ESRF

Experiment title:
Martensitic phase transition of InSn nanocrystals

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Report:

We used X-ray powder diffraction during in-situ cooling to investigate the β to α transition of Sn nanocrystals as well as the incorporation of Pt and Ag in such Sn nanocrystals by post-growth galvanic exchange. Experiments were performed at an energy of 11.5 keV and a Mythen strip detector was used for data collection.

The nanocrystals were wet-chemically synthesized and galvanic exchange was performed after the growth in the coordinating solvent oleylamine. A chloroform solution of Sn nanocrystals was injected into a heated solution of Pt acetylacetonate or silver trifluoroacetate in oleylamine. After a certain time the mixture was cooled to room temperature and the nanocrystals were precipitated with ethanol and separated by centrifugation. This step was repeated a few times to remove all residuals of silver or platinum precursors. A series of ex-situ prepared samples with different treatment times was used to identify the crystallographic change introduced during the galvanic exchange. The study of a martensitic phase transition in InSn nanocrystals has been spoiled by oxidation of the nanocrystals: it turned out that during heating oxidation occurs at the same time scale than the phase transistion but is not reversible. This is true even for samples kept in nitrogen atmosphere and studied at low pressure ($\sim 1 \times 10^{-5}$ mbar). The cooling of the Sn nanocrystals from room-temperature to $\leq$ 160 K showed the absence of any phase transition if the

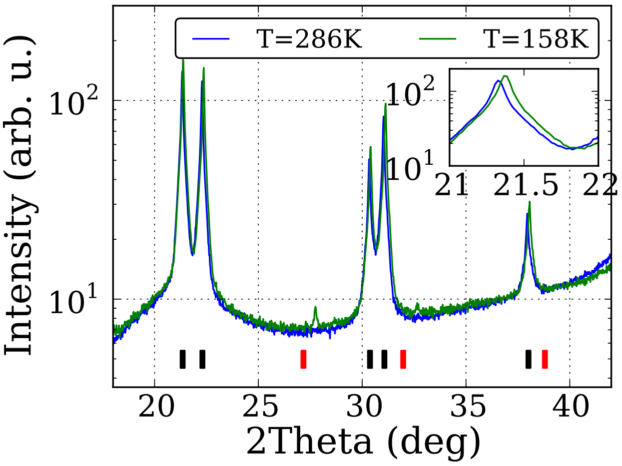

Figure 1: *X-ray diffraction from Sn nanocrystals close to room-temperature and after cooling to $\sim$ 160 K. Evidently at both temperatures the nanocrystals possess the same crystalline structure, namely the β-Sn phase. Black marks show the position of the β-Sn phase, whereas red marks indicate the diffraction positions of the diamond like α-Sn phase. The inset shows the shift of the peaks due to thermal expansion. Measurements were performed at an wavelength of $\lambda = 1.0781$ Å.*

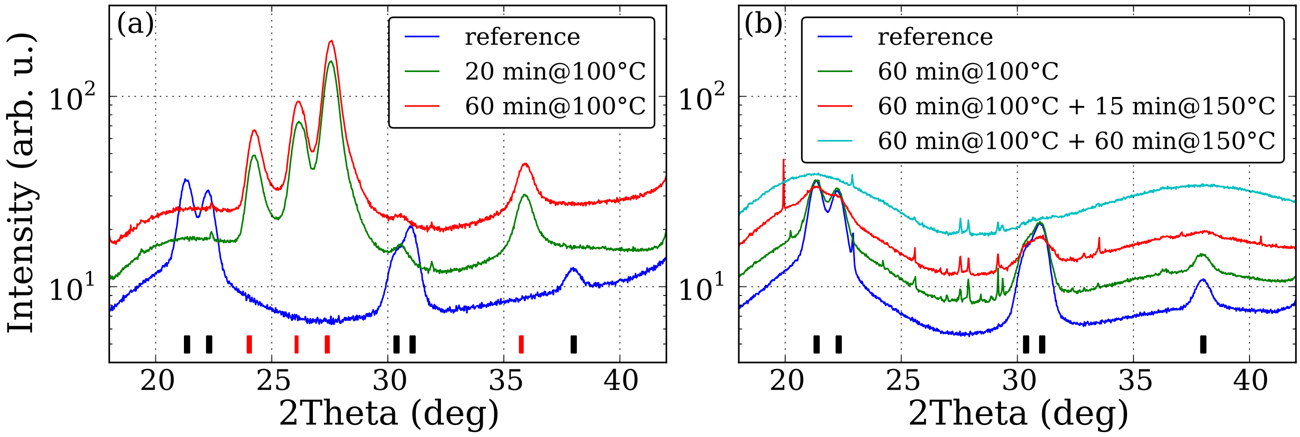

Figure 2: *X-ray powder diffraction scans recorded from Sn nanocrystals treated with (a) Ag and (b) Pt. During the silver treatment (panel (a)) the β-Sn nanocrystals transform to $Ag_{1-x}Sn_x$ with space group Pmmn(59). Black marks show the position of the β-Sn phase, whereas red marks indicate the diffraction positions as reported for the Ag_3Sn structure in Ref. 2. In panel (b) the effect of the Pt treatment is shown. The diffraction signal of the nanocrystals, which in the beginning exhibit the β-Sn phase, disappears after the Pt treatment. Measurements were performed at a wavelength of* $\lambda = 1.0781$ *Å and the curves were vertically shifted for illustrative purposes.*

nanocrystals remained at low temperature for several hours as can be seen in Fig. 1. We conclude that this transition is therefore not accelerated in this nanoscale system and might have similar transition times as in bulk, which varies from few hours to years [1] depending on chemical purity.

Upon treatment with silver trifluoroacetate of Sn nanocrystals, which exhibit the β-Sn phase after the synthesis, a full conversion of the crystal structure to a new phase similar to the Ag_3Sn crystal structure with space group Pmmn(59) [2] was found. This can be seen by the comparison of powder diffraction scans shown in Fig. 2a. We find the new phase to have lattice parameters of $a = 5.88$ Å, $b = 4.76$ Å, $c = 5.15$ Å with considerable differences to the bulk phase of Ag_3Sn, most probably due to a different chemical composition. The Ag content in these structures was determined by energy-dispersive X-ray spectroscopy (EDX) varies from 46 to 56 atomic % for the different treatment times. Peaks associated with the β-Sn phase completely vanish already for treatment times of 20 min. Powder spectra recorded for aliquotes treated for longer times or at higher temperature showed no further change of the crystal structure.

In contrast to the change of the crystal structure observed for the Ag-treated nanocrystals, the platinum treatment provided no changes of the chemical composition. After the treatment the shape and size of nanocrystals was preserved. Also the chemical composition was unchanged, which was proven by EDX analysis. Upon the treatment the Bragg diffraction peaks associated with the β phase of Sn vanished, although no other diffraction peaks associated with the nanocrystals appeared. This is either due to a substantial noise signal generated by amorphous byproducts which were formed by decomposition of platinum acetylacetonate during the heat treatment or due to a decrease of the crystallite size in the Sn-nanocrystals or a mixture of both effects.

References

[1] W.J. Plumbridge *Journal of Materials Science (2007)* 18, 307-318.

[2] C.W. Fairhurst, J.B. Cohen *Acta Crystallographica B* (1972) 28, 371-378.