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Effect of microstructure and fusion temperature on the electrical and optical properties of vanadate glasses

M. N. KHAN
Department of Physics, Bahrain University, PO Box 1082, Bahrain

The electrical and optical properties of binary semiconducting oxide glasses containing 45 mol % V_2O_5 and 55 mol % GeO_2 fused and equilibrated at various temperatures (T_ϕ) in air were measured. T_ϕ was varied over the range from 1000 to 1350° C. Their electrical and optical properties are shown to be sensitive to microstructure and melt temperature. We suggest that the change in T_ϕ caused progressive microstructure changes of these glasses, which dramatically affected the electronic conductivity and the activation enthalpy for conduction.

1. Introduction

The influence of fusion conditions upon the physical properties of GeO_2 glasses have been a subject of continuing interest. Chung and Mackenzie [1] have shown that the electrical conductivity of vanadium germanate glasses was much smaller than that reported by Rao [2]. Recently Khan *et al.* [3] have measured the electrical conductivity of annealed and unannealed vanadium germanate glasses. These measurements clearly elaborated the discrepancies between the two results. The conductivity of annealed samples at room temperature was found to be about five orders of magnitude greater than that of the unannealed samples containing a similar amount of vanadium oxide. The increase in conductivity on annealing was attributed to changes in the microstructure of the glasses. It has also been suggested [4] that the increase in the electrical conductivity of the annealed samples could be attributed to the increase of reduced valence states of vanadium ions (V^{3+} and V^{4+}) which accompany the microstructure formation, and not to the structural changes alone. It has been reported [5] that the glass-forming oxide might not be simply a non-interacting solvent in the conduction process as described by Ioffe *et al.* [6] for the V_2O_5–P_2O_5 system.

There are numerous reports [7–14] in the literature which conclude or can be interpreted to argue that the structure of the glass is dependent upon the structure of the liquid from which it was cooled. The local environment of the sodium ion does not totally relax to a structure characteristic of a glass transition temperature, but instead retains a structure determined by the equilibrium established in the liquid at a temperature T_ϕ from which it was quenched. This argument is, of course, contrary to the conventional view that the structure of a glass is in metastable equilibrium at temperatures above the glass transition. This argument is supported by the work of Galeener and Geils [7] who reported Raman measurements of GeO_2 glasses held in the liquid state at different temperatures but quenched through the glass transition regime at the same rate. They concluded that Raman results indicate differences in structure among glasses quenched in such a fashion. Bohm [8, 9] reported differences in photoconductivity and thermoluminescences in GeO_2 glasses held at different temperatures in the liquid state. Kordas *et al.* [15] have shown that the intensity of two paramagnetic states observed in GeO_2 glasses is dependent upon the temperature T_ϕ at which their glass melts were equilibrated. The dependence of the concentration of each defect upon T_ϕ was of the Arrhenius kind. Primak [11] reviewed the Douglas and Isard [12] density measurements upon SiO_2 glasses with differing glass transition temperatures and concluded that remnants of the high-temperature structure are responsible for the observed density differences. Douglas and Isard stated that "the high temperature phases are readily quenched", and Primak added the observation that these configurational differences are quite stable at lower temperatures.

The purpose of the present study is to examine the effect of microstructure and glass-forming conditions on the optical and electrical properties of vanadate glasses containing 45 mol % V_2O_5.

TABLE I Preparation, density and activation energy of glasses

Notation	Composition (mol %)	Melt temperature, T_ϕ (° C)	Melt time (h)	Activation energy, W (eV)	Density (g cm^{-3})
A	$45V_2O_5$–$50GeO_2$	1000	3	0.670 ± 0.0013	2.980
B	$45V_2O_5$–$50GeO_2$	1200	3	0.393 ± 0.0013	3.085
C	$45V_2O_5$–$50GeO_2$	1350	3	0.291 ± 0.0013	3.098

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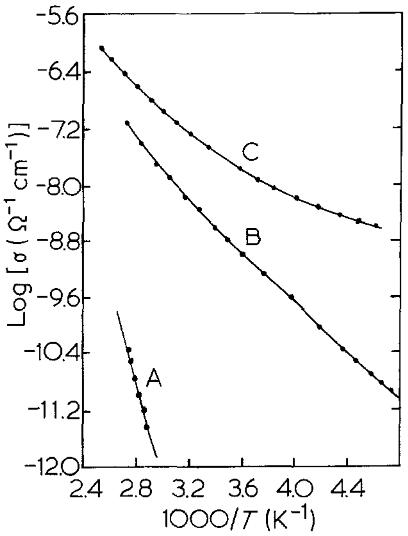


Figure 1 Logarithm of electrical conductivity σ as a function of reciprocal temperature for a series of V_2O_5–GeO_2 samples, prepared under different conditions (see Table I).

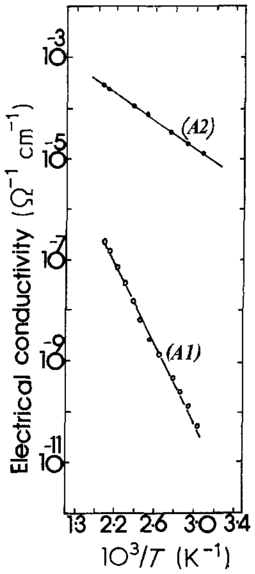


Figure 3 The logarithm of conductivity against $10^3/T$ for (A_1) unannealed V_2O_5–GeO_2, (A_2) annealed V_2O_5–GeO_2 glass.

2. Experimental procedure

Glasses were prepared by heating dry mixtures of analytical-grade chemicals in alumina crucibles. Prior to melting the mixture, the alumina crucible was placed in a furnace maintained at 300° C for 1 h in order to minimize material volatilization. The crucible was then transferred to a melting furnace maintained at a selected temperature, given in Table I. The melt was frequently stirred with an alumina rod. Melted samples were held at various T_ϕ values for the times listed in Table I and then cooled to 25° C at an average rate of 5° C sec^{-1} from T_ϕ to 400° C. The homogenized melts cast on to a stainless steel plate were disc-shaped with diameter approximately 2.5 cm and thickness 0.5 to 1.0 mm.

Thin glass films which were necessary for the optical and infrared measurements were obtained by a blowing technique. The as-blown glass film was mounted on to a machinable glass–ceramic specimen holder having the capability of being placed into an annealing furnace as well as the spectrophotometer.

Measurements of d.c. conductivity were made using evaporated gold electrodes, which make good ohmic contacts, and a guarding configuration to eliminate surface leakage current. The polishing was done with diamond paste in kerosene. A stabilized power supply was used to provide a voltage source and circulating currents were measured using a Keithley 610C electrometer. The temperature of the sample was monitored using a chromel–alumel thermocouple attached to the sample. The infrared absorption spectra were measured using the KBr pellet technique on a double-beam spectrophotometer. The instrument was calibrated using a standard polystyrene sheet and the absorption bands were reproducible to ±2 cm^{-1}. SEM pictures were taken from the surfaces of polished samples etched in distilled water for 20 sec by means of a Cambridge Stereoscan 250 MK2 scanning microscope. Density was measured by the Archimedes principle.

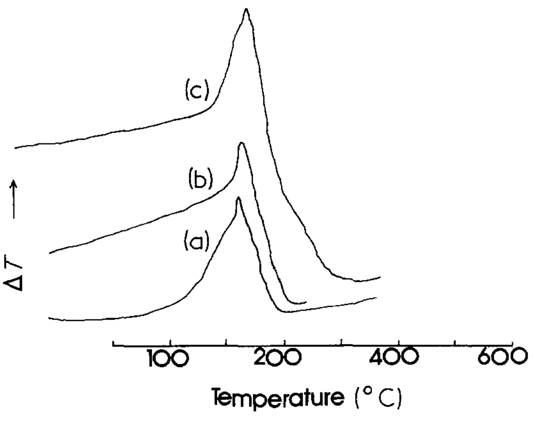


Figure 2 DTA curves for $45V_2O_5$–$55GeO_2$ samples, melted at (a) 1350° C, (b) 1200° C, (c) 1000° C.

3. Results and discussion

Fig. 1 shows the logarithm of conductivity σ against $1000/T$ for germanate glasses containing 45 mol % vanadium oxide for various values of T_ϕ. The values of the activation energy as shown in Table I were calculated from the slopes of the curves, using the relation

$$\sigma = \sigma_0 \exp(-W/kT)$$

It is clear from Fig. 1 that in germanate glasses the electrical conductivity dramatically changed, which could be ascribed to the difference in the microstructure, governed by melting conditions. The results of differential thermal analysis (DTA) shown in Fig. 2 also indicated that these three samples are not identical. Fig. 3 shows the temperature variation of electrical conductivity of unannealed and annealed samples of V_2O_5–GeO_2 glasses taken from our published data [3].

The activation energy calculated for $45V_2O_5$–$55GeO_2$ glasses agrees quite well with Chung and Mackenzie [1]. However, it is less than the reported values of Rao [2].

Figs 4a to c show scanning electron micrographs in order to provide some direct evidence about the difference in the microstructure. It is clear from these SEM pictures that a homogeneous glass was only obtained when melting was at 1300° C.

It was also found that the resistivity was a function of the temperature of the liquid, T_ϕ, from which the glass was cooled. These changes in the resistivity were also reported by Magruder *et al.* [14]. They ascribed the changes in resistivity to structural changes affecting the potential wells of the interstitial sites through which the Na^+ ion moved. These structural changes bring about a change in the anharmonic term for the vibrational energy levels and as a consequence a change in the entropy of activation. These changes in structure could be manifested in changes in resistivity of the glasses. Actually T_ϕ is only one parameter among several that can affect the resistivity of glasses. The thermal treatments at temperatures below the glass transition temperature T_g also affect the resistivity [16]. For glasses with differing T_ϕ values the differences in reaching equilibrium indicate that the stabilization processes in these glasses are different. These differences in stabilization may be in part due to the defect concentration in the glasses. Primak [17] has suggested that the E^- centre may play a role in the compaction of fused silicas. Kordas *et al.* [18] have reported the E^- centre concentration in as-quenched glasses. Jackson *et al.* [19] have reported the defect centre concentration

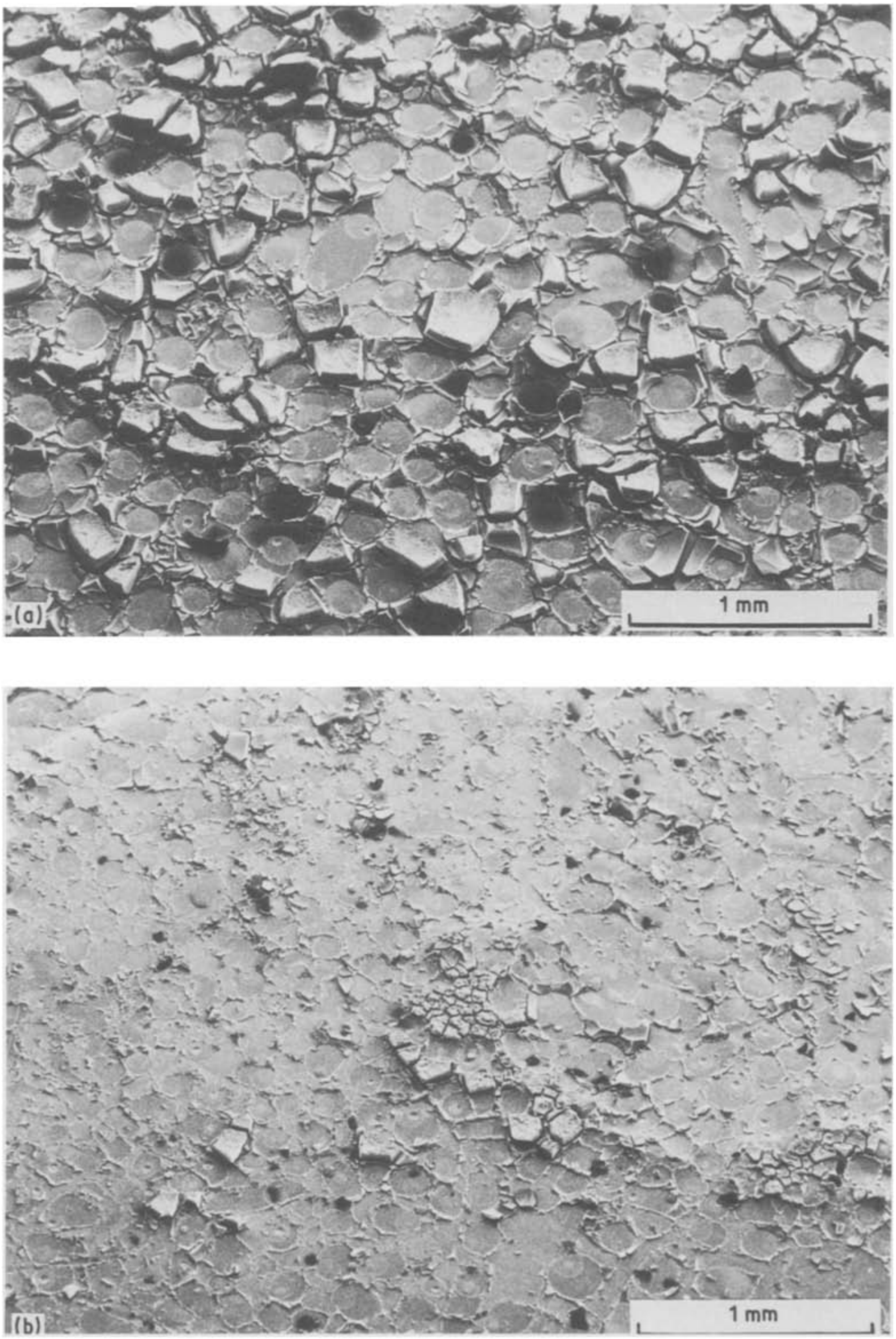


Figure 4 Scanning electron micrographs of $45V_2O_5$–$55GeO_2$ glasses prepared by melting at (a) 1000° C, (b) 1200° C, (c) 1350° C.

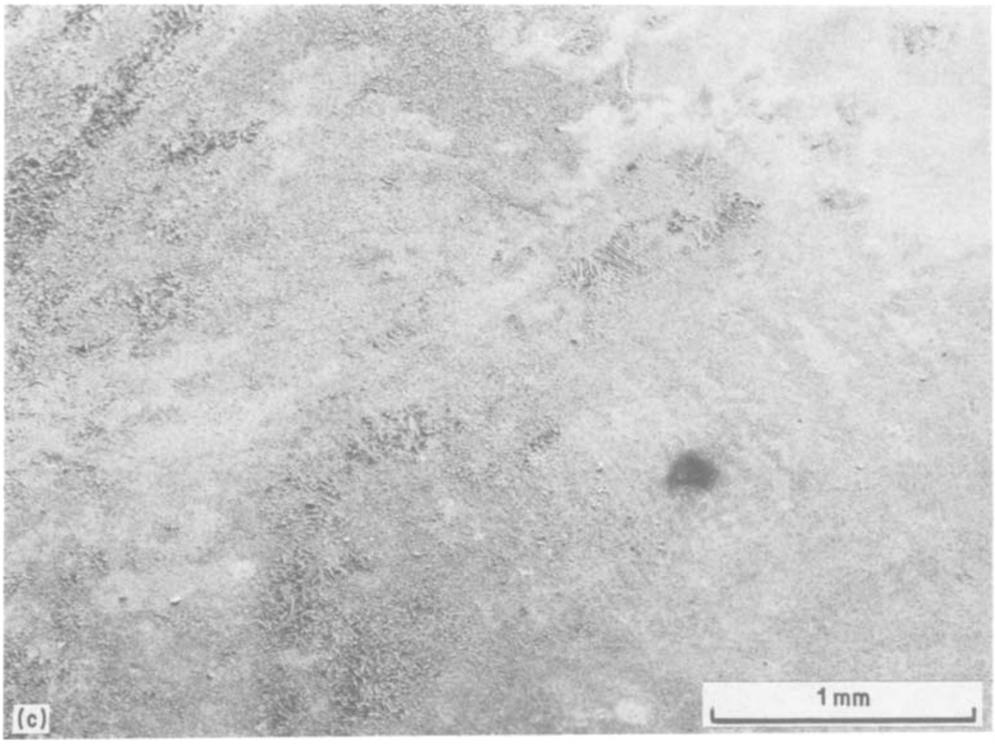


Figure 4 Continued.

associated with a 245 nm absorption peak to be largest for a T_ϕ of 1650° C and lowest for a T_ϕ of 1350° C. It may be plausible that the defect structure of the glass controls the stabilization processes, allowing for points of motion in the network to relieve stresses induced by thermal compaction. The values of the density as a function of melting conditions are listed in Table I.

Infrared spectra of KBr discs in the 1200 to $200\,\mathrm{cm}^{-1}$ range for pure V_2O_5 and GeO_2 are shown in Fig. 5, for ready reference. The spectra for the same region of KBr discs of equimolar mixtures, unannealed and annealed glass films of V_2O_5–GeO_2 glass samples are shown in Fig. 6. The data of Fig. 6 are from Khawaja *et al.* [4]. The infrared spectral data for the KBr pellets of all pure oxides agree with those reported in the literature [20]. The infrared spectrum (Fig. 6) of the KBr disc of an equimolar mixture of crystalline V_2O_5 and GeO_2 is equivalent to a composite spectrum of the two oxides. The sharpness of the peaks in the crystalline material is retained in the spectrum of the equimolar mixture as expected. The infrared data for the V_2O_5–GeO_2 glasses are different from the composite spectra of the two oxides, indicating the formation of different structural units in the glass samples than in the starting materials. Annealing of a V_2O_5–GeO_2 glass sample at 300° C clearly indicated microstructure formation as shown in Fig. 6c.

Figs 7a to c show the absorption spectra of the glass held at various T_ϕ values. It is clear that in the glass

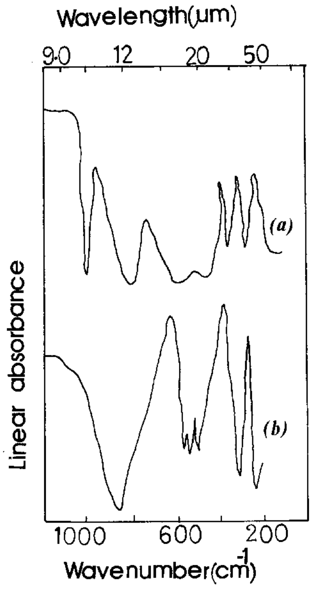


Figure 5 Infrared absorption of (a) pure crystalline V_2O_5, (b) GeO_2 powder.

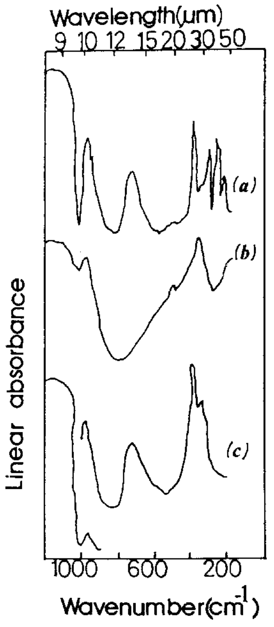
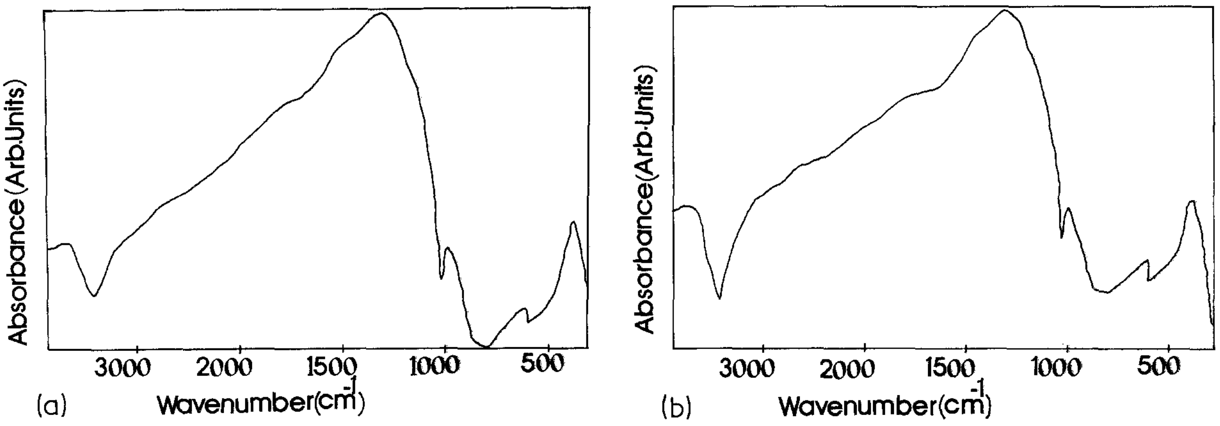


Figure 6 Infrared absorption spectra of (a) equimolar mixture of V_2O_5 and GeO_2 powder, (b) unannealed V_2O_5–GeO_2 glass film, (c) V_2O_5–GeO_2 glass film after annealing.



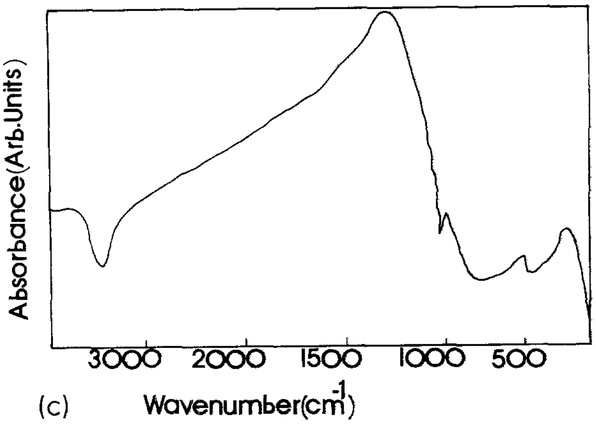


Figure 7 Infrared absorption spectra for a series of V_2O_5–GeO_2 glasses, prepared at (a) 1000° C, (b) 1200° C, (c) 1350° C.

samples of V_2O_5–GeO_2, the V=O stretching band at 1010 cm^{-1} was retained, but the strong absorption at 825 cm^{-1} in V_2O_5 and at 875 cm^{-1} in GeO_2 appeared as a broad absorption, centred at 800 cm^{-1}. Instead of strong and sharp peaks at 600 cm^{-1} in V_2O_5 and 550 cm^{-1} in GeO_2, a broad peak centred at 600 cm^{-1} with a shoulder at 480 cm^{-1} appeared in the equimolar mixture. This set of peaks in the region 600 to 500 cm^{-1} disappeared in the V_2O_5–GeO_2 glass system (Fig. 6b). If we compare the absorption spectra of the glass held at various T_ϕ values (Fig. 7), the general appearance of the absorption spectrum for the three glasses, keeping in mind the specimen thickness, is similar. The infrared peaks as indicated in Fig. 7a remained unchanged at various T_ϕ values as shown in Figs 7b and c. The various T_ϕ values, therefore, have very little effect on the absorption.

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References

1. C. H. CHUNG and J. D. MACKENZIE, *J. Non-Cryst. Solids* **42** (1980) 357.
2. B. V. J. RAO, *J. Amer. Ceram. Soc.* **48** (1965) 311.
3. M. N. KHAN, E. E. KHAWAJA, D. SAVE, A. A. KUTUB and C. A. HOGARTH, *Int. J. Electron.* **56** (1984) 395.
4. E. E. KHAWAJA, J. S. HWANG, F. TEGALLY, A. A. KUTUB and A. S. W. LI, *J. Mater. Sci.* **20** (1985) 3074.
5. B. W. FLYNN, A. E. OWEN and J. M. ROBERTSON, in Proceedings of International Conference on Amorphous and Liquid Semiconductors, edited by W. E. Spear (CICL, Edinburgh, 1977) p. 673.
6. V. A. IOFFE, J. B. PATRINA and I. S. POBEROVSHAYA, *Sov. Phys. Solid State* **2** (1960) 609.
7. F. L. GALEENER and R. H. GEILS, in "The Structure of Non-Crystalline Materials", edited by P. H. Gaskell (Taylor and Francis, London, 1977) p. 223.
8. H. BOHM, *J. Non-Cryst. Solids* **7** (1972) 192.
9. *Idem, Phys. Chem. Glasses* **11** (1977) 177.
10. G. KORDAS, R. A. WEEKS and D. L. KINSER, *J. Appl. Phys.* **45** (1983) 5394.
11. W. PRIMAK, *Phys. Chem. Glasses* **24** (1983) 8.
12. R. W. DOUGLAS and J. O. ISARD, *J. Soc. Glass Technol.* **35** (1951) 206.
13. G. H. HETHERINGTON, K. H. JACK and J. C. KENNEDY, *Phys. Chem. Glasses* **5** (1971) 206.
14. R. H. MAGRUDER, D. L. KINSER, R. A. WEEKS and J. M. JACKSON, *J. Appl. Phys.* **57** (1985) 345.
15. G. KORDAS, R. WEEKS and D. KINSER, *ibid.* **54** (1985) 5394.
16. R. H. MAGRUDER, D. L. KINSER and R. A. WEEKS, *J. Non-Cryst. Solids* **71** (1985) 95.
17. W. PRIMAK, "The Compacted States of Vitreous Silica" (Gordon and Breach, New York, 1975).
18. G. KORDAS, R. A. WEEKS and D. L. KINSER, *J. Appl. Phys.* **54** (1983) 5394.
19. J. M. JACKSON, M. E. WELLS, G. KORDAS, D. L. KINSER and R. A. WEEKS, *ibid.* **58** (1985) 2308.
20. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds (Wiley, New York, 1963).

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