

Synthesis and Characterization of $\text{Na}_6\text{Cd}_7\text{S}_{10}$: A New Framework Sulfide with 1-D Channels Containing 12- and 16-Member Rings and a Sulfide Anion in an Umbrella-like Geometry

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Recently, it has been suggested that bulk compounds possessing low-dimensional covalent frameworks could possibly be considered to display quantum confinement along certain crystallographic directions.^{1,2} These new compounds possess lower framework connectivity, higher bandgaps, and brighter luminescence than their parent binaries, characteristics they share with quantum-confined particles. We have been actively seeking other compounds that display these characteristics, in the hope of correlating the effects of bulk dimensionality and atomic connectivity with the optical and other properties of these new materials. Continuing investigations of the A/Cd/Q system, (A = alkali metal, Q = S, Se, Te)³ have yielded the new, tunneled, three-dimensional (3-D) compound $\text{Na}_6\text{Cd}_7\text{S}_{10}$. The only known compounds in the Na/Cd/Q system before this work were $\text{Na}_6\text{Cd}_4\text{S}_4$,⁴ $\text{Na}_2\text{Cd}_2\text{S}_2$,⁵ and $\text{Na}_4\text{Cd}_3\text{Se}_5$.⁶ In fact, $\text{Na}_6\text{Cd}_7\text{S}_{10}$ is only the second ternary cadmium chalcogenide known to possess a 3-D structure, the other being $\text{K}_2\text{Cd}_2\text{S}_3$.¹

The structure of $\text{Na}_6\text{Cd}_7\text{S}_{10}$ ⁷ contains a unique three-dimensional (3-D) Cd_xS_y ^z framework. All four crystallographically unique Cd atoms possess tetrahedral coordination. While four S atoms are coordinated by three Cd atoms in a trigonal-pyramidal fashion, a fifth S atom, S1, is coordinated by four Cd atoms, and it displays a rare, umbrella-like geometry. The 3-D

$(\text{Cd}_7\text{S}_{10})_n^{6n}$ framework features various types of tunnels running parallel to the crystallographic *b* axis (see Figure 1). One tunnel is composed of a stack of 16-member, Cd_8S_8 rings, which is one of the largest known for cadmium chalcogenides. The long, thin rectangular cross section of the channel (containing atoms Na2 and Na3) indicates that Cd–S framework wraps tightly around the columns of the Na atoms and underscores the importance of the Na cations in stabilizing this structure. A view approximately down the crystallographic *c* axis reveals the octahedral coordination of Na2 and the irregular, 5-coordinate nature of Na3 (see Figure 2A). A second channel is built of 12-member, Cd_6S_6 rings, in which two columns of Na1 atoms are present, each surrounded by four sulfur atoms (see Figure 2B).

The Cd–S bond lengths for Cd1 and Cd2 are normal, ranging from 2.528(6) to 2.632(5) Å, while for Cd3 and Cd4, some bonds are longer, ranging from 2.526(3) to 2.783(6) Å. S–Cd–S angles for Cd1 and Cd2 are close to the ideal tetrahedral value, ranging from 101.7(1) to 114.3(1)°, while those for Cd3 and Cd4 are slightly more distorted, ranging from 90.8(2) to 120.9(2)°. Another difference between the two pairs of Cd atoms is their crystallographic site occupancy. Cd1 and Cd2 are both situated on mirror planes and are fully occupied (multiplicity = 0.5), while Cd3 and Cd4, also situated on mirror planes, possess occupancies of 0.405 and 0.345, respectively.⁸ In retrospect, the reduced occupancies of Cd in these sites are necessary for charge balancing. A material with fully occupied metal sites would have the formula $\text{Na}_6\text{M}_8\text{S}_{10}$ or $\text{Na}_3\text{M}_4\text{S}_5$. Four tetrahedral metals whose ionic charges add to seven would result in full occupancy of the metal sites. Attempts are underway to place suitable substitutions into this lattice. The occupancies of the Cd3 and Cd4 sites are such that one vacancy can be expected for every four formula units or in every other unit cell. Removal of cadmium atoms from the lattice results in “dangling” sulfide bonds,

(7) $\text{Na}_6\text{Cd}_7\text{S}_{10}$ was prepared by the reaction of 0.351 g (4.5 mmol) of Na_2S , 0.084 g (0.75 mmol) of Cd metal, and 0.096 g (3.0 mmol) of S in an $3/8$ in. o.d. $\times 1/4$ in. i.d. $\times 3$ in. long alumina thimble. This thimble was sealed in an evacuated ($\sim 1.0 \times 10^{-4}$ Torr), 13 mm o.d. $\times 11$ mm i.d. carbon-coated quartz tube and heated at 800 °C for 3 days, followed by cooling at a rate of -10 °C/h to 400 °C and -20 °C/h to room temperature. This reaction afforded light yellow rods of $\text{Na}_6\text{Cd}_7\text{S}_{10}$ in 62% yield, based on Cd. The product was isolated with methanol and washed with diethyl ether, under a N_2 atmosphere. This compound is stable in air and water and is insoluble in common organic solvents. Purity was ensured by comparison of experimental powder patterns to that calculated from the appropriate structural parameters.^{7a} $\text{Na}_6\text{Cd}_7\text{S}_{10}$ crystallizes in the monoclinic space group $C2/m$ (no. 12), with $a = 26.564(3)$ Å, $b = 4.2385(4)$ Å, $c = 10.523(2)$ Å, $\beta = 108.48(1)$ °, $V = 1123.7(2)$ Å³, $Z = 2$, $d_{\text{calc}} = 3.68$ g/cm³, $\mu(\text{Mo K}\alpha) = 76.85$ cm⁻¹, $2\theta_{\text{max}} = 60.00$ °, total data collected = 1868, number of unique data = 1831, number of reflections with $F_0^2 > 3\sigma(F_0^2) = 995$. Complete anisotropic refinement (73 variables) resulted in $R = 5.5\%$, $R_w = 6.6\%$. The structure was solved using the SHELXS 86^{7b} direct methods program, incorporated into the TEXSAN software package.^{7c} An empirical absorption correction based on ψ scans followed by the DIFABS correction^{7d} was applied to all data. (a) D. K. Smith, M. C. Nichols, M. E. Zolensky, POWD10: A FORTRAN IV Program for Calculating X-ray Powder Diffraction Patterns, Version 10; Pennsylvania State University, 1983. (b) G. M. Sheldrick, In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Doddard, R., Eds.; Oxford University Press: Oxford, England, 1985; pp 175–189. (c) TEXSAN: Single Crystal Structural Analysis Software, Version 5.0; Molecular Structure Corp.: The Woodlands, TX 77381, 1981. (d) Walker, N; Stuart, D. *Acta Crystallogr.* **1983**, 39A, 158.

(8) Preliminary X-ray photographic examination of crystals of this compound did not reveal signs of a superstructure which may be due to Cd vacancy ordering. An electron diffraction study would be more appropriate to address this issue.

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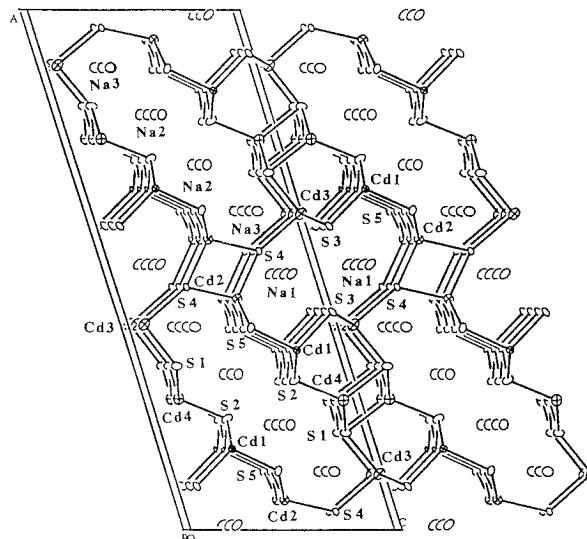


Figure 1. ORTEP view of the structure of $\text{Na}_6\text{Cd}_7\text{S}_{10}$ parallel to the crystallographic b axis (crossed ellipsoids: Cd; open, bonded ellipsoids: S; open, stranded ellipsoids: Na).

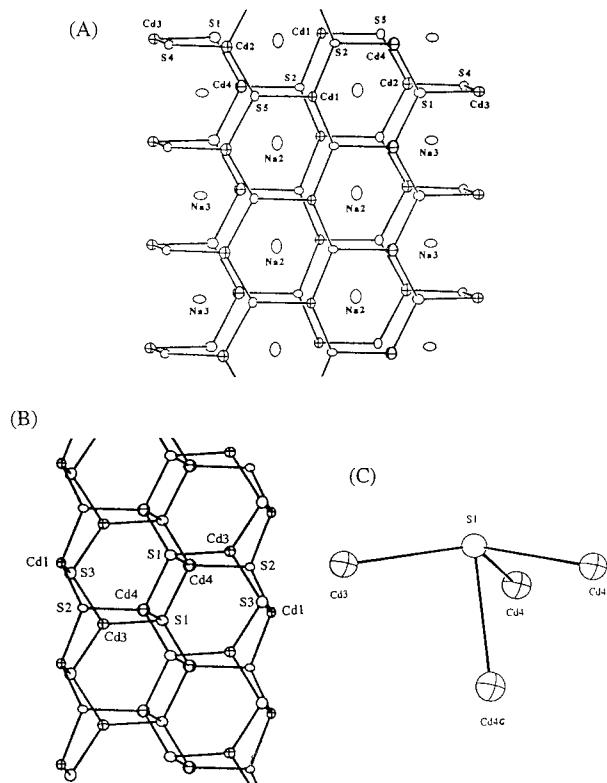
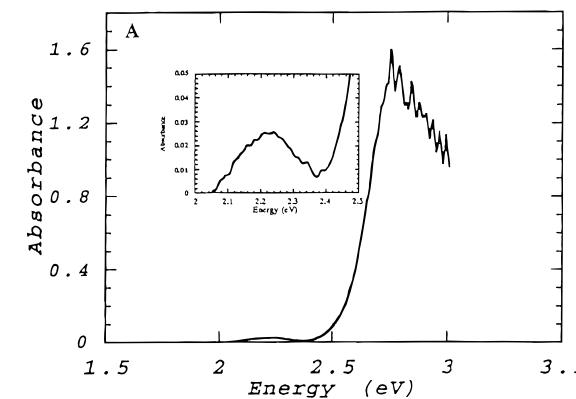


Figure 2. (A) The 16-sided channel of $\text{Na}_6\text{Cd}_7\text{S}_{10}$ approximately parallel to the crystallographic c axis. (B) The two six-sided channels of $\text{Na}_6\text{Cd}_7\text{S}_{10}$. (C) The local structure of S1. Cd3–S1–Cd4a: $122.0(1)^\circ$ ($2\times$); Cd4a–S1–Cd4b: $105.6(2)^\circ$; Cd3–S1–Cd4c: $87.5(2)^\circ$; Cd4a–S1–Cd4c: $74.4(2)^\circ$ ($2\times$).

which could act as traps for excited electrons, affecting the optical properties of the compound (see below).

The unusual, umbrella-like coordination geometry of the S1 atom in this new compound is noteworthy. The mineral sultanite, Cu_3VS_4 ,⁹ is one of few compounds with a similar structural feature. The umbrella is formed from one S1 atom surrounded by a triangle of one Cd3 and two Cd4 atoms. The triangle of Cd atoms is slightly below the S1 atom (see Figures 3B). The

(A)



(B)

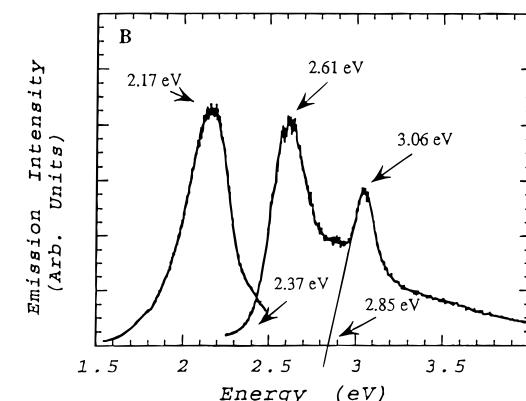


Figure 3. (A) Room-temperature, single-crystal absorption spectrum of $\text{Na}_6\text{Cd}_7\text{S}_{10}$. Inset: the midgap feature of the single-crystal absorption spectrum of $\text{Na}_6\text{Cd}_7\text{S}_{10}$. (B) K emission ($E_{\text{em},\text{max}} = 2.17$ eV) and excitation ($E_{\text{em},\text{max}} = 2.61$, 3.06 eV) spectra of $\text{Na}_6\text{Cd}_7\text{S}_{10}$.

Cd–S–Cd angles around the top of the umbrella are $122.0(1)^\circ$ ($2\times$) and $105.6(2)^\circ$, close to values expected for an equilateral triangle of Cd atoms. Another Cd4 atom forms the “handle” of the umbrella. The Cd–S–Cd angles between each of the Cd atoms that form the top, S1 and the Cd4 atom that forms the handle are less than 90° , at $87.5(2)^\circ$ and 74.4° ($2\times$), as expected for a true umbrella-like coordination. This coordination geometry apparently has a significant influence on the properties of $\text{Na}_6\text{Cd}_7\text{S}_{10}$ (see below).

$\text{Na}_6\text{Cd}_7\text{S}_{10}$ is semiconductor with a room-temperature bandgap of 2.62 eV¹⁰ (see Figure 3A). This result is in line with results obtained from other $\text{A}_x\text{Cd}_y\text{S}_z$ compounds.^{1c,3} A blue-shifted bandgap, compared to that of CdS, at 2.53 eV, is expected to result from the narrowing of the conduction and valence bands as the amount of Cd–S bonding decreases in going to the ternary phase. The single-crystal transmission experiment used to obtain the bandgap also revealed another feature in the midgap region, with a maximum at 2.22 eV (559 nm). Though weak, this feature appears to be real (see Figure 3A). The dangling bonds created by the above-mentioned vacancies may be one cause of the mid gap absorption in this material.

(10) Single-crystal absorption spectra were obtained on a Hitachi U-6000 Microscopic FT spectrophotometer mounted on an Olympus BH2-UMA Microscope. Crystals lying on a glass slide were positioned over the light source and the transmitted light was detected from above. The transmission values were converted to absorbance units. We have obtained a value of 2.62 eV for the bandgap by extrapolating the linear region of the $(\text{absorbance})^2$ versus energy plot to $(\text{absorbance})^2 = 0$.

The likely existence of a direct gap and the interesting structural features of this compound, including the large number of vacancies and the strange coordination geometry around the S1 atom, prompted us to examine its light-emitting properties.¹¹ No emission from $\text{Na}_6\text{Cd}_7\text{S}_{10}$ was visible or detectable at room temperature, but the compound emitted strongly at 77 K. The emission was yellow, with a maximum of 2.17 eV (571 nm). The excitation spectra monitoring the 2.17 eV emission revealed two sharp features. The first feature has a maximum at 2.61 eV (475 nm) which falls to zero by 2.37 eV (525 nm), while the second has a maximum at 3.06 eV (405 nm). This higher energy drop in the excitation profile can be extrapolated to a value of 2.85 eV (435 nm; see Figure 3B). The behavior observed in the excitation profile is consistent with the single-crystal absorption data. The higher energy band represents the true bandgap of the material. Its extrapolated value of 2.85 eV is slightly higher than the 2.62 eV bandgap obtained from absorption, consistent with the lower temperature used in the photoluminescence experiment.

(11) Photoluminescence spectra were obtained on a Spex Fluorolog-2, Model F111A1 spectrofluorometer according to procedures reported in ref 3.

The lower energy band arises from the midgap states formed by the presence of Cd vacancies. Excitation across both gaps results in the same yellow emission.

In summary, $\text{Na}_6\text{Cd}_7\text{S}_{10}$ possesses a tunnelled 3-D framework, displays a sulfur atom in a rare coordination geometry and contains numerous "built-in" cadmium vacancies. These characteristics give rise to the interesting light-absorbing and -emitting properties of this compound.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and calculated and observed powder patterns (13 pages). Ordering information is given on any current masthead page.

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