

A study of the optical absorption edge in silicate glasses containing TiO₂ oxide

A. A. HIGAZY, A. HUSSEIN, M. A. AWALDA

Physics Department, Faculty of Science, El-Menoufia University, Shebin El-Koam, Egypt

A detailed study of the optical absorption as a function of temperature and composition for a series of soda–lime–silica glasses doped with TiO₂ oxide is presented. The variations of the optical energy gap with temperature in the range 296 to 483 K are reported. The UV results are analysed assuming optical absorption by indirect transitions. It was found from these optical absorption data that the present glass system can be divided into three compositional regions.

1. Introduction

The study of the variation of optical absorption spectra in solids or liquids with photon energy, temperature and composition provides essential information on phonon and electron states in a material. Analysis of these absorption spectra in the lower energy part gives information about the atomic vibrations, and higher energy part of the spectrum gives a knowledge about electronic states in the normal material.

Optical absorption in solids or liquids can occur by various mechanisms, all of which involve coupling of the electric vector of incident radiation to dipole moments in the materials and a consequent transfer of energy results. In general there are three kinds of absorption.

(i) Free carrier absorption, which is observed in metals and semiconductors whenever there is a sufficient density of free carriers (n) in a single band.

(ii) Lattice absorption, which gives rise to absorption of radiation normally in the infra-red region of the spectrum. This kind of absorption can occur in covalent materials under “single-phonon” processes, and in ionic and covalent crystals under “multi-phonon” processes.

(iii) Electronic interband absorption, in which the electron is excited from a filled to an empty state by photon absorption which is very important in semiconductors.

In fact there are uncertainties concerning the nature of the exponential absorption edges in amorphous semiconductors. Many attempts [1–7] have been made to explain the exact nature of the physical origin of the absorption edge. Dow and Red Field [2] have suggested that this exponential absorption edge may arise from the random fluctuations of the internal fields associated with structural disorder in many amorphous solids. Tauc [3] has suggested that such an edge can arise from interband transitions involving the tails of the localized states where the density of states falls off exponentially with energy. At a photon energy higher than that of which the exponential behaviour is observed in chalcogenide glasses, which do not exhibit exponential absorption edges, the absorption occurs by the excitation of electrons across the gap into the band. Davis and Mott [5] reported that the density of states at the band edges is a linear function of the energy. Their assumptions are different from those of Tauc, mentioned above.

For many amorphous materials an exponential dependence of absorption coefficient on photon energy $\hbar\omega$ is deduced in a general form by Davis and Mott [5]

$$\alpha(\omega) = \frac{B}{\hbar\omega} (\hbar\omega - E_{\text{opt}})^r \quad (1)$$

where B is a constant and r is an index determined by

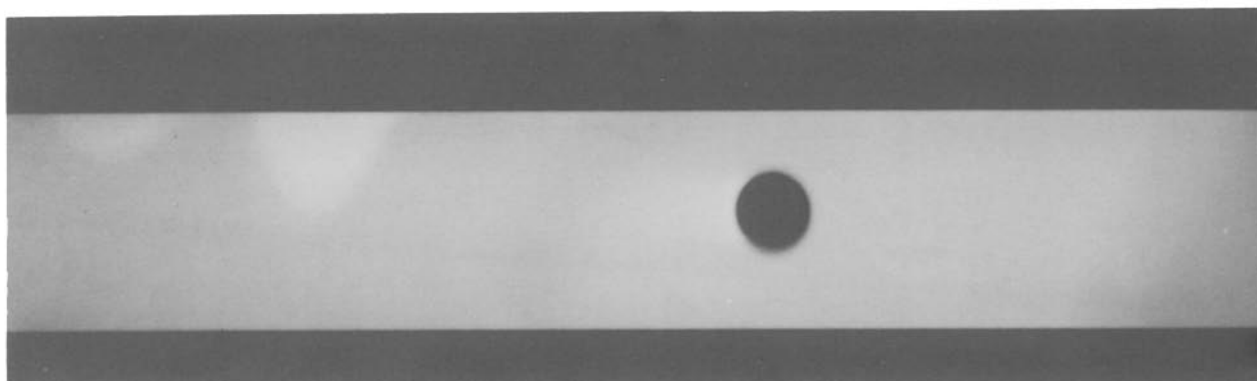


Figure 1 Typical X-ray photograph of TiO₂-doped soda–lime–silica glass.

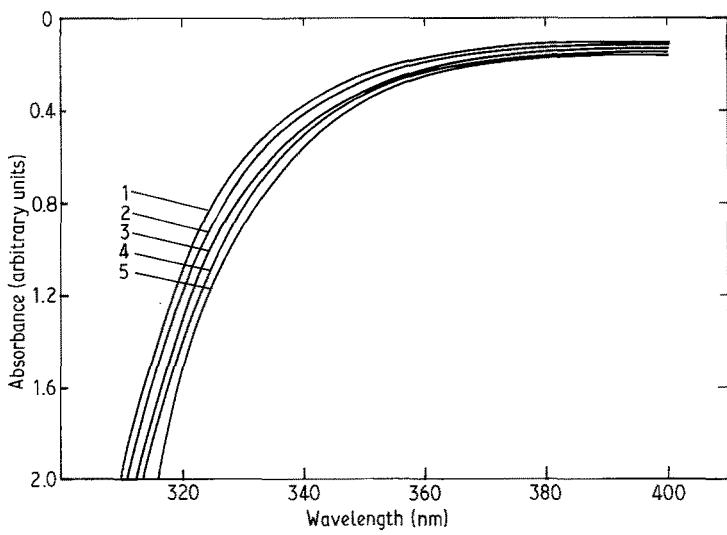


Figure 2 Variation of the optical absorption spectra with wavelength at different temperatures for 0 mol % TiO_2 soda lime-silica glass (1, 2, 3, 4 and 5 represent temperatures 296, 343, 383, 433 and 483 K, respectively).

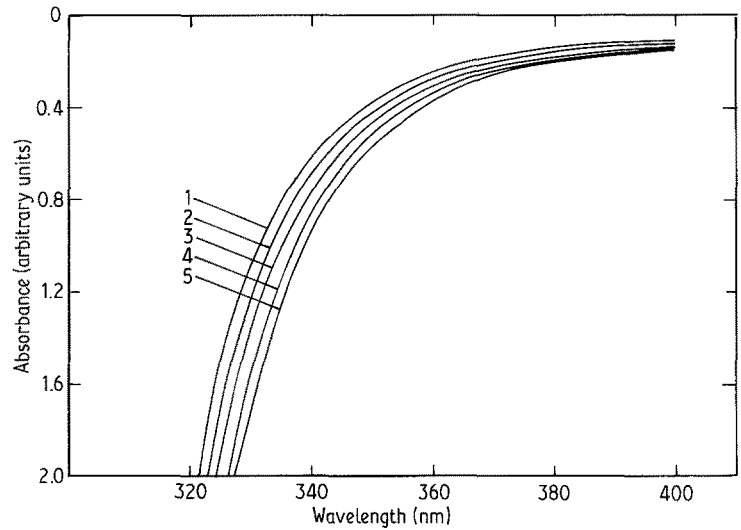


Figure 3 As Fig. 2 for 1.47 mol % TiO_2 .

the nature of the electronic transitions during the absorption process. An earlier form of Equation 1 was given by Tauc [3] who gives $r = 2$, consistent with the Davis and Mott equation for indirect transitions. It has been found that [7] a reasonable fit of Equation 1 with $r = 2$, particularly at the higher absorption values of the edge, for many amorphous materials is achieved.

In the present work we investigate the composition and temperature variations of the optical absorption

edge for a series of soda-lime-silica glasses doped with TiO_2 oxide.

2. Experimental technique

2.1. Glass preparation

The specimens used for the UV spectroscopy were prepared from laboratory reagent grades of Analar SiO_2 , Na_2CO_3 , CaCO_3 and TiO_2 using Pt-Rh crucibles. The weighing of these reagent grades was carried

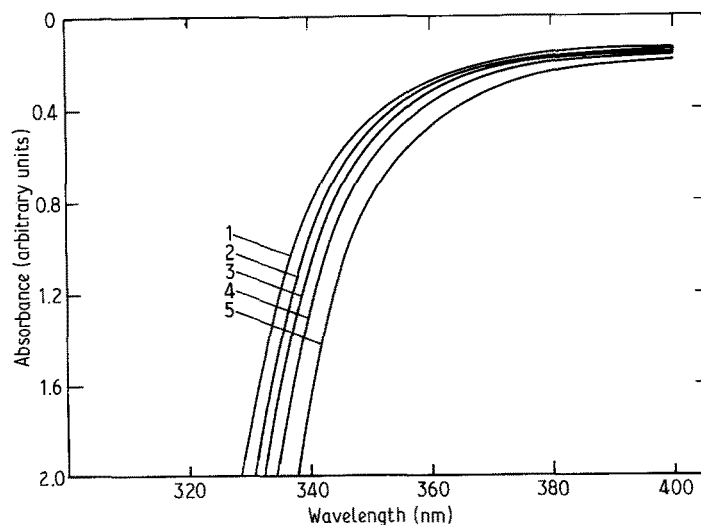


Figure 4 As Fig. 2 for 2.9 mol % TiO_2 .

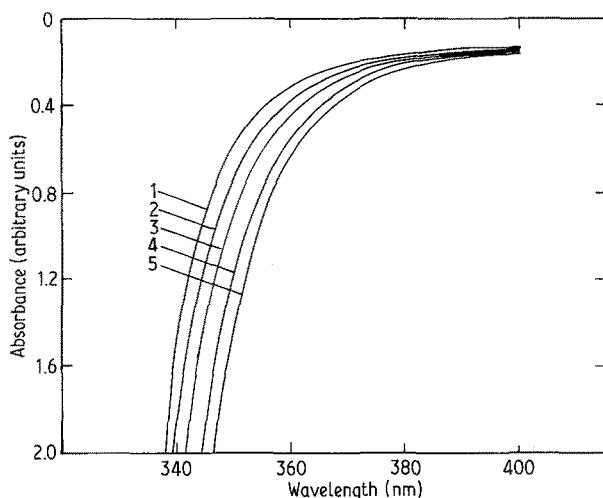


Figure 5 As Fig. 2 for 8.21 mol % TiO_2 .

out using an Oertling type of electric balance with an accuracy of ± 0.2 mg. All glasses were prepared from 30 to 50 g quantities, initially heated in an electric furnace at 500°C for 1 h and then the mixes were placed for 3 h in a second furnace held at 1450°C . The glass melts were stirred occasionally to ensure homogeneous melts. The melt was cast into two mild-steel split moulds heated to 200°C to form glass rods ~ 0.5 cm long and 1.6 cm in diameter. Glass samples were then replaced in the annealing furnace held at 400°C for 1 h. After this, the furnace was switched off and the samples were allowed to cool to room temperature gradually. It was found that glass preparation history, such as melting temperature, melting time, annealing time and rate of cooling could affect the properties of glasses, therefore, we tried to keep all these parameters as constant as possible.

2.2. X-ray and UV measurements

Dry ground glass powders were investigated by using an X-ray Debye Scherrer Camera.

The absorption measurements for our glass samples were made using a SP 8-100 Pye Unicam spectrophotometer in the wavelength range of 200–700 nm. The temperature of the sample was varied from 286 to 483 K.

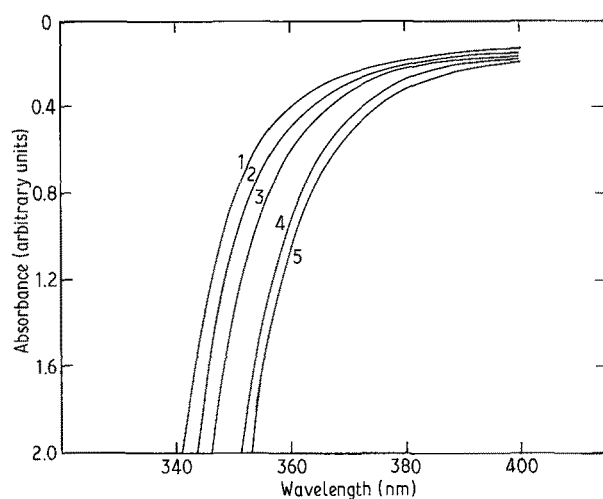


Figure 6 As Fig. 2 for 10.66 mol % TiO_2 .

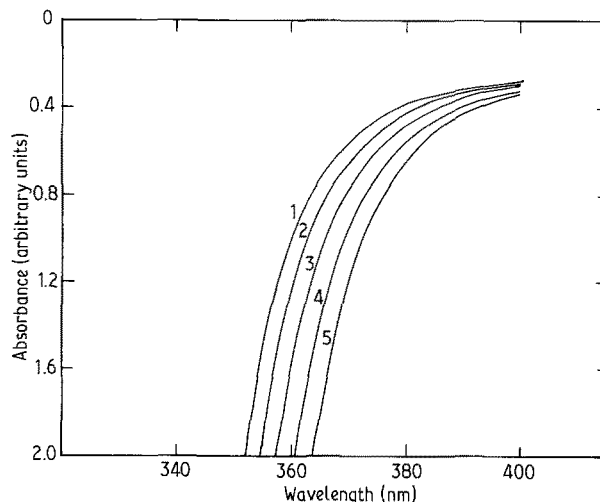


Figure 7 As Fig. 2 for 18.28 mol % TiO_2 .

3. Results and discussion

X-ray photographs of all the studied glasses showed the diffuse bands characteristic of the X-ray diffraction patterns of amorphous materials. Fig. 1 shows an X-ray photograph for one of our glass samples; no sharp line spectra were obtained, so there was no evidence of crystalline phases present in our prepared glass specimens.

Figs 2 to 8 show the plots of the optical absorption spectra against wavelength λ at different temperatures for TiO -doped soda–lime–silica glasses. It is clear that there is no sharp absorption edge and this is a characteristic of the glassy state. For all glass samples the change of absorption edge with temperature shows a real shift in the absorption edge to lower energies (see Figs 2–8). The optical data in these figures could be analysed in terms of non-direct transitions in K space. The variations of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ are shown in Figs 9–15. As seen from these figures the optical absorption data follow Equation 1 with $r = 2$. The values of E_{opt} can be obtained from the extrapolation of a linear part of each curve in these figures to the point $(\alpha\hbar\omega)^{1/2} = 0$. These E_{opt} values were obtained from our data using the least square method.

The temperature dependence of E_{opt} (see Figs 11 and 12) showed a linear decrease with increasing values of

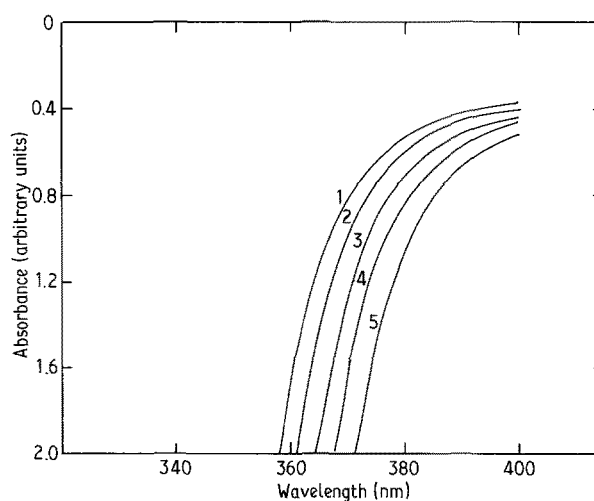


Figure 8 As Fig. 2 for 23 mol % TiO_2 .

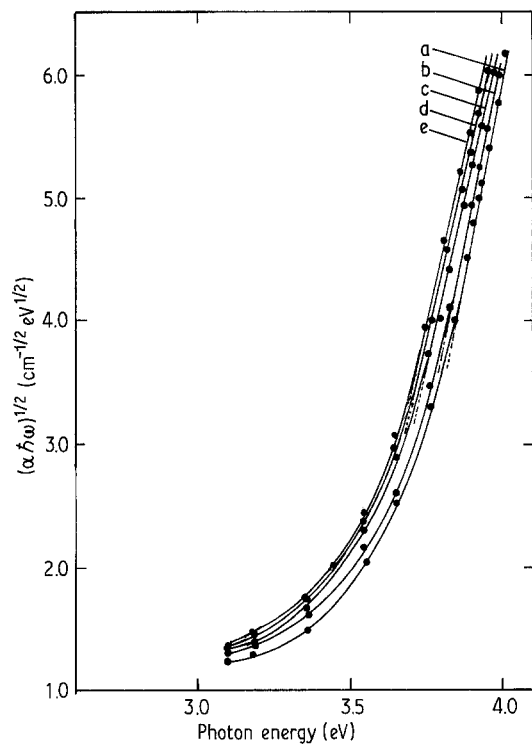


Figure 9 The variation of $(\alpha\hbar\omega)^{1/2}$ with photon energy $\hbar\omega$ at different temperatures for 0 mol % TiO_2 soda-lime-silica glass (a, b, c, d and e represent temperatures 296, 343, 383, 433 and 483 K, respectively).

temperature (the other samples show the same trend). From the density-of-states model it is known that the value of E_{opt} is decreased as the degree of disorder in the amorphous structure is increased. Also, as the temperature is increased the disorder in such materials increases and the band tailing shifts to lower energies and extends further into the forbidden band. As a consequence the value of E_{opt} is expected to decrease with temperature as shown by the results of this work (see Fig. 16).

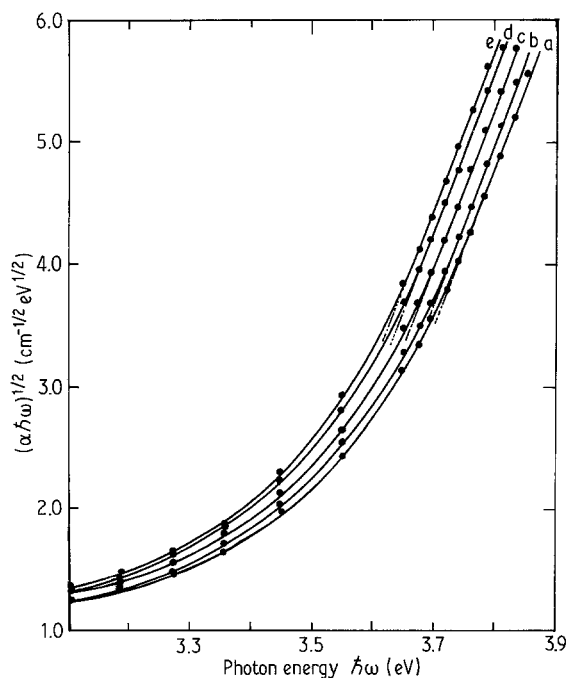


Figure 10 As Fig. 9 for 1.47 TiO_2 .

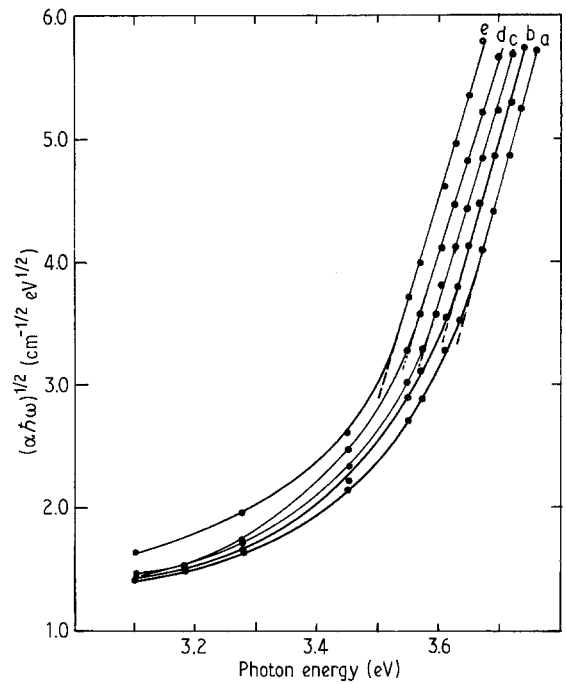


Figure 11 As Fig. 9 for 2.90 mol % TiO_2 .

Fig. 16 shows the variation of E_{opt} with TiO_2 mol % content at five different temperatures. The values of E_{opt} are seen to display a decrease with increasing TiO_2 content from 0–24 mol % (for example at 296 K, E_{opt} varies from 3.524 eV to 3.203 eV) and are consistent with an increase in band tailing arising from localization as may be expected. It is clear, from Fig. 16 that the compositional dependence of E_{opt} could be divided into three compositional regions. The addition of TiO_2 to the soda-lime-silica glasses in the compositional region 0–4 mol % TiO_2 leads to decrease the E_{opt} value from 3.524 to 3.433 eV at 296 K. This decrease may be due to introducing TiO_4 units into network forming positions, which will increase the electronic transitions between localized states in band edge tails. The above

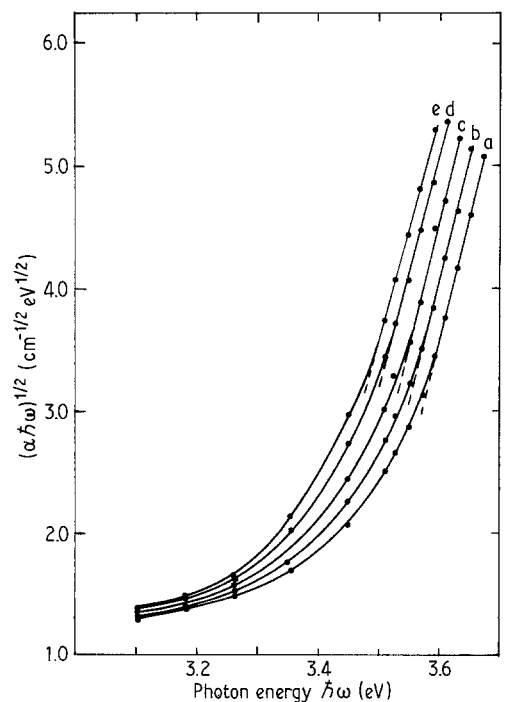


Figure 12 As Fig. 9 for 8.21 mol % TiO_2 .

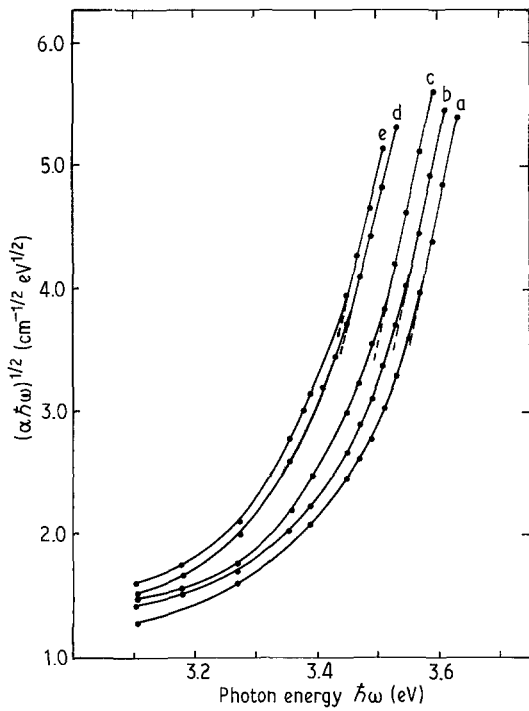


Figure 13 As Fig. 9 for 10.66 mol % TiO₂.

explanation may be attributed to the electronic configuration in both silicon and titanium atoms, especially the outer orbital electrons. It has been reported [8] that, the first ionization energy for silicon atom is 8.2 eV however, for titanium atom is 6.8 eV. Then one can argue that, the increasing of the number of titanium atoms in network position increases the electronic transitions and will lead to decreasing the value of E_{opt} . Beyond 4 mol %, there is a critical compositional region (4–11 mol %) in which almost constant variation in E_{opt} is found (E_{opt} varies from 3.433 to 3.395 eV at 296 K). At the present time we have no explanation for the E_{opt} behaviour in this critical compositional region.

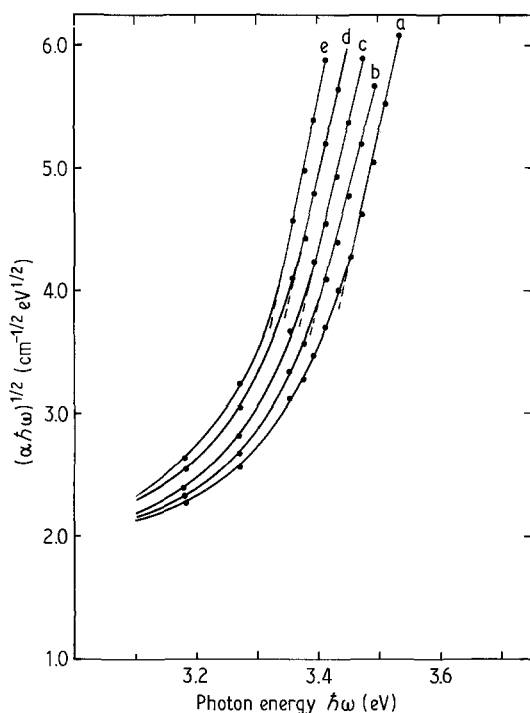


Figure 14 As Fig. 9 for 18.28 mol % TiO₂.

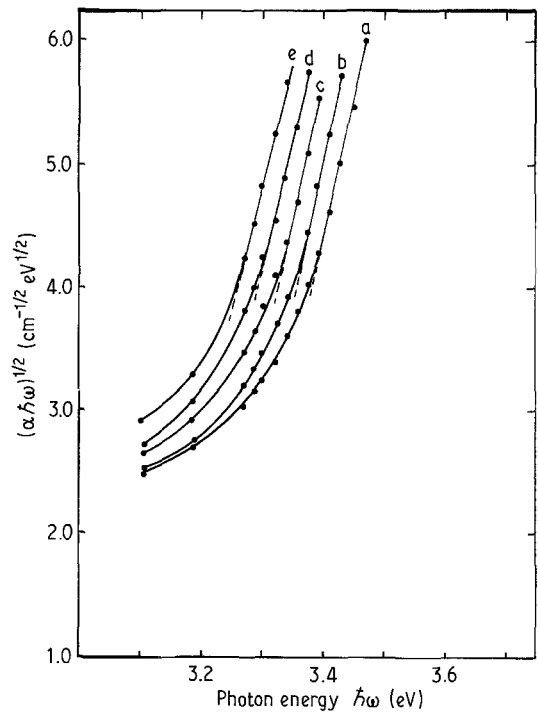


Figure 15 As Fig. 9 for 23 mol % TiO₂.

Now as we increase the TiO₂ content from 11 to 23 mol %, the E_{opt} value decreased rapidly from 3.395 to 3.203 eV at 296 K. In this compositional region Ti⁴⁺ cations fill octahedral vacancies in the glass, i.e. they are coordinated with six oxygen anions [9]. The residing Ti⁴⁺ ion in glass interstitially as network modifiers in the range 11–23 TiO₂ mol % will break down some of the bridging bonds in the glass network. Therefore, we can argue that, as the TiO₂ oxide increases beyond 11 mol % the number of non-bridging oxygen atoms will increase. Stevels [10] has suggested that the movement of UV absorption band to longer wavelengths corresponds to transitions from the non-bridging oxygen which bind an excited electron less tightly than

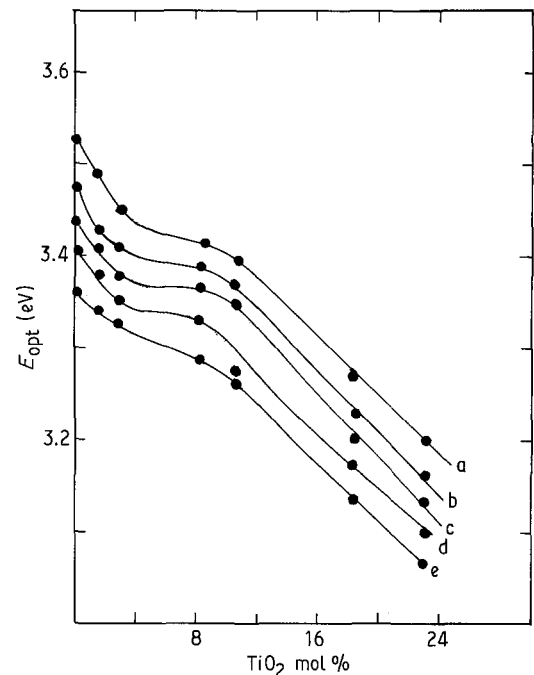


Figure 16 Compositional and temperature dependence of E_{opt} for soda-lime-silica glasses (a, b, c, d and e represent temperatures 296, 343, 383, 433 and 483 K, respectively).

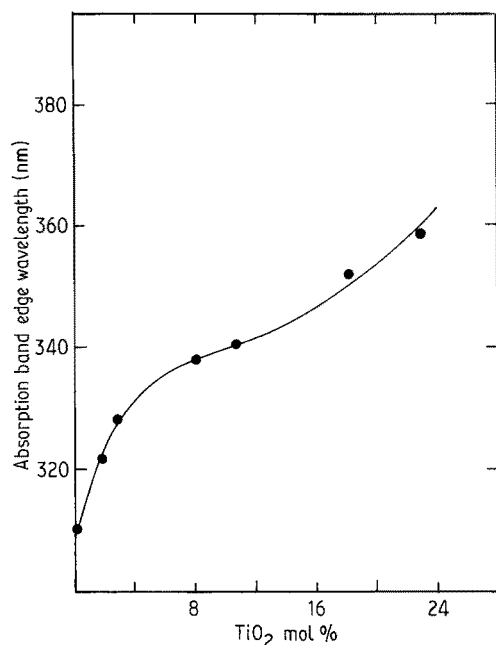


Figure 17 The variation of absorption band edge wavelength with TiO₂ mol % for soda-lime-silica glasses at temperature 296 K.

a bridging oxygen. Therefore, the E_{opt} variations in the compositional region 11–23 mol % can be explained by suggesting that the non-bridging oxygen ion content increases with increasing TiO₂ content, shifting the absorption band edge to the longer wavelengths (see Fig. 17); and this will lead to a decrease in the value of E_{opt} (see Fig. 16).

In our previous work [11] the compositional dependence of the ultrasonic properties for the soda-lime-silica glass system doped with TiO₂ oxide has shown three compositional regions; which their boundaries in agreement with the three compositional behaviour regions observed in the present work.

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