

Synthesis of Microscale Particles of Ternary Sulphides *via* an Adjusted Polyol-Route

Stephan Blöß and Martin Jansen

Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Stuttgart

Reprint requests to Prof. Dr. M. Jansen. E-mail: m.jansen@fkf.mpg.de

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The chalcocuprites Roquesite (CuInS_2), Mohite (Cu_2SnS_3) and Famatinite (Cu_3SbS_4) have been synthesised from metal chlorides and thiourea in form of microscale particles *via* an adjusted polyol-route. The samples were characterised by means of SEM/EDX and XRD. The as prepared chalcocuprites were found to crystallise in metastable, cation disordered cubic structures. The particle sizes vary in the range of 0.2 to 3 micrometers. Thermal annealing transforms the samples into the thermodynamically stable polymorphs with ordered cationic substructures.

Key words: Polyol-Route, Chalcocuprite, Copper

Introduction

In recent years the family of ternary chalcocuprites has attracted much attention because of their important potential applications as non-linear optical or piezoelectric materials [1], in photovoltaic cells [2] or as semiconductors [3]. The polyol-method, as developed by Fievet [4], has proven its high applicability in the synthesis of small metallic particles under gentle conditions. Adapting this method by adding water offers the opportunity to produce small particles of binary and ternary oxides [5]. In addition, replacing water by thiourea opens a new access to metal sulphides. The synthesis of the group 12 sulphides [6] represents a further example demonstrating the flexibility of the polyol-route. Up to date, however, this approach has been restricted to binary sulphides; ternary sulphides, that do not readily precipitate from solution, are not yet accessible by this route. Our work shows, that the adjusted polyol-method has a high potential for establishing a new synthesis route also to multinary sulphides. By applying an adjusted polyol-route, we have synthesised submicron particles of ternary chalcocuprites, *i.e.* CuInS_2 , Cu_2SnS_3 and Cu_3SbS_4 .

Experimental Section

Synthesis

All starting chemicals were used as purchased: anhydrous copper(II) chloride (*Merck*, > 98%), antimony(III) chloride (*Merck*, > 99%), thiourea (*Merck*, > 99%), tin(IV) chloride

(*Riedel-de-Haën*, > 99%) and indium(III) chloride (*Heraeus*, > 99%). Diethylene glycol (DEG, *Merck*, > 99%) was distilled at 4,5 mbar and 117 °C, for further removal of water.

Microscale ternary copper sulphides (CuInS_2 , Cu_2SnS_3 and Cu_3SbS_4) have been synthesised under nearly the same reaction conditions as described for oxides [5]. Roquesite (CuInS_2) was synthesised by mixing 2 mmol of CuCl_2 and 2 mmol of InCl_3 , Mohite (Cu_2SnS_3), or Famatinite (Cu_3SbS_4), by mixing 2,5 mmol of CuCl_2 and 2,5 mmol of SnCl_4 , and SbCl_3 , respectively, with an excess of thiourea (5 mmol) in 50 ml of DEG. The mixtures were heated for 1,5 h at 175 °C. In order to prevent the formation of the binary phase Covellite (CuS), one has to use an excess of the main group metal in the case of tin and antimony.

The as prepared suspensions were allowed to cool down to room temperature. Afterwards, these suspensions were centrifuged and the solids resuspended twice in ethanol *via* ultrasonic irradiation, and centrifuged again in order to remove surface-adsorbed DEG. Finally, the solids were dried at room temperature *in vacuo* (10^{-3} mbar).

Characterisation

SEM-studies were performed on a *Philips* XL 30 TMP (tungsten cathode, 25 kV) with an integrated EDAX-EDX-system (S-UTW-Si(Li)-detector; res. < 135 eV for Mn- K_α / 1000 cps). In order to achieve a better resolution of the SEM-images the samples were sputtered with gold ($\approx 100 \text{ \AA}$). The EDX-measurements were performed with a free working distance (FWD) of 10 mm.

X-ray powder diffraction data were collected at room temperature in transmission geometry (STOE StadiP, linear PSD, curved Ge(111)-monochromator, Mo- K_α) in the range

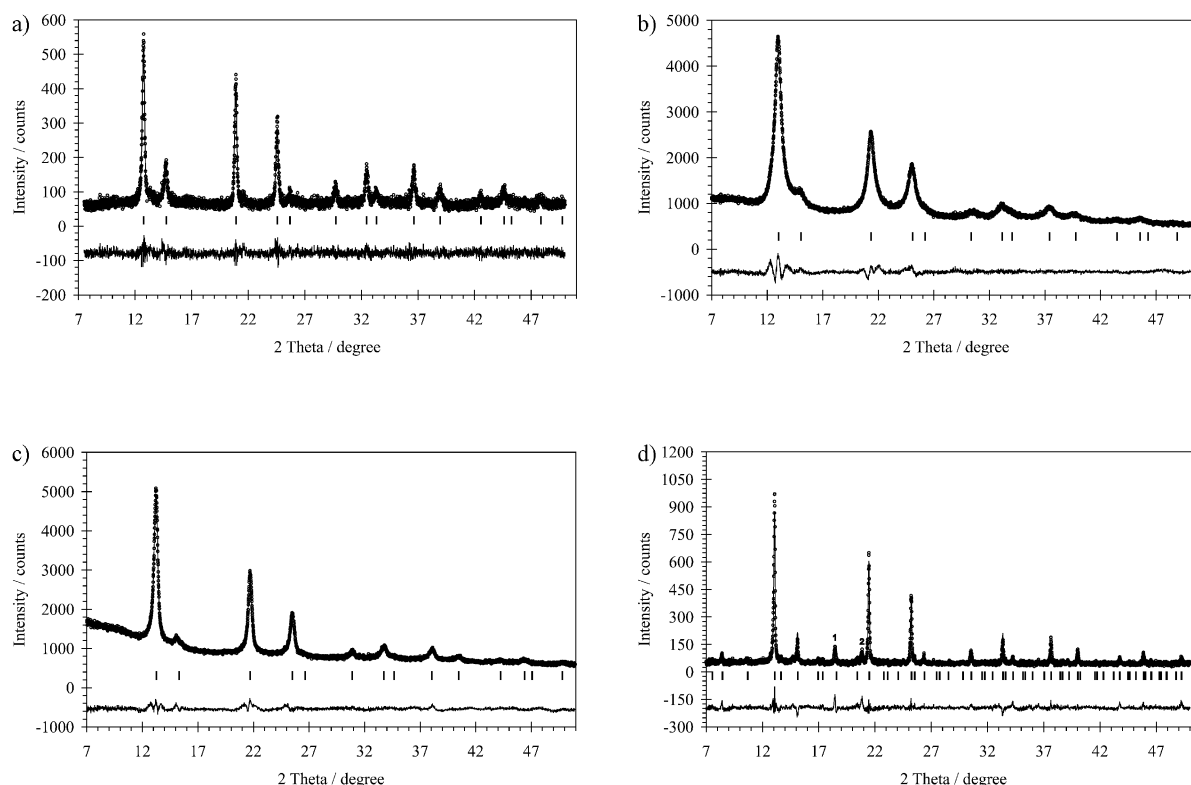


Fig. 1. Powder diffraction patterns: a) CuInS_2 (circles: observed, line: calculated), Bragg positions (assuming a disordered structure in space group $F\bar{4}3m$) and difference plot; b) Cu_2SnS_3 (circles: observed, line: calculated), Bragg positions (assuming a disordered structure in space group $F\bar{4}3m$) and difference plot; c) Cu_3SbS_4 (circles: observed, line: calculated), Bragg positions (assuming a disordered structure in space group $F\bar{4}3m$) and difference plot; d) Cu_3SbS_4 after annealing (circles: observed, line: calculated), Bragg positions (assuming an ordered structure in space group $\bar{A}2m$) and difference plot; (1: Byproduct CuS ; 2: Tungsten from colimator-foil).

Table 1. Crystallite and particle sizes determined by XRD and SEM.

	Crystallite size / nm (Debye-Scherrer equation)	Particle size / nm (average in SEM)
CuInS_2	14.9	200–250
Cu_2SnS_3	3.4	750–850
Cu_3SbS_4	6.9	1700–2100
After annealing	29.8	3000–3300

$7^\circ \leq 2\theta \leq 50^\circ$ in steps of 0.1° . The samples were placed between two Mylar-films or in capillaries (Lindemann Glass, Hilgenberg GmbH, 0.3 mm). Zero-point corrections were applied referring to silicon as an external standard. The lattice parameters were refined by using Le-Bail-fits.

Results and Discussion

For the first time, ternary sulphides have been prepared *via* the polyol-route. The versatility of the pro-

cess has been demonstrated on CuInS_2 (Roquesite), Cu_2SnS_3 (Mohite) and Cu_3SbS_4 (Famatinite). The powder diffraction patterns of all samples obtained can be indexed, based on a cubic crystal system assuming the sphalerite (space group $F\bar{4}3m$) structure type. Thus the cation positions are occupied randomly by copper and indium, tin, and antimony, respectively. The powder diffraction patterns exhibit exclusively the peaks of the pure compounds (see Figures 1 a–c). Quantitative EDX studies confirm purity.

As indicated by the SEM images, the particles of all samples exhibit a more or less spherical shape (see Figures 2 a–c). In the case of Roquesite they are spherical to ellipsoidal and agglomerate to bigger needles and plates. The spherical particles of Famatinite are composed of small needles and resemble sand roses. The Mohite particles resemble solid spheres

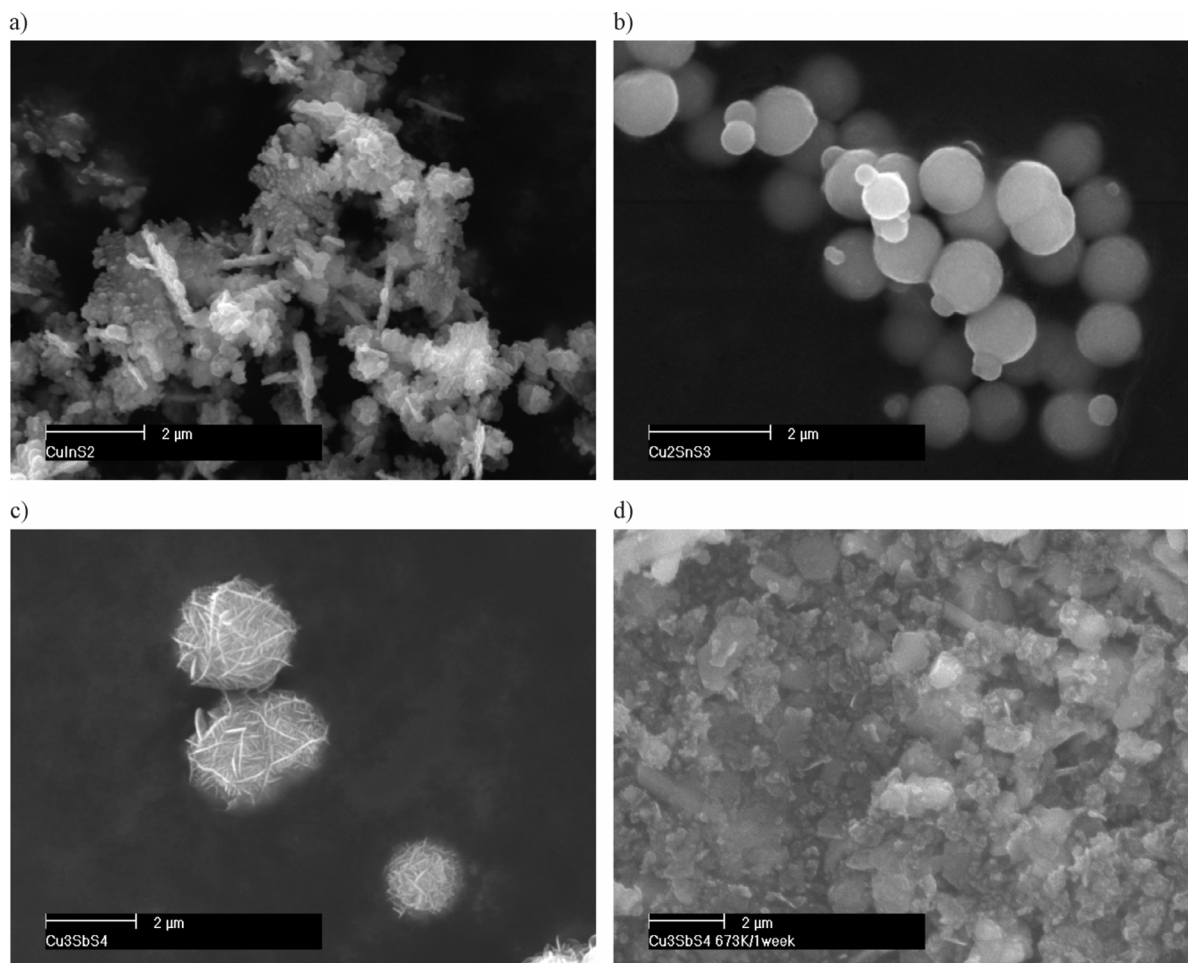


Fig. 2. SEM images: a) CuInS_2 ; b) Cu_2SnS_3 ; c) Cu_3SbS_4 ; d) Cu_3SbS_4 after annealing.

with a small variation of size. The annealed samples exhibit morphologies corresponding to bulk materials with grain sizes of one to three micrometers (see Figure 2 d).

Mean crystallite sizes were determined from FWHM of powder diffraction patterns using the Debye-Scherrer equation. The values obtained are by one to two orders of magnitude smaller than the diameters observed in the SEM images (see Table 1). Thus, in the latter case, agglomerates have been visualized.

Conventionally prepared Roquesite is reported to crystallise in the tetragonal space group $I\bar{4}2d$ [1, 7, 8], Mohite cubic in $F\bar{4}3m$ [11], tetragonal in $I\bar{4}2m$ [9] and monoclinic in Cc [10], respectively, and Famatinite tetragonal in $I\bar{4}2m$ [12–15], orthorhombic in

$Pmn2_1$ [12] and cubic in $Fm\bar{3}m$ [16], respectively. The observed powder diffraction patterns of pristine samples do not give any indication for lattice symmetries lower than cubic. The average crystallite size leads to fairly broad peaks. Thus, the reflections of the lower symmetry structure alternatives might be too weak to be recognized against the background. Also no splitting of cubic peak positions has been observed. After annealing the Famatinite sample in glass tubes under inert gas conditions at temperatures up to 400 °C for one week, an XRD pattern corresponding to the $I\bar{4}2m$ structure type had developed (see Figure 1 d). The refined cell parameters (Mo- $K\alpha$, Le-Bail-fit) of the annealed sample are in reasonable agreement with those found by Garin and Parthé [14] previously (see Table 2).

	Space group	a / Å	c / Å	V _{cell} / Å ³	Ref.
CuInS ₂ (Roquesite)	<i>F</i> $\bar{4}3m$	5.5294(4)		169.06(2)	this work
Literature	<i>I</i> $\bar{4}2d$	5.52279(7)	11.13295(22)	339.6	[1]
Cu ₂ SnS ₃ (Mohite)	<i>F</i> $\bar{4}3m$	5.4190(6)		159.13(3)	this work
Literature	<i>F</i> $\bar{4}3m$	5.43		160.103	[11]
	<i>I</i> $\bar{4}2m$	5.413(1)	10.824(1)	317.15	[9]
Cu ₃ SbS ₄ (Famatinite)	<i>F</i> $\bar{4}3m$	5.3286(4)		151.30(2)	this work
Literature	<i>Fm</i> $\bar{3}m$	10.74		1238.833	[16]
After annealing	<i>I</i> $\bar{4}2m$	5.3831(4)	10.7722(9)	312.15(4)	this work
Literature	<i>I</i> $\bar{4}2m$	5.385(1)	10.754(2)	311.84(2)	[14]

Table 2. Lattice parameters and cell volumes of the prepared chalcocuprites.

Conclusion

We have developed an adjusted polyol-route which is an efficient approach to produce pure ternary sulphides at moderate temperatures. Annealing at 400 °C

transforms the metastable, disordered sphalerite type structures into the stable, ordered structures. This route appears to be a new and economic preparative pathway to multinary sulphides.

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