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$RbIn(OH)PO_4$: an indium(III) phosphate containing spirals of corner-sharing InO_6 octahedra *

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An indium(III) phosphate, $RbIn(OH)PO_4$, was synthesized using a high temperature, high pressure hydrothermal method and characterized by single-crystal X-ray diffraction. The compound crystallizes in the tetragonal space group $P4_32_12$ (no. 96) with $a = 9.400(2)$, $c = 11.179(4)$ Å, $U = 987.8(4)$ Å^3 and $Z = 8$. The structure consists of spirals of *cis* corner-sharing InO_6 octahedra running parallel to the *c* axis. The hydroxyl oxygen is the bridging atom. The In–O–In bonds are nearly equidistant. The composition was further defined by thermogravimetric and infrared spectroscopy measurements. Second harmonics were generated in powdered $RbIn(OH)PO_4$ to confirm the absence of a centre of symmetry in the structure.

Aluminophosphates have been extensively studied because they are known to be very useful materials for catalysis, adsorption and ion exchange.[1,2] The replacement of aluminium by gallium has yielded both novel structure types[3–8] and phases that are analogous to known aluminophosphates and aluminosilicates.[9–11] In contrast, the heavier Group 13 phosphates are rare and there are only three structurally characterized indium phosphates in the literature, namely, $Li_3In_2(PO_4)_3$,[12] $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$[13] and $[(CH_2NH_3)_2][In_2(HPO_4)_4]$[14] and the phosphite $In(PO_3)_3$.[15] The last compound is particularly interestingly because its octahedral–tetrahedral framework consists of large one-dimensional channels in which the organic cations reside. As part of a continuing study on the structural chemistry of phosphates containing mixed octahedral–tetrahedral frameworks, the alkali-metal indium phosphate system has been examined. The synthetic methods are two-fold, *viz.* the hydrothermal and the flux-growth methods. The phosphate $RbIn(OH)PO_4$ has been identified as a new member of this system and its synthesis and crystal structure is described. The structure consists of spirals of InO_6 octahedra sharing *cis* corners. To date, this compound does not have an aluminium or gallium analogue.

Experimental

Synthesis and initial characterization

High temperature, high pressure hydrothermal syntheses were performed in gold ampoules contained in a Leco Tem-Pres autoclave where pressure was provided by water pumped by a compressed air-driven intensifier. The phosphate $RbIn(OH)PO_4$ was synthesized from starting reagents of analytical grade or better: $Rb_2(HPO_4)$ (aq) (0.18 cm^3, 2.5 mol dm^{-3}), $Rb(H_2PO_4)$ (aq) (0.15 cm^3, 3 mol dm^{-3}) (Rb:P molar ratio = 1.5) and In_2O_3 (0.0555 g) were sealed in a gold ampoule (3.5 × 0.5 cm inside diameter) and heated to 550 °C at 32 000 lbf in^{-2} for 8 h. The autoclave was cooled at 5 °C h^{-1} to 250 °C and quenched to room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried in a desiccator at ambient temperature. The product contained pale yellow polycrystalline material and small colourless crystals of $RbIn(OH)PO_4$. A suitable colourless crystal was selected and its structure determined by single-crystal X-ray diffraction (see below). An X-ray powder pattern of the bulk product indicated that it contained a small amount of the cubic form of In_2O_3[16] and all other reflections in the pattern were in excellent agreement with those calculated from single-crystal data. A single-phase product was not obtained, although several different reaction conditions were tested. Subsequently, a reaction mixture of $Rb_2(HPO_4)$ (aq) (1.35 cm^3, 2.5 mol dm^{-3}), $Rb(H_2PO_4)$ (aq) (1.125 cm^3, 3 mol dm^{-3}) (Rb : P = 1.5) and In_2O_3 (0.4165 g) was heated in a larger gold ampoule (7 × 0.9 cm) at 550 °C and 32 000 lbf in^{-2} for 5 d, cooled to 250 °C at 5 °C h^{-1}, and then quenched to room temperature. The product contained many colourless crystals of nearly 1 mm in each dimension. The large size of the $RbIn(OH)PO_4$ crystals allowed for hand sorting of enough pure sample to carry out physical measurements.

Thermogravimetric analysis (TGA) for $RbIn(OH)PO_4$ was performed on a DuPont thermal analyser: the sample was heated to 950 °C at 5 °C min^{-1} in air. Infrared data were collected on a Perkin-Elmer 882 infrared spectrometer (KBr pellet method). The second harmonic generation (SHG) response of powder $RbIn(OH)PO_4$ was measured in the reflection mode. A Q-switch pulsed Nd : YAG laser (Continuum Powerlite 8020) operating at 1064 nm with a 20 Hz repetition rate and a 6–8 ns pulse width was used as source radiation. The average power incident on the reflector was 10–20 mW before focus. The sample was loaded in a capillary of inner diameter 1 mm.

Single-crystal X-ray diffraction

A colourless crystal of dimensions 0.17 × 0.13 × 0.10 mm was selected for indexing and intensity data collection on an Enraf-Nonius CAD4 diffractometer with κ-axis geometry using monochromated Mo-Kα radiation. Unit-cell parameters and the orientation matrix were determined by a least-squares fit of 25 peak maxima having $22 < 2\theta < 30°$. Axial oscillation photographs were taken to check the cell parameters and symmetry properties. Of the 1320 reflections collected, 622 unique reflections were considered observed $[I > 2.5\sigma(I)]$ after Lorentz polarization and empirical absorption corrections. Correction for absorption was based on ψ scans of a few suitable reflections with χ values near 90° using the NRCVAX program package.[17] The systematic-absence conditions were consistent with space groups $P4_12_12$ (no. 92) and $P4_32_12$ (no. 96). The space group $P4_12_12$ was initially selected. The heavy-atom positions were located using a direct method with the oxygen atoms being found from successive difference maps. At this point a parameter, η, that multiplies the imaginary components of the atomic scattering factors was refined.[18] The parameter refined to −1.14(6). A value of −1 with a small estimated standard deviation indicates that the assumed absolute

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* *Non-SI unit employed:* lbf in^{-2} ≈ 6895 Pa.

configuration is incorrect and that the structure must be inverted. Therefore, the space group $P4_32_12$ was used for the remainder of the crystallographic analysis. On the basis of bond-length bond-strength calculations,[19] both indium atoms are trivalent, oxygen O(5) was found to be considerably undersaturated, and all other oxygen atoms have bond-valence sums close to 2.0. Since a hydrogen atom must be included to balance the charge and a valence sum of 1.12 was calculated for O(5), it is probable that O(5) is a hydroxyl oxygen. The hydrogen atom was located from a Fourier-difference map. Subsequent refinement including the atomic coordinates, anisotropic thermal parameters and secondary extinction coefficient converged at $R = 0.0253$ and $R' = 0.0283$. The atomic coordinates and isotropic thermal parameter of the hydrogen atom were fixed. The occupancy factor for Rb was allowed to refine but did not deviate significantly from full occupancy. Neutral-atom scattering factors for all atoms were used. Anomalous dispersion corrections were applied. Calculations were performed on a Vax computer system using SHELXTL PLUS programs.[20]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Physical measurements

A one-step weight loss of 2.8% in the range 500–700 °C was observed for $RbIn(OH)PO_4$. The weight loss corresponds to the loss of $0.5H_2O$ and can be compared with the calculated value of 2.88%. The decomposition product was not characterized. The IR spectrum for $RbIn(OH)PO_4$ shows bands in the 800–1200 cm^{-1} region associated with In–O and P–O resonances, as well as a sharp band at 3520 cm^{-1} due to the O–H stretch. Second harmonic generation provides a highly sensitive and definitive test of the absence of a centre of symmetry of crystalline materials.[21] The $RbIn(OH)PO_4$ powder sample had an SHG signal about 0.6 times that of quartz. The sample gave a clearly positive SHG, indicating that the structure has no centre of symmetry.

Crystal structure

The crystallographic data are listed in Table 1. The atomic coordinates, interatomic distances, bond angles and bond-valence sums are given in Tables 2 and 3, respectively. Both indium atoms sit on two-fold rotation axes and all other atoms are at general positions. The indium and phosphorus atoms are six- and four-co-ordinated, respectively. Valence sums of Rb–O, In–O and P–O bonds are in agreement with their formal oxidation states. The co-ordination number of the rubidium cation was determined on the basis of the maximum gap in the Rb–O distances ranked in increasing order. The maximum Rb–O distance agrees with the 3.42 Å limiting value of Donnay and Allmann.[22] The Rb^+ cation is therefore nine-co-ordinated. The tenth oxygen atom is at a distance of 3.92 Å.

Table 1 Crystal data and intensity collection parameters for $RbIn(OH)PO_4$

Formula	$RbIn(OH)PO_4$
M	312.27
Crystal system	Tetragonal
Space group	$P4_32_12$ (no. 96)
a/Å	9.400(2)
c/Å	11.179(4)
U/Å^3	987.8(4)
Z	8
D_c/g cm^{-3}	4.200
$F(000)$	1136
μ(Mo-Kα)/cm^{-1}	148.2
T/°C	23
λ(Mo-Kα)/Å	0.709 30
Scan mode	θ–2θ
Scan width/°	$0.60 + 0.35 \tan\theta$
2θ Range/°	2–55
Standard reflections	Three measured every 2 h (no decay)
No. of reflections collected	1320
Unique observed reflections	622 $[I > 2.5\sigma(I)]$
Parameters refined	75
R^a	0.0253
R'^b	0.0283
$(\Delta\rho)_{max,min}$/e Å^{-3}	1.15, −0.99

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$, where $g = 0.000\,978$.

Table 2 Atomic positions for $RbIn(OH)PO_4$

Atom	x	y	z
Rb(1)	0.484 0(1)	0.183 4(1)	0.953 7(1)
In(1)	0.099 85(6)	0.099 85(6)	0
In(2)	0.652 76(6)	0.652 76(6)	0
P(1)	0.339 6(2)	0.815 0(2)	0.996 4(2)
O(1)	0.327 9(7)	0.997 8(6)	0.260 9(6)
O(2)	0.215 0(7)	0.201 2(7)	0.141 9(5)
O(3)	0.278 7(6)	0.962 8(6)	0.968 3(5)
O(4)	0.276 1(6)	0.752 5(7)	0.111 0(5)
O(5)	0.954 6(6)	0.014 3(6)	0.875 8(5)
H	0.619 9	0.463 3	0.845 3

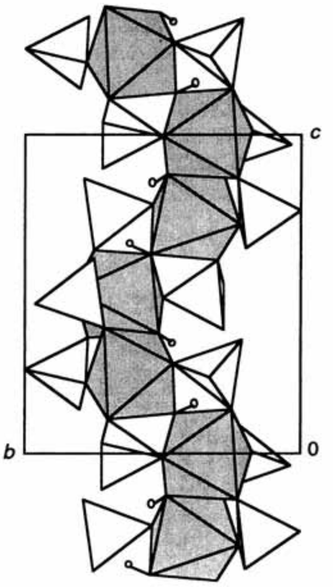

Fig. 1 Section of a spiral in $RbIn(OH)PO_4$ viewed along the [100] direction. The small open circles are H atoms

The phosphate $RbIn(OH)PO_4$ crystallizes in the space group $P4_32_12$ and therefore the unit-cell contents are chiral. The structure consists of spirals of *cis* corner-sharing InO_6 octahedra running along the *c* axis (Fig. 1). The In(1) and In(2) atoms are arranged in alternate order along the spiral. The hydroxyl oxygen, O(5), is the bridging atom. The H atom is not involved in hydrogen bonding. There are four InO_6 octahedra per spiral of unit-cell length along the *c* axis. The central axis of each spiral is a two-fold screw axis and therefore the spiral does not appear to have a square cross-section when viewed in projection down [001]. These spirals are connected by phosphate tetrahedra to form a three-dimensional framework structure (Fig. 2). Each phosphate tetrahedron shares two oxygen vertices with two adjacent InO_6 octahedra within a spiral and the remaining two vertices with two adjacent octahedra in a neighbouring spiral. The framework encloses large cavities in which nine-co-ordinated rubidium cations are

Table 3 Interatomic distances (Å), bond angles (°) and bond valence sums (Σs) for $RbIn(OH)PO_4$

$In(1)O_6$ octahedron *

In(1)	O(2)	O(2′)	O(3)	O(3′)	O(5)	O(5′)
O(2)	**2.144(6)**	3.18(1)	3.025(9)	2.769(9)	2.995(9)	
O(2′)	95.7(3)	**2.144(6)**	2.769(9)	3.025(9)		2.995(9)
O(3)	89.6(2)	80.4(2)	**2.148(6)**		3.037(8)	3.253(8)
O(3′)	80.4(2)	89.6(2)	165.1(3)	**2.148(6)**	3.253(8)	3.037(8)
O(5)	89.6(2)	169.6(2)	91.1(2)	99.8(2)	**2.107(6)**	2.89(1)
O(5′)	169.9(2)	89.6(2)	99.8(2)	91.1(2)	86.5(3)	**2.107(6)**

Σs[In(1)–O] = 3.23

$In(2)O_6$ octahedron *

In(2)	O(1)	O(1′)	O(4)	O(4′)	O(5)	O(5′)
O(1)	**2.175(6)**		2.892(9)	3.042(9)	3.345(9)	2.953(9)
O(1′)	171.4(3)	**2.175(6)**	3.042(9)	2.892(9)	2.953(9)	3.345(9)
O(4)	84.3(2)	89.8(2)	**2.134(6)**	3.13(1)	3.113(8)	
O(4′)	89.8(2)	84.3(2)	94.4(3)	**2.134(6)**		3.113(8)
O(5)	100.8(2)	85.7(2)	92.8(2)	167.7(2)	**2.166(6)**	2.84(1)
O(5′)	85.7(2)	100.8(2)	167.7(2)	92.8(2)	82.0(3)	**2.166(6)**

Σs[In(2)–O] = 2.99

$P(1)O_4$ tetrahedron

P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	**1.541(6)**	2.560(9)	2.499(9)	2.504(9)
O(2)	111.9(4)	**1.548(7)**	2.488(9)	2.483(8)
O(3)	108.7(3)	107.6(4)	**1.535(6)**	2.540(8)
O(4)	109.2(4)	107.5(4)	111.9(4)	**1.531(6)**

Σs[P(1)–O] = 4.94

Rb(1)–O(1)	3.267(7)	Rb(1)–O(1)	3.407(6)
Rb(1)–O(2)	3.294(6)	Rb(1)–O(2)	2.977(6)
Rb(1)–O(2)	2.881(7)	Rb(1)–O(3)	2.838(6)
Rb(1)–O(3)	2.986(6)	Rb(1)–O(4)	2.766(6)
Rb(1)–O(5)	3.286(6)		

Σs[K(1)–O] = 1.18

O(5)–H	0.909	In(1)–O(5)–In(2)	120.0(3)

* The distances between the *trans* oxygen atoms are not shown.

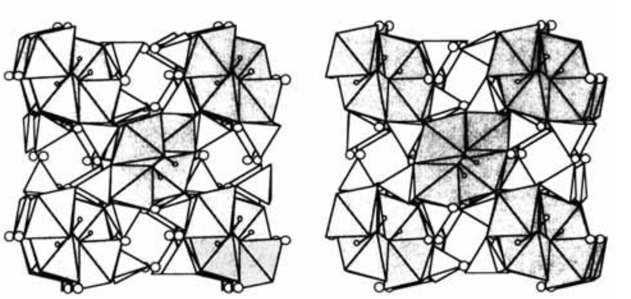

Fig. 2 Stereoscopic view of the $RbIn(OH)PO_4$ structure along the [001] direction. The large open circles are Rb atoms, the small open circles H atoms

located. These cavities are interconnected such that channels parallel to the *c* axis with square windows are formed. The two adjacent RbO_9 polyhedra share an edge. Each channel is surrounded by four spirals which are related to each other by the 4_3 axis.

Both the $In(1)O_6$ and $In(2)O_6$ octahedra are quite regular. Atom In(2) is displaced from the centroid of its In–O octahedron by 0.061 Å, whereas In(1) is nearly at the centroid of its octahedron. The PO_4 tetrahedron is also regular. In $RbIn(OH)PO_4$, the –In–O–In–O– backbone of InO_6 spirals shows nearly equal In–O bond lengths. The difference between In(1)–O(5) and In(2)–O(5) is 0.059 Å. In contrast, the TiO_6 chains in the outstanding non-linear optical crystal $KTiOPO_4$ show a short–long bond alternation. The differences between the short and long Ti–O bonds are 0.275 and 0.363 Å, which are considerably greater than that in $RbIn(OH)PO_4$. The short, highly polarizable titanyl Ti=O bonds play a key role in defining non-linear optical properties, and therefore, $KTiOPO_4$ produces a large SHG intensity (*ca.* 6000 times that of quartz). In $RbIn(OH)PO_4$ the indium atoms are little displaced from the centroids of their octahedra and the observed SHG response is consequently small.

In summary, the synthesis and crystal structure of $RbIn(OH)PO_4$, the first rubidium compound in the family of alkali-metal indium phosphates, is reported. Although the three-dimensional framework shows interesting spirals of *cis* corner-sharing InO_6 octahedra, $RbIn(OH)PO_4$ has a small SHG because the $In^{III}O_6$ octahedra are regular and there are no anomalously short In–O bonds equivalent to the titanyl bonds in $KTiOPO_4$. Recent exploratory syntheses of alkali-metal indium phosphates using the high temperature, high pressure hydrothermal and flux-growth methods reveal a rich structural chemistry. Further investigation of the A–In–P–O phase space is in progress.

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