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Review

Structural investigations of phosphate glasses: a detailed infrared study of the $x(\mathrm{PbO})$–$(1-x)\,\mathrm{P_2O_5}$ vitreous system

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The results and detailed discussion of an extensive experimental study of infrared spectra of the $x(\mathrm{PbO})$–$(1-x)\mathrm{P_2O_5}$ vitreous system ($x = 0.3$–0.75) together with a brief review of infrared spectra of phosphate compounds, are presented. Theoretical models employed in the interpretation of infrared spectra of glasses have been reviewed. The frequency ranges of various infrared bands belonging to $\mathrm{PO_4^{3-}}$ and $\mathrm{P_2O_7^{4-}}$, observed in different phosphate compounds, are discussed. The glassy and quenched samples were prepared from PbO and $\mathrm{NH_4H_2PO_4}$ by the rapid quenching technique. The infrared spectra of the constituents of the system, PbO and $\mathrm{P_2O_5}$, in their polycrystalline and glassy forms, have been discussed. The intensity and wavenumbers of the infrared bands around 1600 and 3300 $\mathrm{cm^{-1}}$, assigned to the bending and stretching modes in $\mathrm{H_2O}$ trapped by the hygroscopic glasses, have been followed for different compositions with $x < 0.5$. The changes observed in these infrared bands established the role of water as an additional glass modifier. The intensity and frequency variations of the infrared bands have been followed through all the compositions for characteristic phosphate group frequencies including P=O, P–O–P stretching and bending modes and P–O bending mode. The results clearly suggest that the $x(\mathrm{PbO})$–$(1-x)\mathrm{P_2O_5}$ system undergoes gradual structural changes from metaphosphate ($x = 0.5$), to pyrophosphate ($x = 0.66$) and to orthophosphate ($x = 0.75$). The continuing presence of the infrared band, in varying intensity, in the region 1200–1280 $\mathrm{cm^{-1}}$ attributed to P=O, suggests that the glass-forming ability of the binary system is extendable at least up to $x = 0.66$ composition, and that no complete rupture of P=O bond by $\mathrm{Pb^{2+}}$ takes place. The ionic character of the phosphate groups, $\mathrm{P{-}O^{(-)}}$, $\mathrm{PO_4^{3-}}$ is well revealed by significant changes with the PbO content in the spectral features of the infrared bands around 1120 and 980 $\mathrm{cm^{-1}}$ respectively. The maximum intensity of the $\mathrm{P{-}O^{(-)}}$ band at 1120 $\mathrm{cm^{-1}}$ for 55 mol% PbO suggests a partial breakdown of the covalent vitreous network of the phosphates and formation of a crystalline phase consisting of ionic groups $\mathrm{PO_4^{3-}}$, $\mathrm{P_2O_6^{2-}}$ and $\mathrm{P_2O_7^{4-}}$ for PbO greater than 55 mol%. The observed pattern of variation in the intensity of the infrared bands in the 940–1080 $\mathrm{cm^{-1}}$ region attributed to the ν_3-mode in $\mathrm{PO_4^{3-}}$, suggests a gradual transformation of $\mathrm{PO_4^{3-}}$ units to $\mathrm{PO_3^{-}}$ groups in lead *meta*-phosphate glass and then their restoration to $\mathrm{PO_4^{3-}}$ groups of *pyro*- and *ortho*-phosphate quenched samples. The results indicate a gradual decrease in the number of bridging oxygens and increase in the resonance behaviour of non-bridging oxygens as the mole percentage of metal oxide (PbO) increases in the glass. The infrared spectra of several binary phosphate glasses have been reviewed in the context of the study of effect of the cation on the infrared spectra. It is found that the influence of the cation on the infrared spectra of phosphate glasses does not show any striking regularity. Theoretical calculations of these band frequencies were found to agree well only in the case of pure stretching (P=O and O–H) vibrations and pure bending (P–O–P and O–H) vibrations. The disagreement in the case of $\mathrm{P{-}O^{(-)}}$, P–O–H and other modes of P–O–P groups, has been attributed to the mixed nature of modes occurring in glasses. The changes in the positions of the characteristic bands and their relative intensities are strongly dependent on the structural units and PbO content in the phosphate glasses and the results emphasize the role of PbO as a network modifier.

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1. Introduction

The vibrations of structural units in a glass are independent [1–3], unlike the vibrations of complex ions in a crystalline matrix which are dependent on the lattice. In a vitreous system, it is assumed that vibrations of the characteristic groups of atoms in the network are independent of the vibrations of other groups. In probing the structural units and changes that take place in the network with composition of a binary or a ternary glass, infrared (IR) spectroscopy lends itself as an effective tool, because the technique is sensitive to short-range ordering and local interactions.

Alkali metal oxide or divalent metal oxide phosphate glasses form an attractive family of insulating vitreous systems as they are potential candidates for many desirable applications in optical systems because of their interesting optical properties [4]. However, most binary phosphate glasses are chemically unstable except in certain compositions, i.e. $\geqslant 50$ mol% alkali or metal oxide (M_2O). For these reasons there have been very few detailed structural studies of phosphate glasses with $P_2O_5 < 50$ mol% [5, 6]. However, the phosphate glasses with $M_2O > 50$ mol% have received enormous attention [6] and the infrared spectra [7] of thin films of binary phosphate glasses have been reported in addition to a few IR studies on non-alkali metal oxide binary phosphate glasses [7–10].

Thus, chemical stability, such as hygroscopicity and volatility, of phosphate glasses poses a serious problem for any viable applications and hence it is felt that there is a need for detailed and systematic investigation of the nature of structural units and their network in the divalent metal oxide phosphate glasses of composition both with $P_2O_5 \gtrless 50$ mol%.

Among the various metal oxides that play the role of glass modifiers in forming a P_2O_5 glass system, lead oxide (PbO) is considered as outstanding from the standpoint of its applications as shields against high-energy radiations, including nuclear radiations [11, 12]. Therefore, we have undertaken a detailed investigation of the $PbO–P_2O_5$ glass system, which has not been studied so far, although a brief mention of it was made by Chakraborty and Paul [13].

Unlike the simple alkali metal oxides such as K_2O which acts only as a network modifier, the role of PbO is known [14] to be unique, because it plays a dual structural role both as a network modifier [15] and as a network former [16–20]. Similarly, it is well-known [16, 17, 21, 22] that P_2O_5 exhibits a pronounced tendency to form a glass in two- or three-dimensional networks. In these networks, the coordination number of network-forming phosphorus, P, atom is typically low [22]. The bonding in these oxides is predominantly covalent, the bonds being strong and directional. With such a simple covalent oxide, P_2O_5, it is possible that glasses are prepared in a binary system of a transition metal oxide, such as CrO, Cr_2O_3 or V_2O_5, or of a post-transitional metal oxide, such as PbO.

Infrared absorption spectra of glasses can provide significant and valuable information on the arrangement of atoms, the nature of chemical bonding between them, the changes in atomic configurations caused by increase or decrease of concentration of glass-forming systems and, in general, facilitate probing of the short- and intermediate-range orders in glasses.

In addition, the investigation of infrared spectra of glasses enables the assignment of characteristic frequencies to molecular groups in the glass and hence correlation of IR absorption bands with different units of vitreous structure. In the case of phosphate glasses, the basic glass contains a double bond in the phosphate network and when a cation such as Pb^{2+} is added, it may enter the network or reside interstitially. Such information about the changes in the basic glass structure that take place upon the addition of a cation can also be studied from the IR spectra.

The present work on phosphate glasses seeks information on the structural changes that take place in the $x(PbO)–(1-x)P_2O_5$ system as the lead content is increased. It is observed [4, 23] that, in this system, as the lead content is progressively increased, the crystallization begins for $x = 0.55$ or 55 mol% PbO. The process of glass crystallization can be studied from the IR spectra because the vibrations of the anions become progressively dependent on the lattice. That is, beyond $x = 0.55$ composition of PbO, the system tends to attain partly a crystalline nature and the nature of the chemical bond in the system is expected to show a variation from covalent to ionic character. This tendency of the chemical bond also can be understood from a study of the vibrational spectra of vitreous $PbO–P_2O_5$ solids. Moreover, as the lead phosphate glass samples with $x < 0.5$ are hygroscopic in nature, the presence of network water and hydrogen bonding may affect the group vibrations in the system, and this should be manifested in the IR spectra.

Recently, numerous investigators [5–10, 24–28] have studied the infrared absorption spectra of binary phosphate glasses in an attempt to investigate the structure of glassy materials through the technique of IR spectroscopy. However, the effect of a heavy cation such as Pb^{2+} on the basic phosphate network has not been studied so far and this paper presents, in addition to a review, wide and specific, qualitative and quantitative data on the vibrational band frequencies and their relation to structural changes in the $x(PbO)–(1-x)P_2O_5$ system covering important compositional ranges which extend through *meta-*; *pyro-* and *ortho*-phosphates of lead.

2. A brief review of IR spectra of binary phosphate glasses

2.1. Theoretical approach

Before we attempt to describe and interpret our results in the present work, it is felt that a brief review of theoretical approaches available for interpretation of infrared spectra of solids in the vitreous state [25, 29] is appropriate.

In a vitreous phosphate, starting with pure P_2O_5, an infinite covalent network of PO_4^{3-} tetrahedra is assumed. The assumption is supported by radial distribution function (RDF) studies [30] which lead to an important inference that phosphate glasses are made up of PO_4 tetrahedra linked together by P–O–P bridges. The structural aspects of P_2O_5 are further discussed in Section 4.2. Therefore, compared to a crystalline matrix containing a lattice-dependent PO_4^{3-} tetrahedron, the IR spectrum of a glass network is expected to contain only a diffuse version of bands corresponding to lattice vibrational modes of the crystalline analogue. According to this "lattice model", one would thus, not expect to see any IR bands corresponding to the normal vibrations of free PO_4^{3-} tetrahedra. However, because the oxygen, O, atom is much lighter than the phosphorus atom, it is expected that characteristic bond frequencies corresponding to P–O–P groups in the phosphate glasses appear in the IR spectra, and these frequencies differ little from what would be expected for the oxygen atom vibrating by itself.

Borrelli and Su [31] proposed a different viewpoint to be adopted in the interpretation of IR absorption spectra of phosphate glasses. According to their model, called the "localized model", the IR spectrum of the glass is regarded as a diffuse version of the spectrum produced by a tightly clamped tetrahedron. Thus, the localized model essentially acknowledges the lack of long-range order in a glass and 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. In view of this distribution of P–O–P bond angles in the clamped tetrahedron, the localized model does not expect pure stretching and bending vibrations corresponding to ν_1(A) and ν_2(E) modes of free PO_4^{3-}, respectively, to occur in the IR spectra of phosphate glasses. In addition, the $\nu_4(F_2)$ corresponding to asymmetric bending is also not expected. However, exceptions have been observed in several vitreous phosphate compounds. It is to be noted that in the assumption of characteristic P–O–P frequencies in the "lattice model", it is the phosphorus atoms that are effectively clamped, whereas the bridging oxygens are clamped in the localized model of Borelli and Su [30] as shown in Fig. 1. It is much more significant to note that in either model, one expects to observe P=O vibration as a characteristic bond-group frequency. This frequency is unaffected to a large extent by the changes in other bonds in the glass network, as long as short-range order is preserved and even when it coexists with the long-range order. However, P=O vibration is certainly affected by the nature of the cation.

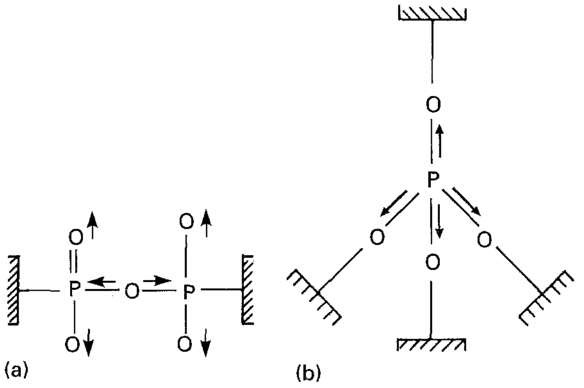


Figure 1 In the lattice model (a) of a phosphate network, P atoms are clamped while O atoms are treated as clamped in the localized model (b).

2.1.1. Relevance of the theory to the $PbO–P_2O_5$ system

When a relatively heavy cation such as Pb^{2+} is added to the P_2O_5 network in the form of PbO, and if PbO acts as a "network former", the IR spectrum is expected [29] to show only slight changes from the IR spectrum of P_2O_5 but with gradual shifts of characteristic bond-group frequencies. These shifts, which are generally red shifts, are attributed to the replacement of phosphorus (P), atoms by the new cation (Pb^{2+}). Thus, addition of PbO will not show any substantial effect on group frequencies. Further, if Pb^{2+} acts as a network former, gradual weakening of P=O may occur and finally the P=O bond may be ruptured completely by the Pb^{2+} ion.

On the other hand, if the cation enters the glass network interstitially as an ion, which is the case anticipated for PbO, known rather more [32] as a network modifier than as a network former, the network is gradually broken down and new IR spectral bands may appear, corresponding to the vibrational character of free-charged structural units.

One of the objectives of the present work was to ascertain whether the addition of lead atoms in the form of PbO to P_2O_5 conforms to its known role as a network modifier, though it is anticipated that lead will not go into the network. PbO may simply modify the network and therefore no P=O bond rupture is expected, unlike the case of cobalt–phosphate ($CoO_3–P_2O_5$) glasses [29], where cobalt atoms are lighter than lead atoms.

2.2. Experimental review

The prominent and strong absorption bands in both crystalline and glassy phosphate materials occur in the frequency region 900–1100 cm^{-1}. A large number of phosphate compounds exhibit well-defined IR absorption bands in this region, although a free phosphate ion, PO_4^{3-}, exhibits [33] four fundamental modes of vibrations in the regions mentioned below.

ν_1(A) (symmetric stretching) $\sim 980\ cm^{-1}$

ν_2(E) (symmetric bending) $\sim 420\ cm^{-1}$

$\nu_3(T_2)$ (asymmetric stretching) $\sim 1000–1100\ cm^{-1}$

$\nu_4(T_2)$ (asymmetric bending) $\sim 560\ cm^{-1}$

Out of these fundamentals, only ν_3 and ν_4 modes (both triply degenerate) are expected to be IR active. In a glassy compound, however, the random nature of bonding makes only the ν_3 mode in PO_4^{3-} tetrahedron appear prominently in the IR spectra in the region 1000–1100 cm^{-1}, as was concluded by Kalbus [34].

The ν_3 mode in the free PO_4^{3-} ion is triply degenerate, and in a compound it is expected to appear generally as a single band in a wide range of energy (990–1020 cm^{-1}) depending on the chemical environment of the phosphate. However, in a crystalline and glassy environment, the degeneracy of this ν_3 mode is likely to be removed as a result of interaction between the PO_4^{3-} ion and its neighbouring atoms. Consequently, the wide range of 960–1020 cm^{-1} could be occupied by a maximum of three bands. Interestingly, it was observed [29] in several glassy compounds, that this region is covered sometimes by more than three bands attributable to the ν_3 mode. The literature indicates that so far no common reason has been agreed upon for the appearance of more than three bands in this region of IR spectra of phosphates. Higazy and Bridge [29] are of the view that the splitting of the ν_3 mode is indicative of the expected association of PO_4^{3-} tetrahedra into dimers of $P_2O_7^{4-}$ or polymers formed out of groups represented by $P_nO_{(3n+1)}^{(n+2)-}$ with $n > 2$. Here, the superscript $(n + 2)$ refers to the charge the group would have if it existed in the ionic state. Thus, the idea of the occurrence of $P_nO_{(3n+1)}^{(n+2)-}$ polymeric chains is valid only if ionic bonding exists for a short range, but it is not valid in glasses where covalent bonding predominates.

The results of extensive studies made by Kalbus [34] and Corbridge and Lowe [35, 36] on about 170 crystalline and non-crystalline inorganic phosphate compounds indicate that the infrared absorption bands around ~ 2100–2400, 900 and 600 cm^{-1} are due to combinational modes $(2\nu_3 + \nu_4)$, ν_1 and ν_4 normal vibrations of PO_4^{3-} tetrahedra, respectively. Shih and Su [37] have briefly reviewed the IR and Raman spectra of various binary phosphate glasses, but no work has been reported on $PbO–P_2O_5$ glasses.

The earliest IR spectrum on crystalline sodium *meta*-phosphate ($Na_2P_2O_6$) in its four forms I, II, III, IV, and on sodium *meta*-phosphate ($Na_2P_2O_6$) glass was reported by Partridge [38]. The glass was obtained by melting NaH_2PO_4 at 700–725 °C for 0.5 h and then "chilling it" by pouring it on to a stainless steel plate. However, the observation of Corbridge and Lowe [35, 36] that the spectra of crystalline and glassy sodium phosphates are all of the same type with only some divergences, is now not acceptable because over the last four-decades the sensitivity of the IR spectrophotometer has been enhanced markedly with the advent of new technology and precision instrumentation, and now the divergences that do occur in the IR spectra of a compound in crystalline and glassy states can be detected with much more precision.

2.2.1. Main absorption bands and their range observed in the IR spectra of phosphates

The literature available [29, 35, 36] on the IR spectra of phosphate salts indicates that the following vibrational frequencies are observable in general in phosphates in the different IR regions.

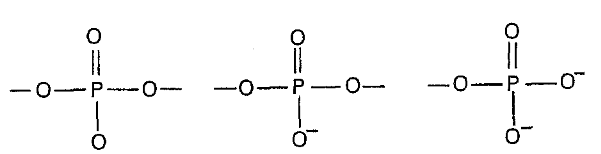
2.2.1.1. P–O linkages. The phosphate tetrahedron (PO_4^{3-}) that has been proved [30] to occur in all P_2O_5 glasses exhibits two fundamental vibrational frequencies at about 1080 and 980 cm^{-1} which are also observed in Raman spectra. The latter band (980 cm^{-1}) is due to the ν_1 mode and is expected to be IR inactive but appears because of solid-state effects. Colthup [39] reported an IR absorption band at 1100–1040 cm^{-1} for the phosphate ion. This band at 1100 cm^{-1} was considered to be a $P–O^{(-)}$ bond-stretching vibration and is also called the P–O ionic stretching frequency.

It is known [9, 35, 36] that in any member of the family of glasses $RO–P_2O_5$ with R = Li, Na, Ag and Pb, there exists a P=O unit. The IR band corresponding to this P=O bond stretching has been identified in several phosphate glasses, including $PbO–P_2O_5$ [6] and the general range suggested for this band is from 1300–1190 cm^{-1}.

Miller and Wilkins [40] considered that the PO_4^{3-} ion exhibits normal vibrations in the region 1100–1040 cm^{-1}. They 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 and $P–O^{(-)}$ groups produce characteristic vibrational bands at 1282 and 1205 cm^{-1}, respectively. However, if in the phosphate glass PO_4^{3-} dominates, the band due to $P–O^{(-)}$, which is basically present in P_2O_5, does not appear. Or, when PO_4^{3-} or $P_2O_7^{4-}$ is also present in the system in monomer form, the band due to $P–O^{(-)}$ does not appear. Miller and Wilkins also suggested that the P=O (double) bond is more strongly localized in central-position phosphate groups than in the end-position group as shown in Fig. 2.

Bartholomew [41] has studied the IR spectra of sodium *meta*-phosphate [$Na_2P_2O_6$] glasses and silver *meta*-phosphate [$Ag_2P_2O_6$] glasses and they observed a shift in the band positions of P=O and $P–O^{(-)}$ in silver glasses in comparison to their positions in the sodium glasses. The shift has been attributed to the effect of metal on the bonding of non-bridging oxygens.

2.2.1.2. P–O–P linkages. The extensive IR investigations on phosphorus compounds by Corbridge and Lowe [35, 36] indicate that if a P–O–P link is present in a compound, characteristic absorptions near 900 and 700 cm^{-1} should appear. While the bands near 900 cm^{-1} have been attributed to P–O–P symmetric



Branching point (a) Middle group (b) End group (c)

Figure 2 The P=O bond is more strongly localized in the central position phosphate groups than in the end position groups.

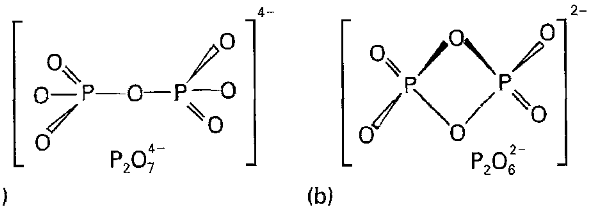


Figure 3 (a) Pyrophosphate $(P_2O_7)^{4-}$ contains only a single P–O–P linkage. (b) *Meta*-phosphate $(P_2O_6)^{2-}$ contains two P–O–P units.

bond stretching vibrations, the bands around 700 cm^{-1} have been suggested to be due to P–O–P anti-symmetric stretching mode. In the Ag_2O–P_2O_5 glass system [41], the formation of a covalent bond between the non-bridging oxygen ions and the silver ions gave rise to P–O–Ag units in the system, and it was assumed that the P–O–Ag stretching frequency is somewhat lower than a P–O–P stretching frequency.

The P–O–P stretching bands near 900 cm^{-1} have been observed [35, 36] to shift towards lower frequencies with increasing length of the P–O–P chain which probably occurs in the following order in phosphate compounds: *pyro*-phosphate ($P_2O_7^{4-}$), triphosphate [$P_3O_{10}^{5-}$] and linear *meta*-phosphate [$P_2O_6^{2-}$] series. While *pyro*-phosphate ($P_2O_7^{4-}$) contains only a single P–O–P linkage [40–43] (Fig. 3a) and correspondingly exhibits only one peak near 700 cm^{-1} due to vitreous nature, *meta*-phosphates ($P_2O_6^{2-}$), however, were found to exhibit two peaks which are attributed to the presence of two P–O–P units as shown in Fig. 3b.

According to Corbridge and Low [35, 36], cyclic *meta*-phosphates show absorption near 700 cm^{-1} and also near 770 cm^{-1}. In the chain compounds like glasses, the band at 770 cm^{-1} replaces the usual band near 900 cm^{-1} corresponding to symmetric stretching vibration. Thus, "the lower vibrational frequencies in the cyclic derivatives may be characteristic of P–O–P linkages in such rings or polymeric systems" [35, 36].

The P–O–P stretching frequency region (940–850 cm^{-1}) in phosphates can be compared with Si–O–Si stretching at 1050–1025 cm^{-1} in silicates. Wright and Hunter [42] attribute very strong absorption in silicates near 400 cm^{-1} to Si–O bending in Si–O–Si chains. Therefore, in phosphates with P (phosphorus-15) of higher atomic weight replacing Si (silicon-14), the bending vibration of P–O should appear below 400 cm^{-1}. However, there are difficulties in instrumentation in recording the IR spectra below 400 cm^{-1}, and the information that one looks for below 400 cm^{-1} can be obtained at higher frequencies in the form of harmonics. Because the harmonics of Si–O bending vibration could be observed near 800 cm^{-1} in several methyl siloxanes, "the bands observed near 700 cm^{-1} in the phosphates containing P–O–P linkages are likewise attributed to harmonics of P–O bending".

2.2.1.3. Other IR bands in phosphate glasses. In the IR spectra of phosphate compounds or phosphate glasses, bands other than those attributed to P–O and P–O–P linkages are quite likely to appear because of several reasons arising from the different routes available for preparation of phosphates. For any reason, such as the salt being acidic or the glass sample trapping water molecules because of hygroscopicity, P–H stretching is expected to appear in the form of an IR absorption band (sharp and medium intensity) near 2400–2300 cm^{-1} [44]. A weak band due to P–H bending is also expected in the region 1150–950 cm^{-1}, besides the bands due to P–O–P linkages [43].

P–O–H stretching: a weak, broad absorption near 2700 cm^{-1} is characteristic of acid *ortho*-phosphates ($PO_4^{3-} + H_2O$) and acid *pyro*-phosphates ($P_2O_7^{4-} + H_2O$). Absorption in this region is assigned to P–O–H stretching [45].

3. Experimental procedure

3.1. Preparation of samples

3.1.1. Lead phosphate $x(PbO)$–$(1-x)P_2O_5$ glasses ($x < 0.5$)

The glasses $x(PbO)$–$(1-x)P_2O_5$ were prepared by a single-step melting process according to the chemical reaction

$$\begin{aligned} x(PbO) + (1-x)(2NH_4H_2PO_4) &\rightarrow x(PbO) \\ &- (1-x)P_2O_5 + (1-x)(2NH_3)\uparrow \\ &+ (1-x)(3H_2O)\uparrow \qquad (1) \end{aligned}$$

where x gives the mole percentage of the PbO. Thus, the lead phosphate glasses of starting compositions expressed in mole per cent, were prepared from AR grade PbO and ADP, both of which were British Drug House (BDH) make. The components were thoroughly mixed in a clean alundum mortar initially, and the mixture was placed in an open alumina crucible. For PbO glass preparation, a porcelain crucible was used. The crucible was inserted into an electric furnace, open to the atmosphere, initially held at 250 °C for about 15 min. The temperature of the furnace was then increased to 550 °C and was maintained at that temperature for about 10 min. Although the melting point of PbO is as high as 886 °C and that of ADP is known to be (around 360 °C) this temperature ($\sim$550 °C) was found to be adequate for melting the PbO–ADP mixtures of all compositions up to $x = 0.5$ or 50 mol% PbO, corresponding to *meta*-phosphate [PbP_2O_6 or $Pb(PO_3)_2$] glass. The reaction takes place according to

$$\begin{aligned} PbO + 2NH_4H_2PO_4 &\rightarrow Pb(PO_3)_2 \\ &+ 2NH_3\uparrow + 3H_2O\uparrow \qquad (2) \end{aligned}$$

3.1.2. $x(PbO)$–$(1-x)P_2O_5$ glasses ($0.5 < x < 0.60$)

The glasses with 55 mol% PbO required a higher temperature ($\sim$600 °C) and the glass obtained was not as homogeneous as that with 50 mol% PbO, indicating that this procedure limits the glass-forming region to $x = 0.55$ or 55 mol% PbO as reported earlier by Weber *et al.* [23].

During the procedure followed for the preparation of glass samples, it was observed that different compositions of lead phosphate glass require different melt temperatures and the range of glass-forming melt temperature is found to be 550–650 °C with the highest being that applied to the mixture rich in PbO.

The glass samples for recording IR spectra were obtained in the form of spheroids by pouring the liquid rapidly on to the smooth surface of a cylindrical steel block maintained at room temperature.

3.1.3. Preparation of quenched samples of lead pyro-phosphate (x = 0.66) and lead ortho-phosphate (x = 0.75)

The lead *pyro*-phosphate ($Pb_2P_2O_7$) samples were prepared by taking the stoichiometric ratio (2:1) of PbO and P_2O_5 through the reaction given by

$$2PbO + 2NH_4H_2PO_4 \rightarrow [2PbO + P_2O_5] + 2NH_3\uparrow + 3H_2O\uparrow \text{ (primary)} \quad (3)$$

$$(2PbO + P_2O_5) \rightarrow Pb_2P_2O_7(Q) \text{ (quenched) (secondary)} \quad (4)$$

The components, however, were melted at 800 °C and were rapidly quenched on to the steel surface. The $Pb_2P_2O_7$ quenched samples were white in colour and opaque.

The lead *ortho*-phosphate samples were similarly prepared by taking the PbO and P_2O_5 in stoichiometric ratio (3:1) through the reaction

$$3PbO + 2NH_4H_2PO_4 \rightarrow (3PbO + P_2O_5) + 2NH_3\uparrow + 3H_2O\uparrow \quad (5)$$

$$(3PbO + P_2O_5) \rightarrow Pb_3(PO_4)_2(Q) \text{ (quenched samples)} \quad (6)$$

These $Pb_3(PO_4)_2$ samples required a higher temperature (~900 °C) for quenching. The samples were opaque and were white in colour.

The amorphous nature of the prepared glasses was confirmed by X-ray diffraction study made on Jeol-XRD-8030 X-ray diffractometer. The X-ray spectra indicate the onset of crystalline phase only for compositions $x = 0.55$ and above.

3.2. Recording of IR spectra

The IR absorption measurements on various phosphate glasses and quenched samples were made by employing the KBr pellet technique. The glass and quenched phosphate samples were ground into a fine powder and a weighed quantity (~0.005 g) of the powder was mixed with highly purified and desiccated KBr powder (0.2 g). The mixtures were then pressed using an evacuated die at 0.1–0.2 kbar pressure to yield transparent pellets suitable for mounting in the spectrometer.

The IR spectra were recorded on NIC Nicolet 740 Fourier transform–infrared (FT–IR) spectrophotometer in the range 400–4000 cm^{-1}. The resolution of the instrument was 4 cm^{-1}. Because the spectrophotometer was maintained in a dust-free room with dry atmospheric conditions, the IR bands due to water contaminating the pellets in the form of atmospheric moisture are considered to be either eliminated or of negligible intensity.

4. Results and discussion of the IR spectra of the constituents

Before any attempt is made to analyse the IR spectra of lead phosphate glasses and draw conclusions about the behaviour of structural units in the glasses, acquiring some knowledge about the IR spectral behaviour of the constitutents, namely PbO and P_2O_5, is in order. Therefore, the IR spectra of these compounds are discussed.

4.1. IR spectra of lead monoxide (PbO) glass

The IR spectrum of lead monoxide (PbO) polycrystalline samples exhibits a few weak bands in the region 463–816 cm^{-1} and some more bands of medium intensity in the range 1250–1400 cm^{-1}. While the weak bands below 700 cm^{-1} have been attributed to various non-degenerate modes in the silicate (SiO_4^{4-}) present in small percentages as an impurity in PbO material, the other bands have been assigned to the nitrate (NO_3^-) impurity present as lead nitrate. The IR spectrum of PbO in different polymorphic forms [46] has been investigated earlier [46–48] and also recently from this laboratory [49] in the context of a structural investigation of PbO glass.

It is known [48, 50–52] that PbO, which cannot form a glass on its own, gains the glass-forming ability in the presence of a small amount of SiO_2 which is provided by the porcelain crucible. The detailed analysis [49] of the IR spectrum of such a PbO glass containing a small amount of silica (SiO_2), indicates that a very strong band appearing at 844 cm^{-1} and a medium intensity band at 463 cm^{-1} are attributable only to the internal vibrations of SiO_2 [53]. Thus, no Pb–O vibration, due to the presence of PbO extensively as a modifier in lead phosphate glasses, is expected in their IR spectra, particularly in the region above 400 cm^{-1}. It is, thus, imperative to attribute the IR bands observed in lead phosphate glasses to any P_2O_5-related units, but not to PbO vibrations.

4.2. IR spectra of P_2O_5

The P_2O_5 glass sample obtained by decomposing $NH_4H_2PO_4$ and rapidly quenching it above 360 °C was used for recording the IR spectrum shown in Fig. 4. Two strong and sharp bands at 494 and 714 cm^{-1} and another strong band at 1243 cm^{-1} are assigned to the vibrations in P_2O_5. The band positions evaluated in the present work are compared with the bands reported by various investigators [14, 22] in Table I. It is seen that there are wide variations in the band positions and the variations are probably due to the slight variations in the method of sample preparation. However, there are at least four commonly observed well-defined bands and their average positions are approximately at 1280, 1080, 700 and 490 cm^{-1}.

The vibrational spectrum of vitreous P_2O_5 as a single-oxide glass former has received much less thorough investigation than the spectra of B_2O_3, SiO_2, GeO_2 and As_2O_3, because the hygroscopic nature and volatility of vitreous P_2O_5 (V–P_2O_5) prevented a thorough examination of its glass state. Only in one earlier study [54] was the Raman spectrum of vitreous P_2O_5 reported together with the effect of adding alkali, alkaline-earth and other multivalent oxides on the spectra of the resultant phosphate glasses. Recently, Hudgens and Martin [5] have reported the IR spectrum of nearly anhydrous (< 1 mol% H_2O) P_2O_5. The structure of pure V–P_2O_5 is shown [43] in Fig. 5.

It is worthwhile to compare the IR spectrum of P_2O_5 glass with that of crystalline P_2O_5. Because P_2O_5 is known [55] to exist in two crystalline modifications – a rhombohedral polymorph at low temperatures and an orthorhombic polymorph at high or room temperature – comparison must be made only with one of them. P_2O_5 in orthorhombic form consists of PO_4 tetrahedra shared by neighbouring tetrahedra such as in P_2O_5 glass, thus comparison has to be made only with orthorhombic P_2O_5 at room temperature (RT). However, no vibrational spectrum has yet been reported for this orthorhombic polymorph of P_2O_5.

The high-temperature or RT form, P_4O_{10}, is the glass-forming polymorph where the P atom has been shown to be four-coordinated with one non-bridging oxygen (NBO) and the remaining as bridging oxygens (BO).

The laser Raman spectral studies [56] on pure V–P_2O_5 indicated that the spectrum of V–P_2O_5 is similar to that of four-coordinated POF_3 molecule. Further, the X-ray photoelectron spectroscopy (XPS) studies [5, 57] on crystalline P_2O_5 (C–P_2O_5) together with the reasonable assumption that the first coordination sphere bonding in C–P_2O_5 and in V–P_2O_5 should be the same, led to the structural model of V–P_2O_5 shown in Fig. 6. Thus, the first-coordination sphere around the P atom is similar in C–P_2O_5 and in V–P_2O_5. In this model, a doubly bonded (P=O) oxygen and three singly bonded oxygens are bonded

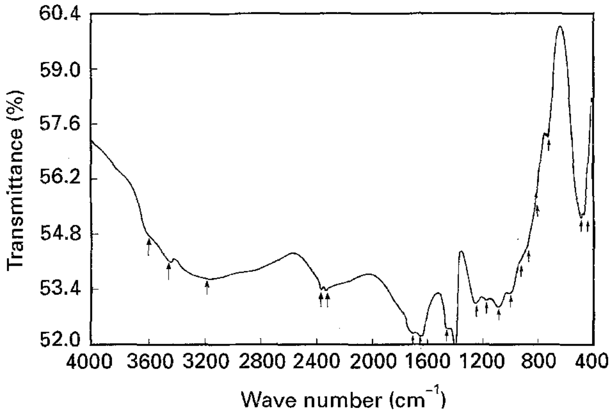


Figure 4 The IR spectrum of P_2O_5 glass recorded on the FT–IR spectrophotometer.

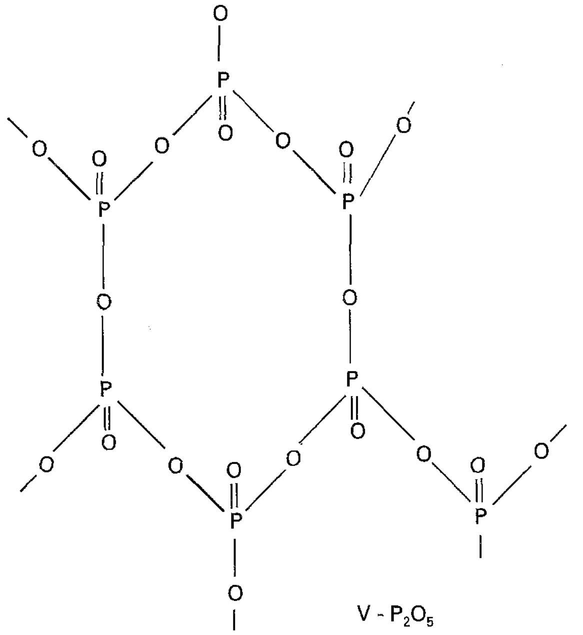


Figure 5 Structure of pure vitreous P_2O_5 [45] which consists of infinite sheets with a T_d environment around the P atom and a distinct P=O (bond) which is considered as terminal oxygen or a non-bridging oxygen. The oxygen that links two P atoms in the P–O–P unit is the bridging oxygen.

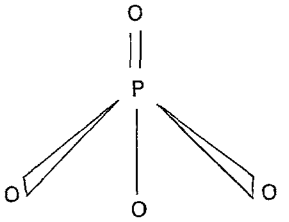


Figure 6 The four-coordinated P atom with one distinct P=O in C – P_2O_5 and V–P_2O_5.

TABLE I The frequencies of IR bands reported for P_2O_5

No.	Specimen	P=O stretching vibrations (cm^{-1})	P–O–P bending vibrations (cm^{-1})	P–O–P stretching vibrations (cm^{-1})	Harmonics of bending O–P–O and O=P–O (cm^{-1})	Ionic groups		Reference
						(PO_4^{3-}) (cm^{-1})	P–O$^-$ (cm^{-1})	
1.	P_2O_5 crystal	1240–1270	910–940	700–730	500	1015 + 15	–	[29]
2.	P_2O_5 glass	1240–1270	915	700–730	500	1015	–	[29]
3.	P_2O_5 glass	1285 (s)	780 (vw)	650 (w)	475 (s)	–	–	[14]
4.	P_2O_5 crystal	1230–1300	800–870	–	600	1100	–	[5]
5.	P_2O_5 glass	1390	–	530	650–800	–	–	[5]
6.	P_2O_5 glass	1240 (s)	780 (w)	780 (s)	470 (w), 530 (w, sh)	930 (sh) 1040 (s, b)	1120(w, sh)	This work

to the phosphorus P centre. While doubly bonded oxygen (P=O) is an NBO, the other three oxygens are BOs.

It was convincingly shown by Wright *et al.* [58] that the intermediate-range order in V–P_2O_5 closely resembles that of GeO_2 and SiO_2 and consists of a three-dimensional network of tetrahedral PO_4 units in a manner similar to that of GeO_2 and SiO_2.

It is important to note that the number of bands expected and obtained for P_2O_5 glass is much smaller than those predicted by factor-group analysis [22] for crystalline P_2O_5 and therefore no analogy of the vitreous structure with any of the crystalline polymorphs can yet be made from vibrational studies.

The possible IR vibrational modes in P_2O_5 correspond to the vibrations of P=O bonds, bridge vibrations of P–O–P chains (Fig. 5) of the glass lattice and P–O–P, O–P–O deformations. All these modes give rise to IR bands below 1300 cm^{-1}. Therefore, the bands in Fig. 4 above 1300 cm^{-1} and around 2400 cm^{-1} are attributed to overtones and combinational modes, as already mentioned [35, 36].

It is significant to note that the band at 1243 cm^{-1} (Fig. 4 and Table I) in V–P_2O_5 has to be assigned to P=O vibrations. This frequency is far less than the value (1390 cm^{-1}) observed [5] for pure, anhydrous V–P_2O_5 obtained by special techniques. The lowering of the P=O frequency in the V–P_2O_5 sample prepared in the present work ought to be attributed to the ordinarily unavoidable H_2O content present in the sample. At the same time, the magnitude of the shift to a value even below the value observed for the highest phosphate content PbO–P_2O_5 glass ($\simeq 1288$ cm^{-1}) should be examined carefully in the context of the role of water (H_2O) in PbO–P_2O_5 as a glass modifier. The result should suggest that in the absence of the other glass modifier, i.e. PbO, the water (H_2O) in P_2O_5 acts as a total modifier (*vide infra*), even stronger than PbO and thus reduces the P=O bond frequency to as low as 1243 cm^{-1}.

Notwithstanding this broad understanding of the IR behaviour of the P_2O_5-containing system, the effect of adding a metal oxide on the structure of V–P_2O_5 and change in the nature of the P=O as the metal oxide is added, is as yet unknown or is not understood clearly in low-phosphate ($x > 0.5$) glasses. An attempt has been made in this direction in the study on IR spectra of the $x\text{PbO} - (1 - x)P_2O_5$ system.

5. Results and discussion of the IR spectra of the xPbO–(1 – x)P_2O_5 glass system

The results of infrared investigations on the vitreous x(PbO)–(1 – x)P_2O_5 system are discussed in the following sections in three parts corresponding to the three compositional regions (or three ranges for values of x). To begin with, a detailed discussion is given on glasses with $x = 0.3$, 0.35, 0.4, 0.45 and 0.5 (first region). The last composition, $x = 0.5$, corresponds to lead *meta*-phosphate [PbP_2O_6] glass. Therefore, discussion is carried on to the IR spectra of glasses and quenched samples with the composition range (second region) of $x = 0.55$ and 0.60. Because $x = 0.666$ and 0.75 compositions correspond to *pyro*- and *ortho*-phosphate samples, a separate discussion is made on these quenched samples (the third region) to indicate the trends of bond-forming tendency in the phosphate system as the metal oxide (PbO) content is increased. However, before the IR spectra arising due to PO_4 tetrahedra in the glass system are discussed, a general description of the results and the suggested attribution of the observed IR bands in different ranges are given below.

5.1. General description of the results

The IR spectra of lead phosphate glasses with PbO content corresponding to $x = 0.3$, 0.35, 0.4 and 0.45, are given respectively in Fig. 7 by curves (a–d), respectively. The IR spectrum of lead *meta*-phosphate glass (PbP_2O_6) with $x = 0.5$ is given by curve (e) while the spectra for the glasses with compositions $x = 0.55$ and 0.6 are given by curves (f) and (g), respectively in Fig. 7. Then the spectra corresponding to *pyro*-, *ortho*-phosphate samples with $x = 0.667$ and 0.75 are given in Fig. 8 by curves (a and b), respectively. These figures should facilitate any quick comparison to enable one to draw important conclusions about the changes in the structural units of the lead phosphate glass network.

From all these spectra, one can find that there are weak but well-defined IR bands in the 3300 cm^{-1} region and around 1600 cm^{-1} which are known [27] to be due to H_2O molecule. The bands (Fig. 7) in the 950–900 cm^{-1} region may be due to P–O–H bending and harmonics of P–O–P bending vibrations. The spectra also display strong bands around 1260, 1015

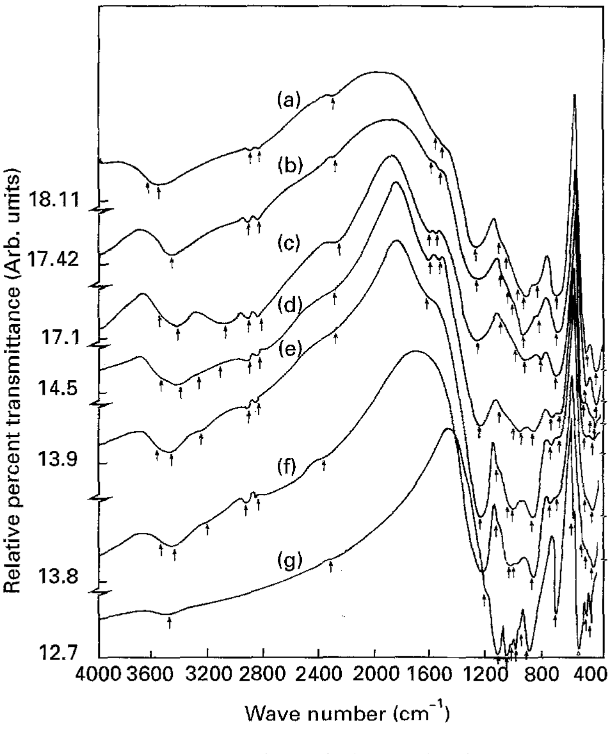


Figure 7 The IR spectra of the x(PbO)–(1 – x)P_2O_5 glass system. Curves (a–g) correspond to $x = 0.3$, 0.35, 0.4, 0.45, 0.5, 0.55 and 0.6, respectively.

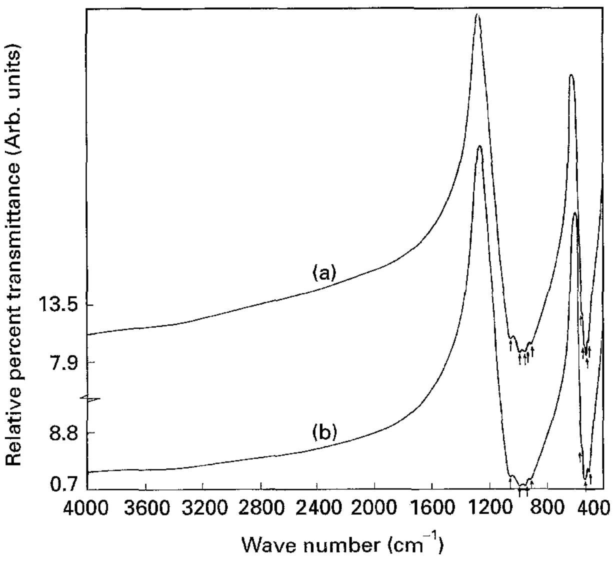


Figure 8 IR spectra of (a) the quenched lead *pyro*-phosphate sample with $x = 0.66$, and (b) the quenched lead *ortho*-phosphate sample with $x = 0.75$, in the x(PbO)–$(1-x)P_2O_5$ system.

and 500 cm^{-1}, which are possibly due to the P=O stretching vibration, a normal vibrational mode in PO_4^{3-} arising out of v_3-symmetric stretching and harmonics of the P–O bending vibrations, respectively. Besides these bands, the sharp and medium-intensity bands around 700 cm^{-1} are known [29] to be due to P–O–P stretching vibrations. The weak bands around 1120 cm^{-1} in Fig. 7 are assigned to P–O$^{(-)}$ ionic stretching vibration.

5.2. IR spectra and hygroscopicity of lead phosphate glasses

In general, the recording of IR spectra of the glass sample by the KBr pellet technique is likely to be influenced by a number of factors, including the atmospheric conditions in the room of the spectrophotometer. In particular, the atmospheric moisture is easily absorbed by the sample or by the pellet, causing the appearance of IR bands belonging to H_2O molecules although the sample under investigation does not contain H_2O as a unit in the network. Because the intensity of the IR bands shows a quantitative dependence on the molecules causing them, it is felt that an approximate idea about the structural units, local order and hydrogen bonding in the lead phosphate glasses can also be gained through comparison of IR bands of the water trapped in the samples, particularly under uniform recording conditions. It is assumed here that IR bands of water arise mainly because of the hygroscopic nature of the glasses with higher phosphate content, and any change in these bands with composition is indicative of changes in their hygroscopicity and hence changes in the glass structure or *vice versa.* Thus, the hygroscopic nature of $PbO–P_2O_5$ glasses should permit one to refer to them as $PbO \cdot P_2O_5 \cdot H_2O$ composition [59].

In all the phosphate glasses examined by earlier investigators [6, 7, 58, 60, 61], the glasses were prepared from hydrated phosphate salts, especially $(NH_4)_2HPO_4$ (di-ammonium H-phosphate) which is chemically analogous to the phosphate, $NH_4H_2PO_4$ (ammonium di-H-phosphate) used in the present work. “It has been the observation of most of these workers that in the ultra phosphate region ($x < 0.5$) this always leads to glasses with very high water contents”.

It has also been shown that water in these glasses acts like an alkali or like a PbO modifier, leading to the formation of additional non-bridging oxygens (NBOs) [5].

In the case of phosphate glasses with a PbO content less than 33%, it is assumed with near certainty that volatile P_4O_{10} exists, and these glasses can retain as much as 25 mol% water, as was established in most phosphate glasses including lithium phosphate glasses [5]. It is for these reasons that the investigations on lead phosphate glasses, x(PbO)–$(1-x)P_2O_5$, in the present work begin with 30 mol% PbO (i.e. $x = 0.3$ only). However, Hudgens and Martin [5], for these same reasons carried out IR studies on anhydrous ultraphosphate ($x < 0.3$) glasses prepared by employing special techniques.

All the hygroscopic glasses are expected to show absorption due to network water or coordinated water around 3600 cm^{-1} and at ~1600 cm^{-1}. These bands presumably [33] correspond to O–H stretching and O–H bending. The presence of bands with frequencies around 3450 cm^{-1} and above indicates that free O–H stretching occurs due to the contaminated water, which has no role in the glass network, but involves intermolecular H-bonding.

The positions of IR bands attributed to water molecules, together with their observed nature in the lead phosphate glasses, have been summarized in Table II. A general observation made in the case of lead phosphate glasses is that as the content of network modifier (PbO) increases, stable glasses are formed, as probably the strength of bonding in the glass samples increases and hence leads to a progressive decrease in their hygroscopicity and increase in their chemical durability until the stoichiometry between PbO and P_2O_5 is complete for $x = 0.5$. It is probable that interstitials or voids are available in large numbers only in the glasses with $x < 0.5$. This indicates definite structural changes in the glasses which seem to manifest indirectly in the form of certain trends in the IR bands of water, corresponding to O–H stretching and O–H bending vibrations.

It is seen from Table II that the O–H stretching vibrational band shows a shift towards a lower frequency from 3600 cm^{-1} to 3440 cm^{-1}. From the IR band positions of water given in Table II for various glass compositions, the following features of the glass structure are discernible.

(i) Initially, in the high-phosphate (70 mol%) glasses which are highly hygroscopic, the water seems to be nearly free or is loosely held by the glass network. Even the vibrational band corresponding to the bending mode at 1660 cm^{-1} falls within the frequency region of partially bound water.

TABLE II The position and nature of IR bands of H_2O in different lead phosphate glasses and quenched samples

No.	Compound	State[a]	Range of O–H stretching modes (cm^{-1})	Range of O–H bending modes (cm^{-1})	Other bands (cm^{-1})
1.	$(PbO)_{0.3}(P_2O_5)_{0.7}$	G	3600 (b)	1660 (w), 1610 (vw)	2940, 2880[b]
2.	$(PbO)_{0.35}(P_2O_5)_{0.65}$	G	3520 (b)	1660 (m), 1610 (w)	2940, 2880
3.	$(PbO)_{0.4}(P_2O_5)_{0.6}$	G	3500 (b)	1640 (m, sh) 1610 (vw)	3552, 3480,[c] 3232 (s, b), 3040 2928 (w), 2848 (w) 2400 (vw), 2320 (vw)
4.	$(PbO)_{0.45}(P_2O_5)_{0.55}$	G	3450 (b)	1656 (m) 1600 (vw)	3560, 3464 (m, b) 3392, 3264, 2944[d] 2864, 2400 (vw)
5.	$(PbO)_{0.5}(P_2O_5)_{0.5}$	G	3445(b)	No band	2930, 2860
6.	$(PbO)_{0.55}(P_2O_5)_{0.45}$	M	3440 (b, w)	No band	2930, 2850
7.	$(PbO)_{0.6}(P_2O_5)_{0.4}$	M	3440 (b, vw)	No band	–
8.	$(PbO)_{0.66}(P_2O_5)_{0.33}$	M	No band	No band	–
9.	$(PbO)_{0.75}(P_2O_5)_{0.25}$	M	No band	No band	–

[a] G, glass; M, mixed phase.

[b] These could be due to one type of OH group [33].

[c] The bands above 3400 cm^{-1} may be due to OH stretching vibrations in the network water. Other bands may be due to various modes in H_2O.

[d] The band around 2400 cm^{-1} is attributed to P–H stretching vibrations.

(ii) It is significant to note that for $x = 0.35$, stretching frequency decreases approximately to 3520 cm^{-1} (see Fig. 7 and Table II). At this stage it is probable that H_2O enters the phosphate network as a modifier and develops bonds with P or O atoms. Consequently, perhaps the freedom of H_2O vibrations is reduced and the stretching frequency decreases. However, it is possible that together with this "network water", some amount of free water is also present in the sample which should exhibit its stretching frequency above 3520 cm^{-1}. In that case, the band corresponding to O–H stretching of free water becomes superposed or overlaps with that due to network water. The broad nature of the band (see curve e of Fig. 7) indicates that such a structure is indeed present and is unresolved. In agreement with this argument, it is seen that in the case of the bending mode, a weak band due to free water at 1610 cm^{-1} appears, together with the bound water band at 1660 cm^{-1}. This behaviour of IR bands of water suggests that the water is bonded to the glass network and acts as a modifier together with PbO, for $x < 0.5$.

(iii) These tentative conclusions seem to be supported by the shifts further to lower frequencies observed in the case of stretching modes (Fig. 7 and Table II) of network water. As Table II indicates, in all these cases the band at 1610 cm^{-1} (attributed to free water) persists, while that at 1660 cm^{-1} (due to bound water) gains intensity.

(iv) When $x = 0.5$, PbO and P_2O_5 bear a 1:1 ratio and form lead *meta*-phosphate (PbP_2O_6) glass; it is worthy to note that in Fig. 7, the IR band corresponding to the H–O–H bending mode shifts to a frequency as low as 1600 cm^{-1} and becomes very weak. This may be due to gradual expulsion of network water. The IR band corresponding to the stretching mode decreases in intensity and shifts to 3445 cm^{-1}. Further, it also exhibits unresolved fine structure and approximate peak positions of the structure are given in Table II under "other bands".

These features distinguish the lead *meta*-phosphate glass from the other glasses with $x < 0.5$ and indicate that now O–H vibrations are subjected to a stronger influence of the glass network. Probably under this influence, the IR absorption becomes broadened and shows splitting. Thus, in the case of ultraphosphate glasses with a modifier content less than 50% ($x < 0.5$), water acts like a partial modifier and the metal oxide (PbO) as a total modifier.

The fine structure in the IR band at 3445 cm^{-1} is due to not only the high resolution but also probably due to the onset of crystalline phase as indicated by the X-ray studies. The structure could be due to various symmetric and antisymmetric OH stretching modes in water. Such fine structure in the IR bands of lattice water was also observed in $CaSO_4 \cdot 2H_2O$ [62] and detailed vibrational studies have been made for a number of inorganic salts having lattice water [63, 33] including sodium triphosphate hexahydrate $Na_5P_3O_{10} \cdot 6H_2O$ [35, 36]. The other bands in Table II around 2900 cm^{-1} may be due to overtones of the rocking and wagging modes of the OH group in water molecules [64] and similarly the weak bands around 2400 cm^{-1} (Table II) may be due to the combinations of bending modes and the wagging modes.

(v) It is interesting to note that the lead phosphate quenched samples with compositions of $x = 0.55$ and 0.6 are not completely glassy in nature and exhibit mixed phase, as revealed by the X-ray spectra. These samples are also found to be physically stable and no hygroscopic nature has been noticed. The IR spectra together for these samples are shown in Fig. 7 (curves f and g). In these spectra, it is seen that the IR bands of O–H stretching and bending modes are either very weak or altogether absent (see Table II).

TABLE III The IR bands of water (H_2O) in various phosphate glasses

No.	Compound	Structure	Range of O–H stretching mode (cm^{-1})	Range of O–H bending mode (cm^{-1})	Other bands (cm^{-1})	Reference
1.	($Li_2O + P_2O_5 + SiO_2$)	Glass	3440	1640	2925	[67]
2.	($K_2O + Al_2O_3 + P_2O_5$)	Glass	–	1660	2350	[13]
3.	($PbO + Al_2O_3 + P_2O_5$)	Glass	–	1660	–	[13]
4.	($KHPO_4 + PbO + P_2O_5$)	Glass	–	1640	–	[13]
5.	($CdO–P_2O_5$)	Glass	3450	–	–	[68]
6.	($CdO–ZnO–P_2O_5$)	Glass	3450	–	–	[68]
7.	(Pb–Sn–F–P)	Glass	3440	1640	–	[69]
8.	($SnO–P_2O_5$)	Glass	3440	1620	–	[69]
9.	($Co_3O_4–P_2O_5$)	Vitreous	–	1640–1700	–	[29]
10.	($V_2O_5–P_2O_5$)	Glass	3400–3600	1600–1700	–	[70]

Thus, for $x > 0.5$, in low-phosphate glasses, the role of water is eliminated and the metal oxide (PbO) alone acts as the glass modifier. In both the cases of glass (with $x < 0.5$ and $x > 0.5$), Brow *et al.* [61] observed that with increasing modifier content in the glass, the fraction of NBOs increases in a fashion predicted by the ionic models proposed long ago by Van Wazer [65]. Such an increase in NBOs decreases the network structure, as is observed by the breakdown of the glass network in lead phosphate glasses for $x \geqslant 0.6$.

(vi) This observation of the elimination of water is further supported by the fact that IR bands of O–H stretching and bending modes are totally absent in the spectra corresponding to $x = 0.667$ (67 mol% PbO) and $x = 0.75$ (75 mol% PbO), respectively, in Fig. 8 (see Table II). In these samples, the stoichiometry of PbO and P_2O_5 bear 2:1 and 3:1 ratios and hereafter will be referred to as lead *pyro*-phosphate and lead *ortho*-phosphate samples, respectively. These are obviously stable samples and although they are prepared by the quenching method, they exhibit clear crystallinity which is evinced by their X-ray spectra.

Thus, the above correlation between the IR bands of H_2O and the composition of lead phosphate samples offers sufficient indication of structural changes and rearrangement of atoms for stronger packing taking place in the vitreous solid. For example, in the case of $Na_5P_3O_{10} \cdot 6H_2O$, in addition to two absorption bands at 3350 and 3260 cm^{-1}, a very sharp, strong band at 3630 cm^{-1} was also observed. This indicates, according to Corbridge and Lowe [35, 36] that out of the six water molecules in the unit cell, some molecules of water of crystallization are probably only loosely held in the structure.

For a broad comparison, the IR bands of water (H_2O) observed in various phosphate glasses [66–70] are given in Table III. From the table it is seen that in almost all phosphate glasses, the IR band corresponding to O–H stretching is around 3450 cm^{-1}, indicating that water is bonded to the network to a certain extent in these glasses. The compositional dependence of wave numbers corresponding to stretching and bending modes of H_2O in lead *meta*-phosphate glasses is shown in Fig. 9.

It is possible, therefore, that differences in the structure of glasses of a given material occur due to the differences in the way the water molecules are held in the structure. From these results and the discussion made so far, the following important conclusions can be drawn.

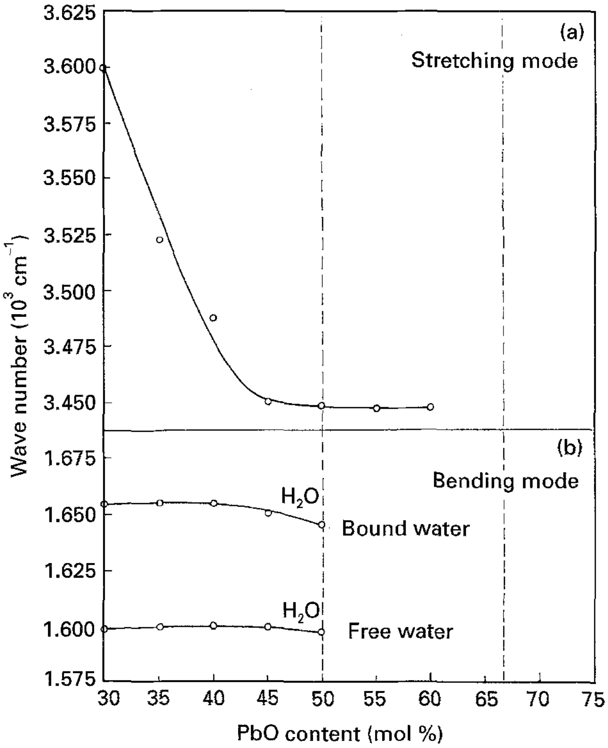


Figure 9 (a) Compositional dependence of the wave number corresponding to the stretching mode of H_2O in the lead phosphate glass system. (b) Variation of the wave number corresponding to the bending mode of H_2O in the lead phosphate glass system.

(a) The hygroscopicity and chemical durability of lead phosphate glasses can be judged from their IR spectra because the frequencies of IR bands of the water show a marked dependence on the composition.

(b) There exists a relation between the structure of glass and the way the water molecule is accommodated in the network. This relation can be understood from the study of IR spectra of the water molecules in the glass.

(c) The variations in the ν_{O-H} stretching and ν_{O-H} bending frequencies with the composition of the glass clearly suggest that extensive hydrogen bonding

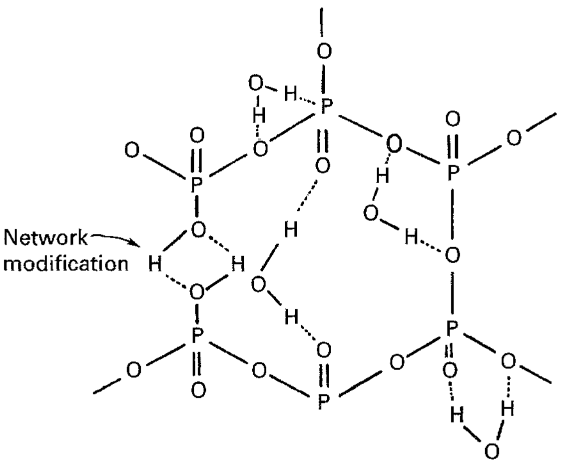


Figure 10 Probable loose binding of water molecules to the network of $x(\mathrm{PbO})\text{–}(1-x)\mathrm{P_2O_5}$ glass for $x < 0.5$ (positions of PbO are not shown).

occurs for lower PbO (or higher phosphate) compositions of the glass, and water acts as a partial network modifier.

Probably, it is for this reason that several bands other than $\nu_{\mathrm{O-H}}$ stretching and $\nu_{\mathrm{O-H}}$ bending appear in the region 3400–2320 cm^{-1} (Table II) which are limited to the composition $x < 0.50$. These bands may be ascribed to more than one type of OH-group hydrogen bonding in lead phosphate glasses as shown in Fig. 10. This was also observed in ternary glasses [67].

6. Detailed discussion of the results of the individual phosphate group frequencies, intensities and their compositional dependence

In general, the phosphate glasses exhibit six well-defined IR bands characteristic of six molecular groups identified as P=O, P–O$^{(-)}$, $\mathrm{PO_4^{3-}}$, P–O–P (bending) and P–O–P (stretching) and P–O. The frequency of each of these groups is dependent on its bonding to other groups in the glass network which, in turn, varies with the composition.

Thus, the method of following the shift of the characteristic IR band frequencies belonging to these groups in the network leads to an understanding of the glass structure. The results of such an effort are summarized in Table IV.

The analysis of these data and important conclusions that could be drawn are given in the following sections. The discussion is based mainly on Fig. 7 as well as Table IV.

6.1. Characteristic frequencies of P=O group stretching vibrations (P=O stretching)

In the first compositional region (I) ($x = 0.3$–0.5 mol%), the IR band at ~1280 cm^{-1}, assigned to P=O bond stretching mode, shifts to lower wave numbers with increasing lead oxide content. The steady decrease in the $\nu_{\mathrm{P=O}}$ continues up to $x = 0.5$ which is the end of the first composition region. Beyond $x = 0.5$, there is a discontinuity as shown in Fig. 11 which depicts the variation of $\nu_{\mathrm{P=O}}$ with composition.

In the second composition region (II) ($x = 0.55$–0.6) where a homogeneous glass is not obtained, the decrease of $\nu_{\mathrm{P=O}}$ with increasing PbO continues, but on an increased gradient.

6.1.1. Interpretation

6.1.1.1. Frequency. It is seen both from Figs 7 and 11 and also from Table IV that the band corresponding to P=O in the region 1210–1280 cm^{-1} is well preserved during the structural changes in the phosphate glasses as the composition is varied, but with changes in their width (widening and then narrowing as seen from Fig. 7). Interestingly, the intensity of the $\nu_{\mathrm{P=O}}$ band also increases steadily until *meta*-phosphate glass is formed ($x = 0.5$) and then the intensity decreases in the compositional regions of II and III as shown in Fig. 11b.

Also, according to Hudgens and Martin's model [5] of π-bonds in P=O, the frequency of the vibration mode of the phosphoryl group, P=O, should move to lower wave numbers due to the reduced force constant between P and O. As the PbO content increases, this frequency shift is also expected to arise from the

TABLE IV The positions of characteristic IR bands assigned to individual (molecular) groups of atoms in the lead phosphate glass system for different compositions (Figs 7 and 8)

No.	Curve	Specimen	P =O stretching vibrations (cm^{-1})	P–O–P bending vibrations (cm^{-1})	P–O–P stretching vibrations (cm^{-1})	Harmonics of bending O–P–O and O =P–O (cm^{-1})	Ionic groups	
							($\mathrm{PO_4^{3-}}$) (cm^{-1})	P–O$^-$ (cm^{-1})
1.	(7a)	$(\mathrm{PbO})_{0.3}\text{–}(\mathrm{P_2O_5})_{0.7}$	1288 (s, b)	856 (m)	720 (s)	448 (m), 526 (w, sh)	944 (s), 1000 (vw)	1120 (w, sh)
2.	(7b)	$(\mathrm{PbO})_{0.35}\text{–}(\mathrm{P_2O_5})_{0.65}$	1284 (s, b)	852 (m)	720 (s)	448 (m), 526 (w, sh)	950 (s), 1010 (vw)	1120 (w, sh)
3.	(7c)	$(\mathrm{PbO})_{0.4}\text{–}(\mathrm{P_2O_5})_{0.6}$	1280 (s, b)	852 (m)	720 (s)	448 (m), 526 (w, sh)	950 (s), 1024 (vw)	1120 (w, sh)
4.	(7d)	$(\mathrm{PbO})_{0.45}\text{–}(\mathrm{P_2O_5})_{0.55}$	1268 (s, b)	880 (m)	716 (s)	448 (m), 526 (w, sh)	950 (s), 1024 (vw)	1136 (w, sh)
5.	(7e)	$(\mathrm{PbO})_{0.5}\text{–}(\mathrm{P_2O_5})_{0.5}$	1260 (vs)	910 (s)	712 (s), 758 (w)	464 (m), 526 (w, sh)	960 (s), 1024 (vw)	1120 (w, sh)
6.	(7f)	$(\mathrm{PbO})_{0.55}\text{–}(\mathrm{P_2O_5})_{0.45}$	1240 (vs)	912 (s)	712 (s), 758 (w)	464 (m), 520 (w, sh)	960 (s), 1008 (vw)	1120 (w, sh)
7.	(7g)	$(\mathrm{PbO})_{0.6}\text{–}(\mathrm{P_2O_5})_{0.4}$	1216 (w, sh)	900 (vs)	704 (vs), 758 (w)	464 (s), 544 (s)	960 (s), 1004 (vw)	1120 (w, sh)
8.	(8a)	$(\mathrm{PbO})_{0.667}\text{–}(\mathrm{P_2O_5})_{0.33}$	1224 (sh)	900 (vs)	700 (s), 736 (m)	496 (m), 560 (w, sh)	960 (m), 1000 (m)	1120 (w, sh)
9.	(8b)	$(\mathrm{PbO})_{0.75}\text{–}(\mathrm{P_2O_5})_{0.25}$	–	900 (vs)	700 (w, sh), 728 (m)	500 (m), 570 (w, sh)	940 (m), 990 (s, b)	1120 (s)

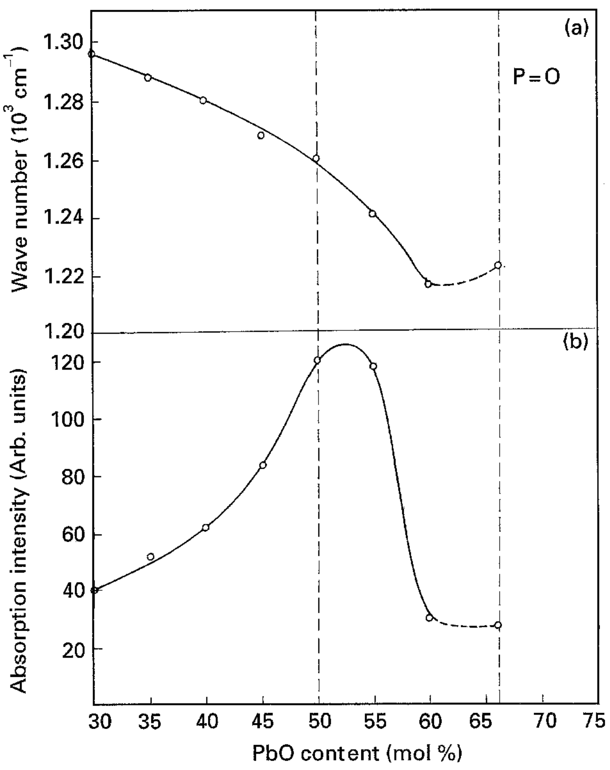


Figure 11 (a) Compositional dependence of the characteristic IR band frequencies for P=O in lead phosphate glasses. (b) Variation of the absorption intensity with composition for the P=O IR band in the $x(\text{PbO})$–$(1-x)\text{P}_2\text{O}_5$ glass system.

increasing charge density on the PO_4 tetrahedral group, leading to more ionic (hence less covalent) and weaker bonding.

6.1.1.2. Intensity. The increase in the intensity of the $\nu_{P=O}$ band is attributed to the decrease in the presence of network water (as discussed under hygroscopicity) with increase in the content of PbO which causes the replacement of P–OH bonds by P=O bonds. This is verifiable from the fact that the IR bands corresponding to P–OH bonds around 850 cm^{-1} weaken and vanish completely for $x = 0.5$, causing a progressive increase in the number of P=O bonds and hence the observed increase in the intensity. Thus, the effects of the hygroscopicity seem to dominate in the IR spectra of lead phosphate glasses for $x < 0.5$ over the effect of PbO on the number of P_2O_5 affected polyhedra as proposed by Dimitriev and co-workers in the case of PbO–V_2O_5 glass [71, 72] which are not hygroscopic in nature.

For a metal oxide content greater than 50 mol%, the intensity of the P=O absorption band (Fig. 11b) then starts to decrease rapidly and becomes lowest in the case of *pyro*-phosphate ($Pb_2P_2O_7$) samples. However, the characteristic band due to $\nu_{P=O}$ associated with the glass network of higher P=O bond order, is conspicuously absent in the IR spectra of lead *ortho*-phosphate quenched samples (Fig. 8, Table IV) obviously due to the absence of P_2O_5 polyhedra in $Pb_3(PO_4)_2$ samples.

The fact that the IR band due to P=O continues to appear for the oxide content up to $x = 0.666$ in lead phosphate glasses, though in varying intensity, means that P=O bonds from the P_2O_5 polyhedra are preserved in the vitreous samples, as well as in the quenched $Pb_2P_2O_7$ samples. Conversely, the appearance of this characteristic IR band due to the P=O bond should suggest the presence of P_2O_5 polyhedra and, therefore, the presence of a glass phase even in the $Pb_2P_2O_7$ (quenched) samples.

This is again supported by Hudgens and Martin's [5] observation that each phosphorus is always coordinated with one phosphoryl group, even though the coordination of the briding P–O–P groups is always decreasing with increasing PbO.

The decrease in the wave number of $\nu_{P=O}$ with the increasing oxide content can further be explained on the mechanism suggested by Dimitriev and co-workers [71, 72]. According to this mechanism, Pb^{2+} ions occupy a position between P–O–P layers. This is why they have a direct influence on P=O bonds of P_2O_5 groups according to the scheme [72, 73] Pb^{2+}–O=P^{5+}.

Under this interaction, the oxygen atom of the phosphoryl (P=O) group is included into the lead coordination polyhedron, as shown sequentially in Figs 12–14. The probable role of PbO as network modifier in lead phosphate glasses is depicted in these structures. Thus, the inclusion of an oxygen atom into the lead sphere leads to an elongation of the affected P=O bonds and a drop in the frequency from 1288 cm^{-1} for $x = 0.3$ to 1260 cm^{-1} for $x = 0.5$ in the composition region I and then to 1216 cm^{-1} for $x = 0.666$ in the composition region II.

At this point, it is worth noting the earlier IR observations made on V–P_2O_5 and alkali-metal-added

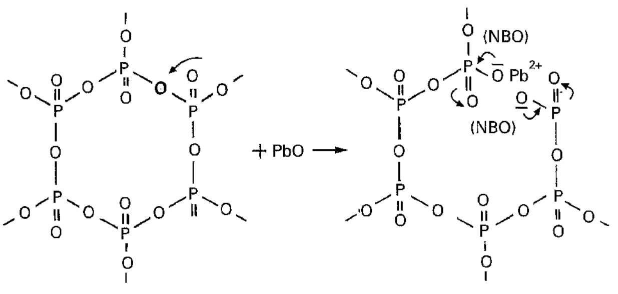


Figure 12 The probable structural mechanism by which PbO enters into the P_2O_5 network and creates additional NBOs in the phosphate tetrahedra by cleaving the P–O–P links for $x < 0.5$.

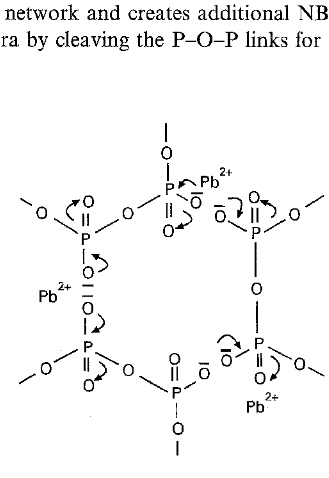


Figure 13 Increase in the number of additional NBOs as the PbO content increases towards $x = 0.5$ but $x < 0.5$.

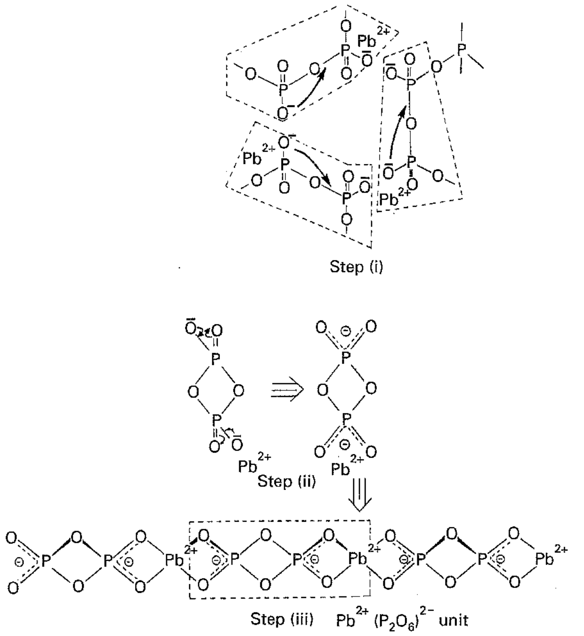


Figure 14 Step (i) Firm settlement of lead atoms for lead *meta*-phosphate glass composition ($x = 0.5$) in the glass network. Steps (ii) and (iii): reorganization of P–O bonds to include two P–O–P links in $P_2O_6^{2-}$ units. The probable four-coordination (T_d) of Pb^{2+} is also indicated (step iii); (random distribution of three-dimensional units, marked by the dashed line boundary, is left to the imagination).

P_2O_5. In the nearly anhydrous $V–P_2O_5$, the IR absorption band corresponding to P=O vibration appears at 1390 cm^{-1} [5]. Addition of a metal oxide in the range 10–30 mol% ($x = 0.1–0.3$) is found to influence this band in shifting it to lower energies. One of the reasons for this is stated [74] to be the formation of additional NBOs (Figs 12 and 13) as confirmed by XPS studies. Another reason given is the displacement of the $P_\pi - d_\pi$ bond of the P=O unit towards the new NBO, due to the increased electron density (resonance structures) around the $P–O^-–R^+$ unit, which in the present work on lead phosphate glasses is replaced by $P=O–Pb^{2+}–O^-$ which is distinctly shown in Fig. 14. When the stoichiometry of PbO and P_2O_5 reaches 1:1, leading to the formation of lead *meta*-phosphate, PbP_2O_6 glass [66] for $x = 0.5$, PbO finds itself in the network firmly settled with 4 – oxygen coordination (T_d) around it (Fig. 14, step (i)). Thus, the entry of PbO at this stage of composition into P_2O_5 glass leads to structural reorganization. In the process, one of the BOs is converted into one NBO for each PbO unit addition. It may be noted that for every pair of PO_4 tetrahedra, there is one Pb^{2+} in stoichiometric proportion leading to glass modification. Further, asymmetric severing of P–O–P links takes place with simultaneous creation of symmetric $\begin{smallmatrix} & O & \\ P & & P \\ & O & \end{smallmatrix}$ links, as shown in Fig. 14, step (ii), which are in turn connected to other such similar units (step iii) through Pb^{2+} forming a three-dimensional structure.

It is surmised that beyond $x = 0.5$, such a one-to-one situation is no longer available in the network, and additional PbO units should find themselves unfavourable to enter into the network as efficient modifiers. As such, the formation of additional phosphoryl (P=O) groups is restricted in the compositions $x > 0.5$.

The observation that beyond $x = 0.5$, the intensity of the P=O band (Fig. 11b) decreases, indicates that their number decreases as a greater number of P_2O_5 polyhedra are affected with increasing PbO content in the absence of counter-effective P–OH bonds. This effectively means that as the PbO content increases above $x = 0.5$, the number of bridging oxygens in the P_2O_5 decreases further, and beyond $x = 0.55$, there is a tendency to attain higher ionic character in the compounds by forming *pyro*-phosphate crystalline samples.

Thus, the IR spectra give an indication of the elongation of bonds in the P_2O_5 groups during glass–crystal transition. The interpretation indicates the presence of P_2O_5 groups in *meta*-phosphate glasses and *pyro*-phosphate (quenched) samples and shows that the glass-forming ability of lead phosphate glasses is extendable up to $x = 0.666$. This conclusion is in conformity with the experimental observation of Weber *et al.* [23] who could obtain homogeneous glasses with 66 mol % PbO by special techniques such as precipitation. This 66 mol% PbO is therefore the limit of glass formation for the $x(PbO)–(1 - x)(P_2O_5)$ system [11, 12].

6.2. Characteristic frequencies of $\begin{smallmatrix} P & & P \\ & O & \end{smallmatrix}$ group stretching and bending vibrations

The IR bands in the range of 950 and 712 cm^{-1} in the first compositional region have, in general, been attributed basically to deformation vibrations in $\begin{smallmatrix} P & & P \\ & O & \end{smallmatrix}$ linkages (hereafter referred to as P–O–P) in various phosphate glasses [27, 30, 67, 71]. In this range, two or three characteristic bands are observed and are assigned to symmetric stretching, anti-symmetric stretching and bending modes in the P–O–P group. However, the bending and stretching modes have not been unambiguously assigned. While Higazy and Bridge [29] assigned the bands in the vicinity of 720 cm^{-1} (Table IV) the P–O–P bond stretching, Motoya Anma *et al.* [69] have assigned the same bands to the bending mode in P–O–P. Further, Khafagy *et al.* [27] have attributed the bands in the region 850–910 cm^{-1} to the bending modes and the bands in the region 712–720 cm^{-1} have been identified by them as absorptions due to P–O–P stretching. Thus there seems to be a controversy in the attribution of IR bands corresponding to P–O–P bending and P–O–P stretching. This controversy could have been resolved if quantitative justification from the theory was made available. However, the force constants for only P–O–P stretching mode are available and for the bending mode no such force constants are available in the literature.

In this background, the bands observed around 720 cm^{-1} (Fig. 7, Table IV) in the present work are treated as due to P–O–P stretching mode, and the bands in the region 850–910 cm^{-1} are assigned to the bending mode in the P–O–P group. In fact, according to Corbridge and Lowe [35, 36], in polymeric systems such as glasses, the band around 720 cm^{-1} replaces the usual band near 900 cm^{-1} corresponding to P–O–P stretching vibration.

In Fig. 15a, the variation of wave number for P–O–P stretching mode with composition is given and Fig. 15b gives the intensity variation for the same band. In the first composition region the band shifts gradually to lower wave number with increasing lead oxide and in the second region the decrease in wave number is rapid. In the third composition region, where glass phase is nearly absent, the band frequency seems to be independent of the composition. However, the intensity of the band decreases rapidly in the first region and becomes independent in the other two regions.

The possible explanation of the decrease in both the wave number and intensity of the band can be given from the main trend, that is, the replacement of P–O–P linkages by O–Pb–O links as PbO enters the network. As the Pb–O stretching force constant is substantially lower than the P–O stretching force constant, the frequency of the P–O–P stretching vibration might tend to be lower. Obviously, as the number of P–O–P groups in the network decreases with increasing oxide content, the intensity of the IR band should decrease, as observed in Fig. 15b. It is interesting to note from Fig. 15a, and b and also from Table IV that this trend is limited to the first compositional region where, as the formation of *meta*-phosphate is complete, the replacement of P–O–P by O–Pb–O (see Fig. 14, Step (i)–(iii)) is complete so that for later compositions, both the wave number and intensity become independent of PbO content.

In this region of P–O–P stretching band, weak bands due to P–O bending are also expected [42] and the weak band at 758 cm^{-1} in the spectrum (Fig. 7) of the $x = 0.5$ sample might be due to the occurrence of the harmonics of P–O bending.

While the decreasing trend is observed in the wave number of P–O–P stretching, an opposing trend seems to dominate P–O–P bending mode around 856 cm^{-1}, as shown in Fig. 16a. Although the wave number seems to be unaffected by the oxide content up to $x = 0.4$ mol%, in general there is an increasing trend in the wave number of P–O–P bending mode. This is attributed to the effect of the electrostatic field of the strongly polarizing Pb^{2+} ions which might serve to increase the wave number of the P–O–P bending vibration and the effect seems to influence P–O–P bending clearly only beyond 40 mol% oxide content (Fig. 16a).

In the second and third composition regions, the effect does not seem to be as dominant. The decrease in the relative intensity of the IR band in Fig. 16b can again be explained as due to the progressive replacement of P–O–P linkages by O–Pb–O links.

It is worthwhile to mention that this IR region of P–O–P bending, that is 850–900 cm^{-1} may also be associated with P–O–H bond vibrations. Because the hygroscopicity of the glass samples decreases with PbO content, the increase of P–O–P bending wave number from 40 mol% onwards is in reasonable agreement with the observed decrease in the hygroscopicity. Probably, the expected increase of P–O–P

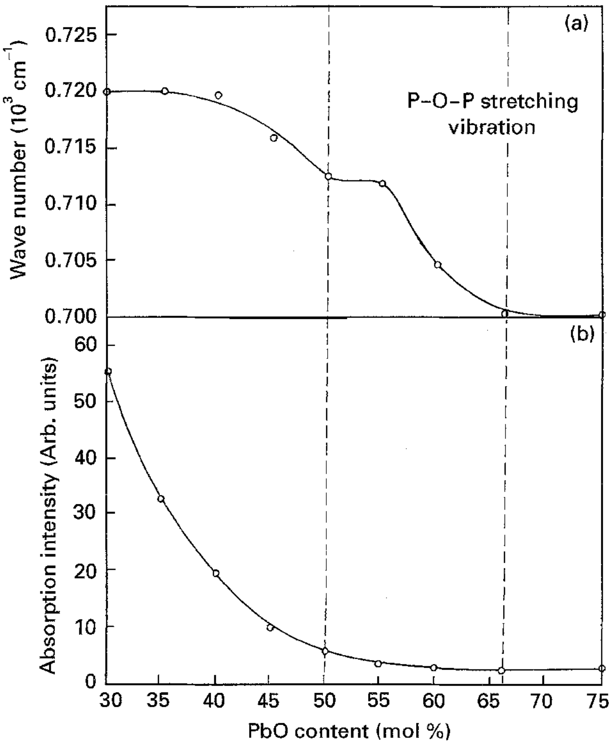


Figure 15 (a) Compositional dependence of the IR band frequencies assigned to P–O–P stretching mode in lead phosphate glasses. (b) Compositional dependence of the intensity of the IR band.

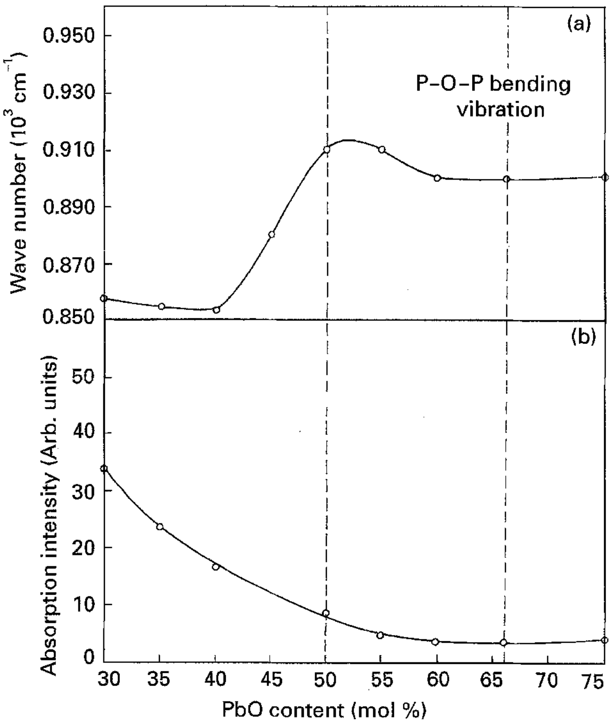


Figure 16 (a) Variation of wave number of the IR band corresponding to P–O–P bending vibrations in lead phosphate glasses. (b) The corresponding compositional dependence of the intensity of the IR band assigned to the P–O–P bending.

wave number even below 40 mol% PbO is masked by the dominant P–O–H vibrations.

6.3. Characteristic frequencies (harmonics) of P–O bending modes

Write and Hunter [42] attribute the very strong absorption near 400 cm^{-1} in silicate glasses to Si–O bending in Si–O–Si chains. However, Tsai and Greenblatt [67] have assigned the bands in the region 450–550 cm^{-1} to the possible modes in O–P–O linkages (see Fig. 14, Step (iii)) based on the earlier IR investigations [75]. In accordance with these investigations discussed in the literature [67, 75], the sharp and strong band at 448 cm^{-1} (Fig. 7 and Table IV) is assigned to O–P–O bending vibrations (see Fig. 14, Step (ii)). The weak shoulder-like band around 526 cm^{-1} (Fig. 7 and Table IV) is attributed to O=P–O bending vibrations. However, Higazy and Bridge [29] have attributed these bands at 500 cm^{-1} to the "harmonics of P–O–P bending".

The wave numbers of these bands are not affected by the composition in the first region of glass samples where P_2O_5 polyhedra continue to remain intact. However, their wave numbers are affected by the onset of crystalline phase from 50 mol% oxide content as seen from Table IV. This may be due to the appearance of the band due to the ν_4 mode in PO_4^{3-} which is expected to overlap with these bands [33].

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

The IR spectral data in the present work offer evidence of ionic groups in the lead oxide-rich glasses. The gradual growth of ionic character of some phosphate groups with progressive increase in PbO content indicates partial breakdown of the supposedly covalent vitreous network at high lead content. For instance, the very weak band appearing as a shoulder (on the very strong band at 944 cm^{-1}) at 1120 cm^{-1} in Fig. 7 (curve a) can be attributed to stretching vibrations of the P–O$^{(-)}$ group which is basically present in P_2O_5. As the PbO content increases, the band position (at 1120 cm^{-1}) remains nearly unaffected as shown in Fig. 17a, until the P_2O_5 content reaches 50 mol%, i.e. when *meta*-phosphate glass is formed. The slight increase in the wave number at $x = 0.5$ is attributed to the increase in the network packing which probably, in turn, causes a shortening of the P–O$^{(-)}$ bond in the compositional region.

In the second compositional region of the quenched samples containing both polymeric and crystalline phases, it is seen from Fig. 17a and also from Fig. 7, that the band position of the P–O$^{(-)}$ group continues to remain at 1120 cm^{-1}, probably due to the presence of mixed phases.

The intensity variation of the P–O$^{(-)}$ band at 1120 cm^{-1} is shown in Fig. 17b which also conforms to the above interpretation. The band intensity, though very weak initially for low oxide contents, reaches a fairly strong maximum at ~ 55 mol % PbO content. This is a region where the breakdown of the covalent vitreous network of the phosphates into small ionic groups including PO_4^{3-}, $P_2O_6^{2-}$ and $P_2O_7^{4-}$ might be expected. As the PbO content increases further beyond 55 mol%, it is obvious that the content of glass-former P_2O_5 decreases and hence correspondingly the intensity of P–O$^{(-)}$ (which is present only as long as the P_2O_5 network exists), decreases as seen from Fig. 17b. It is interesting to note that in the quenched Orthophosphate samples, the band due to P–O$^{(-)}$ does not appear at all (Fig. 8, and Table IV) indicating near total absence of network P_2O_5 and hence the glass phase. That is, despite the quenching technique, the composition of PbO–P_2O_5 in 3:1 ratio does not yield itself to the glass formation. Once again, it is established that the glass-forming ability of the lead phosphate compound is limited to 66.66 mol%, that is, to *pyro*-phosphate composition.

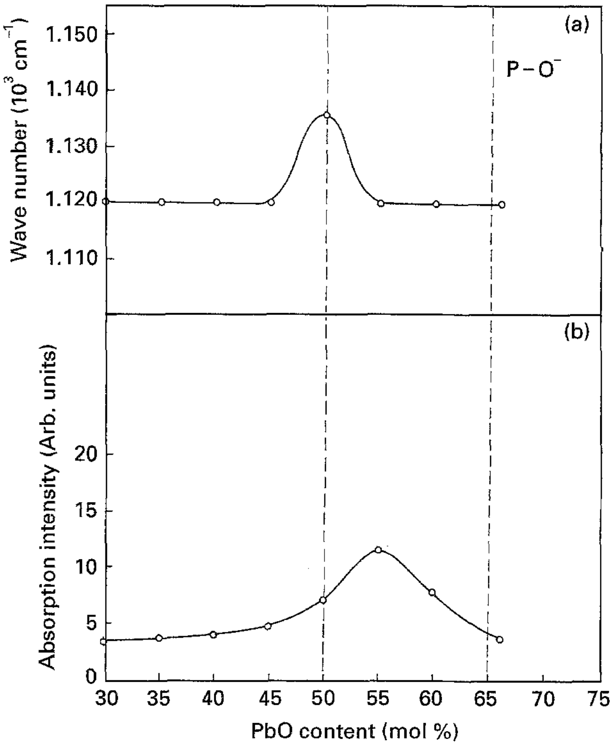


Figure 17 (a) The compositional dependence of the stretching vibrational frequency of the ionic P–O$^{(-)}$ group. (b) Variation of the intensity of the IR band due to the P–O$^{(-)}$ group.

Thus, the ionic P–O stretching band seems to display a "three compositional region" behaviour.

6.5. Structural changes in the lead phosphate from the IR behaviour of ionic PO_4^{3-} groups

Another important IR spectral region that gives information about the structural changes and ionic character of structural units in the phosphate materials is 900–1100 cm^{-1}. In this range, besides the bands due to triply degenerate IR-active ν_3 normal mode of the PO_4 tetrahedron, the bands due to PO_3^- in the compositions close to *meta*-phosphate ($x = 0.5$) are expected. Although a diffuse version of IR bands is expected for pure glass phases, trends such as activation of IR-forbidden ν_1 mode in the phosphate are also expected to be observed in this region.

The results observed in this IR range for the lead phosphate compounds in three compositional regions are summarized in Figs 7, 8 and in Table IV, which can be described briefly as follows: for the hygroscopic glass with 30 mol% ($x = 0.3$) PbO, there is a well-defined, gaussian-shaped band with peak position at 944 cm^{-1} (Fig. 7a) superposed on which are a shoulder at 994 cm^{-1} and a weak shoulder-like structure at 1080 cm^{-1}. These are attributable to weakly resolved components of $\nu_3(T_2)$ asymmetric stretching mode in the PO_4^{3-} tetrahedron which is an inherent group in P_2O_5 chains, particularly dominating in high phosphate glasses. For the composition $x = 0.35$, the main strong band shifts to higher wave number at 950 cm^{-1} and a strong shoulder appears at 1020 cm^{-1} while the band at 1060 cm^{-1} becomes very weak, indicating structural changes in the glass. For $x = 0.4$, the main band changes to medium intensity, probably because of broadening, and the weak shoulder at 1020 cm^{-1} (Fig. 7c) is almost on the verge of disappearing. Even for $x = 0.45$, the main band position continues to be at 950 cm^{-1} with medium intensity, with a very weak shoulder at 1010 cm^{-1}. Lastly, for $x = 0.5$ where the stoichiometry of the metaphosphate compound is complete and where homogeneous glass phase exists (as indicated by X-ray spectra) only one strong band with a maximum at 960 cm^{-1} appears Fig. 7e).

These changes in the IR band at 944 cm^{-1} initially attributed to the ν_3 mode indicate the gradual decrease in the PO_4^{3-} tetrahedra and hence decrease in the number of bridging oxygens (BOs). This is understandable from the fact that as the lead oxide content is increased, PO_4^{3-} tend to change to PO_3^- ionic groups [33] and the band at 950 cm^{-1} in the IR spectrum ($x = 0.5$) *meta*-phosphate glass (Fig. 7e) is attributable to PO_3^-. Thus, the band at 950 cm^{-1} in the spectra close to 50 mol% PbO can be attributed to PO_3^- groups in $Pb(PO_3)_2$. Higazy and Bridge [29] similarly attributed the band in the 910–960 cm^{-1} range to PO_3^-. Sayer and Mansingh [76] obtained a band in the region 931–892 cm^{-1} and attributed to PO_3^- vibrations in $Co(PO_3)_2$ glass. Khafagy *et al.* [27] also obtained a band at 930 cm^{-1} which they attributed to ν_3 of PO_4^{3-} in V_2O_5–P_2O_5 glass. Similar results about the changes in the IR spectra with changes in the environment of P_2O_5 polyhedra in phosphate glasses have been discussed by other authors [77]. These results on the IR bands in the ν_3 region are indicated in Fig. 18a.

It is interesting to note that as the PbO content increases in the second composition region, there is a clear transformation of the IR band at 960 cm^{-1} for $x = 0.5$ to 1008 cm^{-1} for $x = 0.55$, (Fig. 7f) and the band at 960 cm^{-1} now appears only as a shoulder. Because for $x = 0.55$, the band at 1008 cm^{-1} is clearly the main band, it should be attributed to the ν_3 mode in PO_4^{3-}. This certainly suggests that the structure of the glass changes in such a way that again phosphate tetrahedra dominate the network. Obviously, this is due to the tendency of the composition towards constituting *pyro*-($P_2O_7^{4-}$) phosphate structure. Because $P_2O_7^{4-}$ can be considered as a dimer of the PO_4^{3-} tetrahedron, the attribution of 1008 cm^{-1} to ν_3 mode is justified (see Fig. 3).

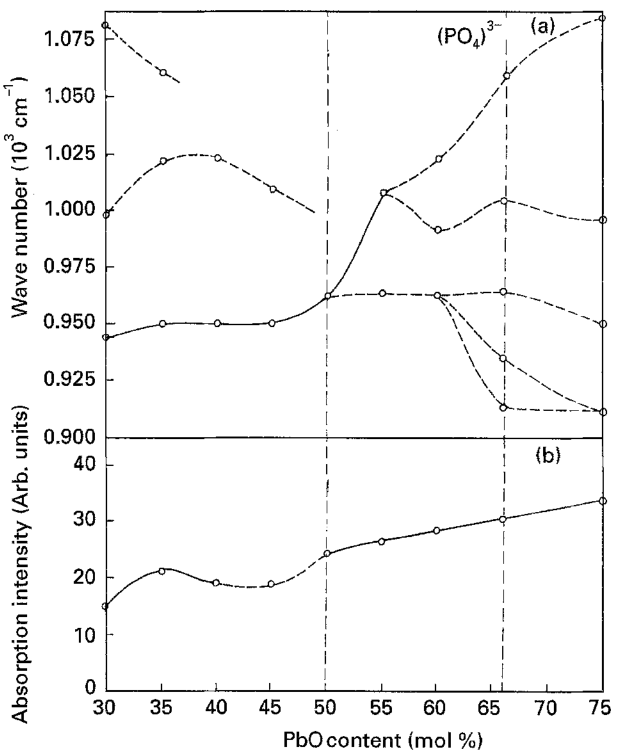


Figure 18 (a) Variation in the wave number of the ν_3- mode in PO_4^{3-} and its later conversion to PO_3^- vibration in the first composition region. The branches indicate the splittings in the ν_3-mode for other compositions. (b) Variation of the intensity of the band in the range 940–1080 cm^{-1}, assumed to be mainly due to the ν_3-mode in PO_4^{3-} in lead phosphate compounds.

Further, for $x = 0.55$ and above, X-ray spectra indicate the presence of crystalline phase where phosphate tetrahedra might be distorted in the structure leading to the splitting of the ν_3 mode. That this, indeed, is the case can be verified from Fig. 7g in which the main band at 1008 cm^{-1} splits into three well-resolved bands at 960, 990 and 1020 cm^{-1} with an average value of 988 cm^{-1}. The splitting is indicated by the branches in Fig. 18 in the second compositional region.

For the quenched samples of lead *pyro*-phosphate, which is found to contain both crystalline and glass phases, these three bands become five in number with positions at 910, 935, 965, 1005 and 1065 cm^{-1} (Fig. 8a). If three of these are considered as due to the ν_3-mode of PO_4^{3-} in the crystalline phase, others could be due to the same mode in the glass phase which is known to cause a shift in the band positions. Also, one or two of these bands could be due to the ν_1 (totally symmetric stretching) mode in the phosphate tetrahedron which is expected to show a band at 938 cm^{-1} [33] in crystals.

All these IR spectral results clearly suggest changes in the lead phosphate compound towards structures which predominantly or primarily consist of PO_4^{3-} tetrahedra. Such a trend is carried forward up to $x = 0.75$, as seen from Fig. 8b and from third composition region of Fig. 18, where the strong band with an average absorption maximum at 992 cm^{-1} consists of

TABLE V Comparison of the main IR absorption band maxima observed in lead phosphate glasses with those reported in the literature for other phosphate glasses

No.	Description of mode	Structural groups	Absorption band (cm^{-1})	Corresponding references
1.	Characteristic frequencies of stretching and bending vibration	P–O–P stretching	900, 700	[35, 36]
			915–880	[45]
			780–730	[29]
			758–700	Present work
		P–O–H bending	910–850	[35, 36]
			910–850	Present work
			930–915	[29]
		$\text{P–O}^{(-)}$ stretching	1036–1030	[45]
			1050	[41]
			1100	[35, 36]
			1110	[40]
			1136–1120	Present work
		P=O stretching	1240, 1220	[41]
			1280–1250	[45]
			1282–1205	[40]
			1300–1200	[35, 36]
			1288–1216	Present work
		PO_4^{3-} ionic group	1100–1040	[40]
			1082–980	[35, 36]
			1025–940	[29]
			1024–940	Present work
2.	Normal vibrational mode (bond bending)	Free H_2O molecules	1640	[35, 36]
			1640–1620	[29]
			1660	[41]
			1660–1600	Present work
			1650–1610	[45]
3.	Normal vibrational mode (bond stretching)	Either free H_2O molecules or OH ions	2860–2380	[41]
			3300	[35, 36]
			3600–3400	[45]
			3600–3440	Present work
4.	Harmonics of P–O–P bending vibrations		565–495	[29]
			570–448	Present work

a clear, fine structure with peak positions at 905, 950, 995, 1080 cm^{-1}. The structure is suggestive of crystal-field effects in the compound with $x = 0.75$ which is mostly crystalline in phase.

It is also important to take note of the other significant features of the IR spectra belonging to PO_4^{3-} groups. The other IR active mode in PO_4^{3-} is ν_4 which is also triply degenerate and is expected to show a degenerate maximum at 560 cm^{-1}. In the IR spectra of the lead phosphate compounds with PbO composition greater than 50 mol% ($x = 0.5$), the band at $\cong 560\ \text{cm}^{-1}$ begins to show splitting. The splitting seems to be partial in Fig. 8a (for $x = 0.66$) and nearly total in Fig. 8b (for $x = 0.75$). Both in the case of ν_3-bands and ν_4-bands of PO_4^{3-}, the gradual sharpening of band maxima in Figs 7 and 8 for composition $x > 0.5$ is indicative of the onset of the crystalline phase in the glass, very much in agreement with the results of X-ray diffraction spectra.

The intensity variation for all these bands could not be followed. However, the variation of intensity of the band assigned to the ν_3-mode in high phosphate ($x = 0.3$) glasses has been given in Fig. 18b. A comparison of the main IR absorption band maxima observed in the present work with those reported for other phosphate glasses is given in Table V.

These results confirm the role of PbO as a glass modifier because it is an increase in the PbO content in the samples that causes the changes in the observed IR spectra which are actually due to changes in the structural units of the vitreous compounds.

7. Effect of cations on the IR spectra of binary phosphate glasses

The study of the effect of cations on the characteristic group frequencies in the IR spectra of the metal oxide phosphate glasses is expected to give interesting information which when correlated with the IR data obtained from various compositions may lend support to some conclusions drawn from the IR spectra. Although no systematic study such as shift in band positions with increase in the mole percentage of the cation in the glass, seems to have been made, the literature available on these aspects, when organized as shown in Table VI, reveals certain interesting features. The effect seems clearly to manifest only in the case of certain IR-band frequencies which involve vibrations of the groups that are sensitive to electrical polarization properties of the cations. Therefore, it is appropriate to review briefly the effect of cations on individual group frequencies in different phosphate glasses, including the lead phosphate glasses. For the sake of clarity, the comparison has been limited to the compositions up to the *meta*-phosphate glasses (in Table VI).

TABLE VI Effect of cation (50 mol%) on IR group frequencies in binary phosphate glasses

Compound	P–O–P stretching vibrations (cm^{-1})	P–O–P bending vibrations (cm^{-1})	PO_4^{3-} (cm^{-1})	$P–O^{(-)}$ (cm^{-1})	P =O (cm^{-1})	H_2O bending (cm^{-1})	Reference
V^{5+} in $V_2O_5 + P_2O_5$ glass	600	790	930	1195	–	–	[27]
Co^{2+}, Co^{3+} in $CoO + Co_2O_3$ glass	710	800	910	1118	1280	1635, 3000	[29]
Cd^{2+} in $CdO + P_2O_5$ glass	–	780	920	1090	1290	1630, 3450	[68]
Sn^{2+} in $(SnO)_{0.4}(P_2O_5)_{0.6}$ glass	725	–	900	1050	1250	1620, 3500	[69]
Pb^{2+} in $(PbO)_{0.5}(P_2O_5)_{0.5}$ glass	721 (s) 758 (w)	910 (s)	960 (s) 1024 (vw)	1120	1260 (vs)	1568, 3445	Present work

P–O–P stretching vibrations (in the region around 750 cm^{-1}) considered in vanadium V^{5+}), cobalt (Co^{2+}), lead (Pb^{2+}) *meta*-phosphate glasses, and tin (40 mol%) glasses, in general, indicate a shift towards higher frequencies with the exception of Sn^{2+}. It is possible that in low phosphate-content glasses, the strength of the covalent bond progressively decreases as the atomic weight of the cation increases. Conversely, as the ionic character of the bonding in the compound increases, probably the P–O–P groups gain greater internal vibrational freedom in stretching. This probably leads to the observed shift of P–O–P stretching frequencies to higher wave numbers.

P–O–P bending modes, on the other hand, seem to follow roughly the opposite trend, that is, as the mass of cation increases, the frequency shifts to lower frequencies, probably due to the greater proximity of the cation during the bending mode. However, V^{5+} and Pb^{2+} are apparently exceptions to this trend (Table VI). Given the ambiguity in the assignment made by Motoya Anma *et al.* [69] in respect of P–O–P bending mode, in tin phosphate glass, one can safely say that there is no marked variation of P–O–P bending frequency with the atomic weight of cation.

In the case of the v_3-vibrational mode in PO_4^{3-}, it is seen from Table VI, that there seems to be a regular increase in the wave number as we go from Co^{2+} to Pb^{2+}; however, vanadium and tin exhibit the opposite trend.

Similarly, the frequencies of ionic groups $P–O^{(-)}$ show a gradual decrease in the wave number, lead phosphate glass being an exception. The expected regularity, if any, is also missing in the vibrational frequencies of P=O and also in the frequencies of normal modes of water considered to be present in phosphate glasses.

Thus, this review of the data and our results clearly support the view expressed by Corbridge and Lowe [35, 36] that the influence of cations on the IR spectra of phosphate glasses does not show any striking regularity in their trend, despite the fact that some influence does exist. This may be attributed to the sensitivity of the structure of glass network to the specific procedure followed in their preparations, including variations in the quenching rate, melt temperature before quenching, etc.

However, the shifts reported for various *pyro*- and *ortho*-phosphates in crystalline form as shown in Table VII show a marked regularity with the atomic weight of the cation, although our results concentrate only on quenched *pyro*- and *ortho*-phosphates. There are, however, negligible exceptions. Thus, it is the presence of a rigid, periodic lattice sensitive to the nature of a given cation that should be made responsible for the observed (Table VII) regularity in the IR spectra of the crystalline phosphate materials.

7.1. Other bands observed in the IR spectra of lead phosphate glasses

A closer inspection of Fig. 7 reveals the presence of several other IR bands around 2400 and 3400 cm^{-1}. The positions of these bands and their probable assignments are indicated in Table II. It may be noted from this table, as well as from Fig. 7, that FT–IR spectra reveal the presence of numerous bands that can be assigned to vibrational modes in the H_2O molecule [27], as discussed earlier. Some of them could be due to P–O–H stretching vibrations (see Fig. 10). Besides these water bands, the weak bands at 2400 cm^{-1} observable up to $x = 0.45$ composition, are attributed to P–H stretching, assuming that phosphorus develops bonds with hydrogen in hygroscopic samples.

8. Quantitative justification for the assignment of the IR bands in lead phosphate glasses

The assignment of the important IR bands observed in lead phosphate glasses of the present work is, in general, made by comparison of the data with the bands reported in the literature, even though some band attributions have their own support from the theory. However, it is possible to provide quantitative justification from the theoretical calculations available in the literature [29] for some of the vibrational frequencies assigned to phosphate groups and for some frequencies in water molecules. Such justification could have been offered even for the IR spectrum observed for PbO glass, provided the force constants corresponding to Pb–O stretching or O–Pb–O bending are

TABLE VII The variation in IR band positions with atomic number of the cations in *pyro*- and *ortho*-phosphates

No.	cation	P–O–P stretching vibrations (cm^{-1})	P–O–P bending vibrations (cm^{-1})	$\nu_3(PO_4^{3-})$ (cm^{-1})	$P–O^-$ (cm^{-1})	P=O (cm^{-1})	H_2O (cm^{-1})	Reference
Pyro-phosphate								
1.	Li^+	738 (m)	896 (m)	940 (vs), 1107 (vs)	1128 (vs), 1150 (vs), 1170 (vs), 1195 (m),	–	1640 (m), 2860 (vw), 3350 (m)	[35, 36]
2.	Na^+	735 (vs)	895 (m)	921 (vs, b), 1031 (s)	1124 (vs), 1150 (vs), 1165 (vs, sh), 1180 (s, sh)	–	–	[35, 36]
3.	Mg^{2+}	725 (m)	907 (m)	932 (m), 1008 (w)	1049 (m), 1122 (vs), 1161 (vs)	–	–	[35, 36]
4.	Ca^{2+}	720 (m)	–	927 (m b), 1000 (w)	1035 (w), 1080 (m), 1153 (vs)	–	–	[35, 36]
5.	Sr^{2+}	722 (m)	888 (s)	981 (w)	1030 (m), 1072 (m), 1125 (vs), 1142 (vs)	–	–	[35, 36]
6.	Pb^{2+}	728 (m)	–	914 (s), 972 (m)	1003 (m), 1061 (vs), 1117 (vs)	–	–	[35, 36]
7.	Pb^{2+}(Q)	700 (s)	736 (m)	900 (s), 960 (m)	1000 (m), 1120 (s)	1224 (sh)	–	This work
Ortho-phosphate								
1.	Li^+	–	–	1035 (vs), 1050 (vs)	1100 (vs)	–	–	[35, 36]
2.	Na^+	–	–	914 (vw), 1028 (vs, b)	1125 (s)	–	–	[35, 36]
3.	Mg^{2+}	–	–	1030 (m)	1068 (vs), 1110 (s, sh) 1140 (s)	–	–	[35, 36]
4.	Ca^{2+}	–	–	1045 (vs)	1070 (vs), 1093 (vs, sh)	–	–	[35, 36]
5.	Sr^{2+}	–	–	1015 (vs), 1040 (vs)	1068 (vs), 1140 (m, sh)	–	–	[35, 36]
6.	Pb^{2+}	–	–	981 (vs, b), 1056 (vs)	–	–	–	[35, 36]
7.	Pb^{2+} (Q)	700 (w, sh)	728 (m)	910 (vs), 940 (m), 990 (s, b)	1060 (s)	–	–	This work

Q = Quenched sample, m = medium, s = strong, vs = very strong, b = broad, sh = shoulder.

TABLE VIII The values of wave numbers calculated from Equation 7 where the stretching force constants have been taken from [29]. The experimental wave numbers obtained in the present work are given for comparison

No.		Bond length (nm)	Stretching force constant (nm^{-1})	Wave number, $\bar{\nu}$, (cm^{-1})	
				Theoretical	Experimental
1.	P–O–P	0.156	826	1334	712 (stretching) 886 (bending)
2.	$P–O^{(-)}$	0.156	413	814	1122
3.	P=O	0.140	930	1221	1251
4.	O–H	0.157	409	2718	2863, 3485
5.	P–O–H	0.170	822	3908	3039

known. No such data on the force constants of Pb–O have come to the notice of the authors in the literature. Therefore, this quantitative justification is limited to the group vibrations in the P_2O_5 or H_2O in the $x(PbO)–(1-x)(P_2O_5)$ system.

When the characteristic group frequencies arise from the vibrations of pure stretching character or of pure bending nature, the wave number, $\bar{\nu}^-$, is to be given by the straightforward formula

$$\bar{\nu} = \frac{1}{2\pi c}\left(\frac{K}{\mu}\right)^{1/2} \tag{7}$$

where c is the velocity of light, μ is the reduced mass of the diatomic or triatomic group, and K the stretching force constant or the bending force constant. For certain diatomic and triatomic groups, various empirical formulae, such as Badger's rule [78–81] are available to calculate the force constants, K, and have been reported in the literature [29].

If a particular band frequency, assigned to a stretching or bending mode in a given group, cannot be made to fit Equation 7 with a reasonable, assumed value of K (with or without the assumption of harmonics), the conclusion must be that the attribution is wrong and the band is not due to a pure stretching or a pure bending mode but due to a more complicated form of vibration, like a normal mode which is a correlated motion (internal vibration) of all the atoms in an ion (say PO_4^{3-}) or a molecule.

In Table VIII, the values of wave numbers calculated from Equation 7 are presented together with the force constants taken from Higazy and Bridge [29]. The experimental wave numbers included in Table VIII are the average IR band positions observed for individual groups in the first and second compositional regions, that is, $x = 0.3$–0.66, because the glass phase is observed to be present in the quenched samples of even *pyro*-phosphate.

On inspection of Table VIII, one can find that the theoretical values of ν agree very well in the case of P=O and O–H, which are known for their pure stretching vibrations. There is such a semblance of agreement in the case of P–O–P wave number if the bands are assumed to be due to the bending mode. There is some disagreement in the case of $P–O^{(-)}$ and P–O–H stretching vibrations.

In the case of the P–O–P group, it is observed that the experimental band wave number, even if assumed to be due to bending, is less than the theoretical value. This suggests that the group frequency is not due to pure stretching mode but it might involve a mixed bending and stretching character. As stated in the brief review, this is hardly surprising, considering the P–O–P bond angles [72].

In the case of $P–O^-$, the experimental wave number is higher than the theoretical one, suggesting that the assignment of the band to this group may be incorrect, or perhaps that it could be a band combining a stretching motion with the harmonics of bending motion. It may be noted here that precise formulae such as Equation 7 are not available for bending force constants, though their values are known to be less than the values of the stretching force constants.

In the case of the disagreement between the theoretical and experimental ν for the P–O–H group, the reason must again be the mixed bending and stretching character of the vibrations involved.

Because bending force constants cannot be evaluated precisely from the theory, it is possible to substitute experimental wave numbers in Equation 7 and derive the effective values of force constants in such cases where a pronounced bending character is expected. The effective force constants derived by this method for certain groups in phosphates are presented in the Table IX. A comparison of these force constants with those obtained in Table VIII indicates that effective force constants do not show good agreement with the expected ranges for stretching and bending force constants. This suggests one thing clearly, that among the observed wave numbers, either the bands associated with the harmonics of pure bending vibrations are present or that the vibrations with mixed bending and stretching character are present in the vitreous state of the materials. This may also suggest the inadequacy of the available theories of the IR spectra for glassy or polymeric solids containing a random network of chemical bonds. It appears that the attribution of the IR bands in glasses (unlike in crystals) to either pure bending or pure stretching, is not justified or is not reasonable.

9. Conclusions

The infrared spectra of the lead phosphate system of glasses and quenched samples, in general, indicate that the local order in the structure and the type of chemical bonds that develop with cations (Pb^{2+}) are strongly influenced by PbO content. The IR spectra clearly establish that for compositions $x = 0.3$–0.666 PbO, the initially dominating covalent character of the bond gradually gives way to ionic character of the bond, although the covalent character is retained in the quenched samples up to 66.6 mol% PbO.

Thus, the glass-modifying role of PbO is extendable up to 66.6 mol% with the glass former P_2O_5. The differences in the IR spectra of phosphate glasses of various compositions arise presumably from the chains being polymerized to different extents. The role of PbO as glass modifier is almost quantitatively determined by the amount of P_2O_5.

The fact that the characteristic IR band due to the P=O bond in the P_2O_5 network is retained until the composition of *pyro*-phosphate quenched samples ($x = 0.66$), suggests that PbO does not act as a "glass former" and no complete rupture of the glassy network by Pb^{2+} takes place. Rather, the cation enters the network interstitially [32] acting more as a network modifier, leading to gradual changes. The appearance of several new sharp IR spectral bands in the 950–1100 cm^{-1} region attributed to the groups in PO_4^{3-} for compositions beyond $x = 0.55$, indicates the vibrational character of free-charged structural units.

Because pure PbO glass cannot be obtained and SiO_2 has to be an unavoidable impurity in any PbO glass, it is not possible to make any comparison between the IR spectrum of PbO glass and that of polycrystalline PbO. Thus, the claim that the IR spectrum of a material in its vitreous state is its crystalline analogue is subject to several limitations. It is possible that drastic changes in the coordination and bonding of the metal (Pb^{2+}) in the glass network from those in

TABLE IX Effect of force constants calculated from Equation 7 with the experimental wave numbers obtained in the present work

No.	Structural group	Bending vibrations		Stretching vibrations	
		Band (cm^{-1})	K (bending) (nm^{-1})	Band (cm^{-1})	K (stretching) (nm^{-1})
1.	Pb–O[a]	–	–	844	625
2.	O–P–O	532	134	713	260
3.	$P–O^{(-)}$	712	317	1122	780
4.	P=O	–	–	1251	971
5.	O–H	1660	154	2863, 3485	660
6.	P–O–H	–	–	2940	465
7.	P–H	–	–	2400	328

[a] Bond length reported for Pb–O is 0.23 nm [82].

the crystal lattice [82] may take place. This might introduce changes in the IR spectrum which need not, in general, be the crystalline analogue of the glass.

The IR spectra of lead phosphate glasses with hygroscopicity provide a wealth of information about structural units of glass and their relation to different types of OH– groups in the glass. The information is helpful in drawing conclusions about the chemical durability of the lead phosphate glasses. The detailed study of variation in the characteristic frequencies and their relative intensities of several important, individual molecular groups indicates that the structural units in the lead phosphate glass network strongly depend on PbO content. For example, the data in the present work offer strong support for the presence of ionic groups whose independence seems to grow to the full extent only beyond $x = 0.55$.

As PbO is added, the network of P_2O_5 is modified by the formation of more and more NBOs (which cause large decrease in T_g) below 33 mol% as observed earlier [5]. Further, the IR spectra reveal that a resonance structure is developed where the bond of the P=O group is distributed across the newly formed NBO. Also, the IR spectra show the presence of terminal $P–O^-–Pb^{2+}–O^-$ groups.

Addition of PbO beyond $x = 0.35$ or 35 mol%, strengthens the glass (resulting in an increase of T_g values) [83, 84] though chain entanglement mechanisms and IR spectra indicate that, in these glasses, long chains or ring structures are developed until $x = 0.55$ (see Fig. 12). Higher compositions ($x > 0.33$) of PbO require higher melting points in accordance with the observation of Uhlmann and Kreidl [83] and in contradiction to Hudgens and Martin [5]. The glass network breaks down completely for more than 66 mol% PbO, i.e. above *pyro*-phosphate.

The effect of cations on the IR spectra of phosphate glasses has been studied and it is found that the random network in a glass does not lend itself to any regular change with atomic number of the cation. The results in the present work can be described in terms of the $(1 - x)PbO–xP_2O_5$ system with $x = 0.25$ for *ortho*-phosphate compound. In that case, an important conclusion that can be drawn from the data is that as the M(metal)/P atomic ratio is reduced, short-chain molecule ions are replaced progressively and smoothly by long chains, and finally partially by rings in high phosphate glasses. Consequently, abrupt changes in physical properties with composition are not expected.

The quantitative justification attempted in the present work for the assignment of various IR bands is found to be still wanting in several respects. This brings out the inadequacy of the presently available theories of IR spectra of glasses.

In brief, the trends in IR spectra on the lead phosphate glasses show that PbO causes a change of the short-range order of the phosphate glass network. Different types of polyhedra seem to build up the network of binary glasses between P_2O_5 and PbP_2O_6, up to $x = 0.5$. The further increase in the PbO content leads to the breaking up of the *meta*-phosphate chain and the formation of *pyro*- and *ortho*-groups.

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