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The vibrational spectra and characteristic features of the orthophosphates of Group I – III elements

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Abstract. The results of the spectroscopic studies (IR absorption, spontaneous Raman scattering) on orthophosphates of Group I – III elements are presented. The characteristic features of the vibrational spectra and the influence of the characteristics of the crystal structure on such features are discussed. The bibliography includes 58 references.

I. Introduction

The orthophosphates of various elements and the materials based on them have found extensive application in many branches of modern engineering and technology. This constitutes a natural stimulus to the search for new compounds and to the investigation of their physicochemical properties. It is not surprising that a number of monographs and reviews containing extensive information concerning the crystal structure of orthophosphates have appeared in recent years. Thus the nomenclature and certain characteristic features of the structure of the phosphates of Group I and II elements have been described in a review,[1] numerous data on the phosphates of divalent elements have been compiled in a monograph,[2] and a classification of the phosphates and X-ray diffraction data for the latter are presented in a book.[3] A review has been devoted to the X-ray diffraction and spectroscopic methods for the investigation of materials based on inorganic phosphates.[4] The IR absorption spectra of many phosphates are presented in the atlas of Mel'nikova et al.,[5] while those of double phosphates are in the atlas of Pechkovskii et al.[6]

However, despite the fact that vibrational spectroscopy (IR absorption and spontaneous Raman scattering) constitutes a powerful method for the investigation of the details of the structure and of the nature of the chemical bonds in compounds, while orthophosphates are convenient objects for study by this method by virtue of the characteristic features of their structure (the presence of discrete tetrahedral PO_4 groups in the structure) and the ratio between the atomic masses and bond energies, the known spectroscopic studies have not been far-reaching and systematic. Qualitative approaches have been used as a rule for the interpretation of the experimental data obtained.

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In all the known investigations, the vibrational spectra have been described, quite justifiably, on the assumption that the vibrations can be divided into internal vibrations (stretching and deformation vibrations of the PO_4 groups) and external vibrations (translational vibrations of the cations and the librations of the PO_4 groups). The assignment of the internal vibration frequencies is in its turn based, as has become customary in the case for compounds with tetrahedral anions such as $[SO_4]^{2-}$, $[CrO_4]^{2-}$, $[MoO_4]^{2-}$, $[ReO_4]^-$, etc., on the vibration frequencies of the 'free' ion. Group-theoretic analysis yields the following distribution of the vibrations of the free ion in terms of irreducible representations of the T_d symmetry point group and their activities in the IR absorption and Raman spectra:

$$\Gamma_{vib} = A_1(R) + E(R) + 2F_2(IR, R).$$

(R = Raman).

Frequencies of 980 cm^{-1} and 1082 cm^{-1} have been found[7] respectively for the fully symmetrical $\nu_1(A_1)$ stretching vibration of the free $[PO_4]^{3-}$ ion and the triple degenerate $\nu_3(F_2)$ stretching vibration. The deformation vibrations are characterised by lower frequencies: 363 cm^{-1} for the doubly degenerate $\nu_2(E)$ vibration and 515 cm^{-1} for the triply degenerate $\nu_4(F_2)$ vibration.

Naturally, in the vibrational spectra of crystalline substances containing phosphate anions, the frequencies of the corresponding vibrations vary as a function of the nature of the cations and the crystal structure. The latter determines the symmetry of the PO_4 groups in the crystal lattice and the possibility of the splitting of the degenerate modes and of the resonance interaction of the vibrations, which increases the number of bands in the spectra and gives rise to appreciable difficulties in their interpretation. Unfortunately, the occurrence of such interaction, leading to the factor-group (Davydov) splitting is by no means always taken into account by investigators. A correct analysis of the manifestations of this effect is possible only when studies are performed on single crystal specimens in polarised light.

In the present review, the authors' aim was to survey as fully as possible the results of studies on the orthophosphates of Group I – III elements by vibrational spectroscopic methods, promoting thereby further researches on these lines.

II. Alkali metal orthophosphates

The vibrational spectra of alkali metal orthophosphates have been investigated for solutions,[8] melts,[9] and the crystalline state.[9,10] The tetrahedral symmetry of the $[PO_4]^{3-}$ anions is retained in aqueous K_3PO_4 and Na_3PO_4 solutions. This follows from the maintenance of the selection rules determined for the free ion.

The intense absorption band at 1004 cm^{-1} has been recorded in the IR absorption spectra. It corresponds to the triply degenerate F_2 stretching vibration to which corresponds a line at a frequency of 1014–1026 cm^{-1} in the Raman spectrum. The fully symmetrical stretching vibration is manifested only in the Raman spectrum by a line at 936 cm^{-1}.

Despite the fact that the phosphate anion does not include hydrogen atoms, in aqueous solutions there is a possibility of the formation of hydrogen bonds as a result of the interaction of the oxygen atoms of the anions with the protons of the water molecules. These fairly strong bonds influence the nature of the spectrum of the $[PO_4]^{3-}$ anions and are manifested significantly in the region of the stretching vibration frequencies of water molecules. In particular, an intense broad shoulder is observed[8] on the low-frequency slope of the IR absorption band due to the ν(OH) stretching vibration at 2900–3000 cm^{-1} (at 2200–2300 cm^{-1} in solutions in D_2O).

It has been noted that the hydrogen bonds involving phosphate anions are much stronger than those between water molecules. On partial deuteriation of water, the fully symmetrical stretching vibration becomes active in the IR absorption spectrum at a frequency of 936 cm^{-1} as a consequence of the decrease in the symmetry of the hydrogen-bonded phosphate ion. The strength of the phosphorus–oxygen covalent bonds in the $[PO_4]^{3-}$ tetrahedra ensures the stability of the latter as structural assemblies also in alkali metal phosphate melts.[9] Whereas the vibrational spectra of lithium and sodium phosphates in the condensed state[5] are fairly complex and differ appreciably owing to the differences between their crystal structures, in the Raman spectra of their melts only four lines corresponding to the internal vibrations of the free phosphate anion remain: at 1012, 930, 587, and 442 cm^{-1} for Li_3PO_4; at 1017, 907, 571, and 412 cm^{-1} for Na_3PO_4.

The observed frequencies differ somewhat from those obtained for solutions of orthophosphates,[8] which is explained by the influence of the solvent already mentioned. On the other hand, the Raman spectra of $M^{I}_3PO_4$ phosphate melts differ as regards the positions of the lines, which is a consequence of the influence of the alkali metal cation on the vibrations of the anions. The existence of a prefusion region at 100–200 °C for alkali metal orthophosphates is characterised by a smooth decrease in the intensities of certain Raman lines corresponding to the external vibrations of the anions up to their complete disappearance and has been attributed by the investigators to the orientational disordering of the PO_4 tetrahedra. Unfortunately, the vibrational spectra of alkali metal phosphates have been studied at an insufficiently high level of sophistication[11] and cannot be discussed in the present review. Recently the crystal structures of these salts have attracted the attention of investigators.[12,14]

III. Alkaline earth metal orthophosphates

A more detailed analysis of the vibrational spectra has been carried out for the alkaline earth metal orthophosphates $M^{II}_3(PO_4)_2$, in particular for barium and strontium orthophosphates, on the basis of experimental IR absorption spectra[14] in the region up to 50 cm^{-1} and the Raman spectra for polycrystalline specimens, resorting to the results of the calculation of the frequencies and modes of the normal vibrations of the crystals.[15]

For the crystal lattices of the isostructural $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ (space group $R3m = D^5_{3d}$), the representation of the vibration of the crystals is

$$\Gamma_{vib} = 5A_{1g} + A_{2g} + 6E_g + A_{1u} + 5A_{2u} + 6E_u,$$

among which the $A_{2g} + E_g + E_u + A_{1u}$ librational modes and the $2A_{1g} + 2E_g + 2E_u + 2A_{2u}$ translational modes correspond to the lattice vibration.

The two translationally nonequivalent PO_4 groups in the unit cell occupy positions with the C_{3v} local symmetry. Table 1 presents a scheme for the correlations between the irreducible representations of the vibrations of the free ion and the PO_4 groups in the $Sr_3(PO_4)_2$ or $Ba_3(PO_4)_2$ structure. According to the results of group-theoretic analysis, the alternative prohibition rule holds in these spectra and, out of the twelve internal vibrations of the PO_4 group in each set, six should be active in IR absorption and six in the Raman spectrum.

Table 1. A scheme of correlations between the irreducible representations of the vibrations of the PO_4 group in $Ba_3(PO_4)_2$.

Vibration	'Free' ion (T_d point group)	C_{3v} symmetry of the position	Factor-group of the D_{3d} space group of the crystal
ν_1	A_1	A_1	A_{1g}(R) + A_{2u}(IR)
ν_2	E	E	E_g(R) + E_u(IR)
ν_3	F_2	$A_1 + E$	A_{1g}(R) + E_g(R) + A_{2u}(IR) + E_u(IR)
ν_4	F_2	$A_1 + E$	A_{1g}(R) + E_g(R) + A_{2u}(IR) + E_u(IR)

R = Raman (Ed. of Translation).

All the predicted modes have been recorded in the experimental Raman spectra of $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ crystals.[15] The frequencies and the assignments are presented in Table 2. The most intense lines correspond to the fully symmetrical $\nu_1(A_{1g})$ vibration and their frequencies, 955 cm^{-1} for $Sr_3(PO_4)_2$ and 931 cm^{-1} for $Ba_3(PO_4)_2$, agree well with the values obtained for the $[PO_4]^{3-}$ ion in solution. By analogy with data for the free ion, the next lines in terms of intensity were assigned to the $\nu_2(E)$ vibration. The high vibration frequencies (together with ν_1) and the relatively low intensity of the Raman lines served as the criteria for the assignment of the $\nu_3(A_{1g} + E_g)$ components. However, the lack of data for single crystal specimens precludes a correct assignment of the components of both stretching and deformation triply degenerate vibrations. As in the case of the alkali metal phosphates in the crystalline state, a relation between the internal vibration frequencies and the nature of the cation cannot be traced. Apart from those listed above, three lines due to the external vibrations of the crystal lattice were recorded in the Raman spectra[14] and these proved to be fairly sensitive to the replacement of the cation.

Table 2. The vibration frequencies (cm^{-1}) in the spectra of $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ and their assignments.[14]

Raman		Assignment	IR absorption		Assignment
$Sr_3(PO_4)_2$	$Ba_3(PO_4)_2$		$Sr_3(PO_4)_2$	$Ba_3(PO_4)_2$	
142	108	External			
163	163	modes	166	146	External
242	203	(E_g)	232	220	modes
416	412				
			450	450	$\nu_2(E_u)$
572	564	$\nu_4^1(E_g)$	570	561	$\nu_4^1(E_u)$
621	602	$\nu(A_{1g})$		580	$\nu_4(A_{2u})$
998	982	$\nu_3^1(E_g)$	951	928	$\nu_1(A_{2u})$
1072	1046	$\nu_3(A_{1g})$	1029	1007	$\nu_3^1(E_u)$
955	931	$\nu_1(A_{1g})$	1099	1053	$\nu_3(A_{2u})$

It has been suggested that the IR absorption bands be assigned similarly. The two intense absorption bands in the high-frequency part of the spectra have been assigned to the A_{2u} and E_u components of the ν_3 mode. It is assumed that the higher-frequency moderately intense band corresponds to a vibration of the A_{2u} type of symmetry, while the most intense band corresponds to E_u. The low-intensity IR band in the spectra of the phosphates considered has been assigned to $\nu_1(A_{2u})$. The lack of evidence for this mode in studies on the spectra of other phosphates is probably

due to its unduly low intensity and its being masked by the two much more intense ν_3 components. However, this assignment is based on general considerations and is not sufficiently well founded.

The assignment of the $\nu_4(A_{2u} + E_u)$ and $\nu_2(E_u)$ deformation vibration bands has been extremely arbitrary. In each of the regions of the manifestation of these modes, two bands are recorded instead of the three predicted by the group-theoretical study of the vibrations of the crystals. Such a situation is actually observed for $Sr_3(PO_4)_2$: the absorption band at 570 cm^{-1} has been assigned to ν_4 (without resolution into components), while the band at 450 cm^{-1} has been assigned to $\nu_2(E_u)$. A fuller experimental picture has been obtained for $Ba_3(PO_4)_2$. The components of the ν_4 mode are manifested by two IR bands with different intensities at 580 and 561 cm^{-1}, whilst the ν_2 mode is manifested by a weak band at 450 cm^{-1}.

As a rule, the deformation vibration frequencies of the EO_4 oxo-anions depend on the nature of both the central atom and the external cation. The measured frequencies change slightly on passing from strontium to barium, demonstrating that the deformation vibrations of the PO_4 group are characteristic.

In the absence of polarisation measurements, the applicability of the alternative prohibition rule to the vibrations of the centrosymmetrical $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$ crystals is an extremely significant factor, ensuring that the assignments of the frequencies are to some extent well founded. Since the inversion operation converts one of the PO_4 groups, within the framework of the unit cell, into another both components are not observed simultaneously in either IR or Raman spectra for any of the resonance doublets. This factor was taken into account by the authors of the proposed assignment.

The conclusions described above have been confirmed by calculations of the frequencies and modes of the normal vibrations [16] of these typical representatives of orthophosphates.

The zeroth approximation for the force constants of the PO_4 group was devised by resorting to the corresponding quantities obtained in the study of aqueous solutions of phosphoric acid.[7] The results of the calculation demonstrate that the interaction of the internal vibrations of the PO_4 groups and the crystal lattice vibrations is insignificant. This makes it possible to regard the complex anions as rigid fragments participating in the lattice vibrations and characterised by their mass, moments of inertia, and the forces linking the terminal oxygen atoms to the cations.

Analysis of the calculated lattice vibrational modes confirmed the legitimacy of a clear-cut separation of the orientational and translational modes not only in those cases where their symmetries differ but also within the framework of the same irreducible representations. The authors were able to subdivide comparatively reliably the translational lattice vibrations into those induced predominantly by the displacements of the PO_4^{3-} anions and the alkaline earth metal cations.

The double orthophosphates $Ca_{3-x}M^{II}_x(PO_4)_2$, where M = Sr or Ba, have been described.[17] At normal pressure, usually two phases of these substances coexist, undergoing a transition to a new phase with orthorhombic symmetry at 50 kbar. The double phosphate $BaZn_2(PO_4)_2$, crystallising in the monoclinic system (space group $P2_1/c$, $Z = 4$) is also known. The ZnO_4 and PO_4 tetrahedra are linked into a three-dimensional framework via their common vertices. The crystal structure of β-$Cd_3(PO_4)_2$ has been described.[17] In the monoclinic crystal lattice (space group $P2_1/c$, $Z = 12$), the cadmium atoms, distributed among nine non-equivalent positions, are surrounded by five oxygen atoms of the PO_4 groups arranged in a trigonal bipyramidal arrangement. We are not aware of any spectroscopic studies on these compounds.

IV. Lanthanide orthophosphates

The vibrational spectra of lanthanide orthophosphates have been investigated in fair detail.[18–21] It has been suggested that the spectroscopic data for $LnPO_4$ be interpreted [22] in accordance with their subdivision into the following three groups: La–Tb orthophosphates with the monazite structure, Sc, Y, Er, Tm, Yb, and Lu orthophosphates crystallising with the xenotime structure, and Dy and Ho orthophosphates, the symmetry of the crystal lattices of which is reduced compared with the second group of compounds.

Lanthanide phosphates crystallising with a monazite type of structure are characterised by a monoclinic system (space group $P2_1n = C^5_{2h}$) with four formula units in the unit cell.[19–21] The model of the crystal structure is made up of the coordination nonagons of the lanthanide cations linked to one another via distorted phosphate groups.

The crystal lattice of the orthophosphates with the xenotime structure has a tetragonal symmetry [18] [space group $I4_1/amd = D^{18}_{4h}$ ($Z = 4$)]. The lanthanide cations in crystals of this type are coordinated to eight oxygen atoms with two sets of interatomic spacings. The phosphate groups in compounds of this type have a distorted tetrahedral structure. The study of the EPR spectra of the impurity ions [23] in YPO_4 single crystals made it possible to obtain information about the crystal field parameters for the cations in this structure.

In crystals with the monazite structure, the anions can occupy only general positions, since the symmetry group of the possible specific positions of the C_i space group $P2_1/c$ is not a subgroup of the intrinsic symmetry group of the tetrahedral ion. This factor implies the complete removal of the degeneracy of the internal vibrations of the PO_4 group and the activity of all the modes in the IR absorption and Raman spectra. A detailed analysis of the IR absorption spectra of compounds of this type [24,25] confirmed the latter hypothesis. Nevertheless, all three components of the triply degenerate ν_3 stretching vibration of the tetrahedron of the orthophosphate anion could be resolved only in the spectrum of $EuPO_4$. The magnitude of the splitting of these components and the intensity of the fully symmetrical ν_1 vibrational band, which is not active in the spectrum of the free ion, constitutes quantitative characteristics of the distortion of the tetrahedron of the orthophosphate ion in the inner field of the crystal. The strength and anisotropy of the crystal field are determined by the interaction between the cations and anions. In the series of lanthanide elements from La to Eu, the intensity of the ν_1 band and the splitting of ν_3 into components increase, these increases being attributed to an increase in the strength of the inner field with decrease in the size of the lanthanide cation. An increase in the frequencies of the vibrations under consideration is observed at the same time.

A greater number of IR absorption bands have been recorded [22] in the spectra of phosphates of the first group than has been postulated on the basis of the results of a group-theoretic analysis (Table 3). In particular, in the range of ν_3 stretching vibration frequencies, five bands were observed in each case, while in the range of the ν_4 deformation frequencies four bands were observed for each compound. The authors believe that the reason for the appearance of the additional band is the manifestation of fairly intense overtones and compound vibrations. In the region of the ν_3 vibration, these bands can correspond to the $2\nu_4$ overtone or the $\nu_4 + \nu_2$ combination. Considerable difficulties arise when an attempt is made to explain the nature of the spectrum in the region of the ν_4 deformation vibration frequencies.

For the orthophosphates of the second group with the tetragonal xenotime symmetry,[18] the distribution of the PO_4 groups among positions with the D_{2d} symmetry leads to the splitting of the $\nu_3(F_2)$ vibration into two components with the E and B_2 symmetries. Both modes should be active in the IR absorption spectra. According to the scheme of correlations between the irreducible representations of the vibrations (Table 4), the $\nu_1(A_1)$ mode should retain its type A_1 symmetry and its activity in the IR absorption spectrum. Doublets corresponding to the ν_3 stretching vibration of the phosphate anion have been recorded in the experimental [25] IR spectra of

Table 3. The vibration frequencies (cm^{-1}) in the IR absorption spectra of lanthanide orthophosphates.[23]

Compound	Vibration frequencies											
$LaPO_4$	1087	1075	1053	1025	1010	980	946	621	575	559	532	487
$CePO_4$	1107	1092	1058	1014	994		953	623	576	564	538	490–460
$PrPO_4$	1111	1093	1058	1015	995		955	625	578	565	538	486
$NdPO_4$	1111	1095	1055	1017	999		958	626	578	567	539	493
$SmPO_4$	1099	1062	1040	1018	1000		962	635	580	568	539	488
$EuPO_4$	1104	1050	1031	1015	1000		963	629	581	570	542	485
$GdPO_4$	1105	1070	1042	1028	1007		967	629	583	575	545	488
$TbPO_4$	1124	1105	1070	1044	1026	1010	969	635	583	575	542	490
YPO_4		1058	990					641	521			
$LuPO_4$		1068	1010					644	518			
$YbPO_4$		1081	1020					649	521			
$TmPO_4$		1075	1020					646	519			
$ErPO_4$		1058	995					645	521			
$DyPO_4$		1053	1020					635	524			
$HoPO_4$		1058	1020					639	523			

Table 4. A scheme of the correlations of the irreducible representations of the vibrations of the PO_4 group in the xenotime structure.

Vibration	'Free' ion (T_d point group)	Symmetry of the D_{3d} position	Factor-group of the D_{4d} space group of the crystal
ν_1	A_1	A_1	$A_{1g}(R) + B_{2u}(in)^a$
ν_2	E	$A_1 + B_1$	$A_{1g}(R) + B_{2g}(R) + A_{1u}(in)^a + B_{2u}(in)^a$
ν_3	F_2	$B_2 + E$	$B_{1g}(R) + E_g(R) + A_{2u}(IR) + E_u(IR)$
ν_4	F_2	$B_2 + E$	$B_{1g}(R) + E_g(R) + A_{2u}(IR) + E_u(IR)$

[a] in = the given vibration is inactive in the spectra.
R = Raman (Ed. of Translation)

YPO_4, $GdPO_4$, and $YbPO_4$ (Table 3), but no absorption bands were observed in the range of frequencies where the ν_1 vibration might be manifested. The frequencies of the triply degenerate vibration of the PO_4 groups increase with decrease in the ionic radius of the lanthanide, similarly to the frequencies of the orthophosphates of the monazite group.

The presence of two PO_4 groups in the unit cells of compounds with the xenotime structure and the possibility of the resonance interaction of their vibrations have led to the hypothesis that the number of the corresponding IR absorption bands should be doubled. However, the authors[25] were unable to detect this effect apparently because of the small splitting of the vibration frequencies.

The decrease in the symmetry of the phosphate anions from T_d to D_{2d} also leads to the partial removal of the degeneracy of the ν_2 and ν_4 modes. The $\nu_2(E)$ mode is split into two components with the A_1 and B_1 symmetries, while the $\nu_4(F_2)$ mode is split, similarly to ν_3, into B_2 and E. All these vibrations are active in the Raman spectrum, whereas in the IR absorption spectrum the appearance of only components of the B_2 and E types is possible.

According to the results of group-theoretic analysis,[26] carried out taking into account the overall symmetry of the xenotime crystal lattice, the normal vibrations are distributed among the following irreducible representations of the factor-group D_{4h} of the space group

$$\Gamma_{mech} = 2A_{1g} + A_{2g} + 4B_{1g} + B_{2g} + 5E_g + A_{1u} + 4A_{2u} + B_{1u} + 2B_{2u} + 5E_u,$$

including the $A_{2u}+E_u$ acoustic modes, the $2B_{1g} + B_{2g} + 2E_u + 2E_g + A_{1u} + 2A_{1g} + 2A_{2u} + 2B_{2u}$ internal modes of the PO_4 groups, the $A_{2g} + E_g + B_{1u} + E_u$ librational modes, and the $2B_{1g} + 2E_g + A2_u + E_u$ translational modes.

In the case of $DyPO_4$, it was possible to record[26,27] virtually all the vibrations with even symmetry active in the Raman spectrum. The absence of two modes (B_{1g} and E_g) from the spectrum is apparently caused by their low intensity or masking by the more intense lines. The results of the IR spectroscopic study of $LnPO_4$ (Ln = Y, Er, Tm, Yb, Lu) [22] agree fully with the theoretical ideas. However, $DyPO_4$ and $HoPO_4$ have been segregated as a separate subgroup of the xenotime group, because their absorption spectra demonstrate the presence in each case of three ν_3 components and four components in the ν_4 region, ν_1 remaining inactive as before.

The X-ray diffraction patterns of these compounds also shows certain differences. On the basis of the analysis of the entire set of experimental data, Hesel and Ross[22] suggested that $DyPO_4$ and $HoPO_4$ have a structure with a symmetry higher than that of monazite but lower than that of xenotime.

Apart from the dependence of the nature of the spectrum on the symmetry in the arrangement of the PO_4 groups and the crystal lattice as a whole, the above investigators[22] considered the influence of the coordination of cations on the P–O bond. It has been suggested that the polarising effect of the cation be estimated in terms of the ratio e/r^2, where e is the formal charge of the cation and r is the ionic radius, and also from the decrease in the frequencies of the symmetrical stretching vibrations of the phosphate anion. It has been postulated that the Ln–OPO_3 bond is strongest for the polarised Tb^{3+}, which agrees with the minimal frequency of the symmetrical stretching vibration of the PO_4 groups. The steady tendency towards an increase in frequency with decrease in the polarising power of the cation was discovered in this connection.

The authors were unable to estimate the polarising power of the cations in the spectra of the phosphates of the second group owing to the absence of the ν_1 vibration bands from the IR spectrum.

A small number of absorption bands, compared with the number recorded in the IR spectra of phosphates with the monazite structure, are characteristic of these compounds,[22] again due to characteristic features of the symmetry. Thus in the region corresponding to the manifestation of the ν_3 and ν_4 vibrations, only two modes were measured in each case. As in the interpretation of the spectra of phosphates with the monazite structure, the authors attempted to explain the appearance of additional bands by the activity of harmonics or combined vibrations. However, selection rules prohibit the activity of harmonics and compound frequencies of the ν_4 components in

the IR spectra, although they become allowed on decrease to the overall C_1 symmetry. The authors were also unable to explain the appearance of additional bands in the region of the ν_4 frequencies.

In the spectra of the orthophosphates of the monazite group, two doublets are recorded in each case in the region of the ν_4 frequencies. The splitting for the high-frequency doublet is ~ 45 cm^{-1}, while that for the low-frequency doublet is ~ 25 cm^{-1}. The corresponding frequencies increase along the series of lanthanides. The latter factor does not permit the assignment of the measured bands to combinations with lattice modes because the frequencies of all of them should decrease in the La – Tb series.

The ratio of the ν_4 and ν_2 band intensities renders improbable, in its turn, the hypothesis that the additional band in the ν_4 frequency region is due to combinations with participation of the ν_2 component.

Somewhat different results were obtained by Elliott et al.[27] In particular, the orthophosphate $TbPO_4$ was assigned to compounds of the xenotime series and doubts were cast on the justification of the segregation of $DyPO_4$ and $HoPO_4$ in a separate group. Detailed analysis of experimental data (Table 3) revealed a series of spectroscopic features of lanthanide orthophosphates of the xenotime type. The theoretically predicted splitting of the ν_3 mode of the PO_4 tetrahedron into two components in conformity with D_{2d} symmetry of its position in the crystal lattice was manifested in the Raman spectra. A line at 1020 – 1040 cm^{-1} has been observed, together with the line at 1000 – 1030 cm^{-1}, for a series of compounds in the range of frequencies assigned to ν_3, while in the spectra of $TbPO_4$, $DyPO_4$, and $LuPO_4$ there is a distinct asymmetry of the lines at 990 – 1015 cm^{-1}. The $\nu_3(B_2)$ bands at 1040 – 1075 cm^{-1} correspond to them in the IR spectrum. The Raman lines corresponding to the high-frequency $\nu_3(E)$ shoulder at 1135 – 1140 cm^{-1} in the IR spectrum were not detected. The most intense Raman line at 986 – 1015 cm^{-1} was assigned to $\nu_1(A_1)$ with a high degree of probability.

Major difficulties arose in the analysis of the region corresponding to the deformation vibrations of the PO_4 groups. The bands referring to the ν_4 vibration have been measured in the IR spectra in the range 500 – 600 cm^{-1} and in the Raman spectra of $TbPO_4$ (525 cm^{-1}), $HoPO_4$ (580 cm^{-1}), and $YbPO_4$ (578 cm^{-1}). The ν_2 modes have been detected in the form of Raman lines (A_{1g}, B_{1g}) in the range 360 – 500 cm^{-1} but are absent from the IR absorption spectra. Although the frequencies below 350 cm^{-1} have in fact been assigned to ν(Ln – O), no well founded analysis of the vibrations in this part of the spectrum have been carried out.

The dependence of the positions of the Raman lines of $HoPO_4$ on the exciting light wavelength and the appearance of a series of additional narrow fluorescence lines create additional difficulties in the interpretation of the experimental data.[26]

The Raman spectra of xenotime type YPO_4 and $YbPO_4$ crystals have also been investigated by Richman.[28] The vibrational frequencies were assigned on the basis of semiempirical data, by using the results of factor-group analysis of the vibrations of the crystals.

A precision study of the Raman spectra of the isostructural YPO_4, $HoPO_4$, and $ErPO_4$ single crystals in polarised light, supplemented by calculation of the frequencies and modes of normal vibrations, has been carried out at a higher level.[29] It was shown that in the previous studies[28] it was not possible to detect all the resolved Raman lines for YPO_4 and $YbPO_4$.

The frequencies of the symmetrical and the antisymmetrical stretching vibrations of the orthophosphate ions in the compounds investigated increase somewhat with decrease in the ionic radius of the cation, i.e. with increase in the packing density in the isostructural crystal cells of the xenotime type, which corresponds to the known tendency for other lanthanide salts. Analysis of the behaviour of the deformation vibration frequencies demonstrated their parallel variation, apparently caused by the significant interaction of these vibrations with external lattice vibrations, which are strongly influenced by a change in the mass of the cation in the series of lanthanides.

The complex problem of the separation of the external lattice vibrations into librations and translational vibrations in the case where it is impossible to distinguish them in terms of symmetry in polarisation spectra has been solved[29] on the hypothesis of a significant dependence of the translational vibrations, in contrast to the librations, on the mass of the cations. Such a dependence has been noted for two E_u vibrations and a single type A_{2u} vibration. However, the assignment of the E_g (translational vibrations and librations) and B_{1g} (translational vibrations) frequencies on the basis of these postulates did not prove to be quite so unambiguous. Some increase in frequencies on moving along the series of cations Y – Ho and Er has actually been noted for one of the B_{1g} vibrations. These data indicate the limited nature of the quasi-isotopic approximation used in the study of the influence of the geometrical characteristics of the crystal lattice on its dynamic parameters.

In contrast to lanthanide orthophosphates of the monazite series, representatives of the xenotime series are characterised by an appreciable resonance interaction of the vibrations. Thus the factor-group splitting for the doubly degenerate component of the ν_3 mode of the free ion is of the order of 30 cm^{-1}, while for the ν_4 vibration it reaches 60 cm^{-1}.

The study of the IR reflection spectra[29] of YPO_4, $HoPO_4$, and $ErPO_4$ single crystals demonstrated a decrease in the band intensities in the series of lanthanides. Since the band intensities in the IR reflection spectra are determined, in particular, by the effective atomic charges, the authors suggested that the decrease in the deformation vibration frequencies of the PO_4 groups in the spectra of the orthophosphates of the series considered is determined by the weakening of the electrostatic oxygen – oxygen interaction within the framework of the phosphate tetrahedron.

In the same study,[29] an attempt was undertaken to estimate the contribution of the dipole – dipole mechanism to the splitting of the bands due to the internal vibrations of the PO_4 groups in xenotime type crystals. In this case where it exerts a dominant influence on the nature of the spectrum, one would observe a decrease in the splitting of the bands in the series of orthophosphates YPO_4, $ErPO_4$, and $LuPO_4$. However, this was not confirmed experimentally. Furthermore, the large splittings ($\sim 60 - 80$ cm^{-1} for ν_1) are also difficult to account for because, according to the symmetry conditions, this vibration in the given crystal lattice does not alter the dipole moment. The influence of the quadrupole moment, determined merely by the slight distortion of the phosphate anion, for which the fully symmetrical vibration is not accompanied by a change in the quadrupole moment in the case of an ideal tetrahedral symmetry, should also be small. Thus the above considerations led the authors to the conclusion that the dipole – dipole interactions model is inapplicable to the description of the splittings of the internal vibrations of the PO_4 groups in crystals with a xenotime type of structure observed experimentally in both Raman spectra and IR reflection spectra.

The normal vibrations of the crystal have been calculated for YPO_4.[29] The valence force field zeroth approximation was devised by resorting to the force constants obtained for the free ion $[PO_4]^{3-}$ in solution and the force constants of the Y – O bonds for the first coordination sphere of the cation. In the calculation, account was taken of the interaction between the oxygen atoms of the neighbouring PO_4 tetrahedra and between the yttrium and phosphorus atoms (Y – Y, P – P, Y – P). The results of the calculation of the frequencies and modes of the normal vibrations and of the distribution of the potential energy made it possible to specify in detail and refine the assignment of the vibration frequencies. A significant correction to the assignment of the vibration frequencies was made on the basis of theoretical data for the E_g and E_u modes of the translational vibrations and librations. It was found that in these representations it is impossible to separate fully the two types of external lattice vibrations and that the change in the mass of the cation exerts a definite influence on

the frequencies of predominantly those translational vibrations for which significant amplitudes of the displacements of atoms have been established. The distribution of the potential energy obtained demonstrates a slight mixing of the modes of the internal vibrations of the phosphate ions with those of the lattice vibrations. The latter confirms the legitimacy of the approach used to interpret the vibrational spectra of all the phosphates and based on the separation of the internal and external vibrations. Among the stretching vibrations, the symmetrical pulsating vibration of the PO_4 groups proved to be mixed to the greatest extent, in terms of mode, with the vibrations of the cationic sublattice.

Comparison of the partial derivatives of the frequencies with respect to the force constants led to the conclusion that the Davydov resonance splitting of modes with identical symmetries in the IR spectra may be predicted in the case where it is determined by the dipole–dipole interactions. Analysis of the data obtained led the authors to the conclusion that the force field model employed is of limited applicability because it cannot be used to describe the elastic forces arising in the reorientation of complex phosphate anions.

Agreement with the results described above was achieved in the study of the Raman spectra of the single crystals of the orthophosphates of all the lanthanides (with the exception of promethium), yttrium, and scandium,[30] the Raman spectra being recorded for the first time for the orthophosphates of the lanthanides of the monazite group. The polarisation measurements permitted a correct assignment of the fundamental frequencies in terms of the symmetry types (Table 5). The data presented agree well with those of Lazarev et al.[29] for YPO_4, $HoPO_4$, and $ErPO_4$, and of Elliott et al.[27] for $DyPO_4$, but there is some discrepancy between the frequencies and those found earlier[26] for other compounds with the xenotime structure.

Table 5. The vibration frequencies (cm^{-1}) in the Raman spectra of the tetragonal orthophosphates $LnPO_4$ (Ln = Y, Tb–Lu).[31]

Y	Tb	Dy	Ho	Er	Tm	Yb	Lu	Assignment
96							98	
121	130	132	132	132	132	132	138	$B_{1g}(T)$
157	141	141	141	132	132	138	144	$E_g(T)$
185	183	185	184	185	185	186	191	$B_{1g}(T)$
210								
267	267				266	268		$E_g(T)$
299	293	295	297	300	303	302	302	$E_g(R)$
332	331	331	336	330	330	330	334	B_{2g}
484	484	485	486	477	488	491	493	A_{1g}
581	576	578	578	580	580	582	587	E_g
660	649	654	656	659	660	663	670	B_{1g}
10011	995	998	1001	1004	1006	1009	1014	A_{1g}
1027	1014	1019	1021	1024	1027	1030	1032	E_g
1048	1043					1048		
1058	1049	1054	1055	1061	1064	1068	1069	B_{1g}

The complete set of twelve allowed Raman vibrations has been recorded for orthophosphates with the xenotime structure. The interpretation of the spectra became possible only when account was taken of the resonance interaction of the vibrations within the framework of the unit cell in terms of the factor-group representations of the space group of the crystals.

The crystals of the phosphates with the monazite structure have much more complex spectra as a consequence of the low symmetry. The spectra were analysed resorting to IR absorption data.[22] The group-theoretic analysis of the vibrations of the orthophosphates with the monazite structure presupposes that 36 modes are active in the Raman spectrum and that 33 modes, obeying the alternative prohibition rule, are active in the IR spectra, but only 23 modes were recorded experimentally in the Raman spectra. Swanson et al.[31] suggest, on the basis of these data, that the vibration frequencies be assigned in terms of the representations of the local symmetry group C_1 for PO_4. In this case, it is assumed that all the internal vibrations of the PO_4 groups are active in both IR absorption and Raman spectra (Table 6).

Table 6. The vibration frequencies (cm^{-1}) in the Raman spectra of the monoclinic orthophosphates $LnPO_4$ (Ln = La–Gd).[31]

La	Ce	Pr	Nd	Sm	Eu	Gd	Assignment
90	88	90	89	88	87	87	B_g
100	100	105	106	107	108	108	A_g
120	118	122	123	123	124	123	A_g, B_g
131	129	133	133	132	132	130	B_g
151	152	158	155	156	158	158	B_g, A_g
170	172	177	164	170	175	178	B_g, A_g
183	188	188	180	185	189	192	B_g, A_g
220	219	224	227	232	233	236	B_g
227	227	230	230	242	244	247	B_g
255	254	251	263	265	265	270	A_g
271	270	282	286	294	310	308	B_g
414	414	417	420	423	423	429	A_g
465	467	469	470	473	471	480	A_g
537	536	538	539	538	538	540	A_g
572	571	572	574	575	576	579	A_g
589	589	592	595	595	597	599	B_g
619	618	623	625	627	629	632	A_g, B_g
					945		
967	970	974	977	982	989	987	A_g
991	990	994	997	999		1004	A_g
1025	1024	1028	1032	1035		1043	B_g
1055	1054	1058	1062	1065	1069	0172	A_g
1065							
1073	1070	1075	1079	1083	1082	1092	B_g
					1093		

However, this approach does not appear to be well founded. Firstly, the occurrence of a fairly strong resonance interaction of the vibrations has been established experimentally. Only five of the recorded Raman lines have the same frequencies as those measured in the IR spectra. In particular, the frequency of the $\nu_1(PO_4)$ symmetrical stretching vibration in the Raman spectra proved to be higher by 20 cm^{-1} than in the IR absorption spectra. Secondly, in the experiment on a single crystal in polarised light, the identity of certain frequencies of the A_g and B_g components cannot be an obstacle to their assignment regardless of whether this is due to the inadequate resolving power of the instrument or to the small factor-group splitting.

The frequencies of the internal vibrations of the PO_4 groups in the spectra of lanthanide orthophosphates increase linearly with the atomic number and ionic radius of the lanthanide. Thus the symmetrical stretching vibration frequencies vary from 967 cm^{-1} ($LaPO_4$) to 1011 cm^{-1} ($LuPO_4$). On the other hand, the frequencies of the lattice vibrations demonstrate a very slight dependence on the atomic number of the lanthanide.

Such tendencies in the variation of the vibration frequencies in the series of lanthanide orthophosphates conflict with those established previously[29] but do agree with those presented for lanthanide hydroxides.[31] The decrease in ionic radius from lanthanum to lutitium ensures a closer packing of the PO_4 groups. The contraction of the latter is accompanied by the deformation of the anion, a decrease in the interatomic phosphorus–oxygen distances, and an increase in the stretching and deformation vibration frequencies.

V. Double orthophosphates

Much attention has been devoted in recent years to the investigation of the structures and properties of double orthophosphates.[1,6,32] The existence of structural information for representatives of this class facilitates the interpretation of their vibrational spectra, which have been investigated in fair detail. A number of studies[33–35] have been devoted to the analysis of the vibrational spectra of the double phosphates $M^{I}M^{II}PO_4$ (M^{I} = Li, Na; M^{II} = Mg, Sr, Ba, Pb, Cd, Mn, Fe, Co, Ni).

X-ray diffraction data[36] have shown that the double phosphates $NaM^{II}PO_4$ (M^{II} = Mn, Fe, Co, Cd) are isostructural with Na_2SO_4-III and have the $Cmcm = D_{2h}^{17}$ symmetry space group. The internal vibrations of the PO_4 groups lie in the same frequency ranges within the spectrum as in the case of the individual phosphates.[33] The lattice vibration frequencies at 100–350 cm^{-1} depend, as expected, on the nature of the divalent cation. In order to refine the assignments in this part of the spectrum, the cadmium isotope ($^{106}Cd-^{116}Cd$)-substituted $NaCdPO_4$ specimens were investigated. However, the data obtained did not permit a reliable differentiation of the librational and translational modes. The authors believe that one of the probable causes of this is the interaction of lattice modes of identical symmetry. Certain features observed in the spectrum led the authors to the idea that the Na_2SO_4-III structural type has been modified for the series of compounds considered despite the similarity of the ionic radii. The lower symmetry of the unit cell in the phosphates considered (factor-group C_{2v}) was postulated. Under these conditions, agreement is achieved between the number and activity in the spectra of the vibrations predicted by the group-theoretic analysis and observed experimentally. In this connection, it is useful to recall the X-ray and neutron diffraction studies on $LiCaPO_4$,[37] isostructural with $LiNaSO_4$, which showed that this compound crystallises in the trigonal system with the space group $P31c = C_{3v}^{4}$.

The interpretation of the IR absorption and Raman spectra of the orthophosphates $LiM^{II}PO_4$ (M^{II} = Mg, Cd, Mn, Fe, Co, Ni) with the olivine structure by Paques-Ledent and Tarte[34] was based on a comparative analysis of data for the individual compounds, their solid solutions, and specimens with isotope substitution of the cations. The crystal structure of olivine is described by the space group $Pnma = D_{2h}^{16}$ ($Z = 4$). In the unit cell, there are two types of positions with a distorted octahedral environment: the divalent M^{II} cations occupy positions with the C_s symmetry, while the alkali metal cations M^{I} occupy C_i positions. There is also a possibility of a statistical distribution of the cations among these positions. Phosphate groups occupy positions with the C_s symmetry. The frequency assignment was carried out in terms of the approximation involving the subdivision of the vibrations into internal and external. The IR absorption spectra of the isotope-substituted $LiMgPO_4$ ($^{6}Li-^{7}Li$, $^{24}Mg-^{26}Mg$) and $LiNiPO_4$ ($^{6}Li-^{7}Li$, $^{62}Ni-^{68}Ni$) specimens as well as the Raman spectra of $LiMnPO_4$ and $LiCdPO_4$ specimens have been studied in greatest detail. The spectra of the isostructural series of compounds $LiM^{II}PO_4$, differing significantly only in the low-frequency region, which is associated with the manifestation of the vibration of the cations of different chemical nature, have been recorded.[34] In the remaining regions (stretching and deformation vibrations of the PO_4 groups), they are similar.

The four intense fairly broad IR bands at 960–1200 cm^{-1} were assigned to the components of the antisymmetrical ν_3 stretching vibration of the phosphate anion, while the weak, narrow, and lower-frequency bands were assigned to the ν_1 symmetrical vibration. The argument used in support of this conclusion was the agreement between the observed frequencies ν_1 and those of the most intense Raman lines and the ν_1 frequency in the IR absorption spectrum of a solution of the orthophosphate. However, the proposed assignment is not entirely correct in view of the possibility of the complete removal of the degeneracy of the vibrations and of the interaction of components with identical symmetries. The factor-group, resonance interaction is not manifested in the spectra of dilute $LiM^{II}(P_{0.02}As_{0.98})O_4$ solid solutions, while the site-group splitting of the ν_3 mode of the anion is observed in the form of three components, which agree with the C_s symmetry of its position.

Table 7. The vibration frequencies (cm^{-1}) for the isotope-substituted specimens[35] in the IR spectrum of $LiMgPO_4$.

$^{6}Li^{24}MgPO_4$	$^{7}Li^{24}MgPO_4$	$^{7}Li^{26}MgPO_4$	Assignment
158	157.5		Predominantly translations of Mg cations
230	229	226	
245	241.5	240.5	
290	280		
296	294	289	Predominantly translations of Li cations
235	322	318	
374	372	371	
416	407	399	
495	479	479	Translations of Li and Mg cations
518	517	515	
	535	534	
559	558	558	
594	593	592	Predominantly $\nu_4(PO)_4$
659	655	655	
673	669	688.5	

Analysis of the changes in the spectra of the isotope-substituted $LiM^{II}PO_4$ specimens (Tables 7–9) made it possible to differentiate three types of absorption bands:

the IR absorption bands at 550–700 cm^{-1}, for which isotopic shifts have not been detected or are insignificant, were assigned to the deformation vibrations of the anions;

several bands in the low-frequency part of the spectrum, which are also insensitive to the mass of the cation (the band at 372 cm^{-1} is the most characteristic in this respect), were assigned to librations bearing in mind that the frequencies are too low for deformation vibrations;

bands with appreciable isotopic shifts were assigned to external translational vibrations.

On the basis of the selective sensitivity to a particular isotope, it was possible in a number of instances to assign bands of the last type to the translational vibrations of various sublattices of the cations (Tables 7–9). Here one should note the fairly high (350–550 cm^{-1}) frequencies of the translational vibrations of

Table 8. The vibration frequencies (cm^{-1}) for the isotope-substituted specimens[34] in the IR spectrum of $LiNiPO_4$.

$^{7}LiNiPO_4$	$^{6}LiNiPO_4$	$^{7}Li^{62}NiPO_4$	$^{7}Li^{58}NiPO_4$	Assignment
163	163	163	163	Librations
192	192	187		
	203	194	192	Translations of Li cations
226	226	224	226	
246.5	250	246	246	
256	257	254.5	256	
304	306	303	304	Predominantly translations of Ni cations
313	313	312.5	313	
327	339	326	328	
360	357	359	361	
396	412	395	395	Predominantly translations of Li cations
477	509	477.5	477	
510				
529		528	528	Predominantly $\nu_4(PO)_4$
550	553	551	551	
650	650	650	650	
661	661	660.5	661	

Table 9. The frequencies (cm^{-1}) in the Raman spectrum of $LiM^{II}PO_4$ and their assignments.[35]

$LiMnPO_4$	$LiCdPO_4$	Assignment
148	94	Translations and librations of M^{II}
203	217	
237	217	
305	297	
410	410	$\nu_2(PO)_4$
442	438	
580	570	$\nu_4(PO)_4$
590	580	
626	622	
948.5	944	$\nu_1(PO)_4$
999		$\nu_3(PO)_4$
1006	988	
1018	1005	
1067	1064	
1080	1073	

the cations in the lithium sublattices, demonstrating the isotopic effect in the $^6Li-^7Li$ replacement. These vibrations may be mixed with the deformation vibrations of the anions, hindering the assignment of the latter.

The most intense line at 950 cm^{-1} in the Raman spectra of $LiM^{II}PO_4$ was assigned to the symmetrical ν_1 stretching vibration of the anion. The lower-intensity lines at higher frequencies (1000–1100 cm^{-1}) were attributed to the components of the triply degenerate ν_3 vibration (Table 9). Raman lines sensitive to lithium isotope substitution were not detected. This situation agrees fully with the theoretical postulates. The lithium cations occupying positions with the C_i symmetry cannot participate in the vibrations active in the Raman spectra. This permitted a more reliable assignment of the deformation vibration frequencies of the PO_4 groups. The ν_2 and ν_4 deformation frequencies were assigned on the basis of the relative intensities of the corresponding Raman lines and the vibration frequencies of the free anion in solution. The Raman lines at frequencies below 350 cm^{-1} were assigned to librations and translation vibrations without further specification. On the basis of the results, the authors[34] suggest that the approximation involving the subdivision of the vibrations into internal and external is justified. However, allowance for the factor-group splitting of the vibrations and for the subsequent interaction of their components with identical symmetries may introduce corrections to the results.

The available data for dilute solid solutions of a series of compounds $LiM^{II}PO_4$ showed that the observed splittings of the degenerate stretching vibration are not associated with geometrical distortions. The study of the crystal structure of $LiMnPO_4$ demonstrated the similarity of the four phosphorus–oxygen interatomic distances in the PO_4 groups (the differences between them do not exceed the experimental error). The deformation of the tetrahedral anions, expressed by changes in the bond angles from 106° to 112°, should most probably affect the behaviour of the deformation modes but cannot induce a significant splitting of ν_3.

Since appreciable splittings of ν_3 have been observed for compounds of different composition with the olivine structure ($M^{II}_2SiO_4$, $M^{II}_2GeO_4$, $M^{I}M^{II}AsO_4$, $M^{I}M^{III}SiO_4$, and $M^{I}M^{III}GeO_4$) as well as the orthophosphates considered, the authors[34] concluded that this effect is determined not only by the chemical nature of the cations or the anions but also by the crystal structure. Even when the cations in two different octahedral positions in the olivine structure are chemically identical, two sets of nonequivalent cation–oxygen distances are postulated in the compounds $M^{II}_2SiO_4$. Each oxygen atom of the tetrahedral anion is linked to three cations located in different positions, namely $2\,M^{II}(C_i) + 1\,M^{II}(C_s)$ or $1\,M^{II}(C_i) + 2\,M^{II}(C_s)$. The difference between the energies of the cation–oxygen bonds leads in this case to the appearance of two types of bonds in the tetrahedral anions and is responsible for the splitting of the ν_3 mode. This is naturally also responsible for the dependence of the splitting on the nature of the cations in the octahedral positions. Indeed, there is a quantitative dependence of the splitting on the second ionisation potential of the divalent cation, which demonstrates the validity of the proposed explanation of the observed effect.[34]

The structures of the double phosphates $LiSrPO_4$, $LiBaPO_4$, and $LiPbPO_4$ have not been investigated, although it is known that they are not isomorphous. The crystal structure of $LiBaPO_4$ resembles[35] the orthorhombic structure of $LiKSO_4$ with the symmetry space group $Pna2_1 = C^9_{2v}$ ($Z = 4$). Despite the similarity of the ionic radii of strontium and lead, their double orthophosphates with lithium salts crystallise differently. The $LiPbPO_4$ crystals have the $Pna2_1 = C^9_{2v}$ symmetry with eight formula units in the unit cell, while the space group $P2_1/b = C^5_{2h}$ has been proposed for $LiSrPO_4$. Using vibrational spectroscopic methods, the investigators[35] attempted to establish certain details of the structures of these compounds. The measured IR absorption spectrum of $LiBaPO_4$ proved to be similar to those obtained for $LiKSO_4$ and $LiCsSO_4$ over the entire range (up to 50 cm^{-1}). The vibration frequencies and their assignments for $LiBaPO_4$ are compiled in Table 10. Apart from the stretching and deformation vibration frequencies of the PO_4 groups, the IR absorption spectra contain bands at 400–500 cm^{-1}, undergoing an appreciable isotopic shift following the $^6Li-^7Li$ substitution which permitted their assignment to the vibrations of the lithium sublattice cations. The relatively high corresponding frequencies suggest a tetrahedral coordination of the lithium cations and agree with X-ray diffraction data. The three IR absorption bands recorded in the low-frequency region were assigned to lattice vibrations with participation of the heavy barium atoms.

Analysis of the isotopic shifts enabled the authors[36] to conclude that there are no appreciable interactions between the internal and external vibrations of the crystals having the structure investigated. It was possible to detect experimentally only some of the theoretically predicted vibration frequencies. In many cases, it was noted that the frequencies in the Raman and IR absorption spectra do not agree, which is consistent with the centrosymmetrical space group proposed for $LiBaPO_4$.

The observed isotopic effect assisted significantly also in the assignment of the Raman spectroscopic frequencies. The 954 and 930 cm^{-1} lines were assigned to the components of the symmetrical stretching vibration of the PO_4 groups, while the three lines in the range 1000–1150 cm^{-1} were assigned to the components of the triply degenerate vibration. The intense line at 424 cm^{-1} as well as the 580 and 570 cm^{-1} lines, which do not shift following lithium isotope substitution, have been assigned to the components of the ν_2 deformation vibration. Lines assigned to the vibrations of the cations of the lithium sublattice have been detected in the same range (390–500 cm^{-1}). A more complex vibrational spectrum has been obtained[35] for $LiSrPO_4$, which is due to the lower symmetry of the crystals. However, the range of the stretching vibration frequencies of the PO_4 groups proved to be similar to that for $LiBaPO_4$. The most significant shifts following lithium isotope substitution ($^7Li-^6Li$) have been recorded for the 618 (639), 516 (555), and 343 (393) cm^{-1} bands in the frequency range corresponding to the tetrahedral coordination of lithium in the crystal lattice. The components of the ν_4 vibrations of the PO_4 group are manifested at 590 and 576 cm^{-1}, while those of the ν_2 vibrations are manifested at 428 cm^{-1}. The authors note an appreciable, compared with $LiBaPO_4$, interaction of the deformation vibrations of the PO_4 groups with the vibrations of the lithium cations.

The presence of two bands, at 964 and 919 cm^{-1}, in the range of the stretching vibration frequencies of the anions in the IR spectrum of $LiPbPO_4$, has been attributed[35] to the presence in the

Table 10. Frequencies of the vibrations (cm^{-1}) of $LiM^{II}PO_4$ (M = Ba, Pb).[35]

$LiBaPO_4$				$LiPbPO_4$				Assignment
IR		Raman		IR		Raman		
^7Li	^6Li	^7Li	^6Li	^7Li	^6Li	^7Li	^6Li	
64	64	107		71	71			Lattice modes
82	83	168		75	75	37	37	including
154	160	295		93	93	57	57	predominantly
		398	405	115	116	71	71	M – O vibrations
				135	135	94.5	94.5	
				169	169	137	137	
				202	202	247	247	
				246	246			
				257	257			
				380	385			
	426	424	426	405	410	395	393.5	$\nu_2(PO)_4$
420	445			443	459		408	
						422	433	
463	487	455	473	482	508	433	455	
482	510					482.5	495.5	
572	573	570	576			560	560	$\nu_4(PO)_4$
587	592	580	585	580	584	582	582	
		600	600					
958	958	930.5		919	919	926		$\nu_1(PO)_4$
		954		964	926			
1037	1039	1021.5		1000	1000	1015		$\nu_3(PO)_4$
		1033.4		1034	1034	1058		
		1108		1062	1062	1078		

crystal lattice of two sets of nonequivalent PO_4 groups. The Raman lines sensitive to lithium isotope substitution have been detected in the frequency range 500–600 cm^{-1}. Identical absorption frequencies have been noted for many vibrations of $LiPbPO_4$, which agrees with the absence of a centre of symmetry in the crystal lattice (space group $Pna2_1 = C_{2v}^9$). The authors[35] do not propose any approaches to a detailed interpretation of the long-wavelength (below 300 cm^{-1}) part of the spectra of the group of compounds considered, postulating the manifestation in this region of vibrations involving the heavy cations. Nevertheless, comparison of the spectra of compounds differing appreciably in the mass of the cations permits the analysis also of this spectral region, thus differentiating also the librations of the PO_4 groups.

The IR absorption spectra of polycrystalline specimens (mulls in liquid paraffin) of $RbMgPO_4$ and $CsMgPO_4$ have been measured[37] in the restricted range 400–1800 cm^{-1}. The very great similarity of the spectra enabled the authors to conclude that the compounds have the same structure. The splitting of the bands due to the stretching and deformation vibrations of the PO_4 groups as well as the activity in the IR spectrum of the fully symmetrical ν_1 stretching vibration suggest a decrease in the symmetry of the anion in the crystal lattice. The lack of sufficient experimental data made it impossible to secure more complete information about the structure of these phosphates.

Apart from the compounds considered here, the crystal structures have been described for a further two orthophosphates $M^IM^{II}PO_4$. X-Ray diffraction analysis of $RbZnPO_4$ led to the conclusion[38] that this compound crystallises in the monoclinic system [space group $P2_1 = C_2^2$ ($Z = 4$)]. It was shown that the structure is based on a three-dimensional skeleton made up of ZnO_4 and PO_4 tetrahedra related to the tridymite skeleton. The heptacoordinated rubidium cations are located in the channels of the skeleton. The crystal structure of $KBaPO_4$[23] with the $Pnma = D_{2h}^{16}$ ($Z = 4$) symmetry belongs[39] to the β-K_2SO_4 (arcanite) type in which some of the potassium cations have been replaced by barium. Unfortunately, we do not possess spectroscopic data on these compounds.

The crystal structures and vibrational spectra of double orthophosphates of Group I and III elements have been most fully investigated. Extensive information about these substances has been surveyed in a series of reviews.[32,40–42] X-Ray and physicochemical studies on phases of the type of nasicon $Na_3M_2^{III}(PO_4)_3$, where M is Sc, Cr, or Fe, demonstrated[40,42] the possibility of the occurrence in the latter of a high-temperature orthorhombic γ-phase with superionic conductivity, an intermediate phase (β-phase), and a low temperature α-phase. A detailed analysis of the structure, ion transport, and phase transitions in compounds of the type of nasicon has been carried out.[43] On the basis of X-ray diffraction and spectro-scopic studies,[44,45] the structure of nasicon $M_3^IM_2^{III}(PO_4)_3$ has been described as a superposition of the sublattices of PO_4 tetra-hedra and the M^I and M^{III} cations which fill the existing cavities. For compounds with a wide range of cations (M^I = Li, Na, K, Cu, Ag; M^{III} = Fe, Sc), the distortion of the structure relative to the initial prototype[40] $NaZr(PO_4)_3$ with the space group $R3c = C_{3v}^6$ as the cavities in the skeleton are filled has been studied.[44] In the course of the investigation of the vibrational spectra, both the range of symmetrical and antisymmetrical stretching vibration frequencies of the PO_4 groups, sensitive to the distortions of the tetrahedral anion, and the long-wavelength range (50–300 cm^{-1}), analysis of the bands in which makes it possible to estimate the degree of ordering of the cations, were examined. The minimum activation energy for conduction was found for compounds with most local disorder in the distribution of the cation. The conductivity diminishes as the cavities are filled.

An interpretation of the temperature-induced changes in the IR absorption and Raman spectra of orthophosphates of the type of nasicon $M_3^ISc_2(PO_4)_3$, where M = Li, Na, K, or Ag, in the range 100–300 K has been proposed.[45] In particular, the frequencies of the internal vibrations of the PO_4 groups and the vibrations of the scandium sublattice and of the conducting M^I cations as well as the librations of the tetrahedral anions were assigned. A correlation was established between the local disorder, the phase transitions, and the changes in the activation energy for conduction. Studies of the Raman spectrum of

$Li_3Fe_2(PO_4)_3$ as a function of temperature were continued.[46] Investigation of the α–β and β–γ phase transitions demonstrated that the disordering of the cationic sublattice of the orthorhombic γ-phase leads to the broadening of the lines due to both the internal stretching vibrations of the PO_4 groups and the lattice modes. Analysis of the calculated and experimental frequencies of the relaxation modes led the authors[28] to the assumption that low-frequency phonons are involved in the activation process.

The crystals of alkali metal lanthanide double phosphates can be divided into several types.[32] The parent of this structural family is glaserite $K_3Na(SO_4)_2$ [48] having a layered structure. The layers are formed by the tetrahedral sulfate anions and sodium cations, the potassium cations occupying the interatomic space.

Among compounds of this series, lithium compounds have been least investigated. The structure of the monoclinic $Li_3Sc_2(PO_4)_3$, corresponding to the space group $P2_1/n = C_{2h}^2$ ($Z = 4$), is known.[48] The crystal lattice is made up of the scandium coordination octahedra linked via the common vertices to the PO_4 tetrahedra. The lithium cations occupy the tetrahedral and trigonal-bipyramidal (two types) positions. The lithium polyhedra linked via common vertices form infinite chains. The results of a neutron diffraction study of $Li_3Sc_2(PO_4)_3$ [49] revealed insignificant differences between the parameters of the monoclinic cell and those obtained by X-ray diffraction.

A study of the structural features of the double sodium lanthanide orthophosphates $Na_3Ln(PO_4)_2$ showed[47] that the nature of the ordering of the cations in the glaserite-like lattice depends on the size of the lanthanide. Most of them have the orthorhombic symmetry and form a group of the $Na_3La(VO_4)_2$ structural type.[32] However, the available literature data are contradictory.[32,47]

Double potassium lanthanide orthophosphates have been investigated in greater detail[32,50] and, in conformity with their crystal structure, they can be divided into three groups:

Ln = La, or Sc—compounds with the triple glaserite unit cell;

Ln = Gd–Yb—compounds with a monoclinic distortion of the $K_3Lu(PO_4)_2$ lattice and the lattice volume increased by a factor of eight;

Ln = Nd—the intrinsic $K_3Nd(PO_4)_2$ structural type.

Among recent studies on the double orthophosphates, mention should be made of the investigation[51] devoted particularly to the phase relations in the $K_2O-Y_2O_3-P_2O_5$ system, where the existence of the $K_3Y(PO_4)_2$ phase was confirmed by the results of physicochemical and X-ray diffraction analysis and by IR spectra.

The more symmetrical trigonal structure occurs in the rubidium compounds of similar composition. This is ensured, firstly, by the 'moving apart' of the layers of the PO_4 tetrahedra and the lanthanide octahedra by the larger rubidium cations and their smoothing and, secondly, by the displacement of electron density and the increase in the covalent component of the Ln–O bond when potassium is replaced by rubidium, which also increases the symmetry of the layers. The intrinsic structural type occurs for $Rb_3Sc(PO_4)_2$.[32] According to the available data,[32] the double orthophosphate $Ag_3Sc(PO_4)_2$ has no structural analogues among the compounds described above. Silver compounds with lanthanides having this composition are unknown.

The vibrational spectra of $M_3^IM_2^{III}(PO_4)_3$, where M^I = Li or Na and M^{III} = Sc, Cr, Fe, or In, have been investigated.[52] Attention was concentrated on the temperature-induced changes in the Raman and IR absorption spectra of $Na_3Fe_2(PO_4)_3$. The two crystalline modifications of this phosphate differ by the distribution of the sodium cations—it is fully ordered for the monoclinic α-phase but is only partly ordered for the hexagonal β-phase. The authors[52] were able to discover certain significant differences between the vibrational spectra of these two modifications of $Na_3Fe_2(PO_4)_3$.

Analysis of the temperature dependence of the behaviour of the IR absorption bands of $Na_3Fe_2(PO_4)_3$ made it possible to divide the spectrum arbitrarily into two regions:

the 300–650 cm^{-1} frequency range, assigned to the deformation vibrations of the PO_4 groups and the translational vibrations of the iron cations, this part of the spectrum hardly changing in the given temperature range;

the higher frequency range 900–1250 cm^{-1}, corresponding to the stretching vibrations of the PO_4 groups, in which the fine structure of the absorption bands undergoes changes (a slight bathochromic shift and a broadening of the bands) at 84 °C.

More significant changes in the spectrum were recorded in the temperature range of the α–β polymorphic transition at 95–102 °C. The spectrum of β-$Na_3Fe_2(PO_4)_3$ obtained resembles that of $NaZr_2(PO_4)_3$ with a structure having hexagonal symmetry. However, solely on the basis of symmetry consideration without allowance for the disordering of the cations, the authors were unable to interpret all the recorded temperature-induced changes.

The results of the studies on the IR spectrum agree satisfactorily with the results of Raman measurements as a function of temperature. The fine structure of the Raman lines in the range 400–1250 cm^{-1} is almost completely smeared on raising the temperature to 110 °C, whilst in the region of moderate and low frequencies no significant changes take place. The 238 cm^{-1} line, which completely disappears with increase in temperature, is an exception.

The synthesis and study[53] of the double orthophosphates $Na_3Ln(PO_4)_2$ and $Na_3Ln_2(PO_4)_3$, where Ln = Tb–Lu, have been described. The formation of several polymorphic modifications with different symmetries is characteristic of each of the compounds investigated. The authors obtained the γ-phase for the first time. The phosphates of the series considered can be divided into four structural types. The X-ray diffraction pattern and the Raman spectrum of the γ-phase isolated differ from those known for any other phosphates. The temperature-induced changes in the Raman spectrum of the double phosphate $Na_3Ho(PO_4)_2$ are of considerable interest. At 465 °C, the three most intense lines of the Raman spectrum in the range of the stretching vibration frequencies of the PO_4 groups were broadened and exhibited two absorption shoulders on their slopes. The frequencies of the maxima increased and then remained unchanged up to 940 °C. A roughly similar behaviour has been demonstrated by the Raman lines of $Na_3Dy(PO_4)_2$. The single line generated when the three components merge in the region of the stretching vibration frequencies of the PO_4 groups at 750 °C has a frequency 16 cm^{-1} lower than that of the most intense initial line. The authors explained the observed effect by the occurrence of a phase transition. Manifestations of a phase transition have been noted[53] also in the Raman spectra of $Na_3Yb_2(PO_4)_2$. On the basis of the spectroscopic data obtained, the authors established the temperature limits of the stability of different polymorphic modifications of the phases studied.

The double orthophosphates $M_3^{II}M^{III}(PO_4)_3$ have been examined.[54,55] The formation of cubic crystals with the space group $I43d = T_d^6$ is characteristic of compounds of the series with M^{II} = Sr, Ba, or Pb and M^{III} = Y, Sc, Ln, or Bi. $Ca_3Bi(PO_4)_3$ and $Ca_3Eu(PO_4)_3$ have also been obtained. The results of the X-ray diffraction and IR spectroscopic study of the double calcium europium orthophosphate indicate[55] that its structure is the same as that of β-$Ca_3(PO_4)_2$.

Double lanthanide orthophosphates have been vigorously investigated in recent years.[56–58] They are isostructural with monazite or zircon and with the lanthanide orthophosphates. It may be expected that the distribution of lanthanides of different masses at the cationic sites would lead to changes in the longer-wavelength part of the vibrational spectra.

* * *

The foregoing demonstrates the possibility of securing extensive information, which is also predictive in character, in those cases where systematic spectroscopic studies have been carried out using all the possibilities of the method. Unfortunately, such investigations have been carried out fully for a very limited number of phosphates. The existing frequently controversial results have not been confirmed by theoretical calculations of the vibrations of the crystals. The vibrational spectra of alkali metal orthophosphates have not been investigated. On the other hand, vigorous studies are being prosecuted on the synthesis and X-ray diffraction of new complex orthophosphates and also compounds with systems of condensed phosphate anions. Reliable information can be secured from the analysis of the vibrational spectra of the latter only on the basis of a detailed knowledge of the nature of the vibrations of simpler orthophosphates.

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