

The Crystal Structure of a β - V_3S -Type Modification of Ta_3P

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Ta_3P occurs in two modifications: low-temperature α - Ta_3P with the Ti_3P -type structure, and high-temperature β - Ta_3P with the β - V_3S -type structure. The crystal structure of β - Ta_3P has been refined from X-ray single-crystal diffraction data: space group $P4_2/nbc$ (No. 133), $a=10.1542(4)$ Å, $c=5.0137(3)$ Å, Ta(1) in 8j: $x=0.1576(1)$, Ta(2) in 8j: $x=0.5490(1)$, Ta(3) in 8i: $x=0.6048(1)$, P in 8h: $x=0.544(1)$, (origin at $\bar{1}$).

The occurrence of a tantalum phosphide with the approximate composition Ta_3P was observed in a cursory examination of the Ta–P system at elevated temperatures.¹ The powder diffraction pattern was indexed on a primitive tetragonal unit cell of dimensions $a=10.154$ Å, $c=5.012$ Å. In analogy to a number of Me_3P -type phosphides previously discovered in systems related to Ta–P it was assumed that Ta_3P crystallizes with the Ti_3P -type structure.²

During studies of various alloys containing transition metals and phosphorus, the X-Ray Crystallography Group at Chulalongkorn University isolated a tantalum phosphide single crystal fragment. Photographic X-ray data obtained by the Weissenberg method for this crystal indicated a primitive tetragonal symmetry, with unit cell dimensions closely the same as those reported previously for Ta_3P .¹ The Laue symmetry was $4/mmm$, however, while a Ti_3P -type structure should possess the lower Laue symmetry $4/m$. Subsequent structure analysis made by the Chulalongkorn group showed that the crystal was in fact isostructural with β - V_3S .³

In a re-examination of the Ta–P system at Uppsala,⁴ preliminary studies of crystals obtained in tantalum-rich alloys showed that Ta_3P actually

occurs in two modifications: one with the β - V_3S -type and the other with the Ti_3P -type structure. For both types of crystal, X-ray diffraction data were collected by single-crystal diffractometry. The present paper gives an account of the structure analyses made at the Chulalongkorn and Uppsala Universities for the β - V_3S -type tantalum phosphide.

EXPERIMENTAL DETAILS AND RESULTS

Preparation and powder diffraction work. Tantalum monophosphide was synthesized by heating tantalum metal (S.A. Lindberg & Co.) and red phosphorus, both of purities higher than 99 %, at 1040 °C in evacuated and sealed silica tubes. Ta_3P alloys were prepared by heating appropriate mixtures of tantalum monophosphide and tantalum in an arc furnace or an induction furnace under a protective atmosphere of argon. β - V_3S -type Ta_3P crystals were obtained directly from the as-cast arc-melted alloys, while Ti_3P -type crystals were found in alloys, which had been annealed at 1700 °C in the induction furnace. This indicates that the β - V_3S and the Ti_3P -type phases are high- and low-temperature modifications of Ta_3P , respectively. In the following, the low-temperature form is denoted by α - Ta_3P , and the high-temperature form by β - Ta_3P .

Powder diffraction patterns were recorded in Hagg-Guinier-type focussing cameras (Philips XDC-700) with $CuK\alpha_1$ or $CrK\alpha_1$ radiation and silicon ($a=5.431065$ Å)⁵ as internal calibration standard. The powder patterns of the two forms of Ta_3P were very similar, with almost insignificant differences in diffraction angles and only minor differences in intensity between corresponding lines.

The unit cell dimensions were refined by the least-squares method using the local program CELNE.⁶

Structure refinement based on photographic data. Intensity data were recorded with zirconium-filtered MoK radiation in a Nonius Weissenberg camera. The multiple-film technique was used with thin iron foils interleaved with the films. The needle-shaped crystal was mounted with the tetragonal axis as rotation axis and $hk0$ and $hk1$ reflexions were recorded. The intensities of the reflexions were measured by visual comparison with an intensity scale obtained by timed exposures of one reflexion. Absorption corrections were applied to the intensity data, the crystal shape being approximated to a cylindrical form. The structure was refined by the least-squares method, initial values for the positional parameters being taken from the β -V₃S structure.³ Atomic scattering factors and anomalous dispersion corrections were taken from International Tables.⁷ Weights were applied according to Cruickshank's formula.⁸ The calculations were carried out on IBM 1800 and IBM 370/155 computers using programs described in Ref. 9. The refinement converged with a final conventional R -value of 0.135 for the 102 independent observed reflexions. The results are given in Table 1.

Structure refinement based on diffractometer data. Intensities were recorded with a PDP8/A-controlled Nonius CAD-4F diffractometer using graphite-monochromatized MoK α radiation. An ω - $3/4\theta$ scanning mode was used, and instrumental stability was checked by remeasuring three standard reflexions regularly. A total number of 1590 reflexions, of these 862 independent, was recorded up to 90° in 2θ . In the region $0 < 2\theta \leq 15^\circ$, the corresponding

indices were $-7 \leq h \leq 7$, $-7 \leq k \leq 7$, $-3 \leq l \leq 3$, and for $15 < 2\theta \leq 90^\circ$, $0 \leq h \leq 20$, $0 \leq k \leq 20$, $0 \leq l \leq 9$. Corrections for absorption were applied using the Gaussian grid method. Due to unavoidable errors in the description of the crystal form in combination with the extremely strong absorption ($\mu = 1254 \text{ cm}^{-1}$, transmissions varying between 0.07 and 0.22), some systematic absorption errors affected the final intensity material. Equivalent reflexions were averaged and refinement of the structure was performed by the least-squares method in a similar manner as for the photographic intensity data. The function minimized was $w(|F_o^n| - |F_c^n|)^2$. Weights were assigned to the reflexions according to the formula $w^{-1} = \sigma^2(F_o^n) + (pF_o^n)^2$, where $\sigma^2(F_o^n)$ is based on counting statistics and the empirical factor p was set to 0.03. A scale factor, positional parameters and individual isotropic temperature factors were refined. The three strongest reflexions were affected by extinction and were eventually assigned zero weight in the refinement.

For the 859 reflexions refined the following agreement factors were finally obtained: $R(F^2) = 0.134$, $R(F) = 0.108$, $R_w(F^2) = 0.224$, where $R(F^n) = \sum |F_o^n| - |F_c^n| / \sum |F_o^n|$, and $R_w(F^n) = [\sum w(|F_o^n| - |F_c^n|)^2 / \sum w|F_o^n|^2]^{1/2}$.

The final structure data obtained are presented in Table 1. Interatomic distances, based on the positional parameters and standard deviations derived from the diffractometer data, are given in Table 2.

Table 1. Structure data for β -Ta₃P, based on space group $P4_2/nbc$, origin at $\bar{1}$.

Atom	x	y	z	B
Diffractometer data				
Ta(1) in 8j	0.1576(1)	(=x)	1/4	0.14(2)
Ta(2) in 8j	0.5490(1)	(=x)	1/4	0.21(2)
Ta(3) in 8i	0.6048(1)	1/4	1/2	0.20(2)
P in 8h	0.544(1)	1/4	0	0.4(1)
Film data				
Ta(1) in 8j	0.1563(7)	(=x)	1/4	0.38(12)
Ta(2) in 8j	0.5497(6)	(=x)	1/4	0.13(9)
Ta(3) in 8i	0.6038(8)	1/4	1/2	0.14(9)
P in 8h	0.544(6)	1/4	0	0.6(8)

Table 2. Interatomic distances in β -Ta₃P. Distances shorter than 3.5 Å are listed.

Distance	Å	Distance	Å
Ta(1)–2P	2.579(8)	Ta(3)–2P	2.557(8)
– Ta(1)	2.653(2)	– 2P	2.581(2)
– 2Ta(2)	2.952(1)	– Ta(2)	2.859(1)
– Ta(2)	2.968(2)	– Ta(2)	2.859(1)
– 2Ta(3)	3.091(1)	– Ta(3)	2.948(3)
– 4Ta(1)	3.131(1)	– 2Ta(1)	3.091(1)
– 2Ta(2)	3.176(1)	– 4Ta(3)	3.260(1)
		– 2Ta(2)	3.333(1)
Ta(2)–2P	2.575(4)	P–2Ta(3)	2.557(8)
– 2Ta(3)	2.859(1)	– 2Ta(2)	2.575(4)
– 2Ta(2)	2.875(1)	– 2Ta(1)	2.579(8)
– 2Ta(1)	2.952(1)	– 2Ta(3)	2.581(2)
– Ta(1)	2.968(2)	– 2Ta(2)	3.285(1)
– 2Ta(1)	3.176(1)		
– 2P	3.285(1)		
– 2Ta(3)	3.333(1)		

CONCLUDING REMARKS

The principal features of the β -V₃S-type structure were presented and discussed by Pedersen and Grønvold,³ and our results for β -Ta₃P are in general agreement with those obtained for β -V₃S. The close relationship between the four tetragonal structure types Fe₃P, Ti₃P, α -V₃S and β -V₃S has been stressed in many previous discussions.^{10,11} With the discovery of β -Ta₃P, all four of these types are now represented among the transition metal phosphide structures. A more detailed crystal chemical analysis of this structure family is deferred to a forthcoming paper.

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