

Incommensurate Structural Modulation as a New route toward Strong Phonon Scattering in Cu-Sn-Se Chalcogenides

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In recent years, copper-rich sulfides and selenides have attracted increased interest as thermoelectric materials due to their low-cost and environmentally benign nature, as compared to state of art tellurides. Within the Cu-Sn-Q (Q= S; Se) phase diagram, several compounds have been reported, including Cu₂SnS₃, Cu₂₂Sn₁₀S₃₂, Cu₅Sn₂S₇, Cu₄SnS₄, Cu₂SnSe₃, Cu₅Sn₂Se₇ exhibiting promising thermoelectric properties ^{[1],[2]}. Variations in the Cu/Sn ratio give rise to different cationic ordering and crystal structures, often derived from the sphalerite-type structure, and lead to diverse electrical and thermal transport behaviors. However, the Cu-Sn-Se crystal structures remains poorly investigated and understood, with compounds displaying a high sensitivity to synthesis conditions and composition, therefore offering an opportunity to unravel new structure types and new mechanisms for electrical conduction and phonon suppression ^[3].

By using advanced structural characterization techniques, such as 3D electron diffraction (3D ED) and HAADF-STEM analyses, we have elucidated the complex crystal structure of a new compound in the Cu-Sn-Se system. Exhibiting an original crystal arrangement characterized by an incommensurately occupation modulation, this new phase is the first incommensurate structure in the Cu-Sn-Se system. This unusual arrangement has shown to directly impact the thermal transport properties, therefore suppressing the lattice thermal conductivity through strong phonon scattering. These results establish incommensurate modulation as a previously unexplored mechanism for controlling charge and phonon transport in Cu–Sn–Se compounds and highlight structural modulation as a promising crystal-chemistry strategy for designing low-thermal-conductivity thermoelectric materials.

[1] Kumar, V. P. et al, *Inorg. Chem.* **2021**, 60 (21), 16273–16285 and references therein

[2] Fan, J. et al, *Inorg. Chem.* **2013**, 52 (19), 11067–11074 and references therein

[3] Fan, J. et al, *Dalton Trans.* **2014**, 43 (44), 16788–16794 and references therein