Reduced Phonon Conductivity of $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$ by Phase-Segregation Scattering

Filled skutterudites are promising high-temperature, high-performance thermoelectric materials and we show how their phonon conductivity is greatly influenced by the topology of the filler species. We predict (ab initio) the phase diagram of $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$ and find several stable configurations of Ba ordering over the intrinsic voids. The phonon conductivity predicted using equilibrium molecular dynamics shows a minimum in the two-phase mixture regime, dominated by significantly reduced long-range acoustic phonon transport.

The diagram of calculation methodology. Our computational approach is two-fold. We begin with finding the phase diagram using ab initio calculations, the cluster expansion (CE) method, and the Monte Carlo (MC) simulations. Thereafter, using molecular dynamics (MD) simulations and the Green-Kubo fluctuation-dissipation linear response theory and $k_p$ decomposition, along with the phase diagram, we predict the $k_p$ of partially-filled $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$ as a function of concentration and temperature.

Calculation of Solid-State Phase Diagram

- **Cluster Expansion (CE) and Ab Initio Calculations**
  - A set of 28 configurational energies were calculated from DFT.
  - Energies of the five ordered configurations predicted by the CE have been verified using DFT.

- **Monte Carlo Simulations**
  - By applying MC simulations to the cluster expanded Hamiltonian for the configurational energy, it is possible to construct a temperature-composition phase diagram.

The results of phase diagram calculations: The CE was parameterized by $\Delta E_f$ of Ba-Va configurations calculated from first principles. Below $x_{\text{Ba}} \leq 0.5$, We identified three ground-state ordered phases: $\text{CoSb}_3$ at $x_{\text{Ba}}=0$, $\gamma$-phase at $x_{\text{Ba}}=0.25$ and $\alpha$-phase at $x_{\text{Ba}}=0.5$. At higher temperatures, Ba-Va solid solution occurs, and coexistence can be achieved between any two of the phases. From the phase diagram, MD calculations were done using three ground-state configurations, two Monte Carlo snapshots, and three $\gamma$- and $\alpha$-phase mixtures at 300K.

**Prediction of Phonon Conductivity ($k_p$)**

**Dependence on various Ba compositions at RT**

- For the solid solution structure, phonons propagate through the ordered CoSb, and the randomly distributed Ba atoms act as point defects (PD). Such PDs cause significant phonon scattering in Regime-I.

- In the two-phase mixture (Regime-II), the mixture of two ordered phases causes significant alloy scattering. We concluded that these two regimes can be characterized predominantly by these scattering mechanisms.

**Temperature effects for several fill fractions**

- The single-phase crystal follows the Slack relation ($k_p \sim T^{-1}$), while the two-phase mixtures reaches a plateau, similar to amorphous solid $k_{p\text{init}}$. This reconfirms that the two-phase mixtures can be considered as pseudo-amorphous structures with significant reduction in $k_p$ for such crystalline TE materials.