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Some studies of the optical properties of molybdenum–phosphate glasses

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A series of binary MoO_3–P_2O_5 and ternary MoO_3–In_2O_3–P_2O_5 glasses was prepared and their optical properties were investigated. The optical absorption edge of the glasses was measured for specimens in the form of thin blown films. It was found that the fundamental absorption edge of these glasses usually occurs in the ultraviolet region. The linear variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ where α is the absorption coefficient and $\hbar\omega$ is the incident photon energy, is taken as evidence of non-direct interband transitions. The linear dependence of optical gap with molybdenum content indicates that the molybdenum content controls the absorption phenomena in this glassy system. The infrared spectra of all the glasses appeared to be almost the same, indicating that the infrared bands arise primarily from the vibrations of the phosphate and molybdate groups. The structure of molybdenum phosphate glasses is discussed in terms of the formation of mixed phosphate and MoO_4 tetrahedra.

1. Introduction

The electrical and optical properties of transition metal oxide glasses have been investigated by a number of workers [1–3]. The transition metal ion exists in different valency states within the glass, which enables the electrons to hop from a low to a higher valency state.

We have studied a range of molybdenum–phosphate glasses. The electron paramagnetic resonance (EPR) studies clearly show the existence of molybdenum in different valency states [4]. The ion concentration ratios of $[Mo^{5+}]/[Mo^{6+}]$ have been measured for glasses with different compositions and it was shown earlier that the spin concentration is independent of temperature [4]. We have also studied the electrical properties of these glasses [5] and have shown that the electrical conduction is by a hopping mechanism in which electrons transfer from Mo^{5+} to Mo^{6+} ion sites. The electrical conductivity increases with increasing MoO_3 content and the electrical activation energy, W, of these glasses decreases as the MoO_3 content of the glass increases [5].

Here we report the optical properties of MoO_3–P_2O_5 glasses. The optical absorption in solids can occur by several different mechanisms. For example, the absorption can arise by transfer of electrons from one neighbouring atom to another. It may also be caused by internal transitions between d-shell electrons, and such absorption normally appears in the infrared region. In this region the absorption may cause molecular vibrations which may provide useful information concerning the local atomic arrangements within the solid.

In terms of the band theory of crystalline solids there are two main types of optical transitions at the fundamental absorption edge, namely, direct transitions where momentum is conserved and indirect transitions which is a phonon-assisted process. According to Mott and Davis [6] for non-direct transitions in amorphous semiconductors, the absorption coefficient is given by

$$\alpha(\omega) = \frac{A}{\hbar\omega}(\hbar\omega - E_{\mathrm{opt}})^2 \qquad (1)$$

where A is constant, E_{opt} is the optical energy gap, $\hbar\omega$ is the photon energy and it is assumed that the matrix element for optical transitions has the same value whether or not the initial and final states are localized. It was reported that in oxide glasses containing copper [7] and tungsten [8], the energy dependence of the absorption coefficient fits Equation 1 very well.

The infrared spectra of binary phosphate glasses have been measured by a number of authors. Bartholomew [9] studied the infrared spectra of glasses in the Ag_2O–P_2O_5 system and showed that the structure of silver phosphate glasses can be interpreted on the basis of a polymeric chain structure. In the frequency ranges where the P=O and P–O stretching frequencies should occur, there is a shift of band position in glasses containing sodium. Such a shift can be discussed in terms of the existence of covalent bond formation between the non-bridging oxygen ions and the silver ions to form P–O–Ag units [9]. Müller [10] has concluded that the principal absorption of the P=O group lies at 1282 to 1205 cm^{-1} and the P–O–P ring frequency in cyclic phosphates occurs between 805 and 740 cm^{-1}. Sayer and Mansingh [11] investigated the infrared spectra of a number of transition metal oxide glasses and suggested that phosphate tetrahedra dominate the structure of manganese, nickel, cobalt and copper glasses, while structures of the form MO_n, where M is the transition metal ion, dominate in the glasses formed with vanadium, molybdenum and tungsten. Hogarth and Moridi [12] showed that in copper calcium phosphate glasses, the phosphate tetrahedra dominate the structure of the glass and a partially covalent P–O–Cu^+ bond is created in glasses having a higher copper content.

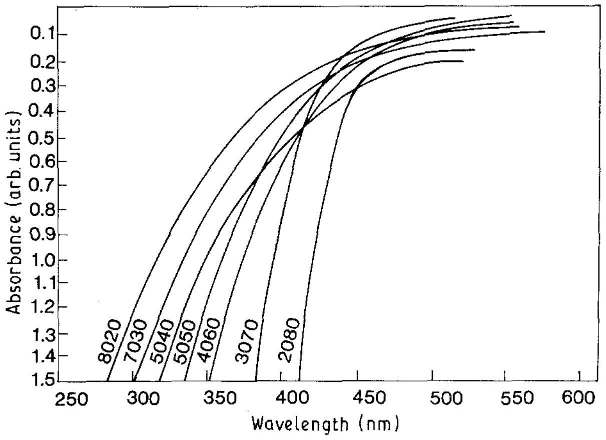

Figure 1 Typical absorption edge characteristic for MoO_3–P_2O_5 glasses.

2. Experimental procedure

The glasses were prepared by mixing appropriate proportions of reagent grade P_2O_5, MoO_3–P_2O_5 and In_2O_3 powders. The materials were melted in an alumina crucible in an electrically heated furnace at 1200 °C for 3 h in an atmosphere of air. The melts were quenched by pouring on to a steel plate. The optical absorption of the glasses was measured at room temperature for specimens in the form of thin blown films having a thickness of about 5 to 10 μm, using a Perkin–Elmer 137 UV spectrophotometer.

The infrared spectra of the glasses were recorded with the aid of a CsC pellet in a Unicam SP 2000 double-beam infrared spectrometer. In this technique glass samples were ground into a fine powder and then a small amount of the glass powder was mixed and ground with CsCl. The pellets were made by pressing the mixture at 15 ton (1 ton = 1.0160 × 10^3 kg) for a few minutes under vacuum. Table I shows the batch compositions of the glasses reported in the present work.

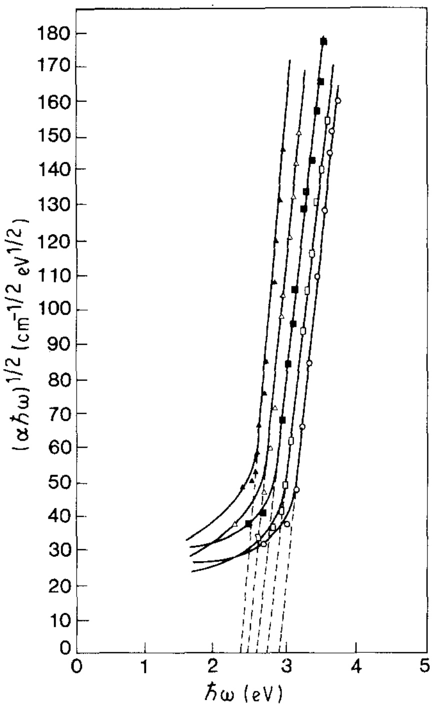

Figure 2 $(\alpha\hbar\omega)^{1/2}$ as a function of energy for MoO_3–P_2O_5 glasses: (▲) 2030, (△) 3070, (■) 4060, (□) 5050, (○) 6040.

3. Results and discussion

3.1. Optical absorption edge

The optical absorption spectra for molybdenum phosphate glasses as a function of wavelength are shown in Fig. 1. It may be noted that the optical absorption edge is rather less steep compared with those characteristic of mono-crystalline semiconductors. As can be seen, the fundamental absorption edge moves towards the longer wavelengths as the MoO_3 content is increased. Fig. 2 illustrates a typical plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ in accordance with Equation 1 and there is a well-defined linear region in the curves particularly at the higher energies. The E_{opt} values are taken to be the intercept of the extrapolation of the linear portion

TABLE I Composition, density, optical gap and electrical activation energy of glasses examined

Glass no.	P_2O_5 content (mol %)	MoO_3 content (mol %)	In_2O_3 content (mol %)	Relative density	E_{opt} (eV)	W[5] (eV)
8020	80	20	0	2.80	3.10	0.76
7030	70	30	0	2.82	3.00	0.74
6040	60	40	0	2.94	2.88	0.71
5050	50	50	0	3.00	2.67	0.67
4060	40	60	0	3.17	2.58	0.65
3070	30	70	0	3.37	2.44	0.62
2080	20	80	0	3.60	2.34	0.57
405505	40	55	5	3.39	2.86	0.77
405010	40	50	10	3.48	2.92	0.75

of the curves with the horizontal axis. Table I and Fig. 3 represent the decrease of E_{opt} with increase of MoO_3. Such behaviour was also noted for the variation of electrical activation energy as a function of MoO_3 content [5]. Fig. 4 shows the variation of electrical activation energy, W, with optical energy gap, E_{opt}. Such a linear relationship between W and E_{opt} has also been reported earlier for glasses containing copper [7], and tungsten [8].

The optical absorption data at the lower values of absorption in molybdenum–phosphate glasses can also be fitted to an expression known as the Urbach rule, namely $\alpha(\omega) \sim \exp(\hbar\omega/\Delta)$ where Δ is a constant and generally lies in the range 0.05 to 0.7 eV for amorphous semiconductors. Fig. 5 shows a typical exponential dependence of $\alpha(\omega)$ as a function of $\hbar\omega$ for these glasses. The value of Δ was reported to vary between 0.12 and 0.4 eV in tungsten–tellurite glasses [8], and to lie between 0.16 and 1.06 eV for copper–phosphate glasses [7]. For molybdenum–

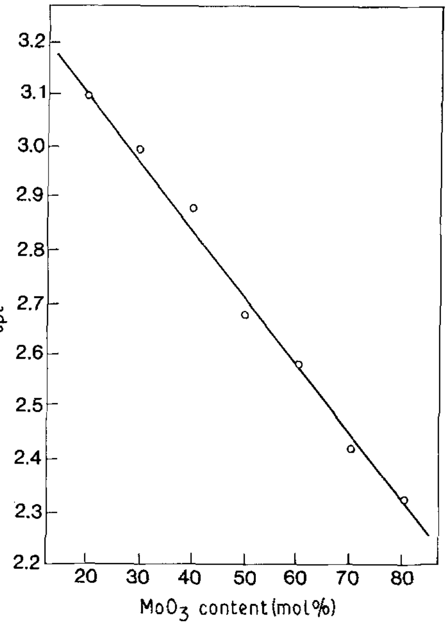

Figure 3 E_{opt} as a function of MoO_3 content for MoO_3–P_2O_5 glasses.

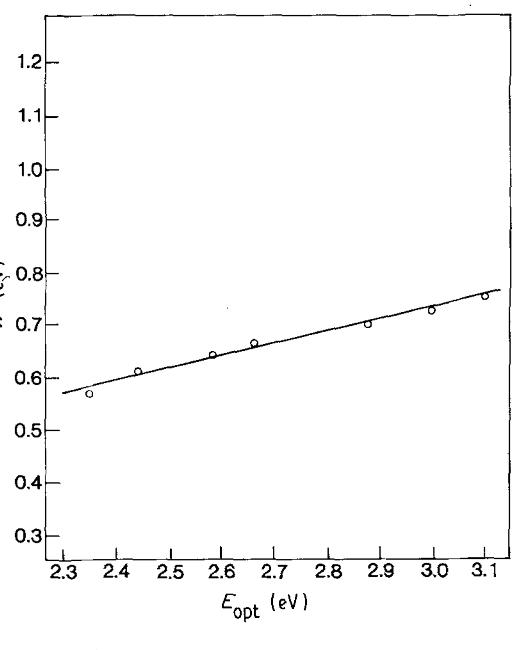

Figure 4 Activation energy, W, as a function of E_{opt} for MoO_3–P_2O_5 glasses.

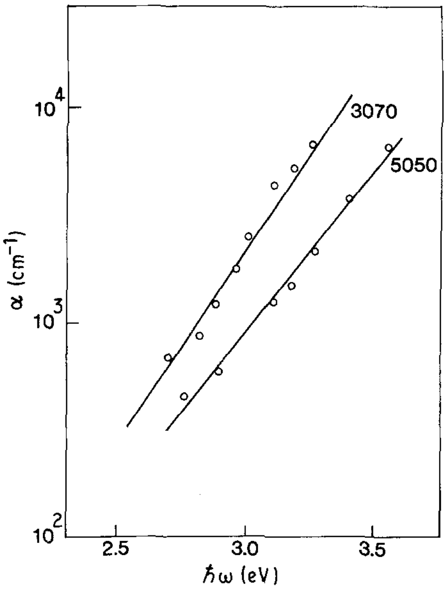

Figure 5 Optical absorption as a function of energy for MoO_3–P_2O_5 glasses.

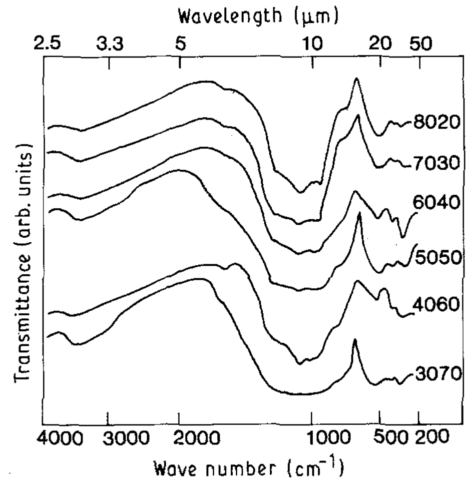

Figure 6 Infrared absorption spectra of MoO_3–P_2O_5 glasses.

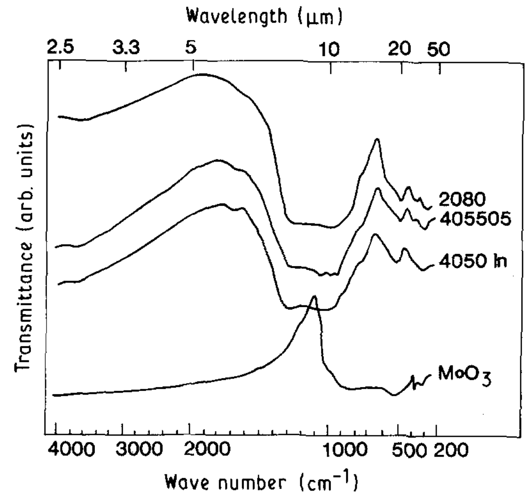

Figure 7 Infrared absorption spectra for a series of MoO_3–P_2O_5 and MoO_3–P_2O_5–In_2O_3 glasses and for MoO_3.

TABLE II Infrared absorption band positions for molybdenum–phosphate glasses

Glass no.	Absorption band position (cm^{-1})									
2080	300	390	500	760–780	930	980	1055	1300	1650	3440
3070	300	390	500	760–780	930	980	1070	1300	1650	3440
4060	300	390	500	760–780	930	980	1090	1300	1650	3440
5050	300	390	500	760–780	930	980	1100	1300	1650	3440
6040	300	390	500	760–780	930	980	1100	1300	1650	3440
7030	300	390	500	760–780	930	980	1020	1300	1650	3440
8020	300	390	500	760–780	930	980	1020	1300	1650	3440
405505	300	390	500	760–780	930	980	1060	1300	1650	3440
405010	300	390	500	760–780	930	980	1060	1300	1650	3440
P_2O_5	–	–	500	760–780	930	980	1020	1260	–	–
MoO_3	300	390	550	–	870	995	–	–	–	–

phosphate glasses, Δ was previously reported to be 0.16 eV [13], but according to our experimental results it is in the range of 0.23 to 0.39 eV depending on glass composition.

The nature of this exponential tail absorption is not clearly known. Tauc [14] suggested that it arises from transitions between the localized states in the band-edge tails, the density of which is assumed to fall exponentially with energy. Mott and Davis [6] believed this to be unlikely as the slopes of the observed exponential absorption edges are very much the same in a large number of materials. Dow and Redfield [15] believe that the spectral Urbach rule is due to the random internal electric field associated with the structural disorder which broadens the exciton line.

3.2. Infrared spectra

The infrared spectra of molybdenum phosphate glasses were recorded from 200 to 4000 cm^{-1}, and are shown in Figs 6 and 7. As can be seen, the bands for some compositions are broad and possibly overlapped. Table II represents the position of the absorption bands for molybdenum–phosphate glasses and these are found to be close to those reported by Minami *et al.* [11]. Two bands at 300 and 390 cm^{-1} can be identified on the basis of the reference data for MoO_4^{2-} ions [16].

Comparison with the infrared spectra of crystalline P_2O_5 shows that some of the absorption bands of glasses are the same as for P_2O_5. The absorption band at 500 cm^{-1} which appears in all glasses and in crystalline P_2O_5 is known to be a fundamental frequency of the $(PO_4)^{3-}$ group and the absorption band at 930 cm^{-1} may be related to the MoO_4^{2-} ions. The absorption bands of glasses at 760 to 780, 100 and 130 cm^{-1} would seem to be attributable to the P–O–P ring frequency, the P–O stretching frequency and the P=O double bond.

It is clear that as the MoO_3 content increases, there is only a small shift of band position in molybdenum–phosphate glasses to lower frequencies where the P–O stretching frequencies should occur. Such a shift was observed by Bartholomew [9] in sodium–phosphate glasses when replacing sodium with silver. Hogarth and Moridi [12] also observed such a shift towards the lower frequencies in copper–calcium–phosphate glasses. Following these authors, this sort of shift can be discussed in terms of the creation of partial covalent bonds between non-bridging oxygen ions and molybdenum ions to form P–O–Mo units in high molybdenum content glasses. Two absorption bands were observed in all spectra at 1640 and 3340 cm^{-1}. These are weak bands and seem to be related to the small amounts of water trapped in the glass or possibly to overtones. The absorption spectra of the glasses was also recorded in the range 0.5 to 2.5 μm but no significant absorption was observed.

4. Conclusion

The linear variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ in molybdenum phosphate glasses can be taken as evidence of indirect interband transitions as discussed by Mott and Davis [6]. The linear variation of E_{opt} with molybdenum content indicates that this is mainly responsible for the absorption phenomena in this glassy system. Furthermore the linear variation of E_{opt} with Mo^{5+} content could be taken as evidence that the absorption edge is related to the Mo^{5+} concentration and indeed is of electronic origin. The exponential dependence of the absorption coefficient on energy may be explained on the basis of internal field broadening of an exciton line. As in many other glasses, $2W$ is less than the value obtained for E_{opt} on the same glasses. This is consistent with the idea that the electronic activation is not across the whole mobility gap but is possibly from one or more trapping level to the conduction band or from bonding states to a trapping level.

The infrared spectra of the binary and ternary glasses appeared to be almost the same. It is difficult to obtain detailed quantitative information from the infrared spectra, but because there is correlation between the infrared spectra for the molybdenum trioxide and the glass, as the fundamental frequency of $(PO_4)^{3-}$ group is maintained in the glass, the behaviour may be qualitatively summarized by suggesting that the structure of the mixed form of phosphate and MoO_4 tetrahedra dominate the structure of molybdenum–phosphate glasses. This suggestion is broadly consistent with the conditional glass-forming nature of MoO_3.

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