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A spectroscopic study of vanadium–phosphate glasses containing vanadium chloride

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The optical properties of vanadium–phosphate glasses containing various amounts of $(V_2O_5)_{50}(P_2O_5)_{50-x}(VCl_3)_x$, where $x = 0.05$, 0.06, 0.08 and 0.1, were measured as a function of VCl_3 content. It is found that by adding VCl_3 to the melt when the glass is formed, the added chlorine which acts as an oxidizing agent alters the ratio of concentration of vanadium ions and thus the absorption coefficient. Data on absorption in this study show that the power law, $\alpha(\omega) = B(\hbar\omega - E_0)^n/\hbar\omega$ is best followed for $n = 3$, and the absorption is solely due to vanadium oxide. Furthermore, the infrared absorption spectra of this system were investigated in the wave number range 400 to 4600 cm^{-1}. The addition of VCl_3 to the vanadium–phosphate glasses does not seem to introduce any new absorption band in this range as compared with the spectrum of a pure vanadium–phosphate glass. Furthermore, no significant difference in the absorption spectra was observed by annealing the V_2O_5–P_2O_5 glasses up to 200° C.

1. Introduction

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. In glasses and amorphous materials the disorder in the materials is associated with a tailing into the normally forbidden energy band gap of the density-of-states curve, and the amount of tailing can be estimated to a first approximation by plotting the absorption edge data in terms of an equation originally published by Urbach [1]:

$$\alpha(\omega) = A \exp \frac{\hbar\omega}{E_e} \qquad (1)$$

where ω is the angular frequency of the incident radiation, $\hbar = h/2\pi$ where h = Planck's constant, A is a constant and E_e is taken as an indication of the width of the band tails of the electrons. Tauc [2] and Davis and Mott [3] gave an equation, derived independently, for the absorption coefficient $\alpha(\omega)$ as a function of photon energy $\hbar\omega$ in an amorphous semiconductor,

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

where n is an exponent, B a constant and E_0 the optical energy gap of the semiconductor. Tauc [2] obtained $n = 2$ on the assumption that the conduction and valence band edges are both parabolic. Davis and Mott [3] obtained $n = 2$ for a different assumption. However, recently Vorlíček *et al.* [4] and others [5] have reanalysed the data on germanium and also reported the optical constants for silicon films in a wider spectral range (1.4 to 3.2 eV). They have found that in the case of germanium and silicon Equation 2 gives a better fit for $n = 3$. Klazes *et al.* [6] obtained the best fit for their data on silicon films for $n = 3$. Fagan [7] and Khawaja and Khattak [8] also reported a cubic fit to the absorption data for multicomponent chalcogenide and vanadate glasses.

Several transition metal oxides, when heated with glass-forming substances such as P_2O_5, TeO_2 and GeO_2, form glasses on quenching from the melt. The loss of oxygen from the melt produces lower valency transition metal ions. Electrical conduction in these glasses occurs by electron hopping from an ion of low valency state (V^{4+}) transition metal to an ion of high valence state (V^{5+}) [9].

It has recently been shown [10] that the admixture of chlorine has a great influence on the conductivity, which seems to be related to the ratio and relative concentrations of the ions in the different valency states (Mott [11], Linsley *et al.* [12], Moridi and Hogarth [13] and Kutub *et al.* [14]). We have already reported [15–21] various properties of germanate glasses of various systems.

In power reflection spectroscopy to determine the frequency-dependent complex dielectric response function $E(v)$, the power reflectivity $R(v)$ is measured, at near normal incidence, over as large a spectral range as possible. To obtain the phase spectrum $\theta(v)$ one has to use the Kramers–Krönig relation (Wootten [22]),

$$\theta(v) = \frac{2v}{\pi}\int_0^\infty \frac{\ln r(v')\mathrm{d}v'}{v'^2 - v^2} \qquad (3)$$

In the above equation $r(v) \exp [i\theta(v)]$ is the complex amplitude reflection coefficient and $r(v) = [R(v)]^{1/2}$. The Fresnel relation for normal incidence is

$$E(v) = E_1(v) + E_2(v) = [N(v) + iK(v)]^2$$
$$= \left(\frac{1 + r(v) \exp [i\,\theta(v)]}{1 - r(v) \exp [i\,\theta(v)]}\right)^2 \qquad (4)$$

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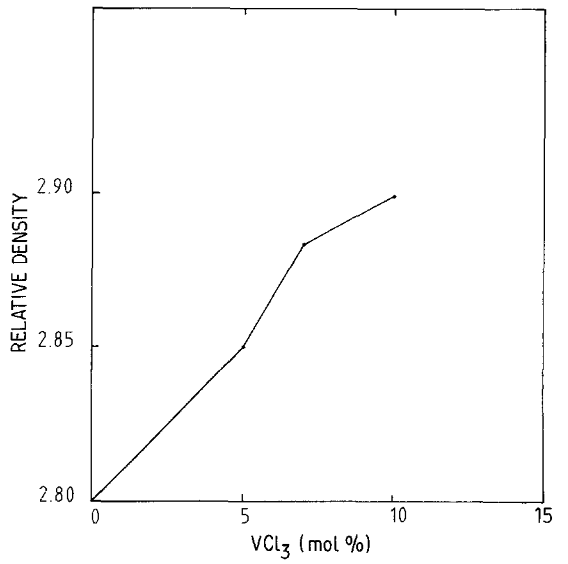


Figure 1 Density as a function of VCl$_3$ content for vanadium–phosphate glasses.

Here $E_1(\nu)$ and $E_2(\nu)$ are the real and imaginary parts of the dielectric response function and n and K are respectively the refractive index and absorption index. The measured power reflectivity $R(\nu)$ and the phase $\theta(\nu)$, with the aid of Equation 4, are used to evaluate various optical parameters like E_1, E_2, the absorption coefficient $\alpha(\nu)$ and the optical conductivity $\sigma(\nu)$. To cover the desired frequency range in the above calculation, the conventional extrapolation procedures were used.

The aims of the present report are threefold: firstly to find a fit to the power law (Equation 2), secondly to study the effect of VCl$_3$ on the absorption, and thirdly to determine the effect of heat treatment on the parameters describing the course of crystallization. These measurements provide reliable optical data in the infrared region for both annealed and unannealed samples of the V$_2$O$_5$–P$_2$O$_5$ system.

2. Sample preparation and experimental details

Glasses in the system having the composition (in mol %) $(V_2O_5)_{50}$ $(P_2O_5)_{50-x}$ $(VCl_3)_x$ where x varied from 0 to 10 mol % were prepared from chemically pure grades of materials. The crucible containing the mixture was pre-heated at 300° C for one hour and then placed into a closed high-temperature furnace where it was held for 6 h at a temperature of about 950° C. The melt was stirred from time to time using an alumina rod. By slow heating it was hoped to

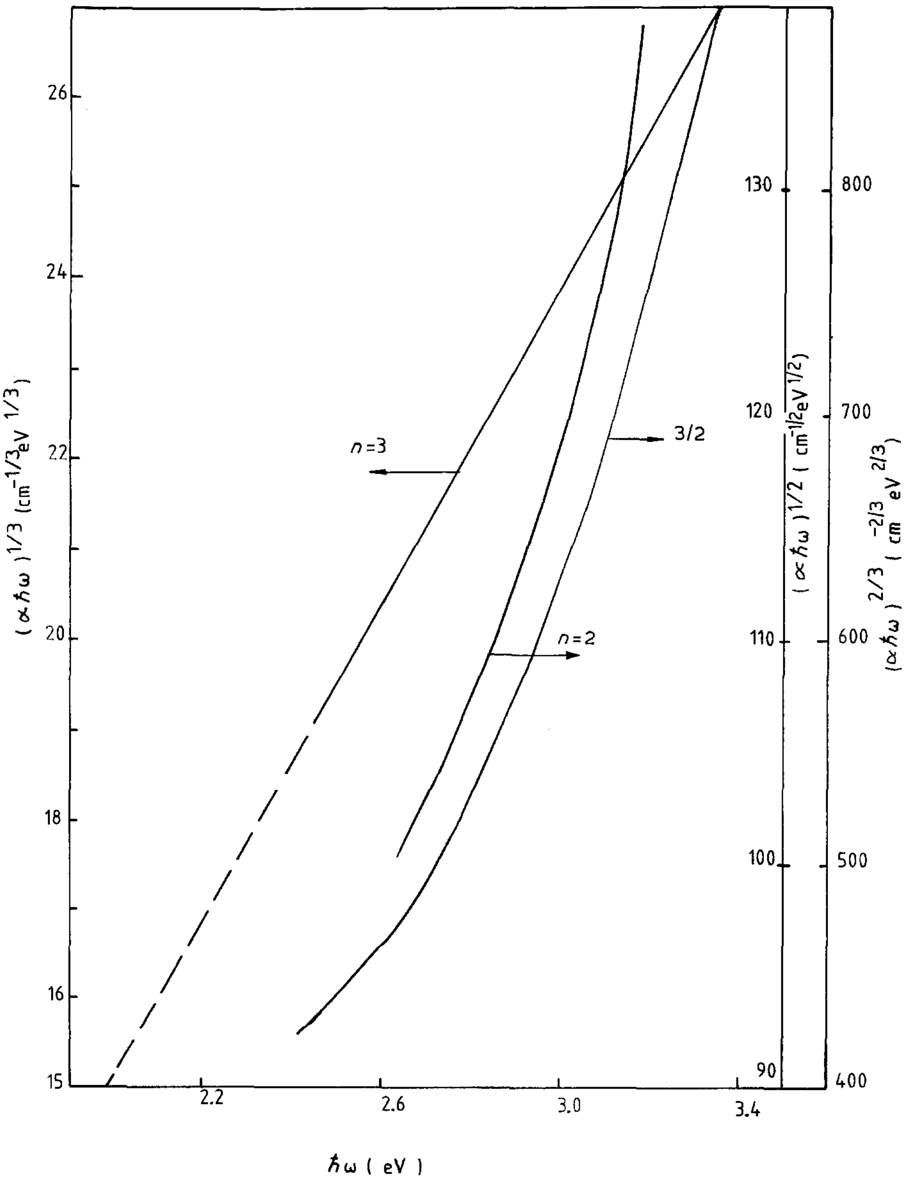


Figure 2 $(\alpha\hbar\omega)^{1/n}$ as a function of photon energy for $(V_2O_5)_{0.5}$ $(P_2O_5)_{0.5}$ glass, n = 3/2, 2 and 3.

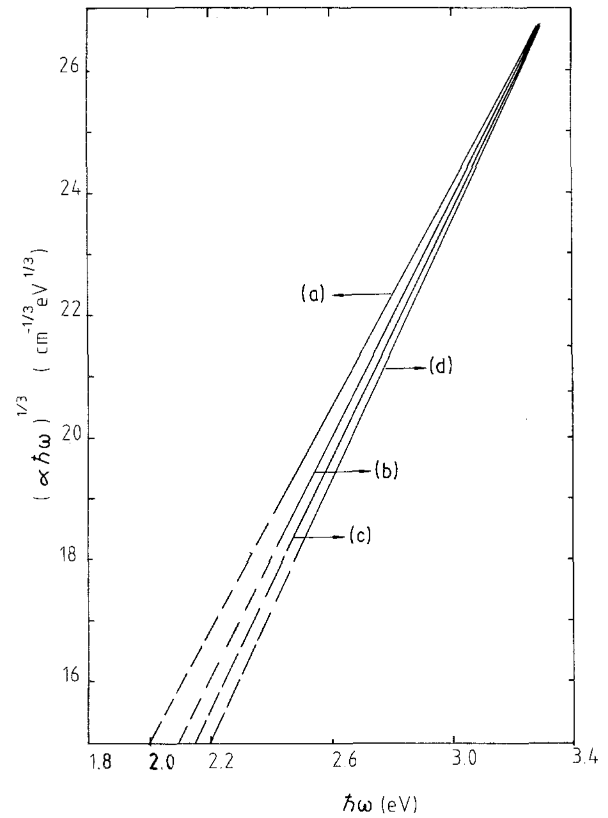


Figure 3 $(\alpha\hbar\omega)^{1/3}$ as a function of photon energy for $(V_2O_5)_x(V_2O_5)_{1-x}$ glass systems where x is (a) 0.0, (b) 0.5, (c) 0.8, (d) 1.0.

reduce mechanical and volatilization losses. The melts were finally poured on to a clean stainless steel plate and cast into the shape of discs of 20 mm diameter and 2 to 3 mm thickness. Two discs of each composition were cast, one on a stainless steel plate which was at room temperature and the other on a steel plate maintained at a temperature of 200° C, and introduced to a furnace which was already at this temperature. The furnace was maintained at this temperature for 2 h and was then switched off to cool down to room temperature. These samples were polished optically flat for the infrared measurements. Thin blown films of the glasses were prepared by dipping an alumina tube into the molten material and collecting a small amount of glass melt on the end of the tube and blowing it into the air. Films ranging in thickness from 4.00 to 8 μm were prepared. Optical measurements were made on the thin films while the density was measured of bulk samples (Fig. 1) by Archimedes' principle using acetone as a fluid. The optical absorption of these glasses was measured at room temperature in the wavelength range from 350 to 900 nm using a Perkin-Elmer Lambda 3 uv/visible spectrophotometer. For each composition the optical density was measured for two samples which varied in thickness such that reflection effects could be eliminated. The results included in the present study include the high absorption region (absorption coefficient $\alpha \gg 10^4\,\mathrm{cm}^{-1}$), wherein the multiple interference effects were insignificant.

In this case the absorption coefficient is then given by

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

where A_1 and A_2 are the optical densities and d_1 and d_2 are the thicknesses of Specimens 1 and 2. In the low-absorption region ($\alpha < 10^4\,\mathrm{cm}^{-1}$) multiple interference effects were very pronounced. It might be appropriate to mention that determination of α in the low-absorption region is not possible from a single measurement of the optical density, and hence values of less than $10^4\,\mathrm{cm}^{-1}$ are not included.

For infrared measurements, glassy samples of specific compositions were prepared by blowing specimens in the thickness range from 5 to 12 μm. The as-blown thin glass film was mounted on a specially designed specimen holder, which was directly placed into the compartment of the infrared spectrophotometer. The infrared absorption spectra of these samples were determined by using a Nicolet DX spectrophotometer in the wave number range 400 to $4600\,\mathrm{cm}^{-1}$. In order to study the infrared optical properties of the bulk samples at ambient temperature, power reflectance measurements were performed using a Perkin-Elmer monochromator. Since the reflectance measurements cover an extremely large frequency range, the Kramers–Krönig [22] relation was used to analyse the spectra.

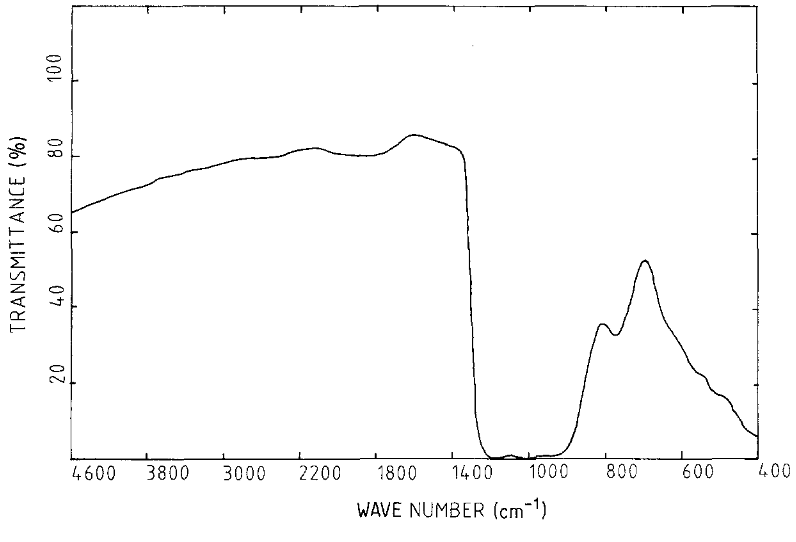
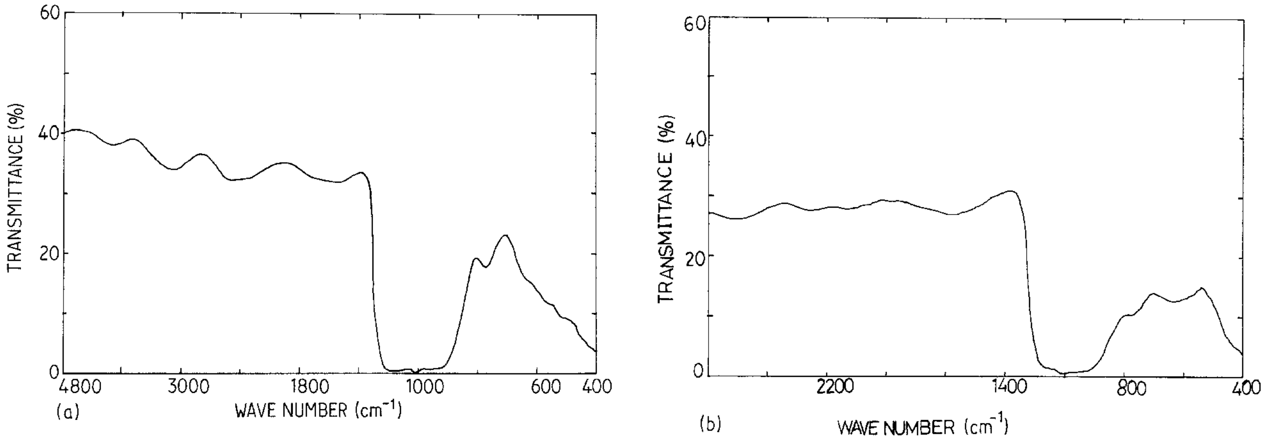


Figure 4 The infrared transmittance spectra of V_2O_5–P_2O_5 glasses.



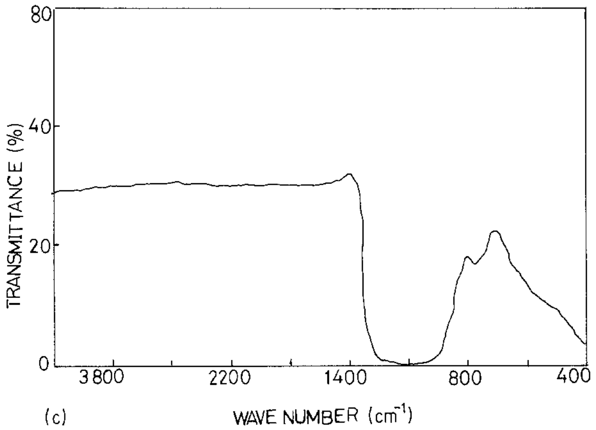


Figure 5 The infrared transmittance spectra of V_2O_5–P_2O_5 glasses: (a) containing 5 mol % VCl_3 taken unannealed, (b) containing 10 mol % VCl_3 unannealed, (c) containing 10 mol % VCl_3 annealed at 200° C for 2 h.

3. Results and discussion

Fig. 2 shows $(\alpha\hbar\omega)^{1/n}$ against $\hbar\omega$ for $n = \frac{3}{2}$, 2 and 3 for films of the V_2O_5–P_2O_5 glass system containing VCl_3. The power $\frac{3}{2}$ is included because some investigators [23, 24] used this for their absorption data on the V_2O_5–P_2O_5 glass system. They obtained reasonable fits with the $\frac{3}{2}$ power, in the small-energy region that they were concerned with (less than 3 eV). However, in the present study a wider energy range up to 3.6 eV is covered. It is clear from Fig. 2 that $n = 3$ gives a better fit to the data on the present system. Similar results were obtained for other compositions. Fig. 3 shows the plots for different compositions for $n = 3$.

The absorption spectra obtained in the present work are similar to the ones obtained by Sanchez *et al.* [25], Khawaja and Khattak [8] and Al-Ani and Hogarth [26]. Sanchez *et al.* attributed the high-energy strong absorption spectra to be arising from allowed charge transfer transitions from the V_{2P} valence band to the empty V_{3P} conduction band. Austin and Mott [27] attribute this absorption to the optical excitation of a carrier from its polarization well and subsequent transfer to another lattice site, corresponding, in a vanadate glass, to the transfer of an electron from a V^{4+} site to a V^{5+} site.

It is clear from Fig. 3 that by increasing the chlorine content, the absorption edges shift towards higher energies which range from 2.0 to 2.2 eV.

The absorption characteristic in these glasses may be described on the generally accepted qualitative

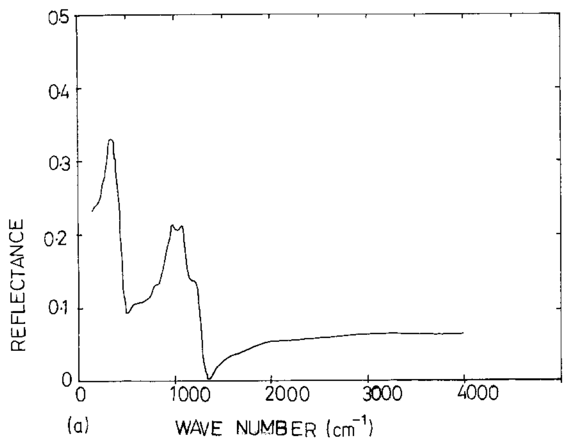
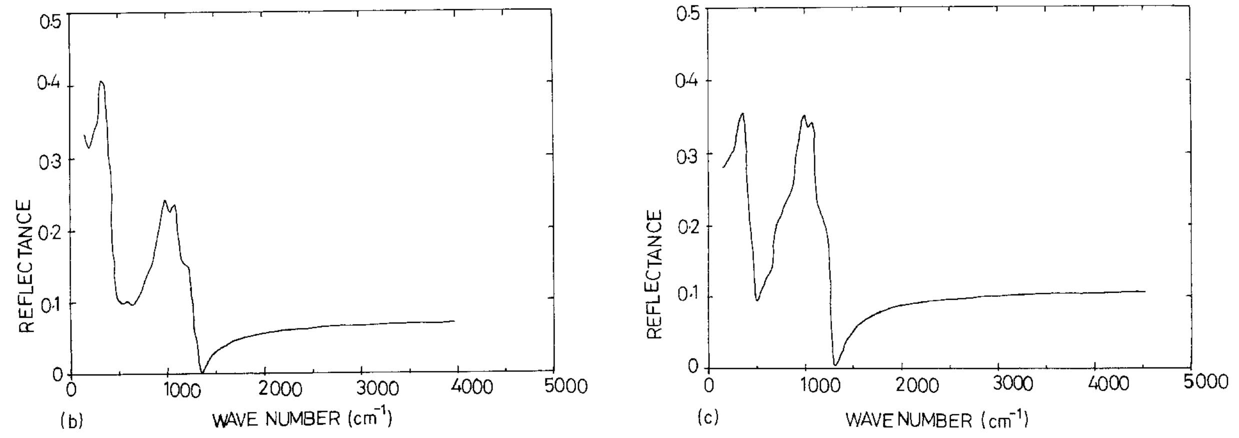
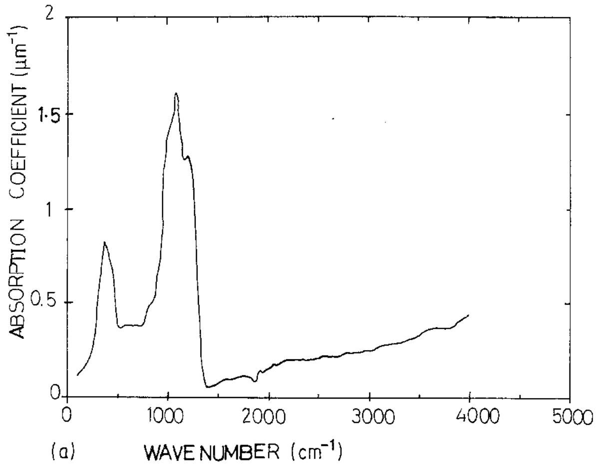
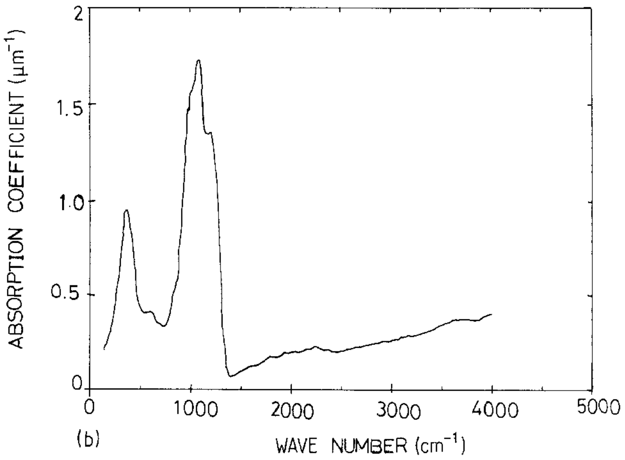


Figure 6 Measured infrared reflectance spectra for (a) unannealed V_2O_5–P_2O_5 glass, (b) annealed V_2O_5–P_2O_5 glass at 200° C, (c) unannealed V_2O_5–P_2O_5 glass containing 5 mol % VCl_3.







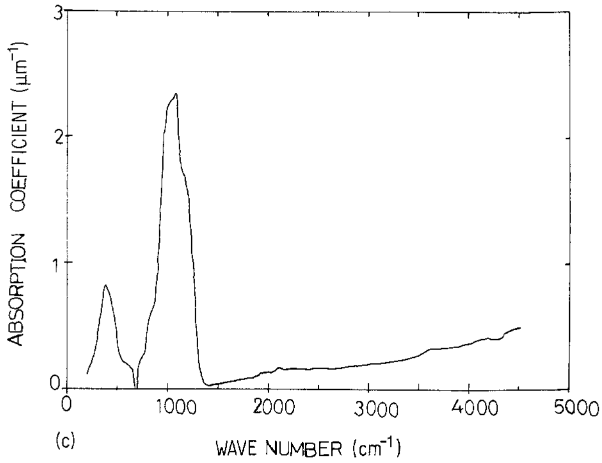
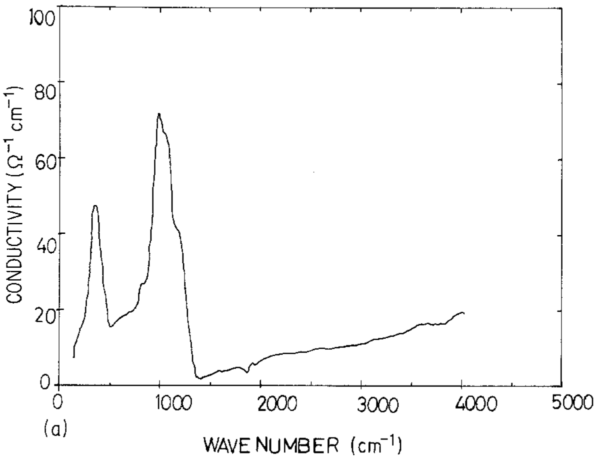


Figure 7 Infrared absorption coefficients of (a) unannealed V_2O_5–P_2O_5 glass, (b) annealed V_2O_5–P_2O_5 glass at 200° C, (c) unannealed V_2O_5–P_2O_5 glass containing 5 mol % of VCl_3.

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 characteristic [28]. This could be ascribed to the added chlorine which acts as an oxidizing agent.

The infrared absorption spectrum for the vanadate glasses is well established. A typical spectrum is shown in Fig. 4 for a vanadium phosphate glass. Assignment of each absorption band can be found in Nakamoto [29].

The vibrational absorption peaks observed for V_2O_5–P_2O_5 glasses are at 780 cm^{-1}, which could be ascribed to the P–O–P ring frequency of P_2O_5. Another very strong and broad absorption band observed in our glasses appeared within the 900 to 1200 cm^{-1} range. The vibrational absorption bands in the range 400 to 2000 cm^{-1} could be due to a number of causes such as bridging and non-bridging oxygen ions which are doubly and singly bonded, to the high and low states of vanadium ions, to phosphate ions, and possibly to some combinations of these. It has been reported [30] that the peak due to the vanadium–oxygen



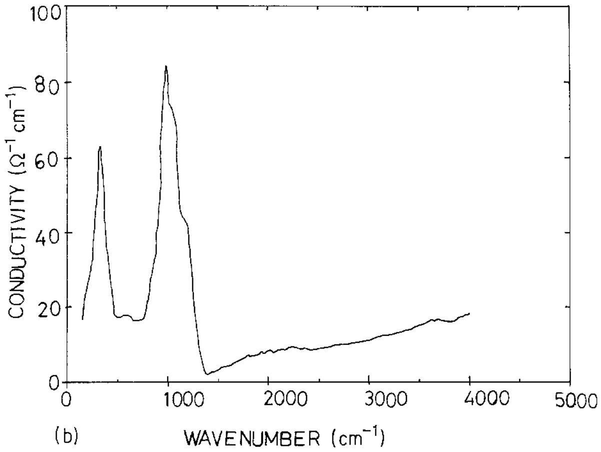
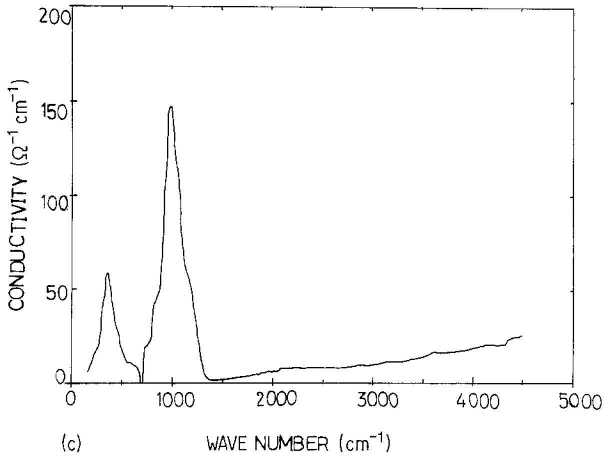


Figure 8 Infrared optical conductivity of (a) unannealed V_2O_5 glass, (b) annealed V_2O_5–P_2O_5 glass at 200° C, (c) unannealed V_2O_5–P_2O_5 glass containing 5 mol % VCl_3.



stretching vibration appears at 1015 cm^{-1}. The presence of V^{4+} ions appears to reduce the V–O stretching frequency to 900 to 1015 cm^{-1}.

Phosphate ions introduce weak vibrational absorption in some phosphate glasses in the range 1020 to 1100 cm^{-1}, and in some crystalline phosphate networks in the range 1150 to 1400 cm^{-1} [23]. Therefore the broad absorption spectra between 1080 and 1150 cm^{-1} could be due to phosphate–oxygen vibrations as has been reported by Janakirama-Rao [30, 31]. Thus the strong and broad band at 900 to 1200 cm^{-1} seems to be the combination of both V_2O_5 and P_2O_5. This observation is consistent with the results of Khan *et al.* [32] and Hogarth and Hosseini [33].

The experimentally measured transmittance and reflectance spectra for the annealed and unannealed glasses containing various amounts of VCl_3 are presented in Figs 5 and 6, respectively. To calculate the phase shift on reflection, Equation 3 was used. The measured reflectance and the phase were then used to calculate the absorption coefficient $\alpha(\nu)$ and optical conductivity $\sigma(\nu)$. The measured parameters for annealed and unannealed samples are respectively shown in Figs 7 and 8. The peaks in these spectra have been identified in the earlier discussion. By comparing Fig. 7a with Fig. 7b we see no significant effect on the absorption coefficient by annealing the V_2O_5–P_2O_5 sample up to 200° C. Similarly no new absorption band was observed in the absorption spectra of the glasses containing 5 mol % VCl_3 as shown in Fig. 7c.

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