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Short Communications

Synthesis and Structural Data of SiP

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The existence of a compound of the composition SiP in the silicon-phosphorus system has been reported by several authors.[1–8] The conditions of synthesis have been rather different, some investigators using straightforward heating of mixtures of the elements under exclusion of air while some recent reports describe preparation performed at very high pressures or by transport or diffusion reactions. The products which are likely to vary in purity have been characterized by chemical analyses, IR-spectra, and X-ray and electron diffraction photographs. Some of the X-ray patterns thus reported are given in Table 1.

Table 1. X-Ray powder diffraction data of SiP. The Guinier powder patterns obtained in the present study which are in full concordance with the single-crystal photographs, were taken with KCl ($a = 6.2930$ Å) as an internal standard.

Ref. 2	Ref. 4	Ref. 6	This work			
d_{obs}[a]	d_{obs}	d_{obs}	d_{obs}	d_{calc}	I_{obs}[c]	$h\,k\,l$
		10.25				
		8.25	8.20	8.18	w	2 1 0
6.80	6.81	6.82	6.81	6.80	m	0 2 0
5.03		5.10	5.12	5.12	w	4 0 0
		4.15	4.15	4.14	v w	2 3 0
4.08		4.10	4.09	4.09	v w	4 2 0
	3.40_5	3.40	3.40_1	3.40_0	w	0 4 0
3.33		3.31	3.31_1	3.30_9	v w	6 1 0
		3.10	3.12_3	3.12_2	m	3 0 1
		3.04	3.04_5	3.04_2	st	3 1 1
2.81		2.83	2.83_9	2.83_7	m	3 2 1
		2.72	2.74_6		v w(d)	
		2.65	2.66_6	2.66_5	w	5 0 1
			2.61_5	2.61_5	v w	5 1 1
2.54		2.55	2.56_0	2.55_7	m	8 0 0
		2.50	2.51_6	2.51_5	w	8 1 0
			2.48_2	2.48_1	v w	5 2 1
		2.40	2.39_9	2.40_1	w	4 5 0
	2.27					
		2.13	2.14[b]		v w(d)	
		2.05	2.02[b]		v w(d)	
		1.94	1.96_0	1.96_0	v w	10 2 0
		1.91	1.90_9	1.90_9	st	9 0 1
			1.75_5	1.75_5	v st	0 0 2
1.71	1.70		1.70_0	1.69_9	v w	0 8 0

[a] *d*-Values recalculated from a "Strichdiagramme".
[b] Very diffuse powder reflections omitted in the least square refinement.
[c] Intensity observed is probably incorrect due to orientation effects.

In the present investigation SiP was obtained by a transport reaction performed in a way previously applied for the synthesis of SiAs. The temperatures of the two-zone furnace were 1100° and 450°C. The starting materials were elementary silicon (99.999 % pure) and red phosphorus (99.9 % pure). A trace of iodine acted as the transporting agent.

The product which was obtained at the 900°C level after a 24 h run consisted of crystals of two different morphological types, *viz.* very thin "fibers", several mm in length, and highly reflecting, very thin plates with two dimensions of several mm. Under mechanical pressure the plates split into fibers. The crystals are transparent with a gold-reddish metallic lustre.

X-Ray powder photographs of the two types of crystals were found to be identical. Single-crystal pictures taken with X-ray and electron diffraction techniques helped to index the powder pattern, which is given in Table 1. The agreement with the powder data reported by previous authors is rather satisfactory and shows that the various samples are essentially the same. The IR-spectrum, given by the present preparation is also in fair agreement with the one obtained by Fritz and Berkenhoff.[2]

The X-ray and electron diffraction data show SiP to be orthorhombic. The reflections systematically missing in the three-dimensional X-ray data collected with CuK radiation using the Weissenberg technique are those characteristic of the space-group *Pnna* (No. 52). The unit cell dimensions, refined by least squares techniques on the basis of powder photographs taken in a Guinier-Hägg type camera with Cu$K\alpha_1$ radiation, are $a=20.47\pm1$ Å, $b=13.59\pm1$ Å, $c=3.510\pm1$Å, $V=977$ Å^3.

The density of the present material measured by flotation techniques is 2.37 g/cm^3 in good agreement with data reported by previous authors, *viz.* 2.40 ± 2 g/cm^3. The density calculated for a unit cell content of 24 SiP is 2.39 g/cm^3.

It is of interest to compare the unit cell dimensions of SiP with those found for SiP_2 and for members of the group of isomorphous phases including SiAs, GeP, and GeAs. SiP_2 is orthorhombic (*Pbam*) with unit cell dimensions rather close to or in simple relation to those of SiP, *viz.* $a=13.99$ Å, $b=10.09$ Å, and $c=3.43$ Å. It is not likely, however, that this similarity of dimensions reflects a basic structural relationship as the character of the diffraction patterns are rather different as is obvious from a comparison of the powder patterns (*cf.* Tables 1 and 2).

Table 2. X-Ray powder diffraction data of SiP_2 taken with KCl ($a=6.2930$ Å) as an internal standard.

d_{obs}	d_{calc}	Intensity	$h\ k\ l$
6.99	6.99	w	2 0 0
5.75	5.75	w	2 1 0
3.30_5	3.30_5	m	4 1 0
3.26_9	3.27_1	w	1 3 0
3.03_4	3.03_2	w	2 3 0
2.87_3	2.87_5	vw	4 2 0
2.77_9	2.78_1	m	1 2 1
2.63_1	2.63_0	st	2 2 1
2.44_6	2.44_7	vw	5 2 0
2.42_4	2.42_5	m	3 2 1
2.20_5	2.20_4	vw	4 2 1
1.95_1	1.95_2	m	2 4 1
1.68_9	1.68_9	st	2 5 1

The possible structural relationship between SiP and the phases of the group of SiAs isomorphs has been pointed out in a previous paper.[9] A structure analysis along those lines is in progress.

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