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Study of optical absorption edges in $MgO–P_2O_5$ glasses

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A series of glass specimens were prepared from the binary glasses ($MgO–P_2O_5$) and their densities and optical absorption edges in the ultraviolet–visible ranges were measured. It was found that the fundamental absorption edge is a function of glass composition and at lower values of the absorption coefficients $\alpha(\omega)$ it follows the so-called Urbach edge. From this edge the value of E_e, the width of the tail of localized states in the bandgap, did not vary significantly with glass composition. In the higher energy region, the behaviour of $\alpha(\omega)$ suggests that there are two different transition energies for electrons, namely direct allowed transitions and non-direct transitions in k space. From these results some information about the band structure of $MgO–P_2O_5$ glass is presented.

1. Introduction

The optical absorption edges in amorphous non-metallic materials are less abrupt and well defined than for materials having the corresponding crystalline form. Nevertheless those edges have similar shapes in many amorphous materials in spite of the distinct differences of the chemical bonds and co-ordinations.

The exponential dependence of the absorption coefficient $\alpha(\omega)$, at angular frequency of radiation ω on photon energy $\hbar\omega$ is found to hold over several decades of an amorphous material and takes the form

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{E_e}\right) \qquad (1)$$

where α_0 is a constant, $\hbar$ the reduced Planck constant and E_e an energy which is interpreted as the width of the tails of localized states in the normally forbidden band gap, which are associated with the amorphous nature. Relation 1 was first proposed by Urbach [1] to describe the absorption edge in alkali halide crystals at high absorption levels when $\alpha(\omega) \geqslant 10^4\ \mathrm{cm}^{-1}$. This relation has been found to hold for many amorphous or glassy materials at lower ranges of the absorption edge, while for higher photon energy (higher $\alpha(\omega)$) the absorption data follow a power law

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

and to yield values of the optical energy gap, E_{opt}. B is a constant and r an index which can assume values of 1, 2, 3, $\frac{1}{2}$ and $\frac{3}{2}$ depending on the nature of the interband electronic transitions.

Equation 2 with $r = 2$ was first proposed by Tauc *et al.* [2] to represent the data of amorphous germanium films and later Davis and Mott [3] gave this general form. Equation 2 with $r = 1$ was found to fit the optical data in amorphous selenium and $In_{30}Se_{70}$ films [4–6] whereas for $r = 2$, it has agreed well for most thin amorphous oxide films [7–9] and for chalcogenide and oxide glasses [10–12]. Other values of the index have been found appropriate for particular amorphous materials, for example $r = \frac{3}{2}$ is the best index for amorphous vanadium pentoxide films and vanadate glasses [13, 14] and Vorlíček *et al.* [15] show that $r = 3$ provides a much better fit for optical data to both amorphous germanium and silicon than $r = 2$. The data on indium tin oxide films agreed with Equation 2 for two values: $r = 3$ and $\frac{1}{2}$ indicating two electronic transition mechanisms.

As a part of a programme of work on $MgO–P_2O_5$ glasses, we have devoted this paper to the preparation of different compositions of this glass as well as to the study of their density, structure and optical absorption in the ultraviolet and visible ranges.

2. Experimental procedure

2.1. Glass preparation

The glass samples were prepared from laboratory reagent grades of analar MgO and P_2O_5 oxides, using alumina crucibles. The reagents were mixed and heated in an electric furnace for 1 h at 400 °C; this allowed the phosphate to decompose and react with other batch constituents before melting would ordinarily occur. Then, the crucible with the mixture was transferred to an electric furnace kept at 1200 °C. After the mixture had melted, it was kept for 2 h and stirred by an alumina rod every 20 min to ensure homogeneity and proper mixing. Each melt was cast into two mild-steel split moulds heated to 200 °C, to form glass rods ~ 1 cm long by 1.6 cm diameter. After casting,

TABLE I Derived characteristic energies for MgO–P_2O_5 glasses

MgO Composition (mol %)	E_{opt} (eV) N-D T[a]	E_{opt} (eV) DAT[b]	The constant B ($cm^{-1}eV^{-1}$)	Slope of Urbach plot (eV^{-1})	The constant E_p (eV)
20	3.71_2	4.60	14.33	2.77	0.36
30	3.79_0	4.31	42.46	3.75	0.27
40	3.70_5	4.52	15.34	2.50	0.40
45	3.62_0	4.30	23.41	2.60	0.38
53	3.80	4.28	44.44	3.75	0.27
60	3.48	3.92	39.06	4.06	0.25

[a] Non-direct transitions, Equation 2 with $r = 2$.

[b] Direct allowed transition, Equation 2 with $r = \frac{1}{2}$.

each glass was immediately transferred to an annealing furnace, held at 400 °C for 1 h. After this time the furnace was switched off and the glasses were allowed to cool down to room temperature at an initial cooling rate of $\sim 3\,°C\,min^{-1}$.

2.2. Structural, density and optical measurements

X-ray diffraction measurements using a Debye–Scherrer camera, were made and showed only the diffuse diffraction rings characteristic of amorphous materials and gave no evidence of crystallinity.

The densities were measured by a simple displacement method using toluene as the immersion liquid. Repeated density measurements agreed to within ± 0.05%. Even very thick glass specimens were transparent to light and thus a range of $d = 0.54$ to 0.65 cm thicknesses was chosen.

The optical absorption data were measured in the wavelength range ($\lambda = 190$ to 850 nm) using a Perkin–Elmer Spectrophotometer Model 402. The absorption coefficients $\alpha(\lambda)$ were calculated from the absorbance, A using the following simple formula

$$\alpha(\lambda) = 2.303\frac{A}{d} \qquad (3)$$

These measurements were made at room temperature.

3. Results and discussions

The compositions of the samples used are listed in Table I. The density measurements on these glasses are shown in Fig. 1. In the range 20 to 35% MgO, the density value reduced to a value of 2.414 and rose to 2.425 for 40% composition. From 40% the density decreases again to a value of 2.402 for 53% and then starts to increase smoothly reaching 2.517 for 60% MgO constituent. A comparison of the density values obtained in the present work with those measured previously by Elyard *et al.* (1959) [17] is of interest and has been included in Fig. 1. Although the similarity between those data is qualitatively good nevertheless it is seen that the present values are significantly lower than those of Elyard *et al.* One possible reason for this difference arises from the fact that different raw materials were used in preparing the two series of glasses. A second possible cause is that they used "Pythagoras" crucibles for melting the glasses as opposed to our alumina crucible and thus it could be responsible for part of the difference in density of the two series of glasses. The variation of density values, as well as other physical properties with composition may be used to obtain some structural information, but because of the lack of such complete data we will not consider this possibility here.

Fig. 2 shows the optical absorption spectra at different compositions of MgO–P_2O_5 glasses. It is clear that there is no sharp absorption edge and this is a characteristic of the glassy state. As can be seen from this figure, the absorption edge moves to long wavelengths as the percentage of MgO in the glass increased. The values of absorption coefficient $\alpha(\omega)$ estimated using Equation 1 are shown on the Urbach plot, in Fig. 3 for various MgO–P_2O_5 glasses. The values of E_e in Equation 1 are calculated from the slopes of the linear portions of these curves and listed in Table I.

The origin of this exponential dependence of $\alpha(\omega)$ on $\hbar\omega$ in both crystalline and amorphous semiconductors is not clearly known. Dow and Redfield [18] suggested it may arise from the random fluctuations of the internal fields associated with structural disorder in many amorphous solids. Tauc [19] believes that it

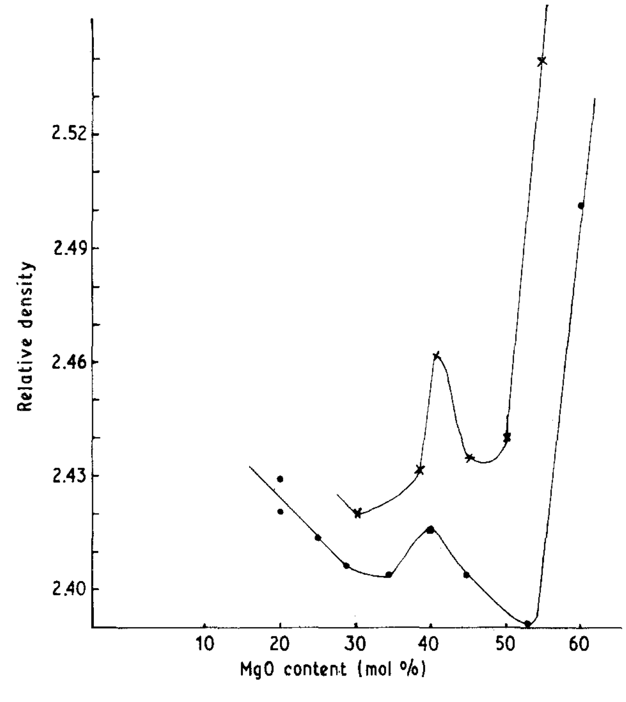

Figure 1 Density measurements of MgO–P_2O_5 glasses.

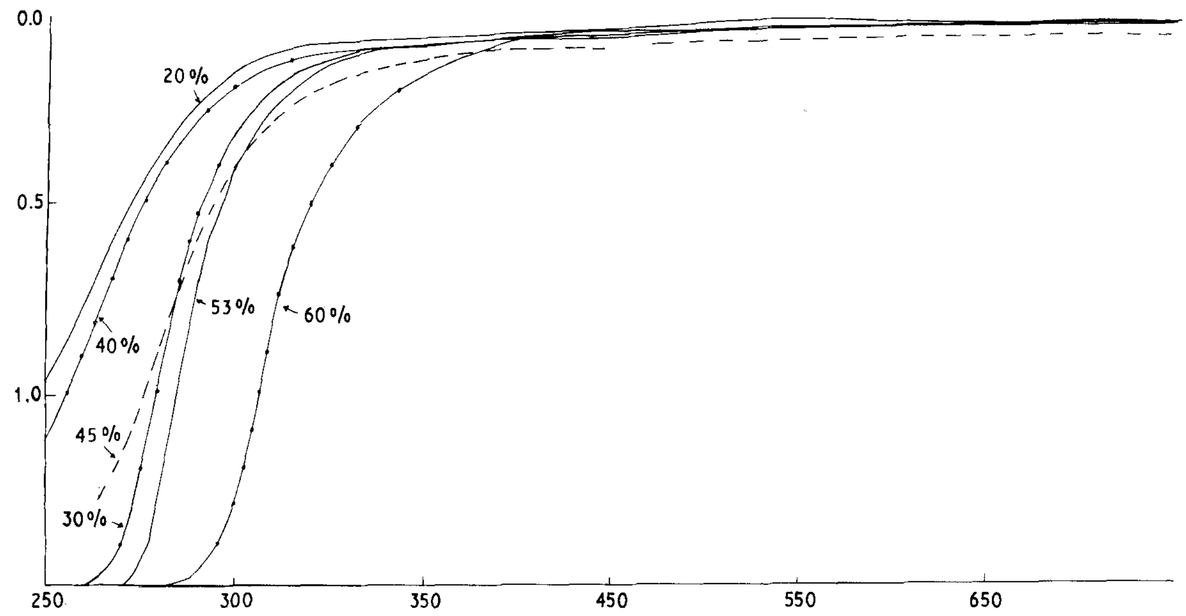

Figure 2 The optical absorbance of different compositions of $MgO-P_2O_5$ glasses.

arises from electronic transitions between localized states in the band edge tails the density of which is assumed to fall off exponentially with energy. Davis and Mott [3] argue to the contrary. One possible reason suggested by them is that the slopes of the measured exponential edges obtained from Equation 1 are very much the same in many semiconductors and the values of E_e for a range of amorphous semiconductors [10] are reported to lie between 0.045 and 0.67 eV. For molybdenum phosphate glasses [20], the value of E_e was 0.16 eV and for copper–calcium–phosphate glasses [11] as high as 0.66 to 1.06 eV depending on the copper concentration. Many other theories have also been given elsewhere [21–27]. Whatever the details of the mechanism needed to interpret the Urbach edge, it appears from the available data here that an exponential dependence of $\alpha(\omega)$ on $\hbar\omega$ is observed suggesting that the Urbach rule is obeyed. The values of E_e obtained in this work are larger than those observed [28, 29] in the range 0.05 to 0.08 eV for various glasses below and at room temperature, and as they vary slightly with composition, a model based on electronic transitions between localized states is not preferable. Measurements at temperatures far below and above room temperature are necessary to give a reliable decision about whether the exponential tail follows the Urbach rule or not.

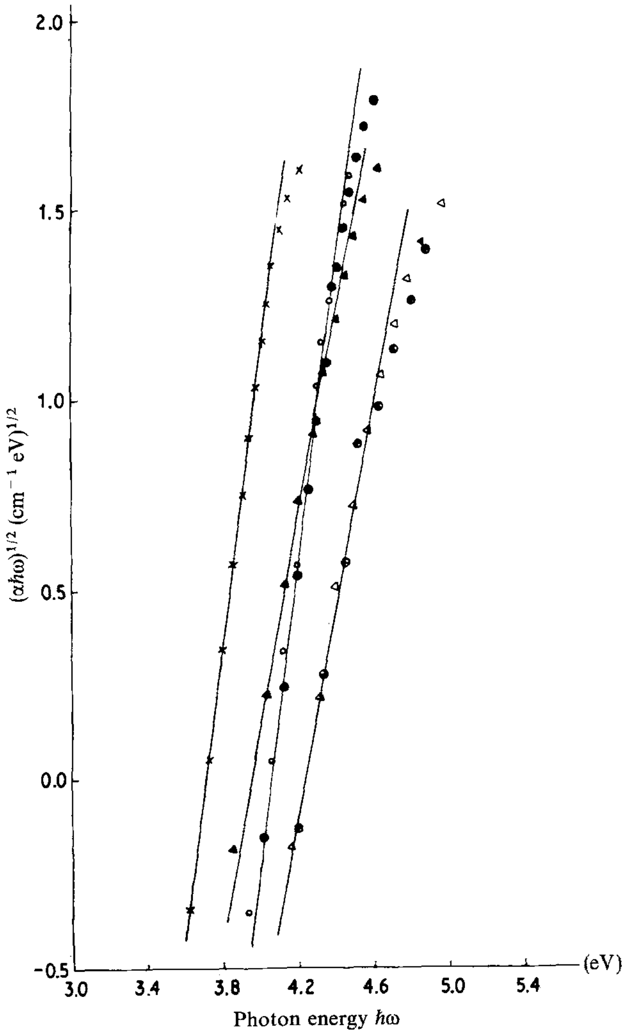

Figure 3 Urbach plots of $MgO-P_2O_5$ glasses. (● 30 mol %, △ 40 mol %, ⊗ 20 mol %, ▲ 45 mol %, ○ 53 mol %, × 60 mol %)

The optical absorption data of 60 mol % MgO has been presented in Fig. 4 in accordance with Equation 2 and possible values of r. It seems that the index $r = \frac{1}{2}$ fits the experimental data especially at the higher values of $\alpha(\omega)$ indicating that direct allowed transitions are involved. Fig. 5 represents the absorption data of other glass compositions in accordance with Equation 2 taking $r = \frac{1}{2}$ and the extrapolated values of E_{opt} are listed in Table I. However, in Fig. 6 we have also plotted those data with $r = 2$ assuming non-direct transitions in k space. The results are of linear form in the high absorption region since the matrix element for optical transition remains constant. The values of the extrapolated E_{opt} and B obtained from the slopes of the derived curves are given in Table I. Tauc and colleagues [2] derived the quadratic equation assuming the electronic density-of-states to be a parabolic function of energy and consequently E_{opt} may represent an extrapolated gap rather than a real

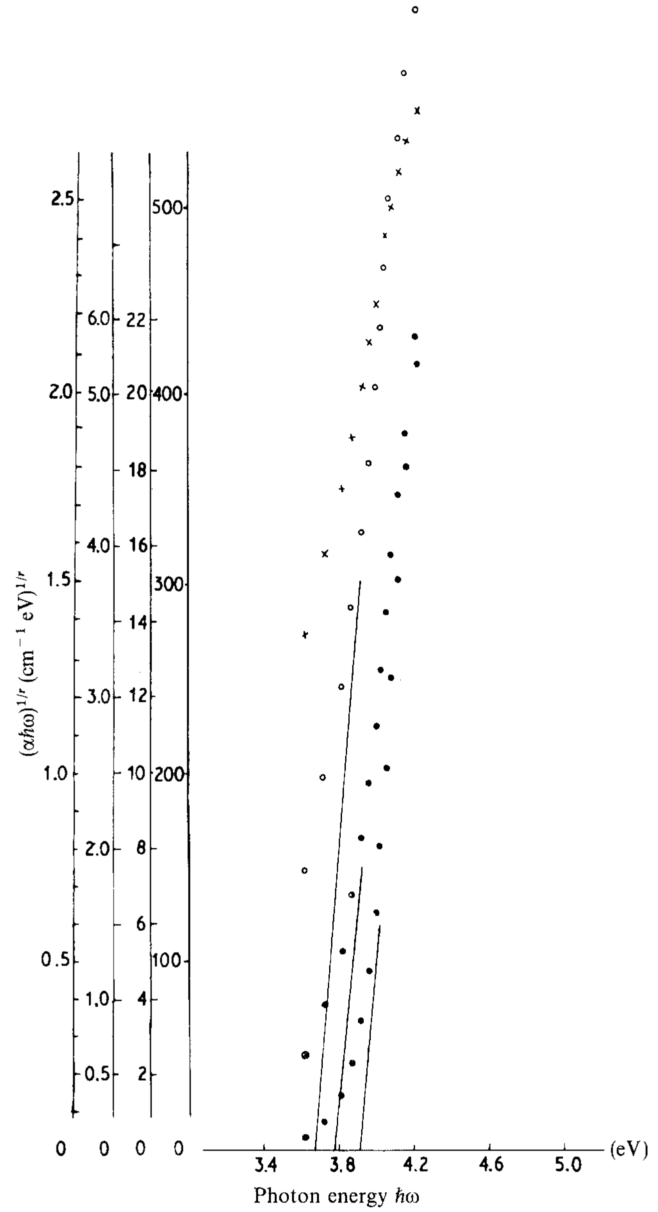

Figure 4 Optical data of 60 mol % MgO glass plotted in accordance with Equation 2 and possible values of r.

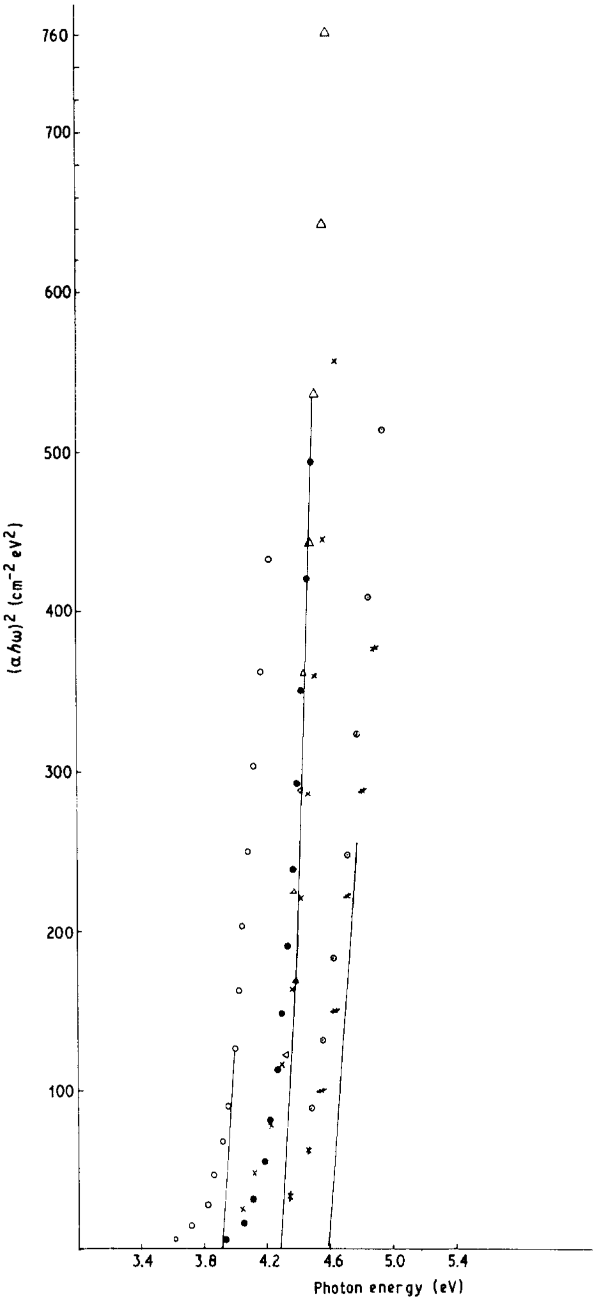

Figure 5 The optical data of MgO–P_2O_5 glasses in accordance with Equation 2 and $r = \frac{1}{2}$. (○ 60 mol %, ● 53 mol %, × 45 mol %, ⊙ 40 mol %, △ 30 mol %, * 20 mol %)

zero in the density-of-states curve. Davis and Mott [3] obtained Equation 2 with $r = 2$ assuming a linear dependence of the electronic density-of-states on $\hbar\omega$, and thus they have interpreted E_{opt} as corresponding to transitions from localized states at the top of the valence band into the delocalized states in the conduction band or vice versa. For both Figs 5 and 6 there is a general shift in the edge to higher $\hbar\omega$ and a consequent increase in the value of E_{opt} with the addition of P_2O_5.

As we can deduce from Figs 5 and 6 and for each glass composition, there are two optical transitions in k space. Assuming that the lowest minimum of the conduction band and the highest maximum of the valence band lie in different regions of k space, the direct allowed transitions may occur as in Fig. 7 and the observed non-direct transitions may be associated with a transition from the top of the valence band to the bottom of the conduction band.

To conclude, these results are reasonably well understood, at least qualitatively, with reference to the density-of-states diagram expected for such amorphous materials. Essentially, the mobility gap and the optical energy gap are related to the point of inflection in the curve of $N(E)$ against E, the electron energy, which determines when band tailing into localized states becomes significant. Hence, our data are consistent with the interpretation that both E_e and E_{opt} are controlled by the amount of disorder in the network and need not change in the same sense.

The MgO–P_2O_5 glass is distinguished by its good optical transmission in the visible region. The transparency of this glass is hence comparable with well known fused silica (cf. [30]) and could be used in solar energy applications. Whatever the type of optical transitions, it is noted that the values of E_{opt} are high as stated in Table I.

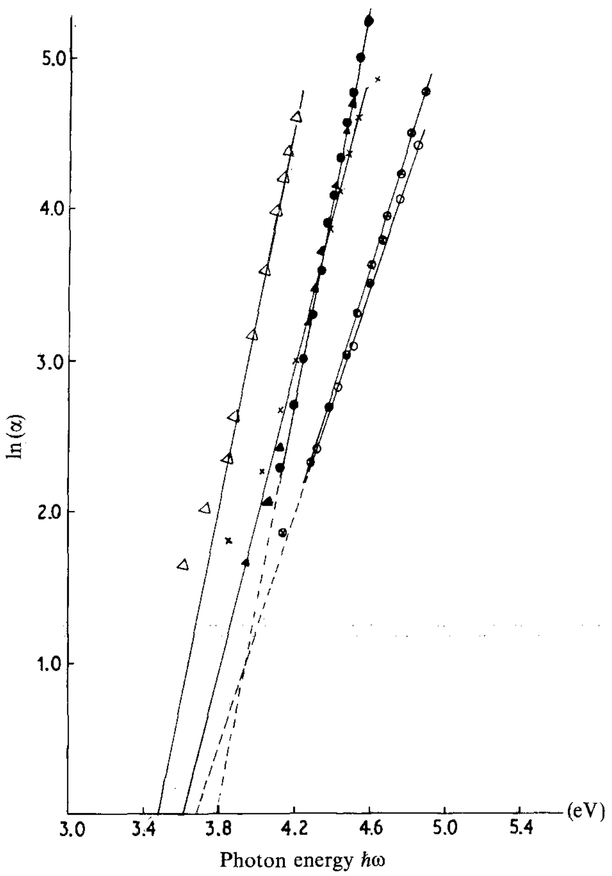

Figure 6 The optical absorption data of MgO–P_2O_5 glasses assuming a non-direct transition is involved. (△ 60 mol %, × 45 mol %, ○ 20 mol %, ⊗ 40 mol %, ● 30 mol %, ▲ 53 mol %.)

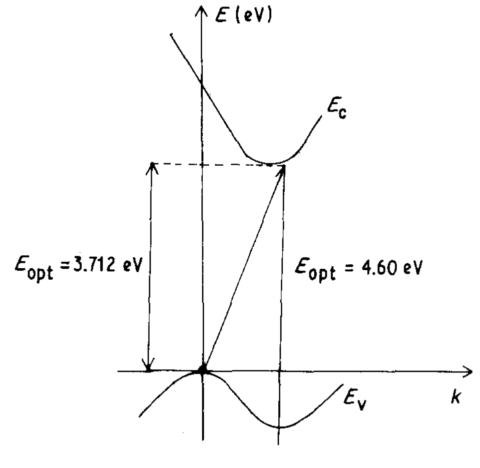

Figure 7 Suggested energy band diagram (electron energy *E* against wave vector *k*) for magnesium phosphate glass.

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