Cage Breathing Lattice Dynamics of Skutterudites for Low Conductivity

Dominant heat-carrying modes in skutterudites are associated with vibrations of the pnicogen rings. To reduce thermal conductivity, disrupting pnicogen rings by Ge/Te substitution has proved effective. We explore configurations of pnicogen rings that yield particularly low thermal conductivity. Our ab initio calculations, guided by cluster expansion, identify stable arrangements of the rings, and subsequent molecular and lattice dynamics simulations establish the range of atomic displacement parameters and values of the thermal conductivity.

Introductions

Filling cages in CoSb₃ has effectively lowered lattice thermal conductivity, making filled skutterudites one of the best novel thermoelectric (TE) materials. An alternative approach is to distort the near-square pnicogen (Sb) rings, which are a characteristic feature of skutterudites. Ge/Te substitution in CoSb₃ has been achieved and it is competitive with the best values of filled-CoSb₃. These exciting findings reveal a compelling theoretical puzzle surrounding the role of pnicogen ring configuration in skutterudite heat transport.

Lattice Dynamics of Double-Substituted Pnicogen Rings

We studied heat transport mechanisms on CoSb₃₋ₓGeₓ₋₁Teₓ, using density functional theory. While the Ge ADP is large for all compositions, it is maximized at x = 0.5 where it becomes comparable to that of a Ba filler atom. Ge exhibits similar projected phonon dispersion curves to those of Ba, showing negligible dispersion, characteristic of local deformational modes with low group velocity. The dominant vibrational distortions of Ge responsible for its large ADP are along the diagonal of the CD Ge₂Te₂ rings, corresponding to a breathing mode of the cage.

Predicted Phonon Conductivity

The experimental minimum of κₙ near x = 0.5 coincides with the maximum of the calculated Ge ADP. In order to analyze the effect of pnicogen ring substitution on κₙ, we use experimentally- and DFT-parameterized analytical models for phonon-phonon and point-defect scattering, as well as non-equilibrium ab initio molecular dynamics (NEAIMD) simulation. The theoretical and computational predictions were verified experimentally by judiciously replacing a specific group of atoms with foreign atoms, which dampened the local atomic vibrations and thus reduced thermal conductivity.