

# A study of the electrical and optical properties of the $\text{GeO}_2\text{-TeO}_2$ glass system

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Results of measurements of the d.c. electrical conductivity, optical absorption edge and infrared optical absorption of  $\text{GeO}_2\text{-TeO}_2$  glasses are reported. Conduction in these glasses is found to be electronic and the hopping of polarons seems to be the dominant process in the transport mechanism. The electrical activation energy decreases with the increase of tellurium content and this decrease corresponds to a decrease in the optical energy gap. The optical gap is of the order of 2.74 eV, somewhat lower than for many other oxide based glasses. Most of the sharp absorption bands characteristic of the basic materials  $\text{GeO}_2$  and  $\text{TeO}_2$  are modified with the formation of broad and strong absorption bands in the process of going from the crystalline to the amorphous state. Density measurements show the glasses to have a compact structure.

## 1. Introduction

Several transition metal oxides when heated with glass-forming substances such as  $\text{P}_2\text{O}_5$ ,  $\text{TeO}_2$  and  $\text{GeO}_2$  form glasses on quenching the melt. The general condition for semiconducting behaviour is that the transition metal ion should be capable of existing in more than one valency state so that conduction occurs by the movement of charge carriers from the lower to the higher valency state. Much of the work on the electrical properties of semiconducting oxide glasses is based on the theories of Mott [1] and of Austin and Mott [2]. Several groups have studied the  $\text{V}_2\text{O}_5\text{-TeO}_2$  glasses and published data which include the equilibrium [3], structure [4], switching mechanism [5, 6], electron paramagnetic resonance [7, 8], phase equilibrium and electrical conductivity [9]. Recently, a detailed analysis of the d.c. conductivity has been reported by Flynn *et al.* [10] on the low concentration (10 to 50 mol%)  $\text{V}_2\text{O}_5$  and by Dhawan *et al.* [11] on the high concentration (50 to 80 mol%)  $\text{V}_2\text{O}_5$  glasses. In the present paper we report the results of our measurements on the  $\text{GeO}_2\text{-TeO}_2$  glasses in the range of 10 to 30 mol%  $\text{TeO}_2$ .

## 2. Experimental work

Several glasses were prepared from reagent grades of  $\text{GeO}_2$  and  $\text{TeO}_2$  in alumina crucibles at a temperature of  $1400^\circ\text{C}$ . The samples were annealed at a constant temperature of  $500^\circ\text{C}$  for one hour and allowed to cool slowly. Silver paint was applied to ground and well-polished glasses to produce silver-glass-silver sandwich samples including a guard-ring arrangement on one side of each of the samples. A special sample holder was designed for the electrical measurements which could hold five glass samples at a time and help in the measurement of different parameters under similar conditions. Current-voltage characteristics were recorded in air with a Keithley 610C electrometer and a stabilized voltage supply unit. The homogeneity of all glasses was checked by X-ray diffraction and the films showed no sharp lines and were characteristic of glassy materials. The density values were measured by the standard displacement method, using toluene as an immersion liquid. Optical measurements were recorded in the ultraviolet, visible and infrared regions. Samples of the same thickness used for the electrical measurements were also used in the ultraviolet

and visible spectroscopic studies. The measurements were carried out at room temperature with a Perkin-Elmer spectrometer in the wavelength range of 190 to 750 nm. As there is no significant absorption in the ultraviolet region, the spectra are shown only in the visible range. The infrared absorption spectra of the present glasses were measured at room temperature using a Unicam SP 2000 double-beam infrared spectrophotometer in the frequency range of 200 to 4000  $\text{cm}^{-1}$ . The spectra are shown in the range of 200 to 2000  $\text{cm}^{-1}$  as there is no measurable absorption above this range.

### 3. Results and discussion

Table I shows a range of density values of  $\text{GeO}_2$ - $\text{TeO}_2$  glasses. With increasing concentration of  $\text{TeO}_2$  from 10 to 30 mol%, the relative density increases from 3.83<sub>1</sub> to 4.11<sub>9</sub>. Fig. 1 represents the density as a function of  $\text{TeO}_2$  content. It is clear from the figure that there is a smooth variation of density with increasing concentration of  $\text{TeO}_2$ . This tends to suggest that the structure of these glasses does not change over the range of compositions studied. The high temperature d.c. conductivity of  $\text{GeO}_2$ - $\text{TeO}_2$  glasses was measured in the range between room temperature and 320° C. The conductivity,  $\sigma$ , varies very slowly with temperature below 150° C and displays no single activation energy, whereas above 150° C the conductivity behaviour seems to be quite consistent and shows a smooth variation with inverse temperature. The activation energies were calculated from the slopes of  $\log \sigma$  against  $1/T$  plots (Fig. 3) and are found to decrease with increasing  $\text{TeO}_2$  content. The conductivity against inverse temperature graph shows that the magnitude of the conductivity becomes smallest in the glasses having highest thermal activation energy. This is consistent with the general formula proposed by Mott [1] and agrees with our previous results [12]. The graphic representation of resistance against

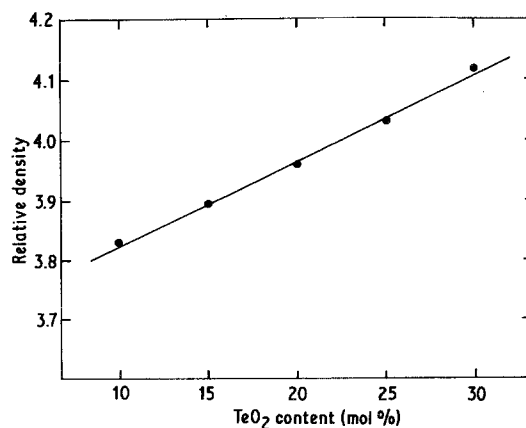


Figure 1 Density of  $\text{GeO}_2$ - $\text{TeO}_2$  glasses as a function of composition.

time is shown in Fig. 2. The resistance of all glasses was measured at 200° C by applying a constant voltage of 200 V and it was found to be constant with time. This could be taken as evidence that there is no measurable polarization effect and that these glasses behave as electronic conductors. The temperature dependence of conductivity (Fig. 3) is consistent with a polaron model for conduction which predicts that an appreciable departure from linearity should occur for a  $\log \sigma$  against  $1/T$  plot below a temperature of  $\frac{1}{2}\theta_D$ , where the Debye temperature,  $\theta_D$ , is given by  $\hbar\omega_0 = k\theta_D$ ,  $\omega_0$  being the phonon frequency and  $k$  the Boltzmann constant. Fig. 3 shows that the departure from linearity is at a temperature of 170° C which suggests that  $\frac{1}{2}\theta_D$  may be of the order of 170° C for these glasses. Different workers have made the assumption that the polaron radius,  $r_p$ , can be calculated from the relation  $r_p = \frac{1}{2}(\pi/6N)^{1/3}$ . The density measurements enable us to calculate  $N$ , the concentration of tellurium ions in each composition, and following the procedure described by Ahmed and Hogarth [12] the estimated polar radius and the total ion concentration are given in Table I. Now one of the parameters which may help us to explain our results is the ion spacing,  $R$ . The

TABLE I Some parameters of  $\text{GeO}_2$ - $\text{TeO}_2$  glasses

Glass no.	$\text{TeO}_2$ content (mol%)	$\text{GeO}_2$ content (mol%)	Relative density	Total Te ion concentration $N \times 10^{-21}$ ( $\text{cm}^{-3}$ )	Mean Te-Te spacing (nm)	Polaron radius $r_p$ (nm)	Conductivity at 250° C	Activation energy $E_a$ (eV)	Optical gap $E_{opt}$ (eV)
a	10	90	3.83 <sub>1</sub>	2.09	0.92 <sub>1</sub>	0.37 <sub>2</sub>	$2.6 \times 10^{-12}$	1.01	2.74
b	15	85	3.89 <sub>6</sub>	3.11	0.80 <sub>7</sub>	0.32 <sub>6</sub>	$4.8 \times 10^{-12}$	0.90	—
c	20	80	3.95 <sub>9</sub>	4.03	0.74 <sub>1</sub>	0.29 <sub>9</sub>	$1.1 \times 10^{-11}$	0.80	2.45
d	25	75	4.03 <sub>1</sub>	5.12	0.68 <sub>5</sub>	0.27 <sub>6</sub>	—	—	—
e	30	70	4.11 <sub>9</sub>	6.14	0.64 <sub>5</sub>	0.26	—	—	2.15

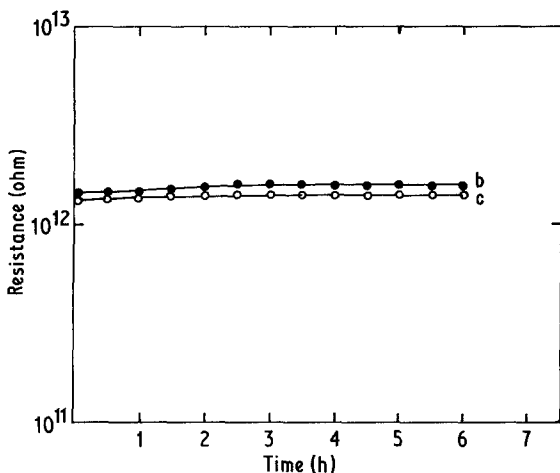


Figure 2 Resistance against time plots for  $\text{GeO}_2\text{-TeO}_2$  glasses.

relation  $R = (1/N)^{1/3}$  was used to calculate the mean spacing between tellurium ions, as listed in Table I. The polaron radius  $r_p$  and the mean Te-Te ion spacing are a function of  $\text{TeO}_2$  content (Fig. 4) and increase with increasing  $\text{TeO}_2$  content

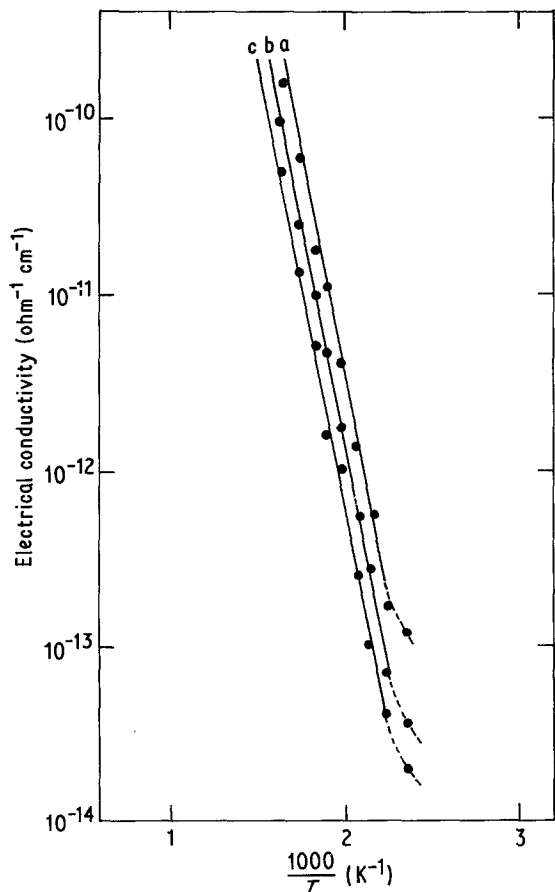


Figure 3 Conductivity as a function of inverse temperature for  $\text{GeO}_2\text{-TeO}_2$  glasses.

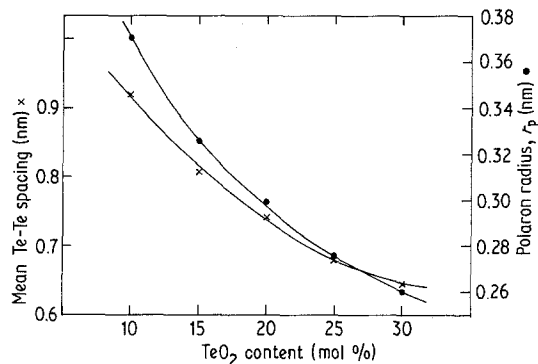


Figure 4 Polaron radius and Te-Te ion spacing as a function of  $\text{TeO}_2$  content.

in the glass. The value of  $r_p$  for each composition is less than the Te-Te distance. The decrease in activation energy with increasing  $\text{TeO}_2$  may well be related to the smaller distance between the tellurium ions. The values of  $\sigma_0$  as calculated by extrapolation of the  $\log \sigma$  against  $1/T$  plot are found to be in the range  $10^{-2}$  to  $10^{-3}$   $\text{ohm}^{-1} \text{cm}^{-1}$  and to decrease slightly with added  $\text{TeO}_2$  content.

The optical spectra of  $\text{GeO}_2\text{-TeO}_2$  glasses are shown as a function of wavelength in the range of 350 to 600 nm (Fig. 5). The fundamental absorption edge moves towards higher wavelength with the addition of  $\text{TeO}_2$ . The absorption coefficient,  $\alpha(\omega)$ , was derived in the usual way on the basis of indirect transitions. The plots corresponding to Fig. 5 are given in Fig. 6. The data for all glasses examined here are presented in accordance with the relation

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^2/\hbar\omega$$

The extrapolation from the linear regions of the  $(\alpha\hbar\omega)^{1/2}$  against  $\hbar\omega$  plots yield the different values of the optical energy gaps at different compositions (Fig. 6) and these values are plotted against the  $\text{TeO}_2$  concentration in Fig. 7. The

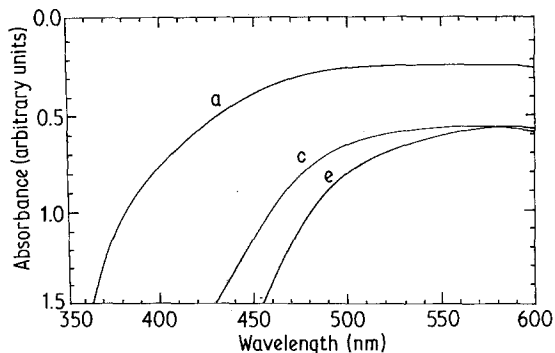


Figure 5 The optical absorption spectra of  $\text{GeO}_2\text{-TeO}_2$  glasses as a function of wavelength.

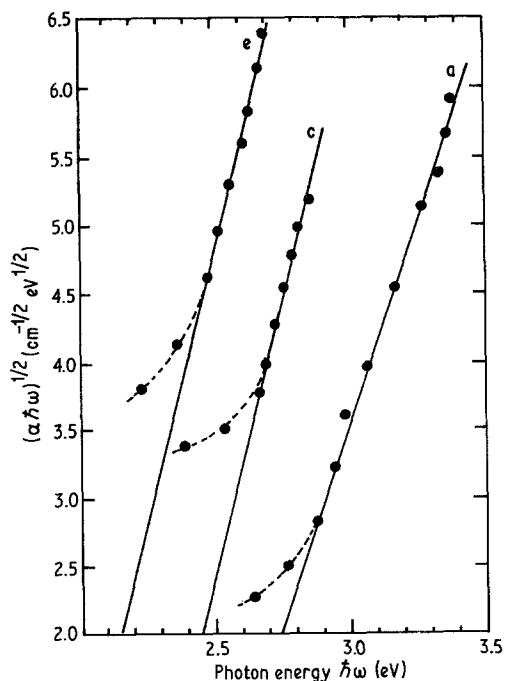


Figure 6  $(\alpha\hbar\omega)^{1/2}$  against  $\hbar\omega$  for five  $\text{GeO}_2$ - $\text{TeO}_2$  glasses.

analysis of the absorption edge is made in accordance with the formula for indirect transitions, and the plot gives a reasonably systematic series of values of optical activation energy. The so-called optical gap is found to decrease with the increase of  $\text{TeO}_2$  content and is about three times greater than the electrical activation energy. The agreement seems to be with the supposition that the electronic activation is not across the whole mobility gap but possibly from one or more trapping levels to the conduction band. The density of localized states or traps will probably have an effective influence and may involve the transport of carriers via many trapping events and a potentially high density of localized states makes

it necessary to consider the hopping of carriers between traps as a probable mechanism of transport.

The infrared absorption spectra of germanium-tellurium oxide glasses along with the spectra for crystalline  $\text{GeO}_2$  and  $\text{TeO}_2$  are shown in Fig. 8. The positions of the absorption peaks are given in Table II. Comparing the spectra of the present glasses with their crystalline constituents, it seems that most of the sharp bands characteristic of crystalline  $\text{GeO}_2$  and  $\text{TeO}_2$  have disappeared in the formation of the glass. The germanium dioxide bands are more significant than the tellurium dioxide absorption peaks in the final glasses. The spectra do not show any change in the band positions with composition. The bands at 350, 610 to 700 and 780  $\text{cm}^{-1}$  for  $\text{TeO}_2$  and at 340, 520, 560, 590 and 878  $\text{cm}^{-1}$  for  $\text{GeO}_2$  are close to the previously reported values [13]. The bands for  $\text{TeO}_2$  are assigned to  $\text{TeO}_{ax}$ ,  $\text{TeO}_{eq}$  stretching vibrations [14]. The spectra of crystalline  $\text{GeO}_2$  resemble that of hexagonal  $\text{GeO}_2$  in which the coordination number of  $\text{Ge}^{4+}$  is 4 and the absorption due to  $\text{Ge-O-Ge}$  stretching occurs at about 878  $\text{cm}^{-1}$ . The intensity of the absorption band in our glass system is centred across a broad region from 800 to 900  $\text{cm}^{-1}$  which may be associated with  $\text{Ge-O-Ge}$  stretching vibrations [15, 16]. The three band positions at 520, 560 and 590  $\text{cm}^{-1}$  in crystalline  $\text{GeO}_2$  changed to a strong band at 520 to 600  $\text{cm}^{-1}$  on the formation of glass. We assign this band to vibrations of the local atomic configuration of amorphous germanium. The band centred at 720  $\text{cm}^{-1}$  is usually attributed to the tetragonal rutile structure of  $\text{GeO}_2$  which appeared in the present system at 730  $\text{cm}^{-1}$  [17]. The band at 260 to 320  $\text{cm}^{-1}$  is a lower shift from 340 and 350  $\text{cm}^{-1}$  of crystalline  $\text{GeO}_2$  and  $\text{TeO}_2$ , respectively, and this may be due to the combined

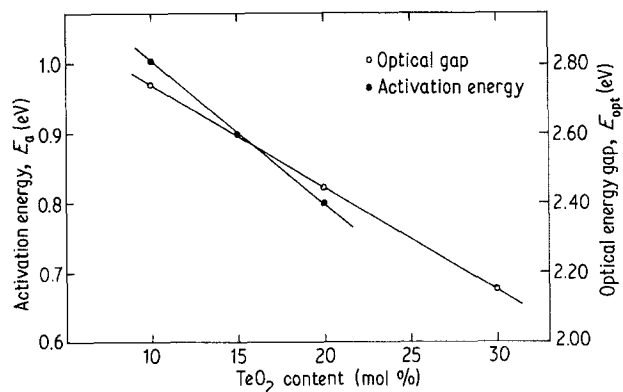


Figure 7 Dependence of activation energy and optical gap on the concentration of  $\text{TeO}_2$  in germanium-tellurium-oxide glasses.

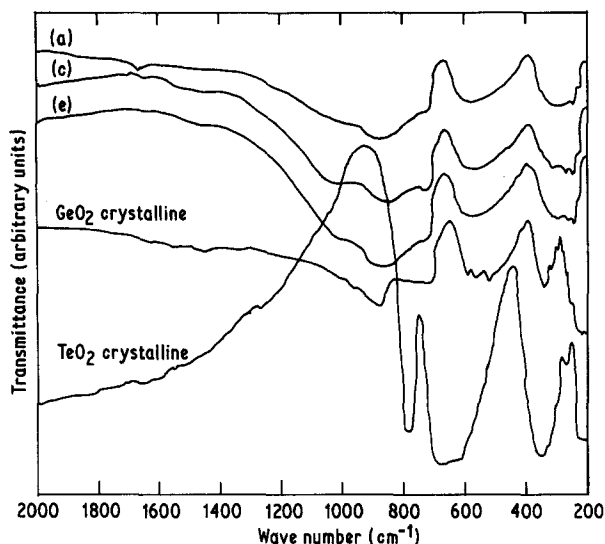


Figure 8 The infrared absorption spectra of  $\text{GeO}_2$ - $\text{TeO}_2$  glasses.

effect of both starting materials. It is seen that all the bands have broadened in going from the crystalline to the amorphous state. The structure of the glass varies very slightly as  $\text{GeO}_2$  bonds are replaced by  $\text{TeO}_2$  bonds in the germanate network. As the  $\text{TeO}_2$  content is increased, the continuous network breaks down because some of  $\text{Ge-O-Ge}$  bonds are broken in the formation of non-bridging oxygens, or on the other hand  $\text{TeO}_2$  tetrahedra probably form tellurite chains which are connected by  $\text{Ge-O-Te}$  bridges to the germanium chains in the glass network. Generally, in a glass which may itself be regarded as possessing a defect structure, it is reasonable to suppose that oxygen defect complexes are present. The  $\text{Ge-O}$  defect band should still persist but be less significant than in the film discussed by Tauc *et al.* [17].

## References

1. N. F. MOTT, *J. Non-Cryst. Solids* **1** (1968) 1.
2. I. G. AUSTIN and N. F. MOTT, *Adv. Phys.* **18** (1969) 41.
3. G. A. CHASE and C. J. PHILLIPS, *J. Amer. Ceram. Soc.* **49** (1964) 467.
4. Y. DIMITRIEV and V. DIMITROV, *Mater. Res. Bull.* **13** (1978) 1071.
5. Y. B. DIMITRIEV, M. R. MARINOV and E. M.

- GATTEFF, *Acad. Bulg. Sci.* **26** (1973) 675.
6. E. M. GATTEFF and Y. B. DIMITRIEV, *Phil. Mag.* **B40** (1979) 233.
7. R. MUNCASTER and S. PARKE, *J. Non-Cryst. Solids* **24** (1977) 399.
8. E. A. ZAMOTRINSKAYA and N. P. KULEWIN, *Izv. Vuz. Fiz. (USSR)* **7** (1969) 143.
9. V. S. KOZHOUHAROV and N. R. MARINOV, *Acad. Bulg. Sci.* **27** (1974) 577.
10. B. W. FLYNN, A. E. OWEN and J. M. ROBERTSON, Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, edited by W. E. Spear (CICL, Edinburgh, 1977) p. 679.
11. V. K. DHAWAN, A. MANSINGH and M. SAYER, *J. Non-Cryst. Solids* **51** (1982) 87.
12. M. M. AHMED and C. A. HOGARTH, *J. Mater. Sci.* **18** (1983) 3305.
13. R. A. NYQUIST and R. A. KAGEL, "Infra-red Spectra of Inorganic Compounds" (Academic Press, New York and London, 1971) pp. 212, 221.
14. Y. O. S. BOBOVICH and A. K. YAKHKIND, *J. Struct. Chem.* **4** (1963) 851.
15. M. K. MURTHY and E. M. KIRBY, *Phys. Chem. Glasses* **5** (1964) 144.
16. W. KAISER, P. H. KECK and C. F. LANGE, *Phys. Rev.* **101** (1956) 1265.
17. J. TAUC, A. ABRAHAM, R. ZALLEN and M. SLADE, *J. Non-Cryst. Solids* **4** (1970) 279.

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TABLE II Positions of infrared absorption bands in  $\text{GeO}_2$ - $\text{TeO}_2$  glasses

Glass	Infrared band positions ( $\text{cm}^{-1}$ )			
a	260-320	520-600	730	800-900
b	260-320	520-600	720	800-900
c	260-320	520-600	730	800-900
d	260-320	520-600	730	800-900
e	260-320	520-600	730	800-900
$\text{GeO}_2$	340	520, 560, 590	-	878
$\text{TeO}_2$	350	-	610-700	780