ISOMORPHISM AND POLYMORPHISM OF THE COMPOUNDS Li$_3$PO$_4$, Li$_3$AsO$_4$ AND Li$_3$VO$_4$

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Abstract—The structural study of the compounds Li$_3$PO$_4$, Li$_3$AsO$_4$ and Li$_3$VO$_4$ has been made by X-ray powder diffractometry and i.r. absorption spectroscopy. In addition to a previously described structure, which has been found for Li$_3$PO$_4$ and Li$_3$AsO$_4$ only and must be considered as a high temperature form, a new, low-temperature form, has been found for Li$_3$PO$_4$, Li$_3$AsO$_4$ and Li$_3$VO$_4$. The following unit cell dimensions (in angstroms) have been deduced from X-ray powder patterns:

Low temperature form:		orthorhombic		$Pmn2_1$–C_{2v}^7
		a	*b*	*c*
Li$_3$PO$_4$		6·13	5·25	4·87
Li$_3$AsO$_4$		6·27	5·38	4·95
Li$_3$VO$_4$		6·33	5·45	4·96

High temperature form:	orthorhombic		$Pmna$–D_{2h}^{16}
Li$_3$PO$_4$	6·12	10·48	4·93
Li$_3$AsO$_4$	6·28	10·76	5·05

Both structures are extremely similar, and are characterized by four-fold co-ordination of lithium, as deduced from the study of the ^{6}Li–^{7}Li isotopic shifts in the spectra. Vibrational interactions between some LiO$_4$ stretching frequencies and the PO$_4$, AsO$_4$ or VO$_4$ bending frequencies are revealed by abnormal ^{6}Li–^{7}Li isotopic shifts.

INTRODUCTION

THE STRUCTURE of Li$_3$PO$_4$ has been accurately determined by ZEMANN[1] who found that all cations (P and Li) are tetrahedrally co-ordinated. No similar detailed study has been done for Li$_3$AsO$_4$ and Li$_3$VO$_4$, but isotypism between these three compounds is suggested by X-ray powder diffraction data of ZEMANN[1] and BLASSE.[2]

The i.r. spectra of these compounds were investigated in this laboratory as a part of a more general study of the vibrational behaviour of Li—O bonds;[3] but lack of reproducibility of some preliminary results induced a systematic reinvestigation by both X-ray and i.r. methods, which eventually led to the conclusion that Li$_3$PO$_4$ and Li$_3$AsO$_4$ exhibit polymorphism, with very intimately related structures.

EXPERIMENTAL

Synthesis of the compounds was first attempted by wet methods, starting from moderately concentrated solutions of LiCl and Na$_3$PO$_4$ (or Na$_3$AsO$_4$). This leads, however, to badly crystallized precipitates, irrespective of temperature or concentration conditions. Only by hydrothermal treatment (4 days at 245°C) was precipitated Li$_3$PO$_4$ converted into a fairly well crystallized phase (some diffuseness remained however, in the X-ray powder diagram) which, as will be shown later on, is the low-temperature form of Li$_3$PO$_4$.

All other phases (pure compounds and solid solutions) were prepared by dry methods, starting

[1] J. ZEMANN, *Acta crystallogr.* 13, 863 (1960).
[2] G. BLASSE, *Z. anorg. allg. Chem.* 331, 44 (1964).
[3] P. TARTE, *Spectrochim. Acta* 20, 238 (1964); *ibid.* 21, 313 (1965).

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from Li_2CO_3, $NH_4H_2PO_4$, $(NH_4)_2HAsO_4$ and V_2O_5: the stoicheiometric quantities of the necessary compounds are thoroughly mixed and ground, then slowly heated in covered Pt crucibles up to 900°C. This temperature is maintained for 4–5 hr, this duration being quite sufficient for completion of the reaction. The samples are, either air quenched, or submitted to a slow cooling in the furnace. ^7Li and ^6Li compounds are not isotopically pure: the former corresponds to the natural isotopic abundance (92·6% ^7Li), the latter is 95% pure in ^6Li.

The i.r. spectra were registered with Unicam SP100 (NaCl and KBr prisms) and Perkin–Elmer 112 (CsBr prism) spectrometers. The KBr disc method has been used throughout; no ionic exchange occurred in the discs, as shown by running some nujol mulls.

The X-ray powder diffraction diagrams were obtained by the reflection method with a CGR diffractometer, using CuKα radiation.
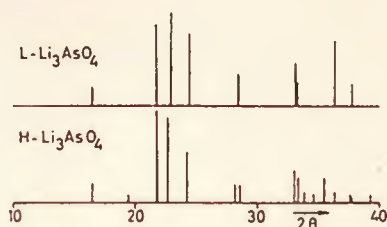

FIG. 1.—Schematic diagram of the X-ray diffraction patterns of the high and low-temperature forms of Li_3AsO_4 (low-angle region only).

RESULTS

X-ray powder diffraction data

All samples of Li_3PO_4 prepared by the dry method give identical powder diffraction diagrams, irrespective of the type of thermal treatment (quenching or slow cooling). Apart from a slight discrepancy in the value of the *b* axis, this diagram may be completely indexed on the basis of the structure and cell dimensions proposed by ZEMANN,[1] and there is no doubt about the identity of the phases.

The behaviour of Li_3AsO_4 is, however, somewhat different: samples removed from the furnace at 900 or 850°C and air quenched give an X-ray powder diagram which is very similar to, and is easily indexed by comparison with the Li_3PO_4 pattern. But samples slowly cooled down, and removed from the furnace at 600°C exhibit a diagram which, although clearly related to the preceding, is more simple (Fig. 1).

This diagram may be tentatively indexed by comparison with the preceding one, the same *h k l* indices being assigned to corresponding low-angle reflexions. This leads to a complete indexing of the new diagram where, however, all *k* indices are even: this suggests that the *b* axis should be halved. The observed reflections seem to follow the limiting conditions: $h00$ and $00l$: *h* and $l = 2n$, $0k0$: no conditions, $hk0$: no condition; $h0l$: $h + l = 2n$; $0kl$: no conditions.

The corresponding space group is $Pmn2_1-C_{2v}^7$. This type of structure (which will be called the low temperature form) is easily reconverted into the high-temperature form by heating to 850° and air-quenching: the transformation is thus reversible. The following unit cell dimensions have been deduced from the X-ray powder diagrams:

Li_3AsO_4, high: $a_0 = 6·28_0$ $b_0 = 10·76_4$ $c_0 = 5·05_6$ Å
Li_3AsO_4, low: $a_0 = 6·27_6$ $b_0 = 5·38_6$ $c_0 = 4·95_6$ Å

The assumed error is $\pm0·01$ Å.

TABLE 1.—X-RAY POWDER DIAGRAM OF L–Li_3AsO_4

Relative intensity	$d_{obs.}$	h k l	$d_{calc.}$*	$d_{calc.} - d_{obs.}$
44	5·383	0 1 0	5·385	+0·002
≫100	4·087	1 1 0	4·087	0·000
≫100	3·889	1 0 1	3·888	−0·001
>100	3·646	0 1 1	3·647	+0·001
74	3·146	⌈2 0 0	3·138	−0·008
		⌊1 1 1	3·153	+0·007
94	2·710	2 1 0	2·711	+0·001
(60)	2·693	0 2 0	2·693	0·000
100	2·476	⌈0 0 2	2·477	+0·001
		⌊1 2 0	2·474	−0·002
48	2·377	2 1 1	2·378	+0·001
?	2·365	0 2 1	2·366	+0·001
10	2·249	0 1 2	2·250	+0·001
24	2·212	1 2 1	2·213	+0·001
40	2·118	1 1 2	2·118	0·000
7	2·042	2 2 0	2·043	+0·001
24	1·946	⌈2 0 2	1·944	−0·002
		⌊3 1 0	1·949	+0·003
18	1·927	3 0 1	1·927	0·000
31	1·888	2 2 1	1·889	+0·001
28	1·829	2 1 2	1·829	0·000
17	1·814	3 1 1	1·814	0·000
12	1·794	0 3 0	1·795	+0·001
16	1·750	1 2 2	1·750	0·000
3	1·726	1 3 0	1·726	0·000
3	1·688	0 3 1	1·688	0·000
14	1·652	3 2 0	1·652	0·000
26	1·630	1 3 1	1·629	−0·001
14	1·598	⌈3 0 2	1·598	0·000
		⌊1 0 3	1·597	−0·001
13	1·579	⌈0 1 3	1·579	0·000
		⌊2 2 2	1·577	−0·002
26	1·567	3 2 1	1·567	0·000
47	1·558	2 3 0	1·558	0·000
15	1·553	⌈3 1 2	1·532	−0·001
		⌊1 1 3	1·531	−0·002
5	1·506	4 1 0	1·506	0·000·
7	1·454	0 3 2	1·453	−0·001
13	1·441	4 1 1	1·441	0·000
30	~⌈1·410	2 1 3	1·410	0·000
	~⌊1·408	0 2 3	1·407	−0·001
12	1·374	⌈3 2 2	1·374	0·000
		⌊1 2 3	1·374	0·000
8	1·355	4 2 0	1·355	0·000
24	1·320	2 3 2	1·319	−0·001
21	1·317	1 4 0	1·316	−0·001
21	1·315	3 3 1	1·313	−0·002
8	1·308	4 2 1	1·307	−0·001
30	1·297	⌈0 4 1	1·299	+0·002
		⌊3 0 3	1·296	−0·001
30	1·286	4 1 2	1·287	+0·001
15	1·273	1 4 1	1·272	−0·001
12	1·261	3 1 3	1·260	−0·001
12	1·238	⌈0 0 4	1·239	+0·001
		⌊2 4 0	1·237	−0·001

* For the following unit cell dimensions: $a_0 = 6.276$, $b_0 = 5.386$, $c_0 = 4.955$ Å.

As mentioned above, no change in the crystal structure is observed when Li_3PO_4 is slowly cooled down; but samples prepared by hydrothermal methods (see experimental part) show the same X-ray powder diagram as the low-temperature Li_3AsO_4.

$$Li_3PO_4 \text{ low: } a_0 = 6 \cdot 13, \quad b_0 = 5 \cdot 25, \quad c_0 = 4 \cdot 87 \text{ Å}$$

It is thus evident that Li_3PO_4 exhibits the same polymorphism as Li_3AsO_4, the structure described by ZEMANN[1] being related to the high-temperature form. In this case, the transformation does not seem to be reversible; it is very probable, however, that the transformation takes place at a much lower temperature for Li_3PO_4 than for Li_3AsO_4, and thus is too sluggish to be easily detected.

Up to the present time, one type of structure only has been found for Li_3VO_4 and is of the low-temperature type, with the unit cell dimensions: $a_0 = 6 \cdot 33_5$, $b_0 = 5 \cdot 45_5$, $c_0 = 4 \cdot 96_0$ Å. All attempts to prepare a high temperature structure by heating Li_3VO_4 up to 950°C and quenching were unsuccessful, either because the transformation temperature is higher than 950°C, or because the high temperature structure cannot be quenched. The matter should be re-investigated by high-temperature diffractometry.

Some solid solutions $Li_3(P, As)O_4$ and $Li_3(P, V)O_4$ were also prepared. Their type of structure depends on the relative amounts of P, As and V.

The indexed spacings of the low temperature form of Li_3AsO_4 are collected in Table 1. Indexed powder diagrams of the other phases (Li_3PO_4 high and low, Li_3AsO_4 high and Li_3VO_4) are available on request to the author.

I.R. absorption spectra

Assignment of the bands. It has been shown in previous papers[3] that the absorption bands related to the stretching vibrations of LiO_4 tetrahedra are generally found in the 400–550 cm^{-1} region. Apart from the totally symmetric mode v_1 (which, anyway is i.r. inactive), these vibrations are easily identified by a ^6Li–^7Li isotopic shift which amounts to about 6 per cent of the observed frequency. This is true, however, only in the absence of important vibrational interactions between LiO_4 tetrahedra and the other co-ordinated groups present in the structure.

According to these principles, the value of the ^6Li–^7Li isotopic shift has been used to class the bands into three different categories:

(a) The bands free from any significant isotopic shift are assigned to the tetrahedral anion (PO_4, AsO_4 or VO_4) vibrational frequencies. This is always the case for the stretching frequency v_3. This is also true, but only as a first approximation, for the PO_4 bending frequency.

(b) The bands which exhibit an isotopic shift of about 20–25 cm^{-1} must be assigned to stretching vibrations of the LiO_4 tetrahedra.

(c) Some bands in the Li_3AsO_4 and Li_3VO_4 spectra are characterized by low or erratic values of the isotopic shift. It is highly probable that these bands are related to mixed vibrations involving both a stretching motion of the LiO_4 tetrahedra, and a bending motion of either AsO_4 or VO_4 tetrahedra.

Representative spectra of the different phases are given in Figs. 2–4. The observed frequencies and the assignments are collected in Tables 2–4. These results confirm, for the high temperature structure, the tetrahedral co-ordination of lithium, already
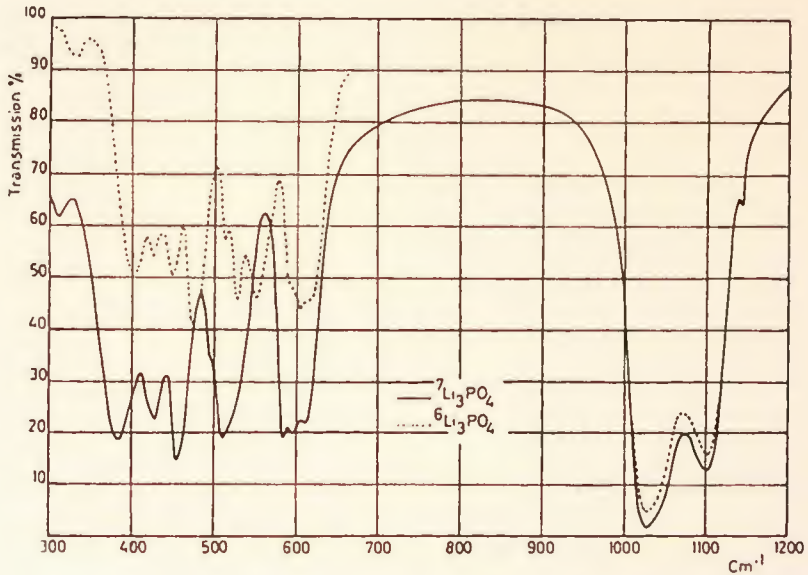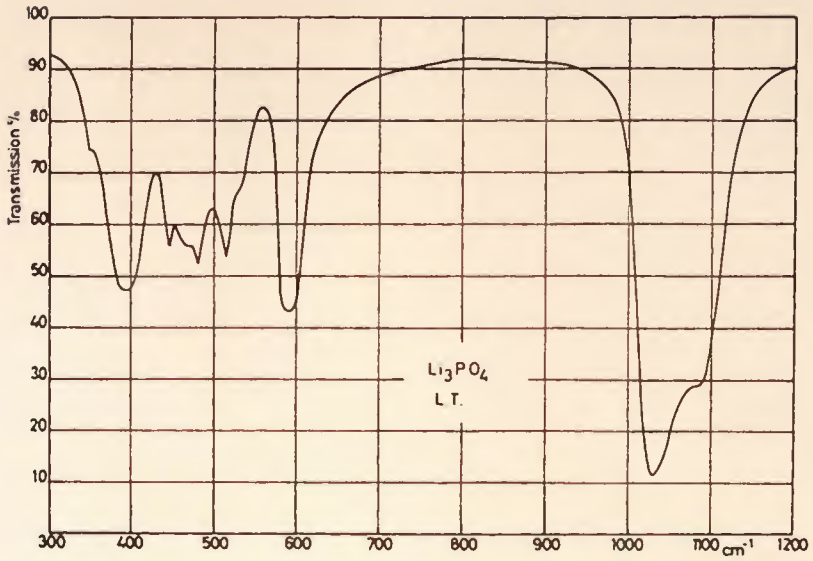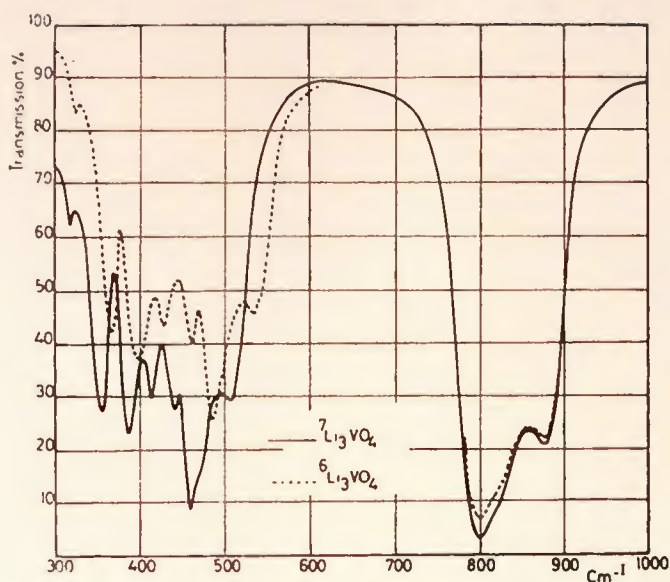
FIG. 2.—I.R. spectra of the high- and low-temperature forms of Li_3PO_4.

FIG. 3.—I.R. spectrum of Li_3VO_4.

TABLE 2.—I.R. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR Li_3PO_4

| L–$^7Li_3PO_4$ | H–Li_3PO_4 | | | Assignment |
	^6Li	^7Li	Δ_ν	
	1153	1153	0	
~1093	1109	1109	0	ν_3PO_4
1038	1035	1036	(+1)	
	622	620	−2	
~598	608	604	−4	ν_4PO_4
	601	592	−9	
	554	516		
~534	532			
519	517	~500	~−17	
484	479	460	−19	LiO_4
~472	452	431	−21	stretching
449	427			
~392	403	385	−18	
(348)	330	307	−23	

deduced from X-ray data by ZEMANN,[1] and show that the tetrahedral co-ordination of lithium is retained in the low temperature structure.

Deformation of the PO_4, AsO_4 *and* VO_4 *tetrahedra.* In all compounds investigated, the ν_3 antisymmetric stretching vibration of the anion is represented by 2 bands of unequal intensity. This doubling may be due to some deformation of the PO_4, AsO_4 or VO_4 tetrahedron, or to vibrational couplings between anions in the same unit cell, or both. This problem is easily solved by the study of dilute solid solutions:[4,5]

[4] K. WICKERSHEIM, R. LEFEVER et B. HANKING, *J. chem. Phys.* **32**, 271 (1960).

[5] P. TARTE, *Bull. Acad. R. Sci. Belg.* **46**, 169 (1960); *idem. Spectrochim. Acta* **18**, 467 (1962).
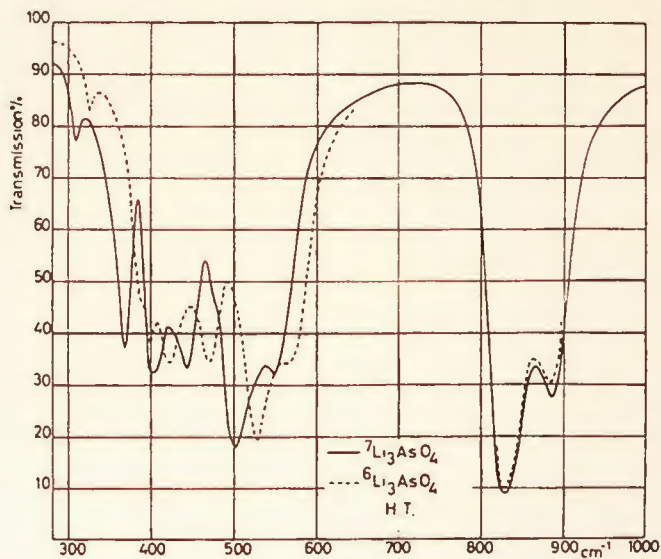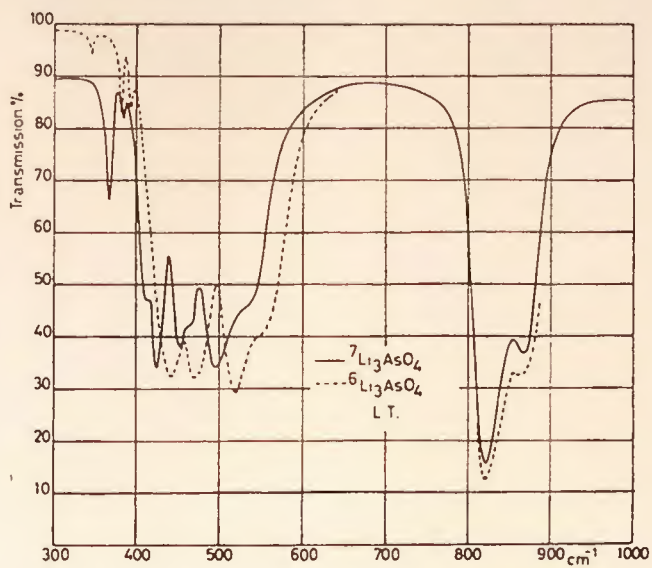
Fig. 4.—I.R. spectra of the high- and low-temperature forms of Li₃AsO₄.

TABLE 3.—I.R. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR Li_3VO_4.

$^6Li_3VO_4$	$^7Li_3VO_4$	Δ_ν	Assignment
884	884	0 ⎤	$\nu_3 VO_4$
805	803	(−2) ⎦	
537	512	−25 ⎤	
490	463	−27	LiO_6
463	443	−20	stretching
430	415	−15 ⎦	
397	387	−10 ⎤	Mixed frequencies
366	355	−11 ⎦	LiO_4 stretching and VO_4 bending
314	317	(+3)	

in this case, the vibrational couplings are suppressed, and any multiplicity of the absorption corresponding to a degenerate vibrational mode, here the ν_3 mode of the tetrahedron, must be assigned to the suppression of the degeneracy, and thus to some deviation from the ideal T_d symmetry.

In the dilute solid solutions studied, namely $Li_3(X, Y)O_4$ with $(X, Y) = (P_{0.08}As_{0.02})$, $(P_{0.08}V_{0.02})$, $(As_{0.98}P_{0.02})$ and $(V_{0.98}P_{0.02})$, the absorption corresponding to the triply degenerate ν_3 mode of the *dilute* anion is always represented by one single band, thus proving that the anion has retained its full tetrahedral T_d symmetry.

This is true for both types of structures studied here, namely the high- and low-temperature forms, and this result is in full agreement with ZEMANN's structural data on the high temperature form of Li_3PO_4.

Structural relations between the low- and the high-temperature forms. The great similarity between the X-ray powder diagrams of the low- and the high-temperature forms and the reversible character of the transformation suggest that the transition does not involve important structural rearrangements.

This hypothesis is fully substantiated by the i.r. spectra: both types of structures are characterized by the occurrence of non-deformed PO_4 tetrahedra, and by the four

TABLE 4.—I.R. VIBRATIONAL FREQUENCIES AND ASSIGNMENT FOR Li_3AsO_4.

	L-Li_3AsO_4			H-Li_3AsO_4			
^6Li	^7Li	Δ_ν	^6Li	^7Li	Δ_ν		Assignment
~869	870	(+1)	888	888	0 ⎤		
824	824	0	831	831	0 ⎦		$\nu_3 AsO_4$
~556	539	~−17	~567	~553	~−14 ⎤		LiO_4
523	499	−24	531	507	−24		stretching
	468						
473	456	−17	474	447	−27		
445	424	−21	424	402	−22 ⎦		
	~413						
394	385	−9	400	368	(−32) ⎤		Mixed frequencies
380	366	−14					LiO_4 stretching and
345			322	306	−16 ⎦		AsO_4 bending

fold co-ordination of lithium. Moreover, the extreme similarity of the i.r. patterns shows that the structural analogy between the two forms goes very far indeed, and that the two structures should differ by minor details only.