JOURNAL OF MATERIALS SCIENCE 27 (1992) 1343–1346

Spectroscopic and DSC studies of vanadium–copper–phosphate glasses

A. A. KUTUB, F. H. AL-GHORABIE, S. S. NATTO
Department of Physics, Umm Al-Qura University, Makkah, Saudi Arabia
A. M. ALSANOOSI, S. S. BABKAIR, A. S. FAIDAH
Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

A series of glass samples were prepared from admixtures of P_2O_5, V_2O_5 and CuO and results are reported for optical absorption, infrared absorption spectra and differential scanning calorimetry (DSC) as a function of copper content up to 10 mol %. It is found that the addition of CuO shifts the optical absorption edges towards lower energies in the range from 3.15–2.89 eV. The addition of CuO does not seem to introduce any new absorption band as compared with the spectrum of a pure vanadium phosphate glass. DSC measurements showed endothermal peaks varying from 475–510 °C depending on the CuO content.

1. Introduction

Measurement of the optical absorption coefficient, particularly near the fundamental absorption edge provides a standard method for the investigation of optically induced electronic transitions and provides some ideas about the band structure and energy gap in both crystalline and non-crystalline materials.

Several transition metal oxides, when heated with glass-forming substances such as P_2O_5, TeO_2 and GeO_2, form glasses on quenching from the melt. The loss of oxygen from the melt produces lower valency transition metal ions and indeed the electronic conduction in these glasses is associated with hopping of electrons from reduced to normal valency ions as discussed in detail by Mott [1].

A great deal of work has been carried out on many glass systems, including a number of semiconductor glasses based on the vanadium phosphate system [2–6]. During the last few years many workers have studied the oxide glasses containing mixed transition metal ions.

Bogomolova *et al.* [7–9] 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. Khan and Memon [10] studied the optical properties of vanadium phosphate glasses containing various amounts of VCl_3 and found that the addition of chlorine acts as an oxidizing agent and alters the ratio of concentration of vanadium ions. Bandyopadhyay [11] investigated the BaO–B_2O_3 glasses containing single and mixed transition metal oxides and suggested that out of various types of interactions taking place in the system, strong interaction between V^{4+} and Fe^{3+} or Cu^{2+} ions may result in the formation of V^{4+}–O–Fe^{3+} or V^{4+}–O–Cu^{2+}associates.

In this work we have studied the effect of the addition of cupric oxide on the optical and infrared absorption of vandium phosphate glasses.

2. Experimental procedure

All glasses in the P_2O_5–V_2O_5–CuO system were prepared from analytical grade materials, according to their molar composition (Table I). The alumina crucible containing the mixture was heated at 200 °C for 1 h. This initial heating served to minimize material volatilization. The crucible was then transferred to a melting furnace maintained at a selected temperature of 1000 °C for 2 h with frequent stirring. The homogenized melts were then cast on a clean stainless steel plate mould (pre-heated to 250 °C) in the form of circular discs of 2 cm diameter and 2 mm thick. The disc was immediately transferred to another furnace which was already maintained at 300 °C. The furnace was kept at this temperature for 1 h and then was switched off to cool down to room temperature. The glass samples were polished using diamond paste down to a minimum grit size of 0.1 μm. X-ray diffraction measurements confirmed the glassy nature of all samples used. For optical measurements, thin blown films of the glasses were prepared by dipping an alumina tube into the molten material and collecting a

TABLE I Composition data for vanadium phosphate glasses containing cupric oxide

Glass sample	Composition (mol %)	Density (g cm^{-3})
1	$(P_2O_5)_{50}$–$(V_2O_5)_{50}$–$(CuO)_0$	2.8134
2	$(P_2O_5)_{50}$–$(V_2O_5)_{47.5}$–$(CuO)_{2.5}$	2.8428
3	$(P_2O_5)_{50}$–$(V_2O_5)_{45}$–$(CuO)_5$	2.8710
4	$(P_2O_5)_{50}$–$(V_2O_5)_{42.5}$–$(CuO)_{7.5}$	2.890
5	$(P_2O_5)_{50}$–$(V_2O_5)_{40}$–$(CuO)_{10}$	2.9211

small amount of glass melt on the end of the tube and blowing it into the air. Films ranging in thickness from 5–10 μm were prepared. 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 from 185–900 nm using a Varian model cary 2390 spectrophotometer.

The infrared absorption of thin-film glasses was measured at room temperature in the range 400–4000 cm^{-1} using an IR-460 Shimadzu double-beam recording infrared spectrophotometer. Also, for comparison, infrared measurements were made for powdered glass samples using a Perkin–Elmer 1320 infrared spectrophotometer in the range 600–4000 cm^{-1}. The glass samples were ground in a clean mortar to a fine powder. A few milligrams of glass powder were mixed and ground with a large quantity of KBr. KBr pellets, transparent to light, were formed by pressing the mixture at 10 ton for a few minutes under vacuum. The differential scanning calorimetry (DSC) measurement was carried out at atmospheric pressure in a Mettler TA 3000 thermal analysis system in the temperature range 303–873 K. The heat flow to the sample was measured under thermally controlled conditions. The sample was ground well to powder form and about 10 mg were contained in an aluminium crucible for measurement. The DSC pattern was then measured relative to an empty aluminium crucible which served as a reference.

The densities of the glass samples were measured at room temperature by the displacement method using xylene as the immersion liquid and a single pan balance of 10^{-4} g sensitivity.

3. Results and discussion

3.1. Optical absorption spectroscopy

The optical absorption measurements were made at room temperature for P_2O_5–V_2O_5 glass system and for glasses containing CuO as indicated in Table I. Fig. 1 shows the absorbance as a function of the wavelength for glass films of different compositions. It is clear from the optical absorption spectra that there are no absorption peaks due to CuO in vanadium phosphate glasses. This may be due to the high concentration of vanadium in the glass compositions. The region of high absorption of all glass samples in the visible range seems to move to longer wavelength. The general appearance of the absorption spectrum (Fig. 1) is similar to those observed by Khan *et al.* [4] for P_2O_5–V_2O_5 containing different rare-earth oxides, to those reported by Hogarth and Hosseini [12] for V_2O_5–P_2O_5–TeO_2 and to the results of Khawaja *et al.* [13] for V_2O_5–P_2O_5 glasses.

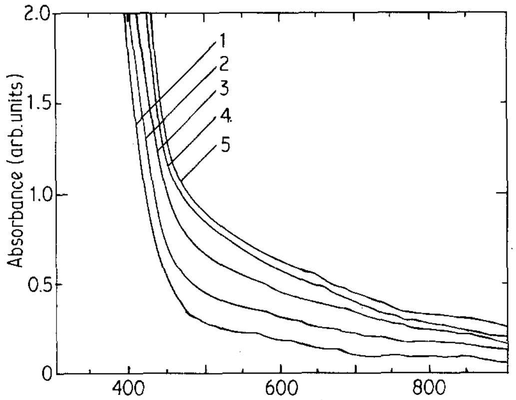

Figure 1 Absorption as a function of wavelength for unannealed thin blown glass films. Numbers by curves refer to Table I.

By increasing the CuO content, the absorption edges shift towards lower energies within the energy range from 3.15 eV (394 nm) to 2.89 eV (429 nm). Khan and Memon [10] found that by increasing the VCl_3 content in the V_2O_5–P_2O_5 glass system, the absorption edges shift towards higher energies from 2.0 to 2.2 eV due to the addition of chlorine which acts as an oxidizing agent and alters the ratio of concentration of vanadium ions and thus the absorption coefficient. It was reported by Bamford [14] that vanadium in various glasses can exist in three oxidation states, V^{5+}, V^{4+} and V^{3+} In the soda–lime silica glass system, the absorption band at 350 nm was assigned to V^{5+}, the bands at 425 and 645 nm to V^{3+}, and the band at 1100 nm to V^{4+}. Following this, we may suggest that the absorption spectra reported in the present work have no appreciable contribution from V^{5+}. Because the glass former has very little effect on the optical absorption, we may, therefore, assume that the observed high absorption region is due to the band of V^{3+} ions. The absorption tail extending from 500–900 nm (Fig. 1) arises from a combination of the bands associated with V^{3+} and V^{4+} ions in the glass.

It has been reported by McSwain *et al.* [15] that the absorption characteristics of these glasses may be described on the generally accepted qualitative understanding that the absorption edge is determined by the oxygen bond strength in the glass-forming network; the formation of non-bridging oxygens, for instance, changes the absorption characteristics.

3.2. Infrared absorption

The spectral curves in the 4000–400 cm^{-1} region obtained for thin blown films of P_2O_5–V_2O_5 glass and glasses containing various amounts of CuO are shown in Fig. 2. The general shape of the infrared spectra for various CuO concentrations resembles that of the undoped P_2O_5–V_2O_5 glass. No new peaks that could be attributed to CuO content are found within the wavelength range studied. The spectra of the same glass compositions obtained on KBr discs and annealed at 300 °C for 1 h are presented in Fig. 3. It is evident that the spectra recorded for blown thin film are sharper and better defined than those obtained with KBr discs.

The absorption peaks observed in all the glasses at 420, 600, 780, 900–1200, 1620 and 2000 cm^{-1} are in good agreement with the spectra obtained by Khan and co-workers [4, 10]. Shih and Su [16] have carried out an extensive study of the infrared spectra of binary phosphate glasses and they found the spectra of these glasses to be essentially the same. Ghosh and

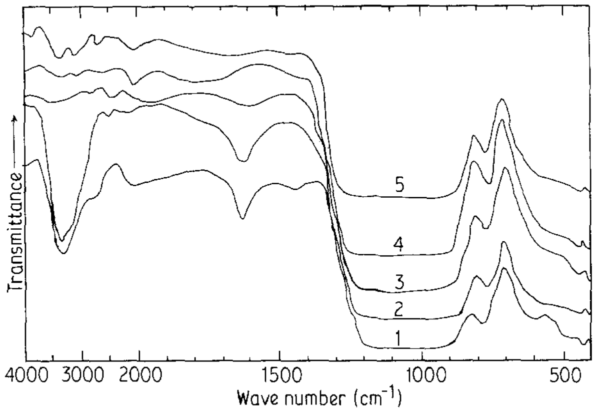

Figure 2 The infrared absorption spectra of vanadium phosphate glasses containing CuO (Table I), taken with thin blown films.

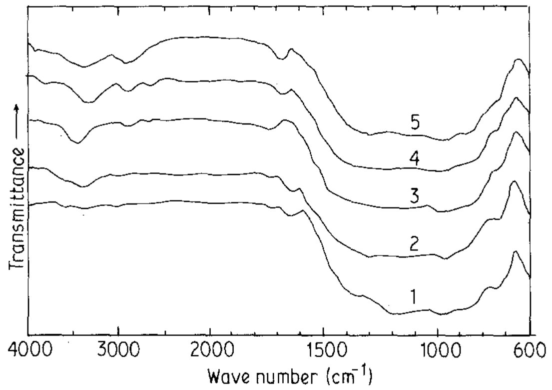

Figure 3 The infrared absorption spectra taken on KBr discs of glass samples (Table I) annealed at 300 °C for 1 h.

Chaudhri [17] have reported an infrared spectrum of crystalline V_2O_5 having peaks at 1640, 1030, 840, 810, 610, 495, 400, and 320 cm^{-1}. The intensity of the absorption peak at 1620 cm^{-1} observed in our glasses decreased with decreasing the V_2O_5 content, i.e. increasing the CuO content. It has been reported [18] that the peak due to the vanadium–oxygen stretching vibration appears at 1015 cm^{-1}. The presence of V^{4+} ions seems to reduce the V–O stretching frequency to 900–1015 cm^{-1}.

Phosphate ions introduce weak vibrational absorption in some phosphate glasses in the range 1020–1100 cm^{-1}, and in some crystalline phosphate networks in the range 1150–1400 cm^{-1} [19]. Thus, the strong and broad band at 900–1200 cm^{-1} seems to be a combined effect of both V_2O_5 and P_2O_5. The P–O–P ring frequency of P_2O_5 has been reported at 780 cm^{-1} [20] which agrees with our results. The general position of Cu–O frequency is not detectable in P_2O_5–V_2O_5–CuO glasses. This band may be buried in the broad transmission region at 6000–7000 cm^{-1}. This is supported by results of Hogarth and Moridi [21] who reported that the phosphate tetrahedra dominate the structure of copper–calcium–phosphate glasses and that a partially covalent P–O–Cu^+ bond is created at high copper contents.

The absorption band which appeared at 3400 cm^{-1} is believed to be associated with water trapped in the glass.

3.3. DSC measurements

The DSC patterns measured for different glass samples are shown in Fig. 4 for a heating rate of 20 K min^{-1}. It was found that all samples showed an endothermal peak, which shifts to higher temperature as the CuO content is increased. Fig. 5 shows the variation of endothermal peak temperature with the CuO content in the glass samples. It is clear from this figure that the phase-transition temperature increased from 475 °C in the undoped sample to 510 °C for a sample doped with 7.5 mol % CuO, then decreased to 500 °C at 10 mol % CuO. It is clear from Fig. 4 that the undoped glass sample (Sample 1) showed also

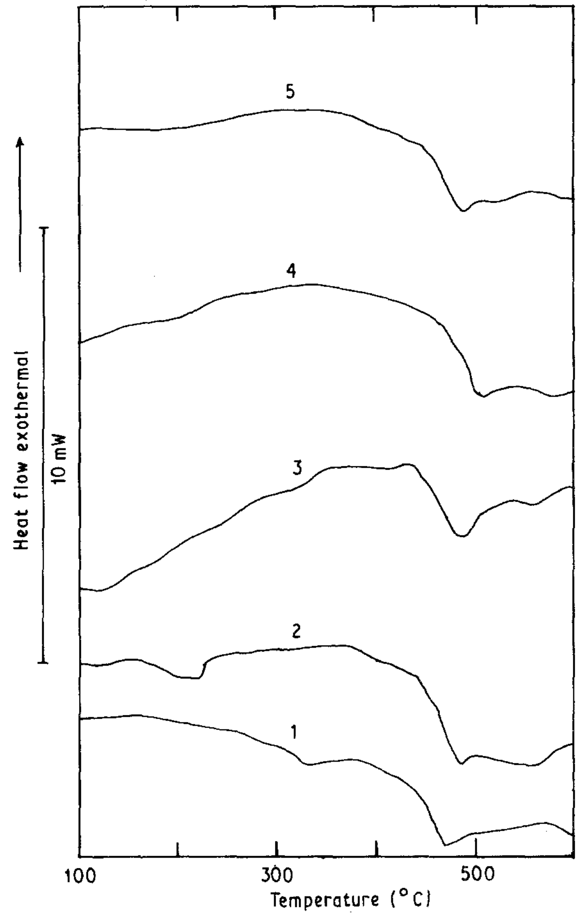

Figure 4 DSC curves of glass samples taken at a heating rate of 20 K min^{-1}.

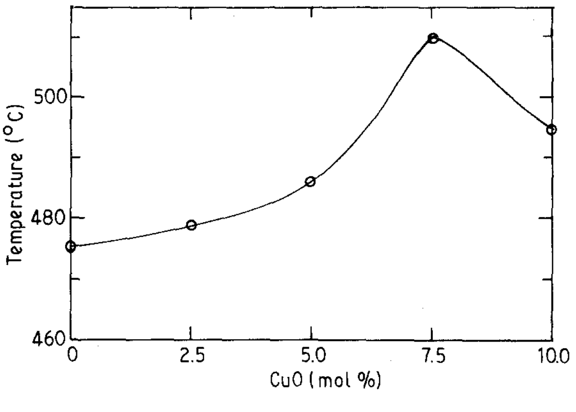

Figure 5 Variation of endothermal phase-transition temperature with CuO content of glass samples.

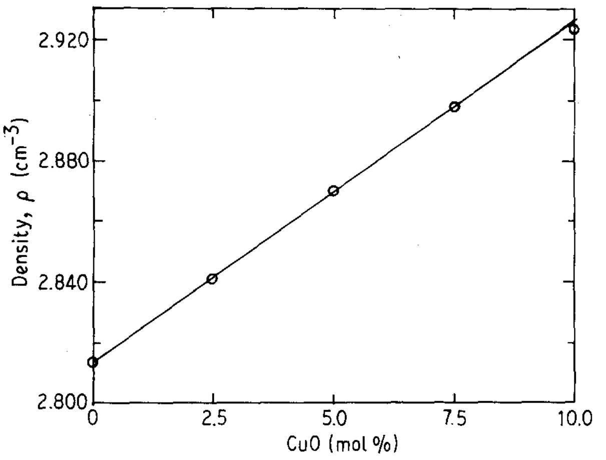

Figure 6 Density, ρ, of P_2O_5–V_2O_5–CuO glasses as a function of CuO content.

another phase transition at around 310 °C. With the addition of a small amount of CuO (2.5 mol %) the phase transition at 310 °C shifted to lower temperature at 240 °C. With further addition of CuO this phase transition disappeared. Ghosh and Chaudhri [17] found that the transition temperatures of V_2O_5–Bi_2O_3 glasses lie in the range 260–270 °C and increase with decrease of V_2O_5 content in the glasses.

It has been reported that for the V_2O_5–P_2O_5–B_2O_3 glass system there are two phase separations, and any subsequent crystallization of V_2O_5 is at 290 and 410 °C [22]. 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 samples were cooled down to room temperature and DSC curves re-measured, the same endothermal peak reappeared for all glass samples. This indicates that the glass transition temperature in the first measurement was not permanent but reversible.

3.4. Density variation with composition

The density of the glass samples is shown in Fig. 6 as a function of the concentration of CuO in the glasses. It is observed that the density increases almost linearly with decreasing V_2O_5 content and increasing CuO content in the glasses. This indicates that the structure becomes more compact as a result of copper content. Khan *et al.* [4] reported a sharp variation in the relative density of vanadium phosphate glasses containing rare-earth oxides from 2.92 to 3.12. Ghosh and Chaudhri [17] observed that the density increases with decreasing V_2O_5 content in the V_2O_5–Bi_2O_3 glasses.

References

1. N. F. MOTT, *J. Non-Cryst. Solids* **1** (1968) 1.
2. N. A. GHONEIM, *ibid.* **56** (1983) 367.
3. E. E. KHAWAJA and G. D. KHATTAK, *Phys. Status Solid.* (*a*) **93** (1986) 621.
4. M. N. KHAN, R. HARANI, M. M. AHMED and C. A. HOGARTH, *J. Mater. Sci.* **20** (1985) 2207.
5. A. YADAV and V. P. SETH, *ibid.* **22** (1987) 239.
6. M. SAYER, A. MANSINGH, J. M. REYES and G. ROSENBLATT, *J. Appl. Phys.* **42** (1) (1971) 2857.
7. L. D. BOGOMOLOVA, *J. Non-Cryst. Solids* **30** (1979) 379.
8. L. D. BOGOMOLOVA, M. P. GLASSOVA and V. A. SHMUDER, *Phys. Khim. Stecla* **5** (1979) 26.
9. L. D. BOGOMOLOVA and M. P. GLASSOVA, *J. Non-Cryst. Solids* **37** (1980) 423.
10. M. N. KHAN and A. MEMON, *J. Mater. Sci.* **22** (1987) 3309.
11. A. K. BANDYOPADHYAY, *ibid.* **16** (1981) 189.
12. C. A. HOGARTH and A. A. HOSSEINI, *ibid.* **18** (1983) 2697.
13. E. E. KHAWAJA, M. S. HUSSAIN, M. A. KHAN and J. S. HWANG, *ibid.* **21** (1986) 2812.
14. C. R. BAMFORD, "Colour Generation and Control in Glass" (Elsevier, Amsterdam, 1977).
15. B. D. McSWAIN, N. F. BORRELLI and SU GOUQ-JEN, *Phys. Chem. Glasses* **4** (1) (1963) 1.
16. C. K. SHIH and G. J. SU, in "Proceeding of the VIIth International Conference on Glass", Brussels (1965) p. 1.3.3.48.
17. A. GHOSH and B. K. CHAUDHRI, *J. Mater. Sci.* **22** (1987) 2369.
18. B. H. V. JANAKIRAMA RAO, *J. Amer. Ceram. Soc.* **48** (1965) 311.
19. G. W. ANDERSON and W. D. COMPTON, *J. Chem. Phys.* **52** (1970) 6166.
20. M. A. GHAURI, *J. Mater. Sci. Lett.* **2** (1983) 660.
21. C. A. HOGARTH and G. R. MORIDI, *ibid.* **3** (1984) 481.
22. Y. LIMB and R. F. DAVIS, *J. Amer. Ceram. Soc.* **62** (1978) 403.
23. N. H. RAY, *J. Non-Cryst. Solids* **15** (1974) 423.

Received 7 January
and accepted 18 March 1991