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Composition-dependence of photoconduction band gap in cadmium zinc phosphate glasses

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Photoconduction in cadmium zinc phosphate glasses of various compositions has been measured in the spectral energy range 1.5 to 6.2 eV. With the P_2O_5 percentage remaining fixed at 60 mol %, CdO and ZnO contents have been varied between 0 and 40 mol %. Photocurrents start at about 3.85 eV and rise sharply above 4.5 eV. The optical band gap obtained by the extrapolation of the linear region of the photoresponse curve shows a slow decrease with an increase in the applied field. The optical band gap at a particular applied field decreases with increasing ZnO content. The field-dependence of the optical band gap may be explained in terms of an energy band scheme for non-crystalline solids. The composition-dependence may be due some structural changes in the glasses.

1. Introduction

The absorption coefficient shows an exponential behaviour in vanadium phosphate glasses with Ni, Cu, Co, ions [1], but tails in the absorption have been reported in cadmium phosphate glasses [2]. These tails were proposed to be due to the presence of impurities, structural defects or other kinds of inhomogeneities. The d.c. photoconductivity measurements follow the optical absorption edge which yields the mobility gap, E_g, only indirectly. This is based on the assumption that the density of states at the band edges is a linear function of energy in glassy materials and a narrow band of localized states exists near the centre of the band gap [3]. The optical band gap, E_{opt}, is greater than E_g in chalcogenide glasses [4]. Caslavska *et al.* [5] reported that the spectral response is dependent on the purity and composition in ($CdO-B_2O_5-SiO_2$) glasses. Minami *et al.* [6] suggested that photocurrent in oxychalcogenide glasses containing CdO, ZnO, is affected by the presence of a crystalline phase in these glasses and the gap of As_2Se_3-CdO glasses is 1.72 eV. Nazar *et al.* [7] showed that optical band gap obtained from photoconduction measurements decreases slowly with increasing applied fields in cadmium phosphate glass. The research described in the present paper is partly an extension of our recently reported work on the band gap of cadmium zinc phosphate glass [8]. The photoconduction band gap was found to be field-dependent. In the present investigations, d.c. photoconduction measurements have been made on ($CdO-ZnO-P_2O_5$) glasses of various compositions. The deduced values for band gap show a decrease with ZnO content and, for a particular composition, the band gap also decreases with an increase in the applied field.

2. Experimental techniques

Glass specimens used in the present investigations were prepared as 60 g specimens from the admixtures of analytical reagent grade CdO, ZnO and P_2O_5. The P_2O_5 percentage was kept constant at 60 mol% in various samples while the percentage of CdO and ZnO was changed between 0 and 40 mol%. After mixing the compositions, the alumina crucible was placed initially in a furnace at 500° C to minimize the tendency of P_2O_5 to evaporate and was then transferred to a crucilite

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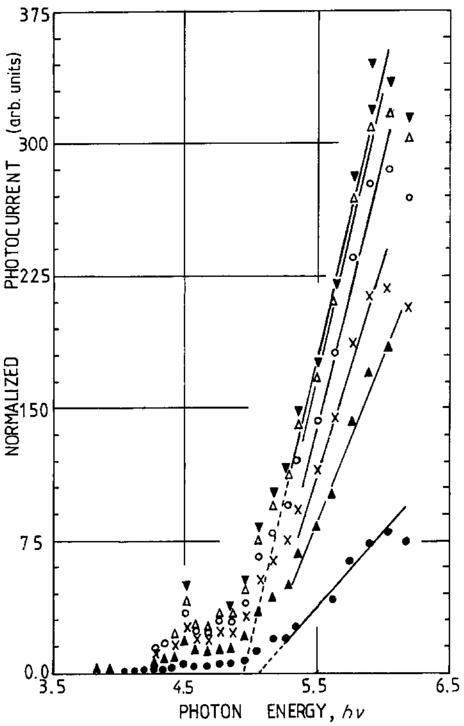

Figure 1 Spectral response curves, i.e. plots of normalized photocurrent (ΔI) against photon energy ($h\nu$) for a (30% CdO–10% ZnO–60% P_2O_5) glass specimen at different applied voltages. ●, 100 V; ▲, 200 V; X, 300 V; ○, 400 V; △, 500 V; ▼, 600 V.

furnace at a temperature of 1150 ± 10° C. The crucible was kept at 1150° C for 2 h and the melt was stirred from time to time to ensure homogeneity. The melt was cast into small discs about 4 cm diameter. These discs were then annealed at 500° C for 3 h. After preparation, the glasses were polished to optical quality. The specimens were then stored in vacuum. The X-ray diffraction patterns showed no discrete lines.

Semi-transparent electrodes of Al and thick Al guard rings were evaporated on one side while thick Al electrodes were deposited on the other side of the samples. All depositions were made in a vacuum better than 10^{-5} torr using Edwards 306 Coating Unit. The electrical contacts were made using silver conductivity paint. For photoconduction measurements, the samples were mounted on a Keithley 6104 test shield. The monochromatic output of a Bausch & Lomb Monochromator Model 5-UV-VIS was used to irradiate the samples. Measurements were made in the photon energy range 1.5 to 6.2 eV. The photocurrents were measured using Keithley 610 C and 616 electrometers. The photocurrents were normalized to unit radiant flux incident on the sample at any wavelength.

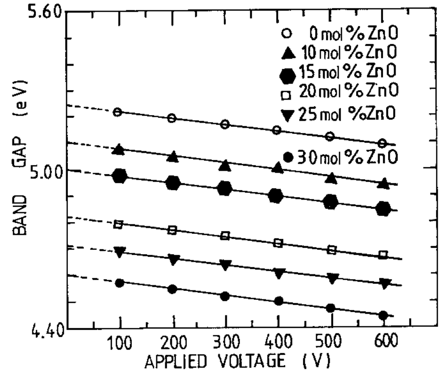

Figure 2 Field-dependence of photoconduction band gaps for various compositions of (CdO–ZnO–P_2O_5) glasses.

3. Experimental results and discussion

Fig. 1 shows the photoresponse curves for a (30 mol% CdO–10 mol% ZnO–60 mol% P_2O_5) glass specimen at different applied voltages. The extrapolations of the linear regions of these curves give the optical band gaps at the corresponding fields. The variation of the optical band gap with the applied field for different compositions is drawn in Fig. 2. The optical band gap, E_{photo}, shows a slow decrease with an increase in the applied field for any particular glass composition. The curves for the field-dependence of optical band gaps for various compositions are almost parallel straight lines having the same slope. At a particular applied field, the band gap decreases with an increase in the ZnO content (Fig. 3).

Conventional semiconductor concepts are

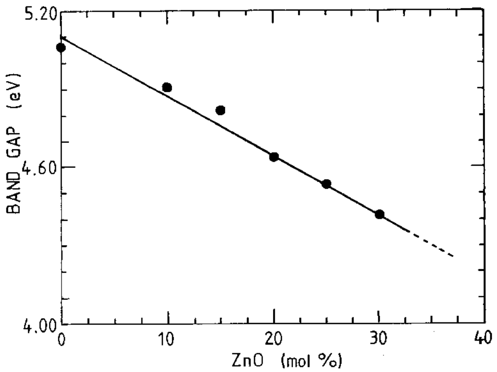

Figure 3 Photoconduction band gap variation with mol% ZnO content at 600 V.

employed to understand the electronic behaviour of glassy materials which have relatively large forbidden energy gaps [2, 3]. The spectral dependence of d.c. photoconductivity involves the use of illumination of the sample and sufficiently high electric fields to ensure that drifting carriers do not suffer much due to deep trapping during their transport. The region prior to the steep rise in photoconduction is nearly exponential, indicative of localized states in the band gap. The slow variation of the optical band gap, E_{photo}, with applied field may be due to the fact that as the field increases, more and more localized states deeper in energy may release their charge carriers under optical excitation. The amorphous materials normally contain a number of trapping levels and hence one gets such a "density of states tail" near the band edges [9, 10]. Similar phenomena have been observed in cadmium phosphate glass samples [7]. The increase in the ZnO content may lead to certain structural changes such that the photoconduction band gap decreases.

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