

# Infrared spectra of the vitreous system $\text{Co}_3\text{O}_4\text{--P}_2\text{O}_5$ and their interpretation

A. A. HIGAZY\*, B. BRIDGE

*Department of Physics, Brunel University, Kingston Lane, Uxbridge, Middlesex, UK*

The infrared absorption spectra of the vitreous  $\text{Co}_3\text{O}_4\text{--P}_2\text{O}_5$  system have been measured in the frequency region 4000 to 200  $\text{cm}^{-1}$ . Absorption bands and mode attributions have been fully discussed. Absorption frequencies and intensities are found to be strongly and systematically dependent on glass composition. On this basis it is found that this glass system can be divided into three distinct "compositional regions". Similar "three region" behaviour is reported for the compositional dependence of density and molar volume of mixing of  $\text{Co}_3\text{O}_4\text{--P}_2\text{O}_5$  glass. Quantitative justification for the band attributions has been attempted.

## 1. Introduction

Infrared absorption spectra of glasses can give valuable information about atomic configurations in glasses even though quantitative analysis is rarely possible. For example, the extent to which added cations enter the network of the basic glass or reside interstitially and the extent to which the double bond in phosphate networks is broken, can be qualitatively assessed. This is the kind of information that we sought for the Co–P–O glass system, to aid the interpretation of ultrasonic studies of the same.

Experimental and theoretical investigations of the vibrational spectra of vitreous solids have been undertaken by numerous investigators [1–3]. Recently several papers have dealt with the infrared absorption spectra of binary phosphate glasses, using the infrared spectroscopy technique. Attempts to apply this technique to study the structure of glassy materials were made by Su *et al.* [4]. Quantitatively the vibrational spectra of several glass systems, including silicate [4], borate, boron oxide [5] and metaphosphate [6] were analysed, based on either the "localized model" or the "lattice model" as summarized in a recent paper by Borrelli and Su [7]. However, in spite of the wealth of literature on infrared absorption in glasses, it is relatively rare to find data covering as

broad a continuous compositional range as is presented here.

## 2. Theoretical review of the infrared absorption spectra of phosphate

In order to interpret our data we find it helpful to first summarize the general form of the spectra that should be expected of a vitreous phosphate. Starting with pure  $\text{P}_2\text{O}_5$ , if an infinite covalent network of  $\text{PO}_4^{3-}$  tetrahedra is assumed, one might expect a diffuse version of the spectrum of the lattice vibrational modes of the crystalline analogue. In other words one would not expect to see any bands corresponding to the normal vibrations of free  $\text{PO}_4^{3-}$  tetrahedra. However, another viewpoint following Borrelli and Su [7] is to regard the glass spectrum as a diffuse version of the spectrum produced by a tightly clamped tetrahedron. This is essentially a localized model which, acknowledging the lack of long range order in a glass, represents the effect of an infinite irregular covalent network by setting the mass of the atoms connecting each tetrahedron equal to infinity. The broadening of vibrational bands is then interpreted in terms of a distribution of angles of clamping in the disordered array. Returning to the lattice model the fact that the oxygen atom is much lighter than the phosphorus atom suggests that there might exist

\*On leave from the Physics Department, Faculty of Science, Monofia University, Shebeen El-Kome, Egypt.

characteristic bond (group) frequencies for P—O—P vibrations, i.e. that some lattice modes frequencies differ little from what would be expected for the oxygen atom vibrating by itself. However, in view of the P—O—P bond angles it is difficult to see how pure stretching and bending vibrations can exist as frequently proposed in the literature. It will be noted that in the assumption of characteristic P—O—P frequencies, it is the phosphorus atoms that are effectively clamped, whereas the bridging oxygens are clamped in the model of Borrelli and Su. In either model one expects to observe P=O vibrations as a characteristic bond group frequency, unaffected by the network bond.

When different cations are added to the  $P_2O_5$  network two kinds of behaviour can be expected. If the cation enters the network and is relatively heavy compared with oxygen the spectrum should remain recognizably as described above but with gradual shifts of characteristic bond group frequencies as phosphorus atoms are replaced by the new cations. Lighter cations, however, might have more substantial effects on group frequencies. In addition a weakening of the P=O spectrum might be expected with this bond being ruptured by network forming cations. If instead the cation enters the network interstitially as an ion, the network is gradually broken down and new spectral bands may appear corresponding to the vibrational character of free charged structural units. Such is the case with sodium, and Almeida and Mackenzie [8] have described in detail the types of ionic groups which might exist in sodium phosphate glasses. One of the purposes of the present study is to see to what extent the addition of cobalt atoms to  $P_2O_5$  follows the latter or former behaviour — though we anticipate that this cation will go predominantly into the network.

### 3. Experimental review of the infrared absorption spectra of phosphates

The position of the main absorption bands in both crystalline and glassy phosphates occur between 1000 and 1111  $cm^{-1}$ . The majority of the phosphates exhibit a number of strong absorption bands in this region. It has been concluded by Kalbus [9] that these bands are due to the  $\nu_3$  vibration of a  $PO_4^{3-}$  tetrahedron. As already men-

tioned, for the free  $PO_4^{3-}$  ion, the  $\nu_3$  mode is triply degenerate, which appears as a single band at  $1015 \pm 15 cm^{-1}$ . However, in the crystalline and glassy state one could expect that interaction between any  $PO_4^{3-}$  ion and neighbouring atoms and ions could remove the degeneracy and cause three bands to appear. The reason for the appearance of more than three bands for some of the phosphates is not generally agreed, but in our view may be indicative of the expected association of  $PO_4^{3-}$  phosphate ions into dimers (i.e.  $P_2O_7^{4-}$  ions) or polymers (i.e.  $P_nO_{\{3n+1\}}^{(n+2)-}$  groups with  $n > 2$ )\*.

In all, seventeen crystalline phosphates have been examined by Kalbus [9]; two absorption bands due to water have been observed at 3571 to 2857 and 1667 to 1613  $cm^{-1}$ . The absorption bands at 2439 to 2174, 926 and 625  $cm^{-1}$  have been explained as due to the  $2\nu_3 + \nu_4$ ,  $\nu_1$ , and  $\nu_4$  normal vibrations of  $PO_4^{3-}$  tetrahedra, respectively.

Infrared spectra of 153 inorganic phosphate compounds, both in the crystalline and glassy state, have been investigated by Corbridge and Lowe [10, 11]. They found that the orthophosphate compounds displayed a very strong broad band at 1060 to 1000  $cm^{-1}$ , with two or more weaker bands in the same region also occurring.

In pyrophosphates two strong bands at 1060 to 1170 and 940 to 870  $cm^{-1}$ , two peaks with different intensity at 1045 to 970  $cm^{-1}$ , and one peak of medium intensity at 735 to 690  $cm^{-1}$  were found. In the triphosphates strong absorption bands at 1170 to 1100, 1085 and 920 to 885  $cm^{-1}$  with two absorption bands in the region 755 to 690  $cm^{-1}$ , were observed. In cyclic meta-phosphates a very strong triplet absorption in the region 1315 to 1205  $cm^{-1}$ , with a very strong and broad absorption band near 1000  $cm^{-1}$ , and two strong absorptions near 770  $cm^{-1}$ , in addition to medium or weak bands near 700  $cm^{-1}$  appeared. For all the hydrated phosphate compounds two absorption bands at 3300 and 1640  $cm^{-1}$  were found which were assumed to correspond to O—H bond stretching vibrations and O—H bending vibrations, respectively. Two absorption bands at 1082 and 980  $cm^{-1}$  have been ascribed to two of the normal vibrational modes of the  $PO_4^{3-}$  ions, the latter

\*The subscript  $n + 2$  refers to the charge the group would have if it existed in the ionized state (for example when in solution). In some glassy structures (for example certain composition ranges of our cobalt-phosphate glasses) these groups form parts of infinite covalently bonded networks and it is no longer appropriate to attribute to them the ionic charge ( $n + 2$ ).

band being the  $\nu_1$  symmetrical stretching mode. On the other hand, Colthup [12] Bellamy and Beecher [13] and Miller and Wilkins [14] considered that the  $\text{PO}_4^{3-}$  ion exhibits normal vibrations at  $1100$  to  $1040\text{ cm}^{-1}$ . For the phosphates generally, Corbridge attributes the bands at  $900$ , and  $700\text{ cm}^{-1}$  to symmetric and antisymmetric P—O—P bond stretching vibrations, respectively. Further absorption bands at  $910$  to  $850\text{ cm}^{-1}$  were associated with P—O—H bond vibrations; and a band at  $1100\text{ cm}^{-1}$  was considered to be due to a P—O<sup>(-)</sup> bond stretching vibration (also called P—O ionic stretching). The absorption bands at  $1300$  to  $1200\text{ cm}^{-1}$  were attributed to P=O bond stretching vibrations. The bands at about  $1400$  to  $1200\text{ cm}^{-1}$  generally of medium intensity, in the acid phosphates, may be due to a P—O<sup>(-)</sup> bond stretching vibration combined with a lattice mode as has also been suggested by Oberley and Weiner [15]. Corbridge and Lowe have concluded from their study of inorganic phosphate compounds that the absorption frequencies in infrared spectra are mainly dependent on the nature of the anion rather than the positive ion.

Miller and Wilkins have used the assignment of spectra according to Corbridge and Lowe to determine the average chain length of polyphosphates by infrared spectroscopy. They used the argument that in polymerized phosphate chains the P=O group and the P—O<sup>(-)</sup> group produce characteristic vibration frequencies of  $1282$  and  $1205\text{ cm}^{-1}$ , respectively. However, the monomers  $\text{P}_2\text{O}_7^{4-}$  and  $\text{PO}_4^{3-}$  exhibit no splitting into these two bands. They have one band at  $1160\text{ cm}^{-1}$ . They argue that the P=O double bond is more strongly localized in central-position phosphate groups than in the end-position group. Miller and Wilkins are also reported [14] to have defined a band occurring at  $805$  to  $740\text{ cm}^{-1}$  in cyclic phosphates as a "P—O—P ring frequency".

Bartholomew [16] has studied the IR spectra of sodium metaphosphate glasses and silver metaphosphate glass. In the frequency range where the P=O and P—O<sup>-</sup> stretching frequencies should occur, there is a shift of band positions in the silver glass to lower wave numbers, in comparison to their positions in the sodium glass. Such shifts

can be discussed in terms of the existence of covalent-bond formation between the non-bridging oxygen ions and the silver ions to form P—O—Ag units, i.e. it is assumed that a P—O—Ag<sup>†</sup> stretching frequency is somewhat lower than a P—O—P stretching frequency and also that the proximity of the added silver ions to other unruptured P=O bonds also weakens the P=O bond strength.

Glasses of higher phosphorus content in the  $\text{Ag}_2\text{O—P}_2\text{O}_5$  system show a shift of the P=O stretching frequency to a higher frequency ( $1240\text{ cm}^{-1}$ ), and this is considered to be due to a stronger localization of the P=O bond in the central-position  $\text{PO}_4$  groups in the  $\text{Ag}_2\text{O} \cdot 2\text{P}_2\text{O}_5$  glass. However, the P—O<sup>(-)</sup> stretching vibration which is characterized by a strong absorption band around  $1050\text{ cm}^{-1}$ , is apparently absent in these glasses with higher phosphorus content.

#### 4. Experimental techniques

The glasses examined were prepared by melting the appropriate weights of analytical reagent grades of  $\text{Co}_3\text{O}_4$  and  $\text{P}_2\text{O}_5$  oxides. The entire range of glasses that can be obtained from these reagents using open crucibles, is discussed. Details of the techniques for the preparation of these glasses are to be presented elsewhere [17].

The infrared absorption spectra of the  $\text{Co}_3\text{O}_4\text{—P}_2\text{O}_5$  glass system were measured for glass samples over the range  $400$  to  $200\text{ cm}^{-1}$ . A Unicam SP 2000 double beam infrared spectrometer was used in conjunction with the CsCl disc technique. Samples of glass weighing  $0.004\text{ g}$  were mixed and ground with  $0.200\text{ g}$  caesium chloride; after which the mixtures were pressed at  $15\text{ ton}$  for  $3\text{ min}$  under vacuum, to yield transparent discs suitable for mounting in the spectrometer. The infrared spectra of the glasses are shown in Figs. 1 and 2.

The absorption band positions of Co—P—O glasses and the related crystalline phases are shown in Table I together with the specification of vibrational modes or characteristic group frequencies (P—O, P=O,  $\text{PO}_4^{3-}$ , etc) to which we have attributed these bands. In Table II the Co—P—O absorption bands and their attributions are compared with those previously reported, for other phosphate compounds.

<sup>†</sup>When bond groups exhibit characteristic frequencies in an infrared spectrum one could ordinarily expect to find two bands corresponding to symmetrical and antisymmetrical stretching vibrations and two bands corresponding to symmetrical and antisymmetrical bending vibrations. Often, however, only single, broad "stretching" and "bending" bands are observed.

TABLE I Infrared spectra band positions of Co-P-O glasses and their crystalline phases (cm<sup>-1</sup>)

Specimen	CoO + Co <sub>2</sub> O <sub>3</sub> (mol %)	Co <sup>3+</sup> -O ionic vibrations	Harmonics of P-O-P bending vibrations	P-O-P stretching vibrations	P-O-P bending vibrations	PO <sub>3</sub> <sup>-</sup> normal mode ( $\nu_3$ symmetric stretching)	P-O <sup>(C)</sup> ionic stretching vibration	P=O stretching vibration	H <sub>2</sub> O normal mode (bond bending)
P <sub>2</sub> O <sub>5</sub> crystal	-	-	500	700-730	910-940	1015	-	1240-1270	1630-1700
P <sub>2</sub> O <sub>5</sub> glass	-	-	500	700-730	915	1015	-	1240-1270	1640-1700
C-1	4.05	320	490-510	710-745	910-950	990-1045	-	1240-1290	1640-1700
C-3	5.19	325	490-518	730-750	910-950	1000-1050	-	1240-1300	1650-1690
C-5	6.02	325	490-515	750-810	910-950	975-1030	1080-1120	1260-1398	1660-1700
C-8	6.61	325	490-515	755-810	910-950	965-1025	1090-1120	1320-1370	-
C-9	7.14	325	485-518	755-785	-	965-1010	1150-1190	1310-1350	1640-1890
C-15	15.61	-	478-525	755-790	-	950-1000	1150-1180	1300-1350	1640-1690
C-19	24.39	-	480-525	755-795	-	940-990	1050-1100	1295-1350	1635-1670
C-22	37.63	-	475-528	755-795	-	930-985	1045-1095	1280-1329	1635-1670
C-24	40.17	-	470-530	750-795	-	925-972	1040-1095	1275-1322	1635-1670
C-27	43.80	-	470-530	750-805	-	915-960	1045-1100	1265-1315	1635-1675
C-32	47.37	-	470-532	750-802	-	915-960	1045-1118	1260-1310	1635-1675
Co(PO <sub>3</sub> ) <sub>2</sub> crystal	50.00	-	460-530	710.0	-	890-910	1030-1070	1240-1310	-
C-38	54.64	-	485-555	750-800	-	915-960	1055-1122	1250-1305	1635-1670
C-42	57.78	-	490-558	740-780	-	918-960	1060-1130	1205-1265	1630-1660
C-45	59.21	-	500-570	740-785	-	920-975	1060-1130	1200-1265	1630-1660
Co <sub>3</sub> P <sub>2</sub> O <sub>7</sub>	66.67	-	530-600	730	-	950-1000	1050-1090	1190-1200	-
Co <sub>3</sub> O <sub>4</sub> *	-	-	560-590	660-670	-	-	-	-	-
crystal	-	-	580-600	-	-	-	-	-	-
CoO*	-	-	-	-	-	-	-	-	-
crystal	-	-	-	-	-	-	-	-	-

\*In these cases the band attribution is not as given at the head of the table.

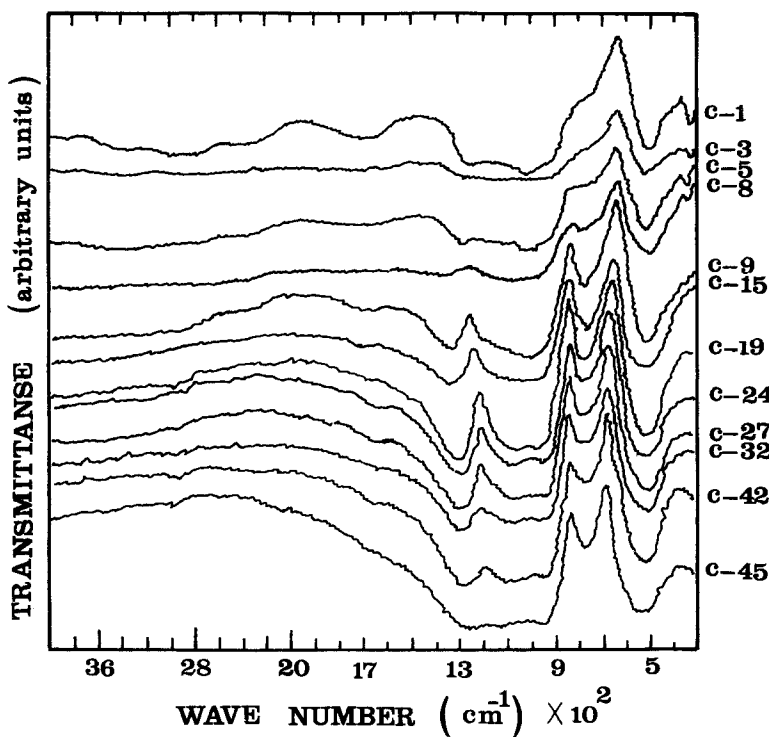


Figure 1 Infra-red absorption spectra for Co-P-O glasses in CsCl matrix

## 5. General description of results and suggestion attribution of bands

The infrared spectra of the vitreous Co-P-O glass system (Figs. 1 and 2) showed weak, broad bands in the regions 1640 to 1620, 940 to 910 and 730 to 700  $\text{cm}^{-1}$  which may be due to free  $\text{H}_2\text{O}$  molecules, P-O-H bending and harmonic P-O-P bending vibrations, respectively. The spectra also displayed strong bands at 1255, 1015 and 500  $\text{cm}^{-1}$ , which possibly may be due to the P=O stretching vibration, a normal vibrational mode ( $\nu_3$  symmetric stretching) of the  $\text{PO}_4^{3-}$  ion, and harmonics of the P-O bending vibrations respectively. All of our Co-P-O glasses showed a very weak, broad band in the region 1700 to 1640  $\text{cm}^{-1}$ , which may be attributed to the bending vibrations of free  $\text{H}_2\text{O}$  molecules [8]. The presence of these water molecules in our glasses was probably because the mixtures had absorbed some water during the preparation of pellets. A very weak peak also appeared at 950 to 910  $\text{cm}^{-1}$  in the glass composition range from pure  $\text{P}_2\text{O}_5$  up to 7.0 mol% cobalt oxide, which may have been related to a P-O-H bending vibration [11].

In Figs. 3 to 6 we have plotted for each band (attributed to a given vibrational mode) the mid-bond wave number and the absorption intensity against glass composition. From these figures one can identify shifts of the band positions with

compositions, but additionally there is some evidence, particularly in Figs. 3c, 4a, b and c that the glass series can be divided into three compositional regions which are basically the same as the region much more clearly classified by our ultrasonic measurements [18]. The first ranges from pure  $\text{P}_2\text{O}_5$  up to 16 mol% cobalt oxide, which corresponds to the glass regime defined in another paper [17], in which the  $\text{Co}^{2+}$  content expressed as a ratio of  $\text{Co}^{2+}/\text{Co}^{3+}$  varies from very high to very low. The second starts from 16 mol% and continues up to 50 mol% cobalt oxide, and the third ranges from 50 mol% up to 60 mol% cobalt oxide (see Figs. 7 and 8). These latter two regions correspond to the second regime of the analysed cobalt phosphate glasses in which the cobalt content is almost entirely in the form of  $\text{Co}^{2+}$  [17]. The absorption bands and mode attributions will now be discussed more fully, in the above context.

## 6. Detailed discussion of the results in terms of compositional dependence

### 6.1. Characteristic frequencies of $\geq\text{P}=\text{O}$ group stretching vibrations (P=O stretching)

In the first compositional region the P=O bond stretching band shifts to higher wave numbers with increasing cobalt oxide content and displays a maximum at the highest oxide content. Thereafter

TABLE II Positions of the infrared absorption bands of phosphate compounds

Remarks	Structural groups	Absorption band (cm <sup>-1</sup> )	Corresponding references
Characteristic frequencies of bond group stretching and bending vibrations	P—O—P stretching	780– 730	Present work
		805– 740	[14]
		915– 880	[8]
	P—O—H bending	900, 700	[10, 11]
		910– 850	[10, 11]
		930– 915	Present work
	P—O(°) stretching	1036–1030	[8]
		1050	[16]
		1100	[10, 11]
		1110	[14]
1170–1070		Present work	
Symmetric stretching of P—O(°) bonds in the PO <sub>3</sub> <sup>2-</sup> end group	P=O stretching	1300–1006	[8]
		1240, 1220	[16]
		1280–1250	[8]
	PO <sub>3</sub> <sup>2-</sup> ionic group	1282–1205	[14]
		1300–1200	[10, 11]
		1340–1235	Present work
		931– 892	[21]
Normal vibrational mode (ν <sub>3</sub> symmetric stretching)	PO <sub>3</sub> <sup>2-</sup> ionic group	938	Present work
		1000– 990	[8]
		1022– 990,	
		1000– 980,	
		990– 970	[10]
	Free H <sub>2</sub> O molecules	1015	[9]
		1025– 940	Present work
		1082– 980	[10, 11]
		1100–1040	[14]
		1160	[16]
Normal vibrational mode (involving bond bending)	Free H <sub>2</sub> O molecules	1640–1620	Present work
		1660	[16]
		1640	[10, 11]
		1650–1610	[8]
		1667–1613	[9]
Normal vibrational mode (involving bond stretching)	Either free H <sub>2</sub> O molecule or OH <sup>-</sup> ion	2860–2380	[16]
		3300	[10, 11]
		3400–3600	[8]
		3571–2857	[9]
		495–565	Present work
Harmonics of P—O—P bending vibration			
Co <sup>3+</sup> —O(°) ionic vibration		320– 325	Present work

in the second compositional region, the wave number decreases with increasing oxide content, and in the third compositional region, this decrease continues but on an increased gradient. Starting from the lowest oxide contents, the intensity of the P=O absorption band increases steadily with oxide content. We attribute this to the increasing presence of water with decreasing oxide content which caused the replacement of some P=O bonds by P—OH bonds. For oxide content greater than 15 mol% the intensity of the P=O absorption band then starts to decrease steadily up to the highest oxide content and we attribute this to the

increasing replacement of P=O bonds by P—O—Co bridging units.

## 6.2. Characteristic frequencies of ≧P—O—P≦ group stretching vibrations (P—O—P stretching)

The band in the vicinity of 736 to 706 cm<sup>-1</sup> which was attributed to P—O—P bond stretching displays clearly the “three-composition region” behaviour. Thus in the first region the band shifts rapidly to increasing wave number with increasing oxide content. Then, in the second compositional region, the band position becomes independent of

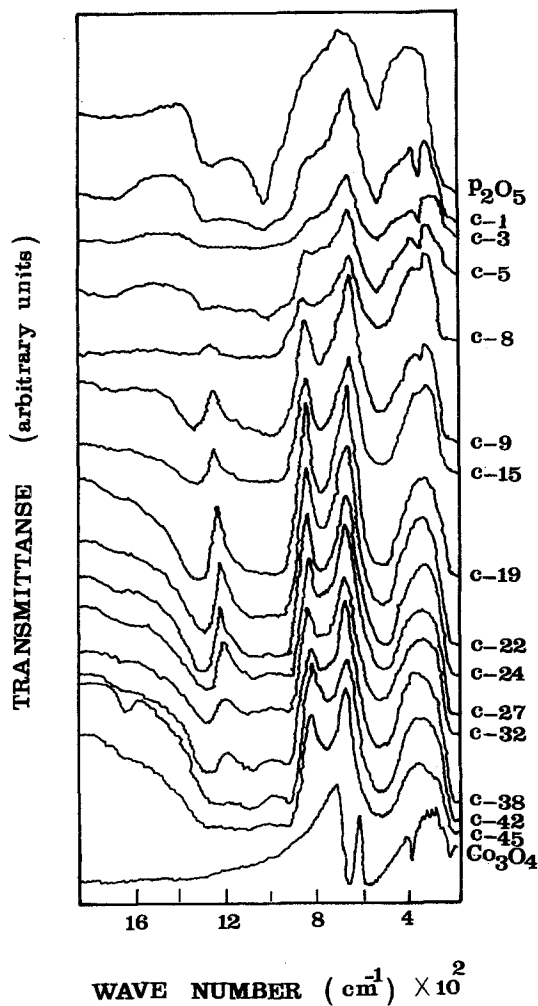


Figure 2 Infra-red absorption spectra for Co-P-O glasses in CsCl matrix.

oxide content, and further in the third compositional region the band shifts rapidly to decreasing wave number, with increasing oxide content. The possible explanation of the broad maximum in band wave number at intermediate oxide contents could be explained as a balance between two opposing trends: (1) the replacement of -P-O-P- linkages by O-Co-O links as cobalt so enters the network, the wave number of the -P-O- stretching vibrations might tend to lower, because the Co-O stretching force constant is substantially lower than the P-O stretching force constant. This effect will increase with increasing cobalt content. On the other hand, (2) the electrostatic field of the strongly electronegative cobalt ions may serve to increase the wave number of the -P-O- stretching vibrations and this effect would tend to decrease when the cobalt ion content was increased

above a certain amount, because of the rapid reduction of  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ .

### 6.3. Characteristic frequencies of $\geq\text{P-O-P}\leq$ group bending vibrations (P-O-P bending)

Wright and Hunter [19] attribute the very strong absorption near  $400\text{ cm}^{-1}$  to Si-O bending in Si-O-Si chains, so in Co-P-O glasses the band observed near to  $500\text{ cm}^{-1}$  can be compared with Si-O-Si linkages, and may likewise be due to harmonics of P-O-P bending. In the first and second composition regions, this band associated with P-O-P bending remains nearly constant, with just slight shifting to lower wave numbers, while in the third composition region this band shifts to higher wave numbers coming close to the pyrophosphate  $\text{P}_2\text{O}_7^{4-}$  group characteristic frequency which appears at  $600$  to  $530\text{ cm}^{-1}$ .

### 6.4. Characteristic group frequencies and normal vibrations involving groups with ionic character

Our infrared data give evidence of some ionic content in the cobalt-rich glasses i.e. the partial breakdown of the supposedly covalent vitreous network at high cobalt content. For instance, the very weak band appearing at  $1120$  to  $1000\text{ cm}^{-1}$  can be attributed to stretching vibrations of the  $\text{P-O}^{(-)}$  group. The peak intensity, though very weak at low oxide contents, reaches a fairly strong maximum at  $\sim 55\%$  CoO oxide content, i.e. in the region when the breakdown of the covalent vitreous network into small ionic groups ( $\text{PO}_4^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$ , etc) might be expected. This ionic P-O stretching band also seems to display "three-compositional region" behaviour, i.e. the band wave number displays a maximum in the first composition region, a minimum in the second composition region and a further maximum in the third composition region.

Another sign of some ionic character to the glasses is provided by the absorption band lying between  $1095$  and  $990\text{ cm}^{-1}$  which is probably due to the  $\nu_{3abc}$  normal modes (symmetric stretching) of the  $\text{PO}_4^{3-}$  ion, which has previously been observed by Corbridge [10] at about  $1082$  and  $980\text{ cm}^{-1}$ . Colthup [12], Bellamy and Beecher [13], Miller and Wilkins [14] and others have also observed this  $\text{PO}_4^{3-}$  band at  $1100$  to  $1040\text{ cm}^{-1}$ . Kalbus [9], too has recorded a band at  $1111$  and  $1000\text{ cm}^{-1}$  for the  $\text{PO}_4^{3-}$  group.

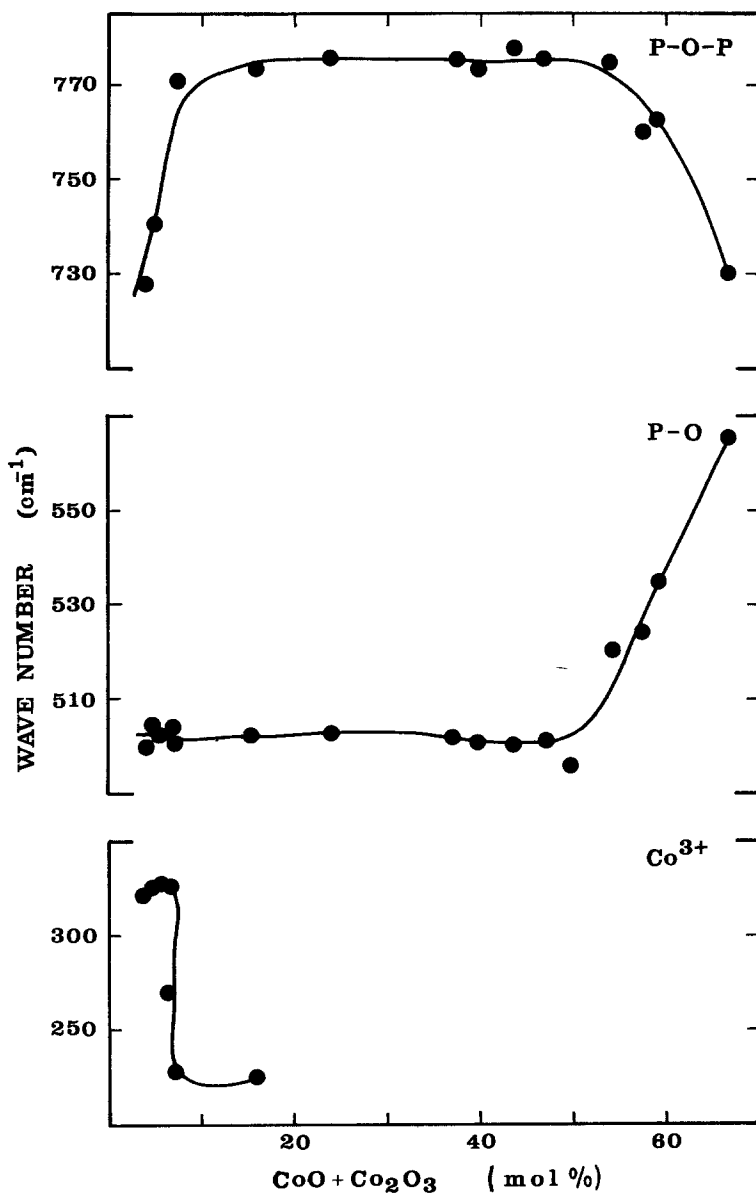


Figure 3 Compositional dependence of the wave numbers for P-O-P, P-O and  $\text{Co}^{3+}$  absorption bands (attributed to a given vibrational mode) in the infrared spectra of Co-P-O glasses.

As the oxide content is progressively increased, the wave number of the absorption band behaves in the following manner. The characteristic frequency related to the ionic  $\text{PO}_4^{3-}$  groups shifts rapidly to low wave number in the first composition range. This shift continues, though more slowly, in the second composition region. At this point, the wave number is very close to what might be expected from the symmetric stretching vibrations of the two P-O<sup>(-)</sup> bonds in the  $\text{PO}_3^-$  ionic group [20]. In the case of cobalt-metaphosphate crystal ( $\text{Co}(\text{PO}_3)_2$ ), the characteristic band for the  $\text{PO}_3^{2-}$  ionic group appeared at 910 to 980  $\text{cm}^{-1}$  [20], while for a glass of the same com-

position it appeared at 931 to 892  $\text{cm}^{-1}$  [21]. Then in the third composition region, the wave number starts to increase again rapidly. It may be due to an increasing presence of  $\text{P}_2\text{O}_7^{4-}$  groups which would produce characteristic vibration frequencies appearing in the band at 1000 to 950  $\text{cm}^{-1}$ . Infrared spectra for pure  $\text{Co}_3\text{O}_4$  crystals [22] (see Fig. 1) show absorption bands at 390  $\text{cm}^{-1}$  which might be due to the  $\text{Co}^{3+}$  ion. In the first glass composition region (high  $\text{Co}^{3+}$  ions concentrations) an absorption band appeared at 325  $\text{cm}^{-1}$ , it may be attributed to the  $\text{Co}^{3+}$  ions. The intensity of this peak decreases and eventually disappears as the  $\text{Co}^{3+}$  ion concentration reduces.



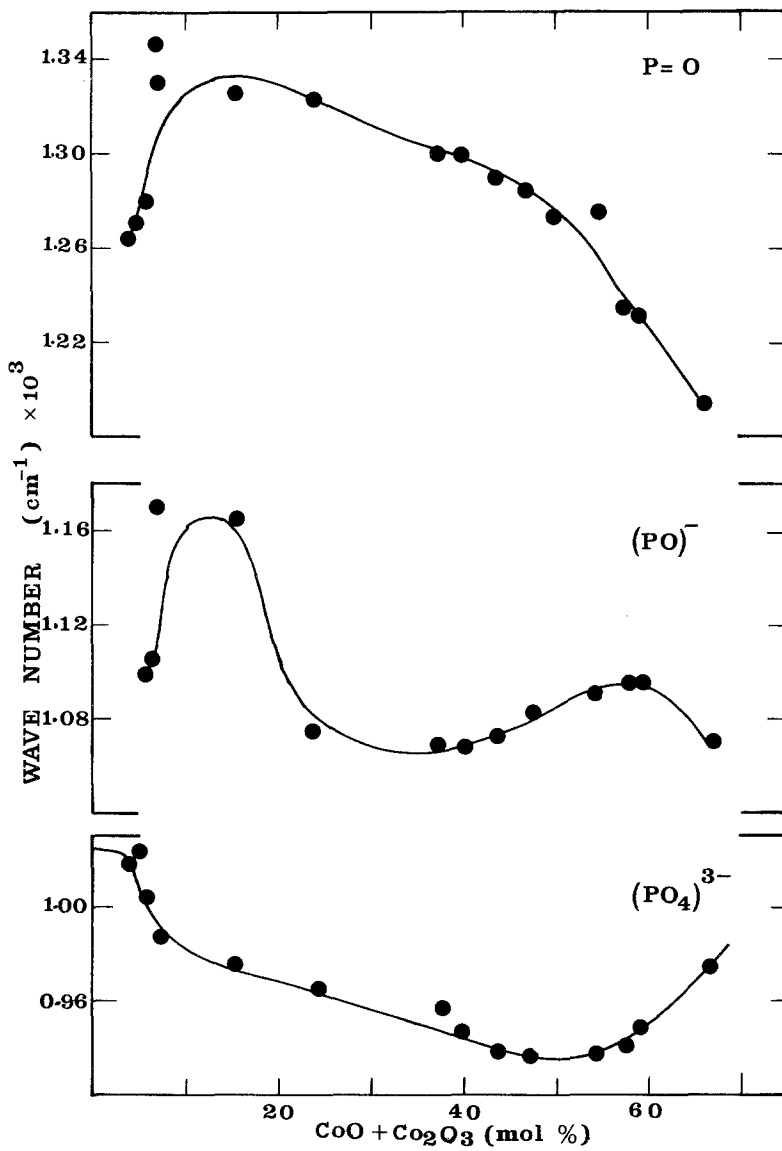


Figure 4 Compositional dependence of the wave numbers for  $\text{P}=\text{O}$ ,  $\text{PO}^-$  and  $\text{PO}_4^{3-}$  absorption bands (attributed to a given vibrational mode) in the infra-red spectra of Co-P-O glasses.

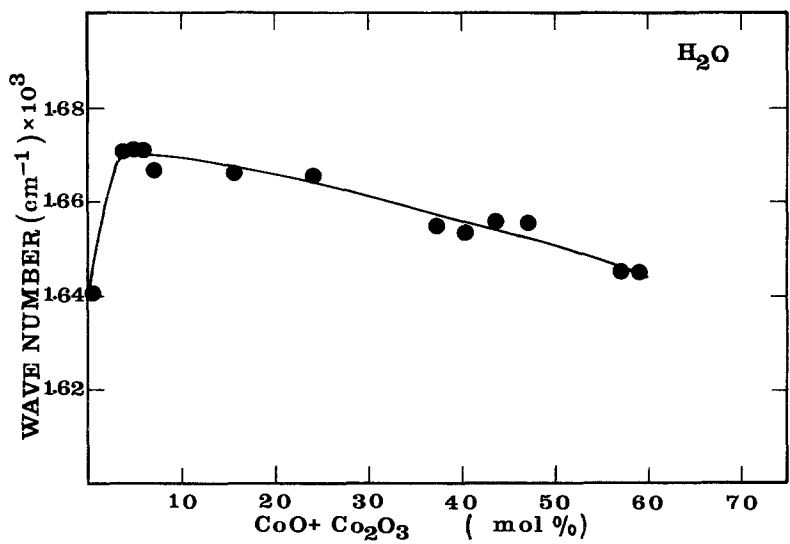


Figure 5 Compositional dependence of the wave number for  $\text{H}_2\text{O}$  band in the infra-red spectra of Co-P-O glasses.

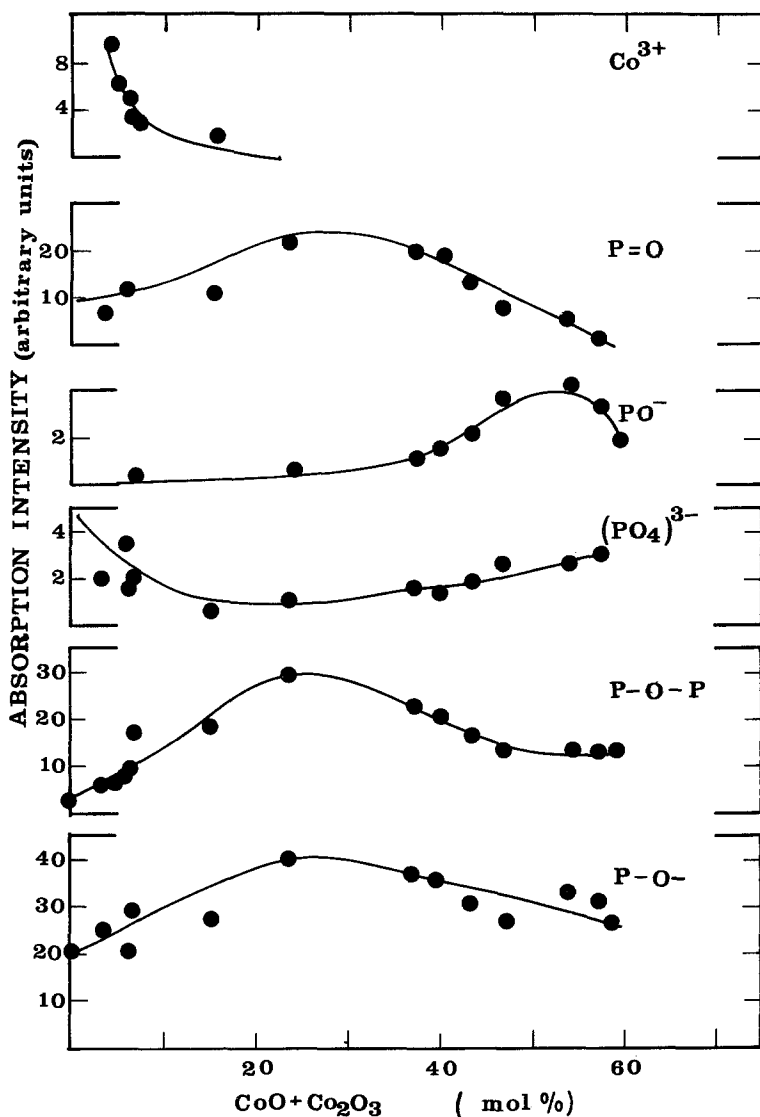


Figure 6 Variation of the absorption intensity for  $\text{Co}^{3+}$ ,  $\text{P}=\text{O}$ ,  $\text{PO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{P}-\text{O}-\text{P}$  and  $\text{P}-\text{O}-$  absorption bands, in the infrared spectra of  $\text{Co}-\text{P}-\text{O}$  glasses with composition.

## 7. Quantitative justification of the band attributions

In the above account our attribution of bands was made by comparison of our data with past literature. However, in this section we attempt to provide quantitative justification of these attributions. In the cases where the vibrations are assumed to be characteristic group frequencies either of pure bending or pure stretching character, the wave number (frequency)  $\lambda^{-1}$  ( $\text{cm}^{-1}$ ) ought to be given by the straightforward formula:

$$\lambda^{-1} = \frac{1}{2\pi c} (F/\mu)^{1/2} \quad (1)$$

where  $c$  is the velocity of light,  $\mu$  is the reduced mass, and  $F$  is the bending or stretching force

constant. In the case of stretching forces,  $F$  can be obtained from a number of empirical formulae, for example the expression [9]

$$F = 1.67 N \left( \frac{X_a X_b}{r^2} \right)^{3/4} + 0.30 \quad (2)$$

where  $N$  is the bond order.  $X_a$  and  $X_b$  are the electronegativities and  $r$  is the bond length. For a single bond group like  $\text{P}-\text{O}^{(-)}$  the reduced mass takes the form  $\mu^{-1} = M_1^{-1} + M_2^{-1}$ , where  $M_1$  and  $M_2$  are the masses of the two atoms, but for groups involving two bonds with respective force constants  $F_1$  and  $F_2$ , and three atoms of masses  $M_1$ ,  $M_2$  and  $M_3$ , we write  $F = F_1 + F_2$  and  $\mu^{-1} = M_1^{-1} + M_2^{-1} + M_3^{-1}$  in Equation 2.

If a particular band frequency cannot be made

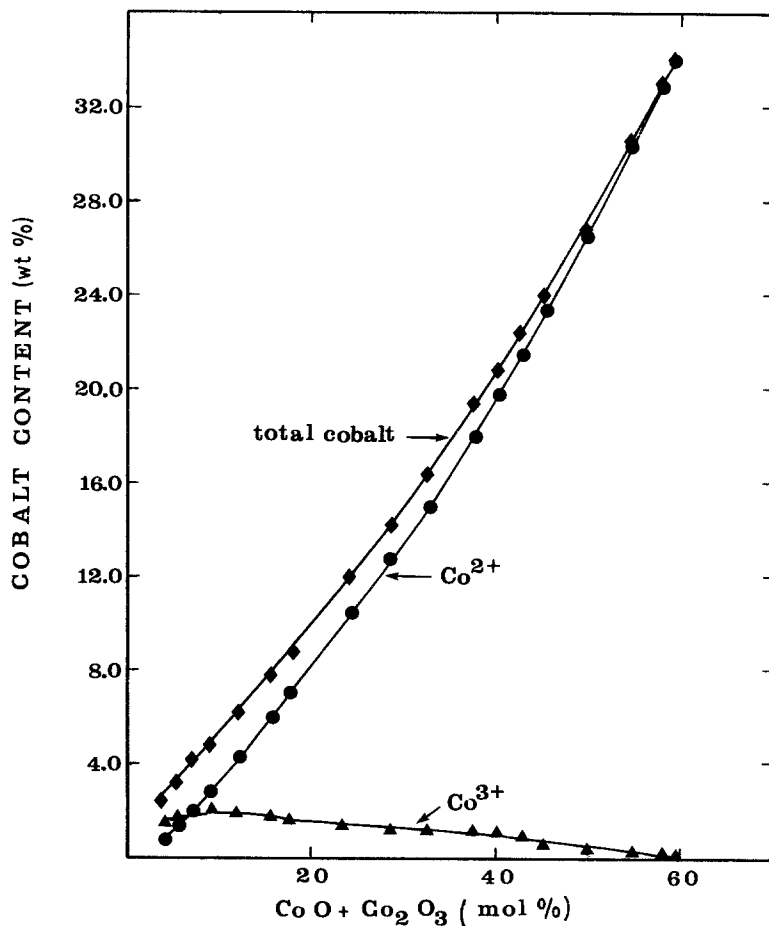


Figure 7 Variations of total cobalt,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  in wt% contents with  $\text{CoO} + \text{Co}_2\text{O}_3$  (mol%) for  $\text{Co}_3\text{O}_4\text{-P}_2\text{O}_5$  glasses.

to fit Equation 1 with a reasonable assumed value of  $F$  (with or without the assumption of harmonics) the conclusion must be that the attribution is wrong and that the band is due to a more complicated form of vibration, e.g. a normal mode.

The calculated values of  $\nu$  ( $\text{cm}^{-1}$ ) using Equations 1 and 2, are tabulated in Table III. Also in this table are values of  $\nu$  experimental. From inspection of Table IV, we found that the theoretical values of  $\nu$  agree reasonably well with experiment for all the (assumed) stretching vibrations,

except that for  $\text{P-O-P}$  and  $\text{P-O}^{(-)}$  stretching. In the case of  $\text{P-O-P}$ , it is found that the experimental band wave number is less than the theoretical value obtained from Equation 1 assuming stretching force constants, suggesting that the vibrations might involve mixed bending and stretching character. As stated in our theoretical review (Section 2) this is hardly surprising, considering the  $\text{P-O-P}$  bond angles. In the case of  $\text{P-O}^{(-)}$  the experimental wave number is higher than the theoretical one, suggesting that the

TABLE III The calculated values of wave numbers using Equation 1 with stretching force constants evaluated from Equation 2, compared with experimental wave numbers

	Bond length (nm)	Stretching force const ( $\text{N m}^{-1}$ )	Wave length ( $\mu\text{m}$ )	Wave number $K_{\text{theor}}$ ( $\text{cm}^{-1}$ )	Experimental wave $K_{\text{exp}}$ ( $\text{cm}^{-1}$ )
$\text{Co}^{3+}\text{-O}$	0.188	294	15.88	630	325
$\text{P-O-P}$	0.156	826	7.49	1335	780
$\text{P-O}^{(-)}$	0.156	413	12.27	815	1120
$\text{P=O}$	0.14	930	8.18	1223	1285
$\text{P-O-H}$	0.17	822	2.56	3908	3000*
$\text{O-H}$	0.157	409	3.68	2716	2860*
$\text{P-N}$	0.1785	308	13.58	736.4	738*

\*Results taken from Corbridge and Lowe [10].

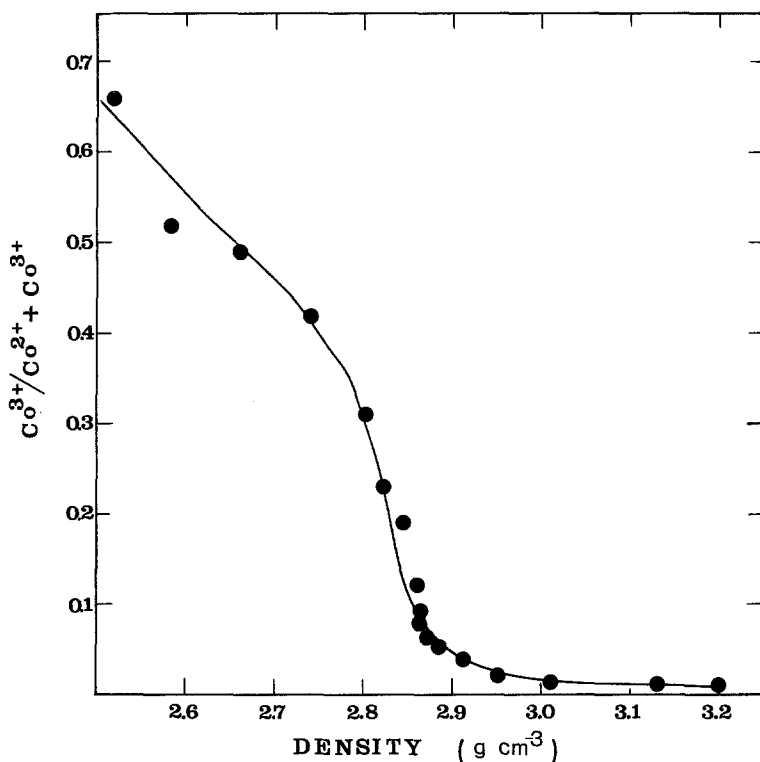


Figure 8 Variation of  $\text{Co}^{3+}/\text{Co}$  total with density ( $\text{g cm}^{-3}$ ) in  $\text{Co}_3\text{O}_4\text{-P}_2\text{O}_5$  glasses (density-composition data given in Table V).

attribution of the bond to this group may be incorrect, or perhaps that it could be a band combining a stretching motion with harmonics of bending motion. Precise formulae such as Equation 1 are unavailable for bending force constants, though they are generally known to be about one-tenth to one-twentieth the value of stretching force constants, for bonds of pronounced covalent character. So for the cases where a pronounced bending compound is expected we substitute experimental wave numbers in Equation 1 to derive effective values of force constant (Table IV). In all instances we find effective force constants intermediate between the expected

TABLE IV Effective force constants calculated using Equation 1 with experimental wave numbers

	Bending vibrations		Stretching vibrations	
	( $\text{cm}^{-1}$ )	$F$ (bend) ( $\text{N m}^{-1}$ )	( $\text{cm}^{-1}$ )	$F$ (stretch) ( $\text{N m}^{-1}$ )
P-O-P	500	155	780	378
			915 <sup>†</sup>	520
P-O( <sup>-</sup> )	700	306	1120	780
O-H	1640	149	3300 <sup>†</sup>	604
P-H	1150*	75	2400*	328
P-O-H	880*	481	3000*	5294

\*Data taken from [9].

†Data taken from [17].

ranges for stretching and bending force constants, suggesting that either bands associated with harmonics of pure bending vibrations are present, or that vibrations with mixed bending and stretching character are present.

### 8. Compositional dependence of the densities and molar volume of mixing of Co-P-O glass

To throw more light on the nature of the "three composition regions", tentative evidence for the existence of which is given by the infrared spectra, the molar volumes of mixing of the analysed components of our glasses were determined from the equation

$$\Delta V_M = V_M - V_0 \quad (3)$$

where  $V_M$  is the experimental molar volume obtained from the equation

$$V_M = (M_{\text{P}_2\text{O}_5} X_{\text{P}_2\text{O}_5} + M_{\text{CoO}} X_{\text{CoO}} + M_{\text{Co}_2\text{O}_3} X_{\text{Co}_2\text{O}_3}) / \rho \quad (4)$$

Here  $M$  refers to the molecular weight of the component,  $X$  refers to its mole fraction,  $\rho$  is the experimentally determined density of the glass, and  $V_0$  is the ideal additive molar volume given by

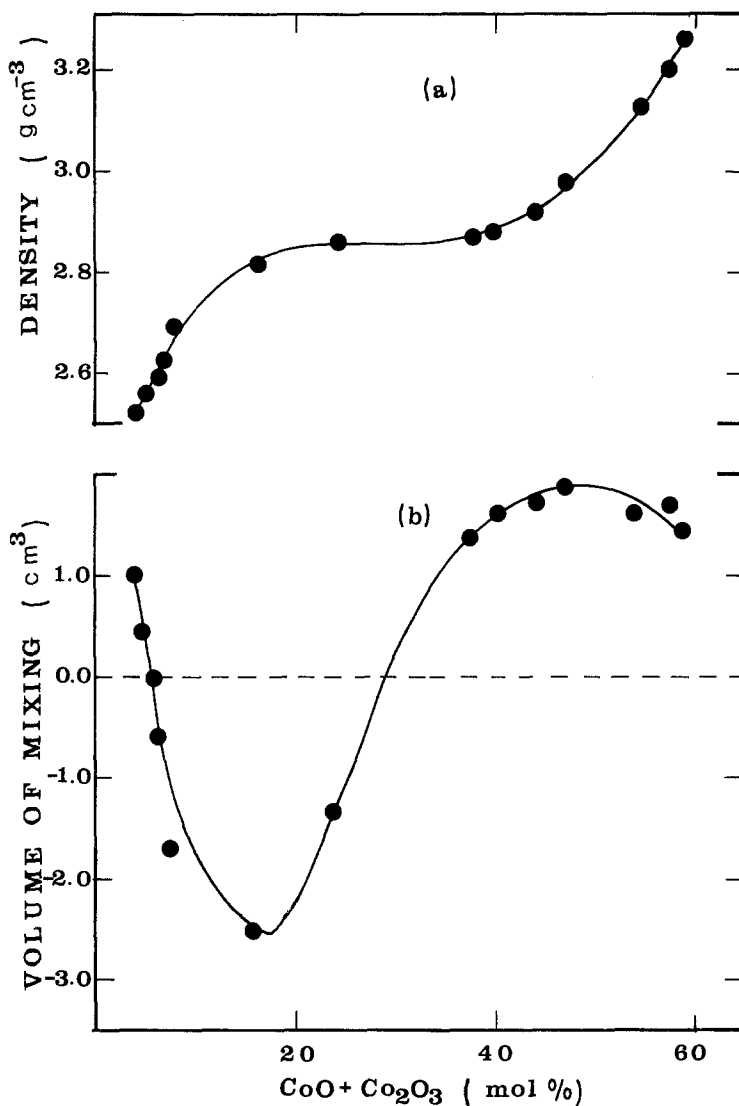


Figure 9 Compositional dependence of (a) the glass densities and (b) the volume of mixing  $\Delta V_m$  for Co-P-O system.

TABLE V Composition, density and the molar volume of mixing in Co-P-O glasses

Specimen	CoO + Co <sub>2</sub> O <sub>3</sub> (mol %)	density (g cm <sup>-3</sup> )	CoO (mol %)	Co <sub>2</sub> O <sub>3</sub> (mol %)	P <sub>2</sub> O <sub>5</sub> (mol %)	V <sub>M</sub> (cm <sup>3</sup> )	V <sub>0</sub> (cm <sup>3</sup> )	ΔV <sub>M</sub> (cm <sup>3</sup> )
C-1	4.05	2.5220	2.07	1.98	95.95	55.36	54.37	0.99
C-3	5.19	2.5560	3.19	2.00	94.81	54.59	54.12	0.47
C-5	6.02	2.5847	3.92	2.10	93.98	53.89	53.86	0.03
C-8	6.61	2.6192	4.25	2.26	93.39	53.11	53.71	-0.60
C-9	7.14	2.6850	4.81	2.33	92.86	51.56	55.28	-1.72
C-15	15.61	2.8241	13.55	2.60	84.39	46.94	49.46	-2.52
C-19	24.39	2.8572	22.88	1.51	75.61	44.38	45.67	-1.29
C-22	37.63	2.8652	36.37	1.26	62.37	41.14	39.76	+1.38
C-24	40.17	2.8849	39.01	1.16	59.83	40.26	38.64	+1.62
C-27	43.80	2.9302	43.02	0.78	56.20	38.66	36.90	+1.76
C-32	41.37	2.9751	46.95	0.42	52.63	37.18	35.25	+1.93
C-38	54.64	3.1330	54.44	0.20	45.36	33.76	32.12	+1.64
C-42	57.78	3.2012	57.65	0.13	42.22	32.30	30.56	+1.74
C-45	59.21	3.2557	59.12	0.09	40.79	31.52	30.05	+1.47

$$V_0 = V_{P_2O_5}X_{P_2O_5} + V_{CoO}X_{CoO} + V_{Co_2O_3}X_{Co_2O_3} \quad (5)$$

where  $V$  is the molar volume of the pure component.

The glass densities and the volume of mixing  $\Delta V_M$  are shown in Table V. On the basis of how these two properties vary with glass composition (Table III and Fig. 9) one can divide our Co-P-O glasses into three distinct "compositional regions". The first, extending from 0 to 17.5 mol%, the second from 18 to 50 mol% and the last from 50 to 60 mol% cobalt oxide content, which shows a good agreement with those compositional regions observed in the infrared spectra, as well as the other measured properties, mainly ultrasonic, to be discussed in subsequent papers.

To summarize the infrared data, it should be stated that a complete quantitative analysis of the infrared bands obtained is beyond the scope of this paper. Therefore, the conclusions that can be drawn are necessarily limited. However, we feel that two firm conclusions can definitely be drawn:

1. That at high oxide contents there is evidence of the rupture of the P=O bond by cobalt atoms to produce P-Co-O-P crosslinkages; and

2. at high cobalt oxide contents there is substantial evidence of the presence of ionized groups, i.e. of the breakdown of the covalent Co-P-O network into  $P_nO_{\frac{n+2}{3n+1}}^-$  groups of low  $n$  value, for example 1 and 2.

These two pieces of information will be used as an aid to the interpretation of our ultrasonic data on the glasses, in subsequent papers.

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