

Electronic Supporting Information

Precursor driven one pot synthesis of Wurtzite and Chalcopyrite CuFeS₂

*Prashant Kumar, Sitharaman Uma and Rajamani Nagarajan**

Materials Chemistry Group, Department of Chemistry,

University of Delhi, Delhi-110007INDIA

Experimental Section

I. Synthesis of Copper (I) thiourea precursor [Cu₄(tu)₉](NO₃)₄·4H₂O

[Cu₄(tu)₉](NO₃)₄·4H₂O was prepared following the procedure reported by Bott *et al.*¹ 3.0 g (12.4 *mmol*) Cu(NO₃)₂·3H₂O (Kemphasol, 98 %) was dissolved in 10 mL of double distilled water and the solution was slowly added to a solution containing 2.4 g (31.0 *mmol*) of thiourea (SRL, 98 %) in 10 mL of double distilled water. The solution was stirred for few hours and allowed to evaporate at room temperature. The product was recrystallized and characterized using elemental analysis, IR, Raman spectroscopy and thermogravimetric analysis techniques. (Fig. S11-S13)

II. Synthesis of CuFeS₂

3.12 g (2.5 *mmol*) of freshly prepared [Cu₄(tu)₉](NO₃)₄·4H₂O) was reacted with 1.6224 g (10 *mmol*) FeCl₃ (Thomas Baker, A.R. Grade) and 2 g (5 *mmol*) of Fe₂(SO₄)₃·xH₂O (Alfa Aesar, A.R. Grade) separately under the same refluxing conditions. The weighed solids were mixed magnetically over a hot plate to which 50 mL of Ethyleneglycol (Merck, A. R. Grade) was added. Refluxing was carried out for 1.5 h followed by separating the product by centrifugation. The black colored solid obtained was washed several times with CS₂, ethanol, and double distilled water and dried naturally (average yield of 80 %).

IV. Characterization

The powder X-ray diffraction (PXRD) patterns were collected using High resolution D8 Discover Bruker diffractometer, equipped with point detector (scintillation counter), employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) obtained through a göbel mirror with a scan rate of 1.0 second/step and step size 0.02° at 298 K as well as using PANalytical's Empyrean diffractometer, equipped with PIXcel-3D detector, employing Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with scan step size of 0.01313° and 63.495 seconds/step. UV-Visible absorbance spectra of the samples were recorded by dispersing them in *n*-hexane using a Thermo Scientific UV-Visible spectrophotometer (Model Evolution 300). Raman spectra of the samples, in compact form, were collected using a Renishaw spectrophotometer equipped with a microscope having laser wavelength of 514 nm. Photoluminescence (PL) measurements were performed on a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer at room temperature. The morphology of the final products was examined from the SEM images obtained using FESEM, FEI Quanta 200F microscope. Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED) were carried out on an FEI Technai G² 20 electron microscope operating at 200 kV. The FT-IR spectrum was collected using Perkin-Elmer 2000 Fourier-Transform infrared spectrometer in the range $400\text{-}4000 \text{ cm}^{-1}$ using KBr disks. Thermogravimetric (TG) analysis was carried out using Shimadzu simultaneous TG/DTA thermal analyzer (DTG-60). The samples were heated at the rate of $10^\circ\text{C}/\text{min}$. The concentration of copper and iron in the samples was determined using a Shimadzu, AA-6300 atomic absorption spectrometer by subjecting the solution of them in dilute nitric acid yielding a ratio of 1:0.85 for the copper: iron in the samples. The chemical analysis of chalcopyrite and wurtzite structured CuFeS₂ has also been carried out combining gravimetric and titrimetric procedures.² 0.1014 g of the sample was dissolved in 10 mL of 1:1 nitric acid producing a blue colored solution indicative of the oxidation of copper to +II state. To this solution, 2 mL of 10 % barium nitrate solution was

added. A white colored precipitate appeared instantly on the addition of the barium nitrate solution. It was digested over the water bath for 3 h. The precipitate was filtered through the standard G4 crucible and dried overnight at 110°C. From the weight of the barium sulphate, the amount of sulphur present in the sample was determined. The filtrate from the above experiments was made up to 100 mL. Iodometric titration of the filtrate using starch as the indicator yielded the total concentration of copper and iron. By masking the iron with ammonium fluoride, the amount of copper was determined.^{2 (b)} The concentration of iron was determined from the difference between these two set of experiments. The amount of Cu, Fe and S in the sample was determined to be 34 %, 31.9 % and 34 % by weight respectively.

References:

1. R. C. Bott, G. A. Bowmaker, C.A. Davis, G.A. Hope, and B. E. Jones, *Inorg. Chem.* 1998, **37**, 651-657.
2. (a) *VOGEL'S Text Book of Quantitative Chemical Analysis*, 6th, ed.; J. Mendham, R. C. Denney, J. D. Barnes, M. Thomas, and B. Sivashankar, Eds.; Pearson Education: New Delhi, **2007**.
(b) J. Agterbenbos and E. J. V. Tellinghen, *Talanta*, 1961, **8**, 532-534.

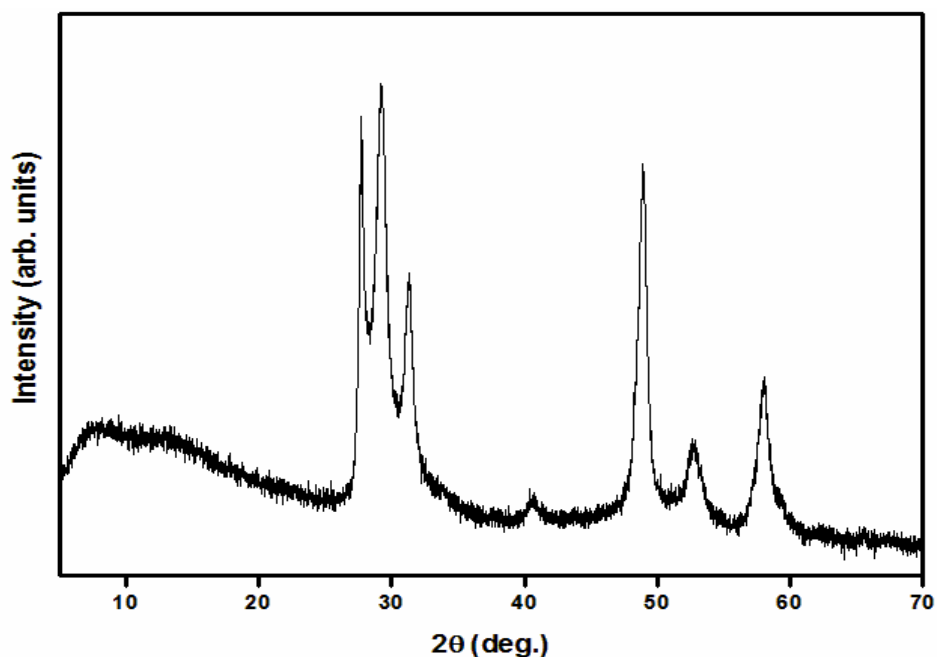


Fig. S1 Powder X-ray diffraction (PXRD) pattern of the product obtained by refluxing $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ in ethylene glycol for 1.5 h.

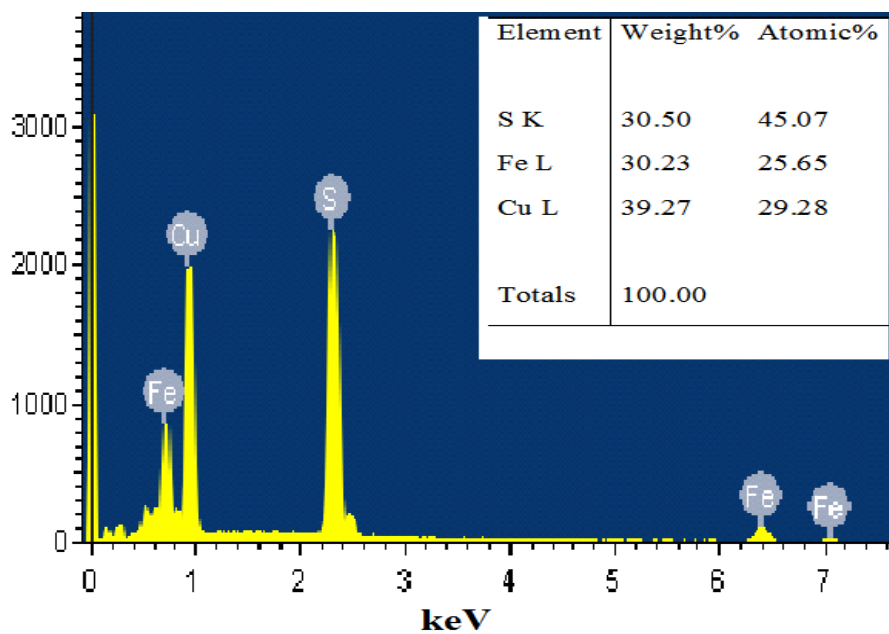


Fig. S2 EDX analysis of the product obtained by refluxing $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ in ethyleneglycol for 1.5 h.

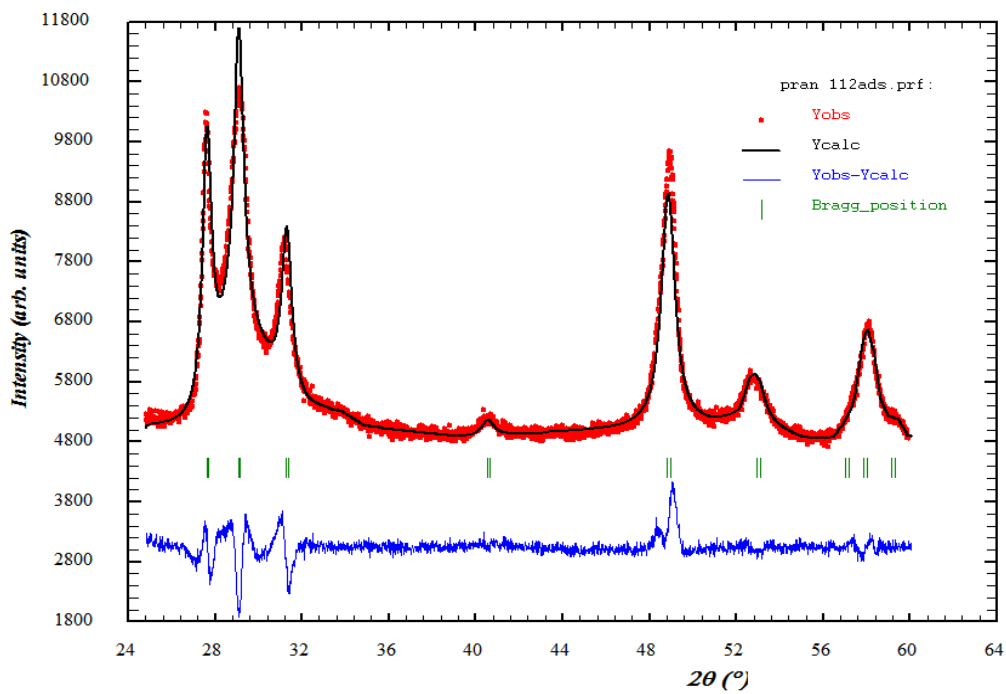


Fig. S3 Rietveld refinement plot of WZ- CuFeS₂. The observed, calculated (profile matching), and difference profiles given respectively as red, black, and blue lines.

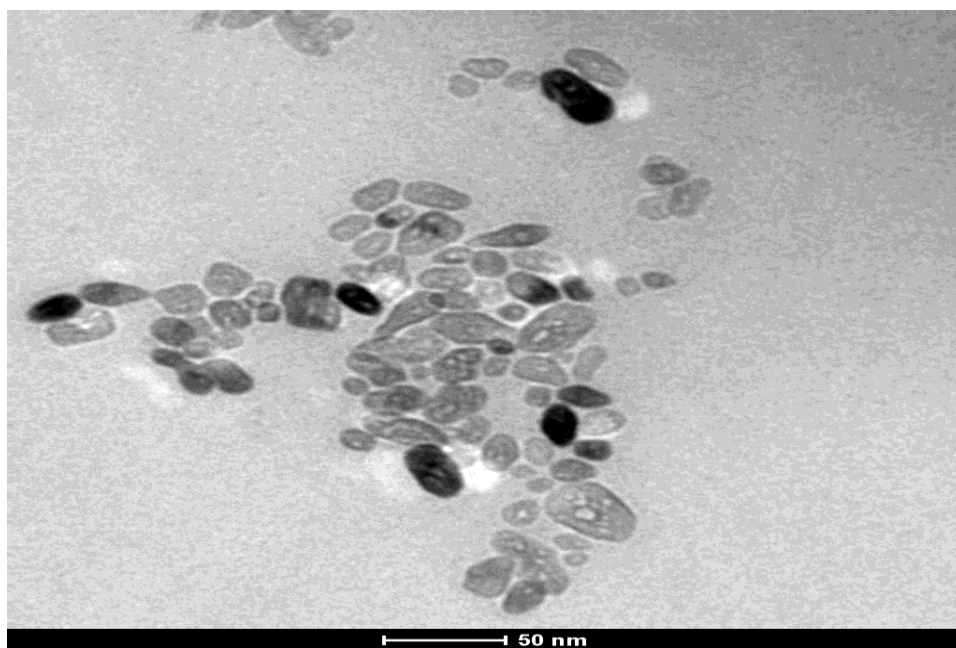


Fig.S4 TEM image of WZ-CuFeS₂

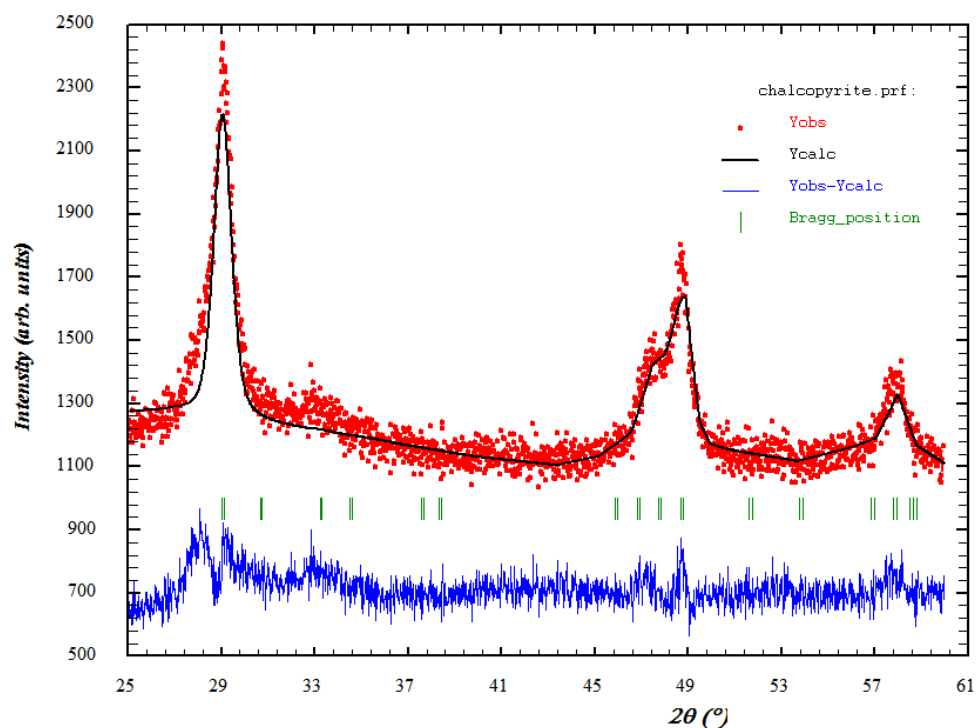


Fig. S5 Rietveld refinement plot of the PXRD pattern of chalcopyrite CuFeS_2 . The observed, calculated (profile matching), and difference profiles given respectively as red, black, and blue lines.

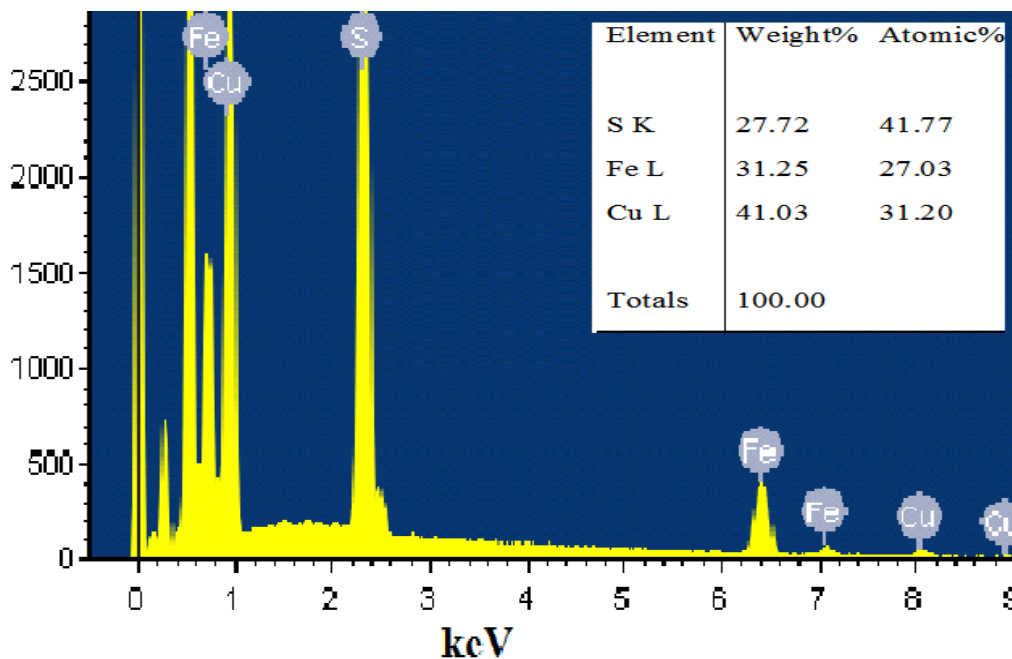


Fig. S6 EDX analysis of the product obtained by refluxing $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ with FeCl_3 in ethyleneglycol for 1.5 h.

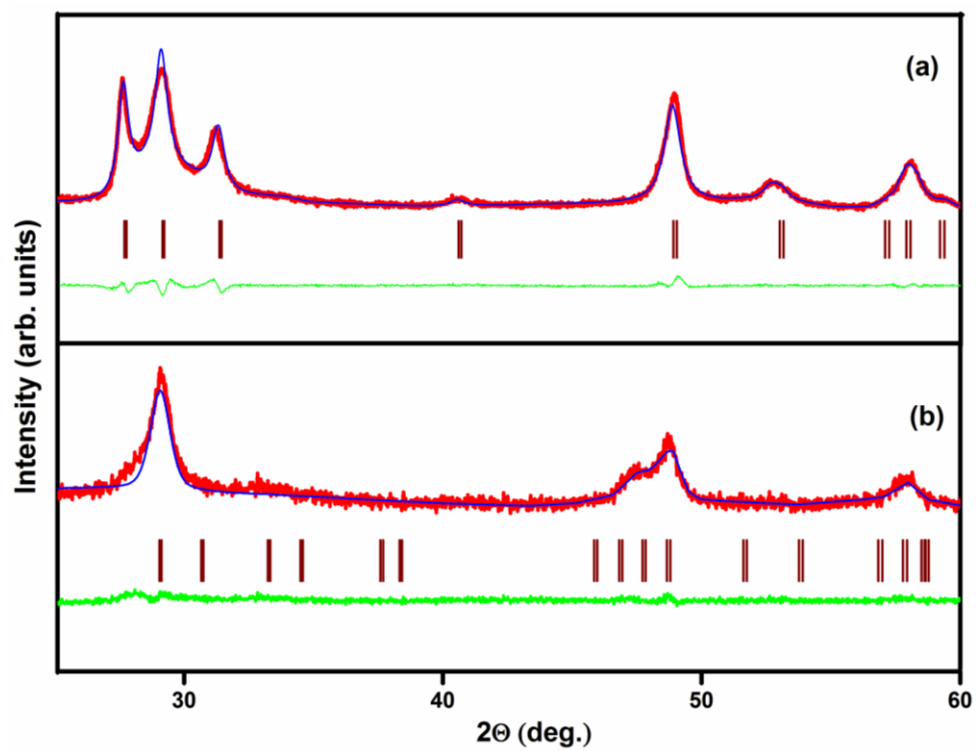


Fig. S7 Comparison of Rietveld fit of the PXRD patterns of WZ and CH-CuFeS₂.

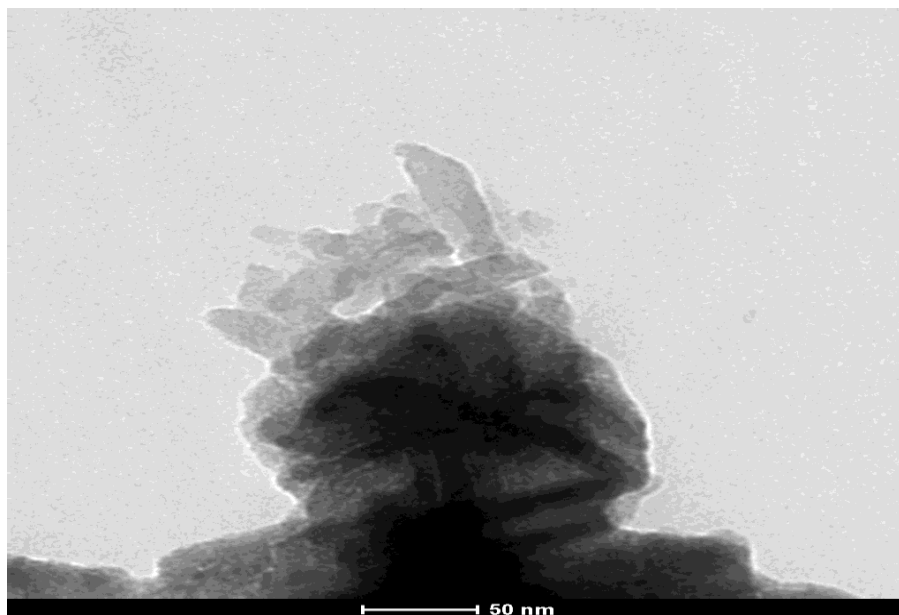


Fig. S8 TEM image of CH-CuFeS₂.

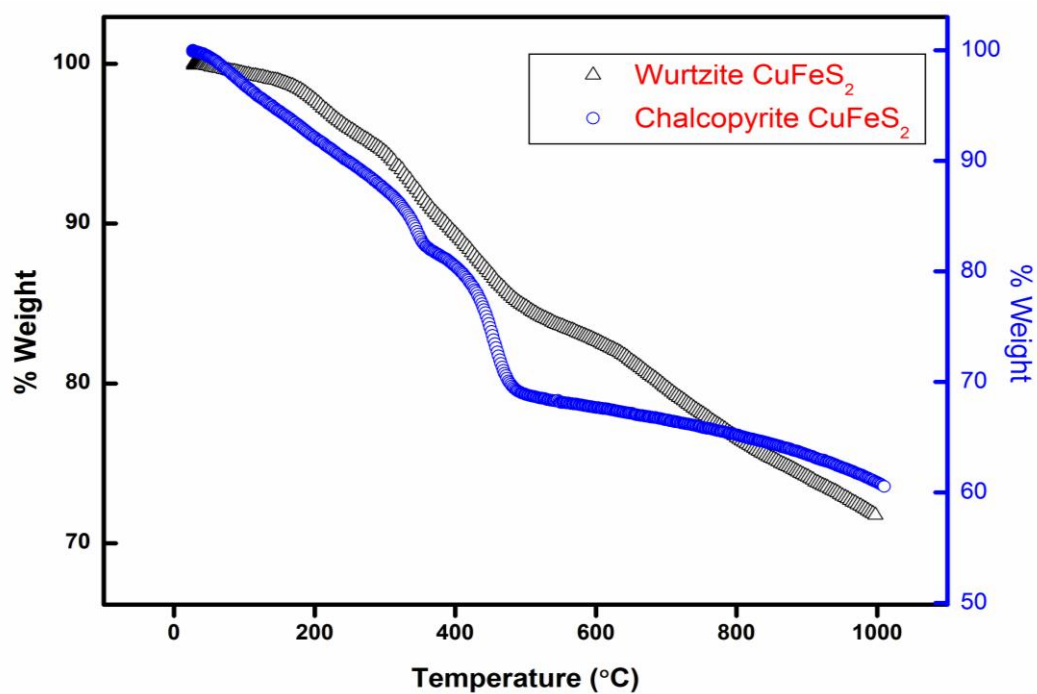


Fig.S9 TGA traces of wurtzite and chalcopyrite CuFeS₂ in nitrogen atmosphere.

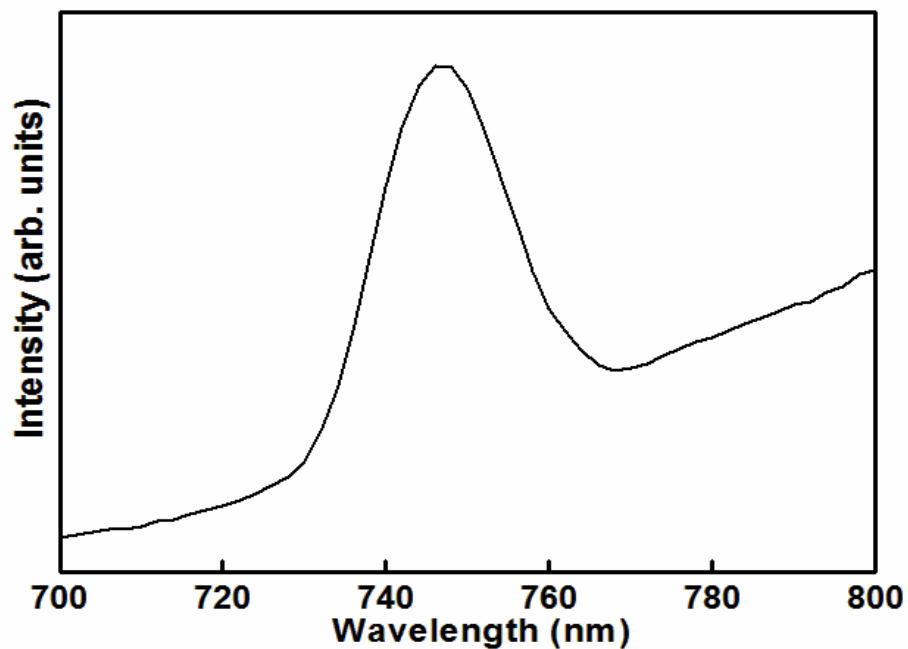


Fig. S10 Photoluminescence spectrum of chalcopyrite structured CuFeS₂ obtained by exciting it with $\lambda = 500$ nm.

Table S1 Crystallographic data and structure refinement parameters of wurtzite structured CuFeS₂.

Empirical formula	CuFeS ₂
Crystal system	Hexagonal
Space group	P6 ₃ mc (186)
Lattice parameter <i>a</i> (Å)	3.726 (3)
Lattice parameter <i>c</i> (Å)	6.132 (4)
Volume <i>V</i> (Å ³)	73.744 (1)
λ (Å)	1.5418
2 θ range (°)	25-60
2 θ increment	0.01313°
No. of reflections	9
R _p	20.7
R _{wp}	17.8
R _{exp}	0.032(7)
R _B	3.142
Global user-weighted (χ^2)	3.77(3)

Table S2 Position coordinates of various atoms in representative wurtzite structured CuFeS₂.
The B factor for all the atoms (S, Cu and Fe) were set to 0.25 as a reasonable value.

Atom	Site	S.O.F	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>_{iso}
S1	<i>2b</i>	1.0	0.3333	0.6666	0.0	0.25
Cu	<i>2b</i>	0.5	0.3333	0.6666	0.384(5)	0.25
Fe	<i>2b</i>	0.5	0.3333	0.6666	0.384(5)	0.25

Table S3 Crystallographic data and structure refinement parameters of Chalcopyrite structured CuFeS₂.

Empirical formula	CuFeS ₂
Crystal system	Tetragonal
Space group	I-42 _d (122)
Lattice parameter <i>a</i> (Å)	5.386 (5)
Lattice parameter <i>c</i> (Å)	10.391 (1)
Volume <i>V</i> (Å ³)	301.500(2)
λ (Å)	1.5418
2 θ range (°)	25-60
Scan rate	1.2 s/step
Step size	0.02°
No. of reflections	15
R _p	76.7
R _{wp}	38.1
R _{exp}	26.5
R _B	26.3
Global user-weighted (χ^2)	2.07(3)

Table S4 Position coordinates of various atoms in representative chalcopyrite structured CuFeS_2 .
The B factor for all the atoms (S, Cu and Fe) were set to 0.25 as a reasonable value.

Atom	Site	S.O.F	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{iso}</i>
S	<i>8d</i>	1.0	0.2695(4)	0.25	0.125	0.25
Cu	<i>4a</i>	1.0	0	0	0	0.25
Fe	<i>4b</i>	1.0	0	0	0.5	0.25

Table S5 Comparison of the observed 2θ , d value, height and relative intensity for the synthesized wurtzite and chalcopyrite CuFeS_2 .

Wurtzite CuFeS_2				Chalcopyrite CuFeS_2			
2θ	d (Å)	Height	Relative intensity	2θ	d (Å)	Height	Relative intensity
27.71	3.2196	10233.9	96.4	29.064	3.0722	2429.9	100
29.23	3.0552	10619.6	100	32.001	2.7966	1351.0	55.6
31.35	2.8531	8104.6	76.3	32.811	2.7294	1417.0	58.3
40.81	2.2111	5142.1	48.4	47.518	1.9133	1514.6	62.3
48.92	1.8615	9570.4	90.1	48.681	1.8703	1791.3	73.7
52.80	1.7336	5867.3	55.2	57.708	1.5974	1403.4	57.8
58.06	1.5885	6715.9	63.2	58.151	1.5863	1423.1	58.6

Characterizations of the precursor $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$

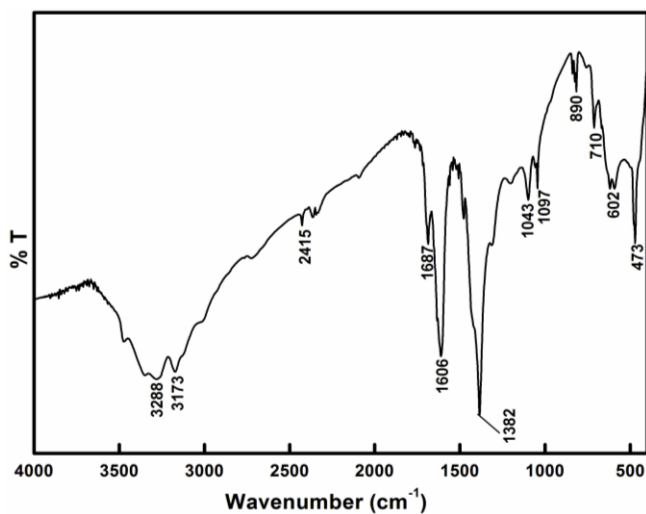


Fig. S11 FT-IR spectrum of $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$

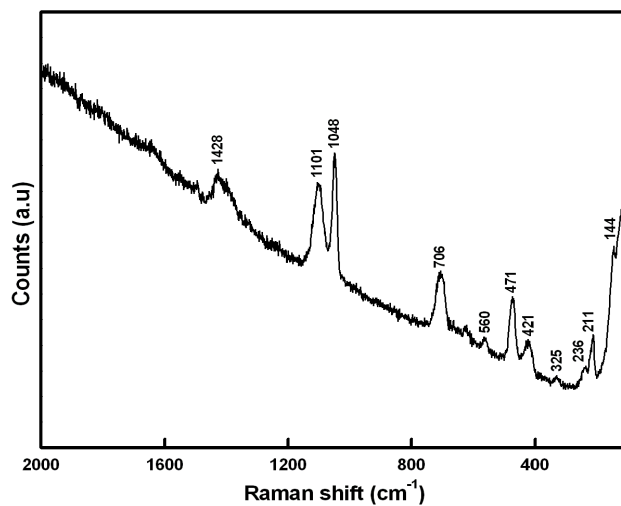


Fig. S12 Raman spectrum of $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$

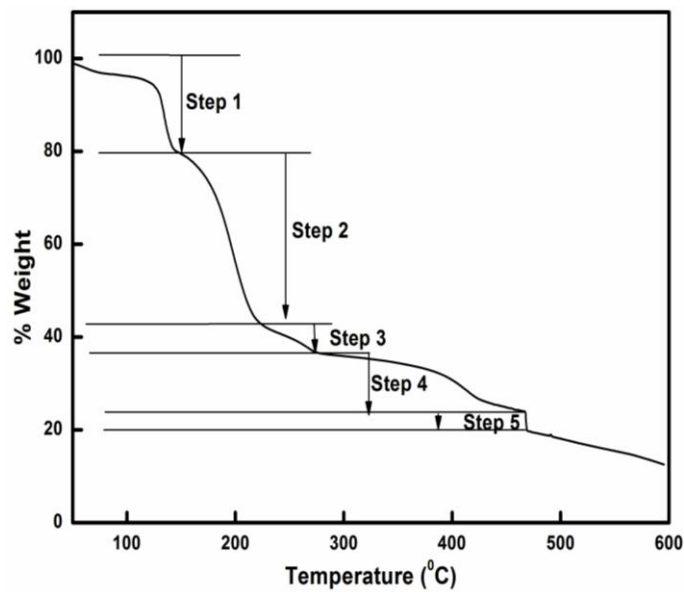


Fig. S13 TGA trace of $[\text{Cu}_4(\text{tu})_9](\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ in air.