Characterization of FeS_2 pyrite microcrystals synthesized in different flux media

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Supporting information

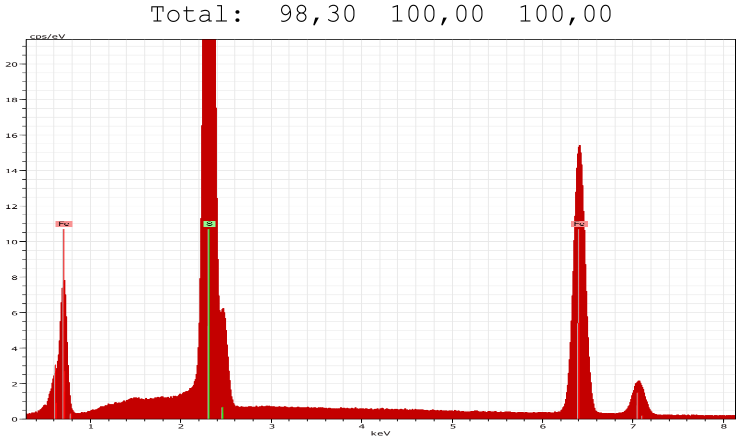
Energy dispersive X-ray spectroscopy (EDX) data

The chemical composition of FeS_2 powder crystals was determined by energy dispersive X-ray spectroscopy (EDX) using Bruker Esprit 1.8 system. EDX data of the pyrite materials considered in this manuscript:

FeS_2 synthesized with no flux (3N FeS precursor)

Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Iron	K-series	46,27	47,07	33,80	1,3
Sulfur	K-series	52,03	52,93	66,20	1,9
	Total:	98,30	100,00	100,00	

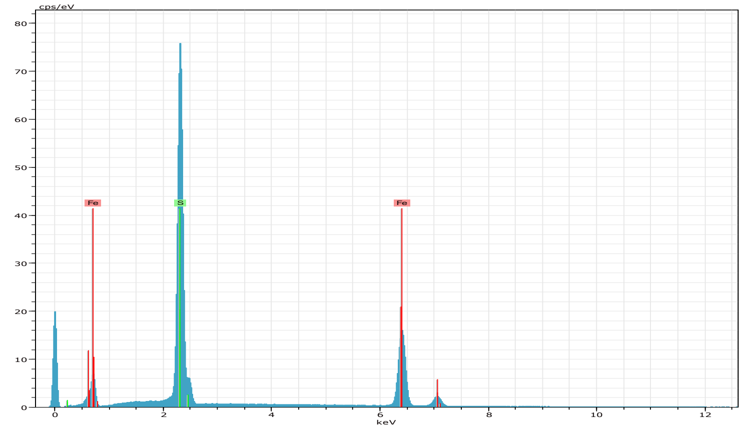


FeS_2 synthesized with potassium iodide flux (3N FeS precursor)

Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Iron	K-series	46,98	46,96	33,70	1,3

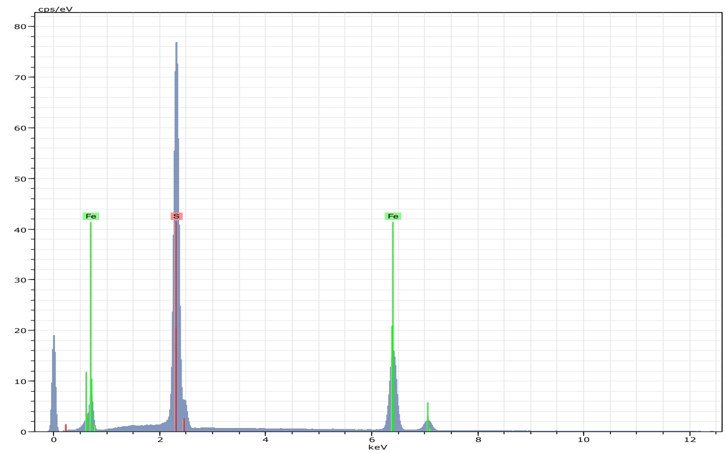
Sulfur	K-series	53,07	53,04	66,30	1,9
	Total:	100,05	100,00	100,00	



FeS_2 synthesized with lithium iodide (3N FeS precursor)

Spectrum:

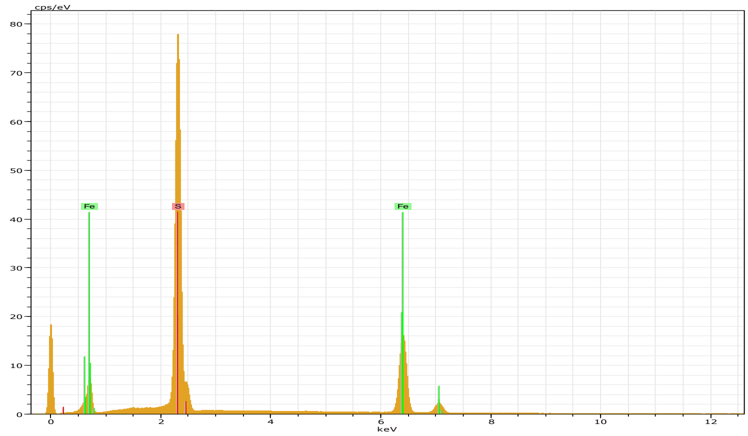
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Sulfur	K-series	50,88	52,85	66,12	1,8
Iron	K-series	45,40	47,15	33,88	1,2
	Total:	96,28	100,00	100,00	



FeS_2 synthesized with cesium iodide (3N FeS precursor)

Spectrum:

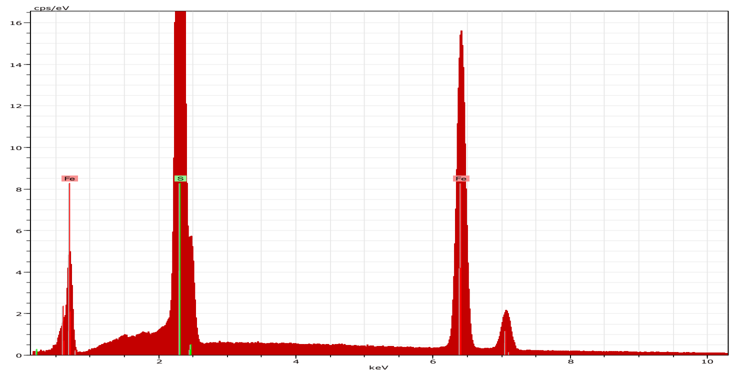
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Sulfur	K-series	50,77	53,08	66,33	1,8
Iron	K-series	44,89	46,92	33,67	1,2
	Total:	95,66	100,00	100,00	



FeS_2 synthesized with sodium polysulfide (3N FeS precursor)

Spectrum:

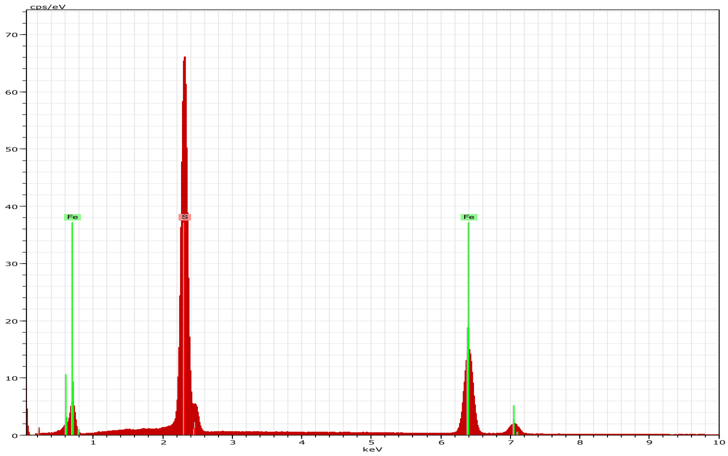
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Iron	K-series	45,80	46,49	33,28	1,2
Sulfur	K-series	52,73	53,51	66,72	1,9
	Total:	98,53	100,00	100,00	



FeS_2 recrystallized with 4x potassium iodide (3N FeS precursor)

Spectrum:

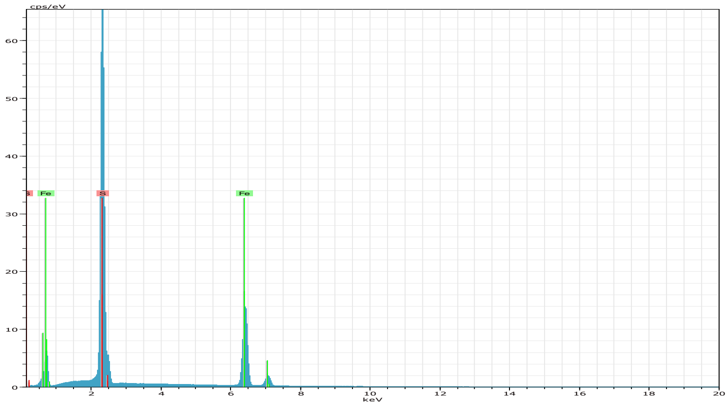
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Sulfur	K-series	51,08	52,95	66,21	1,9
Iron	K-series	45,39	47,05	33,79	1,2
	Total:	96,47	100,00	100,00	



FeS_2 recrystallized with 10x potassium iodide (3N FeS precursor)

Spectrum:

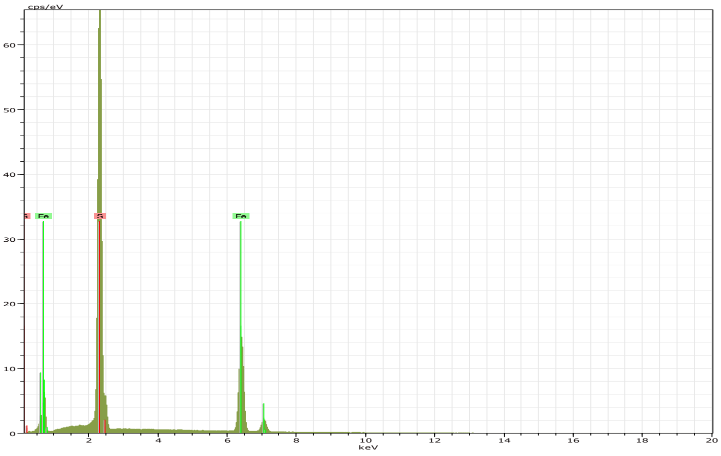
Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Sulfur	K-series	51,28	52,82	66,10	1,9
Iron	K-series	45,80	47,18	33,90	1,2
	Total:	97,08	100,00	100,00	



FeS_2 synthesized with potassium iodide flux (4N FeS precursor)

Spectrum:

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Sulfur	K-series	50,54	52,86	66,13	1,8
Iron	K-series	45,08	47,14	33,87	1,2
	Total:	95,62	100,00	100,00	


cps/eV
60
50
40
30
20
10
0
Fe
S
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2
4
6
8
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12
14
16
18
20
keV

Impurities in sulfur

Impurities reported in the 5N sulfur that is used in the experiments of this manuscript are obtained from the chemical data sheet.

Table 1. Impurities in the sulfur precursor as stated by the supplier.

Element	**Mass%**
Aluminum	$2\text{-}4*10^{-5}$
Bitumen	$2*10^{-3}$
Gallium	$1*10^{-6}$
Iron	$1\text{-}3*10^{-5}$
Indium	$1*10^{-6}$
Cobalt	$3*10^{-6}$
Manganese	$1*10^{-6}$
Vask	$2\text{-}4*10^{-6}$
Molybdenum	$1*10^{-6}$
Arsenic	$5*10^{-6}$
Nickel	$1\text{-}3*10^{-6}$
Tin	$1*10^{-6}$
Lead	$2\text{-}4*10^{-6}$
Selenium	$2*10^{-4}$
Silver	$1*10^{-6}$
Tellurium	$5*10^{-6}$
Phosphorus	$1*10^{-5}$
Chloride	$2*10^{-5}$

Supporting data from the inductively coupled plasma mass spectroscopy (ICPMS) analyses

Impurities concentrations in the pyrite crystals were determined by the inductively coupled plasma mass spectroscopy (ICPMS). 0.1 g of sample material was dissolved with Anton Paar Multiwave PRO microwave digestion system in NXF100 vessels (PTFE/TFM liner) using an acid mixture of 8 mL of HNO_3 (65%; Carl Roth, ROTIPURAN® Supra) and 2 mL of H_2O_2 (30%; Carl Roth, ROTIPURAN®). Samples were digested at 230 °C and pressures between 45-50 bar. After dissolution, the samples were diluted with 2% HNO_3 solution. Elemental impurities were measured using Agilent 8800 ICPMS/MS. ^{7}Li, ^{127}I and ^{133}Cs were measured in NoGas mode and ^{23}Na, ^{39}K, ^{40}Ca, ^{59}Co using He collision gas on mass. ^{52}Cr, ^{60}Ni, ^{63}Cu were measured in O_2 mode as $M^{16}O^{+}$ reaction products. Indium was used as internal standard element added online via mixing T and NIST 1643f, which were used as references for quality control.

The FeS presursors used in the syntheses were analyzed by ICPMS and the results in mg/kg were obtained from the measurements:

Material	*Li mg/kg*	*Cr mg/kg*	*Cu mg/kg*	*Co mg/kg*	*Ni mg/kg*	*Cs mg/kg*
FeS 3N precursor	1,92	185,11	22,57	119,99	223,65	0,02
FeS 4N precursor	5,72	216,22	333,28	29,01	203,61	0,31

The calculated results in at/cm^3 were used in the Discussion of the article.

Material	*Li at/cm^3*	*Cr at/cm^3*	*Cu at/cm^3*	*Co at/cm^3*	*Ni at/cm^3*	*Cs at/cm^3*
FeS 3N precursor	8,3* 10^{17}	1*10^{19}	1,1*10^{18}	6,1*10^{18}	1,2*10^{19}	4,5*10^{14}
FeS 4N precursor	2,5*10^{18}	1,3*10^{19}	1,6*10^{19}	1,5*10^{18}	1*10^{19}	7*10^{15}

All data from the ICPMS measurements is brought in the following table:

Table 2. All ICPMS results of the pyrite materials, precursors, and fluxes.

	Li	+/- error	Cr	+/- error	Co	+/- error	Ni	+/- error	Cu	+/- error	Cs	+/- error	I	+/- error
	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³	at/cm³
FeS (3N) prec.	8,33E+17	3,90E+16	1,07E+19	2,78E+17	6,13E+18	1,23E+16	1,15E+19	2,87E+17	1,07E+18	6,73E+16	4,53E+14	0,00E+00	3,60E+17	9,72E+15
FeS (4N) prec.	2,48E+18	1,30E+17	1,25E+19	1,75E+17	1,48E+18	3,06E+15	1,04E+19	1,88E+17	1,58E+19	8,21E+17	7,02E+15	0,00E+00	8,22E+17	1,40E+16
FeS_2 (no flux)	0	0	6,93E+18	1,39E+17	3,32E+18	6,98E+16	6,91E+18	1,94E+17	6,93E+17	4,23E+16	1,37E+15	8,38E+13	1,39E+16	2,36E+14
FeS_2 (Na_2S_x flux)	0	0	5,42E+18	5,96E+16	2,29E+18	7,55E+16	5,44E+18	9,8E+16	3,85E+18	3,08E+17	9,17E+14	1,93E+13	1,92E+16	5,2E+14
FeS_2 (LiI flux)	4,04E+19	4,28E+18	4,5E+18	9E+16	2,84E+18	3,7E+16	5,95E+18	1,19E+17	6,76E+17	4,26E+16	5,68E+16	5,91E+15	4,67E+19	2,01E+18
FeS_2 (CsI flux)	5,49E+17	6,92E+16	4,45E+18	4,9E+16	3,23E+18	6,13E+16	6,9E+18	1,24E+17	9,55E+17	5,83E+16	8,52E+18	2,47E+17	1,86E+19	7,25E+17
FeS_2 (KI flux)	4,87E+17	1,2E+17	4,77E+18	1,91E+16	3,11E+18	1,12E+17	6,6E+18	5,94E+16	7,31E+17	6,21E+16	1,76E+15	7,92E+13	9,45E+18	2,93E+17
FeS_2 (4x KI flux)	5,72E+17	1,73E+16	1,75E+18	8,68E+15	4,82E+18	2,84E+17	9,29E+18	3,69E+16	2,30E+17	7,58E+15	2,26E+14	0,00E+00	1,78E+17	6,88E+15
FeS_2 (10x KI flux)	4,60E+17	1,30E+16	3,98E+18	1,15E+17	4,76E+18	1,89E+16	8,30E+18	2,49E+17	3,17E+16	5,21E+15	2,26E+14	0,00E+00	1,27E+17	4,03E+15
FeS_2 (KI flux) 4N prec.	6,42E+17	2,17E+16	2,57E+18	1,13E+17	1,22E+18	1,23E+16	8,04E+18	3,46E+17	3,50E+18	1,64E+17	4,53E+14	0,00E+00	2,48E+17	1,07E+16
Na_2S_x	1,34E+18	2,60E+16	2,08E+16	1,74E+15	5,11E+14	0,00E+00	2,62E+16	2,05E+15	0,00E+00	0,00E+00	2,26E+14	0,00E+00	1,80E+17	1,19E+15
LiI	2,65E+22	1,22E+21	1,74E+16	2,32E+15	1,53E+15	0,00E+00	2,15E+16	1,03E+15	5,07E+16	6,63E+15	4,35E+16	2,04E+15	4,23E+19	2,96E+17
KI	4,32E+18	9,97E+16	7,06E+16	2,32E+15	2,04E+15	0,00E+00	4,72E+16	1,03E+15	1,61E+16	4,26E+15	4,53E+14	0,00E+00	3,28E+19	6,56E+17

Red – unreliable measurements, equipment had become compromised

Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) data

Impurities in powder materials were qualitatively determined by TOF-SIMS 5 by IONTOF. Oxygen etching at 2 keV was used for the negative mode measurement, while cesium etching at 0.5-1 keV was used for the positive mode. The measurements were carried out with vanadium primary ions with the ion gun working at 25 keV. The ToF-SIMS measurements were taken in the so-called "static" regime, where only the first few atomic layers are removed prior/during the measurement. The elemental data is obtained as a graph of counts vs time, where the elemental concentrations stabilize over a few hundred seconds of sputtering time, for example:

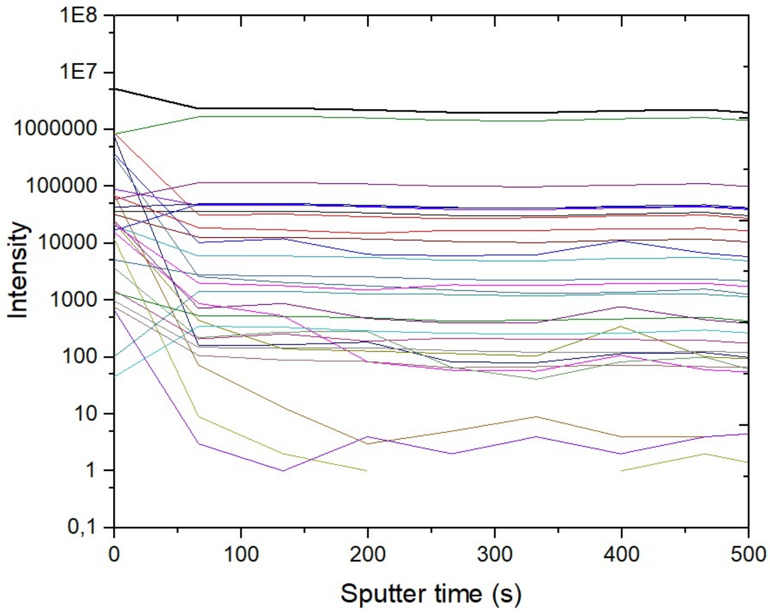

Figure 1. Example of raw ToF-SIMS data. Each colored line represents a different element/ion.

Each colored line represents a different elemental signal from the sample. The intensity values are considered from the parallel region of the graph, after at least 200 s of sputter time.

The following table summarizes the ToF-SIMS data gathered from the materials:

Table 3. ToF-SIMS data of pyrite materials synthesized in different fluxes.

	KI flux	**Na_2S_x flux**	**LiI flux**	**CsI flux**	**no flux**
Impurity ion	intensity ratio to matrix	intensity ratio to matrix	intensity ratio to matrix	intensity ratio to matrix	intensity ratio to matrix
Cu^+	4,55E-05	8,00E-06	2,73E-05	3,64E-05	3,85E-05
Ni^+	2,73E-03	5,00E-02	3,64E-03	0,00E+00	1,15E-02
K^+	4,55E-03	1,00E-03	3,64E-03	2,73E-03	--------
Li^+	--------	2,00E-05	--------	--------	1,31E-04
Na^+	1,82E-02	3,00E-02	1,82E-02	1,00E-02	4,11E-02
Cs^+	9,09E-04	--------	3,64E-04	5,45E-04	3,85E-05
I^-	9,09E-05	--------	2,50E-05	0,00E+00	--------
Cl^-	2,73E-04	8,33E-02	2,75E-04	0,00E+00	--------