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Vibrational Spectra and Structure of $LiB^{2+}PO_4$ Compounds with $B = $ Sr, Ba, Pb

MARIE-THÉRÈSE PAQUES-LEDENT

Department of General Chemistry, Sart Tilman-4000 Liege, Belgium

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The vibrational spectra of $LiB^{2+}PO_4$ compounds with B = Ba, Sr, Pb are studied. Typical vibrations of LiO_4 and PO_4 tetrahedral have been identified. This work leads one to propose structural types to which the three compounds belong: $LiBaPO_4$ is isomorphous with orthorhombic $LiKSO_4$ while $LiSrPO_4$ is related to monoclinic $RbLiSO_4$; $LiPbPO_4$, with a more distorted structure, most likely contains lithium atoms with a tetrahedral coordination.

Introduction

$LiB^{2+}PO_4$ (B = Sr, Ba, Pb) compounds have been reported in the literature (*1*, *2*, *4*). First, Wanamaker and Spier (*1*) have studied the luminescent properties of copper-activated Sr and Ba orthophosphates, but the crystal structures of the Sr and Ba compounds are not discussed. Nevertheless the samples of their two compounds do not correspond to pure orthophosphates. The X-ray diagrams of our samples which are obtained after short cookings, are similar to the published X-ray data. But the ir spectra show that no such samples correspond to pure orthophosphates. Our studied samples are submitted to prolonged cookings: We obtain pure orthophosphates without any increase of the maximal temperature (*2*). So far, the crystal structures of Sr and Ba phosphates were unknown.

Recently $LiPbPO_4$ single crystals have been prepared and an orthorhombic unit cell has been determined by Brixner and Foris (*4*). Our powdered sample corresponds exactly with their $LiPbPO_4$.

We have studied the ir and Raman spectra of the three compounds with the object of improving on the structural determination. On the basis of our X-ray powder diagrams and our vibrational spectra, it is indicated that $LiKSO_4$ and $LiBaPO_4$ have strongly related structures.

$LiSrPO_4$ is not isomorphous with $LiPbPO_4$, despite the fact that the ionic radii of Sr^{2+} and Pb^{2+} are virtually identical. For the three compounds, we propose tetrahedral coordination of Li atoms.

B. Experimental

Synthesis

All the compounds have been synthetized by a solid-state reaction between lithium carbonate, $(NH_4)_2HPO_4$ and $BaCO_3$, $SrCO_3$ or $PbCO_3$. The mixtures are slowly heated in corundum crucibles at various temperatures: 920°C during 3 weeks for $LiBaPO_4$, 950°C during 1 week for $LiSrPO_4$, 800°C during 2 days for $LiPbPO_4$ (*4*), with several intermediate mixings and grindings, particularly for the Ra compound. $^6Li_2CO_3$ is obtained from metallic lithium containing 95.68% of ^6Li (by reaction between LiOH and pure gaseous CO_2).

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Spectra and X-Ray Diffraction

The ir spectra have been recorded by a conventional pressed disk technique with a Beckman ir spectrometer (200–1000 cm^{-1}) and a Polytec FIR 30 interferometer (40–350 cm^{-1}). The Raman spectra were obtained with a Coderg PH O monochromator, equipped with a 50-mW He–Ne laser. The powdered sample is introduced into a glass capillary and formed into a cone which is illuminated along its axis by the laser beam. The scattered light is collected at a 90° angle. The X-ray powder diagrams are obtained with a C.G.R. diffractometer using CuK_α and CoK_α radiation.

C. Results and Discussion

1. X-Ray Powder Diagrams

The powder patterns for Sr and Ba compounds are shown in Fig. 1. The $LiBaPO_4$ diagram shows strong analogies with the orthorhombic phase of $LiKSO_4$ (*3*); the same is indicated independently by the vibrational study. Therefore, owing to the observed reflections, we propose for $LiBaPO_4$ an orthorhombic $LiKSO_4$ structure and the C_{2v}^9 space group with $Z = 4$. The cell dimensions are: $a = 8.72$ Å, $b = 5.19$ Å, $c = 8.63$ Å. The Sr compound is less symmetric. Its X-ray powder diagram shows many similarities with the monoclinic double sulfate $RbLiSO_4$ (*3*) whose structure is strongly related to the $LiKSO_4$ orthorhombic phase. The X-ray diagram can be interpreted assuming a monoclinic unit cell with C_{2h}^5 symmetry as for $RbLiSO_4$. $LiPbSO_4$ belongs to the C_{2v}^9 space group with eight formula units in the cell (*4*) but is *not* isomorphous with the Ba compound.

$LiKSO_4$ crystal structures. $LiKSO_4$ structures are built upon 3 LiO_4 and 3 SO_4 shared tetrahedra which form mixed rings, normal to the "*c*" axis (Fig. 2). This layer model forms big cavities available for larger ions such as K, Rb, and Cs. The orthorhombic phase (or phase II) of $LiKSO_4$ belongs to the C_{2v}^9 space group and all the atoms are located on sites with C_1 symmetry. Three adjacent tetrahedra are placed at the "up" position with regard to the "c" axis, the three latter at "down" positions.

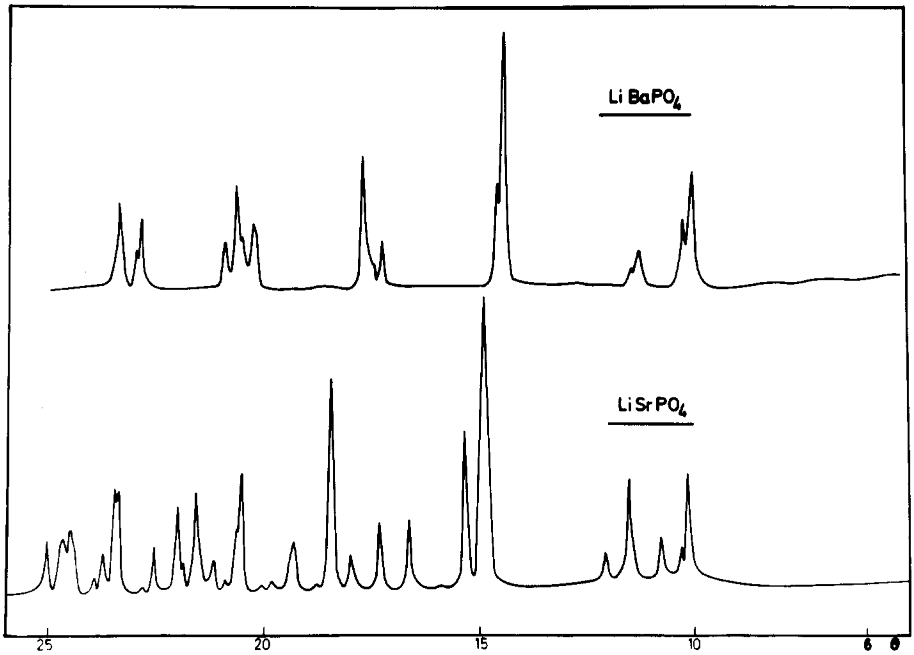
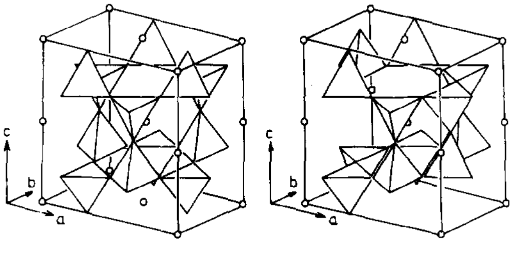


FIG. 1. X-Ray pattern of $LiBaPO_4$ and $LiSrPO_4$. CoK_α radiation.



(a) (b)

FIG. 2. Tridymite (a) and *Imma* (b) structure types.

This structure type is a *Imma* structure type (Fig. 2b) and is also observed for other compounds: $RbLiSO_4$, $CsLiSO_4$, $RbLiBeF_4$, $CsLiBeF_4$. The hexagonal phases of $LiKSO_4$ (I and III) show mixed rings with alternately "up" and "down" tetrahedra. They belong to the tridymite structure type (Fig. 2a).

2. *Infrared and Raman Spectra*

LiBaPO$_4$. An obvious analogy exists between the ir spectra of $LiKSO_4$ (*5*), $CsLiSO_4$, and of $LiBaPO_4$, not only in the spectral range 550–1200 cm^{-1} assigned to internal bending and stretching modes of sulfate or phosphate ions, but also in the range below 550 cm^{-1}. The vibrational representation related to the $LiKSO_4$ orthorhombic crystal is: $\Gamma_{\text{vibr}} = 20A_1 + 21A_2 + 20B_1 + 20B_2$ (Table I). A_2 modes are infrared-inactive

In our ir experimental data, the most interesting features are the strong isotopic mass effects observed when ^{6}Li substitutes ^{7}Li: between 400 and 500 cm^{-1}, large shifts appear, while the other two bands (above and below this region) are weakly displaced (Table II).

These frequency shifts allow one to indentify unambiguously the vibrational modes involving motion of Li atoms (*6*). Moreover, the narrow frequency range (400–500 cm^{-1}) where such modes are observed, indicates a tetrahedral coordination of lithium. This last inference confirms the X-ray powder study.

Between 550 and 700 cm^{-1}, the bands correspond essentially to the PO_4 antisymmetric bending modes, while between 900 and 1200 cm^{-1} appear the stretching PO_4 modes. We see at 958 cm^{-1} one weak component from the symmetric stretching mode ν_1. In the low-frequency region, the three bands correspond to lattice modes with motion of heavy Ba atoms.

TABLE I

VIBRATIONAL CORRELATION DIAGRAM: C_{2v}^9 SPACE GROUP, C_1 SITE SYMMETRY

$LiKSO_4$: 4 (=n) equivalent sets of each atom. $LiPbPO_4$: 2 × 4 equivalent sets of each atom

Site group C_1 $n = 4$	Correlation	Factor group C_{2v}
$(x, y, z)\,A$ (×4)		A_1 (ir, R) A_2 (R) B_1 (ir, R) B_2 (ir, R)

$LiKSO_4$: $\Gamma_{\text{vibr}} = 20A_1 + 21A_2 + 20B_1 + 20B_2$
$Z = 4$
$LiPbPO_4$: $\Gamma_{\text{vibr}} = 41A_1 + 42A_2 + 41B_1 + 41B_2$
$Z = 8$
Internal modes: XO_4 tetrahedron

Molecular point group T_d	Site group C_1 $n = 4$	Factor group C_{2v}
$A_1(\nu_1)$	A (×4)	$A_1 + A_2 + B_2 + B_1$
$E(\nu_2)$	$2A$ (×4)	$2A_1 + 2A_2 + 2B_1 + 2B_2$
$T_2(\nu_3, \nu_4)$	$3A$ (×4)	$3A_1 + 3A_2 + 3B_1 + 3B_2$

TABLE II

FREQUENCIES, ISOTOPIC SHIFTS, AND ASSIGNMENTS FOR $LiBaPO_4$. INFRARED AND RAMAN

ir (cm^{-1})				Raman (cm^{-1})			
$^7LiBaPO_4$	Δ_{isot}	$^6LiBaPO_4$	Assignments	$^7LiBaPO_4$	Δ_{isot}	$^6LiBaPO_4$	Intensity
64		64	Lattice modes with motion of Ba atoms	107			w
82	+1	83		168			m
				259			vw
154	+6	160		398 sh	7	405 sh	
	+6	426	Internal $\nu_2(PO_4)$	424		424	vs
420	+35	445	Vibrations related to the internal LiO_4 modes				
463	+24	487		~455	~18	473	vw
482	+28	510					
				570	6	576	s
572	+1	573	Internal $\nu_4(PO_4)$	580	5	585	s
587	+5	592		600 sh		600 sh	
958		958	Internal $\nu_1(PO_4)$	930.5			vw
				954			vs
~1037	~+2	~1039	Internal modes $\nu_3(PO_4)$	1021.5			m
				1033.4			m
				1108			w

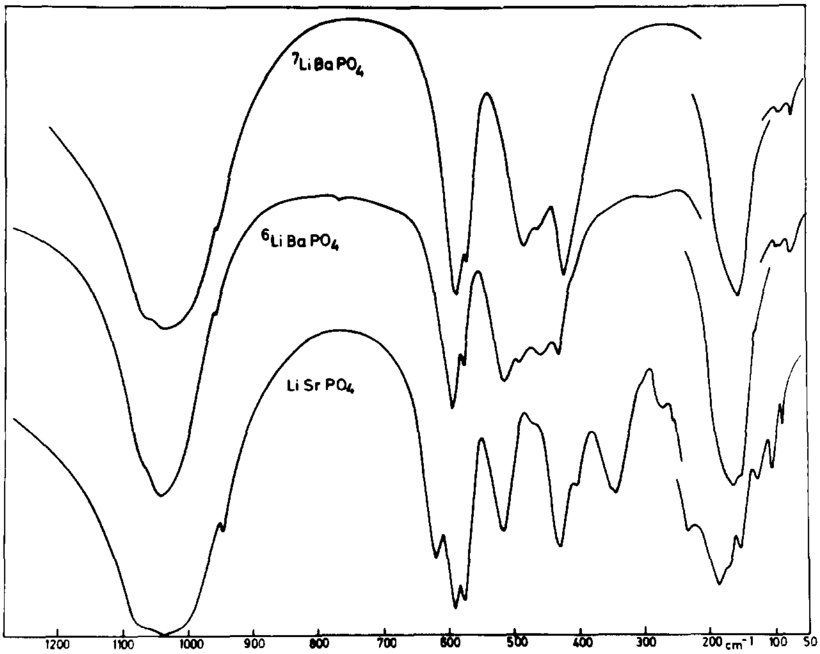


FIG. 3. Infrared spectra of $^{7,6}LiBaPO_4$ and $^7LiSrPO_4$.

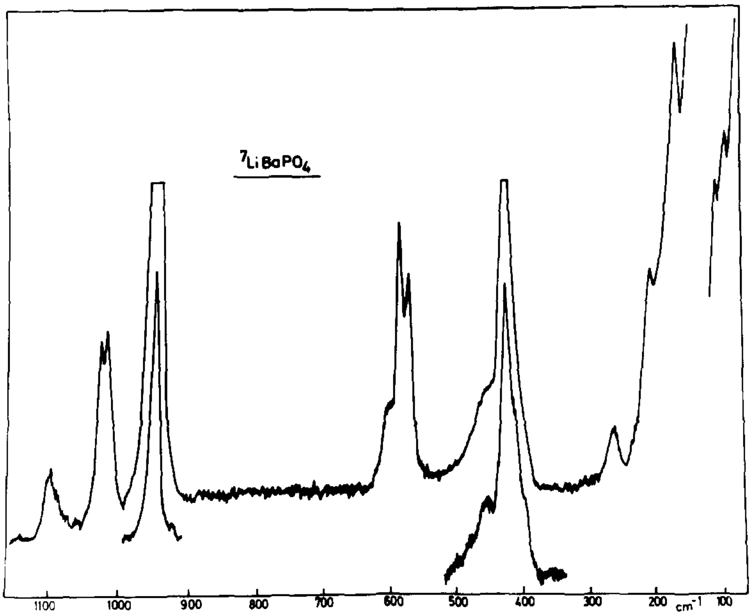


FIG. 4. Raman spectrum of LiBaPO$_4$. Slit = 2 cm^{-1}.

Owing to the values of the observed isotopic shifts, it is clear that the vibrational interactions between the modes related to the internal SO$_4$ and PO$_4$ vibrations are those related to the next LiO$_4$ groups, are weak in this structure. Moreover, the quite similar pattern of the ir spectra for hexagonal LiKSO$_4$, CsLiSO$_4$, RbLiSO$_4$, LiBaPO$_4$ between 300 and 1200 cm^{-1} indicates the vibrational modes in these cases to be weakly sensitive to the mixed rings symmetry.

Only a few frequencies are available from the numerous predicted active modes but we observe many coincidences between the Raman and ir frequencies. This is in accord with a noncentered crystallographic unit cell and confirms the C_{2v}^9 space group.

The ^{7}Li–^{6}Li isotopic shifts led to the

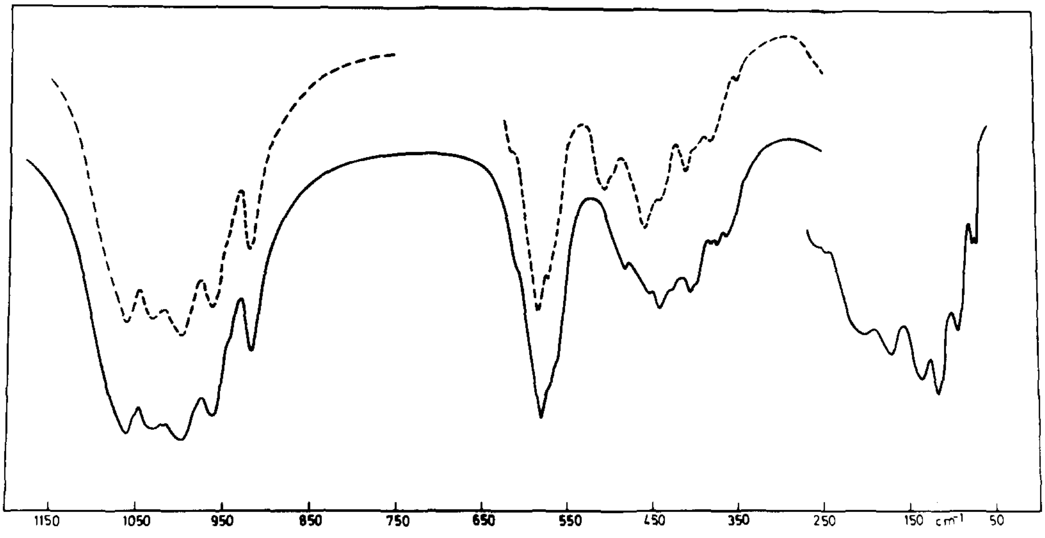


FIG. 5. Infrared spectrum of LiPbPO$_4$.

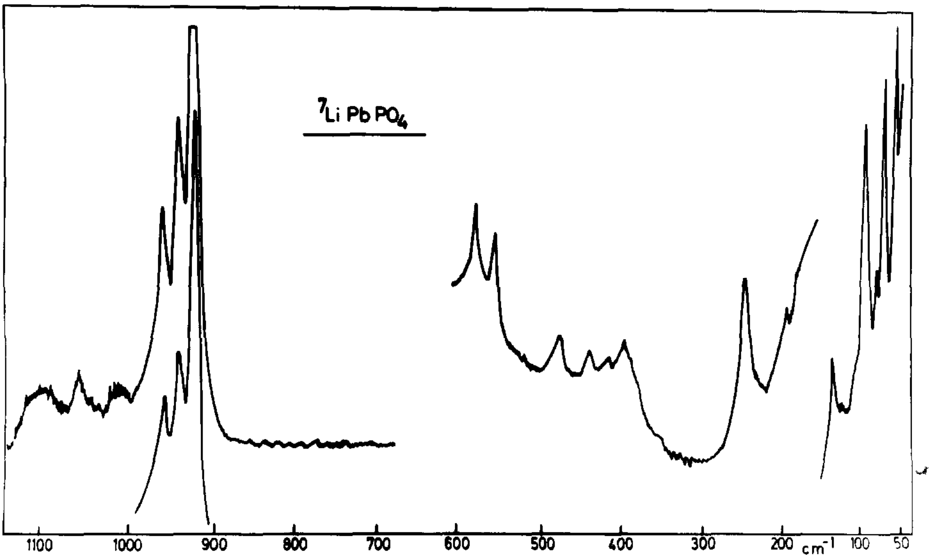


FIG. 6. Raman spectrum of $LiPbPO_4$; 50 to 150 cm^{-1}: slit = 1 cm^{-1}, 150 to 1200 cm^{-1}: slit = 2 cm^{-1}.

following assignments in Raman. The strong peak at 424 cm^{-1}, is unaffected and assigned to the symmetric ν_2 bending PO_4 mode; at 570 and 580 cm^{-1} antisymmetric modes appear. The very strong peak at 954 cm^{-1} is assigned to the A_1 component of the ν_1 mode; at 930 cm^{-1} we see another split component (with A_2 or B symmetry) of the ν_1 mode; three other peaks between 1000 and 1150 cm^{-1} are related to antisymmetric stretching vibrations.

From 398 to 500 cm^{-1} we detect frequencies related to vibrations of LiO_4 groups in the mixed rings. As expected, the low polarizability of Li ions has as a consequence a very weak Raman intensity for the modes involving primarily vibration of Li atoms. Lattice modes with motion of barium atoms appear below 300 cm^{-1}.

$LiSrPO_4$. This double phosphate has a more complicated spectrum; an obvious correlation appears between this one and the $LiBaPO_4$ spectrum but the lower crystal symmetry leads to observation of more bands, chiefly below 700 cm^{-1} (Table III). For this reason the isotopic substitution does not allow simple assignments for the bands: Between 300 and 700 cm^{-1}, three bands are strongly shifted and correspond to translational modes with motion of lithium. The 576, 590 bands are essentially related to the $\nu_4(PO_4)$ mode, the

TABLE III

FREQUENCIES, ISOTOPIC SHIFTS FOR $LiSrPO_4$

Δ_{isot}	$^7LiSrPO_4$	$^6LiSrPO_4$
	87	
	106	
	126	
	153	
	174	
	188	
	215 sh	
	233 sh	
~8	~270 ff	~278 ff
50	343	393
	~405 sh	
7	428	435
6	468 sh	474
39	516	555
1	576	577
5	590	595
21	618	639
	948	948
~3	~1037	~1040

428 cm^{-1} band being assigned to the $\nu_2(PO_4)$ mode. These assignments are very close to those of $LiBaPO_4$; nevertheless the vibrational interactions here seem to be stronger between antisymmetric bending PO_4 mode and Li–O vibration (see the 618-cm^{-1} band). The breadth of the spectral region where characteristic frequencies of Li–O vibration are observed suggests very distorted LiO_4 tetrahedra.

Between 900 and 1200 cm^{-1} we recognize one component of the $\nu_1(PO_4)$ mode (at 948 cm^{-1}); components of the $\nu_3(PO_4)$ mode appear in the same range as for $LiBaPO_4$ compound.

The many low-frequency bands correspond to lattice modes involving primarily Sr–O vibration.

$LiPbPO_4$. The vibrational analysis for a $LiPbPO_4$ crystal with 8 units per cell, leads to the irreducible representation

$$\Gamma_{\text{vibr}}: 41A_1 + 42A_2 + 41B_1 + 41B_2.$$

The vibrational pattern shows no strong analogy with the former Sr and Ba compounds.

Isotopic frequencies and detailed assignments are listed in Table IV. We comment on some results. Between 500 and 1100 cm^{-1} we observe the frequencies typical of internal modes of PO_4 tetrahedra; the band corresponding to the vibrational modes especially related to motion of lithium (see isotopic shifts) appears in the 400–525-cm^{-1} range. That allows us to propose tetrahedral coordination for the Li atoms in $LiPbPO_4$ and so

TABLE IV

INFRARED AND RAMAN FREQUENCIES, ISOTOPIC SHIFTS, AND ASSIGNMENTS FOR $LiPbPO_4$

ir (cm^{-1})				Raman (cm^{-1})			
$^7PoPbPO_4$	Δ_{isot}	$^6LiPbPO_4$	Assignments	$^7LiPbPO_4$	Δ_{isot}	$^6LiPbPO_4$	Intensity
71		71	Lattice modes involving primarily Pb–O vibrations				
75		75					
93		93		37		37	
115	1	116		57		57	vs
135		135		71		71	vs
169		169		94.5		94.5	vs
~202		~202		137		137	m
246 sh		246 sh		247		247	s
257 sh		257 sh					
380 sh	~5	~385 sh					
405	5	410	Internal $\nu_2(PO_4)$	395	−1.5	393.5	w
			Modes related to internal Li–O vibration in the $Li\text{–}O_4$ groups			408 sh	
				422	+11	433	w
443	16	459		433	+12	455	w
482	26	508		482.5	+13	495.5	w
580.	4	584	Internal $\nu_4(PO_4)$	560		560	m
				582		582	m
919		919	Components of $\nu_1(PO_4)$	926			vs
964		964		944			s
				961			s
~1000		~1000	Components of $\nu_3(PO_4)$	1015			w
1034		1034		1058			w
1062		1062		1078			w

to resolve partly the structural model; without doubt this is the most interesting consequence of this study.

Two ir frequencies with quite distinguishable values, correspond to two components of internal $\nu_1(PO_4)$ modes and appear likely here in connection with the presence of two different sets of PO_4 groups in the structure, as required by 8 units per cell.

For the Raman spectra we are led to analogous assignments: All the peaks shifted by ^7Li–^6Li substitution appear between 400 and 500 cm^{-1} and are assigned to LiO_4 modes. At ~408 cm^{-1} and between 500 and 600 cm^{-1} we observe, respectively, the symmetric and antisymmetric bending PO_4 vibrations. Peaks at 926, 944, and 961 cm^{-1} correspond to internal PO_4 modes from the symmetric stretching vibration; above 1000 cm^{-1} appear corresponding antisymmetric modes.

As for $LiBaPO_4$, many but no systematic coincidences, occur between ir and Raman frequencies, which is in accordance with the C_{2v}^9 space group. In ir and Raman spectra, we observe frequencies below 250 cm^{-1} that correspond to lattice modes involving primarily Pb–O vibration.

D. Conclusion

A comprehensive survey of the vibrational assignments for the two nonisomorphous phosphates $LiBaPO_4$ and $LiPbPO_4$, shows that the different spectral regions (500–1100 and 400–500 cm^{-1}) receive quite analogous assignments. This last result comes evidently from the presence of heavy atoms (Ba, Pb) next to the very light Li and P atoms, a situation that is favorable for the observation of the tetrahedral coordination of Li atoms.

From this study, the structure of $LiBaPO_4$ is now cleared up: $LiBaPO_4$ and orthorhombic $LiKSO_4$ are isomorphous, the tetrahedral coordination of lithium being established from ^7Li–^6Li isotopic mass effects in the vibrational spectrum. The structure of $LiSrPO_4$ is partly resolved because we have shown the connection between this structure and $RbLiSO_4$.

Finally, the vibrational data strongly support the tetrahedral coordination for lithium in $LiPbPO_4$.

On the whole, this work leads both to the resolution of a large share of the crystal structure for the three compounds and to the proposal of a rather detailed assignment of their vibrational spectrum.

Acknowledgments

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