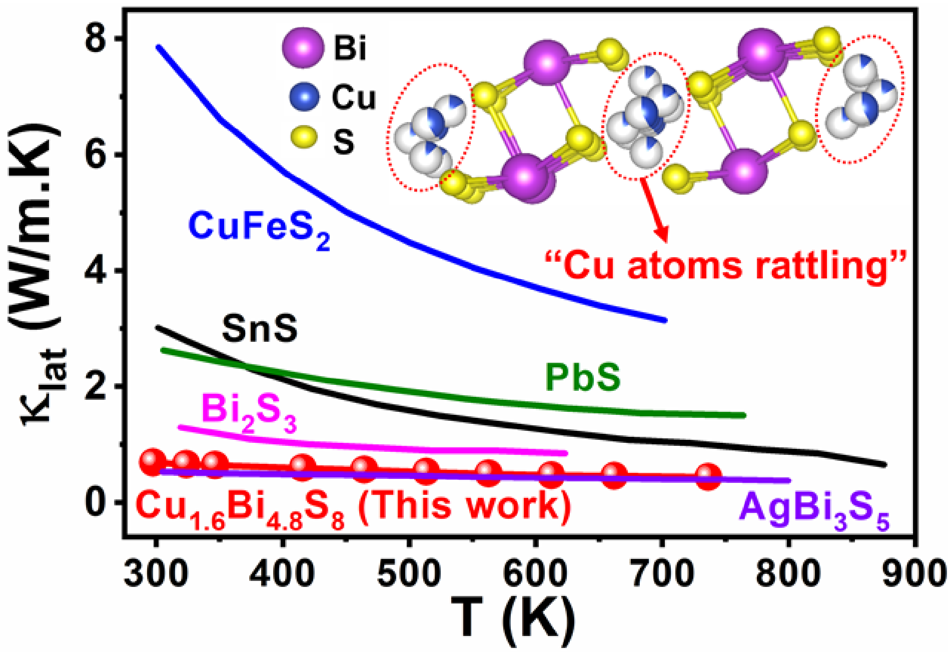
Ultralow Thermal Conductivity in Earth-Abundant $Cu_{1.6}Bi_{4.8}S_8$: Anharmonic Rattling of Interstitial Cu

Animesh Bhui, Moinak Dutta, Madhubanti Mukherjee, Kewal Singh Rana, Abhishek K. Singh, Ajay Soni, and Kanishka Biswas*

JNCASR



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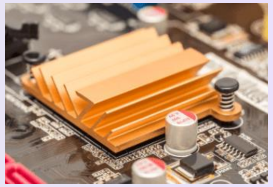
International Winter School-2021

Thermal Conductivity

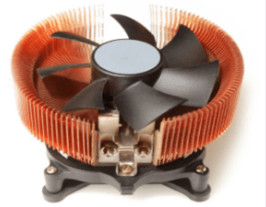
- Insulator



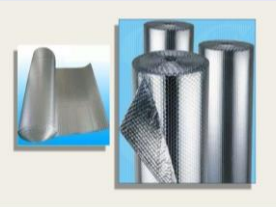
- Heat Sink

Low thermal conductivity

High thermal conductivity



- Refractories



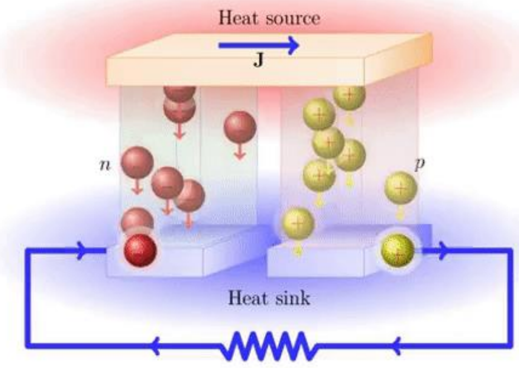
- Radiators

Seebeck effect (ΔT → ΔV)

Waste Heat

Thermoelectricity

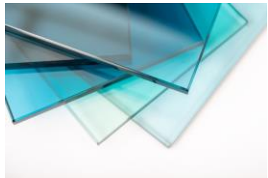
Electricity



Nat. Mater. **2008**, *7*, 105-114

Lattice Vibration

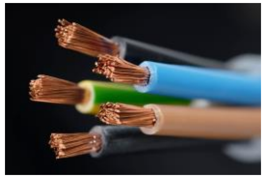
Glass



Low thermal Conductivity (κ)

+

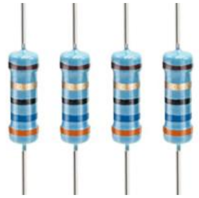
Metal



High electrical conductivity (σ)

+

Semiconductor



High Seebeck coefficient (S)

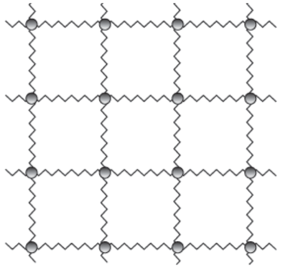
$$ZT = \frac{S^2\sigma}{\kappa} . T$$

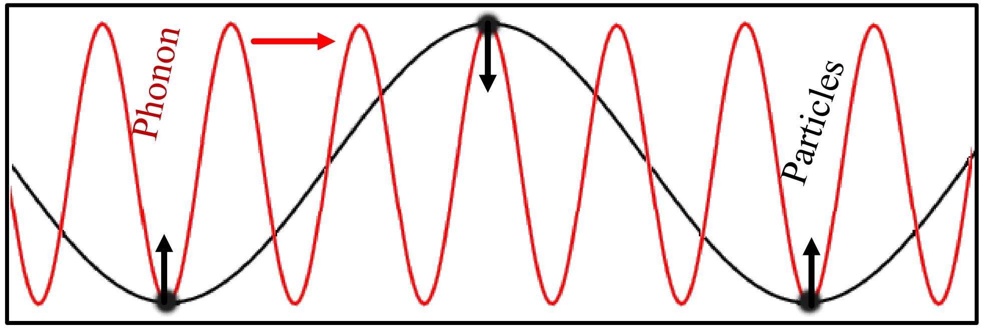
[electrical κ_e + lattice κ_{lat}]

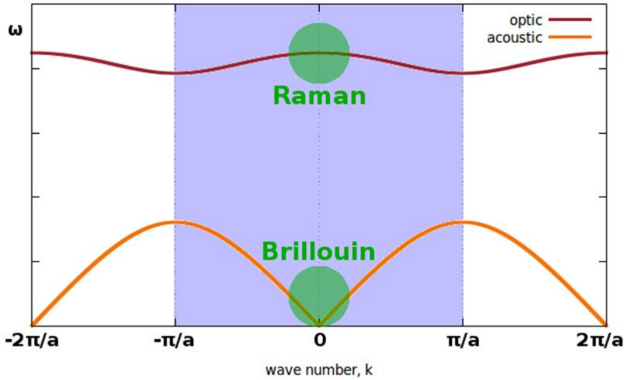
All the parameters are related via carrier concentration

❖ The only independent parameter is κ_{lat}

Crystal Lattice





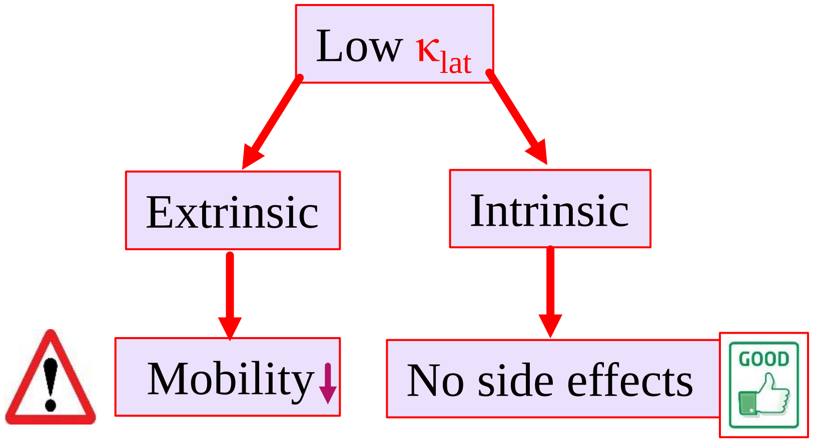


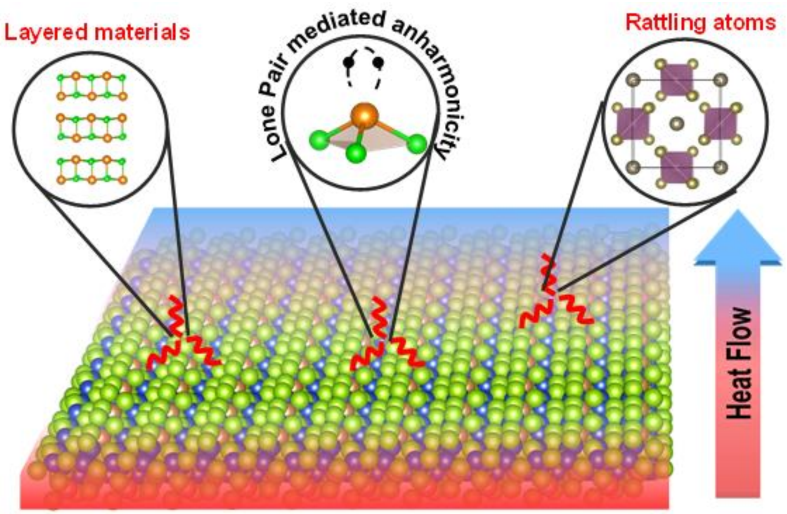
Atomic vibrations in solids: Phonons

$\kappa_{lat} = (1/3)C_v v_a l$

(C_v = Heat capacity at constant volume, v_a = Sound velocity, l = Phonon mean free path)

Intrinsic Approaches





❖ Additional structural features: complex crystal structure, heavy constituent elements, statistical disorder and bonding heterogeneity.

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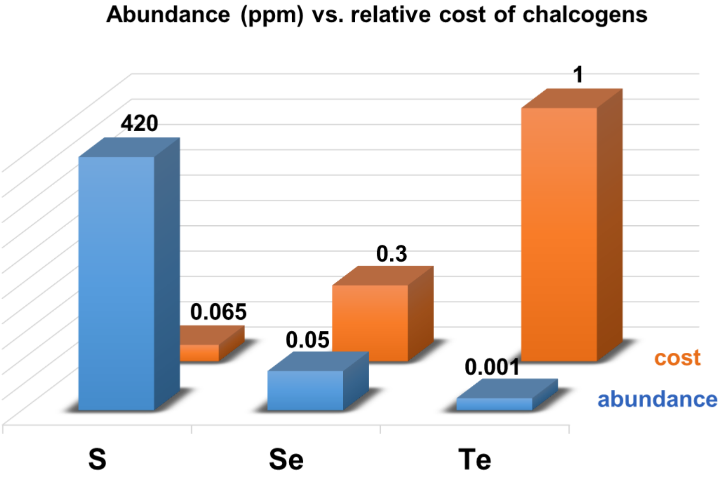
Why S Based Material $Cu_{1.6}Bi_{4.8}S_8$?

$$\kappa_{latt} T = \frac{R^{3/2}}{3\gamma^2 \varepsilon^3 N_0^{1/3}} \frac{T_m^{3/2} \rho^{2/3}}{A^{7/6}}$$

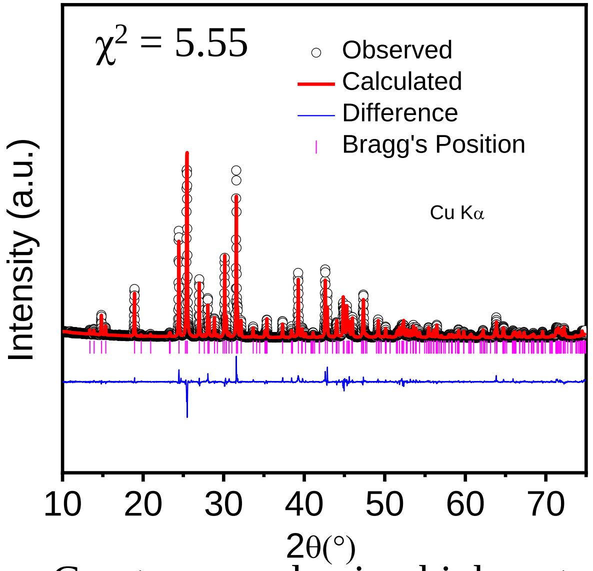


- κ_{lat} increases with decreasing atomic mass (A).
- Telluride and selenides are mostly used.

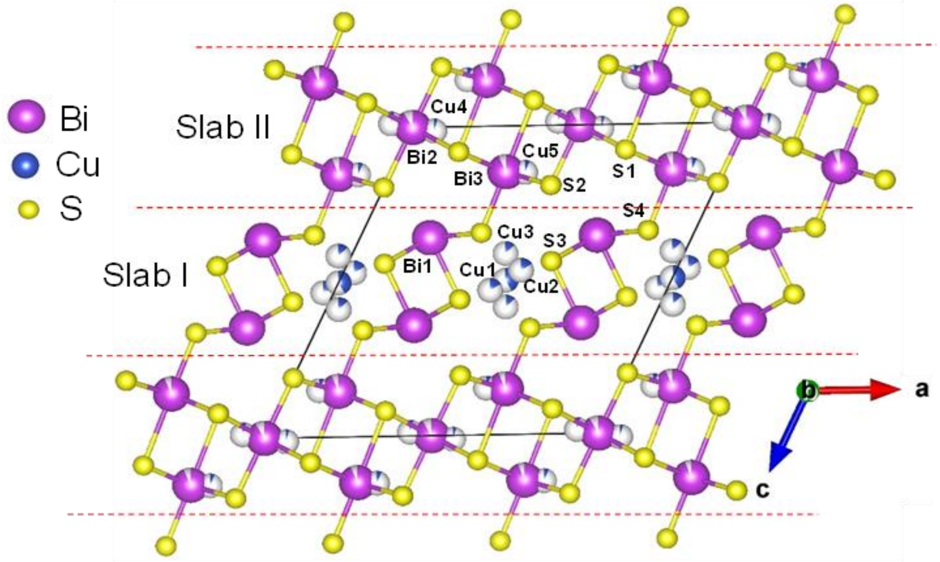
Te: Toxic and costly.

S: Earth-abundant and less expensive.

- Synthesized by high-T vacuum seal tube reaction.

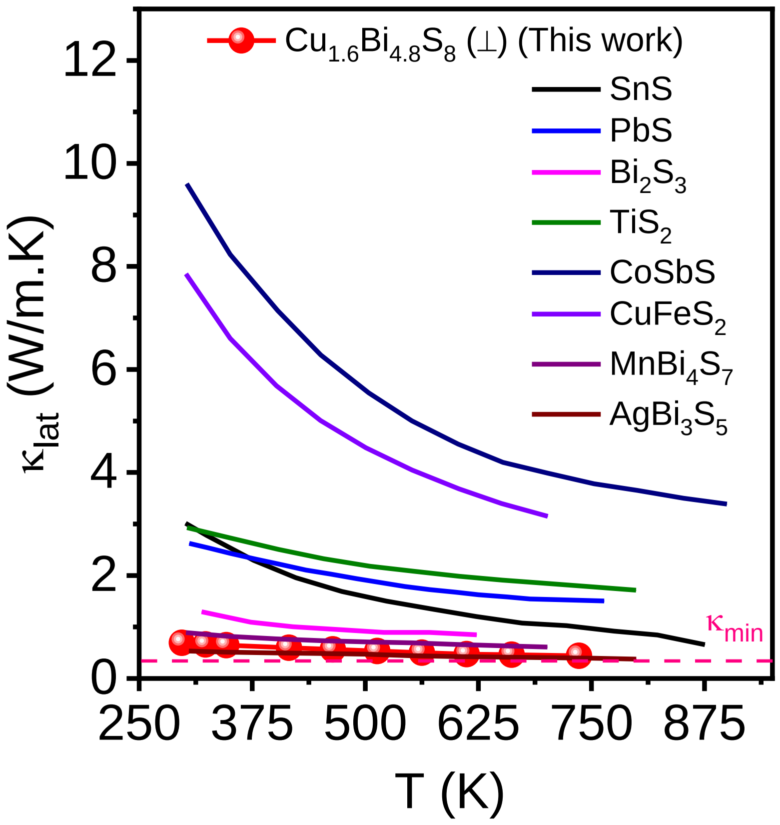


$Cu_{1.8}Bi_{4.8}S_8$ (*C2/m*)



- Cu-atoms are having higher atomic displacement parameters than Bi and S.

Low Thermal Conductivity and It's Origin



- κ_{lat} of $Cu_{1.6}Bi_{4.8}S_8$ has an exceptionally low value compared with the state-of-the-art metal sulfides.

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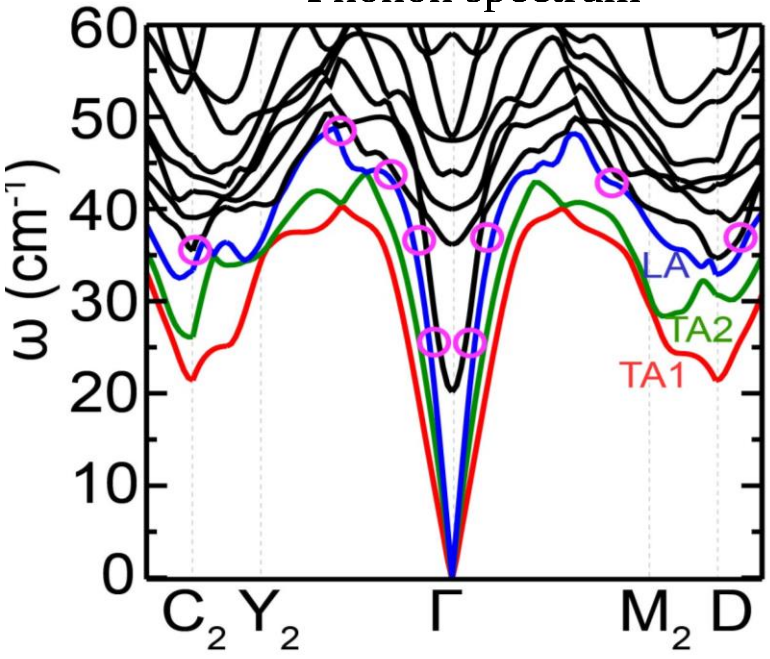
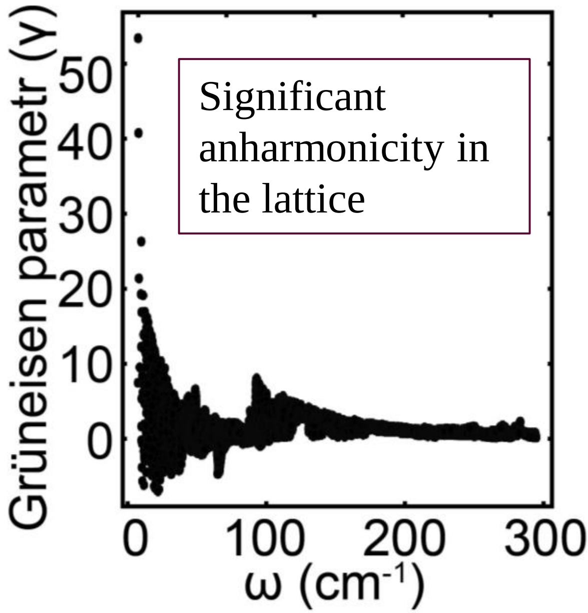
Phonon spectrum

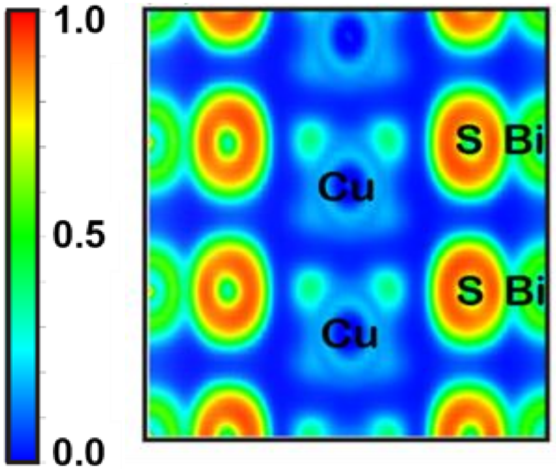


Low-frequency optical phonons

Scatters heat-carrying acoustic phonons



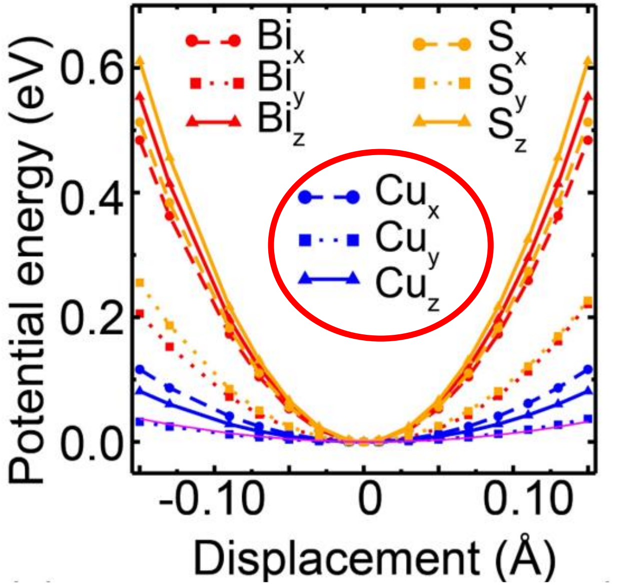
Significant anharmonicity in the lattice



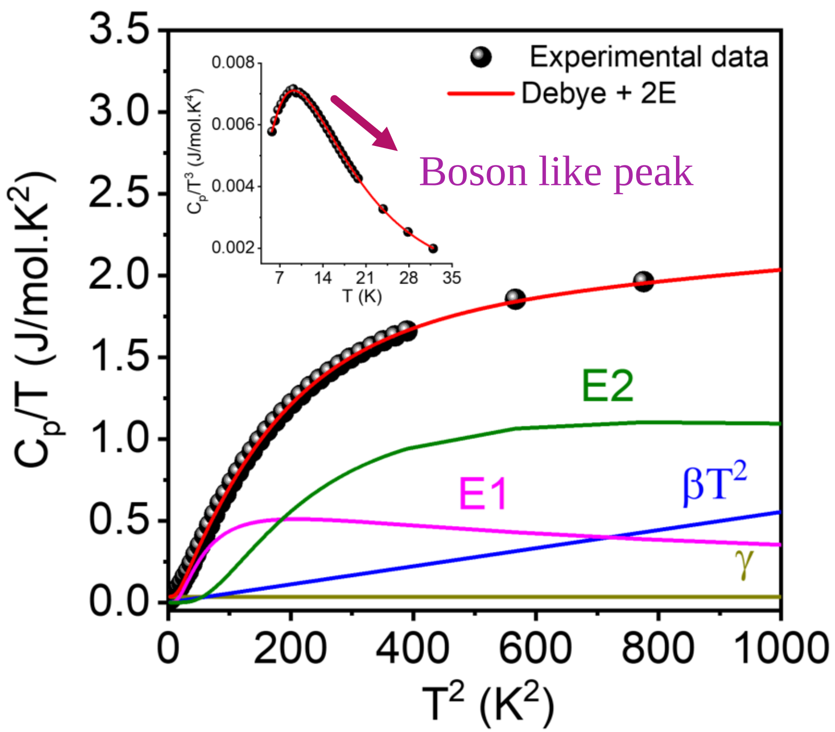
Electron localization function

Bonding heterogeneity

Rattling atoms



Heat Capacity and Raman Spectrum: Experimental Proof



$$\frac{C_p}{T} = \Upsilon + \beta T^2 + \sum_n \left(A_n\left(\theta_{E_n}\right)^2 . \left(T^2\right)^{-\frac{3}{2}} . \frac{e^{\frac{\theta_{E_n}}{T}}}{\left(e^{\frac{\theta_{E_n}}{T}} - 1\right)^2} \right)$$

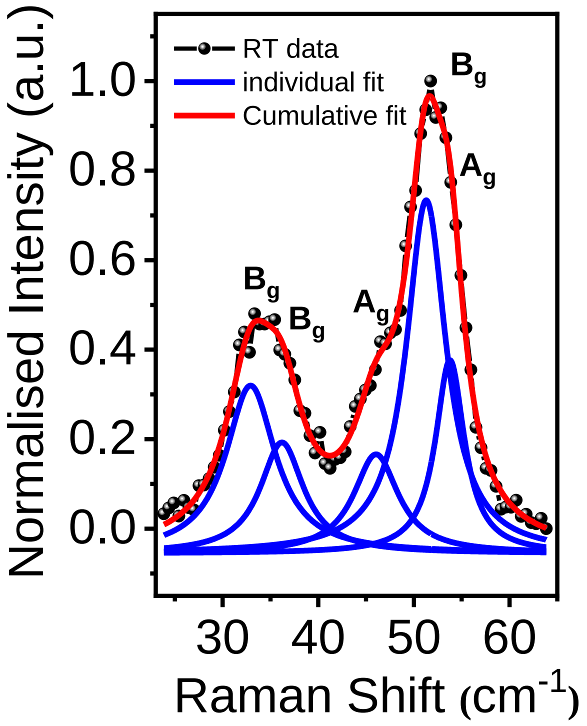
Electronic contribution

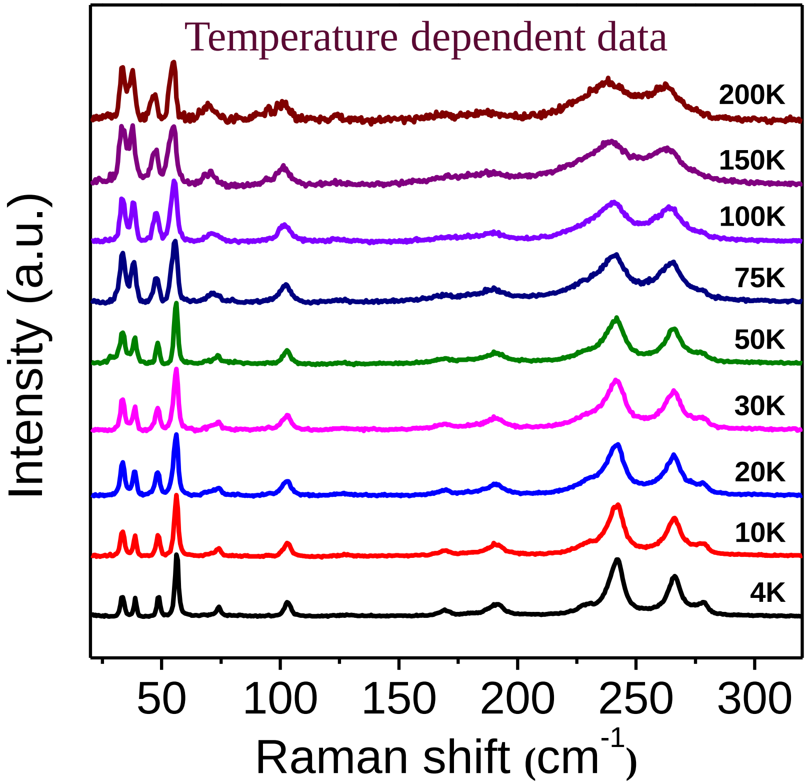
Debye modes

Einstein modes

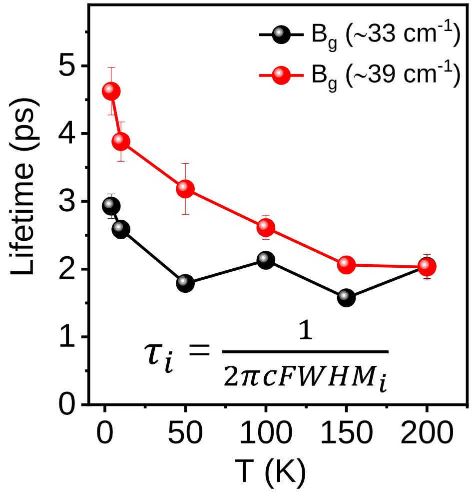
Θ_{E1} = 37.31 K (~ 26 cm^{-1})
Θ_{E2} = 74.21 K (~ 51.5 cm^{-1})

Low lying optical modes

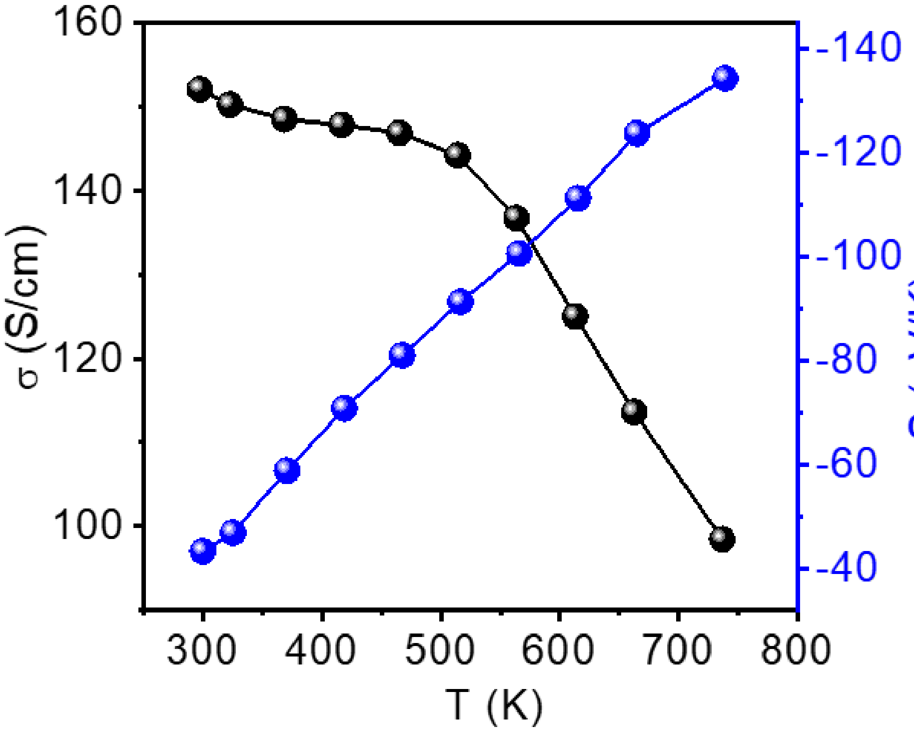


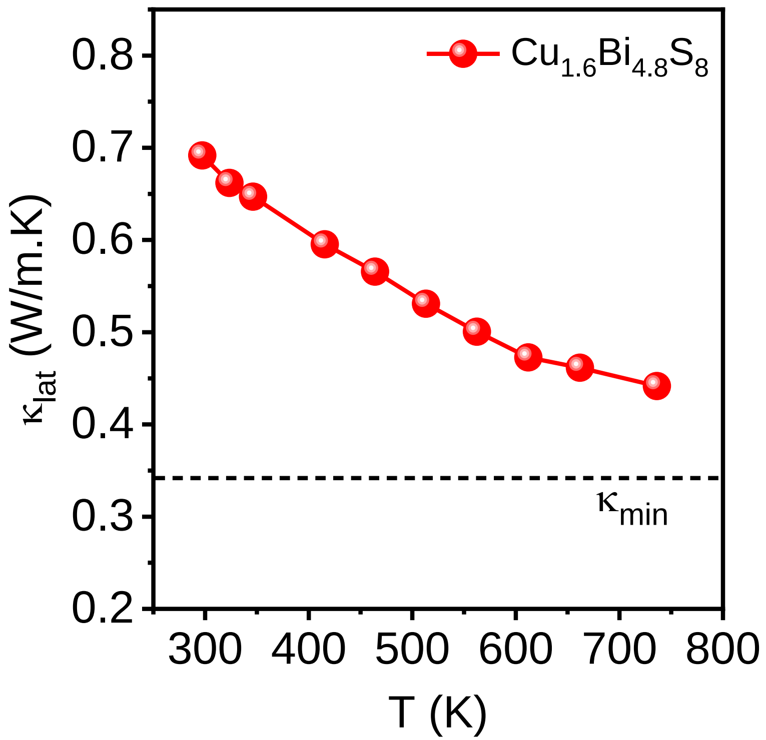


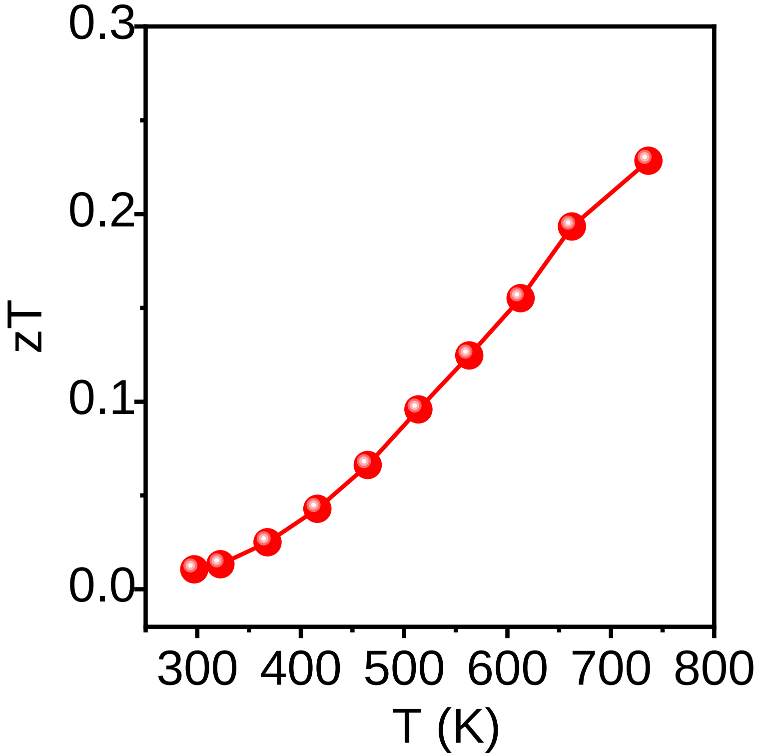
- ✓ Several low frequency optical modes are present.
- ✓ Ultrashort phonon lifetime (τ_i = 2-4.5 ms) due to large number of phonon scattering and leads to ultralow κ_{lat}.



Conclusions







- Low κ_{lat} w.r.t several state-of-the-art low thermal conductive materials in terms of earth-abundant and low-cost S-based materials.
- Reasonable zT in terms of pristine n-type earth-abundant metal sulfide.
- Presence of bonding hierarchy, rattling atoms and lattice anharmonicity generates the low-frequency optical phonon branches and strongly scatter the heat-carrying acoustic phonons to reduce κ_{lat}.

Bhui, A.; Dutta, M.; Mukherjee, M.; Rana, K. S.; Singh, A. K.; Soni, A.; Biswas, K., ***Chem. Mater.*** 2021, *33*, 2993-3001

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