Supplemental Material for "Nanowires with Dislocations for Ultralow Lattice Thermal Conductivity"

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Thermal Properties of PbSe via Molecular Dynamics Simulations

The large scale simulations are carried out with equilibrium molecular dynamics (MD) with LAMMPS.[1] For PbSe structures, we adopted the interatomic potentials developed by Schapotschnikow et al., [2] which is a combination of Lennard-Jones (LJ) and Coulomb potentials,

$$U_{ij}(r_{ij}) = U_{coulomb}(r_{ij}) + U_{LJ}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \quad (1)$$

where r_{ij} is the distance between i and j, ε_{ij} and σ_{ij} are the LJ parameters, q_i and q_j are partial charges on atom i and j, and ε_0 is the dielectric constant of vacuum. Parameters of the LJ potential for same type of atoms are defined as in Ref [2]; and for different types of atoms, the Lorentz-Berthelot mixing rules have been applied. In order to improve the simulation efficiency, instead of using 10 nm as the cut-off radius for electrostatic interactions as indicated in their paper, we applied Ewald summation to describe the long range electrostatic interactions. The lattice constant at 0 K and the bulk modulus in the rocksalt structure are 6.06 Å and 52.9 GPa respectively with our adapted method, which are comparable to the values obtained in their paper, 6.06 Å and 54.3 GPa, and other experimental measurements [3,4] and first principle calculations.[5,6] Thus, the cut-off radius approach can be safely replaced with the Ewald summation one.

To verify the potential we are using for MD simulations to calculate thermal conductivity (κ), we firstly calculated a series of cubic bulk PbSe structures with different sizes, side lengths varying

from 2.4 nm to 7.3 nm with periodic boundary conditions (PBC) applied in three directions. Initially, the structures were fully relaxed with a conjugate gradient energy minimization algorithm. The structures were evolved for 10 ps in the isothermal-isobaric ensemble to raise the temperature to 300 K in vacuum. Then they were thermally equilibrated at 300 K for another 10 ps each in canonical and microcanonical ensembles. The MD time step was set to 1 fs. Another 100 ps of microcanonical ensembles were carried out with the velocity Verlet integral after the equilibrium to calculate the heat flux:

$$j(t) = \frac{1}{2}\sum_{i,j,i\neq j} r_{ij}(F_{ij}\cdot v_i) \tag{2}$$

where v_i is the velocity of particle *i*, F_{ij} is the force on atom *i* due to its neighbor *j* from the pair potential (1), where m_i is the mass of atom *i.* Then Green-Kubo formula is applied to calculate κ:

$$\kappa = \frac{1}{3Vk_BT^2}\int_0^\infty \langle j(0)j(t)\rangle dt \tag{3}$$

where V is the volume, k_B is the Boltzmann constant and T is the temperature at equilibrium. The results are shown in Figure S1. We can see that the κ is converged at around 3.2 W/mK when side length reaches 3.7 nm, which is comparable to the results of the first principle calculations in Ref.[7]. We then took the similar procedures to calculate a series of pristine PbSe NWs with 2.45×2.45 nm^2 cross-sectional area (xy plane) and different lengths in z direction. PBC was applied only in z direction. The length of the calculated pristine structures vary from 3.06 nm to 30.13 nm in z direction. κ has converged when the length is approximately 5 nm. These results are presented in Figure S2.

The thermal conductivity was obtained by averaging the calculated thermal conductivities over the number of ensembles. Figure S3 shows that the averaged thermal conductivity of a pristine SiGe NW converges to 5.1 W/mK after 25 ensembles. The error bar is ± 0.15 W/mK.

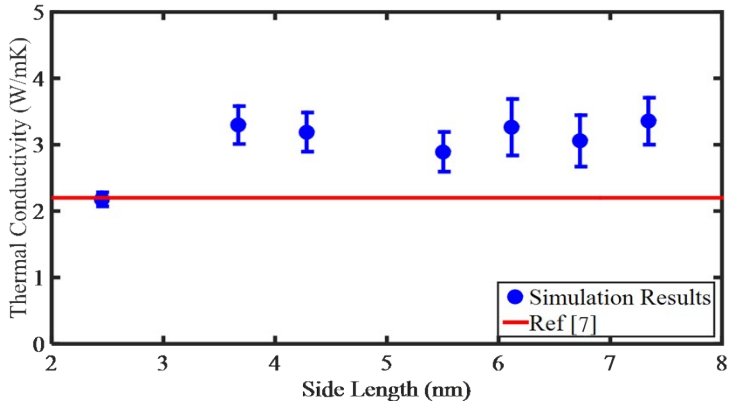

Figure S1. Thermal conductivity of bulk PbSe structures with different side lengths. The blue circles are calculated with MD simulation. The red line is the result from first-principle calculations[8].

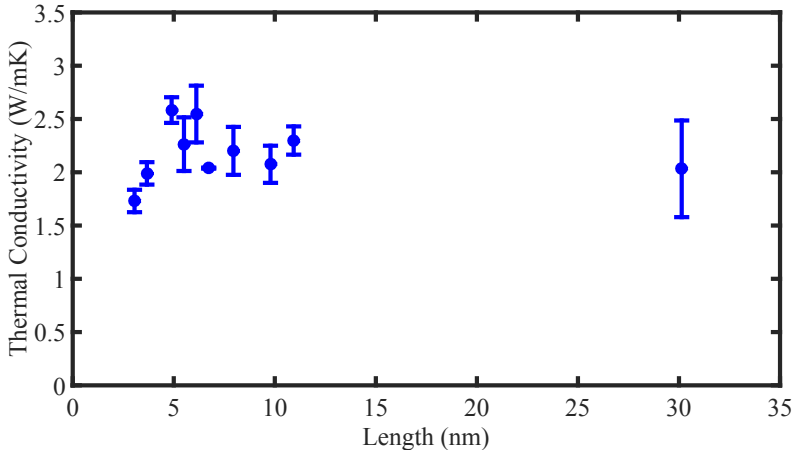

Figure S2. Thermal conductivity of pristine PbSe NWs with different lengths. The blue circles are the simulated results for pristine NWs.

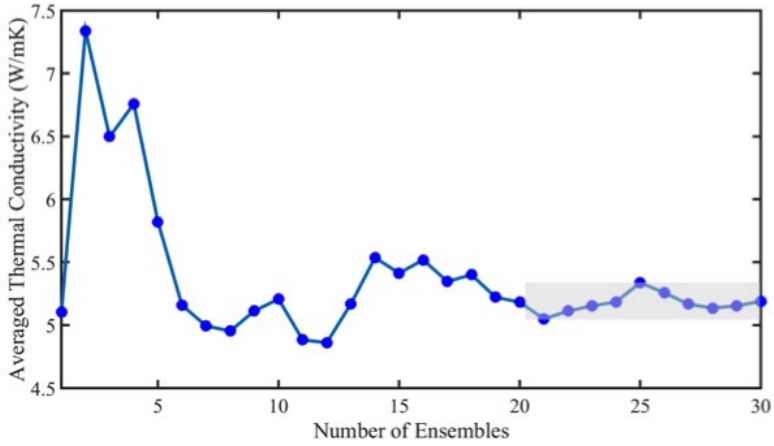

Figure S3. Convergence of thermal conductivity of pristine SiGe NWs with the number of ensembles. The shaded area represents the error bar.

References

1. S. J. Plimpton, *J. Comp. Phys.*, 1995, **117**, 1-19.
2. P. Schapotschnikow, M. A. v. Huis, H. W. Zandbergen, D. Vanmaekelbergh and T. J. H. Vlugt, *Nano Lett.*, 2010, **10**, 3966–3971.
3. *Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology*, Springer, Berlin, 1983.
4. R. Dalven, *Infrared Phys.*, 1969, **9**, 141-184.
5. S.-H. Wei and A. Zunger, *Phys. Rev. B*, 1997, **55**, 13605.
6. Y. Zhang, X. Ke, C. Chen, J. Yang and P. R. C. Kent, *Phys. Rev. B*, 2009, **80**, 024304.
7. Z. Tian, J. Garg, K. Esfarjani, T. Shiga, J. Shiomi and G. Chen, *Phys. Rev. B*, 2012, **85**, 184303.