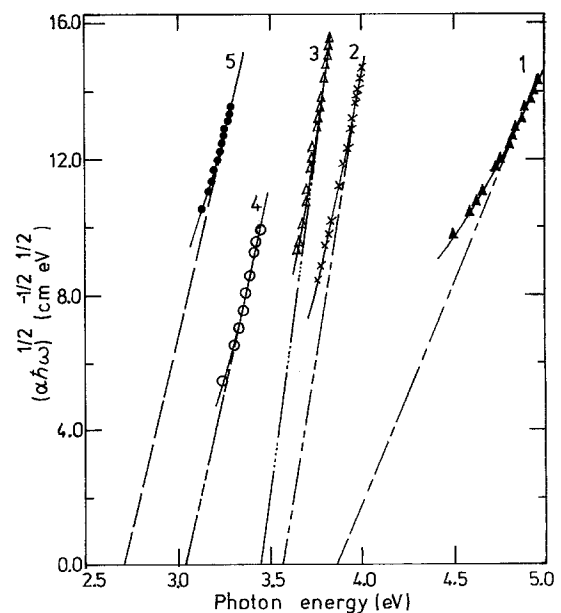
Figure 2 Absorption coefficient as a function of photon energy for $Na_2B_4O_7$–Pb_3O_4 glass samples (numbered as in Table I).
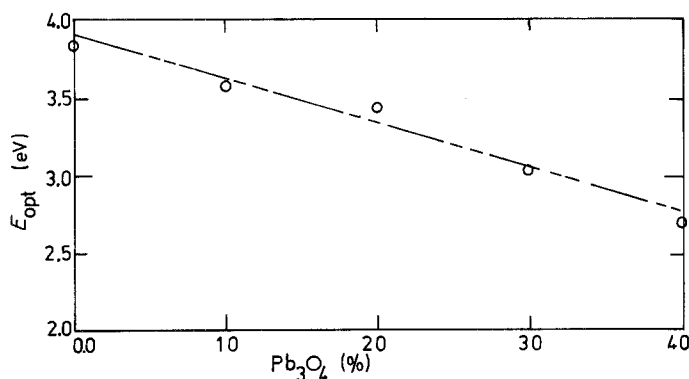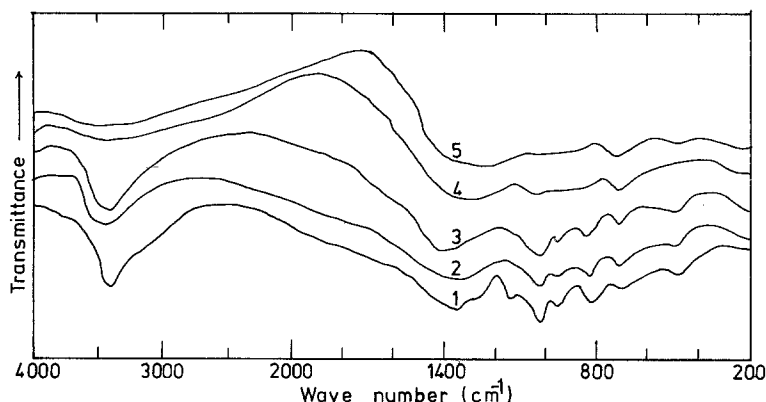
Figure 4 The infrared absorption spectra of glass samples (numbered as in Table I).

bonded, to the high BO_4 groups and low-state BO_3 groups, to sodium ions, and possibly some combination of these.

It seems that Pb_3O_4 can easily give the oxygen required for the formation of BO_4 groups, and the maximum BO_4/BO_3 ratio will depend on the amount and the nature of the Pb^{2+} ions. It may be that the non-bridging oxygens present in $(Na_2 0.2B_2O_3)$ glasses remain almost unchanged upon the addition of lead in small quantities, but that this leads to a reduction in the number of vibrational bonds.

Figure 5 DSC curves of glass samples (numbered as in Table I) taken at heating rate of $20 \, K \, min^{-1}$.

The absorption band at $3400 \, cm^{-1}$ is believed to be associated with water trapped in glasses during the experiment. Borrelli *et al.* [7] observed the absorption peaks in $Na_2B_4O_7$ glass at 710, 840, 1050, 1360 and $3400 \, cm^{-1}$. Khan and Al-Rfooh [12] observed peaks at 790 and $1190 \, cm^{-1}$ for $Na_2B_4O_7$ glass and reported that the infrared spectra for various nickel-doped sodium tetraborate glasses are quite similar in shape to the spectrum of undoped $Na_2B_4O_7$ glass, without the appearance of any new peaks.

3.3. DSC measurements

The DSC patterns for different glass samples were obtained and are shown in Fig. 5 for a heating rate of $20 \, K \, min^{-1}$. It was found that all samples showed an endothermal peak, and this peak shifts to lower temperatures as the Pb_3O_4 content is increased. Fig. 6 shows the variation of endothermal peak temperature with the Pb_3O_4 content in the glass samples. Glass samples containing Pb_3O_4 also exhibited an exothermal peak, and this peak shifts toward higher temperature as the Pb_3O_4 content is decreased.

In pure $Na_2B_4O_7$ samples and glass samples containing $10 \, mol \%$ of Pb_3O_4, the exothermal peak appears to be shifted to temperatures above $600° \, C$, as is evident from Fig. 5. Therefore it is worth mentioning that sodium tetraborate glass containing lead oxide shows two phase transitions, and the phase transition temperatures shift to lower temperatures as the Pb_3O_4 content is increased in the glass system.

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 [22], the glass transition temperature is strictly linked to the density of cross-linking rather than to the bond strength. When the
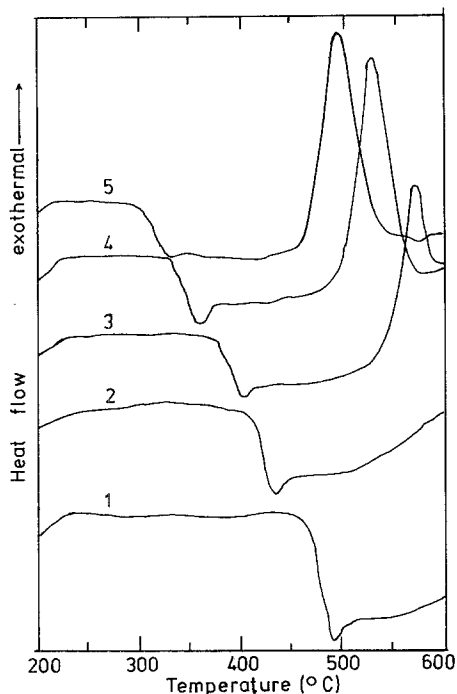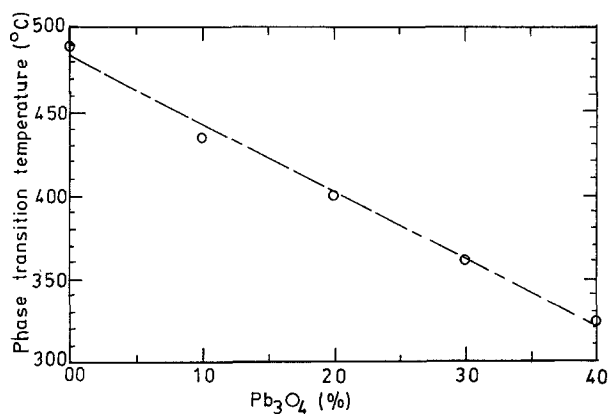
Figure 6 Variation of endothermal phase transition temperature with Pb_3O_4 content.

samples were cooled down to room temperature the DSC curves were re-measured and the same endothermal peak reappeared for all glass samples, while the exothermal peaks for Samples 3, 4 and 5 disappeared. This indicates that the first phase transition in the first measurement was not permanent and reversible, while the second glass transition for Samples 3, 4 and 5 obtained in the earlier measurement was permanent and irreversible.

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. It has been reported that for the $V_2O_5-P_2O_5-B_2O_3$ glass system there are two phase separations, and any subsequent crystalliztion of V_2O_5 is at 290 and 410° C [23]. El-Bayoumi and Subramanian [15] reported that lead borate glasses containing CeO_2 exhibited endotherms over the temperature range 400 to 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. The exothermic maximum disappeared upon the addition of CeO_2.

Acknowledgements

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