Optical absorption near the fundamental absorption edge in some vanadate glasses

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The fundamental absorption edges of some samples of $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses were measured in the short wavelength part of the visible region, and it was found that the fundamental absorption of these glasses is dependent on composition and arises from direct forbidden transitions and occurs at a photon energy in the range 1.9 to 2.6 eV, depending on composition.

1. Introduction

In transition metal oxide glasses, in general, and in vanadate glasses in particular, a photon with a certain range of energy could be absorbed by transition metal ions present in the glass, by two different processes.

(i) The absorption may be due to internal transitions between the d-shell electrons and

(ii) The absorption may be due to a transfer of an electron from a neighbouring atom to the transition metal ion and vice versa.

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically-induced transitions and for the provision of information about the band structure and energy gap in both crystalline semiconductors and non-crystalline materials. The principle of this technique is that a photon with energies greater than the band gap energy will be absorbed. The absorption edge in many disordered materials follows the Urbach [1] rule given by

$$\alpha(\omega) \propto \exp\left(\frac{\hbar\omega}{\Delta E}\right) \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient at an angular frequency of $\omega = 2\pi\nu$ and ΔE is the width of the tail of localized states in the band gap.

There are two kinds of optical transition at the fundamental edge of crystalline and non-crystalline semiconductors, direct transitions and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band, which is then raised across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band it is essential that the wave vector for the electron be unchanged. In the case of indirect transitions the interactions with lattice vibrations (phonons) take place; thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons. In other words, if the minimum of the conduction band lies in a different part of k-space from the maximum of the valence band, a direct optical transition from the top of the valence band to the bottom of the conduction band is forbidden. Mott and Davis [2] suggested the following expression for direct transitions

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

where $n = 1/2$ or $3/2$ depending on whether the transition is allowed or forbidden.

It has been suggested by Anderson and Compton [3] that the fundamental absorption edge of the vanadate glasses and crystalline V_2O_5 near 2.5 eV fits the condition for direct forbidden transitions in which the absorption coefficient is given by

$$\alpha(\omega) = A(\hbar\omega - E_{opt})^{3/2}/\hbar\omega \qquad (3)$$

where $\alpha(\omega)$ is the absorption coefficient, E_{opt} is the optical gap and B is a constant.

2. Sample preparation and experimental technique

Thin blown films of some glasses listed in Table

TABLE I Values of some physical parameters for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses

Composition (mol %)	Glass number	E_{opt} (eV)	E_{el} (eV)	$A \times 10^3$ (cm$^{-2/3}$ eV$^{-1/3}$)	C	ΔE (eV)
$V_2O_5-P_2O_5$						
50−50	101	2.43	0.98	3.70	0.44	0.39
60−40	103	2.32	0.88	3.44	0.28	
70−30	105	2.21	0.76	3.33	0.18	
80−20	107	2.12	0.68	3.10	0.08	0.54
90−10	109	2.02	0.62	2.80	0.05	0.61
$V_2O_5-P_2O_5-TeO_2$						
60−30−5	201	2.44	0.86	4.95	0.33	0.41
60−30−10	202	2.38	0.84	4.82	0.29	
60−20−20	204	2.30	0.78	4.67	0.24	0.35
60−10−30	206	2.13	0.74	4.56	0.21	
60−5−35	207	2.10	2.22	4.38		0.31

I were prepared by dipping a silica tube into the molten material and gathering a small amount of glass melt on the end of the tube and blowing it into the air. The optical absorption edge of these glasses after annealing at 200° C for two hours was measured in the wavelength range of 200 to 700 nm using a Perkin−Elmer model 137 UV spectrometer at room temperature.

The general formula for the optical absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{1}{L} \ln\left(\frac{I_0}{I_t}\right) \qquad (4)$$

where $\alpha(\omega)$ is the absorption coefficient (cm^{-1}), I_0 and I_t is the intensity of incident and transmitted light, respectively, and L is the thickness of the sample (cm).

3. Results and discussion

The optical absorption spectra for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses as a function of wavelength in the visible range are shown in Figs. 1 and 2, respectively. These figures show that firstly, in contrast to crystalline V_2O_5, there is no sharp absorption edge and this is a characteristic of the glassy state, and secondly
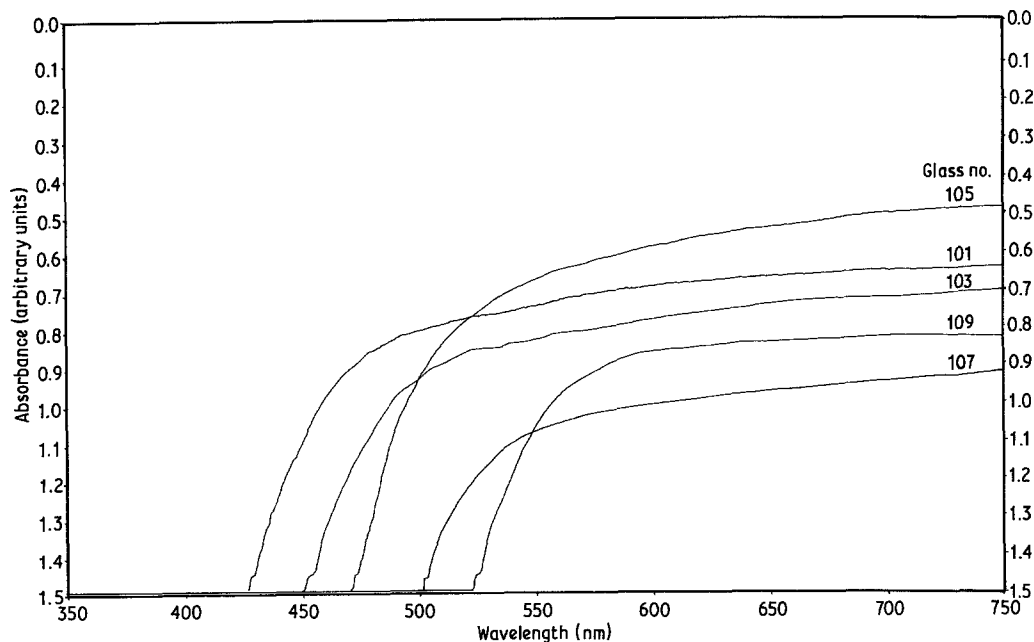

Figure 1 Absorption edge characteristic in the visible range for $V_2O_5-P_2O_5$ glasses.
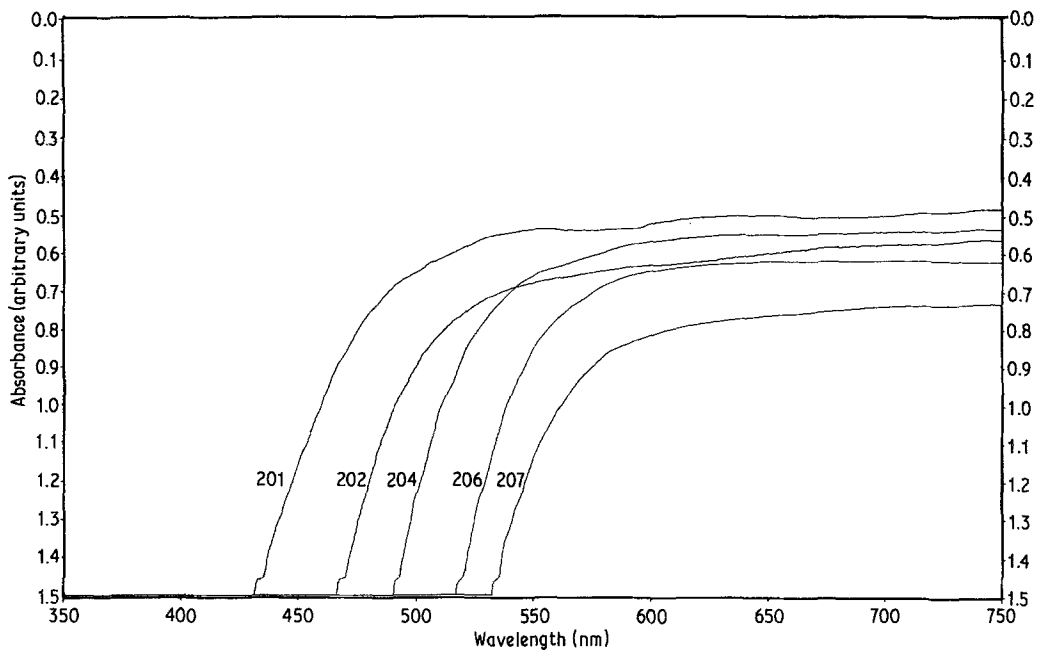
Figure 2 Absorption edge characteristic in visible range for $V_2O_5-P_2O_5-TeO_2$ glasses.

the position of the fundamental absorption edge shifts to higher energy with increasing P_2O_5 content.

The absorption coefficient $\alpha(\omega)$ was determined at different photon energies, near the absorption edge for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses, and the quantity $(\alpha\hbar\omega)^{2/3}$ is plotted against photon energy $(\hbar\omega)$ as mentioned earlier in this paper, for direct forbidden transitions. Figs. 3 and 4 show the linear dependence of $(\alpha\hbar\omega)^{2/3}$ on photon energy $(\hbar\omega)$ for both binary and ternary glass systems which tends to deviate from linearity at low values of photon energy. The values of optical gap E_{opt} are obtained by extrapolation of the linear region of the plots of $(\alpha\hbar\omega)^{2/3}$ against $(\hbar\omega)$ in Figs. 3 and 4 to $(\alpha\hbar\omega)^{2/3} = 0$ and these values for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses are given in Table I. These figures show that for both glass systems the value of E_{opt} increases with increasing P_2O_5 content, which is due to the increase of V^{4+} ion concentration with P_2O_5 content in glass [4].

It has been established that the concentration of the non-bridging oxygen ions decreases with increasing P_2O_5 content. This is due to the increase in V^{4+} ion concentration with P_2O_5 content, because the charged non-bridging oxygen associated with the V_2O_5 network would introduce $2p$-like energy levels which are higher than those of the bridging oxygen ions. Therefore

E_{opt} increases with increasing V^{4+} ion concentration or P_2O_5 content.

The variations of E_{opt} with P_2O_5 content for both $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses are shown in Figs. 5 and 6, respectively. In Figs. 7 and 8 E_{opt} is plotted as a function of C, the ratio of the concentration of reduced valency states to the total vanadium ion concentration measured in previous work by these authors [4] for both glass systems. The value of A in Equation 3 can be determined from the slope of the linear part of the curves showing $(\alpha\hbar\omega)^{2/3}$ against $(\hbar\omega)$ in Figs. 3 and 4. These values for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses are found and listed in Table I. It is found that the value of A in these glasses increases with increasing P_2O_5 content. The dependence of A on P_2O_5 content in both glass systems is shown in Figs. 9 and 10, respectively.

In many crystalline and non-crystalline semiconductors, the absorption coefficient $\alpha(\omega)$ depends exponentially on photon energy $(\hbar\omega)$. The exponential dependence known as the Urbach [1] rule may be written in the form

$$\alpha(\omega) = B \exp\left(\frac{\hbar\omega}{\Delta E}\right) \qquad (5)$$

where B is constant and ΔE is the width of the band tails of the localized states.
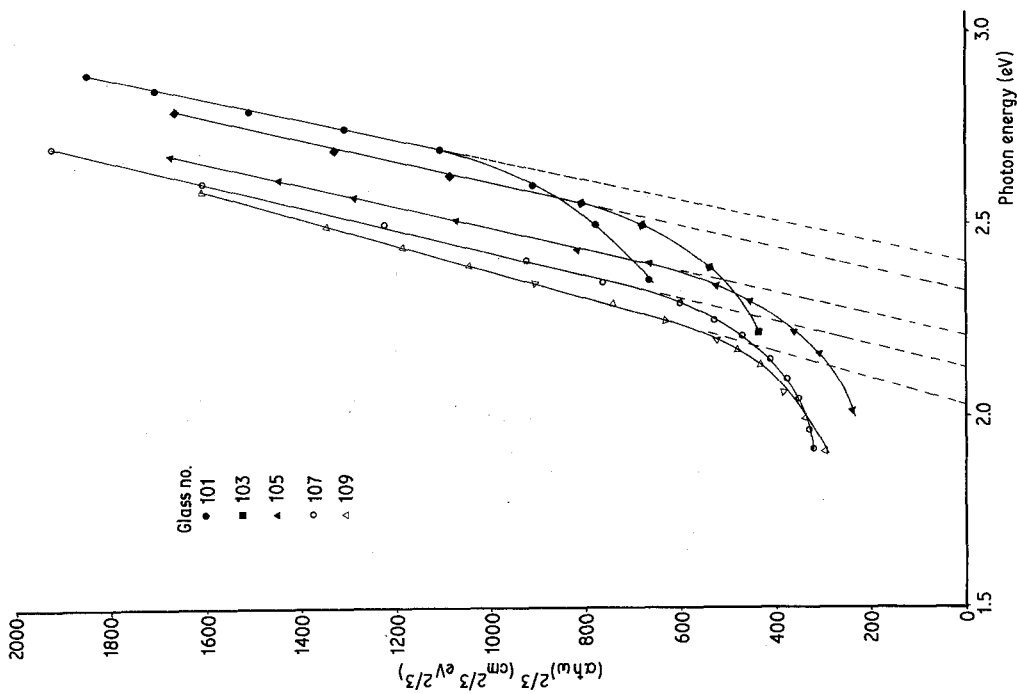
The origin of the exponential dependence of
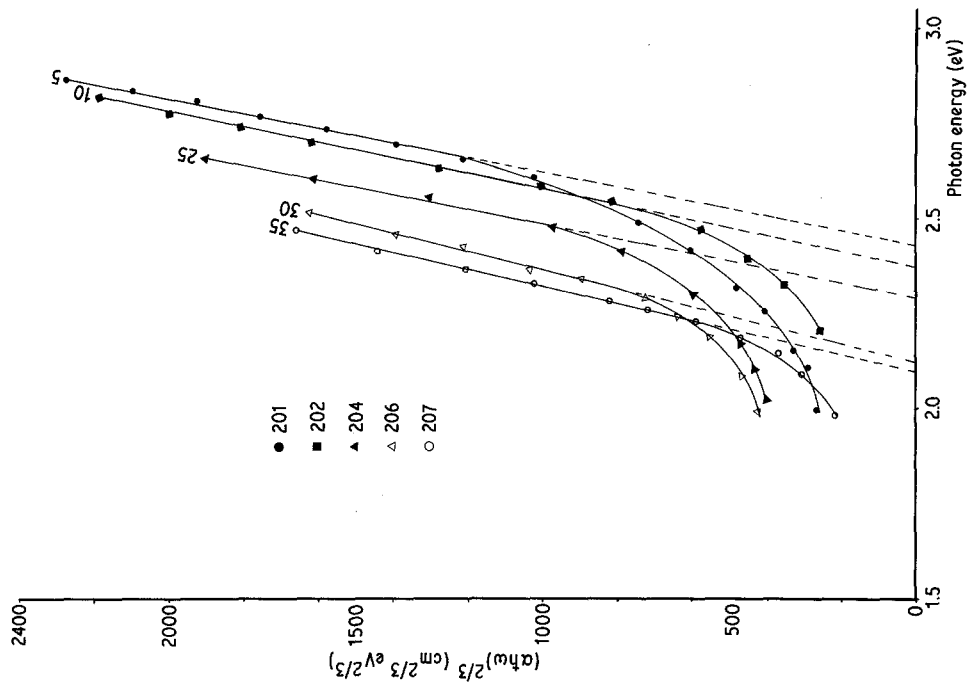
Figure 3 Optical absorption of V_2O_5—P_2O_5 glasses.

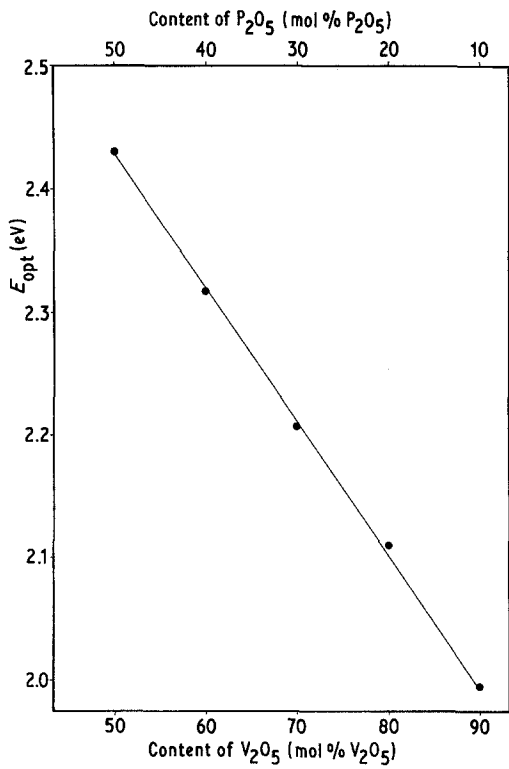*Figure 4* Optical absorption edge for V_2O_5—P_2O_5—TeO glasses.

Figure 5 E_{opt} against V_2O_5 content for $V_2O_5-P_2O_5$ glasses.
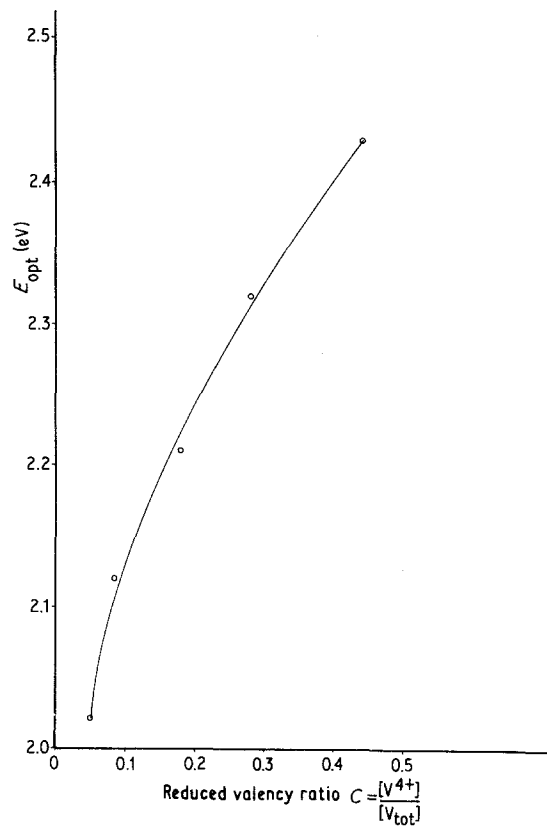

Figure 7 Dependence of optical gap on ratio of reduced valency states in $V_2O_5-P_2O_5$ glasses.
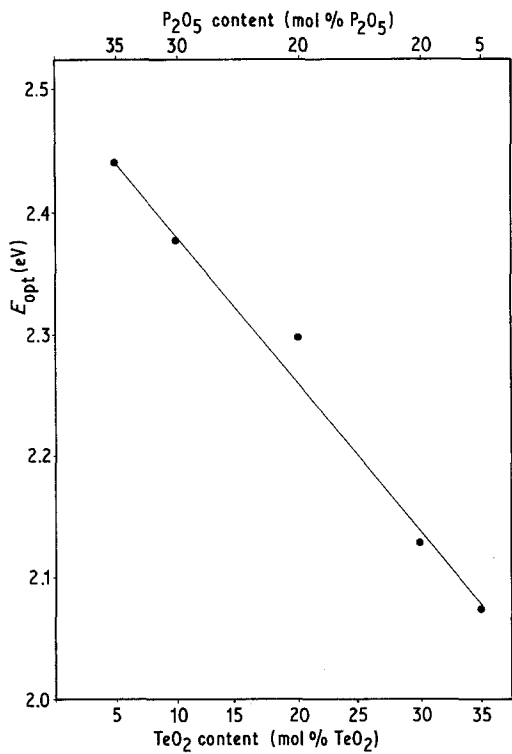

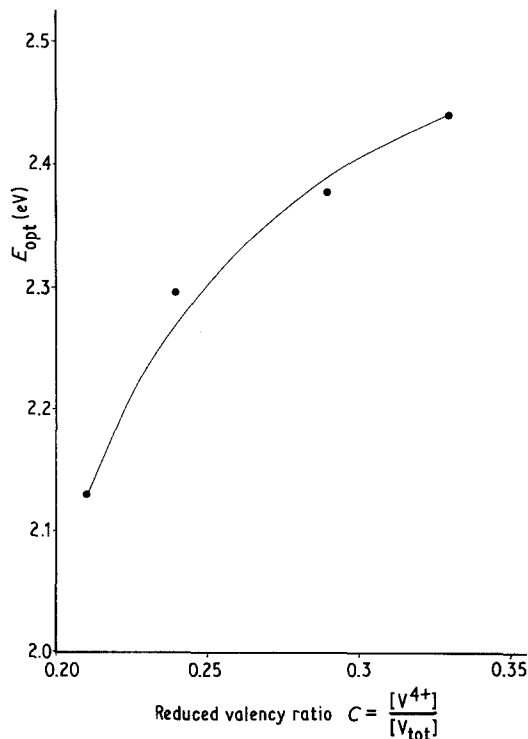*Figure 6* Variation of optical gap with glass composition for $V_2O_5-P_2O_5-TeO_2$ glasses.

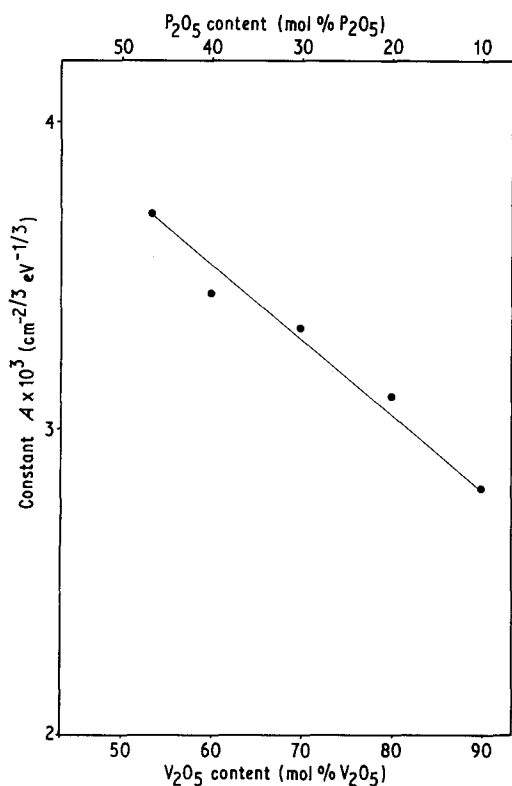*Figure 8* Variation of E_{opt} with C for $V_2O_5-P_2O_5-TeO_2$.

Figure 9 Variation of A (slope of $(\alpha\hbar\omega)^{2/3}$ against $\hbar\omega$) with glass composition for $V_2O_5-P_2O_5$ glasses.
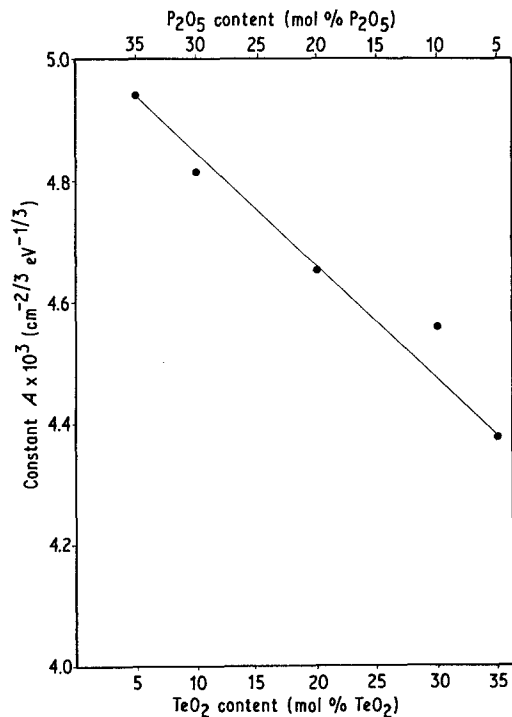

Figure 10 Variation of A with glass composition for $V_2O_5-P_2O_5-TeO_2$ glasses.

absorption coefficient on photon energy $\hbar\omega$ is not clearly known. Tauc [5] has suggested that it arises from electron transitions between localized states where the density of localized states is exponentially dependent on energy. But Davis and Mott [6] reported that this explanation is not valid for all disordered materials since the slope of the observed exponential behaviour remains unchanged for many crystalline and non-crystalline materials. Figs. 11 and 12 show the variation of $\ln(\alpha)$ with photon energy $(\hbar\omega)$ for some $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses, respectively. The values of ΔE in Equation 5 are calculated from the slope of the straight line of these curves and are given in Table I. Mott and Davies [7] reported that the values of ΔE for a range of amorphous semiconductors are very close together in value and lie between 0.046 and 0.066 eV. For highly disordered crystalline GeTe, ΔE is reported by Lewis [8] to be 0.1 eV and in the case of molybdenum phosphate glasses Austin *et al.* [9] reported the value of ΔE to be as high as 0.16 eV.

For the glasses investigated in the present work the exponential behaviour is observed and the value of ΔE varies between 0.31 and 0.68 eV depending on the composition. In the case of vanadate glasses, the exponential dependence of absorption coefficient $\alpha(\omega)$ on photon energy $(\hbar\omega)$ (Figs. 11 and 12) suggests that these materials obey the Urbach rule.

If the glass behaves as a quasi-intrinsic semiconductor, then the Fermi energy will be in the middle of the band gap and the electrical energy gap E_{el} would be given by twice W, where W is the activation energy, and would be expected to be equal to E_{opt}. If twice the value of W is much less than E_{opt}, it is clear that the electrical activation process is certainly not across a band gap but must be between bands and trapping levels.

The electrical activation energy values at high temperature (W) for some of these glasses were measured by the present authors [4] and showed that the value of $E_{el} = 2W$ is much less than E_{opt}. It is also found that the value of E_{el} varies with E_{opt} and these variations are shown in Figs. 13 and 14 for $V_2O_5-P_2O_5$ and $V_2O_5-P_2O_5-TeO_2$ glasses, respectively. From these figures a simple correlation is found between E_{el} and E_{opt} for $V_2O_5-P_2O_5$ glasses as
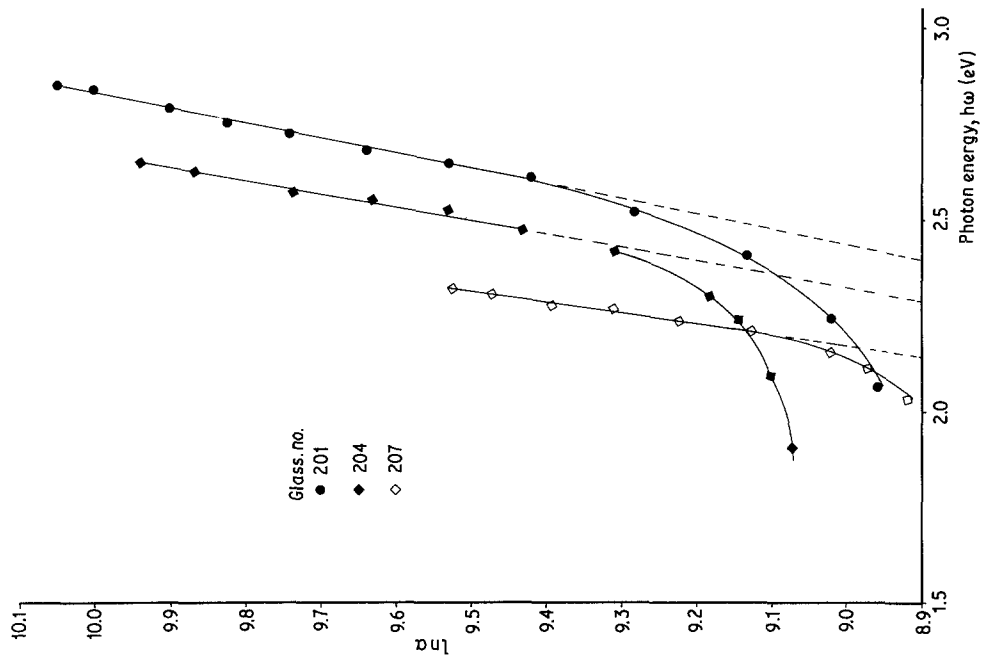
$$E_{el} = 0.97\,E_{opt} - 1.37$$

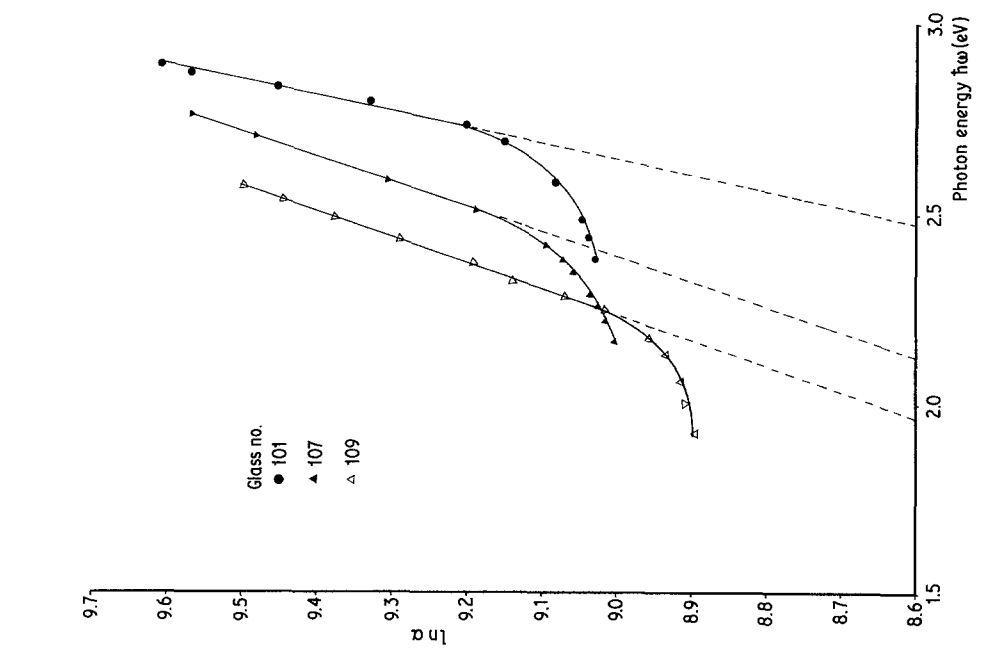*Figure 12* Optical absorption coefficient against photon energy for $V_2O_5-P_2O_5-TeO_2$ glasses.

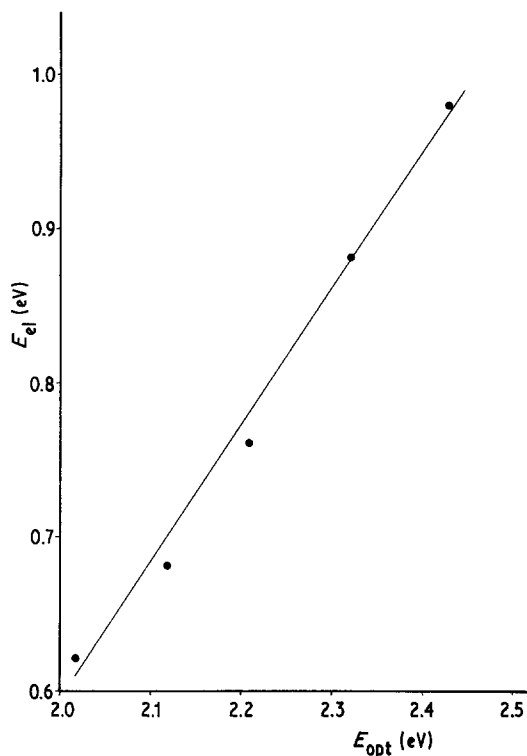*Figure 11* Optical absorption coefficient against photon energy for $V_2O_5-P_2O_5$ glasses.

Figure 13 Optical gap against E_{el} for $V_2O_5 - P_2O_5$ glasses.

and a similar relationship was found for $V_2O_5 - P_2O_5 - TeO_2$ in empirical form of

$$E_{el} = 0.39 E_{opt} - 0.09.$$

4. Conclusion

It appears that there is an exponential absorption edge in the visible spectral range $1.9 < \hbar\omega < 2.6\,eV$ (Figs. 3 and 4) which could be explained as due to the exponential distribution of localized states in the normally forbidden gap. The carrier concentration in the localized levels (band tails) depends upon the total number of available sites which in the case of vanadium phosphate glasses are different for V^{4+} and V^{5+} ions.

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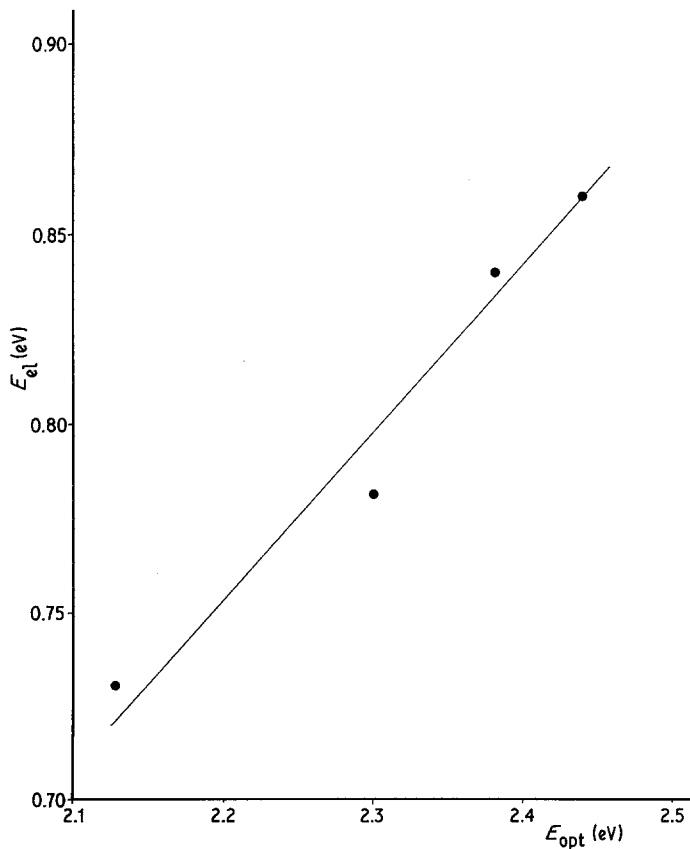5. J. TAUC and M. ZANINI, *Non-cryst. Solids* **23** (1977) 349.

Figure 14 Variations of E_{opt} with E_{el} for $V_2O_5 - P_2O_5 - TeO_2$ glasses.

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