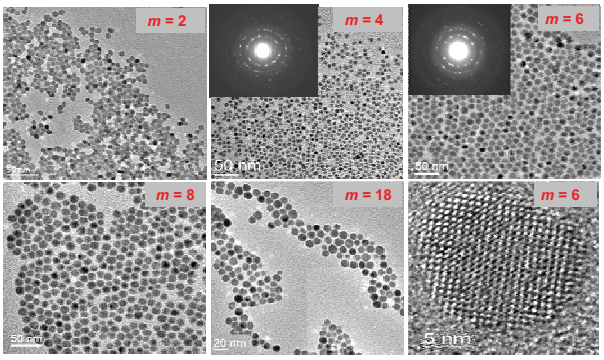
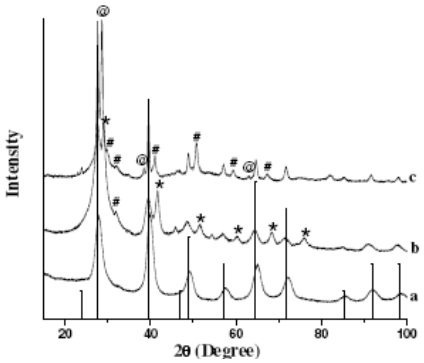
Nanoparticle Transformations: From Solid Solution to Nanoscale Phase Segregation

The discovery of record high thermoelectric performance in recently synthesized bulk $AgPb_{18}SbTe_{20}$ has been attributed to the unexpected presence of phase-segregated endotaxial (lattice-matched) nanodots. Rather than solidifying from the molten reaction mixture as a homogeneous solid solution, the 2-20 nm nanodots that segregate upon slow cooling appear to be somewhat enriched in Ag and Sb. The effective mass difference between the nanodots and matrix leads to the scattering of phonons, thus decreasing thermal conductivity, while the lattice coherence allows unimpeded electron flow. The decoupling electron and phonon transport in this manner has opened up a new direction of exploration with the potential for further significant improvements in conversion efficiency.

To study the driving force for the formation in of the nanodots Arachchige, Kanatzidis and colleagues at Northwestern University, have now developed low temperature, one pot solution syntheses for nanoparticles of composition $AgPb_mSbTe_{m+2}$ (m=1-18). This is the only quaternary system reported to date to successfully produce nanoparticles and, in contrast to the bulk materials, all the nanoparticles are homogeneous in composition. Upon heating to ~150-200°C, however, the nanocrystals undergo phase transformations to a mixture of PbTe, $AgSbTe_2$, Ag_2Te, and Sb_2Te. Thus, the bottom-up, low temperature synthesis approach gives access to a metastable solid solution state with nanoparticle size and composition control for a class of materials of interest for thermoelectrics, infrared sensing. phase change memory, and photovoltaics.





Transmission electron micrographs (TEM) of as-synthesized nanoparticles of $AgPb_mSbTe_{m+2}$, (m=2-18) Insets show the selected area electron diffraction pattern from a 200nmx200nm area of nanocrystals that are indexable to a cubic Fm3m lattice.The high resolution TEM micrograph of $AgPb_6SbTe_8$ nanocrystals shows a regular NaCl-type crystal structure viewed down the [200] direction.	Powder X-ray diffraction spectra of the $AgPb_4SbTe_6$ nanocrystals annealed at (a) 25 °C (b) 150 °C and 400 °C for 3 hours under vacuum. Powder X-ray diffraction peaks correspond to cubic PbTe (vertical lines), $AgSbTe_2$ (*), Ag_2Te (#) and Sb_2Te_3 (@).

Reference: Arachchige, I.U.; Wu, J.; Dravid, V.P.; Kanatzidis, M.G., *Adv. Mater.* **2008**, *20*, 3638–3642.

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