# $I_2$–II–IV–$VI_4$ Nanocrystals: Synthesis and Thermoelectric Properties

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Today's main strategy to produce materials with high thermoelectric figures of merit is to trigger phonon scattering at multiple length scales without disturbing the charge carrier transport. The goal is to minimize the lattice thermal conductivity in highly electrically conductive materials; the so-called electron-crystal phonon-glass paradigm. This strategy is implemented by two main approaches: i) the scattering of phonons at the atomic length scale by the synthesis of complex crystal phases that include 1D phonon scattering centers, such as vacancies or rattling atoms, and/or 2D layered crystallographic structures; ii) the scattering of phonons at the 1-100 nm scale by reducing the crystal domain dimensions to the nanoscale.

In this scenario, colloidal synthesis routes are particularly well suited for the production of thermoelectric materials. Solution-processing methods have a high potential for the production of low-cost, high-yield, large-scale, high-output and shape-adaptable devices. Moreover, bottom-up approaches allow to directly obtain nanocomposites with reduced crystal domain size and controlled geometry.

At the same time, some quaternary chalcogenides have the required attributes to be potentially excellent thermoelectric materials. Not only the complex structures of these quaternary compounds are associated with intrinsically low thermal conductivities, but also their different cationic valences provide a means of controlling their Fermi level by adjusting their cation ratios. Besides, some $I_2$-II-IV-$VI_4$ materials crystallizing in the stannite phase are characterized by a convenient structure layering, which allows decoupling the electrical conductivity from both the thermal conductivity and the Seebeck coefficient.

We will present a novel colloidal synthetic route to prepare I2–II–IV–VI4 quaternary nanocrystals with controlled size, shape and composition. We put special effort in designing a cost-effective and scalable process susceptible of being implemented in real applications. The synthetic route is applied to the preparation of grams of the quaternary chalcogenide $Cu_{2+x}Cd_{1-x}SnSe_4$ ($0 \leq x \leq 0.5$) with accurately controlled composition and narrow size distributions. The electrical and thermoelectric properties of these materials were characterized over a wide temperature range. We will show how these materials have high Seebeck coefficients (150-300μV/K), electrical conductivities up to 14000 S/m, and thermal conductivities down to 0.3 W/mK, leading to ZT values up to 0.4 at 700 K. Besides, the advantages and disadvantages of this bottom-up approach to produce thermoelectric nanomaterials will be discussed.