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A comparative study of the effects of rare-earth oxides on the physical, optical, electrical and structural properties of vanadium phosphate glasses

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The physical parameters such as density, X-ray diffraction, infra-red absorption spectra and optical absorption measurements are discussed with respect to all compositions. The d.c. conductivity was measured for semi-conducting vanadium phosphate glasses containing 5 mol % rare-earth oxides. The conductivity of vanadium phosphate glasses is slightly higher than the corresponding compositions with rare-earth oxides. The heat treatment in the range 300 to 500° C caused progressive microstructural changes which dramatically affected the electronic conductivity (σ) and the activation energy for conduction (W). It was also found that the incorporation of rare-earth oxides did not affect the limits of the ultra-violet absorption edge of the base glass.

1. Introduction

Vanadium phosphate glasses have been investigated by many authors [1–7]. There are also many papers available on the structure of glasses containing ions of the first transition series and on the role of the more metallic p elements. Less work has been devoted to glasses containing oxides of the rare-earths, particularly their effects on the optical, electrical and structural properties of vanadium phosphate glasses. At present there is an increasing interest in studying such oxides. Makishima *et al.* [8] prepared aluminosilicate glasses containing yttrium and lanthanum with high refractive index, elastic moduli and hardness. Recently, Magruder and Kinser [9] have reported on the electrical conductivity of glasses made from oxides of praseodymium and phosphorous pentoxide and have suggested that the conduction mechanism is similar to the variable valency hopping proposed by Mott. Some spectroscopic studies of lanthanide salts [10, 11] have been reported and traditional glasses doped with small quantities of rare-earth oxides [12, 13] have been investigated. The spectra of rare-earth ions are characterized by absorption bands which are very sharp, almost line-like. These sharp bands are due to forbidden transitions involving the $4f$ levels which are allowed by electric dipole effects, and these $4f$ orbitals are very effectively shielded from interaction with external forces by the overlying $5s^2$ and $5p^6$ shells. Hence the states arising from the various $4f^n$ configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in the various compounds. Therefore in general the rare-earth elements do not change the limits of the ultra-violet absorption edge of the base glass. The spectra of the rare-earths reflect the stability of the empty,

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half-filled and filled $4f$ levels. In order to study the role of the rare-earth oxides on the optical, electrical and structural properties of vanadium phosphate glasses, it was thought useful to study glasses having higher concentrations of V_2O_5–P_2O_5 glasses with a fixed added concentration of several different rare-earth oxides.

In the present paper we report the results of our measurements of infra-red spectra, the physical properties such as density, the d.c. conductivity and optical absorption, in order to study, (1) the effect of the addition of rare-earth oxides and (2) the effect of heat treatment on the parameters describing the course of crystallization. Scanning electron microscopy was used since it provides a direct image of the microstructure and, via selected-area diffraction, distinguishes glassy and crystalline phases and is a technique which provides particularly valuable information for investigating the early stages of phase separation and crystallization.

2. Experimental techniques

2.1. Glass preparation

Glasses in the system having the composition expressed in mol% $(P_2O_5)_{50}$, $(V_2O_5)_{50-x}$, (RE, rare-earth oxides)$_x$, where x was kept at 5 mol% $(RE)_2O_3$, were prepared from chemically pure reagent grades of P_2O_5, V_2O_5 and rare-earth oxides of Ce_2O_3, Pr_6O_{11}, Eu_2O_3, Gd_2O_3, Tb_4O_7, Yb_2O_3 and CeO_2 materials. Melting of the glasses which were placed in a recrystallized alumina crucible was done in an electrically heated furnace at 1200° C for 3 h. The melt was stirred from time to time using an alumina rod and was molten at 1200° C. By slow heating it was hoped to reduce mechanical and volatilization losses. The melt was finally poured on to a clean stainless steel plate and cast into a disc shape. The disc was immediately transferred to another furnace which was already at 300° C. This furnace was then switched off to cool down to room temperature. The glass samples were polished using diamond paste, down to ~~minimum grit~~ size of 0.1 μm.

Thin glass films, which are necessary for optical absorption measurements, were obtained by blowing techniques. Specimens in the thickness range from 2 to 10 μm were obtained as measured using a Sigma Comparator. All thin films were un-annealed when used for optical measurements. The optical absorption measurements were made on thin blown films at room temperature in the wavelength range 190 to 850 nm using a Perkin-Elmer 402 Spectrophotometer.

For infra-red examination, samples of the listed compositions were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with a relatively large quantity of KBr. KBr pellets transparent to light were formed by pressing the mixture at 10 to 15 tons for a few minutes under vacuum. The infra-red absorption spectra of these samples were determined by using a Unicam SP2000 double-beam recording infra-red spectrometer in the range 200 to 4000 cm^{-1}. Also the infra-red spectra of freshly blown thin films were determined for comparison.

2.2. Measurements

The densities of specimens annealed at 300 and 500° C as given in Table I were measured at room temperature by a displacement method using ethyl-methyl-ketone as the displaced liquid.

The d.c. conductivity of the samples was measured in the temperature range 300 to 473 K. Electrodes were placed on the samples in a guarded configuration using silver. The samples were placed in a sample holder which could take five samples at a time, thereby ensuring accurate comparison of five samples with different compositions under similar conditions. The measurements were made using a conventional d.c. supply with a Keithly 610C electrometer on V_2O_5–P_2O_5 and V_2O_5–$(RE_2)O_3$–P_2O_5 glasses and heated at two different annealing temperatures.

Heat treatment was applied to several glasses in order to introduce a tendency towards ordering and even crystallization. This was done in the same electric furnace as that used for the preparation of the original glasses.

The examination of microstructural changes after the heat treatments was conducted by means of a Cambridge Steroscan 250 Mk 2 scanning microscope. Furthermore X-ray diffraction patterns were also obtained in order to provide definite evidence of crystallinity. Powdered samples of the prepared glasses were tested by X-ray diffraction using a Debye-Scherrer powder camera using Ni-filtered Cu$K\alpha$ radiation.

3. Results and discussion

3.1. Density variation with composition and annealing temperature

The relative density of glasses with different compositions shows a quite sharp variation from 2.92

TABLE I Chemical compositions, physical parameters, optical and electrical properties of vanadium-phosphate glasses, containing rare-earth oxides

Notation	Glass Sample	Composition (mol%)	Relative density (annealed at 300° C)	Relative density (annealed at 500° C)	Activation energy (eV)	Optical gap, E_{opt} (eV)	Urbach energy, E (eV)
A	V_2O_5–P_2O_5	45–55	2.92_7	2.94_9	0.45	2.20	0.38
B	V_2O_5–CeO_2–P_2O_5	45–5–50	2.96_2	2.99_1	0.53	2.37	0.30
C	V_2O_5–Ce_2O_3–P_2O_5	45–5–50	2.98_0	3.00_9	0.55	2.34	0.33
D	V_2O_5–Eu_2O_3–P_2O_5	45–5–50	3.02_0	3.10_0	0.52	2.37	0.43
E	V_2O_5–Gd_2O_3–P_2O_5	45–5–50	3.07_0	3.15_0	0.56	–	–
F	V_2O_5–Tb_2O_3–P_2O_5	45–5–50	3.08_8	3.21_4	0.57	2.37	0.43
G	V_2O_5–Yb_2O_3 P_2O_5	45–5–50	3.12_3	3.21_3	0.57	2.21	0.42

to 3.12. It may be pointed out that the density shows a regular increase when taken on samples annealed at the higher temperatures showing a compaction of the structure as a result of annealing, as shown in Fig. 1.

3.2. Microstructure

Figs. 2a and b are representative of the microstructural evolution as a function of temperature of three ternary glasses annealed at different temperatures.

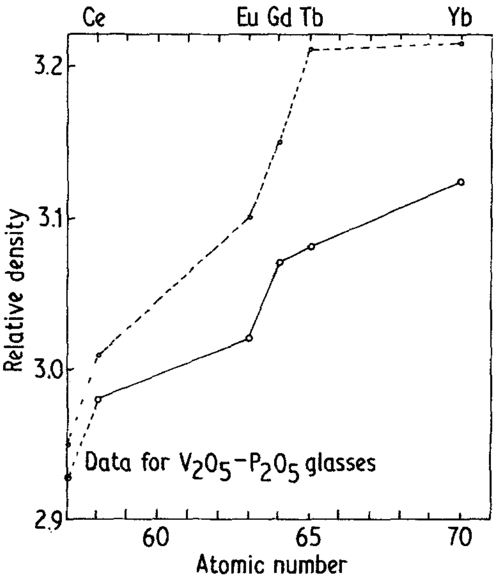

Figure 1 Relative density as a function of rare-earth atomic number for glasses annealed at two different temperatures.

The annealed glasses at 300° C (Fig. 2a) possess unclustered, apparently interlocking, rod-shaped crystals, showing a polycrystalline type structure, whereas the annealed materials at 500° C in Fig. 2b exhibit a distinct morphology resembling a collection of petal- or sheaf-like particles emanating from their common centres, strongly implying a crystalline nature.

Despite the scanning electron micrographic evidence suggesting that crystallization occurred after heat treatment, it is still necessary to provide some direct evidence in order to prove that the petal-like particles which were observed are indeed of crystalline nature. The annealed samples were examined by X-ray diffraction as shown in Fig. 3, which provided positive evidence of crystallization occurring in the annealed glasses.

3.3. Temperature dependence of conductivity

The results of conductivity measurements as a function of temperature in the range 300 to 473 K for different compositions are shown in Fig. 4. The general form of the curves is similar to that reported for V_2O_5–P_2O_5 glasses [14–17]. The d.c. conductivity is found to be well described at high temperatures by the relation

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right).$$

The values of the activation energy, W, above room

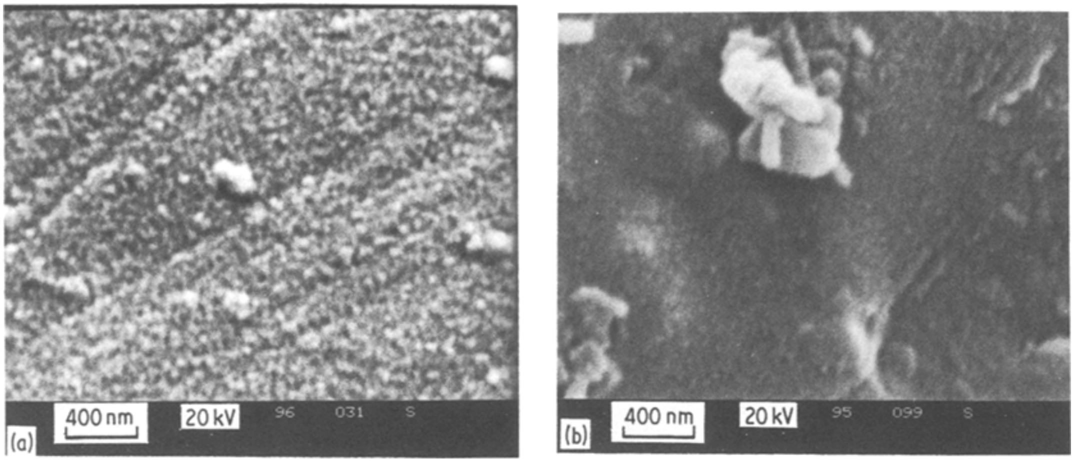

Figure 2 Scanning electron micrographs of (a) V_2O_5–CeO_2–P_2O_5 heated at 300° C, (b) V_2O_5–$CeO_2P_2O_5$ annealed at 500° C.

temperature are typically 0.45 to 0.57 eV and as such are considerably less than the calculated values of the optical gap, as shown in Table I. A comparison of conductivity for V_2O_5–P_2O_5 glasses and V_2O_5–P_2O_5 glasses containing 5 mol% rare-earth oxides shows that for the latter glasses the conductivity decreases.

Fig. 4 shows the changes in d.c. conductivity and activation energy which accompany the progressive crystallization of the annealed phase-separated glasses. The latter values from these plots are given in Table I. It was found that the conduction mechanism in V_2O_5–$(RE)_2O_3$–P_2O_5 glasses in the composition range examined here is electronic which is in agreement with the earlier results of Magruder and Kinser [9].

Bogomolova *et al.* [18, 19] studied vanadium phosphate glasses doped with copper oxide and explained the results in terms of cross-relaxation processes between the two spin systems and also by spin diffusion. They explained the decrease in the V^{4+} ESR signal by spin diffusion and with V_2O_5 and CuO invoked a chemical exchange mechanism in the form

$$V^{4+} + Cu^{2+} \rightarrow V^{5} + Cu^{+}$$

Previous workers [20] also suggested that if there are two elements in the system which forms ions of variable valency, then interaction between them usually takes place as follows

$$Mn^{3+} + Ce^{3+} \rightleftharpoons Mn^{2+} + Ce^{4+}$$

In the systems studied by us by the incorporation of $(RE)_2O_3$ an oxidation–reduction mechanism may be taking place with the reduction of V^{4+} ions which reduced the concentration ratio $C = (V^{4+})/(V^{\text{total}})$ and hence the conductivity decreases. Therefore the decrease of conductivity by adding the rare-earth oxide may, in our case, be ascribed to the different possible oxidation states, which

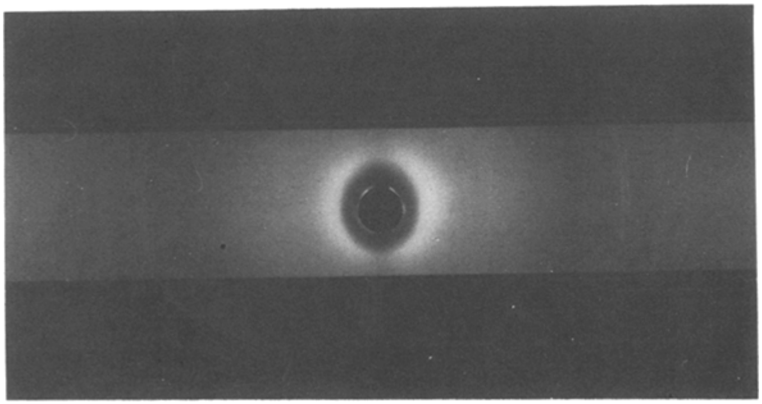

Figure 3 X-ray diffraction pattern of the same glass after annealing at 500° C.

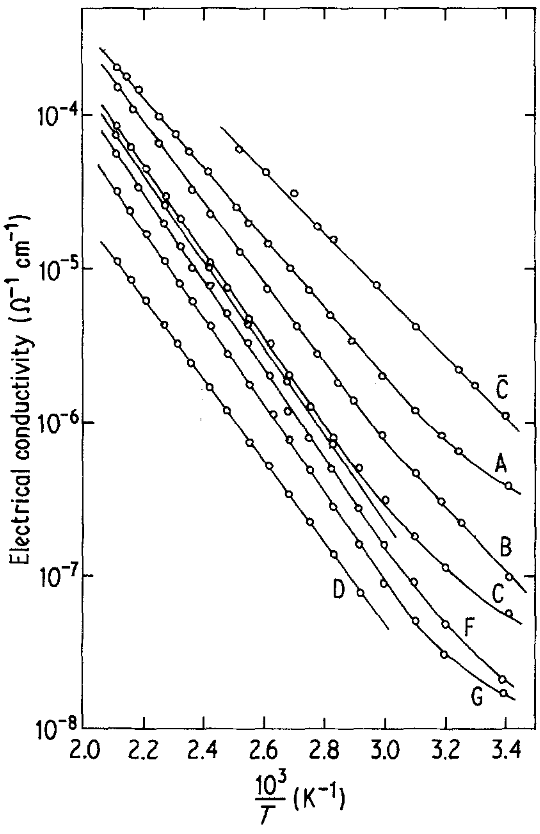

Figure 4 Electrical conductivity as a function of temperature for various glass compositions.

exist due to the mixed ions with the possible pairing of mixed ions in the form of oxygen-bridged associates.

3.4. Infra-red absorption spectroscopy

The infra-red spectra of V_2O_5–P_2O_5 and V_2O_5–RE_2O_3–P_2O_5 (where the RE oxides are CeO_2, Ce_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7 and Yb_2O_3) glasses were carried out in the range 200 to 4000 cm^{-1}. Fig. 5 shows the spectra of glasses A, D and G, with KBr pellets and blown thin films. Comparing the spectra of thin blown films with KBr pellets of the same composition, it appears that all the glasses show great similarity in their general shape of absorption spectra, with the exception that in the blown thin films the peaks become sharper and well defined.

The absorption peaks observed in all the glasses are at 300 to 500 cm^{-1}, 780 cm^{-1} and 900 to 1250 cm^{-1} except for V_2O_5–P_2O_5 glass where absorption occurs at 320 and 390 cm^{-1} instead of a broad peak at 300 to 500 cm^{-1}. As it appears from the literature [21] that rare-earth oxides used in these glasses show absorption peaks between 268 and 569 cm^{-1}, it seems that the rare earth oxides have some contribution in the formation of a strong and broad peak observed at 300 to 500 cm^{-1}. Sayer *et al.* [6] observed an absorption peak at 380 cm^{-1} and showed that the intensity of this peak increases with the increase of P_2O_5 content. In our glasses P_2O_5 is constant so the broadening of this peak could not be due to P_2O_5. Therefore, this broad and strong peak does not seem to be a feature of V_2O_5, P_2O_5 or rare-earth oxides but it may be a combined effect of all the constituents with the formation of V–O–P–O–RE-units. The P–O–P ring frequency of P_2O_5 appears at 780 cm^{-1} [22] which agrees with our results.

Another very strong and broad absorption band observed in our glasses appeared within the 900 to 1250 cm^{-1} range. It has been reported [23] that the peak due to the vanadium–oxygen stretching

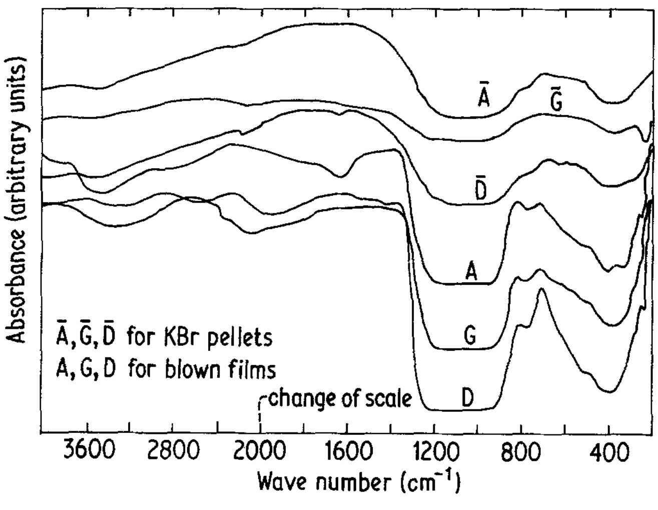

Figure 5 Room temperature infra-red absorption spectra of vanadium phosphate glasses containing rare-earth oxides.

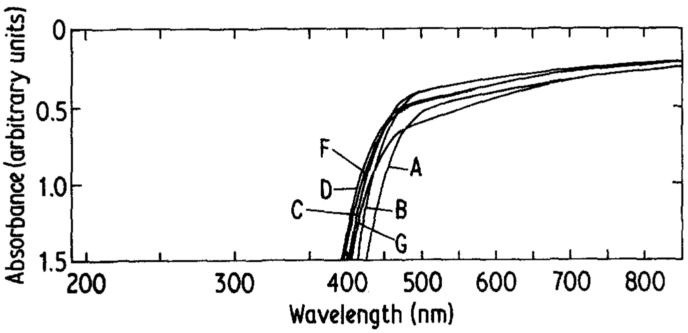

Figure 6 Variation of optical absorbance with wavelength for glass films of different compositions.

vibration appears at 1015 cm^{-1}. The presence of V^{4+} ion appears to reduce the V–O stretching frequency to 900 to 1015 cm^{-1}. The strong and broad band at 900 to 1250 cm^{-1} seems to be the combination of both V_2O_5 and P_2O_5 as the P–O vibration at 1080 to 1150 cm^{-1} and P=0 double bond at 1280 cm^{-1} have been reported earlier [22–24] for P_2O_5.

3.5. Optical absorption

The measurements of the optical absorption coefficient particularly near the fundamental absorption edge, provide a standard method for the investigation of optically induced electronic transitions and provide some ideas about the band structure and energy gap in both crystalline and non-crystalline materials. The absorption coefficients $\alpha(\omega)$ of the optical absorption near the band edge in many amorphous semiconductors show an exponential dependence on photon energy, $\hbar\omega$, and obey an empirical relation due to Urbach [25].

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

where B is constant, E is the width of the band tails of the localized states and ω is the angular frequency of the radiation. The origin of the exponential dependence of absorption coefficient on photon energy $\hbar\omega$ is not clearly known. Zanini and Tauc [26] have suggested that it arises from electron transitions between localized states where the density of the localized states is exponentially dependent on energy. But Davis and Mott [27] reported that this explanation is not valid for all disordered materials.

Optical absorption measurements were made as a function of photon energy at room temperature (~300 K). Considering our optical absorption results, Fig. 6 shows the absorbance in arbitrary units as a function of the wavelength in nm for glass films of different compositions. It is clear from the optical absorption spectra that there are no absorption peaks due to rare-earth oxides in vanadium phosphate glasses. This may be due to high optical absorption up to 410 nm, as a consequence of high percentage of vanadium.

The absorption coefficients, α, were determined near the edge for the whole range of glass compositions and the results 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 Davis and Mott [27]. For absorption by indirect transitions their equation takes the form,

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

and applies particularly in the region of absorption for which the absorption coefficient $\alpha(\omega) \geqslant 10^4$ cm^{-1}. B is constant and $\hbar\omega$ is the photon energy.

Fig. 7 shows the plot of $(\alpha\hbar\omega)^{\frac{1}{2}}$ against $\hbar\omega$ and the equivalent Urbach plot is presented in Fig. 8, in which the absorption coefficients are plotted as functions of ħ for various compositions of V_2O_5–P_2O_5 and V_2O_5–$(RE)_2O_3$–P_2O_5, respectively. From such exponential edges (Equation 1) the widths of the band tails of the localized states are estimated and listed in Table I.

The values of E_{opt} determined Fig. 7 by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{\frac{1}{2}} = 0$ lie within close limits between 2.20 to 2.37 eV ± 0.01 eV and these values may be compared with the values obtained from films containing V_2O_5 and P_2O_5 only. It is clear that the position of the absorption edge and the values of E_{opt} (however derived) are not particularly sensitive to the incorporation of rare-earth oxides. It may be ascribed to the unusual electronic configuration in these materials. For the same basic reason, i.e. the shielding of the $4f$ electrons from external forces by

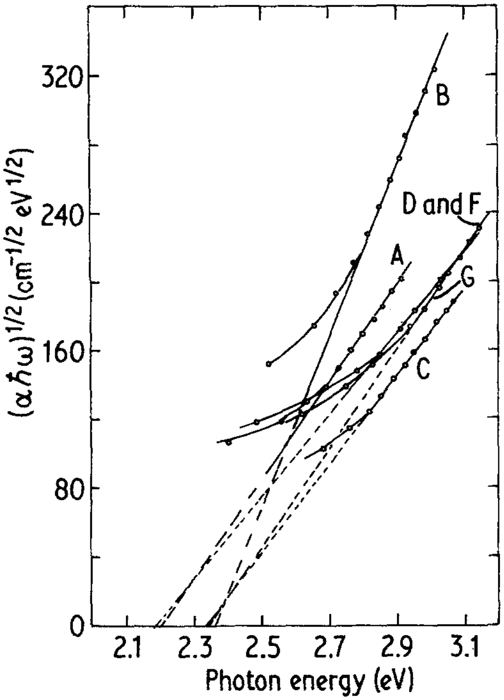

Figure 7 Optical absorption $(\alpha\hbar\omega)^{\frac{1}{2}}$ as a function of photon energy, plotted to confirm absorption by indirect transitions in vanadium phosphate glasses.

overlying $5s^2$ and $5p^6$ shells, we expect the states arising from the various $4f^n$ configurations to remain invariant for a given ion in various compounds including oxide glasses. Additional evidence for these phenomena has also been presented by Smith and Cohen [12] and others [28].

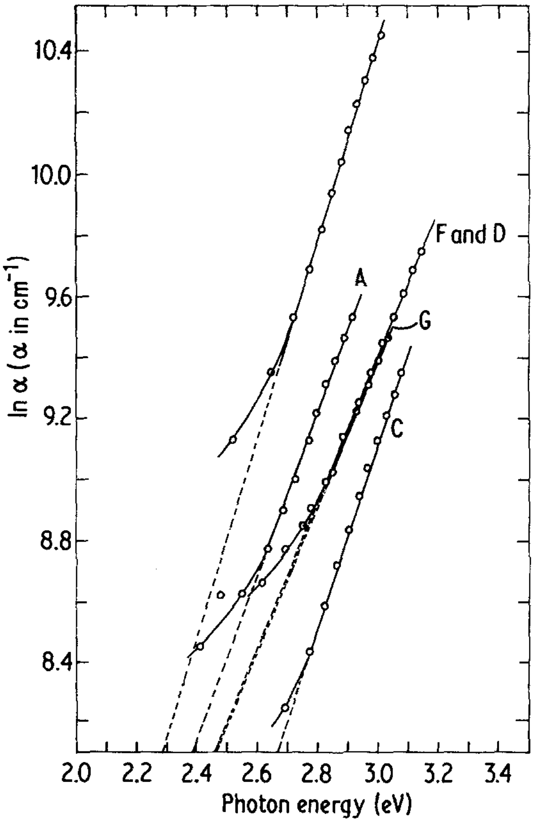

Figure 8 Absorption coefficient as a function of photon energy for vanadium phosphate glasses.

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