

The Crystal Structure of α -SrZn₂(PO₄)₂: A Hurlbutite Type

A. HEMON AND G. COURBION

*Laboratoire des Fluorures (UA 449), Faculté des Sciences,
Université du Maine, 72017 Le Mans Cedex, France*

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α -SrZn₂(PO₄)₂ is monoclinic (space group: $P2_1/c$) with $a = 8.3232(4)$ Å, $b = 9.5101(4)$ Å, $c = 9.0317(4)$ Å, $\beta = 92.293(3)^\circ$, and $Z = 4$. The crystal structure is refined from 3426 reflections to $R = 0.026$ ($R_w = 0.034$). Zinc and phosphorus tetrahedra build up a three-dimensional network isotopic to the hurlbutite-type CaBe₂(PO₄)₂. The strontium atoms form isolated SrO₇ polyhedra located between large octagonal holes. The difference from the α -CaZn₂(PO₄)₂ structure is pointed out. © 1990 Academic Press, Inc.

Introduction

The orthophosphates $M_3(\text{PO}_4)_2$, with $M = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} , Cd^{2+} , and Zn^{2+} , have been extensively studied in the past years for their luminescence applications (1-4). Ternary compounds $M_2M'(\text{PO}_4)_2$ have also been evidenced. Generally, the orthophosphates show polymorphic transitions and their luminescence properties are dependent from the polymorph (4). If the structures of the $M_3(\text{PO}_4)_2$ compounds are well known (5-8), this is not the case for the ternary phosphates. For example, the structure resolution of α -CaZn₂(PO₄)₂ was achieved in 1988 by Cheetham (9) and for SrZn₂(PO₄)₂ phases only nonindexed X-ray powder data are available.

During crystal growth of fluorophosphate compounds containing Na, Sr, and Al atoms by a chloride flux method (NaCl + ZnCl₂), specimens of α -SrZn₂(PO₄)₂ were isolated. This incited us to solve the struc-

ture of this phase on the basis of single-crystal diffraction data.

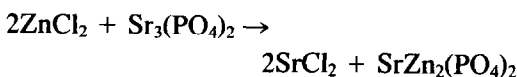
Preparation

Crystals of α -SrZn₂(PO₄)₂ were synthesized, as by-products, with a chloride flux method (10, 11) during a growth of fluorophosphates. They were obtained from the flux mixture, 2NaF + SrF₂ + 0.33Sr₃(PO₄)₂ + 0.67AlF₃ + 0.33AlPO₄ + 5.4NaCl + 3.3ZnCl₂, by slow cooling (6°C/hr) from 700°C, with a large amount of Na₂Sr₂Al₂(PO₄)F₉ (12).

The X-ray pattern of the crushed crystals allows to identify the compound as the low temperature form (α) by comparison with the JCPDS diffraction file 14-208. This result is in agreement with the transition temperature previously reported: $\alpha \rightleftharpoons \beta$ at 1035°C (2) and corresponds to the following possible exchange inside the melt:

TABLE I
CRYSTAL DATA AND CONDITIONS OF DATA COLLECTION AND REFINEMENT FOR α -SrZn₂(PO₄)₂

Symmetry	Monoclinic
Space group	$P2_1/c$ (No. 14)
Cell parameters	$a = 8.3232(4) \text{ \AA}$, $b = 9.5101(4) \text{ \AA}$, $c = 9.0317(4) \text{ \AA}$, $\beta = 92.293(3)^\circ$, $V = 714.32 \text{ \AA}^3$, $Z = 4$
Crystal volume (10^{-3} mm^3)	1.14
Radiation	MoK α (graphite monochromatized)
Aperture (mm)	3.5×3.5
Scanning mode	$\omega/2\theta$, 36 steps of $\Delta\omega$, $0.03 \leq \Delta\omega \leq 0.035$, time per step: 1–4 sec
Range registered	$2\theta_{\min}$ – $2\theta_{\max}$, 4–80 hkl_{\max} , 15 17 16
Absorption correction	Gauss method, $\mu = 145.15 \text{ cm}^{-1}$, $t_{\min} = 0.263$, $t_{\max} = 0.377$
Reflections measured:	Total 4626 (one independent set) Used in refinement 3426 ($I/\sigma(I) > 3$)
Number of refined parameters	119
Weighting scheme	$\omega = 0.4484(\sigma^2(F) + 0.001745F^2)$
Secondary extinction	$\epsilon = 3.8 \times 10^{-7}$
Maximum height in final Fourier difference map	$0.11 e^{-}/\text{\AA}^3$



Structure Resolution

A crystal with an approximate volume of $1.14 \times 10^{-3} \text{ mm}^3$ was chosen for the structure determination. Laue and precession

photographs indicate a monoclinic symmetry and lead to the space group $P2_1/c$ (No. 14). Intensities data collection was made on an AED2 Siemens–Stoe four circles diffractometer. Table I gathers the experimental conditions. The cell parameters were refined from the positions of 32 reflections with $2\theta \approx 30^\circ$ by the double scan technique.

TABLE II
ATOMIC PARAMETERS, ANISOTROPIC TEMPERATURE FACTORS ($U_{ij} \times 10^4$),^a AND B_{eq} (\AA^2) FOR α -SrZn₂(PO₄)₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Sr	0.2456(0)	0.0819(0)	0.6074(0)	104(1)	87(1)	109(1)	2(1)	10(1)	−7(1)	0.79(1)
Zn ₁	0.5739(0)	0.5711(0)	0.2887(0)	115(1)	103(1)	100(1)	−1(1)	8(1)	−16(1)	0.83(1)
Zn ₂	0.9195(0)	0.3197(0)	0.4510(0)	100(1)	85(1)	100(1)	5(1)	10(1)	6(1)	0.75(1)
P ₁	0.5428(1)	0.2941(1)	0.4314(1)	84(2)	71(2)	80(2)	−4(1)	12(1)	−5(1)	0.61(1)
P ₂	0.0576(1)	0.0847(1)	0.2507(1)	82(2)	84(2)	68(2)	−10(1)	12(1)	−6(1)	0.61(1)
O ₁	0.4746(2)	0.3866(2)	0.3024(2)	158(7)	100(5)	110(6)	23(4)	16(5)	0(5)	0.97(5)
O ₂	0.4178(2)	0.2059(2)	0.0528(2)	145(6)	125(6)	109(6)	8(4)	55(5)	19(5)	0.99(5)
O ₃	0.2276(2)	0.0621(2)	0.3200(2)	99(6)	233(8)	110(6)	9(5)	−7(5)	−3(5)	1.17(5)
O ₄	0.0174(2)	0.4490(2)	0.3135(2)	145(6)	97(5)	154(6)	34(5)	44(5)	27(5)	1.03(5)
O ₅	0.0637(2)	0.3033(2)	0.6287(2)	150(6)	125(6)	101(6)	−14(5)	3(5)	29(5)	0.99(5)
O ₆	0.5658(2)	0.1413(2)	0.3796(2)	146(7)	111(6)	147(6)	−35(5)	−24(5)	14(5)	1.07(5)
O ₇	0.6999(2)	0.1407(2)	0.9909(2)	91(6)	180(7)	218(8)	72(6)	1(5)	25(5)	1.29(6)
O ₈	0.9510(2)	0.3729(2)	0.8793(2)	164(7)	91(5)	141(6)	31(5)	71(5)	23(5)	1.03(5)

^a The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^{*}b^{*}U_{12} + 2hla^{*}c^{*}U_{13} + 2klb^{*}c^{*}U_{23})]$.

Intensities were corrected for Lorentz-Polarisation effects as well as for absorption. All the calculations were performed with SHELX76 (13). Atomic scattering factors and dispersion correction factors were taken from "International Tables for X-ray Crystallography" (14). The structure was solved from the TANG option of direct methods. The refinement of atomic parameters and isotropic thermal motion for all atoms converged to the reliability factor $R = 0.045$ ($R_w = 0.059$). The introduction of the anisotropic thermal motion led to the values 0.026 and 0.034 for R and R_w , respectively. Table II gathers the atomic coordinates and the thermal motion parameters whereas Table III gives the main interatomic distances and angles. A list of F_o/F_c values can be obtained on request to the authors.

Structure Description

The α - $\text{SrZn}_2(\text{PO}_4)_2$ structure is made from connected zinc and phosphorus regular tetrahedra which build up a three-dimensional network $[\text{ZnPO}_4]_n$. Each zinc

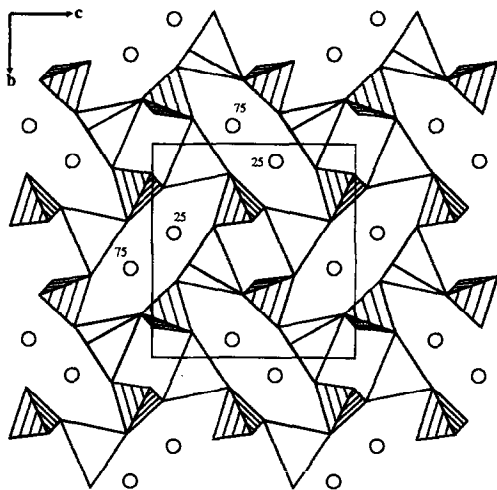


FIG. 1. (100) projection of a pseudo-layer of zinc and phosphorus (shaded) tetrahedra at $x \approx 0.5$. Strontium atoms are represented by circles.

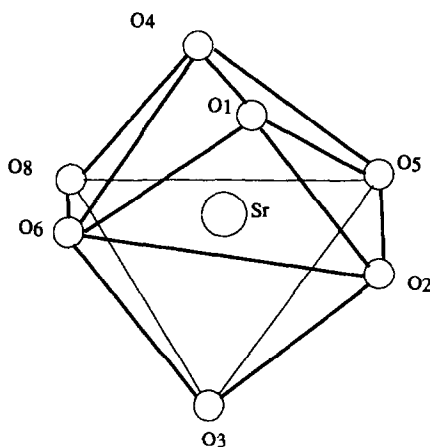


FIG. 2. Strontium polyhedron: a distorted monocapped trigonal prism.

tetrahedron shares corners with four phosphorus tetrahedra, and vice versa. In this framework, it appears as pseudo-layers of tetrahedra in the plane (b, c) around $x \approx 0$ and $\frac{1}{2}$ as shown in Fig. 1. In these layers, the large cavities surrounded by the eight tetrahedra are occupied by the strontium atoms ($x \approx 0.25$ and 0.75) which are sevenfold coordinated (Fig. 2). The connection mode between the sheets along the a -axis is shown in Fig. 3. This kind of arrangement is

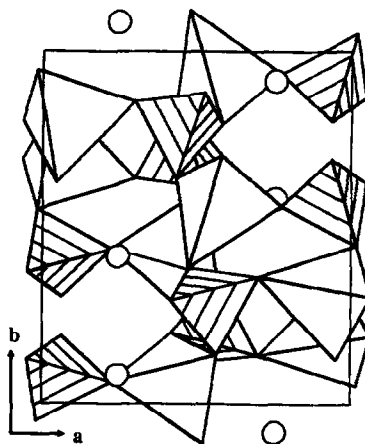


FIG. 3. (001) projection of connection mode between layers.

TABLE III
DISTANCES (Å) AND ANGLES (°) IN α -SrZn₂(PO₄)₂

Sr polyhedron $\langle \text{Sr}-\text{O} \rangle = 2.607 \text{ \AA}$							
Sr	O ₂	O ₁	O ₈	O ₃	O ₅	O ₆	O ₄
O ₂	2.535(1)	2.859(3)	5.098(2)	3.395(2)	3.054(2)	4.187(2)	4.756(1)
O ₁	68.3(2)	2.561(1)	4.473(2)	4.768(2)	4.122(2)	2.939(3)	3.857(2)
O ₈	170.7(1)	120.9(1)	2.580(1)	3.625(2)	4.095(2)	3.209(2)	2.451(4)
O ₃	82.7(1)	134.9(1)	88.8(1)	2.601(1)	3.898(2)	3.699(2)	4.854(2)
O ₅	72.9(1)	105.9(1)	104.3(1)	97.0(1)	2.605(1)	5.235(3)	2.956(3)
O ₆	108.0(1)	68.8(2)	75.9(1)	89.8(1)	173.2(1)	2.640(1)	4.348(2)
O ₄	129.3(1)	93.6(1)	54.9(2)	131.3(1)	67.3(2)	108.2(1)	2.728(1)
Zn ₁ tetrahedron $\langle \text{Zn}_1-\text{O} \rangle = 1.954 \text{ \AA}$							
Zn ₁	O ₂	O ₁	O ₃	O ₆			
O ₂	1.921(1)	3.411(1)	3.241(1)	3.212(2)			
O ₁	123.9(1)	1.945(2)	3.220(2)	2.939(2)			
O ₃	113.4(1)	111.2(1)	1.957(1)	2.942(2)			
O ₆	110.3(1)	96.6(1)	96.3(1)	1.992(2)			
Zn ₂ tetrahedron $\langle \text{Zn}_2-\text{O} \rangle = 1.950 \text{ \AA}$							
Zn ₂	O ₇	O ₄	O ₈	O ₅			
O ₇	1.914(1)	3.258(2)	3.230(2)	3.271(2)			
O ₄	115.0(1)	1.949(2)	3.171(2)	3.176(1)			
O ₈	112.7(1)	108.3(1)	1.965(1)	2.931(2)			
O ₅	114.7(1)	108.2(1)	96.3(1)	1.971(1)			
P ₁ tetrahedron $\langle \text{P}_1-\text{O} \rangle = 1.539 \text{ \AA}$							
P ₁	O ₇	O ₆	O ₂	O ₁			
O ₇	1.525(1)	2.543(2)	2.513(2)	2.494(2)			
O ₆	112.1(2)	1.541(1)	2.496(1)	2.542(2)			
O ₂	110.1(2)	108.1(2)	1.542(2)	2.489(2)			
O ₁	108.5(2)	110.7(2)	107.3(2)	1.549(2)			
P ₂ tetrahedron $\langle \text{P}_2-\text{O} \rangle = 1.539 \text{ \AA}$							
P ₂	O ₅	O ₄	O ₃	O ₈			
O ₅	1.534(2)	2.512(2)	2.509(1)	2.571(2)			
O ₄	109.7(2)	1.537(1)	2.564(2)	2.451(1)			
O ₃	109.5(2)	112.9(2)	1.539(1)	2.463(2)			
O ₈	113.3(2)	105.4(2)	106.1(2)	1.544(1)			

encountered in the framework of the natural minerals hurlbutite CaBe₂(PO₄)₂ (15) and paracelsian BaAl₂(SiO₄)₂ (16); however, in the latter there is a small degree of

Al/Si disorder. The main difference between α -SrZn₂(PO₄)₂ and CaBe₂(PO₄)₂ comes from the coordination of strontium and calcium atoms; respectively isolated

SrO₇ polyhedra and zig-zag strip of CaO₉ polyhedra.

The α -SrZn₂(PO₄)₂ structure is very different from that of α -CaZn₂(PO₄)₂ (9). Indeed in the calcium compound, there are two zinc sites, one four- and the other five-coordinated, linked to the phosphate tetrahedra to form layers between which the calcium ions lie.

The luminescence properties of the strontium orthophosphate have been reported by Hummel (2) for tin-activated compounds and by Brown (4) for Eu²⁺-activated ones. For α -SrZn₂(PO₄)₂ a blue emission (0.02 Sn²⁺ activated) at about 470 nm is observed with 253.7 nm radiation or cathode ray excitation. Taking into account our structural results, we can say that the blue emission of α -SrZn₂(PO₄)₂ is characteristic of tin in sevenfold coordination due to the vicinity of ionic radii between Sr²⁺ and Sn²⁺ (respectively 1.21 and 1.22 Å).

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