Preparation and Crystal Structure of the Copper Silicon Polyphosphide Cu₄SiP₈

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In memoriam Professor Wilhelm Klemm

Abstract. The new compound Cu_4SiP_8 was prepared by solid state reaction of the elemental components. It crystallizes with a new structure type, which was determined from singlecrystal X-ray diffractometer data: $I4_1/a$, a = 1218.6(2) pm, c = 573.2(2) pm, Z = 8, R = 0.023 for 970 structure factors and 31 variable parameters. Tetrahedral SiP₄ groups are linked via additional phosphorus atoms to a three-dimensionally infinite silicon phosphorus network, accommodating Cu_2 pairs with octahedral phosphorus coordination as is known for the closely related structure of CuP_2 . Using oxidation numbers the compound may be rationalized by the formula $(Cu^{+1})_4 Si^{+4}(P^0)_4 (P^{-2})_4$ in agreement with the Zintl-Klemm concept.

Keywords: Copper silicon polyphosphide, Cu_4SiP_8 ; crystal structure

verknüpft, das Cu₂-Paare mit oktaedrischer Phosphorumge-

bung umschließt, wie das von der nahe verwandten Struktur

von CuP₂ her bekannt ist. Die Verbindung kann mit Hilfe von

Oxidationszahlen durch die Formel $(Cu^{+1})_4Si^{+4}(P^0)_4(P^{-2})_4$

beschrieben werden, im Einklang mit dem Zintl-Klemm-Kon-

Silicium-Phosphor-Netzwerk

Darstellung und Kristallstruktur des Kupfer-Silicium-Polyphosphids Cu₄SiP₈

Inhaltsübersicht. Die neue Verbindung Cu_4SiP_8 wurde durch eine Festkörperreaktion aus den Elementen hergestellt. Sie kristallisiert mit einem neuen Strukturtyp, der aus Röntgen-Einkristalldiffraktometerdaten bestimmt worden ist: I4₁/a, a = 1218,6(2) pm, c = 573,2(2) pm, Z = 8, R = 0,023 für 970 Strukturfaktoren und 31 variable Parameter. Tetraedrische SiP₄-Gruppen sind über zusätzliche Phosphoratome zu einem

Introduction

Most transition metals (T) form polyphosphides with a rather high content of phosphorus. In these compounds the phosphorus atoms are usually tetrahedrally coordinated by transition metal and phosphorus atoms. In contrast, the silicides of the transition metals with the highest silicon content usually have compositions close to TSi₂, and the silicon atoms in these silicides have relatively high coordination with coordination numbers of 7 to 12 [1, 2]. We have recently determined the crystal structure of NiSi₂P₃ [3], where we gained the experience, that it is well possible to distinguish silicon and phosphorus atoms on the basis of their X-ray scattering power. As a consequence we have now started a systematic investigation of ternary compounds containing both silicon and phosphorus, and we report here on the new compound Cu₄SiP₈.

Sample Preparation and Lattice Constants

dreidimensional-unendlichen

zept.

Starting materials were powders of copper and silicon (both with nominal purities $\geq 99.9\%$) and red phosphorus (Hoechst, "ultrapure"). Cold-pressed pellets of the ideal composition were annealed in evacuated and sealed silica tubes (tube volume 2 cm³, P content 0.1 g). To prevent the rupture of the tubes the temperature was raised slowly: 1 d at 450 °C, 1 d at 700 °C, 5 d at 900 °C, and 21 d at 800 °C. Finally the samples were quenched in air. The resulting products consisted of crystals of the new polyphosphide. In addition we frequently observed black powders of the binary phosphide CuP₂. The energy-dispersive X-ray fluorescence analysis of the ternary compound showed the ratio Cu:Si:P = 4.4:1:8.6 and no impurity elements heavier than sodium.

The tetragonal lattice constants of Cu_4SiP_8 were refined by least-squares fits of the Guinier powder data using α quartz (a = 491.30 pm, c = 540.46 pm) as an internal standard: a = 1218.6(2) pm, c = 573.2(2) pm, and $V = 0.8512 \text{ nm}^3$.

Structure Determination

Single crystals of Cu₄SiP₈ were investigated first with a precession camera to establish their symmetry and suitability for the data collection. Intensity data were collected from a crystal of dimensions $60 \times 50 \times 40 \ \mu\text{m}^3$ on a CAD4 single-crystal diffractometer, using MoK α radiation, a graphite monochromator, and a scintillation counter with pulse-height discriminator. Backround counts were collected at both sides of the $\theta/2\theta$ scans. An absorption correction was carried out on the basis of psi scan data. The ratio of the highest to the lowest transmission was 1.25. A total of 7660 reflections were measured in one half of the reciprocal space up to $2\theta = 90^\circ$. Of these 4420 reflections had intensities greater than three standard deviations.

The intensitiy distribution had the Laue symmetry 4/m and the space group extinctions led to the unique space group $I4_1/a$ (No. 88), which proved to be correct during the structure refinements. The stucture was solved by Patterson and difference Fourier syntheses [4] and refined by a full-matrix leastsquares program [5] using atomic scattering factors [6], corrected for anomalous dispersion [7]. The weighting scheme reflected the counting statistics and a parameter correcting for secondary extinction was refined as a least-squares parameter.

Silicon and phosphorus differ in their scattering power by only one electron. Thus the correct atom distribution was initially based on chemical arguments. Nevertheless, our data set was good enough to distinguish the phosphorus and silicon atoms, because a sufficient number of high angle reflections was present. It was even possible to refine the occupancy and anisotropic thermal parameters simultaneously. The results are summarized in Table 1. All refinements led to residuals of between 0.023 and 0.024 for the 970 unique structure factors with $F > 3\sigma(F)$ and 34 variable parameters. For the final refinement the ideal occupancy parameters were assumed: R = 0.023 for 31 variables. The highest electron densities of a final difference Fourier synthesis were 0.66 and 0.32 e/Å³. The atomic parameters and interatomic distances are listed in the Tables 2 and 3.

Table 3 Interatomic distances (pm) in Cu_4SiP_8 . All distances shorter than 260 pm are listed. The standard deviations are all 0.1 pm or less

Cu:	1 P1 1 P2 1 P2	228.6 232.0 234.0	P1:	1 P2 2 P1 1 Cu	217.5 221.4 228.6
	1 P2 1 Cu	257.2 251.3	P2:	1 P1 1 Si	217.5 224.5
Si:	4 P2	224.5		1 Cu 1 Cu 1 Cu	232.0 234.0 257.2

Discussion

Cu₄SiP₈ crystallizes with a new structure type, which is closely related to the structures of CuP₂ [9, 10], ZnP₄ [11], and CdP₄ [12] (Fig. 1). The Cu atoms form pairs, which are octahedrally coordinated by P atoms (Fig. 2). This is exactly the same environment as for the Cu atoms in CuP₂. The Cu—Cu bond distance of 251 pm in Cu₄SiP₈ compares well with the corresponding distance of 248 pm in CuP₂, and the average Cu—P distance of 238 pm in the ternary compound is practically the same as the average Cu—P distance of 237 pm in CuP₂. The silicon atoms in Cu₄SiP₈ are tetrahedrally coordinated by phosphorus atoms with a bond distance of 225 pm, which is similar to the average Si—P distances of 225, 223, and 225 pm in ZnSiP₂ [13], CeSiP₃ [14], and

Table 1 Occupancy parameters (%) as obtained from the least-squares refinements with differing distributions of silicon and phosphorus atoms in the structure of the copper silicon polyphosphide. The corresponding compositions are indicated in the column headings. Anisotropic thermal parameters for all atoms were allowed to vary always together with the occupancy parameters, however, the thermal parameters did not vary greatly. The lowest equivalent B value of 0.272(7) Å² was obtained for a Si atom on a P position and the highest value of 0.53(1) Å² resulted for a silicon position occupied by a phosphorus atom. The atom distribution considered as the correct one is listed first

I4,/a	Cu_4SiP_8	Cu ₄ Si ₄ P ₅	$Cu_4Si_4P_5$	$Cu_4Si_5P_4$	$Cu_4Si_5P_4$	Cu ₄ Si ₉	Cu ₄ P ₉
16f	Cu 100	Cu 100	Cu 100	Cu 100	Cu100Si199.9(4)Si2103.9(2)P100.7(2)	Cu 100	Cu 100
4a	Si 99.7(4)	P1 95.7(4)	P1 94.6(4)	Si1 98.8(4)		Si1 99.1(4)	P1 95.4(4)
16f	P1 99.9(2)	Si 103.9(2)	P2 99.9(2)	P 100.0(2)		Si2 104.0(2)	P2 99.9(2)
16f	P2 100.6(2)	P2 100.9(2)	Si 105.0(2)	Si2 104.9(2)		Si3 104.9(2)	P3 100.9(2)

Table 2 Atomic parameters of Cu₄SiP₈. The program STRUCTURE TIDY [8] was used to standardize the positional parameters

Atom	I4 ₁ /a	x	у	Z	\mathbf{U}_{11}	U ₂₂	U_{33}	\mathbf{U}_{12}	U_{13}	U_{23}	U _{eq} (pm ²)
Cu Si P1 P2	16f 4a 16f 16f	0.20051(2) 0 0.15464(4) 0.41238(4)	0.23869(2) 1/4 0.02224(4) 0.13490(4)	0.55918(5) 1/8 0.10212(9) 0.13257(9)	158(1) 48(2) 56(2) 60(2)	$ \begin{array}{r} 114(1) \\ U_{11} \\ 53(2) \\ 67(2) \end{array} $	84(1) 58(4) 48(2) 59(2)	$ \begin{array}{r} 42(1) \\ 0 \\ -4(1) \\ -3(2) \end{array} $	22(1) 0 3(2) 6(2)	$ \begin{array}{r} 19(1) \\ 0 \\ -2(2) \\ -12(2) \end{array} $	119(1) 51(2) 52(1) 62(1)

The anisotropic thermal parameters are defined by $T = \exp[-2\pi^2 \{h^2 a^{*2} U_{11} + \ldots + 2k l b^* c^* U_{23}\}]$.



Fig. 1 The crystal structure of Cu_4SiP_8 as compared to the structures of CuP_2 , CdP_4 , and ZnP_4



Fig. 2 Near-neighbor environments in the structure of Cu_4SiP_8 . Single-digit numbers correspond to the atom designations. Interatomic distances are indicated in pm units

 $NiSi_2P_3$ [3]. The two phosphorus sites in Cu_4SiP_8 have remarkably different coordinations. The P1 atoms are tetrahedrally coordinated by one Cu and three P atoms, while the P2 atoms have five neighbors: three Cu, one Si, and one P.

The P-P bonds of 218 and 221 pm in Cu₄SiP₈ are similar to the typical two-electron bond lengths of $222 \pm 2 \text{ pm}$ in the modifications of elemental phosphorus [15] and in polyphosphides [16]. We assume the octet rule to be valid for the silicon and the phosphorus atoms. To determine oxidation numbers we count the bonding electrons of the Cu-P and Si-P bonds at the more electronegative partners, the phosphorus atoms. In this way the P1 atoms obtain the oxidation number zero, while the P2 atoms obtain the formal charge -2. The compound may than be written with the formula $(Cu^{+1})_4Si^{+4}(P1^0)_4(P2^{-2})_4$, i.e. Cu obtains a d¹⁰ system. Assuming the 18-electron rule to be valid for the copper atoms one may count two electrons for the Cu-Cu bond of 251 pm and two electrons for the short Cu-P1 bond of 229 pm. The three Cu-P2 bonds of 232, 234, and 257 pm together would then account for four more electrons. Obviously these are very crude assignements.

Above we have assumed that the octet rule is obeyed for the silicon and phosphorus atoms and we have counted two valence electrons for each of the bonds between the main group elements. As a result we found that the copper atoms have the oxidation number +1. This procedure is closely related to the Zintl-Klemm concept [17-21]. This concept was originally applied to compounds of the alkali and earth alkali elements with metallic or semimetallic main group elements. There the oxidation number of the alkali and earth alkali element is usually known (+1 or +2, respectively). One counts the corresponding electrons as belonging to the main group elements and these form a structure with as many two-electron bonds as is appropriate for a main group element with that many electrons. Thus, in one of the first known examples, LiAl with NaTl-type structure [17] each Al atom has to accommodate a total of four valence electrons and accordingly - like elemental silicon - it forms four two-electron bonds to adjacent Al atoms. In another early, most impressive example, KGe, prepared by a graduate student of Klemm in Münster and structurally characterized under the guidance of Zemann in Göttingen [22] the Ge atoms achieve an electron count of five and consequently they form three bonds to neighboring Ge atoms, as is appropriate for an element of the fifth main group. In this case they form Ge4 tetrahedra (as is known for the white modification of phosphorus), however, any other structure with three Ge-Ge bonds per Ge atom would also be in agreement with this concept. Thus, the Zintl-Klemm concept has some predictive character: it predicts the number of bonds between the main group elements.

In applying this concept to Cu_4SiP_8 one has to assume that the Cu atoms have the oxidation number +1 (not the valence; we like to think that copper is divalent in this compound because of the Cu—Cu bond). With this assumption the Si and P atoms obtain four additional valence electrons from the four Cu atoms. In ternary compounds with two different main group elements these additional valence electrons can usually be assigned to the more electronegative main group element. Thus four of the P atoms attain a total of six valence electrons and accordingly (like sulfur in its various elemental modifications) they should form two bonds to other main group atoms. These are the four P2 atoms, while the Si and P1 atoms have no additional valence electrons and therefore they form four and three (two-electron) bonds within the polyanion, as is appropriate for elements of the fourth and fifth main group. Therefore, assuming the Cu atoms in Cu_4SiP_8 to have the oxidation number +1 the bonding within the silicon-phosphorus polyanion is entirely in agreement with the Zintl-Klemm concept.

Today, with the wealth of structural information on solid state compounds available, the *Zintl-Klemm* concept may look trivial to some readers. However, at the time when it was envisioned and recognized to be generally applicable for compounds like LiAl and KGe it was not generally accepted by the scientific community, because at that time the predominant opinion was, that not much could be understood about the bonding in such intermetallics without calculating a band structure.

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