

## POSSIBILITY OF THE FORMATION OF MIXED CRYSTALS IN THE INDIUM PHOSPHATE-SCANDIUM PHOSPHATE SYSTEM

Bohumil HÁJEK, Eva ŠANTAVÁ and Alexander MUCK

*Department of Inorganic Chemistry,*

*Prague Institute of Chemical Technology, 166 28 Prague 6*

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The powder X-ray diffraction patterns and vibrational spectra were studied for the  $\text{InPO}_4$ - $\text{ScPO}_4$  system. The two cations were found mutually partly replaceable in the two phosphate structures involved,  $D_{2h}^{17}$  and  $D_{4h}^{19}$ : the orthorhombic  $D_{2h}^{17}$  structure of  $\text{InPO}_4$  is apt to accept 25 mol.%  $\text{ScPO}_4$ , whereas the tetragonal  $D_{4h}^{19}$  structure of  $\text{ScPO}_4$  only accepts  $\text{InPO}_4$  in amounts not exceeding 5 mol.%. The vibrational spectra of  $\text{TiPO}_4$  are also investigated.

The ionic radii of  $\text{In}^{3+}$  and  $\text{Sc}^{3+}$  ions in crystals of their compounds, which lie in the region of 80–90 pm (refs<sup>1-3</sup>), approach each other closely; due to the different electronic configuration, however, their coordination is different. The possibility of their mutual replacement is therefore studied in this work for two different phosphate structure types, *viz.* the orthorhombic  $D_{2h}^{17}$ -*Cmcm* structure for  $\text{InPO}_4$  ( $a = 530.8$  pm,  $b = 785.1$  pm,  $c = 676.7$  pm;  $Z = 4$ ; refs<sup>4,5</sup>) and the tetragonal  $D_{4h}^{19}$ -*I4<sub>1</sub>/amd* structure for  $\text{ScPO}_4$  ( $a = 657.4$  pm,  $c = 579.1$  pm;  $Z = 4$ ; refs<sup>4,6,7</sup>).

Interpreting the hitherto unpublished vibrational spectra of  $\text{InPO}_4$  we found them better consistent with the initially considered<sup>5</sup> structure  $C_{2v}^{12}$ ; for a comparison the vibrational spectra were therefore also interpreted for the isostructural  $\text{TiPO}_4$  ( $D_{2h}^{17}$ -*Cmcm*,  $a = 539.5$  pm,  $b = 801.0$  pm,  $c = 707.1$  pm,  $Z = 4$ ; ref.<sup>5</sup>).

### EXPERIMENTAL

The samples of indium and scandium phosphates and their mixed samples were prepared<sup>8-10</sup> from the corresponding oxides (Lachema, Brno) and annealed at 800, 900, or 1 000°C. The water content of  $\text{InPO}_4$  prepared at room temperature was determined by thermogravimetric and differential thermal analysis; the crystallization temperature of anhydrous indium phosphate<sup>10</sup> was also verified. The data for scandium phosphate were taken from ref.<sup>11</sup>.

Thallium phosphate was prepared from  $\text{Tl}_2\text{O}_3$  (Merck, Darmstadt) by long-run dissolution in a fiftyfold excess of 85%  $\text{H}_3\text{PO}_4$  *p.a.* ( $\text{Tl}_2\text{O}_3$  dissolved in acids such as  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  considerably more reluctantly than as reported in the literature<sup>12,13</sup>). The clear sirup obtained was diluted with water, and the precipitated hydrate was decanted to weakly acid pH, filtered out, washed with diethyl ether, dried freely in air, and annealed at 200–280°C and 300–360°C.

TABLE I  
Structural data of pure InPO<sub>4</sub>, ScPO<sub>4</sub> and TIPO<sub>4</sub>

Parameter	InPO <sub>4</sub>	ScPO <sub>4</sub>	TIPO <sub>4</sub>
<i>a</i> , pm	530·8(5)	657·8(2)	541·0(4)
<i>b</i> , pm	796·9(6)	657·8(2)	801·3(6)
<i>c</i> , pm	676·4(5)	579·5(2)	707·0(5)
(P–O) <sub>PO<sub>4</sub></sub> distance, pm	2 × 153·8 2 × 156·1	4 × 153·4	2 × 156·2 2 × 155·8
(O–O) <sub>PO<sub>4</sub></sub> distance, pm	4 × 252·2 254·4 254·8	4 × 256·9(2) <sup>a</sup> 2 × 237·4(3) <sup>a</sup>	5 × 254·7 254·6
M–O distance, pm	4 × 219·2 2 × 200·5	4 × 215·3(1) <sup>a</sup> 4 × 226·0(1) <sup>a</sup>	2 × 202·5 4 × 228·5
Coordination number of M <sup>3+</sup>	6	8 <sup>a</sup>	6
Symmetry of the coordination MO <sub>x</sub> polyhedron	distorted octahedron C <sub>2v</sub>	dodecahedron (bisbisphenoid) D <sub>2d</sub>	distorted octahedron C <sub>2</sub>
Own symmetry of PO <sub>4</sub> anion	C <sub>2v</sub>	D <sub>2d</sub>	T <sub>d</sub>

<sup>a</sup> Ref. 7.

TABLE II  
Composition of the samples studied

InPO <sub>4</sub> content mol.%	Number of diffraction lines <sup>a</sup>		Substance	InPO <sub>4</sub> content mol.%	Number of diffraction lines <sup>a</sup>		Substance
	ScPO <sub>4</sub>	InPO <sub>4</sub>			ScPO <sub>4</sub>	InPO <sub>4</sub>	
100	0	13	InPO <sub>4</sub>	30	6	10	<sup>c</sup>
95	0	12	<sup>b</sup>	25	7	5	<sup>c</sup>
90–75	0	11	<sup>b</sup>	20	7	3	<sup>c</sup>
70	1	11	<sup>c</sup>	15	7	1 (?)	<sup>c</sup>
60	3	11	<sup>c</sup>	10	7	3	<sup>c</sup>
50	5	11	<sup>c</sup>	5	7	1	<sup>c</sup>
40	5	9	<sup>c</sup>	0	7	0	ScPO <sub>4</sub>

<sup>a</sup> Number of mutually noncoincident lines within the region of  $\theta$  2–25°; <sup>b</sup> mixed crystal with the InPO<sub>4</sub> structure; <sup>c</sup> mixed crystal + ScPO<sub>4</sub>.

The powder X-ray diffraction measurements over the region of  $\theta = 2-35^\circ$  were performed on a Geigerflex instrument (Rigaku Denki) equipped with a Cu anode and a Ni filter. The infrared spectra over the  $4000-200\text{ cm}^{-1}$  range were measured in KBr disks on a Perkin-Elmer 325 spectrophotometer. The Raman spectra of the powdered pure components were measured in the free state or in a capillary on a Jeol JRS S1 spectrometer using the 488 nm line of an Ar<sup>+</sup> laser (power 15.5 mW), the Raman spectra of the powdered pure samples were also measured in a capillary on a Coderg LRDH-800 spectrometer using the 514.5 nm line of a CR-3 Ar<sup>+</sup> laser of Coherent Radiation.

### RESULTS AND DISCUSSION

According to the thermogravimetric and differential thermal analysis data, the water content of the freely dried indium phosphate precipitate corresponds to the formula  $\text{InPO}_4 \cdot x \text{H}_2\text{O}$  with  $x = 2.91$ . The single endothermic effect observed at  $130-200^\circ\text{C}$  is due to the loss of all water, the single exothermic effect at  $700^\circ\text{C}$  arises from the crystallization of the anhydrous amorphous  $\text{InPO}_4$ . The scandium phosphate sample dried freely in air has a composition of  $\text{ScPO}_4 \cdot x \text{H}_2\text{O}$  with  $x = 3.2$ . The two exothermic effects at  $800$  and  $830^\circ\text{C}$  correspond to the crystallization<sup>11</sup> of  $\text{ScPO}_4$ . The lowest temperature of  $800^\circ\text{C}$  was therefore chosen for the sample preparation. Attempted DTA determination of the temperature of crystallization for thallium phosphate failed because of the too low temperature change involved. The best-developed infrared spectra were obtained for samples annealed at  $200-360^\circ\text{C}$ ; at  $650-700^\circ\text{C}$ , melting and decomposition took place (endothermic effect).

TABLE III  
Correlation table for the phosphate anion in the structures considered

$T_d$ (24)	$C_{2v}$ (4)	$D_{2h}$ (8) $C_2 \rightarrow C_2^y$
$\nu_1$ $A_1$	$A_1(\text{IR, RA})$	$A_g(\text{RA}) + B_{2u}(\text{IR})$
$\nu_2$ $E$	$A_1(\text{IR, RA}) + A_2(\text{RA})$	$B_{2g}(\text{RA}) + A_u(\text{ia}) + A_g(\text{RA}) + B_{2u}(\text{IR})$
$\nu_3, \nu_4$ $F_2$	$A_1(\text{IR, RA}) + B_1(\text{IR, RA}) + B_2(\text{IR, RA})$	$A_g(\text{RA}) + B_{2u}(\text{IR}) + B_{3g}(\text{RA}) + B_{1u}(\text{IR}) + B_{1g}(\text{RA}) + B_{3u}(\text{IR})$
$T_d$ (24)	$C_s$ (2)	$C_{2v}$ (4)
$\nu_1$ $A_1$	$A'(\text{IR, RA})$	$A_1(\text{IR, RA}) + B_1(\text{IR, RA})$
$\nu_2$ $E$	$A'(\text{IR, RA}) + A''(\text{IR, RA})$	$A_1(\text{IR, RA}) + B_1(\text{IR, RA}) + A_2(\text{ia}) + B_2(\text{IR, RA})$
$\nu_3, \nu_4$ $F_2$	$2A'(\text{IR, RA}) + A''(\text{IR, RA})$	$2A_1(\text{IR, RA}) + 2B_1(\text{IR, RA}) + A_2(\text{ia}) + B_2(\text{IR, RA})$

The crystallographic data of the three phosphates were taken from refs<sup>4-7</sup>. The own symmetry of the anions was verified by calculating the (O—O)<sub>PO<sub>4</sub></sub> and (P—O)<sub>PO<sub>4</sub></sub> distances (Table I). The vibrational spectra of scandium phosphate have been interpreted previously<sup>14,15</sup> in terms of the  $T_d \rightarrow D_{2d} \rightarrow D_{4h}$  correlation. The activation of the  $\nu_1$  vibration in the infrared spectrum of ScPO<sub>4</sub> is related with the lowering in the site symmetry of the anion to the effective site symmetry by the correlation<sup>16</sup>  $D_{2d} \rightarrow C_2$ .

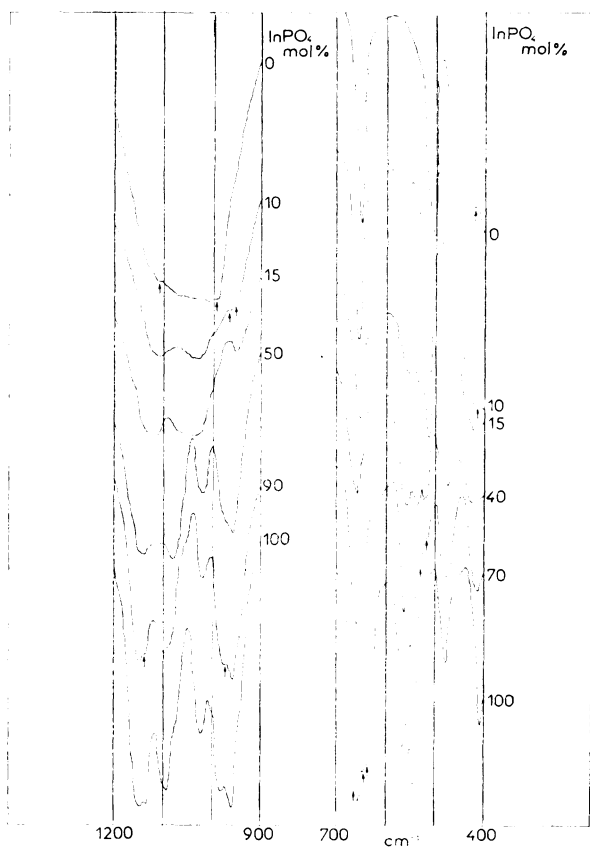


FIG. 1  
Infrared spectra of the indium phosphate–scandium phosphate system

TABLE IV  
Wavenumbers ( $\text{cm}^{-1}$ ) of the bands in the vibrational spectra of  $\text{InPO}_4$ ,  $\text{ScPO}_4$ , their mixed

$\text{InPO}_4$ mol. %	$\nu_1$		$\nu_2$ and lattice vibrations					
IR 100	980	960	408	338	317 and 305		264	238
90	975 sh	960	412	338 sh	320 — 305		295 sh	285 sh 235
70	980 — 950		410		325 — 305		280	
50	975 sh	955	420	360 — 325				
40	970 sh	955	420	360	330			
15		945	415	370	325		250	
10	965 sh	950 sh	415 sh	370	325			
0	990 sh		420 sh	365	315			
RA $\text{InPO}_4$	953	914	416	350	320		243	220 130
IR $\text{TIPO}_4$	985	950	375 sh	360	330	305	265 — 255	226
RA $\text{TIPO}_4$	920	895	400				255	205 143
RA $\text{ScPO}_4$	1 026		333		324 sh		241	235 sh 185

Annealed at  $1\ 300^\circ\text{C}$ ,  $\text{ScPO}_4$  exhibits values of 1 110, 1 080, 1 020  $\text{cm}^{-1}$  in the  $\nu_3$  region. The Ti-O vibration in the spectra of  $\text{TIPO}_4$  appears at 440  $\text{cm}^{-1}$ .

### X-Ray Diffraction Measurements

The lattice parameters of the pure substances (Table I) were calculated based on the indices of the most intense diffraction lines of the starting substances and the corresponding lines of the mixed samples, and refined by the least squares method employing the X RAY-72 program (University Computer Centre, Prague); the data are in accordance with the published values<sup>4-7</sup>. The lattice parameters of indium and scandium phosphates containing the cations in various proportions (Table II) are identical with those of the starting components to within the limits of error of powder X-ray diffraction measurements.

Samples containing 100–75 mol. %  $\text{InPO}_4$  can be indexed as orthorhombic with the lattice parameters of  $\text{InPO}_4$ , the parameters being constant to within the experimental error. The patterns of the remaining samples except for pure  $\text{ScPO}_4$  are superpositions of the diffraction lines of the orthorhombic and tetragonal structures, the lattice parameters of which are concentration-independent.

### Infrared and Raman Spectra

The vibrational spectra of scandium phosphate have been interpreted previously<sup>14-16</sup>. Indium (or thallium) phosphate crystallizes in the space group  $D_{2h}^{17}-Cmcm: C_1(16)$ ,

TABLE IV  
system, and  $\text{TiPO}_4$

$\nu_3$				$\nu_4$				
1 160 and 1 143	1 093	1 030		672 668 662 sh	655 sh	563	552	545
1 157 and 1 145 sh	1 100	1 027				662	560 sh	555 545
	1 140	1 080	1 025			660	560	550 525 sh 515 sh
	1 140	1 080	1 020			660	555	530 520
	1 150 —	1 075	1 015			660	555	530 520
	1 120	1 070 —	1 030			660	560	515
	1 110		1 035			660	560	515
	1 110 sh	1 070 —	1 010			650		510
1 165	1 145	1 050	1 028			665	550	430
		1 060	1 026			625	535	520
		1 095	1 000			650	530	
		1 082	1 043				593	473

In—O vibration at  $475 \text{ cm}^{-1}$  appears in the spectra of samples with 100 — 20 mol.%  $\text{InPO}_4$

$2C_{2h}(4)$ ,  $C_{2v}(4)$ ,  $C_i(8)$ ,  $C_2(8)$ ,  $2C_s(8)$ . The own symmetry of the anion is  $D_{2d}$  with the subgroups  $D_{2d}$ ,  $S_4$ ,  $D_2$ ,  $C_{2v}$ ,  $C_2$ ,  $C_s$ ,  $C_1$ , the number of formula units in an elementary cell is  $Z = 4$ , or  $Z_p = 2$ . Thus the corresponding site symmetry is unambiguously  $C_{2v}$ .

If the space group  $C_{2v}^{12} : C_1(8)$ ,  $C_s(4)$ , also suggested<sup>7</sup> for this substance, and the same own symmetry of the anion with  $Z = 4$ , or  $Z_p = 2$ , are considered, the site symmetry of the anion is  $C_s \equiv S_1$ . The correlation for the phosphate anion in these structure is as given in Table III.

The  $\nu_1$  vibration at  $950 \text{ cm}^{-1}$ , appearing for samples containing  $\text{InPO}_4$  in amounts of 15 — 100 mol.% and absent for pure  $\text{ScPO}_4$ , is indicative of mixed crystals of the  $\text{InPO}_4$  structure. The X-ray diffraction patterns show the line of indium phosphate at its concentrations as low as 5 mol.%.

The infrared spectra of pure indium phosphate can be better interpreted in terms of the factor symmetry  $C_{2v}$ , as is clear from a comparison of the correlation table (Table III) with the experimental wavenumbers (Table IV, Fig. 1). Unique interpretation based on the approximation applicable to the isolated particles, however, is hampered by the partially covalent nature of the In—O bond. For thallium phosphate, the  $D_{2h}$  factor symmetry is appropriate.

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