

Crystal Structure Refinement of α -Ti₅P₃

WILDER CARRILLO-CABRERA and TORSTEN LUNDSTRÖM

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of α -Ti₅P₃ has been refined using X-ray single-crystal diffractometry. α -Ti₅P₃ crystallizes in the space group *Pnma* (No. 62) with the cell dimensions: $a=9.7475(5)$ Å, $b=7.4403(3)$ Å, $c=6.5056(5)$ Å. α -Ti₅P₃ is iso-structural with β -Yb₅Sb₃. The structure has been refined on F^2 to an R -value of 0.124 without excluding any reflexions.

In previous investigations of the Ti–P and Ti–Cu–P systems three phases of the ideal composition M₅P₃ have been reported, namely orthorhombic α -Ti₅P₃ with the β -Yb₅Sb₃ type structure, orthorhombic β -(Ti,Cu)₅P₃ with the Nb₅P₃ type structure and hexagonal γ -Ti₅P₃ with the Mn₅Si₃ type structure. The notation α - γ is used here merely to distinguish between the different M₅P₃ phases and it does not include information, for instance, regarding thermal stability. Of these phases the hexagonal modification is likely to contain light-atom impurities (N or O).^{1,2} Crystals of the β -(Ti,Cu)₅P₃ modification were obtained from a copper melt and contained 1.6 atom-% copper. It is not known presently whether this phase actually occurs in the binary Ti–P system. α -Ti₅P₃ was prepared by Snell⁴ as a binary Ti–P phase and was denoted Ti_{1.7}P. This phase was found to crystallize³ in the β -Yb₅Sb₃ type structure⁵ in agreement with a suggestion by Berger.⁶ In the present paper we report the results of a single-crystal structure investigation of α -Ti₅P₃ containing ~0.2 atom-% copper.

EXPERIMENTAL

Preparation. Single crystals were prepared³ by cooling a ternary melt (approx. 2.5 g) of nominal composition Ti_{0.02}Cu_{0.97}P_{0.01} to room tempera-

ture. Subsequently the solidified melt was heat treated at 800 °C for 12 days. The crystals were isolated by dissolving the copper matrix in nitric acid. A binary alloy of nominal composition Ti_{1.78}P was prepared by arc-melting³ and used to obtain powder intensity data. The titanium and red phosphorus used in the syntheses were from Koch-Light Laboratories, Colnbrock, England, and had a claimed purity of 99.95 and 99.999 % respectively. The copper was from Outokumpu Oy, Pori, Finland, and had a purity, as analyzed, of 99.99 %.

X-Ray diffraction measurements and data reduction. The cell dimensions were determined using a Guinier-Hägg focussing camera with CuK α ₁ radiation ($\lambda=1.540598$ Å) and silicon as internal calibration standard ($a=5.431065$ Å). The powder diffraction intensities were measured using a SAAB Mark II film scanner.^{7,8} Powder data are presented in Table 1.

The crystal, selected for the intensity measurements, had a pseudooctahedral shape and was bounded by faces with the indices (101) and (011), and slightly truncated by the planes (100). The external crystal symmetry was *mmm*. The size of the crystal was approximately 0.03 × 0.04 × 0.05 mm. The intensity data were recorded using a computer-controlled Stoe-Philips four-circle diffractometer with graphite monochromatized MoK α radiation and an NaI scintillation detector. The integrated intensities were measured using the θ - 2θ step-scan technique. Instrumental stability and crystal setting were checked by remeasuring three standard reflexions every 40 reflexions and no significant changes were observed. Up to $2\theta=25^\circ$ all reflexions were measured and for $25^\circ < 2\theta \leq 95^\circ$ reflexions with $5 \leq h \leq 20$, $4 \leq k \leq 15$ and $3 \leq l \leq 12$.

The single-crystal intensities were corrected for Lorentz, polarization and absorption effects, using the Gaussian grid method, and a linear absorption coefficient of 88.7 cm⁻¹, calculated with data from Ref. 9. The transmission varied between 0.67 and

Table 1. Powder diffraction data for α -Ti₅P₃. Cell dimensions: $a=9.7539(4)$ Å, $b=7.4263(3)$ Å, $c=6.5032(2)$ Å.

<i>h k l</i>	<i>Q</i> ×10 ⁵ obs	(Å ⁻²) calc	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	Intensity obs calc	<i>h k l</i>	<i>Q</i> ×10 ⁵ obs	(Å ⁻²) calc	<i>d</i> _{obs} (Å)	<i>d</i> _{calc} (Å)	Intensity obs calc
1 0 1		3416		5.411	- 0	1 3 2		26829		1.931	- 4
0 1 1		4178		4.892	- 0	2 1 3		27298		1.914	185 ^d 14
2 0 0		4204		4.877	- 2	4 1 2		28089		1.887	- 1
1 1 1		5229		4.373	- 0	3 3 1	28135	28144	1.885	1.885	4 3
2 1 0		6018		4.076	- 0	5 0 1		28642		1.871	- 1
2 0 1	6562	6569	3.904	3.902	- 3	0 4 0	29013	29012	1.857	1.857	24 40
0 2 0	7249	7253	3.714	3.713	- 4	1 2 3		29585		1.839	- 0
2 1 1		8382		3.454	- 0	2 3 2	29985	29982	1.826	1.826	3 5
0 0 2		9458		3.252	- 0	5 1 1		30455		1.812	- 0
1 0 2		10509		3.085	- 1	3 0 3		30741		1.804	- 0
1 2 1		10669		3.062	- 1	1 4 1		32428		1.756	- 1
2 2 0	11449	11457	2.955	2.954	- 2	3 1 3		32554		1.753	- 0
3 0 1		11824		2.908	- 0	2 2 3	32750	32738	1.747	1.748	6 10
1 1 2		12322		2.849	- 1	4 3 0	33137	33137	1.737	1.737	6 5
3 1 1		13638		2.708	- 0	2 4 0		33217		1.735	- 0
2 0 2		13663		2.705	- 2	4 2 2		33529		1.727	- 2
2 2 1	13823	13822	2.690	2.690	31 30	3 3 2		35237		1.685	- 3
2 1 2	15473	15476	2.542	2.542	3 2	4 3 1		35501		1.678	- 0
0 2 2	16719	16711	2.446	2.446	5 5	2 4 1		35581		1.676	- 1
4 0 0	16820	16818	2.438	2.438	13 11	5 0 2		35736		1.673	- 0
1 2 2	17765	17762	2.373	2.373	90 100	5 2 1	35888	35895	1.669	1.669	9 10
4 1 0		18631		2.317	- 3	5 1 2		37549		1.632	- 0
0 3 1	18679	18684	2.314	2.313	51 ^a 21	0 3 3		37600		1.631	- 0
3 0 2	18907	18918	2.300	2.299	36 37	0 0 4		37833		1.626	- 1
3 2 1	19067	19078	2.290	2.289	66 ^b 53	6 0 0		37840		1.626	- 0
4 0 1	19184	19182	2.283	2.283	60 61	3 2 3		37994		1.622	- 0
1 3 1		19735		2.251	- 3	4 0 3		38098		1.620	- 1
2 3 0		20524		2.207	- ^c 8	0 4 2		38470		1.612	- 1
3 1 2		20731		2.196	- 1	1 3 3		38651		1.608	- 1
2 2 2	20911	20916	2.187	2.187	96 84	1 0 4	38881	38884	1.604	1.604	5 5
4 1 1		20995		2.182	- 7	1 4 2		39521		1.591	- 1
1 0 3	22324	22332	2.117	2.116	38 33	6 1 0		39653		1.588	- 0
2 3 1	22898	22888	2.090	2.090	13 10	4 1 3	39914	39912	1.583	1.583	2 3
0 1 3	23112	23094	2.080	2.081	6 4	6 0 1		40204		1.577	- 1
4 2 0	24064	24071	2.039	2.038	49 46	1 1 4		40697		1.568	- 1
1 1 3		24145		2.035	- 1	3 4 1		40837		1.565	- 0
2 0 3	25482	25485	1.981	1.981	21 10	2 3 3	41783	41805	1.547	1.547	3 2
3 2 2		26171		1.955	- 2	6 1 1		42017		1.543	- 0
4 0 2		26271		1.951	- 2	2 0 4	42037	42037	1.542	1.542	8 6
4 2 1		26435		1.945	- 3						

^a Overlapped by unidentified phase, uncorrected. ^b Overlapped by unindexed titanium phosphide, corrected. ^c Overlapped, not measurable. ^d Overlapped by Si.

0.90. An internal consistency index, defined as $\Sigma|F_o(hkl)^2 - \bar{F}_o^2|/\Sigma F_o(hkl)^2$, where \bar{F}_o^2 is the average of eight symmetry equivalent reflexions and the summations are taken over all measured reflexions with $2\theta \leq 25^\circ$, was calculated as 0.04 after the correction for absorption. Totally 2818 reflexions were recorded, of which eight reflexions were excluded from the calculations due to obviously misread data. Equivalent reflexions were averaged after absorption correction. These procedures left 2235 symmetry independent reflexions.

Calculations. All calculations were performed with IBM 370/155 and IBM 1800 computers using a system of programs described by Lundgren.¹⁰

STRUCTURE ANALYSIS AND RESULTS

The conditions for observed reflexions were $h=2n$ for $hk0$ and $h+k=2n$ for $0kl$, which is consistent with space groups $Pnma$ and $Pn2_1a$. The centrosymmetric alternative was chosen and finally confirmed in the refinement. The structure was refined using a full-matrix least-squares program and the atomic coordinates¹⁵ of Ca₅Sb₃ as initial values for the positional parameters. The atomic scattering factors for neutral atoms were used and corrected for anomalous dispersion⁹ (real as well as imaginary parts). The quantity minimized was $\Sigma w(|F_o^n| - k^n|F_c^n|)^2$ with $n=1$ or 2 and the weight w given by

$$w^{-1} = \sigma_c^2(F^n) + (p|F_o^n|)^2$$

Table 2. *R* factors from isotropic and anisotropic refinements on F^2 of α -Ti₅P₃.

Refinement	No. of refl.	No. of param.	$R(F^2)$	$R_w(F^2)$	$R(F)$
Isotropic	936 ($> 3\sigma$)	21	0.0694	0.0640	0.0533
Isotropic ^a	2234	21	0.1294	0.0854	0.1492
Anisotropic	2234	43	0.1231	0.0811	0.1452
Anisotropic ^b	2234	44 ^c	0.1229	0.0810	0.1453

^a Isotropic temperature factors from this refinement are included in Table 3. ^b Parameters from this refinement are given in Table 3. ^c Final refinement with Cu in Ti(4) position.

where σ_c is the standard deviation of F^n based on counting statistics and p an empirical parameter, chosen to obtain a satisfactory weight analysis (p was 0.013 in the final anisotropic refinement). The agreement indices are defined as

$$R(F^n) = \frac{\sum(|F_o^n| - |F_c^n|)/\sum|F_o^n|}{\sum w(|F_o^n| - |F_c^n|)^2/\sum|F_o^n|^2}^{1/2}$$

with $n=1$ or 2, and where F_o has been multiplied by $1/k^n$.

Extinction effects were hardly discernible and thus no correction was applied. The strongest reflexion (040) was, however, excluded from the refinements ($F_o(040) \sim 0.97F_c(040)$). After four refinement cycles an $R(F)$ value of 0.039 was obtained, based on the 522 strongest reflexions. In subsequent refinements all reflexions were included to avoid bias of the input data from exclusion of "unobserved" reflexions.^{11,12} Results are presented in Table 2 from refinements of models with isotropic as well as anisotropic temperature factors. According to Hamilton's R factor significance test¹³ the ratio of the agreement factors ($R_{wk2}(\text{iso})/R_{wk2}(\text{aniso})$

= 1.05) is more than sufficient to reject the isotropic model at the 99.5 % confidence level (required ratio 1.01).

The low isotropic B -value (Table 3) and the low C. N. for Ti(4) indicated a partial occupancy by copper. The least-squares refinement gave an occupancy of 0.490 ($\sigma=0.003$) for Ti and 0.010 for Cu (reset). Attempts to locate copper in the other metal positions did not reveal any significant copper occupancy. Structure data from the final refinement, based on 2234 reflexions, are presented in Table 3 and interatomic distances in Table 4. The total number of parameters varied was 44 (one scale factor, one occupancy and 14 positional parameters, and 28 temperature factors). The largest shift of any parameter in the last cycle was 2 % of the standard deviation. A normal ΔR probability plot¹⁴ after the final refinement was close to a straight line, with a slope of 1.09 and an intercept at -0.06 . No value fell outside the range $\pm 4\sigma$. The standard deviation of an observation of unit weight was $S=0.99$. A final difference map had $1.3 \text{ e}/\text{\AA}^3$ (corresponding to 1.5 % of a phosphorus peak in the F_o map) as the largest peak value.

Table 3. Structure data for α -Ti₅P₃. Standard deviations are given in parentheses. Space group $Pnma$ (No. 62), $Z=4$. Cell dimensions: $a=9.7475(5) \text{ \AA}$, $b=7.4403(3) \text{ \AA}$, $c=6.5056(5) \text{ \AA}$. The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{23}klb^*c^*)]$.

Atom	Position	Positional parameters			$U_{ij} \times 10^5 (\text{\AA}^2)$						$B(\text{\AA}^2)$
		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
Ti(1)	8d	0.07220(6)	0.04668(8)	0.19203(9)	754(22)	495(20)	543(22)	-16(21)	-175(22)	-64(21)	0.47(1)
Ti(2)	4c	0.22576(9)	1/4	0.83655(14)	717(39)	599(35)	628(38)	0	-141(32)	0	0.52(2)
Ti(3)	4c	0.29356(9)	1/4	0.35132(4)	538(34)	747(38)	590(36)	0	-77(31)	0	0.49(2)
Ti(4) ^a	4c	0.00142(10)	1/4	0.53000(13)	440(32)	650(35)	413(34)	0	4(33)	0	0.36(1)
P(1)	8d	0.32673(8)	0.49073(12)	0.06897(14)	598(31)	567(34)	546(34)	5(33)	12(31)	-11(33)	0.45(2)
P(2)	4c	0.48567(14)	1/4	0.58033(21)	788(56)	482(51)	566(51)	0	-160(48)	0	0.49(2)

^a Occupancy 98.0(6) % Ti, the remainder Cu.

Table 4. Interatomic distances (Å) for α -Ti₅P₃. Distances shorter than 3.8 Å are listed. The estimated standard deviations lie in the ranges 0.000–0.001, 0.001–0.002 and 0.000–0.002 for Ti–Ti, Ti–P and P–P distances, respectively.

Ti(1)–P(2)	2.391	Ti(4)–P(2)	2.540
–P(2)	2.478	–2P(1)	2.554
–P(1)	2.622	–2P(1)	2.568
–P(1)	2.675	–2Ti(1)	2.756
–Ti(4)	2.757	–Ti(2)	2.824
–Ti(3)	2.832	–2Ti(1)	2.942
–P(1)	2.867	–Ti(2)	2.960
–Ti(4)	2.942	–Ti(3)	3.076
–Ti(1)	2.951	–Ti(3)	3.203
–Ti(1)	3.025	–2Ti(4)	3.741
–Ti(2)	3.104		
–Ti(3)	3.122	P(1)–Ti(2)	2.542
–Ti(2)	3.143	–Ti(4)	2.554
–Ti(3)	3.391	–Ti(4)	2.568
–Ti(2)	3.653	–Ti(3)	2.586
		–Ti(1)	2.622
Ti(2)–P(2)	2.402	–Ti(2)	2.648
–2P(1)	2.542	–Ti(3)	2.665
–2P(1)	2.648	–Ti(1)	2.675
–Ti(4)	2.824	–Ti(1)	2.867
–Ti(4)	2.960	–P(1)	3.498
–P(2)	3.033	–P(2)	3.503
–2Ti(1)	3.104	–P(1)	3.582
–2Ti(1)	3.143	–2P(1)	3.583
–Ti(3)	3.225	–P(2)	3.605
–Ti(3)	3.414		
–2Ti(1)	3.653	P(2)–2Ti(1)	2.391
–2Ti(3)	3.726	–Ti(3)	2.393
		–Ti(2)	2.402
Ti(3)–P(2)	2.393	–2Ti(1)	2.478
–2P(1)	2.586	–Ti(4)	2.542
–2P(1)	2.665	–Ti(2)	3.033
–2Ti(1)	2.832	–2P(1)	3.503
–Ti(4)	3.076	–2P(1)	3.605
–2Ti(1)	3.122		
–Ti(4)	3.203		
–Ti(2)	3.225		
–2Ti(1)	3.391		
–Ti(2)	3.414		
–2Ti(2)	3.726		

The agreement factors for a refinement omitting observations with $F^2 < 3\sigma(F^2)$ were much lower than those from the refinement of the complete intensity material (see Table 2). The standard deviations were, on the average, 18 % larger than those from the latter refinement, however.

A list of observed and calculated structure factors can be obtained on request from the Institute of Chemistry, Uppsala, Sweden.

DISCUSSION

Since the β -Yb₅Sb₃ structure type was described in detail in earlier work^{5,15} we restrict the discussion to some brief remarks on characteristic features of α -Ti₅P₃. The present single-crystal refinement confirms that α -Ti₅P₃ crystallizes in the β -Yb₅Sb₃ type structure. In a general discussion of the β -Yb₅Sb₃ type structure, Berger¹⁴ distinguished two sub-classes within this structure family. In one of the classes, represented by for instance β -Yb₅Sb₃, Ca₅Bi₃ and Ca₅Sb₃, coordination numbers of the two non-metal atoms are seven and eight, respectively, (disregarding in both cases one further very remote metal neighbour). In the other sub-class, represented for instance by Ti₅Sb₃, the corresponding coordination numbers are eight and nine, respectively. Berger found a correlation between the coordination numbers of the non-metal atoms and the b/a ratio of the unit cell and used this correlation to predict low coordination numbers for phosphorus in α -Ti₅P₃. From Table 4 it can be seen that the P(1) and P(2) atoms have eight and seven close titanium neighbours, respectively, (disregarding the neighbours at 2.87 Å and 3.03 Å, respectively). Consequently α -Ti₅P₃ belongs to the β -Yb₅Sb₃ sub-class as predicted by Berger. Table 4 also shows that some interatomic distances fall considerably below the sum of the atomic radii of titanium (1.45 Å) and phosphorus (1.10 Å). The shortest Ti–Ti distance is 2.76 Å as compared to the radius sum of 2.90 Å, and the shortest Ti–P distance is 2.39 Å as compared to the corresponding radius sum of 2.55 Å.

As mentioned above, the anisotropic refinement gave a significantly lower discrepancy index than the isotropic refinement. The magnitudes and orientations of the thermal ellipsoids were calculated and analyzed. As a result it was found that for all atoms with the exception of Ti(1) and P(1) the differences between the largest and smallest principal axis range between 3.5σ and 4.4σ , where σ is the standard deviation of the differences. The difference is only 1.3σ for P(1), which accordingly vibrates isotropically. Ti(1) displays the greatest thermal vibration as shown by the r.m.s. components along the principal axes: $u_1=0.0924(14)$ Å, $u_2=0.0733(18)$ Å and $u_3=0.0633(22)$ Å. An analysis of the atomic environment of Ti(1) reveals that the largest (u_1) axis is directed approximately along the P(1)–Ti(1)–P(1) direction with the fairly long Ti–P distances of 2.87 and 2.62 Å. The significantly

smaller thermal vibrations in the plane perpendicular to this direction are consistent with short Ti–P distances (indicating tighter bonding) in the plane (Ti(1)–P(2) 2.39 Å and Ti(1)–P(2) 2.48 Å) as well as short Ti–Ti distances [Ti(1)–Ti(4) 2.76 Å and Ti(1)–Ti(3) 2.83 Å], although the latter are not situated exactly in the plane.

From the present refinement the copper content of the crystal used was found to be 0.25(8) atom-%. Micro-probe analysis of other α -Ti₅P₃ crystals, selected from the same alloy specimen, gave values of 0.5 and 0.7 atom-%.³ In view of the low accuracy of the microprobe analysis for such small copper contents these results are not conflicting. Furthermore, since the specimen had not been in complete equilibrium, it is possible that different crystals actually had slightly different copper contents.

The unit cell volume of arc-melted and quenched binary Ti–P specimens varied from 471.06(5) Å³ (Table 1) for a titanium-rich to 471.57(6) Å³ for a titanium-poor composition, which indicates a range of homogeneity. The cell volume of the ternary alloy, from which the single crystal was selected, was 471.92(8) Å³ (Table 3). This value is larger than that of the titanium-poor binary alloy at the 99% confidence level. The ternary alloy was, however, heat-treated at 800 °C and is probably close to equilibrium at that temperature while the arc-melted alloys probably do not represent equilibrium. To sum up, the cell dimensions of Tables 1 and 3 were measured on specimens of different heat treatments and composition.

Acknowledgements. This investigation was supported by the Swedish Natural Science Research Council. One of us (W.C.-C.) is indebted to the Swedish Institute for financial support.

REFERENCES

1. Bärnighausen, H., Knausenberger, M. and Brauer, G. *Acta Crystallogr.* 19 (1965) 1.
2. Lundström, T. and Snell, P.-O. *Acta Chem. Scand.* 21 (1967) 1343.
3. Carrillo-Cabrera, W. and Lundström, T. *Acta Chem. Scand. A* 33 (1979) 401.
4. Snell, P.-O. *Acta Chem. Scand.* 22 (1968) 1942.
5. Brunton, G. D. and Steinfink, H. *Inorg. Chem.* 10 (1971) 2301.
6. Berger, R. *Acta Chem. Scand. A* 31 (1977) 514.
7. Abrahamsson, S. *J. Sci. Instr.* 43 (1966) 931.
8. SAAB 1967. *Film scanner Manual*, SAAB AB, Datasaab, Linköping, Sweden.
9. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
10. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1975, UUIC-B13(04-2).
11. Hirshfeld, F. L. and Rabinovich, D. *Acta Crystallogr. A* 29 (1973) 510.
12. Wilson, A. J. C. *Acta Crystallogr. A* 32 (1976) 781.
13. Hamilton, W. C. *Acta Crystallogr.* 18 (1965) 502.
14. Abrahams, S. C. and Keve, K. T. *Acta Crystallogr. A* 27 (1971) 157.
15. Martinez-Ripoll, M. and Brauer, G. *Acta Crystallogr. B* 30 (1974) 1083.
16. Berger, R. *Thesis, Acta Univ. Ups. (Faculty of Science)* (1978). No. 478.

Received January 29, 1980.