

On the Crystallography and Morphology of SiAs

TOMMY WADSTEN

*Institute of Inorganic and Physical Chemistry,
University of Stockholm, Stockholm, Sweden*

The synthesis and crystal structure analysis of SiAs have been reported in a previous article by the present author.¹ The preparative method used in that study was melting of a mixture of the finely powdered elements in a sealed evacuated silica tube. The tube was kept at 1100°C for 2 h and then slowly cooled down to room temperature. The product thus obtained consisted of small balls which when crushed gave small crystal plates with a shiny metallic appearance. The product also contained tiny crystal needles grown perpendicular to the surface of the balls and also on the wall of the tube. X-Ray powder photographs of the plates and of the needles showed them to be just different forms of the same phase.

The preparations of SiAs from the elements by a vapour-transport method with a small amount of iodine as a carrier substance has been reported by Beck and Sticler² and by Ing, Chiang and Haas.³ Some results obtained by the present author when applying this technique of synthesis give some additional information about the crystallography and morphology of SiAs.

The reaction vessel, which consisted of a sealed evacuated silica tube about 25 cm long and 0.5 cm inner diameter, was placed in a two-zone furnace to give the necessary temperature gradient. The samples to be reacted (0.1 g) were a pellet of elementary silicon (99.999 % pure) at the hot end (1100°C) and a pellet of arsenic (99.99 %) at the low-temperature end (450°C) of the tube. The amount of iodine was 0.0005 g. After heating for one day, the tube contained a considerable amount of a condensed crystalline phase in an intermediary temperature region estimated to be at 900°C. Under the microscope, this deposit was found to contain crystals very different in character, *viz.* thin needles up to 15 or 20 mm in length and about 0.001 mm thick and transparent ribbons or plates of thickness also within the μm region. The lateral extension of the plates was often several mm.

Samples of the various types of crystals were picked out and investigated by X-ray powder photographs in a Guinier-Hägg camera with strictly monochromatized $\text{CuK}\alpha_1$ radiation. All the powder photographs were identical as far as the positions of the diffraction lines are concerned. They were also in full agreement with the patterns given by the SiAs samples prepared by reaction of the elements without the presence of a transport agent. Minor differences in the intensities of the various photographs may be attributed to orientation effects caused by the very different shape of the crystallites. It was thus obvious that all these preparations are chemically identical.

Table 1. Unit cell dimensions and volume of SiAs

	Ref. 1	Ref. 4	Ref. 2	This work
<i>a</i>	15.98 Å	21.0 kX	6.95 Å	21.23 Å
<i>b</i>	3.668 Å	3.7 kX	9.25 Å	3.667 Å
<i>c</i>	9.529 Å	9.7 kX	7.70 Å	9.530 Å
β°	106.0	45.0		46.3
<i>V</i>	533 Å ³	537 kX ³	495 Å ³	537 Å ³

X-Ray single crystal photographs of the needle-shaped crystals showed that these are extended along the *b* axis of the monoclinic structure (*cf.* Table 1 and Fig. 1).

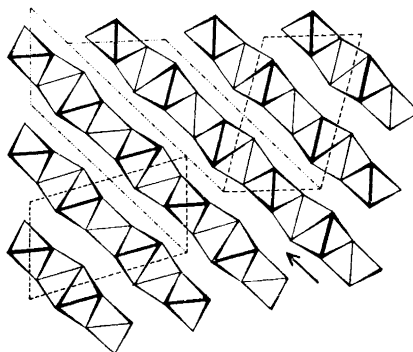


Fig. 1. *h0l*-Projection at two SiAs crystals, silicon atoms excluded, with the direction of the twin plane shown by the arrow. The dotted lines refer to the two different monoclinic settings.

As the extremely thin crystal plates often gave very poor X-ray photographs, these were also investigated by electron diffraction techniques. A considerable number of crystals were thus studied. Some were found to be single crystals, giving diffraction photographs in agreement with the crystal structure previously deduced.¹ Most of the crystals, however, were found to be more or less twinned, some specimens evidently with about equal proportions of the twin individuals, yielding diffraction

photographs which could at the first sight be mistaken for having orthorhombic symmetry.

It was thought to be of interest to find out whether the statement by Beck and Stickler² that SiAs possesses orthorhombic symmetry could be associated with this marked tendency of twinning in SiAs plate crystals. The X-ray powder data given by these authors are compared, in Table 2, with data obtained in the present investigation. It seems obvious that the two sets of powder patterns are equivalent and can thus be referred to the same phase.

Table 2. X-Ray powder diffraction data of SiAs. The powder patterns obtained in the present study, which are in full concordance with the single-crystal photographs, were taken with KCl ($a = 6.2930 \text{ \AA}$) as an internal standard.

Ref. 2	This work			
d_{obs}	d_{obs}	d_{calc}	Intensity	hkl
9.25	9.13	9.16	v w	$\bar{2}01$
7.7	7.65	7.67	v w	200
6.95	6.88	6.89	v w	001
5.22	5.21 ₈	5.21 ₉	m	$\bar{4}01$
4.6	4.57 ₈	4.58 ₉	w	$\bar{4}02$
4.52	4.52 ₉	4.52 ₉	w	$\bar{2}02$
3.98	3.94 ₉	3.95 ₉	w	201
3.84	3.83 ₈	3.83 ₉	m	400
3.52	3.52 ₉	3.52 ₉	m	$\bar{6}02$
3.45	3.44 ₈	3.44 ₇	st	002
3.35				
	3.25 ₈	3.25 ₄	v w	$\bar{3}11$
3.24	3.23 ₇	3.23 ₇	v st	$\bar{6}01$
3.17	3.14 ₇	3.15 ₉	m	$\bar{4}03$
3.06	3.05 ₁	3.05 ₃	v st	$\bar{6}03$
3.02				
2.96	2.98 ₀	2.98 ₀	v st	$\begin{cases} 310 \\ 111 \end{cases}$
2.86	2.90 ₅	2.90 ₈	m	$\bar{3}12$
2.80				
	2.70 ₉	2.71 ₀	m	$\bar{5}11$
2.67	2.66 ₂	2.66 ₂	v w	401
2.61	2.60 ₂	2.60 ₂	st	$\bar{8}03$
2.56	2.55 ₉	2.56 ₉	w	600
2.36	2.39 ₇	2.39 ₇	w	$\bar{5}13$
	2.32 ₈	2.32 ₈	m	$\bar{3}13$
2.31	2.30 ₅	2.30 ₆	w	$\bar{8}01$
	2.29 ₀	2.29 ₁	v w	$\bar{8}04$
2.26	2.26 ₀	2.26 ₀	v w	$\bar{4}04$
	2.25 ₀	2.25 ₀	w	$\bar{7}13$
	2.17 ₃	2.17 ₃	v w	$\bar{7}11$
	2.09 ₁	2.09 ₁	w	$\bar{1}13$
2.05	2.04 ₈	2.04 ₈	w	$\bar{1}04$
				0

When studying the character of twinning in the SiAs plate crystals it was found convenient to choose the a and c axes of the unit cell in another way than in Ref. 1. The new cell, which is actually in conformity with the one adopted in an early study by Schubert *et al.*,⁴ may be said to emphasize the layer character of the structure. The relations between the two unit cell settings are the following (dashed symbols for the setting in Ref. 1)

$$\begin{aligned} \vec{a} &= \vec{a}' + 2\vec{c}' \\ \vec{b} &= \vec{b}' \\ \vec{c} &= \vec{c}' \end{aligned}$$

The electron and X-ray diffraction investigation showed that twinning occurs in SiAs on the ab -plane of the new setting. This is the plane of the layers and the mechanism of twinning can be referred to a mistake in the stacking of adjacent layers. This is illustrated in Fig. 1 which, besides the mutual relations of the orientations of adjacent layers (A and B) of two twin individuals, also suggests a plausible mechanism of stacking which leads to a conservation of the coordination around the atoms situated at the plane of twinning.

If, however, the stacking of adjacent layers were to appear with a periodicity $-A-B-A-B-$ etc. this would result in a different structure with orthorhombic symmetry and approximate cell parameters $a = 21.2 \text{ \AA}$, $b = 3.67 \text{ \AA}$, and $c = 13.8 \text{ \AA}$. The length of the c -axis is thus twice the interplanar distance between the ab -planes and corresponds to two layers of polyhedra. This hypothetical structure seems to be represented by SiP, the structure of which is now under study by the present author. The unit cell dimensions found for this compound are $a = 20.50 \text{ \AA}$, $b = 3.51 \text{ \AA}$, and $c = 13.61 \text{ \AA}$.

By electron diffraction and electron microscopy methods data were obtained on growth direction, symmetry and cell dimensions in the new monoclinic *ab*-projection, which are confirmed by the results found by X-ray techniques.

A Zeiss EM-9A 60 kV electron microscope has been used, with a selected area of about 1 μm in diameter. The grids were supported with a collodium film. The camera constant 2 λ L was externally calibrated with TlCl and also indirectly calibrated by the X-ray parameters of the SiAs sample.

This investigation was carried out within a research program financially supported by the *Swedish Natural Science Research Council*. Thanks are due to Professor Ivar Hessland and Dr. R. Hallberg of the Geological Institute, University of Stockholm, for the use of the electron microscope and electron diffraction instrument and also to Professor A. Magnéli for valuable discussions.

1. Wadsten, T. *Acta Chem. Scand.* **19** (1965) 1232.
2. Beck, C. G. and Stickler, R. J. *Appl. Phys.* **37** (1966) 4683.
3. Ing, S. W., Chiang, Y. S. and Haas, W. *J. Electrochem. Soc.* **114** (1967) 761.
4. Schubert, K., Dörre, E. and Günzel, D. *Naturwiss.* **41** (1954) 448.

Received December 20, 1968.

Revised Analysis of Molecular Vibrations of Sulphur Trioxide

S. J. CYVIN and J. BRUNVOLL

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

and

R. STØLEVIK

Kjemisk institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

Three events have moved us to repeat the previous analysis¹ of molecular vibrations of sulphur trioxide: (i) the criticism by L. H. Jones,² who has questioned the correctness of some of our results, (ii) the appearance of an improved experimental value³ of ζ_3 for SO_3 , and (iii) an interesting study of AlCl_3 by Zasorin and Rambidi,⁴ which suggests that an analysis of mean amplitudes of SO_3 similar to the previous one,¹ but studying the quantities at high temperatures, might be valuable and interesting.

(i) We realize the correctness of Jones' results² and are thankful to him for having pointed out the errors in our previous calculations. According to our revised calculations the limits of accuracy (± 5 and $\pm 1 \text{ cm}^{-1}$) for ν_3^* and ν_4^* (in S^{18}O_3), as given in the last lines of the bottom paragraph on p. 1584 in the cited paper,¹ should be corrected to ± 0.5 and $\mp 0.2 \text{ cm}^{-1}$, respectively. This correction also changes some of the conclusions of the same paragraph, inasmuch as the revised calculations are well compatible with the statements of Duncan and Mills referred to in the paragraph.¹

(ii) A slight refinement of the force field for SO_3 was performed using the Coriolis constant of $\zeta_3 = 0.465 \pm 0.020$ from Milne and Ruoff³ along with $\nu_3 = 1391.3 \text{ cm}^{-1}$ from the same work, and otherwise the same spectral data as previously.¹ The derived force constants in the E' species, *viz.* (in $\text{mdyne}/\text{\AA}$)

$$F_1 = 10.58 \mp 0.10, F_{12} = -0.34_6 \pm 0.06_3,$$

$$F_2 = 0.621 \pm 0.002 \quad (1)$$

are very similar to those recently published by Ruoff.⁵