

Synthesis and Structure of $\text{Na}_2\text{Cu}_2\text{ZrS}_4$

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The new compound $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ has been synthesized through direct reaction of the elements with an Na_2S_n flux at 375°C . The structure has been determined by single-crystal X-ray methods. The compound crystallizes in space group $C_{2h}^3 - C2/m$ of the monoclinic system with two formula units in a cell of dimensions $a = 13.657(9)$, $b = 3.720(3)$, $c = 7.025(5)$ Å, $\beta = 112.44(3)^\circ$ ($T = 113$ K). The structure is composed of ${}^2_0[\text{Cu}_2\text{ZrS}_4^{2-}]$ layers separated by Na^+ cations. A ${}^2_0[\text{Cu}_2\text{ZrS}_4^{2-}]$ layer is composed of pairs of CuS_4 tetrahedra alternating with ZrS_6 octahedra. © 1995 Academic Press, Inc.

INTRODUCTION

After the initial demonstration of the reactive flux method (1), many new metal chalcogenides and polychalcogenides have been synthesized (1-14). The present compound $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ was synthesized at 375°C by this method. It exhibits a new structural motif that we describe and compare with those of several known chalcogenides.

EXPERIMENTAL

Synthesis. $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ was synthesized by combining Na_2S (65 mg, 0.84 mmol; Alfa) with powders of the elements Cu (35 mg, 0.56 mmol; Johnson-Matthey 99.999%), Zr (51 mg, 0.56 mmol; Johnson-Matthey 99.9%), and S (98 mg, 3.07 mmol; AESAR 99.9999%). The reaction mixture was loaded into a fused silica tube in a dry box under an Ar atmosphere. The tube was evacuated to approximately 10^{-3} Torr, sealed, and heated in a furnace at 375°C for 4 days before being cooled to room temperature at $4^\circ\text{C}/\text{hr}$.

Single crystals formed in the presence of the melt. Small red needles were extracted by washing the excess flux away with water. The compound is stable in air and water. Its quaternary nature and approximate composition were established with the microprobe of an EDAX (energy dispersive analysis by X rays)-equipped Hitachi S-570 scanning electron microscope.

Structure determination. The unit cell constants were determined from a least-squares analysis of the setting

angles of 26 reflections in the range $14^\circ < 2\theta(\text{MoK}\alpha_1) < 30^\circ$ that had been automatically centered at 113 K on a Picker diffractometer operated from a PC (15). Six representative standard reflections measured every 100 reflections during the course of the data collection showed no significant variations in intensity. Additional crystallographic details are described in Table 1. Intensity data were processed and corrected for absorption (16) on an IBM RS/6000 series computer with programs and methods standard in this laboratory.

The observed Laue symmetry and the systematic absences are consistent with the monoclinic space groups $C_2^3 - C2$, $C_3^3 - Cm$, and $C_{2h}^3 - C2/m$. Intensity statistics favor the centrosymmetric space group $C2/m$ and the structure was solved in this space group with the direct methods program XS in the SHELXTL PC program package (17). The structure was refined with the use of the program SHELXL-93 (18) by full-matrix least-squares techniques, the function $\sum w(F_o^2 - F_c^2)^2$ being minimized. Anisotropic thermal motion was included. The final refinement led to a value of $R_w(F_o^2)$ of 0.075. The conventional R index (on F for $F_o^2 > 2\sigma(F_o^2)$) is 0.031. The final difference electron density map shows no features with a height greater than 1% that of a Zr atom.

Final values of the atomic parameters and equivalent isotropic displacement parameters are given in Table 2. Final anisotropic displacement parameters and structure amplitudes are available as supplementary material.¹ The SHELXTL PC program package was used to produce the figures.

RESULTS AND DISCUSSION

The structure of $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ consists of ${}^2_0[\text{Cu}_2\text{ZrS}_4^{2-}]$ layers (Fig. 1, Slab A) separated by Na^+ cations (Fig. 1,

¹ See NAPS document No. 05182 for 3 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or \$7.75 for photocopy. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, \$1.75 for postage of any microfiche orders.

TABLE 1
Crystal Data and Intensity Collection for Na₂Cu₂ZrS₄

Formula	Na ₂ Cu ₂ ZrS ₄
Formula mass (amu)	392.5
Space group	C _{2h} ³ - C2/m
<i>a</i> (Å)	13.657(9) ^a
<i>b</i> (Å)	3.720(3)
<i>c</i> (Å)	7.025(5)
β (°)	112.44(3)
<i>V</i> (Å ³)	329.9(4)
<i>Z</i>	2
ρ _c (g cm ⁻³)	3.95
<i>T</i> of data collection (K) ^b	113
Crystal shape	Needle ≈ 0.021 × 0.029 × 0.095 mm bounded by {100}, {103}, {010}
Crystal volume (mm ³)	0.58 × 10 ⁻⁴
Radiation	Graphite monochromated MoKα (λ(Kα ₁) = 0.7093 Å)
Linear absorption coefficient (cm ⁻¹)	92.1
Transmission factors ^c	0.763–0.839
Detector aperture (mm)	Horizontal, 6.5; vertical, 6.5; 32 cm from crystal
Scan type	θ–2θ
Scan speed (deg min ⁻¹)	1
Scan range (deg)	–0.75 to +0.65 in 2θ
Takeoff angle (degrees)	2.5
λ ⁻¹ sin θ limits (Å ⁻¹)	0.079–0.629
Background counts	15 sec
Weighting scheme	w ⁻¹ = σ ² (F _o ²) + (0.04 × F _o ²) ²
Data collected	± <i>h</i> ± <i>k</i> ± <i>l</i>
Number of data collected	1356
Number of unique data, including	395
0 ≤ F _o ² ≤ 3σ(F _o ²)	
Number of unique data, with F _o ² > 2σ(F _o ²)	296
Number of variables	29
R _{ave}	0.056
R _w (F _o ²)	0.075
<i>R</i> (on <i>F</i> for F _o ² > 2σ(F _o ²))	0.031
Error in observation of unit weight	1.04

^a Obtained from a refinement with the constraints α = γ = 90°.

^b The low temperature system is based on a design by Huffman (22).

^c The analytical method as employed in the Northwestern absorption program, AGNOST, was used for the absorption correction (16).

Slab B). Figure 2 shows that an isolated [Cu₂ZrS₄]²⁻ layer is composed of *pairs* of CuS₄ tetrahedra alternating with ZrS₆ octahedra. These polyhedra edge share in the *a* direction. In the *b* direction the tetrahedra share a corner through an axial S(1) atom and the octahedra share an edge through two equatorial S(2) atoms. As a result, the structure comprises zigzag chains of edge-shared CuS₄ tetrahedra connected through edge-sharing to chains of edge-shared ZrS₆ octahedra. In slab **B** the Na⁺ cations are coordinated by seven S atoms in a distorted monocapped trigonal prismatic arrangement. These Na-centered poly-

TABLE 2
Atomic Coordinates (× 10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Na₂Cu₂ZrS₄

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Zr	1387(3)	0	5594(6)	16(1)
Cu	3206(1)	0	137(2)	10(1)
Zr	0	0	0	8(1)
S(1)	2034(2)	0	2019(3)	9(1)
S(2)	4909(2)	0	2482(3)	8(1)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

hedra share faces in the *b* direction. The polyhedra of slab **B** are connected to those of slab **A** through edge sharing with both the tetrahedra and the octahedra. The compound K₂Cu₂CeS₄ (14) is isostructural with Na₂Cu₂ZrS₄.

Selected bond distances and angles for Na₂Cu₂ZrS₄ are given in Table 3. The Zr–S distances of 2.585(2) and 2.593(3) Å are comparable to those found in the quaternary compound NaCuZrS₃ (2.568(2) to 2.624(2) Å) (10) and roughly comparable to those in the binary sulfide ZrS₃ (2.602(3) to 2.724(4) Å) (19). The Cu–S distances of 2.280(3), 2.342(2), and 2.434(3) Å are in good agreement with those found in KCu₄S₃ (2.312(3) to 2.451(1) Å) (20), β-KCuS₄ (2.298(4) to 2.432(4) Å) (4), and NaCuZrS₃ (2.276(2) to 2.322(2) Å) (10). The closest S⋯S distance of 3.451(4) Å indicates that there are no significant S–S bonding interactions. Thus the formal oxidation states Na(I), Cu(I), Zr(IV), and S(–II) may be assigned.

Na₂Cu₂ZrS₄ shares some common structural features with KCuZrQ₃ (Q = S, Se, Te) (9), NaCuMQ₃ (M = Ti, Zr; Q = S, Se, Te) (10), and Ta₂NiQ₅ (Q = S, Se) (21). Each of these layered compounds is composed of MQ₄ tetrahedra (M = Cu or Ni) and M'Q₆ octahedra (M' =

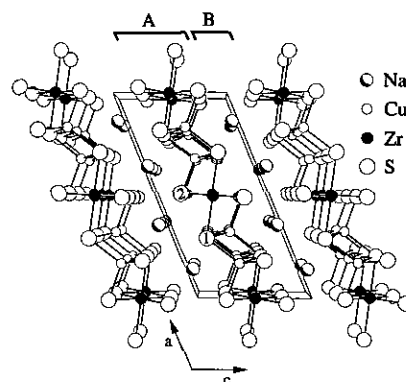


FIG. 1. View down [010] of the structure of Na₂Cu₂ZrS₄ with layers and atoms labeled. Here and in succeeding figures the atoms are shown as circles of arbitrary size.

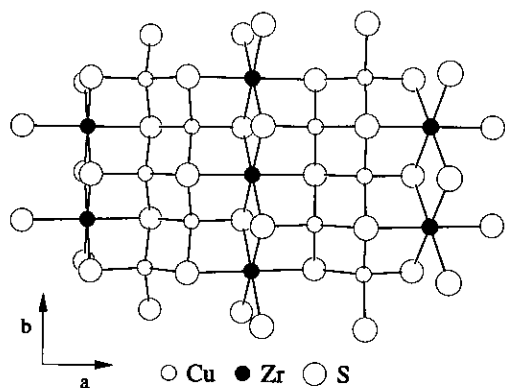


FIG. 2. Perspective drawing of an isolated $\frac{1}{2}[\text{Cu}_2\text{ZrS}_4]^{2-}$ layer in the a - b plane.

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for $\text{Na}_2\text{Cu}_2\text{ZrS}_4$

Na-S(1) ^a	(2)	2.857(4)
Na-S(1)		2.963(5)
Na-S(2) ^b	(2)	2.991(4)
Na-S(2) ^c	(2)	3.201(4)
Cu-S(2)		2.280(3)
Cu-S(1) ^d	(2)	2.342(2)
Cu-S(1)		2.434(3)
Cu-Cu ^d		2.632(2)
Cu-Zr ^e		3.107(2)
Zr-S(2) ^d	(4)	2.585(2)
Zr-S(1)	(2)	2.593(3)
S(1) ^a -Na-S(1) ^c		81.26(13)
S(1) ^a -Na-S(1)		95.46(11)
S(1) ^a -Na-S(2) ^b		169.0(2)
S(1) ^c -Na-S(2) ^b		99.89(7)
S(1)-Na-S(2) ^b		73.56(10)
S(2) ^b -Na-S(2) ^f		76.92(12)
S(1) ^a -Na-S(2) ^c		123.06(14)
S(1) ^c -Na-S(2) ^c		77.81(9)
S(1)-Na-S(2) ^c		138.57(9)
S(2) ^b -Na-S(2) ^c		67.64(10)
S(2) ^f -Na-S(2) ^c		110.01(13)
S(2) ^c -Na-S(2) ^a		71.04(10)
S(2)-Cu-S(1) ^d		108.64(7)
S(1) ^b -Cu-S(1) ^d		105.19(11)
S(2)-Cu-S(1)		107.97(10)
S(1) ^a -Cu-S(1)		113.13(6)
S(2) ^b -Zr-S(2) ^f		180.0
S(2) ^b -Zr-S(2) ^d		92.05(9)
S(2) ^f -Zr-S(2) ^c		87.95(9)
S(2) ^f -Zr-S(1)		87.03(6)
S(2) ^d -Zr-S(1)		92.97(6)
S(1)-Zr-S(1) ^h		180.0

Symmetry transformations used to generate equivalent atoms

- | | |
|----------------------------------|------------------------------|
| (a) $-x + 1/2, -y + 1/2, -z + 1$ | (b) $x - 1/2, y - 1/2, z$ |
| (c) $-x + 1/2, -y - 1/2, -z + 1$ | (d) $-x + 1/2, -y + 1/2, -z$ |
| (e) $x + 1/2, y + 1/2, z$ | (f) $x - 1/2, y + 1/2, z$ |
| (g) $-x + 1/2, -y - 1/2, -z$ | (h) $-x, -y, -z$ |

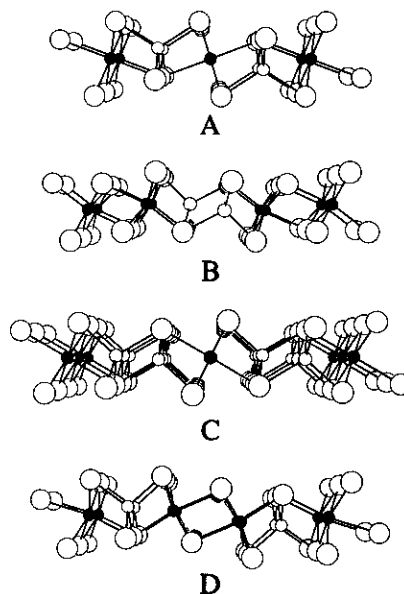


FIG. 3. Variations in the alternation of metal-centered polyhedra in KCuZrQ_3 (A), NaCuMQ_3 (B), $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ (C), and Ta_2NiQ_5 (D).

Ti, Zr, or Ta). In the quaternaries the layers are separated by A^+ cations whereas in Ta_2NiQ_5 , the layers are separated by a van der Waals gap. Structural differences among these compounds arise in the manner in which the metal-centered polyhedra alternate with the layers (Fig. 3). In the two compounds where octahedra (oct) and tetrahedra (tet) occur in equal numbers, an alternation of a single octahedron and tetrahedron in the fashion *oct : tet* is observed for KCuZrQ_3 (A) whereas an alternation of *pairs* of octahedra and *pairs* of tetrahedra in the fashion *oct : oct : tet : tet* is seen for NaCuMQ_3 (B). In the two compounds where octahedra and tetrahedra occur in unequal numbers an alternation of a single octahedron with *pairs* of tetrahedra (*oct : tet : tet*) is observed for the present compound $\text{Na}_2\text{Cu}_2\text{ZrS}_4$ (C), whereas an alternation of *pairs* of octahedra with a single tetrahedron in the fashion *oct : oct : tet* occurs in the compounds Ta_2NiQ_5 (D).

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