# On the role of polymorphism, crystal disorder, and microstructure evolution in materials for energy conversion and storage

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Thermoelectric materials can convert temperature gradients into electricity via the Seebeck effect, offering opportunities for waste heat recovery. High thermoelectric efficiency calls for an uncommon combination of good electrical conductivity and high Seebeck coefficient, as well as suppressed thermal transport properties, which requires an extensive engineering of the crystal structure and microstructure of candidate materials.

In this talk, earth-abundant, quaternary chalcogenides of the $Cu_2ZnSnS_4$ (CZTS) family will be discussed, as their pronounced polymorphism and crystal disorder were shown to benefit the thermoelectric properties. [1] As synthesized, CZTS forms a metastable disordered $F\bar{4}3m$ phase, which transitions to an ordered tetragonal phase upon thermal treatment. Rietveld refinement of temperature-dependent XRD data reveals that disordered CZTS can be modelled as a random occupation of cations, giving rise to a static, temperature-independent component of the Debye-Waller coefficients. This is confirmed by *ab-initio* simulations, supporting an increase in the atomic mean-square displacement for the cubic compared to the tetragonal polymorph. [2] A considerable amount of stacking faults appears to be stabilized in the disordered cubic polymorph. Upon heating, the domain growth leads to an ordering of Sn atoms first, followed by fault healing and concurrent ordering of the other cations, ultimately leading to the tetragonal CZTS phase. [3] Tetragonal CZTS also presents an order-disorder phase transition from a $I\bar{4}$ to a $I\bar{4}2m$ arrangement, involving the randomization of the Cu and Zn atoms in the 4d Wyckoff sites. This transition leads to a sharp enhancement in the Seebeck coefficient, associated with more converged electronic bands. The band structure modification is linked to an increased crystal symmetry, which can be observed in the temperature evolution of lattice parameters. [4]

Lastly, a study of microstructural evolution in FeTi for solid-state hydrogen storage will be presented. In this system, a combination of XRD whole-powder pattern modelling and transmission microscopy allows to detect a progressive increase in the density of dislocations with hydrogenation and de-hydrogenation cycles. Contrary to what previously reported, dislocations do not compromise the hydrogenation capacity, and contribute to improving hydrogen adsorption/desorption kinetics by providing hydride nucleation sites and by promoting the formation of crack networks, which increase the surface area available for the process.

These examples showcase how a detailed understanding of the structural and microstructural evolution of compounds can offer critical insights for interpreting functional properties in energy conversion and storage, pointing to relevant directions for performance enhancement.

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