Structure–Property Interplay in $Cu_6Te_{3-x}S_{1+x}$: An Analytical Approach to Thermoelectric Optimization

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In this contribution, we present an analytical interpretation of structure–property relationships in the $Cu_6Te_{3-x}S_{1+x}$ chalcogenide system, based on experimental transport data and classical physical models. We show in our previous work [1] that progressive substitution of Te by S leads to a substantial increase in the electronic band gap (from ~0.07 eV at x = 0 to ~0.2 eV at x = 0.7), which correlates with a strong enhancement of the Seebeck coefficient (from ~9 μV/K to ~200 μV/K) and a more than 40-fold decrease in electrical conductivity (from ~3600 S/cm to ~85 S/cm at 298 K).

Simultaneously, ultralow lattice thermal conductivity is observed across the series. For the parent compound Cu_6Te_3S, the lattice contribution drops to ~0.2 W/m·K at room temperature and remains nearly temperature-independent—an effect attributed to strong phonon scattering induced by partial occupancy of Cu sites (site occupancy factor ≈ 0.5) and local Te/S anionic disorder. This "crystalline-glass" behavior, confirmed independently by Liu et al. [2], is further supported by phonon mean free paths approaching the minimum limit (~3 Å) and the emergence of Einstein-type vibrational modes in specific heat analysis.

These results provide a foundation for a crystallochemically motivated design strategy for thermoelectric materials: combining globally ordered lattices with local structural and chemical disorder (cationic nonstoichiometry and anionic contrast) offers an efficient route toward phonon-glass electron-crystal behavior. We propose site occupancy, electronegativity contrast, and local symmetry disruption as key analytical descriptors for predicting low κ_lat and optimized thermoelectric performance without relying on numerical simulation..

[1] O. Cherniushok, T. Parashchuk, G. J. Snyder, K. T. Wojciechowski, *Adv. Mater.* 2025, **37**, 2420556.

[2] Z. Liu, W. Zhang, W. Gao, T. Mori, *Energy Environ. Sci.* 2021, 14, 3579

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