Short Communications

A Note on the V − P, V − As and Cr − As Systems

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In previous work on compounds in the V − As and Cr − As systems the samples have generally been synthesized in evacuated silica tubes. This method, however, has to be used with some reservation since the arsenides can readily become contaminated by reaction with the silica. These hazards are particularly serious in the case of the vanadium arsenides, where V_5As_3 and V_3As are isotypic with the corresponding silicides. The author has in fact observed chemical attack on the tube walls, accompanied by considerable variations in unit cell dimensions, during attempts to prepare or anneal metal-rich vanadium arsenides in silica tubes.

The method of arc-melting on a water-cooled copper hearth under a protective atmosphere offers a considerable advantage from the contamination point of view, and in addition provides higher temperatures than those attainable in silica tubes. In the present study, arc-melting has therefore been utilized as a complement to the silica tube technique in a survey on the metal-rich parts of the V − P, V − As and Cr − As systems.

The phase-analytical work was based on powder diffraction investigations performed with a Guinier-Hägg type focusing camera, using $CrK\alpha_1$ radiation ($\lambda = 2.28962$ Å) with silicon ($a = 5.43054$ Å) or germanium ($a = 5.65771$ Å) as internal calibration standards.

The V − P system. The phases VP_2, VP, V_4P_3, $V_{12}P_7$, and V_3P have been characterized in previous work.[1-5] In addition, Boller[3] has reported an intermediate phase of approximate composition $V_{2.4}P$. In the present study the occurrence of a phase between $V_{12}P_7$ and V_3P was confirmed. This phase could be prepared both by silica tube synthesis and arc-melting. The powder photograph could be indexed on the basis of orthorhombic symmetry, yielding the cell parameters $a = 6.204$ Å, $b = 3.307$ Å, $c = 7.536$ Å. The structure is most probably of the Co_2P (anti-$PbCl_2$) type.[6] Intensity calculations using the atomic coordinates of Co_2P as refined by Rundqvist[7]

showed a very good agreement with the observed values. A complete structure analysis has been started.

The V − As system. The use of the higher temperatures attainable in the arc furnace has yielded a number of phases which were not obtained in earlier work using the silica tube technique. The occurrence of β-V_4As_3 has already been reported in an earlier communication.[9] In addition, two new orthorhombic phases have been found. Single-crystal diffraction data indicate that both phases crystallize with $Pnma$ or $Pn2_1a$ symmetry. The phase denoted β, which has also been prepared by silica tube syntheses at temperatures above 1000 °C, shows a marked homogeneity range. The unit cell dimensions have been found to vary from $a = 6.437$ Å, $b = 7.673$ Å, $c = 9.280$ Å and $V = 458.4$ Å^3 to $a = 6.414$ Å, $b = 7.628$Å, $c = 9.299$ Å and $V = 454.9$ Å^3. The other orthorhombic phase, γ, stable only at elevated temperatures, has the dimensions $a = 9.463$ Å, $b = 7.519$ Å, $c = 6.471$ Å and $V = 460.5$ Å^3. Intensity calculations strongly suggest that γ is isotypic with β-Yb_5Sb_3 reported by Brunton and Steinfink.[8] It is notable that the cell volumes of β and γ are nearly equal. In fact, the phases might be related by a polymorphic transformation, since, in one experiment β was found after treating γ at 800 °C in a silica tube for four days in the presence of traces of iodine. The occurrence of β at this temperature is thought not to correspond to equilibrium, but can be explained on the basis of a relatively rapid polymorphic transformation followed by a rather sluggish eutectoid decomposition. Heat-treatments of β at 1000 °C for several days support this latter assumption, since, despite a kinetically more favourable situation, only a partial decomposition into tetragonal V_3As_2[9] and tetragonal V_5As_3 (W_5Si_3 type)[10] occurred. The latter phase is considered to be arsenic deficient[11] and shows a considerable homogeneity range. The phase-analytical data in combination with considerations of atomic volumes suggest a composition of V_5As_3 for both the orthorhombic phases, with four formula units to the cell. A single-crystal structure analysis of β has been made and will soon be reported in this journal. The phase-analytical studies have also indicated the occurrence of a phase with the approximate composition V_2As. No single crystals of this phase have yet been obtained, but powder photographs

indicate a hexagonal unit cell of dimensions $a = 7.6519$ Å, $c = 3.3584$ Å, containing four formula units.

The Cr—As system. Arc-melting of a mixture of CrAs and Cr_4As_3 has yielded a new high-temperature phase, which could be indexed according to orthorhombic symmetry. The comparison of powder photographs and intensity calculations strongly suggested that this new phase — occurring together with CrAs — is isotypic with γ in the V—As system of the β-Yb_5Sb_3 structure type. The cell parameters found were $a = 9.263$ Å, $b = 7.446$ Å, $c = 6.393$ Å and $V = 440.9$ Å³. In arc-melted alloys no intermediate phase more chromium-rich than Cr_2As was found. The Cr_3As (A15) phase as reported by Yuzuri[12] and Hollan et al.[13] was thus not obtained. Arc-melted specimens did not contain the high-temperature polymorph of Cr_2As (Fe_2P type).[14–16] This might be due to insufficiently rapid quenching. One specimen heat-treated in an induction furnace at 1450 °C showed, however, weak lines of the hexagonal phase together with the tetragonal form (Cu_2Sb type).

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On the Crystal Conformation of 1,3,9,11-Tetraoxacyclohexadecane at Room Temperature

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16-Membered rings have been studied by Dale and co-workers.[1,2] A marked tendency for the saturated ring skeleton to assume the diamond lattice is observed. Semiquantitative calculations of the conformational energies[3] show that the "square" conformation has the lowest enthalpy. This conformation was found in the crystals of 1,1,9,9-tetramethylcyclohexadecane.[4] Ring substitution by hetero atoms (oxygen) may reduce the *gauche* interactions at corner positions of the "square" conformation,[5] which indeed is the preferred crystal conformation of 1,5,9,13-tetraoxacyclohexadecane.[6] The compact "rectangular" conformation has only 5.03 kJ/mol higher enthalpy than the "square".[3] The symmetry number is 4 for both, but since only the "rectangular" form is a *d,l*-pair, it has an entropy term (at 300 K) of 1.7 kJ/mol in its favour, and the free-energy difference is only 3.4 kJ/mol.

The crystals of $C_{12}O_4H_{24}$ belong to the triclinic system with dimensions $a = 5.799(1)$ Å, $b = 7.731(1)$ Å, $c = 7.815(1)$ Å, $\alpha = 70.21(1)°$, $\beta = 82.46(1)°$, $\gamma = 88.19(1)°$ for Dirichlets reduced cell, and one molecule in the unit cell. 527 observed reflections were measured on an automatic four-circle diffractometer at room temperature ($MoK\alpha$-radiation). Statistical tests strongly indicated the space group $P\bar{1}$. The structure was solved by direct methods[7] and refined by full-matrix least squares technique

Table 1. Final fractional coordinates (multiplied by 10^4) and thermal parameters for carbon and oxygen atoms.

Atom	X	Y	Z	B
O1	1194(43)	5805(29)	2081(29)	4.0(.6)
O2	7586(16)	6774(12)	6604(11)	4.4(.2)
O3	7636(23)	3908(18)	8940(16)	4.6(.3)
O4	4350(31)	3729(20)	2488(23)	4.3(.5)
C1	2131(23)	4551(16)	1652(17)	5.3(.3)
C2	2529(26)	7468(18)	1190(18)	3.8(.3)
C3	1787(29)	8887(21)	2262(24)	3.9(.4)
C4	2366(15)	8103(11)	4199(11)	4.0(.2)
C5	4909(33)	7804(20)	4447(22)	3.6(.4)
C6	5158(16)	6965(13)	6458(12)	5.4(.2)
C7	7899(25)	5940(19)	8379(17)	2.5(.3)
C8	9152(31)	2956(22)	8008(21)	4.7(.4)
C9	8001(22)	1312(15)	8205(16)	3.3(.3)
C10	5789(28)	1430(18)	7277(18)	4.0(.3)
C11	6172(27)	2521(17)	5194(19)	3.4(.3)
C12	3916(16)	2871(11)	4401(12)	3.4(.2)