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$AlSiP_3$, a Compound with a Novel Wurtzite–Pyrite Intergrowth Structure*

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$AlSiP_3$ is formed by heating aluminum and silicon powder with red phosphorus and adding small amounts of iodine or $AlCl_3$. Small, black crystals with metallic lustre grow at 1200°K. The compound crystallizes in the orthorhombic space group Pmnb (No. 62) with $a = 987.2$ pm, $b = 586.1$ pm, $c = 608.8$ pm and four formula units. In the structure isolated P atoms as well as P_2 pairs are present (P–P = 218.2 pm). Silicon is tetrahedrally bonded (Si–P = 224.2 – 228.2 pm) whereas aluminum has octahedral coordination (Al–P = 244.2 – 260.8 pm). The structure can be described as an intergrowth structure of wurtzite and pyrite type.

Introduction

In the last few years we have been deeply involved with the chemistry and structural chemistry of metal-polyphosphides. Due to improved chemical synthesis, we have succeeded in detecting many unexpected compounds, especially in the little explored phosphorus-rich parts of binary systems (*2*). The reaction of aluminum with phosphorus excess, too, yields a new compound which was deposited at the surface of a quartz ampoule. The X-ray structure analysis, together with classical valence rules, show that the ternary compound $AlSiP_3$ is present. This result was confirmed by electron microprobe analysis. The preparation, properties and structure of this novel compound will be discussed in detail.

Preparation and Properties

$AlSiP_3$ was first observed by reactions of aluminum powder with red phosphorus at the surface of a quartz ampoule. This reaction is reproducible. However, the ratio of $AlSiP_3$ to other reaction products as AlP, SiP and SiP_2 vary with the reaction conditions. In our opinion the very slow formation of $AlSiP_3$ from the originally formed binary compounds is important. We performed many experiments with variation of reaction conditions (temperature, temperature gradient, reaction time, ratio of components) as well as with different materials ([Al + P + Si] or [Al + P + SiO_2(powder)] or [Al + P + SiO_2(splints)]) but we were not able to clarify all details of the reaction.

Preparation: Aluminum (powder or tape), silicon (powder) and red phosphorus (all substances p.a. MERCK, Darmstadt) are filled in a quartz ampoule of 200 mm in length and 20 mm in diameter. To do this e.g. 0.75 g aluminum and 0.45 g silicon are filled into a small quartz crucible. For the support of crystallization about 250 mg of

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* Chemistry and Structural Chemistry of Phosphides and Polyphosphides, Part 18; for Part 16 compare Ref. (*1*); for Part 17 compare Ref. (*2*)

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a salt mixture of NaCl, CsCl and KI can be added (*2*). A second crucible is charged with 2.0 g red phosphorus and some milligrams $AlCl_3$ or I_2 (*2, 3, 4*). The external ampoule is sealed and heated very slowly during four days up to 1200°K and kept at that temperature for three weeks at least. The furnace is about 15° inclined to the horizontal. In the course of one hour the temperature then is reduced to 900°K and at this temperature the ampoule is shifted so that one quarter of its length is sticking out of the furnace. In a short time, excess phosphorus is precipitated in the cooler part and the ampoule can be removed.

At the bottom of the metal filled internal crucible a compact, hard grey product is formed, composed of AlP, SiP and $AlSiP_3$. Within a few hours, AlP is completely decomposed in moist air, PH_3 as well as $AlPO_4$ and other products are formed during the process. From the reaction products $AlSiP_3$ can be separated as follows: First the reaction product is treated by concentrated hydrochloric acid for one hr. Then the liquid is decanted and the residue is washed several times with water. The procedure is repeated with concentrated sodium hydroxide solution. The treated product consists of black glittering crystals of $AlSiP_3$. The yield amounts to 20–25%.

Properties: The compound $AlSiP_3$ grows as dark reflecting crystals in the shape of rhombic prisms and platelets up to 1 mm diameter. In most cases the synthesis described above produces well developed crystals. The compound is remarkably resistant against concentrated acids and bases (HCl, NaOH etc.). For identification the *d* values and powder intensities are given in Table I. The stoichiometry was determined by the X-ray structure analysis given below and by dispersive X-ray analysis with a scanning electron microscope, yielding the approximate ratios $Al:Si \approx 1:1$ and $Al:P \approx 2.5-3.0$ respectively. Chemical analysis with sufficient precision is lacking because of the small quantities of pure substance.

Structure Determination

For structure determination a prismatic crystal was used ($0.05 \times 0.05 \times 0.20$ mm). Lattice parameters and intensities were measured with a SYNTEX $P\bar{1}$ diffractometer (Mo$K\alpha$ radiation; graphite monochromator; scintillation counter; ω-scan with $\Delta\omega = \pm 1°$). In the range $0 \leq 2\theta \leq 60°$ 537 intensity data were collected. 500 I(*hkl*) with $I > 2 \cdot \sigma(I)$ were used in a least squares refinement (SYNTEX-XTL system). The

TABLE I

d VALUES AND RELATIVE POWDER INTENSITIES[a]

hkl	*d*	I_0	*hkl*	*d*	I_0	*hkl*	*d*	I_0
101	518.1	17	400	246.8	67	032	164.4	24
200	493.6	14	221	232.8	52	520	163.7	33
011	422.2	20	022	211.1	27	132	162.2	17
022	304.4	82	312	208.8	31	331	161.9	28
020	293.0	65	402	191.7	29	422	160.4	21
301	289.5	100	420	188.8	26	512	159.4	15
120	280.9	69	213	178.7	36	223	158.1	37
012	270.1	69	231	174.1	76	611	153.3	22
112	260.6	13	303	172.7	56	532	126.3	16
311	259.5	76						

[a] *d* values are given in pm.

Laue symmetry and the systematic absences are specific to the space groups *Pmnb* and $P2_1nb$. The intensity statistic shows *Pmnb* to be most probable.

The structure determination was started with the assumption that the compound under investigation was an aluminum polyphosphide AlP_x with $x > 1$. The unit cell volume is $352.3 \times 10^{-30}\,\mathrm{m}^3 \triangleq 212.2\,\mathrm{cm}^3\cdot\mathrm{mole}^{-1}$. From the symmetry *Pmnb* and $\mathrm{P2_1nb}$ follows that at least 4 formula units should be present with a mole volume of $53.0\,\mathrm{cm}^3\cdot\mathrm{mole}^{-1}$. According to Biltz (*5*) as well as our own results (*6*) the volume increments of Al and P indicate that the formula unit should contain five atoms (AlP_4 or $\mathrm{Al}_2\mathrm{P}_3$). Partially they may be connected by symmetry in *Pmnb*. In the space group *Pmnb* direct methods immediately lead to a structure model with five atoms (two of them connected by mirror plane) whose scattering power is nearly identical (MULTAN (*7*); 63 *hkl* with $|E| \geq 1.60$). The lowest peak of the resulting *E* map at the position (4*c*) was assigned to an Al-atom, the other peaks at the positions (4*a*), (4*c*)′ and (8*d*) were explained as P atoms. After six cycles of full-matrix isotropic refinement the conventional *R* value dropped to $R = 0.032$. The refined isotropic *B* values for the atom at position (4*c*) and for the atom at position (4*a*) indicate that the scattering power f_i must fulfill the conditions $f(4c) > f(\mathrm{Al})$ and $f(4a) < f(\mathrm{P})$. The interatomic distances show:

1. The atoms at position (4*c*) are tetrahedrally bonded to the atoms P(1) at position (4*c*)′ and P(2) at position (8*d*).
2. The atoms at position (4*a*) are octahedrally bonded to two P(1) atoms and four P(2) atoms.
3. The P(1) atoms are tetrahedrally bonded to two atoms at position (4*c*) and two atoms at position (4*a*).
4. The P(2) atoms are tetrahedrally bonded to one (4*c*) atom, two (4*a*) atoms and one atom P(2).

Using classical valence rules and considering the interatomic distances it follows that the octahedrally coordinated (4*a*) atom must be a cation *M* with $f(M) < f(\mathrm{P})$, e.g. aluminum or silicon. Furthermore, the atom P(1) can formally be described as P^{3-}, whereas the atom P(2) can formally be viewed as P^{2-} or rather P_2^{4-}. Thus the composition was $[\mathrm{Al}^{3+}M^{4+}\mathrm{P}^{3-}\mathrm{P}_2^{4-}]$. The reasonable assumption $M \triangleq \mathrm{Si}$ could be verified by the analysis of the examined crystal described above. Another problem was the assignment of Al and Si to the tetrahedral and octahedral positions. Two different least-squares refinements produced the following results:

1. Al(tetr.) $B = 0.25\ \text{Å}^2$
   Si(oct.) $B = 1.10\ \text{Å}^2$
   P(1), P(2) $B = 0.58\ \text{Å}^2$
   $R = 0.028$
2. Si(tetr.) $B = 0.61\ \text{Å}^2$
   Al(oct.) $B = 0.72\ \text{Å}^2$
   P(1), P(2) $B = 0.59\ \text{Å}^2$
   $R = 0.023$

Apart from the *R* values the second distribution seems to be the correct solution due to the more similar *B* values. Another important support for this second model comes from the mean bond lengths: $(M_{\mathrm{tet}}\text{–}\mathrm{P}) = 226$ pm and $(M_{\mathrm{oct}}\text{–}\mathrm{P}) = 253$ pm. The sums of bond radii for tetrahedral and octahedral coordination are $d_{\mathrm{tet}}(\mathrm{Al\text{–}P}) = 236$ pm, $d_{\mathrm{tet}}(\mathrm{Si\text{–}P}) = 227$ pm, $d_{\mathrm{oct}}(\mathrm{Al\text{–}P}) = 248$ pm and $d_{\mathrm{oct}}(\mathrm{SI\text{–}P}) = 239$ pm. Therefore, the bond lengths also prove that the silicon atoms are tetrahedrally and the aluminum atoms octahedrally bonded to phosphorus atoms.

Result: AlSiP_3 crystallizes in the space group *Pmnb* $-D_{2h}^{16}$ (No. 62) with $a = 987.2(5)$ pm, $b = 586.1(2)$ pm, $c = 608.8(2)$ pm and $Z = 4$ formula units per unit cell ($d_x = 2.790\,\mathrm{g\cdot cm}^{-3}$). The atoms occupy the positions given in Table II. With these parameters the conventional *R* value is $R = 0.023$ both for isotropic and anisotropic

TABLE II

POSITIONAL AND THERMAL PARAMETERS[a]

Atom	Position	x	y	z	B	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al	4(*a*)	0	0	0	0.75(2)	0.87(3)	0.67(3)	0.69(3)	−0.07(2)	0.02(2)	0.00(2)
Si	4(*c*)	1/4	0.4992(1)	0.0616(1)	0.60(1)	0.48(3)	0.71(3)	0.60(3)	0	0	−0.02(2)
P(1)	4(*c*)	1/4	0.3876(1)	0.4139(1)	0.60(1)	0.53(3)	0.66(3)	0.62(3)	0	0	0.01(2)
P(2)	8(*d*)	0.0586(1)	0.3890(1)	0.8920(1)	0.56(1)	0.50(2)	0.63(2)	0.53(2)	−0.01(1)	−0.02(1)	−0.02(1)

[a] Standard deviations are given in parentheses; B_i and B_{ij} are given in units of 10^{-20} m^2; the anisotropic B_{ij} are defined for $\exp(-1/4 \cdot (B_{11}h^2 \cdot a^{*2} + \ldots + 2 \cdot B_{12}hk \cdot a^* \cdot b^* + \ldots))$.

refinement and including the 500 nonzero reflexions. Bond lengths and bond angles are listed in Table III. The structure factor list will be sent on request (HGS).

Discussion

In this new structure type the Si atoms are tetrahedrally bonded to four P atoms whereas the Al atoms are octahedrally coordinated by six P atoms. The two different phosphorus atoms P(1) and P(2) are bonded tetrahedrally, too, but whereas P(1) has four bonds to Si and Al atoms exclusively, the atoms of type P(2) have one homonuclear P–P bond with 218.2 pm bond length. The P_2-pairs correspond to similar groups in pyrites like SiP_2 (*8*, *9*) and PtP_2 (*10*) of tetravalent metals. The compound $AlSiP_3$ has, therefore, to be described as a phosphid–diphosphid and belongs with the formal charges $[Al^{3+}Si^{4+}P^{3-}(P_2)^{4-}]$ to the ZINTL phases (*11*).

TABLE III

BOND DISTANCES AND BOND ANGLES

Bond Distances in pm[a]

P(1)	-Al	260.8(1) 2*x*	Al	-P(1)	260.8(1) 2*x*
	-Si	224.2(2) 1*x*		-P(2)	244.2(1) 2*x*
	-Si′	228.2(1) 1*x*		-P(2)′	254.0(1) 2*x*
P(2)	-Al	244.2(1) 1*x*	Si	-P(1)	224.2(2) 1*x*
	-Al′	254.0(1) 1*x*		-P(1)′	228.2(2) 1*x*
	-Si	224.8(2) 1*x*		-P(2)	224.8(2) 2*x*
	-P(2)′	218.2(2) 1*x*			

Bond Angles in degree[b]

Al	P(1)	P(1)	P(2)	P(2)	P(2)
P(2)	95.2	84.8	86.1	180.0	93.9
P(2)	93.8	86.2	180.0	86.1	
P(2)	84.8	95.2	93.9		
P(2)	86.2	93.8			
P(1)	180.0				

Si	P(1)	P(1)	P(1)
P(2)	110.8	108.5	114.4
P(2)	110.8	108.5	
P(1)	103.2		

P(1)	Si	Si	Si
Al	96.8	103.8	142.3
Al	96.8	103.8	
Si	110.7		

P(2)	Si	P(2)	Al
Al	123.3	107.0	116.0
Al	110.1	105.6	
P(2)	89.9		

[a] Standard deviations are given in parentheses.

[b] Standard deviations for the angles are 0.1°.

Figure 1 gives a stereoscopic view of the structure perpendicular to the (011) plane. Figure 2 shows a section of the structure with the numbering of the atoms (Table II) and the bond length (Table III) as well as the indication of the 'Intergrowth Planes' (*12*). Along [100] layers of the pyrite type alternate with those of the wurtzite type producing a hitherto unknown type of monoatomic lamellar structure with wurtzite–pyrite-intergrowth. Dimensions and shapes of the intergrowth planes are compared in Table IV. $AlSiP_3$ is formed from the binary components AlP and SiP_2 with slight expansion in volume. The areas of the intergrowth planes, however, become smaller with simultaneous equilibration of their axial ratios. The relatively strong contraction of the hypothetical hexagonal (11.0) plane of AlP as well as the smooth expansion of the cubic (100) plane of SiP_2 is remarkable and is in good agreement with the changed cation distribution. In the $AlSiP_3$ structure the wurtzite planes include Si^{4+} cations whereas Al^{3+} is at the pyrite plane positions. Thus the observed alterations are due to changed charges. This can be described with the formalism $(SiP)^+(AlP_2)^-$.

We have tried to rationalize this atomic distribution by lattice energy calculations. Surely the bonds will be mainly covalent, especially in the P–P-bond region, but we have supposed that this energy term will be nearly unchanged in the two atomic distributions $(AlP)(SiP_2)$ and $(SiP)(AlP_2)$ taken into consideration. With ideal point charges (Si^{4+}, Al^{3+}, P^{3-}, P^{2-}) the MADELUNG constants MF(1) = 31.298 and MF(2) = 31.605 resulted for distribution 1 [$(AlP)(SiP_2)$; Al^{3+} at tetrahedral position] and distribution 2 [$(SiP)(AlP_2)$; Si^{4+} at tetrahedral position]. Both values are defined for the lattice parameters and positional parameters given in Table II and for the shortest distance M–P(1) = 224.2 pm. Thus the two structures differ by $\Delta(\text{MAPLE})^1 = 190$ kJ·mole^{-1} (45 kcal·mole^{-1}) favoring the distribution of type 2 found by us, although normally the electrostatic potentials at octahedral positions favor the occupation of those positions by the higher charged particles.

In detail the bond distances (see Table III and Fig. 2) are very close to common data (*15*). Only a few bond angles differ from ideal tetrahedral and octahedral angles up to 14 degrees (see P(2)). These deviations as well as the somewhat longer Al–P(1) bonds clearly result from the lamellar packing of pyrite and wurtzite planes.

From the X-ray result as well as from the electrostatic calculations, the distribution Si(tet), Al(oct) seems to be well established. The refined isotropic B-values give no indication for noticeable distribution disorder (B_{Al} should be smaller than B_{Si}). But this does not absolutely exclude a small disorder.

[1] MADELUNG Part of Lattice Energy, according to Hoppe (*14*)

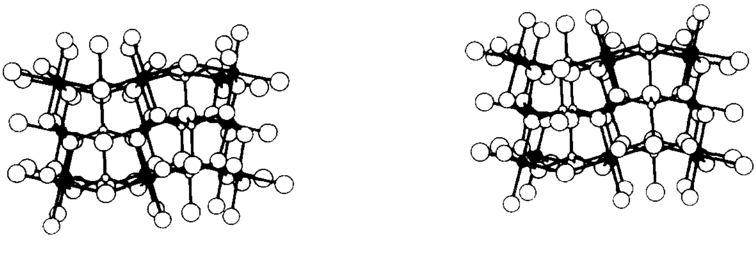

FIG. 1 Stereo plot of the $AlSiP_3$ structure viewed down [001]; phosphorus atoms are represented by large spheres, aluminum atoms by black spheres. The a-axis corresponds to the horizontal.

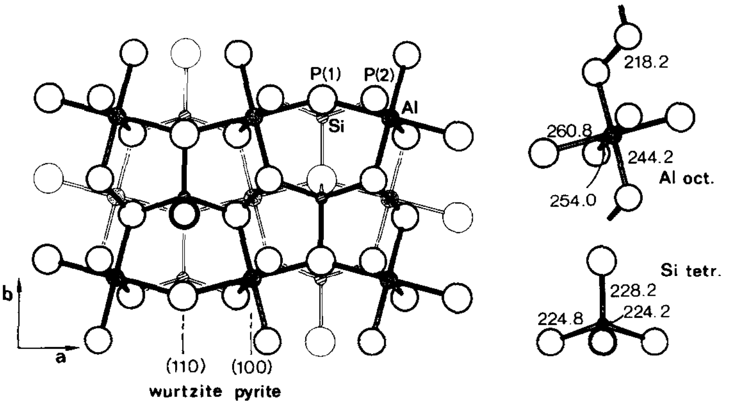

FIG. 2 $AlSiP_3$ structure projected down [001]. Phosphorus atoms are represented by large circles, silicon atoms by small line-shaded circles and aluminum atoms are dotted. The numbering of the atoms (Table II) and the bond distances (Table III) as well as the intergrowth planes are indicated.

Further Investigations

According to the description of $AlSiP_3$ being a ZINTL phase the compound will be a semiconductor or possibly a semimetal as SiP_2 (*9*). We are now trying to synthesize single crystals suitable for reliable measurements.

Finally, this novel type of solid-state phase is of general interest because the structure may allow important variations of physical properties, e.g. two-dimensional magnetic ordering and anisotropic electric properties. Attempts to synthesize compounds like $AlGeP_3$, $GaSiP_3$ and $ZnFeS_3$ ($ZnS{\cdot}FeS_2$) have failed until now, but will be continued.

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References

1. H. G. VON SCHNERING AND K. G. HÄUSLER, *Rev. Chim. Miner.* **13**, 71 (1976).
2. H. G. VON SCHNERING, "Catenation of Phosphorus Atoms" *in* (A. Rheingold, ed., "Homoatomic Rings, Chains and Macromolecules of Main Group Elements," Elsevier, Amsterdam (1977).
3. H. SCHÄFER AND M. TRENKEL, *Z. Anorg. Allg. Chem.* **391**, 11 (1972).

TABLE IV

COMPARISON OF STRUCTURAL DATA

	AlP^a	SiP_2	$AlSiP_3$	Change^e
Volume^b	24.60	27.94	53.04	+0.9%
Intergrowth	$c = 631.3$	$c = 570.4$	$b = 586.1$	−2.5%
	$a\sqrt{3} = 669.6$	$a = 570.4$	$c = 608.8$	−1.7%
	$A = 42.27$	$A = 32.54$	$A = 35.68$	−4.6%
plane^{c,d}	$c/a' = 0.9428$	$c/a = 1.0000$	$b/c = 0.9627$	

[a] hypothetical hexagonal form calculated from cubic AlP ($a_{cub} = 546.7$ pm (*13*)) with constant mole volume.

[b] in cm^3 per mole.

[c] lengths are given in pm.

[d] areas are given in 10^{-20} m^2.

[e] compared with the mean values of the binary phases.

4. H. SCHÄFER AND M. TRENKEL, *Z. Anorg. Allg. Chem.* **420**, 261 (1976).
5. W. BILTZ, "Raumchemie der festen Stoffe," Leipzig (1934).
6. H. G. VON SCHNERING, H. SCHMIDT, W. WICHELHAUS, W. DAHLMANN, AND W. HÖNLE (1970), unpublished results.
7. G. GERMAIN, P. MAIN, AND M. M. WOOLFSON, *Acta Crystallogr. A* **27**, 368 (1971).
8. T. WADSTEN, *Acta Chem. Scand.* **21**, 1374 (1967).
9. P. C. DONOHUE, W. J. SIEMONDS, AND J. L. GILLSON, *J. Phys. Chem. Solids* **29**, 807 (1968).
10. E. DAHL, *Acta Chem. Scand.* **23**, 2677 (1969).
11. H. SCHÄFER, B. EISENMANN, AND W. MÜLLER, *Angew. Chem.* **85**, 742 (1973); *Angew. Chem. Int. Edit.* **12**, 694 (1973).
12. A. D. WADSLEY, *in* "Nonstoichiometric Compounds," (L. Mandelcorn ed.), Academic Press, New York (1964).
13. C. C. WANG, M. ZAHERUDDIN, AND L. H. SPINAR, *J. Inorg. Nucl. Chem.* **25**, 326 (1963).
14. R. HOPPE, *Advan. Fluorine Chem.* **6**, 387 (1970).
15. D. E. CORBRIDGE, "The Structural Chemistry of Phosphorus," Elsevier, Amsterdam (1974).