Vibrational spectrum of nasicon-like, rhombohedral orthophosphates $M^I M^{IV}_2 (PO_4)_3$

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Abstract—The Raman and i.r. spectra of nasicon-type $M^I M^{IV}_2 (PO_4)_3$ rhombohedral phosphates (M^I = Li, Na, K, Rb, Cs, Tl; M^{IV} = Ge, Sn, Ti, Zr, Hf) exhibit intricate relationships between the spectra and the chemical composition. The pattern of the PO_4 stretching frequencies is more or less strongly modified by the nature of both M^{IV} and M^I cations. Still greater variations are observed in the medium and low frequency region, although some external modes have been identified by the study of mass effects (^{6}Li–^{7}Li, ^{70}Ge–^{76}Ge, Zr–Hf etc.). The origin of this complex behaviour is discussed in relation to the structure.

INTRODUCTION

Solid inorganic compounds characterized by the same structure and the same complex anion (carbonate, silicate, phosphate etc.) generally give a very similar high frequency vibrational pattern, which is characteristic of the stretching frequencies of the anion engaged in the structure under consideration. This is not always true, however, when the anion is associated with a highly charged (e.g. tetravalent) cation. We present here the results of a study of $M^I M^{IV}_2 (PO_4)_3$ rhombohedral phosphates, which belong to the so-called nasicon family of ionic conductors. This study was initiated in 1978 [1]; similar studies have been published in the meantime [2–5]. They will be discussed later on.

EXPERIMENTAL

All compounds were synthesized by conventional solid state reaction techniques. Stoichiometric quantities of $M^I_2 CO_3$, $M^{IV} O_2$ and $(NH_4)_2 HPO_4$ were well ground and mixed, and progressively heated in covered platinum crucibles up to a final temperature of 900–1200°C, depending on the nature of the M^I and M^{IV} cations. The progress of the reaction and the purity of the compounds were checked by both X-ray diffractometry (monochromatized Co $K\alpha$ radiation) and i.r. spectroscopy: the i.r. spectrum must be free from any absorption in the 700–900 cm^{-1} region (presence of a *meta*- or a pyrophosphate).

The i.r. spectra were recorded with a Beckman 4250 spectrometer (1500–250 cm^{-1}) and a Polytec FIR 30 interferometer (350–20 cm^{-1}); KBr or polythene discs were used in the appropriate regions. Some spectra were also run in Nujol to check the lack of ionic exchange between the KBr and the sample. The Raman spectra were obtained with a Coderg PHO double monochromator equipped with a Spectra Physics Ar$^+$ laser (5145 Å green line, 200 mW).

CHEMICAL AND STRUCTURAL DATA

All the compounds investigated and discussed in this paper correspond to the general formula $M^I M^{IV}_2 (PO_4)_3$, restricted to a $R\overline{3}c$ rhombohedral structure. The full structure has been determined for two compounds only: $NaZr_2(PO_4)_3$ [6, 7] and $KZr_2(PO_4)_3$ [8]. For all the other compounds, iso-

morphism was deduced, either from Weissenberg diffraction photographs (Zr and Hf compounds; M^I = Na, K, Rb, Cs, Tl) [9] or from powder diffraction data: Ti (M^I = Li, Na, K, Rb, Tl) [10], Sn (M^I = Na, K, Rb, Tl) [11] or Ge (M^I = Li, Na, K) [1, 6] compounds. Some of the existing Li compounds are not rhombohedral [3, 12]. They are not discussed in this paper.

CRYSTAL STRUCTURE, SITE AND FACTOR GROUP ANALYSIS

The space group of these compounds is D^6_{3d}–$R\overline{3}c$, with $Z = 6$ in the hexagonal cell, but $Z = 2$ in the primitive cell. The PO_4 tetrahedron is somewhat distorted, with two types of oxygen atoms. One of them (O_1) is also bound to one M^{IV} cation, whereas the second (O_2) is bound to one M^{IV} and one M^I cation. Both M^I and M^{IV} possess a distorted octahedral environment. The Pauling rule is not strictly satisfied, with a cationic contribution of 23/12 for O_1, and of 25/12 for O_2. The positions and symmetry properties of the atoms are given in Table 1.

Internal modes

By assuming separation of the vibrations into internal and external modes (the validity of this assumption will be discussed hereafter), factor group analysis leads to the following internal modes of the PO_4 anion.

	Point group T_d	Site group C_2	Factor group D_{3d}
v_1	A_1	A	$A_{1g} + E_g + A_{1u} + E_u$
v_2	E	$2A$	$2A_{1g} + 2E_g + 2A_{1u} + 2E_u$
v_3, v_4	F_2	$A + 2B$	$A_{1g} + 2A_{2g} + 3E_g + A_{1u} + 2A_{2u} + 3E_u$

Thus, we expect for the stretching vibrations: Raman active: v_1: $A_{1g} + E_g$; v_3: $A_{1g} + 3E_g$; i.r. active: v_1: E_u; v_3: $2A_{2u} + 3E_u$ and for the bending vibrations: Raman active: v_2: $2A_{1g} + 2E_g$; v_4: $A_{1g} + 3E_g$; i.r. active: v_2: $2E_u$; v_4: $2A_{2u} + 3E_u$.

Table 1. Positions and symmetry properties in rhombohedral phosphates

Atoms	Wyckoff position	Site symmetry
$2 M^I$	$2b$	S_6
$4 M^{IV}$	$4c$	C_3
$6 P$	$6e$	C_2
$12 O_1$	$12f$	C_1
$12 O_2$	$12f$	C_1

External modes

These include the translational modes of the M^I, M^{IV} and (PO_4) ions, and the (PO_4) librations. Group theoretical analysis [1] leads to the following results:

(PO_4) translations: $\Gamma_{T(PO_4)} = A_{1g}(\text{Ra}) + 2A_{2g}$
$+ 3E_g(\text{Ra}) + A_{1u} + 2A_{2u}(\text{i.r.}) + 3E_u(\text{i.r.})$

M^I translations: $\Gamma_{T(M^I)} = A_{1u} + A_{2u}(\text{i.r.}) + 2E_u(\text{i.r.})$

M^{IV} translations: $\Gamma_{T(M^{IV})} = A_{1g}(\text{Ra}) + A_{2g} + 2E_g(\text{Ra})$
$+ A_{1u} + A_{2u}(\text{i.r.}) + 2E_u(\text{i.r.})$

(PO_4) librations: $\Gamma_{\text{lib}} = A_{1g}(\text{Ra}) + 2A_{2g} + 3E_g(\text{Ra})$
$+ A_{1u} + 2A_{2u}(\text{i.r.}) + 3E_u(\text{i.r.})$.

Sum of the external modes (after subtracting the acoustical modes): Raman active: $8A_{1g} + 17E_g$; i.r. active: $9A_{1u} + 18E_u$.

Some salient features of this analysis may now be pointed out:

i. For the Raman active, stretching vibrations, the components issued from v_1 and v_3 belong to the same representation (either A_{1g} or E_g), and vibrational interactions are thus possible; as a limiting case, the discrimination between symmetric and antisymmetric motions could become irrelevant. The situation in the i.r. is somewhat (but not completely) different, since v_1 can only couple with v_3 in the E_u symmetry crystal normal modes. The other A_{2u} active modes are only related to v_3.

ii. There is no Raman active translation for the M^I cation.

iii. The number of external modes is fairly high, and they belong to a limited number of representations. Vibrational interactions are thus expected and, in some instances at least, it will be impossible to assign a given frequency to a definite type of motion.

RESULTS AND ASSIGNMENTS

PO_4 Stretching vibrations

Raman spectra. It is evident from Fig. 1 that, for the K compounds, two rather different types of spectra are observed, depending on the fact that M^{IV} is either a transition metal (Ti, Zr, Hf) or a main group element (Ge, Sn). In this latter case, the pattern remains essentially the same, irrespective of the nature of M^I (except LiGe phosphate; but in this case, the whole spectrum is different). If, however, M^{IV} is a transition
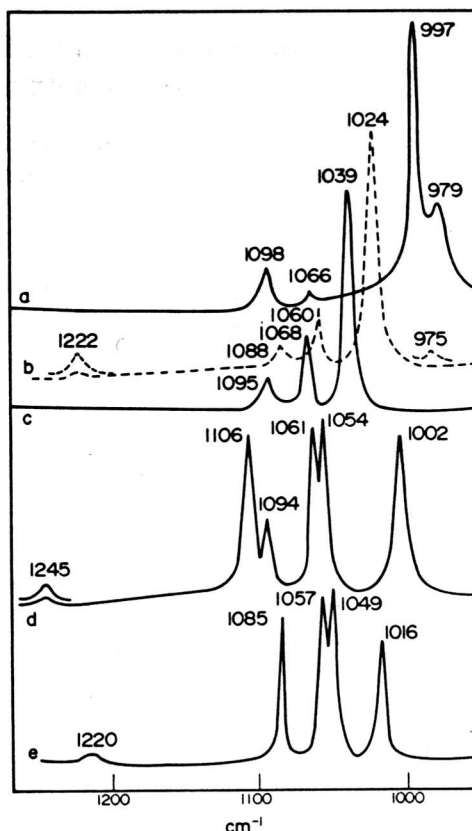

Fig. 1. Raman spectrum of PO_4 stretching vibrations of $KM_2^{IV}(PO_4)_3$. M^{IV} = Ti, Zr, Hf, Ge and Sn for a, b, c, d and e, respectively.

metal, and if K is replaced by another monovalent cation (Na, Rb, Cs, Tl), weak additional bands may appear on the sides of the strongest peaks, as illustrated in Fig. 2.

Assignments. The simplest case is that of $KHf_2(PO_4)_3$ (Fig. 1c), with one strong band assigned to v_1, and two weaker bands assigned to components of v_3. This is the situation expected for pseudo C_3 symmetry (the true local symmetry of PO_4 being C_2) and negligible influence of factor group splitting. The additional band observed in $KTi_2(PO_4)_3$ (Fig. 1a) suggests effective C_2 symmetry, and thus a greater distortion, probably related to the smaller size of the Ti cation. Other spectra (Fig. 2) may be deduced by taking into account the factor group splitting. On the contrary, the intensity is nearly the same for most of the bands of the Ge and Sn compounds (Fig. 1d, e), and this precludes any assignment to v_1 or v_3 modes.

Infrared spectra. The results are not so clear-cut here, since the high-frequency i.r. pattern seems to depend equally well on both M^{IV} and M^I cations (Figs 3, 4). There is just one evident systematic difference in the behaviour of main group or transition M^{IV}, namely the occurrence, near 1200 cm^{-1}, of either a single band (M^{IV} = Ti, Zr, Hf) or a doublet (M^{IV} = Ge, Sn). For NaGe and KSn compounds, the
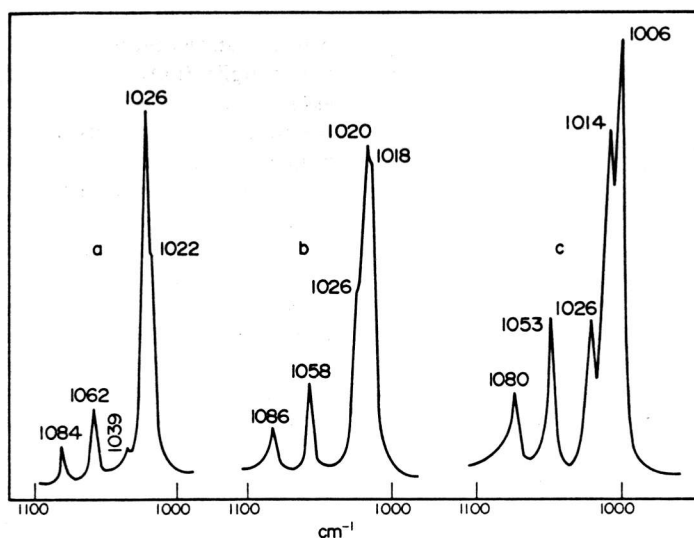
Fig. 2. Raman spectrum of PO_4 stretching vibrations of $M^I Zr_2(PO_4)_3$. M^I = Na, Rb and Cs for a, b and c, respectively.

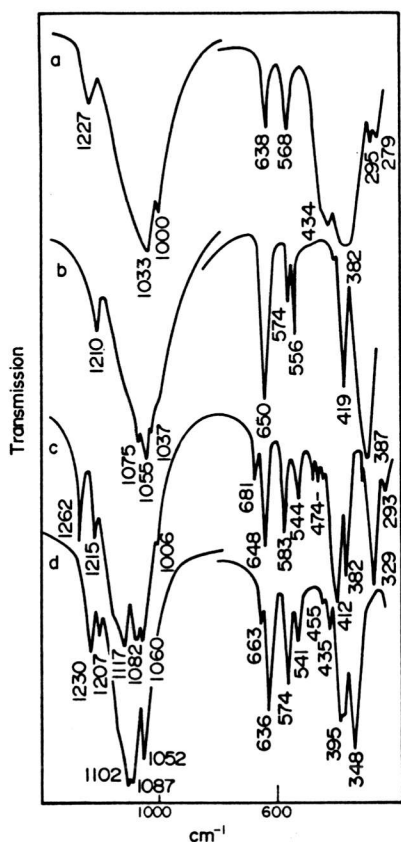Fig. 3. Infrared spectrum of $NaM_2^{IV}(PO_4)_3$ compounds. M^{IV} = Ti, Hf, Ge and Sn for a, b, c and d, respectively.
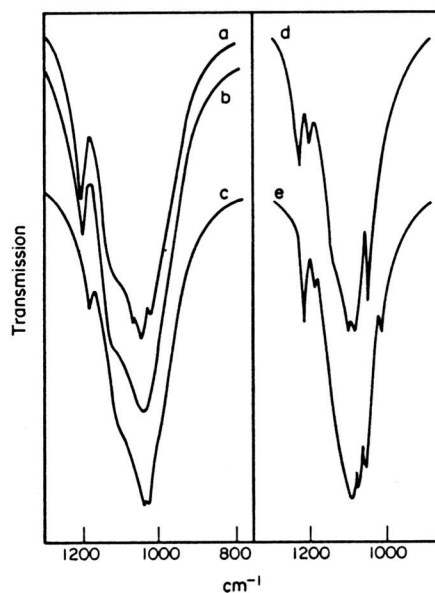

Fig. 4. High frequency i.r. spectrum of $M^I M_2^{IV}(PO_4)_3$ compounds. $M^I M^{IV}$ = NaZr, KZr, CsZr, NaSn and KSn for a, b, c, d and e, respectively.

$1200 \ cm^{-1}$ will be considered in the Discussion.

PO_4 bending vibrations

Raman spectra. All the compounds investigated show three or four bands in the $700–500 \ cm^{-1}$ region (systematically four bands in the Ge and Sn compounds) of weak to moderate intensity (Fig. 5). Some (if not all) of them can be reasonably assigned to ν_4 (for which the group theoretical analysis predicts four Raman active components).

One or two strong bands are observed near $450 \ cm^{-1}$. Their frequency is slightly, but systemati-

spectrum exhibits the six bands predicted by group theory, including near $1000 \ cm^{-1}$ a weak band which can reasonably be assigned to ν_1. The extension of the PO_4 stretching modes to frequencies higher than
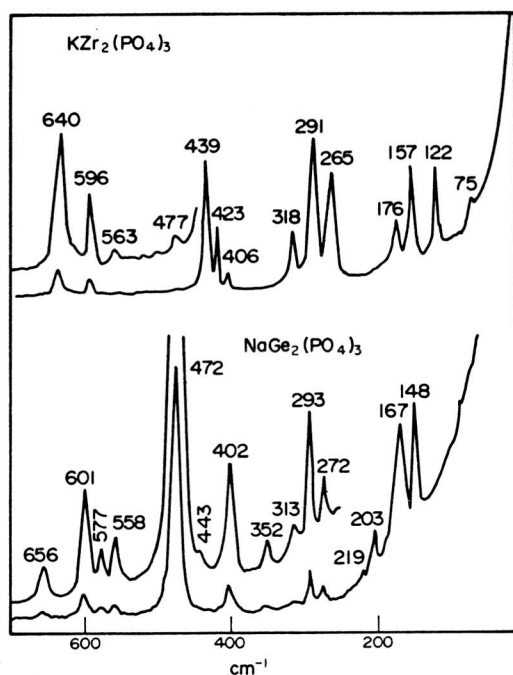
Fig. 5. Examples of Raman spectra in the medium and low frequency region.

cally, higher for Hf than for Zr compounds, and they cannot be assigned to a translation of the M^{IV} cation: these bands are most probably components of v_2. One or two additional weak bands may also be present in the same frequency region, in agreement with the fact that we expect four Raman active components of v_2. It appears from the results that, by and large, there is no general characteristic relationship between the nature of M^{IV} and the Raman active PO_4 bending modes.

Infrared spectra. Apart from the noticeable exception of $NaTi_2(PO_4)_3$, with only two bands at 638 and 568 cm^{-1}, the 700–500 cm^{-1} region shows three or four bands, against a total of five components expected for v_4 (Fig. 3).

The identification of v_2 is more difficult for at least two reasons: first, its expected low intensity in the i.r. and second the increased possibility of overlapping or mixing with external modes.

Weak bands are generally observed in the 500–400 cm^{-1} region, but the lack of analogies between the spectra precludes any systematic assignment.

External modes

Preliminary remarks. A detailed assignment of the external modes is, for many bands, difficult or even impossible for several reasons. First, because, especially for the weak bands, it is impossible to find an unquestionable band to band correlation between suitable compounds and second, because the fairly numerous external modes are distributed among a small number of representations (25 Raman active, A_{1g} and E_g; 27 i.r. active, A_{2u} and E_u), a situation which greatly facilitates vibrational interactions.

M^I *translations.* After BARJ et al. [2], the lowest-lying i.r. band is observed at 83, 72 and 32 cm^{-1} for Na, K and $AgZr_2(PO_4)_3$, respectively, and thus must be assigned to a translation of the monovalent cation. According to our results, this relationship does not hold for the larger cations Rb, Cs and Tl: the frequency slightly *increases* when going from Rb to Cs compounds, very probably because the available octahedral holes are too small for the usual ionic radius of these large cations.

The peculiar case of Li translations was investigated with the help of ^6Li–^7Li isotopic species. A significant isotopic shift (175–167 cm^{-1}) was observed in the low-frequency spectrum of $LiGe_2(PO_4)_3$, whereas $LiTi_2(PO_4)_3$ gave only small shifts distributed over the bands of the 150–350 cm^{-1} region. No correlation could be found with the band(s) assigned to the translation of the other M^I cations.

M^{IV} *translations.* Infrared spectra: The study of the corresponding Hf and Zr compounds (Fig. 6) shows that four low-frequency bands [155, 201, 240 and 334 cm^{-1} in $KZr_2(PO_4)_3$] exhibit a systematic Hf–Zr mass effect, with a still higher frequency for the corresponding Ti compounds. Since the translations of M^{IV} are represented by three i.r. active modes only $(1A_{2u} + 2E_u)$, it may be inferred that some (if not all) of these four bands must be assigned to complex modes including, besides the M^{IV} translation, a contribution of (PO_4) translations or librations.

The Ge translations in $NaGe_2(PO_4)_3$ may be identified by Ge isotopic shifts (^{70}Ge, ^nGe and ^{76}Ge): the

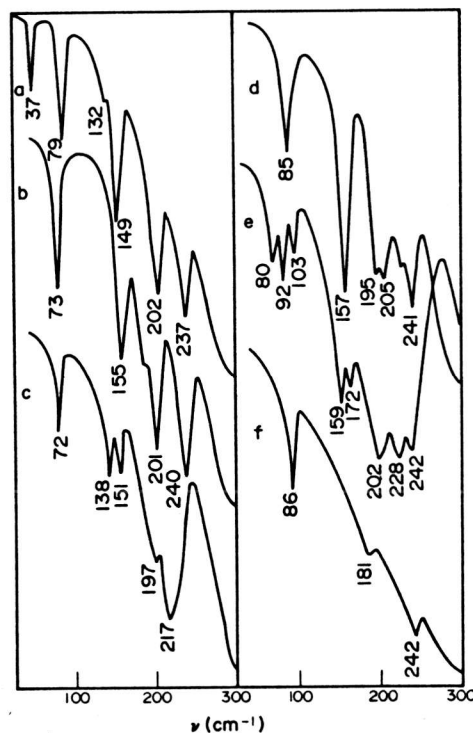

Fig. 6. Examples of far i.r. spectra. M^IM^{IV} = TlZr, KZr, KHf, NaZr, NaSn and KTi for a, b, c, d, e and f, respectively.

actual isotopic compositions are given in Table 2, and the observed isotopic frequencies are collected in Table 3. Two bands only (at 203 and 474 cm^{-1} in the "Ge compound) exhibit an isotopic shift which is unquestionable. There is little analogy with the mass effects observed for the Ti–Zr–Hf series. But this is easily justified by the increased covalency of the Ge–O bond and by a different amount of mixing with other external modes.

Raman spectra: Two bands [122 and 265 cm^{-1} in $KZr_2(PO_4)_3$], against three predicted modes, exhibit an evident Hf–Zr mass effect and are thus assigned to a M^{IV} translation. Three bands in the Raman spectrum of $NaGe_2(PO_4)_3$ exhibit a ^{76}Ge–^{70}Ge isotopic shift which, although small, may be considered as significant in view of the sharpness of the bands and of the very good reproducibility of the frequency measurements (Table 3).

PO_4 translations and librations. These modes are essentially characterized by their low frequency and by the lack of a mass effect of both M^I and M^{IV} cations. This is clearly the case for the lowest-lying Raman band, which has a frequency practically the same for the corresponding Zr and Hf compounds. Since M^I translations are Raman inactive, this band is necessarily a (PO_4) external mode (translation or libration, or both).

The same behaviour (no Zr–Hf mass effect) is observed in the Raman spectrum for bands located near 160–170, 285–295 and 320 cm^{-1}. On the contrary, all the low-frequency i.r. bands of the Zr and Hf compounds are sensitive to the mass of either M^I or M^{IV}, and none of these bands can be assigned to a specific motion of the PO_4 group.

Here again, the extension of these assignments to compounds with another M^{IV} cation (Ti, Sn, Ge) is generally difficult or even impossible, because of the lack of analogies between the spectra. Moreover, a simple change of the monovalent cation M^I (without modification of M^{IV}) may, in some cases at least, lead in the low frequency region to spectral modifications which preclude the finding of a band-to-band correspondance between the spectra (Fig. 7).

DISCUSSION

Two points will be considered here:
i. a comparison between our results and assignments, and those already published by Barj et al. [2];
ii. the search for correlations between specific structural features and some peculiar vibrational properties.

Table 2. Actual isotopic compositions of Ge

Isotope	Atomic percentage		
	^{70}Ge	"Ge	^{76}Ge
70	91.38	20.45	7.69
72	3.73	27.41	6.65
73	1.01	7.77	1.69
74	2.70	36.58	10.08
76	1.18	7.79	73.89
Average atomic mass	70.28	72.60	75.02

Table 3. Isotopic frequencies of $NaGe_2(PO_4)_3$

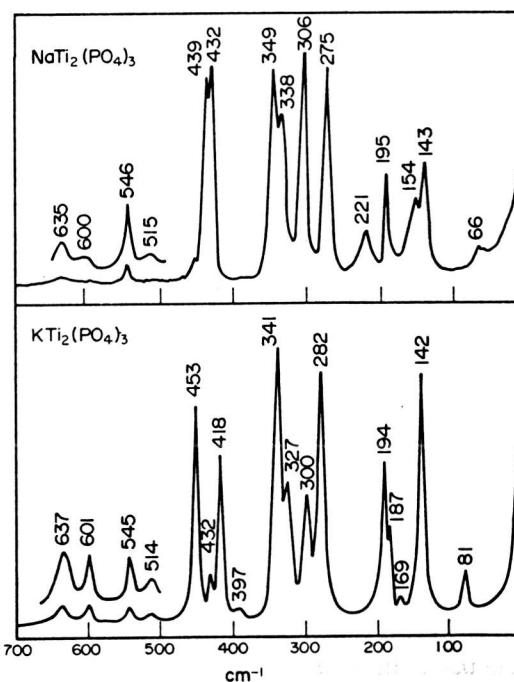| Infrared			Raman		
^{70}Ge	"Ge	^{76}Ge	^{70}Ge	"Ge	^{76}Ge
1261	1262	1261	1243	1244	1243
1215	1215	1215	1128	1128	1127
1118	1117	1118	1105	1105	1105
1083	1082	1082	1072	1072	1072
1060	1060	1060	1053	1053	1053
1006	1006	1006	1007	1007	1007
681	681	680	655.5	656	655.5
648	648	648	601	601	600
583	583	583	577	577	577
545	544	545	557	558	557
495	495	495			
475	474	472	472	472	472
457	457	457			
412	412	412	401	402	401
383	382	·381	352	352	351
330	329	329			
292	293	290	295	293	292.5
253	253	253	274	272	272
216	215	216			
205	203	201	204	203	200.5
			166	167	164
137	137	137	148.5	148	146.5
115	115	115			
93	93	93			

Fig. 7. Comparison of Raman spectra of $NaTi_2(PO_4)_3$ and $KTi_2(PO_4)_3$ in the medium and low frequency region.

Comparison with BARJ *et al.'s results and assignments* [2]

A large part of BARJ *et al.*'s paper deals with the influence, on the vibrational spectrum, of stoichiometric variations and of disorder effects. Our paper does not consider these aspects, but presents a more systematic investigation of the influence of both M^I and M^{IV} cations on the vibrational spectrum. The two papers may thus be considered as complementary. There are, however, some points of disagreement which must be discussed.

Choice of an appropriate vibrational analysis. BARJ *et al.* [2] consider glaserite $K_3Na(SO_4)_2$ as a model structure and suggest discussing the vibrational spectrum on the basis of a simplified $M^I M^{IV}(PO_4)_2$ "spectroscopic cell", with a local symmetry of C_3, C_2 or C_s for the PO_4 tetrahedron. This approximation is certainly useful for discussing the case of compounds with variable stoichiometry, for which a rigorous factor group analysis is impossible; but it is clearly unsatisfactory for most of the stoichiometric compounds investigated in our paper: the factor group contribution must be taken into account.

Assignment of the Raman PO_4 stretching frequencies. Another point is the assignment, in the Raman spectrum, of the (PO_4) stretching vibrations to either symmetric (v_1) or antisymmetric (v_3) modes.

In simple cases such as $KZr_2(PO_4)_3$ (Fig. 1b), we have tentatively assigned the strongest Raman peak to v_1; but for the same compound, BARJ *et al.* [2] assign to v_1 the very weak band located near 975 cm^{-1}, whereas the strongest Raman peak at 1024 cm^{-1} is assigned to a component of v_3. This assignment of v_1 to a weak band is used nearly systematically throughout the paper. This seems to come from a misinterpretation of a paper by CHANTRY and PLANE [13], who have shown that the absolute intensity of the v_1 Raman band of (XO_4) anions in aqueous solution decreases in the series $(ClO_4)^-$, $(SO_4)^{2-}$ and $(PO_4)^{3-}$ as a consequence of the decreasing covalent character of the X–O bond. In fact, CHANTRY and PLANE investigated the intensity change of v_1 only; they never consider the case of v_3, or the intensity ratio I_{v_1}/I_{v_3}. Thus, the intensity decrease of v_1 in the series $(ClO_4)^-$ → $(PO_4)^{3-}$ is by no means a proof that the intensity ratio I_{v_1}/I_{v_3} will also decrease so that $I_{v_3} > I_{v_1}$. Moreover, these intensity measurements were carried out in aqueous solution, and the conclusions cannot be extended to solids. Additional experiments carried out in this laboratory show that, for compounds where the identification of v_1 and v_3 is unquestionable, the intensity of v_1 is generally greater than, or at least equal to, that of v_3.

Thus, we have no reason to believe that, for the phosphates investigated in this paper, the Raman intensity of the v_3 modes must be significantly greater than that of the v_1 modes.

One point remains unsolved, namely the amount of mixing between v_1 and v_3; this possibility has been ignored in BARJ *et al.*'s paper. There is no definite answer to this question; but it may be suspected that the large differences in the patterns given by, say, $KHf_2(PO_4)_3$ and $KGe_2(PO_4)_3$ (Fig. 1) are, at least in part, the result of a different degree of mixing between v_1 and v_3.

Other assignments. There is generally good agreement between the assignments proposed by BARJ *et al.* and by ourselves, for the low frequency bands (e.g. translations of M^{IV} or of M^I). Nevertheless, our results show that, in most cases, these assignments are restricted to a limited number of compounds and cannot be extended to the whole $M^I M_2^{IV}(PO_4)_3$ family. This is the result of the interconnected and complex influence of both M^I and M^{IV} cations.

Discussion of some vibrational features in relation with the structure

To approach this problem, we shall first consider some specific aspects of the structure.

For our purpose, it is useful to consider the structure as constituted of endless columns, directed along the hexagonal c axis, of alternating PO_4 tetrahedra, $M^{IV}O_6$ octahedra and $M^I O_6$ polyhedra which may be described as a trigonal prism or a distorted octahedron strongly elongated along the c_{hex} axis. These columns are interconnected by PO_4 tetrahedra to form a tridimensional lattice including holes which are responsible for the mobility of the M^I cations (Fig. 8). These columns constitute the rigid part of the crystal lattice, and there is a nearly linear relationship between the value of the c_{hex} axis and the ionic radius of either M^{IV} or M^I.

However, the a_{hex} axis *decreases* with *increasing* size of M^I. This may be understood qualitatively if we
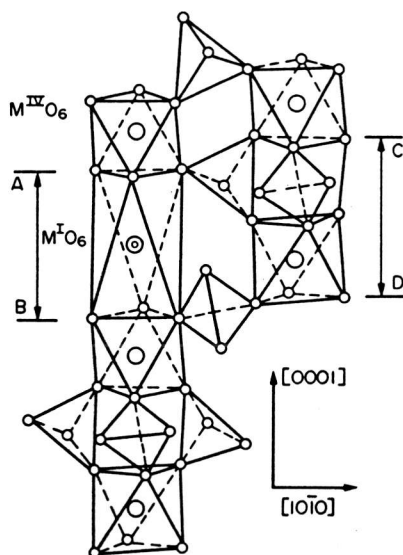
Fig. 8. Part of the structure, showing the columns of $M^I O_6$, ZrO_6 and PO_4 polyhedra, and their interconnection by PO_4 tetrahedra.

Table 4. Influence of M^I on the Raman frequencies of $M^IZr_2(PO_4)_3$

Na	K	Tl	Rb	Cs	Assignment	General trend
1084	1088	1085	1086	1080	ν_3	−
1062	1060	1057	1058	1053	ν_3	−
1026	1024	1013	1020	1014	ν_1	−
				+1006		
643	640	633	638	636	ν_4	−
597	596	593	595	592	ν_4	−
438	439	442	443	451	ν_2	+
425	423	421	422	425	ν_2	
295	291	288	289	288	L or T_{PO_4}	−
263	265	261	265	262	T_{Zr}	
?	157	158	160	169	L or T_{PO_4}	+
127	122	128	126	135	T_{Zr}	+
72	75	83	85	106	L or T_{PO_4}	+

− Frequency decreases with increasing ionic radius of M^I.
+ Frequency increases with increasing ionic radius of M^I.
This table considers only those bands for which the correspondence is unequivocal.

consider the replacement [e.g. in $NaZr_2(PO_4)_3$] of Na by Cs (with ionic radii of 1.02 and 1.67 Å, respectively). This results in a significant increase of the A–B distance (Fig. 8) which in turn will bring some misfit with the corresponding C–D distance in the adjacent column, since the size of the PO_4 and ZrO_6 groups remains essentially the same. This misfit may be reduced by tilting and rotating the interconnecting PO_4 tetrahedra, but this will decrease the column-to-column distance, and hence the value of the a_{hex} axis. It should be realized that this contraction along the a_{hex} axis is allowed by the existence of the empty sites which are characteristic of the $M^IM_2^{IV}(PO_4)_3$ composition. If these sites are totally or partially occupied [e.g. in $Na_4Zr_2(SiO_4)_3$ or $Na_3Fe_2(PO_4)_3$], a contraction along the a axis is impossible, and the nasicon structure can be obtained only with relatively small monovalent cations such as Na^+. These structural adjustments, which depend on the ionic radii of both M^I and M^{IV} cations, are most probably responsible for the great diversity of the spectra.

High frequency infrared band. This band is characterized by a rather high frequency, going from 1185 cm^{-1} [lowest value, in $CsZr_2(PO_4)_3$] to 1269 cm^{-1} [highest value, in $LiGe_2(PO_4)_3$]. This frequency is essentially influenced by the ionic radius of M^{IV}. These facts may be explained by an interaction between the P–O and the adjacent M^{IV}–O bonds.

From the atomic positions given by HONG [7] for $NaZr_2(PO_4)_3$, we have calculated the following distances and angles: P–O_1: 1.521 Å; Zr–O_1: 2.044 Å; P–O_1–Zr: 157.50°; P–O_2: 1.551 Å; Zr–O_2: 2.068 Å; P–O_2–Zr: 143.85°. The large P–O_1–Zr angle suggests that the force constant of the P–O_1 stretch may contain some contribution from the Zr–O_1 bond; moreover, this P–O_1 combines the shortest P–O distance, the shortest Zr–O distance and the largest P–O–Zr angle which may explain the high P–O frequency and the strong influence, at this frequency, of the nature of the M^{IV} cation.

The influence of the ionic radius of M^I is smaller, but it is not negligible, especially for the largest M^I cations (Rb, Cs). It may be qualitatively explained by the structural adjustments previously discussed (Fig. 8).

Influence of M^I on the vibrational frequencies. Besides the specific influences discussed above, the vibrational frequencies of a series of isomorphic compounds are often slightly modified by second-order effects, such as the molecular volume. For most of the internal modes (and some of the external ones), there is generally a small frequency decrease when the molecular volume (or the ionic radius of the cation) increases. This general trend is verified for the high or medium frequency bands of the phosphates discussed here (Table 4). But for some of the lower frequency bands, a reverse trend is observed: the frequency *increases* with the ionic radius of M^I; the largest variation is observed for the lowest-frequency band, going from 72 cm^{-1} in the Na compound to 106 cm^{-1} in the Cs compound. This behaviour is not exceptional, since it is also observed for other M^{IV} compounds, and for some i.r. bands. Moreover, it is not restricted to one specific type of vibration, since it is observed on one component of ν_2, one translation of M^{IV} and two PO_4 external modes.

It must be pointed out that the frequency increase is the smallest for the $Na^+ \rightarrow K^+$, and the largest for the $Rb^+ \rightarrow Cs^+$, replacement. This may be compared with the contraction of the a_{hex} axis with increasing size of the M^I cation, and we suspect that the vibrations under discussion have a predominant component along the a axis.

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