Supplementary Materials

Lattice thermal conductivity reducing in Ca_3AlSb_3 and $Ca_5Al_2Sb_6$ by manipulating the covalent tetrahedral chain

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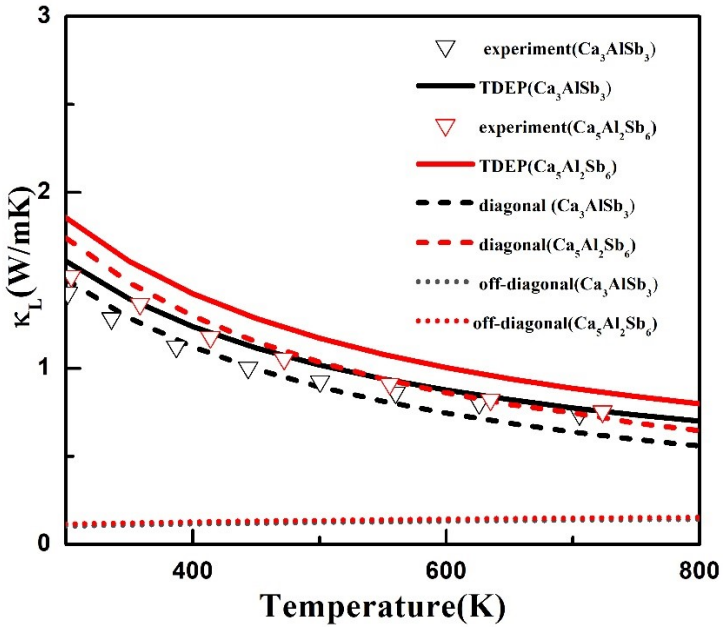

Fig. S1. (a) Computed lattice thermal conductivities of Ca_3AlSb_3 and $Ca_5Al_2Sb_6$. The black and red triangles are experimental measurements of Ca_3AlSb_3 and $Ca_5Al_2Sb_6$, respectively. The black and red solid lines represent the TDEP theoretical thermal conductivities of Ca_3AlSb_3 and $Ca_5Al_2Sb_6$, respectively. The black and red dotted lines (dashed lines) represent the off-diagonal (diagonal) contributions in the thermal conductivities of Ca_3AlSb_3 and $Ca_5Al_2Sb_6$, respectively.

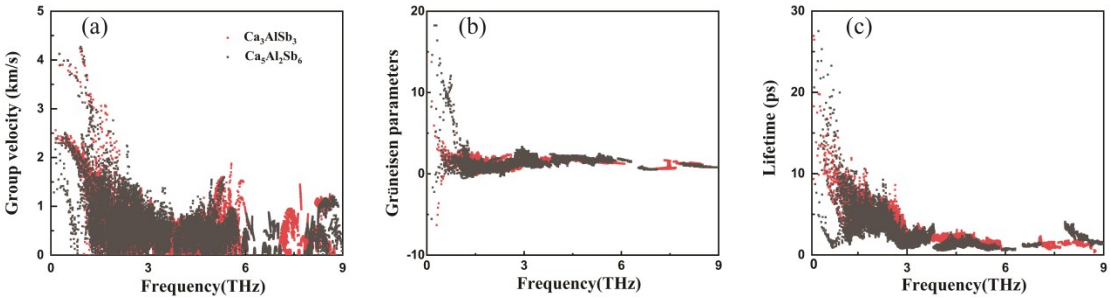

Fig. S2. Calculated (a) phonon group velocities, (b) Grüneisen parameters and (c) phonon lifetime as a function of frequency for Ca_3AlSb_3 (red dots) and $Ca_5Al_2Sb_6$ (black dots).

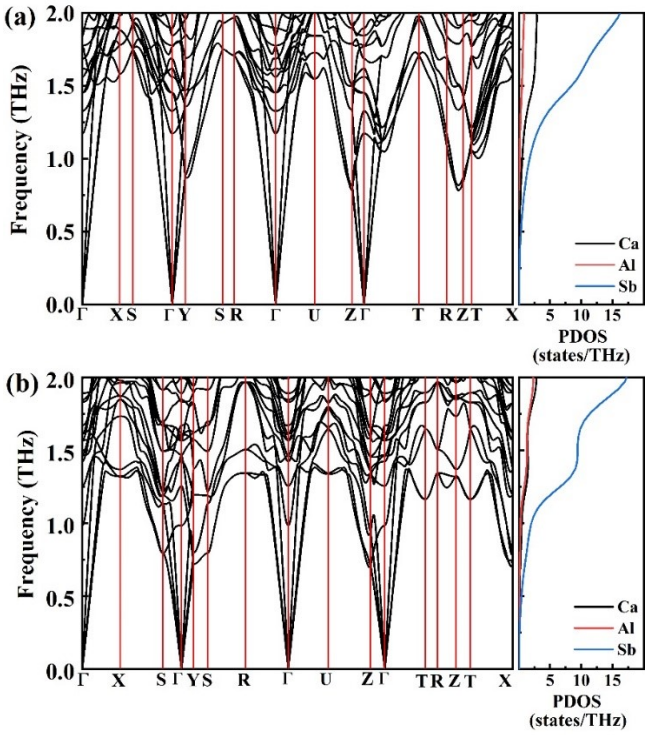

Fig. S3. The phonon dispersions and density of states of (a) Ca_3AlSb_3 and (b) $Ca_5Al_2Sb_6$, respectively.

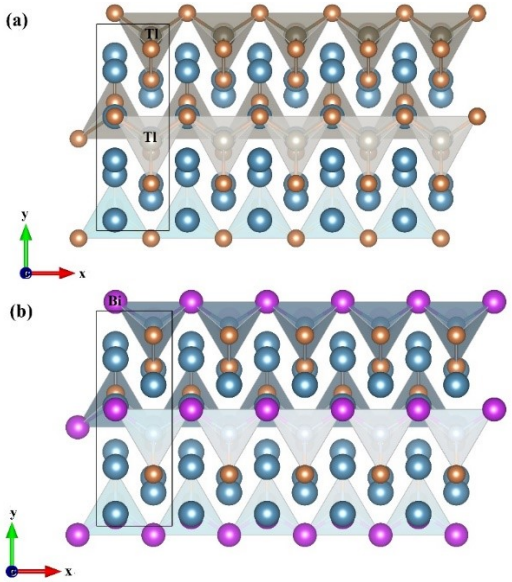

Fig. S4. Crystal structures of Tl-doped Ca_3AlSb_3 (the top three panels: a) and Bi-doped Ca_3AlSb_3 (the bottom three panels: b). Sb = pink, Al = green, Ca = blue, Tl=grey, Bi=purple.

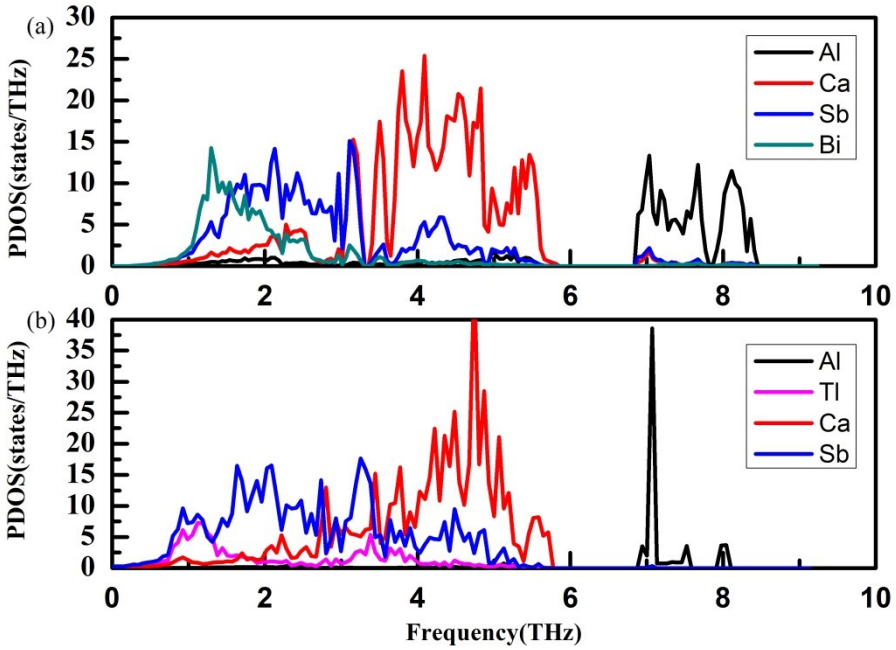

Fig. S5. The phonon density of states of (a) Bi- and (b) Tl-solid solution Ca_3AlSb_3, respectively.

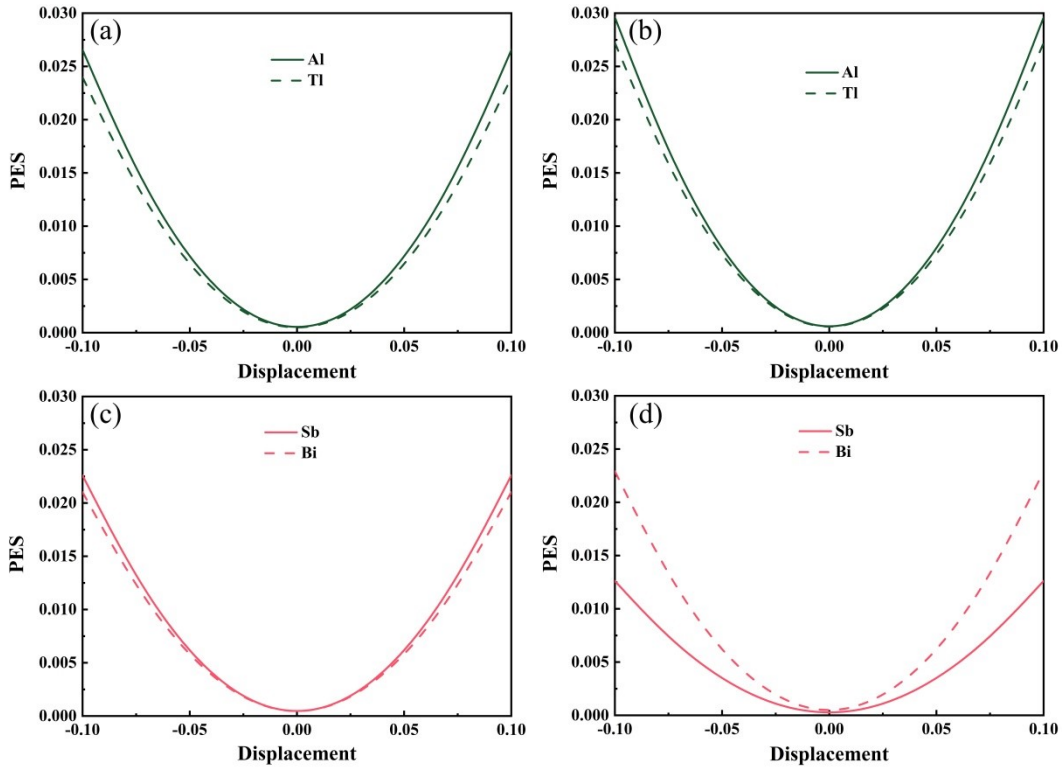

Fig. S6. The potential energy surfaces (PES) of replacing Al with Tl atom in (a) Ca_3AlSb_3 and (b) $Ca_5Al_2Sb_6$. PES of replacing Sb with Bi in (c) Ca_3AlSb_3 and (d) $Ca_5Al_2Sb_6$. The solid green line, dashed green line, solid red line and dashed red line represent the PES of Al, Tl, Sb and Bi, respectively.

Computational details

A. The tests of convergence

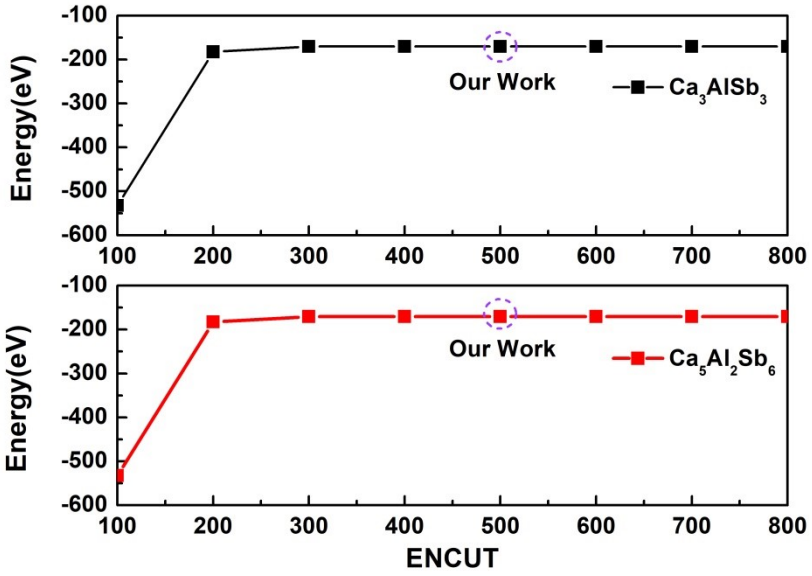

Fig. S7. The test results of ENCUT for (a) Ca_3AlSb_3 and (b) $Ca_5Al_2Sb_6$, respectively. The total energy is converged at the 200 eV energy cutoff, and we use a high energy cutoff (500 eV) for the calculations.

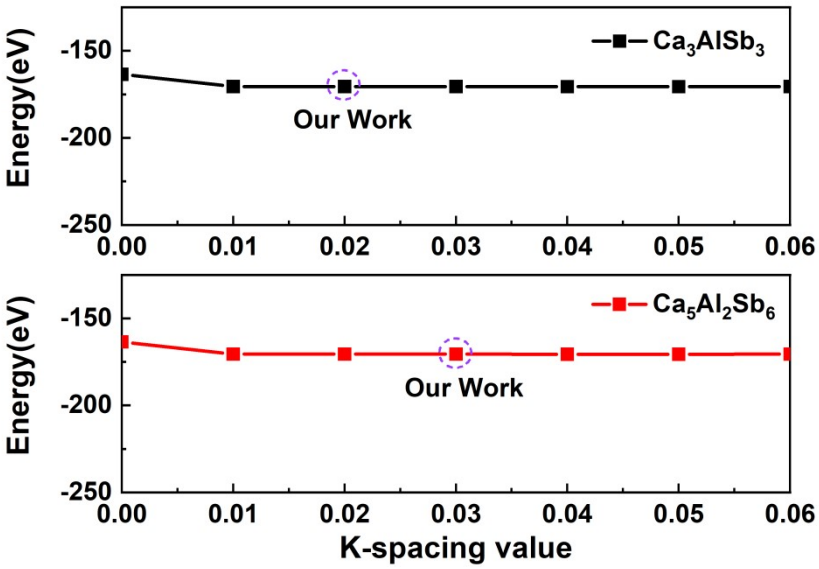

Fig. S8. The test results of K-spacing value for (a) Ca_3AlSb_3 and (b) $Ca_5Al_2Sb_6$, respectively. The total energy is converged at the K-spacing value of 0.01 (a 4×1×1 K-mesh). We choose densed K-spacing values [0.02 (k-mesh of 3×3×8) and 0.03 (k-mesh of 10×4×3) for Ca_3AlSb_3 and Ca_5AlSb_6, respectively] for the calculations.

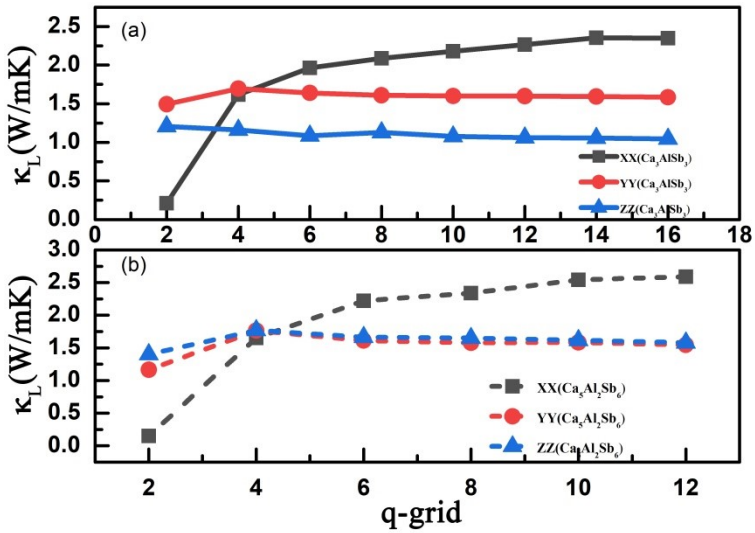

Fig. S9. The test results of thermal conductivity for (a) Ca_3AlSb_3 and (b) $Ca_5Al_2Sb_6$, respectively. Here, N=2-12 represent N×N×N q grid, respectively. The q-grid of 6×6×6 is good enough to get converged lattice thermal conductivity values, and we utilize a densed 8×8×8 grid.

B. The atomic displacement parameter (ADP)

The ADP can be calculated based on the dynamical matrix:

$$D_{\alpha\beta}(jj',q) = \frac{1}{\sqrt{m_j m_{j'}}} \sum_{l'} \Phi_{\alpha\beta}(j0,j'l') exp\left(iq \cdot [r(j'l') - r(j0)]\right)$$

where m is the atomic mass and q is the wave vector. An equation of motion is written as

$$\sum_{j'\beta} D_{\alpha\beta}(jj',q) e_\beta(j',qv) = [\omega(qv)]^2 e_\alpha(j,qv)$$

where the eigenvector of the band index v at q is obtained by the diagonalization:

$$\sum_{j\alpha j'\beta} e_\alpha(j',qv)^* D_{\alpha\beta}(jj',q) e_\beta(j',qv') = [\omega(qv)]^2 \delta_{vv'}$$

The atomic displacement parameter (ADP) u is given as

$$u_\alpha(jl,t) = \left(\frac{\hbar}{2Nm_j}\right)^{\frac{1}{2}} \sum_{q,v} [\omega(qv)]^{-\frac{1}{2}} [\hat{a}(qv) exp(-i\omega(qv)t) + \hat{a}^\dagger(-qv) exp(i\omega(qv)t)) e_\alpha(j,qv)$$

where $\hat{a}^{\dagger}$ and $\hat{a}$ are the creation and annihilation operators of phonon, $\hbar$ is the reduced Planck constant, and t is the time.

C. The force constant approximation

To further check the effect of temperature-dependent force constants on κ_L, we perform the molecular dynamics (MD) calculations at 500 K and directly calculate κ at this temperature using the second and third force constants from the 500 K molecular dynamics. We notice that the lattice thermal conductivities at 500 K using the force constants from 300 and 500 K MD simulations are highly similar (Table S1, error is smaller than 4 %). These results indicate that it is reasonable to use the renormalized force constants from the simulations at 300 K to calculate the lattice thermal conductivities at other temperatures.

Table S1 Comparison of the lattice thermal conductivity at 500 K using the renormalized force constants from the MD simulations at 300 K and 500 K. (unit: W/mK)

	X	y	z
Ca_3AlSb_3 (300 K)	1.31	1.04	0.71
Ca_3AlSb_3 (500 K)	1.35	1.07	0.71
$Ca_5Al_2Sb_6$ (300 K)	1.46	1.10	1.14
$Ca_5Al_2Sb_6$ (500 K)	1.49	1.12	1.18