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Crystal structure of zirconium chromium phosphide, $ZrCr_5P_3$

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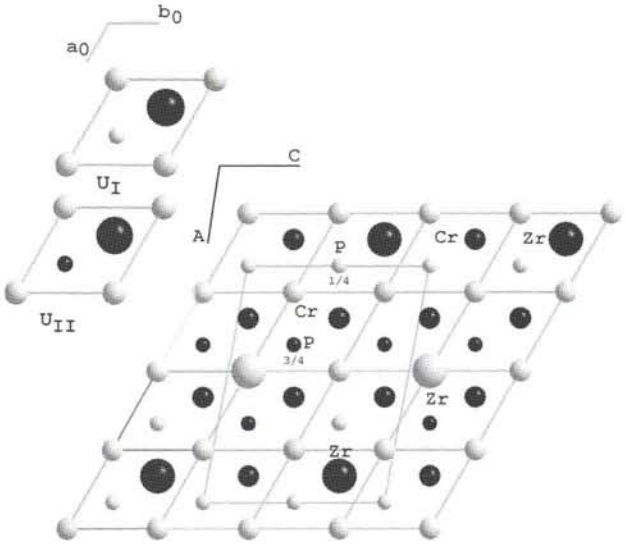

Abstract

$Cr_{10}P_6Zr_2$, monoclinic, $P12_1/m1$ (No. 11), $a = 9.465(5)$ Å, $b = 3.638(2)$ Å, $c = 6.983(2)$ Å, $\beta = 100.55(5)°$, $V = 236.4$ Å^3, $Z = 1$, $R_{gt}(F) = 0.027$, $wR_{gt}(F) = 0.028$, $T = 293$ K.

Source of material

Synthesis was done by the tin flux method. Samples in the atomic ratio Zr : Cr : P : Sn = 4 : 13 : 7 : 76 were heated in evacuated silica tubes up to 1173 K for one week and then slowly cooled in air. Tin-rich matrix was dissolved in diluted hydrochloric acid and led to shiny black needles. Energy-dispersive analysis of the single crystals in a scanning electron microscope confirmed the absence of tin in the single crystals.

Discussion

The ternary phosphide $ZrCr_5P_3$ is isostructural with UCr_5P_3 [1]. Its crystal structure reveals the usual coordination scheme for ternary phosphides with a metal/non me tal ratio equals or close to 2, i. e. the Zr atoms are in trigonal-prismatic, the Cr atoms are either in tetrahedral (Cr1, Cr3-Cr5) or in "square planar" pyramidal (Cr2) phosphorus coordination, while the P atoms are in tricapped trigonal prisms of metal atoms. There is no P—P bond in the structure and the mean distances Zr—P (2.78 Å) and Cr—P (2.40 Å) are in good agreement with similar distances previously reported in other zirconium chromium phosphides with identical metal/non metal ratio. These distances are in accordance with the sum of covalent radius of phosphorus (1.10 Å) and of the metal radius of zirconium (1.60 Å) or chromium (1.28 Å). From our recent classification scheme [2], based upon two fundamental units U_I and U_{II} corresponding to two hexagonal prisms (differing from the metalloid location) with the fundamental vectors $\vec{a}_0, \vec{b}_0, \vec{c}_0$, $\omega = 120°$ and the volume $V_0 = (\vec{a}_0 \wedge \vec{b}_0) \cdot \vec{c}_0$, the crystal structure of $ZrCr_5P_3$ can be viewed as being built from three units U_I and three units U_{II} displayed in such a way that the vectors $\vec{A}, \vec{B}, \vec{C}$ of its unit cell are depending to $\vec{a}_0, \vec{b}_0, \vec{c}_0$, by the vectorial relations $\vec{A} = 3\vec{a}_0 + \vec{b}_0$, $\vec{B} = \vec{c}_0$, $\vec{C} = 2\vec{b}_0$ and the corresponding magnitudes $A = a_0\sqrt{7}$, $B = c_0$ and $C = 2a_0$. Expected values for unit cell parameters, deducted from our classification scheme (A/C, B/C and B/A ratios of 1.322, 0.500, 0.378 and monoclinic angle of 100.89°) compare well with the experimental ones which have been found for $ZrCr_5P_3$ (1.355, 0.520, 0.384 and 100.55°).

Table 1. Data collection and handling.

Crystal:	shiny black, parallepiped form, size 0.01 × 0.05 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	144.3 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	70°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2376, 1169
Criterion for I_{obs}, $N(hkl)_{gt}$:	$F_{obs} > 4\,\sigma(F_{obs})$, 948
$N(param)_{refined}$:	56
Program:	CSD [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr	2e	0.22122(4)	1/4	0.80787(6)	0.0051(2)	0.0055(2)	0.0070(2)	0	0.00119(1)	0
Cr(1)	2e	0.50575(8)	1/4	0.12861(1)	0.0034(3)	0.0102(3)	0.0135(3)	0	0.0014(2)	0
Cr(2)	2e	0.27457(8)	1/4	0.31581(1)	0.0046(3)	0.0059(3)	0.0080(3)	0	0.0010(2)	0
Cr(3)	2e	0.91950(8)	1/4	0.54156(1)	0.0051(3)	0.0071(3)	0.0049(3)	0	0.0002(2)	0
Cr(4)	2e	0.91572(8)	1/4	0.91649(1)	0.0048(3)	0.0076(3)	0.0050(3)	0	0.0016(2)	0

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Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(5)	2*e*	0.49228(8)	1/4	0.62142(1)	0.0047(3)	0.0082(3)	0.0131(3)	0	0.0008(2)	0
P(1)	2*e*	0.67414(1)	1/4	0.4292(2)	0.0043(4)	0.0060(5)	0.0075(4)	0	0.0010(3)	0
P(2)	2*e*	0.00864(1)	1/4	0.2501(2)	0.0053(4)	0.0059(5)	0.0067(4)	0	0.0008(3)	0
P(3)	2*e*	0.66854(1)	1/4	0.9070(2)	0.0051(4)	0.0063(5)	0.0076(4)	0	0.0009(3)	0

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