## Electronic Supporting Information

# The Interplay of Chemical Bonding and Thermoelectric Properties in Doped Cubic GeTe

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**Number of Bands for projections:**

To determine the required number of wavefunctions for the projection from plane waves to atomic orbitals for COHP calculation, the DFT calculations must include enough bands in the self-consistent calculations. The number of bands depends on the structure and the basis used for the projection in LOBSTER. The calculation of the minimum number of bands for different supercells is discussed here.

For GeTe,

With the basis: Ge($4s^2 4p^2 3d^{10}$), Te($5s^2 5p^4 4d^{10}$).

There are 27 Ge atoms and 27 Te atoms in the supercell.

Minimum number of bands:

$$\frac{27[2(Ge-4s)+2(Ge-4p)+10(Ge-3d)+\ 2(Te-5s)+4(Te-5p)+10(Te-4d)]}{2}=405$$

For Pb:GeTe, 2 Ge atoms is replaced by Pb atoms

With the basis: Pb($6s^2 6p^2 5d^{10}$)

Minimum number of bands:

$$\frac{25[2(Ge-4s)+2(Ge-4p)+10(Ge-3d)]+27[\ 2(Te-5s)+4(Te-5p)+10(Te-4d)]+2}{2}=405$$

For Bi:GeTe, 2 Ge atoms is replaced by Bi atoms

With the basis: Bi($6s^2 6p^3 5d^{10}$)

Minimum number of bands:

$$\frac{25[2(Ge-4s)+2(Ge-4p)+10(Ge-3d)]+27[\ 2(Te-5s)+4(Te-5p)+10(Te-4d)]+2}{2}=406$$

For Sb:GeTe, 2 Ge atoms is replaced by Sb atoms

With the basis: Sb($5s^2 5p^3$)

Minimum number of bands:

$$\frac{25[2(Ge-4s)+2(Ge-4p)+10(Ge-3d)]+27[\ 2(Te-5s)+4(Te-5p)+10(Te-4d)]+2[2(Sb-5s)+3(Sb-5p)]}{2}=396$$

For In:GeTe, 2 Ge atoms is replaced by In atoms

With the basis: In($5s^2 5p^1 4d^{10}$)

Minimum number of bands:

$$\frac{25[2(Ge-4s)+2(Ge-4p)+10(Ge-3d)]+27[\ 2(Te-5s)+4(Te-5p)+10(Te-4d)]+2}{2}=404$$

**Summary of dopant elements in GeTe:**

As-grown GeTe is predominantly a highly p-doped degenerate narrow gap semiconductor due to a high level of Ge vacancies. The introduction of additional dopants in GeTe is to lower the high hole concentration by effective suppression of intrinsic Ge vacancies and concurrently modifying the electronic structure. In recent years, significant efforts have been made to improve the performance of GeTe by introducing different dopants in it as shown in Fig. 1 in the main text. Fig. S1 summarizes the collective insights gleaned from the literature, showcasing the impactful advancements made in recent years.


Fig. S1 Summary of recently used dopant materials (orange color) in GeTe achieving zT>1.0

**Phonon Dispersion:**

As cubic-GeTe is not thermodynamically stable at room temperature, vibrational modes are stabilized by a finite temperature of 800 K in TDEP calculations as depicted in Fig. 5(b) whereas density functional perturbation calculation reveals imaginary phonon modes as shown in Fig. S2.

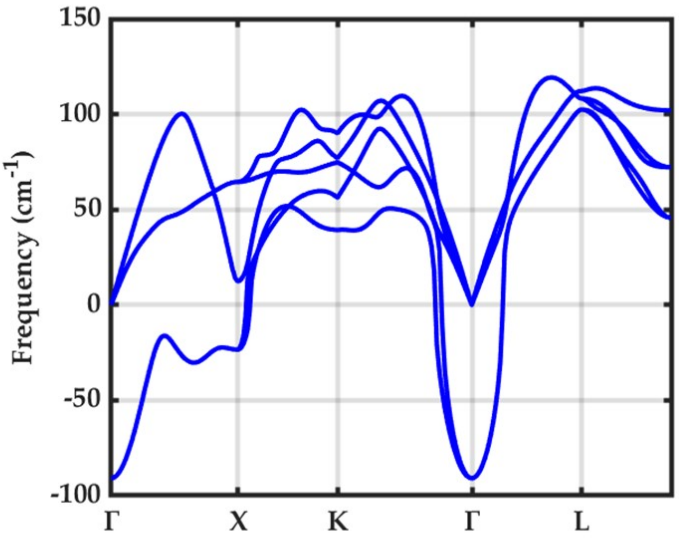


Fig. S2 Phonon dispersion computed from dynamical matrix using 4x4x4 q-point mesh.

**Elastic constants from group velocities:**

In a cubic crystal, using elasticity theory, it is possible to extract the 3 independent elastic constants from the acoustic group velocities along [110] direction. We have used the following relations to complete the table 2 in the main text:

$$\rho v_{t,z}^2 = C_{44}\,;\, \rho v_{t,xy}^{\ 2} = \frac{(C_{11} - C_{12})}{2}\,;\, \rho v_l^2 = \frac{(C_{11} + C_{12})}{2} - C_{44}$$

Where the mass density $\rho$=6115.5 kg/m$^3$; and for q=[110] the two transverse group velocities are polarized along z (for the shear mode $C_{44}$), and in the xy plane.

**Convergence Study of K-mesh and q-mesh:**

Before performing the transport calculations, convergence of electron-phonon scattering rates has been performed with varying k-mesh and q-mesh. Fig. S3(a-b) depicts the change in electron-phonon scattering rates with q-mesh and k-mesh. It is evident that k-mesh of $60 \times 60 \times 60$ and q-mesh $5 \times 10^6$ would be enough to reach convergence. This has been further validated by transport properties as shown in Fig. S3(c-d).

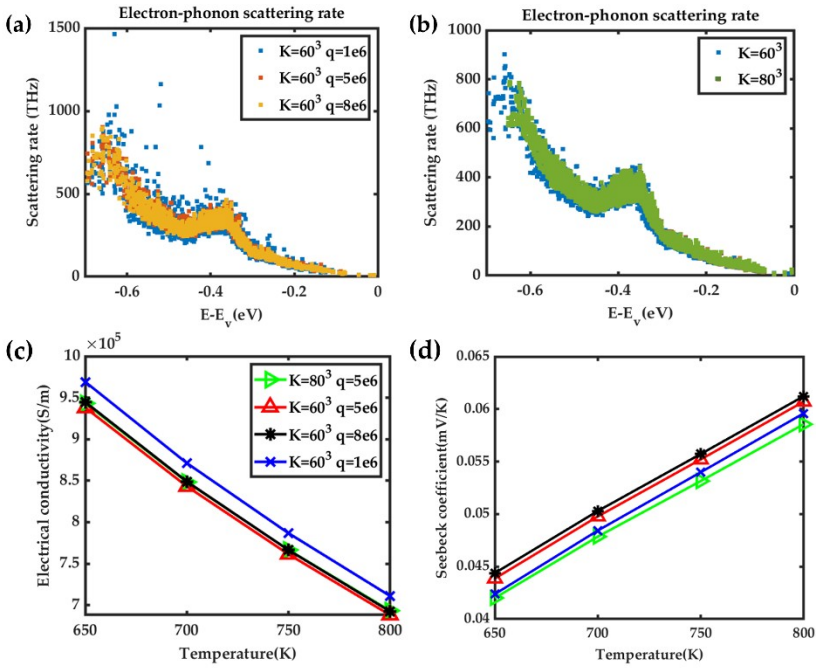


Fig. S3 Convergence study of K-mesh and q-mesh (a) q-mesh dependent electron-phonon scattering rates with fixed k-mesh 60 $\times$ 60 $\times$ 60, (b) K-mesh dependent electron-phonon scattering rates with fixed q-mesh of 5 $\times$ $10^6$, (c) electrical conductivity, (d) Seebeck coefficient including only electron-phonon scattering with respect to different k-mesh and q-mesh.

**Valence electron wavefunction:**

As explained in the main text, the conduction band of cubic-GeTe is governed by Ge(p) orbital and the valence band is from Ge(s) and Te(p) orbitals. This is revealed by electron wavefunction plot in Fig. S4 where Fig. S4(a) & (b) shows the Ge(p)-Te(p) interactions and Ge(s)-Te(p) interactions, respectively.

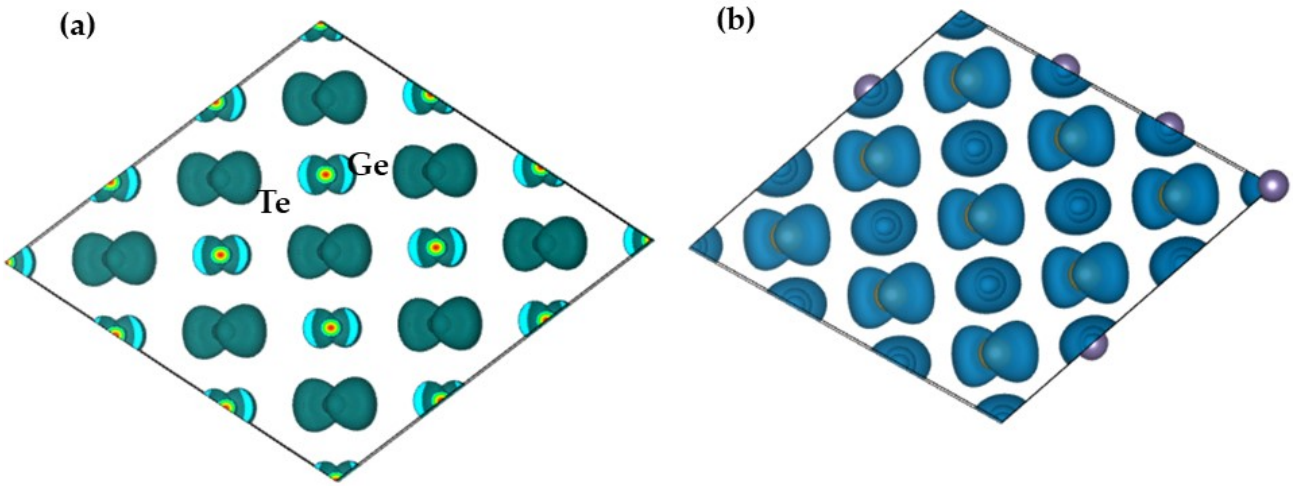


Fig. S4 Isosurfaces of the valence electron wavefunction at (a) 20% of the isovalue (Ge(p)-Te(p) interactions), (b) 10% of isovalue (Ge(s)-Te(p) interactions).

**Projected Density of States:**

Projected density of states (PDOS) for all supercells is shown in Fig. S5.

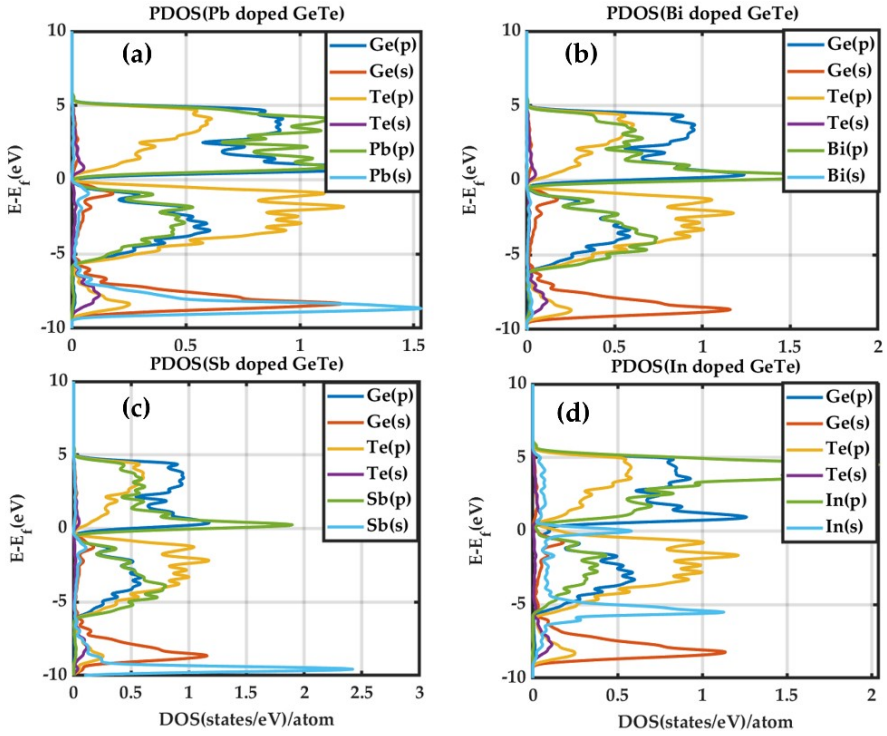


Fig. S5 Projected density of states (PDOS) (a) Pb doped GeTe, (b) Bi doped GeTe, (c) Sb doped GeTe, and (d) In doped GeTe.

The contribution of orbital projected PDOS to total DOS in Fig. S6 shows that s-contribution from dopants (X) in valance band decreases as X=In, Pb, Sb, Bi. Except Indium, other dopants do not have significant effect on total dos (Fig. S6(e)) rather than changing the fermi level.

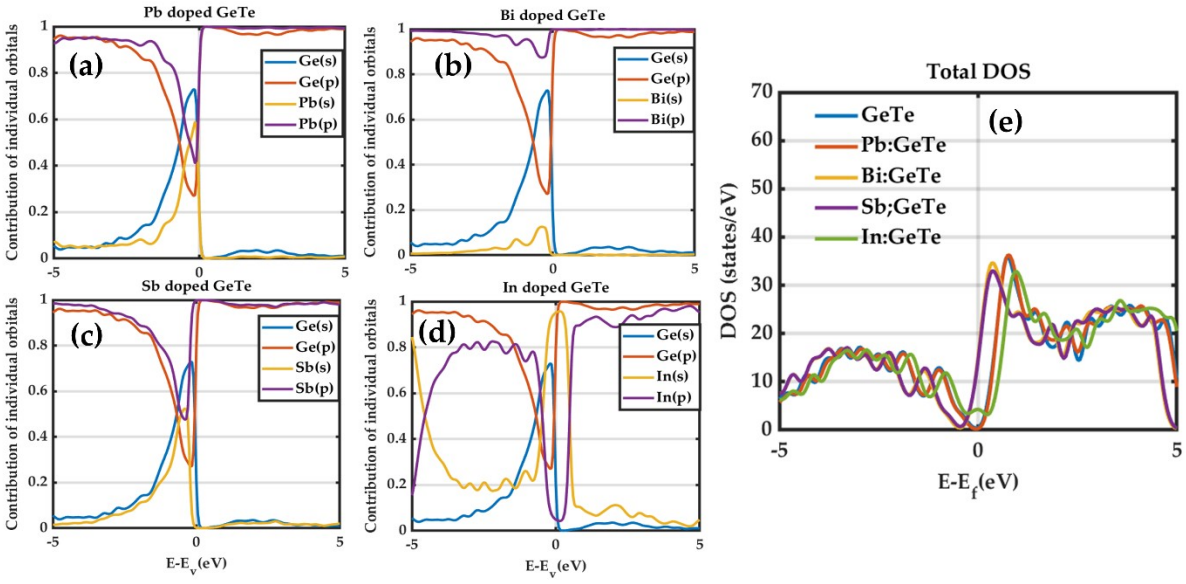


Fig. S6 Contribution of s and p orbital on DOS (a) Pb doped GeTe, (b) Bi doped GeTe, (c) Sb doped GeTe, (d) In doped GeTe, w.r.t valence band minimum and (e) total DOS w.r.t fermi level for all samples.

Table S1: ICOHP of s-p interactions in doped GeTe showing that the Te-X bonds become more antibonding (weaker) as X=In, Ge, Sb, Pb, Bi

| Bonding | ICOHP for s-p (eV) |
|---|---|
| In-Te | -0.34 |
| Ge-Te | -0.132 |
| Sb-Te | -0.11 |
| Pb-Te | -0.094 |
| Bi-Te | -0.072 |

**Electronic Band Structure comparison:**

Fig. S7 (a) shows the electronic band structure with and without spin-orbit coupling (SOC). There is no significant effect of SOC on electronic band structure near the fermi level. Also wannierized band structure coincides well with DFT band structure.

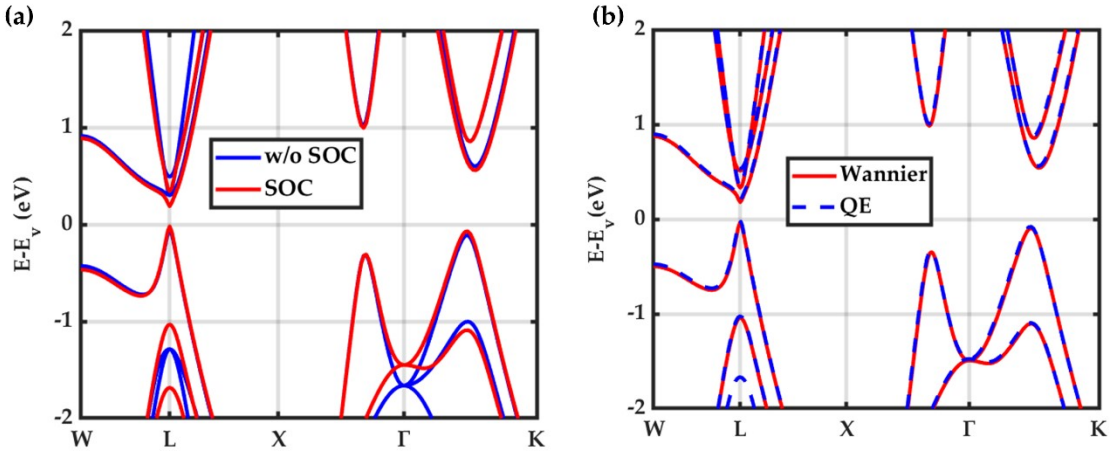


Fig. S7 (a) Electronic band structure with and without SOC, (b) Comparison between wannierized and DFT band structure.

**Screening length:**

Screening length is a strong function of carrier concentration compared to temperature as depicted in Fig. S8. At very high concentrations, electron-impurity screening length is shorter than low concentrations.

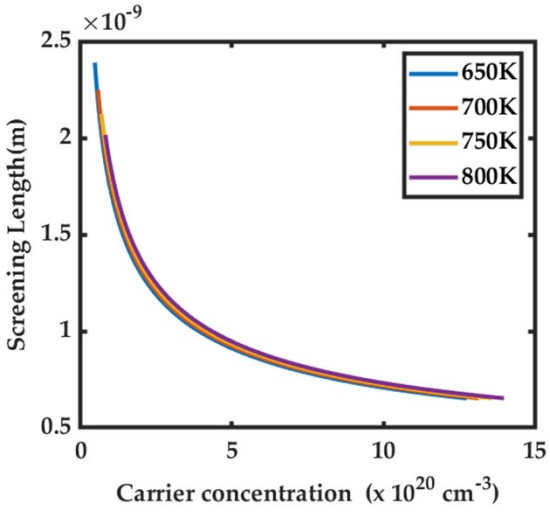


Fig. S8 Screening length versus carrier concentration at different temperatures.

**Transport Properties of cubic-GeTe:**

Semiclassical Boltzmann Transport formula under energy dependent relaxation time has been used for transport calculation. Temperature and carrier concentration dependent transport coefficients are shown in Fig. S9.

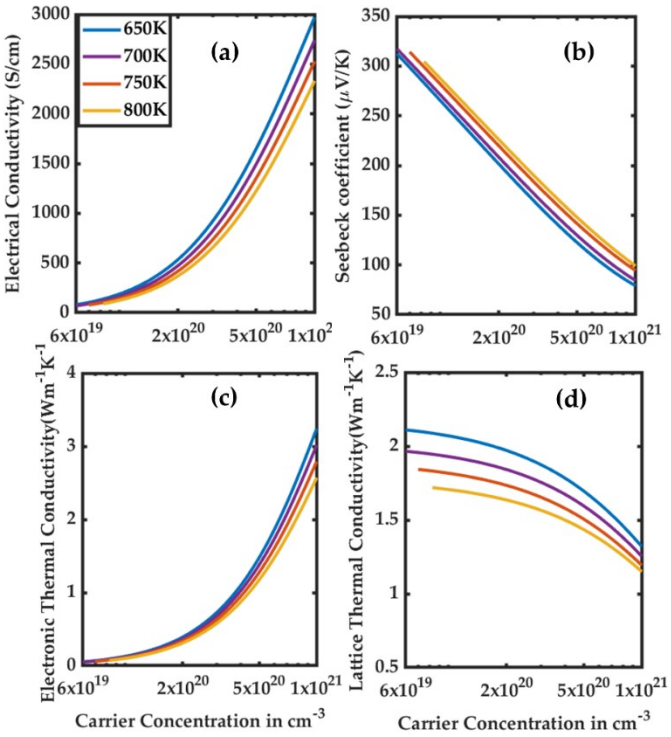


Fig. S9 Transport properties based on RTA (a) electrical conductivity, (b) Seebeck coefficient, (c) Electronic thermal conductivity, and (d) Lattice thermal conductivity.