An investigation of the electrical, optical and DSC properties of a copper-phosphate glass composition

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The variation of some physical properties of equimolar copper-phosphate glasses has been reported in the literature. The present work studied a 60 mol% P_2O_5-40 mol% CuO glass system using electrical conductivity, infrared absorption, optical absorption spectroscopy and differential scanning calorimetry. The results revealed an increase in the activation energy and the optical energy gap compared with that for equimolar P_2O_5-CuO, which could be attributed to the variation of reduced valence states of the copper ion in the process of glass formation. The relation between the a.c. electrical conductivity with frequency was found to be almost temperature-independent. Infrared measurement revealed similar trends to those reported for the same glass composition. DSC measurements showed endothermal peaks at 360, 520, 560 and 580 °C for this glass composition.

1. Introduction
The general condition for semiconducting behaviour is that the transition metal ion should be capable of existing in more than one valence state, so that conduction occurs by the movement of carriers from lower valence states to higher valence states. The electrical conductivity has been shown to be related to the ratio and relative concentration of the ions in the different valence states [1, 2]. In particular, the copper phosphate glasses are electronic conductors in which the transport mechanism involves the exchange of electrons between Cu^+ and Cu^{2+} ions [3].

Several papers have appeared recently reporting the properties of glassy and amorphous semiconductors based on the phosphate glass system [4–9]. During the last few years, many workers have studied glasses containing mixed transition metal ions. Bogomolova and co-workers [10–12] have studied the P_2O_5-BaO-V_2O_5-CuO and P_2O_5-CaO-V_2O_5-CuO glasses, and reported that a strong exchange interaction exists between Cu^{2+} and V^{4+} ions, leading to the mixed exchange Cu^{2+} and V^{4+} pairs formation.

Various properties of copper-phosphate glass containing small amounts of rare-earths have been reported [13, 14]. Kutub *et al.* studied the effect of the addition of cupric oxide on the optical, infrared absorption [15] and electrical measurements [16] of vanadium-phosphate glasses.

In the present work we report some electrical, optical absorption, infrared absorption spectrum and differential scanning calorimetry measurements of glasses containing 60 mol% P_2O_5 and 40 mol% CuO.

Owing to the differences in the results obtained here from those previously published for 50 mol% P_2O_5-50 mol% CuO [17], a comparison of the two glass compositions is included.

2. Experimental procedure
2.1. Glass preparation
60 mol% analytical reagent grade phosphorus pentoxide and 40 mol% cupric oxide were carefully mixed in an alumina crucible and heated at 300 °C for 1 h. This initial heating served to minimize material volatilization. The crucible was then transferred to another furnace maintained at a selected temperature of 1000 °C and left for 2 h with frequent stirring.

The homogenized melts were then poured on to a clean stainless steel plate and cast into a disc shape with diameter 2 cm and thickness about 2 mm. The disc was immediately transferred to another furnace which was already maintained at 300 °C. The furnace was kept at this temperature for 2 h and then was switched off to cool down to room temperature.

X-ray diffraction measurements confirmed the glassy nature of the samples examined.

2.2. Electrical measurements
For d.c. conductivity measurements, the disc-shaped sample was ground to a thickness of about 1 mm. After grinding, the sample was polished and then evaporation of gold electrodes was carried out in vacuum. Because of the high resistance of the glass sample, it is preferable to use guard-ring electrode configuration in order to eliminate the surface leakage and to measure the true bulk resistance of the glass. The sample was then heated at 200 °C for 1 h in order

to harden the gold electrodes. The electrical measurements were made by standard techniques. The circulating current was measured using a Keithley 610 electrometer, and a stabilized 247 Keithley power supply was used as a voltage source. The temperature of the sample was monitored using a chromel–alumel thermocouple attached to it.

For a.c. measurements, the frequency range covered was from 1–500 kHz. A voltage signal of 5 V was supplied across the sample using a BK-Precision function generator 3010.

2.3. Optical measurements

For optical measurements, thin blown films of the glass sample were prepared by blowing in air using an alumina tube. Films ranging in thickness from 3–15 μm were obtained. All thin films were unannealed when used for optical absorption measurements. The optical absorption measurements were carried out at room temperature in the wavelength range 185–900 nm using a Varian model Cary 2390 spectrophotometer. In the low absorption region $(\alpha < 10^4 \text{ cm}^{-1})$ multiple interference effects were well pronounced and use of this was made in determining the thickness of the films.

The infrared absorption of thin film glass was measured at room temperature in the range 400–4000 cm^{-1} using an IR-460 Shimadzu double-beam recording infrared spectrophotometer.

2.4. DSC measurements

Thermal stability of the glass was studied at atmospheric pressure in a Mettler TA-3000 thermal analysis system. The differential scanning calorimetry (DSC) technique was applied in the temperature range 303–873 K, where the heat flow to the sample is measured under thermally controlled conditions. The sample was well ground into a powder form and about 10 mg was contained in an aluminium crucible for measurement.

The DSC pattern was then measured relative to an empty aluminium crucible which served as a reference.

3. Results

3.1. Electrical conductivity

Typical current–voltage characteristics are shown in Fig. 1 for a glass sample containing 60 mol % P_2O_5–40 mol % CuO. Because of the difficulties in measuring current less than 10^{-14} A with the equipment available, it was not possible to measure currents at temperatures lower than 100 °C.

At higher temperatures, the conduction was ohmic and plots of log V versus log I give straight lines. With increasing temperature, the linear region extends to lower values of field. The departure from linearity and the appearance of non-ohmic behaviour occurs at fields below 3×10^3 V cm^{-1} and temperatures higher than 205 °C. A further increase in temperature (256 °C) causes the departure from linearity to occur at lower fields (below 2×10^3 V cm^{-1}). A similar characteristic
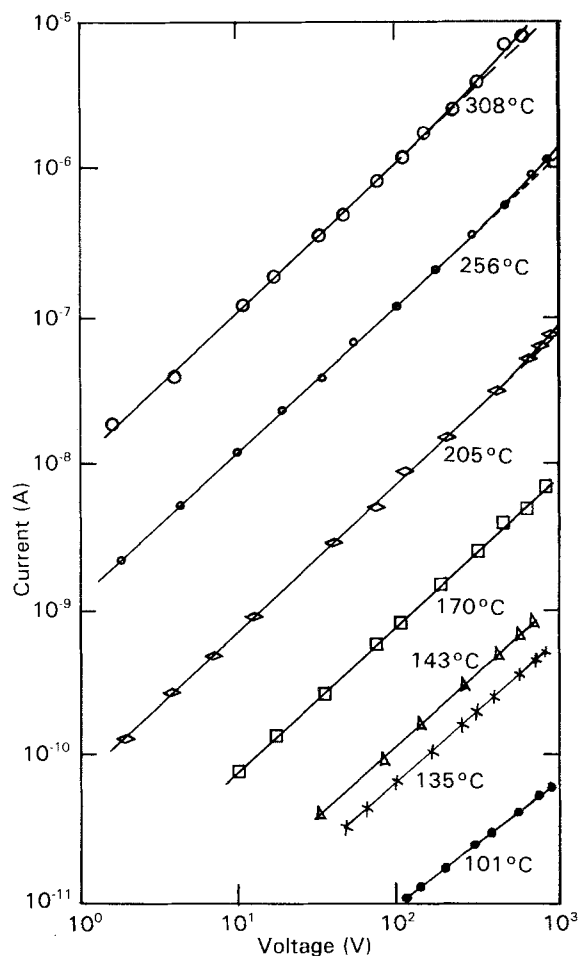

Figure 1 I–V characteristic for a 60 mol % P_2O_5–40 mol % CuO glass sample at different temperatures.

has been observed for a phosphate glass containing 50 mol % V_2O_5, but the departure from linearity, occurred at fields below 135 V cm^{-1}, and temperature above 170 °C [16]. Hogarth and Ghauri [18] reported that for a glass sample of composition 50 mol % P_2O_5, 50 mol % CdO, the conductance is ohmic at fields below 4×10^4 V cm^{-1}, while the non-ohmic behaviour occurs at fields above 4×10^4 V cm^{-1}.

Fig. 2 shows the temperature dependence of d.c. conductivity, σ. The results of the temperature variations of σ showed that in the modest range investigated, log σ is a linear function of $1/T$ for the present glass sample. The value of the activation energy was found to be about 1.23 eV which was calculated from the slope of the curve using the relation

$$\sigma = \sigma_o \exp(-E_a/kT) \qquad (1)$$

where E_a is the activation energy, k the Boltzmann constant, T the absolute temperature, and σ_0 is a constant. It is found that for a glass sample of composition 50 mol % P_2O_5–50 mol % CuO [17], the value of E_a is 1.05 eV. This indicates that the increase of CuO in the glass composition increases the electrical conductivity and decreases the activation energy. Hekmat-Shoar et al. [19] found that the value of E_a for a glass composition of 60 mol % P_2O_5, 40 mol % MoO_3 is 0.71 eV and decreases to 0.67 eV for a 50 mol % P_2O_5, 50 mol % MoO_3 glass composition.

The a.c. conductivity variation with frequency at different temperatures has been measured for the glass
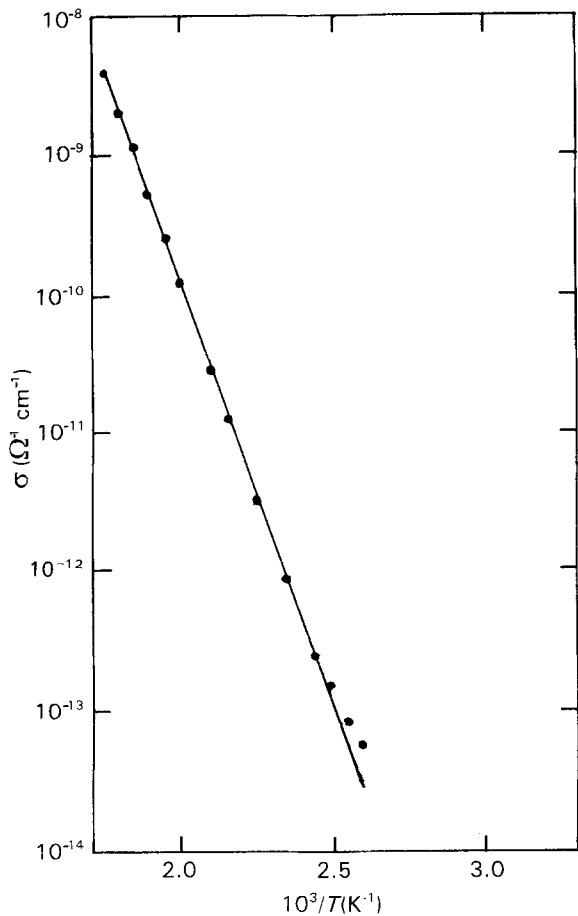
Figure 2 Electrical conductivity as a function of reciprocal temperature for a 60 mol % P_2O_5–40 mol % CuO glass composition.
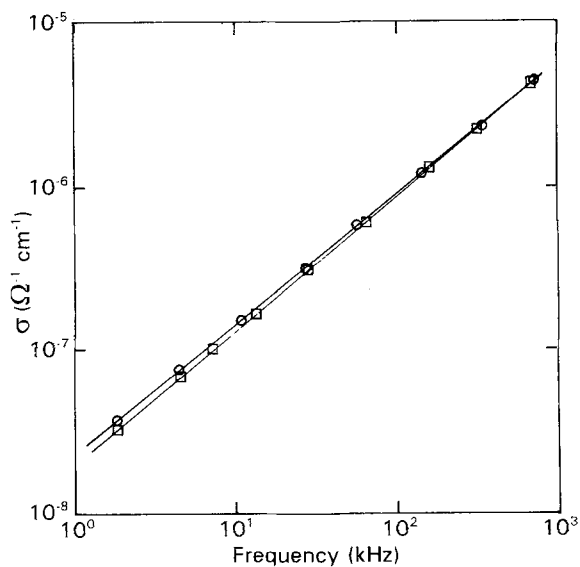

Figure 3 Variation of a.c. conductivity with frequency at ($\square$) 50 and ($\bigcirc$) 250 °C.

sample. It was found that the conductivity at a fixed frequency varied very slightly with temperature. Fig. 3 shows the variation of conductivity with frequency at 50 and 250 °C.

Similar behaviour has been reported for other glass compositions [4, 13]. For semiconducting glasses, the frequency variation of conductivity is usually expressed by the relation

$$\sigma = A\omega^s \tag{2}$$

where A is a constant, ω is the angular frequency of a.c., σ is the a.c. conductivity and s is an index; s usually lies within the range $0.5 < s < 1$. It is about 0.79 for our glass sample, and is slightly temperature-dependent.

3.2. Infrared absorption

The infrared spectrum for 60 mol % P_2O_5–40 mol % CuO thin blown film was carried out in the range 400–4000 cm^{-1} and is shown in Fig. 4.

The absorption peaks observed at 420, 500, 750–780, 920, 1080 and 1250 cm^{-1} are in good agreement with the spectra obtained for the copper–phosphate glasses [13, 14, 20].

The bands observed in our study at 1250, 1080 and 750–780 cm^{-1} could be attributed to the $P=O$ double bond, the $P–O^-$ stretching frequencies and the $P–O–P$ ring frequency, respectively. The absorption band at 420 cm^{-1} is known to be at the fundamental frequency of the $(PO_4)^{3-}$ group, which is in close agreement with the results reported by Hogarth and Moridi [21]. The broad band at 500 cm^{-1} observed in our glass seems to be due to CuO in the glass [13]. This peak is broadened at high copper content [14]. Other workers have noted a shift of band position and broadening of the band when a transition metal oxide, such as CuO, is added to P_2O_5 [13].

3.3. Optical absorption

The optical absorption measurements were made for a thin blown film of 60 mol % P_2O_5–40 mol % CuO glass sample. Fig. 5 shows the absorbance as a function of the wavelength. The general appearance of the absorption spectrum is similar to that observed by Khawaja *et al.* [17] for a 50 mol % P_2O_5–50 mol % CuO glass system. The optical absorption coefficient, $\alpha(\omega)$, may be displayed in a number of ways as a function of photon energy, $\hbar\omega$. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ as suggested by Davis and Mott [22]. The coefficient $\alpha(\omega)$ for many amorphous and
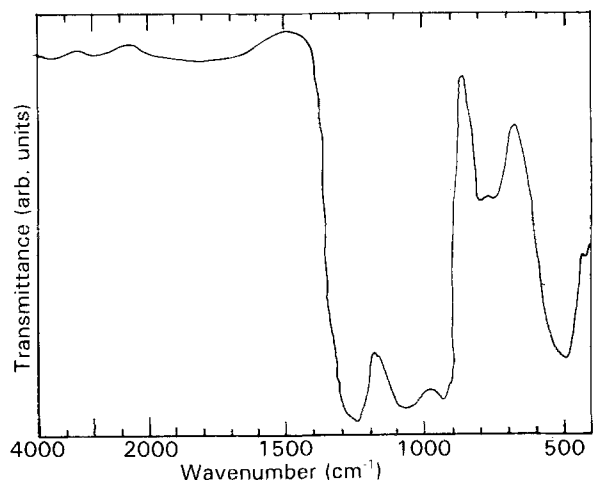

Figure 4 The infrared absorption spectrum of thin blown film of copper–phosphate glass.
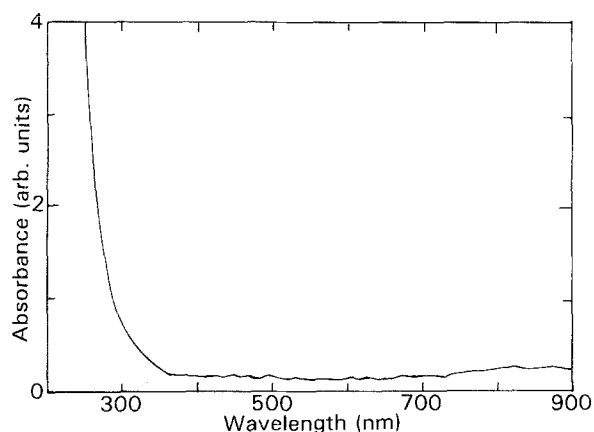
Figure 5 Optical absorption as a function of wavelength for a copper–phosphate glass sample.

glassy materials is found to obey the relation

$$\alpha(\omega)\,\hbar\omega \;=\; \beta(\hbar\omega - E_{opt})^2 \qquad (3)$$

and applies particularly in the region of absorption for which $\alpha(\omega) > 10^4\ cm^{-1}$. E_{opt} is the optical gap, β is a constant and $\hbar\omega$ is the photon energy. Fig. 6 shows the plot of $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$. The value of E_{opt}, determined by extrapolating the linear part of the curve to $(\alpha\hbar\omega)^{1/2} = 0$, is 3.90 eV. E_{opt} obtained for a 50 mol % P_2O_5–50 ml% CuO was 3.42 eV [17]. Arzeian and Hogarth [13] found the value of E_{opt} was of the order of 3.95 eV for a 65 mol % P_2O_5–35 mol % CuO glass system. This indicates that the value of E_{opt} decreases with increasing CuO content in the phosphate glass.

3.4. DSC measurements

The DSC pattern measured for the 60 mol % P_2O_5–40 mol % CuO glass sample is shown in Fig. 7 for a heating rate of 25 K min^{-1}. It is clear from the figure that the sample showed endothermal peaks at 360, 520, 560 and 580 °C, while the glass composition containing 50 mol% P_2O_5–50 mol% CuO showed only two endothermal peaks at 310 and 475 °C [15]. This indicates that increasing P_2O_5 content and decreasing CuO content shifted the 310 °C peak to 360 °C, and the 475 °C peak to 520 °C. The 560 and 580 °C peaks did not appear in the 50 mol % P_2O_5–50 mol% CuO, due to the lower concentration of P_2O_5.

A process of bond switching or transfer of bonds occurs, whereby segments of the network can become detached and able to move relative to the rest of the network. According to Ray [23], the glass transition temperature is strictly linked to the density of cross linking rather than to the bond strength. When the sample was cooled to room temperature and the DSC curve re-measured, the same endothermal peaks reappeared. This indicates that the glass transition temperatures in the first measurement were not permanent, but reversible.

4. Discussion

We believe that the mechanism of conduction in copper–phosphate glasses is similar to that of vanadium–phosphate glasses. ESR studies on
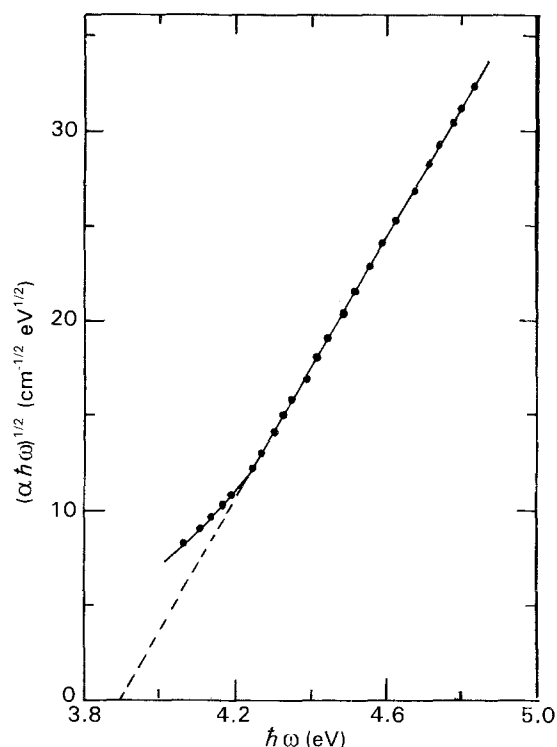

Figure 6 $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy for a copper–phosphate glass sample.
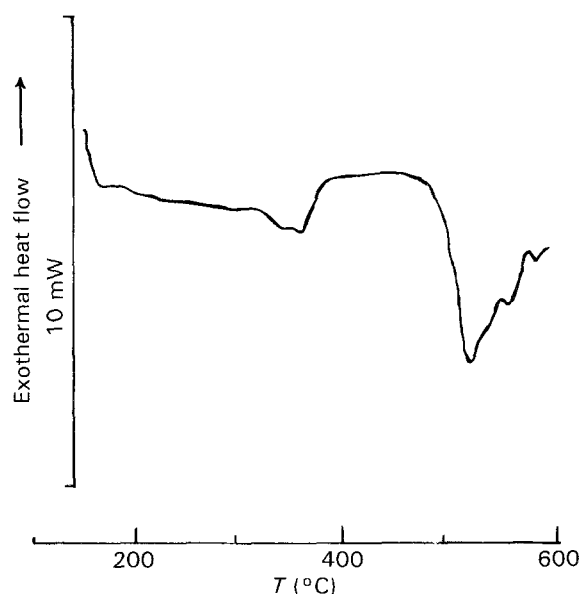

Figure 7 DSC curve of copper–phosphate glass sample taken at a heating rate of 25 K min^{-1}.

copper–phosphate glasses showed that the reduced valency states of Cu^{2+} and Cu^+ ions were both present in the glass in varying amounts [13].

In view of these results the conduction in copper–phosphate glasses may be assumed to be due to hopping of electrons from the low valence state, Cu^+, to the higher state, Cu^{2+}. Thus, the change in the CuO content in the glass composition is expected to alter the ratio (Cu^+/Cu_{total}) and consequently controls the transition probabilities of the conduction electrons and hence the electrical conductivity and the optical absorption.

In the light of the above discussion, the values of the activation energy and the optical gap of

copper–phosphate glasses could be ascribed to a dependence on the concentration ratio of Cu^+/Cu^{2+} ions in the glasses with various CuO contents.

The infrared spectrum obtained (Fig. 4) is similar to those spectra of copper–phosphate glasses studied by Hogarth and Moridi [24]. The absorption peak for CuO, which appeared at $620\,cm^{-1}$ [24], did not appear in our glass composition. This band seems to be completely broken down as a consequence of the P–O–Cu stretching vibration. It has been suggested that a partial bond such as P–O–Cu^+ may be created in the region $900–1250\,cm^{-1}$ and the band shifts with increasing CuO content [13]. It can be said that the whole behaviour of phosphate glasses is generally dominated by their P_2O_5 content which represents the major constituent.

References

1. N. F. MOTT, *J. Non-Cryst. Solids* **1** (1968) 1.
2. G. S. LINSLEY, A. E. OWEN and F. M. HAYATEE, *ibid.* **4** (1970) 208.
3. C. F. DRAKE, I. E. SCANLAN and A. ENGEL, *Phys. Status Solidi (a)* **32** (1969) 193.
4. C. A. HOGARTH and M. JAMEL BASHA, *J. Phys. D Appl. Phys.* **16** (1983) 869.
5. I. KASHIF, S. A. EL-SAHHAR, A. M. SANAD and S. A. EL-HENAWII, *J. Mater. Sci.* **5** (1986) 827.
6. A. MANSINGH, A. DHAWAN, R. P. TANDON and J. K. VAID, *J. Non-Cryst. Solids* **27** (1978) 309.
7. A. KLONKOWSKI, *Phys. Chem. Glasses* **26** (1985) 11.
8. A. A. HOSSEINI and C. A. HOGARTH, *J. Mater. Sci.* **20** (1985) 261.
9. C. ANANTHAMOHAN, C. A. HOGARTH, C. R. THEOCHARIS and D. YEATES, *ibid.* **25** (1990) 3956.
10. L. D. BOGOMOLOVA, *J. Non-Cryst. Solids* **30** (1979) 379.
11. L. D. BOGOMOLOVA, M. P. GLASSOVA and V. A. SHMUDER, *Phys. Khim. Stecla* **5** (1979) 26.
12. L. D. BOGOMOLOVA and M. P. GLASSOVA, *J. Non-Cryst. Solids* **37** (1980) 423.
13. J. M. ARZEIAN and C. A. HOGARTH, *J. Mater. Sci.* **26** (1991) 5353.
14. A. A. KUTUB, A. E. MOHAMED-OSMAN and C. A. HOGARTH, *ibid.* **21** (1986) 3517.
15. A. A. KUTUB, F. H. AL-GHORAIBIE, S. S. NATTO, A. M. ALSANOOSI, S. S. BABKAIR and A. S. FAIDAH, *ibid.* **27** (1992) 1343.
16. A. A. KUTUB, S. S. BABKAIR, A. M. ALSANOOSI and A. S. FAIDAH, *Int. J. Electron.* **72** (1992) 567.
17. E. E. KHAWAJA, M. N. KHAN, A. A. KUTUB and C. A. HOGARTH, *ibid.* **58** (1985) 471.
18. C. A. HOGARTH and M. A. GHAURI, *J. Mater. Sci.* **15** (1980) 409.
19. M. H. HEKMAT-SHOAR, C. A. HOGARTH and G. R. MORIDI, *ibid.* **20** (1985) 889.
20. C. K. SHIH and G. J. SU, in "Proceedings of the VIIth International Conference on Glass", Brussels (1965) p. 1.3.3.48.
21. C. A. HOGARTH and G. R. MORIDI, *Int. J. Electron.* **54** (1983) 169.
22. E. A. DAVIS and N. F. MOTT, *Philos. Mag.* **22** (1970) 903.
23. N. H. RAY, *J. Non-Cryst. Solids* **15** (1974) 423.
24. C. A. HOGARTH and G. R. MORIDI, *J. Mater. Sci. Lett.* **3** (1984) 481.