Synthesis and stability of single-phase chalcopyrite – a potential reference material for key investigations in chemistry and metallurgical engineering

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Supporting information

Table S1: Results of Mößbauer spectroscopy for the compositions between 48 and 50.5 at% S in the reactant mixtures. Bornite and pyrite are given as references. Line width (WID), Isomer shift (ISO), quadrupole splitting (QUA) and hyperfine field (B) are reported relative to an α-Fe reference at room temperature. Parameters are given with fit uncertainties (unc.). Numbers written in bold were fixed before fitting. Abbreviations: cpy = chalcopyrite, tal = talnakhite, py = pyrite, bo = bornite, isocub = isocubanite; sext = sextet, doub = doublet.

at% S	sub-band	phase	portion / at%	WID / mm s^{-1}	unc.	ISO / mm s^{-1}	unc.	QUA / mm s^{-1}	unc.	B / T	unc.	X^2 Fit
48.00	sext1	cpy	54.8	0.40	0.01	0.27	0.01	-0.03	0.01	34.7	0.1	2.3
	doub1	bo	0.4	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
	doub2	isocub	6.7	**0.60**	-	**0.50**	-	**0.90**	-	-	-	
	doub3			**0.60**	-	**0.50**	-	**0.50**	-	-	-	
	sext2	tal	38.0	**1.00**	-	0.43	0.04	-0.16	0.03	28.5	0.1	
48.50	sext1	cpy	69.6	0.34	0.01	0.26	0.01	0.00	0.01	35.1	0.1	5.7
	doub1	bo	0.5	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
	doub2	isocub	5.9	**0.60**	-	**0.50**	-	**0.90**	-	-	-	
	doub3			**0.60**	-	**0.50**	-	**0.50**	-	-	-	
	sext2	tal	24.1	**1.00**	-	0.43	0.02	-0.15	0.04	28.8	0.1	
49.00	sext1	cpy	81.2	0.32	0.01	0.26	0.01	0.00	0.01	35.3	0.1	2.8
	doub1	bo	0.4	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
	doub2	isocub	3.5	**0.60**	-	**0.50**	-	**0.90**	-	-	-	
	doub3			**0.60**	-	**0.50**	-	**0.50**	-	-	-	
	sext2	tal	14.8	**1.00**	-	0.42	0.03	-0.06	0.06	30.0	0.2	
49.25	sext1	cpy	81.4	0.31	0.01	0.25	0.01	0.00	0.01	35.2	0.1	2.6
	doub1	bo	0.4	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
	doub2	isocub	4.2	**0.60**	-	**0.50**	-	**0.90**	-	-	-	
	doub3			**0.60**	-	**0.50**	-	**0.50**	-	-	-	
	sext2	tal	14.0	**1.00**	-	0.28	0.03	0.03	0.05	32.5	0.4	
49.50	sext1	cpy	98.8	0.30	0.01	0.25	0.01	0.00	0.01	35.7	0.1	1.4
	doub1	bo	1.2	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
49.62	sext1	cpy	100	0.31	0.01	0.25	0.01	0.00	0.01	35.5	0.1	1.2
49.76	sext1	cpy	100	0.29	0.01	0.25	0.01	0.00	0.01	35.8	0.1	1.2
49.88	sext1	cpy	96.2	0.28	0.01	0.25	0.01	0.00	0.01	35.7	0.1	1.0
	doub1	py	3.4	**0.40**	-	**0.31**	-	**0.61**	-	-	-	
	doub2	bo	0.4	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
49.91	sext1	cpy	93.6	0.29	0.01	0.25	0.01	0.00	0.01	35.8	0.1	1.0
	doub1	py	6.2	0.35	0.07	0.31	0.02	0.60	0.05	-	-	
	doub2	bo	0.1	**0.40**	-	**0.47**	-	**0.18**	-	-	-	

at% S	sub-band	phase	portion / at%	WID / mm s^{-1}	unc.	ISO / mm s^{-1}	unc.	QUA / mm s^{-1}	unc.	B / T	unc.	X^2 Fit
50.01	sext1	cpy	86.5	0.29	0.01	0.25	0.01	0.00	0.01	35.8	0.1	1.1
	doub1	py	13.2	0.44	0.03	0.31	0.01	0.61	0.02	-	-	
	doub2	bo	0.3	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
50.51	sext1	cpy	80.8	0.28	0.01	0.25	0.01	0.00	0.01	35.7	0.1	1.2
	doub1	py	17.8	0.35	0.02	0.31	0.01	0.61	0.01	-	-	
	doub2	bo	1.4	**0.40**	-	**0.47**	-	**0.18**	-	-	-	
bornite	doub	bo	100	0.37	0.04	0.47	0.01	0.18	0.03	-	-	1.1
pyrite	doub	py	100	0.37	0.01	0.31	0.01	0.63	0.01	-	-	2.2

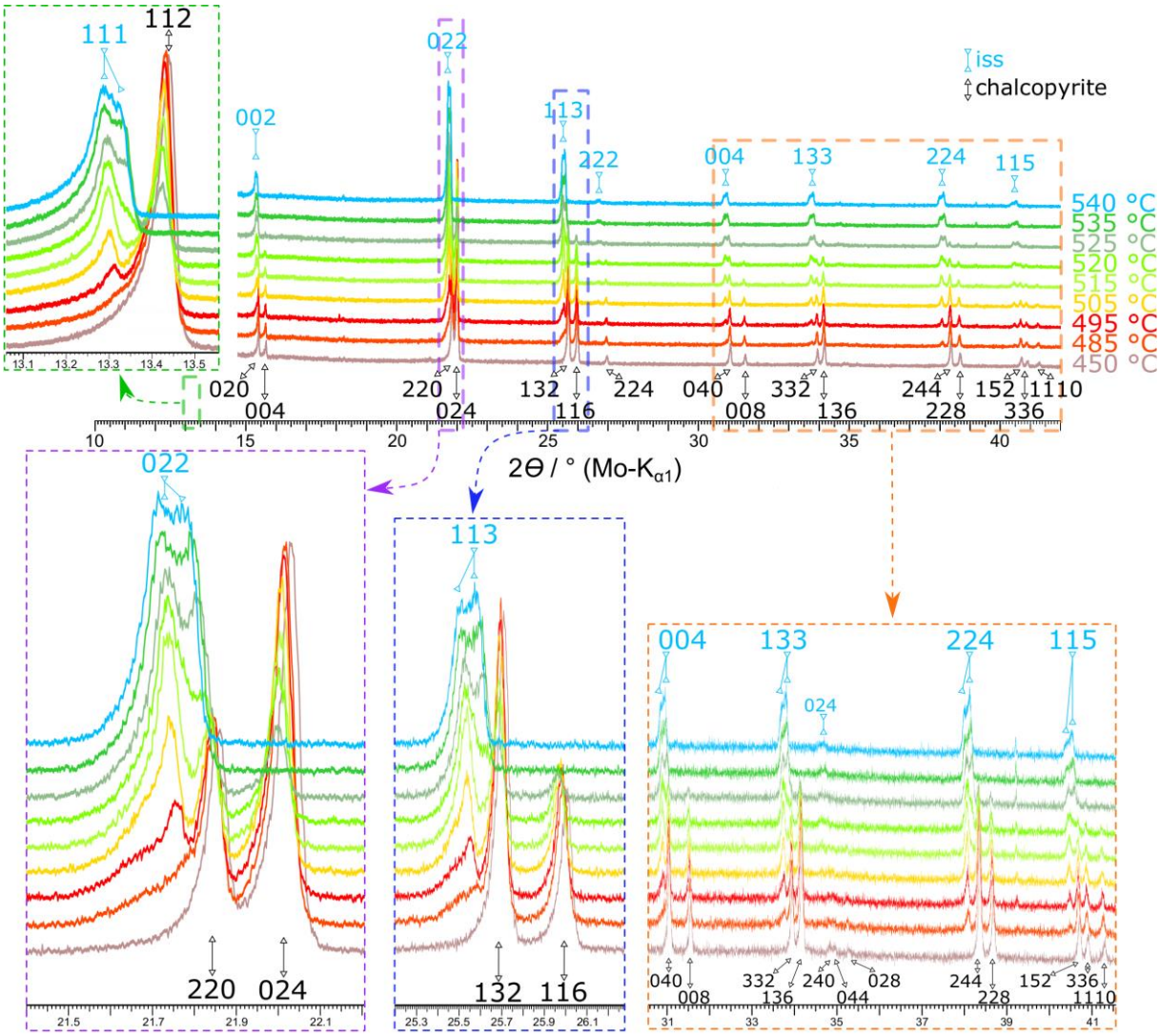

Figure S1: Detailed version of Figure 9: stacked XRPD pattern of the 49.76 at% S composition at different temperatures. Reflections for the tetragonal chalcopyrite cell are indexed black, the cubic high-temperature phase is indexed in light blue.

Crystallographic data for chalcopyrite's high temperature intermediate solid solution (obtained after heating the 49.50 at% S sample) are given in Table S2 and were submitted to the CCDC database under the deposition number 2033752.

Table S2: Crystallographic and Rietveld refinement data of chalcopyrite's high temperature intermediate solid solutions at 545 °C (samples synthesised at 450 °C with 49.50 at% S).

substance name	copper iron sulfide
sum formula	$Cu_{0.5}Fe_{0.5}S$
molecular weight / g mol^{-1}	91.76
temperature / °C	545
space group	*F*$\bar{4}$3*m* (216)
Z	4
a / Å	5.3261(1)
V / Å³	151.089(3)
ρ_{calc} / g cm^{-3}	4.03
wavelength / Å	0.7093
R-p / % *	5.91
R-*w*p / % *	7.59
R-*F*² / % *	4.56
R-exp / % *	6.18
GOF *	1.23
starting angle / ° 2ϑ	10
final angle / ° 2ϑ	75
step width / ° 2ϑ	0.003
time/scan / h	12
no. of variables	20

Atom	**Wyck.**	**Site**	**S.O.F.**	***x* / *a***	***y* / *b***	***z* / *c***	**B / Å²**
Cu(1)	4*c*	-43m	0.5	1/4	1/4	1/4	3.4(1)
Fe(1)	4*c*	-43m	0.5	1/4	1/4	1/4	3.4(1)
S(1)	4*a*	-43m	1	0	0	0	3.4(1)

* *R*-p, *R*-*w*p, *R*-*F*², R-*exp* and GOF as defined in TOPAS (Bruker AXS)

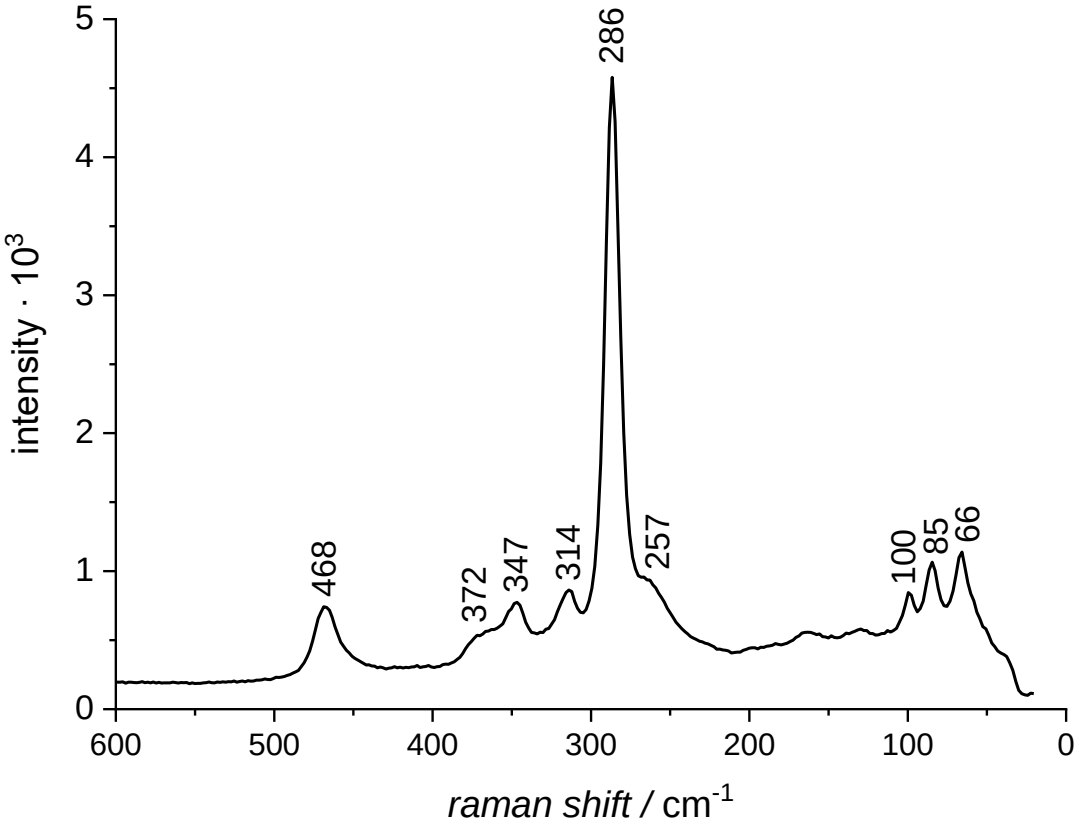

Figure S2: A typical Raman spectrum for single-phase chalcopyrite which is in good agreement with the literature.[I-V] Measurements were carried out using a HORIBA Scientific XploRA-PLUS Raman Microscope, with a laser operating at 532 nm using the LabSpec 6 - Horiba Scientific software. The displayed measurement was recorded with an 1800(450-850nm) grid and an object lens x100_VIS_LWD.

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