

Crystallographic Data on New Arsenides and Antimonides of Titanium and Scandium

ROLF BERGER

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

In the course of a study of the vanadium arsenides, the common technique of performing syntheses in evacuated silica tubes was supplemented with arc-melting. Some aspects of these two methods have been discussed earlier.¹ In view of the fact that the arc-melting technique often reveals phases not obtainable in silica tube syntheses, it was considered worthwhile to extend this supplementary method to other related systems.

Starting materials. The elements used for the syntheses were titanium (Koch-Light Ltd., 99.95%), scandium (Rare Earths Prod., 99.99%), arsenic (Koch-Light Ltd., 99.9999%) and antimony (Johnson & Matthey, 99.9999%). The figures indicate the claimed purity. The actual purity is probably slightly lower, primarily owing to the presence of oxide films. As₂O₃ was removed from the elemental arsenic by vacuum sublimation, but the other elements were not treated for impurities before the syntheses.

X-Ray equipment and methods. The phase analyses were based on powder diffraction, using Guinier-Hägg focussing cameras equipped with CuK α_1 radiation ($\lambda = 1.540598 \text{ \AA}$). Silicon ($a = 5.431065 \text{ \AA}$)² or germanium ($a = 5.657906 \text{ \AA}$)³ were used as primary internal calibration standards. Cell parameters refined by the least-squares method are presented together with other crystallographic data in Table 1.

The Ti-As system. TiAs (TiP type) was formed by reacting the elements in a silica tube at 900 °C for 7 days. The powdered product was compressed to a pellet and melted in an arc furnace in a protective argon atmosphere. Additional lines formed on the corresponding powder photograph, since the melting caused an uncontrolled but intentional loss of arsenic from the sample. The same method was used for preparing β -V₄As₃ from VAs.⁴ The cell dimensions of TiAs showed no significant deviation from those obtained from the single-phase starting product and were in good agreement with those reported by Łukaszewicz and Trzebiatowski.⁵ There was no sign of β -TiAs of the NiAs type, which was assumed by Bachmayer *et al.* to be stable on the metal-rich side or to be a high-temperature phase.⁶ Neither were there any indications as to stacking disorder, since all TiAs lines were sharp. The additional lines were indexed on a body-centred cubic cell. The new compound is assigned the composition Ti₄As₃, an analogue existing in

the Ti-P system.⁷ Preliminary investigations using less pure starting materials did not yield Ti₄As₃ but instead the hexagonal phase reported by Boller and Nowotny,⁸ and assigned the composition Ti₅As₃. This difference might be due to the stabilizing effect of a contaminant. The formation of ternary compounds with the Mn₃Si₂-type structure ("Nowotny phases") requires only minute amounts of nitrogen, carbon or oxygen; it is therefore often difficult to ascertain whether the presence of these phases corresponds to thermodynamic stability in the binary system. A moderate addition of titanium to the two-phase product made the TiAs phase disappear. In addition to the Ti₄As₃ lines that remained, the resulting product showed new diffraction lines. A few of these, very weak and blurred, belonged to the Mn₃Si₂-type phase, while the rest could be indexed on a primitive orthorhombic cell of the same magnitude as those of the two high-temperature V₄As₃ polymorphs.⁹ This new phase is probably isostructural with γ -V₄As₃ (β -Yb₃Sb₃ type¹⁰). It cannot be inferred with certainty whether the Ti₁₁P phase reported by Snell⁷ also belongs to this class of compounds, but the cell dimensions and the powder line indices do not contradict such a hypothesis. Still more metal-rich specimens indicated the presence of further phases in the system. One powder pattern was interpreted as belonging to Ti₃As, isostructural with Ti₃P. Again there is an obvious similarity between the Ti-As and the Ti-P systems. The phase analysis is far from complete, and one must bear in mind that the arc-melting technique creates conditions where it is difficult to attain equilibrium.

The Sc-As system. ScAs (NaCl type) was synthesized in a silica tube at 900 °C for 4 days. Powder diffraction showed the presence of Sc₂O₃ in minute amounts, its strongest lines being detected as weak traces. The cell parameter of ScAs was compatible with that given by Brixner.¹¹ The method of arc-melting the monoarsenide was used to obtain a phase containing less arsenic. The cell parameters of ScAs in this two-phase region did not differ significantly from that of the initial monoarsenide. The lines of the new phase were indexed on a primitive tetragonal cell. Its volume suggests a cell content of 20 atoms, and it is likely that the new compound has the composition Sc₃As₂, being isostructural with V₃As₂.¹² Preliminary intensity calculations suggest that this might very well be the case. The cell dimensions of Sc₃As₂ were refined, ScAs being used as a secondary internal standard. There exist still further phases in the system, and one was confirmed as being identical with a tetragonal phase found by Rundqvist and Nyarko.¹³ Their crystallographic data are given in Table 1. The exact composition of this phase is unknown; it is approximately 70 atomic % Sc, and the cell volume indicates about 80 atoms to the cell. A literature search for a

Table 1. Crystallographic data of phases obtained in the present study. Cell dimensions in Å units with standard deviations in parentheses.

Phase	Space group	Structure type	Cell dimensions	Internal standard	No. of reflexions
TiAs	$P6_3/mmc$	TiP	$a = 3.6419(2)$ $c = 12.055(1)$	Ge	25
Ti ₄ As ₃	$I\bar{4}3d$	<i>anti</i> -Th ₃ P ₄	$a = 7.6795(2)$	Ge	15
Ti ₅ As ₃	$Pnma$	β -Yb ₅ Sb ₃	$a = 9.8521(4)$ $b = 7.7363(11)$ $c = 6.7232(4)$	Ti ₄ As ₃	63
Ti ₃ As	$P4_2/n$	Ti ₃ P	$a = 10.1618(2)$ $c = 5.1098(2)$	Si	75
ScAs	$Fm\bar{3}m$	NaCl	$a = 5.4640(2)$	Ge	9
Sc ₃ As ₂	$P4/m$	V ₃ As ₂	$a = 10.3755(3)$ $c = 3.8064(2)$	ScAs	58
Sc _{2,3} As	$I4/mmm$	—	$a = 14.3743(9)$ $c = 8.0257(6)$	Si	60
Ti ₅ Sb ₃	$Pnma$	β -Yb ₅ Sb ₃	$a = 10.2173(5)$ $b = 8.3281(5)$ $c = 7.1459(4)$	Ge	76
ScSb	$Fm\bar{3}m$	NaCl	$a = 5.8517(4)$	Ge	10
Sc ₅ Sb ₃	$Pnma$	β -Yb ₅ Sb ₃	$a = 11.0792(8)$ $b = 8.7126(5)$ $c = 7.6272(5)$	Si	102
Sc ₂ Sb	$P4/nmm$	Cu ₂ Sb	$a = 4.2049(2)$ $c = 7.7902(4)$	Ge	38

report on an isostructural phase was not successful.

The Ti-Sb system. Kjekshus *et al.*¹⁴ reported an orthorhombic phase of the approximate composition Ti_{1.7}Sb. The cell parameters indicated that this phase might be assigned the formula Ti₅Sb₃ and be related to either the β -Yb₅Sb₃ type¹⁰ or the Y₅Bi₃ type.^{9,15} In their paper, Kjekshus *et al.* stated that the only systematic extinctions occurred for the $hk0$ reflexions when $h = 2n + 1$. This is not compatible with either of the two suggested structure types which, with the similar axis setting, respectively belong to the $Pnma$ and $Pcmn$ space groups. However, investigations of single crystals from a sample obtained by arc-melting titanium and antimony in the atomic ratio 5:3 clearly showed that the space-group assignment ought rather to be $Pnma$ (or $Pn2_1a$) with an axis setting corresponding to β -Yb₅Sb₃. The compound obtained is obviously identical with that found by Kjekshus *et al.*, despite the differences in our indexing of high-angle lines.

A single-crystal structure determination has been started, and the preliminary results support this structure hypothesis.

The Sc-Sb system. As is often the case with compounds of the Group V non-metals with Sc, Y or the rare-earth elements, only the 1:1 compound has been reported.¹¹ On arc-melting the elements in a ratio corresponding to Sc_{1.2}Sb, a phase mixture was obtained. One phase was identified as ScSb, its cell parameter being not very different from that reported by Brixner.¹¹ The remaining lines were not indexed. Heat-treatment in a silica tube at 950 °C for 7 days yielded a new pattern, which still contained lines attributed to ScSb. The remainder could be indexed on a primitive orthorhombic cell. On the basis of atomic volume considerations including comparisons with the Y-Sb system,¹⁶ the cell volume agreed very well with a content of 32 atoms. It is likely that this phase is also of the β -Yb₅Sb₃ type. The indexing of the powder lines is similar to that of Ti₅Sb₃. No single-crystal data are available as yet.

In the metal-rich region there also exists a phase indexable on a primitive tetragonal cell. This compound seems to be isostructural with Cu_2Sb . No corresponding phase was found in the Y-Sb system.¹⁶ The specimens initially showed a silvery lustre, but tended to turn dark on long exposure to air, probably because of the formation of a superficial oxide film.

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