JOURNAL OF MATERIALS SCIENCE 19 (1984) 99–104

The infrared spectra of CdO–P_2O_5 and CdO–ZnO–P_2O_5 glasses

M. A. GHAURI*, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex, UK

The infrared absorption spectra of cadmium phosphate and cadmium zinc phosphate glasses were measured. The structure of cadmium phosphate glasses was found analogous to cadmium zinc phosphate glasses at 30% of ZnO but a further decrease in ZnO content causes a 30 to 40 cm^{-1} change towards higher wave number of the absorption band at the stretching frequency. Annealing at different temperatures does not show a prominent change in absorption band positions.

1. Introduction

The early investigation by infrared spectroscopy of the structure of phosphate glasses, especially those containing alkali metal oxides, was reported by Miller and Wilkins [1] who used the KBr pellet technique. The fundamental absorption range for the orthophosphates was found to be at 1030 to 1000 cm^{-1}. The only other fundamental frequency allowed in the infrared appears near 500 cm^{-1}. More recently, the fundamental frequencies of all types of phosphate ions, such as metaphosphates, pyrophosphates and hypo-phosphates in crystalline and glassy inorganic phosphate compounds have been investigated by Corbridge and Lowe [2–4].

Shih and Su [5] reviewed the work of Corbridge and Lowe [2–4], and Bues and Gehrke [6], made a systematic investigation of phosphate glasses containing either alkali (Li, Na, K, Rb) or alkaline earth (Ca, Sr, Ba) elements in the range 2 to 200 μm, and concluded that the spectra of these glasses are essentially the same except for a slight diffuseness which appears in the spectra of the alkaline earth metaphosphates. Müller [7] argued that P=O double bond lies in the range 1282 to 1205 cm^{-1} in the polyphosphate chain and the P–O group is characterized by a stretching frequency at 1110 cm^{-1} whereas the P–O–P ring frequency should occur between 805 and 740 cm^{-1} for cyclic phosphates. Williams *et al.* [8] measured the infrared spectra of a series of binary phosphate glasses with molar ratio of metal oxide to P_2O_5 of 1 to 2 using a KBr-pellet sampling technique. It was found that the absorption band in the region of 900 cm^{-1} moves to higher frequencies.

The infrared spectra of transition metal oxides have been studied by a number of investigators [9, 10]. Sayer and Mansingh suggested that phosphate tetrahedra dominate the structure of manganese, cobalt, and copper glasses [10]. The evidence is supported by measurements on copper–calcium–phosphate glasses where covalent P–O–Cu^+ bonds would be created in the glasses having a higher copper content.

2. Experimental procedure

The infrared absorption spectra of specimens of cadmium phosphate and cadmium zinc phosphate glasses, annealed at 500° C for three hours, were studied at room temperature and in the frequency region 4000 to 400 cm^{-1} with a Unicam SP2000 double-beam recording infrared spectrophotometer. A 30% by weight sample of the selected glass specimen was ground with 70% by weight of KBr (laboratory reagent for infrared spectroscopy, BDH Chemicals Ltd.) in a clean alundum mortar into a fine powder. KBr pellets of thickness of 1 mm, transparent to light, were formed by pressing the mixture at 10 tons for a few minutes under vacuum.

---

*Present address: Government College of Science, Lahore, Pakistan.

0022–2461/84 $03.00 + .12

TABLE I Main features of the absorption spectra of cadmium phosphate and of cadmium zinc phosphate glasses

Specimen number	Composition mol %			Infrared absorption band positions (cm^{-1}) for CdO–P_2O_5 and CdO–ZnO–P_2O_5 glasses								
	P_2O_5	CdO	ZnO									
a	50	50	–	–	480	530	750–780	920	1090	1290	1630	3450
b	55	45	–	–	480	–	780	920	1080	1290	1630	3450
c	60	40	–	–	480	–	780	920	1080	1290	–	3450
d	65	35	–	–	480	–	750	920	1040–60	1300	–	3450
e	70	30	–	–	480	–	750	920	1040–60	1300	–	3450
f	75	25	–	–	480	–	750	920	1050	1300	–	3450
g	80	20			460–500	–	750	920	1050–80	1300–20	–	3450
m	85	15	–	–	480	–	750	920	1020–60	1300	–	3450
n	90	10	–	–	480	–	750	920	1050	1300	–	3450
Z_1	–	CdO	–	–	–	–	–	–	–	–	1400	–
Z_2	P_2O_5	–	–	430	480	530	–	–	–	–	–	–
Z_3	–	–	ZnO	430–500	–	540	–	–	–	–	–	–
l	70	25	5	–	480	–	750	920	1050–80	1290	–	3450
k	70	20	10	–	480	–	750	910–50	1050–80	1260–1300	–	3450
j	70	15	15	–	480	–	750	920	1080	1290	–	3450
i	70	10	20	–	480	–	750	920	1080	1290	–	3450
h	70	5	25	–	480	–	750	920	1080	1290	–	3450
P	70	–	30	–	480	–	750	920	1050	1290	–	3450

3. Results and discussion for cadmium phosphate glasses

The infrared absorption maeasurements in binary CdO–P_2O_5, and ternary CdO–ZnO–P_2O_5, glasses of the compositions given in Table I, were made. Fig. 1 shows the infrared absorption spectra of all the specimens containing CdO–P_2O_5, along with the spectra of crystalline CdO and P_2O_5. Table I shows the positions of the absorption bands obtained in these measurements. The comparison of the position of the absorption band of crystalline CdO is very close to the spectra reported by Nyquist and Kagel [11]. The CdO fundamental frequency lies somewhere towards higher frequencies and there is no bond vibration in the range 400 to 400 cm^{-1} arising from an ionic character such as for NaCl. The absorption peaks present in the infrared spectra are probably due to combination tones.

The absorption band at 480 cm^{-1} which appears in all glasses and in crystalline P_2O_5 is known to be the fundamental frequency of the $[P_2O_5]^{3-}$ group [10, 12]. The most important point in cadmium phosphate glasses is that the weaker absorption peaks at higher concentrations of P_2O_5 at the P=O double bond and P–O bond positions are difficult to locate with an accuracy of position to within ± 10 cm^{-1}. The P=O double bond, $P-\bar{O}$ stretching frequency and P–O–P ring frequency in 50 mol % CdO–50 mol % P_2O_5 glass occur at 1290, 1090 and 750 to 780 cm^{-1}, respectively.

Our conclusions for cadmium phosphate glasses are as follows.

(i) The fundamental absorption frequency is not dependent on the concentration of P_2O_5 or CdO present in cadmium phosphate glasses.

(ii) The bridging oxygen absorption bands are much weaker. When the percentage of CdO is increased in P_2O_5, the intensity of the infrared band at about 780 cm^{-1} decreases. The same infrared band becomes progressively broader with increasing percentages of CdO, another sign of disordering of the original structure. A new band begins to emerge when the concentration of CdO exceeds approximately 20 mol %.

Our values for the P=O, P–O, P–O–P absorptions are in accordance with the expected values for metaphosphates given by Müller [7]. So we may regard these glasses as cadmium metaphosphate glasses because their density and molar volume vary linearly with composition.

4. Results and discussion for cadmium zinc phosphate glasses

Fig. 2. shows the absorption spectra of CdO–ZnO–P_2O_5 glasses with 70 mol % P_2O_5, together with the spectra of crystalline ZnO. Table I shows the positions of the absorption bands obtained. Zinc oxide as compared to cadmium oxide has fourfold coordination in its crystalline compounds and this behaviour is expected to be preserved in glassy materials. Hurt and Philips [13], while

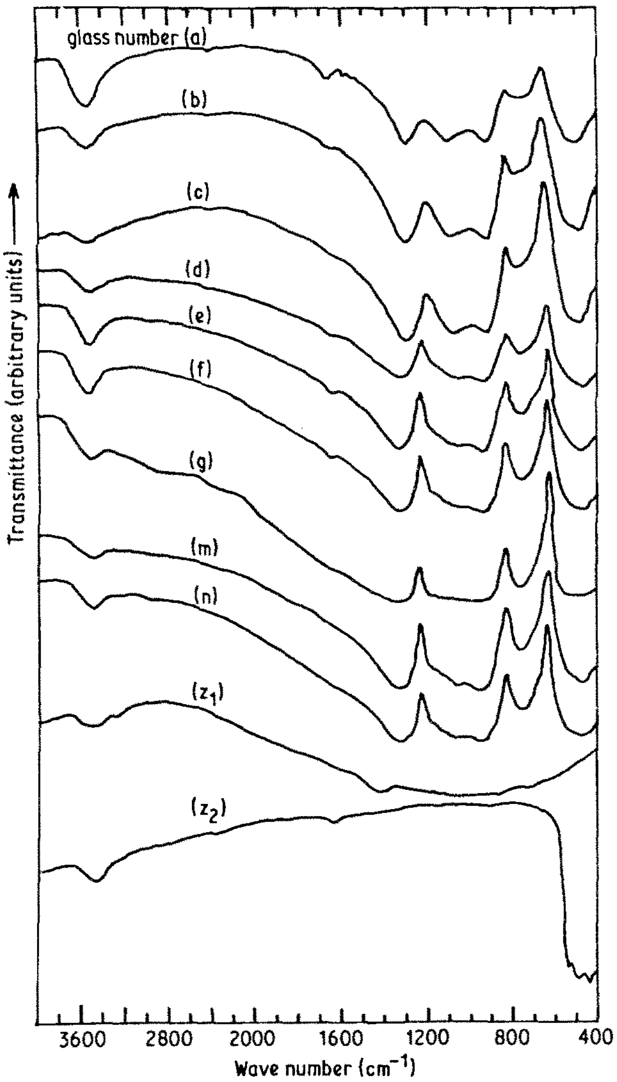

Figure 1 Infrared absorption spectra for a series of $CdO-P_2O_5$ glasses.

studying the infrared absorption band of SiO_2–ZnO–Na_2O glasses, found that Zn–O tetrahedral bonds are in the range of 600 to 400 cm^{-1} and suggested that Zn–O octahedra should lie at 300 to 100 cm^{-1}. Moreover the increase of ZnO concentration results in shifting the latter region to 600 to 400 cm^{-1}. Such a shift indicates an increase in the number of tetrahedrally-surrounded zinc cations.

Tarte [14] studied the infrared spectra of silicate glasses containing oxides of aluminium, magnesium, zinc, titanium and lithium. He found a downward shift of the strong SiO_4 band near 1050 cm^{-1} with increasing wt % ZnO content but an upward shift of the 475 cm^{-1} band. The shift possibly suggests the presence of a superimposed band related to ZnO_4 tetrahedra. The number of tetrahedrally coordinated zinc ions can be affected by water in phosphate glasses. Krivovyazov *et al.* [15] showed that zinc caesium phosphate glasses absorb water when kept for a certain time in air. As this water diffuses into the glass body, the traces of tetrahedrally coordinated zinc are converted to the octahedrally coordinated form. This transition was observed visually from the change in colour of the glass with incorporated $Co(PO_3)_2$ from violet to pink.

The addition to the ZnO content in cadmium phosphate glasses at 70 mol % P_2O_5 has no significant effect on the position of the absorption band associated with crystalline P_2O_5. The P=O double bond and P–O–P ring frequency are unaffected except they are broadened, but the $P-\bar{O}$ stretching frequency band, with the increase of ZnO content, moves 30 cm^{-1} towards the higher wave-numbers in comparison with 30 mol % CdO–70 mol % P_2O_5.

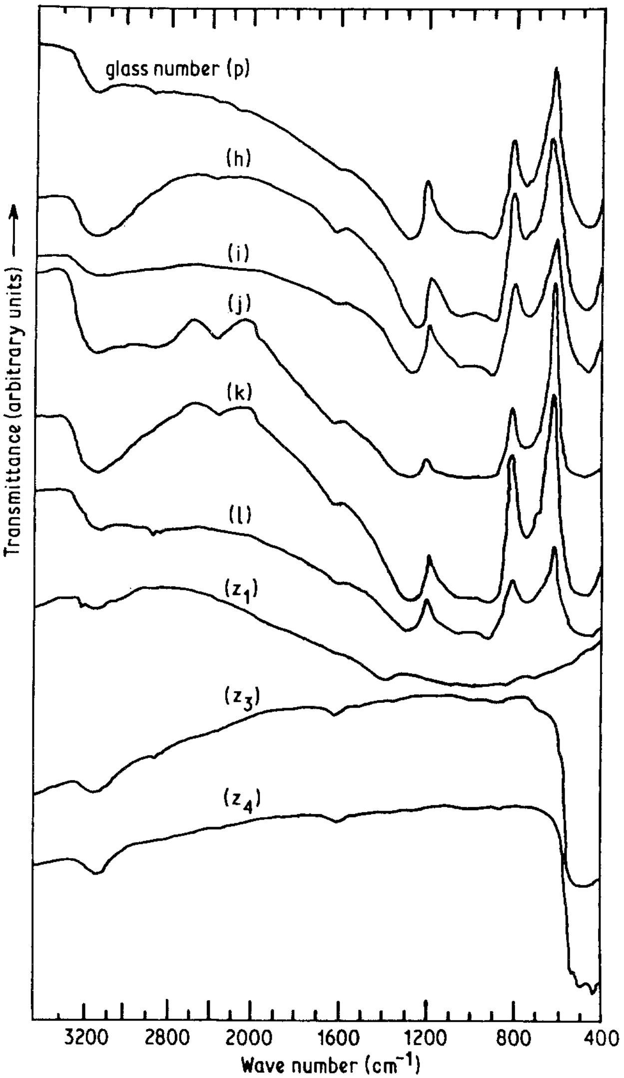

Figure 2 Infrared absorption spectra for a series of CdO–ZnO–P_2O_5 glasses.

Such a change indicates that, as the ion–oxygen attraction increases, the phosphate chain length appears to decrease. The values of P=O frequency, double-bond P–$\bar{O}$ stretching frequency and P–O–P ring frequency are shown in Table I for each composition.

By replacing 30 mol% with CdO in 70 mol% P_2O_5 glass, the bands at 1290, 1050 and 750 cm^{-1} would seem to be, as in Fig. 3, attributed to the P=O double bond, and P–$\bar{O}$ stretching frequencies and the P–O–P ring frequency, respectively. This is a clear indication that 30 mol% CdO–70 mol% P_2O_5 and 30 mol% ZnO–70 mol% P_2O_5 glasses have similar structures but any further increase in CdO content causes a 30 to 40 cm^{-1} change towards higher wave number at the P–$\bar{O}$ stretching frequency, and the reason for this shift is not clear. It could well be due to a change in coordination number. Kordes and Bonn [16] also has described some abnormality in this range of composition which affects the absorption coefficient. A pronounced shift has been observed by Corbridge and Lowe in their salt [2, 3]. Bartholomew [17] also has a similar result that there is a shift of band position on the frequency ranges appropriate to P–$\bar{O}$ and P=O absorption, which occurs in sodium-phosphate glasses when replaced with silver. Moridi and Hogarth [18] also gave a similar explanation when calcium was replaced by copper in binary phosphate glasses. According to them, such a shift can be discussed in terms of the existence of covalent bond formation between the non-bridging oxygen ions and the silver, P–O–Ag, or copper ion P–O–Cu^+ units.

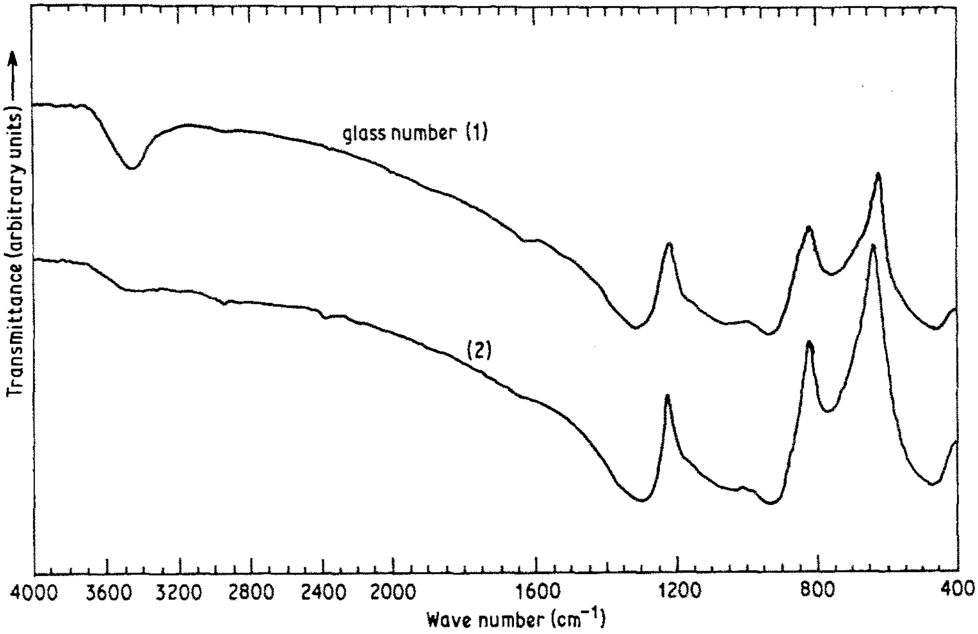

Figure 3 Infrared absorption spectra of (1) 30 mol % CdO–70 mol % P_2O_5 and (2) 30 mol % ZnO–70 mol % P_2O_5 glasses.

The absorption bands appearing in CdO–P_2O_5 and CdO–ZnO–P_2O_5 at 1625 to 1635, 2360, 3450 cm^{-1} are weak bands and are believed to be associated with a small amount of water trapped in the glasses during the experiment, but are possibly due to the overtones.

The infrared spectra of 50 mol % CdO–50 mol % P_2O_5 glass specimens annealed at 400, 500, 600° C, were also recorded and no significant changes were observed in the absorption band position as shown in Fig. 4, demonstrating that there is no structural change as a result of the annealing.

Qualitatively, the infrared spectra of cadmium

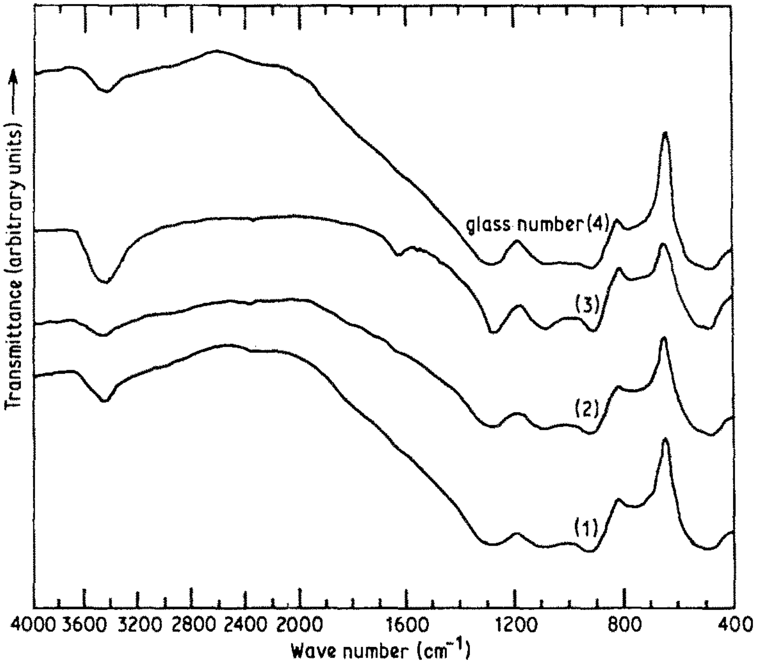

Figure 4 Infrared absorption spectra of 50 mol % CdO–50 mol % P_2O_5 glasses annealed at (1) 300° C (2) 400° C (3) 500° C (4) 600° C.

phosphate or cadmium–zinc-phosphate glasses would suggest that the phosphate tetrahedra dominate the structure of these glasses and that a partial covalent, P–O–Cd, bond would be created at higher cadmium content.

References

1. F. A. MILLER and C. H. WILKINS, *Anal. Chem.* **24** (1952) 1253.
2. D. E. C. CORBRIDGE and E. J. LOWE, *J. Chem. Soc.* Part I (1954) 493.
3. *Idem, ibid.* Part II (1954) 4555.
4. D. E. C. CORBRIDGE, *J. Appl. Chem.* **6** (1956) 456.
5. C. K. SHIH and G. J. SU, Proceedings of the VIIth International Conference on Glass, Brussels. 1.3.3. (1965) p. 48.
6. V. W. BUES and H. W. GEHRKE, *Anorg. Allgem. Chemie.* **288** (1956) 291–307.
7. K. -P. VON MÜLLER, *Glastech. Ber* **42** (1969) 83.
8. D. J. WILLIAM, B. T. BRADBURG and W. R. MADDOCKS, *J. Soc. Glasstechnol.* **43** (1959) 308T.
9. J. C. HADDON, E. A. ROGGERS and D. G. WILLIAMS, *J. Amer. Ceram. Soc.* **52** (1969) 52.
10. M. SAYER and A. MANSINGH, *Phys. Rev.* **B6** (1972) 4629.
11. R. A. NYQUIST and R. O. KAGEL, "Infra-red Spectra of Inorganic Compounds" (Academic Press, New York and London, 1971).
12. K. NAKAMO, "Infra-red Spectra of Inorganic and Co-ordination Compounds" (Wiley, New York, 1963).
13. J. C. HURT and C. J. PHILLIPS, *J. Amer. Ceram. Soc.* **53** (1960) 269.
14. P. TARTE, "Physics of Non-crystalline Solids" edited by J. A. Pins (North-Holland Publishing Company, Amsterdam, 1965) p. 549.
15. E. L. KRIVOVYAZOV, B. F. DZHURTNSKII, Kh. M. RAKHIMBEKOVA and N. K. VOSKRESENSKAYA, *Inorg. Matter* (Consultant Bur. Translations) **8** (1972) 1445.
16. V. E. KORDES and R. N. BONN, *Glasstechnol.* **41** (1968) 41.
17. R. F. BARTHOLOMEW, *J. Non-cryst. Solids* **7** (1972) 221.
18. G. R. MORIDI and C. A. HOGARTH, *Int. J. Electron.* **37** (1974) 141.

Received 13 April
and accepted 26 April 1983