Electronic Supplementary Information (ESI)

A New Nanocrystalline Binary Phase: Synthesis and Properties of Cubic Tin Monoselenide

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Characterization methods

Conventional TEM was carried out using a Tecnai G2 TEM operating at 120 kV. Analytical TEM analyses were performed using a JEOL JEM-2100F microscope system with accelerating voltage of 200 kV, with energy dispersive spectroscopy (EDS) analysis performed using a JEOL JED-2300T energy dispersive X-ray spectrometer. Probe tracking (drift correction), allowed chemical analysis at the nanometer scale. JEOL Analytical Station software (v. 3.8.0.21) was used for the EDS data analysis. Standardless quantitative analysis was performed using the Cliff-Lorimer method. TEM samples were prepared by solvent evaporation from chloroform suspensions. Powder X-ray diffraction was performed on a Panalytical Empyrean powder diffractometer equipped with a position sensitive X'Celerator detector using Cu Kα radiation (λ = 1.5405 Å). Rietveld refinement and quantitative extraction of phase ratios and were carried out using FULLPROF-98, Version 5.06.[1] the data is presented in Figure S1 below.

Optical absorption measurements were performed on a Shimadzu UV 3600 spectrophotometer from chloroform suspensions using Hellma 110-QX cells. The Raman system comprised of a Jobin-Yvon LabRam HR 800 micro-Raman system, equipped with a Synapse CCD detector. The excitation source was an Argon laser (514.5 nm) He-Ne laser (632.8 nm) and diode laser (785 nm) with a power of 3 mW on the sample. In most of the measurements the laser power was reduced by x100 using ND filters. The laser was focused and with an x100 objective to a spot of about 1μ in diameter. The grating used was a 600 g mm^{-1} with a confocal hole of 100 μm. Samples were drop casted to a 10 mm cuvette and sealed using a rubber septum. The cuvette was evacuated and flushed with argon gas 4 times in order to remove oxygen and moisture. This action was necessary in order to obtain Raman spectra with good signal to noise ratio, as it was

found that all samples were sensitive to the laser beam which causes the material to transform from SnSe to $SnSe_2$. Data analysis and processing was carried out using "OriginPro 9.0.0 SR2".

Density functional theory based calculations of the atomic and electronic structure were performed within the plane-wave pseudopotential approach using Quantum Espresso[2] and scalar relativistic norm-conserving pseudopotentials included therein. Exchange correlation was represented in the GGA by the PBE functional[3] and a 75 Rydberg energy cutoff was employed in the plane-wave expansion of the wavefunctions and 300 Ry for the density. Electronic structure total energy calculations were converged to better than 10-8 Rydberg per unit cell. Atomic structure was determined by allowing relaxation of the system until forces were less than 10-3 Ry/Bohr.

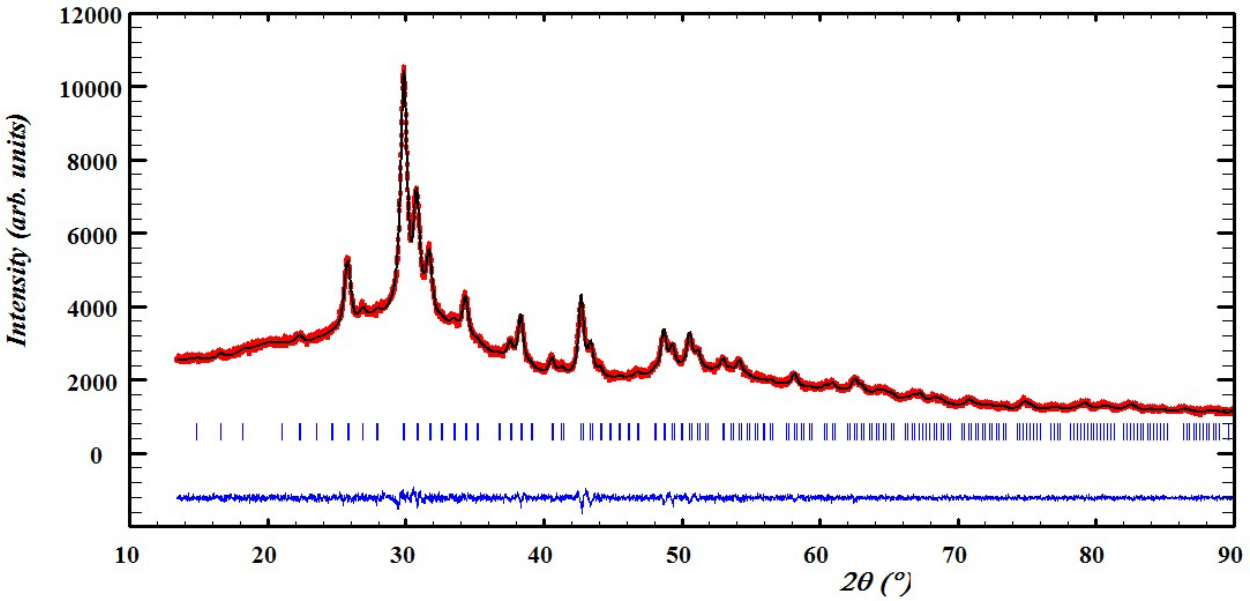

Figure S1. Plot of the Rietveld refinement of the π-SnSe structure showing: observed X-ray profile (in black), calculated profile (red line), and difference between them (on the bottom). The calculated profile was based on the π-SnSe structural model proposed in current work. Vertical bars refer to the calculated peak positions of the π-SnSe phase. Negligible difference between these profiles indicates a considerably good match of the fitted crystallographic model to the experimental results. The Rietveld refinement of π-SnSe structure, led to agreement factors of Rp=1.65, Rwp=2.11. These low values of reliability factors not only demonstrate good fit of the model but also provide strong proof for the correctness of the theoretical π-SnSe model.

REFERENCES

1. J. Rodrigues-Carvajal, Program FULLPROF-98, Version 5.06, 2015.

2. Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Dal Corso, A.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J Phys Condens Matter* 2009, 21, 395502.

3. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865-3868.