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Some studies of the optical properties of copper phosphate glasses containing praseodymium

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A range of copper phosphate glasses containing praseodymium was prepared and the optical absorption edges and infrared optical absorption spectra were measured. The optical energy gap of copper phosphate glass doped with praseodymium is slightly higher than the corresponding composition of the base glass. Heat treatment at 400 and 800° C caused some changes in the infrared absorption bands which are related to the characteristics of the Pr_6O_{11} component.

1. Introduction

In recent years many papers have appeared reporting the properties of amorphous and glassy semiconductors, and much of the state of the art is included in a book written by Mott and Davis [1]. Many of the investigations of electronically-conducting oxide glasses have been made in glass systems based on phosphorus pentoxide [2–4]. Spectroscopic studies of lanthanide salts have been reported [5, 6] and traditional glasses doped with varying quantities of rare-earth oxides have been investigated [7–11]. In such systems lanthanide ions may give rise to sharp absorption bands. These sharp bands are due to forbidden transitions involving the 4f levels, 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 various compounds.

Some earlier investigations have been made on praseodymium phosphate glasses [12, 13] but there are no reported studies on copper phosphate glasses doped with praseodymium. Thus it was of some interest to measure the optical absorption edge and infrared absorption spectra in order to study the effect of the introduction of praseodymium into copper phosphate glasses and the effect of annealing on the infrared spectra, which may provide some information about microstructural changes which occur in the glass.

2. Experimental work

2.1. Glass preparation

Glasses in the system having the composition expressed in mol % $(P_2O_5)_{50}$–$(CuO)_{50-x}$–$(Pr_6O_{11})_x$, where x varied from 0 to 5 mol %, were prepared from chemically pure grades of material according to their molar composition, in an alumina crucible. A typical melt contained some 30 g of material. In order to reduce a tendency to volatilization the crucible was initially heated for one hour at 400° C and then transferred to another furnace maintained at a specific temperature for one hour, based on the composition used. This is shown in Table I. The melt was stirred from time to time using an alumina rod, and was finally poured on to a clean stainless steel plate and cast into a disc 2 cm in diameter and about 2 mm thick.

Three discs of each composition were cast, one on a stainless steel plate which was at room temperature (unannealed samples) and the second disc was immediately transferred to another furnace which was already maintained at 400° C. The third disc was transferred to a furnace maintained at 800° C. The furnaces were kept at these temperatures for one hour and then were switched off to cool down to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. X-ray diffraction measurements confirmed the glassy nature of all samples examined.

2.2. Optical measurements

Thin films of specific composition, which are necessary for optical absorption measurements, were obtained by blowing in air using an alumina tube. Specimens in the thickness range from 2 to 10 μm were obtained, as measured using a Sigma comparator (Letchworth, Herts, UK). All thin films were unannealed when used for optical measurements.

TABLE I Composition data for praseodymium copper phosphate glasses

Glass No.	Composition (mol %)	Initial melting point (° C)
1	$(P_2O_5)_{50}$–$(CuO)_{50}$–$(Pr_6O_{11})_0$	1200
2	$(P_2O_5)_{50}$–$(CuO)_{49}$–$(Pr_6O_{11})_1$	1300
3	$(P_2O_5)_{50}$–$(CuO)_{48}$–$(Pr_6O_{11})_2$	1300
4	$(P_2O_5)_{50}$–$(CuO)_{47}$–$(Pr_6O_{11})_3$	1350
5	$(P_2O_5)_{50}$–$(CuO)_{46}$–$(Pr_6O_{11})_4$	1350
6	$(P_2O_5)_{50}$–$(CuO)_{45}$–$(Pr_6O_{11})_5$	1400

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The optical absorption measurements were made on thin blown films at room temperature in the wavelength range 180 to 900 nm using a Perkin-Elmer 402 Spectrophotometer. For infrared measurements, 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 large quantity of KBr. KBr pellets transparent to light were formed by pressing the mixture at 12 tons (1016 kg) for a few minutes under vacuum. The infrared absorption spectra of these samples were determined by using a Unicam SP 2000 double-beam recording infrared spectrometer in the range 400 to 4000 cm^{-1}.

3. Results and discussion

3.1. Optical absorption spectroscopy

Optical absorption measurements were made at room temperature. Fig. 1 shows the absorption in arbitrary units as a function of wavelength for Glasses 1 and 2. From the figure it is clear that there are no sharp absorption edges, and this is a characteristic of most glassy oxide materials including transition metal ion phosphate glasses [14, 15]; there are no absorption peaks just beyond the edge in copper phosphate glass doped with 1 mol % Pr_6O_{11}, and this may be due to the high percentage of copper in the glass. However, an absorption at 850 nm due to Cu^{2+} is observed for copper phosphate glass (Curve 1) [4, 16] and this disappears as the glass is increasingly doped with Pr_6O_{11}. It is clear that the fundamental optical absorption edge of glass doped with Pr_6O_{11} is sharp as for cerium phosphate glass [11] rather than the usual copper phosphate glass, but it is not as sharp as reported for the higher percentages of Pr_6O_{11} in praseodymium phosphate glasses [13].

The reason for this different spectral behaviour in praseodymium glasses lies in the 4f electrons of praseodymium and has been discussed earlier. Thus the optical absorption edge is expected to be sharp rather than diffuse for these materials, but clearly as the relative copper content is increased or the praseodymium content is reduced, then the effectiveness of the 4f electrons in behaving as if they were in a crystal will be reduced.

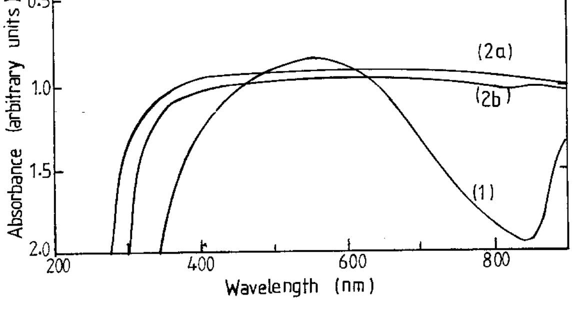

Figure 1 Absorption as a function of wavelength for (1) Glass 1 (Table I) 6 μm thick and (2a, b) Glass 2 of different thicknesses: (a) 3.5 μm, (b) 4.5 μm.

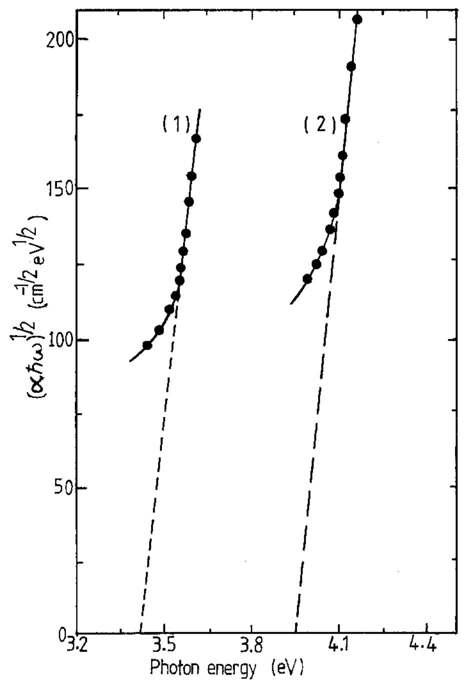

Figure 2 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for Glasses 1 and 2 (Table I).

It is also noted from the figure that the absorption edge seems to move to longer wavelengths as the thickness of the glass sample is increased (Curves 2a and b). The optical absorption coefficient $\alpha(\omega)$ 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 [17]. The coefficient $\alpha(\omega)$ for many amorphous and glassy materials is found to obey the relation

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

and applies particularly in the region of absorption for which $\alpha(\omega) > 10^4 cm^{-1}$. E_{opt} is the optical energy gap, B is a constant and $\hbar\omega$ is the photon energy. Fig. 2 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ for Glasses 1 and 2 and the values of E_{opt} determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = \theta$ are 3.24 eV for Glass 1 and 3.95 eV for Glass 2, which are lower than the values reported for higher doping contents of Pr_6O_{11} in phosphate glasses [15] and may arise from the presence of copper in the glass. It is clear from Fig. 2 that the copper phosphate glass containing a very small quantity of Pr_6O_{11} (1 mol %) had an increased value of E_{opt} as expected. The high value of E_{opt} measured for praseodymium copper phosphate glass is almost certainly related to the high values of glass formation temperature which are generally higher than for copper phosphate glass, as shown in Table I.

The exponential dependence known as the Urbach rule [18] may be written in the form

$$\alpha(\omega) = A \exp \frac{\hbar\omega}{E_e} \qquad (2)$$

where A is a constant and E_e indicates the width of the band tails of the localized states. The relation is found to apply particularly at the lower values of $\alpha(\omega)$ for many non-crystalline materials. Tauc and Zanini [19] believe that it arises from electron transitions between

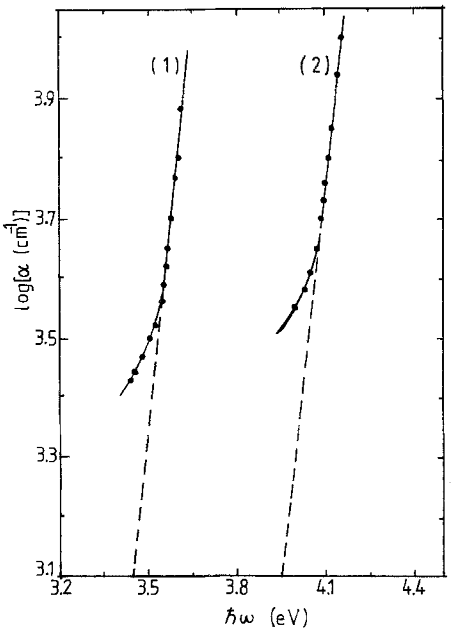

Figure 3 Absorption coefficient as a function of photon energy for Glasses 1 and 2 (Table 1).

localized states where the density of the localized states is exponentially dependent on energy. Dow and Redfield [20] suggested that it may arise from the random fluctuations of the internal fields associated with structural disorder in many amorphous solids. Davis and Mott [17] are uncertain about the precise explanation. One possible reason suggested by them is that the slope of the observed exponential edges obtained from Equation 2 are very much the same as in many semiconductors, and the values of E_e for a range of amorphous semiconductors lie between about 0.045 and 0.67 eV. For cerium phosphate glasses [11], the value of E_e was as low as 0.03 eV. Fig. 3 shows the variation of log α with photon energy and values of E_e in Equation 2 are calculated from the slopes of the straight lines and found to be 0.09 and 0.10 eV for Glasses 1 and 2, respectively, rather higher than the value of 0.06 eV reported for Pr_6O_{11}–P_2O_5 glasses [13]. This confirms that the bonding in rare-earth copper phosphate glass is different from that of other traditional phosphate glasses.

3.2. Infrared absorption

The infrared absorption spectra of unannealed glasses given in Table I are shown in Fig. 4. Table II summarizes the positions of the absorption bands obtained. Comparing the infrared spectrum of CuO–P_2O_5 (Glass 1) with those doped with Pr_6O_{11},it appears that all glasses show great similarity in their general shape of absorption spectra with the exception that for Glasses 5 and 6 new well-defined peaks appeared at 540 and 620 cm^{-1} instead of the broad peak at 500 to 650 cm^{-1}, and also at 960 cm^{-1} instead of the broad peak at 920 to 1150 cm^{-1}. It has been reported [21] that glasses doped with Pr_6O_{11} show absorption peaks between 260 and 655 cm^{-1}, and it seems that Pr_6O_{11} makes some contribution to the formation of the new peaks observed at 540 and 620 cm^{-1}. Shih and Su [22] have carried out an extensive study of the infrared spectra of binary phosphate glasses and they found the spectra of these glasses to be essentially the same. The bands observed in our study at 1300, 1100 and 750 to 780 cm^{-1} could be attributed to the P=O double bond, the P–O$^-$ stretching frequencies and the P–O–P ring frequency, respectively. The absorption band at 430 cm^{-1} which appeared in all glasses is known to be at the fundamental frequency of the $(PO_4)^{3-}$ group, which is in close agreement with the results of Hogarth and Moridi [23].

In our glasses P_2O_5 is constant so that the observed peaks could be due to $(PO_4)^{3-}$. Therefore the new peaks which appeared may be due to the replacement of copper ions by praseodymium ions in the glass. Smith and Cohen [7] reported that the spectra of rare-earth ions are characterized by absorption bands which are very sharp. The usual absorption band at the Cu–O main frequency is not detectable in the praseodymium–copper–phosphate glasses although it is fully developed in the simpler copper phosphate glass.

The absorption band which appeared at 3500 cm^{-1} is a weak band and is believed to be associated with a small amount of water trapped in the glasses during the experiment.

Samples annealed at 400° C for one hour did not show any great changes in the infrared spectra, as shown in Fig. 5. Fig. 6 shows the infrared absorption spectra for the glass sample annealed at 800° C for one hour. It is clear from this figure that all peaks became sharper and new peaks developed at 440, 580 and 740 cm^{-1}. These peaks subsequently increased in magnitude with increasing Pr_6O_{11} content in the copper phosphate glasses.

The appearance of these peaks suggests the possibility that some type of microstructural changes occurred in addition to the reduction of the Cu^{2+} content on annealing [23], probably leading to a less disordered glass network.

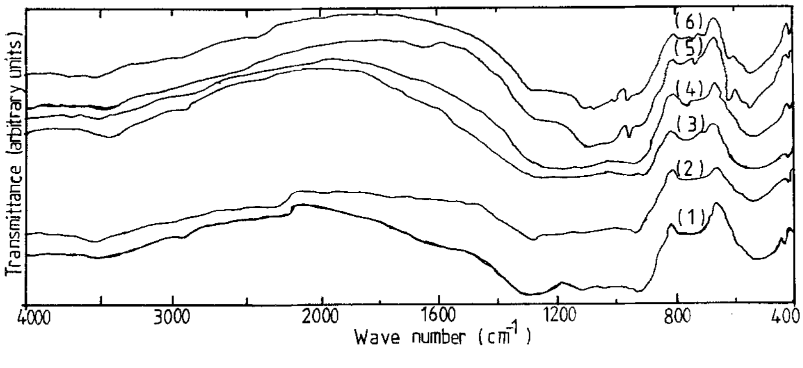

Figure 4 The infrared absorption spectra of unannealed samples of Glasses 1 to 6 (Table I).

TABLE II Characteristic infrared absorption band positions for praseodymium copper phosphate glasses

Glass No.	Band positions (cm^{-1})									
1	430	540	–	690	750–780	920	–	1100	1300	3500
2	430	540	–	690	750–780	920	–	1100	1300	3500
3	430	540	–	690	770	920	–	1100	1300	3500
4	430	540	–	690	770	920	–	1100	1300	3500
5	430	540	620	690	730, 770	920	960	1100	1300	3500
6	430	540	620	690	730, 770	920	960	1100	1300	3500

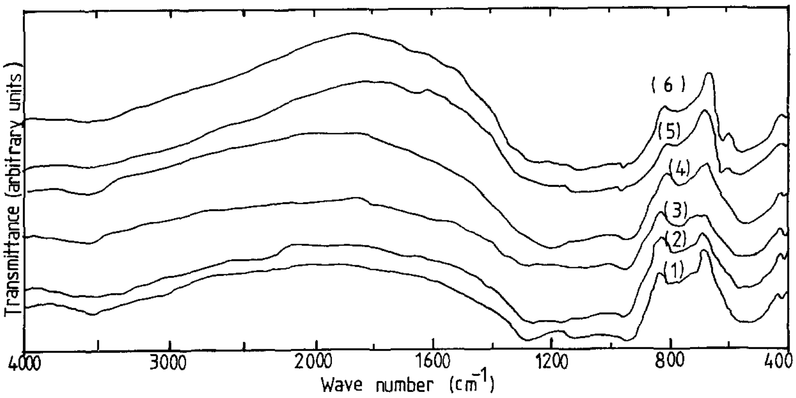

Figure 5 The infrared absorption spectra of Glasses 1 to 6 (Table I) taken after annealing at 400° C for 1 h.

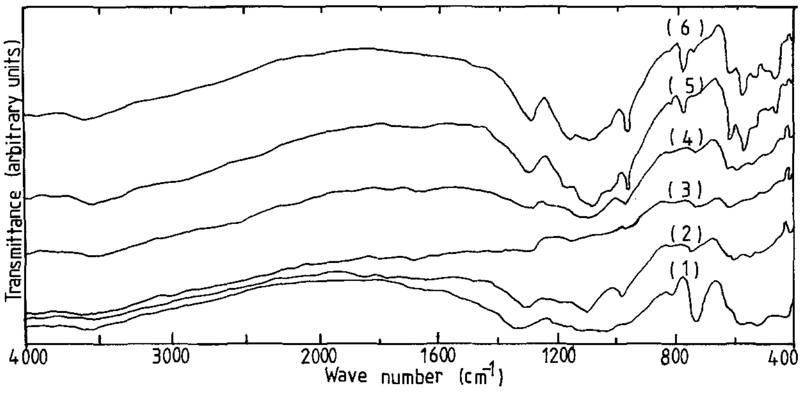

Figure 6 The infrared absorption spectra of Glasses 1 to 6 (Table I) taken after annealing at 800° C for 1 h.

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