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Crystal growth and structure determination of potassium zirconium phosphate $K_2Zr(PO_4)_2$

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Abstract. During the investigation of the system $K_2O - P_2O_5 - ZrO_2$, a new potassium zirconium phosphate, $K_2Zr(PO_4)_2$, was found. The crystals grown from melt solutions were merohedrally twinned. $K_2Zr(PO_4)_2$ crystallizes in the space group $P\bar{3}$ with $a = 5.176(1)$ Å, $c = 9.011(2)$ Å, $V = 209.1$ Å^3, $Z = 1$, $\varrho_x = 2.854$ g/cm^3. Its structure was refined to $R = 0.029$ and $R_w = 0.041$. $K_2Zr(PO_4)_2$ shows a layer structure consisting of close packed ZrO_6 layers perpendicular to the c-axis. The PO_4 tetrahedra are slightly distorted. Further, the isostructural compound $K_2Sn(PO_4)_2$ could be prepared.

Potassium zirconium phosphates of varying contents of K and H_2O have been obtained as products of ion-exchanged $Zr(HPO_4)_2 \cdot H_2O$ (Clearfield and Stynes, 1964; Clearfield and Smith, 1968; Dyer et al., 1971). However, the anhydrous stoichiometric compound $K_2Zr(PO_4)_2$ seems to be not yet known. We, therefore, were interested to prepare this compound and to determine its crystal structure.

$K_2Zr(PO_4)_2$ was obtained by solid state reaction of a carefully ground powder mixture of KPO_3 and ZrO_2 (both analytical grade) in a molar ratio of 2:1. After pre-firing at 1023 K for one day and subsequent re-grinding the temperature was held at 1073 K for 3 days. Under these conditions a complete reaction had taken place as was found by X-ray studies. The diffractograms had no similarity to those mentioned for the ion-exchanged phases and could be hexagonally indexed with lattice constants $a = 5.176(4)$ Å, $c = 9.012(8)$ Å, $V = 209.1$ Å^3.

In order to look for an isostructural Sn compound the preparation of $K_2Sn(PO_4)_2$ was tried in the way described above. It was observed that the desired phase was formed only in the small temperature range $1033\ K < T < 1083\ K$. The resulting diffractogram showed clear resemblance to that of $K_2Zr(PO_4)_2$ indicating both phases to be isostructural. The lattice constants were found to be $a = 4.980(4)$ Å, $c = 9.124(8)$ Å, $V = 196.0$ Å^3. Compared with $K_2Zr(PO_4)_2$ a is somewhat decreased and c slightly increased which confirms the assumption of isotypism. The smaller cell volume corresponds to the smaller size of Sn.

In spite of some efforts $K_2Ti(PO_4)_2$ could not be prepared. So, it must be concluded that Ti is too small to fit into the crystal structure of the $K_2Zr(PO_4)_2$-type.

Single crystals of $K_2Zr(PO_4)_2$ could be grown from melt solutions in the system $K_2O-P_2O_5-ZrO_2$. A typical procedure consisted of melting a mixture of 5 g K_2CO_3, 20 g KPO_3 and 1.5 g ZrO_2 at 1273 K for several hours, cooling rapidly to 1193 K and then cooling slowly with 0.4 K/h to 1063 K. The excess of K_2O prevented the formation of $KZr_2(PO_4)_3$. Hexagonal plates (diameter up to 3 mm, thickness about 0.1 mm) of the desired phase could be isolated from the solidified melt with boiling water.

Microscopic inspection of the $K_2Zr(PO_4)_2$ crystals showed the optical character to be uniaxial negative. X-ray photographs (Laue and Buerger precession) revealed the Laue group $\bar{3}m$ and the absence of systematic extinctions. No second harmonic generation could be detected exposing a powder sample to laser light of 1064 nm. This suggests the existence of an inversion symmetry. Differential scanning calorimetry up to 493 K proved that the crystals were strictly anhydrous.

The structure determination was carried out on two crystals from different growth batches. The results of the first investigation will be reported in detail. Here we used a crystal of irregular shape with dimensions $0.15 \times 0.2 \times 0.3$ mm. The crystal was mounted on an Enraf-Nonius CAD4 four-circle diffractometer (MoK_α-radiation, graphite monochromator). The lattice constants were refined from 25 well-centered reflections in the angular range $20° < \Theta < 36°$. We obtained $a = 5.176(1)$ Å, $c = 9.011(2)$ Å. The intensities of 3702 reflections were collected with a Θ-range up to 35° (full sphere: $h, k \in (-8, 8)$, $l \in (-14, 14)$, $\omega-2\Theta$-scan-mode). An empirical absorption correction, based on the Ψ-scans of six reflections, was applied, together with corrections for Lorentz and polarization effects. The data reduction resulted in 573 independent reflections with $I \geq 4\,\sigma(I)$. The structure was solved by direct methods using MULTAN 82 (Main et al., 1982).

The two space groups $P\bar{3}m1$ and $P\bar{3}1m$ are compatible with the Laue group $\bar{3}m$, the presence of inversion symmetry, and the absence of systematic extinctions. Attempts to solve the structure in $P\bar{3}1m$ failed. Solving the structure in $P\bar{3}m1$ made it necessary to introduce an occupation factor q of

Table 1. Atomic coordinates and isotropic thermal parameters of the atoms. q = occupation factor, $B_{eq} = \frac{4}{3}(a_1^2 \cdot B_{11} + \ldots + 2B_{23} \cdot a_2a_3 \cos\alpha_1)$.

Atom	x	y	z	q	B_{eq} [$Å^2$]
Zr	0	0	0	1	0.537(6)
P	1/3	2/3	0.1939(1)	1	0.68(1)
K	1/3	2/3	0.6504(1)	1	1.51(1)
O1	1/3	2/3	0.3612(4)	1	1.44(5)
O2A	0.6405(7)	0.9102(7)	0.1349(4)	0.6	0.84(5)
O2B	0.6430(10)	0.7310(10)	0.1342(7)	0.4	0.90(9)

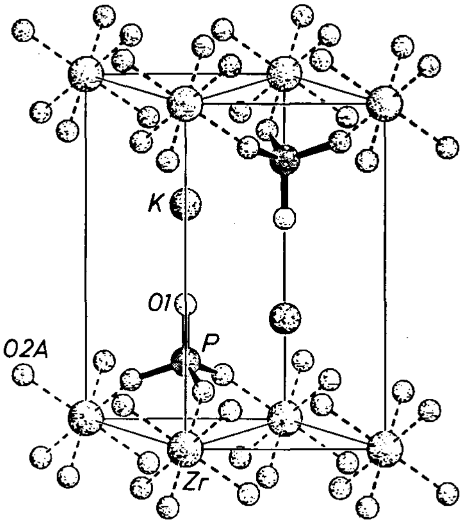

Fig. 1. Crystal structure of $K_2Zr(PO_4)_2$. The Zr coordination is indicated by dashed lines.

one half for the general position 12 j occupied by 6 O. In spite of the low resulting R-value of about 0.04 the structure can not be correct because shortest O–O distances of 0.94 Å occur.

Therefore, the subgroup $P\bar{3}$ was tried. Here the final R-values are R = 0.029 and $R_w = 0.041$ ($w = 1/\sigma^2(F)$) with anisotropic thermal parameters for all atoms. Extinction was corrected by $F_{corr} = F/(1 + E \cdot F^2 \cdot Lp)$, $E = 6.85 \cdot 10^{-6}$. The atomic parameters and equivalent isotropic temperature factors are listed in Table 1.[1] The partial occupation of about one half –

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[1] Additional material to this paper including the F_o/F_c-lists can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 54366, names of the authors and the title of the paper.

Table 2. Interatomic distances in Å and angles in degree with e.s.d.'s given in parentheses in terms of the last digit (*i*: three times; *ii*: six times). For O2B we find within the standard deviations identical values for bond lengths and angles as with O2A.

PO_4 tetrahedron			
P–O1	1.508(4)	O1–P–O2A	110.1(1)^{i}
–O2A	1.548(6)^{i}	O2A–P–O2A	108.8(3)^{i}
O1–O2A	2.504(4)^{i}		
O2A–O2A	2.518(5)^{i}		
ZrO_6 octahedron			
Zr–O2A	2.072(6)^{ii}	O2A–Zr–O2A	180.0(2)^{i}
			89.1(2)^{ii}
			90.9(2)^{ii}
KO_7 polyhedron			
K–O1	2.606(4)	O1–K–O1	119.9(1)^{i}
	2.990(1)^{i}		88.0(1)^{i}
–O2A	2.874(4)^{i}	O1–K–O2A	132.3(1)^{i}
			130.0(1)^{i}
			93.7(1)^{i}
			50.5(1)^{i}
		O2A–K–O2A	79.7(1)

Table 3. Thermal parameters of $K_2Zr(PO_4)_2$. The temperature factor has the form $T = \exp\{-2\pi^2 \Sigma_{ij} U_{ij} h_i h_j a_i^* a_j^*\}$, where a^* are reciprocal lattice constants.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	0.0051(1)	U_{11}	0.0102(2)	U_{11}	0	0
P	0.0086(4)	U_{11}	0.0087(4)	U_{11}	0	0
K	0.0215(4)	U_{11}	0.0144(4)	U_{11}	0	0
O1	0.023(2)	U_{11}	0.009(1)	U_{11}	0	0
O2A	0.0068(9)	0.0086(9)	0.013(1)	0.0015(6)	0.0036(9)	0.0001(9)
O2B	0.007(2)	0.013(2)	0.015(2)	0.006(1)	0.001(2)	0.003(2)

for the second crystal q was exactly 0.5 — is not avoided because now the positions (O2A and O2B) were found independently for 6 g. Moreover, the arrangement of the atoms is essentially the same as in $P\bar{3}m1$ because O2A and O2B are mirror positions. Fully occupied O2A and empty O2B sites or vice versa led to the not acceptable R-value of about 0.08.

The only possible interpretation of the low R-value obtained in $P\bar{3}$ is to assume merohedral twinning of the two crystals with nearly equal amounts of both individuals. Then the true structure has space group $P\bar{3}$ and full occupation of either O2A or O2B on each individual. The merohedrally twinned crystals exhibit Laue group $\bar{3}m$ as observed.

The crystal structure of $K_2Zr(PO_4)_2$ is drawn in Figure 1 regarding O2A, the interatomic distances and bonding angles are summarized in Table 2. The structure is dominated by the presence of isolated and slightly distorted PO_4 tetrahedra. The mean value for the P – O bond of 1.538(10) Å is in good agreement with those of other orthophosphates. Zirconium shows octahedral coordination. The ZrO_6 octahedra consist of oxygen atoms from six different PO_4 tetrahedra. Each O2A atom of the phosphate tetrahedra is involved in two other polyhedra, one ZrO_6 and one KO_7. The oxygen atom O1 takes part in four potassium polyhedra.

References

Clearfield, A., Stynes, J. A.: The preparation of crystallline zirconium phosphate and some observation on its ion exchange behaviour. J. Inorg. Nucl. Chem. **26** (1964) 117–129.

Clearfield, A., Smith, S. D.: The crystal structure of zirconium phosphate and the mechanism of its ion exchange behaviour. J. Colloid Interface Sci. **28** (1968) 325–330.

Dyer, A., Leigh, D., Ocon, F. T.: Studies on crystalline zirconium phosphate-I. J. Inorg. Nucl. Chem. **33** (1971) 3141–3151.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declerq, J. P., Woolfson, M. M.: MULTAN 11/82. A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data. University of York, England (1982).