Atomic Hopping Induced Dynamic Disorder Phonon Scattering and Suppressed Thermal Transport

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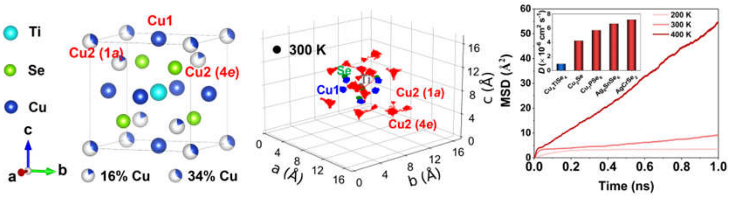
Introduction

Thermal transport in insulators is primarily mediated by phonons and is highly sensitive to atomic motion. While rapid atomic diffusion in superionic materials enhances phonon scattering, it also introduces uncompromising convectional heat flux, often increasing lattice thermal conductivity (κ_L) with temperature. Here, we uncovered that partial Cu2 occupancy and moderate atomic hopping in Cu_4TiSe_4 introduce strong dynamic disorder that intensifies phonon scatterings. This intermediate atomic mobility effectively connects rigid crystalline lattices and superionic phases, enabling substantial suppression of κ_L.

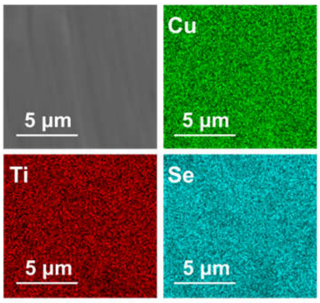


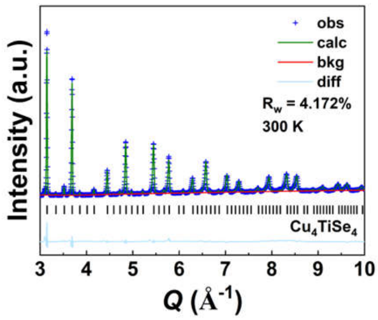
Methodology

➢ **Materials Synthesis and Characterization**

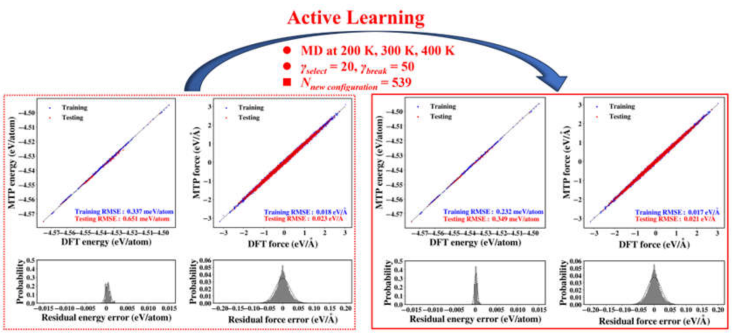
◆ **Scanning Electron Microscopy (SEM) and the Corresponding EDS Mapping**

◆ **Rietveld Refinement of Neutron Diffraction Data**



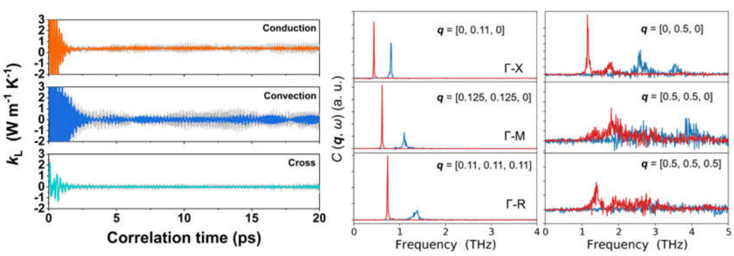


➢ **Construction of Machine Learning Moment Tensor Potential**

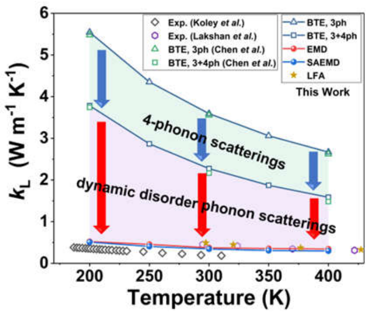


➢ **Molecular Dynamics (MD) Simulations**

◆ **The Running κ_L for Different Components** ◆ **Velocity and Current Correlation Functions**



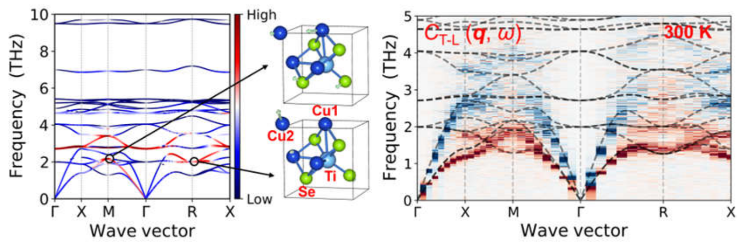
Thermal transport measurements and simulations



T (K)	κ_v (W m^{-1} K^{-1})	κ_c (W m^{-1} K^{-1})	κ_{vc} (W m^{-1} K^{-1})
200	0.535	0.007	0.0003
250	0.464	0.009	-0.0247
300	0.381	0.010	0.0018
350	0.347	0.011	0.0142
400	0.360	0.014	-0.0152

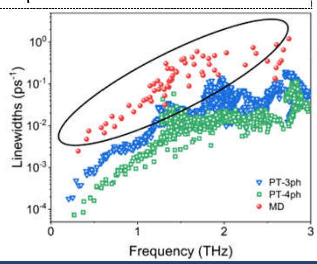
- The phonon scattering caused by dynamic disorder is critical for explaining the low κ_L.
- The thermally excited hopping of Cu2 atoms is observed in Cu_4TiSe_4, while the corresponding thermal convection term is negligible due to the lower D of Cu2 compared to the liquid-like atoms in superionic materials.

Anharmonic lattice dynamics



- Most acoustic phonon modes can be clearly observed, and their frequencies match reasonably with the phonon dispersions obtained based on the quasi-harmonic approximation.
- Some phonon modes dominated by the vibrations of Cu2 atoms diminish, such as the transverse acoustic (TA) modes near the M point and the longitudinal acoustic (LA) modes near the R point.

- The phonon linewidths extracted from MD simulations are much larger than those obtained from the perturbation theory at 300 K, suggesting that the phonon scattering induced by atomic hopping is strong.



Conclusions

❖ **Moderate Atomic Hopping with Negligible Convection**

- Cu2 atoms exhibit thermally activated hopping behavior.
- Due to the low diffusion coefficients, the convectional heat flux is negligible.

❖ **Dynamic Disorder Enhances Phonon Scattering**

- Cu2-induced dynamic disorder leads to the collapse of Cu2-dominated phonon modes near the Brillouin zone boundary.
- Broadening of low-frequency phonon linewidths indicates enhanced phonon scattering.
- The enhanced phonon scattering from dynamic disorder is the key mechanism behind the low κ_L of Cu_4TiSe_4.

❖ **Implications for Material Design and Discovery**

- These insights highlight the interplay between atomic dynamics and phonon scattering, offering new strategies for engineering materials with ultralow thermal conductivity.

➢ **References**

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