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 $CoSb_3$ 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 $CoSb_3$ has been achieved and it is competitive with the best values of filled-$CoSb_3$. These exciting findings reveal a compelling theoretical puzzle surrounding the role of pnicogen ring configuration in skutterudite heat transport.

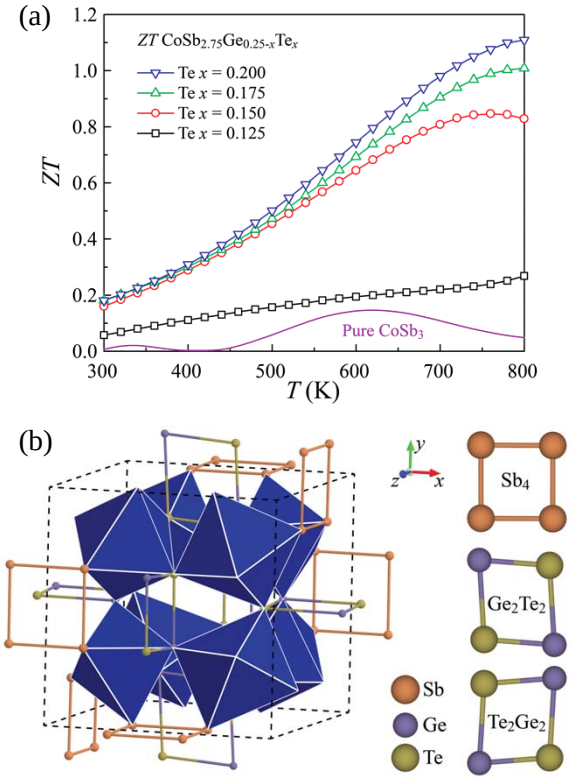

Figure 1. (a) Reported figure-of-merit (ZT) of Co(Sb,Ge,Te)$_3$. (b Crystal structure of $CoSb_{3(1-x)}Ge_{1.5x}Te_{1.5x,}$ where Ge and Te atoms are the foreign atoms substituted for Sb atoms. Predicted low-energy pnicogen rings are also shown.

Lattice Dynamics of Double-Substituted Pnicogen Rings

We studied heat transport mechanisms on $CoSb_{3(1-x)}Ge_{1.5x}Te_{1.5x}$ 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.

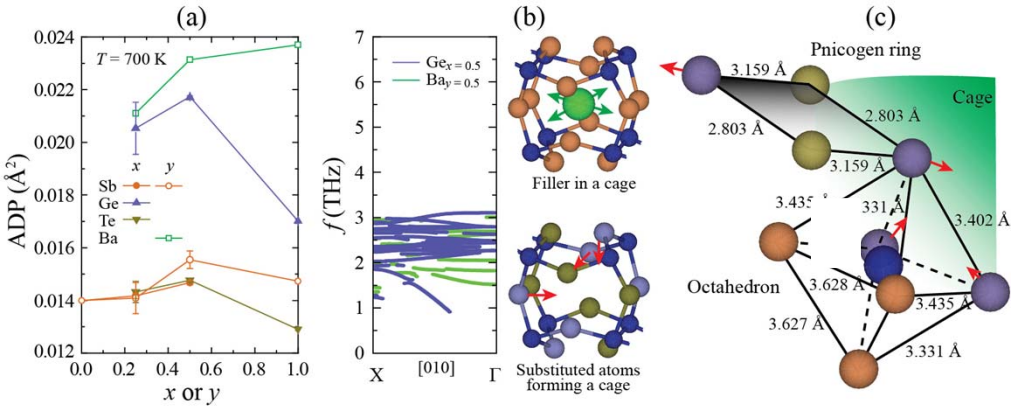

Figure 2. (a) ADP in $CoSb_{3(1-x)}Ge_{1.5x}Te_{1.5x}$ and $Ba_yCo_4Sb_{12}$. (b) Projected phonon dispersion for $x = 0.5$ and $y = 0.5$, with vibration modes. (c) Pnicogen ring and octahedron.

Predicted Phonon Conductivity

The experimental minimum of κ_L near $x = 0.5$ coincides with the maximum of the calculated Ge ADP. In order to analyze the effect of pnicogen ring substitution on κ_L, 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.

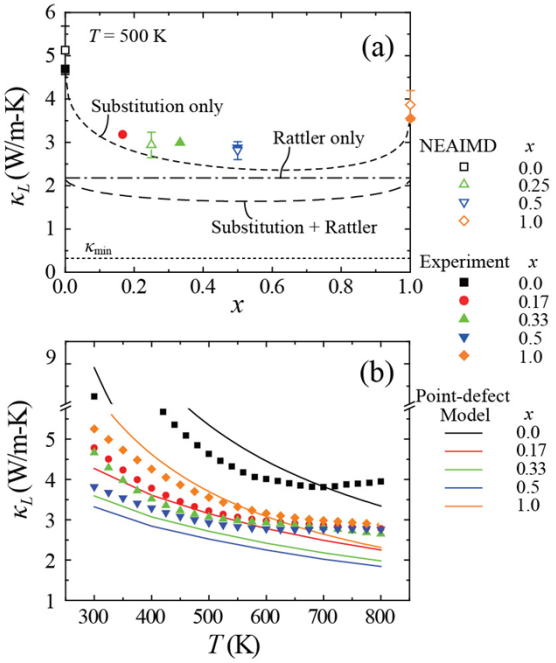

Figure 3 . (a) Concentration dependence, and (b) temperature dependence of lattice thermal conductivity of $CoSb_{3(1-x)}Ge_{1.5x}Te_{1.5x}$.