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Optical, infrared and electrical conductivity of glasses in the TeO_2–B_2O_3 system

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Infrared (IR) and optical absorption spectra were measured in order to study the structure of some tellurite glasses containing boric oxide. The compositions (mol%) were (100-X) TeO_2, XB_2O_3 where $X = 5, 10, 20, 25, 30$. The optical spectra were measured at room temperature in the wavelength range 350–450 nm, and the results show that the fundamental absorption edge is a function of composition, with the optical absorption due to indirect transitions. The optical band gap increases with increasing B_2O_3 content. The validity of the Urbach rule was investigated. The IR results prove the distribution of the TeO_4 polyhedra which determines the network and the basic oscillations of the building units in the tellurite glasses. The IR results also prove the distribution of the boroxal group. The electrical conductivity was measured as a function of temperature in the temperature range (300–573 K). Both the conductivity and activation energy were found to be a function of added oxide type.

1. Introduction

Tellurite glasses are considered to be important because of their optical and electrical properties, and as potential optical CD memory devices. In tellurite glasses, the main glass-former is tellurium oxide (TeO_2), which under normal conditions does not have the ability to transform into the glassy state without a modifier [1]. Recently there has been a considerable interest in semiconducting glasses in which tellurium oxide is a glass forming factor [2, 3]. The distinguishing factor about the matrix of this glass is that the tellurium atoms have unshared pairs of electrons which do not take part in bonding. On the other hand, their relatively low temperature of crystallization and melting [4] makes these types of glass an active candidate for CD memory devices. The glasses of the binary system TeO_2–B_2O_3 studied in this work belong to a group of multicomponent glasses with extreme optical properties.

The composition range between 5 and 30 mol % B_2O_3 is characterized by crystal-free, homogeneous, clear and colourless glasses which are formed by the method of hammer and anvil. [5] By this method, the glass-forming region can be extended by between 5 and 30 mol % B_2O_3, extending the region (11–26.5 mol % B_2O_3) previously reported [6].

The study of the optical absorption spectra has been one of the most productive methods in developing and understanding the band structure and energy gap of amorphous non-metallic materials. Measurement of the optical absorption coefficient, particularly near the fundamental absorption edge, provides a standard method for the investigation of optically induced electronic transitions. The fundamental absorption edges in such solids are less abrupt. Generally, the absorption coefficient $\alpha(w)$ in the optical region near the band edge in many amorphous semiconductors shows an exponential dependence on photon energy ($\hbar w$) and obeys an empirical relation due to Urbach [7],

$$\alpha(w) = \alpha_0 \exp(\hbar w/E_e) \qquad (1)$$

where w is the angular frequency of radiation, α_0 is a constant, and E_e is related to the width of the tail of localized states in the band gap.

Different suggestions about the band tail have been made. Tauc [8] believes that the exponential variation of α with $\hbar w$ is due to transitions between localized states and will vary from sample to sample, whereas Davis and Mott [9] assumed that the value of E_e will be much the same for most amorphous semiconductors. Tauc *et al.* [10] and Davis and Mott [9] gave an equation, derived independently, for the absorption coefficient $\alpha(w)$ as a function of photon energy in an amorphous material:

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

where B is a constant, E_{opt} is the optical band gap of the material, and the exponent M may take the value of 2 for an indirect allowed transition, 1/2 for a direct allowed transition, 3/2 for a direct forbidden transition, and 3 for indirect forbidden transition.

Equation 2 with $M = 2$ seems to offer the best fit for the optical absorption data in many amorphous or glassy materials, and indeed it has been applied to estimate the optical band gap in many tellurite glasses [11–15]. It has also recently been successfully applied to other glasses [16, 17]. The electrical conduction process is carried out by electrons in these tellurite glasses because the tellurium atoms have unshared pairs of electrons which do not take part in bonding [1].

The aim of the present work is to study the effect of the added B_2O_3 oxide on the optical and electrical properties at room temperature and at high temperatures. IR absorption spectra were measured to give an idea about the structure of these tellurite glasses. The infrared spectra of tellurite glasses have been measured by many previous workers [1, 13, 14, 18, 19].

2. Experimental procedure

In the glass-forming region of the system, B_2O_3–TeO_2 glasses were prepared with 95, 90, 80, 75, and 70 mol % TeO_2. The preparations were carried out with extremely pure substances (TeO_2 p.a. and H_3BO_3 p.a.) melted in platinum crucible at 800 °C, where the melt was stirred from time to time. The melts were sudden-quenched using the hammer and anvil technique (sudden impact of the melt). The final glass samples were homogeneous, clear and colourless glasses. The glassy nature was confirmed by X-ray diffraction (XRD), as well as by visual inspection.

The optical absorption of the glasses was measured at room temperature in the wavelength range from 350 to 450 nm, using a varian model DMS 100 S double-beam spectrophotometer. Samples of each composition, but of different thicknesses, were measured so that reflection effects could be eliminated. The d.c. conductivity measurements were made in the temperature range from room temperature up to 573 K, and the IV characteristics were found to be linear, using the two-probe method. The infrared absorption spectra were measured as usual using KBr discs, and a Unicam SP300 double-beam infrared spectrophotometer in the frequency range 200–4000 cm^{-1}. The spectra are shown in the range of 200–1500 cm^{-1} as there are no measurable bands above this range.

3. Results and discussion

XRD patterns for the 95, 70 mol % TeO_2 glass samples are shown in Fig. 1. It is clear from this figure that no clear, sharp diffraction lines are present, confirming the amorphous nature of the samples, although traces of crystalline impurity could be observed. Fig. 2 shows optical absorption spectra of different thicknesses and having the same composition as the binary TeO_2–B_2O_3 glasses. It may be seen that there is no sharp absorption edge, as could be expected to be characteristic of the glassy network, but there is a shift of the absorption edge to higher wavelengths as the thickness of the sample is increased.

Fig. 3 shows the optical absorption spectra of binary TeO_2–B_2O_3 glasses of different compositions, of thickness 1.4 and 0.8 mm. It may be seen that there is no sharp absorption edge, but there is a shift of the absorption edge to lower wavelengths as the B_2O_3 content was increased. The reflectivity, R, of glasses is considerable and is independent of sample thickness. Even without a knowledge of R, the absorption coefficient, $\alpha(w)$, can be estimated from the absorbance, A, measured for two specimens of the same composition but having different thickness, from

$$\alpha(\lambda) = 2.303 \frac{A_1(\lambda) - A_2(\lambda)}{d_1 - d_2} \tag{3}$$

where A_1 and A_2 are the absorption at a given wavelength, λ, of the two samples of thicknesses d_1 and d_2, respectively. The absorbance is defined by

$$A = \ln(I_0/I_t)$$

where I_0 and I_t are the intensities of the incident and transmitted light, respectively.

The usual method for determining the value of E_{opt} involves plotting a graph of $(\alpha\hbar w)^M$ against photon energy, as given by Equation 2. If the appropriate values of M have been used, the graph is a straight line and the other value of E_{opt} is given by the intercept on the photon energy axis. Fig. 4 presents plots of $(\alpha\hbar w)^{1/2}$ for the data given in Figs 2 and 3 and, as expected from Equation 2, these are linear at the higher values of $\alpha(w)$ but tend to deviate from linearity at low photon energies. These graphs extrapolated to the $\hbar w$ axis give the values of E_{opt} which are given in Table I and Fig. 5 where it may be seen that E_{opt} increases as the B_2O_3 content in the binary system increases from 5 to 30 mol %.

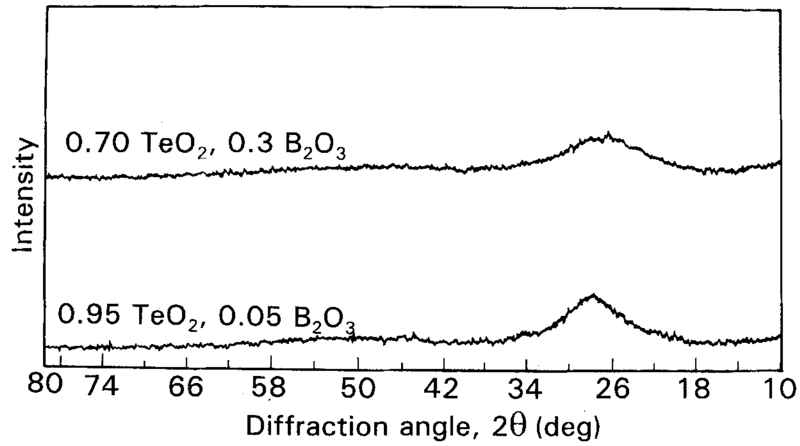

Figure 1 XRD patterns of TeO_2–B_2O_3 glasses.

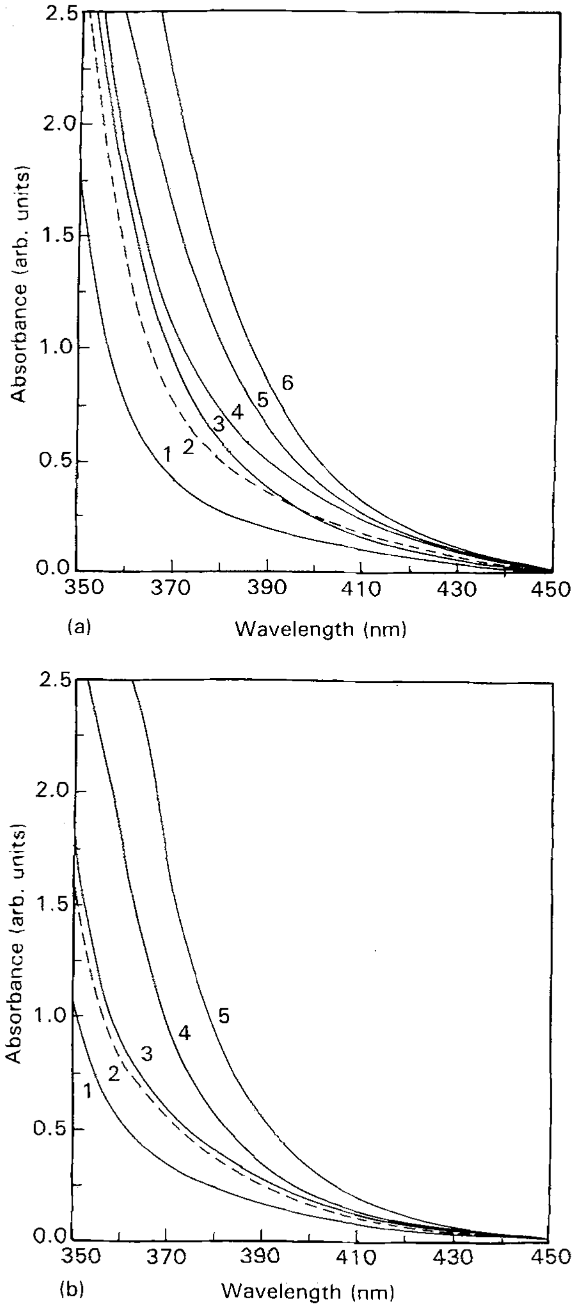

Figure 2 Optical absorption spectra of binary TeO_2–B_2O_3 glasses having different thickness and composition. (a) 0.75 TeO_2–0.25 B_2O_3 (curves 1, 2 and4) and 0.90 TeO_2–0.1 B_2O_3 (curves 3, 5 and 6). d = 1, 0.53; 2, 0.82; 3, 0.96; 4, 0.52; 5, 0.83 mm. (b) 0.7 TeO_2–0.3 B_2O_3 (curves 1, 2 and 3) and 0.95 TeO_2–0.05 B_2O_3 (curves 4, 5 and 6). d = 1, 0.82; 2, 1.43; 3, 0.82; 4, 1.77; 5, 1.27, 6, 2.04 mm.

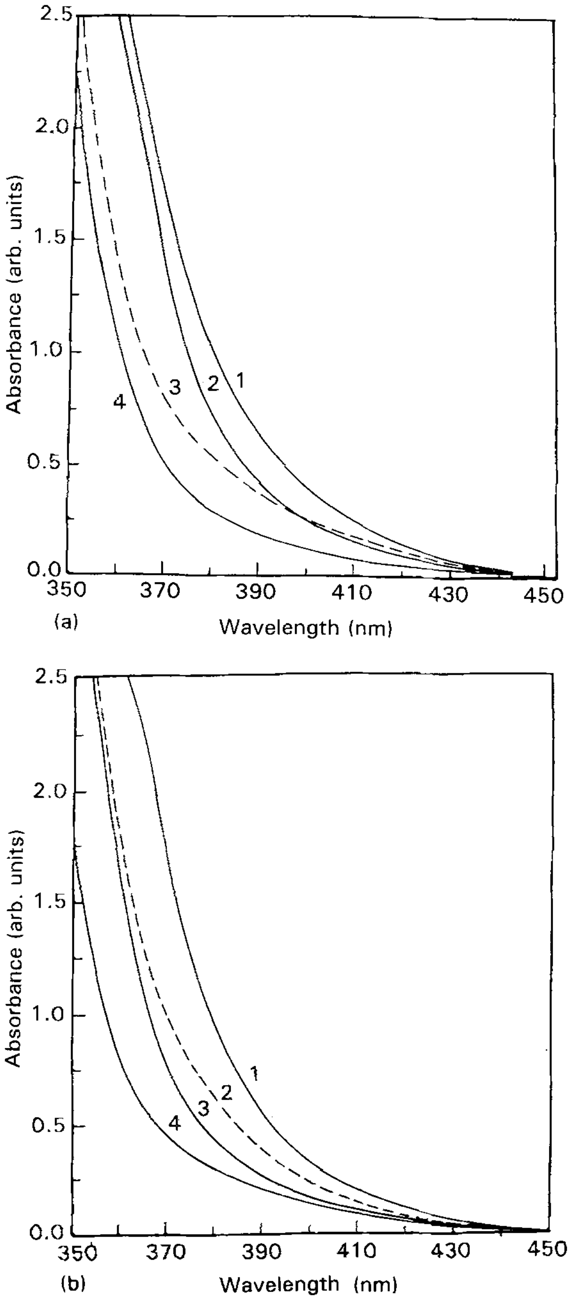

Figure 3 Optical absorption spectra of $(0.95 - x)TeO_2$–XB_2O_3 having different composition. (a) Thickness = 1.4 mm; X = 1, 0.10; 2, 0.20; 3, 0.25; 4, 0.30 B_2O_3. (b) Thickness = 0.8 mm; X = 1, 0.05; 2, 0.10; 3, 0.20; 4, 0.25 B_2O_3.

Stevels [20] and McSwain *et al.* [21] suggested that the shift to lower energies or a change in the absorption band characteristics could be related to a transition to non-bridging oxygens which bind excited electrons less tightly than bridging oxygens. It has been suggested [19–22] that, in tellurite glasses with high TeO_2 contents, the TeO_4 triangular bipyramid is the basic coordination polyhedron. In this configuration, tellurium atoms are surrounded by four oxygens each connected to two tellurium atoms, creating an axial equatorial bonding in which the bonds can easily be deformed. This change in the $Te{-}_{ax}O_{eq}{-}Te$ angle takes place along the C axis through the incorporation of the modifier into the structure, which creates defects and oxygen vacancies and also increases the number of non-bridging oxygens. However the glasses of the binary system TeO_2–B_2O_3 show a behaviour different from those of the glasses of the binary system TeO_2–GeO_2 [15]; it is evident from Fig. 5 that the optical energy gap increases with increasing B_2O_3 content and this may be attributed to the decreased disorder which is a direct consequence of the decrease of non-bridging oxygens as the B_2O_3 content increases, where the number of BO_3 groups increases with increasing B_2O_3 content [23], assuming the existence of BO_3 units only with all bridging oxygens [6].

The values of the Urbach energy (E_e) and the width of the band tail for the glass composition shown in Figs 2 and 3, calculated from plots of ln α against $\alpha\hbar w$

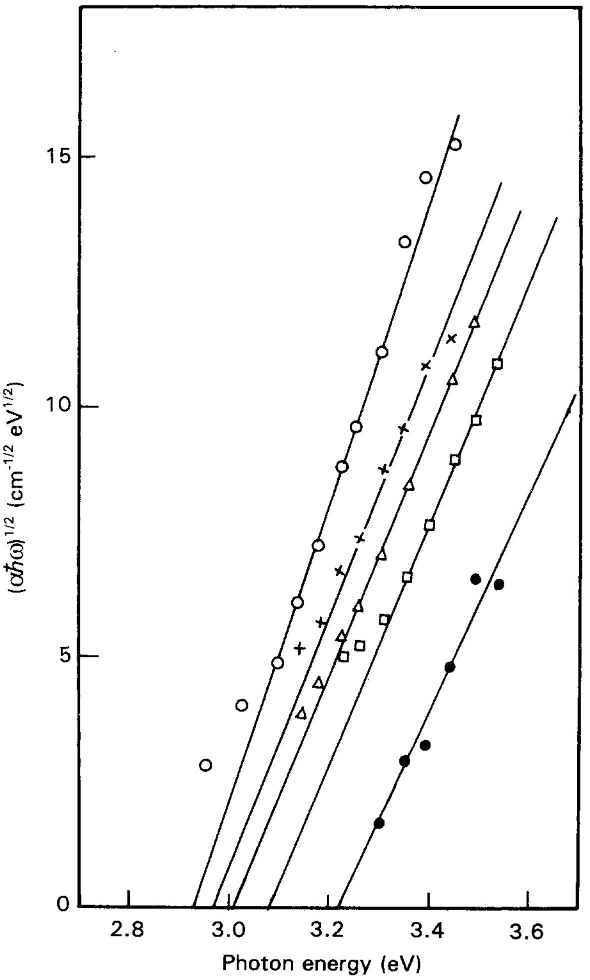

Figure 4 Data of Figs 2 and 3 replotted in accordance with the theory of indirect transitions. ○, 0.95 TeO_2–0.05 B_2O_3; X, 0.90 TeO_2–0.10 B_2O_3; △, 0.80 TeO_2–0.20 B_2O_3; □ 0.75 TeO_2 –0.25 B_2O_3; ●, 0.70 TeO_2–0.30 B_2O_3.

TABLE I The effect of added B_2O_3 on optical and electrical properties of binary TeO_2–B_2O_3 glasses

Glass composition	E_{opt}/(eV)	E_e/(eV)	E_i/(eV)
0.95 TeO_2–0.05 B_2O_3	2.93	0.120	0.726
0.90 TeO_2–0.1 B_2O_3	2.97	0.140	0.684
0.8 TeO_2–0.2 B_2O_3	3.01	0.144	0.633
0.75 TeO_2–0.25 B_2O_3	3.08	0.222	0.594
0.70 TeO_2–0.30 B_2O_3	3.22	0.212	0.554

(Fig. 6) are also given in Table I. From this Table it is clear that there is a systematic change in E_{opt} and E_e with composition, suggesting that the degree of disorder in these systems is decreased as the BO_3 increases. This supports the theory of Mott and Davis [24] which suggests that the extent of the localized states near the mobility edge decreases as the disorder in the amorphous structure decreases.

3.1. Electrical conductivity

The electrical resistivity, ρ, of the glasses of the binary system TeO_2–B_2O_3 were measured as a function of temperature T from 300 up to 573 K. Fig. 7 presents plots of ln ρ against $1/T$ from which it is clear that there is an increase in the electrical conduction of the glasses

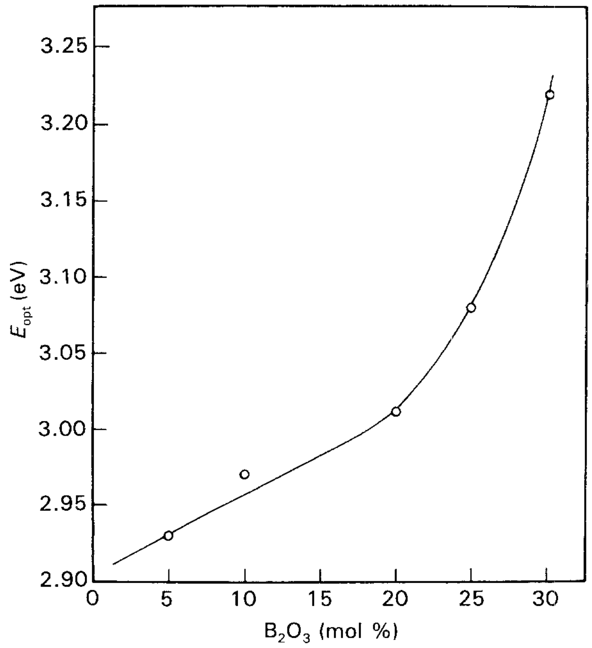

Figure 5 Optical band gap (E_{opt}) as a function of B_2O_3 content (data derived from Fig. 4).

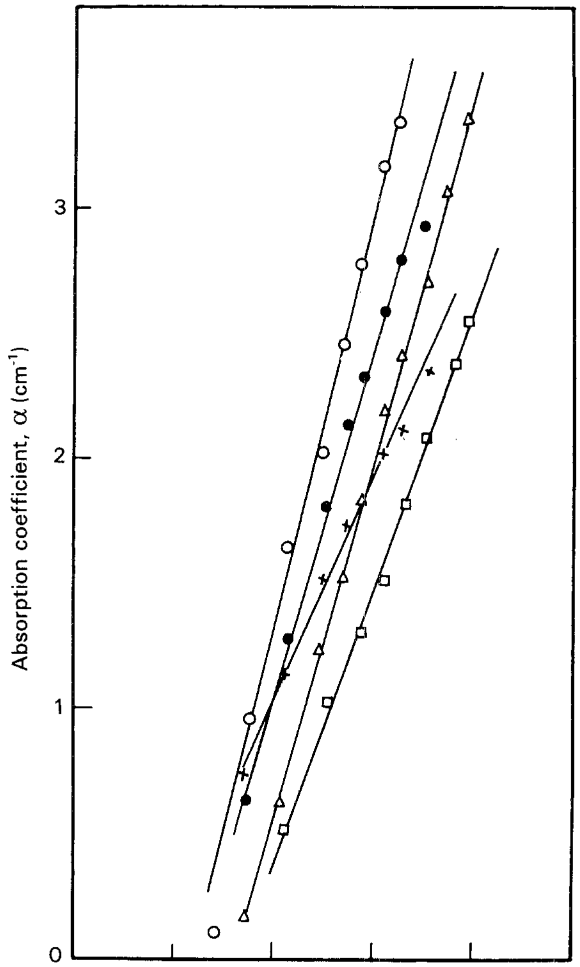

Figure 6 Optical absorption edges of the glass samples replotted in accordance with the Urbach rule. X = ○, 0.05; ●, 0.10; △, 0.20; ×, 0.25; □, 0.30.

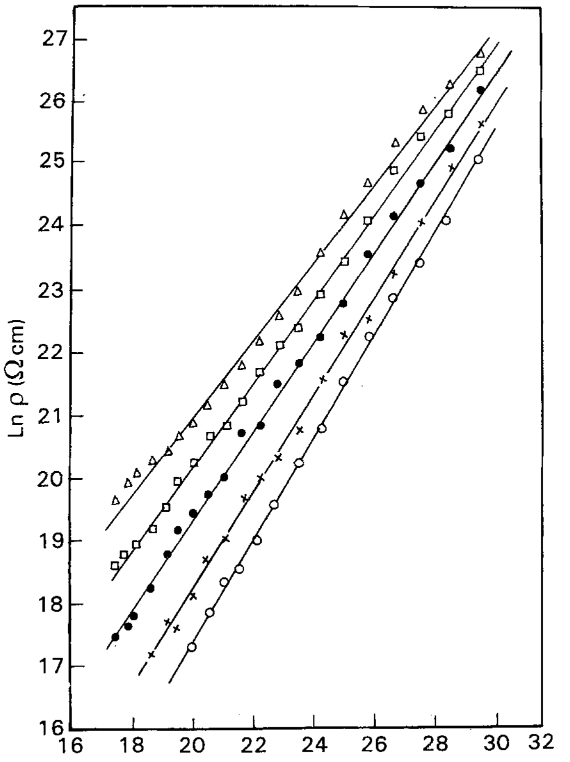

Figure 7 Temperature dependence of the conductivity of $(0.95\text{-}X)TeO_2\text{-}B_2O_3$ glasses. △, 0.95 Te_2O_3–0.05 B_2O_3; □, 0.90 Te_2O_3–0.10 B_2O_3; ●, 0.80 Te_2O_3–0.20 B_2O_3; ×, 0.75 Te_2O_3–0.25 B_2O_3; ○, 0.70 Te_2O_3–0.30 B_2O_3.

with increasing temperature, and on introducing B_2O_3 oxide to the glass a large increase in resistivity is detected. It is also observed that the measurements follow the Arrhenius relation in its simplest form. On the other hand, the activation energies of these glasses were calculated and plotted against B_2O_3 content as shown in Fig. 8. The results show that the activation energy decreases with an increase in B_2O_3 content. Accordingly, we may say that the electrical conduction process is carried out by electrons in these tellurite glasses, where the tellurium network must play the decisive role in electrical conductivity due to the free electron pair of the tellurium atom.

There is agreement between the present results and those reported previously by Ahmed *et al.* [11] that the optical gap is found to decrease with increasing TeO_2 content, and is 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 for the present electrical conductivity results.

3.2. Infrared measurements

The infrared absorption spectra of TeO_2–B_2O_3 glasses are quite similar in shape to those in Fig. 9. The broadening of the bands confirms the amorphous nature of the samples. The IR spectra of TeO_2–B_2O_3 glasses show broad bands at 630 and 330 cm^{-1} and a shoulder at 780 cm^{-1} which could be attributed to the distribution of the TeO_4 polyhedra [25] determining the form of the network and the basic oscillation of the building units in this type of tellurite glass.

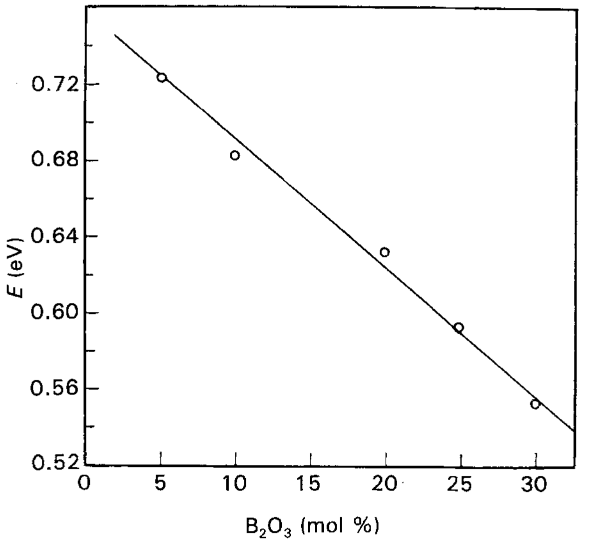

Figure 8 Dependence of electrical activation energy on B_2O_3 content.

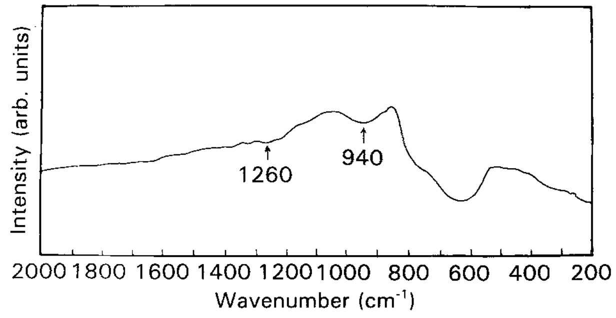

Figure 9 Infrared absorption spectra of 0.95 TeO_2–0.05 B_2O_3 glass.

The IR spectra show two other broad bands at 940 and 1260 cm^{-1}. The 940 cm^{-1} band is due to B–O vibration linkage [26] in BO_4; the 1260 cm^{-1} band involves the vibration of a B–O–B bond constituting the linkage of the boroxol group to neighbouring groups.

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