SUPPORTING INFORMATION (SI)

Calorimetric study of skutterudite (CoAs$_{2.92}$) and heazlewoodite (Ni$_3$S$_2$)

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Table S1. Equilibrium constants for selected reactions considered in this work. The values were calculated by SUPCRTBL (Zimmer et al. 2016). P_{sat} is the saturation H_2O pressure along the water-water vapor curve. For these calculations, the data for heazlewoodite and skutterudite were taken from this work, data for all other phases and species in reactions (11) through (14) from SUPCRTBL.

T (°C)	P_{sat} (bar)	log K_{11}	log K_{12}	log K_{13}	log K_{14}
0.01	1	44.176	29.344	207.802	179.758
25	1	39.929	25.954	190.208	163.51
50	1	36.353	22.91	175.067	149.407
75	1	33.31	20.185	161.915	137.059
100	1.013	30.69	17.725	150.377	126.137
125	2.32	28.405	15.477	140.162	116.385
150	4.757	26.386	13.394	131.04	107.594
175	8.918	24.579	11.438	122.832	99.6
200	15.536	22.942	9.576	115.393	92.267
225	25.479	21.439	7.773	108.606	85.479
250	39.736	20.032	5.987	102.371	79.128
275	59.431	18.693	4.176	96.6	73.107
300	85.838	17.416	2.309	91.223	67.305
325	120.458	16.242	0.371	86.175	61.573
350	165.211	15.304	-1.695	81.37	55.533

Table S2. Adjustable parameters A_1-A_5 for the equation (15) for the chemical reactions (11) through (14). The fitted log K values are listed in Table S1.

	log K_{11}	log K_{12}	log K_{13}	log K_{14}
A_1	3.9819E+00	-3.1778E+03	-1.2690E+03	-5.7571E+03
A_2	-2.1705E-02	-4.8008E-01	-1.9782E-01	-8.3650E-01
A_3	6.3566E+03	1.9026E+05	1.3555E+05	3.8959E+05
A_4	4.3749E+00	1.1444E+03	4.5449E+02	2.0625E+03
A_5	9.1092E+05	-1.0930E+07	-5.4261E+06	-2.1345E+07

Table S3. Adjustable parameters a-f for the equation (16) for the chemical reactions (11) through (14). The fitted log K values are listed in Table S1.

	log K_{11}	log K_{12}	log K_{13}	log K_{14}
a	3.9951E+01	2.5947E+01	1.9020E+02	1.6346E+02
b	-2.4488E+00	1.4112E+00	7.3071E-01	6.8141E+00
c	7.1222E-04	-5.5498E-04	-2.7248E-04	-2.2451E-03
d	4.1998E+05	-1.3204E+05	-2.2692E+04	-9.1423E+05
e	-1.9768E+07	5.1839E+06	2.4850E+06	4.3839E+07
f	1.5208E+03	-6.8653E+02	-3.8370E+02	-3.8921E+03

References

Zimmer, K., Zhang, Y.L., Lu, P., Chen, Y.Y., Zhang, G.R., Dalkilic, M., and Zhu, C. (2016) SUPCRTBL: A revised and extended thermodynamic dataset and software package of SUPCRT92. Computer and Geosciences, 90, 97-111. https://doi.org/10.1016/j.cageo.2016.02.013
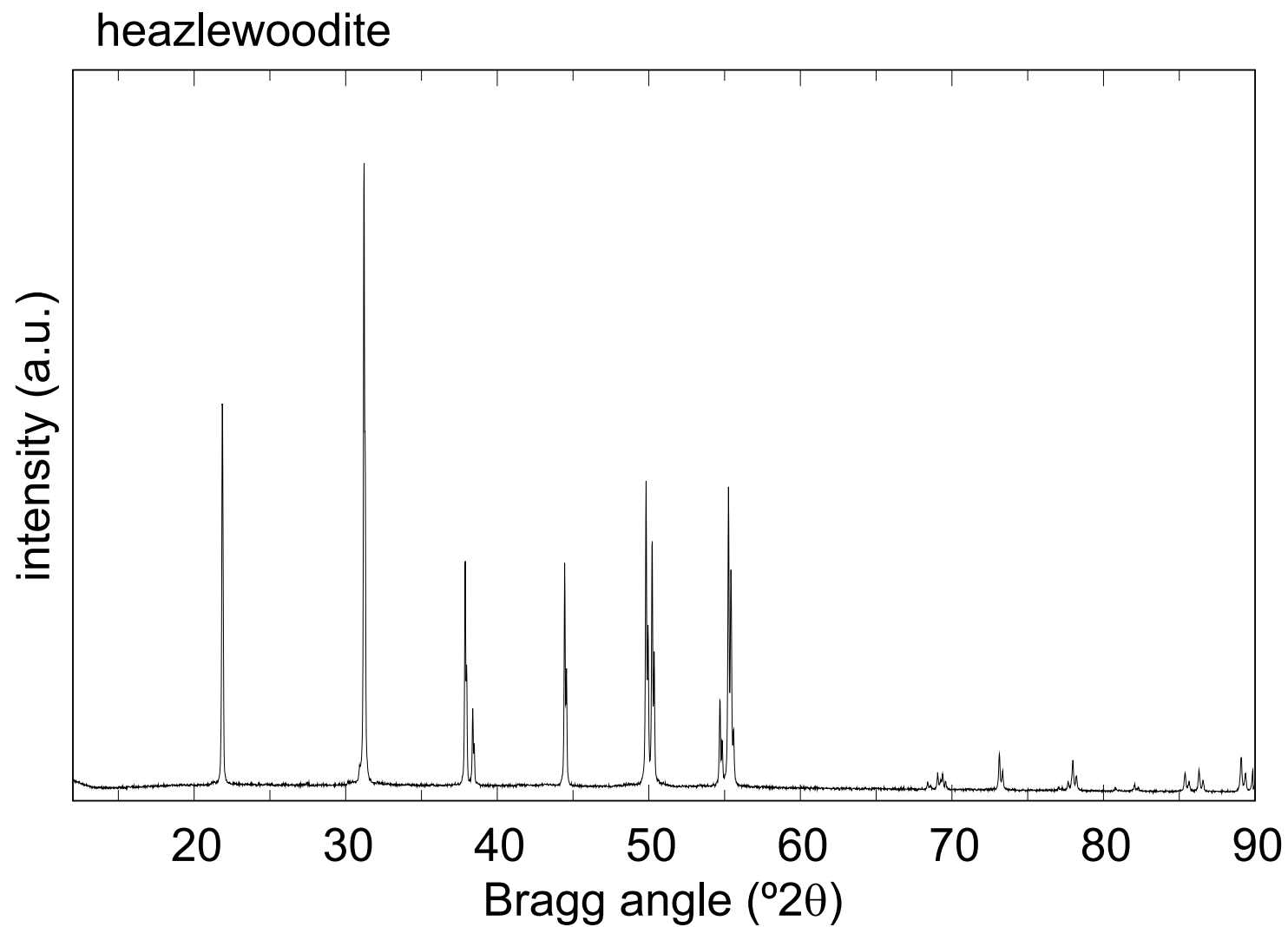
heazlewoodite

Fig. S1. Powder X-ray diffraction pattern of synthetic heazlewoodite used in this work.
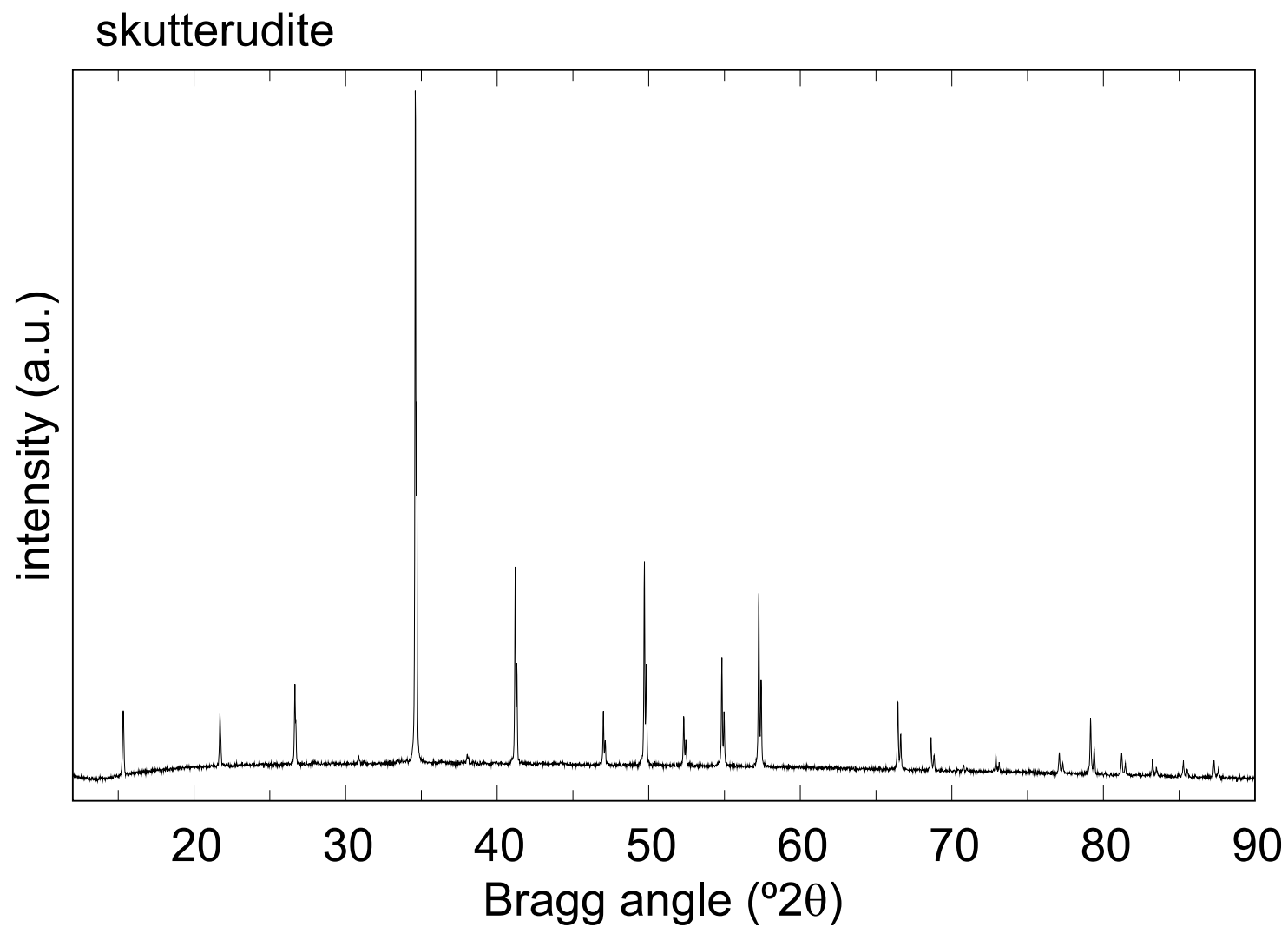
skutterudite

Fig. S2. Powder X-ray diffraction pattern of synthetic skutterudite used in this work.