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Investigation of infrared absorption spectra of copper phosphate glasses containing some rare earth oxides

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The spectra of copper–lutetium–phosphate and copper–erbium–phosphate glasses have been studied within the spectral range 4000 to 400 cm^{-1} by Fourier transform infrared spectroscopy. Incorporation of a small amount of lutetium or erbium influences some band positions compared with binary copper phosphate glasses. The additional bands in the range 491 to 576 cm^{-1} are attributed to the presence of Lu–O and Er–O groups. It has been observed that annealing of the samples at 500° C leads to a slight shift in the peak positions.

1. Introduction

Infrared spectroscopy is well known as an important analytical tool in the study of the structure of both organic and inorganic materials as it enables the arrangement of the molecules, the bond type and the force fields in the material to be investigated. The application of these infrared techniques to glassy materials, on the other hand, is only a relatively recent development.

Spectroscopic studies of lanthanide salts have been reported [1, 2] and traditional glasses doped with small quantities of rare earth oxides have been investigated [3, 5]. The different spectral behaviour from that shown by ions of the d-block transition elements, lies in the fact that the electrons responsible for the spectral and magnetic properties of lanthanide ions are $4f$ electrons, and the $4f$ orbitals are very effectively shielded from the effect of external forces by the overlying $5s^2$ and $5p^6$ shells. The states arising from the $4f^n$ configurations are only slightly affected by the surroundings of the ions and remain practically invariant for a given ion in various compounds. Shih and Su [6] have carried out an extensive study of the infrared spectra of binary phosphate glasses and they found the spectra of these of glasses to be essentially similar.

Müller [7] using the approach of Corbridge and Lowe [8, 9], argued that the P–O stretching lies at 1285 to 1205 cm^{-1}, the P–O^- group is characterized by a frequency at 1110 cm^{-1}, and the P–O–P ring frequency should occur between 805 and 740 cm^{-1}. Hogarth and Moridi [10] showed that in copper-calcium-phosphate glasses the phosphate tetrahedra dominate the structure of glasses and a partially covalent P–O–Cu^+ bond is created in glasses having a high copper content. Baun and McDevitt [11] studied the infrared spectra of rare earth oxides in the region 800 to 240 cm^{-1}.

In a previous paper [12] we have analysed the absorption edges for a series of copper-phosphate-lutetium glasses, and recently we have studied copper-phosphate-erbium glasses in terms of the theory of Davis and Mott [13] for interband non-direct transitions, and found that the edges lie in the visible region of the spectrum in the range 3.72 to 3.92 eV and 4.17 to 4.25 eV, respectively.

Fourier transform infrared spectroscopy is a well-known technique for the study of surface features of materials and also one of the few methods which allow direct examination of absorbed molecules on a solid surface.

2. Experimental procedure

The series of ternary P_2O_5–CuO–Lu_2O_3 and P_2O_5–CuO–Er_2O_3 glass samples containing 65 mol % P_2O_5, (35-x) mol % CuO and x mol % Lu_2O_3 or Er_2O_3, where x varies from 0 to 5, were prepared from analytical reagent grades of P_2O_5, CuO and Lu_2O_3 or Er_2O_3 in 30 g batches. The chemicals were carefully weighed and mixed in an alumina crucible.

In order to minimize a tendency to volatilization,

TABLE I The infrared peak positions of P_2O_5–CuO–Er_2O_3 glasses

Glass compositions (mol %)			Glass no.	Peak positions of infrared bands (cm^{-1})						
P_2O_5	CuO	Er_2O_3								
65	35	0	a	487	–	–	779	916	1267	3448
65	34	1	b	455	492	558	780	913	1279	3413
65	33	2	c	465	491	560	780	902	1260	3438
65	32	3	d	465	498	560	782	913	1260	3438
65	31	4	e	465	492	570	785	905	1268	3439

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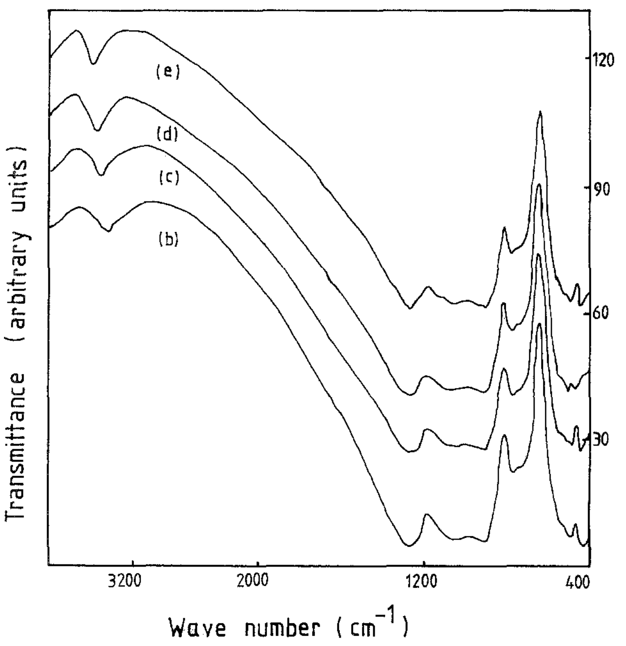

Figure 1 FTIR spectra for four copper–erbium–phosphate glasses.

the mixtures were kept for 1 h in a furnace at 300° C, and then melted at 1300° C for 3 h. The melts were quenched by pouring into disc-shaped depressions in a steel plate. The glass samples were ground in a clean mortar to a fine powder. Small quantities of glass powder were mixed and ground with a relatively large quantity of KBr. KBr pellets, transparent to light, were formed by pressing the mixture at 15 ton for a few minutes under vacuum. The infrared spectra for the unannealed samples were recorded immediately in a Perkin–Elmer 1710 Fourier transform infrared spectrometer over the range 4000 to 400 cm^{-1}.

3. Results

Rare earth oxides give absorption bands in the infrared 800 to 240 cm^{-1} region. The infrared spectrum of copper phosphate glasses lies in the region 4000 to 200 cm^{-1}. The majority of the resonant vibrational frequencies are present in this region.

Figs 1 and 2 illustrate the infrared spectra of four P_2O_5–CuO–Er_2O_3 and five P_2O_5–CuO–Lu_2O_3 samples, respectively, and their corresponding important absorption bands within the frequency ranges 3450 to 450 cm^{-1}, and 3552 to 420 cm^{-1}, are shown in Tables I and II, respectively.

Fig. 3 shows the infrared spectra of crystalline Lu_2O_3, and important absorption bands of Lu_2O_3, Er_2O_3, P_2O_5 and CuO are shown in Table III.

Figs 4 to 6 show the infrared spectra of a binary P_2O_5–CuO sample (Fig. 4), P_2O_5–CuO–Er_2O_3 (sample c) both unannealed and after annealing at 500° C (Fig. 5), and P_2O_5–CuO–Lu_2O_3 (sample j) both unannealed and after annealing at 500° C (Fig. 6).

4. Discussion

Continuing the spectroscopic study of copper phosphate glasses [7–10], our measurements of the infrared absorption spectra for these glasses containing lutetium or erbium add to the information about a basic glassy material of potential application in electronics. In many respects the spectra obtained (Figs 1 and 2) are similar to the absorption spectra of copper phosphate glasses which have been studied by Hogarth and Moridi [10]. The absorption peak for CuO, which appeared at 620 cm^{-1} as reported by Hogarth and Moridi [10] did not appear in either series of glasses. This band seems to be completely broken down as a consequence of the P–O–Cu stretching vibrations being modified by the P–O–Cu–O–Lu and P–O–Cu–O–Er bonds.

The addition of a very small amount of Lu_2O_3 or Er_2O_3 also affects the absorption band positions compared with binary copper phosphate glasses. A very slight shift in the position of some bands is observed. One absorption band varies from 465 to 480 cm^{-1} as the rare earth content is changed from sample to sample. Wong and Angell [13] found that, in binary

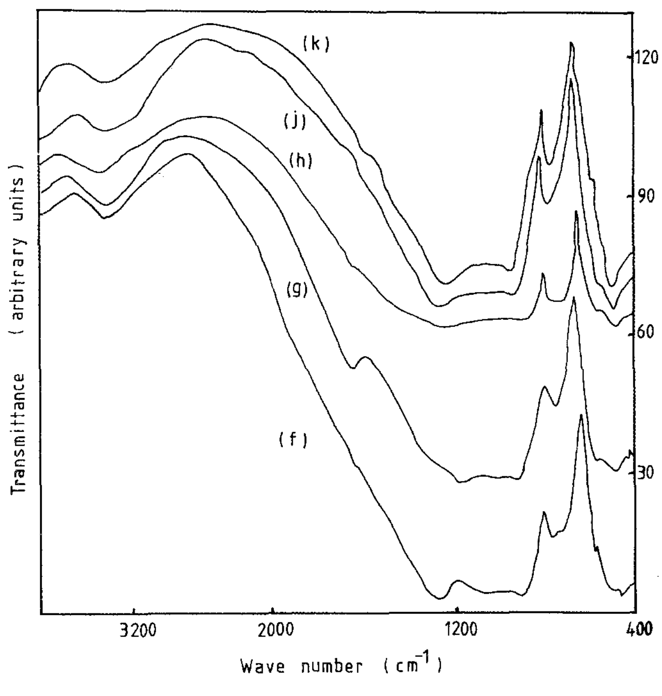

Figure 2 FTIR spectra for five copper–lutetium–phosphate glasses.

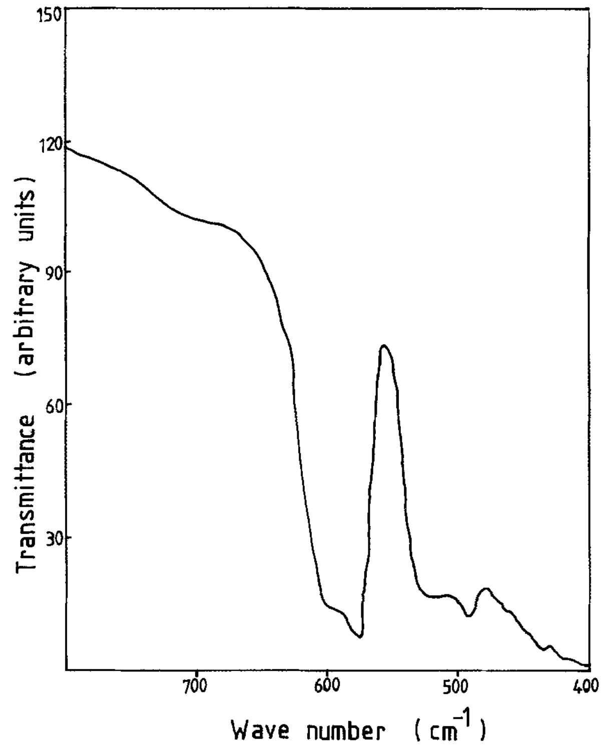

Figure 3 FTIR spectrum for crystalline Lu_2O_3.

phosphate glasses, the P–O band occurred at 1310 cm^{-1}. However, Müller [7] argued that the principal absorption of the P–O group lies at 1282 to 1250 cm^{-1} in a polymeric phosphate chain. In both our series of glasses the absorption band of the P–O group agreed with the results of Müller [7].

A fundamental absorption band at about 500 cm^{-1} which appears in glasses and crystalline P_2O_5 is known to be associated with the $(PO_4)^{3-}$ group [15], probably the wagging mode. Our results show that the $(PO_4)^{3-}$ group absorption band in binary phosphate glass appears at 487 cm^{-1} (Fig. 3). There is a shift in the $(PO_4)^{3-}$ band position in P_2O_5–CuO–RE_2O_3 system glasses (RE = rare earth) to the lower frequencies and appears in the range 465 to 455 cm^{-1} and 480 to 473 cm^{-1} for erbium and lutetium, respectively. The absorption band observed in our study at 780 cm^{-1} would seem to be attributable to the P–O–P ring frequency, which is in close agreement with earlier results [7–10].

The strong broad band at 900 to 1200 cm^{-1} is assigned to P–O^- stretching in P_2O_5–CuO. Two absorption bands were observed in both the P_2O_5–CuO–Lu_2O_3 and P_2O_5–CuO–Er_2O_3 networks at about 1600 and 1640 cm^{-1} and 3400 to 3550 cm^{-1}. These weak bands are probably associated with water trapped in the glass.

The absorption peaks observed in binary P_2O_5–CuO glasses are at 487, 780, 916 and 1267 cm^{-1}, but in the case of the P_2O_5–CuO–Lu_2O_3 glass system there is an additional band position at about 490 to 515 cm^{-1}. Fig. 3 shows that crystalline Lu_2O_3 has two strong

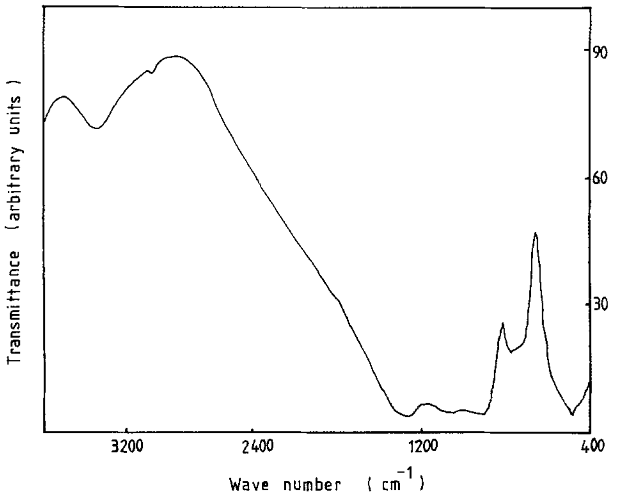

Figure 4 FTIR spectrum for binary copper phosphate glass.

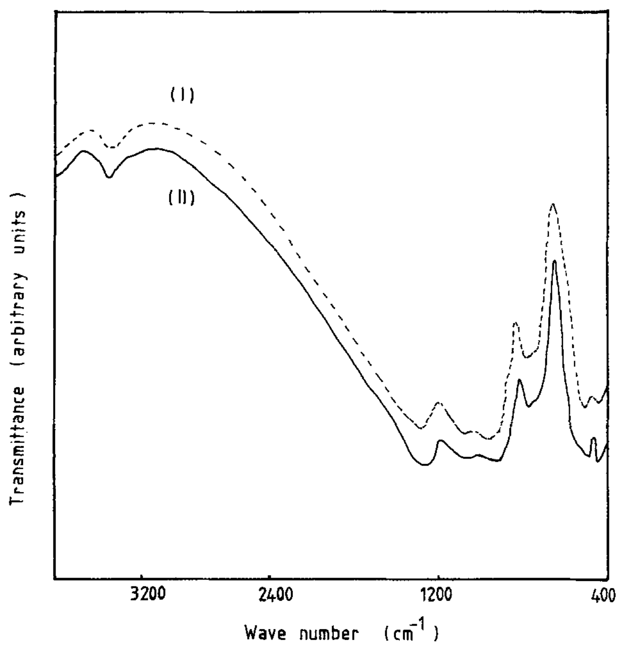

Figure 5 FTIR spectrum for a glass sample of P_2O_5–CuO–Er_2O_3 composition (c). (I) Annealed at 500° C, (II) unannealed.

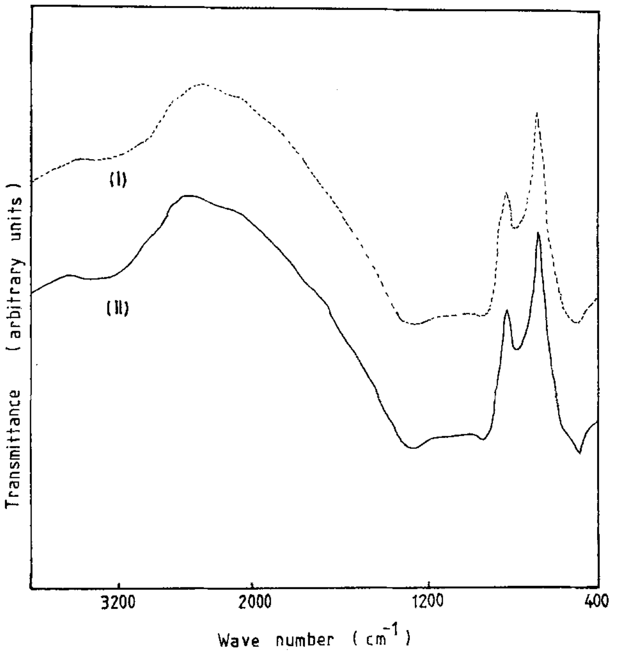

Figure 6 FTIR spectrum for a glass sample of P_2O_5–CuO–Lu_2O_3 composition (j). (I) Annealed at 500° C, (II) unannealed.

TABLE II The infrared peak positions of P_2O_5–CuO–Lu_2O_3 glasses

Glass compositions (mol %)			Glass no.	Position of infrared bands (cm^{-1})					
P_2O_5	CuO	Lu_2O_3							
65	34	1	f	473	576	780	913	1260	3440
65	33.5	1.5	g	474	568	772	915	1200	3400
65	33	2	h	475	568	780	920	1260	3495
65	32	3	j	478	568	780	922	1261	3552
65	31	4	k	480	572	780	925	1260	3567

TABLE III The infrared peak positions of crystalline Lu_2O_3, Er_2O_3, P_2O_5 and CuO

Crystalline materials	Position of infrared bands (cm^{-1})						
Lu_2O_3 [11]	419	435	480	525	576	585	
Er_2O_3 [11]	325		345–500		563		
P_2O_5 [16]	500	780	930	1020	1260	1650	3450
CuO [16]	620						

absorption peaks at 491 and 576 cm^{-1}. This result is in agreement with the results of Baun and McDevitt [11] who also reported the bands at 563 and 500 to 345 cm^{-1} for erbium. We believe the additional bands could be attributed to the formation of Lu–O and Er–O groups. From these results, it is obvious that rare earth oxides in these glasses make some kind of contribution to the formation of a strong and broad peak observed at 491 to 570 cm^{-1} and 568 to 576 cm^{-1} for erbium and lutetium, respectively. On the other hand, in our glasses the P_2O_5 content is constant, so the broadening of this peak could not be due to P_2O_5. It could be a combined effect of all the constituents with the formation of P–O–Cu–O–RE units.

The infrared spectra for two samples of glass (c), one annealed at 500° C for 1 h and the other unannealed, were also examined. Annealing led to a slight shift in the peak positions and the appearance of broad peaks at 902 and 1260 cm^{-1} in erbium (c) and 510 and 1270 cm^{-1} in lutetium (j). This is a clear indication that small microstructural changes have occurred in the glass even after annealing at such a low temperature as 500° C.

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