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A study of optical absorption in tellurite and tungsten–tellurite glasses

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A series of glass specimens was prepared from TeO_2 glass and from the binary tungsten tellurite glasses (TeO_2–WO_3) and their densities, optical absorption edges and infrared absorption spectra were measured. It was found that the fundamental absorption edge is a function of glass composition, and absorption in this region is due to indirect electronic transitions in k-space. The main infrared absorption bands in the TeO_2–WO_3 glasses are related to those characteristics of the TeO_2 component.

1. Introduction

The optical properties of non-metallic solids may be described by two constants, the index of refraction n, and the extinction coefficient, k, which is related to the optical absorption coefficient, $\alpha(\omega)$, at angular frequency of radiation ω by the equation:

$$\alpha(\omega) = 4\pi k/\lambda \qquad (1)$$

where $\omega = 2\pi\nu$ and λ is the wavelength of the radiation in vacuum. In amorphous as in crystalline materials some useful information can be deduced both from absorption edge and infrared absorption spectral measurements even though in such materials the edge is less sharp and the absorption peaks are broader than is normally the case for crystals. For many amorphous materials an exponential dependence of absorption coefficient on photon energy $\hbar\omega$ is found to hold over several decades and takes the form

$$\alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar\omega}{E_e}\right) \qquad (2)$$

where α_0 is a constant, $\hbar$ is the reduced Planck constant and E_e is an energy which is sometimes interpreted as the width of the tail of localized states in the normally forbidden band gap, which are associated with the amorphous nature of the materials. The relation was first proposed by Urbach [1] to describe the absorption edge in alkali halide crystals at high absorption levels when $\alpha(\omega) \geqslant 10^4\ \text{cm}^{-1}$. The relation has been found to hold for many amorphous or glassy materials at the lower ranges of the absorption edge, while for higher absorption values a relationship proposed by Tauc *et al.* [2] and deduced in more general form by Davis and Mott [3]

$$\alpha(\omega) = \frac{B}{\hbar\omega}(\hbar\omega - E_{\text{opt}})^r \qquad (3)$$

is found to describe the experimental data and to yield values of the optical energy gap, E_{opt}. B is a constant and r an index which can assume values of 2, 3, $\frac{1}{2}$ and $\frac{3}{2}$ depending on the nature of the electronic transitions responsible for the absorption. For many glasses [4, 5] and amorphous materials, Equation 3 with $r = 2$ is found to represent the experimental results and this case applies to indirect transitions in such materials when the electron wave vector **k** is no longer a good quantum number. For certain thin oxide films [6] the relation was also found to hold.

Tungstic oxide is one of the transition metal oxides and as a semiconducting oxide has attracted attention over the years. Amorphous films of WO_3 have been studied and their optical and electrical properties reported [7, 8]. Glasses having TeO_2 as a main component, particularly the TeO_2–WO_3 system have been produced over a long period [9] and found to have a low transition temperature. Such glasses are of the dense flint type having refractive indices in the range 2.15 to 2.18 and dispersion coefficients of 15 to 17, and values of 2.20 to 2.35 and 14 to 16 have also been reported [10]. Such glasses exhibit the highest refractive

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indices coupled with average dispersion coefficients for those glasses transparent in the visible and near infrared. The materials have been developed as optical glass [11], laser glass [12] and a very good sonic glass [13]. The aim of the present work is to study the optical properties of the WO_3–TeO_2 glass system with varying composition and to analyse the data in modern terms. In particular we have made measurements on a glass based on pure TeO_2. For many years there was considerable doubt about the existence of TeO_2 in a true glassy state and indeed many workers claimed that such a material could not exist. Recently, however, as part of a programme of work on the elastic moduli and related constants of tellurite glasses, TeO_2 glass was prepared and studied by Lambson *et al.* [14], and their results have kindly been communicated to us. Previous related measurements [5] on the more complex system of tungsten–calcium–tellurite glasses showed that as the tungstic oxide content was increased at the expense of calcium oxide in the glasses, the optical gap decreased and it was therefore of interest to determine whether a similar relationship held for the simpler glass system and also to determine the value of E_{opt} for a pure TeO_2 glass.

2. Experimental work

2.1. Preparation of pure tellurite glass

The technique adopted was different from that reported by Cheremisinov and Zlomanov [16]. An alumina crucible containing analytical reagent grade of TeO_2 was used. The samples were weighed to an accuracy of 0.2 mg. The crucible plus charge was placed in an electric furnace, preheated to a temperature of 800° C and held at this temperature for 30 min, by which time complete fusion has occurred. The melt was then cooled to 700° C in 5 min and a sample was blown using an alumina tube having a fine bore. The high viscosity of the melt at 700° C made this process relatively straightforward. The result was a TeO_2 glass in the form of a thin blown film well-suited for making optical measurements. The glass was annealed in a second furnace for 1 h at 300° C after which the furnace was switched off and allowed to cool down *in situ* for 24 h. The glass contained a very small quantity of aluminium which arose from contact with the crucible, but much less than the 6% Al_2O_3 equivalent reported earlier [16].

TABLE I Composition data for tellurite glasses

Batch No.	WO_3 content (mol %)	Initial melting point (° C)	Colour
T-1	Pure TeO_2	720	Pale green
T-2	5	740	Pale yellow
T-3	10	740	Yellow
T-4	15	800	Yellow
T-5	20	850	Yellow
T-6	25	900	Yellow
T-7	30	950	Brown

All samples were annealed at 300° C.

2.2. Preparation of binary tellurite glasses

TeO_2–WO_3 glasses were prepared by mixing the powders of TeO_2 and WO_3 in an alumina crucible and in order to reduce any tendency to volatilization, the mixture was kept at 400° C for a period of one hour and the crucible was transferred to the melting furnace with a temperature in the range 800 to 950° C, the precise value depending on the composition. During the 1 h melting period the melt was stirred a few times with an alumina rod to improve homogeneity. Thin samples were prepared by blowing molten glass using an alumina tube with a fine bore. All glass samples were annealed at 300° C for 1 h. The furnace was then switched off and allowed to cool overnight at a rate of some 3° C min^{-1}. Kozhukharov *et al.* [17] have reported the glass formation range for this system to be from 11 to 33.3 mol %. In the present work we produced and measured glasses from pure TeO_2 up to 33.3 mol % WO_3: contents are listed in Tables I and II.

2.3. Structural measurements

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

A simple displacement method was used with

TABLE II Derived characteristic energies for tellurite glasses

Batch No.	E_{opt} (eV)	E_e (eV)
T-1	3.79	0.07
T-2	3.49	0.11
T-3	3.43	0.13
T-4	3.40	0.11
T-5	3.38	0.14
T-6	3.38	0.11
T-7	3.32	0.12

toluene as the immersion liquid. Repeated measurements of density agreed to within ± 0.06%.

Sample thicknesses were measured in a traditional manner using a Sigma comparator.

2.4. Optical absorption measurements

These measurements were made in the range 190 to 850 nm using a Perkin–Elmer spectrophotometer Model 402. In the case of blown films of glasses the reflectivity, R, is considerable and is independent of sample thickness. Even without a knowledge of R the absorption coefficient can be estimated from the absorbance, A, measured for two specimens of the same material but having different thickness using the equation

$$\alpha(\lambda) = 2.303\frac{A_1(\lambda)-A_2(\lambda)}{x_1 - x_2} \qquad (4)$$

where A_1 and A_2 are the absorbances at a given wavelength of two samples of thicknesses x_1 and x_2.

The infrared absorption spectra were measured on KBr discs using the following procedure. Glass samples of the compositions given in Table III were ground in a clean mortar to a fine powder and mixed with a constant proportional amount of KBr in each case. The sample pellets were prepared by pressing for a few minutes under vacuum. The infrared spectra were then recorded using a Unicam SP2000 double-beam spectrometer in the range of wave numbers 4000 to 200 cm^{-1}. The refractive index, n, can be estimated from the transmittance spectra using the expression

$$1/2nx = (1/\lambda_1 - 1/\lambda_2) \qquad (5)$$

where λ_1 and λ_2 are the wavelengths of adjacent maxima and minima.

TABLE III Characteristic infrared absorption band positions for tellurite glasses

WO_3 Composition (mol %)		Infrared absorption band position (cm^{-1})		
Pure TeO_2	(glass)	340	640	740
Pure WO_3	(crystalline)	375	–	–
2	(glass)	350	650	750
5	(glass)	350	650	750
7	(glass)	350	650	750
10	(glass)	350	660	750
15	(glass)	355	660	750
20	(glass)	355	660	750
25	(glass)	350	660	750
33	(glass)	350	660	740

3. Results and discussion

3.1. The fundamental optical absorption edge

The compositions of the samples used are listed in Table I. The density measurements on these glasses are shown in Fig. 1. The density increased smoothly with increasing WO_3 content. However, our values are somewhat lower than those found by Yakhkind [11]. Figs. 2 and 3 show the optical absorption spectra at different thicknesses for both TeO_2 glasses and typical TeO_2–WO_3 glasses.

It is clear that there is no sharp absorption edge and this is a characteristic of the glassy state. As seen from these figures, the absorption edge moves to higher wavelengths as the thicknesses of the glass specimens are increased. Fig. 4 shows the absorption spectra at room temperature of some TeO_2 and TeO_2–WO_3 glasses of the same thickness and different compositions. Again the optical absorption edge moves to the long wavelength as the WO_3 percentage in the glass is increased. The values of absorption coefficient $\alpha(\omega)$ estimated by using Equation 4 are shown on an Urbach plot, in Fig. 5, for various TeO_2–WO_3 glasses. The values of E_e in Equation 2 are calculated from the slopes

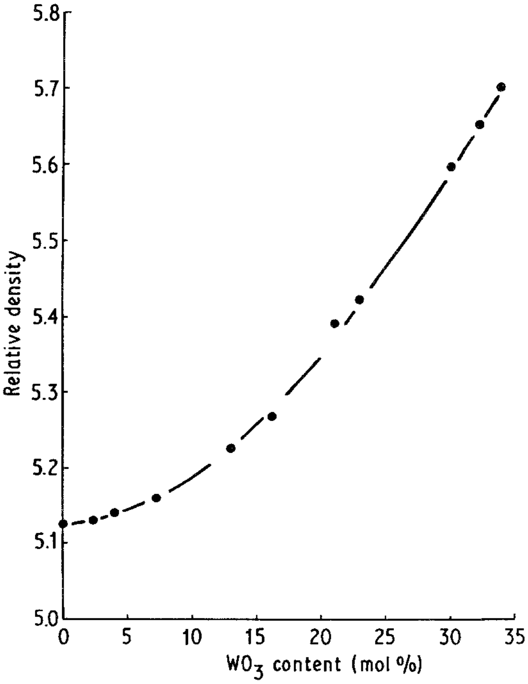

Figure 1 Relative density as a function of composition for TeO_2 and TeO_2–WO_3 glasses.

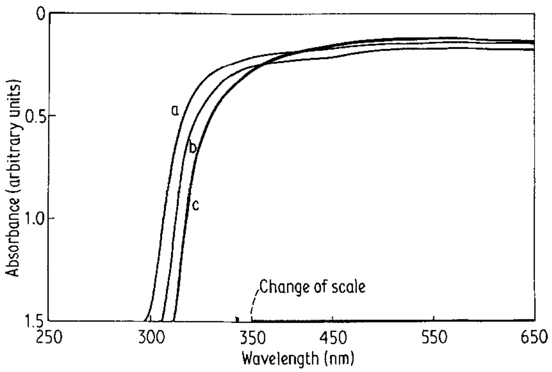

Figure 2 Absorption spectra as a function of wavelength of TeO_2 glasses of different thickness. (a) 1.0 μm. (b) 1.5 μm. (c) 4.0 μm.

of the straight lines of these curves and given in Table II. The origin of the exponential dependence of the absorption coefficient on the energy 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 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] are uncertain about the precise explanation. One possible reason suggested by them is that the slopes of the observed exponential edges obtained from Equation 2 are very much the same in many semiconductors, and the values of E_e for a range of amorphous semiconductors [5] lie between ~0.045 and 0.67 eV. For molybdenum phosphate glasses [20], the value

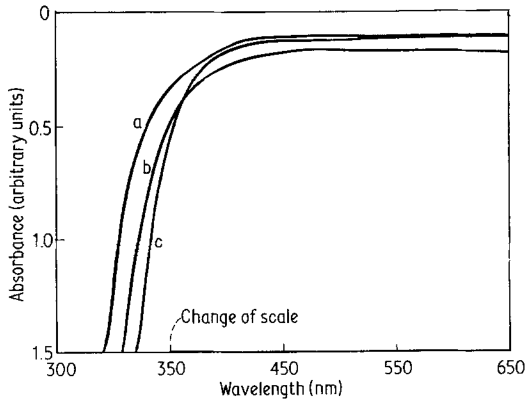

Figure 3 Absorption spectra as a function of wavelength of a typical TeO_2–WO_3 glass (95 mol% TeO_2–5 mol% WO_3) of different thickness. (a) 3.0 μm. (b) 6.5 μm. (c) 10.0 μm.

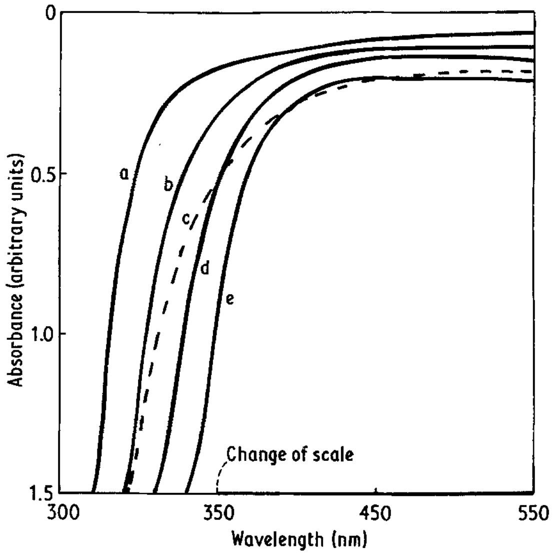

Figure 4 Optical absorption spectra of several TeO_2–WO_3 glasses having the same thickness and different compositions. (a) TeO_2. (b) 95 mol% TeO_2. (c) 90 mol% TeO_2. (d) 80 mol% TeO_2. (e) 70 mol% TeO_2.

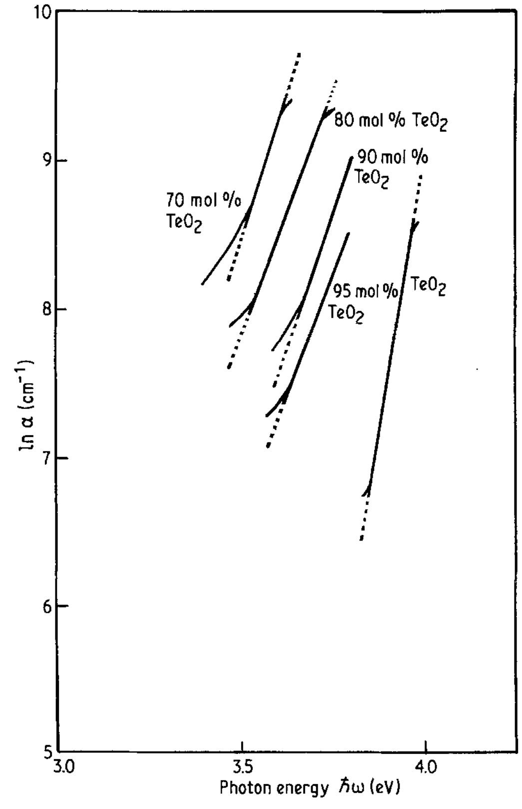

Figure 5 Urbach law plots for several TeO_2–WO_3 glasses.

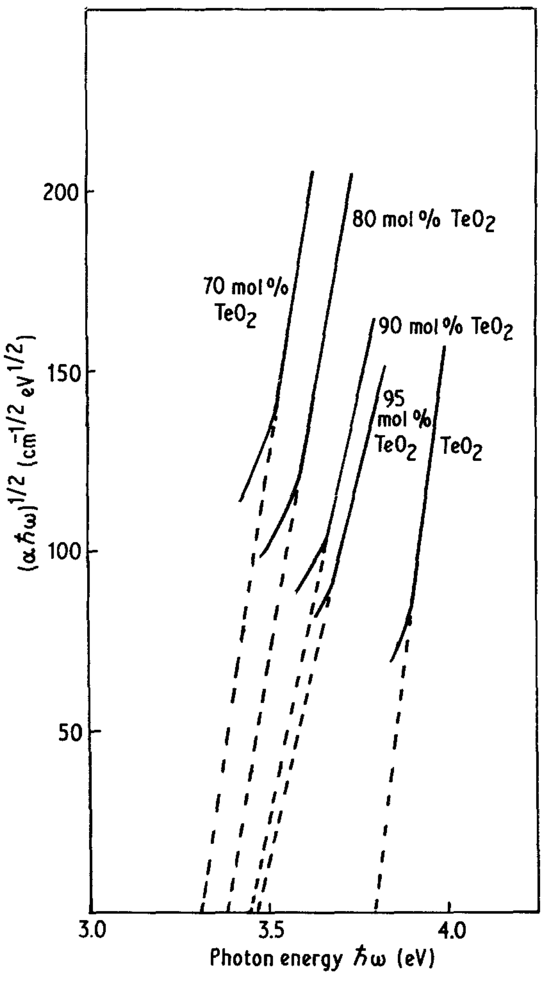

Figure 6 Optical absorption re-plotted in terms of absorption by indirect transitions for TeO_2–WO_3 glasses.

of E_e was as high as 0.16 eV, whereas for triple tellurite systems of the type WO_3–CaO–TeO_2 the reported [15] values of E_e vary between 0.12 and 0.4 eV, depending on the composition. For the glasses investigated in the present work, an exponential dependence of the absorption coefficient on photon energy is observed, suggesting that the Urbach rule is obeyed. The values of E_e obtained here are larger than those observed in some amorphous semiconductors [5, 21] and as they vary slightly with composition, a model based on electronic transitions between localized states is not preferable. We believe, however, that measurements at higher temperatures are needed to give a reliable decision about whether the exponential tail follows the Urbach rule or not.

The optical absorption data of TeO_2 and of TeO_2–WO_3 glasses follow Equation 3 with $r = 2$,

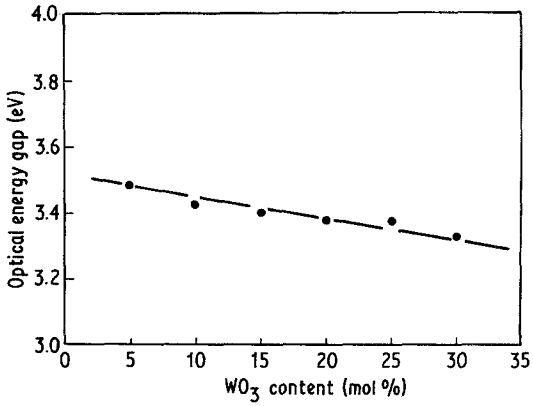

Figure 7 E_{opt} as a function of WO_3 content for TeO_2–WO_3 glasses.

but it may not be enough with only such measurements to indicate with certainty their band structure in the neighbourhood of the mobility edges. Tauc and colleagues [2] derived the quadratic equation assuming the electronic density-of-states at the band edges in the region of localized states to be a parabolic function of energy, and consequently E_{opt} may represent an extrapolated gap rather than a real zero in the density-of-states curve. Davis and Mott [3] reached Equation 3 with $r = 2$ assuming a linear dependence of the electronic density-of-states on energy, and thus they 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*. The optical data in Figs. 2, 3 and 4 could be analysed in terms of non-direct transitions in **k**-space and are re-plotted in Fig. 6 as the quantity $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$. The values of the optical gaps, E_{opt}, are obtained from the extrapolation of the linear portions of these graphs and are listed in Table II. Fig. 7 shows the variation of E_{opt} with composition for TeO_2–WO_3 glasses. The values of E_{opt} decrease linearly with increasing tungsten content and are consistent with an increase in band tailing arising from localization, as may be expected.

Stevels [22] has suggested that the movement of the ultraviolet absorption band to longer wavelengths corresponds to transitions from the non-bridging oxygen which bind an excited electron less tightly than a bridging oxygen. The results in Fig. 7 show that the variation of E_{opt} with composition can be explained by suggesting that the non-bridging oxygen ion content increases with increasing WO_3 content, shifting the band edge to lower energies and leading to a decrease in the value of E_{opt}.

The value of the constant B in Equation 3 can be determined from the slope of the linear part of the curves relating $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$. These values for TeO_2 and TeO_2–WO_3 glasses are of the same order as was reported by Davis and Mott [3]. The refractive index values for TeO_2 glasses obtained from Equation 5 gave values of 1.83 to 2.19 in the 450 to 820 nm range, in fair agreement with earlier findings [10, 11].

3.2. The infrared absorption

According to Zachariasen's theory [23], the structural network in glassy oxides can be formed only by a corner combination of oxygen tetrahedra or triangles. However, an exception to this rule [24] is the two-component tellurite glasses in which a coordination number of 6 is assigned to tellurium.

Fig. 8 shows the infrared spectra of tellurite–tungsten glasses obtained in the present work. Table III summarizes the characteristic infrared absorption band positions. A recent investigation [25] of the infrared spectra of TeO_2–WO_3 binary system glasses has indicated major peaks in the lower wavelength regime which do not appear in our results. The main infrared absorption band of our TeO_2 glass is at 640 cm^{-1} and it is attributed to symmetrical vibration oscillations of the Te–O bonds. The position of all peaks in the TeO_2 spectrum showed a close agreement with those previously reported [26], but the broadened bands are a feature of the glassy state. By adding WO_3, the band positions shift slightly towards higher wave numbers. A Raman study [24] of the TeO_2–WO_3 system has shown that the spectra of these glasses possess a band at 930 cm^{-1} which corresponds apparently to completely symmetrical oscillations of WO_4 tetrahedra. This band, however, has not been detected in our spectra. The intensity and the band positions in these spectra (Fig. 8) show some chemical interaction between the two oxides rather than positions characteristic of a simple oxide mixture.

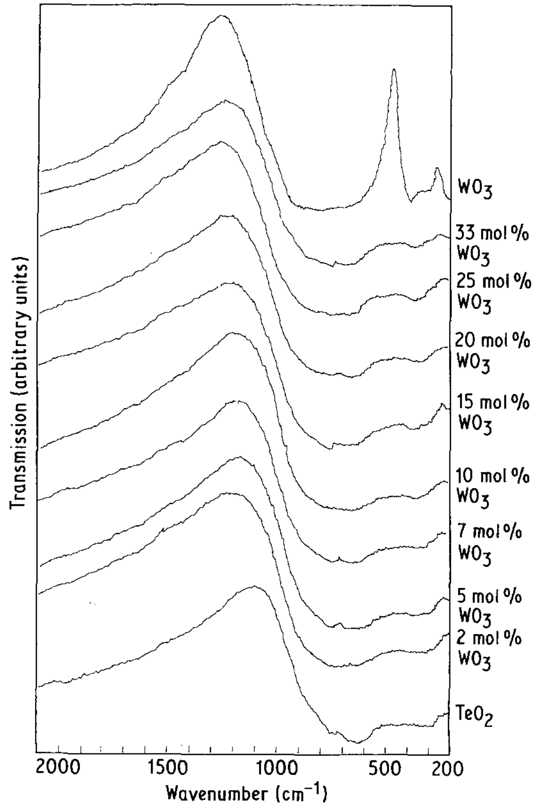

Figure 8 Infrared absorption spectra of WO_3, TeO_2 and TeO_2–WO_3 glasses.

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