JOURNAL OF MATERIALS SCIENCE 25 (1990) 2115–2117

The effects of the incorporation of lutetium oxide on the density and optical properties of copper phosphate glasses

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A range of phosphate glasses containing lutetium was prepared by the melt quenching technique. The densities of annealed and unannealed glass samples, molar volumes and the optical energy gap E_{opt} of thin blown films of the glasses were determined. It was found that the density and molar volume both increased with increase of Lu_2O_3 content. The E_{opt} values showed that they are not sensitive to the incorporation of small amounts of oxides.

1. Introduction

Many recent investigations have been carried out on copper phosphate glasses [1–5]. There is also a considerable literature available on the structures of glasses containing ions of the first transition series and on the role of the more metallic p-elements and their effects on the optical properties. Only relatively little work has been reported on copper phosphate glasses containing rare earth oxides.

The study of the optical absorption and particularly the absorption edge is a useful technique for the investigation of optically induced transitions and it may provide information about the band structure and energy gap in both crystalline and disordered semiconducting materials.

Direct and indirect transitions are the possible optical transitions which can occur at the fundamental absorption edge, of crystalline and non-crystalline materials. For the direct transition the momentum is conserved. In the case of an indirect transition the required change in momentum $\hbar\mathbf{k}$ (where $\mathbf{k}$ is the wave vector) needs co-operation from a phonon.

For many glassy and amorphous non-metallic materials the optical absorption edge can be divided into two regions. If $\alpha(\omega) < 10^4\,cm^{-1}$ the Urbach rule [6] is generally applicable, and is given by

$$\alpha(\omega) = A \exp\left(\frac{\hbar\omega}{E_e}\right) \quad (1)$$

where $\alpha(\omega)$ is the absorption coefficient, A is a constant, $\omega = 2\pi\nu$ is the angular frequency of the radiation and E_e the Urbach energy is identified with the widths of the tails of localized states in the bandgap.

If $\alpha(\omega) \geqslant 10^4\,cm^{-1}$, then an equation of the following form may be used to describe the optical absorption.

$$\alpha(\omega) = \frac{B[\hbar\omega - E_{opt}]^n}{\hbar\omega} \quad (2)$$

The above relation was proposed by Tauc *et al.* [7] with $n = 2$ and deduced in more general form by Davis and Mott [8].

B is a constant, E_{opt} is the optical energy gap of the material and the exponent n can assume the values 1, 2, 3, $\frac{1}{2}$, $\frac{3}{2}$ indicating the type of electron transition in $\mathbf{k}$-space. For our samples $n = 2$ and therefore we plot our results for the absorption edge region as $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$.

In this paper we wish to report the results of our density and optical absorption measurements in order to study the effect of the addition of the lutetium oxide to the glass.

2. Experimental technique

Glasses of composition expressed in mol % $P_2O_{5(65)}$–$CuO_{(35-x)}$–$Lu_2O_{3(x)}$ were prepared from the appropriate analytical grade component oxides where x was in the range 0–4 mol %. The chemicals were carefully weighed and mixed in an alumina crucible. In order to minimise a tendency to volatilization the mixtures were kept for 1 h in a furnace at 300° C, and then for 3 h at 1200° C in a melting furnace. During the 3-h melting period, the melt was stirred a few times with an alumina rod to improve the homogeneity.

The thin blown films of glasses which are necessary for optical measurement were prepared by blowing the molten glasses using an alumina tube having a fine bore. These unannealed thin glass films were kept under vacuum in separate small containers to avoid cracking and the absorption of moisture. The remainder of each molten glass was poured on to a clean stainless steel plate and cast into a disc shape typically 2 mm thick. Some of the glass samples were

TABLE I Some physical parameters of copper phosphate glasses containing lutetium

Glass sample	Composition (mol %)			E_{opt} (eV)	E_e (eV)
	P_2O_5	CuO	Lu_2O_3		
Lu (1)	65	34	1	3.72	0.25
Lu (1.5)	65	33.5	1.5	3.76	0.24
Lu (2)	65	33	2	3.80	0.26
Lu (3)	65	32	3	3.86	0.27
Lu (4)	65	31	4	3.92	0.28

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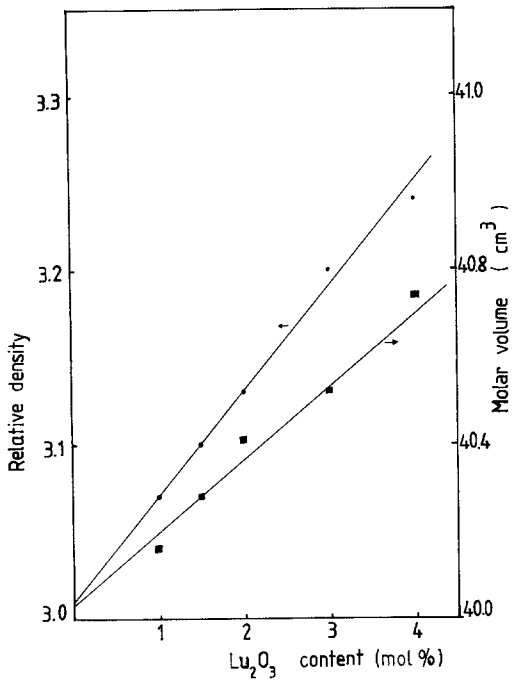

Figure 1 Relative density and molar volume of P_2O_5–CuO–Lu_2O_3 glasses as a function of Lu_2O_3 content.

annealed at 300 and 500° C. Specimens in the thickness range from 2 to 6 μm were obtained by blowing and measured using a Sigma comparator. The optical absorption properties of the glasses were obtained using a Perkin Elmer 402 UV Spectrophotometer, at room temperature, in the wavelength range of 300–700 nm.

3. Results and discussion

The values of density and molar volume for each glass system are given in Table I. Figure 1 shows the density and molar volume as a function of Lu_2O_3 content. The results for the increase of molar volume and density with increase of Lu_2O_3 content, are in agreement with the results reported earlier [10]. The increase of density with increase of Lu_2O_3 probably involves an increase in the density of non-bridging oxygen ions, which can cause the expansion of the network of the system. They tend to develop a more tightly-packed glass structure thereby compacting the electron clouds surrounding these oxygen ions owing to their high charges and co-ordination number.

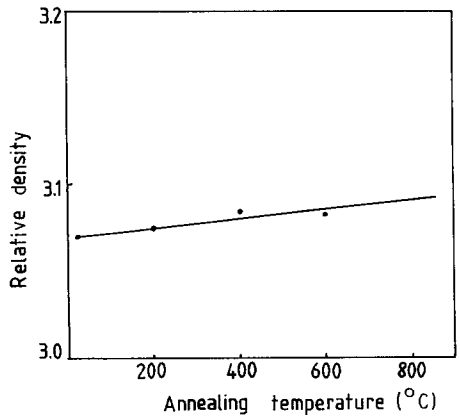

Figure 2 Relative density of $P_2O_{5(65)}$–$CuO_{(34)}$–$Lu_2O_{3(1)}$ glass as a function of annealing temperature.

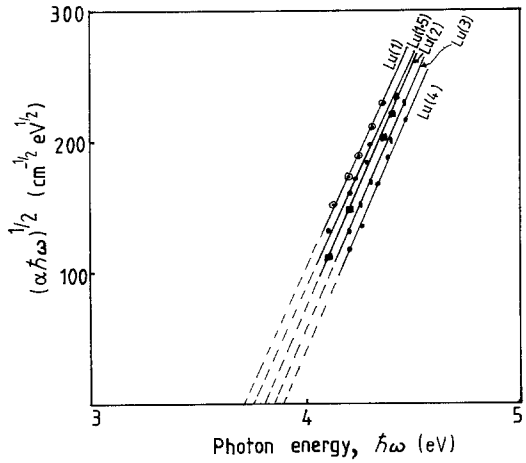

Figure 3 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for $P_2O_{5(65)}$–$CuO_{(35-x)}$–$Lu_2O_{3(x)}$.

Figure 2 shows a typical relationship between relative density and annealing temperature for glasses containing lutetium. The density increases slightly with increase in the annealing temperature. In this case the higher annealing temperatures reduce the average interatomic spacing and hence give a denser glass. These results are in agreement with the earlier results [11, 12].

A plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ is given in Fig. 3. The E_{opt} values were determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$ and lie within close limits between 3.72 and 3.92 $\pm$ 0.01 eV. These values also shift towards higher energies, as the Lu_2O_3 content increases. It is clear from Fig. 3 that the copper phosphate glass containing a very small quantity of Lu_2O_3 (1 mol %) had an increased value of E_{opt}. The values of E_{opt} increase with increasing Lu_2O_3 content as shown in Fig. 4. This may be due to a decrease in the band tailing arising from localization.

According to the results it is also clear that the E_{opt} values are not particularly sensitive to the incorporation of the rare earth oxide. This may be due to the

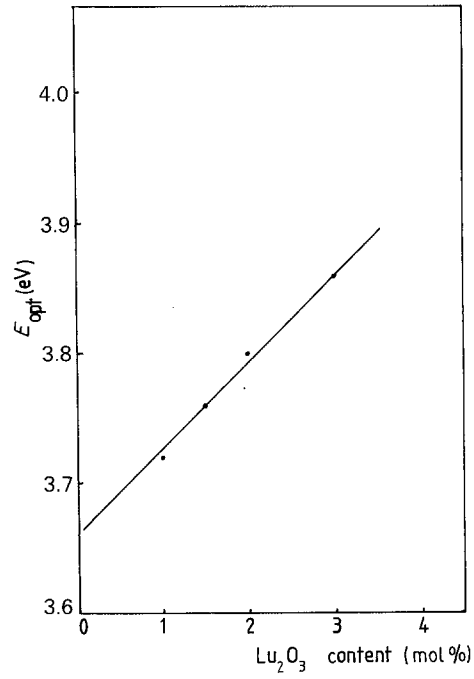

Figure 4 Optical energy gap as a function of Lu_2O_3 content for P_2O_5–CuO–Lu_2O_3 glasses.

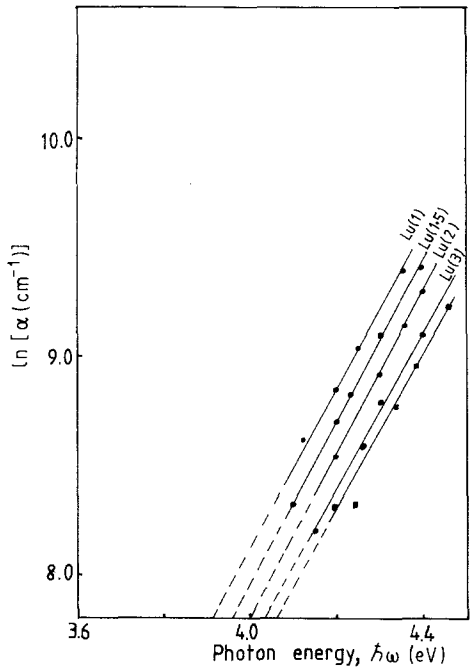

Figure 5 Absorption coefficient as a function of photon energy for copper phosphate glasses containing Lu_2O_3.

unusual electronic configuration in these materials. The 4f orbitals are very effectively shielded from interaction with external forces by the overlying $5s^2$ and $5p^6$ shells. We expect the states arising from the various $4f^n$ configurations to be only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in the various compounds.

Figure 5 shows the variations of ln α with photon energy and the values of E_e in Equation 1 are calculated from the slopes of the straight lines and are found to lie between 0.24 and 0.28 eV. Typical values of E_e for a range of amorphous semiconductors between 0.046 and 0.66 eV were reported by Davis and Mott [12].

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Received 20 January
and accepted 24 August 1989