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Some optical and differential scanning calorimetry studies of sodium tetraborate glasses containing vanadium oxide

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A series of glass samples was prepared from mixtures of $Na_2B_4O_7$ and V_2O_5. Measurements were made for infrared absorption and optical absorption spectra as a function of V_2O_5 content up to 10 mol %. The addition of V_2O_5 did not introduce any new absorption band as compared with the infrared spectrum of pure sodium tetraborate glass. The addition of V_2O_5 shifted the optical absorption edges towards lower energies, and introduced a new absorption band as compared with the optical absorption of pure $Na_2B_4O_7$ glass. Differential scanning calorimetry as a function of V_2O_5 content was also measured.

1. Introduction

Many papers have appeared reporting the properties of amorphous and glassy semiconductors, and the state of the art is reviewed by Mott and Davis [1]. 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 [2] on the soda–lime–silicate glass-based system. Many transition-metal oxides when melted with a 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 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 [3].

Spectroscopic studies have been reported on glass systems based on the borate system [4–11]. Sanad *et al.* [12, 13] studied the effect of heat treatment and irradiation on some properties of barium borate glasses containing iron oxide, and Khawaja *et al.* [14] discusses the effect of annealing on the electrical and optical properties of V_2O_5–GeO_2 glasses. Ahmed and Hogarth report the spectroscopic properties of some borate and vanadate glasses [15]; Khawaja and Khattak [16] have studied the optical absorption edge in vanadate glasses.

In this work we have studied the effects of the addition of vanadium oxide on the optical and differential scanning calorimetry measurements of sodium tetraborate ($Na_2B_4O_7$) glasses.

2. Experimental procedure

Glasses in the system having the composition (mol %) $(Na_2B_4O_7)_{100-x}$-$(V_2O_5)_x$ where $x = 0$, 0.5, 2, 5 and 10 mol % were prepared from chemically pure reagent-grade materials. 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 glass samples were prepared by mixing an appropriate amount of $Na_2B_4O_7$ with V_2O_5 in an alumina crucible. The crucible containing the mixture was preheated at 300 °C for 1 h and then placed into a closed high-temperature furnace where it was held for 1 h under atmospheric conditions at about 1000 °C. During this time the melt was occasionally stirred with an alumina rod. 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 3 μm were obtained. Bulk samples were prepared by pouring the melt onto a massive stainless steel plate and casting into a disc shape 1.5 cm in diameter and ~ 2 mm thick. The disc was immediately transferred to another furnace which was already at 400 °C. The furnace was maintained at this temperature for 1 h and then switched off to cool to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm.

Optical absorption measurements for thin films and bulk glasses were carried out at room temperature in a wavelength range from 185 to 800 nm using a Varian model Cary 2390 spectrophotometer. In the low-absorption region ($\alpha < 10^4\ cm^{-1}$) 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 400 to 4000 cm^{-1} using an IR-460 Shimadzu double beam recording infrared spectrophotometer. Also, for comparison, infrared measurements were made for powdered glass samples using an SP3-100 Pye Unicam

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double-beam infrared spectrophotometer. The glass samples were ground in a clean mortar to a fine powder. A few milligrams of the 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 10 tons for a few minutes. 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 aluminium crucible which served as a reference.

3. Results and discussion

3.1. Infrared absorption spectra

The spectral curves for the 4000 to 400 $\mathrm{cm^{-1}}$ region obtained for thin-blown films of pure sodium tetraborate glass and glasses containing various amounts of V_2O_5 (Table I) are shown in Fig. 1.

Fig. 2 shows the spectra of glasses 1 and 2 with KBr pellets annealed at 400 °C for 1 h. Comparing the infrared spectrum of $Na_2B_4O_7$ (glass 1) with those doped with V_2O_5, it appears that all glasses show great similarity in the general shape of their absorption spectra, with the exception that, for the blown thin films, the peaks are sharper and better defined.

The absorption peaks observed in glasses are at 450, 725, 850 to 1200, 1300 to 1500, and 3400 $\mathrm{cm^{-1}}$. Except for glasses 3, 4 and 5, the absorption band at 450 $\mathrm{cm^{-1}}$ becomes deeper as the V_2O_5 content is increased. Also, it is noticed that the absorption bands occur at 940 and 1060 $\mathrm{cm^{-1}}$ instead of a broad peak at 850 to 1200 $\mathrm{cm^{-1}}$. These results are in agreement with the spectra reported for V_2O_5–B_2O_3 glasses [17].

TABLE I Composition data for ($Na_2B_4O_7$–V_2O_5) glasses

Glass sample	Composition (mol %) $Na_2B_4O_7$	V_2O_5
1	100.0	0.0
2	99.5	0.5
3	98.0	2.0
4	95.0	5.0
5	90.0	10.0

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 and vanadium ions; and possibly to some combination of these.

For the B_2O_3–V_2O_5 system, the infrared absorption spectra of V_2O_5 can be attributed to vibrations of VO_4 tetrahedra and VO_6 octahedra of the V–O bond [18]. Kulieva *et al.* [19] have suggested that the bands at 1019, 820 and 400 to 700 $\mathrm{cm^{-1}}$ are due to stretching vibrations of V=O bonds. The bands reported here at 1060, 940, and 450 $\mathrm{cm^{-1}}$ would seem to be due to the V =O double bond. These peaks become weaker and broader as the V_2O_5 concentration is increased in the glass system. The glasses are water-absorbent and the band at 3400 $\mathrm{cm^{-1}}$ is certainly due to the presence of OH groups in the glass.

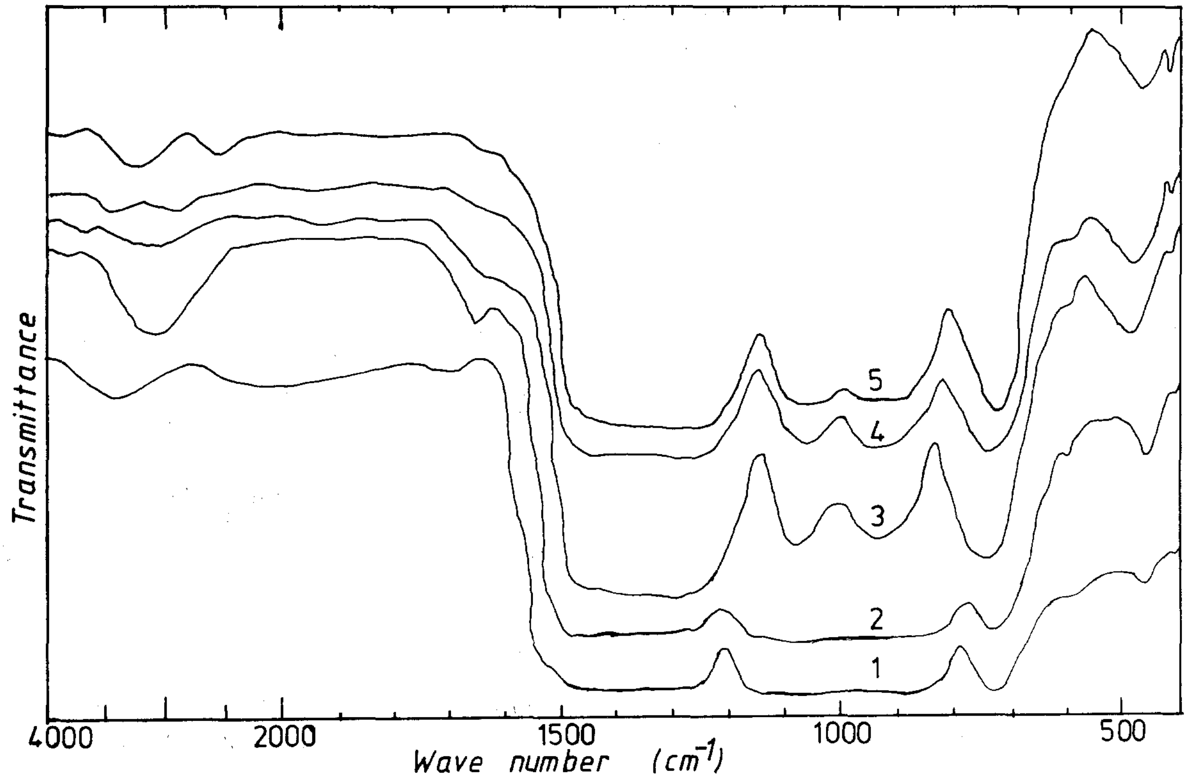

Figure 1 The infrared absorption spectra of ($Na_2B_4O_7$–V_2O_5) glass system with thin blown films (Table I).

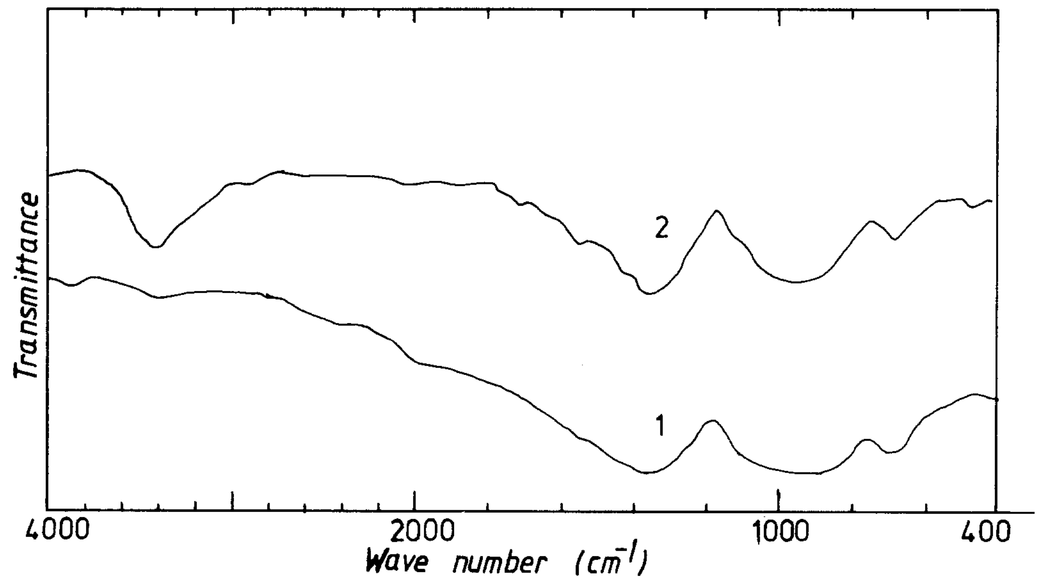

Figure 2 Comparison of the infrared absorption of samples 1 and 2 taken with KBr pellets.

3.2. Optical absorption measurements

Complete optical absorption spectra were made at room temperature for unannealed thin-blown glass films of thicknesses ranging from 1 to 4 μm of the ($Na_2B_4O_7$–V_2O_5) glass system as indicated in Table I. Fig. 3 shows the absorption in arbitrary units as a function of wavelength ranging from 185 to 800 nm. The following points may be noted.

1. The absorption spectra of $Na_2B_4O_7$ thin-film glass showed no characteristic band in the ultraviolet or visible range.

2. The region of high absorption of all glass samples is in the ultraviolet range and seems to move to longer wavelength, approaching the visible range as the V_2O_5 content is increased. By increasing the V_2O_5 content, the absorption edges shift towards lower energies which range from 6.17 to 4.6 eV. Such a change has been reported for nickel-doped sodium tetraborate glasses [7, 10], for ($Na_2B_4O_7$–Pb_3O_4) [20] and for the V_2O_5–B_2O_3 glass system [15].

3. The charge transfer bands centred at about 208 and 256 nm increase in intensity with V_2O_5 content in the thin-film glasses and are absent in glasses which do

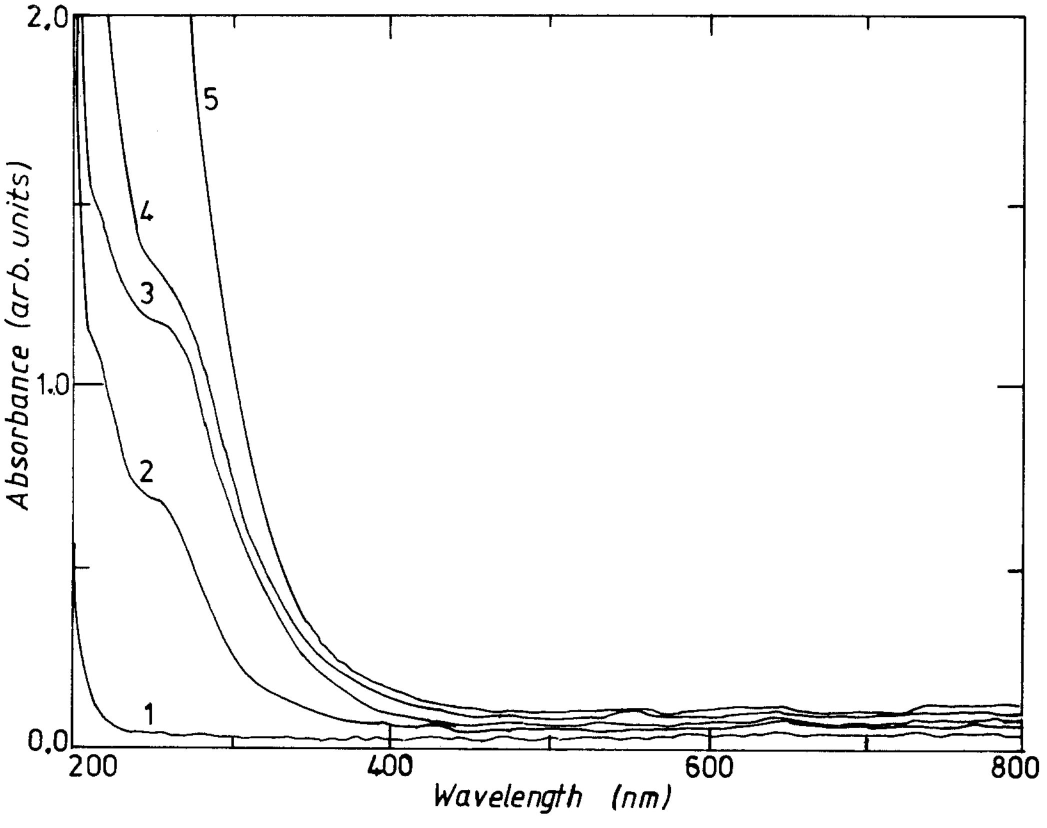

Figure 3 Absorption as a function of wavelength of unannealed thin-blown glass films (Table I).

not contain vanadium. This indicates that the bands are associated with transitions involving vanadium. The band at 208 nm grows more rapidly than that at 256 nm. As a result, these two bands apparently become buried under the region of high absorption edges at higher V_2O_5 content (sample 5). Piguet and Shelby [21] observed absorption bands at about 250, 310, and 410 nm for silver borate glasses. Kutub [22] observed charge transfer band at about 216 nm for the $Na_2B_4O_7$–Fe_2O_3 glass system.

4. There is a broad absorption tail for all glass samples which extends from about 350 to 800 nm without showing any peak in this region.

Optical absorption measurements were also made for annealed-bulk glass samples as indicated in Table I (thickness ranging from 1.2 to 1.5 mm). Fig. 4 shows absorption in arbitrary units as a function of wavelength for annealed-bulk glass samples. It is clear from this figure that the fundamental optical absorption edge of glass doped with V_2O_5 is fairly sharp as compared with that for the usual $Na_2B_4O_7$ glass, as has been observed for other borate glasses for example nickel-doped sodium tetraborate glasses [10] and for the ($Na_2B_4O_7$–Fe_2O_3) glass system [22].

It is also noted that the region of high absorption of all bulk-glass samples doped with V_2O_5 is in the visible range and a broad absorption tail extends without showing any peak.

Similar results have been reported by other workers for the V_2O_5–B_2O_3 [15] and $Na_2B_4O_7$–Pb_3O_4 [20] glass systems. 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 [23].

3.3. DSC measurements

The DSC patterns measured for different glass samples are shown in Fig. 5 for a heating rate of 20 K min^{-1}. All samples showed an endothermal peak which shifts to lower temperature as the V_2O_5 content is increased. Fig. 6 shows the variation of endothermal peak temperature with V_2O_5 content in the glass samples. It is obvious from this figure that the phase-transition temperature changes from 519 °C in the undoped sample to 495 °C for the doped sample with 10 mol % V_2O_5. With the addition of a small amount of V_2O_5 (0.5 mol %), the shift to the lower temperature is greater than that noted with the addition of a large amount of V_2O_5 (5 and 10 mol %) as is evident from Fig. 6. 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.

It has been reported that sodium tetraborate glass containing Fe_2O_3 shows an endothermal peak which shifts to lower temperatures as the Fe_2O_3 content is increased [24]. The addition of Pb_3O_4 to sodium tetraborate glasses shows two phase transitions which shift to lower temperatures as the Pb_3O_4 content is increased [20]. Limb and Davis [25] reported that for

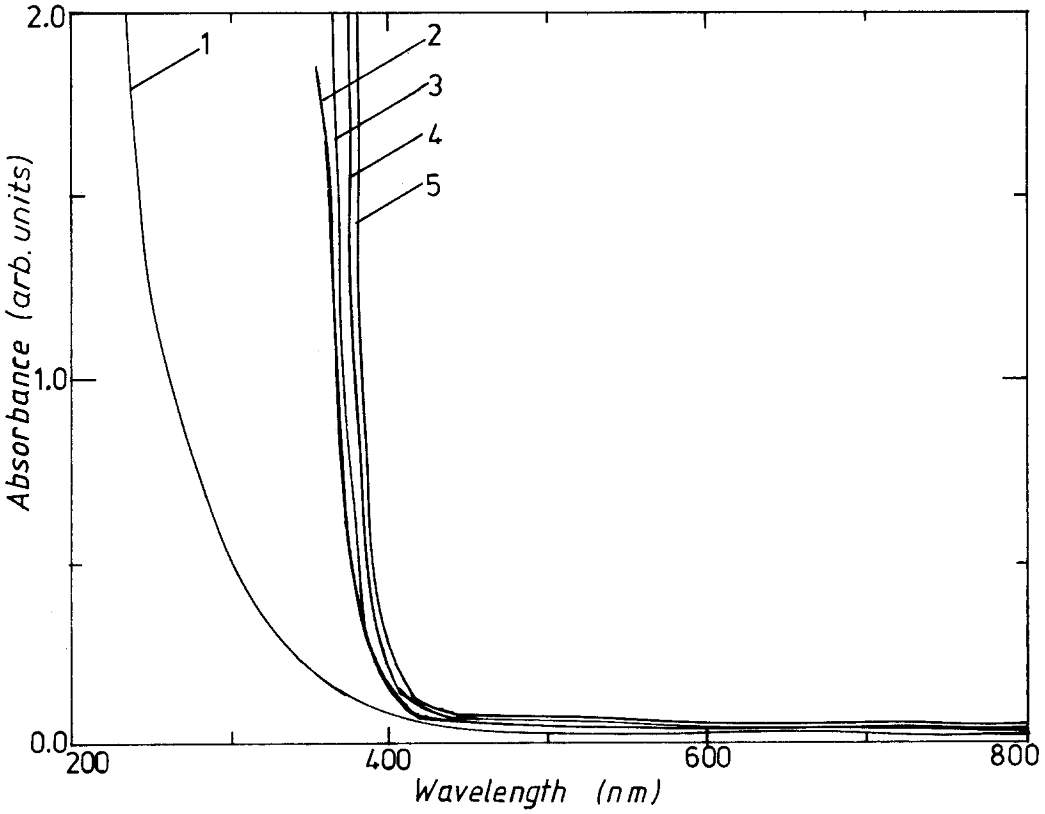

Figure 4 Absorption as a function of wavelength for bulk glass samples (Table I) annealed at 400 °C for 1 h.

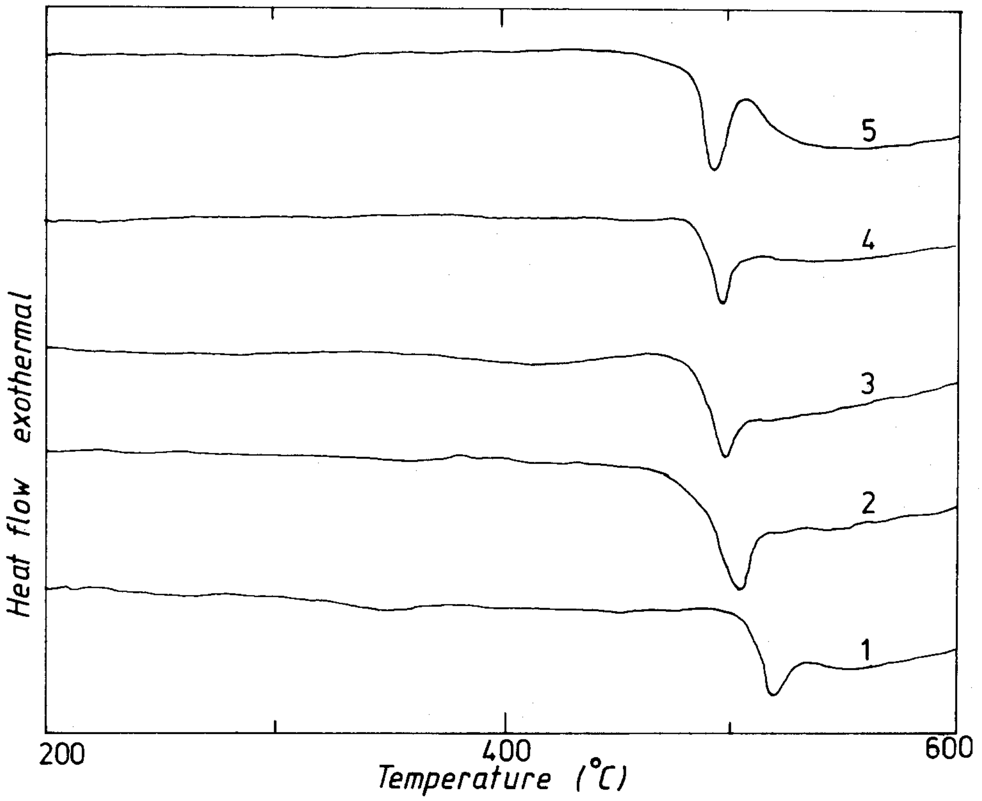

Figure 5 DSC curves of glass samples taken at a heating rate of 20 K min^{-1}.

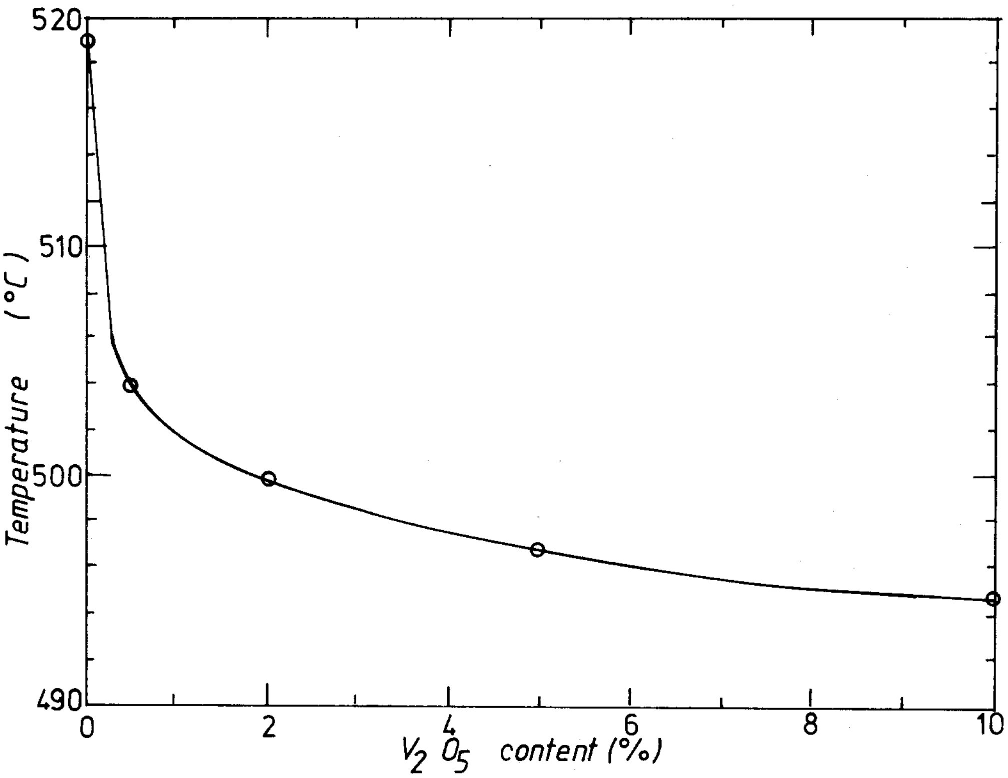

Figure 6 Variation of endothermal phase transition temperature with V_2O_5 content of glass samples.

the V_2O_5–P_2O_5–B_2O_3 glass system there are two phase separations, and any subsequent crystallization of V_2O_5 is at 290 and 410 °C. According to Ray [26], 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 and the same endothermal peak reappeared for all glass samples. This indicates that the phase transition measurements were not permanent and were reversible. No significant change in the weight of the samples was noticed.

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