

Synthesis and characterisation of a new high pressure polymorph of Cu_2WS_4

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In this communication we report the synthesis and structural characterisation of a new body centred polymorph of Cu_2WS_4 prepared using hydrothermal methods. $I\text{-Cu}_2\text{WS}_4$ crystallises in space group $I42m$ with cell parameters $a = b = 5.44427(8)$, $c = 10.0687(2)$ Å and has a new structure type containing layers of edge-sharing CuS_4 and WS_4 tetrahedra.

Chalcogenide materials have been the focus of much interest because of their useful and novel properties. Properties exhibited by this type of material include semiconduction, ferromagnetism, antiferromagnetism and non-linear optical activity.^{1,2} Most chalcogenide materials have been synthesised by traditional solid state, high temperature methods, however methods of synthesis such as molten flux and solvanothermal routes have also been investigated. Interest in these synthetic methods has largely been stimulated by the possibility of targeted syntheses and material design.

The synthesis and structure of layered Cu_2WS_4 by a low temperature ambient pressure route was reported by Pruss *et al.* in 1993.³ In this communication we report the synthesis of Cu_2WS_4 using solvanothermal methods, the preparation of a new higher pressure polymorph of the material and the structural characterisation of this phase by powder diffraction methods.

The synthetic strategy adopted during this work was to react a copper salt with ammonium thiotungstate in a mixture of organic solvents at elevated temperature in a sealed hydrothermal autoclave. $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ and $(\text{NH}_4)_2\text{WS}_4$ were prepared by literature methods and their purities confirmed by elemental analysis and powder X-ray diffraction.^{4,5} In a typical preparation, a solution of 0.07 g (0.22 mmol) of $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ in 4 ml of butyronitrile was added to a solution of 0.039 g (0.11 mmol) of $(\text{NH}_4)_2\text{WS}_4$ in 4 ml of *N,N*-dimethylformamide. The mixture was sealed in a Teflon-lined autoclave and heated to the desired temperature for 48 h. After cooling the powder formed was isolated from solution and washed with diethyl ether before drying in air. This procedure was repeated using a range of temperatures between 110 °C and 250 °C. The samples were analysed to determine their purity and crystallinity by X-ray powder diffraction.

The powder diffraction data showed that at synthesis temperatures of 135 °C and below the product of the reaction was a form of Cu_2WS_4 (primitive, space group $P42m$), identical to that previously reported by Pruss *et al.* However, as temperature was increased, a material with a markedly different X-ray powder pattern began to form; this material proved to be a new polymorph of Cu_2WS_4 . The new material was produced at all synthetic temperatures between 135 °C and 220 °C; at 250 °C an X-ray amorphous brown powder was formed. All materials produced below 220 °C were orange in colour.

The structure of the new polymorph was determined from powder diffraction data of a sample synthesised at 200 °C. Data were collected using a Bruker D8 Advance diffractometer equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å), a Ge(111) incident beam monochromator and an M-Braun linear position-sensitive detector. The sample was sprinkled onto an amorphous SiO_2 disk and data collected over a 2θ range of 15–140 °

with a step size of 0.0144 ° and a measurement time of 7.5 s per step. The measurement was repeated three times on the same sample and data from all three scans summed.

The diffraction pattern was indexed using a locally modified version of ITO.⁶ This gave a tetragonal unit cell with $a = 5.4458$ Å and $c = 10.0643$ Å (figure of merit 148). Systematic absences in the powder pattern were consistent with body centring and a satisfactory structure solution was obtained using direct methods in the EXPO package in space group $I42m$.⁷ The trial structure was refined using the Rietveld method within the TOPAS program.⁸ A minor $(\text{NH}_4)_2\text{SO}_4$ impurity was introduced as a second phase. In final cycles of refinement a total of 45 parameters were refined (2 scale factors, 18 coefficients of a Chebychev polynomial to describe the smoothly varying background, sample displacement, 6 pseudo Voigt peak profile parameters, cell parameters, atomic coordinates and isotropic temperature factors) and R -factors of $wRp = 6.87\%$ and $R_{\text{Bragg}} = 5.02\%$ were obtained. Cell parameters determined using an internal silicon ($a = 5.4312$ Å) standard were $a = 5.44427(8)$ Å and $c = 10.0687(2)$ Å. Fractional atomic coordinates are given in Table 1 and the Rietveld fit is shown in Fig. 1.

The structure of body centred Cu_2WS_4 ($I\text{-Cu}_2\text{WS}_4$) is closely related to that of the primitive material previously characterised by Pruss ($P\text{-Cu}_2\text{WS}_4$) and is shown in Fig. 2. It contains layers of edge-sharing WS_4 and CuS_4 tetrahedra separated by a van der Waals gap. These layers can be viewed as being related to the anti PbO structure, with $\frac{3}{4}$ of the available tetrahedral sites between S layers occupied by metal atoms in an ordered fashion. The intralayer structure in both P and I forms is similar, however in the new polymorph alternate planes of metal atoms are offset by half a unit cell in the a and b directions. This means that tungsten atoms in one layer lie above metal vacancies in adjacent layers, minimising electrostatic interactions between them. This gives a unit cell with body centring and a c axis double the length of the primitive form. To the best of our

Table 1 Fractional atomic coordinates for $I\text{-Cu}_2\text{WS}_4$

Atom	x	y	z	$U_{\text{iso}}/\text{Å}^2$
W	0.0000	0.0000	0.0000	0.0397 (3)
Cu	0.5000	0.0000	0.0000	0.0477 (6)
S	0.2381 (3)	0.2381 (3)	0.1189 (6)	0.0418 (6)

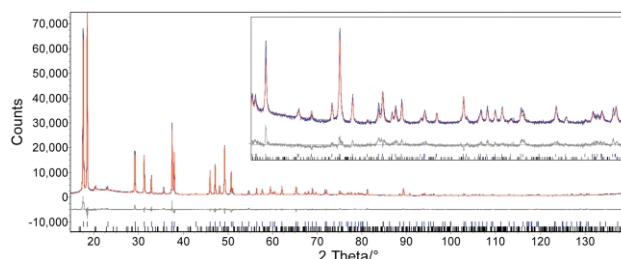


Fig. 1 Rietveld refinement of $I\text{-Cu}_2\text{WS}_4$ showing observed (blue), calculated (red) and difference (grey) plots. The insert shows the region between 80 and 120° 2θ .

knowledge I - Cu_2WS_4 is the first material to be reported with this structure type.

Bond lengths and angles for I - Cu_2WS_4 are given in Table 2. There are small but significant differences between the values determined here and those reported for P - Cu_2WS_4 . Pruss reported W–S bond lengths of 2.354 Å, whilst bond lengths in the new polymorph (2.189(2) Å), are significantly shorter and nearer to the 2.177 Å bond length observed in isolated WS_4^{2-} tetrahedra.⁹ The Cu–S bond length (2.268(1) Å) is also slightly shorter than that observed by Pruss (2.356 Å). The WS_4 tetrahedra show slight deviation from tetrahedral geometry, the range of S–W–S of bond angles is 107.4° to 113.8°. There is more distortion in the CuS_4 tetrahedra, with S–Cu–S angles ranging from 102.4° to 116.3°. Both the W–S and the Cu–S bond lengths are within the range found for S atoms bridging a tungsten and two copper atoms in polynuclear clusters found in the Cambridge Structural Database.¹⁰

The ratio of P to I - Cu_2WS_4 formed varies with synthesis temperature. At temperatures at or below 135 °C the material formed is the primitive polymorph, above 135 °C the body centred polymorph is formed. This ratio is presumably governed largely by the pressure during synthesis. We estimate that at 135 °C the pressure in the autoclave is 150 kPa, whilst by

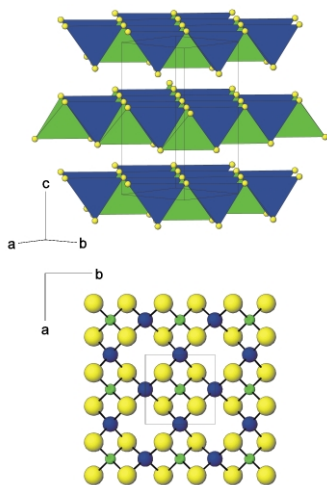


Fig. 2 The structure of body centred I - Cu_2WS_4 viewed down the 110 direction (top) and c axis (bottom). WS_4 tetrahedra are shown in green, CuS_4 tetrahedra are shown in blue and the sulfur atoms are shown in yellow.

Table 2 Bond lengths and bond angles for I - Cu_2WS_4

Bond lengths/Å	Bond angles/°
W–S 2.189(2)	S–W–S 107.4(1)
Cu–S 2.268(1)	S–W–S 113.8(1)
	S–Cu–S 116.3(1)
	S–Cu–S 102.1(1)
	S–Cu–S 110.2(1)

200 °C it has increased to ~500 kPa. The smaller volume per formula unit (149 Å³) of the I form over the P form (154 Å³) suggests the reason for its formation at higher pressure. Presumably the reduction in the interlayer distance ($\Delta a P \rightarrow I = +0.4\%$; $\Delta c P \rightarrow I = -3.8\%$) is sufficient that the body centred cation arrangement, with larger W–W separations, becomes more stable. Interlayer W–W, W–Cu and Cu–Cu distances in the I and P polymorph are 5.723/5.234, 5.034/5.234 and 6.338/5.234 Å respectively. In some later experiments it was possible to form the I centred polymorph at 135 °C, presumably due to seeding of the bomb causing preferential growth of the I polymorph. This suggests that the balance between stabilities of the two polymorphs is subtle.

It is also possible to convert a pre-prepared sample of P - Cu_2WS_4 to the body centred form by heating in a 50 : 50 mixture of butyronitrile and N,N -dimethylformamide at 200 °C for 12 h. Attempts to drive the conversion by application of pressure at room temperature or by heating a pellet under vacuum at 200 °C were not successful. Partial conversion can, however, be achieved by heating a pellet of the material to 200 °C under ~700 kPa of N_2 for 12 h. These observations suggest that the conversion from the P polymorph to the I polymorph requires both elevated temperature and pressure and that whilst it can occur as a solid state process, it is more facile in the presence of solvent.

We have recently been made aware of a newly discovered and as yet unregistered mineral containing a ratio of Cu to W close to 2 : 1, which shows an I centred cell similar to that determined here.¹¹ It is intriguing to speculate that the hydrothermal route has mimicked geological conditions in producing the high pressure form of Cu_2WS_4 .

In summary, a new layered form of Cu_2WS_4 has been synthesised using solvanothermal methods and a new polymorph of the material has been discovered at elevated temperature and pressure. The structure of this polymorph has been solved from powder X-ray diffraction data. Its chemistry and properties are under investigation.

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