Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

New Organometallic Single-Source Precursors for $CuGaS_2$ – Polytypism in Gallite Nanocrystals Obtained by Thermolysis

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1. Rietveld refinements of XRPD pattern obtained from the residues of **4** and **5**

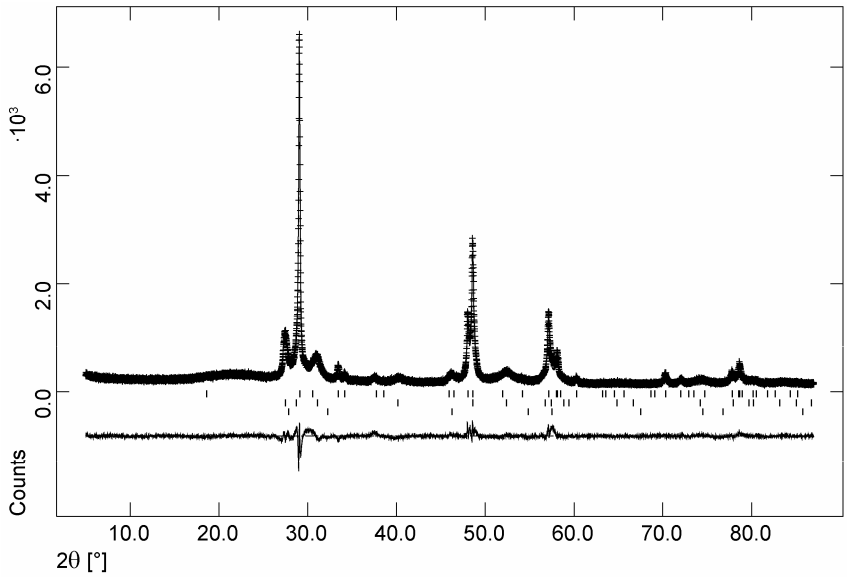

Fig. S1 Rietveld refinement (wR_p = 0.0893, R_p = 0.0689, $R(F^2)$ = 0.0652) of the powder pattern obtained from the residue of **4** heated to T_{max} = 400 °C (heating rate ca. 15 K/min, hold at T_{max} for 4 h) in a quartz tube. Observed (+) and calculated intensities, reflection positions of tetragonal $CuGaS_2$ (first row, 48.55(9) %, a = 535.24(2) pm, c = 1048.60(6) pm), hexagonal $CuGaS_2$ (second row, 42.3(2) %, a = 374.34(3) pm, c = 621.7(2) pm) and cubic $Cu_{2-x}S$ (third row, 9.1(4) %, a = 554.8(2) pm) are displayed.

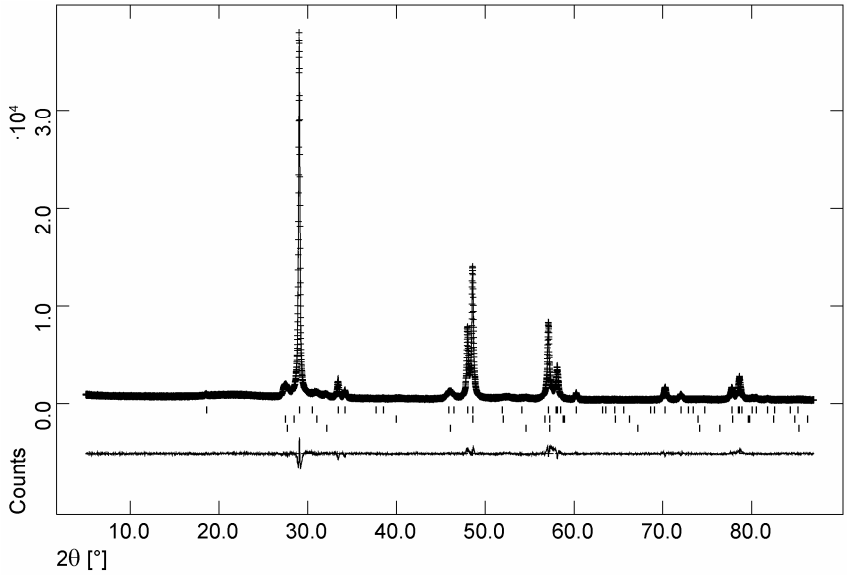

Fig. S2 Rietveld refinement (wR_p = 0.0783, R_p = 0.0557, $R(F^2)$ = 0.0737) of the powder pattern obtained from the residue of **4** heated to T_{max} = 600 °C (heating rate ca. 15 K/min, hold at T_{max} for 1 h) in a quartz tube. Observed (+) and calculated intensities, reflection positions of tetragonal $CuGaS_2$ (first row, 73.85(4) %, a = 535.586(9) pm, c = 1048.24(2) pm), hexagonal $CuGaS_2$ (second row, 12.0(1) %, a = 374.54(4) pm, c = 626.5(7) pm) and cubic $Cu_{2-x}S$ (third row, 14.1(4) %, a = 557.00(7) pm) are displayed.

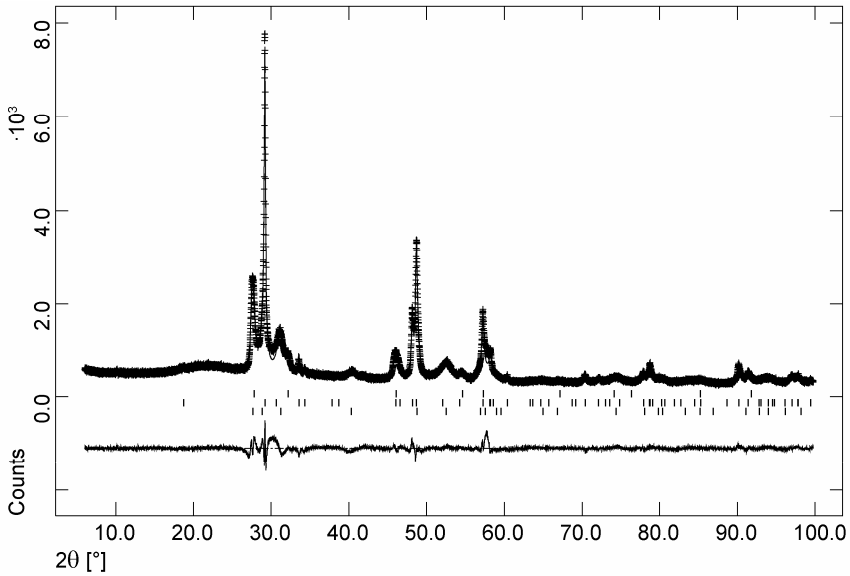

Fig. S3 Rietveld refinement (wR_p = 0.0699, R_p = 0.0512, $R(F^2)$ = 0.0716) of the powder pattern obtained from the residue of **4** heated to T_{max} = 600 °C on a thermobalance (heating rate 10 K/min). Observed (+) and calculated intensities, reflection positions of cubic $Cu_{2-x}S$ (first row, 19.6(3) %, a = 557.99(5) pm), tetragonal $CuGaS_2$ (second row, 32.7(1) %, a = 535.30(2) pm, c = 1048.68(6) pm) and hexagonal $CuGaS_2$ (third row, 47.7(1) %, a = 374.23(2) pm, c = 621.2(1) pm) are displayed.

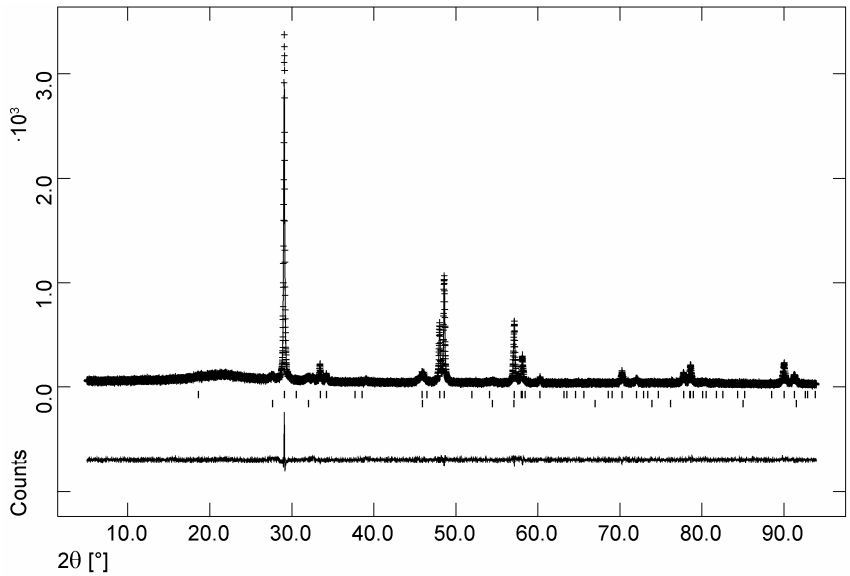

Fig. S4 Rietveld refinement (wR_p = 0.1252, R_p = 0.0969, $R(F^2)$ = 0.0495) of the powder pattern obtained from the residue of **4** heated to T_{max} = 900 °C on a thermobalance (heating rate 10 K/min). Observed (+) and calculated intensities, reflection positions of tetragonal $CuGaS_2$ (first row, 76.0(1) %, a = 535.56(3) pm, c = 1048.17(6) pm) and cubic $Cu_{2-x}S$ (second row, 24.0(5) %, a = 558.58(9) pm) are displayed.

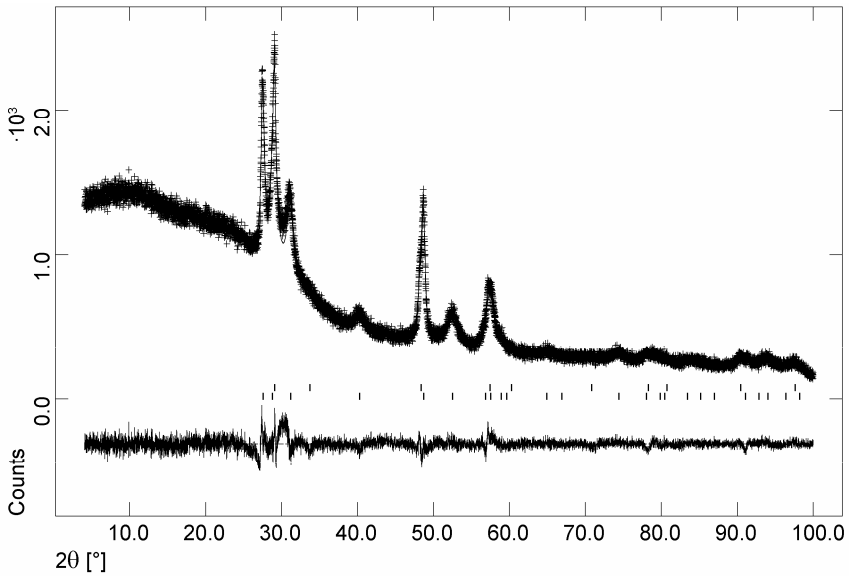

Fig. S5 Rietveld refinement (wR_p = 0.0501, R_p = 0.0375, $R(F^2)$ = 0.0680) of the powder pattern obtained from the residue of **5** heated to T_{max} = 600 °C on a thermobalance (heating rate 10 K/min). Observed (+) and calculated intensities, reflection positions of cubic $CuGaS_2$ (first row, 31.7(2) %, a = 531.98(7) pm) and hexagonal $CuGaS_2$ (second row, 68.3(2) %, a = 373.97(4) pm, c = 620.1(2) pm) are displayed.

2. TEM images and EDX measurements of the residue of **5** heated to T_{max} = 400 °C in a quartz tube.

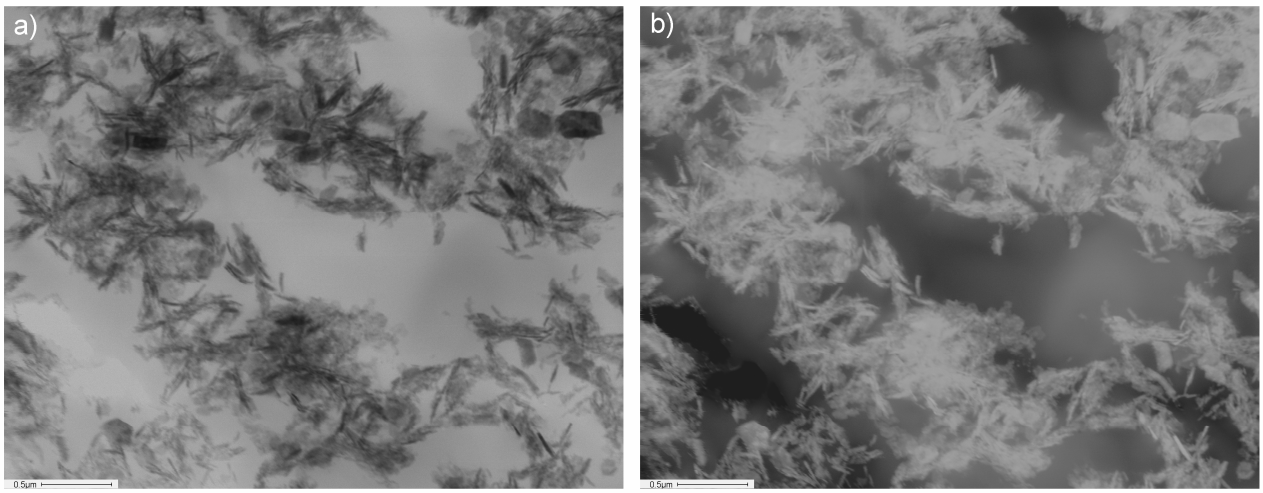

Fig. S6 Scanning TEM of $CuGaS_2$ embedded into epoxy. a) bright-field image; b) dark-field image.

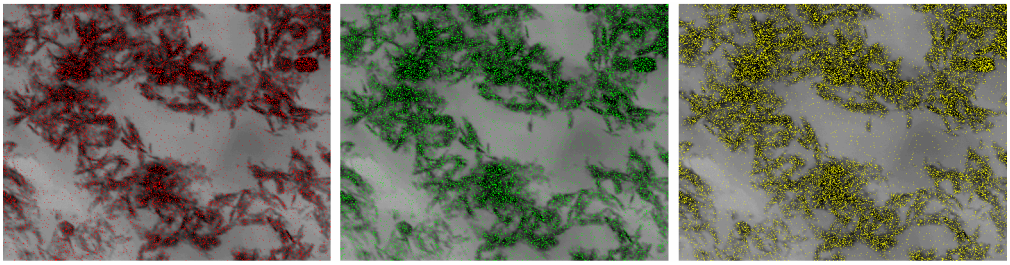

Fig. S7 Scanning TEM of $CuGaS_2$ embedded into epoxy and distribution of Cu (red), Ga (green) and S (yellow) determined by EDX mapping.

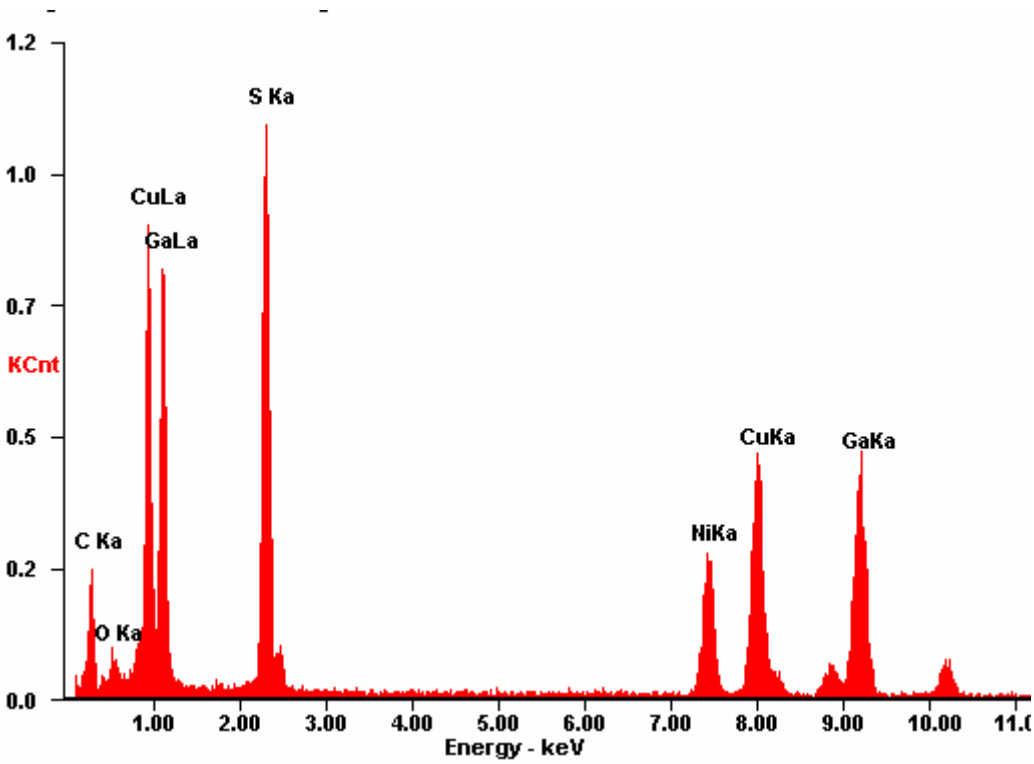

Fig. S8 EDX spectrum of crystal 1 (compare Fig. 8 in the article). Sample tilt 15° during EDX analysis. The Ni-peak stems from the sample holder ring.

Table S1 Chemical composition of crystals 1, 2 and 3 (compare Fig. 8 in the article) as determined by EDX.

element	crystal 1	crystal 2	crystal 3	average
copper	25.2 at%	24.1 at%	24.8 at%	24.7 at%
gallium	25.1 at%	25.1 at%	24.8 at%	25.0 at%
sulphur	49.7 at%	50.8 at%	50.4 at%	50.3 at%

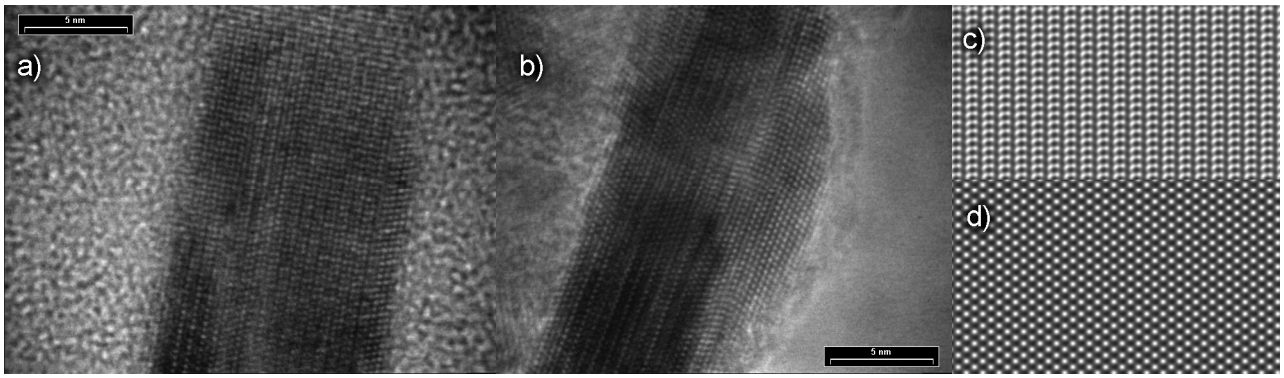

Fig. S9 a) and b) HRTEM lattice images of $CuGaS_2$ crystals. Beam direction perpendicular to [0001]. Simulated HRTEM images for c) hexagonal and d) tetragonal $CuGaS_2$, respectively.