The system Cu₃AsS₄–Cu₃SbS₄ and investigations on normal tetrahedral structures

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Dedicated to Professor Dr. H.-L. Keller on the occasion of his 60th birthday

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X-ray diffraction / Powder diffraction structure analysis / Single crystal structure analysis / Thiometallate / Tetrahedral structures / Wurtzite structure type / Sphalerite structure type

Abstract. In order to develop a novel model to predict if a so called normal tetrahedral compound crystallizes in a wurtzite- or sphalerite superstructure type, the system Cu₃AsS₄–Cu₃SbS₄ was reinvestigated. A solid solution series was prepared and the mixed crystals were characterized by powder X-ray techniques. The crystal structures of Cu₃As₀.₃₃₁Sb₀.₆₇₀S₄, Cu₃As₀.₇₃₆Sb₀.₂₆₄S₄, and Cu₃AsS₄ were refined from single crystal X-ray data. The refinements converged to $R = 0.0209$, $wR_2 = 0.0484$ (Cu₃As₀.₃₃₁Sb₀.₆₇₀S₄, 201 unique reflections, 15 parameters), $R = 0.0235$, $wR_2 = 0.0596$ (Cu₃As₀.₇₃₆Sb₀.₂₆₄S₄, 218 reflections, 15 parameters), and $R = 0.0241$, $wR_2 = 0.0669$ (Cu₃AsS₄, 721 reflections, 45 parameters). Z is 2 for all compounds. The volumes of the tetrahedra [MS₄] were calculated for the investigated compounds. In addition, the corresponding data were calculated for further solids from literature data. The volumes of the tetrahedra used to separate compounds with a sphalerite type anion arrangement from compounds with hexagonal packed anions. A closer inspection of the tetrahedra volumes reveals a greater variation for one given material in the case of wurtzite type superstructures than for sphalerite type superstructures. A critical difference in the tetrahedra volumes is derived from these data.

Introduction

Normal tetrahedral structures have been investigated for a long time because of their interesting electrical and optical properties. Parthé has given easy valence electron rules in order to predict the composition of multinary compounds which crystallize in tetrahedral structures [1]. The cubic sphalerite structure type and the hexagonal wurtzite structure type are distinguished due to the packing of the anions. In ternary or multinary tetrahedral compounds the cation positions may be occupied in an ordered or in a statistic way. An ordered distribution causes a reduction of symmetry, e.g. leading to a tetragonal instead of a cubic cell for Cu₃SbS₄ (famatinite), whereas an orthorhombic cell instead of a hexagonal cell results for Cu₃AsS₄ (enargite) [2]. An even lower symmetry has been observed in some other cases.

The system Cu₃AsS₄–Cu₃SbS₄ is well investigated with respect to the formation of mixed crystals and thermal properties [3, 4]. According to powder data the structure of the mixed crystals Cu₃AsₓSb₁₋ₓS₄ changes at $x = 0.8$. For $x < 0.8$ the tetragonal famatinite type is observed, and for $x > 0.8$ the orthorhombic enargite type is found. Most of the former investigations concentrate on the stability of the different phases in the quasi-binary system. Kanazawa describes the evolution of the lattice parameters in the solid solution series Cu₃AsₓSb₁₋ₓS₄ [5]. Bernardini et al. examine the evolution of the $d_{112}$-values, the most intense reflection in the X-ray powder diagram. The $d_{112}$ spacing increases linearly from luzonite to famatinite [6]. Luconite is the arsenian homologue of famatinite.

In the literature some refinements of natural samples of enargite can be found [7–10]. However, these refinements cannot be used for deriving crystal chemical parameters since the natural samples may contain a manifold of elements. Only Karanović et al. determined the composition of their sample exactly by energy dispersive spectroscopy, it was Cu₃As₀.₆₈₅Sb₀.₃₁₅S₄ [10].

The crystal structure of Cu₃As₀.₆₈₅Sb₀.₃₁₅S₄ was determined by Marumo and Nowacki in 1967 [11]. This composition was reinvestigated, as their data based on film methods.

To date it is not possible to predict which structure type will be formed by a normal tetrahedral compound with a given composition. Some authors suggest that the C cation in quaternary compounds $A_2B_{CQ}$, ($A = Cu$, $B = Mn$, Fe, Co, Ni, Cd, $C = Si, Ge, Sn$, $Q = S$, Se) plays an important role [12]. However, despite numerous efforts, e.g. ref. [13], there is no concept available to de-
rive at least the arrangement of the anions from simple crystal chemical data, e.g. ionic radii of the constituent elements.

A novel approach to predict the preference for either a distorted hexagonal or a distorted cubic arrangement of the anions was recently described [14]. It became obvious that in Cu$_3$PS$_4$ (enargite type) the tetrahedra [MS$_4$] (M = Cu, P) exhibit a significant difference of their volumes while in Cu$_3$SbS$_4$ the tetrahedra [MS$_4$] (M = Cu, Sb) have about the same size.

Herein, we report our investigations of the system Cu$_3$As$_x$Sb$_{1-x}$S$_4$. This system was chosen since Cu$_3$PS$_4$ and Cu$_3$SbS$_4$ do not form a solid solution series. Lattice constants and thermal behaviour of the mixed crystals are reported. In addition, selected compositions are characterized by single crystal X-ray structure determination. Thus, a precise information about the volumes of the tetrahedra [MS$_4$] (M = Cu, As, Sb) is available. It is possible to derive critical volume ratios for the change from the cubic anion arrangement to the hexagonal packing from these data.

**Experimental**

Cu$_3$AsS$_4$ and Cu$_3$SbS$_4$ were prepared by annealing stoichiometric mixtures of the elements in evacuated, sealed quartz ampoules for two weeks at 590 °C. The products were homogenized between two annealing periods. The solid solutions Cu$_3$As$_x$Sb$_{1-x}$S$_4$ (x = 0.1 to 0.9) were prepared from the end members by annealing stoichiometric mixtures at 595 °C for a total of four weeks. Again, the materials were ground between two annealing periods. After that time, no impurities were detected by X-ray powder diffraction.

### Table 1. Crystallographic data for the X-ray structure determinations of Cu$_3$As$_{0.3}$Sb$_{0.7}$S$_4$, Cu$_3$As$_{0.7}$Sb$_{0.3}$S$_4$, and Cu$_3$AsS$_4$ a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cu$<em>3$As$</em>{0.3}$Sb$_{0.7}$S$_4$</th>
<th>Cu$<em>3$As$</em>{0.7}$Sb$_{0.3}$S$_4$</th>
<th>Cu$_3$AsS$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight/(g mol$^{-1}$)</td>
<td>426.56</td>
<td>407.83</td>
<td>393.78</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>0.12 0.10 0.08</td>
<td>0.11 0.09 0.09</td>
<td>0.32 0.20 0.18</td>
</tr>
<tr>
<td>Colour</td>
<td>black</td>
<td>black</td>
<td>black</td>
</tr>
<tr>
<td>Crystal system</td>
<td>tetragonal</td>
<td>tetragonal</td>
<td>orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>1$\bar{2}$m (no. 121)</td>
<td>1$\bar{2}$m (no. 121)</td>
<td>Pm$\bar{3}$m (no. 221)</td>
</tr>
<tr>
<td>Lattice constants/Å</td>
<td>$a = 5.353(1)$</td>
<td>$a = 5.315(1)$</td>
<td>$a = 7.399(1)$</td>
</tr>
<tr>
<td></td>
<td>$c = 10.652(2)$</td>
<td>$c = 10.536(2)$</td>
<td>$b = 6.428(1)$</td>
</tr>
<tr>
<td>Crystal size/mm$^3$</td>
<td>0.12 0.10 0.08</td>
<td>0.11 0.09 0.09</td>
<td>0.32 0.20 0.18</td>
</tr>
<tr>
<td>Colour</td>
<td>black</td>
<td>black</td>
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<td>$a = 5.353(1)$</td>
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<td>$a = 7.399(1)$</td>
</tr>
<tr>
<td></td>
<td>$c = 10.652(2)$</td>
<td>$c = 10.536(2)$</td>
<td>$b = 6.428(1)$</td>
</tr>
<tr>
<td>Cell volume/Å$^3$, Z</td>
<td>305.2(1), 2</td>
<td>297.7(1), 2</td>
<td>292.3(1), 2</td>
</tr>
<tr>
<td>$\varphi$-range/°, $\Delta \varphi$</td>
<td>$0^\circ \leq \varphi \leq 112.5^\circ$, 1.5</td>
<td>$0^\circ \leq \varphi \leq 140^\circ$, 2.0</td>
<td>$0^\circ \leq \varphi \leq 173^\circ$, 1.0</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Numerical, shape optimized with X-SHAPE [15]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiation time/image/min.</td>
<td>15</td>
<td>18</td>
<td>13</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>20</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>2 $\theta$-range/°</td>
<td>$3.8 &lt; 2\theta &lt; 56.3$</td>
<td>$4.2 &lt; 2\theta &lt; 58.3$</td>
<td>$6.3 &lt; 2\theta &lt; 56.0$</td>
</tr>
<tr>
<td>hob-range</td>
<td>$-6 &lt; h &lt; 6$</td>
<td>$-5 &lt; h &lt; 7$</td>
<td>$-9 &lt; h &lt; 9$</td>
</tr>
<tr>
<td></td>
<td>$-6 &lt; k &lt; 6$</td>
<td>$-6 &lt; k &lt; 7$</td>
<td>$-8 &lt; k &lt; 8$</td>
</tr>
<tr>
<td></td>
<td>$-13 &lt; l &lt; 9$</td>
<td>$-14 &lt; l &lt; 14$</td>
<td>$-7 &lt; l &lt; 8$</td>
</tr>
<tr>
<td>No. of reflections, $R_{int}$</td>
<td>894, 0.0408</td>
<td>1257, 0.0398</td>
<td>2276, 0.0322</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>201</td>
<td>218</td>
<td>721</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>15</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>Program</td>
<td>SHEXL97 [16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1(I &gt; 2\sigma(I))$, $R_1$(all reflections)</td>
<td>0.0209, 0.0209</td>
<td>0.0235, 0.0235</td>
<td>0.0240, 0.0251</td>
</tr>
<tr>
<td>$wR_1(I &gt; 2\sigma(I))$, $wR_1$(all reflections) $^b$</td>
<td>0.0484, 0.0484</td>
<td>0.0596, 0.0596</td>
<td>0.0660, 0.0664</td>
</tr>
<tr>
<td>Weighting parameter $a$</td>
<td>0.0269</td>
<td>0.0390</td>
<td>0.0445</td>
</tr>
<tr>
<td>$GooF$</td>
<td>1.083</td>
<td>1.138</td>
<td>1.094</td>
</tr>
<tr>
<td>Largest difference peaks</td>
<td>$\Delta \rho_{max}$, $\Delta \rho_{ave}$(e Å$^{-3}$)</td>
<td>0.613, –0.630</td>
<td>0.739, –0.542</td>
</tr>
</tbody>
</table>

a: Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (Fax: (+49)7247-808-666 Dr. S. Höhler-Schlimm); E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository numbers CSD-413348 (Cu$_3$As$_{0.3}$Sb$_{0.7}$S$_4$), CSD-413349 (Cu$_3$As$_{0.7}$Sb$_{0.3}$S$_4$), and CSD-413350 (Cu$_3$AsS$_4$).

$^b$: Definition of $R_1$ and $wR_1$:

$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_1 = \sqrt{\frac{\sum [w|F_o| - |F_c|]^2}{\sum [w|F_o|^2]}}$$

with $GooF = \sqrt{\frac{\sum [(w|F_o|^2 - \bar{w}|F_o'|^2)]^2}{\sum [w|F_o'|^2]}}$.

$w = 1/(\sigma^2(F_o^2) + (aF_o)^2)$. 

$\Delta \rho_{max}$ and $\Delta \rho_{ave}$ were calculated by difference Fourier synthesis using the program SHELXL97 [16].
Thermal analyses were carried out on a Setaram TMA 92 16.18 high temperature DSC in evacuated sealed quartz ampoules (inner diameter: 2.6 mm). X-ray powder diffraction data were collected in transmission setup on a STOE Stadi P equipped with Cu Kα1 radiation (Ge monochromator, Si as an external standard) and a linear PSD detector.

Single crystal X-ray diffraction data of 
\( \text{Cu}_3\text{As}_{0.333}\text{Sb}_{0.667}\text{S}_4 \), 
\( \text{Cu}_3\text{As}_{0.3}\text{Sb}_{0.7}\text{S}_4 \), 
\( \text{Cu}_3\text{As}_{0.736}\text{Sb}_{0.264}\text{S}_4 \), 
\( \text{Cu}_3\text{As}_{0.7}\text{Sb}_{0.3}\text{S}_4 \), and 
\( \text{Cu}_3\text{As}_{1}\text{S}_4 \) were collected on a STOE IPDS. For all three compositions a numerical absorption correction was performed. The description of the crystal shapes was optimized with X-Shape [15]. The structures were solved by direct methods and refined against \( F^2 \) [16] with anisotropic displacement parameters for all atoms including an extinction parameter. The Flack parameter was used to check for the right setting of the non-centrosymmetric structures. It was 0.00(8) for 
\( \text{Cu}_3\text{As}_{0.3}\text{Sb}_{0.7}\text{S}_4 \), 
\( -0.01(5) \) for 
\( \text{Cu}_3\text{As}_{0.736}\text{Sb}_{0.264}\text{S}_4 \), and 
\( 0.07(2) \) for 
\( \text{Cu}_3\text{As}_{1}\text{S}_4 \). This means, there was no evidence for inversion twinning. Crystallographic data and details of the refinements are collected in Table 1.

Results and discussion

Phase analytical investigations

The system 
\( \text{Cu}_3\text{As}_{1-x}\text{Sb}_{x}\text{S}_4 \) has a two phase region at \( x = 0.8 \). Mixtures with \( x < 0.8 \) crystallize in the famatinite type, compositions with \( x > 0.8 \) crystallize in the enargite type. The sample with \( x = 0.8 \) contains both phases. Fig. 1c shows that the cell volume of the famatinite phase is close to the volume at \( x = 0.7 \), the volume of the enargite phase is close to the volume for \( x = 0.9 \). Skinner et al. found that the antimony richest enargite type composition in their studies was 
\( \text{Cu}_3\text{As}_{0.874}\text{Sb}_{0.126}\text{S}_4 \), (annealing temperature 500 °C). The same authors designated 
\( \text{Cu}_3\text{As}_{0.65}\text{Sb}_{0.35}\text{S}_4 \), grown at 425 °C, as the arsenic richest famatinite type composition they received in their studies [3]. Sugaki et al. determined the composition gap at temperatures of 400 °C, 500 °C, and 600 °C [4]. At 400 °C the immiscibility field reaches from about 2 to 38% \( \text{Cu}_3\text{SbS}_4 \). With higher temperatures the width of the field decreases, reaching from 6 to 33% \( \text{Cu}_3\text{SbS}_4 \) at 500 °C and 14–25% famatinite at 600 °C. For this temperature the authors reported the existence of small amounts of tennantite-tetrahedrite (\( \text{Cu}_2\text{As}_{1-x}\text{S}_3 \)–\( \text{Cu}_2\text{Sb}_{1-x}\text{S}_3 \), both cubic, space group \( I4_3m \) [17]). The evolution of the lattice parameters in the solid solution tennantite-famatinite (both are tetragonal) was described by Kanazawa [5] and Sugaki et al. [4]. In both cases the authors report a linear variation over the whole composition range.

The orthorhombic lattice constants of enargite type solids can be transformed into tetragonal cell parameters using the following formulas:

\[
\frac{a_{\text{tet}}}{\sqrt{2}} = \frac{a_{\text{ortho}}}{\sqrt{2}}, \quad \frac{b_{\text{tet}}}{\sqrt{2}} = \frac{b_{\text{ortho}}}{\sqrt{2}},
\]

and

\[
c_{\text{tet}} = \sqrt[3]{c_{\text{ortho}}}.\]

The value for \( a_{\text{tet}} \) can thus be calculated from \( a_{\text{ortho}} \) and \( b_{\text{ortho}} \). Here the average value of both data \( a_{\text{tet}} \) and \( b_{\text{tet}} \) is used since they are slightly different.

![Fig. 1a. Tetragonal lattice parameter \( a_{\text{tet}} \) vs. the composition of the solid solution \( \text{Cu}_3\text{As}_{1-x}\text{Sb}_{x}\text{S}_4 \).](image)

![Fig. 1b. Tetragonal lattice parameter \( c_{\text{tet}} \) of the compositions in the system \( \text{Cu}_3\text{As}_{1-x}\text{Sb}_{x}\text{S}_4 \).](image)

![Fig. 1c. Cell volumes vs. composition in the system \( \text{Cu}_3\text{As}_{1-x}\text{Sb}_{x}\text{S}_4 \).](image)

The change of the structure with increasing As content around the composition gap becomes obvious from these data. The lattice constants \( a \) and \( c \) decrease linearly to \( x = 0.8 \) and then \( a \) falls to smaller values, while the parameter \( c \) jumps to higher values at this composition, see Fig. 1. The cell volume varies more or less linear over the whole composition range, because the contrary trends for \( c \) and \( a \) compensate each other.

The lattice constants of the famatinite type compositions are in good agreement with the data published in refs. [4, 5].

The ratio \( c/a \) decreases linearly with an increasing content of arsenic. Its value declines from the ideal tetragonal ratio \( c/a = 2 \), which is nearly reached in \( \text{Cu}_3\text{SbS}_4 \) (c/a
Contrary to the linear behaviour for the series famatinite-luzonite [5] a discontinuity is found for the series famatinite-enargite at \( x = 0.8 \). The enargite type compositions have ratios \( c/a > 2.03 \), see Fig. 2. Again, the values of the famatinite compositions agree very well.

The splitting of the reflections in the powder diffraction patterns depends strongly on the \( c/a \) ratio. This splitting becomes more and more evident with an increasing As content due to the increasing structural distortions.

Famatinite is reported to melt congruently at 627 °C [18]. The melting points reported for enargite are not unique. Some authors suggest the congruent melting of enargite at 655 °C [19], and 674 °C [20] while others report a particular decomposition at 600 °C [5]. A detailed survey of the contradictory results is given by Müller and Blachnik who report the melting point of Cu$_3$AsS$_4$ as 694 °C [21].

Melting points of the mixed crystals Cu$_3$As$_x$Sb$_{1-x}$S$_4$ were determined by DTA measurements in order to investigate the thermal behaviour of the system Cu$_3$As$_4$—Cu$_3$Sb$_4$. The compositions were heated twice to 1000 °C with a rate of 10 °C per minute and cooled again with the same rate. The second heating cycle was performed in order to examine if the substances melt congruently.

The melting points for Cu$_3$Sb$_4$ (632 °C) and Cu$_3$As$_4$ (692 °C) are in good agreement with refs. [18, 21]. The melting points of the mixed crystals increase linearly with an increasing content of As, as shown in Fig. 3.

The thermal effects in the two heating cycles are identical within the tolerances. An X-ray powder diffraction diagram was recorded for Cu$_3$As$_{0.7}$Sb$_{0.3}$S$_4$ after melting. The diffraction data show the coexistence of the famatinite type and a second phase belonging to the Cu$_{12}$As$_4$S$_{13}$—Cu$_{12}$Sb$_4$S$_{13}$ series. We also recognized a decomposition upon heating the end members to 700 °C. These results are in agreement with the results of Sugaki et al., who investigated the system Cu$_3$As$_4$—Cu$_3$Sb$_4$ at a temperature of 600 °C. They found a particular decomposition into the tennantite-tetrahedrite system, too [4]. Müller and Blachnik report that heating Cu$_3$As$_4$ above the melting point of enargite increases the amount of by-products [21].

**Single crystal investigations**

The results of the crystal structure analyses are collected in tables 2–5. The compounds consist of corner sharing tetrahedra [Cu$_4$], and [(As/Sb)$_4$] in a ratio 3:1. As and Sb are statistically distributed on the MV positions.

During the refinement only one common position and common displacement parameters for Sb and As were considered. The occupancies of Sb and As were constrained to result in fully occupied positions.

We showed recently for Cu$_3$PS$_4$ and Cu$_3$Sb$_4$ that in Cu$_3$PS$_4$ the tetrahedra [CuS$_4$] and [PS$_4$] differ significantly in size whereas they have about the same size in Cu$_3$Sb$_4$. The higher symmetrical sphalerite structure type cannot be built if the differences between different tetrahedra are too large. In order to verify this idea, the system Cu$_3$As$_4$—Cu$_3$Sb$_4$ was investigated with respect to this assumption. The volumes of the tetrahedra were calculated from the lengths of the edges (see Fig. 5 for assignment).
We have calculated the average volumes of all tetrahedra in the compounds under discussion. From the volumes $V_i$ of the distinct tetrahedra $i$ in a compound we have calculated the following values:

$$ D_V^i = V_i - ar{V}, \quad \bar{D}_V^i = \frac{1}{n} \sum_{i=1}^{n} D_V^i. $$

The values are given in Table 6. The data for Cu$_3$PS$_4$ and Cu$_3$SbS$_4$ were calculated from ref. [14].

Plotting $D_V^i$ of the tetrahedra $[MS_4]$ (M = (As$_x$Sb$_{1-x}$)) of the compositions with $x = 0.0, 0.3, 0.7, \text{ and } 1.0$ against the composition provides a linear dependence, shown in Fig. 6.

For Cu$_3$PS$_4$ $D_V^i$ is quite high as expected. On the other hand for sphalerite type structures we receive small values. $D_V^i$ for enargite is slightly bigger as compared to the sphalerite related compositions.

If we compare the average values $D_V^i$ for the system Cu$_3$AsS$_4$–Cu$_3$SbS$_4$, we expect a minimum at about $x = 0.4$. This is, because the tetrahedra $[SbS_4]$ are larger than the polyhedra $[CuS_4]$, but the tetrahedra $[AsS_4]$ are smaller. If Sb is substituted by As, there exists a composition where the tetrahedra $[(As_xSb_{1-x})S_4]$ reach the same

Table 2. Atomic parameters (e.s.d.s) and $U_{eq}$ (in Å$^2$) for Cu$_3$As$_0.3$Sb$_0.7$S$_4$ and Cu$_3$As$_0.7$Sb$_0.3$S$_4$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff pos.</th>
<th>Occup.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>2a</td>
<td>0.736(3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0119(2)</td>
</tr>
<tr>
<td>As</td>
<td>2a</td>
<td>0.264</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0119(2)</td>
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<tr>
<td>Cu1</td>
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<td>0</td>
<td>0.25</td>
<td>0</td>
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<tr>
<td>Cu2</td>
<td>2b</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.0230(3)</td>
</tr>
<tr>
<td>S</td>
<td>8i</td>
<td>0.2501(1)</td>
<td>$x$</td>
<td>0.1273(1)</td>
<td>0.01613(3)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Anisotropic displacement parameters $U_{ij}$ (in Å$^2$) for Cu$_3$As$_0.3$Sb$_0.7$S$_4$ and Cu$_3$As$_0.7$Sb$_0.3$S$_4$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$ = $U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$ = $U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>0.0119(2)</td>
<td>0.0120(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>As</td>
<td>0.0119(2)</td>
<td>0.0120(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu1</td>
<td>0.0224(3)</td>
<td>0.0251(4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu3</td>
<td>0.0228(3)</td>
<td>0.0233(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S4</td>
<td>0.0156(4)</td>
<td>0.0173(7)</td>
<td>0.0004(3)</td>
<td>0.0008(2)</td>
</tr>
</tbody>
</table>

Table 4. Atomic parameters (e.s.d.s) and $U_{eq}$ (in Å$^2$) for Cu$_3$As$_x$S$_{4-x}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff pos.</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>2a</td>
<td>0.1726(1)</td>
<td>0.0014(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1</td>
<td>2a</td>
<td>0.8467(1)</td>
<td>0.5016(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2</td>
<td>4b</td>
<td>0.7523(1)</td>
<td>0.6745(1)</td>
<td>0.0097(1)</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>2a</td>
<td>0.1777(2)</td>
<td>0.3589(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>2a</td>
<td>0.8517(2)</td>
<td>0.8763(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>4b</td>
<td>0.7436(1)</td>
<td>0.6648(1)</td>
<td>0.3811(2)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Anisotropic displacement parameters $U_{ij}$ (in Å$^2$) for Cu$_3$As$_x$S$_{4-x}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{22}$</th>
<th>$U_{23}$</th>
<th>$U_{33}$</th>
<th>$U_{32}$</th>
<th>$U_{31}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.0103(3)</td>
<td>0.0078(3)</td>
<td>0.0095(3)</td>
<td>0</td>
<td>0</td>
<td>0.0001(3)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu1</td>
<td>0.0222(4)</td>
<td>0.0195(3)</td>
<td>0.0187(4)</td>
<td>0</td>
<td>0</td>
<td>0.0025(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu2</td>
<td>0.0213(3)</td>
<td>0.0183(3)</td>
<td>0.0197(6)</td>
<td>0.0013(1)</td>
<td>0.0008(2)</td>
<td>0.0111(4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S1</td>
<td>0.0130(7)</td>
<td>0.0127(7)</td>
<td>0.0070(7)</td>
<td>0</td>
<td>0</td>
<td>0.0010(5)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S2</td>
<td>0.0134(6)</td>
<td>0.0083(5)</td>
<td>0.0133(7)</td>
<td>0</td>
<td>0</td>
<td>0.0001(6)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S3</td>
<td>0.0110(5)</td>
<td>0.0105(5)</td>
<td>0.0145(9)</td>
<td>0.0017(3)</td>
<td>0.0008(3)</td>
<td>0.0004(3)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 6. Volumes of the different tetrahedra in the investigated compositions.

| Compound          | D of [CuS₄] | V of [CuS₄] | ΔV of [MS₄] | ΔV
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂PS₄</td>
<td>10.4</td>
<td>5.1</td>
<td>−20.6</td>
<td>10.3</td>
</tr>
<tr>
<td>Cu₃AsS₄</td>
<td>5.1</td>
<td>2.7</td>
<td>−10.4</td>
<td>5.2</td>
</tr>
<tr>
<td>Cu₂As₀.₇Sb₀.₃S₄</td>
<td>5.0</td>
<td>0.0</td>
<td>−5.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Cu₃As₀.₇Sb₀.₃S₄</td>
<td>1.8</td>
<td>−1.9</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>Cu₂Sb₄</td>
<td>−0.4</td>
<td>3.1</td>
<td>6.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Note: ΔV = V₂ − V₁.

Table 7. V₄i for different compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space-group</th>
<th>ΔV₄</th>
<th>ref.</th>
<th>Structure-Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃GeS₄</td>
<td>C1c1</td>
<td>3.7</td>
<td>[23] sst*</td>
<td></td>
</tr>
<tr>
<td>Cu₃SnS₄</td>
<td>P2₁m</td>
<td>2.3</td>
<td>[24] sst</td>
<td></td>
</tr>
<tr>
<td>Cu₃SbSe₄</td>
<td>P2₁m</td>
<td>5.8</td>
<td>[17] sst</td>
<td></td>
</tr>
<tr>
<td>CuFeS₂</td>
<td>P2₁d</td>
<td>2.4</td>
<td>[25] sst</td>
<td></td>
</tr>
<tr>
<td>Cu₃TiS₄</td>
<td>P2₁m</td>
<td>2.2</td>
<td>[26] sst</td>
<td></td>
</tr>
<tr>
<td>Cu₃SiS₃ (LT)</td>
<td>C1c1</td>
<td>7.3</td>
<td>[27] sst</td>
<td></td>
</tr>
<tr>
<td>Li₃AsO₄</td>
<td>Pmn2₁</td>
<td>15.2</td>
<td>[28] wst</td>
<td></td>
</tr>
<tr>
<td>Li₃PO₄</td>
<td>Pnma</td>
<td>21.4</td>
<td>[29] wst</td>
<td></td>
</tr>
<tr>
<td>AlLiSe₂</td>
<td>Pmn2₁</td>
<td>10.0</td>
<td>[30] wst</td>
<td></td>
</tr>
<tr>
<td>Ag₃As₂S₄</td>
<td>Pmn2₁</td>
<td>15.0</td>
<td>[31] wst</td>
<td></td>
</tr>
<tr>
<td>Cu₃SiS₃ (HT)</td>
<td>Cm2₁</td>
<td>8.6</td>
<td>[32] wst</td>
<td></td>
</tr>
</tbody>
</table>

*Note: sst: sphalerite superstructure type
wst: wurtzite superstructure type

The largest ΔV was calculated for a famatinite type compound was 8.8 for Cu₃NiS₄S₂. The structure was solved by Schäfer et al. [33]. We refined the structure again [34] in order to verify this relatively large ΔV and observed ΔV = 8.5. This difference is not remarkable. The smallest V₄i for an enargite type compound was found for enargite itself with ΔV = 5.2.

This means that there is an intermediate range where either one or the other packing can be realized, cf. also Cu₃SiS₃ [27, 32]. To date, our model fits crystal structures of chalcogenides quite well. However, an inspection of the structures of more ionic compounds, e.g. ternary nitrides, shows that different critical parameters have to be derived here for a broader applicability of our approach.

Acknowledgments. We thank the Fonds der Chemischen Industrie FCI and the Bundesministerium für Bildung und Forschung BMBF for valuable financial support.

References


[34] Cu₄NiS₆S₇: STOE IPDS, Mo-Anode, oriented graphite monochromator, λ = 0.71073 Å, refinement (SHELX97 [16], numerical absorption correction, shape optimized with X-SHAPE [15], Z = 2, T = 20 °C, a = 11.56 (2) Å, b = 5.32 (1) Å, c = 8.18 (2) Å, β = 98.71°, V = 498.2 (2) Å³. 4.2 < 2θ < 58.6, 3.5956 g cm⁻³, 5996 reflections (Rint = 0.0328), 1300 independent reflections, R1 (I > 2σI) = 0.0318, R1 (all reflections) = 0.0325, wR (I > 2σI) = 0.0940, wR (all reflections) = 0.0945, 65 parameters, Δρmax = 0.614 e Å⁻³, Δρmin = −0.555 e Å⁻³. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) (Fax: (+49)7247-808-666 (Dr. S. Höhler-Schlimm); E-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413347.