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Refinement of the crystal structures of Cu_3PS_4 and Cu_3SbS_4 and a comment on normal tetrahedral structures

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Abstract. The crystal structures of yellow Cu_3PS_4 and of black Cu_3SbS_4 were refined from single crystal X-ray diffraction data. Cu_3PS_4 crystallizes orthorhombic in an ordered wurtzite superstructure type with the space group $Pmn2_1$ (no. 31), $a = 7.282(1)$ Å, $b = 6.339(1)$ Å, $c = 6.075(1)$ Å, $V = 280.38(8)$ Å^3, and $Z = 2$. The refinement converged to $R = 0.0276$, and $wR2 = 0.0710$ for 737 unique reflections and 44 parameters. Cu_3SbS_4 crystallizes tetragonal in an ordered sphalerite superstructure type with the space group $I\bar{4}2m$ (no. 121), $a = 5.391(1)$ Å, $c = 10.764(1)$ Å, $V = 312.83(9)$ Å^3, and $Z = 2$. The refinement converged to $R = 0.0213$, and $wR2 = 0.0532$ for 492 unique reflections and 14 parameters.

The crystal structures of the title compounds and related normal tetrahedral structures are discussed with respect to the preference of either hexagonal or cubic packing of the anions.

Introduction

Ternary copper chalcogenides are an interesting group of compounds due to their semiconducting properties. Especially copper indium chalcogenides are of technological interest as highly resistant photovoltaic materials. Checking the literature for basic structural information about ternary compounds of copper chalcogenides with the general composition Cu_3PnQ_4 (Pn = P, As, Sb, Q = S, Se) one finds a separation into two different structure types for this group of six compounds. They are isotypic either with the mineral enargite Cu_3AsS_4 or the mineral famatinite Cu_3SbS_4. Cu_3PS_4, Cu_3PSe_4, Cu_3AsS_4, and Cu_3AsSe_4 are reported to crystallize in the wurtzite related enargite structure type [1–5]. The structure of Cu_3PS_4 was yet only refined from film data [1]. Cu_3SbS_4 and Cu_3SbSe_4 prefer the sphalerite related famatinite structure type [2, 6, 7]. From electron diffraction data it was concluded that Cu_3SbS_4 is cubic with a cell volume of $V_{\mathrm{cub}} = 4 \cdot V_{\mathrm{tet}}$ [8]. The small tetragonal distortion of the crystal structure was certainly not observed in this study. This discrepancy and the lack of precise structural data was the reason for the refinement of the crystal structures of Cu_3PS_4 and of Cu_3SbS_4.

Both structure types are tetrahedral structures with an ordered distribution of monovalent copper and the pentavalent cations. The question for the separation of these analogous compounds into two different structure types has not yet been answered despite the fact that the principal structural relations are known since a long time. The same holds for related compounds where the cation site of the ZnS structures is occupied even by three different cations, e.g. A_2BCQ_4 compounds, in an ordered manner. Herein we report the refined crystal structures of Cu_3PS_4 and of Cu_3SbS_4, discuss the major differences between both structure types, and comment on related so-called normal tetrahedral structures.

Experimental

Yellow single crystals of Cu_3PS_4 were obtained as a by-product from reaction mixtures of CuI and P_2S_5 in the ratio 1 : 1. They were preheated to 600 °C and then annealed at 300 °C for seven weeks. Black single crystals of Cu_3SbS_4 resulted as a by-product from reaction mixtures with the nominal composition $Cu_3V_{0.25}Sb_{0.75}S_4$ which were originally designed for the synthesis of an antimony bearing colusite analogous compound [9]. Samples were heated to 700 °C for a few hours and were then annealed at 550 °C for several weeks. The syntheses for Cu_3PS_4 and Cu_3SbS_4 were not optimized since the experimental procedure was already described [1, 2]. The compounds can be obtained by the reaction of stoichiometric amounts of the corresponding elements.

The chemical composition of selected crystals of both compounds was checked by EDX measurements on a CamScan microprobe CS44 equipped with an EDAX EDX spectrometer. Single crystal X-ray diffraction data were collected on a STOE IPDS (Cu_3PS_4), and on a CAD4 (Cu_3SbS_4), respectively. The raw data were corrected for Lorentz and polarization effects. A numerical absorption correction was employed before merging symmetry equivalent reflections in the case of Cu_3PS_4. The description of the shape of the crystal was optimized with the X-SHAPE routine [10]. For Cu_3SbS_4 no absorption

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correction was necessary since the crystal had a size of only 0.08 × 0.05 × 0.04 mm^3.

Both structures were solved by direct methods and refined against F^2 [11] with anisotropic displacement parameters for all atoms and including an extinction parameter. The Flack parameter was used to check for the right setting of the non centrosymmetric structures. It was 0.001(10) (Cu_3PS_4), and −0.09(4) (Cu_3SbS_4), i.e. no hint for the formation of an inversion twin was detected. Details of the crystal structure refinements and crystallographic data are collected in Table 1.

Table 1. Crystallographic data for the X-ray structure determination of Cu_3PS_4 and Cu_3SbS_4.^{a}

Compound	Cu_3PS_4	Cu_3SbS_4
Formula weight (g mol^{-1})	349.83	440.61
Crystal size (mm^3)	0.3 × 0.16 × 0.06	0.08 × 0.05 × 0.04
Color	yellow	black
Crystal system	orthorhombic	tetragonal
Space group	$Pna2_1$ (no. 31)	$I\bar{4}2m$ (no. 121)
Lattice constants (Å) from single crystals	$a = 7.282(1)$ $b = 6.339(1)$ $c = 6.075(1)$	$a = 5.391(1)$ $c = 10.764(1)$
Cell volume (Å^3), Z	280.38(8), 2	312.83(9), 2
$\varrho_{X\text{-ray}}$ (g cm^{-3}), μ (cm^{-1})	4.144, 129.0	4.678, 155.3
Diffractometer	STOE IPDS, MoK_α, $\lambda = 0.71073$ Å, oriented graphite monochromator	CAD 4, MoK_α, $\lambda = 0.71073$ Å, oriented graphite monochromator
Image plate distance	60 mm	–
φ-range (°), $\Delta\varphi$ (°)	$0 \leq \varphi \leq 360$, 2	–
Absorption correction	numerical, crystal description with 10 faces, shape optimized with X-SHAPE	none
Irradiation time/image (min.)	3.5	–
Temperature (°C)	20	20
2θ-range (°)	$2\theta < 56.2°$	$2\theta < 90°$
hkl-range	$-9 \leq h \leq 9$, $-8 \leq k \leq 8$, $-8 \leq l \leq 8$	$-10 \leq h \leq 10$, $0 \leq k \leq 10$, $-21 \leq l \leq 0$
No. of reflections, $R_{int.}$	4737, 0.0600	836, 0.0364
No. of independent reflections	737	492
No. of parameters	44	14
Program	SHELX97 program package [11]	SHELX97 program package [11]
R ($I > 2\sigma_I$), R (all reflections)	0.0276, 0.0276	0.0211, 0.0530
wR ($I > 2\sigma_I$), wR (all reflections)	0.0709, 0.0710	0.0213, 0.0532
GooF	1.278	1.065
Extinction coefficient	0.76(3)	0.028(1)
Weighting parameters a, b^b	0.0499, 0.0081	0.0296, 0
Largest difference peaks $\Delta\varrho_{max}$, $\Delta\varrho_{min}$ (e Å^{-3})	1.112, −1.340	2.755 (0.49 Å apart from Sb), −1.730

a: Additional material to this paper can be ordered referring to no. CSD-412240 (Cu_3PS_4), and CSD-412239 (Cu_3SbS_4), name of the author and citation of the paper at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz.de). The list of F_o/F_c-data is available from the author up to one year after the publication has appeared.
b: $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$, $P = [\max(F_o^2, 0) + 2 \cdot F_c^2]/3$

Results and discussion

The results of the crystal structure analyses are summarized in Tables 2 and 3 (Cu_3PS_4), and in Tables 4 and 5 (Cu_3SbS_4), respectively. Selected interatomic distances and angles for both compounds are gathered in Table 6. The close relationship of the famatinite structure, see Fig. 1 and Table 4, to a cubic close packing of the anions becomes immediately obvious from the atomic parameters. The relationship of the crystal structure of Cu_3PS_4, see Figure 2 and Table 2, and the hexagonal close packing of the anions is not as striking but it is still obvious from the data.

At a first glance one might wonder why these homologous compounds crystallize in different structure types. A comparison of the two crystal structures shows the major difference between them. That is, the tetrahedra [CuS_4]

Table 2. Atomic parameters (e.s.d.s) and $U_{eq}{}^a$ (in Å^2) for Cu_3PS_4 at room temperature.

Atom	Wyckoff pos.	x	y	z	U_{eq}
Cu1	2a	0.	0.6476(1)	0.0983(1)	0.018(1)
Cu2	4b	0.7356(1)	0.1784(1)	0.0873(1)	0.017(1)
P	2a	0.	0.3234(1)	0.5999(3)	0.005(1)
S1	2a	0.	0.3175(2)	0.2584(3)	0.009(1)
S2	2a	0.	0.6281(2)	0.7176(2)	0.008(1)
S3	4b	0.7330(1)	0.8320(1)	0.2102(2)	0.009(1)

a: U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic displacement parameters U^{ij} (in Å^2) for Cu_3PS_4.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.020(1)	0.018(1)	0.016(1)	0.	0.	0.003(1)
Cu2	0.017(1)	0.016(1)	0.017(1)	−0.001(1)	0.000(1)	−0.001(1)
P	0.005(1)	0.005(1)	0.005(1)	0.	0.	0.000(1)
S1	0.010(1)	0.012(1)	0.004(1)	0.	0.	−0.001(1)
S2	0.010(1)	0.006(1)	0.008(1)	0.	0.	−0.001(1)
S3	0.008(1)	0.010(1)	0.010(1)	−0.001(1)	−0.001(1)	0.000(1)

Table 4. Atomic parameters (e.s.d.s) and $U_{eq}{}^a$ (in Å^2) for Cu_3SbS_4 at room temperature.

Atom	Wyckoff pos.	x	y	z	U_{eq}
Cu1	2b	0.	0.	$^1/_2$	0.019(1)
Cu2	4d	0.	$^1/_2$	$^1/_4$	0.019(1)
Sb	2a	0.	0.	0.	0.009(1)
S	8i	0.2542(1)	x	0.1289(1)	0.011(1)

a: U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 5. Anisotropic displacement parameters U^{ij} (in Å^2) for Cu_3SbS_4.

Atom	$U^{11} = U^{22}$	U^{33}	U^{12}	$U^{13} = U^{23}$
Cu1	0.019(1)	0.019(1)	0.	0.
Cu2	0.019(1)	0.019(1)	0.	0.
Sb	0.008(1)	0.009(1)	0.	0.
S	0.011(1)	0.012(1)	−0.001(1)	−0.001(1)

Table 6. Selected interatomic distances (in Å) and angles (in °) for Cu_3PS_4 and Cu_3SbS_4.

	Cu_3PS_4		
Cu1–S1	2.307(2)	S1–Cu2–S3	104.44(5)
–S2	2.316(2)	S1–Cu2–S2	105.38(4)
–S3	2× 2.368(1)	S3–Cu2–S3	107.24(4)
Cu2–S3	2.297(2)	S2–Cu2–S3	111.21(5)
–S1	2.300(1)	S1–Cu2–S3	114.02(5)
–S2	2.3086(8)	S2–Cu2–S3	114.17(5)
–S3	2.321(1)		
P1–S2	2.060(2)	S1–P–S3	2× 108.33(7)
–S3	2× 2.073(1)	S2–P–S3	2× 109.48(7)
–S1	2.075(3)	S3–P–S3	109.85(8)
		S1–P–S2	111.35(8)
S2–Cu1–S3	2× 108.22(4)		
S1–Cu1–S3	2× 109.08(4)		
S3–Cu1–S3	110.36(6)		
S1–Cu1–S2	111.88(6)		
	Cu_3SbS_4		
Cu1–S	4× 2.3317(7)	S–Cu1–S	2× 106.95(3)
Cu2–S	4× 2.3092(5)		4× 110.75(2)
Sb–S	4× 2.3838(7)	S–Cu2–S	4× 108.58(1)
			2× 111.28(3)
S–Sb–S	2× 108.80(3)		
	4× 109.81(2)		

and $[SbS_4]$ have almost the same size whereas the polyhedra $[PS_4]$ are significantly smaller than $[CuS_4]$. In detail, the distances d(Cu–S) are about 2.32 Å in both compounds, d(Sb–S) is 2.38 Å, and d(P–S) is 2.07 Å. As a consequence the edges of the different tetrahedra are almost in the same range (3.75–3.9 Å) in Cu_3SbS_4. In Cu_3PS_4 the corresponding distances are 3.65–3.89 Å for $[CuS_4]$ but only 3.36–3.41 Å for $[PS_4]$. In addition, the angles S–Cu–S around Cu2 in Cu_3PS_4 show a deviation of up to 5 degrees from the ideal tetrahedral angle. All other tetrahedra centers show bond angles which are close to the ideal value.

Compounds which are closely related to the enargite and famatinite structure are the members of the wurtzstannite and of the stannite family with the composition A_2BCQ_4 (A = Cu, Ag; B = Mn, Fe, Co, Ni, Zn, Cd, Hg; C = Si, Ge, Sn; Q = S, Se, Te). A survey is given in ref. [12]. As discussed by Parthé et al. [13] the ordering of the cations in the respective tetragonal and orthorhombic structures is very similar for the compounds under discussion. Thus, the same Wyckoff positions are occupied in famatinite and in stannite. The same holds for enargite and wurtzstannite. However, the reason why an actual compound takes the cubic or the hexagonal arrangement of the anions is still a subject of discussion [14].

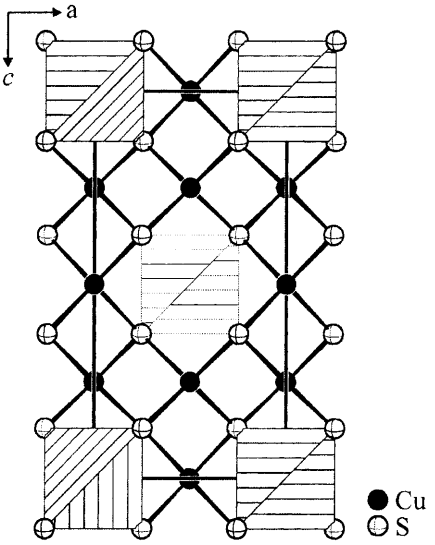

Fig. 1. Section of the crystal structure of Cu_3SbS_4. The tetrahedra are centered by antimony atoms.

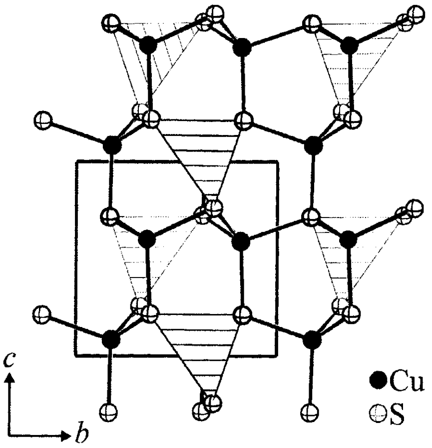

Fig. 2. Section of the crystal structure of Cu_3PS_4. The tetrahedra are centered by phosphorus atoms. Note the different positions of sulfur along the c-axis.

An inspection of the interatomic distances within the basic tetrahedra shows, that the hexagonal arrangement of the anions is preferred when the size of the tetrahedra differs significantly. This finding even holds when the crystal structures of oxides, e.g. Na_2ZnSiO_4 [15] or β-$NaFeO_2$ [16], are analyzed. However, the crystal structures of Cu_2SiS_3, Cu_2SiSe_3, and Cu_2GeS_3 show that a prediction whether the hexagonal or the cubic arrangement of the anions is favorable for a given compound cannot be made easily. Especially for Cu_2SiS_3 both types have been reported. The preparation method and the sample temperature seem to play a crucial role [17–19].

It can be stated that the hexagonal packing of the anions can compensate the distortions much better than a cubic packing. However, the crystal structures of a certain number of these compounds has not yet been determined in detail. Therefore a more detailed analysis of the influence of the size of the tetrahedra on the resulting crystal structure is impossible at the moment.

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