

Ab initio structure study from in-house powder diffraction of a novel ZnS(EN)_{0.5} structure with layered wurtzite ZnS fragment

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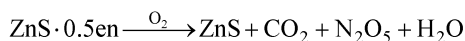
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The solvothermal reaction of elemental zinc with sulfur in ethylenediamine (en) as solvent yields [ZnS·0.5(NH₂CH₂CH₂NH₂)]₁, an unprecedented ethylenediamine pillared ZnS layered compound, containing two dimensional (2-D) boat-type 6-membered rings, which was characterized by *ab initio* structure solution from powder diffraction data (SDPD).

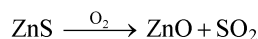
The preparation of nanometer sized crystallites is a subject under intense study because it is often the case that the physical properties of a solid are different in the nano-length scale than in bulk.^{1–4} A great deal of study has been devoted to producing nanoparticles of the well-known II–VI family of semi-conductors, ZnS, Se, Te. Recently, Li *et al.*⁵ summarized the several methods utilized to control the particle size of these semiconductors. They concluded that either agglomerates or near spherical particles are mainly produced by the several methodologies described. The exceptions were CdS nanowires⁶ and rodlike CdSe particles⁷ prepared by electrodeposition. Therefore, they proceeded to examine the solvothermal synthetic routes as a possible means to better control the shape and size of the zinc and cadmium chalcogenides.

Solvothermal reactions of cadmium metal with elemental chalcogens showed that the size and shape of the crystals were greatly influenced by the solvent used. In ethylenediamine (en) rod-like crystals 10–40 nm in diameter and several micrometers in length were obtained in the temperature range 120–200 °C. However, with Zn, thin platelets of the sulfide and selenide were obtained.⁸ The composition of the sulfide platelets was reported as ZnS·0.5en. Because new forms of ZnS have potential applications as a direct band-gap semiconductor and luminescent material, we were interested in determining the structure of the platelets.

The solvothermal reaction of elemental zinc and sulfur powders in ethylenediamine was carried out at 180 °C as reported by Li *et al.*⁸ The precipitated solid was recovered by centrifugation and washed with acetone by decantation. Elemental analysis gave Zn 53.7%, S 27.08% calculated for ZnS·0.5en: Zn 51.27%, S 25.15%. Thermogravimetric analysis carried out in air at a rate of 10° min⁻¹ exhibited two weight loss regions. The first commenced at 263 °C and was complete at 398 °C and amounted to 25.06%. The second loss of 16.62% ranged from 549–669 °C. These weight losses are interpreted in the following way:



and



An X-ray pattern taken after the first weight loss showed the product to be ZnS and at the end of the run ($T = 975$ °C) ZnO. Our observed weight losses were 20.9% and 12.98% compared to 23.57% and 12.60% calculated for reactions one and two, respectively. These results indicate that somewhat less than half a mole of ethylenediamine was incorporated into the compound.

Li *et al.*⁸ only observed the first weight loss (to 600°) at 24.3% under argon. Powder patterns taken of our product matched the one presented by Li *et al.*⁸

The powder pattern for the structural study was collected on a Bruker D8 Discover Powder X-ray diffractometer with diffracted beam graphite monochromator at 50 kV and 40 mA (Cu K α with $\lambda = 1.54187$ Å). Data collection was carried out in variable time step–scan mode with 0.02° per step in the angular range of 5–70° in 2θ at 10 s per step and 60–100° in 2θ at 15 s per step. The pattern was indexed to the orthorhombic system with unit cell dimensions of $a = 17.263(1)$ Å, $b = 6.393(1)$, $c = 6.205(1)$, $V = 684.78(1)$ Å³. The space group was determined to be *Pbca*, $Z = 8$. The structure was solved by direct methods with program EXPO97.⁹ Refinement of the structure was carried out by the Rietveld method, based on a stoichiometry of ZnS·0.5NH₂CH₂CH₂NH₂. The reliability indices, which are a measure of how well the calculated pattern and structure agree with the observed data, are as follows: $R_p = 0.082$, $R_{wp} = 0.110$, $R_F = 0.03$. The final Rietveld refinement plot is shown in Fig. 1. The crosses are the observed data points and the solid lines are calculated based on the structure. The blue line is the difference between the two and it is seen that most of the error is in the first peak. There are two reasons for this large error; that peak is the interlayer distance and suffers from preferred orientation, a phenomenon common for layered compounds. The second reason is the first peak is usually highly asymmetric and therefore difficult to duplicate by an analytical function. However, the fact the R_F is as low as 3% indicates that the location of the atoms on which the intensities are calculated reproduces the observed intensities extremely well.

The zinc atoms are tetrahedrally coordinated by three sulfur atoms and one nitrogen of the ethylenediamine molecule. The

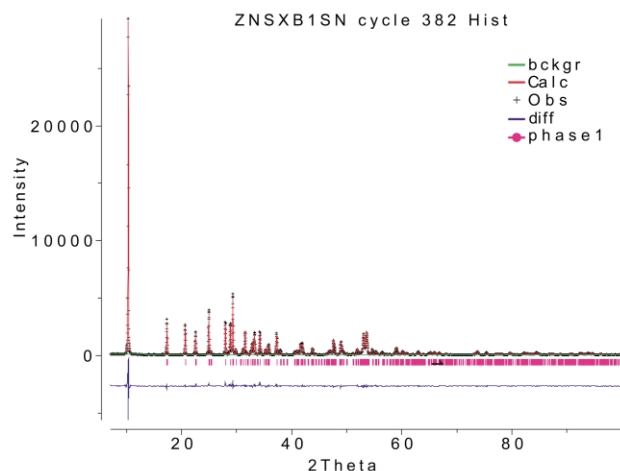


Fig. 1 Rietveld plot of refinement result; observed (+) and calculated (—) profiles for the Rietveld refined structure of compound 1. The bottom curve is the difference plot on the same intensity scale.

alternation of zinc and sulfur atoms forms six-membered rings that have a boat-like shape (Fig. 2). These rings share edges to form layers that are perpendicular to the *a*-axis centered at approximately $\frac{1}{4}$ and $\frac{3}{4}a$. These layers are then connected to each other through bonding of the nitrogen atoms as shown in Fig. 2. If we consider only the zinc sulfur layers, they are similar to those in wurtzite. Fig. 3 is a ball and stick rendering of a portion of the wurtzite structure illustrating the boat-shaped rings running vertically through the structure. By cleaving the bonds intersecting vertical lines enclosing the rings, layers

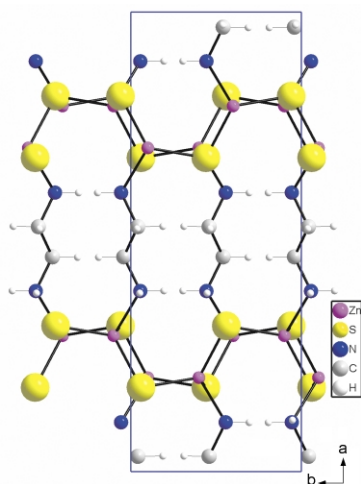


Fig. 2 View of the structure down the *c*-axis showing the undulating nature of the layers at $\frac{1}{4}$ and $\frac{3}{4}$ and the ethylenediamine groups linking the layers together.

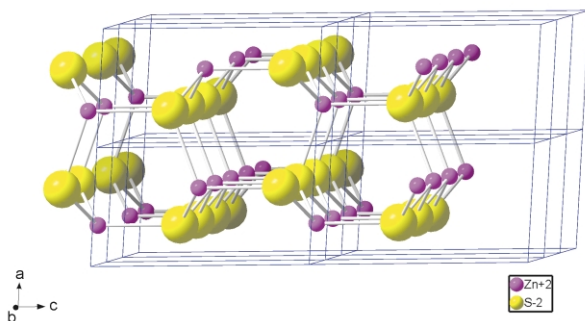


Fig. 3 A portion of the wurtzite structure showing the boat-shaped rings forming layers.

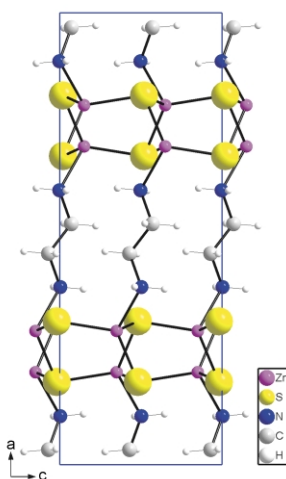


Fig. 4 View of the structure down the *b*-axis showing the overlaying nature of the six-membered rings.

similar to those shown in Fig. 2 are isolated. A second view of the structure as viewed down the *b*-axis is shown in Fig. 4. A line drawing of the ring structure is shown in Scheme 1.



Scheme 1 Line drawing of the boat-shaped six-membered rings of ZnS-0.5en, alternating in up and down fashion as in Fig. 2.

ZnS bond distances† average 2.34(2) Å, quite similar to the values for wurtzite and zinc blende. The Zn–N bonds are shorter at 2.17(4) Å. The bond angles about the Zn are slightly distorted tetrahedral; all the S–Zn–S angles are about 4–5° larger than the ideal tetrahedral value and the S–Zn–N are smaller. However, the average for each coordination sphere is 109.1°.

We have also prepared a similar propylenediamine derivative indicating that the reaction is general in scope. Similar reactions with other bonding solvents may lead to a novel series of compounds with isolated wurtzite-like layers and interesting physical properties.

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Notes and references

† Powder data for **1**: empirical formula CH_4NZnS , $M_r = 127.84$, Orthorhombic, space group *Pbca*, $a = 17.263(1)$ Å, $b = 6.393(1)$ Å, $c = 6.205(1)$ Å, $V = 684.78(1)$ Å³, and $Z = 8$, Cu K α ($K\alpha_1 = 1.54056$ Å, $K\alpha_2 = 1.5430$ Å). Data were collected at room temperature by the step-scan mode in the range 5–100°; 0.02° per step and on a Bruker D8 Discover powder diffractometer with graphite diffract beam monochromator. The structure was solved by direct methods with program EXPO and refined by Rietveld full pattern refinement using the GSAS¹⁰ package on a Pentium III Workstation. Total refinement parameters used 42. Number of observations 4655 (718 reflections). Profile function #4 (18 terms), pseudovoigt function with asymmetry correction of Finger *et al.*,¹¹ micro strain broadening correction by Stephens.¹² Background function #2, Cosine Fourier series. (8 terms). Preferred orientation correction type March-Dollase, axis 110, ratio 3.97, fraction 0.02, axis 100, ratio 1, fraction 0.98. The structure was refined to residuals of $R_p = 0.078$ ($R_{wp} = 0.119$, $R_F = 0.03$) and a goodness of fit $\chi = 1.232$. CCDC 200433. See <http://www.rsc.org/suppdata/cc/b2/b212335p/> for crystallographic data in CIF or other electronic format.

Selected bond lengths and bond angles: Zn1–S2, 2.336(2); Zn1–S2', 2.349(2); Zn1–S2'', 2.343(2); Zn1–N3, 2.171(4); N3–C4, 1.496(5); C4–C4', 1.523(6); S2–Zn1–S2'', 114.54(9); S2–Zn1–S2''', 115.01(8); S2'–Zn1–S2'', 114.54(9); Zn1–S2–Zn1', 102.25(9); Zn1–S2–Zn1'', 104.81(9); Zn1'–S2–Zn1'', 98.87(8); S2–Zn1–N3, 104.8(2); S2'–Zn1–N3, 98.9(2); S2''–Zn1–N3, 106.9(1); Zn1–N3–C4, 109.8(3); N3–C4–C4', 108.7(5).

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