

Infrared spectra of copper-calcium-phosphate glasses

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In previous papers we have studied structural [1], optical [1, 2], electrical [3] and acoustical [4] properties and also switching action [5] in copper-calcium-phosphate glasses. In the present work we report our experimental results on the infrared spectroscopy of these glasses. The infrared measurements have been known to be an important tool in studying the structure of gaseous molecules and organic substance. The application of these infrared techniques to glassy materials is limited, mainly due to the complicated and random nature of the glassy state, but infrared spectroscopy may still be considered as a complementary tool to X-ray diffraction and to the other methods of studying the structure of glass.

The infrared spectra of phosphate glasses have been measured by a number of investigators and the results mainly interpreted qualitatively. Corbridge and Lowe [6] have studied the infrared spectra of a number of both crystalline and glassy inorganic compounds, and concluded that the spectra of crystalline $(\text{NaPO}_3)_n$ -II, III, IV and glasses based on the metaphosphate compositions are generally similar. This has been taken as evidence that the sodium metaphosphate glasses are composed of chain-linked anions of high molecular weight. Shih and Su [7] 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. Using the results of Corbridge and Lowe [6], Müller [8] argued that the P=O double bond 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 to 740 cm^{-1} . Sayer and Mansingh [9] have measured the infrared absorption spectra of a number of transition-metal phosphate glasses and on the basis of the positions of the vibrational frequencies they argued, qualitatively, that the phosphate tetrahedra dominate the structure of manganese, nickel, cobalt and copper

glasses, while in glasses of the composition P_2O_5 - M_aO_b (where M is V, Ti, Mo or W) structures of the form $[\text{MO}_n]$ pre-dominate.

The glass compositions covered the range 55% P_2O_5 -(45-x)% CaO where $35 > x > 0$. The glass preparation methods have been discussed elsewhere [3]. The infrared spectra of glasses were recorded with a Unicam SP 2000 infrared spectrophotometer in the range 350 to 4000 cm^{-1} at room temperature, operating in the double beam mode. Selected glass samples were ground in a clean mortar into a fine powder and then a small amount of glass powder was mixed and ground with KBr. The KBr pellets were formed by pressing the evacuated mixtures at 15 tons for a few minutes.

Infrared absorption measurements have been made on several copper-calcium-phosphate glasses. Fig. 1 shows the spectra of samples of all glasses together with the spectra of crystalline P_2O_5 and CuO. Table I presents the position of

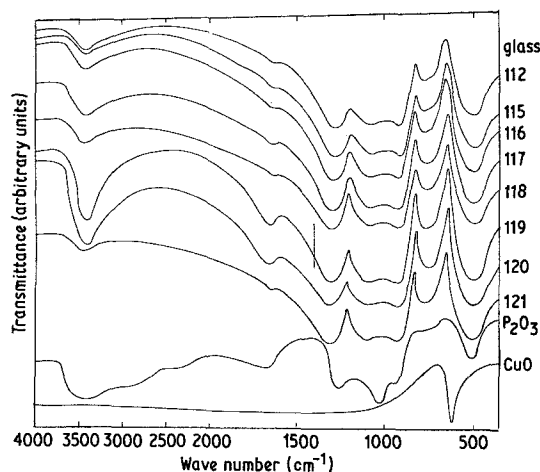


Figure 1 Infrared absorption spectra for a series of copper-calcium-phosphate glasses and for P_2O_5 and CuO.

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TABLE I Infrared absorption bands for a series of copper-calcium-phosphate glasses

Glass number	CuO (mol%)	Infrared absorption band positions (cm ⁻¹)							
112	35	500	740	780	930	1075	1270	1630	3450
115	30	500	740	780	930	1075	1280	1630	3450
116	25	500	740	780	930	1080	1280	1630	3450
117	20	500	740	780	930	1080	1290	1630	3450
118	15	500	740	780	930	1085	1300	1630	3450
119	10	500	740	780	930	1090	1300	1630	3450
120	5	500	740	780	930	1100	1305	1630	3450
121	0	500	740	780	930	1110	1305	1630	3450
P ₂ O ₅	—	500	740	780	930	1020	1260	1650	3450
CuO	—	—	620	—	—	—	—	—	—

the absorption bands obtained in this study. The position obtained for the Cu—O main frequency is close to the reported value [10]. Comparison with the infrared spectrum of P₂O₅ shows that most of the absorption bands in the glasses are the same as for P₂O₅. The absorption bands of glass 121 are in close agreement with the results of Shih and Su [7]. The bands at 1305, 1110 and 780 cm⁻¹ would seem to be attributable to the P=O double bond, the P—O⁻ stretching frequencies and the P—O—P ring frequency, respectively. The absorption band at 500 cm⁻¹ which appears in all glasses and in crystalline P₂O₅, is known to be at the fundamental frequency of the (PO₄)³⁻ group [11]. There is a shift of band positions in copper-calcium-phosphate glasses to lower frequencies where the P=O double bond and P—O⁻ stretching frequencies should occur. Such a shift was observed by Bartholomew [12] in sodium-phosphate glasses when replacing sodium with silver. Corbridge and Lowe [6] also observed a pronounced shift of some absorption bands to lower frequencies in their silver salts. In a similar

way to the explanation for silver phosphate glasses, the shift can be discussed in terms of the creation of covalent bonds between non-bridging oxygen ions and copper ions, to form P—O—Cu⁺ units. By replacing 35% of calcium ions by 35% of copper ions in the glass, a band shift of approximately 35 cm⁻¹ to lower wave numbers was observed. It could be seen that the band shift is dependent on the CuO concentration in the glass. Fig. 2 shows the trend of band shift with CuO content. The absorption bands were observed in both calcium phosphate and copper-calcium-phosphate glasses at 1630 and 3450 cm⁻¹. These are weak bands and are believed to be associated with small amounts of water trapped in the glass and, more likely, to be due to the overtones. The position of the Cu—O frequency is not detectable in copper-calcium-phosphate glasses. This band may be buried in the broad transmission region at 6000 to 7000 cm⁻¹.

Qualitatively, the infrared spectra of copper-calcium-phosphate glasses would suggest that the phosphate tetrahedra dominate the structure of these glasses and that a partial covalent P—O—Cu⁺ bond would be created in high copper content glasses.

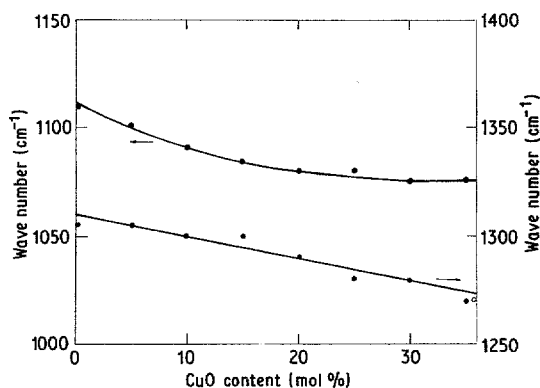


Figure 2 Variation of two infrared absorption band positions with CuO content of glasses.

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