

Short Communication

New Phases in the Zr–P and Zr–As Systems

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In previous communications on the Zr–P¹ and Zr–As^{1,2} systems the occurrence of two subphosphides and three subselenides was reported together with α , β -ZrP, ZrP₂, ZrAs and ZrAs₂. Furthermore, indications of further intermediate phases were observed. The present work was undertaken in an attempt to characterize these phases. The studies provided information on two new phosphides and four new arsenides and these phases are described in this communication.

Mixtures of turnings of zirconium (Foots Mineral Co., claimed purity better than 2N8) and red phosphorus (M.C.P. Electronic Ltd., claimed purity 5N) or arsenic (Boliden Metal Ltd., claimed purity 5N) were heated in evacuated and sealed silica tubes at 900 °C for periods of 3 d. The reaction products were subsequently arc-melted on a water-cooled copper hearth under a protective Ti–Zr-gettered argon atmosphere. Some alloys were annealed at about 1650 °C under a protective argon atmosphere in a high-frequency induction furnace using a cold-crucible levitation technique. The alloys were examined by X-ray powder diffraction using a Philips XDC 700 Guinier-Hägg type focusing camera with CrK α ₁ or CuK α ₁ radiation. Silicon ($a=5.431065$ Å)³ or germanium ($a=5.657906$ Å)⁴ were used as internal calibration standards. In one case single crystal fragments were examined in a Weissenberg camera using filtered CuK α radiation.

The powder diffraction studies showed that the arc-melted alloys were generally inhomogeneous and often contained more than two phases. Annealing at 1650 °C for periods up to 3 d improved the situation but was generally not sufficient for obtaining equilibrium conditions.

All alloys with high zirconium contents contained

Zr₃P and Zr₃As, respectively. The lattice parameters of both phases were in good agreement with those obtained by Lundström.¹ A new phase, provisionally denoted ZrAs_x, $0.4 < x < 0.5$, was found in a two-phase sample together with Zr₃As. Examination of single crystal fragments indicated an orthorhombic symmetry. An isostructural counterpart to ZrAs_x, denoted ZrP_x, was found in the Zr–P system. The composition of these new phases is at present uncertain but will be established more accurately in connection with a complete single crystal structure determination which is in progress.

The occurrence of the isostructural phases, Zr₇P₄, Zr₇As₄ and Hf₇As₄ was established by comparisons of the corresponding powder diffraction films with the film for Nb₇P₄.⁵ The Hf₇As₄ phase has earlier been identified by single crystal methods.⁶ In the same way an isostructural counterpart to Zr₁₄P₉ was discovered in the Zr–As system.⁷

A further new phase was discovered in more arsenic-rich samples together with Zr₃As₂² and minute amounts of ZrAs.⁸ Its powder pattern could be indexed on a face-centred cubic unit cell with $a=5.4335(6)$ Å. Intensity calculations indicated isotypism with the NaCl type structure. By analogy with the phase transformation in ZrP,⁹ this new phase, denoted by α -ZrAs, is a high temperature form of ZrAs, while the low temperature form, denoted by β -ZrAs, crystallizes in the TiP type structure.⁸

Crystallographic data for the new phases in the Zr–P, Zr–As and Hf–As systems are collected in Table 1. The cell parameters of the phosphides in various samples were constant within experimental errors. Variations in the cell dimensions of at most 0.1 % for ZrAs_x and Zr₇As₄ indicate a certain range of homogeneity.

The a axis of Zr₈As₅, crystallizing in the Nb₈P₅¹⁰ type structure, was found to vary considerably with composition (Table 2). This feature is most probably connected with vacancies on one of the zirconium positions.

In the Nb₈P₅ structure, the Nb(4) positions are arranged in pairs with a distance of only 2.54 Å, which would be abnormally short for an Nb–Nb atomic contact. The structure refinement indi-

Table 1. Crystallographic data for phases discovered in the present study.

Phase	Structure type	Space group (or diffraction symbol)	Cell dimensions and standard deviations (Å, °)	Cell volume (Å ³)
ZrP _x (0.4 < x < 0.5)	new	<i>Pb</i>	a=14.7737(12) b=19.0791(13) c=3.6000(4)	1014.7
Zr ₇ P ₄	Nb ₇ P ₄	<i>C2/m</i>	a=15.8111(10) b=3.6049(3) c=14.7357(12) β=104.831(5)	811.9
ZrAs _x ^a (0.4 < x < 0.5)	new	<i>Pb</i>	a=15.0782(9) b=19.5317(10) c=3.6613(3)	1078.3
Zr ₇ As ₄ ^a	Nb ₇ P ₄	<i>C2/m</i>	a=16.2020(7) b=3.6778(3) c=15.0394(8) β=104.656(4)	867.0
Zr ₁₄ As ₉ ^a	Zr ₁₄ P ₉	<i>Pnnm</i>	a=17.0987(10) b=28.2588(16) c=3.7661(3)	1819.7
α-ZrAs ^a	NaCl	<i>Fm3m</i>	a=5.4335(6)	160.4
Hf ₇ As ₄ ^b	Nb ₇ P ₄	<i>C2/m</i>	a=16.1150(21) b=3.5912(3) c=14.9283(15) β=104.24(1)	837.4

^a Metal-rich two-phase sample. ^b Re-examination of Guinier-Hägg X-ray powder diffraction film recorded earlier.⁷

cated that the Nb(4) position was occupied to 50 % only. Accordingly, it seemed very likely that only one site per pair would actually be occupied, and too short Nb-Nb contacts could thus be avoided.

For Zr₈As₅, the distance between the Zr(4) pairs should be 3.14–3.17 Å, as calculated from the positional parameters obtained in the previous single crystal refinement,² and the limiting values of the cell parameters as determined in the present study. Since Zr-Zr distances of 3.14–3.17 Å are quite reasonable, an occupancy greater than 50 % of the Zr(4) position can by no means be excluded. In fact, refinement of the Zr(4) occupancy gave a value of 65 %, although the reliability of this result was uncertain due to uncorrected absorption effects.²

It seems safe to conclude that the extended range of homogeneity for the Zr₈As₅ phase is due

to a variable amount of vacancies on the Zr(4) position, and the correct crystallographic formula should accordingly be written Zr_{17-y}As₁₀ (0 < y < 1).

The unit cell dimensions of Zr₃As₂ (crystallizing in the Hf₃P₂¹¹ type structure) obtained in this work differed significantly from those obtained by Carlsson *et al.*² (Table 2). The X-ray powder pattern for Zr₃As₂ in a two-phase sample with α-ZrAs showed a broadening of reflections with high *l* indices. These reflections had tails extending in the direction of smaller angles, indicating a homogeneity range for Zr₃As₂ associated with an expansion of the *c* axis. The different values of the cell dimensions obtained in this work and by Carlsson *et al.* may be due to differences in *e.g.* the sample sizes which affect the cooling rate after arc melting. Analogous but smaller variations in the unit cell dimensions of Hf₃P₂ in

Table 2. Cell dimensions for Zr_8As_5 and Zr_3As_2 in two-phase samples.

Phase	Cell dimensions and standard deviations (Å)	Cell volume (Å ³)	Coexisting phase
Zr_8As_5	$a=28.449(5)$ $b=10.206(2)$ $c=3.7619(7)$	1092.3	Zr_7As_4
Zr_8As_5	$a=28.156(2)$ $b=10.2111(5)$ $c=3.7894(3)$	1089.5	Zr_3As_2
Zr_3As_2	$a=10.5278(10)$ $b=3.7276(4)$ $c=10.2142(10)$	400.8	Zr_8As_5
$Zr_3As_2^a$	$a=10.5302(6)$ $b=3.7271(2)$ $c=10.2277(18)$	401.4	α -ZrAs
$Zr_3As_2^b$	$a=10.5348(6)$ $b=3.7185(4)$ $c=10.3103(18)$	403.9	α -ZrAs

^a Broadening of reflections with high l indices. ^b Unit cell dimensions from Ref. 2.

samples with different composition have also been reported.¹²

Crystal-chemical considerations of the Zr_3As_2 structure do not indicate any specific mechanism for the extended homogeneity range but the expansion of the unit cell volume with increasing arsenic content suggests the occurrence of arsenic vacancies in metal-rich samples.

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7. Tergenius, L.-E., Nolång, B. I. and Lundström, T. *Acta Chem. Scand. A* 35 (1981) 693.
8. Trzebiatowski, W., Weglowski, S. and Lukaszewicz, K. *Roczniki Chem.* 32 (1958) 189.
9. Irani, K. S. and Gingerich, K. A. *J. Phys. Chem. Solids* 24 (1963) 1153.
10. Anugul, S., Pontchour, C. and Rundqvist, S. *Acta Chem. Scand.* 27 (1973) 26.
11. Lundström, T. *Acta Chem. Scand.* 22 (1968) 2191.
12. Lundström, T. and Tansuriwongs, P. *Acta Chem. Scand.* 22 (1968) 704.

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1. Lundström, T. *Acta Chem. Scand.* 20 (1966) 1712.
2. Carlsson, B., Gölin, M. and Rundqvist, S. *Acta Chem. Scand. A* 30 (1976) 386.
3. Deslattes, R. D. and Henins, A. *Phys. Rev. Lett.* 31 (1973) 972.
4. Baker, J. F. C. and Hart, M. *Acta Crystallogr. A* 31 (1975) 364.
5. Rundqvist, S. *Acta Chem. Scand.* 20 (1966) 2427.
6. Rundqvist, S. and Carlsson, B. *Acta Chem. Scand.* 22 (1968) 2395.