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Some studies of the optical properties of tungsten–calcium–tellurite glasses

C. A. HOGARTH, E. ASSADZADEH-KASHANI
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

A range of tungsten tellurite glasses containing calcium was prepared and the densities, optical absorption edges and infrared optical absorption spectra were measured. The optical energy gap is of order 3 eV, somewhat lower than for many oxide-based glasses. It is established that the main absorption bands are related to the bonds in TeO_2 rather than the other components of the glasses.

1. Introduction

In recent years the properties of glasses have been interpreted in electronic terms rather than simply from the chemical point of view. The understanding of the amorphous and glassy states as described by Mott and Davis [1] and by Borisova [2] and in particular the relationships between structure and properties has led to an increased application of glasses and glassy complexes, in electronic systems for example.

We have studied some tungsten tellurite glasses. The yellowish colours of some glasses of this system have suggested a lower energy gap than is exhibited by many other oxide glass systems, mainly of order 4.5 eV. It is known that in tungsten glasses the electrical conduction arises from electron hopping between variable valency sites (W^{5+} and W^{6+}) and it was thought that some glasses having useful electronic properties would be found in the tungsten tellurite system. A more electronically passive glass-modifying material, CaO, was incorporated in order to produce a background matrix for the glasses.

In this paper we shall describe the preparation technique, measurements of density, and the main optical properties measured at room temperature. Tellurite glasses are known to have high values of refractive index and their known chemical stability is expected to make them useful as optical components. The melting conditions of tellurite glasses containing transition metal ions are confined to the specific behaviour of the tellurite melt (i.e. high volatility and low viscosity) but the composition range of the glass-forming region depends on the nature of the modifier itself and on the type of the corresponding phase diagram [3]. The study of the glass-forming region arises from consideration of optical and electronic properties of the tellurite glasses which in turn relates to energy band structure and to the detailed mechanism of electrical conduction. The properties of the glasses may be determined by melting temperature, melting time, annealing temperature, annealing time, rate of cooling and ambient atmosphere for melting. To produce glasses having constant and reproducible properties the above parameters must be kept constant.

The optical absorption in solids occurs by a number of mechanisms, all of which involve the coupling of the electric vector of the incident radiation to dipole moments in the material and the consequent transfer of energy. For example, the absorption may be caused by internal transitions between d-shell electrons, a process known as Ligand field absorption. The absorption can also arise by the transfer of electrons from a neighbouring atom to the transition metal ions and vice versa in what is called the charge transfer band. The study of the absorption spectrum in the near infrared region of the glass containing tungsten ions is of importance since it can give information about the local arrangement of such ions.

In crystalline non-metallic materials, for example semiconductors, there are two main types of optical transitions that can occur at the fundamental absorption edge, namely direct transitions in which momentum is conserved and indirect

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TABLE I Composition and identification of seven glasses of tungsten–calcium–tellurite

Glass number	CaO (mol%)	WO_3 (mol%)	Relative density	Colour
4040	0	35	6.07	yellowish brown
4041	2.5	32.5	6.05	yellow
4042	5.0	30	5.90	green
4043	7.5	27.5	5.74	green
4044	10	25	5.54	green
4045	15	20	5.52	green
4046	20	15	5.43	light green

transitions in which the required change in momentum $\hbar\mathbf{k}$ (where $\mathbf{k}$ is the wave vector) needs co-operation from a phonon. Neglecting any possibilities of exciton formation or other forms of electron-hole interaction, the absorption coefficient $\alpha(\omega)$ as a function of photon energy depends on the type of energy bands containing the initial and final states. For simple parabolic bands they are, for direct transitions

$$n_0\hbar\omega \propto (\hbar\omega - E_{\text{opt}})^n \tag{1}$$

where $n = 1/2$ or $3/2$ depending on whether the transition is allowed or forbidden in the quantum mechanical sense, and this type of absorption is independent of temperature apart from any temperature variation of the optical gap E_{opt}, and n_0 is the refractive index. There is also a formula for indirect transitions which can also be related to allowed and forbidden transitions. In each case multiple-phonon processes may occur. According to Mott [4] and others, the absorption edge for non-direct transitions in amorphous semiconductors, provided that they have constant matrix elements and that the $\mathbf{k}$-conservation selection rule is relaxed, can be expressed in the following simple form

$$\alpha(\omega) = \frac{A}{\hbar\omega}(\hbar\omega - E_{\text{opt}})^n \tag{2}$$

where A is a constant, n is an index and E_{opt} is the optical energy gap. For our materials $n = 2$ and we therefore plot our results for the absorption edge region as $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$. The optical absorption coefficient of most amorphous semiconductors is also found to increase exponentially with photon energy in the range $1 < \alpha < 10^4$ cm^{-1}. The origin of this Urbach edge behaviour is discussed by Mott and Davis [1]. At values of α larger than 10^4 cm^{-1} the absorption curves begin to level off, where the transitions can take place between two bands of states. Evidence for optical transitions from the valence band (or localized gap states) to unoccupied localized states above the Fermi level may be sought at energies near to and below E_{opt}. The matrix element for a transition between localized and extended states is of the same order of magnitude as that for a transition between band states as shown by Mott and Davis [1]. The localized gap states are not detected optically because the extended conduction band states of the lowest energy are channel states which are essentially excluded from the regions where the electrons are localized. The extended electron states are found only at higher energies. This condition could be

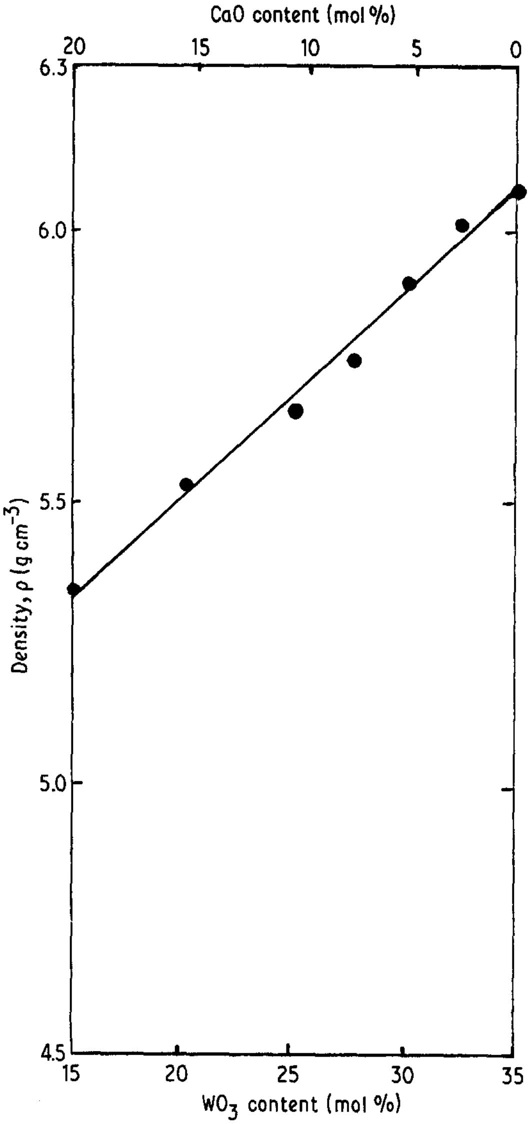


Figure 1 Density of WO_3–CaO–TeO_2 glasses as a function of WO_3 content.

TABLE II Some characteristic energy parameters of five calcium–tungsten–tellurite glasses

Glass number	E_{opt} (eV)	Activation energy (eV)	Break energy (eV)
4040	2.82	1.22	3.51
4041	2.93	1.26	3.58
4042	3.02	1.30	3.61
4043	3.08	1.32	3.64
4044	3.15	1.34	3.65

expressed in terms of a rapidly-decreasing matrix element for optical transitions between localized states and non-localized states, as the photon energy is decreased below the optical gap. Thus on the basis of this model we suppose that tunnelling processes may be taking place. Mott and Davis [1] assumed that the densities of states at the band edges E_C and E_V are linear functions of the energy so that

$$N(E_C) = N(E_V) \qquad (3)$$

and

$$E_C - E_A = E_B - E_V = \Delta E \qquad (4)$$

where ΔE is the width of the tail of localized states in the band gap, and the transition in which both the initial and final states are localized can be neglected. Therefore from Equation 2 we may develop an equation for glassy materials of the form

$$\alpha(\omega) = \frac{4\pi\sigma_0}{n_0 c}(\hbar\omega - E_{\mathrm{opt}})^2/\hbar\omega\Delta E \qquad (5)$$

where we write

$$A = \frac{4\pi\sigma_0}{n_0 c \Delta E}$$

n_0 is the refractive index, σ_0 is the conductivity at $1/T = 0$, and c is the velocity of light.

2. Glass preparation and density measurements

Analytical reagent quality material TeO_2, WO_3 and CaO were carefully weighed and mixed in an alumina crucible. A typical melt used some 45 g of material. In order to reduce a tendency to volatilization the crucible was initially heated for one hour at 430° C and then for two hours at 950° C in the melting furnace. The melt was stirred from time to time using an alumina rod. The melt was finally poured on to a clean steel surface and cast into a disc shape with 3 cm diameter and about 3 mm thickness. All samples were then annealed at 430° C for one hour. This casting procedure served to relieve thermal stress and to minimize cracking of the glasses. The compositions covered the range 65 mol% TeO_2–(35 – x) mol% CaO–x mol% WO_3, where $35 \geqslant x \geqslant 0$. Table I shows the compositions of all the glasses reported in this paper.

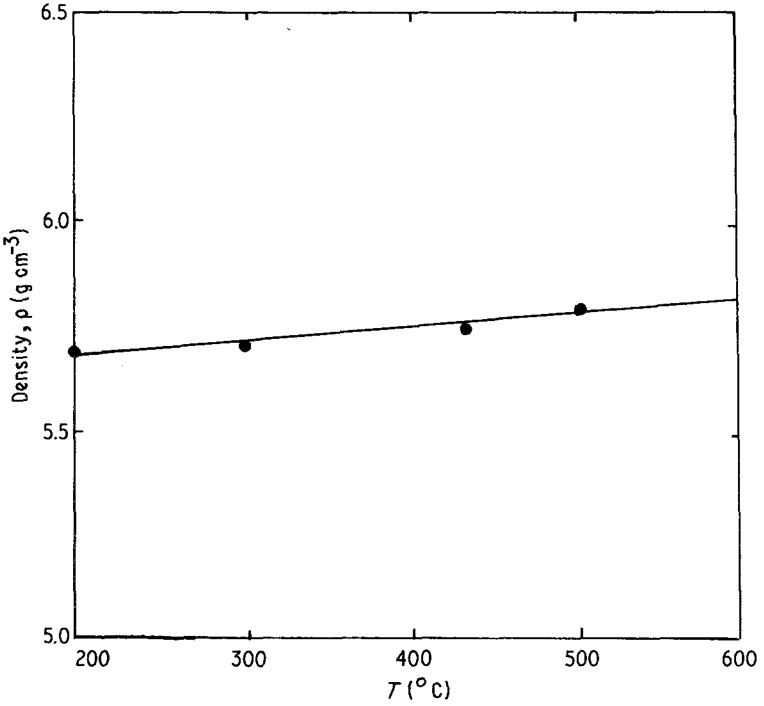
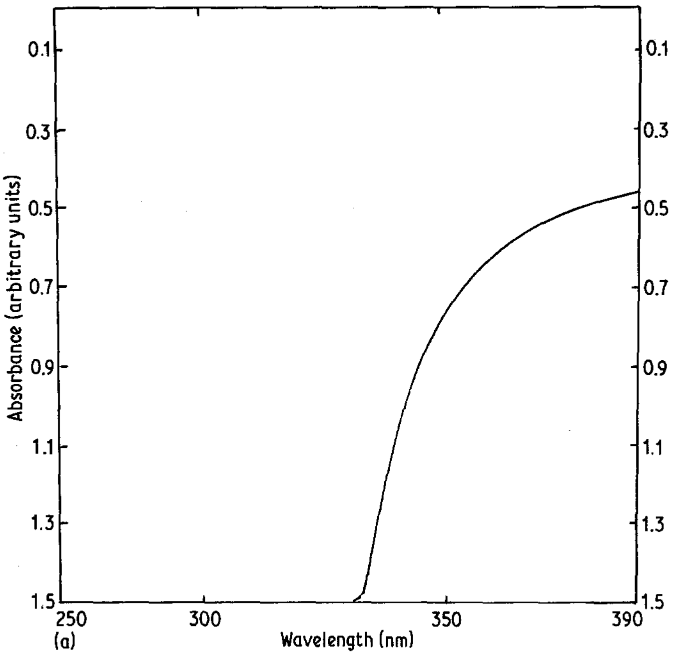


Figure 2 Density of WO_3–CaO–TeO_2 glass (4043) as a function of annealing temperature.



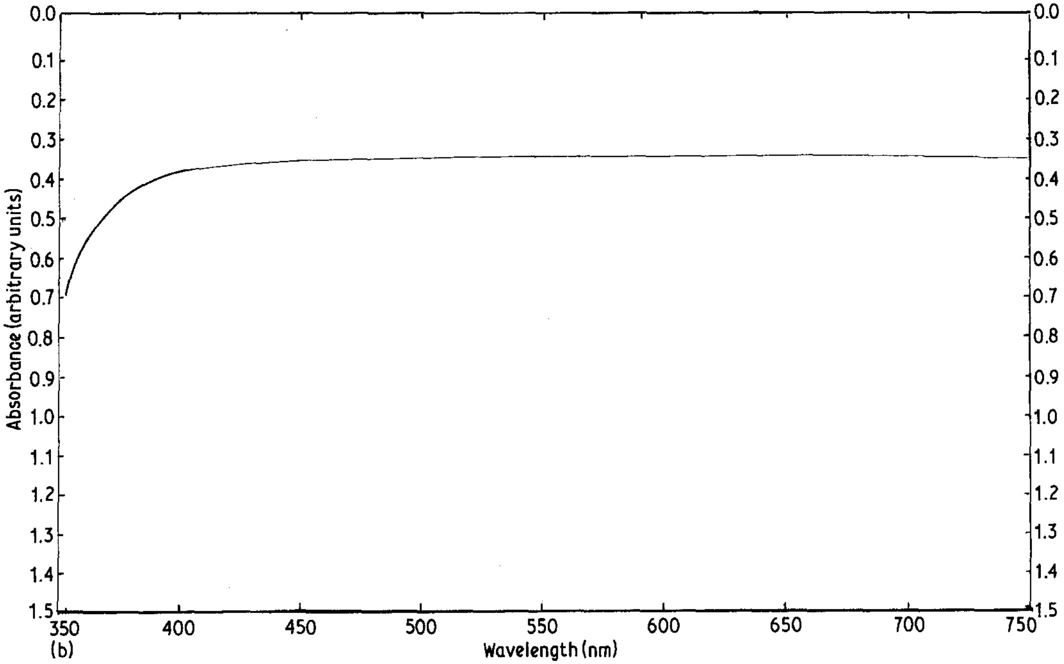


Figure 3 (a) Absorption as a function of wavelength for a glass sample. (b) Absorbance as a function of wavelength for a glass sample.

A study of the X-ray diffraction pattern of a glass sample showed no discrete lines or structure and was thus seen to confirm that our samples were non-crystalline. The densities were measured by a simple displacement technique using toluene as the fluid medium and the results are shown in Table I, which also indicates the colour of the glasses produced. A study of Fig. 1 indicates that there is a linear relationship between the density, increasing with the WO_3 content. Thus the structure becomes more compact as the WO_3 content increases. A typical effect of annealing is shown in Fig. 2 where for a sample of glass no. 4043 a small but significant increase in density with annealing temperature is observed.

3. Optical measurements

Thin films were prepared by a blowing technique

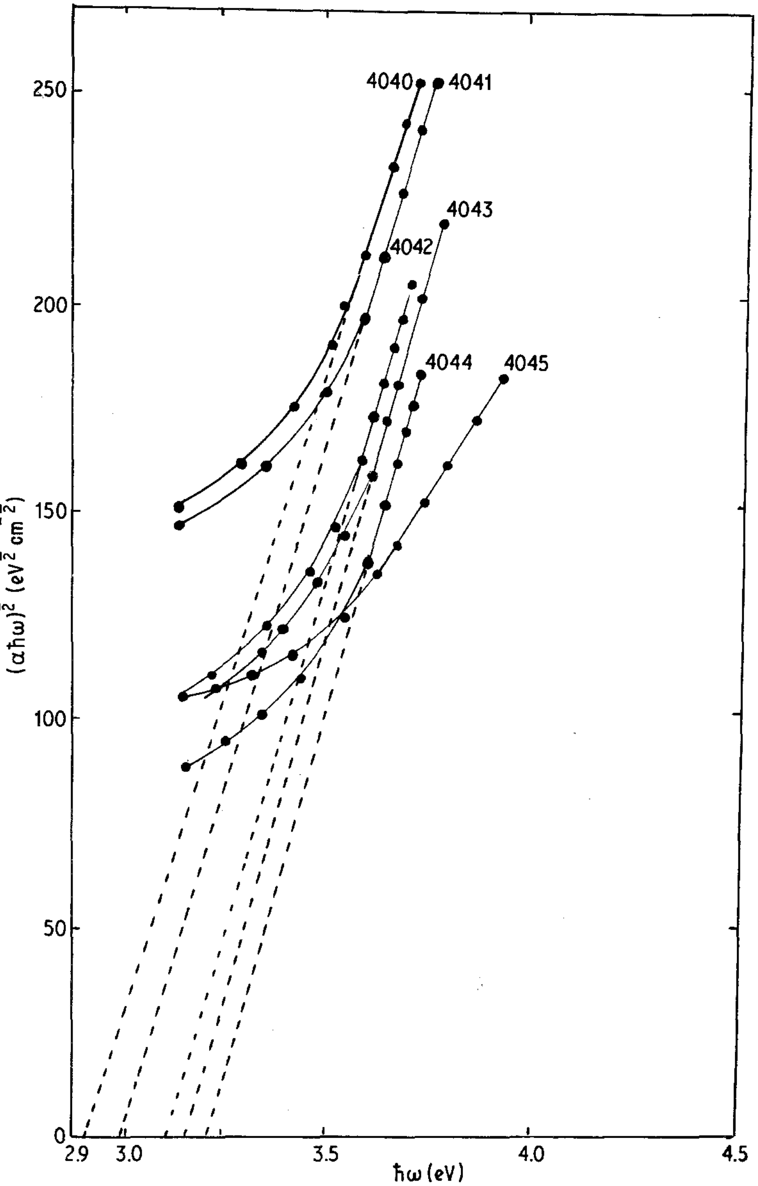


Figure 4 $(\alpha\hbar\omega)^{1/2}$ as a function of energy for WO_3–CaO–TeO_2 glasses.

using a silica rod and the thicknesses of the films of tungsten–calcium–tellurite glasses of different composition (from 1.5 to 2.0 μm) were determined by a Sigma comparator. The optical transmission properties of the glasses were obtained by using a spectrophotometer, at room temperature. The optical absorption coefficient has been derived from the formula.

$$\alpha(\omega) = \frac{1}{d}\ln\frac{I_0}{I_t} \qquad (6)$$

where d is the sample thickness and I_0 and I_t are the intensities of incident and transmitted lights, respectively. Table II shows some characteristic energy parameters of five tungsten–calcium–tellurite glasses.

A typical form of optical absorption edge for a glass sample as a function of wavelength is shown in Fig. 3. It is less sharp than for a typical crystalline material and becomes even less sharp as the WO_3 content is increased. The high absorption ends of the curve of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ shown in Fig. 4 are good straight lines and extrapolate to values of E_{opt} of the order of magnitude suggested in §1. The general trend is not obeyed by glass no. 4045 containing the lowest quantity of tungsten. An energy E_b is defined as that at which the departure from linearity occurs on the

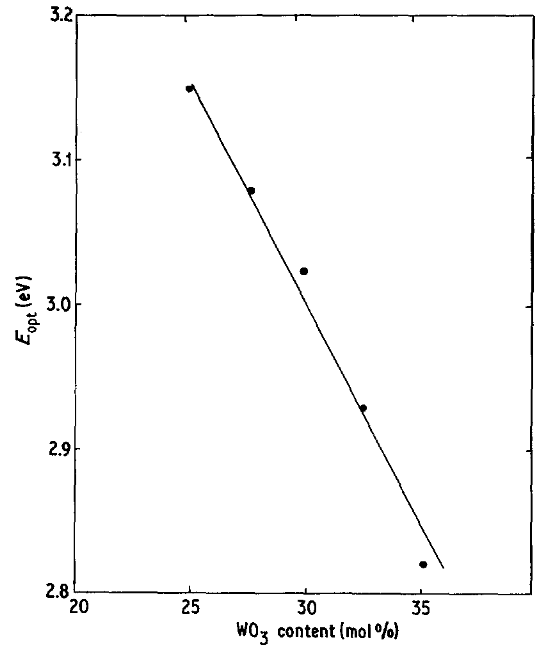


Figure 5 E_{opt} as a function of WO_3 content for WO_3–CaO–TeO_2 glasses.

curves of Fig. 4. These values also shift towards higher energies as the tungsten content decreases. The values of E_{opt} decrease with increasing tungsten content as shown in Fig. 5 and are consistent with an increase in band tailing arising from localization, as expected. The derived values of the constant A of Equation 5 are found to increase with increase of tungsten content as in Fig. 6. The curves in the relationship between ln α and $\hbar\omega$ are shown in Fig. 7. The optical data may be fitted to an exponential of this form

$$\alpha(\omega) = \text{constant} \exp\left(\frac{\hbar\omega}{\Delta}\right) \qquad (7)$$

The above form represents the absorption edge as an exponential function of photon energy.

Similar exponential edges known as Urbach edges [5] have been observed in a number of amorphous and crystalline materials. The origin of this exponential tail absorption is still a matter of conjecture but according to Dow and Redfield [6], it arises from the random fluctuation of the internal fields associated with structural disorder which are considerable in many amorphous solids. The slopes of the exponential form of curve are found to vary between 0.12 and 0.4 eV depending on the composition. This paper does not deal in detail with electrical properties of the glasses, but the values of activation energy W obtained from the linear plots of log conductivity against $1/T$ are included for comparison purposes. The magnitude of W may be roughly half that of the optical gap, which is in accordance with the general rule formulated by Joffe and Regel [7]. Fig. 8 shows a linear functional relationship between W and E_{opt}.

The infrared spectra of tungsten–calcium–tellurite glasses were recorded with a Unicam SP200 infrared spectrophotometer which was operated in the double beam mode. Selected glass samples were ground in a clean mortar into a fine powder and then a small amount of glass powder was weighed and mixed with an already weighed amount of KBr powder in accordance with standard procedures. The mixed powder was shaken by a special machine in order to obtain a well-mixed powder. The pellets were formed by pressing the evacuated mixture at 15 tons for a few minutes. Table III shows the characteristic infrared absorption band position (cm^{-1}) for tungsten–calcium–tellurite glasses. Fig. 9 shows the infrared spectra of the tungsten–calcium–tellurite glasses.

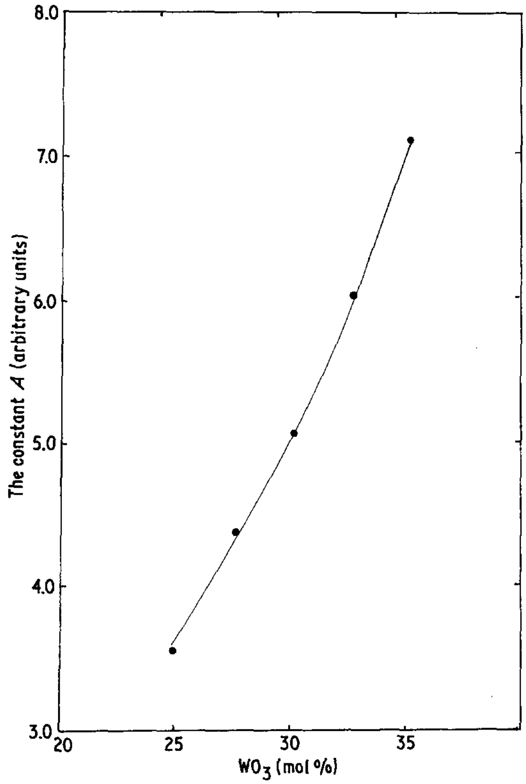


Figure 6 The function A as a function of WO_3 content for some WO_3–CaO–TeO_2 glasses.

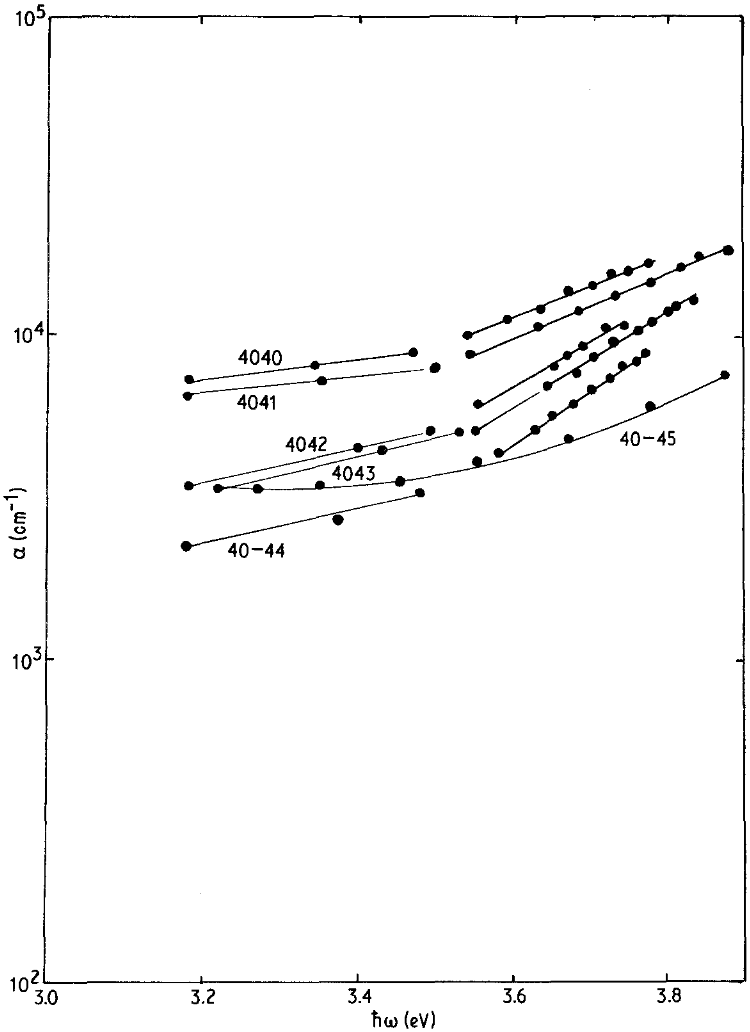


Figure 7 Optical absorption as a function of energy for WO_3–CaO–TeO_2 glasses.

The infrared spectra of glasses with high TeO_2 content resembled that of a para-tellurite ion and showed the remarkable downward shift of the peak position. The position obtained for the TeO_2 is close to the reported value [8]. The bands at 780, 670, 350 cm^{-1} would seem to be attributable to α-TeO_2. These bands are assigned to the TeO_{ax}, TeO_{eq} stretching vibrations, respectively [9]. By the addition of small amounts of WO_3 to the composition, the structure of the glass varies very slightly as the TeO_4 tetrahedra are replaced by WO_3 tetrahedra in the tellurite network. With the increase of concentration of WO_3 in the glass, the WO_4 tetrahedra probably form tungsten chains in the group [9], which are connected by Te–O–W bridges to the tellurite

TABLE III Characteristic infrared absorption band positions (cm^{-1}) for tungsten–calcium–tellurite glasses

Glass number	Infrared absorption band position					
	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
4040	350	420–550	590–720	740–850	930	–
4041	350	420–550	590–720	740–850	930	–
4042	350	420–550	590–720	740–850	930	–
4043	350	420–550	590–720	740–850	930	–
4044	350	420–550	590–720	740–850	930	–
TeO_2	350	–	670	780	–	–
WO_3	–	375, 405, 425	–	772, 833	930	1047

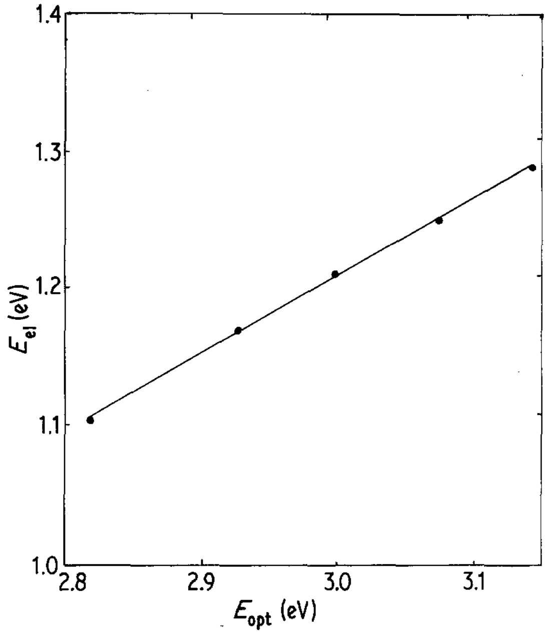


Figure 8 E_{el} as a function of E_{opt} for some WO_3–CaO–TeO_2 glasses.

chain into the glass network. This can perhaps be estimated from the increase in the absorption in the frequency region of 740 to 850 cm^{-1} and 420 to 550 cm^{-1} which may be assigned to asymmetric vibrations v_{as} OWO and v_{as} WOW vibrations of the tungsten chains. The network may include tungsten chains which are in the general form of the distorted WO_4 tetrahedra and of WO_6 octahedra joined by non-symmetrical WOW bridges. There are bands at 920 cm^{-1} and at 1047 cm^{-1} which may be assigned to the v_s $\bar{O}W\bar{O}$ vibration and W=O bond, respectively. Fig. 9 represents the infrared spectra of tungsten–calcium–tellurite glasses.

4. Conclusions

The density measurements showed that by increasing the WO_3 content in these glasses the density increases and the glass acquires a more compact structure. The annealing temperature was found to affect the density of tungsten–calcium–tellurite glasses, the increase in density being associated with a change in the average interatomic spacing. The ESR measurement and chemical analysis indicates that tungsten exists in glass in more than one valency state.

The optical absorption spectra indicate that the optical gap decreases as the WO_3 content in the glass increases and these glasses show an

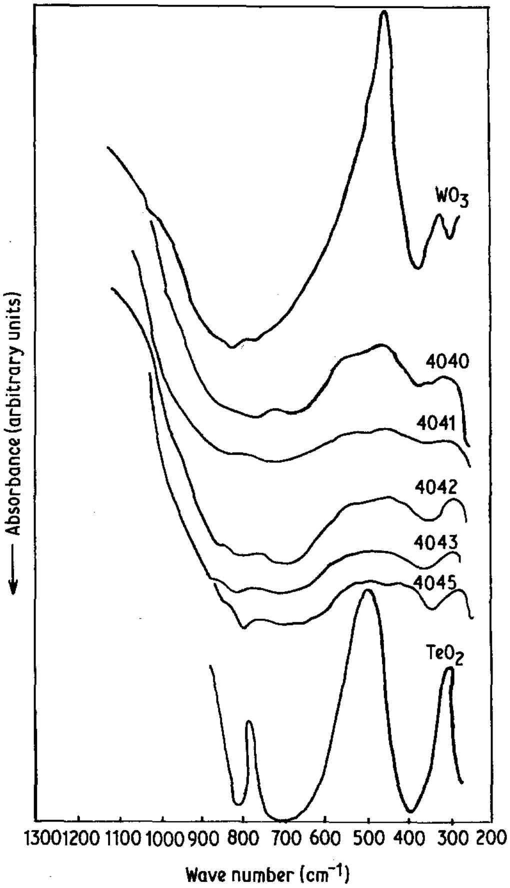


Figure 9 Infrared absorption spectra of some tungsten–calcium–tellurite glasses.

absorption which fits into a non-direct interband transition as discussed by Mott and Davis [1]. The optical data may also be fitted to an exponential Urbach formula with a value Δ in the range of 0.12 to 0.40 eV for different compositions. The exponential form of the absorption coefficient may be explained on the basis of internal field broadening of an exciton line. The value of electrical activation energy was found to be less than half the optical gap on the same glass. This may suggest that the electronic activation is not across the mobility gap but is possibly from one or more trapping levels to the conduction band or from the bonding states to a trapping level. The infrared spectroscopy of tungsten–calcium–tellurite glasses and crystalline TeO_2 and WO_3 indicates that the most important absorption bands in the glasses are the same as for TeO_2. A shift of band position may be observed in these glasses to a lower frequency where Te–O stretching frequencies should be important. This may be due to the creation of single bonds between bridging oxygen ions and a tungsten ion to form a Te–O–W unit, and the TeO_2 tetrahedra will then dominate the structure.

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