

Cu₂ZnSiS₄

Kimberly A. Rosmus and Jennifer A. Aitken*

Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, Pittsburgh, PA 15282, USA
Correspondence e-mail: aitkenj@duq.edu

Received 12 February 2011; accepted 8 March 2011

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{S}-\text{Si}) = 0.002$ Å; R factor = 0.020; wR factor = 0.051; data-to-parameter ratio = 24.5.

Single crystals of Cu₂ZnSiS₄, dicopper(I) zinc silicon tetrasulfide, have been prepared *via* high-temperature solid-state synthesis. Cu₂ZnSiS₄ was found to have the wurtz-stannite structure type, like that of Li₂CdGeS₄, Li₂CdSnS₄, and Cu₂CdSiS₄. Each sulfur anion is tetrahedrally coordinated by two Cu cations, one Si cation, and one Zn cation, forming a three-dimensional honeycomb structure. When viewed along the c axis, the atoms are aligned in rows in which each cation alternates with the sulfur anions.

Related literature

For synthetic procedures, see: Himmrich & Haeuseler (1991); Nitsche *et al.* (1967); Yao *et al.* (1987). For related structures, see: Chapuis & Niggli (1972); Lekse *et al.* (2008, 2009); Schäfer & Nitsche (1974). For optical properties, see: Levenco *et al.* (2010).

Experimental*Crystal data*

Cu ₂ ZnSiS ₄	$V = 292.24$ (1) Å ³
$M_r = 348.78$	$Z = 2$
Orthorhombic, $Pmn2_1$	Mo $K\alpha$ radiation
$a = 7.4374$ (1) Å	$\mu = 12.77$ mm ⁻¹
$b = 6.4001$ (1) Å	$T = 296$ K
$c = 6.1394$ (1) Å	$0.13 \times 0.07 \times 0.06$ mm

Data collection

Bruker SMART APEX diffractometer	5153 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	1078 independent reflections
$T_{\min} = 0.290$, $T_{\max} = 0.500$	1023 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	$\Delta\rho_{\text{max}} = 0.72$ e Å ⁻³
$wR(F^2) = 0.051$	$\Delta\rho_{\text{min}} = -1.01$ e Å ⁻³
$S = 1.14$	Absolute structure: Flack (1983), 449 Friedel pairs
1078 reflections	Flack parameter: 0.02 (1)
44 parameters	
1 restraint	

Table 1

Selected bond lengths (Å).

Cu1—S2 ⁱ	2.3170 (7)	Zn1—S3 ⁱⁱⁱ	2.3650 (7)
Cu1—S3	2.325 (1)	Zn1—S3 ^{iv}	2.3650 (7)
Cu1—S1	2.3270 (6)	Si1—S1	2.131 (1)
Cu1—S3 ⁱⁱ	2.3426 (7)	Si1—S3 ^v	2.136 (1)
Zn1—S2	2.322 (1)	Si1—S3 ^{vi}	2.136 (1)
Zn1—S1	2.322 (1)	Si1—S2 ^{vii}	2.143 (3)

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iii) $-x, y, z + 1$; (iv) $x, y, z + 1$; (v) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (vii) $x, y, z - 1$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: CrystalMaker (Palmer, 2010); software used to prepare material for publication: publCIF (Westrip, 2010).

Special thanks are extended to Dr Tomislav Pintauer and Dr William T. Eckenhoff. The project was funded by the National Science Foundation (CRIF-0234872) and a CAREER Award (DMR-0645304).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2337).

References

- Bruker (1998). SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chapuis, G. & Niggli, A. (1972). *Acta Cryst.* **B28**, 1626–1628.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Himmrich, M. & Haeuseler, H. (1991). *Spectrochim. Acta*, **47A**, 933–942.
- Lekse, J. W., Leverett, B. M., Lake, C. H. & Aitken, J. A. (2008). *J. Solid State Chem.* **181**, 3217–3222.
- Lekse, J. W., Moreau, M. A., McNerny, K. L., Yeon, J., Halasyamani, P. S. & Aitken, J. A. (2009). *Inorg. Chem.* **48**, 7516–7518.
- Levenco, S., Dumcenco, D., Huang, Y. S., Arushanov, E., Tezlevan, V., Tjong, K. K. & Du, C. H. (2010). *J. Appl. Phys.* **108**, 073508.
- Nitsche, R., Sargent, D. F. & Wild, P. (1967). *J. Cryst. Growth*, **1**, 52–53.
- Palmer, D. (2010). *Crystal Maker*. CrystalMaker Software Ltd, Oxfordshire, England.
- Schäfer, W. & Nitsche, R. (1974). *Mater. Res. Bull.* **9**, 645–654.
- Sheldrick, G. M. (2002). SADABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yao, G. Q., Shen, H. S., Honig, E. D., Kershaw, R. & Dwight, K. (1987). *Solid State Ionics*, **24**, 249–252.

supplementary materials

Acta Cryst. (2011). E67, i28 [doi:10.1107/S1600536811008889]

Cu₂ZnSiS₄

K. A. Rosmus and J. A. Aitken

Comment

Cu₂ZnSiS₄ was prepared as crystals *via* iodine vapor transport reactions as early as 1967 (Nitsche *et al.*, 1967); however, only lattice parameters were reported. Using the same synthetic method to prepare Cu₂ZnSiS₄, Yao *et al.* reported the infrared spectrum of this compound (Yao *et al.*, 1987). Alternatively Cu₂ZnSiS₄ can be synthesized by grinding stoichiometric amounts of the elements and reacting them in a vibrational mill multiple times during the heating process (Himmrich & Haeuseler, 1991). More recently, the band gap of the title compound has been reported (Levcenco *et al.*, 2010). In this paper, Cu₂ZnSiS₄ was prepared as relatively small single crystals using a simple high-temperature solid-state synthesis.

Cu₂ZnSiS₄ possesses the wurtz-stannite structure type (Schäfer, & Nitsche, 1974) like that of Li₂CdGeS₄, Li₂CdSnS₄ (Lekse *et al.*, 2009), and Cu₂CdSiS₄ (Chapuis & Niggli, 1972). The asymmetric unit can be observed in Figure 1. Cu₂ZnSiS₄ has a diamond-like structure, where every cation is tetrahedrally coordinated with sulfur anions. The bond lengths for M—S range from 2.3170 (7)–2.3426 (7) Å for *M*=Cu, 2.322 (1)–2.3650 (7) Å for *M*=Zn, and 2.131 (1)–2.143 (3) Å for *M*=Si (Table 1). Every MS₄ tetrahedron points in the same direction along the crystallographic *b* axis rendering the structure non-centrosymmetric (Fig.2). When viewed down the *c* axis, the ions are aligned in rows where each cation alternates with the sulfur anions (Fig.3).

Recently second harmonic generation for a couple of compounds of this structure type, Li₂CdGeS₄ and Li₂CdSnS₄, have been reported on powder samples (Lekse *et al.*, 2009). Therefore it is of interest to further study Cu₂ZnSiS₄.

Experimental

Cu₂ZnSiS₄ was prepared *via* high-temperature solid-state synthesis. Stoichiometric ratios of the elements were weighed and then ground for 30 min in an argon-filled glovebox using an agate mortar and pestle. The sample was placed into a graphite crucible, which was then inserted in a 12 mm outer diameter fused-silica tube. The tube was flame sealed under a vacuum of 10⁻³ mbar and transported to a computer-controlled furnace. The sample was heated to 1000°C in 12hrs, held at 1000°C for 168hrs and then cooled at 7.5°C/hr to room temperature. When removed from the furnace, blue rod-like crystals of approximate size 0.13 x 0.07 x 0.6 mm were found under a light microscope.

Figures

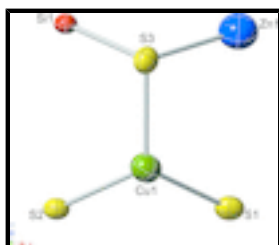


Fig. 1. Asymmetric unit of Cu₂ZnSiS₄ using 95% probability thermal ellipsoids.

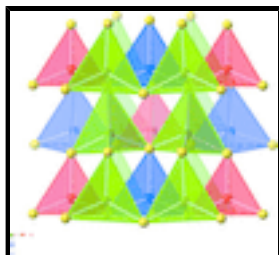


Fig. 2. Polyhedral view down the b axis of $\text{Cu}_2\text{ZnSiS}_4$ with sulfur anions as the corners of each tetrahedron.

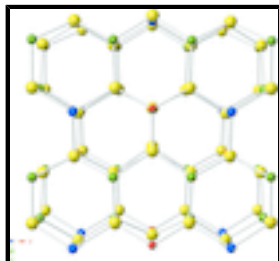


Fig. 3. $\text{Cu}_2\text{ZnSiS}_4$ viewed along the c axis showing a three-dimensional honeycomb structure where the atoms are aligned in rows with each cation alternating with sulfur anions. Color code: Cu - green, Zn - blue, Si - red, and S - yellow.

dicopper(I) zinc silicon tetrasulfide

Crystal data

$\text{Cu}_2\text{ZnSiS}_4$

$M_r = 348.78$

Orthorhombic, $Pmn2_1$

Hall symbol: P 2ac -2

$a = 7.4374$ (1) Å

$b = 6.4001$ (1) Å

$c = 6.1394$ (1) Å

$V = 292.24$ (1) Å³

$Z = 2$

$F(000) = 332$

$D_x = 3.964$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3127 reflections

$\theta = 3.2\text{--}32.2^\circ$

$\mu = 12.77$ mm⁻¹

$T = 296$ K

Rod, blue

$0.13 \times 0.07 \times 0.06$ mm

Data collection

Bruker SMART APEX
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2002)

$T_{\min} = 0.290$, $T_{\max} = 0.500$

5153 measured reflections

1078 independent reflections

1023 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 32.9^\circ$, $\theta_{\min} = 3.2^\circ$

$h = -11 \rightarrow 11$

$k = -9 \rightarrow 9$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$w = 1/[\sigma^2(F_o^2) + (0.0067P)^2 + 0.2702P]$

where $P = (F_o^2 + 2F_c^2)/3$

$R[F^2 > 2\sigma(F^2)] = 0.020$	$(\Delta/\sigma)_{\max} < 0.001$
$wR(F^2) = 0.051$	$\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$
$S = 1.14$	$\Delta\rho_{\min} = -1.01 \text{ e } \text{\AA}^{-3}$
1078 reflections	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
44 parameters	Extinction coefficient: 0.025 (1)
1 restraint	Absolute structure: Flack (1983), 449 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.02 (1)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.24741 (3)	0.17426 (4)	0.33723 (8)	0.0133 (1)
Zn1	0.0000	0.34747 (7)	0.84124 (15)	0.0211 (1)
Si1	0.0000	0.6743 (1)	0.3451 (4)	0.0071 (1)
S1	0.0000	0.3611 (1)	0.4632 (1)	0.0094 (1)
S2	0.0000	0.6784 (1)	0.9961 (2)	0.0089 (2)
S3	0.26269 (8)	0.1724 (1)	-0.0411 (1)	0.0100 (1)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0141 (1)	0.0135 (1)	0.0125 (2)	-0.0007 (1)	-0.0008 (1)	0.0000 (2)
Zn1	0.0235 (2)	0.0210 (2)	0.0191 (3)	0.000	0.000	-0.0016 (3)
Si1	0.0078 (3)	0.0077 (3)	0.0058 (5)	0.000	0.000	0.0007 (4)
S1	0.0126 (3)	0.0072 (3)	0.0085 (5)	0.000	0.000	0.0011 (4)
S2	0.0099 (3)	0.0104 (3)	0.0064 (6)	0.000	0.000	-0.0001 (3)
S3	0.0089 (2)	0.0101 (3)	0.0110 (5)	-0.0012 (1)	0.0006 (3)	0.0000 (3)

Geometric parameters (\AA , $^\circ$)

Cu1—S2 ⁱ	2.3170 (7)	Si1—S3 ^{vi}	2.136 (1)
Cu1—S3	2.325 (1)	Si1—S2 ^{vii}	2.143 (3)
Cu1—S1	2.3270 (6)	S1—Cu1 ^{viii}	2.3270 (6)

supplementary materials

Cu1—S3 ⁱⁱ	2.3426 (7)	S2—Si1 ^{iv}	2.143 (3)
Zn1—S2	2.322 (1)	S2—Cu1 ^{vi}	2.3170 (7)
Zn1—S1	2.322 (1)	S2—Cu1 ^v	2.3170 (7)
Zn1—S3 ⁱⁱⁱ	2.3650 (7)	S3—Si1 ⁱ	2.136 (1)
Zn1—S3 ^{iv}	2.3650 (7)	S3—Cu1 ^{ix}	2.3426 (7)
Si1—S1	2.131 (1)	S3—Zn1 ^{vii}	2.3650 (7)
Si1—S3 ^v	2.136 (1)		
S2 ⁱ —Cu1—S3	112.51 (4)	Si1—S1—Zn1	112.05 (8)
S2 ⁱ —Cu1—S1	106.98 (3)	Si1—S1—Cu1 ^{viii}	111.72 (5)
S3—Cu1—S1	111.92 (4)	Zn1—S1—Cu1 ^{viii}	108.24 (4)
S2 ⁱ —Cu1—S3 ⁱⁱ	106.09 (4)	Si1—S1—Cu1	111.72 (5)
S3—Cu1—S3 ⁱⁱ	108.38 (3)	Zn1—S1—Cu1	108.24 (4)
S1—Cu1—S3 ⁱⁱ	110.82 (4)	Cu1 ^{viii} —S1—Cu1	104.51 (4)
S2—Zn1—S1	112.01 (5)	Si1 ^{iv} —S2—Cu1 ^{vi}	115.21 (4)
S2—Zn1—S3 ⁱⁱⁱ	107.88 (4)	Si1 ^{iv} —S2—Cu1 ^v	115.21 (4)
S1—Zn1—S3 ⁱⁱⁱ	108.84 (4)	Cu1 ^{vi} —S2—Cu1 ^v	108.34 (5)
S2—Zn1—S3 ^{iv}	107.88 (4)	Si1 ^{iv} —S2—Zn1	113.46 (6)
S1—Zn1—S3 ^{iv}	108.84 (4)	Cu1 ^{vi} —S2—Zn1	101.47 (4)
S3 ⁱⁱⁱ —Zn1—S3 ^{iv}	111.40 (5)	Cu1 ^v —S2—Zn1	101.47 (4)
S1—Si1—S3 ^v	108.68 (7)	Si1 ⁱ —S3—Cu1	111.38 (7)
S1—Si1—S3 ^{vi}	108.68 (7)	Si1 ⁱ —S3—Cu1 ^{ix}	110.92 (5)
S3 ^v —Si1—S3 ^{vi}	111.40 (7)	Cu1—S3—Cu1 ^{ix}	108.76 (3)
S1—Si1—S2 ^{vii}	110.60 (9)	Si1 ⁱ —S3—Zn1 ^{vii}	111.42 (5)
S3 ^v —Si1—S2 ^{vii}	108.74 (7)	Cu1—S3—Zn1 ^{vii}	105.21 (4)
S3 ^{vi} —Si1—S2 ^{vii}	108.74 (7)	Cu1 ^{ix} —S3—Zn1 ^{vii}	108.95 (3)

Symmetry codes: (i) $-x+1/2, -y+1, z-1/2$; (ii) $-x+1/2, -y, z+1/2$; (iii) $-x, y, z+1$; (iv) $x, y, z+1$; (v) $-x+1/2, -y+1, z+1/2$; (vi) $x-1/2, -y+1, z+1/2$; (vii) $x, y, z-1$; (viii) $-x, y, z$; (ix) $-x+1/2, -y, z-1/2$.

Fig. 1

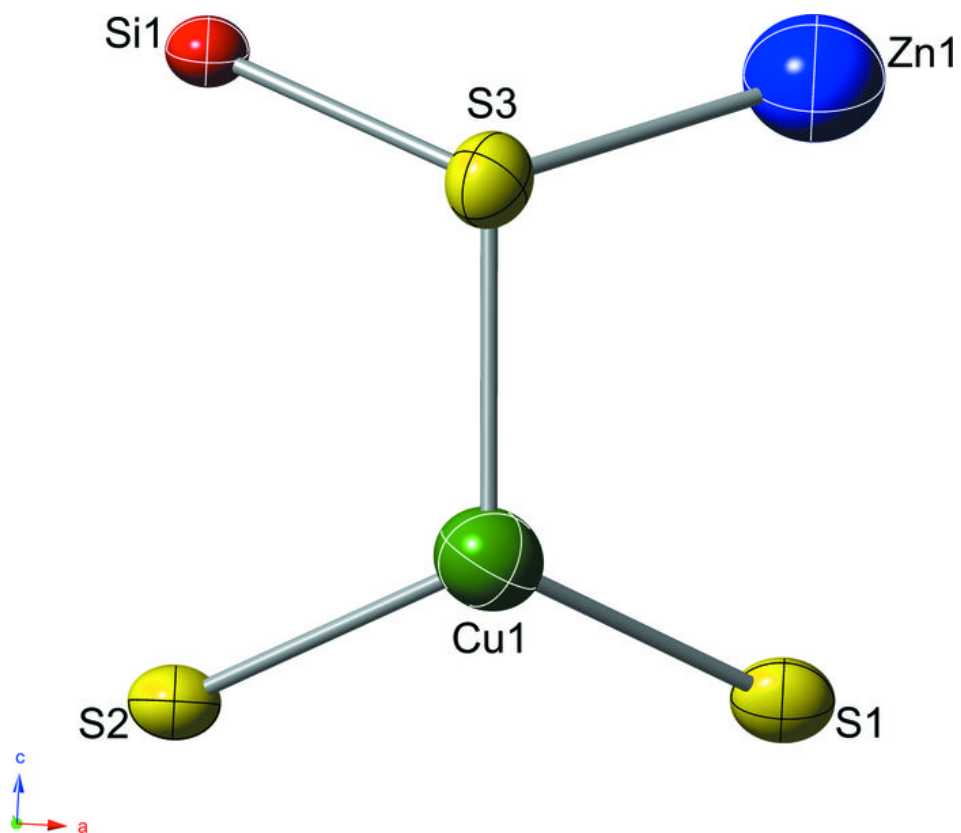


Fig. 2

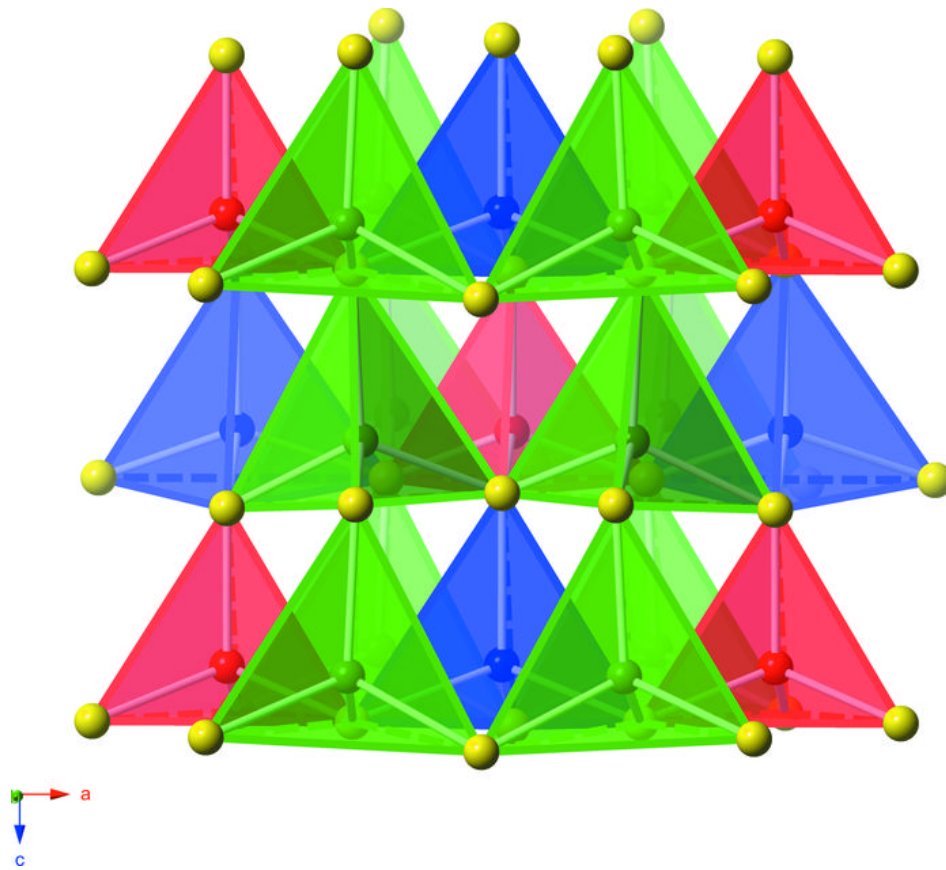


Fig. 3

