

# Optical properties of ternary tellurite glasses

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Test samples of ternary glass tellurite  $[(\text{TeO}_2)_{65}(\text{B}_2\text{O}_3)_{35}]_y[\text{Ag}_2\text{O}]_y$  with  $y = 10, 15, 20, 25, 30$  mol % have been fabricated and their physical and optical properties were investigated. The optical absorption was recorded at room temperature in the wavelength range from 200 to 800 nm. From the absorption edge data, the value of the optical band gap  $E_{\text{opt}}$  and the Urbach energy  $\Delta E$  were evaluated. The value of  $E_{\text{opt}}$  lies between 2.15 eV and 1.85 eV for the indirect transition and for direct transition the values vary from 2.77 eV to 2.35 eV. From the experimental results, values of the optical band gap and Urbach energy were calculated. They were found to be dependent on the glass composition.

Keywords: *tellurite glasses; optical band gap; Urbach energy; density*

## 1. Introduction

Glasses have some unique properties such as high hardness and transparency at room temperature, along with sufficient strength and excellent corrosion resistance. Due to potential applications in various engineering and technological fields, the study of the properties of glasses is of great significance. Glassy materials have acknowledged advantages, like physical isotropy, the absence of grain boundaries, continuously variable composition they are practical to use [1].

Tellurite glasses are very promising materials for laser and non-linear applications in optics, due to some of their important characteristic features, such as high refractive index, low phonon maxima and low melting point [2].  $\text{TeO}_2$  is known as a conditional glass former; it needs a modifier ion to form the glassy state easily. The formation of glass on two glass formers such as borate glass and tellurite glass is of both scientific and practical interest. This may lead to the formation of new structural units [3]. The basic structural unit of tellurite glass is  $\text{TeO}_4$  trigonal bipyramid (tbp) containing a lone pair of electrons and the structural units take the Te–O–Te bond for glass formation. The introduction of  $\text{TeO}_2$  into the matrix of alkali borate glasses decreases its

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hygroscopicity, improves the quality of the glass (less brittle and free from bubbles) and enhances the IR transmission [4, 5]. Silver dioxide,  $\text{Ag}_2\text{O}$  in the borotellurite network modifies the host structure through the transformation of the structural units of the borate network from  $[\text{BO}_3]$  to  $[\text{BO}_4]$  and tellurite network from trigonal bipyramid  $[\text{TeO}_4]$  to trigonal pyramid  $[\text{TeO}_3]$ [6].

The objective of the present work was to study the optical band gap of the silver borotellurite glass system. A systematic study has been performed on the variation of the optical band gap in function of the  $\text{Ag}_2\text{O}$  composition in borotellurite glasses. Densities were also determined, in order to investigate the correlation between density and molar volume in function of  $\text{Ag}_2\text{O}$  content in the silver borotellurite glass.

## 2. Experimental

The ternary  $[(\text{TeO}_2)_{65} (\text{B}_2\text{O}_3)_{35}]_{1-y}(\text{Ag}_2\text{O})_y$  glasses were prepared by mixing together tellurium dioxide (Aldrich 99.5%), boron oxide  $\text{B}_2\text{O}_3$  (Alfa Aesar, 97.5%) and silver dioxide  $\text{Ag}_2\text{O}$  (Aldrich 99%), in a closed alumina crucible,  $y$  being 10, 15, 20, 25 and 30 mol %. Appropriate amounts of powder chemicals were weighed and placed in a crucible. The crucible was covered with a lid and then put inside an electric furnace set at 400 °C. The mixture was maintained at 400 °C for 30 min, the crucible was then transferred to another furnace for 60 min at 800 °C. The crucible was constantly stirred in order to obtain a homogeneous melt. The melt was then poured into a stainless steel, cylindrically shaped split mould which had been preheated, and then the sample was annealed at 350 °C. The samples were cut into pieces having appropriate dimensions for optical absorption and density measurements.

Optical absorption measurements in the wavelength range of 200–800 nm were performed at room temperature using a Camspec M350 double beam UV-visible spectrophotometer. The optical absorption coefficient  $\alpha(\lambda)$  was calculated from the absorbance  $A$ , using the following equation

$$\alpha(\lambda) = 2.303 \frac{A}{d} \quad (1)$$

where  $d$  is the sample thickness. Density measurements were made at room temperature based on Archimedes' Principle, involving weighing in air and in acetone as the buoyancy liquid. The samples were ground into powder for X-ray diffraction measurements, using an X'pert Pro Panalytical mill.

## 3. Results and discussion

The X-ray diffraction patterns of the studied glass system revealed the absence of any discrete or sharp crystalline peaks, indicating that the samples are amorphous (Fig. 1).

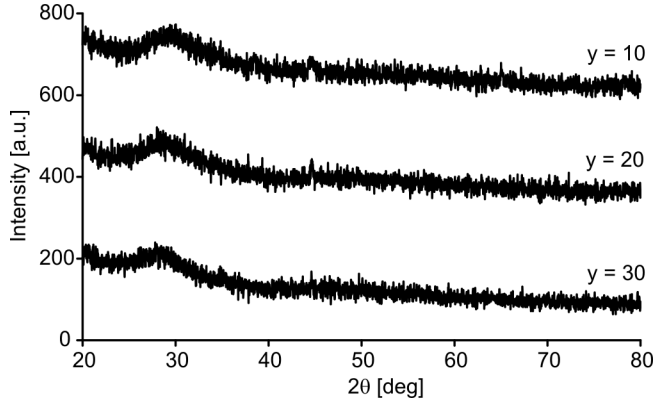


Fig. 1. XRD spectrum of  $[(\text{TeO}_2)_{65} (\text{B}_2\text{O}_3)_{35}]_{1-y} [\text{Ag}_2\text{O}]_y$  glasses

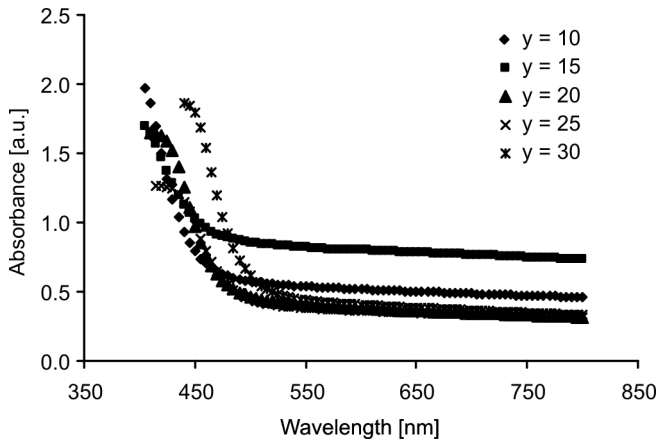


Fig. 2. Optical absorbance spectra of  $[(\text{TeO}_2)_{65} (\text{B}_2\text{O}_3)_{35}]_{1-y} [\text{Ag}_2\text{O}]_y$  glasses

The optical absorption spectra of  $\text{Ag}_2\text{O}-\text{TeO}_2-\text{B}_2\text{O}_3$  are shown in Fig. 2. They do not display any sharp absorption edges, which is characteristic of the glassy state. As the X-ray diffraction spectra, they also show no distinguishable peaks or sharp lines but the pattern does exhibit a broad hump, which shows that the samples are essentially amorphous rather than crystalline (Fig. 1). It is also observed in Figure 2 that the fundamental absorption edge shifts to higher wavelengths as the concentration of  $\text{Ag}_2\text{O}$  increases. This may be due to the lower rigidity of the glass resulting from higher  $\text{Ag}_2\text{O}$  content. The data in Figs. 3 and 4 were obtained from the equation:

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

where  $E_{\text{opt}}$  is the energy of the optical band gap and  $\hbar\omega$  is the photon energy. The values of  $n$  are 1/2 and 2 for the direct and indirect transitions, respectively. Both these

band gaps obtained from the above dependences are interband transitions, but the latter involves the phonon interaction. In order to check whether optical data on the present glasses fit better to the direct or indirect band gap formula; dependences  $(\alpha\hbar\omega)^2$  on  $\hbar\omega$  as well as  $(\alpha\hbar\omega)^{1/2}$  on  $\hbar\omega$  have been plotted in the absorption region for which the absorption  $\alpha(\omega) \geq 10^4 \text{ cm}^{-1}$  as shown in Figs. 3 and 4.

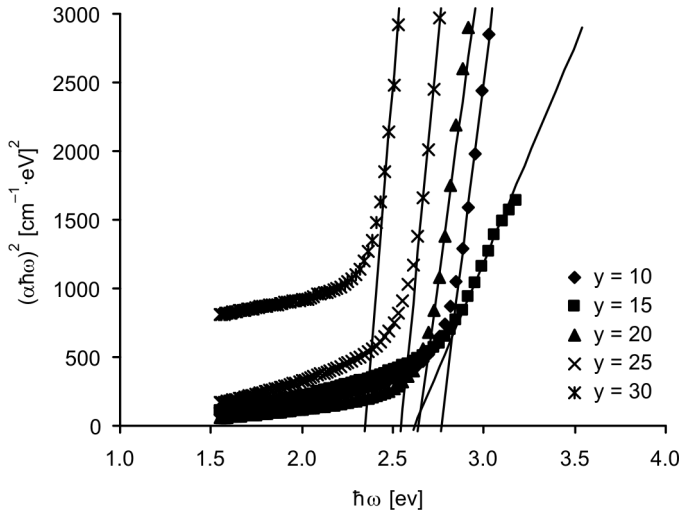


Fig. 3. Plot of  $(\alpha\hbar\omega)^2$  against photon energy for direct band gap measurement in  $[(\text{TeO}_2)_{65} (\text{B}_2\text{O}_3)_{35}]_{1-y}[\text{Ag}_2\text{O}]_y$  glasses

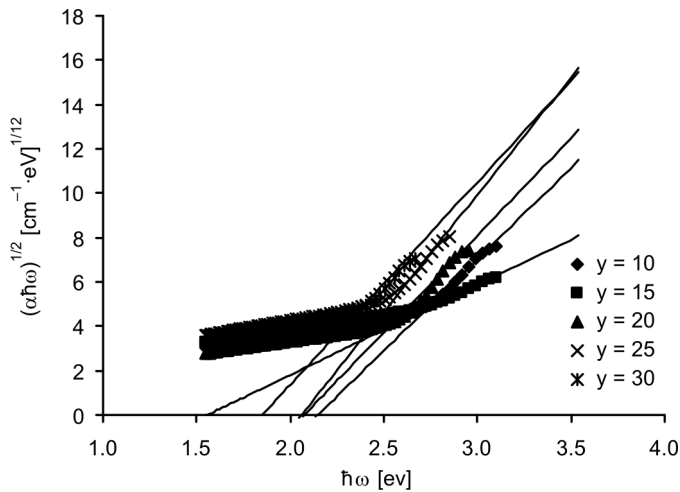


Fig. 4. Plot of  $(\alpha\hbar\omega)^{1/2}$  against photon energy for indirect band gap measurement in  $[(\text{TeO}_2)_{65} (\text{B}_2\text{O}_3)_{35}]_{1-y}[\text{Ag}_2\text{O}]_y$  glasses

The direct and the indirect energy band gaps are determined from the linear regions of the data plots, as shown in the figures, and the corresponding values are pre-

sented in Table 1. The values for the optical band gaps lie between 1.85 eV and 2.37 eV for  $n = 2$ , whereas for  $n = 1/2$  they lie between 2.35 eV and 2.82 eV.

Table 1. Results of optical measurements in  $[(\text{TeO}_2)_{65}(\text{B}_2\text{O}_3)_{35}]_{1-y}[\text{Ag}_2\text{O}]_y$  glasses

| $y$<br>[mol %]<br>$x = 65$ | Direct<br>transition<br>$E_{\text{opt}}^1$ [eV] | Indirect<br>transition<br>$E_{\text{opt}}^2$ [eV] | Urbach<br>energy<br>$\Delta E$ [eV] |
|----------------------------|---|---|-------------------------------------|
| 10                         | 2.77  | 2.15  | 0.37                                |
| 15                         | 2.62  | 2.06  | 0.43                                |
| 20                         | 2.64  | 2.07  | 0.40                                |
| 25                         | 2.55  | 2.06  | 0.45                                |
| 30                         | 2.35  | 1.85  | 0.48                                |

The optical band gaps for direct and indirect transitions for this ternary tellurite system both decrease as the  $\text{Ag}_2\text{O}$  content increases, as shown in Fig. 5.

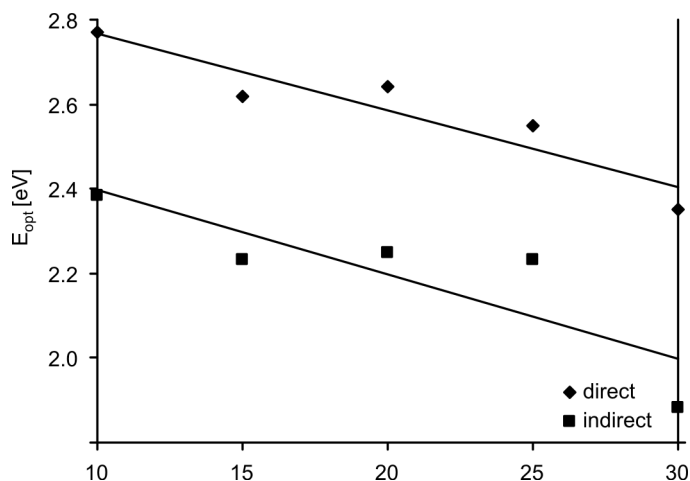


Fig. 5. Dependences of optical band gap on molar percentage of  $\text{Ag}_2\text{O}$  for direct and indirect transitions in  $[(\text{TeO}_2)_{65}(\text{B}_2\text{O}_3)_{35}]_{1-y}[\text{Ag}_2\text{O}]_y$  glasses

This behaviour may be associated with the structural changes occurring after addition of  $\text{Ag}_2\text{O}$ . In binary tellurite, non bridging oxygen atoms are already present, and with the addition of  $\text{Ag}_2\text{O}$  as a modifier, their concentration increases. The glass structure becomes less ordered; addition of  $\text{Ag}_2\text{O}$  causes breaking of the regular structure of borate and tellurite, leading to a decrease of the band gap [7]. The values of the obtained band gaps of tellurite glasses are quite close to the values reported in the literature [8, 9]. This decrease is due to an increase of the disorder and consequently the more extension of the localized states within the gap according to Mott and Davies [10].

From Table 1 and Figure 5, it is observed that the values of the direct band gap are larger than the corresponding values of the indirect band gap. For this ternary tellurite glass system, there are two optical transitions in  $k$  space. Assuming that the lowest minimum of the conduction band and the highest maximum of the valence band lie in different regions of the  $k$  space, direct allowed transitions may occur, as shown in Fig. 6, and the observed indirect transition may be associated with transitions from the top of the valence band to the bottom of the conduction band [11].

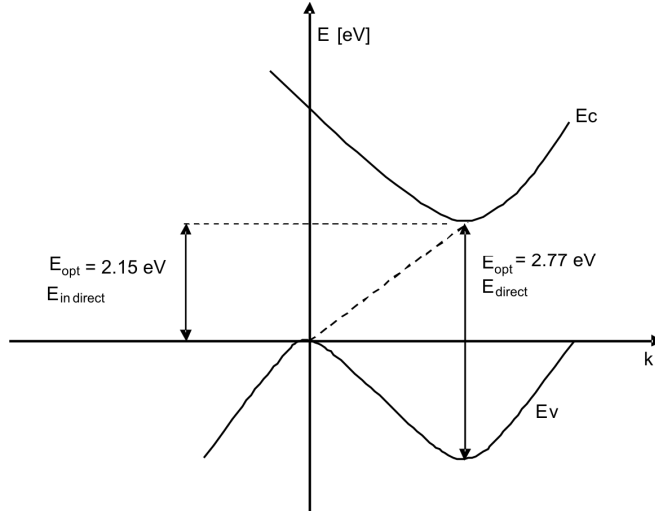


Fig. 6. Suggested energy band diagram (electron energy  $E$  against wave vector  $k$  in  $[(\text{TeO}_2)_{65}(\text{B}_2\text{O}_3)_{35}]_{1-y}[\text{Ag}_2\text{O}]_y$  glasses

The fundamental absorption edge usually follows the Urbach rule [3]

$$\alpha(\omega) = B \exp\left(\frac{\hbar\omega}{\Delta E}\right) \quad (3)$$

where  $B$  is a constant,  $\Delta E$  is a measure of the band tailing and is known as the Urbach energy. The values of the Urbach energy  $\Delta E$  were calculated by taking the reciprocals of the slopes of the linear portion of the  $\ln\alpha(\omega)$  versus  $\hbar\omega$  curves in the lower photon energy regions. These values are given in Table 1.

The values of the Urbach energy increase as the quantity of  $\text{Ag}_2\text{O}$  increases (Fig. 7). An increase in the Urbach energy can be considered being due to a higher number of defects [12]. Hence, the increase in the Urbach energy with  $\text{Ag}_2\text{O}$  content confirms that the number of defects also increases. Mott and Davies [10] reported that the values of  $\Delta E$  for a range of amorphous semiconductors are very close and the range of their values is between 0.046 eV and 0.066 eV. The  $\Delta E$  value of  $\text{Na}_2\text{O}-\text{TeO}_2$  glasses is reported by Prakash et al. [2] to lie between 0.09 eV and 0.26 eV, and in the case of  $\text{V}_2\text{O}_5-\text{P}_2\text{O}_5-\text{TeO}_2$  glasses, Hogarth [8] reported that the value of  $\Delta E$  varies between 0.31 eV to 0.41 eV. In the present work, the exponential behaviour is ob-

served and the value of  $\Delta E$  varies between 0.37 eV and 0.48 eV. The obtained optical band gap energies are of the order reported in the literature, and the Urbach energy values are in the same range as that reported for tellurite glasses [13].

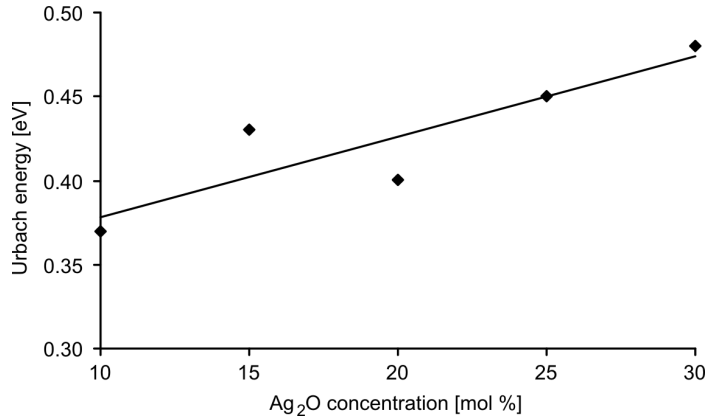


Fig. 7. Dependence of Urbach energy on molar percentage of Ag<sub>2</sub>O in [(TeO<sub>2</sub>)<sub>65</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>35</sub>]<sub>1-y</sub>[Ag<sub>2</sub>O]<sub>y</sub> glasses

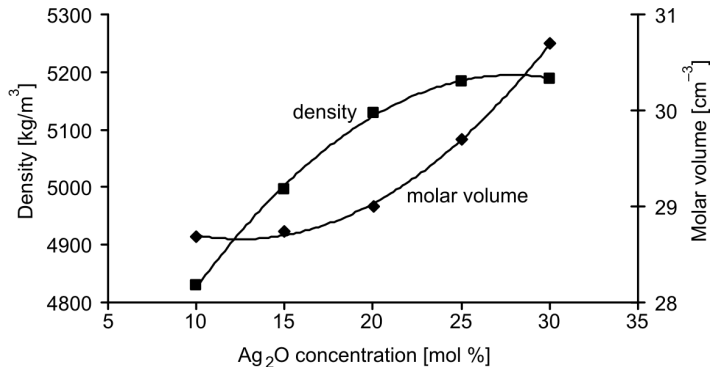


Fig. 8. Density and molar volume of [(TeO<sub>2</sub>)<sub>65</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>35</sub>]<sub>1-y</sub>[Ag<sub>2</sub>O]<sub>y</sub> glasses

The dependences of density and molar volume of [(TeO<sub>2</sub>)<sub>65</sub>(B<sub>2</sub>O<sub>3</sub>)<sub>35</sub>]<sub>1-y</sub>[Ag<sub>2</sub>O]<sub>y</sub> glasses on Ag<sub>2</sub>O content are shown in Fig. 8. They both increase as the molar percentage of Ag<sub>2</sub>O increases. The atomic weight of TeO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> is 229.2 g and the atomic weight of Ag<sub>2</sub>O is 231.7 g, the replacement of the borotellurite atom with the silver atom is explained by the increase in the density resulting from the increase in the content of Ag<sub>2</sub>O. Generally, the density and the molar volume show opposite behaviours, but in this work it is not the case. This anomalous behaviour was shown in a study by Rajendran et al. [3] and Saddeek and Abdul El-Latif [14]. The increase in the molar volume, resulting from the presence of non-bridging oxygen atoms (NBO) causes bond breaking, and thereby leads to an increase in the number of spaces in the network [14]. The observed increase in the molar volume may be due to an increase in

the bond length or an increase in the interatomic spacing between the atoms. The values of the molar volume of the ternary tellurite glass system lie in the same range as those reported by El-Mallawany [15] for the tellurite glasses.

## 4. Conclusions

The ternary tellurite glass system  $[(\text{TeO}_2)_{65}(\text{B}_2\text{O}_3)_{35}]_{1-y}(\text{Ag}_2\text{O})_y$  was fabricated. The optical band gap values have been determined and from the theoretical fitting of the experimental absorption coefficient for all samples, it is concluded that both direct and indirect transitions occur. For both transition types, the values of the optical band gap, are found to decrease as the amount of  $\text{Ag}_2\text{O}$  increases. The Urbach energy is found to be between 0.37 eV and 0.48 eV. Urbach edge behaviour is observed in these glasses, and the slope of the edge was found to increase as the amount of  $\text{Ag}_2\text{O}$  increases. The density depends on the composition: the greater the compactness of the structure, the higher the density.

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## References

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