

Cu₂MnM^{IV}S₄ (M^{IV} = Si, Ge, Sn) – analysis of crystal structures and tetrahedra volumes of normal tetrahedral compounds

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Dedicated to Professor Dr. Hans Hartl on the occasion of his 65th birthday

Tetrahedral structures / Quaternary copper chalcogenides / Wurtzite structure type / Sphalerite structure type / Single crystal structure analysis / X-ray diffraction

Abstract. The crystal structures of the normal tetrahedral compounds Cu₂MnSiS₄, Cu₂MnGeS₄, and Cu₂MnSnS₄ are presented. The structures were refined from single crystal X-ray data. Cu₂MnSiS₄ and Cu₂MnGeS₄ crystallize in the space group *Pmn*2₁ in a wurtzite type superstructure. The refinement of Cu₂MnSiS₄ converged to *R* = 0.0214 and *wR*2 = 0.0477. The redetermination of Cu₂MnGeS₄ converged to *R* = 0.0281, *wR*2 = 0.0739. The tetrahedra volumes of the coordination polyhedra of the cations in these compounds are calculated and compared with those of Cu₂MnSnS₄ (redetermination, spacegroup *I*4̄2*m*, sphalerite type superstructure, *R* = 0.0146, *wR*2 = 0.0425). In the wurtzite type structures the tetrahedra volumes differ significantly for different cations while they differ only in a small range in the sphalerite type structure.

Introduction

Many publications deal with tetrahedral structures because there exists a manifold of compounds with interesting properties for many applications (*e.g.* semiconducting, magnetical or optical properties). The prediction of the structure type or even the estimation of the precision of older structure determinations by simple checking routines is still an open problem although many investigations have been performed in the past. Some approaches have been made, see *e.g.* [1, 2], but a useful concept is not available.

Recently we published a new model to predict the structure type of multinary normal tetrahedral compounds [3]. This model bases on the volumes of the different tetrahedra in a compound. In wurtzite type compounds the tetrahedra volumes differ significantly while in sphalerite type compounds the volumes are similar. We have been able to sup-

port this idea by experimental work on chalcogenides in the systems Cu₃AsS₄–Cu₃SbS₄ [3] and Cu₃PS₄–Cu₃SbS₄ [4]. The model was manifested by using structural data from the literature. Herein, we present the quaternary compounds Cu₂MnSiS₄, Cu₂MnGeS₄, and Cu₂MnSnS₄ and calculations analogous to those described in [3].

Some publications describe quaternary compounds of the type Cu₂M^{II}M^{IV}Q₄ (Q = S, Se) [5, 6] but only a few compounds with Te as the Q atom are known [7]. Mostly lattice constants determined by powder diffraction are given. For a detailed view at the tetrahedra volumes an inspection of the crystal structures is necessary. The interest in the crystal structures of these compounds raised in the last years [8, 9]. A structure determination for M^{II} = Mn and M^{IV} = Ge, Sn can be found in the literature [10, 11]. The given data in [10] were obtained by film methods and therefore a new structure determination by modern methods seems desirable. The data on Cu₂MnSnS₄ in [11] were obtained by single crystal neutron diffraction. We redetermined the structural data by single crystal X-ray diffraction just in order to have the same basis for all compounds for our calculations of the tetrahedral volumes. These Mn²⁺ containing materials are especially interesting due to their magnetic properties [11–13].

Experimental

The title compounds were prepared by heating stoichiometric mixtures of the elements (metals: AlfaAesar 99.999%, sulphur: Riedel de Haën 99.999%) in evacuated sealed quartz ampoules to 800 °C. The reaction mixtures were ground intensively between three heating periods of about one week. For the last heating period the mixtures were pressed to pellets in order to obtain single crystals. This method was very effective in the case of Cu₂MnSiS₄.

The purity of the products was confirmed by powder diffraction on a STOE Stadi P. Single crystals of Cu₂MnGeS₄ and Cu₂MnSnS₄ were measured on a STOE IPDS. Single crystal X-ray data of Cu₂MnSiS₄ were collected on a Siemens P4. For the solution and refinement of the crystal structures we used the SHELX97 program

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Table 1. Crystallographic data for the X-ray structure determinations of Cu₂MnSiS₄, Cu₂MnGeS₄, and Cu₂MnSnS₄¹.

Compound	Cu ₂ MnSiS ₄	Cu ₂ MnGeS ₄	Cu ₂ MnSnS ₄
Formula weight in g mol ⁻¹	338.35	382.88	428.95
Crystal size in mm ³	0.14 0.08 0.12	0.12 0.10 0.08	0.11 0.09 0.09
Colour	black	black	black
Crystal system	orthorhombic	orthorhombic	tetragonal
Spacegroup	<i>Pmn</i> 2 ₁ (No. 31)	<i>Pmn</i> 2 ₁ (No. 31)	$\bar{I}4$ 2 <i>m</i> (No. 121)
Lattice constants in Å	<i>a</i> = 7.543(2)	<i>a</i> = 7.635(1)	<i>a</i> = 5.548(1)
from single crystal data	<i>b</i> = 6.446(1)	<i>b</i> = 6.5267(7)	
	<i>c</i> = 6.193(1)	<i>c</i> = 6.2438(7)	<i>c</i> = 10.844(2)
Cell volume in Å ³ , <i>Z</i>	301.1(1), 2	311.13(6), 2	333.8 (1), 2
$\rho_{X\text{-ray}}$ in g cm ⁻³	3.732	4.087	4.268
Diffractometer	Siemens P4	STOE IPDS	
	MoK α , <i>k</i> = 0.71073 Å, oriented graphite monochromator		
Image plate distance in mm	–	60	55
φ -range, $\Delta\varphi$ in °	–	0° ≤ φ ≤ 359.8°, 1.4	105° ≤ φ ≤ 245°, 2.0
Absorption correction	numerical, shape optimized with X-SHAPE [15]		
No. of faces for crystal description	14	14	15
Irradiation time/image in min.	–	7	4
Temperature in °C	20	20	20
2 θ -range in °	6.3 < 2 θ < 60	6.2 < 2 θ < 55.7	7.2 < 2 θ < 58.2
<i>hkl</i> -range	–10 ≤ <i>h</i> ≤ 10	–10 ≤ <i>h</i> ≤ 10	–7 ≤ <i>h</i> ≤ 7
	–9 ≤ <i>k</i> ≤ 1	–8 ≤ <i>k</i> ≤ 8	–7 ≤ <i>k</i> ≤ 7
	–1 ≤ <i>l</i> ≤ 8	–8 ≤ <i>l</i> ≤ 7	–14 ≤ <i>l</i> ≤ 14
No. of reflections, <i>R</i> _{int}	1279, 0.0233	3328, 0.0345	3037, 0.0271
No. of independent reflections	590	756	245
No. of parameters	45	45	15
Program	SHELXL97 [14]		
<i>R</i> (<i>I</i> > 2 σ ₁), <i>R</i> (all reflections) [#]	0.0194, 0.0214	0.0259, 0.0281	0.0144, 0.0146
<i>wR</i> 2 (<i>I</i> > 2 σ ₁), <i>wR</i> 2 (all reflections) ^a	0.0463, 0.0477	0.0732, 0.0739	0.0424, 0.0425
GooF	1.116	1.190	1.330
Largest difference peaks $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ in e Å ⁻³	0.501, –0.510	0.689, –0.603	0.603, –0.539

a: Definition of *R* and *wR*2:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}}, \quad \text{GooF} = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{n - p}}$$

package [14]. The structure solutions were performed using direct methods. No evidence for inversion twins was found as the Flack parameters for the non-centrosymmetric structures were 0.000(7), 0.01(1), and 0.005(8) for Cu₂MnSiS₄, Cu₂MnGeS₄, and Cu₂MnSnS₄ respectively.

A numerical absorption correction was performed with the STOE X-SHAPE and X-RED routines [15].

Table 1 shows crystallographic data of the title compounds.

Results and discussion

Crystal structures

Atomic and anisotropic displacement parameters for the investigated compounds are collected in Tables 2 and 3. Table 4 shows selected distances *d*(M–S).

Cu₂MnSiS₄ and Cu₂MnGeS₄ crystallize in a wurtzite type superstructure in the spacegroup *Pmn*2₁ while Cu₂MnSnS₄ crystallizes in a sphalerite type superstructure, spacegroup $\bar{I}4$ 2*m*. In both structure types the metal atoms are coordinated tetrahedrally by four sulphur atoms and vice versa. The superstructures are caused by an ordering of the cations on the cation sites. This class of compounds is called normal adamantane structures [16].

¹ Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), Fax: 0049 7247 808 666, E-mail: crysdata@fiz-karlsruhe.de, on quoting the depository number CSD-415452 (Cu₂MnSiS₄), CSD-415453 (Cu₂MnGeS₄), and CSD-415454 (Cu₂MnSnS₄), the name of the authors, and the reference of the publication.

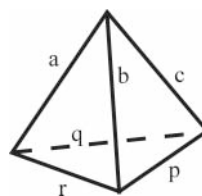
Table 2. Atomic parameters (e.s.d.s) and U_{eq}^a (in \AA^2) for the title compounds.

Atom	Wyckoff position	x	y	z	U_{eq}
Cu₂MnSiS₄					
Cu	4b	0.75239(2)	0.67804(2)	0.17904(4)	0.01999(4)
Mn	2a	0	0.84482(4)	0.66765(4)	0.01622(6)
Si	2a	0	0.17727(6)	0.16974(8)	0.00998(9)
S1	4b	0.72902(3)	0.66449(4)	0.55078(5)	0.01215(6)
S2	2a	0	0.86278(6)	0.06350(7)	0.01233(8)
S3	2a	0	0.19134(6)	0.51437(7)	0.01242(8)
Cu₂MnGeS₄					
Cu	4b	0.2488(1)	0.3240(1)	0.9903(1)	0.0219(1)
Mn	2a	0	0.1587(1)	0.4994(1)	0.0184(1)
Ge	2a	0	0.8251(1)	0.9979(1)	0.0124(1)
S1	4b	0.2646(1)	0.3390(1)	0.6213(1)	0.0140(2)
S2	2a	0	0.8125(1)	0.6411(1)	0.0151(2)
S3	2a	0	0.1491(1)	0.1071(1)	0.0140(1)
Cu₂MnSnS₄					
Cu	4d	0	1/2	3/4	0.02394(5)
Mn	2b	1/2	1/2	0	0.01700(5)
Sn	2a	0	0	0	0.01317(2)
S	8i	0.24779(3)	x	0.13243(2)	0.01497(9)

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

Analysis of the tetrahedral volumes

We calculated a measure for the distortion of the tetrahedra as described in [3]. The tetrahedra volumes were calculated according to Ref. [17]. Figure 1 shows the labelling scheme of the edges of the tetrahedra.

**Fig. 1.** Labelling of the tetrahedra edges.

$$V = \left(\frac{1}{288} \cdot \begin{vmatrix} 0 & r^2 & q^2 & a^2 & 1 \\ r^2 & 0 & p^2 & b^2 & 1 \\ q^2 & p^2 & 0 & c^2 & 1 \\ a^2 & b^2 & c^2 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{vmatrix} \right)^{\frac{1}{2}}$$

The tetrahedra volumes of the compounds under discussion are collected in Table 5.

The tetrahedra $[\text{CuS}_4]$ have about the same size in all compounds (as they have in many other ternary copper chalcogenides, too; see [3]). The volumes of the tetrahedra $[\text{MnS}_4]$ also remain unchanged in the title compounds. As Sn has a bigger radius than Ge and Si the tetrahedra $[\text{SnS}_4]$ are bigger than $[\text{GeS}_4]$ and $[\text{SiS}_4]$, respectively, see Table 5. The combination of these tetrahedra $[\text{M}^{\text{IV}}\text{S}_4]$ with two tetrahedra $[\text{CuS}_4]$ and one tetrahedron $[\text{MnS}_4]$ of almost constant and similar size leads to wurtzite type compounds $\text{Cu}_2\text{MnSiS}_4$ and $\text{Cu}_2\text{MnGeS}_4$, and to $\text{Cu}_2\text{MnSnS}_4$ of the zincblende type, respectively. Figure 2 gives an impression of this fact.

Obviously the relation of the sizes of different tetrahedra plays the most important role with respect to the resulting structure type. In [3] we calculated $\overline{\Delta V}_i$ values for the different compounds in order to receive a measure for the distinction of the structure types. $\overline{\Delta V}_i$ is the average

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu₂MnSiS₄						
Cu	0.02201(6)	0.02146(6)	0.01650(7)	0.00095(6)	-0.00076 (6)	0.00036(8)
Mn	0.01590(9)	0.0177(1)	0.0151(1)	0	0	0.0007(1)
Si	0.0112(2)	0.0101(2)	0.0086(2)	0	0	-0.0002(2)
S1	0.01308(9)	0.0131(1)	0.0103(1)	0.00162(9)	0.0007 (1)	-0.0005(1)
S2	0.0153(1)	0.0105(1)	0.0112(2)	0	0	-0.0004(2)
S3	0.0141(1)	0.0148(2)	0.0083(2)	0	0	-0.0004(2)
Cu₂MnGeS₄						
Cu	0.0234(2)	0.0215(1)	0.0208(2)	0.0016 (1)	-0.0006 (1)	0.0001(2)
Mn	0.0179(2)	0.0183(2)	0.0191(3)	0	0	-0.0011(3)
Ge	0.0124(1)	0.0109(1)	0.0138(2)	0	0	0.0001(2)
S1	0.0144(2)	0.0135(3)	0.0141(3)	0.0019 (2)	0.0023 (2)	-0.0007(2)
S2	0.0158(3)	0.0168(4)	0.0127(4)	0	0	-0.0015(3)
S3	0.0171(3)	0.0111(3)	0.0138(4)	0	0	-0.0023(3)
Atom	$U_{11} = U_{22}$		U_{33}	U_{12}	$U_{13} = U_{23}$	
Cu₂MnSnS₄						
Cu	0.02303(5)		0.0258(1)	0	0	
Mn	0.01595(6)		0.0191(1)	0	0	
Sn	0.01322(2)		0.01307(4)	0	0	
S	0.0149(1)		0.0151(2)	-0.00054(7)	-0.00076(5)	

Table 3. Anisotropic displacement parameters U_{ij} (in \AA^2) for $\text{Cu}_2\text{MnSiS}_4$, $\text{Cu}_2\text{MnGeS}_4$, and $\text{Cu}_2\text{MnSnS}_4$.

Table 4. Selected interatomic distances d in Å for Cu₂MnM^{IV}S₄ (M^{IV} = Si, Ge, Sn).

Cu ₂ MnSiS ₄		Cu ₂ MnGeS ₄		Cu ₂ MnSnS ₄	
Cu–S1	2.3106(6)	Cu–S1	2.3091(7)	Cu–S	4 × 2.3395(3)
–S2	2.4542(7)	–S2	2.3152(6)	Mn–S	4 × 2.4450(4)
–S3	2.4603(5)	–S3	2.3327(6)	Sn–S	4 × 2.4170(4)
–S1	2.3507(5)	–S1	2.3491(7)		
Mn–S1	2 × 2.4603(5)	Mn–S1	2 × 2.4583(6)		
–S2	2.4542(7)	–S2	2.427(1)		
–S3	2.4270(6)	–S3	2.451(1)		
Si–S1	2 × 2.1372(5)	Ge–S1	2 × 2.2295(6)		
–S2	2.1313(6)	–S2	2.229(1)		
–S3	2.1363(8)	–S3	2.2219(9)		

Table 5. Tetrahedra volumes V and $\overline{\Delta V}_i$ values (for definition see text below) for Cu₂MnM^{IV}S₄.

Tetrahedra	$V(\text{Cu}_2\text{MnSiS}_4)$ Å ³	$V(\text{Cu}_2\text{MnGeS}_4)$ Å ³	$V(\text{Cu}_2\text{MnSnS}_4)$ Å ³
[CuS ₄]	6.40	6.44	6.42
[MnS ₄]	7.50	7.53	7.50
[M ^{IV} S ₄]	4.94	5.68	7.24
$\overline{\Delta V}_i$	11.1	7.7	6.1

deviation of the different tetrahedra of their mean volume. Therefore we calculate the average \overline{V} of all tetrahedra volumes

$$\overline{V} = \frac{\sum_1^n V_i}{n}.$$

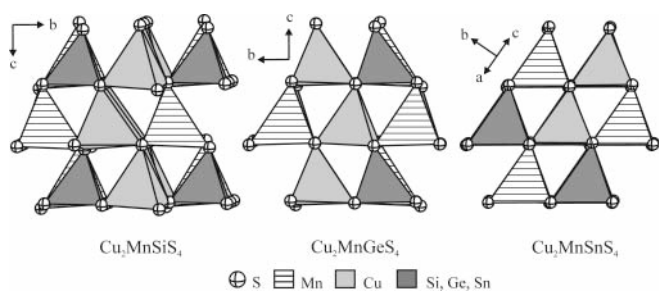
The differences of the different volumes V_i from this average volume are computed for each tetrahedron

$$\Delta V_i = \frac{V_i - \overline{V}}{\overline{V}}.$$

Finally we determine the average value of all these differences as a measure for the distortions of the tetrahedra

$$\overline{\Delta V}_i = \frac{\sum_i \Delta V_i}{i}.$$

The data for the compounds given herein are $\overline{\Delta V}_i = 11.1$ for Cu₂MnSiS₄, $\overline{\Delta V}_i = 7.7$ for Cu₂MnGeS₄, and $\overline{\Delta V}_i = 6.1$ for Cu₂MnSnS₄. Wurtzite type variants are expected to have quite big $\overline{\Delta V}_i$ values while sphalerite type

**Fig. 2.** Comparison of the tetrahedra [MS₄] in Cu₂MnM^{IV}S₄. Notice that the tilting of the tetrahedra decreases from M^{IV} = Si to M^{IV} = Sn. Table 5 quantifies this finding.

variants have smaller ones. As reported earlier there exists no sharp border line in these values but an overlap range $5 \leq \overline{\Delta V}_i \leq 8$. The value for Cu₂MnSiS₄ is greater than 10. This clearly indicates the wurtzite type variant. The closer the differences between the volumes of the tetrahedra, the smaller are the $\overline{\Delta V}_i$ values. The values for Cu₂MnGeS₄ and Cu₂MnSnS₄ fall in the range of the overlap region but the value for the wurtzite type superstructure is significantly bigger than the value of the sphalerite type superstructure. For this region one might expect the existence of the alternative structure types, both for Ge and Sn. Cu₂MnGeS₄ and Cu₂MnSnS₄ form mixed crystals [18]. The miscibility gap is in the range of Cu₂MnGe_{0.3}Sn_{0.7}S₄ and Cu₂MnGe_{0.5}Sn_{0.5}S₄ at 800 °C. Between 0 and 20% Ge content the mixed crystals belong to the stannite type. From 60 to 100% Ge content the wurtzstannite type is formed. Further investigations on the mixed crystals will be presented in the near future.

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