phys. stat. sol. (a) **134**, K77 (1992)

Subject classification: 78.20 and 78.30; S11

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Studies of the Effects of CeO_2 on the Optical Absorption and DSC Measurement of Sodium Tetraborate Glasses

By

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The spectroscopic studies of lanthanide salts and traditional glasses doped with varying quantities of rare-earth oxides, exhibit a variety of scientifically interesting characteristics ([1, 2] and references therein).

In this note a spectroscopic study on the effect of small additions of CeO_2 to sodium tetraborate glasses is discussed. The experiments are based on the optical and infrared absorption techniques.

Details about preparing the glasses and the experimental procedures can be found elsewhere [1]. Briefly, for preparing the glasses a mixture of sodium tetraborate $(N_2B_4O_7)_{100-x}$ and $(CeO_2)_x$ (chemical purity 99.99%; $x = 0$, 0.02, 0.15, 1.0, and 2 mol%) is used and unannealed thin glass films of thickness 4 to 10 μm were obtained by the blowing technique [2].

A Varian model 2390 spectrophotometer in the wavelength range from 185 to 900 nm and an SP3-100 Pye Unicam double-beam infrared spectrophotometer were used for the

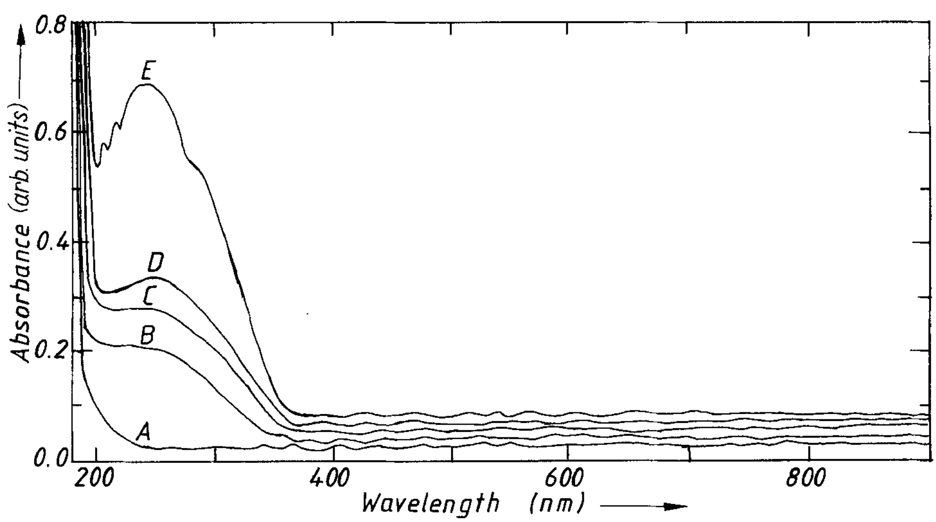

Fig. 1. Absorption as a function of wavelength for the unannealed thin blown films listed in Table 1

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Table 1
Chemical composition and some properties of glasses in the system $Na_2B_4O_7$–CeO_2

glass sample	composition (mol%)		density (g/cm^3)	refractive index	optical gap E_{opt} (eV)
	$Na_2B_4O_7$	CeO_2			
A	100.00	0.00	2.5234	1.6575	6.25
B	99.98	0.02	2.5577	1.6572	5.63
C	99.85	0.15	2.5934	1.6571	5.32
D	99.00	1.00	2.7631	1.6570	5.28
E	98.00	2.00	2.8770	1.6568	5.10

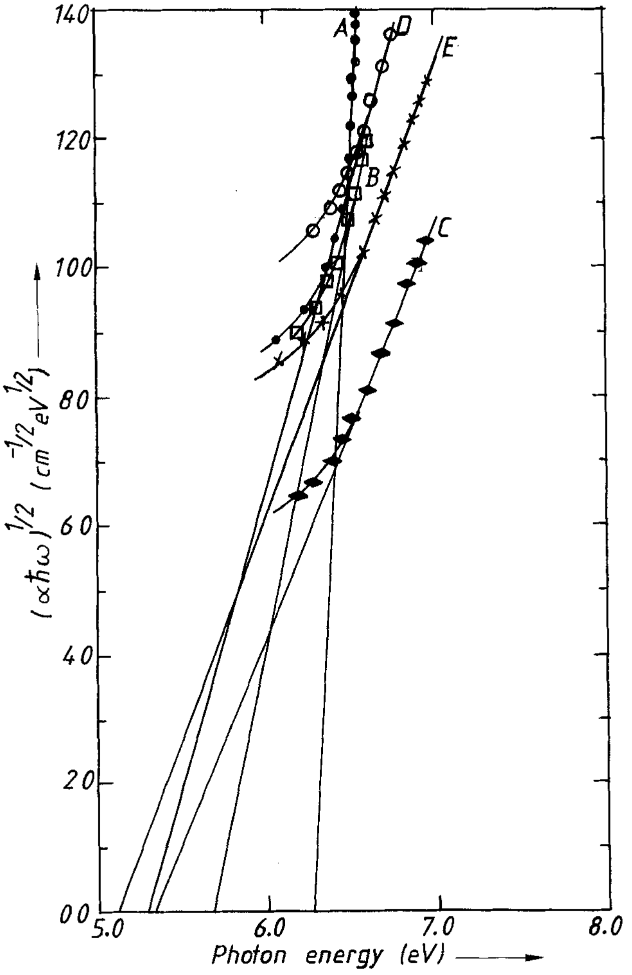

Fig. 2. $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for $(Na_2B_4O_7)$–(CeO_2) glass samples (see Table 1)

optical and infrared absorption measurements, respectively. All measurements were made at room temperature.

The thermal stability of the glasses was studied in a Mettler TA 3000 thermal analysis system in the temperature range from 303 to 873 K. The refractive index of these glasses was measured by an Abbe refractometer with an accuracy of ± 0.0002.

Fig. 1 illustrates the absorbance as a function of wavelength for all samples. High absorption at wavelengths in the ultraviolet region is observed. This absorption region seems to move towards longer wavelengths as the CeO_2 content is increased. Absorption peaks around $\lambda = 245$ nm were observed for all samples, where the absorbance increases as the content of CeO_2 is increased. Also two additional peaks around $\lambda = 215$ and 207 nm were observed for the sample containing 2 mol% of CeO_2. These absorption bands 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.

It is worth mentioning that a similar observation has been reported in [3] and [4] on phosphate glasses and Al_2O_3–B_2O_3–K_2O doped with cerium oxide, respectively.

The optical absorption coefficient $\alpha(\omega)$ (ω is the angular frequency of the incident radiation) is related to the photon energy $\hbar\omega$ by [5],

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

where E_{opt} is the optical energy gap and B a constant. In Fig. 2 the values of $\alpha(\omega)\,\hbar\omega$ are plotted versus the values of $\hbar\omega$ for all samples. The graph shows straight lines with some deviations at lower photon energy. These deviations can be explained due to the imperfection in the material. From Fig. 2, the value of E_{opt} of each sample is extracted. These values

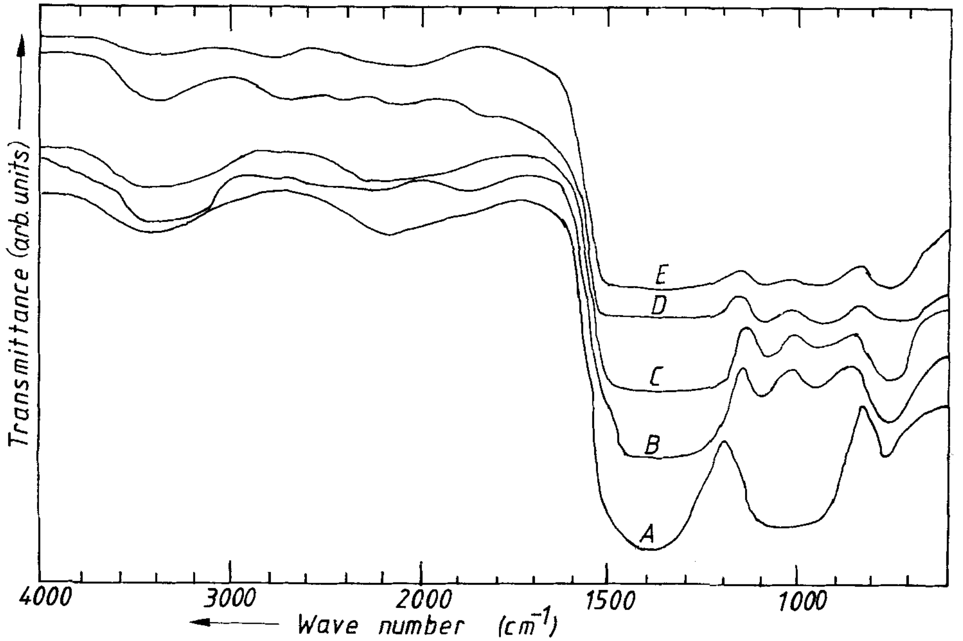

Fig. 3. Room temperature infrared absorption spectra of $(Na_2B_4O_7)$–(CeO_2) glass samples (see Table 1)

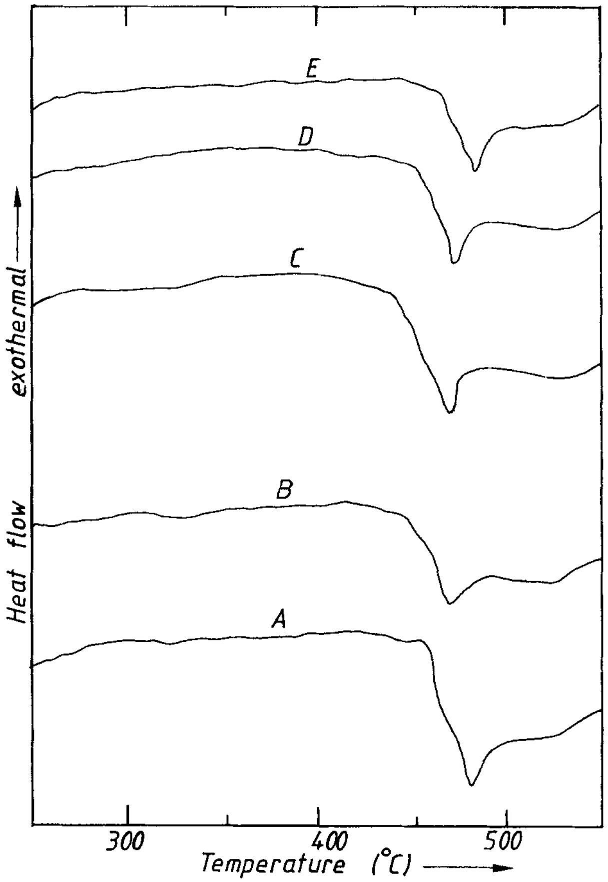

Fig. 4. DSC curves of ($Na_2B_4O_7$)–(CeO_2) glass samples (see Table 1)

together with the corresponding values of the density and the refractive index obtained are listed in Table 1. It has also been found that the absorption edge and the values of E_{opt} (between 6.25 and 5.10 eV) are not particularly sensitive to the incorporation of rare-earth oxides. This phenomenon may be ascribed to the unusual electronic configuration in these materials.

In Fig. 3, the infrared spectra of pure sodium tetraborate glass and glasses containing various amounts of CeO_2 are shown in the range 600 to 4000 cm^{-1}. It appeared that all measured absorption spectra were of the same general shape. The absorption peaks observed in the base glass ($Na_2B_4O_7$) are at 750, 900 to 1150, 1250 to 1500, and 3400 cm^{-1}.

Glasses doped with CeO_2 show absorption bands at 950 and 1100 cm^{-1} instead of the broad band occurring at 900 to 1150 cm^{-1} in the spectrum of the undoped glass.

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 high BO_4 groups and low-state BO_3 groups, to sodium and cerium ions, and possibly to some combinations of these. The absorption band which appeared at 3400 cm^{-1} is a weak band and is believed to be associated with a small amount of water trapped in the glasses during the experiment.

In Fig. 4 the DSC patterns measured for different glass samples are drawn for a heating rate of 20 K min^{-1}. It is found that all samples show an endothermal peak which shifts to lower temperatures as the CeO_2 content is increased, from about 487 °C in the undoped sample to 472 °C for the sample doped with 0.02 mol% CeO_2, and then increased by increasing the CeO_2 content. Our studies showed that the addition of a small amount of CeO_2 (0.15 mol%) caused a greater shift to higher temperatures compared with that caused by high additions of CeO_2 (1 and 2 mol%). These results are in agreement with previous studies on $Na_2B_4O_7$–Fe_2O_3 [6] and lead borate glasses containing CeO_2 [7].

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(Received December 4, 1991; in revised form October 13, 1992)