

THE OPTICAL ABSORPTION OF THE $[TeO_{2(100-x)} - MoO_{3(x)}]$ SEMICONDUCTOR GLASS SYSTEM

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Abstract:

The optical absorption coefficient $\alpha(w)$ of binary glasses $[TeO_{2(100-x)} - MoO_3(x)]$ as a function of MoO₃ content (x) [0<x<55 wt%] were studied. From these measurements, it is found that the fundamental absorption edge is a function of glass composition and the optical absorption is due to non-direct transitions. At lower values of the absorption coefficients $\alpha(w) > 10^4 \text{ cm}^{-1}$ follows the Urbach rule and the value of the width of the tails of localized states in the band gap (ΔE_t) did not vary significantly with glass compositions. It is also noticed that the optical energy gap (E_{opt}) decreases with the increase of the transition metal oxide (TMO) concentration. This is due to d-d transitions and the deep donor levels above the valance band, which arises from the non-bridging oxygen ions (NBOI)

Introduction

Oxide glasses containing transition metal ions were first reported to have semiconducting properties in 1954 [Denton et al (1954)]. The general condition for semiconducting behavior is that the transition metal ion should be capable of existing in more than one valency state so that the conduction occurs by the movement of charge carriers from the lower to the higher valency state. Most the work on the electrical properties of semi conducting oxide glasses is based on theories of Mott (1968), Austin, and Mott (1969).

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Studying optical absorption in particular the shape and shift of the absorption edge, is an extremely useful technique for understanding the basic mechanism of optically induced transitions in crystalline and non crystalline materials as well as providing information about the band structure [Hosseini etal (1994)].

$$\alpha(\omega) = \alpha_0 \exp\left\{\frac{\sigma(\hbar\omega - \Delta E_g)}{kT}\right\} \text{----- (1)}$$

The fundamental absorption edge in such solids is less steep and well defined than in crystalline semiconductor. Two such approaches have been given in literature one by Urbach (1953) and another by Tauc et al (1966) and by Davis and Mott (1970). Urbach assumed that the absorption coefficient $\alpha(\omega)$ at angular frequency of radiation (ω) in the range 1 cm^{-1} - 10^4 cm^{-1} is an exponential function of photon energy $\hbar\omega$ of the following form:

Where α_0 is a constant σ/kT gives a measure of the steepness of the absorption edge and some time interpreted as the width of the tail of localized states in the band gap.

The quantity σ is of the form

$$\sigma = \sigma_0 \frac{2kT \tanh \frac{\hbar\omega_p}{2kT}}{\hbar\omega} \text{----- (2)}$$

Where σ_0 is a constant and $\hbar\omega_p$ is the phonon energy involved in the optical transition. Equation (1) was first proposed by Urbach (1953) to describe the absorption edge in crystalline alkali halides and its practical use was reviewed by Kurik (1971). Al-Ani etal (1984) reported optical data vs temperature dependence using eqn.(2) for silicon oxide thin films

Tauc et al (1966) and Davis and Mott (1970) gave an equation more generally and derived independently, for the absorption

coefficient $d(\omega)$ in the range $\alpha(\omega) > 10^4 \text{ cm}^{-1}$ for an amorphous semiconductor.

$$\alpha(\omega) = B \frac{(h\omega - E_{opt})^r}{h\omega} \quad (3)$$

Where r is an index determined by the nature of the electronic transition during the absorption process, which can assume values 1,2,3,1/2 and 3/2. B is a constant and E_{opt} is the optical energy gap of the semiconductor. Equation (3) with $r=1$ was found to fit the optical data in amorphous selenium, In_2O_3 and Se_2O films [Davis (1970) , Al-Ani etal (1985)] where as for $r=2$, it has a greed well for most thin amorphous oxide film [Hogarth and Nadeem (1981)] and for chalcogenide and oxide glasses [Mott and Davis (1979) , Al-Ani etal (1985)] . Other values of the index have been found appropriate for particular amorphous materials for example $r=3/2$ is the best index for amorphous vanadium pentoxide films and vanadate glasses [Anderson and Compton (1970)]. Vorlicek etal (1981) showed that $r=3$ provides a good fit for optical data to both amorphous germanium and silicon much better than $r=2$. A recent evaluation of the available models and theories of the optical absorption edge in semiconductor materials has been reported by Ibrahim and Al-Ani (1994).

As apart of our work on $[\text{TeO}_{2(100-X)} - \text{MoO}_3(X)]$ glasses we report different composition of this glass system and study of its optical absorption in the range($\lambda=190\text{nm} -2500\text{nm}$)

Experimental

The glasses under study have been prepared by mixing analar TeO_2 and MoO_3 in specified proportions, using alumina crucibles. The mixtures were heated in an electrical furnace for one

hour at 400 C to prevent tendency to volatilization. Then the crucible with the mixture transferred to an electric furnace held at temperature of 800-850 C depending on the ratio of MoO₃ for one hour. The melt was quenched in a graphite mold, which was preheated to 300 C in air. The mold was transferred to another furnace for annealing at 300 C for 1 hour then switched off to cool down to room temperature. The prepared glasses were examined by X-ray diffraction for distinguishing glassy states using X-ray diffractometer.

The absorption measurements in the ultra - violet, visible and near i r regions were carried out at room temperature in the wavelength range ($\lambda=200-2500$ nm) using a Perkin - Elmer $\lambda-9$ spectrophotometer

The absorption coefficient $\alpha(\omega)$ can be calculated from the relation

Where A is the absorbance, d is the thickness of the sample and R is the reflectance

$$\alpha(\omega) = \frac{2.303A + 2\ln(1 - R)}{d} \quad \text{---} \quad (4)$$

Results and discussion

The recorded absorption spectra for all glass compositions studied have been shown in figure 1. It is noted that there is no sharp absorption edge, and this is a characteristic of the glassy state. Further, the fundamental edge becomes less sharp and shifted towards higher wavelength as the MoO₃ percentage increases in the glasses. These results suggested the conduction mechanism is due to the transition between metal ions (TMI).

In order to examine equation (3) and evaluate the exponent (r), graphs of $(\alpha h\nu)^{1/r}$ vs. photon energy ($h\nu$) were plotted with different values of r : [$r=1,2,3,3/2,1/2$]. It was found that $r=2$ give the best fit in the higher absorption region assuming non direct transition in k-space are involved which seems to agree with most oxide glasses [Davis and Mott (1970), Al-Ani et al (1985)].

Figure (2) depicts the variation of $(\alpha h\nu)^{1/2}$ with $(h\nu)$ for all samples , the value of E_{opt} is obtained by extrapolating the linear portion to $(\alpha h\nu)^{1/2}=0$ in the same figure on to the $(h\nu)$ axis .

The optical energy gap (E_{opt}) is found to decrease as the MoO_3 percentage in the glass is increased (fig.4) . It has been suggested that the broad absorption tail and the optical band gap energy may be related to the high concentration of molybdenum ions in the glass system [Dow and Redfield(1972)] . Thus electronic excitations of the d-d type may contribute to this absorption. In addition, as Stevels suggested [Stevens (1953)] the increase in the concentration of non bridging oxygen ion [which is follow the increase in MoO_3] with increasing MoO_3 content would introduce energy levels higher than those of bridging ions resulting a decrease in E_{opt} and this is confirmed by Anderson (1973). The E_{opt} is found to be decreased in similar systems such as $TcO_2.WO_3$ glasses as the W ions increases [Shaltowut etal (1996)].

The value of B in equation (3) can be obtained from the gradient of the curve of figure(2) and are also given in Table 1.

Figure (3) shows the variation of B with concentrations of MoO_3 .

Table I : Values of E_{opt} , ΔE_t and the constant B versus the variations of TMO.

Sample No.	MoO_3 conct. (wt%)	E_{opt} (eV)	ΔE_t (eV)	B ($eV^{-1} .cm^{-1}$)
Ho	-	2.79	0.13	84.89
H2	10	2.25	0.188	58.369
H3	20	1.963	0.207	48.44
H4	30	1.52	0.1125	74.47
H5	40	1.125	0.118	82.26
H6	50	0.8	0.125	98.011
H7	55	0.725	0.122	100.50

Figure(5) shows that the graphs of $\ln\alpha(w)$ vs. (hw) are linear and follow the equation:

$$\alpha(w) = \alpha_0 \exp \frac{hw}{\Delta E_t} \quad (5)$$

where α_0 is a constant and ΔE_t indicates the width of the band tails of the localized states. There have been a number of different interpretations of the origin of the exponential dependence of α on photon energy. One based on the presence of strong internal electric field due to the structural disorder [Dow and Redfield (1972)] whilst Tauc and Zanan (1977) believed that it arises from electronic transitions between localized states in the band edge tails which is assumed to fall off exponentially with energy. Davis and Mott (1970) rejected the latter interpretation because the slopes of the exponential absorption edges are much the same for many crystalline and non-crystalline materials. The width of the band tails ΔE_t have been reported to lie between 0.045 eV and 0.67 eV [Mott and Davis (1979)]. For our glasses ΔE_t have a value between 0.112 eV and 0.207 eV as shown in Table 1 while the value of ΔE_t for Molybdenum phosphate glasses was 0.16 eV [Austin et al (1970)]. The value of ΔE_t for pure TeO_2 as a blown thin film with thickness 2000 nm is 0.166 (eV) [Al-Ani and Hogarth (1985)] where its value for $\text{TeO}_2\text{-WO}_3$ glasses lies between 0.103 and 0.12 eV for concentration 31.5 mol% [Shaltowut et al (1996)].

Conclusion:

From the previous discussion it is concluded that the optical energy gap (E_{opt}) decreases with the increase of (TMI) of the molybdenum and there are two mechanisms of optical absorption , first is due to the d-d type transport of the electrons in the valance band and the second is the charge transport of non bridge oxygen ions which make a donor level higher than the valance band , which result as smaller E_{opt} and shift the absorption edges towarded a longer wavelength.

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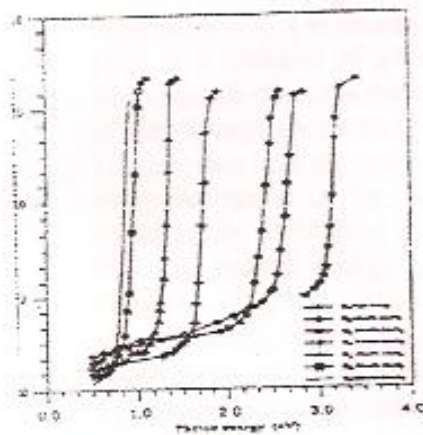


Fig (1): The variation of $\alpha(\omega)$ as a function of photon energy for the glass samples

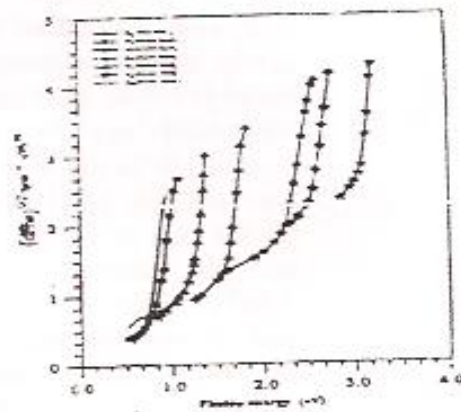


Fig (2): The variation of $(\alpha(\omega))^{1/2}$ as a function of photon energy for the glass samples

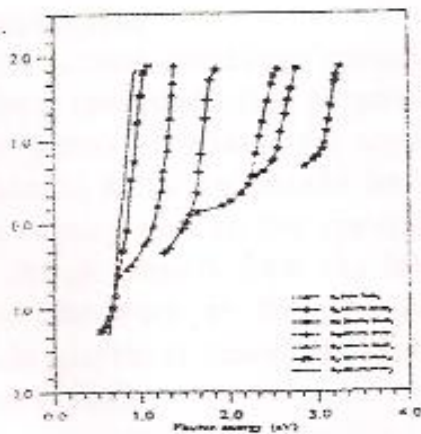


Fig (3): The variation of $\log \alpha$ as a function of photon energy for the glass samples

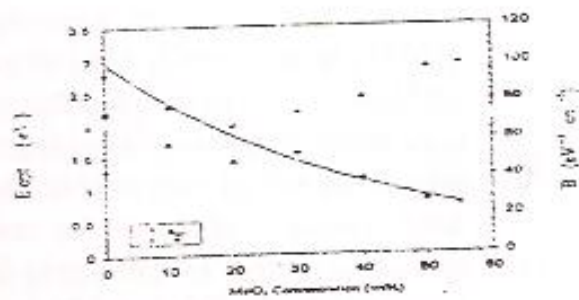


Fig (4): The variation of E_g and the constant B versus the MoO_3 concentration