Understanding Morphology: A Look at Tin Based Nanoparticles

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Exceptional service in the national interest

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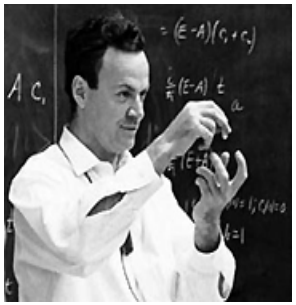

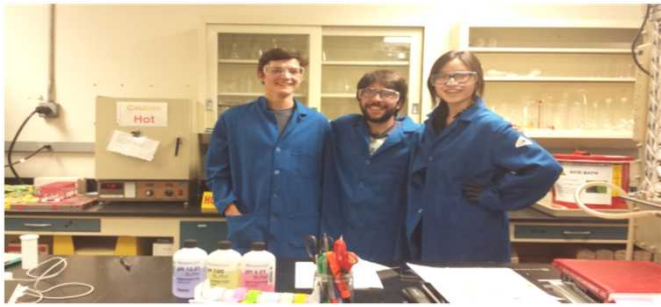

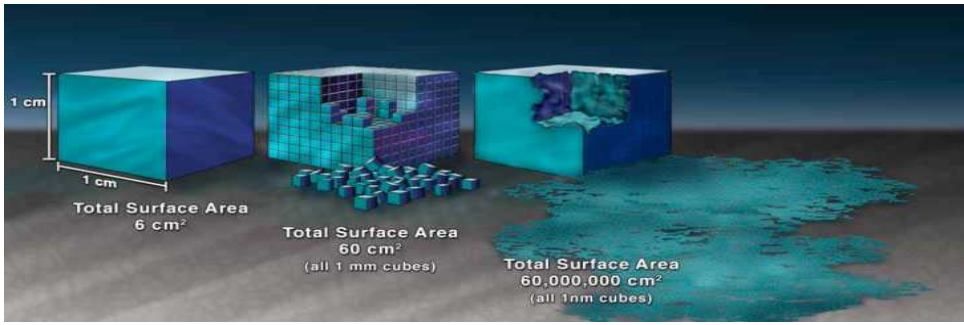

Images from nano.gov

THE UNIVERSITY of NEW MEXICO

AML Advanced Materials Laboratory

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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The Importance of Morphology

Morphology affects

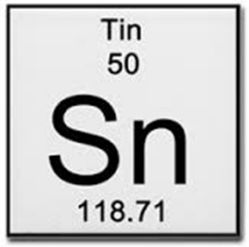
- Phototoxicity[1]
- Photo electrochemical performance[2]
- Tensile and yield strength[3] among other properties

Morphology is affected by

- Reagent choice and ratio
- Reaction temperature
- Method of synthesis

Morphology is hard to predict without precedence

1. Tiezheng Ton et al. 2. N. Naseri et al. 3. A. R. Marder et al.

Working with  based materials

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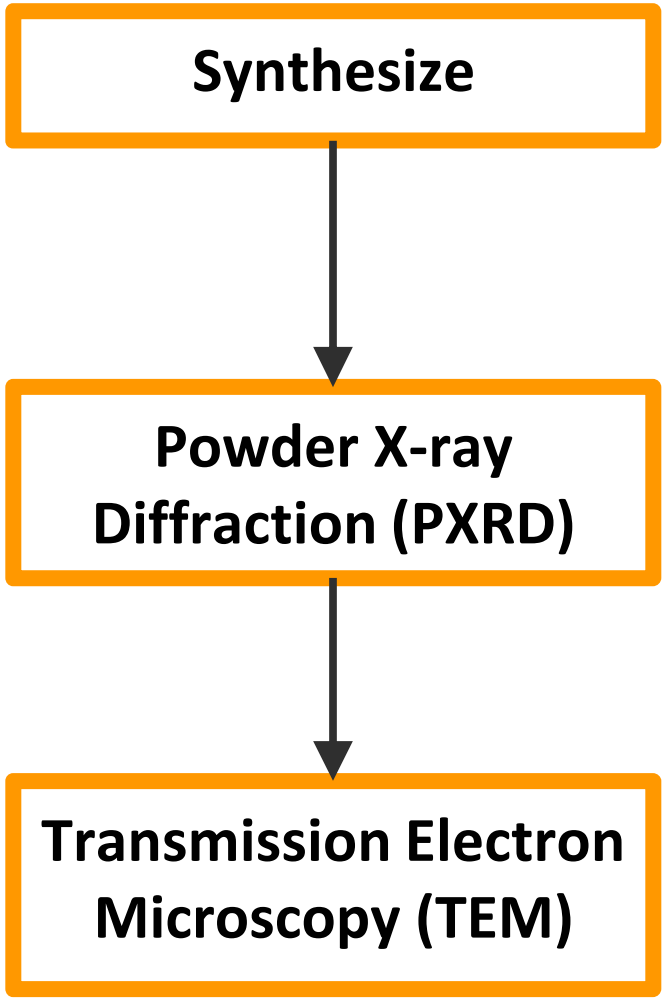
Sn	Anticorrosion, malleable, ductile, conductive, used in coatings, and is abundant
SnO	Used in carbon monoxide detectors, and used in film anodes for Li-ion batteries[4]
SnE	Promising materials due to optical and electrical properties[5]
SnP	Used in anodes for Na-ion batteries[6], and found useful due to semiconductive properties

E = Chalcogenides (Se, Te, S)

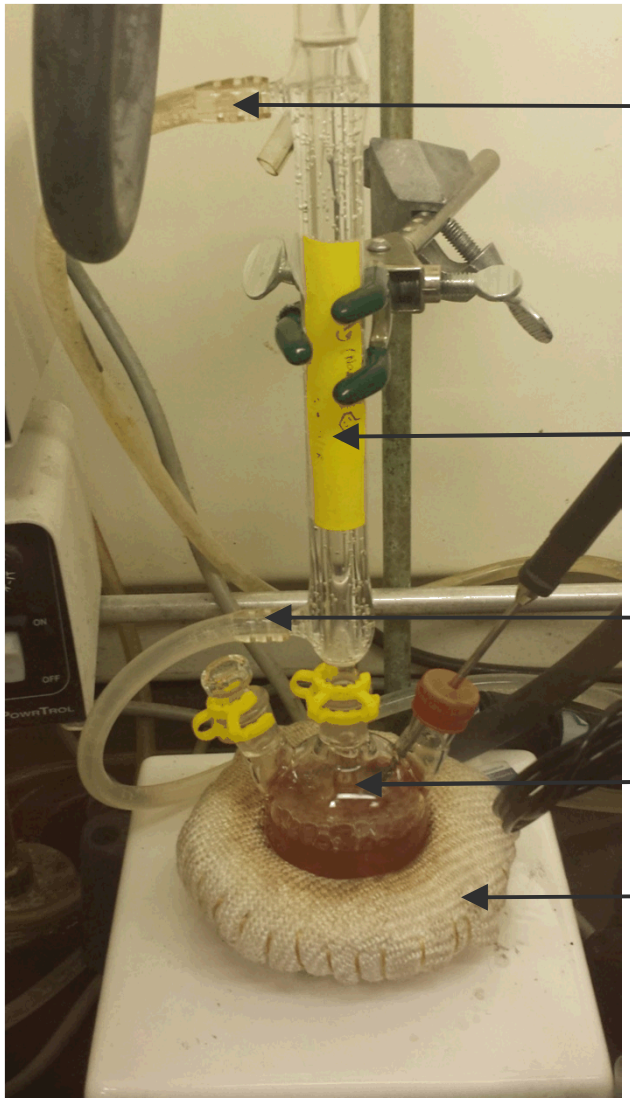
Image from cafepress.com, 4. Yan-Na Nuli et al., 5. O. P. Singh et al. 6. Youngjin Kim et al.

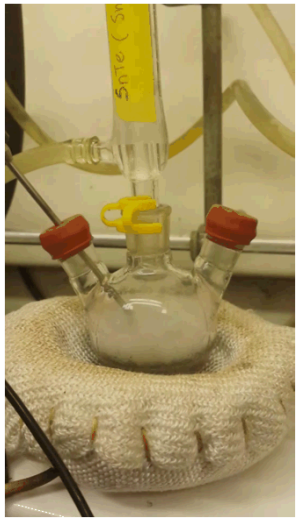
Experimental Overview



Compound	Synthesis	PXRD	TEM
Sn	●	●	●
SnSe	●	●	●
SnTe	●	●	●
SnS	●	●	●
SnP	●	✕	
SnO	●	●	●

Temporal Solution Precipitation



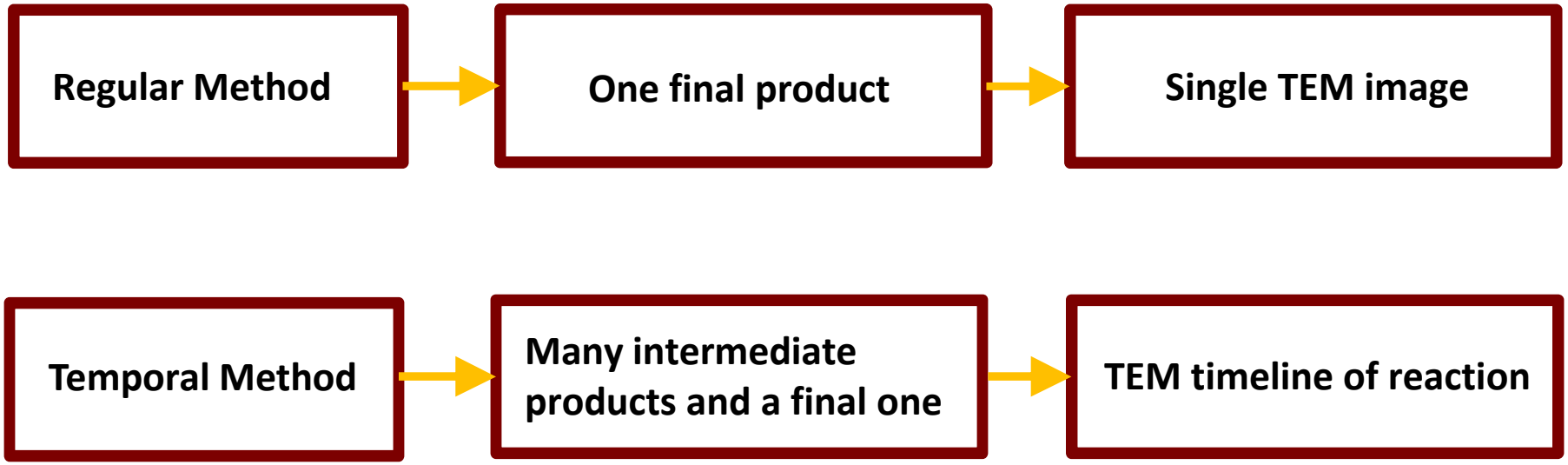


Sample at . . .

- ☐ Color change
- ☐ 5 minutes after
- ☐ 15 minutes after
- ☐ 30 minutes after
- ☐ 60 minutes after
- ☐ Reaction finished (usually 2 hours)

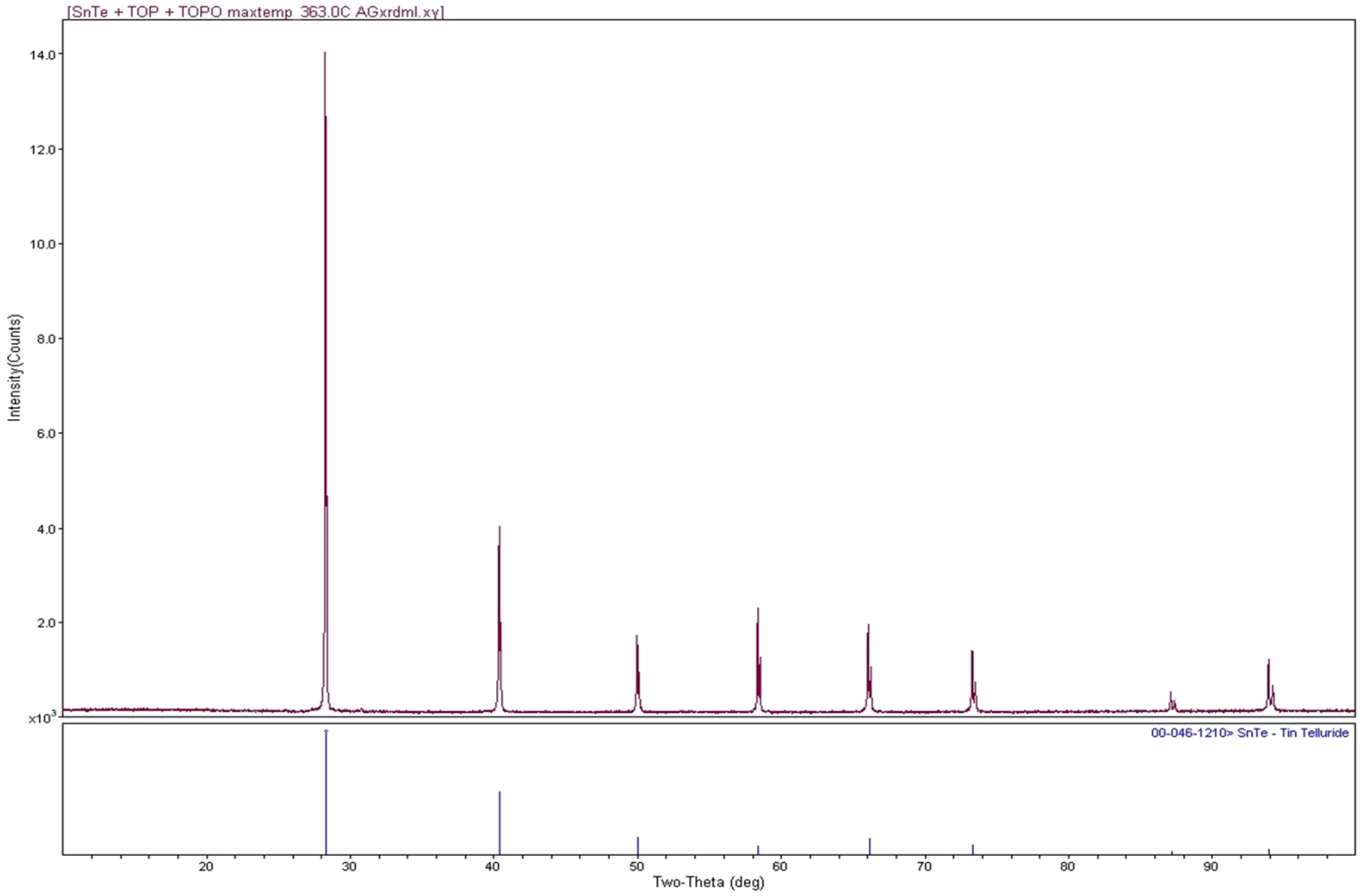
Temporal studies

Temporal studies used to see how the morphology changes as the reaction progresses



A mechanism for morphology and growth can potentially be obtained

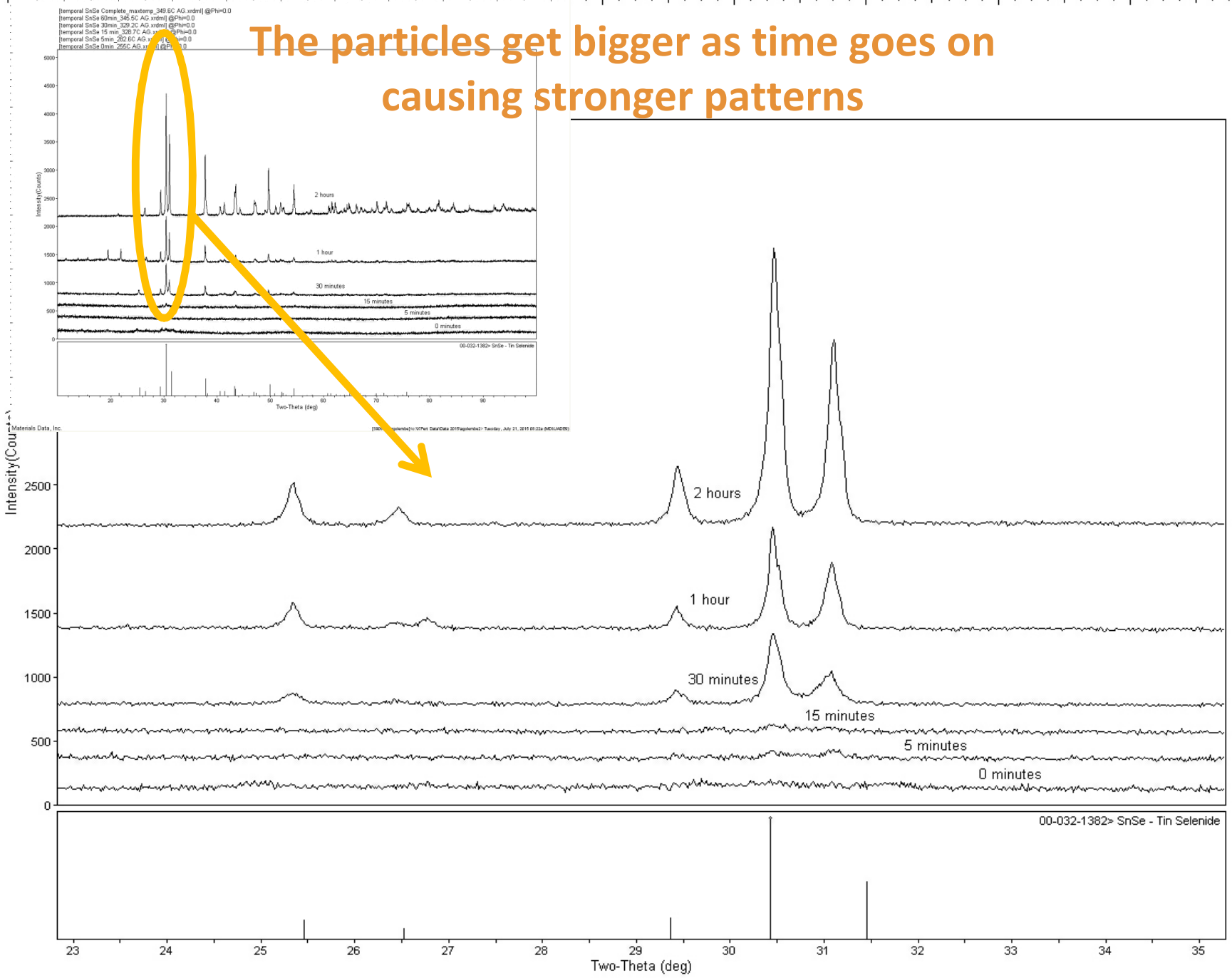
Powder X-ray Diffraction (PXRD)



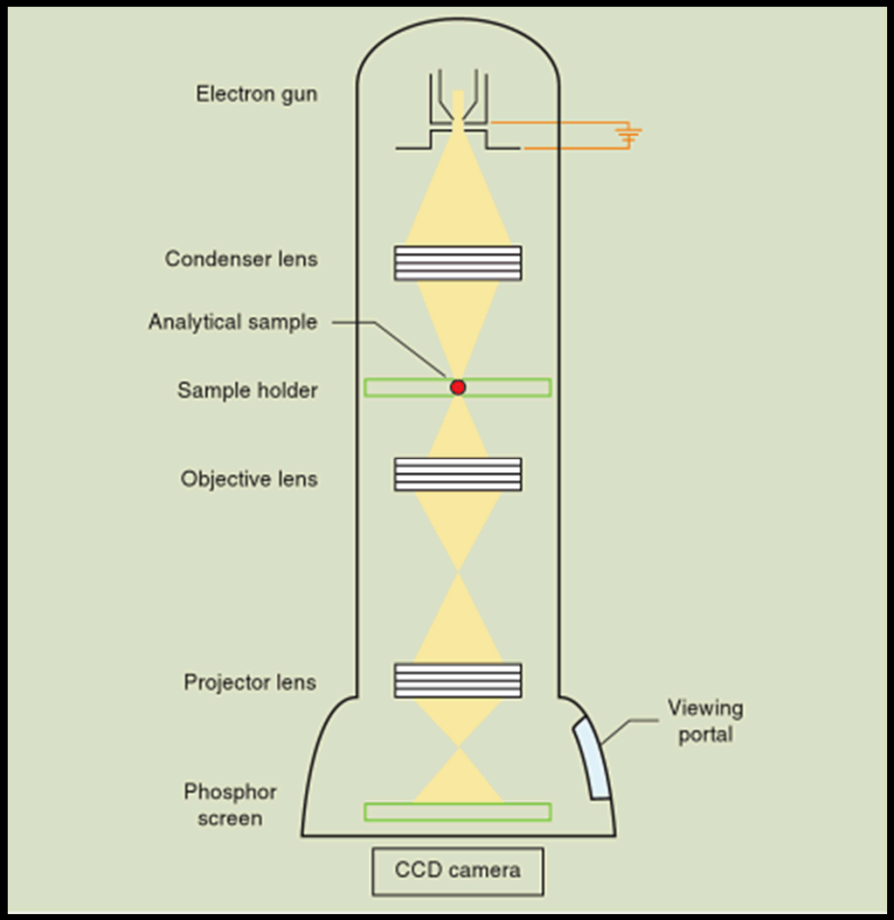
Materials Data, Inc.

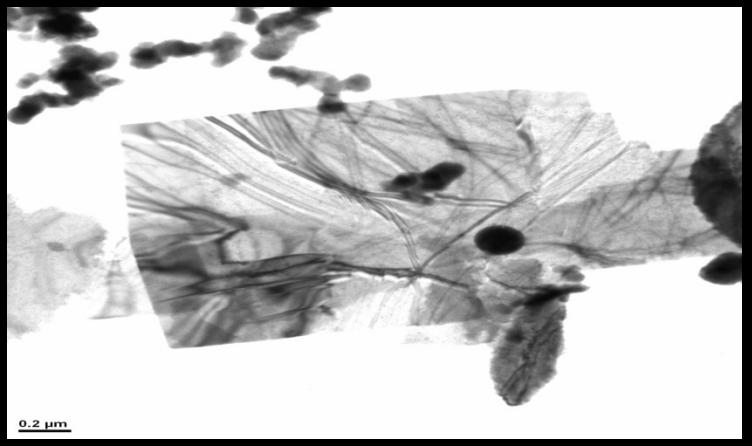
[S905113]agolembe]<c:\Data 2015\agolembe> Monday, June 29, 2015 09:40a (MDI/JADE9)

The particles get bigger as time goes on causing stronger patterns



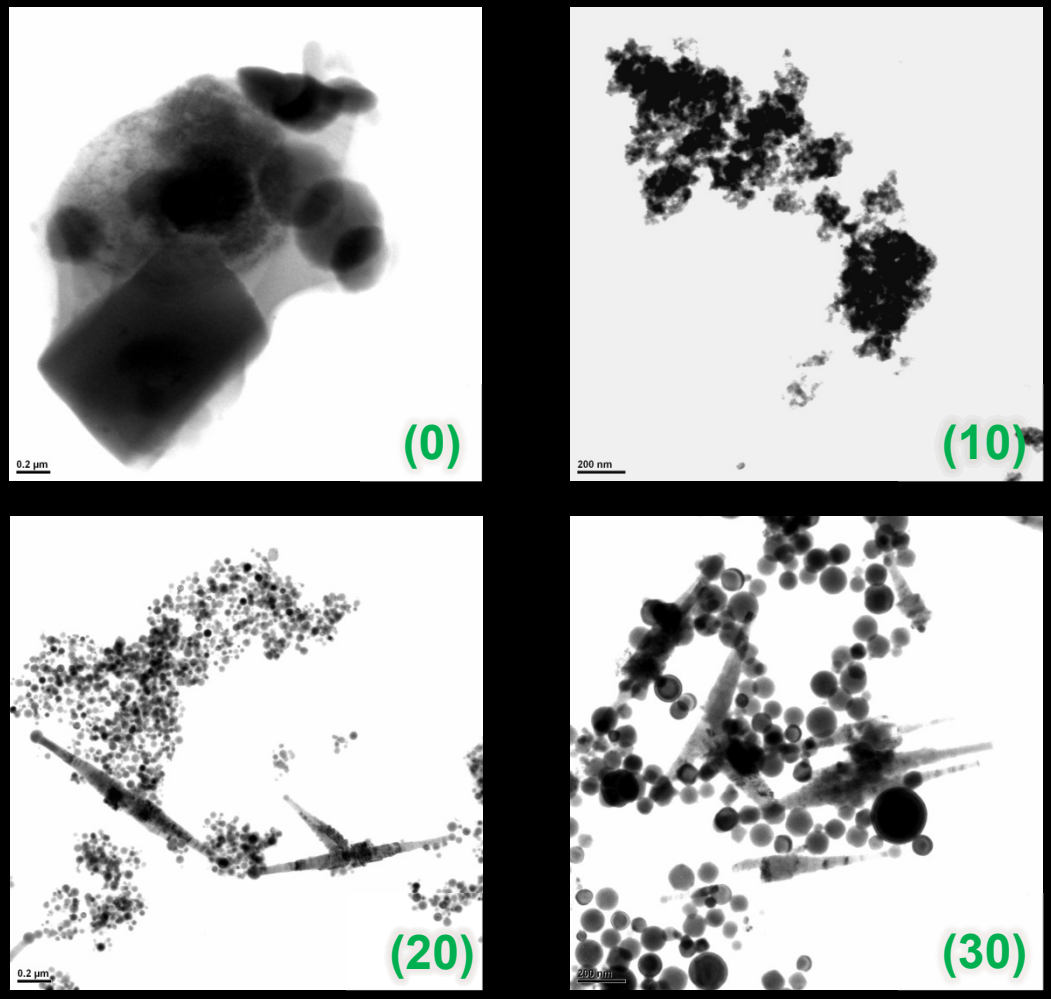
Transmission Electron Microscopy





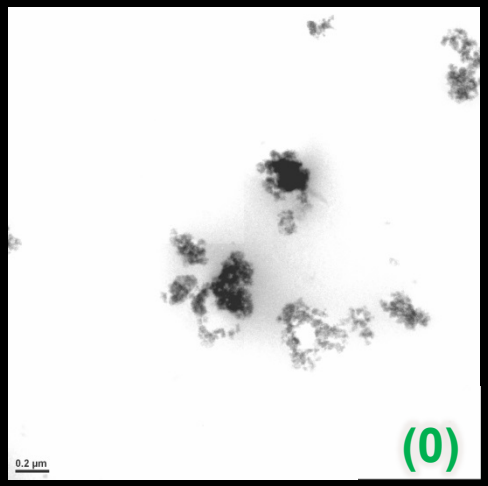
This instrument uses an electron gun to create high resolution images on the nanoscale

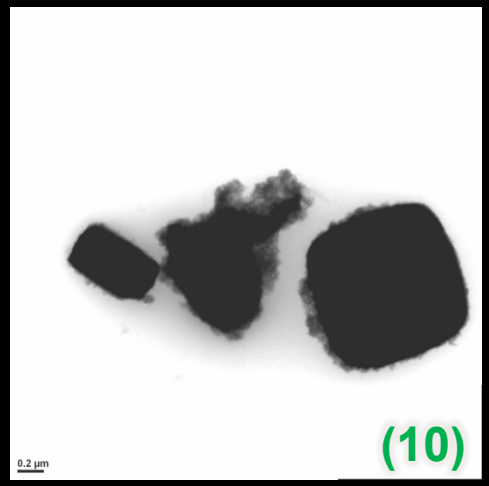
Tin (Sn)

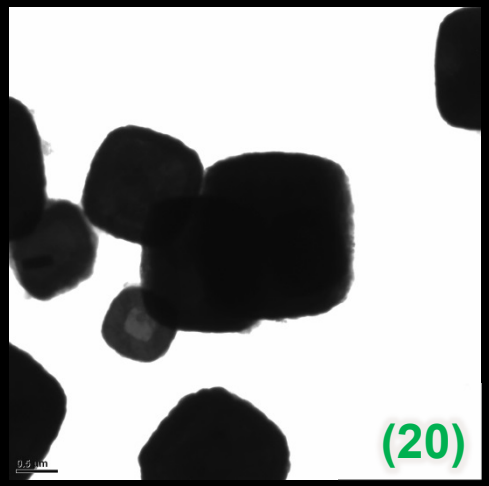


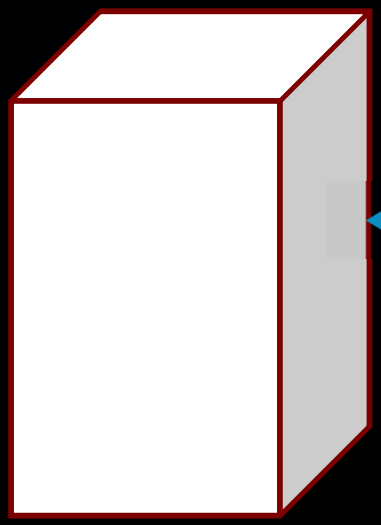
"Tin whiskers" formed after 20 minutes. Morphology is mixed between whiskers and dots.

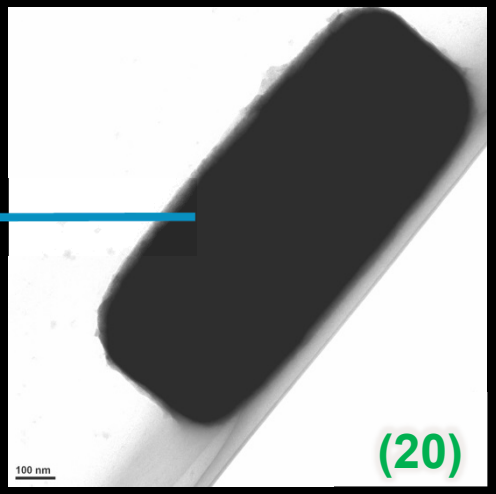
Tin Oxide (SnO)











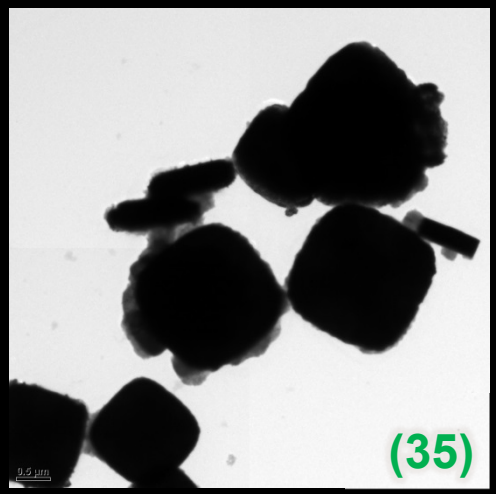
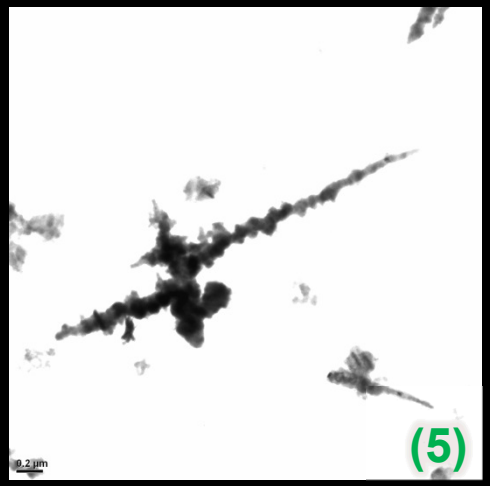
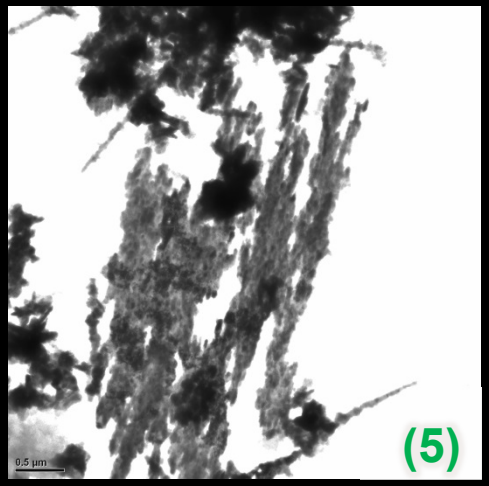
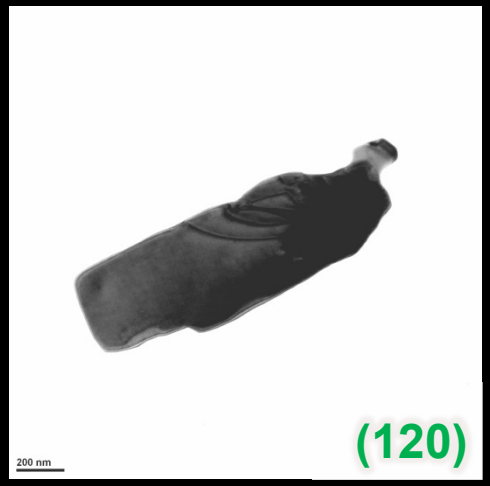


Plate growth is quick. Out of the nano range after 20 minutes.

Tin Selenide (SnSe)

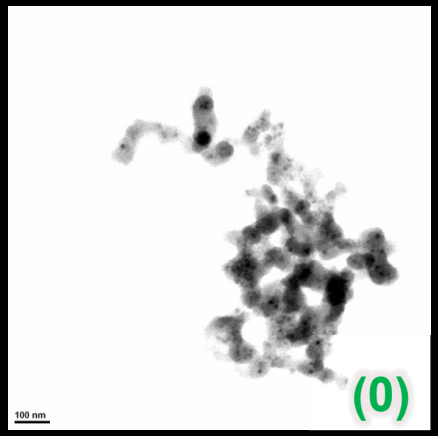


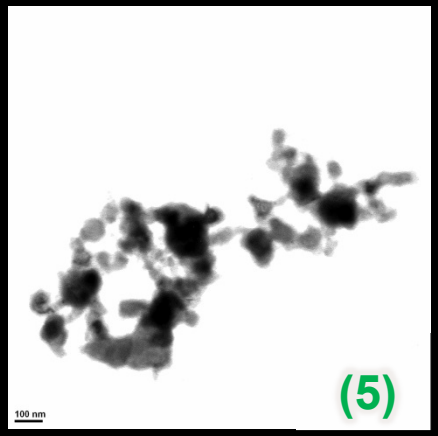


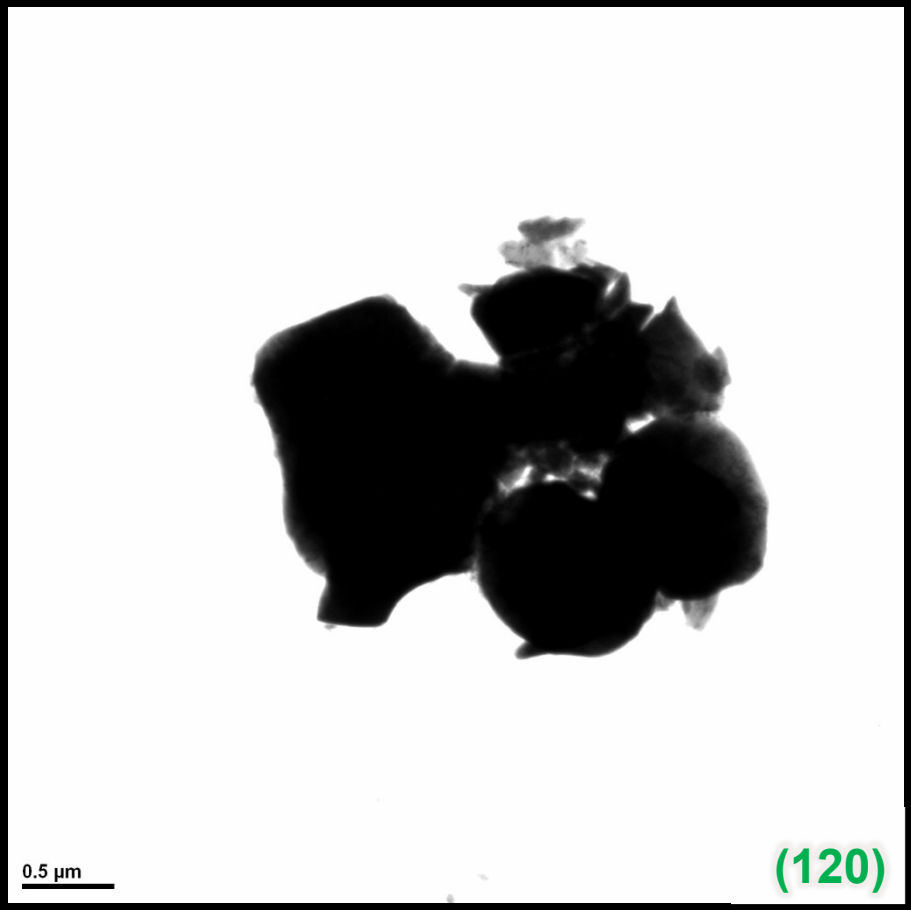


The morphology is not constant throughout the reaction!
It develops over time instead.

Tin Telluride (SnTe)

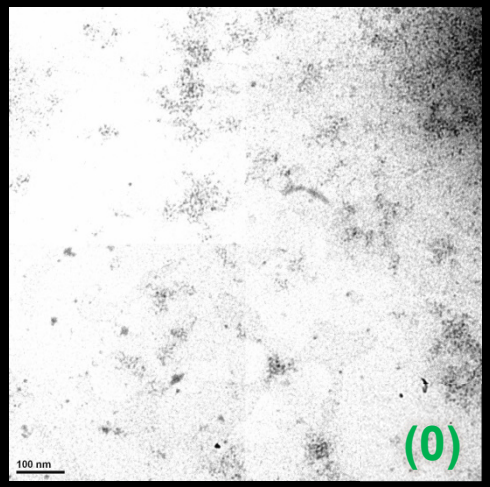


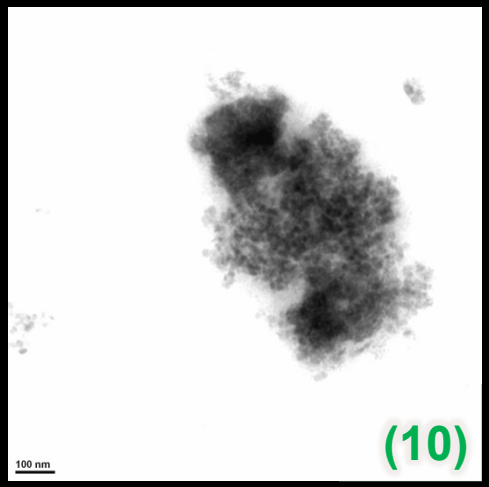


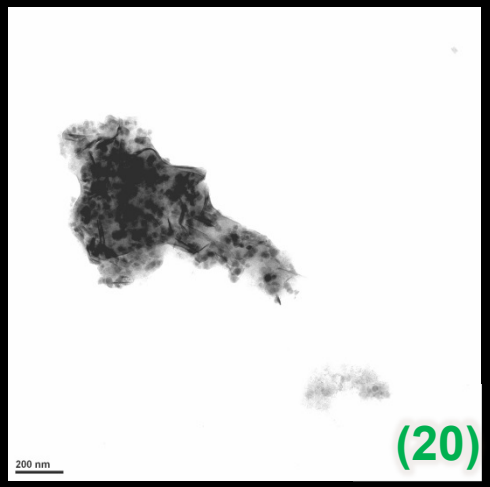


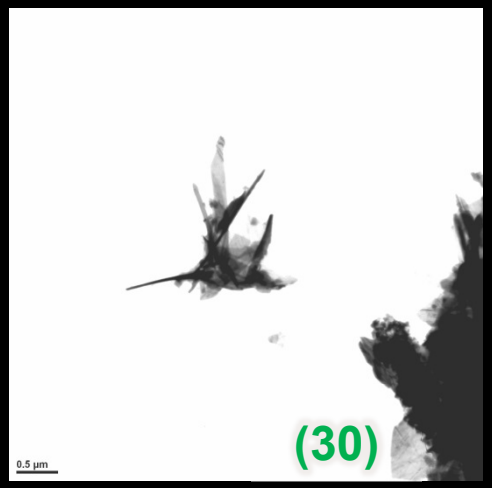
More to be explored here sampling at different times. The end morphology appears to be “sheet like” on the edges.

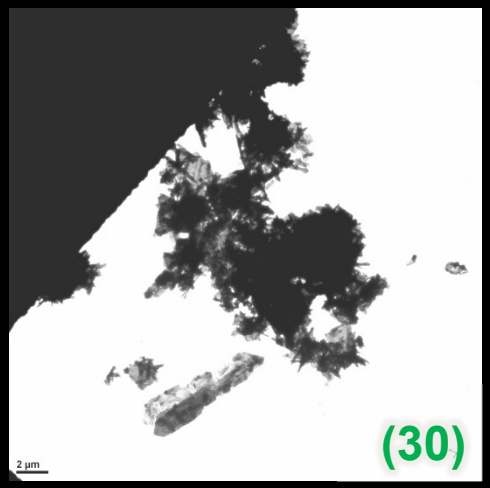
Tin Sulfide (SnS) (Oleic Acid)





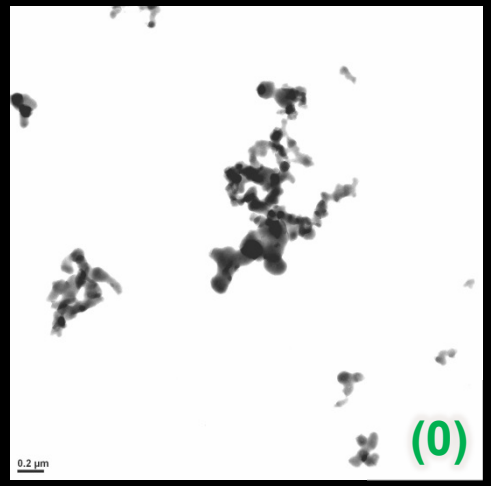


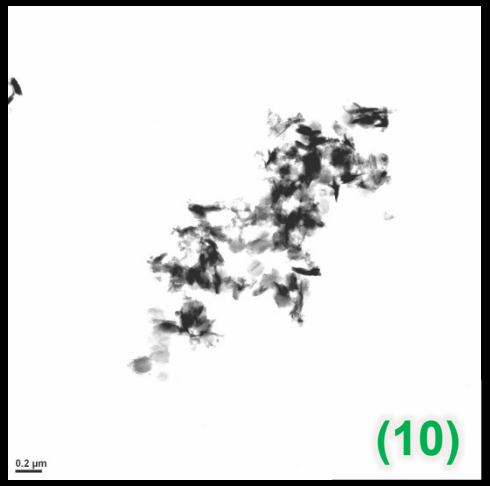


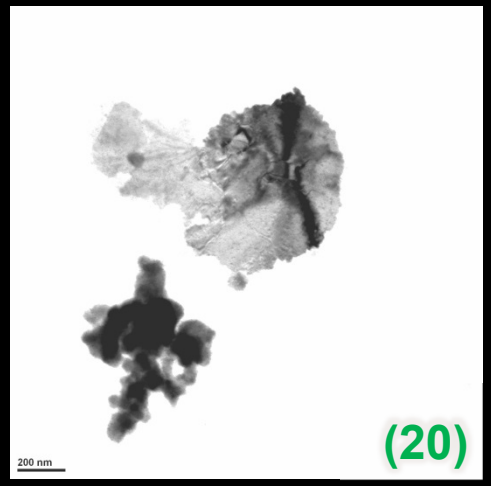


Mixed morphology of nanosheets and nanorods.

Tin Sulfide (SnS) (TOPO)

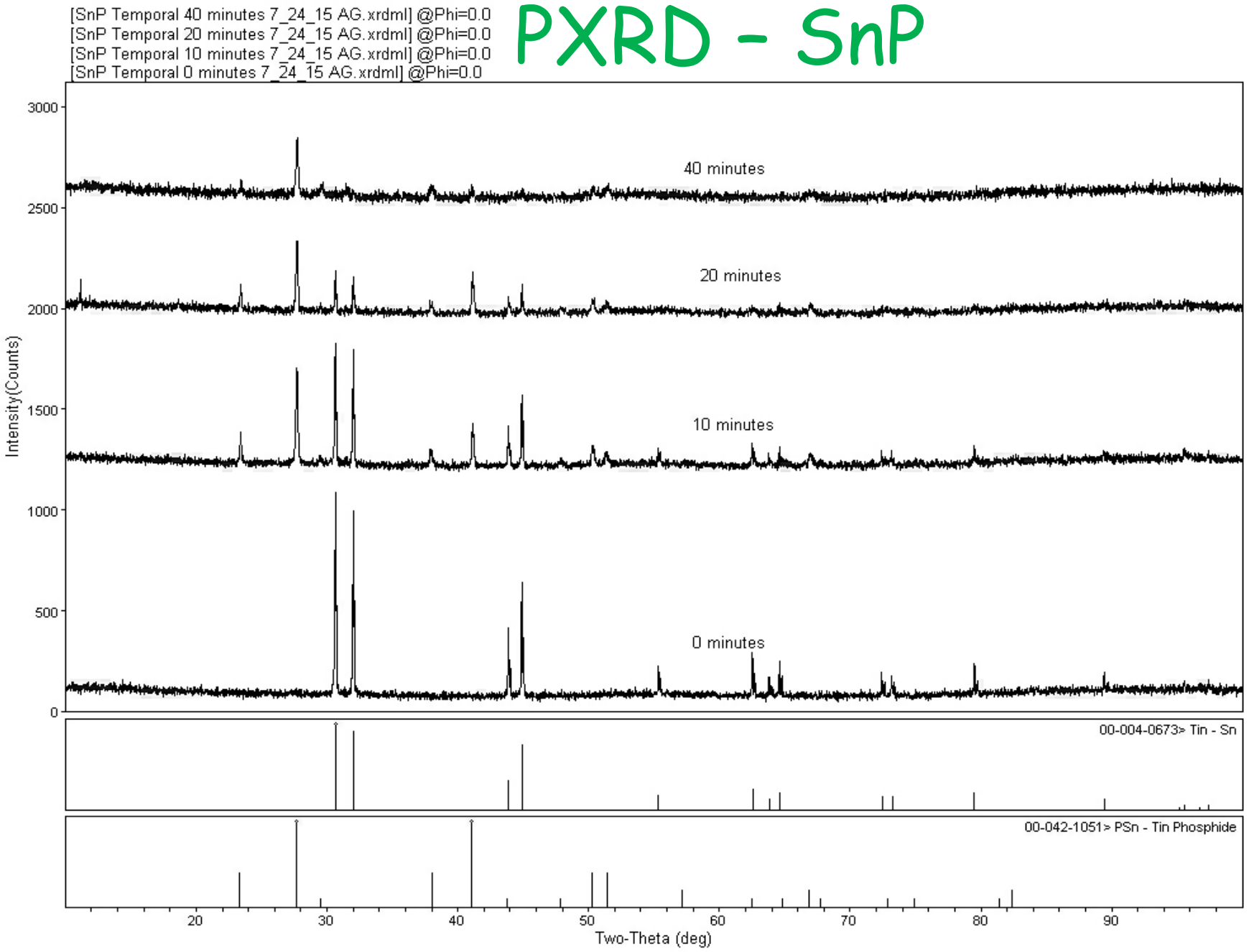






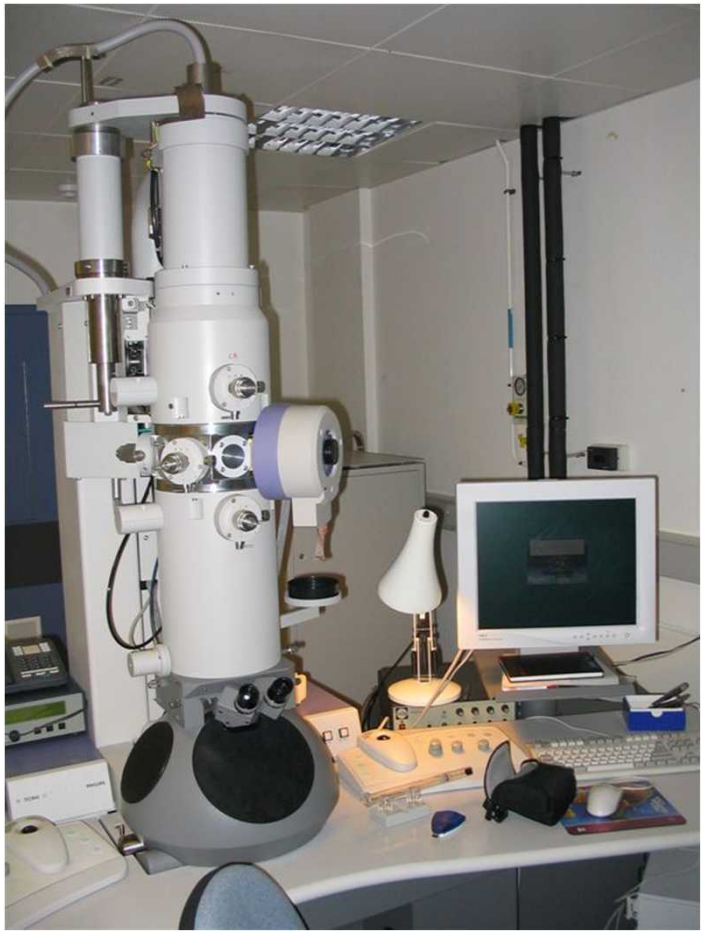
Mixed morphology as well, this time in nanosheets and dots.

PXRD - SnP


[SnP Temporal 40 minutes 7_24_15 AG.xrdml] @Phi=0.0
[SnP Temporal 20 minutes 7_24_15 AG.xrdml] @Phi=0.0
[SnP Temporal 10 minutes 7_24_15 AG.xrdml] @Phi=0.0
[SnP Temporal 0 minutes 7_24_15 AG.xrdml] @Phi=0.0
40 minutes
20 minutes
10 minutes
0 minutes
Intensity(Counts)
3000
2500
2000
1500
1000
500
0
00-004-0673> Tin - Sn
00-042-1051> PSn - Tin Phosphide
20
30
40
50
60
70
80
90
Two-Theta (deg)

Moving further with the project

- Perform additional characteristic analysis on the different morphologies to gather morphology and size specific properties (I^3TEM)
- Look into applications of the materials such as in photovoltaics or in computer applications
- Explore other tin based compounds such as Sn_2P or SnO_2



(TEM Microscope)

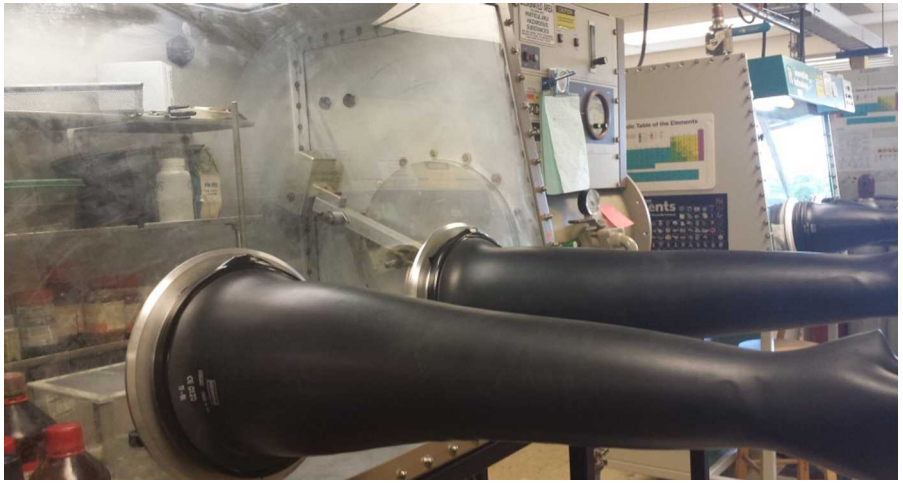


Image on the right from upload.wikipedia.org

Thank you for your time!

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Tin Oxide synthesis yields a skewed geometry, as it develops more in one plane than the other two planes.

Tin Selenide synthesis undergoes a dramatic change in morphology mid reaction.

Tin Phosphide synthesis proved to be tough, as it required a long reaction time to yield phase purity at which point particle size was out of the nanoscale.

Particle Growth

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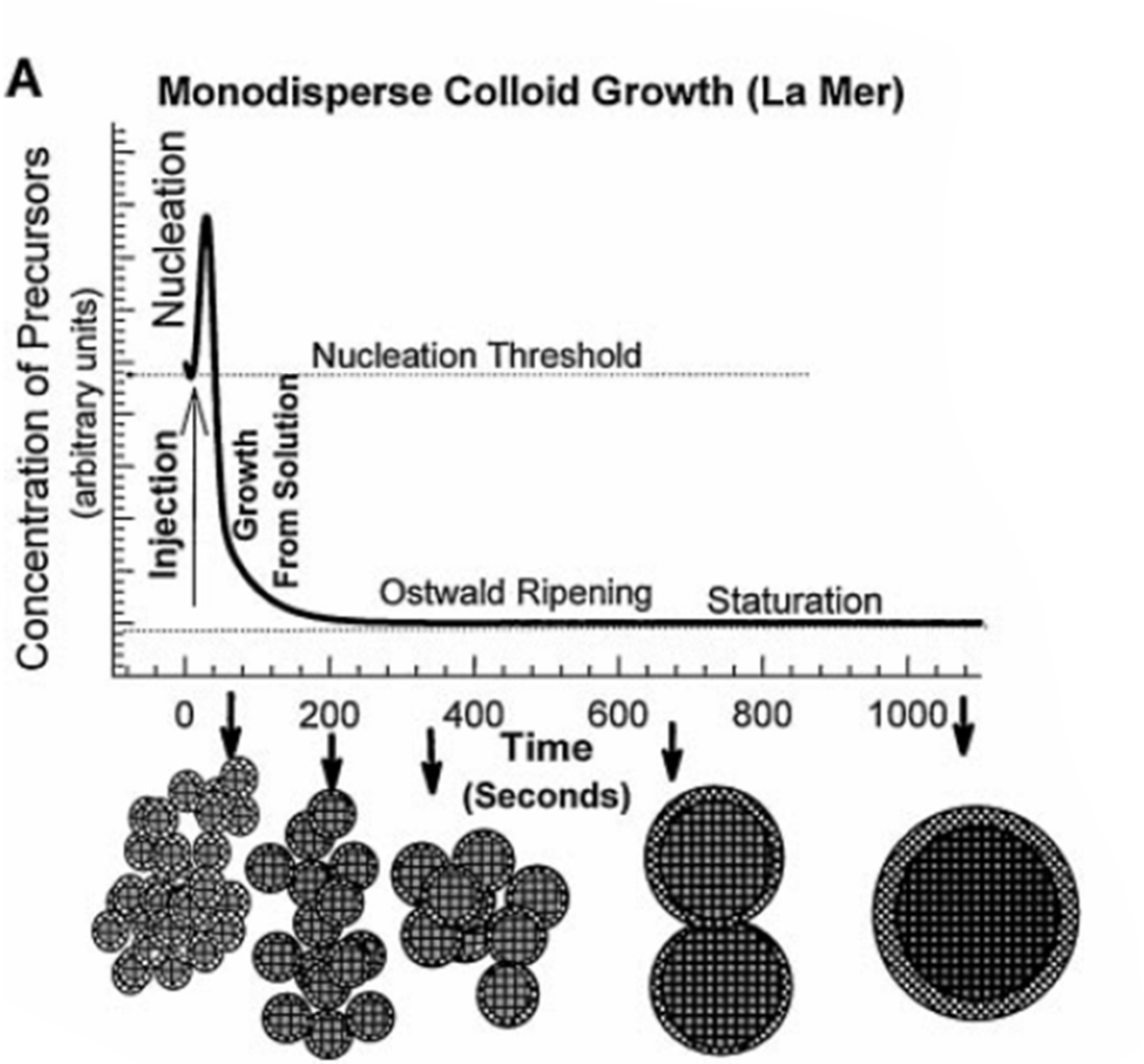

Image from C. B. Murray et al.

Reactions

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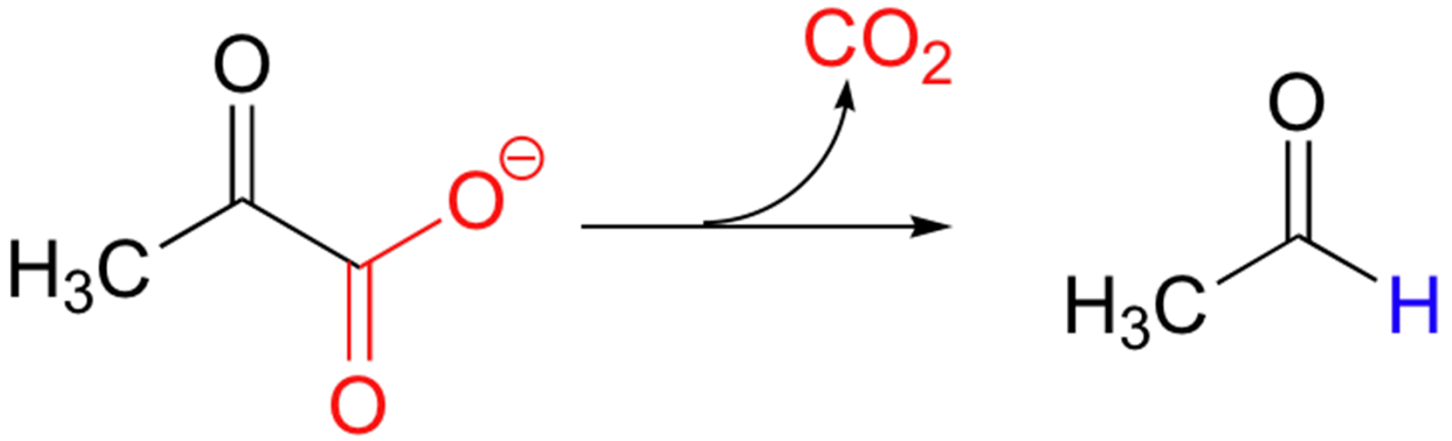
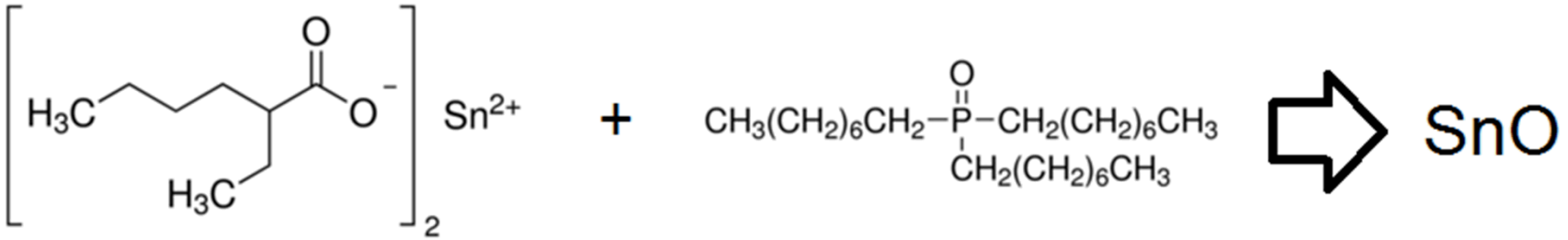
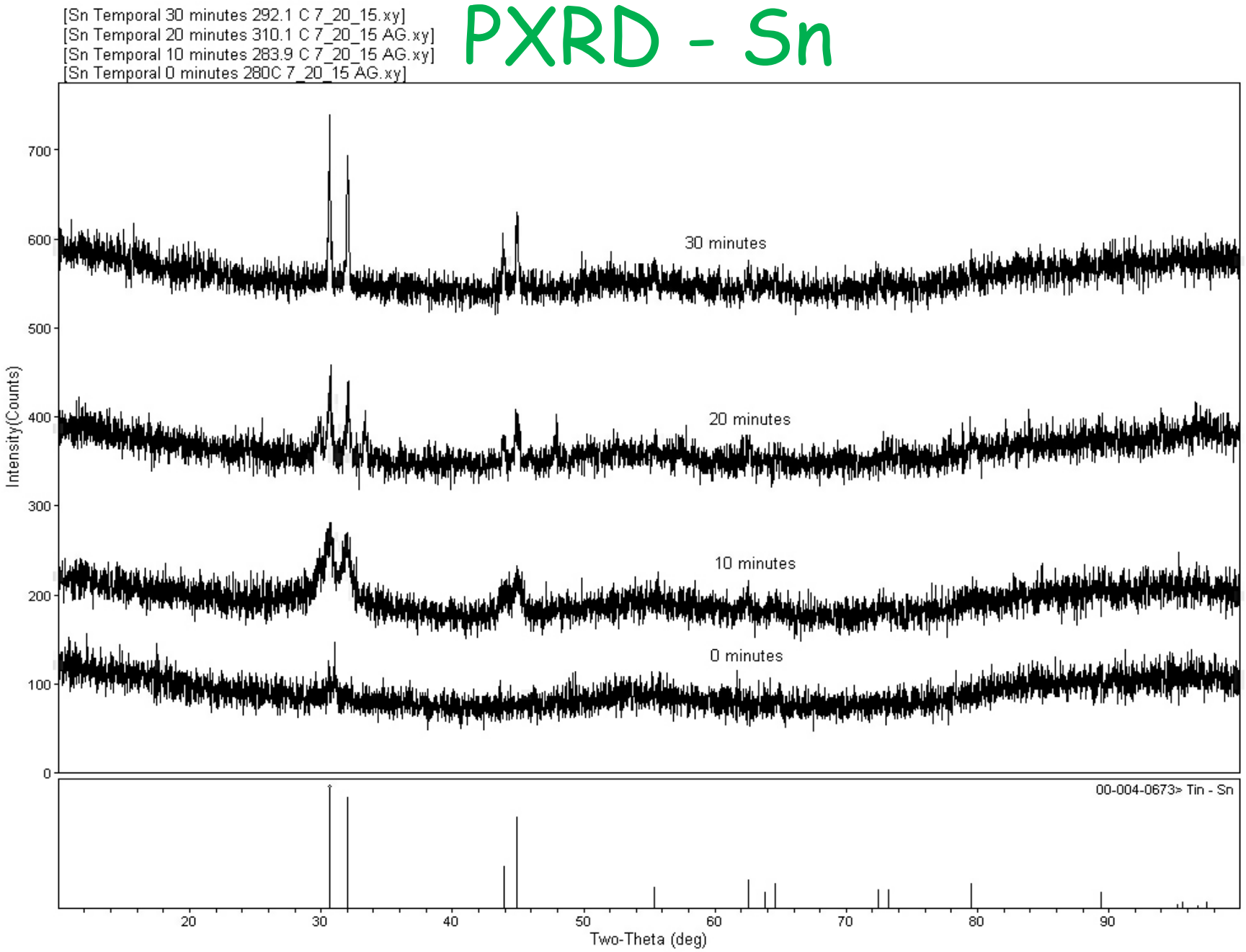
Reagents	Product
$Sn[N(P\text{-}Pr^{i}_{2})_2]_2$ + TOPO	Sn
$Sn(EtHx)_2$ + TOPO	SnO
$Sn(EtHx)_2$ + TOPO + TOP=Se	SnSe
$Sn(EtHx)_2$ + TOPO + TOP=Te	SnTe
$Sn(EtHx)_2$ + OA + Oleylamine	SnS (OA)
$Sn(EtHx)_2$ + TOPO + Oleylamine	SnS (TOPO)
$Sn[N(P\text{-}Pr^{i}_{2})_2]_2$ + TOP+ Oleylamine	SnP

Oxide Formation

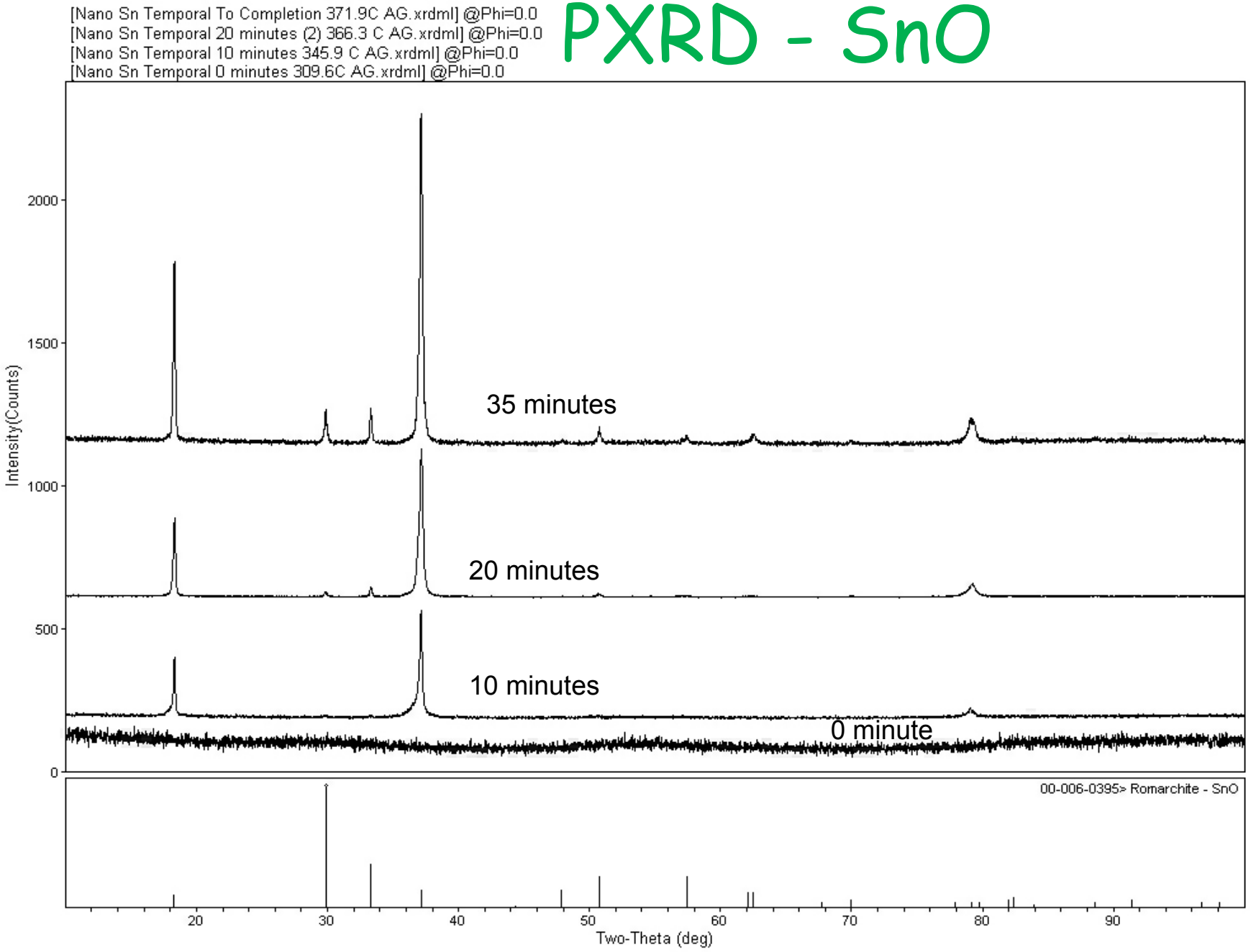




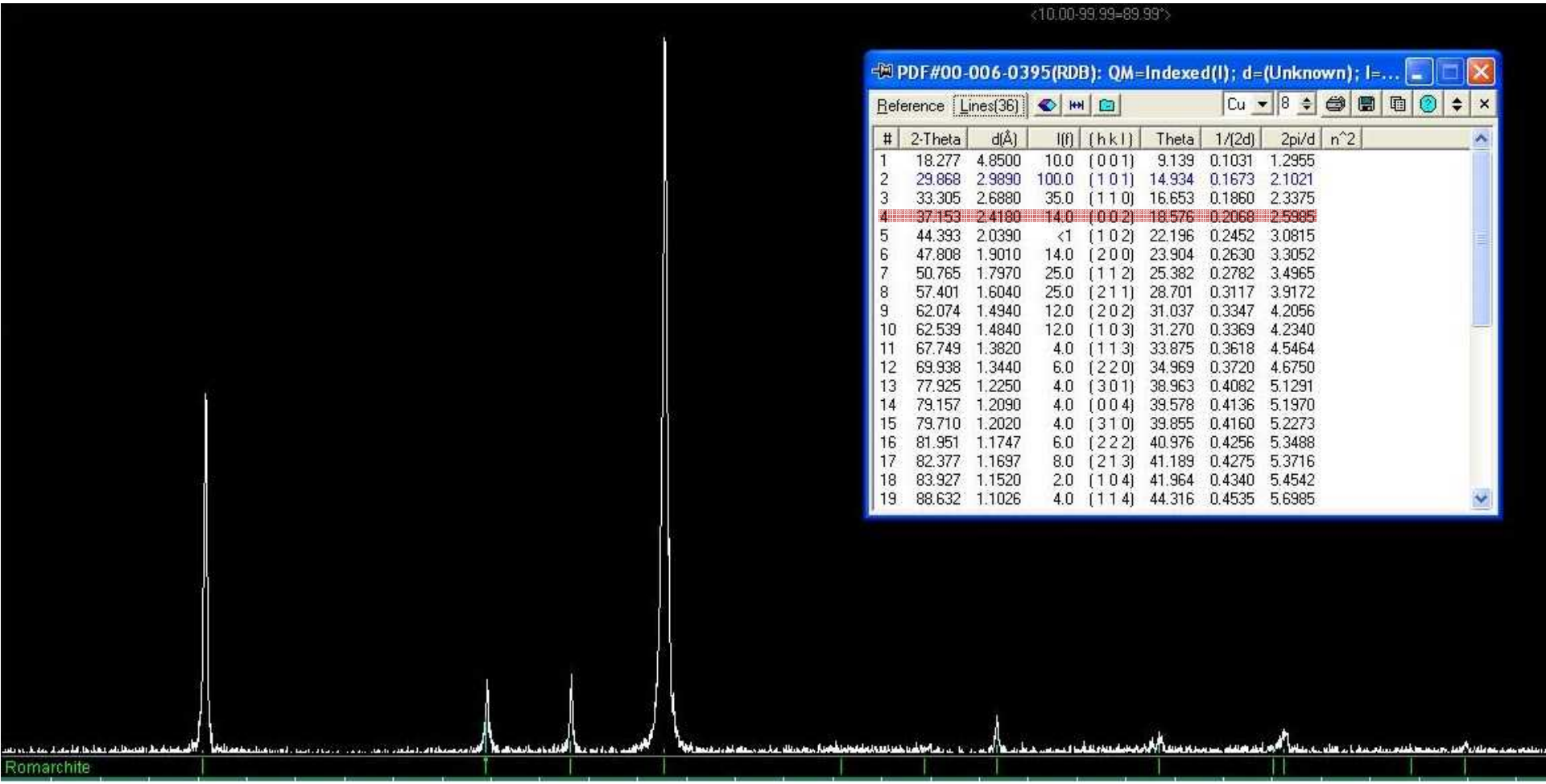
PXRD - Sn


[Sn Temporal 30 minutes 292.1 C 7_20_15.xy]
[Sn Temporal 20 minutes 310.1 C 7_20_15 AG.xy]
[Sn Temporal 10 minutes 283.9 C 7_20_15 AG.xy]
[Sn Temporal 0 minutes 280C 7_20_15 AG.xy]
30 minutes
20 minutes
10 minutes
0 minutes
Intensity(Counts)
0
100
200
300
400
500
600
700
00-004-0673> Tin - Sn
20
30
40
50
60
70
80
90
Two-Theta (deg)

PXRD - SnO

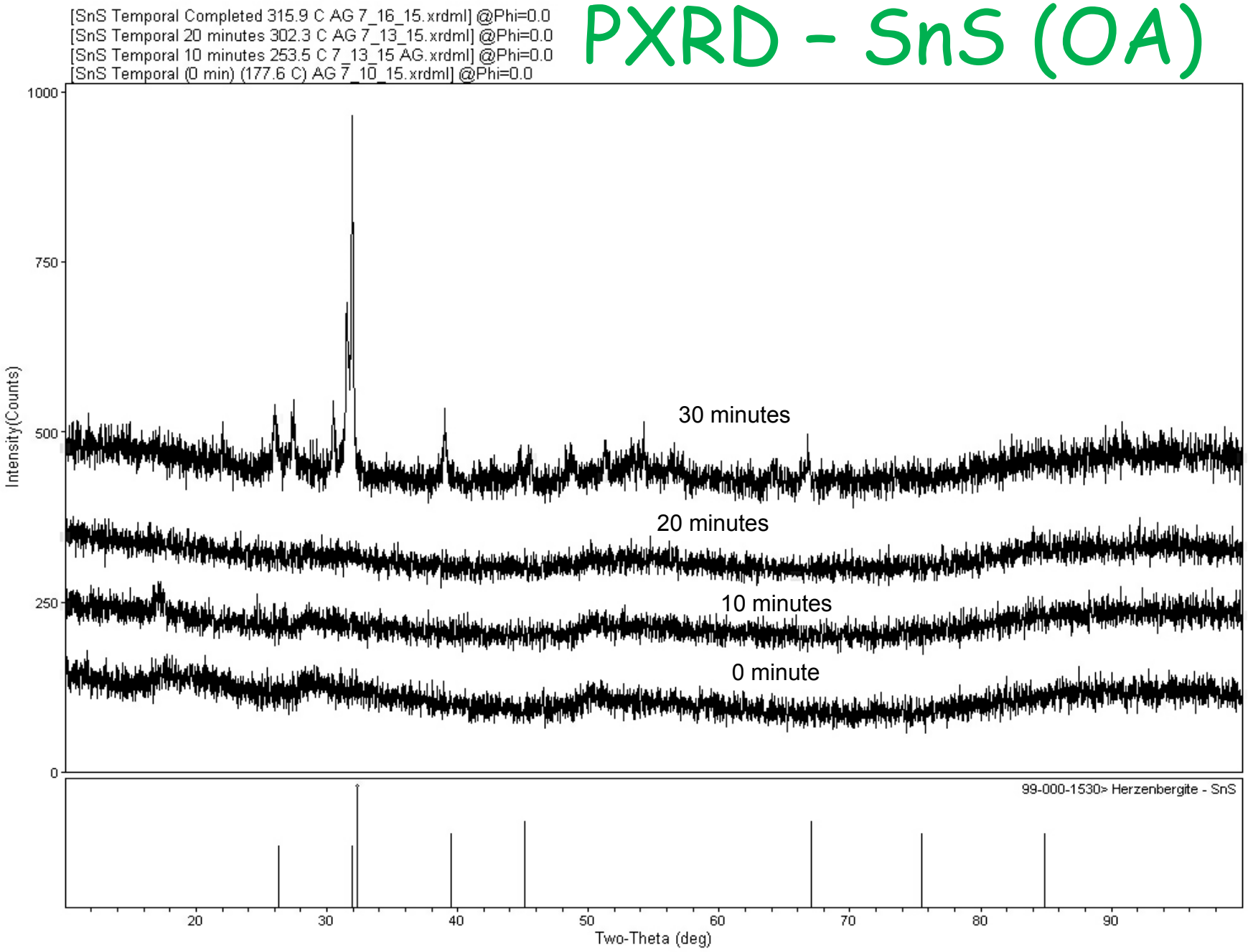

[Nano Sn Temporal To Completion 371.9C AG.xrdml] @Phi=0.0
[Nano Sn Temporal 20 minutes (2) 366.3 C AG.xrdml] @Phi=0.0
[Nano Sn Temporal 10 minutes 345.9 C AG.xrdml] @Phi=0.0
[Nano Sn Temporal 0 minutes 309.6C AG.xrdml] @Phi=0.0
Intensity(Counts)
2000
1500
1000
500
0
35 minutes
20 minutes
10 minutes
0 minute
00-006-0395> Romarchite - SnO
20
30
40
50
60
70
80
90
Two-Theta (deg)

Crystal System = Tetragonal

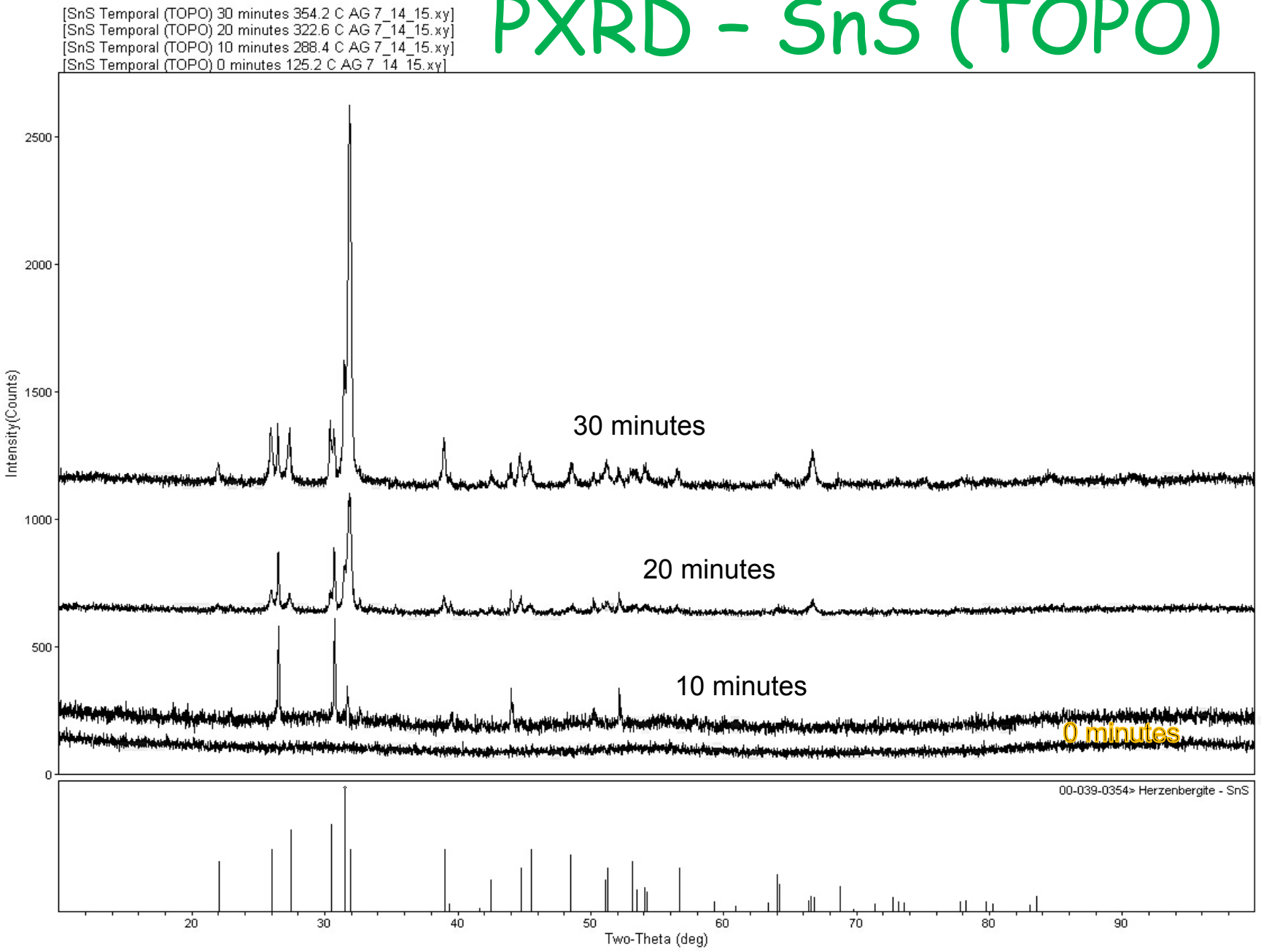


#	2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
1	18.277	4.8500	10.0	(0 0 1)	9.139	0.1031	1.2955	
2	29.868	2.9890	100.0	(1 0 1)	14.934	0.1673	2.1021	
3	33.305	2.6880	35.0	(1 1 0)	16.653	0.1860	2.3375	
4	37.153	2.4180	14.0	(0 0 2)	18.576	0.2068	2.5985	
5	44.393	2.0390	<1	(1 0 2)	22.196	0.2452	3.0815	
6	47.808	1.9010	14.0	(2 0 0)	23.904	0.2630	3.3052	
7	50.765	1.7970	25.0	(1 1 2)	25.382	0.2782	3.4965	
8	57.401	1.6040	25.0	(2 1 1)	28.701	0.3117	3.9172	
9	62.074	1.4940	12.0	(2 0 2)	31.037	0.3347	4.2056	
10	62.539	1.4840	12.0	(1 0 3)	31.270	0.3369	4.2340	
11	67.749	1.3820	4.0	(1 1 3)	33.875	0.3618	4.5464	
12	69.938	1.3440	6.0	(2 2 0)	34.969	0.3720	4.6750	
13	77.925	1.2250	4.0	(3 0 1)	38.963	0.4082	5.1291	
14	79.157	1.2090	4.0	(0 0 4)	39.578	0.4136	5.1970	
15	79.710	1.2020	4.0	(3 1 0)	39.855	0.4160	5.2273	
16	81.951	1.1747	6.0	(2 2 2)	40.976	0.4256	5.3488	
17	82.377	1.1697	8.0	(2 1 3)	41.189	0.4275	5.3716	
18	83.927	1.1520	2.0	(1 0 4)	41.964	0.4340	5.4542	
19	88.632	1.1026	4.0	(1 1 4)	44.316	0.4535	5.6985	

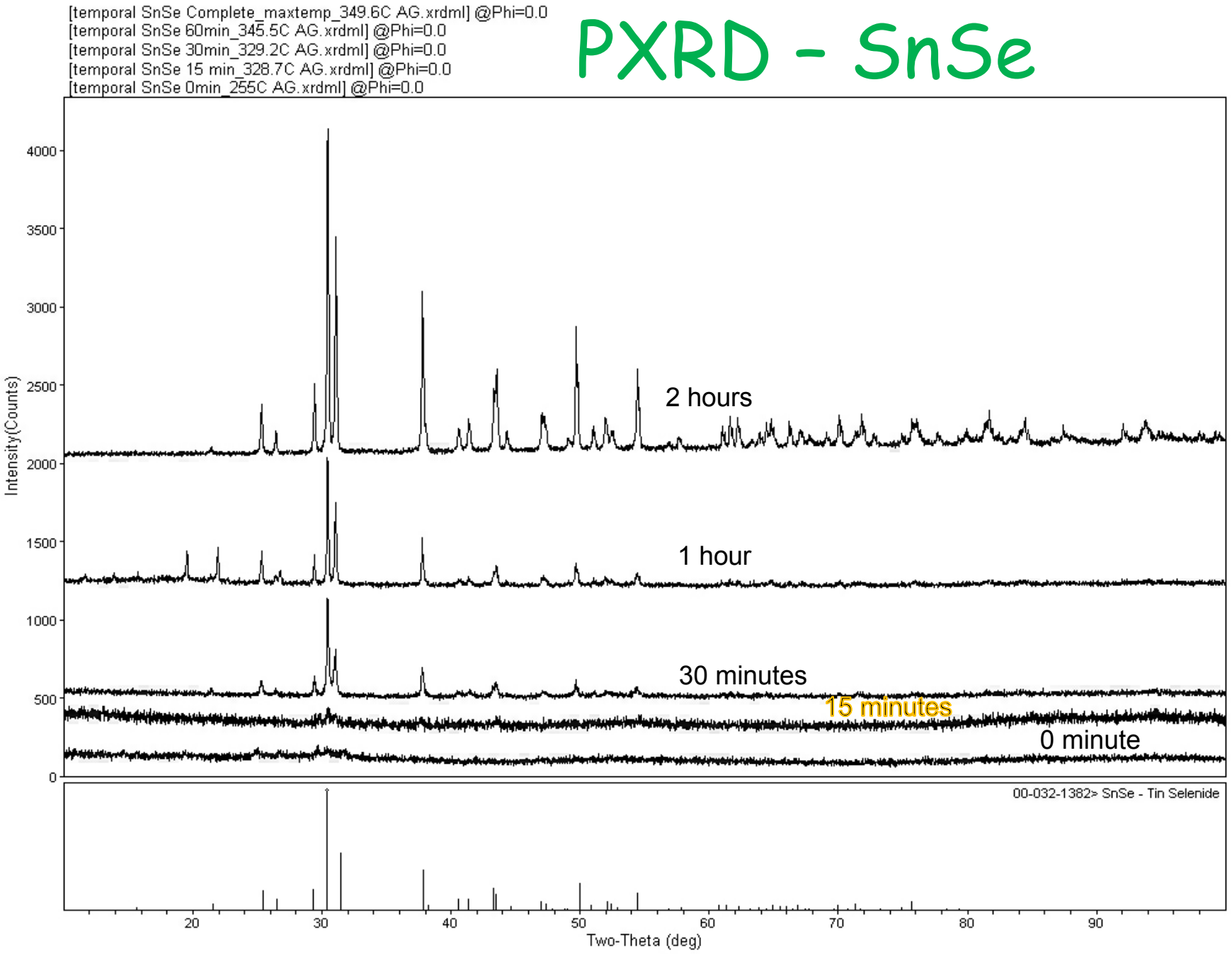
PXRD - SnS (OA)


[SnS Temporal Completed 315.9 C AG 7_16_15.xrdml] @Phi=0.0
[SnS Temporal 20 minutes 302.3 C AG 7_13_15.xrdml] @Phi=0.0
[SnS Temporal 10 minutes 253.5 C 7_13_15 AG.xrdml] @Phi=0.0
[SnS Temporal (0 min) (177.6 C) AG 7_10_15.xrdml] @Phi=0.0
Intensity(Counts)
1000
750
500
250
0
30 minutes
20 minutes
10 minutes
0 minute
99-000-1530> Herzenbergite - SnS
20
30
40
50
60
70
80
90
Two-Theta (deg)

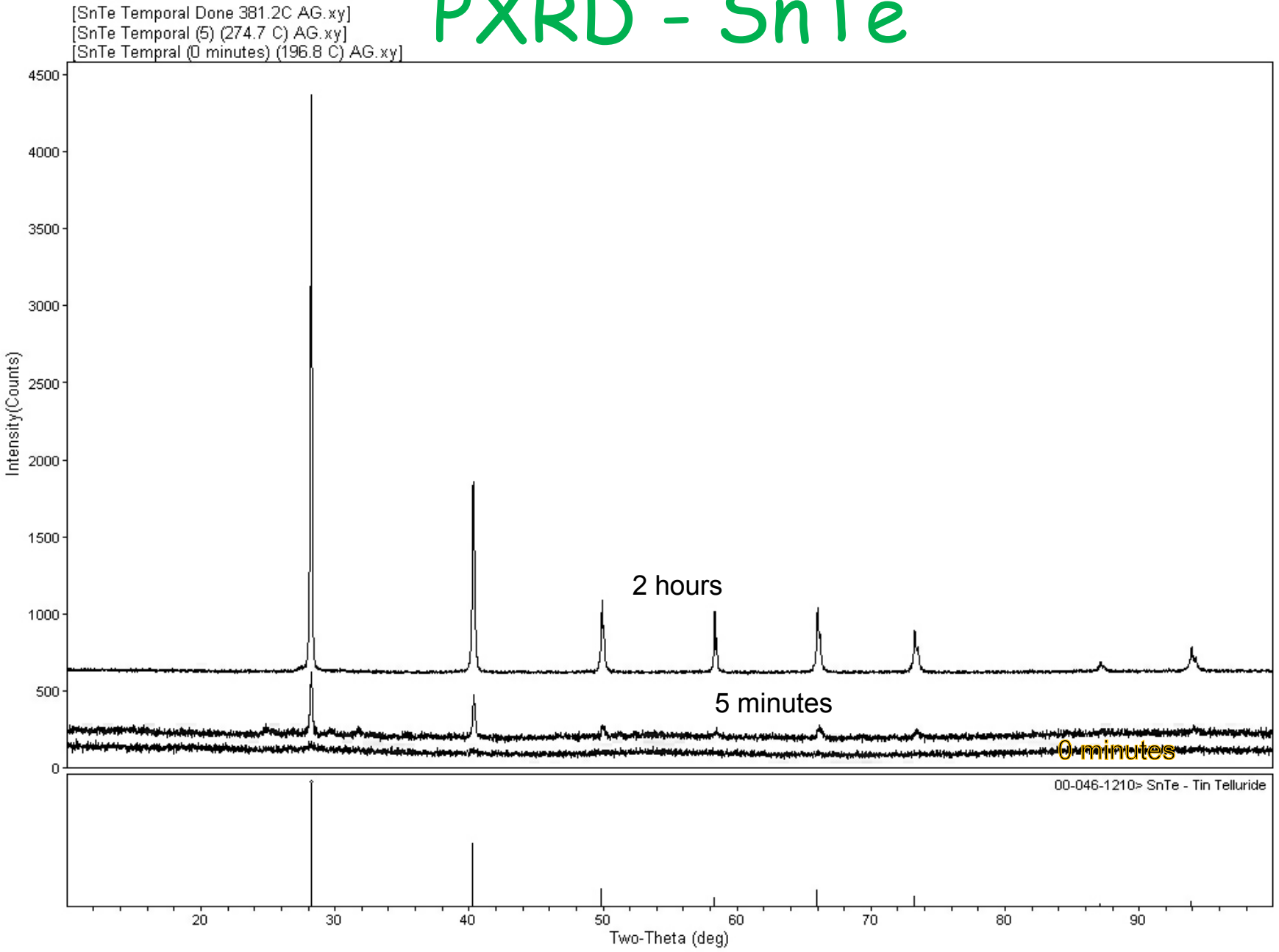
PXRD – SnS (TOPO)



PXRD - SnSe



PXRD - SnTe


[SnTe Temporal Done 381.2C AG.xy]
[SnTe Temporal (5) (274.7 C) AG.xy]
[SnTe Tempral (0 minutes) (196.8 C) AG.xy]
Intensity(Counts)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
2 hours
5 minutes
0 minutes
00-046-1210> SnTe - Tin Telluride
20
30
40
50
60
70
80
90
Two-Theta (deg)

Sherrer Equation

$$D = \frac{k\lambda}{\beta \cos\theta}$$