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The chromium phosphide carbide Cr_8P_6C

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Abstract

The new phosphide carbide with ideal composition Cr_8P_6C was prepared by reacting powers of Cr, Cr_3C_2 and red P in evacuated silica tubes. Small single crystals were obtained by annealing these components in an NaCl/KCl flux. Their structure was determined from four-circle diffractometer data of two different multiple-domain crystals with practically the same results: $P\bar{3}1m$, $a = 668.2(4)$ pm, $c = 460.6(3)$ pm, $R(F^2) = 0.030$ for 517 structure factors and 25 variable parameters, resulting in a composition $Cr_{8.105(5)}P_6C_{0.76(2)}$. The structure is closely related to the higher symmetry ($P6_3/mcm$) structure of Mn_5Si_3 and its filled version Mo_5Si_3C. The lower symmetry results from an ordered arrangement of vacancies at the carbon and at one of the metal sites of Mo_5Si_3C. The crystal chemistry of these structures is discussed.

Keywords: Chromium phosphide carbide; Crystal structure; Interstitial carbides

1. Introduction

The ternary system chromium–phosphorus–carbon has been investigated by Baurecht, Boller and Nowotny, who reported two ternary phases with the compositions $Cr_6P_{2.6}C_{0.4}$ [1] and Cr_3PC [2] for the isothermal section at 1000°C. While the structure of Cr_3PC can be rationalized as a filled-up version of an Re_3B-type structure, the structure of the compound $Cr_6P_{2.6}C_{0.4}$ has great similarity with that of Fe_2P. The ternary compound reported here was prepared at lower temperatures. Its structure is different and may be derived from that of Mn_5Si_3. The structure was determined from X-ray data of two multiple-domain crystals, which resulted in the exact compositions $Cr_{8.103(8)}P_6C_{0.71(3)}$ and $Cr_{8.105(5)}P_6C_{0.76(2)}$. However, for simplicity we use the ideal formula Cr_8P_6C for most purposes.

2. Sample preparation, properties and lattice constants

Starting materials were chromium powder (Certified Chemicals 99.99%), pieces of semiconductor grade red phosphorus (Hoechst-Knapsack, ultrapure) and graphite flakes (Alpha, greater than 99.5%). First the binary carbide Cr_3C_2 was prepared from a stoichiometric mixture of the elements, which were cold pressed to pellets (300 mg) and reacted in an arc-melting furnace. The educts were mixed in various atomic ratios, for example Cr:P:C = 3:2:2, and sealed in evacuated silica tubes. The samples were annealed for up to 2 weeks at 800°C and usually quenched to room temperature. Small single crystals were obtained by annealing these components in an NaCl/KCl flux. The NaCl/KCl matrix was dissolved in water. Various amounts of the binary compounds CrP [3], $Cr_{12}P_7$ [1] and Cr_3C_2 [4] were frequently observed in the reaction products.

The crystals of the ternary compound were separated mechanically from the binary compounds under a microscope. Energy-dispersive X-ray fluorescence analyses did not reveal impurity elements such as silicon. The crystals of the new compound were well developed hexagonal prisms with diameters up to 80 pm and heights up to 60 pm. They are stable in air and not attacked by non-oxidizing acids or bases.

The products were characterized by their Guinier powder patterns using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. Indices could be assigned on the basis of a primitive hexagonal cell. The lattice constants (Table 1) were obtained from least-squares fits.

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Table 1
Crystal data for two crystals of $Cr_{8+x}P_6C_{1-y}$ [a]

	$Cr_{8+x}P_6C_{1-y}$(I)	$Cr_{8+x}P_6C_{1-y}$(II)
Space group	$P\bar{3}1m$ (No. 162)	$P\bar{3}1m$ (No. 162)
Lattice constants from single crystal [and Guinier powder] data		
a (pm)	668.1(1) [668.6(2)]	667.6(2) [668.2(4)]
c (pm)	461.03(4) [460.7(1)]	460.8(3) [460.6(3)]
V (nm^3)	0.1782 [0.1784]	0.1779 [0.1781]
x	0.103(8)	0.105(5)
y	0.29(3)	0.24(2)
Formula units per cell	$Z = 1$	$Z = 1$
Formula weight	613.2	613.8
Calculated density (g/cm^3)	5.72	5.72
Crystal dimensions (μm^3)	20 × 40 × 10	40 × 40 × 60
$\theta/2\theta$ scans up to (deg)	$2\theta = 90$	$2\theta = 90$
Range in h, k, l	±13, ±13, 0 – 9	±13, ±13, −9 + 4
Total number of reflections	3591	4837
Unique reflections	544	544
Ratio of the individual twin domains	1.62(1):1	6.29(2):1
Inner residual (on F^2 values)	$R_i = 0.093$	$R_i = 0.057$
Reflections with $F_o > 4\sigma(F_o)$	489	517
Number of variables	21	25
Highest, lowest residual electron density (e Å^{-3})	1.5, −1.6	2.4, −2.3
Residual (on F^2 values)	$R = 0.047$	$R = 0.030$
Weighted residual (on F^2 values)	$R_w = 0.043$	$R_w = 0.031$

[a] The lattice constants resulting from the Guinier powder data are considered to be more reliable. For calculation of the interatomic distances, those from sample II were used. Standard deviations in the positions of the least significant digits are listed in parentheses throughout the paper.

3. Structure determination

The structure determination was unusally difficult, because the data set of the crystal first investigated suggested a hexagonal axis. It turned out that this crystal was twinned and the real symmetry was trigonal. This was revealed from the intensity data of a second crystal. That crystal was also twinned, however, the ratio of the two differently oriented domains was such that the true trigonal symmetry could be recognized. The two multiple-domain crystals were isolated from samples with different compositions. Crystal I was taken from a sample with the atomic ratio Cr:P:C = 36:28:36, while crystal II originated from a sample with the composition 36:9:55.

The intensity data were collected using a four-circle diffractometer with graphite-monochromated Mo Kα radiation and a scintillation counter with pulse-height discrimination. The background was determined at both ends of each $\theta/2\theta$ scan. Absorption corrections were made from psi scan data.

The structure has the trigonal Laue symmetry $\bar{3}m$, however, as already mentioned, the twinned crystals mimicked the hexagonal symmetry $6/mmm$. There were no space group extinctions and since initially we were not sure of the correct Laue symmetry, a total of six trigonal and five hexagonal space groups was possible. Eventually the structure was refined successfully in a space group of the highest symmetrical trigonal class $P\bar{3}1m$ (No. 162). A full-matrix least-squares program was used with atomic scattering factors [5], corrected for anomalous dispersion [6]. The coincidences of the reflections resulting from the twinning (matrix $\bar{1}00/0\bar{1}0/001$) were accounted for by the program system SHELXL 93 [7]. The secondary extinction was corrected isotropically by one variable parameter and the weighting scheme accounted for the counting statistics. Further details of the two data sets used for refinement of the structure are summarized in Table 1.

The ideal composition of this structure is Cr_8P_6C. However, refinement of the occupancy parameters showed that the carbon position is occupied only to 71(3)% and 76(2)% in crystals I and II respectively. A further complication arose with the position 2d 1/3, 2/3, 1/2. There is a large void at this position with six phosphorus neighbours at 229 pm. It is therefore well suited for occupancy by a chromium atom. The refinement of the occupancy parameter for this position together with the thermal parameters resulted in occupancy parameters of 5.2(4)% and 5.2(3)% chromium for the data sets I and II. When a carbon atom was placed at this position the occupancies refined to 30(2)% in both cases. For both of these refinements the isotropic B values were held constant at 0.4 Å^2. Since the void is rather large for a carbon atom, we considered the possibility that the carbon atom might be situated in a split position 1/3, 2/3, $1/2 \pm z$. However such least-squares refinements moved the carbon atom back to $z = 1/2$. Thus we considered the partial occupancy of this position by chromium atoms as much more likely. The occupancy

Table 2
Atom parameters of $Cr_{8.104(3)}P_6C_{0.76(2)}$ [a]

Atom	$P\bar{3}1m$	Occupancy	x	y	z	B_{eq}
Cr1	6k	1	0.24405(5)	0	0.2527(1)	0.328(6)
Cr2	2c	1	1/3	2/3	0	0.36(1)
Cr3	2d	0.052(3)	1/3	2/3	1/2	0.5(2)
P	6k	1	0.59548(8)	0	0.2713(2)	0.36(1)
C	1a	0.76(2)	0	0	0	0.42(12)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr1	35(1)	39(1)	51(1)	20(1)	−3(1)	0
Cr2	36(1)	36(1)	65(3)	18(1)	0	0
Cr3	40(30)	40(30)	120(60)	20(10)	0	0
P	40(1)	40(2)	73(3)	20(1)	−7(2)	0
C	40(20)	40(20)	60(30)	50(10)	0	0

[a] The anisotropic thermal parameters U ($Å^2 \times 10^4$) are defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$. The equivalent isotropic thermal parameter B_{eq} ($\times 100\ nm^2$) is also given.

parameters for the other three atoms of the more accurate data set II were as follows: Cr1 100.0(2)%, Cr2 98.6(4)%, P 100.5(4)%; they were fixed at the ideal values in the final least-squares cycles. The results of the structure refinements from the two data sets agreed all within four standard deviations of the more accurate data set. Therefore only the results of the more accurate refinement II are listed in Table 2. The results of refinement I and the structure factor tables are available from the authors [8].

4. Discussion

The phase diagram of the ternary system chromium–phosphorus–carbon reported by Baurecht et al. [1] does not contain the compound Cr_8P_6C characterized in the present paper. However, there is no contradiction. We obtained Cr_8P_6C only in samples annealed at 800°C. Samples annealed at 900 to 1000°C did not contain this compound, in agreement with the phase equilibria established for the ternary system at 1000°C [1]. Cr_8P_6C does not seem to have a large homogeneity range, since the two structure refinements resulted in practically the same composition, in spite of the large difference in elemental starting ratios of the two samples mentioned above. The occupancy parameters of crystal I correspond to the composition $Cr_{8.103(8)}P_6C_{0.71(3)}$ and those of crystal II resulted in $Cr_{8.105(5)}P_6C_{0.76(2)}$. The weighted average is $Cr_{8.104(5)}P_6C_{0.74(2)}$.

The Cr3 site has an occupation factor of only 5.2(3)%; the refinement of this position assuming its occupancy by carbon atoms resulted in 30(2)%. However, the coordination polyhedron of that site is too large for its occupancy with carbon atoms (Table 3, Fig. 1). The thermal vibration at high temperatures could be expected to hold the carbon atoms at the metastable central position of that polyhedron, however at room temperature the carbon atoms should prefer to be situated within the bonding distance of at least some atoms. Since the U_{33} parameter of that site is rather large, we had placed the carbon atoms, assumed for that site, in a corresponding split position. However, as already mentioned above, the refinements moved the carbon atoms again to the centre of the polyhedron. Thus, most evidence favours the occupancy of this site by chromium atoms.

Table 3
Interatomic distances of Cr_8P_6C [a]

Cr1:C	200.4	*Cr3*:6P	228.8
1P	235.0	2Cr2	230.3
2P	235.9	6Cr1	281.8
1P	244.0	*P*:(2Cr3	228.8)
1P	264.1	1Cr1	235.0
2Cr1	280.2	2Cr1	235.9
(2Cr3	281.8)	2Cr2	238.5
2Cr1	282.5	1Cr1	244.0
2Cr2	282.9	1P	246.3
2Cr1	284.2	1Cr1	264.1
Cr2:(2Cr3	230.3)	1P	280.6
6P	238.5	*C*:6Cr1	200.4
6Cr1	282.9		

[a] The standard deviations are all 0.1 pm or less. The Cr3 position is occupied to only 5.2%. For this reason the corresponding interatomic distances are in parentheses. All distances shorter than 380 pm involving Cr atoms and 295 pm (P–P, P–C, C–C interactions) are listed.

In discounting the marginally occupied Cr3 site, the Cr–Cr distances in Cr_8P_6C cover the narrow range form 280.2 to 284.2 pm. This may be compared with the range from 267 to 288 pm in $Cr_{12}P_7$ [1] or with that from 253.6 to 292.8 pm found for UCr_5P_3 [9] and the two modifications of UCr_6P_4 [10]. The Cr–P distances

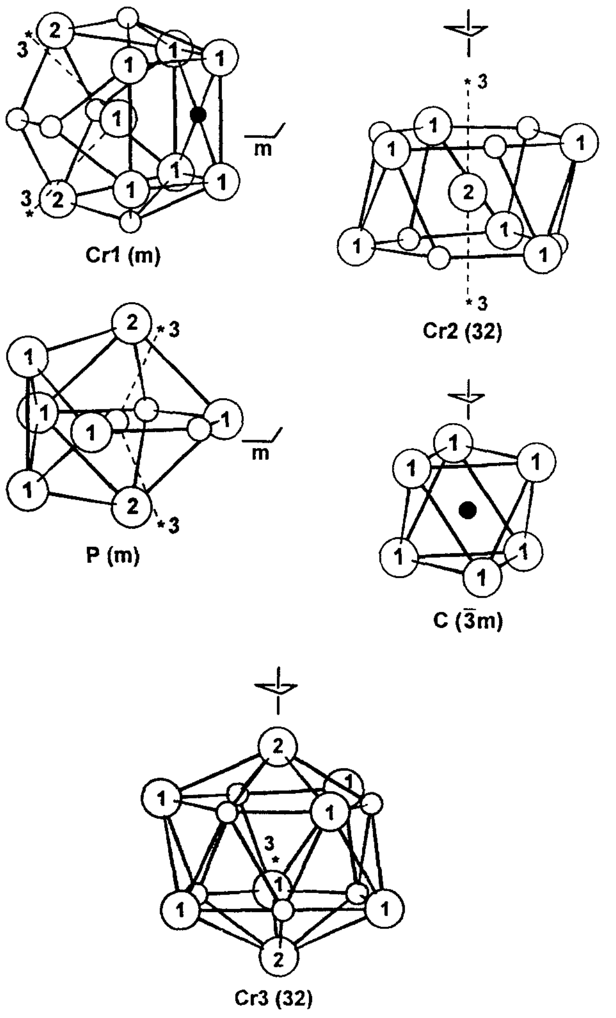

Fig. 1. Coordination polyhedra of Cr_8P_6C. Single-digit numbers correspond to the designations of the chromium atoms. The site symmetries are given in parentheses.

in Cr_8P_6C extend from 235.0 to 244.0 pm. This range is again comparable with those extending from 225 to 246 in $Cr_{12}P_7$, and from 232.3 to 252.3 pm in UCr_5P_3 and in the two modifications of UCr_6P_4.

Most phosphorus atoms in these compounds have nine metal neighbours in the arrangement of a trigonal prism with three metal neighbours outside the rectangular faces of the prims. In Cr_8P_6C the phosphorus atoms have seven chromium neighbours in a rather irregular arrangement, with two more potential chromium neighbours from the marginally occupied Cr3 site. In addition, the phosphorus atoms have one phosphorus neighbour at a distance of 246.3 pm, which is only slightly greater than the typical two-electron bond distance of 223.8 pm [11]. A similar short P–P distance of 248.5 pm was found for one phosphorus site in $LaCo_8P_5$ [12].

The carbon atoms in Cr_8P_6C have an octahedral chromium environment. This is the typical coordination of the carbon atoms in binary carbides of the early transition metals, while trigonal prismatic and square antiprismatic coordination is usually found for carbon atoms in carbides of the late transition metals. Octahedral chromium coordination was also observed for the carbon atoms in Cr_3PC [2], where the Cr–C distances are not known because the positional parameters have not been determined. However, the Cr–C distances of 199 pm in the octahedral Cr_6C groups of Cr_2AlC [13] compare favourably with the Cr–C distances of 200.4 pm found in Cr_8P_6C.

As can be seen from Fig. 2, the structure of Cr_8P_6C is closely related to the structure of Mn_5Si_3, and especially to its "filled up" version, the Nowotny phase Mo_5Si_3C [14]. This is best recognized if the formula of the latter compound is doubled, i.e. $Mo_{10}Si_6C_2$. The phosphorus sites of Cr_8P_6C and the silicon sites of $Mo_{10}Si_6C_2$ exactly correspond to each

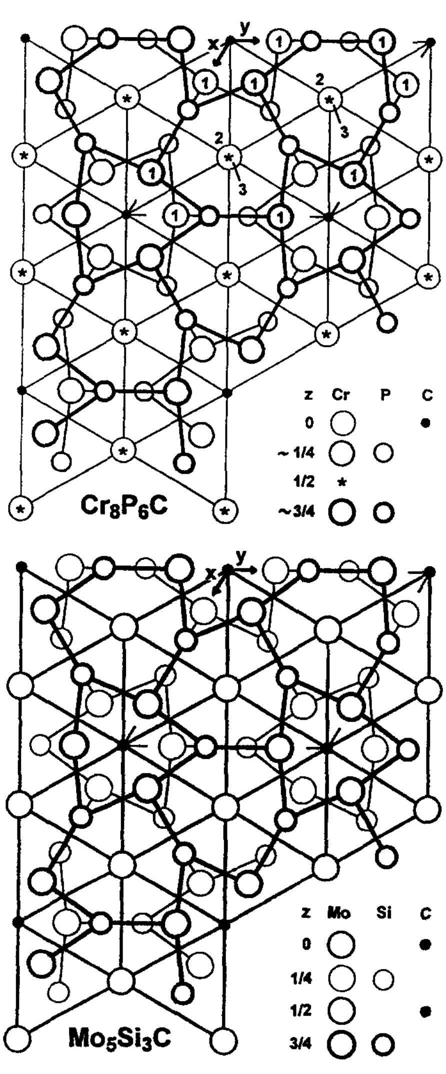

Fig. 2. The crystal structure of Cr_8P_6C as compared with the structure of Mo_5Si_3C. Atoms connected by thick and thin lines are at $z = 3/4$ and $1/4$; these lines do not necessarily represent atomic bonds. Single-digit numbers correspond to the designations of the chromium atoms.

other. One half of one molybdenum site of $Mo_{10}Si_6C_2$ is practically unoccupied in Cr_8P_6C. This is the Cr3 site with an occupancy of only 5.2%. Furthermore, the carbon positions of $Mo_{10}Si_6C_2$ at $z = \frac{1}{2}$ are unoccupied in Cr_8P_6C. The formation of vacant transition metal sites in Cr_8P_6C is probably caused by the higher electron count of the phosphorus atoms. It has been argued before [15,16] that vacant sites in intermetallic compounds may be filled with non-bonding electron similar to the well known space requirements of "lone pairs" in compounds of the main group elements in their lower oxidation states, e.g. Sn(II) or Sb(III). If these vacant Cr3 sites were filled, the non-bonding electrons might become antibonding. In this context it is interesting to know already that in the molybdenum silicide carbide the molybdenum site corresponding to the Cr3 site of $Cr_{8.105}P_6C_{0.76}$ is not completely occupied, i.e. the exact formula is $Mo_{9.6}Si_6C_{1.2}$ [14].

This formula, furthermore, indicates that the carbon positions of the latter compound are also not completely filled. Thus, the main difference between the structures of $Cr_{8.105}P_6C_{0.76}$ and $Mo_{9.6}Si_6C_{1.2}$ is the larger proportion of unoccupied transition metal and carbon sites in the phosphide carbide. This allows an ordered distribution of occupied and unoccupied atomic sites, which lowers the symmetry from $P6_3/mcm$ for the Nowotny phase to $P\bar{3}1m$ for the compound reported here with the ideal composition Cr_8P_6C.

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