

SUPPORTING INFORMATION

Incorporation of Tin affects Crystallization, Morphology and Crystal Composition of Sn-Beta

Søren Tolborg,^{§,†} Anna Katarinopoulou,[§] Derek Falcone,[‡] Irantzu Sádaba,[§] Christian M. Osmundsen,[§] Robert J. Davis,[‡] Esben Taarning,^{*,§} Peter Fristrup,[†] and Martin S. Holm.[§]

[§] Haldor Topsøe A/S, New Business R&D, Nymøllevej 55, 2800-Kgs. Lyngby, Denmark

[†] Technical University of Denmark, Department of Chemistry, Kemitorvet, 2800-Kgs. Lyngby, Denmark

[‡] University of Virginia, Department of Chemistry, McCormick Road, 400319-Charlottesville, VA, USA

* Corresponding author. E-mail: esta@topsoe.dk

Table S1. Physical properties of Sn-Beta samples.

Entry	Nominal Si/Sn	Crystallization days	Crystallinity ^a %	Tin ^b wt %	Si/Sn ^b	S _{BET} ^c m ² /g	V _{micropore} ^d mL/g	ML yield ^e %
1	-	2	72	-	-	451	0.16	-
2	-	3	>95	-	-	428	0.18	-
3	-	4	>95	-	-	459	0.19	0.53 ± 0.02
4	-	7	>95	-	-	465	0.20	-
5	-	14	>95	-	-	483	0.20	-
6	-	30	>95	-	-	474	0.19	1.6 ± 0.1
7	400	2	40	0.46	433	429	0.14	3.6 ± 2.1
8	400	3	>95	0.42	475	490	0.20	-
9	400	4	>95	0.42	475	464	0.19	10.7 ± 0.9
10	400	7	>95	0.44	452	476	0.20	10.0 ± 1.8
11	400	14	>95	0.50	396	465	0.20	12.7 ± 2.8
12	400	30	>95	0.49	400	482	0.19	8.0 ± 1.1
13	200	2	8	0.93	211	395	0.10	2.3 ± 1.4
14	200	4	52	0.90	219	422	0.14	4.8 ± 0.8
15	200	5	60	0.91	217	437	0.16	-
16	200	7	>95	0.97	203	471	0.19	22.8 ± 3.0
17	200	14	>95	0.96	204	473	0.19	28.5 ± 4.2
18	200	30	>95	0.94	209	475	0.20	17.8 ± 4.2
19	150	2	20	1.27	154	470	0.14	1.4 ± 0.2
20	150	4	22	1.16	169	387	0.11	2.0 ± 0.3
21	150	5	35	1.21	161	454	0.14	1.9 ± 0.3
22	150	7	63	1.21	161	486	0.18	3.5 ± 0.5
23	150	10	83	1.19	164	-	-	3.7 ± 0.6
24	150	14	>95	1.24	158	470	0.20	22.1 ± 3.7
25	150	30	>95	1.14	172	471	0.19	25.2 ± 3.8
26	100	7	0	1.77	110	421	0.12	3.6 ± 1.7
27	100	14	16	1.86	105	395	0.11	3.9 ± 1.7
28	100	30	36	1.81	107	392	0.13	5.8 ± 1.5
29	100	60	>95	1.81	107	508	0.20	31.9 ± 5.3

a. Determined by Rietveld refinement of XRD measurements using the PONCKS method.

b. Determined by ICP analysis.

c. BET surface area

d. Micropore volume, calculated using the *t*-plot method.

e. Average ML yield of min. 3 catalytic runs. Conditions: 25 mg catalyst, 300 mg DHA, 6.5 mL methanol, 600 rpm, 75°C, 2 hours

Table S2. Physical properties of Sn-Beta samples prepared using different tin sources, crystallized for 14 days.

Entry	Tin source	Nominal Si/Sn	Tin ^a wt %	Si/Sn ^a	S _{BET} ^b m ² /g	V _{micropore} ^c mL/g	ML yield ^d %
1	Sn(CH ₃ CO ₂) ₄	150	0.67	295	468	0.18	27.4 ± 0.8
2	((C ₂ H ₅) ₄ N) ₂ SnF ₆ ^b	150	1.19	165	478	0.19	13.3 ± 0.3
3	SnO ₂ ^c	150	1.11	177	456	0.19	4.0 ± 0.4

a. Determined by ICP analysis.

b. BET surface area

c. Micropore volume, calculated using the *t*-plot method.

d. Average ML yield of min. 3 catalytic runs. Conditions: 25 mg catalyst, 300 mg DHA, 6.5 mL methanol, 600 rpm, 75°C, 2 hours

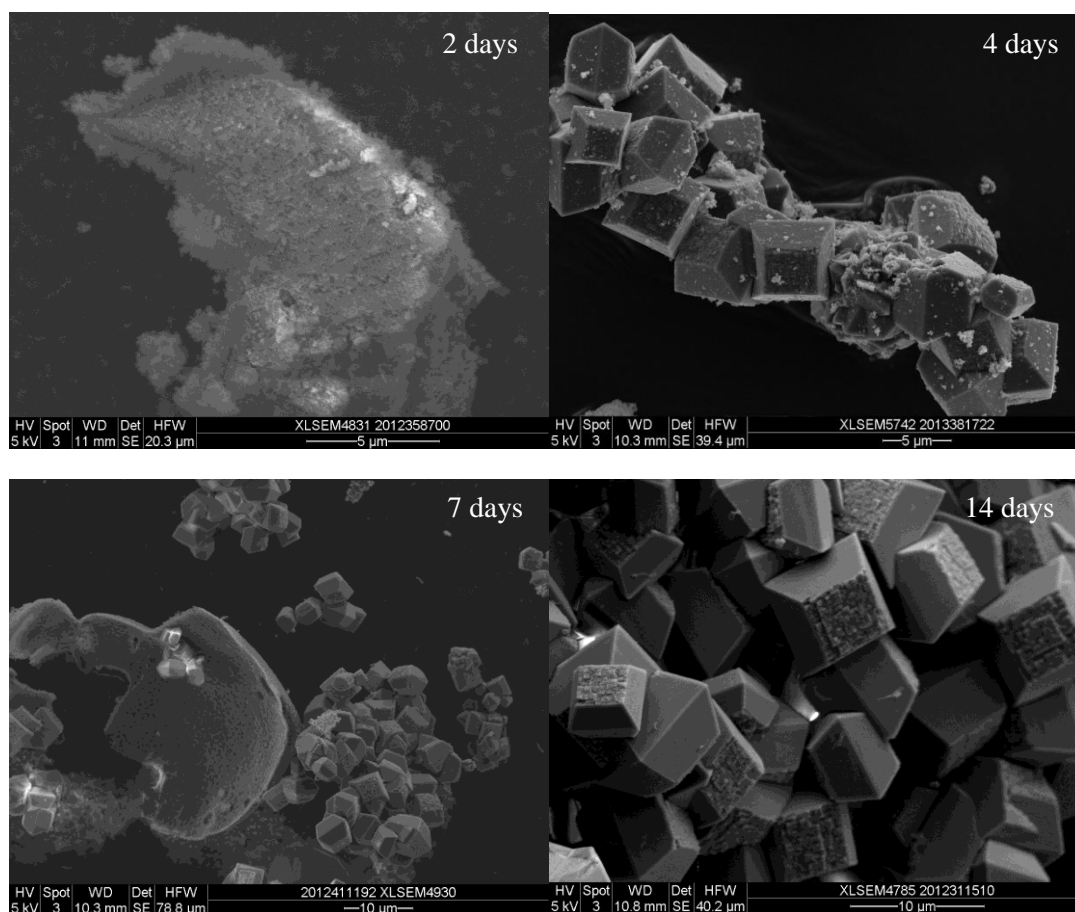


Figure S1. Micrographs of Sn-Beta sample with Si/Sn = 200 amorphous (2 days), 'semi-amorphous' (4 days) and crystalline (7, 14 days)

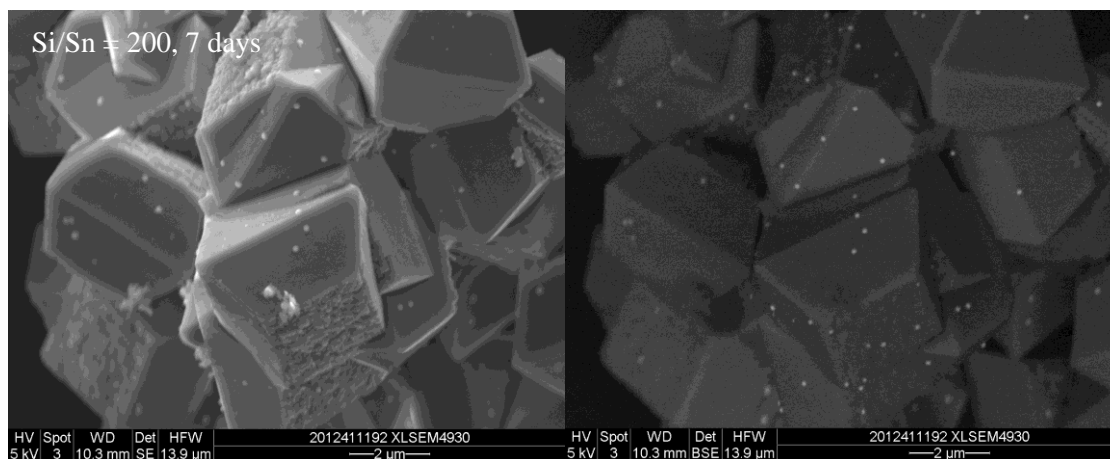


Figure S2. Secondary electron (left) and back-scattered electron (right) image of Sn-Beta (Si/Sn = 200) synthesized for 7 days with SnO₂ particles visible on the surface

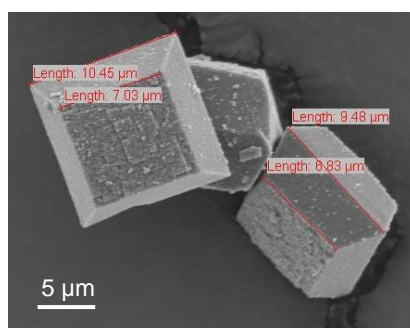


Figure S3. SEM image of Sn-Beta sample with Si/Sn = 150 synthesized for 14 days with measurements of *a* and *b*.

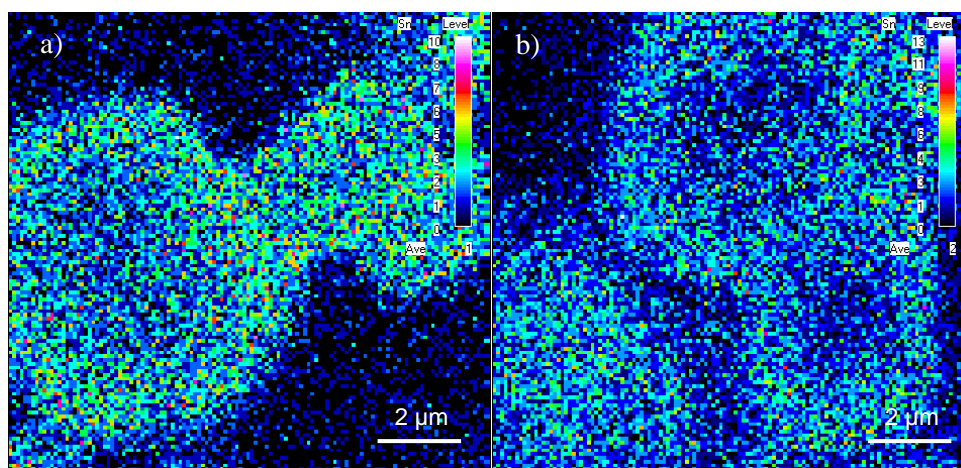


Figure S4. SEM-WDS measurements showing the tin distribution in transverse sections of Sn-Beta zeolite (Si/Sn = 200, synthesized for 7 days). The measurements are done a) before and b) after thermal removal of the organic template at 550°C for 6 hours.

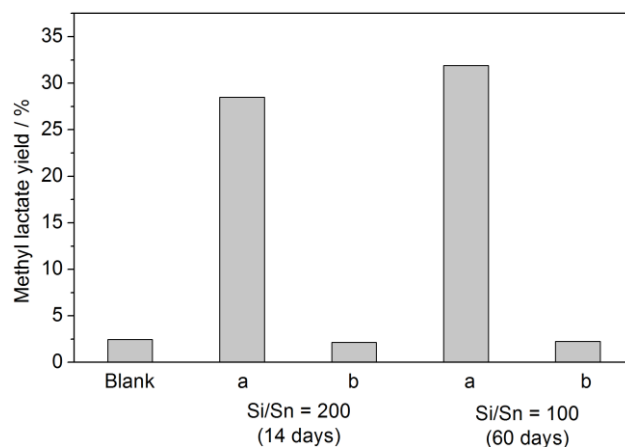
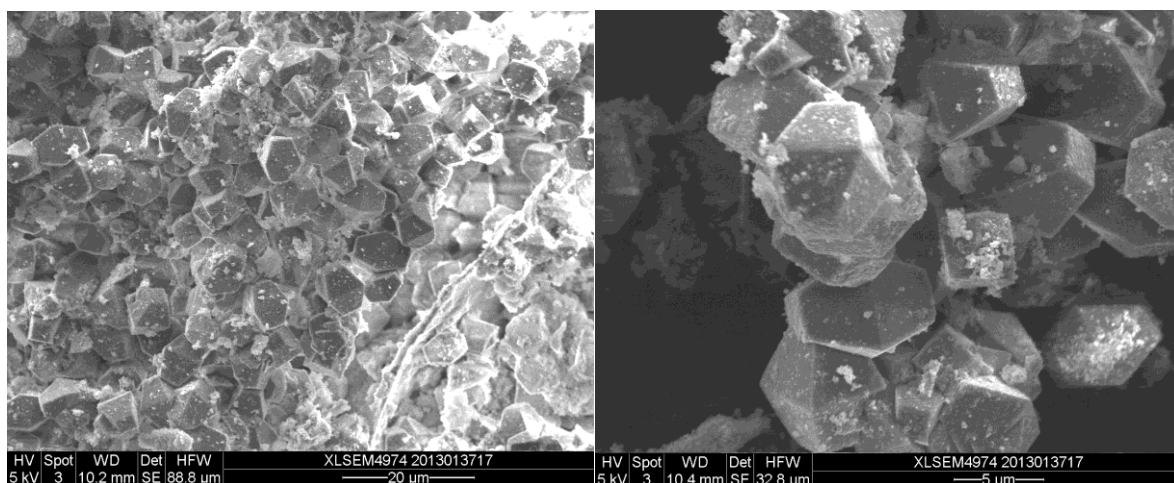


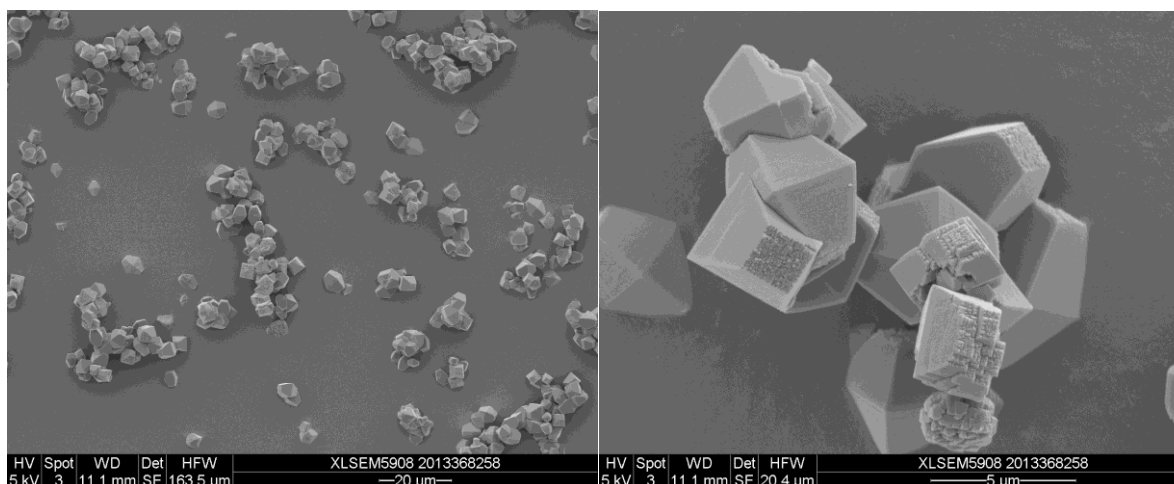
Figure S5. Comparison of the conversion of 1,3-dihydroxyacetone performed using a) the Sn-Beta catalyst and b) Leaching experiment: initially treating the Sn-Beta zeolite in 6.5 mL of methanol at 75°C for 2 hours, filtering off the catalyst and using this methanol as the solvent for the reaction. Reaction conditions: 25 mg catalyst, 300 mg DHA, 6.5 mL methanol, 600 rpm, 75°C, 2 hours.

Additional SE images of samples presented in Table S1.

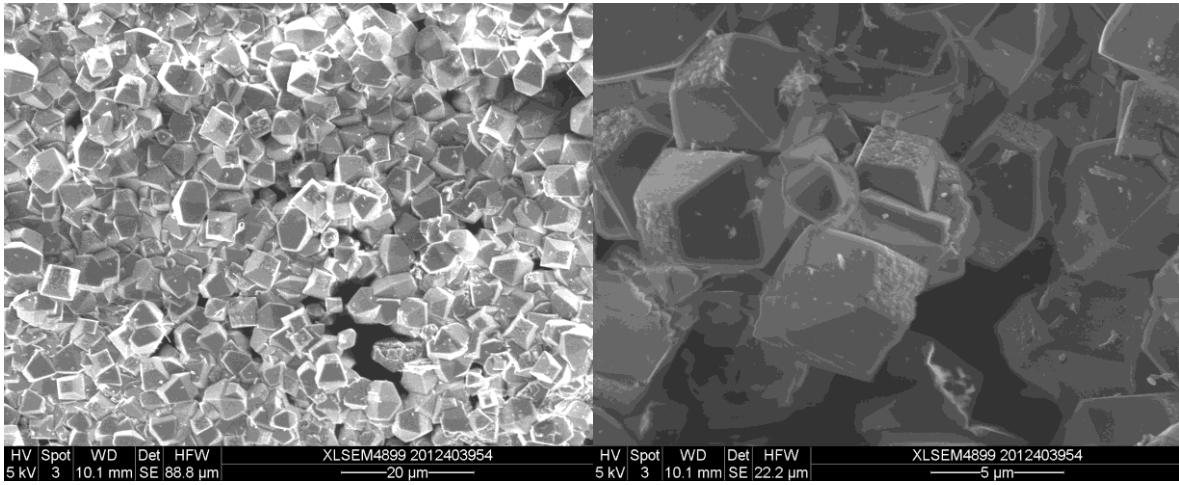
No tin, 2 days (Table S1, entry 1)



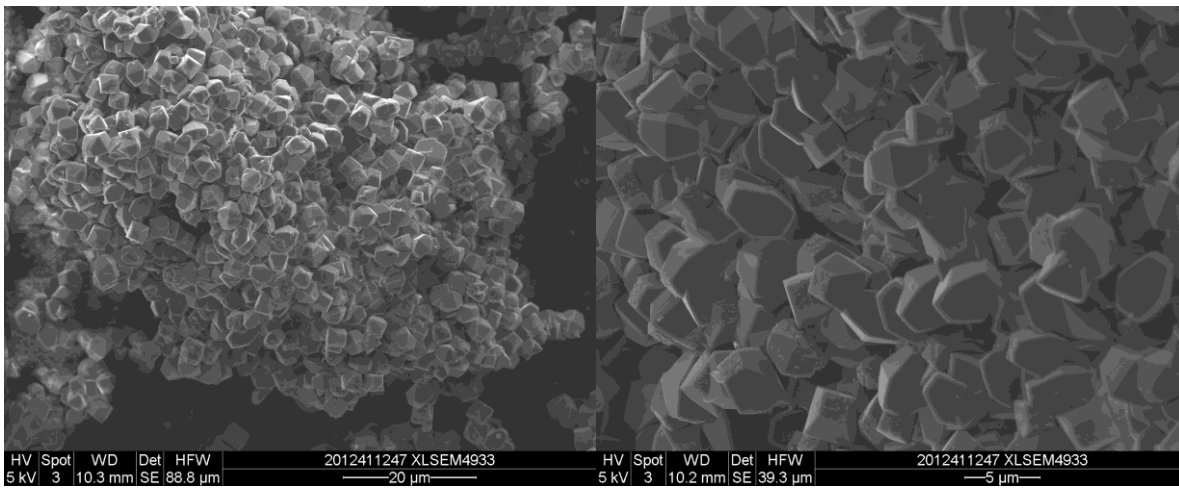
No tin, 4 days (Table S1, entry 3)



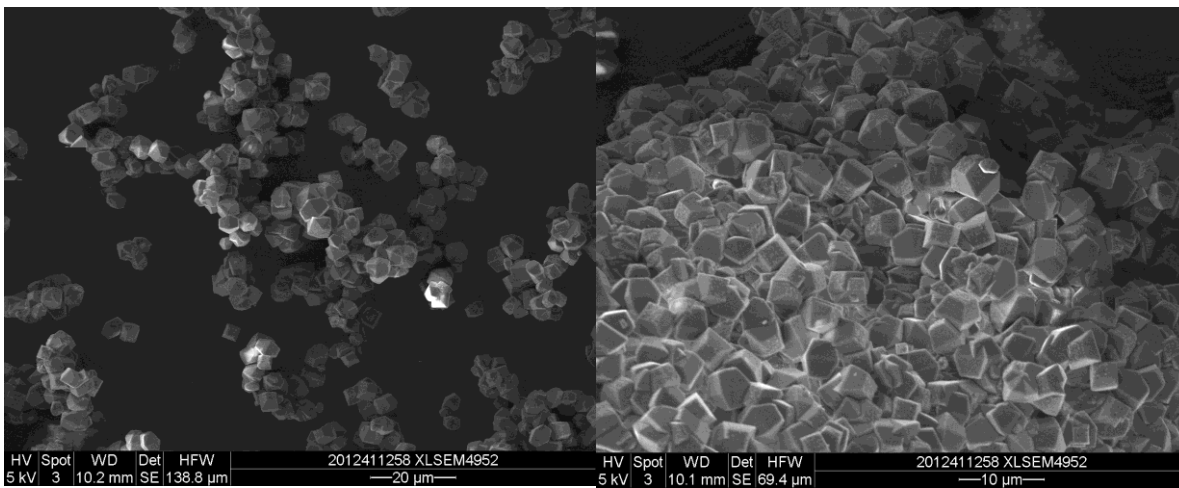
No tin, 7 days (Table S1, entry 4)



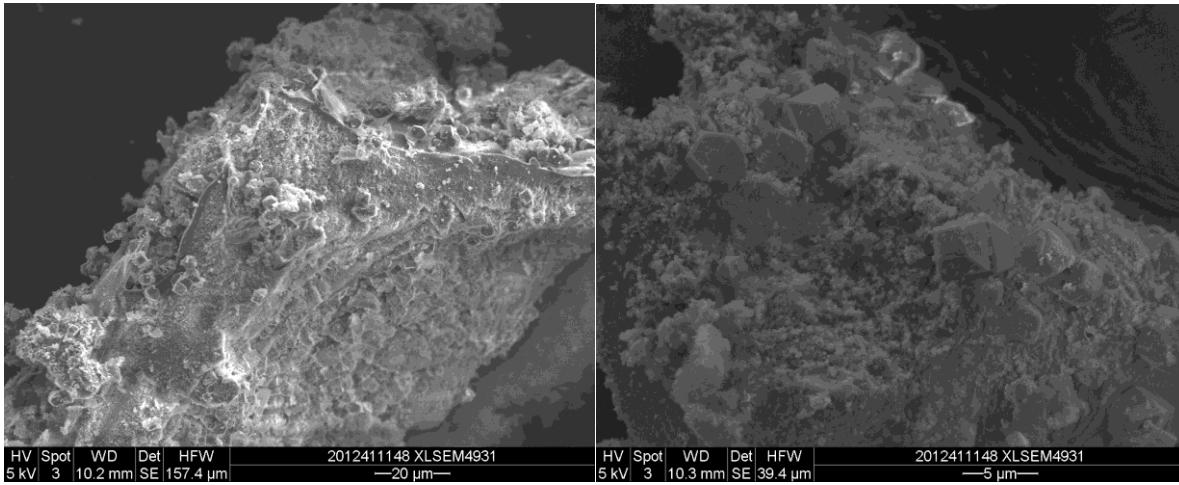
No tin, 14 days (Table S1, entry 5)



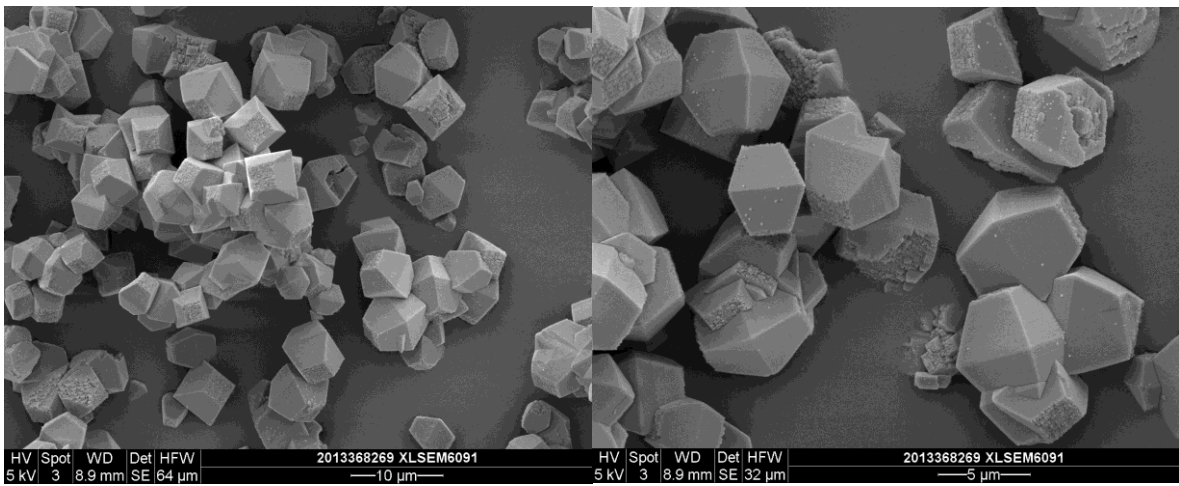
No tin, 30 days (Table S1, entry 6)



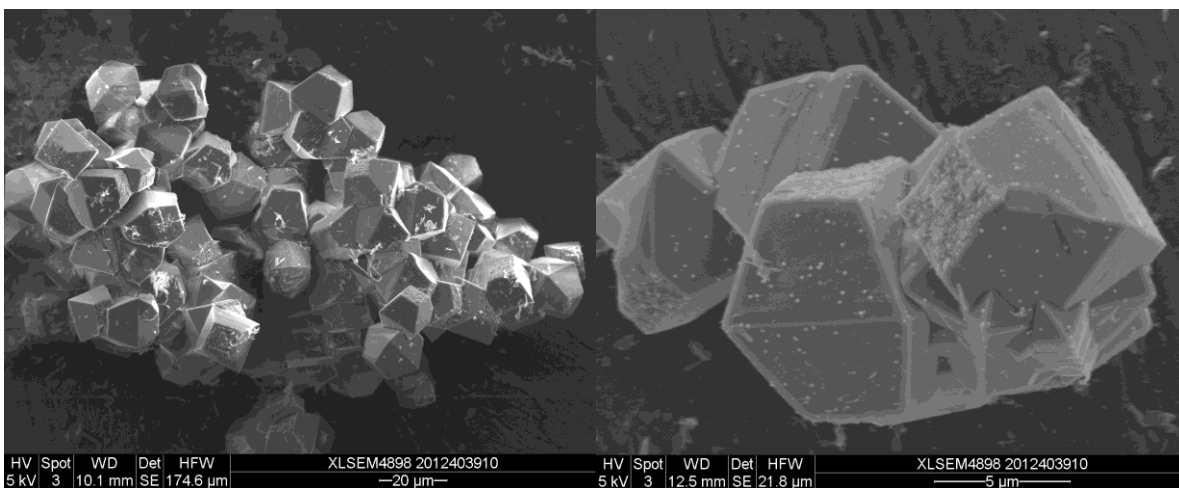
Si/Sn = 400, 2 days (Table S1, entry 7)



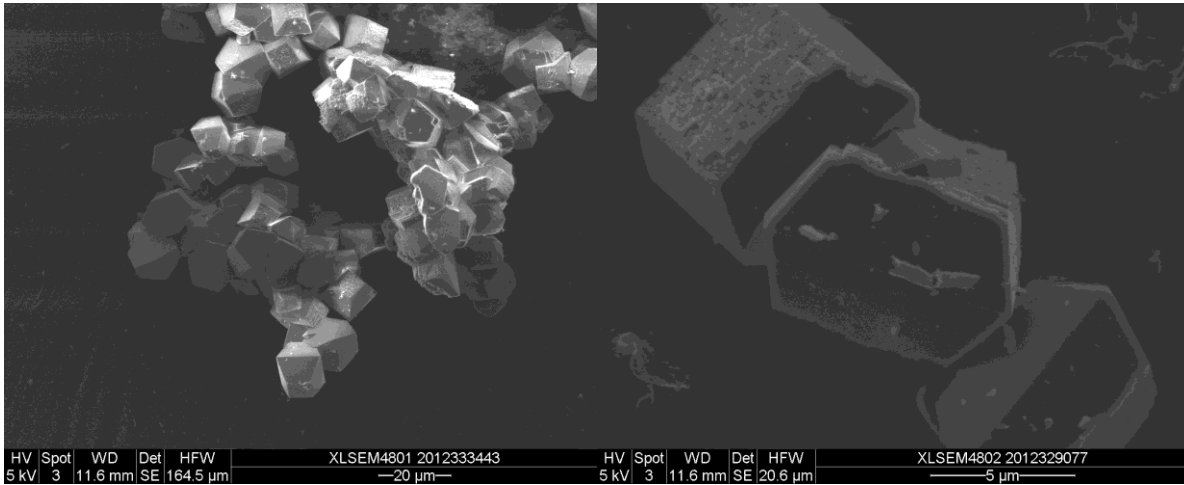
Si/Sn = 400, 4 days (Table S1, entry 9)



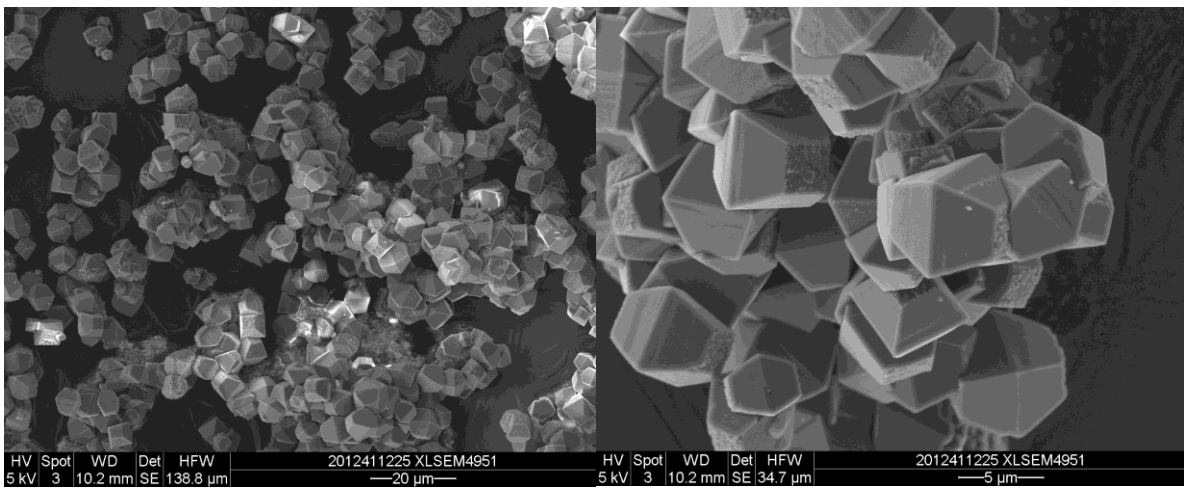
Si/Sn = 400, 7 days (Table S1, entry 10)



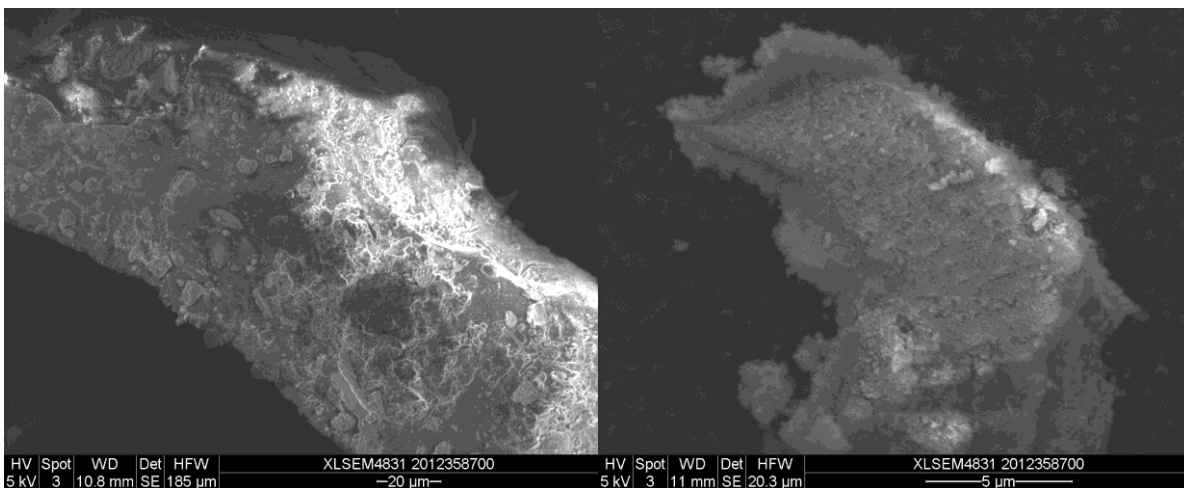
Si/Sn = 400, 14 days (Table S1, entry 11)



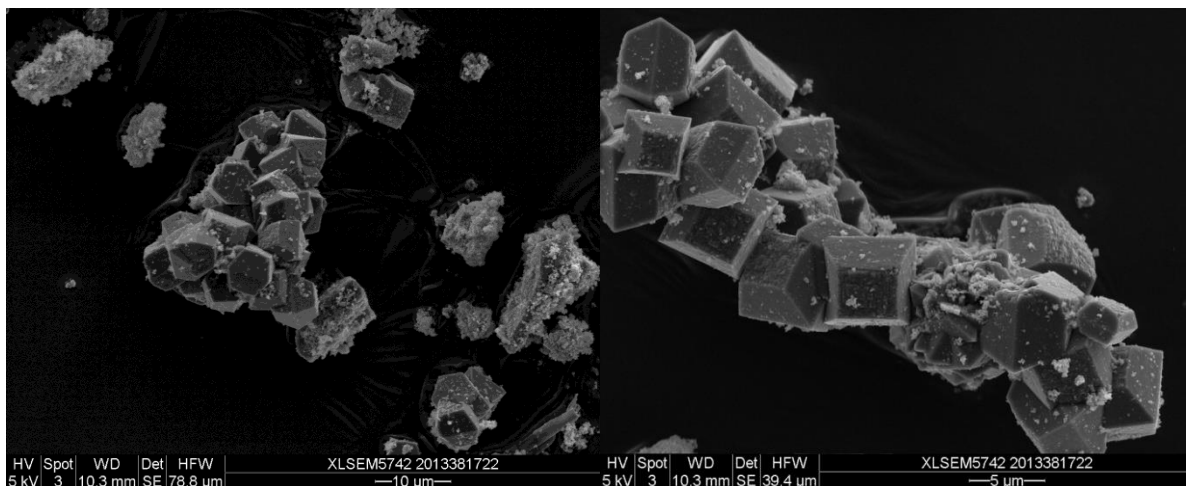
Si/Sn = 400, 30 days (Table S1, entry 12)



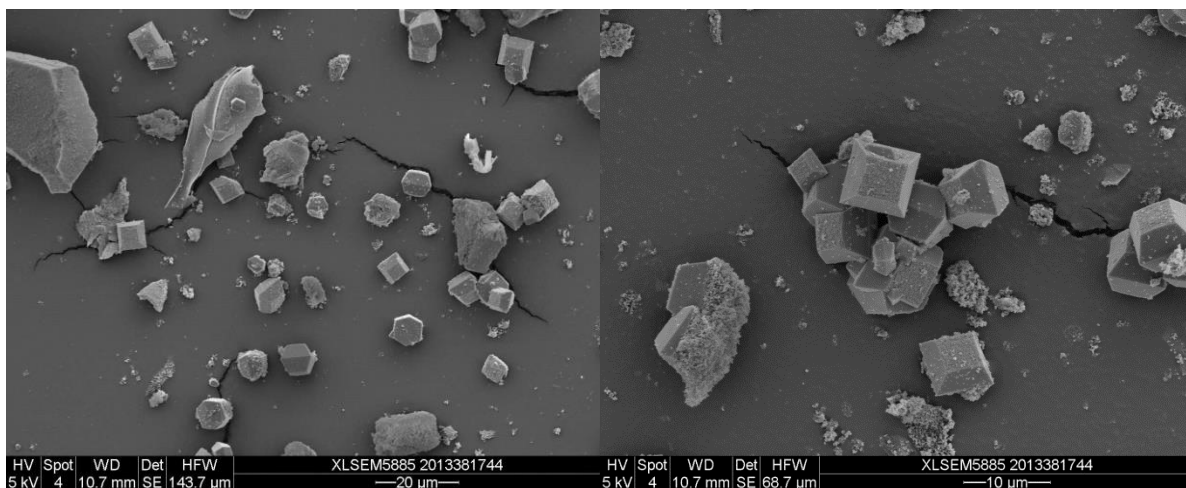
Si/Sn = 200, 2 days (Table S1, entry 13)



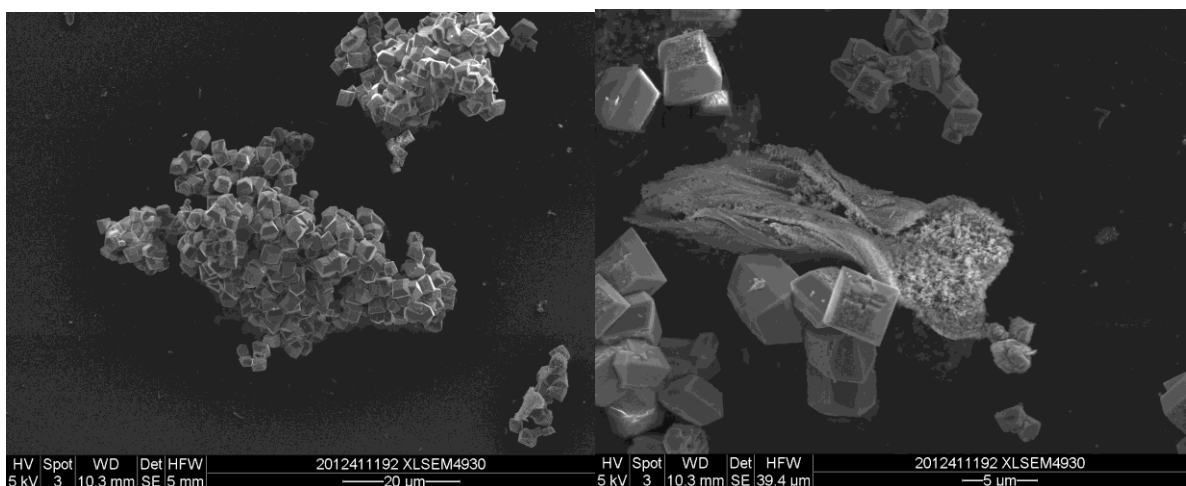
Si/Sn = 200, 4 days (Table S1, entry 14)



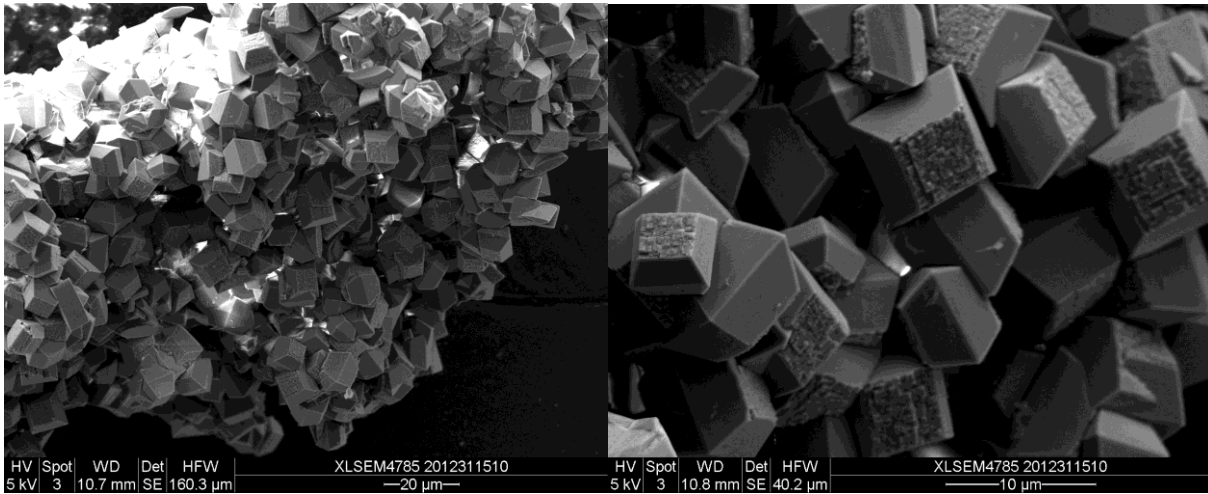
Si/Sn = 200, 5 days (Table S1, entry 15)



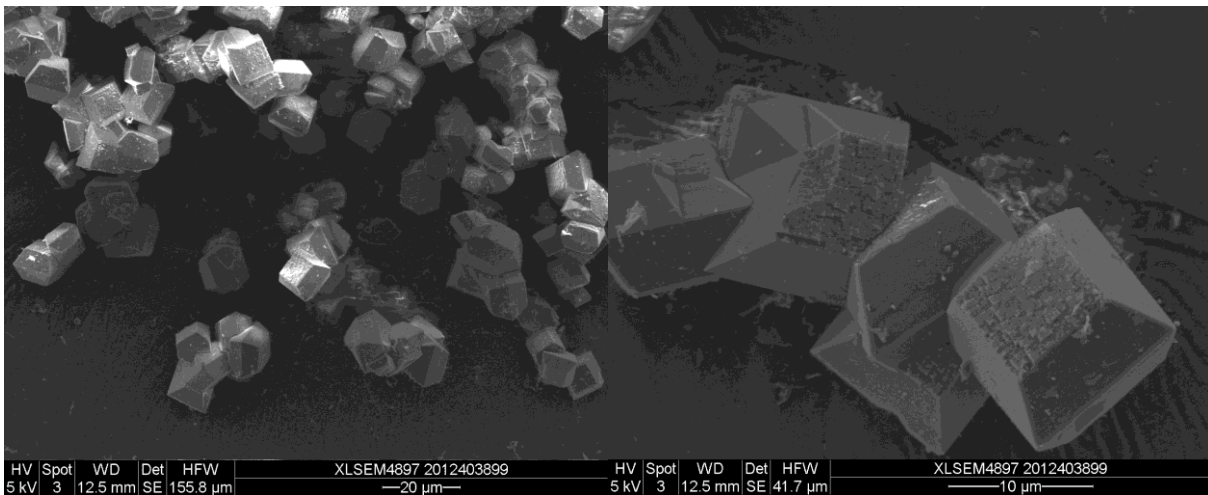
Si/Sn = 200, 7 days (Table S1, entry 17)



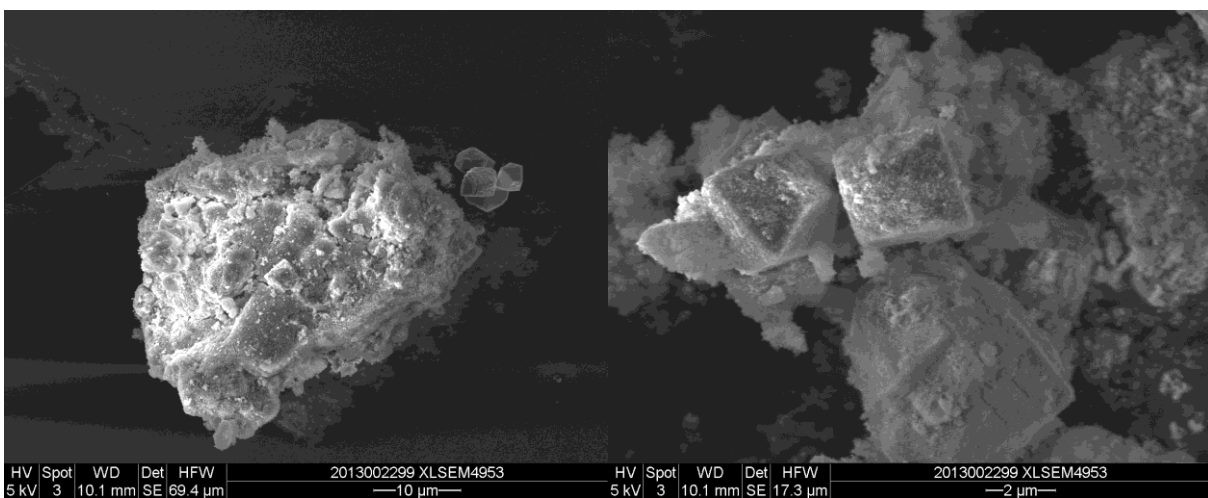
Si/Sn = 200, 14 days (Table S1, entry 17)



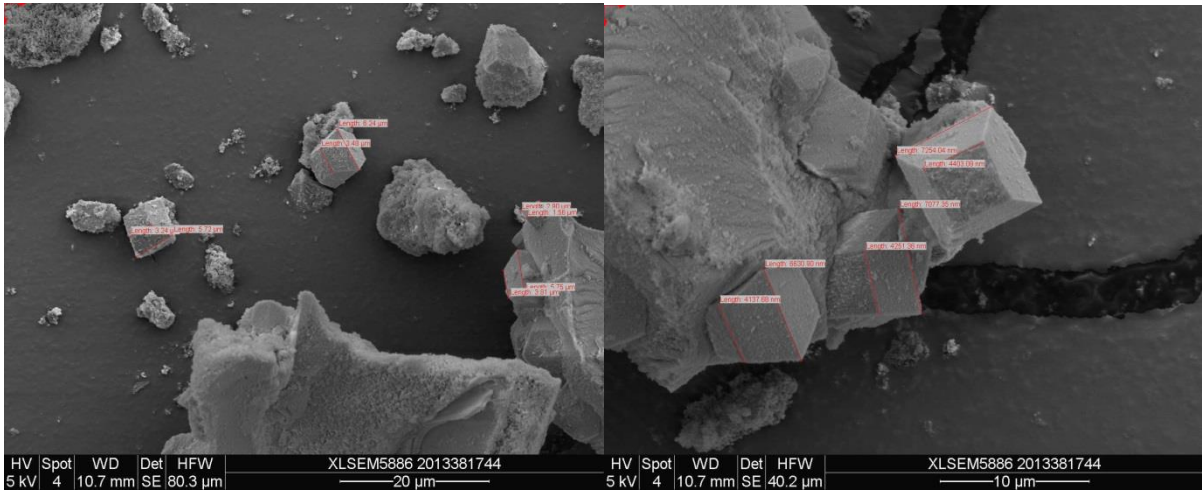
Si/Sn = 200, 30 days (Table S1, entry 18)



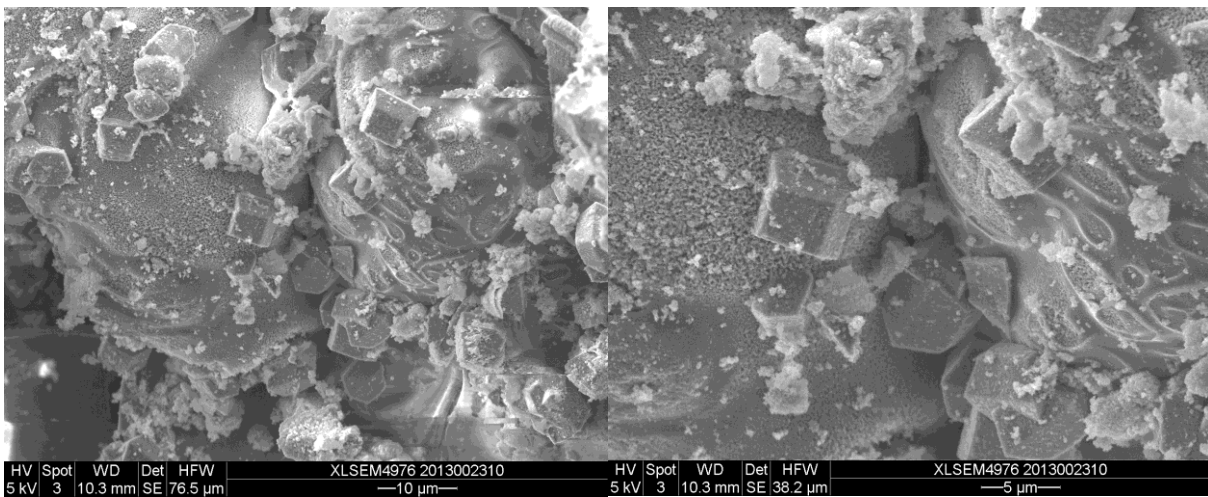
Si/Sn = 150, 2 days (Table S1, entry 19)



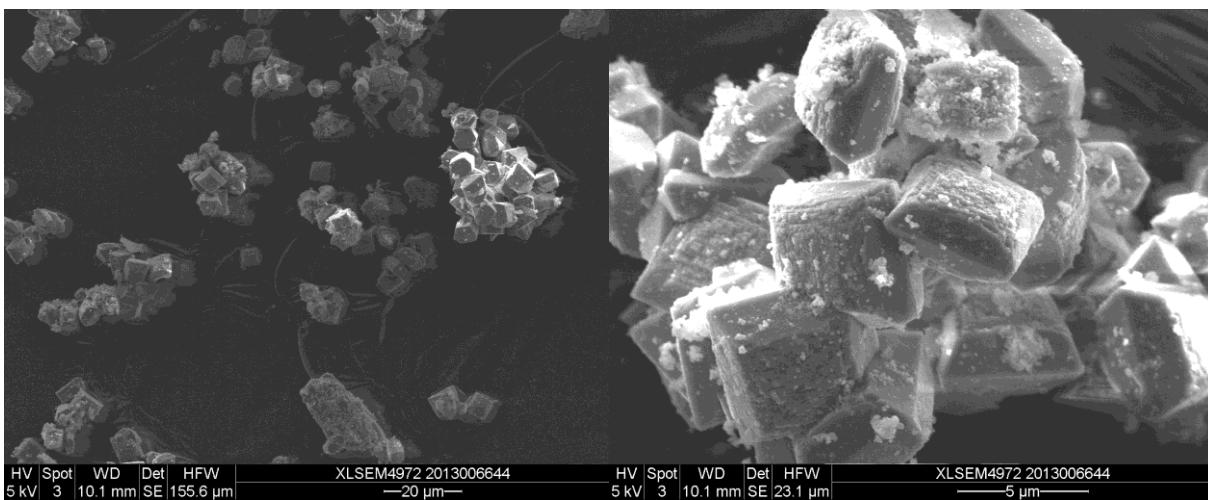
Si/Sn = 150, 4 days (Table S1, entry 20)



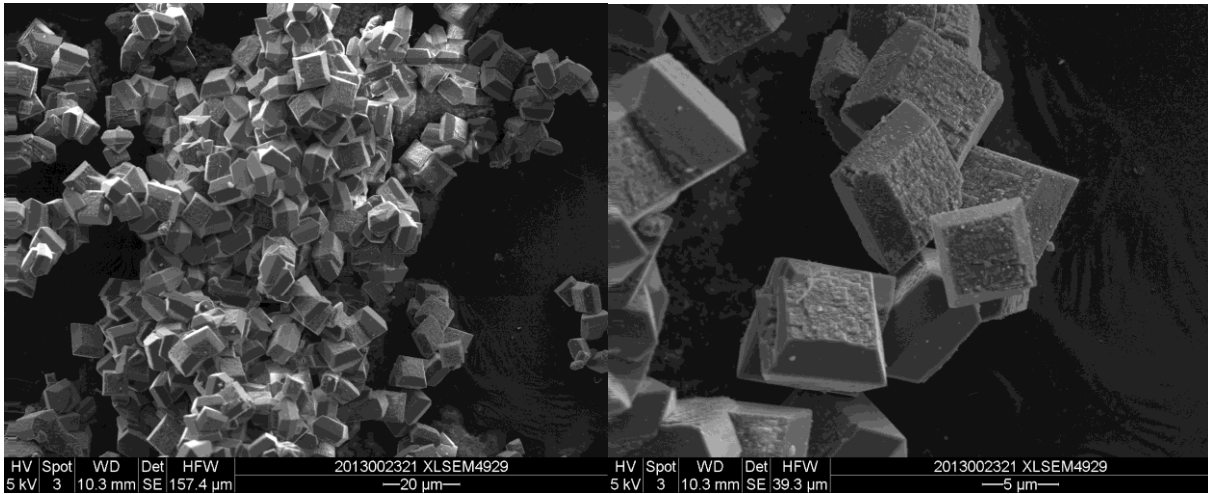
Si/Sn = 150, 5 days (Table S1, entry 21)



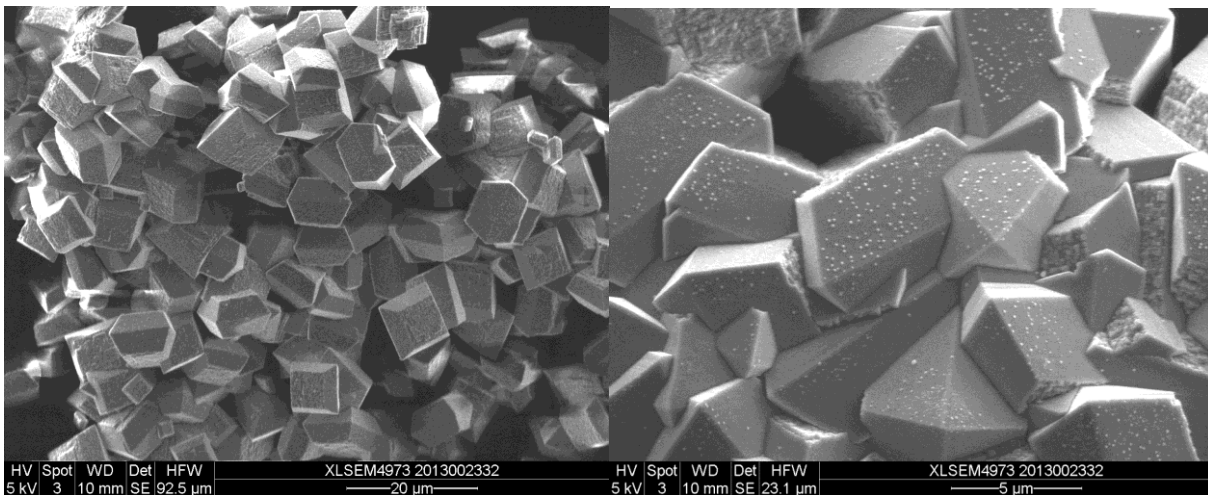
Si/Sn = 150, 7 days (Table S1, entry 22)



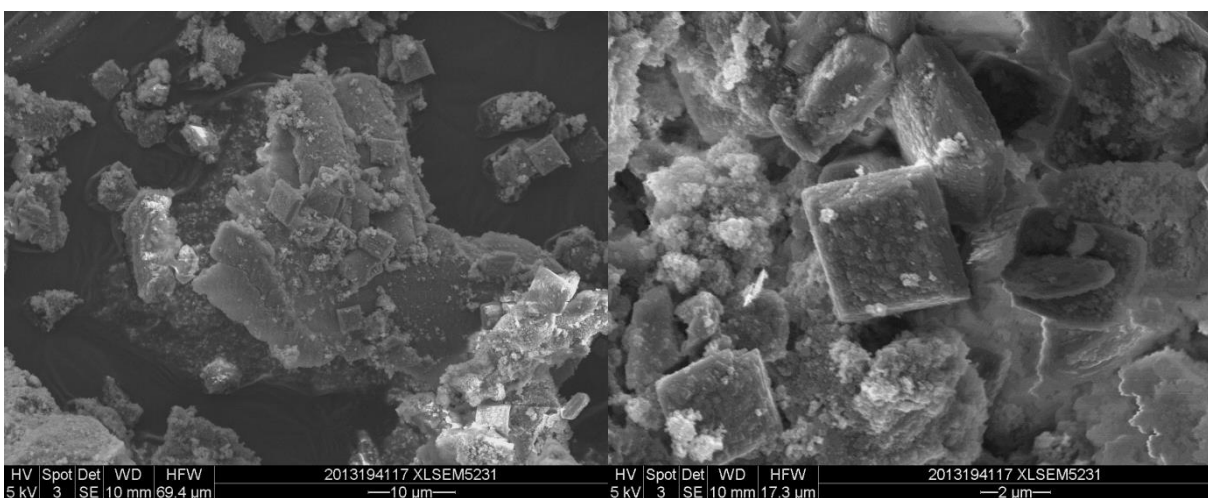
Si/Sn = 150, 14 days (Table S1, entry 24)



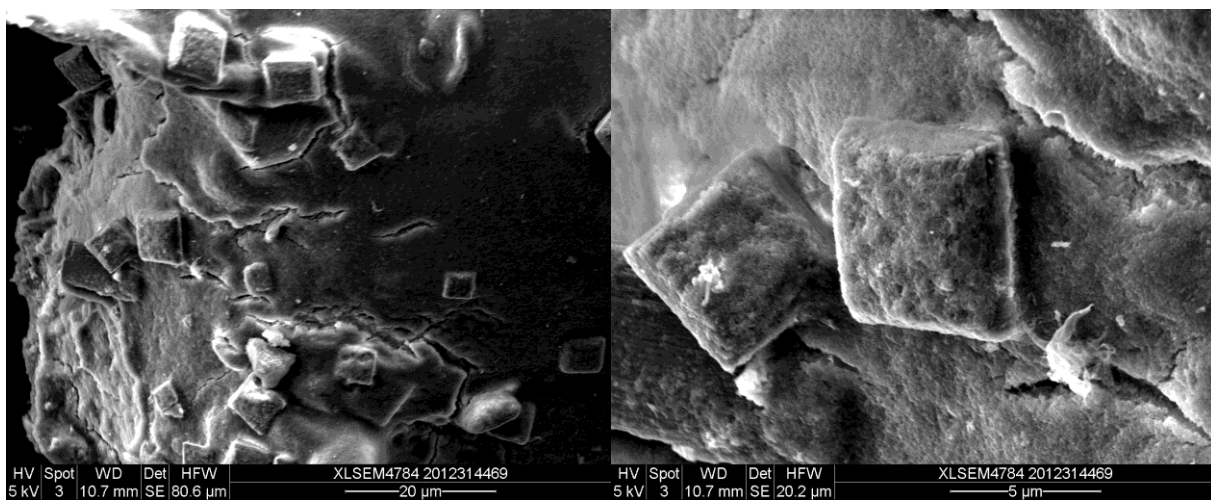
Si/Sn = 150, 30 days (Table S1, entry 25)



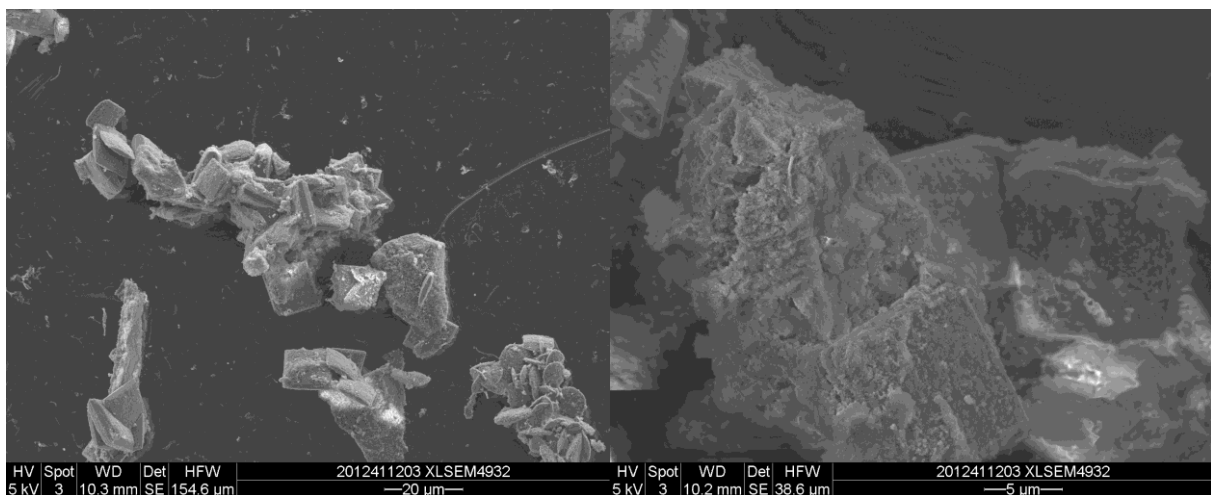
Si/Sn = 100, 7 days (Table S1, entry 26)



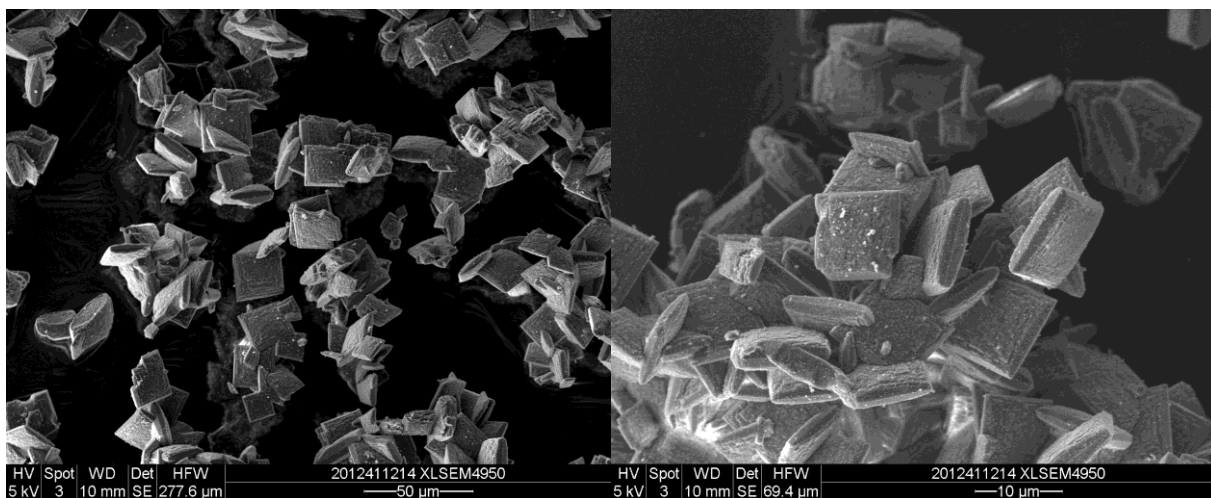
Si/Sn = 100, 14 days (Table S1, entry 27)



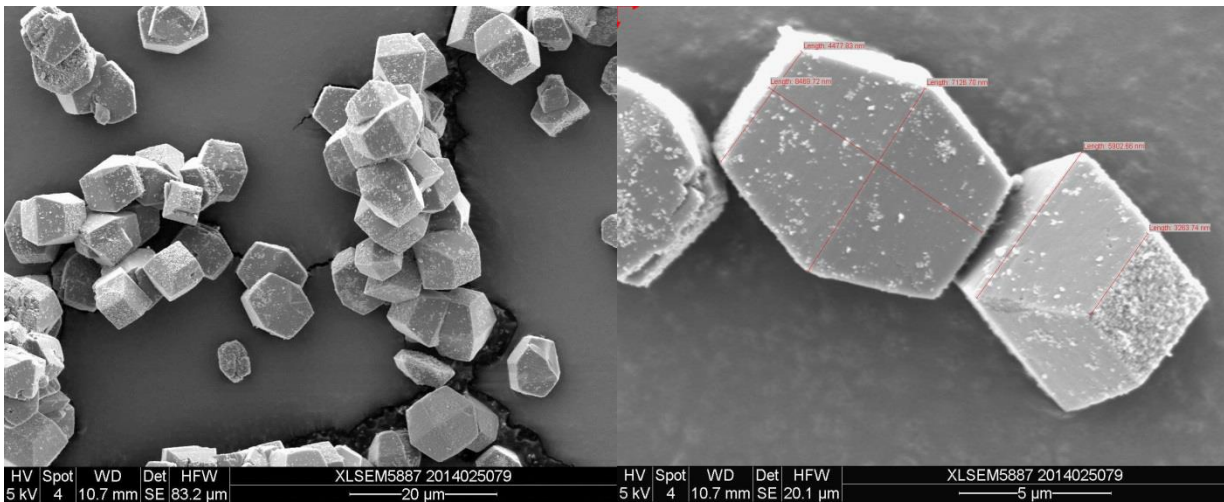
100, 30 days (Table S1, entry 28)



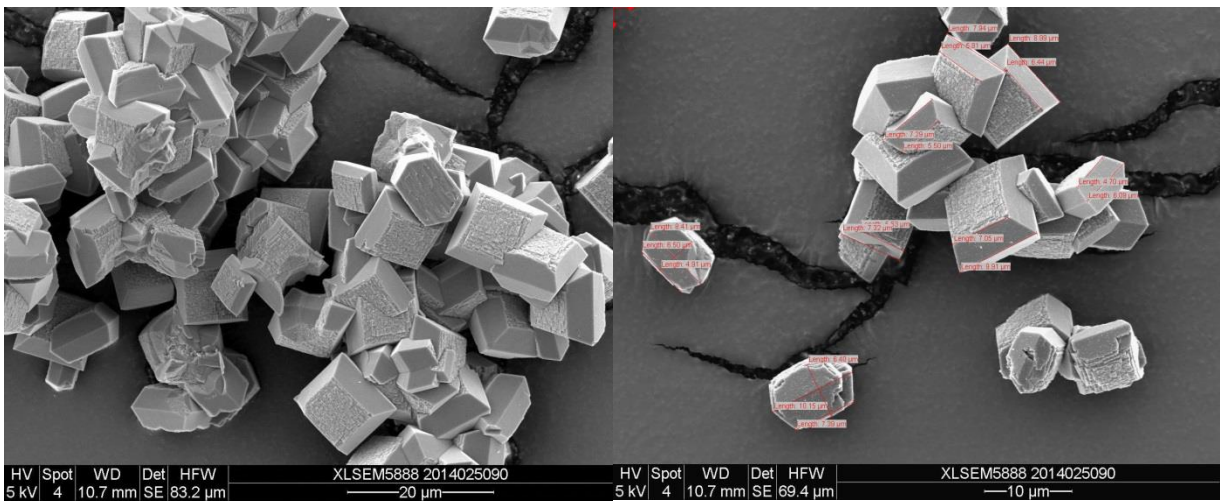
Si/Sn = 100, 60 days (Table S1, entry 29)



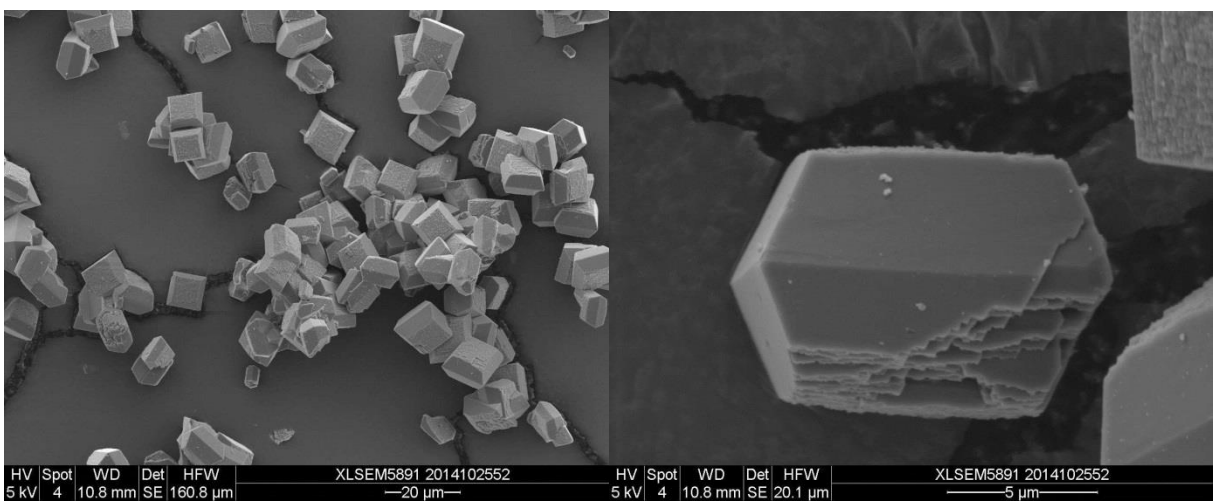
Si/Sn = 150, SnO₂ as tin source



Si/Sn = 150, tin(IV)acetate as tin source

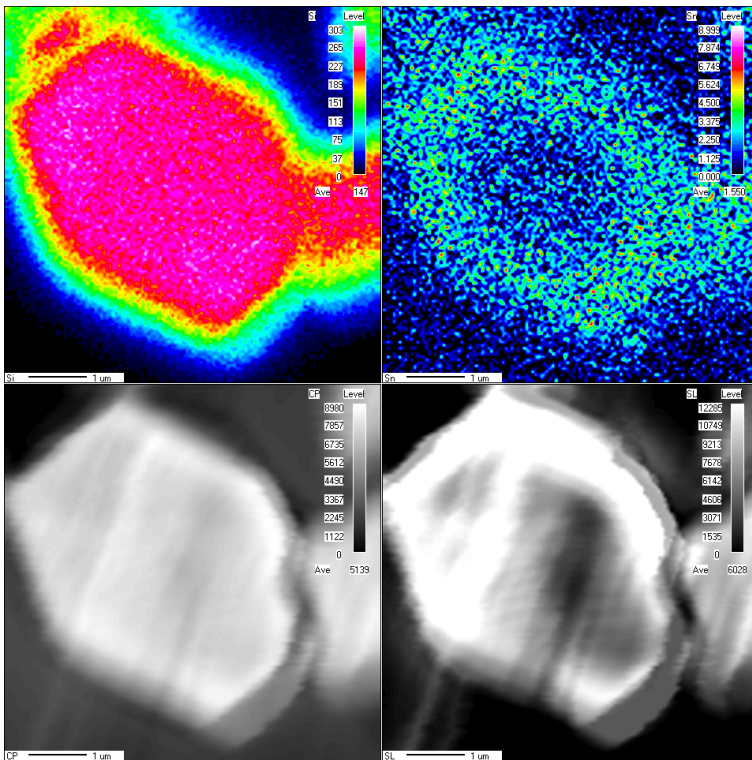


Si/Sn = 150, (TEA)₂SnF₆ as tin source

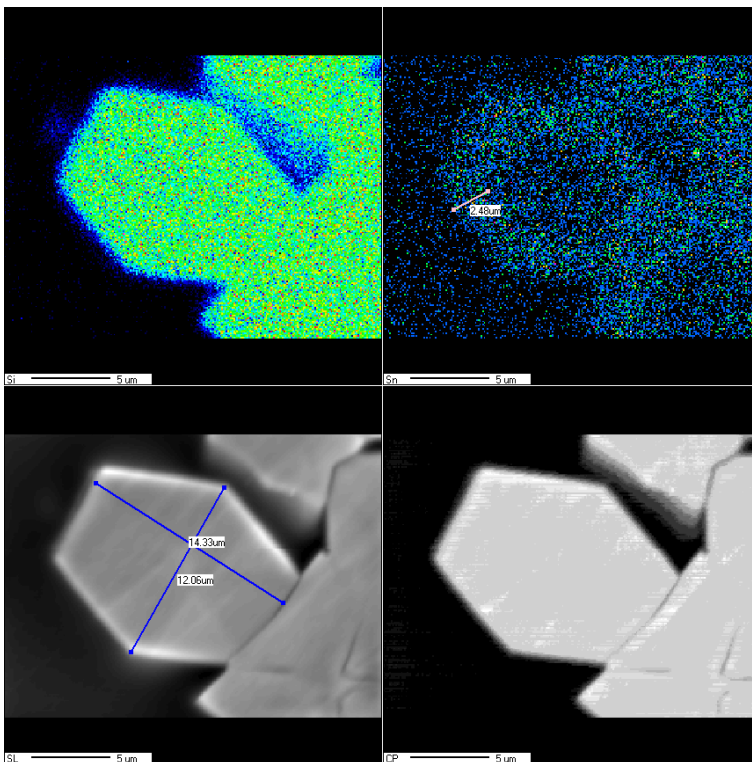


Additional SEM-EMP measurements for samples in Table S1.

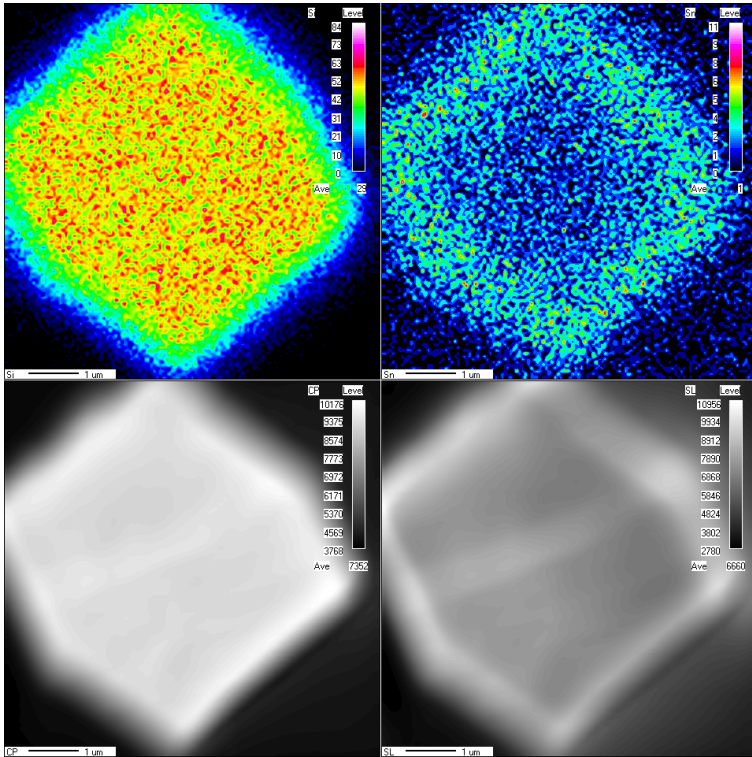
Si/Sn = 400, 4 days



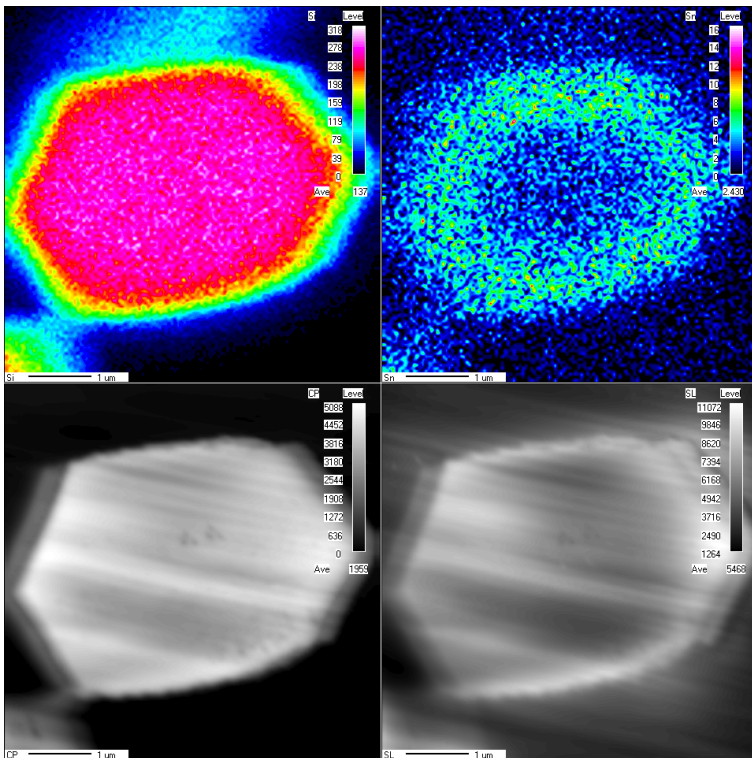
Si/Sn = 400, 14 days



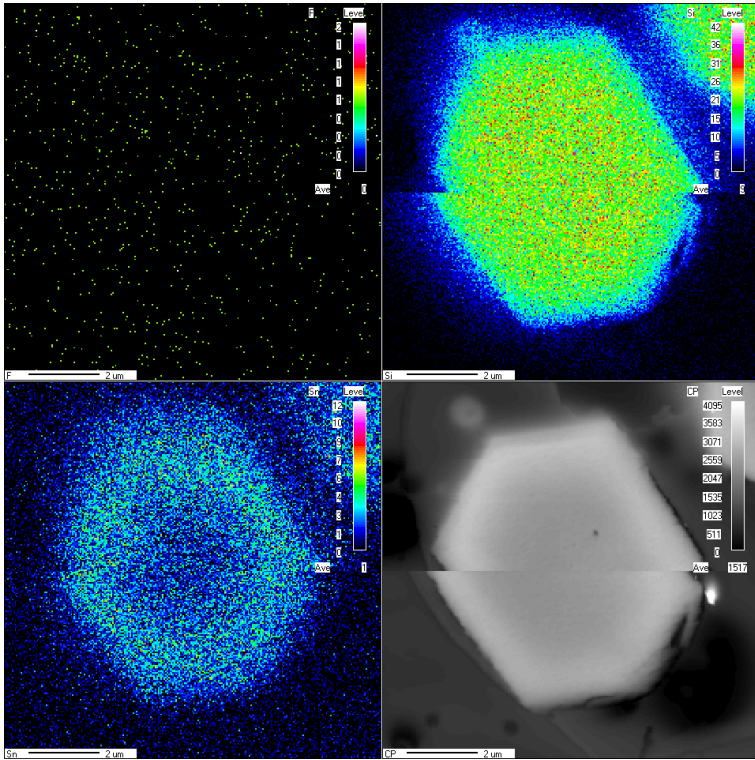
Si/Sn = 200, 4 days



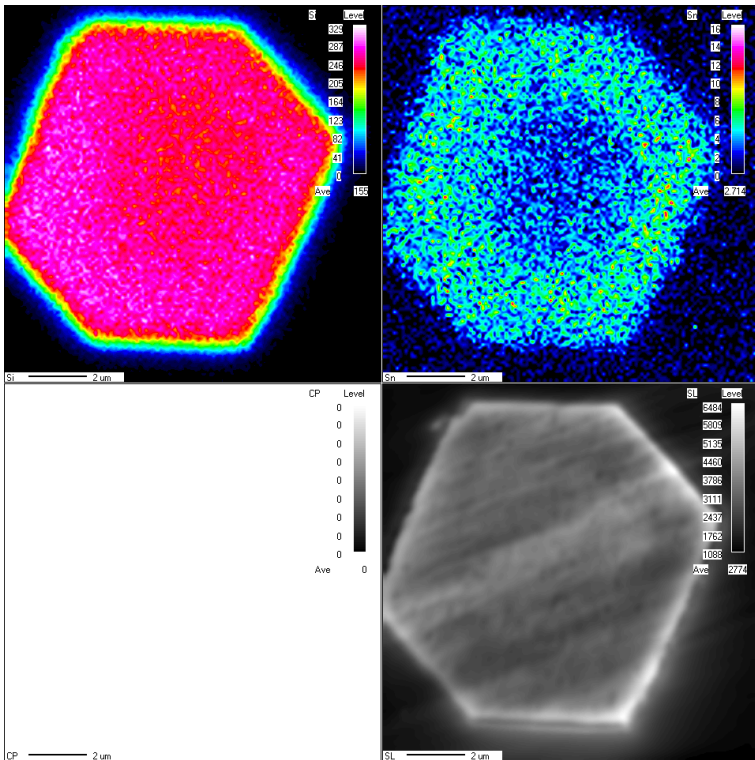
Si/Sn = 200, 7 days



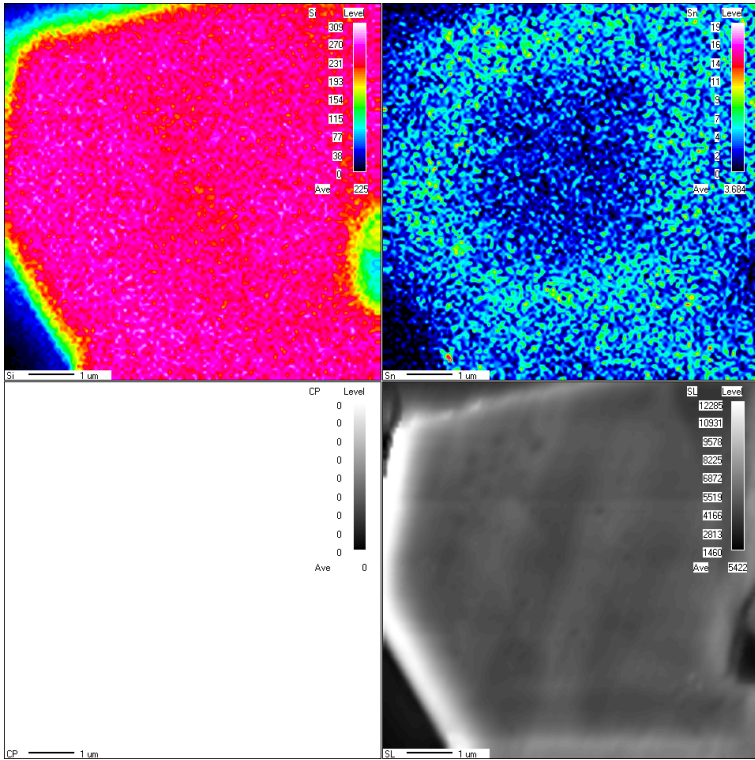
Si/Sn = 200, 14 days



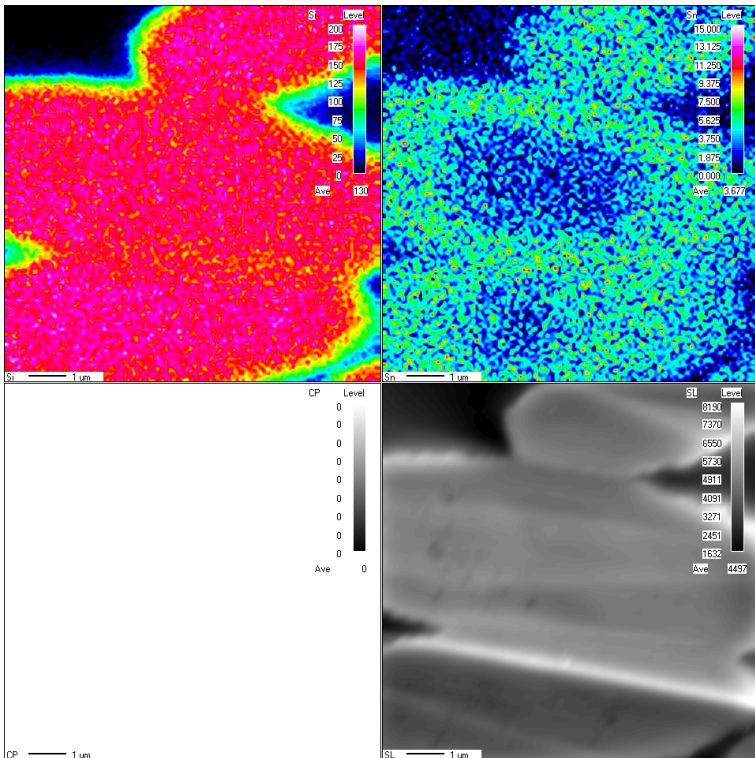
Si/Sn = 200, 30 days



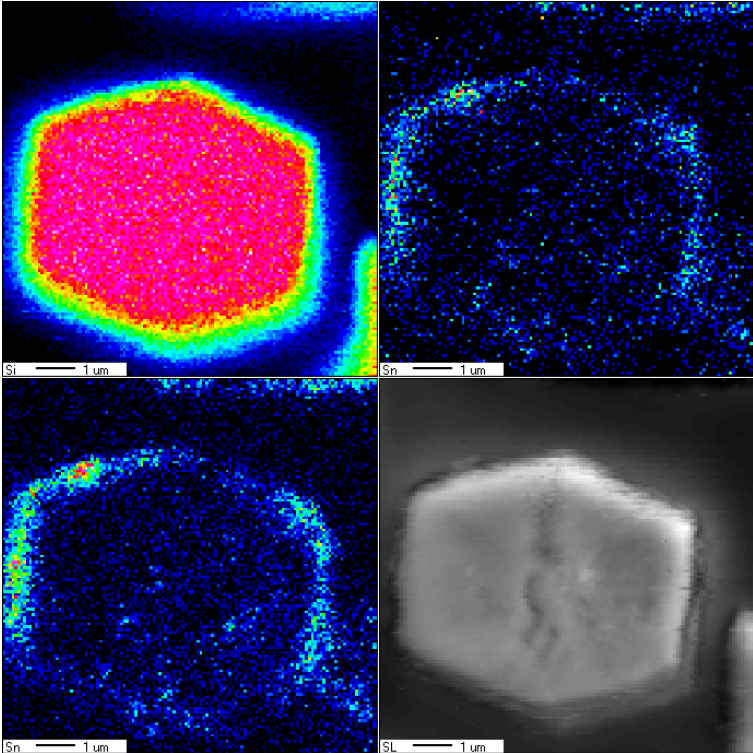
Si/Sn = 150, 14 days



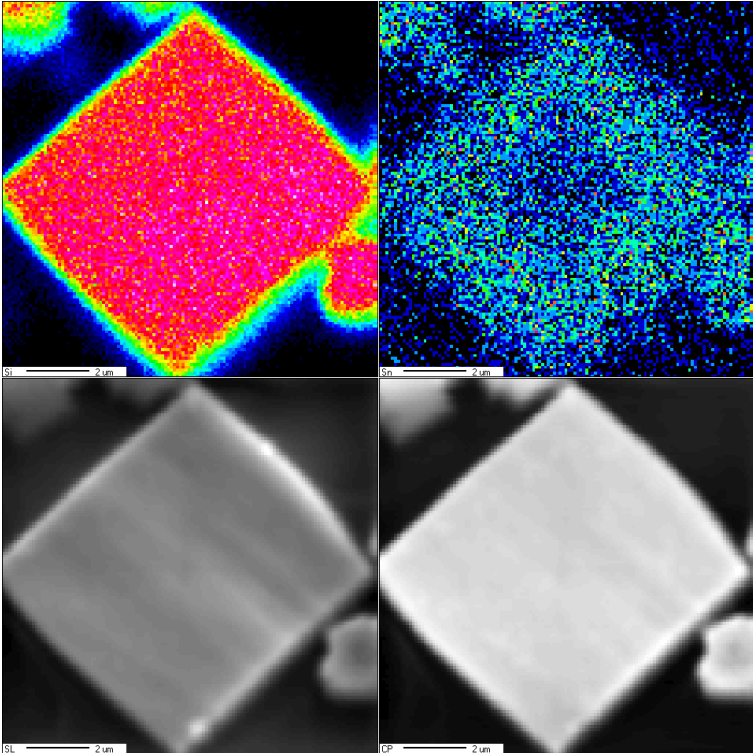
Si/Sn = 100, 60 days



Si/Sn = 150, SnO₂ as tin source



Si/Sn = 150, Tin(IV)acetate as tin source



Si/Sn = 150, (TEA)₂SnF₆ as tin source

