Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Real-time Monitoring of Phase Transitions in π-SnS Nanoparticles

Helena Fridman,[1,3] Nir Barsheshet,[2,3] Sofiya Kolusheva,[3] Taleb Mokari,*[1,3] Shmuel Hayun[2,3] and Yuval Golan*[2,3]

[1]Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel
[2]Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel
[3]Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 8410501, Israel

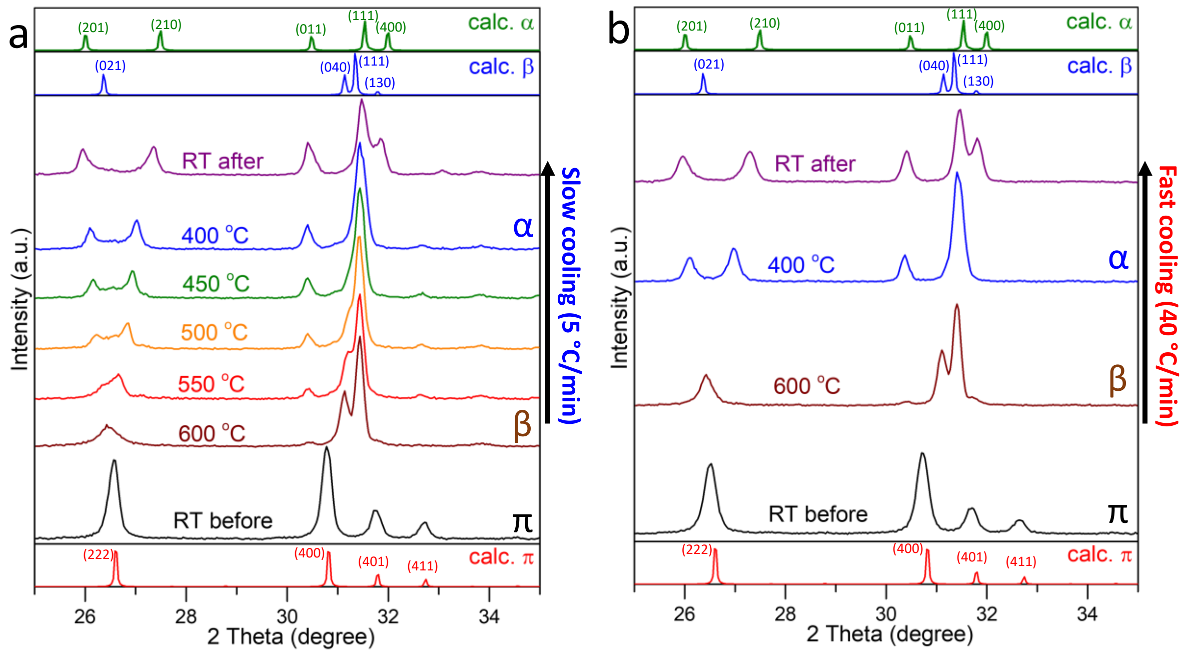

Figure S1 Temperature resolved XRD of π-SnS nanoparticles while cooling back to room temperature after heating to 600 °C. (a) Cool rate was 5 °C/min, with multiple measurements between 600 °C and 400 °C. (b) Cool rate was 40 °C/min, with an immediate cooling from 600 °C to 400 °C. In both cases, the observed transition was from π to β, followed by transformation to α upon cooling.

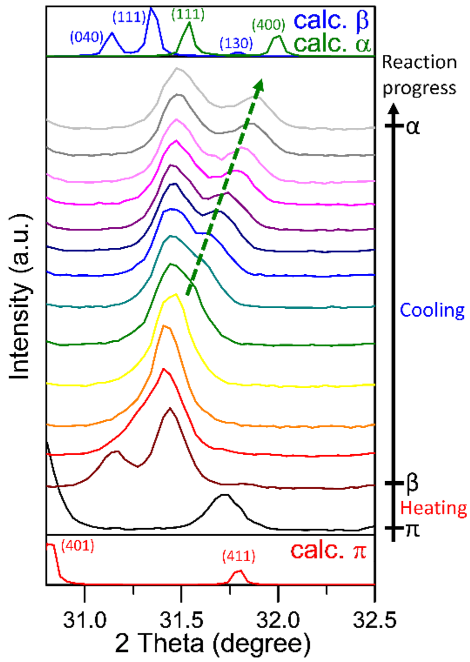

Figure S2 Temperature resolved XRD of π-SnS nanoparticles while cooling back to room temperature after heating to 600 °C. Temperature intervals between scans were 50 °C. The transition from β to α starts immediately after cooling below 600 °C, with a disappearance of the (040) peak of β and gradual appearance of the (400) peak of α as marked with a dashed green arrow.

Refinement of XRD data for the evaluation of thermal expansion coefficient:

To evaluate the thermal expansion coefficient, the raw XRD data was processed by Rietveld refinement calculations. The calculation was conducted using a FullProf[1] software installed on a Match! 3.12 program. For each temperature-dependent XRD pattern, the corresponding unit cell parameter (a_t) of the Si standard was fixed while the cell parameter of the π-SnS was calculated. Other parameters (such as scale factors, background parameters, specimen displacement, etc.) were also set as variables, until reaching the best possible agreement between the experimental diffraction profile and the profile calculated from the model (giving the lowest Bragg R-factor). The calculated cell parameter was used to calculate cell volume. The final calculated cell parameter and cell volume of π-SnS *vs*. the temperature is given in Table 1.

Table S1: Cell parameter of the Si standard used for Rietveld refinement calculations, the calculated cell parameter and volume of π-SnS and the Bragg R-factor.

***t* [°C]**	**a_t of Si powder [Å]**	**a_t of π-SnS [Å]**	**Bragg R-factor**	**Cell volume [Å^3]**
25(1)	5.430840	11.6010(2)	15.5	1561.30
100(1)	5.430841	11.6066(2)	16.5	1563.56
150(1)	5.430842	11.6100(2)	14.3	1564.94
200(1)	5.430842	11.6132(2)	15.1	1566.23
250(1)	5.430843	11.6162(2)	16.5	1567.44
300(1)	5.430843	11.6216(2)	13.0	1569.63

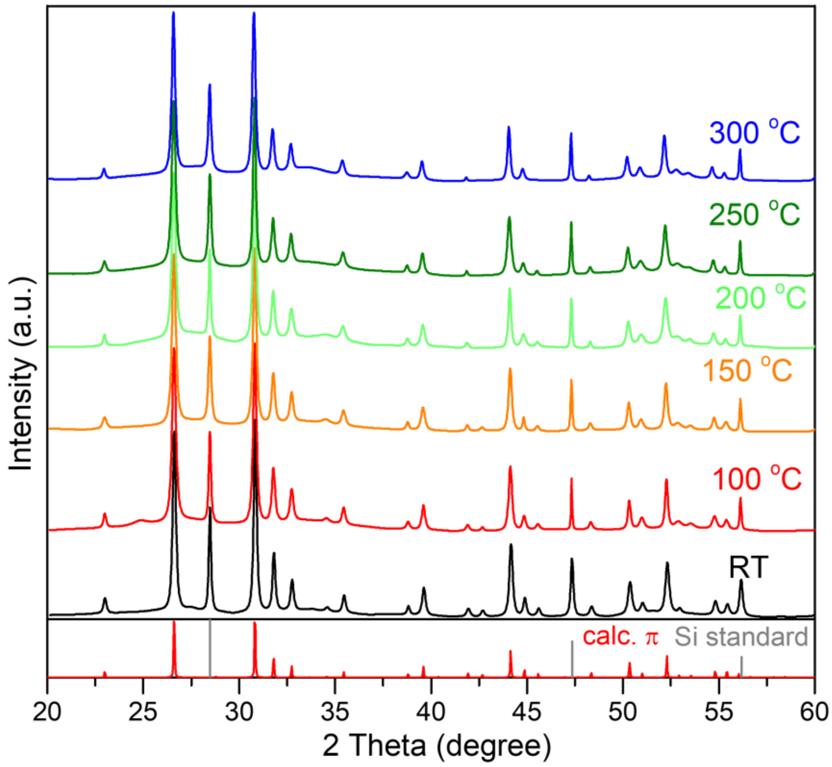

Figure S3 Refined calculation of the temperature-resolved XRD data of π-SnS nanoparticles upon heating to 300 °C. Intervals between temperatures was 50 °C.

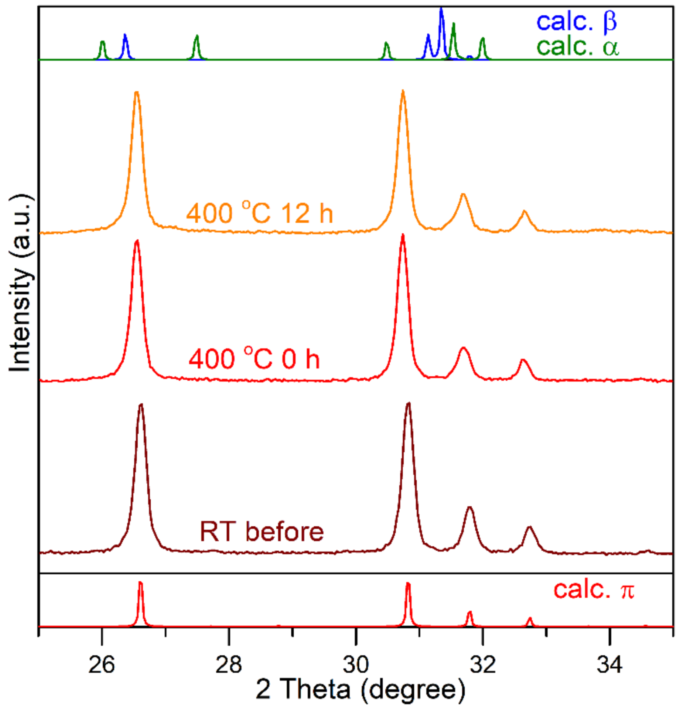

Figure S4 Temperature-resolved XRD of π-SnS nanoparticles held at 400 °C for 12 hours in helium environment. The π phase remains stable and no phase transition accrues.

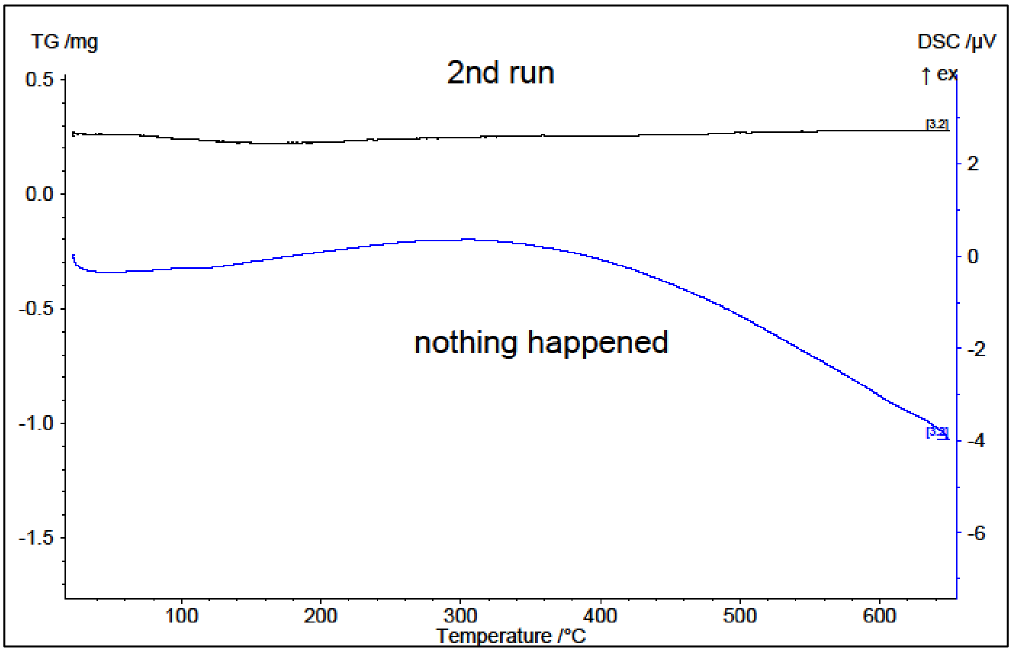

Figure S5 TG-DSC presenting the second heating cycle of π-SnS nanoparticles heated from room temperature to 650 °C. No reaction is observed, meaning that the π to β phase transition is irreversible.

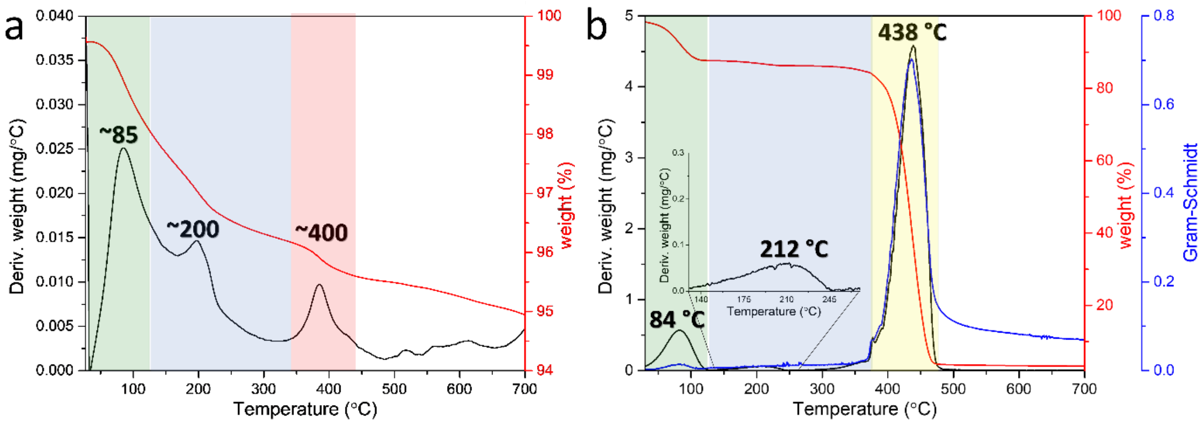

Figure S6 TG-IR measurement of (a) PVP-capped π-SnS nanoparticles and of (b) pure PVP. Both TG-IR measurements correlate nicely with the TG-DSC results in main text.

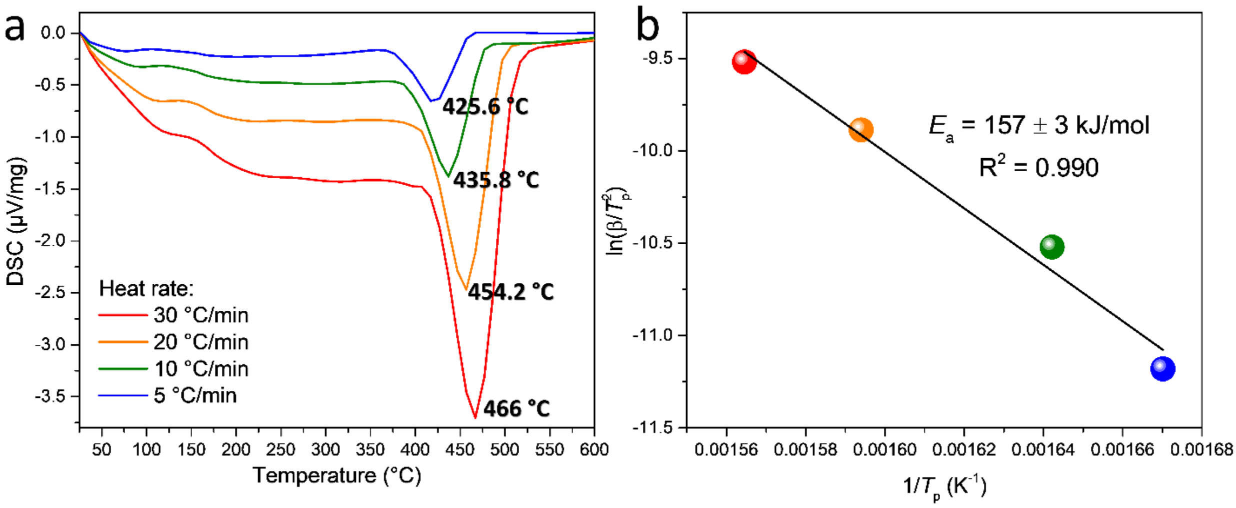

Figure S7 (a) TG-DSC of PVP using at varying scan rates and (b) the corresponding Kissinger equation plot. The peak temperature for each scan rate is mentioned above the corresponding scan in (a).

<u>Supplementary Reference</u>

1. Rodríguez-Carvajal J. Recent advances in magnetic structure determination by neutron powder diffraction. *Phys B Phys Condens Matter*. 1993;192(1-2):55-69. doi:10.1016/0921-4526(93)90108-I