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Optical absorption of vanadium in sodium diborate glasses

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The optical absorption in blown films and bulk specimens of sodium diborate glasses containing vanadium oxide based on the system $[Na_2O–2B_2O_3]_{1-x}$ $[V_2O_5]_x$ where $x = 0$, 0.05, 0.10, 0.15 and 0.20, has been studied in the wavelength range 200 to 900 nm. The fundamental absorption edge has been analysed in the light of the existing models. It is found that glasses containing a higher content of vanadium have fewer defects when compared with those containing a low vanadium content. The absorption spectra are interpreted as due solely to pentavalent vanadium.

1. Introduction

Many glasses containing transition-metal ions, for instance vanadium or iron, are semiconductors. The properties of semiconducting glasses have been of increasing interest since their discovery in 1954 by Denton *et al.* [1]. The optical properties of glasses containing vanadium have received considerably less attention than the electrical properties. These glasses contain a large concentration (generally greater than about 50 mol %) of V_2O_5 and are therefore unsuitable for studies of very intense charge transfer bands in the ultraviolet region due to vanadium. Hence previous studies on binary oxide glasses, such as V_2O_5/P_2O_5, V_2O_5/GeO_2 and V_2O_5/TeO_2 in general have been restricted to low absorption regions in the visible region (e.g. [2–8]). However, Paul and Rusin [9] have studied the ultraviolet absorption of vanadium in binary alkali borate glasses, but with a low concentration of vanadium (0.01 wt %) in the glasses. In the present work, vanadium in sodium diborate glasses was studied spectroscopically in the spectral range 200 to 900 nm with vanadium concentrations of 0, 5, 10, 15 and 20 mol %. The absorption data were analysed in the light of existing theories on optical absorption in amorphous semiconductors. The theories are summarized below.

It is well known that the low-energy electronic edge (Urbach [10]) in most semiconductors rolls off into the forbidden gap as approximately exponential functions of photon energy ($\hbar\omega$). Thus, in the case of the electronic edge, the following expression for the absorption coefficient, $\alpha(\omega)$, can be written

$$\alpha(\omega) = A \exp[\sigma(\hbar\omega - \hbar\omega_0)/kT] \qquad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, $\hbar$ is Planck's constant, and σ, A, and ω_0 are parameters characteristic of the material in question. Various models that have been proposed to explain the Urbach edge are reviewed by Mott and Davis [11], Connell [12], and Tauc and Menth [13].

In the high absorption region, above the exponential tail, the absorption is associated with interband transitions of electrons. Tauc [14] and Davis and Mott [15] gave an equation, derived independently, for the absorption (associated with interband transitions) as a function of photon energy in an amorphous semiconductor,

$$\alpha = B\frac{(\hbar\omega - E_0)^n}{\hbar\omega} \qquad (2)$$

where n is an exponent, B a constant and E_0 the optical energy gap of the semiconductor. In Equation 2, Tauc obtained $n = 2$ on the assumption that the conduction and valence band edges are both parabolic. Davis and Mott obtained $n = 3$ for linear band edges but $n = 2$ for different assumptions.

2. Experimental details

Vanadium oxide-doped sodium diborate glasses were melted from reagent grade B_2O_3, Na_2CO_3 and V_2O_5. The compositions used were $[Na_2O–2B_2O_3]_{1-x}[V_2O_5]_x$ where $x = 0, 0.05, 0.10, 0.15$, and 0.20. Batch materials to yield 25 g of glass were weighed accurately and melted in an alumina crucible at about 1100° C for 5 h under atmospheric conditions in an electric furnace. During this time the melt was occasionally stirred with an alumina rod. For each batch, thin films were obtained by the usual blowing technique while the bulk samples were prepared by casting the melt on a steel plate. The films ranged in thickness from 1 to 5 μm. The bulk samples were in the form of discs which were ground and polished to thicknesses ranging from 1 to 4 mm.

The optical absorption of these glasses was measured at room temperature in the wavelength range 200 to 900 nm using a varian model DMS-90 spectrophotometer. For each composition the optical density was measured for two samples which varied in thickness such that reflection effects could be eliminated. Then the absorption coefficient is given by

$$\alpha = 2.303\frac{A_2 - A_1}{d_2 - d_1}$$

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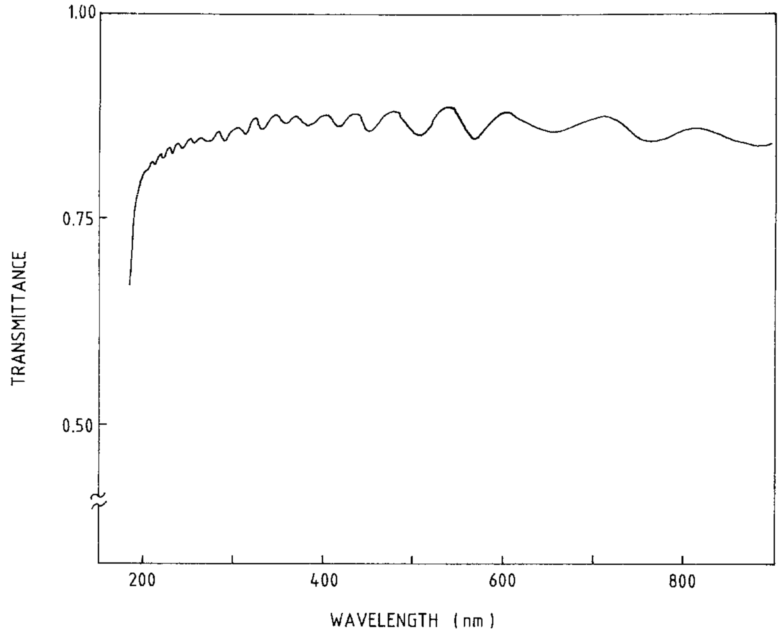

Figure 1 Transmittance plotted against wavelength in $[Na_2O{-}2B_2O_3]_{1-x}[V_2O_5]_x$ glass for $x = 0$.

where A_1 and A_2 are optical densities of specimen of thickness d_1 and d_2, respectively. In the low absorption region (less than $10^3\,cm^{-1}$) measurements were made from the bulk samples, while in the high absorption region they were from the thin films. It may be mentioned that in the high absorption region multiple interference effects were negligible but in the low absorption region these were well pronounced. Multiple interference effects were used in determining the thickness of a film.

3. Results and discussion

The optical absorption/transmission spectra of a glass film and bulk glass of initial composition $[Na_2O{-}2B_2O_3]_{1-x}[V_2O_5]_x$ were measured in the wavelength range 200 to 900 nm for $x = 0$, 0.05, 0.10, 0.15 and 0.20. Fig. 1 shows transmission spectra in a thin film of undoped sodium diborate glass (i.e. $x = 0$). In the undoped sample there is no significant absorption down to a wavelength of about 200 nm. Below this there is a steep absorption, which could not be measured further into the short wavelength region because of the limited range of the equipment. For sodium diborate glass, McSwain *et al.* [16] found the absorption edge to be at about 220 nm. The present results (Fig. 1) show that the edge may be close to this value, keeping in mind that the edge is at a wavelength which is little higher than that corresponding to the onset (200 nm) of the steep absorption.

Fig. 2 shows a plot of the absorption coefficient as a function of wavelength for different concentrations of V_2O_5 (indicated in the figure) in sodium diborate glasses. In this spectral region, undoped glass showed no absorption (Fig. 1) and from this we infer that the absorption shown in Fig. 2 may thus be associated with V_2O_5. Furthermore, the absorption increases as the vanadium oxide content in the glass is increased. In the low photon energy region the absorption indeed follows an exponential law similar to that given by Equation 1. For a constant temperature, Equation 1 may be written in the form

$$\alpha(\omega) = \alpha_0 \exp(\Gamma\hbar\omega) \qquad (3)$$

where α_0 and Γ are parameters characteristic of the material in question. The values of Γ for different compositions were obtained from the slopes of the semilog plots of Fig. 2 and are listed in Table I.

The exponential dependence of absorption coefficient on photon energy is observed in most of the crystalline

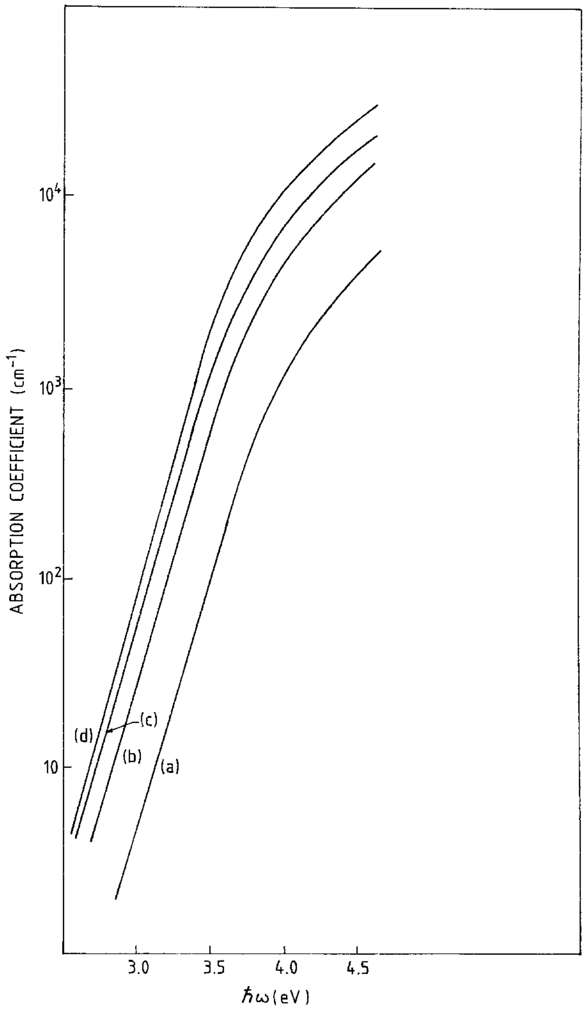

Figure 2 Exponential absorption edges in $[Na_2O{-}2B_2O_3]_{1-x}[V_2O_5]_x$ glasses at room temperature for (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.15$ and (d) $x = 0.20$.

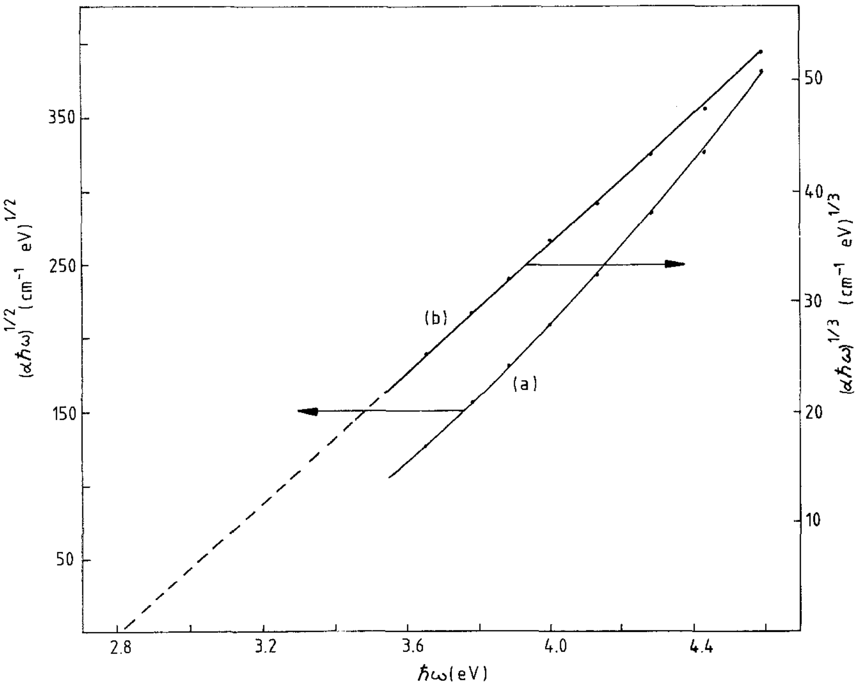

Figure 3 $(\alpha\hbar\omega)^{1/n}$ as a function of photon energy in $[Na_2O–2B_2O_3]_{0.80}[V_2O_5]_{0.20}$ for (a) $n = 2$ and (b) $n = 3$.

and noncrystalline semiconductors. Despite this universal behaviour, the precise origin of the exponential absorption in any particular material is uncertain [11–13]. However, exponential behaviour predicted by Dow and Redfield's theory [17] for electric field broadening of an exciton line, is generally considered to be an attractive model. Furthermore, it has been suggested that there are additional states in the bandgap associated with the disorder inherent in amorphous materials [11]. This could lead to a tail on the Urbach edge. This may also account for lower values of the slopes of the exponential plots in amorphous materials when compared with those in crystalline materials.

For the glasses investigated in the present work, the exponential behaviour is observed and the value of Γ varies between 6.14 and 6.68 eV^{-1} depending on the composition. Mott and Davies [11] reported that the values of Γ for a range of amorphous semiconductors are very close together in value and lie between 6 and 20 eV^{-1} (Fig. 6.46 in [11]). For highly disordered crystalline GeTe, Γ is reported by Lewis [18] to be 10 eV^{-1}, and in the case of molybdenum phosphate glasses Austin *et al.* [19] reported the value of Γ to be as low as 6.25 eV^{-1}. The slope increases slightly as the vanadium oxide content in the glass is increased (Table I). It follows from the above that a decrease in disorder (such as defects, voids, dangling bonds, etc.) could result in an increase of the slope. Therefore the increase in vanadium oxide content may lead to an improved order in the glass.

It is well-known [20] that vanadium in various glasses can exist in three oxidation states: V^{5+}, V^{4+}, and V^{3+}. The absorption bands due to V^{4+} and V^{3+} lie in the visible and near-infrared region [20]. Because there is no significant absorption in these regions in the glasses studied in the present work we therefore conclude that the content of V^{4+} and V^{3+} in these glasses would be negligible. Thus the absorption spectra (Fig. 2) is interpreted as due solely to pentavalent vanadium.

In Fig. 3 $(\alpha\hbar\omega)^{1/n}$ is plotted against $\hbar\omega$ for $n = 2$ and 3. These plots represent high absorption regions at photon energies above the exponential tail. It is clear from the figure that $n = 3$ gives a better fit to the data on $[Na_2O–2B_2O_3]_{0.80}[V_2O_5]_{0.20}$ glass. Similar results were obtained for other compositions. Fig. 4 shows the plots for different compositions with $n = 3$. Thus, above the exponential edge the absorption coefficient follows the power law (Equation 2) for $n = 3$. The parameters B and E_0 obtained from the plots in Fig. 4 are listed in Table I.

Earlier results on the absorption, for example As_2Te_3, Si, As_2S_3, and As_2Se_3, were found to fit Equation 2 for $n = 2$ [11]. However, recently Vorlicek *et al.* [21] have re-analysed the data on germanium [22] and silicon [23] and have also reported the optical constants for silicon films in a wider spectral range. They have found that in the case of germanium and silicon Equation 2 gives a better fit for $n = 3$ while in chalcogenide films the quadratic law ($n = 2$) is followed. Klazes *et al.* [24] obtained the best fit for their data on silicon films for $n = 3$. Fagen also reported a cubic fit to the absorption data for multicomponent chalcogenide glasses (Fig. 6.49, [11]).

4. Conclusion

Combining the measurements made on blown films and bulk specimens of sodium diborate glasses containing vanadium oxide, it was possible to study the optical absorption in the glasses in wavelength ranges

TABLE I Values of some physical parameters for $[Na_2O–2B_2O_3]_{1-x}[V_2O_5]_x$ glass

Composition parameter, x	Γ (eV^{-1})	B (cm^{-1} eV^{-2})	Optical gap E_0 (eV)
0.05	6.14	0.8×10^4	3.15
0.10	6.31	1.5×10^4	2.93
0.15	6.43	2.0×10^4	2.88
0.20	6.68	2.6×10^4	2.82

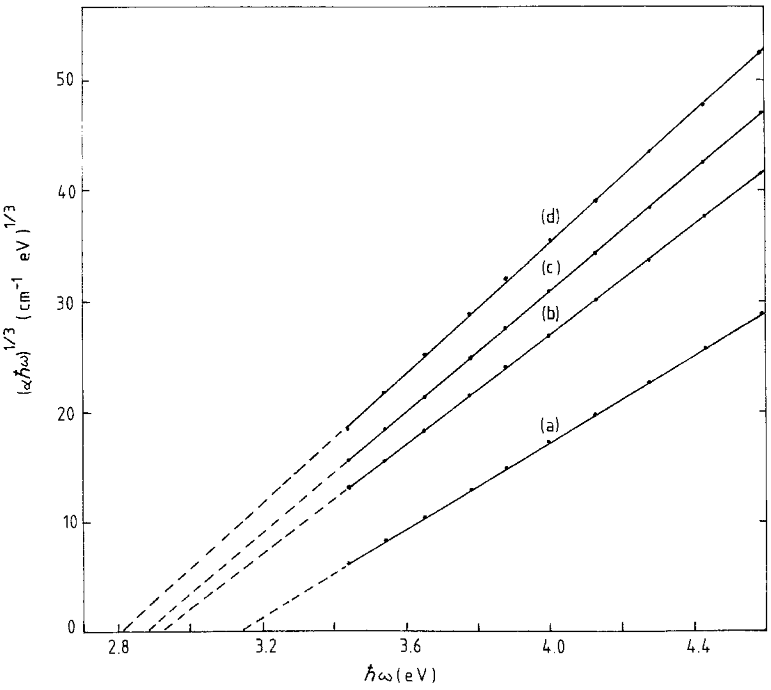

Figure 4 $(\alpha\hbar\omega)^{1/3}$ as a function of photon energy in $[Na_2O-2B_2O_3]_{1-x}[V_2O_5]_x$ for (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.15$ and (d) $x = 0.20$.

from 200 to 900 nm. In the low absorption region (less than about $10^3\ \mathrm{cm^{-1}}$) the usual exponential law is followed by the absorption coefficient. In the high absorption region, the power law (Equation 2) in the glasses is best followed for $n = 3$.

The observed increase in the slope of an exponential plot upon an increase in vanadium content is an indication of improved order in the glass with high vanadium content.

The absorption spectra were interpreted as due solely to pentavalent vanadium. Vanadium in other glasses such as P_2O_5, TeO_2, and GeO_2 is found to exist in three oxidation states: V^{5+}, V^{4+}, and V^{3+} [3, 5, 6, 20]. These glasses had higher concentrations of vanadium oxide (50 mol % or more). The existence of V^{5+} only in the present glass system may be due to the low content of vanadium oxide or perhaps it is the glass former which makes the difference. A further study of higher concentrations of vanadium oxide in these glasses would lead to a better understanding.

The absorption due to V^{4+} and V^{3+} in various glasses is in the visible region [20]. It is expected that this absorption would produce a tail on the Urbach edge, thus reducing the slope of the exponential plot. For example, Hogarth and Hosseini [3] in their study of V_2O_5–P_2O_5 glass sytems which contained a large content of V^{4+} ($C = V^{4+}/V_{\mathrm{total}} \sim 0.3$) obtained a slope value much smaller than those listed in Table I for different compositions in the range 1.5 to $3.2\ \mathrm{eV^{-1}}$.

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References

1. E. P. DENTON, H. RAWSON and J. E. STANWORTH, *Nature* **173** (1954) 1030.
2. G. W. ANDERSON and W. D. COMPTON, *J. Chem. Phys.* **52** (1970) 616.
3. C. A. HOGARTH and A. A. HOSSEINI, *J. Mater. Sci.* **18** (1983) 2697.
4. H. H. NESTER and W. D. KINGERY, Proceedings of the VIIth International Conference on Glass, Brussels (1965).
5. E. E. KHAWAJA, F. TEGALLY, J. S. HWANG, A. W. W. LI and A. A. KUTUB, *J. Mater. Sci.* **20** (1985) 3074.
6. E. E. KHAWAJA, M. SAKHAWAT HUSSAIN, M. A. KHAN and J. S. HWANG, *ibid.* **21** (1986) 2812.
7. E. E. KHAWAJA and G. D. KHATTAK, *Phys. Status Solidi* (*a*) **93** (1986) 621.
8. C. SANCHEZ, F. BABONNEAU, R. MONINEAC, J. LIVAGE and J. BULLOT, *Phil. Mag.* **B47** (1983) 279.
9. A. PAUL and J. M. RUSIN, *J. Amer. Ceram. Soc.* **52** (1969) 657.
10. F. URBACH, *Phys. Rev.* **92** (1953) 1324.
11. N. F. MOTT and E. A. DAVIES, "Electronic Processes in Non-Crystalline Materials" (Clarendon, Oxford, 1979) p. 273.
12. G. A. N. CONNELL, "Amorphous Semiconductors", edited by M. H. Brodsky (Springer-Verlag, Berlin, 1979).
13. J. TAUC and A. MENTH, *J. Non-Cryst. Solids* **8–10** (1972) 569.
14. J. TAUC, "The Optical Properties of Solids", edited by F. Abeles (North Holland, Amsterdam, 1970) p. 277.
15. E. A. DAVIS and N. F. MOTT, *Phil. Mag.* **22** (1970) 903.
16. B. D. McSWAIN, N. F. BORRELLI and G. J. SU, *Phys. Chem. Glasses* **4** (1963) 1.
17. J. D. DOW and D. REDFIELD, *Phys. Rev.* **B5** (1972) 594.
18. J. E. LEWIS, *J. Non-Cryst. Solids* **15** (1974) 352.
19. I. G. AUSTIN, M. SAYER and R. S. SUSSMAN, "Amorphous and Liquid Semiconductors" (Taylor and Francis, London, 1973) p. 1343.
20. C. R. BAMFORD, "Colour Generation and Control in Glass" (Elsevier, Amsterdam, 1977) p. 52.
21. V. VORLICEK, M. ZAVETOVA, S. K. PAVLOV and L. PAJASOVA, *J. Non-Cryst. Solids* **45** (1981) 289.
22. S. G. TOMLIN, E. E. KHAWAJA and G. K. M. THUTUPALLI, *J. Phys. C* **9** (1976) 4335.
23. G. K. M. THUTUPALLI and S. G. TOMLIN, *ibid.* **10** (1977) 467.
24. R. H. KLAZES, M. H. L. M. VAN DEN BROCK, J. BEZEMER and RADELAAR, *Phil. Mag.* **B45** (1982) 377.

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