

The crystal structure of $\text{KZr}_2(\text{PO}_4)_3$

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Auszug

Die Raumgruppe von $\text{KZr}_2(\text{PO}_4)_3$ ist $R\bar{3}c$; die hexagonale Elementarzelle hat die Gitterkonstanten $a = 8,71 \text{ \AA}$, $c = 23,89 \text{ \AA}$ und enthält sechs Formeleinheiten; $D_x = 3,22 \text{ g/cm}^3$. Zr ist von sechs O-Atomen im Abstand von $2,06 \pm 0,01 \text{ \AA}$ oktaedrisch umgeben. Auch K hat sechs O-Nachbarn in den Ecken eines in Richtung der c -Achse stark gestreckten Oktaeders; der Abstand K—O ist $2,81 \pm 0,01 \text{ \AA}$. Die Abstände in der PO_4 -Gruppe weichen nicht wesentlich von den in anderen Strukturen ab.

Abstract

The structure of $\text{KZr}_2(\text{PO}_4)_3$ has been determined from three-dimensional x-ray data. The crystals are rhombohedral with hexagonal unit cell $a = 8.71$, $c = 23.89 \text{ \AA}$, $D_x = 3.22 \text{ g/cm}^3$. The space group is $R\bar{3}c$ and there are six formula units per unit cell. It follows from the interatomic distances that the compound is potassium trisphosphatodizirconate defined by the formula $\text{K}[\text{Zr}_2(\text{PO}_4)_3]$. The coordination of the zirconium atom is sixfold in the shape of octahedron. Zr—O distances are $2.06 \pm 0.01 \text{ \AA}$. Six oxygen atoms are coordinated around a potassium atom in the shape of trigonal antiprism. K—O distances are $2.81 \pm 0.01 \text{ \AA}$. The distances in the PO_4 group do not deviate significantly from the known data.

Introduction

An investigation of the crystal structure of potassium dizirconium trisphosphate was commenced in connection with a series of investigations of similar thorium and tetravalent uranium phosphates. The common formula of these compounds is $\text{M}^{\text{I}}\text{M}_2^{\text{IV}}(\text{PO}_4)_3$ with $\text{M}^{\text{I}} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $\text{M}^{\text{IV}} = \text{Th}, \text{U}, \text{Zr}, \text{Hf}$. Crystal growth and crystal-

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lographic data of $\text{NaTh}_2(\text{PO}_4)_3$, $\text{NaU}_2(\text{PO}_4)_3$ and $\text{KTh}_2(\text{PO}_4)_3$ have been published^{1,2}. The crystals are monoclinic, space group $C2/c$ or Cc with four formula weights per unit cell. The crystal structure of $\text{KTh}_2(\text{PO}_4)_3$ has been also completed³. The thorium atom is nine coordinated and its coordination polyhedron is a distorted trigonal prism with additional ligands outside each of the rectangular faces. Preparation and crystallographic data of alkali-metal salts of zirconium and hafnium phosphates have also been published⁴. These salts are trigonal, space group $R\bar{3}c$ or $R3c$ with six formula weights per hexagonal unit cell. The question was whether Zr atom in $\text{KZr}_2(\text{PO}_4)_3$ had a similar coordination polyhedron as the Th atom in $\text{KTh}_2(\text{PO}_4)_3$. Both compounds could have the same nine coordination of oxygen atoms around the tetravalent metal atom, because the Zr atoms occupy special positions of the $R\bar{3}c$ or $R3c$ space group on the threefold axis (that was evident from crystallographic data) and the trigonal prism with additional ligands outside each of the rectangular faces retains the threefold axis. The results presented in this paper show obviously that $\text{KZr}_2(\text{PO}_4)_3$ compound in comparison with $\text{KTh}_2(\text{PO}_4)_3$ has no similarity in coordination polyhedron or in structural arrangement of the atoms.

Experimental

Single crystals of potassium dizirconium trisphosphate were obtained by heating a mixture of zirconium dioxide, alkali metal phosphate and B_2O_3 (as flux) to a temperature of 1200°C , as described before⁴. Later results suggest that the stoichiometric quantity of ZrO_2 and an excess of alkali-metal phosphate (twice the stoichiometric quantity) has to be used to avoid the formation of small amounts of baddeleyite, the monoclinic modification of ZrO_2 .

Crystals of potassium dizirconium trisphosphate grow as colourless and transparent polyhedra bounded only by the faces of a $\{10\bar{1}2\}$

¹ B. MATKOVIĆ and M. ŠLJUKIĆ, Synthesis and crystallographic data of sodium thorium trisphosphate, $\text{NaTh}_2(\text{PO}_4)_3$, and sodium uranium(IV) trisphosphate, $\text{NaU}_2(\text{PO}_4)_3$. Croat. Chem. Acta **37** (1965) 115–116.

² B. MATKOVIĆ, M. ŠLJUKIĆ and B. PRODIĆ, Preparative and x-ray crystallographic data on potassium dithorium trisphosphate, $\text{KTh}_2(\text{PO}_4)_3$. Croat. Chem. Acta **38** (1966) 69–70.

³ B. MATKOVIĆ, B. PRODIĆ and M. ŠLJUKIĆ, The crystal structure of potassium dithorium triphosphate, $\text{KTh}_2(\text{PO}_4)_3$. Acta Crystallogr. **21** (1966) A 64.

⁴ M. ŠLJUKIĆ, B. MATKOVIĆ, B. PRODIĆ and S. ŠČAVNIČAR, Preparation and crystallographic data of phosphates with common formula $\text{M}^{\text{IV}}\text{M}_2^{\text{IV}}(\text{PO}_4)_3$ ($\text{M}^{\text{I}} = \text{Li, Na, K, Rb, Cs}$; $\text{M}^{\text{IV}} = \text{Zr, Hf}$). Croat. Chem. Acta **39** (1967) 145–148.

rhombohedron. The identity period along the $[\bar{2}4\cdot1]$ direction and the polar distance ϱ of $\{10\bar{1}2\}$, the form of crystal growth, are listed in Table 1 together with the data for rhombohedral and hexagonal unit-cell parameters, axial ratios, hexagonal unit-cell volumes and densities. The $\{10\bar{1}2\}$ rhombohedron, the rhombohedral and the hexagonal unit cells are represented in Fig. 1.

The polar distances ϱ were measured on an optical goniometer; the lattice constants were obtained from oscillation and Weissenberg x-ray diffraction photographs with nickel-filtered $\text{CuK}\alpha$ radiation.

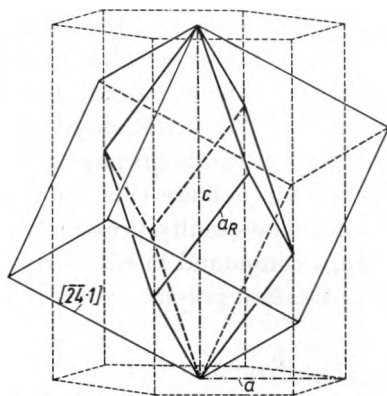


Fig. 1. The hexagonal unit cell (dotted lines), the $\{10\bar{1}2\}$ rhombohedron, the form of the crystal growth (full lines), and the rhombohedral unit cell (heavy full lines)

The densities (D_m), determined by a pycnometer with decalin as liquid, agree with the calculated values (D_x) for six formula weights per hexagonal unit cell. There is good agreement between the values based on morphology and those derived from the lattice constants. The systematically absent reflections indicate space groups $R3c$ or $R\bar{3}c$. Efforts to detect a piezoelectric effect, using relatively large single crystals, were unsuccessful and it was concluded that the most probable space group is $R\bar{3}c$. The choice of space group was also confirmed during the course of crystal-structure determination.

The three-dimensional intensity data were recorded on multiple equi-inclination Weissenberg photographs, with $\text{CuK}\alpha$ radiation. A crystal was ground to a sphere of 0.116 mm radius ($\mu = 258.70 \text{ cm}^{-1}$, $\mu r = 3.00$) in order to apply absorption corrections more easily and accurately. A ground specimen, mounted along the a axis, was used for collecting $h0l$ to $h4l$ intensity data. The same specimen, oriented

Table 1. *The morphology and lattice constants of $\text{KZr}_2(\text{PO}_4)_3$*

{10 $\bar{1}$ 2} rhombohedron—the form of the crystal growth

$$[\bar{2}\bar{4} \cdot 1] = 12.82 \pm 0.01 \text{ \AA}, \quad \varrho_m = 57^\circ 44' \pm 02', \quad \varrho_x = 57^\circ 44'$$

Rhombohedral unit cell

$$a_R = 9.41 \pm 0.01 \text{ \AA}, \quad \alpha = 55^\circ 08'$$

Hexagonal unit cell

$$a = 8.71 \pm 0.01 \text{ \AA}, \quad c = 23.89 \pm 0.02 \text{ \AA}, \quad (c:a)_m = 2.74, \quad (c:a)_x = 2.74$$

$$V = 1569.57 \text{ \AA}^3, \quad Z = 6$$

Space group $R\bar{3}c$

Density

$$D_m = 3.23 \text{ g/cm}^3, \quad D_x = 3.22 \text{ g/cm}^3$$

along [001] was used for collecting $hk0$ reflections. The relative intensities were determined from the optical densities of each spot measured by means of a microdensitometer. The corrections for absorption, polarization and Lorentz factors were made in the usual way and the structure amplitudes derived. The factors for transforming the observed structure amplitude onto absolute scale were found for reflections of each layer and with the help of these factors all structure amplitudes were scaled. These scale factors were improved in the course of structure determination.

Structure determination

The positions of the zirconium atoms were determined from the [100] Patterson projection. Analysis of the interatomic vector projection also permitted the construction of a structural model. K, Zr and P atoms occupy special positions $6b$, $12c$ and $18e$ of the space group $R\bar{3}c$ and only the z coordinate for the Zr atom and the x coordinate for the P atom had to be determined. Two oxygen atoms lie in general positions. The initial coordinates for the atoms of the supposed structure were refined by a least-squares method using a unit weighting system. Other weighting schemes gave no improvement over this one. Several cycles of least-squares refinement on scale factors, atomic positions and isotropic temperature factors were carried out until the shifts in the atomic coordinates were less than standard deviations. When anisotropic temperature factors were introduced, the R factor decreased to the present value of 8.50%

Table 2. *Fractional atomic coordinates and anisotropic thermal parameters in KZr₂(PO₄)₃*

The estimated standard deviations in parenthesis refer to the last digits. The temperature-factor expression used was $\exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. Each thermal parameter is multiplied by 10^4 . Following relationships are required by symmetry for Zr and K atoms: $\beta_{11} = \beta_{22}$, $\beta_{12} = \frac{1}{2}\beta_{11}$, $\beta_{13} = \beta_{23} = 0$; and for P atoms: $\beta_{12} = \frac{1}{2}\beta_{22}$, $\beta_{13} = \frac{1}{2}\beta_{23}$

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|------------|------------|-----------|--------------|--------------|--------------|--------------|--------------|--------------|
| Zr(1) | 0 | 0 | 0.1497(1) | 18(0.2) | 18 | 2(0.3) | 9 | 0 | 0 |
| K(2) | 0 | 0 | 0 | 166(12) | 166 | 6(1) | 83 | 0 | 0 |
| P(3) | -0.2870(5) | 0 | 0.250 | 16(4) | 16(4) | 3(1) | 8 | 0 | 0(3) |
| O(4) | 0.3067(12) | 0.4685(12) | 0.2628(3) | 63(9) | 44(9) | 4(1) | 22(8) | 0(4) | -9(4) |
| O(5) | 0.1680(12) | 0.2112(12) | 0.1994(3) | 64(9) | 42(9) | 3(1) | 21(8) | 0(4) | -3(4) |

$$R_1 = \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o| = 0.085 \text{ (including unobserved reflections)}$$

$$R_2 = \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o| = 0.074 \text{ (omitting unobserved reflections)}$$

Table 3. Observed and calculated structure factors

| <i>h k l</i> | F_o | F_c | <i>h k l</i> | F_o | F_c | <i>h k l</i> | F_o | F_c | <i>h k l</i> | F_o | F_c |
|--------------|--------|--------|--------------|--------|-------|--------------|--------|--------|--------------|--------|-------|
| 0 0 6 | 91.3 | 58.0 | 1 6 7 | 0 | 20.4 | 3 1 20 | 267.2 | 266.0 | 5 0 8 | 64.4 | 47.8 |
| 12 316.5 | 287.4 | | 10 235.5 | -221.9 | | 23 26.7 | -34.5 | | 14 251.1 | 236.1 | |
| 18 275.9 | -275.4 | | 13 0 | 14.4 | | 26 134.0 | 133.2 | | 20 276.7 | 274.8 | |
| 24 60.7 | -55.1 | | 16 150.5 | -133.0 | | 3 2 1 | 49.5 | -48.7 | 26 108.6 | 154.9 | |
| 30 109.6 | -145.5 | | 19 0 | 0.7 | | 4 239.8 | -247.7 | | 5 1 1 | 135.4 | 137.1 |
| 0 1 2 | 161.6 | -135.9 | 22 46.4 | -37.4 | | 7 79.5 | 72.0 | | 4 287.6 | -304.5 | |
| 8 174.2 | 153.9 | | 1 7 0 | 226.2 | 219.7 | 10 209.8 | -199.9 | | 7 185.3 | -177.8 | |
| 14 267.0 | 249.9 | | 9 3 | 37.4 | -36.8 | 13 133.9 | -123.9 | | 10 104.3 | -91.0 | |
| 20 378.8 | 405.6 | | 6 233.7 | 219.4 | | 16 201.2 | -189.8 | | 13 91.8 | | |
| 26 162.1 | 149.8 | | 9 0 | 12.0 | | 19 83.5 | 78.8 | | 16 213.9 | -207.8 | |
| 0 2 4 | 366.3 | -362.8 | 12 109.9 | 94.7 | | 22 0 | 0.1 | | 19 67.3 | -50.1 | |
| 10 284.3 | -276.9 | | 15 0 | -1.9 | | 25 53.8 | -50.7 | | 22 22.4 | 18.3 | |
| 16 165.2 | -163.5 | | 18 50.1 | -46.9 | | 3 3 0 | 349.6 | 355.3 | 25 91.3 | 74.6 | |
| 22 0 | 10.4 | | 1 8 2 | 0 | -8.6 | 3 93.0 | 84.5 | | 5 2 0 | 251.7 | 247.9 |
| 0 3 0 | 407.7 | 451.8 | 5 87.2 | 79.8 | | 6 224.0 | 223.9 | | 3 0 | 5.9 | |
| 6 334.3 | 344.2 | | 8 79.9 | 81.0 | | 9 0 | -16.4 | | 6 290.9 | 304.3 | |
| 12 265.6 | 256.2 | | 11 83.7 | -79.8 | | 12 153.8 | 135.9 | | 9 29.7 | 29.2 | |
| 18 134.4 | -106.2 | | 14 170.8 | 165.7 | | 15 36.3 | 28.5 | | 12 76.8 | 58.7 | |
| 24 120.6 | -116.1 | | 1 9 1 | 0 | 12.2 | 18 100.6 | -87.0 | | 15 0 | 16.3 | |
| 0 4 2 | 176.1 | -178.8 | 4 145.4 | -150.7 | | 21 28.4 | -28.2 | | 18 0 | -18.8 | |
| 8 244.8 | 245.6 | | 2 0 2 | 49.7 | 45.2 | 24 95.6 | -101.2 | | 21 0 | 8.4 | |
| 14 131.0 | 108.0 | | 8 171.9 | 161.3 | | 3 4 2 | 140.6 | -138.2 | 5 3 2 | 34.3 | -30.7 |
| 20 355.0 | 360.8 | | 14 370.4 | 395.3 | | 5 0 | 2.3 | | 5 23.8 | -21.9 | |
| 26 118.1 | 109.0 | | 20 223.9 | 220.5 | | 8 214.8 | 199.8 | | 8 103.7 | 97.7 | |
| 0 5 4 | 260.6 | -271.1 | 26 194.5 | 190.1 | | 11 0 | -27.2 | | 11 58.3 | 49.9 | |
| 10 89.2 | -72.0 | | 2 1 1 | 130.9 | 133.7 | 14 183.7 | 162.5 | | 14 174.6 | 164.0 | |
| 16 250.4 | -229.9 | | 4 142.6 | -152.7 | | 17 0 | -20.8 | | 17 53.3 | -43.8 | |
| 22 0 | 0.0 | | 7 94.4 | 73.6 | | 20 247.8 | 255.1 | | 20 165.5 | 163.8 | |
| 0 6 0 | 419.8 | 398.6 | 10 342.2 | -361.5 | | 23 43.1 | 43.3 | | 5 4 1 | 80.9 | 67.0 |
| 6 171.7 | 167.5 | | 13 66.3 | -61.7 | | 3 5 1 | 92.7 | -41.7 | 4 223.8 | -224.0 | |
| 12 140.8 | 126.5 | | 16 199.9 | -193.4 | | 6 139.5 | -126.8 | | 7 195.5 | -158.5 | |
| 18 101.9 | -90.5 | | 19 52.2 | -49.1 | | 7 49.6 | 43.1 | | 10 166.2 | -154.4 | |
| 24 102.7 | -114.0 | | 22 0 | -12.2 | | 10 221.8 | -213.6 | | 13 52.7 | 49.2 | |
| 0 7 2 | 157.7 | -152.0 | 25 23.8 | 18.8 | | 13 46.8 | -39.4 | | 16 131.3 | -151.2 | |
| 8 229.6 | 219.6 | | 28 98.0 | 99.2 | | 16 182.7 | -176.8 | | 5 5 0 | 207.1 | 189.8 |
| 14 58.6 | 45.9 | | 2 2 0 | 220.7 | 215.8 | 19 31.1 | 26.6 | | 6 0 0 | 368.9 | 398.6 |
| 20 240.9 | 262.9 | | 3 109.5 | -90.6 | | 3 6 0 | 224.1 | 210.7 | 6 1 2 | 164.8 | 161.2 |
| 0 8 4 | 212.5 | -197.6 | 6 391.8 | 386.7 | | 3 0 | -12.7 | | 11 128.7 | -128.7 | |
| 10 242.0 | -236.1 | | 9 100.1 | -90.0 | | 6 184.3 | 166.8 | | 18 110.7 | -94.2 | |
| 16 67.0 | -64.3 | | 12 87.7 | 72.5 | | 9 16.6 | -24.9 | | 24 122.1 | -111.3 | |
| 0 9 0 | 162.5 | 156.2 | 15 46.8 | 41.7 | | 12 66.2 | 56.5 | | 6 1 2 | 76.2 | -67.1 |
| 6 228.4 | 211.8 | | 18 28.9 | 23.6 | | 15 37.0 | 37.8 | | 5 0 | -2.6 | |
| 12 255.5 | -244.9 | | 21 27.3 | -22.1 | | 18 16.3 | -44.8 | | 8 135.0 | 124.4 | |
| 18 208.6 | -202.1 | | 24 178.1 | -178.4 | | 3 7 2 | 130.9 | -127.1 | 11 0 | 12.7 | |
| 22 43.2 | -45.1 | | 27 86.8 | 87.8 | | 5 0 | -1.8 | | 14 178.7 | 174.5 | |
| 0 1 0 | 369.5 | 399.0 | 2 3 2 | 0 | 0.9 | 8 113.2 | 119.4 | | 17 26.6 | -25.5 | |
| 3 307.8 | -302.0 | | 5 108.4 | -98.0 | | 11 26.8 | 27.5 | | 20 195.6 | 225.5 | |
| 6 428.4 | 466.4 | | 8 96.2 | 81.3 | | 4 0 4 | 57.3 | -52.8 | 6 2 1 | 106.4 | -93.3 |
| 12 137.0 | 126.0 | | 11 60.8 | 50.1 | | 10 302.2 | -306.0 | | 4 230.0 | -235.4 | |
| 18 90.3 | 88.1 | | 14 299.6 | 297.4 | | 16 115.6 | -110.6 | | 7 108.3 | 96.1 | |
| 15 145.2 | -126.4 | | 17 0 | -20.0 | | 22 113.0 | -103.6 | | 10 173.6 | -166.4 | |
| 0 2 4 | 0 | 7.6 | 20 216.7 | 199.1 | | 28 388.7 | 129.2 | | 13 87.4 | -83.5 | |
| 21 115.9 | 110.0 | | 23 52.9 | 46.6 | | 4 1 0 | 115.9 | -149.5 | 16 149.5 | -158.5 | |
| 24 188.2 | -190.9 | | 26 180.1 | 200.5 | | 3 141.4 | -136.5 | | 19 68.3 | 73.8 | |
| 27 56.9 | -46.1 | | 2 4 1 | 0 | -10.6 | 6 259.1 | 282.4 | | 6 3 0 | 210.6 | 210.7 |
| 30 104.1 | -117.1 | | 4 177.0 | -170.3 | | 9 120.0 | 110.9 | | 3 46.2 | 41.7 | |
| 1 2 2 | 52.8 | 58.1 | 7 60.7 | -44.1 | | 12 101.3 | 82.9 | | 6 229.5 | 236.5 | |
| 5 67.9 | 58.1 | | 10 203.7 | -184.5 | | 15 58.4 | -44.5 | | 9 71.9 | -64.2 | |
| 8 205.2 | 198.1 | | 13 154.3 | 129.5 | | 18 63.4 | -52.8 | | 12 57.0 | 45.2 | |
| 11 36.1 | -27.9 | | 16 209.4 | -195.9 | | 21 73.3 | 77.8 | | 15 23.3 | 25.5 | |
| 14 274.3 | 280.0 | | 19 67.1 | -60.7 | | 24 157.4 | -159.0 | | 6 4 2 | 89.7 | -80.8 |
| 17 144.0 | 138.8 | | 22 29.6 | -22.4 | | 27 58.2 | -65.1 | | 5 0 | 15.4 | |
| 20 210.6 | 194.4 | | 25 41.5 | 34.1 | | 4 2 2 | 38.7 | -38.3 | 8 113.1 | 108.3 | |
| 23 99.1 | -99.7 | | 2 5 0 | 268.0 | 247.9 | 5 93.3 | 79.5 | | 11 48.0 | -36.5 | |
| 26 211.8 | 218.3 | | 3 90.1 | 78.7 | | 8 96.5 | 90.3 | | 7 0 4 | 0 | -4.0 |
| 29 34.7 | 34.0 | | 6 215.0 | 207.0 | | 11 22.9 | -21.2 | | 10 311.2 | -324.8 | |
| 1 3 1 | 54.2 | -51.2 | 9 46.8 | -26.4 | | 14 22.5 | 208.2 | | 16 82.5 | -85.6 | |
| 4 205.7 | -207.1 | | 12 83.2 | 61.9 | | 17 28.4 | -29.4 | | 7 1 0 | 213.1 | 219.7 |
| 7 178.5 | 161.4 | | 15 0 | 6.6 | | 20 230.8 | 225.1 | | 3 0 | -18.4 | |
| 10 328.3 | -336.0 | | 18 33.7 | -31.5 | | 23 42.4 | -37.1 | | 6 153.0 | 146.8 | |
| 15 95.6 | -76.2 | | 21 46.6 | -42.4 | | 4 3 1 | 0 | 17.3 | 9 0 | 17.8 | |
| 16 95.6 | -79.9 | | 2 6 2 | 17.4 | 11.9 | 4 112.2 | -107.4 | | 12 89.5 | 94.0 | |
| 19 0 | 15.4 | | 5 97.3 | -81.1 | | 7 98.2 | -79.2 | | 15 0 | -11.6 | |
| 22 71.8 | -63.3 | | 8 49.6 | 39.5 | | 10 329.5 | -330.8 | | 18 45.0 | -55.3 | |
| 25 51.0 | -40.8 | | 11 91.0 | 87.2 | | 13 41.7 | 41.7 | | 21 149.5 | -158.5 | |
| 28 134.3 | 125.0 | | 14 256.8 | 256.0 | | 16 49.7 | -36.5 | | 7 2 2 | 0 | -8.4 |
| 1 4 0 | 392.7 | 415.9 | 17 63.5 | -58.8 | | 19 0 | -2.3 | | 8 58.2 | 55.4 | |
| 4 30.0 | -15.1 | | 20 131.3 | 131.7 | | 22 97.7 | -98.2 | | 11 15.5 | -14.6 | |
| 6 274.2 | 279.3 | | 2 7 1 | 0 | 6.1 | 4 4 0 | 258.7 | 247.7 | 14 155.1 | 187.8 | |
| 9 34.5 | 34.2 | | 4 170.2 | -165.7 | | 3 0 | -0.4 | | 7 3 1 | 37.4 | -24.1 |
| 12 101.1 | 76.3 | | 7 17.4 | 8.2 | | 6 200.7 | 185.6 | | 4 92.6 | -87.4 | |
| 15 88.7 | -71.5 | | 10 174.2 | -167.7 | | 9 2.3 | -2.3 | | 7 52.0 | 73.6 | |
| 18 63.6 | -49.4 | | 13 46.4 | -35.0 | | 12 126.2 | 113.6 | | 10 214.2 | -214.2 | |
| 21 0 | 16.0 | | 16 114.6 | -135.9 | | 15 0 | -10.7 | | 8 0 2 | 233.5 | 269.7 |
| 24 163.6 | -160.6 | | 2 8 0 | 209.1 | 197.5 | 18 64.5 | -60.1 | | 8 78.9 | -40.8 | |
| 27 0 | -11.4 | | 3 51.1 | -45.1 | | 21 19.3 | 15.6 | | 8 105.2 | 99.7 | |
| 1 5 2 | 0 | -1.1 | 6 149.1 | 176.7 | | 4 5 2 | 0 | 3.4 | 14 196.7 | 221.8 | |
| 5 106.1 | 92.1 | | 9 51.6 | 43.5 | | 5 72.8 | 62.0 | | 8 1 1 | 72.4 | 73.5 |
| 8 34.5 | 37.1 | | 12 245.2 | 248.0 | | 8 39.1 | 45.3 | | 4 139.7 | -147.9 | |
| 11 171.5 | -150.3 | | 15 88.2 | 87.2 | | 11 31.2 | -25.9 | | 7 64.0 | 64.0 | |
| 14 289.5 | 277.8 | | 18 138.5 | -116.8 | | 14 219.3 | 225.6 | | 10 150.7 | -161.9 | |
| 17 120.0 | 103.8 | | 24 24.9 | -24.6 | | 17 66.1 | 54.1 | | 13 46.8 | 55.7 | |
| 20 235.1 | 224.8 | | 3 1 2 | 91.2 | -88.4 | 4 110.5 | -99.0 | | 3 52.4 | -49.9 | |
| 23 47.4 | -35.9 | | 5 28.0 | -28.3 | | 7 25.9 | -28.6 | | 6 142.0 | 180.2 | |
| 1 6 1 | 30.7 | -38.5 | 8 204.1 | 213.8 | | 10 166.6 | -180.6 | | 9 39.4 | 48.6 | |
| 4 171.7 | -160.4 | | 11 88.2 | 80.9 | | 13 31.3 | -22.6 | | 9 160.4 | 156.2 | |
| | | | 14 261.7 | 267.2 | | 4 7 0 | 250.5 | 269.7 | 9 0 0 | 165.3 | 165.3 |
| | | | 17 0 | 2.5 | | 5 0 2 | 0 | -24.0 | 9 1 2 | 31.4 | -26.7 |

(when unobserved reflections were included) and 7.4% (based only on observed reflections). The atomic scattering factors used in these calculations were from International tables for x-ray crystallography⁵. The atomic coordinates and temperature factors with their standard deviations are listed in Table 2. The whole three-dimensional x-ray

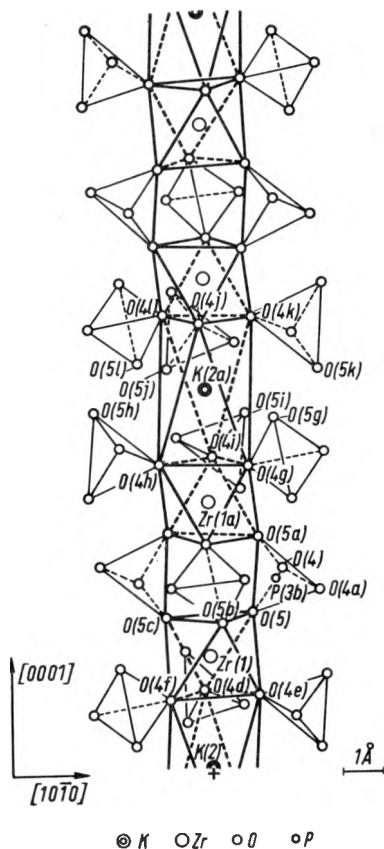


Fig. 2. The arrangement of P, K and Zr polyhedra along the three-fold axis. Only those atoms are numbered whose distances and angles are mentioned in the tables

analysis was undertaken on the basis of 1146 reflections (differing in hkl), which were measured photometrically on integrated Weissenberg films. Later, at the end of refinement, the F_{obs} data for symmetrically-

⁵ *International tables for x-ray crystallography*, Vol. III. Kynoch Press, Birmingham, 1962.

Table 4. *Numbering of atoms*

| Atoms | Coordinates | | |
|---------------|---------------------------|---------------------------|-----------------------|
| | <i>x</i> | <i>y</i> | <i>z</i> |
| Zr(1a); K(2a) | <i>y</i> | <i>x</i> | $\frac{1}{2} - z$ |
| O(4a); O(5a) | <i>y</i> - <i>x</i> | - <i>x</i> | <i>z</i> |
| P(3b); O(5b) | - <i>y</i> | <i>x</i> - <i>y</i> | <i>z</i> |
| O(5c) | $\frac{2}{3} + x - 1$ | $\frac{1}{3} + x - y$ | $\frac{5}{6} + z - 1$ |
| O(4d) | $\frac{2}{3} - y$ | $\frac{1}{3} - x$ | $\frac{5}{6} + z - 1$ |
| O(4e) | $\frac{2}{3} + y - x - 1$ | $\frac{1}{3} + y - 1$ | $\frac{5}{6} + z - 1$ |
| O(4f) | $\frac{1}{3} + x - y$ | $\frac{2}{3} + x - 1$ | $\frac{2}{3} - z$ |
| O(4g); O(5g) | $\frac{1}{3} + y - 1$ | $\frac{2}{3} + y - x - 1$ | $\frac{2}{3} - z$ |
| O(4h); O(5h) | $\frac{1}{3} - x$ | $\frac{2}{3} - y$ | $\frac{2}{3} - z$ |
| O(4i); O(5i) | $\frac{2}{3} + x - 1$ | $\frac{1}{3} + y - 1$ | $\frac{1}{3} + z$ |
| O(4j); O(5j) | $\frac{2}{3} - y$ | $\frac{1}{3} + x - y$ | $\frac{1}{3} + z$ |
| O(4k); O(5k) | $\frac{2}{3} + y - x - 1$ | $\frac{1}{3} - x$ | $\frac{1}{3} + z$ |
| O(4l); O(5l) | | | |

- 1 refers to a unit-cell translation.

equivalent reflections were averaged, reduced to a unique set of indices, and a new list of 397 independent reflections with positive *hkl* indices was obtained. So obtained observed structure factors together with calculated structure factors are listed in Table 3. The refinement cycles, using ORFLS program⁶ (rewritten for the IBM 360-67), and the calculation of bond lengths and angles, using ORFFE program⁷, were carried out on the IBM 360-67 computer at the Washington State University Computing Center. The numbering of the atoms, which is the same in all figures and tables, is explained and listed in Table 4 and Fig. 2. The bond distances and angles are listed in Table 5.

Description and discussion of the structure

Figure 3 represents (001) projection of the structure including symmetry elements. Oxygen atoms are designated by \times and phosphorus atoms by an asterisk; zirconium and potassium atoms are in positions designated by the symbols for threefold axes and threefold

⁶ W. R. BUSING, K. O. MARTIN and H. A. LEVY, ORFLS, a FORTRAN crystallographic least squares program. U.S. Atomic Energy Commission Report ORNL-TM-305, 1962.

⁷ W. R. BUSING, K. O. MARTIN and H. A. LEVY, ORFFE, a FORTRAN crystallographic function and error program. U.S. Atomic Energy Commission Report ORNL-TM-306, 1964.

Table 5. *Interatomic distances and angles in KZr₂(PO₄)₃*

(The estimated standard deviations in parenthesis refer to the last digits)

| | A | B | C | Distances | | Angles |
|--------------------------------|-------|-------|-------|------------|-------------|-----------|
| | | | | A-B | A-C | A-B-C |
| Within Zr polyhedron | O(5) | Zr(1) | O(5c) | 2.061(9) Å | 2.916(16) Å | 90.0(3) ° |
| | O(5c) | | O(5b) | 2.061(9) | 2.916(16) | 90.0(3) |
| | O(5b) | | O(5) | 2.061(9) | 2.916(16) | 90.0(3) |
| | O(4d) | | O(5c) | 2.065(9) | 3.027(12) | 94.4(4) |
| | O(4e) | | O(5) | 2.065(9) | 3.027(12) | 94.4(4) |
| | O(4f) | | O(4e) | 2.065(9) | 2.810(16) | 85.6(4) |
| | O(4e) | | O(4d) | | 2.810(16) | 85.6(4) |
| | O(4f) | | O(4d) | | 2.810(16) | 85.6(4) |
| | O(4d) | | O(5) | | 2.915(12) | 89.9(3) |
| | O(4f) | | O(5c) | | 2.915(12) | 89.9(3) |
| | O(4e) | | O(5b) | | 2.915(12) | 89.9(3) |
| | O(4f) | | O(5b) | | 3.027(12) | 94.4(4) |
| | O(4f) | | O(5) | | 4.125(18) | 175.6(5) |
| | O(4e) | | O(5c) | | 4.125(18) | 175.6(5) |
| | O(4d) | | O(5b) | | 4.125(18) | 175.6(5) |
| Within K polyhedron | O(4g) | K(2a) | O(4h) | 2.813(9) | 2.810(16) | 59.9(3) |
| | O(4h) | | O(4i) | 2.813(9) | 2.810(16) | 59.9(3) |
| | O(4i) | | O(4h) | 2.813(9) | 2.810(16) | 59.9(3) |
| | O(4j) | | O(4g) | 2.813(9) | 4.873(16) | 120.1(3) |
| | O(4k) | | O(4g) | 2.813(9) | 4.873(16) | 120.1(3) |
| | O(4l) | | O(4h) | 2.813(9) | 4.873(16) | 120.1(3) |
| | O(4j) | | O(4k) | | 2.810(16) | 59.9(3) |
| | O(4j) | | O(4l) | | 2.810(16) | 59.9(3) |
| | O(4k) | | O(4l) | | 2.810(16) | 59.9(3) |
| | O(4h) | | O(4j) | | 4.873(16) | 120.1(3) |
| | O(4i) | | O(4k) | | 4.873(16) | 120.1(3) |
| | O(4i) | | O(4l) | | 4.873(16) | 120.1(3) |
| | O(4g) | | O(4l) | | 5.625(18) | 180.0 |
| | O(4h) | | O(4k) | | 5.625(18) | 180.0 |
| | O(4i) | | O(4j) | | 5.625(18) | 180.0 |
| Within the phosphate groups | O(5a) | P(3b) | O(4) | 1.511(9) | 2.485(13) | 109.4(5) |
| | O(5) | | O(5a) | 1.511(9) | 2.502(16) | 111.7(7) |
| | O(4a) | | O(5a) | 1.533(9) | 2.463(12) | 108.0(5) |
| | O(4) | | O(4a) | 1.533(9) | 2.517(19) | 110.3(7) |
| | O(4) | | O(5) | | 2.463(12) | 108.0(5) |
| | O(4a) | | O(5) | | 2.485(13) | 109.4(5) |

Table 5. (Continued)

| | A | B | C | Distance | | Angles |
|--|-------|-------|--------|----------|----------|--------|
| | | | | A—B | A—C | A—B—C |
| The shortest K...O distances which do not belong to K polyhedron | K(2a) | O(5g) | O(5h) | 3.565(3) | 3.565(3) | |
| | | O(5i) | O(5j) | 3.565(3) | 3.565(3) | |
| | | O(5k) | O(5l) | 3.565(3) | 3.565(3) | |
| The shortest distances between the other atoms | Zr(1) | K(2) | Zr(1a) | 3.576(3) | 4.794(4) | |

inversion axes. All PO_4 tetrahedra are discrete groups, that is, no oxygen atom is common to two phosphorus atoms. But each oxygen atom, in addition to being bonded to the phosphorus atom, is also attached to the zirconium atom. When viewed in projection down the c axis, 24 oxygen atoms are shown around each threefold axis. They belong to four zirconium atoms which are located along each of these axes. The coordination of zirconium atom involves six oxygen atoms which are from six phosphate groups. Along the threefold axis two Zr polyhedra are joined together by phosphate groups, which act as bridges, as shown in Fig. 4. These two Zr polyhedra are also bridged by phosphate groups with other Zr polyhedra located along neigh-

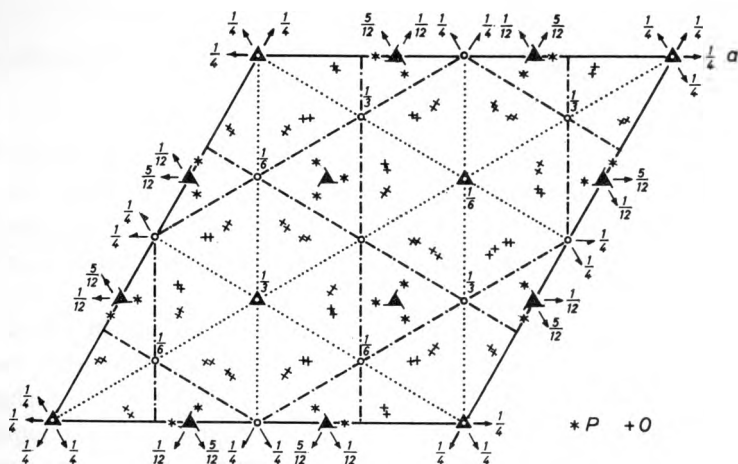


Fig. 3. The (001) projection of the structure including symmetry elements

boring threefold axis, as shown in Fig. 5. This forms a three-dimensional network of $[\text{Zr}_2(\text{PO}_4)_3]$ groupings. The packing of the zirconium atoms and the atoms of the phosphate groups is dense in the whole unit cell except at $\bar{3}$, where holes between the zirconium polyhedra exist. The potassium atoms are located in these holes. The nearest neighbors of the potassium atom are six oxygen atoms. The resulting sixfold coordination around the potassium atom is presented in Fig. 6. All oxygen atoms belong to phosphorus and zirconium atoms, and half of them

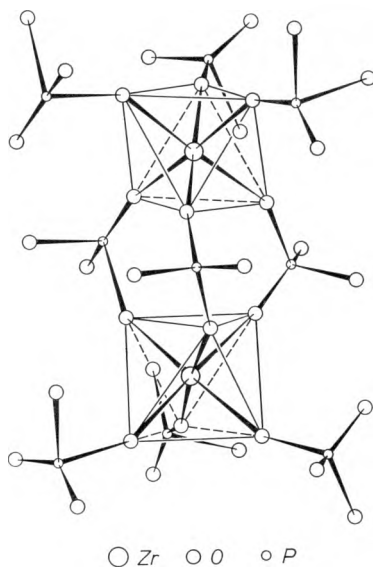


Fig. 4. Detail of the structure. Two Zr polyhedra, lying on the threefold axis, are bridged by PO_4 groups

[in Fig. 2 designated as O(4)] are also coordinated to K atoms. The potassium-oxygen distance is equal to the distance usual for the six-coordinated potassium atom. The compound can be described as potassium trisphosphatodizirconate defined by the formula $\text{K}[\text{Zr}_2(\text{PO}_4)_3]$.

When viewed along the threefold axis, as shown in Fig. 2, the structure is composed of two Zr polyhedra, one K polyhedron, two Zr polyhedra etc. The zirconium polyhedron can be described as a slightly distorted octahedron. The distance between the zirconium atom and the three nearest oxygen atoms is 2.061 Å. The next three closest oxygen atoms are 2.065 Å from the zirconium atom. The difference is smaller

than might be expected from the accuracy of the experiment. These distances are in agreement with those already found in other zirconium compounds, e.g. zirconium-oxygen distances in seven-coordinated Zr polyhedron range from 1.97 to 2.26 Å, as found in $\text{Zr}_4(\text{OH})_6(\text{CrO}_4)_5(\text{H}_2\text{O})_2$ ⁸ and monoclinic ZrO_2 (baddeleyite)⁹; greater zirconium-oxygen dis-

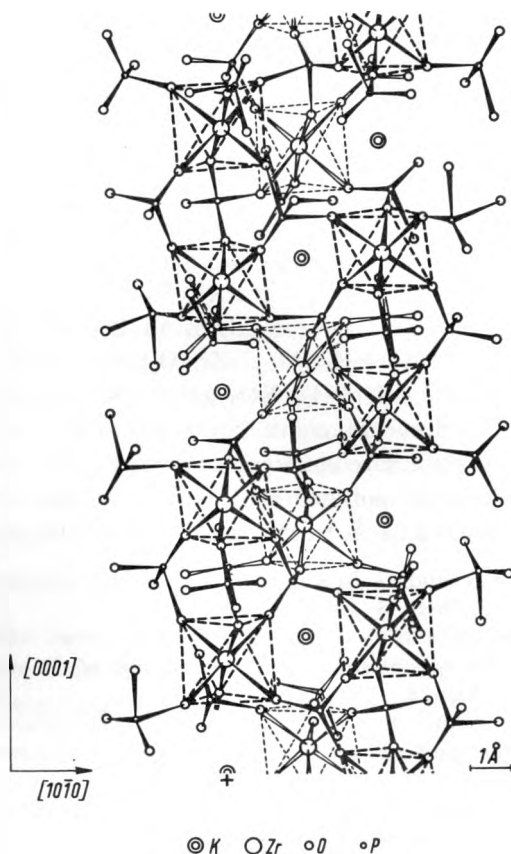


Fig. 5. A view on the structure. Oxygen atoms which belong to a PO_4 tetrahedron and to a ZrO_6 octahedron, are connected with the central atom by full lines. Oxygen-oxygen distances, which belong to a Zr octahedron, are connected by broken lines. Heavy lines are taken for polyhedra ahead and light lines for polyhedra behind

⁸ G. LUNDGREN, On the crystal structure of a zirconium hydroxide chromate. *Arkiv Kemi* **13** (1959) 59–85.

⁹ J. D. McCULLOUGH and K. N. TRUEBLOOD, The crystal structure of baddeleyite (monoclinic ZrO_2). *Acta Crystallogr.* **12** (1959) 507–511.

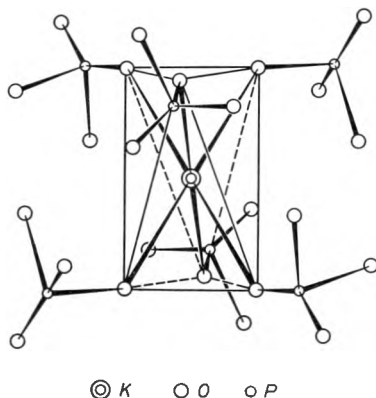


Fig. 6. Detail of the structure. The sixfold coordination of oxygen atoms around the potassium atom

tances from 2.09 to 2.37 Å were found in $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$ ¹⁰, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ ¹¹, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ¹², $\text{Zr}(\text{IO}_3)_4$ ¹³, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ¹⁴, $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ ¹⁵, $\text{Zr}(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_4$ ¹⁶ and ZrSiO_4 ¹⁷ where zirconium has coordination eight. Six-coordinated zirconium atom was found in some fluorozirconate compounds, Cs_2ZrF_6 and Rb_2ZrF_6 ¹⁸, where the coordination polyhedron is an octahedron and the zirconium-fluor distance is 2.04 Å. In the case of $\text{KZr}_2(\text{PO}_4)_3$, the octahedron

¹⁰ D. B. McWHAN and G. LUNDGREN, The crystal structure of $\text{Zr}_2(\text{OH})_2(\text{SO}_4)_3(\text{H}_2\text{O})_4$. *Inorg. Chem.* **5** (1965) 284–289.

¹¹ J. V. SILVERTON and J. L. HOARD, Stereochemistry of discrete eight-coordination. II. The crystal and molecular structure of zirconium(IV) acetylacetonate. *Inorg. Chem.* **2** (1963) 243–249.

¹² A. CLEARFIELD and P. A. VAUGHAN, The crystal structure of zirconyl chloride octahydrate and zirconyl bromide octahydrate. *Acta Crystallogr.* **9** (1956) 555–558.

¹³ A. C. LARSON and D. T. CROMER, The crystal structure of $\text{Zr}(\text{IO}_3)_4$. *Acta Crystallogr.* **14** (1961) 128–132.

¹⁴ J. SINGER and D. T. CROMER, The crystal structure analysis of zirconium sulphate tetrahydrate. *Acta Crystallogr.* **12** (1959) 719–723.

¹⁵ G. L. GLEN, J. V. SILVERTON and J. L. HOARD, Stereochemistry of discrete eight-coordination. III. Tetrasodium tetrakisoxalatozirconate(IV) trihydrate. *Inorg. Chem.* **2** (1963) 250–256.

¹⁶ D. B. McWHAN and G. LUNDGREN, The crystal structure of some zirconium hydroxide salts. *Acta Crystallogr.* **16** A36 (1963).

¹⁷ I. R. KRSTANOVIĆ, Redetermination of the oxygen parameters in zircon (ZrSiO_4). *Acta Crystallogr.* **11** (1958) 896–897.

¹⁸ H. BODE und G. TEUFER, Über Strukturen von Hexafluorozirconaten und Hexafluorhafnaten. *Z. anorg. allg. Chem.* **283** (1956) 18–25.

is slightly distorted, the oxygen edges of the polyhedron vary in length over a fairly narrow range from 2.810 to 3.027 Å. The geometry of the Zr polyhedron can be best understood from Table 5 where all distances between the oxygen atoms, which belong to this polyhedron, and the angles around the zirconium atom are listed.

The potassium atom is surrounded by six oxygen atoms, for which the K—O distance is 2.810 Å. Another six oxygen atoms are 3.565 Å from the potassium atom. The resulting sixfold coordination around the potassium atom may be described as trigonal antiprism. The oxygen edges of this polyhedron range from 2.810 to 4.873 Å. All distances and O—K—O angles inside this polyhedron are also listed in Table 5.

The distances within the phosphate group are 1.511 and 1.533 Å for phosphorus-oxygen atoms; oxygen-oxygen distances range from 2.463 to 2.517 Å and O—P—O angles range from 108.04° to 111.7° . All distances and O—P—O angles in PO_4 tetrahedron are also listed in Table 5. They do not deviate significantly from the results obtained before⁵, e.g. similar distances are obtained in the NbOPO_4 structure¹⁹, where P—O = 1.528 Å, O—O = 2.480 and 2.525 Å, O—P—O = 109.5° ; P—O = 1.54 Å was found in $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ²⁰. Somewhat longer P—O distances (up to 1.58 Å) were obtained in following structures: AlPO_4 ²¹, GaPO_4 ²¹, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ ²² and $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ ²³.

Acknowledgements

We would like to thank Dr. R. WILLETT for his interest and instructive help during the calculations and the Washington State University Computing Center for a grant of computing time.

¹⁹ J. M. LONGO and P. KIERKEGAARD, The crystal structure of NbOPO_4 . *Acta Chem. Scand.* **20** (1966) 72–78.

²⁰ S. C. ABRAHAMS and J. L. BERNSTEIN, Crystal structure of paramagnetic ludlamite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, at 298°K . *J. Chem. Physics* **44** (1966) 2223–2229.

²¹ R. C. MOONEY, The crystal structure of aluminum phosphate and gallium phosphate, low-crystobalite type. *Acta Crystallogr.* **9** (1956) 728–734.

²² S. GHOSE, The crystal structure of pseudomalachite, $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$. *Acta Crystallogr.* **16** (1963) 124–128.

²³ R. C. L. MOONEY-SLATER, The crystal structure of hydrated gallium phosphate of composition $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$. *Acta Crystallogr.* **20** (1966) 526–534.