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Supplementary Information for

Thermoelectric performance of novel single-layer $ZrTeSe_4$

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1. Crystal structure of bulk $ZrTeSe_4$

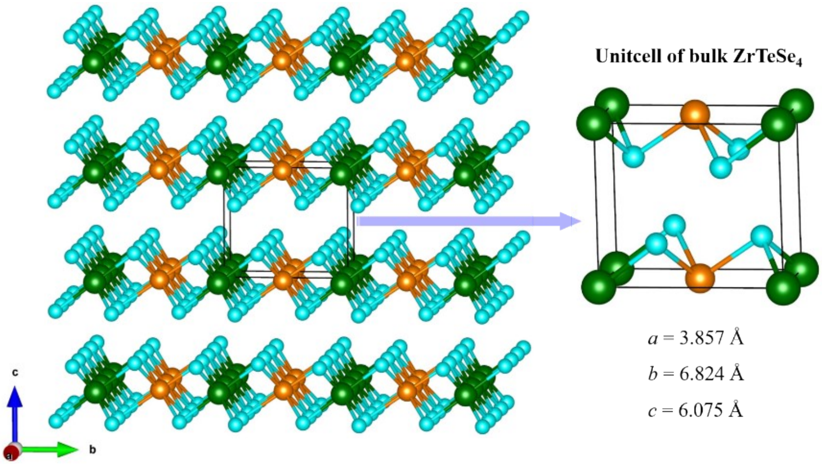

Figure S1. Crystal structure of bulk $ZrTeSe_4$. The black solid line indicates unitcell of bulk $ZrTeSe_4$ in *AAA* stacking fashion.

2. Cleavage energy calculation of $ZrTeSe_4$

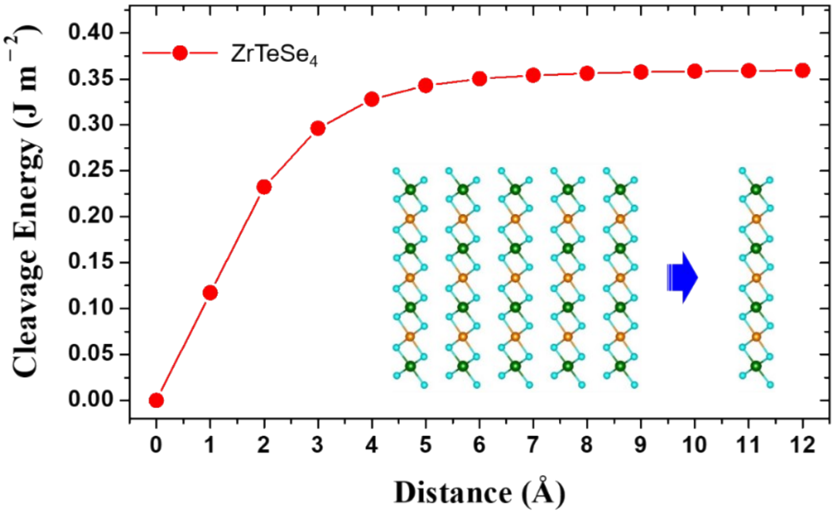

Figure S2. Cleavage energy as a function of the separation distance between quintuple-layer (5L) and single-layer (1L). The inset shows a schematic illustration of the considered exfoliation

To evaluate the possibility of obtaining 1L-$ZrTeSe_4$ from its bulk crystal by the mechanical exfoliation technique, we calculate the cleavage energy (E_{cl}). The E_{cl} is given by $E_{cl} = E_{1L} + E_{5L} - E_{6L}$, where E_{1L}, E_{5L}, and E_{6L} are the total energy (TE) of 1L-$ZrTeSe_4$, the TE of the quintuple-layer (5L) $ZrTeSe_4$ after exfoliation, and the TE of the sextuple-layer (6L) $ZrTeSe_4$ before exfoliation, respectively. Here, 6L-$ZrTeSe_4$ may be regarded as the bulk crystal.

3. Atomic structure and electronic structure of 1L-ZrTeSe$_4$ (2H phase)

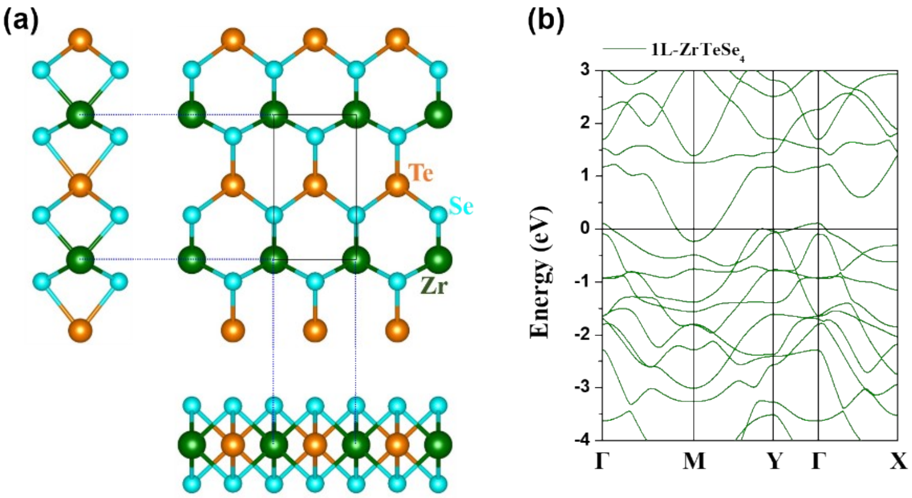

Figure S3. (a) Top- and side-views of the atomic structure of 1L-ZrTeSe$_4$ (2H phase). The black solid line shows a rectangular primitive cell. (b) Electronic band structure with PBE functional.

If the Zr atom and the Te atom in 1L-ZrTeSe$_4$ are the same, the structure of 1L-ZrTeSe$_4$ (initial phase) is nearly identical to the central honeycomb (T) phase. Therefore, it is possible to produce the honeycomb (H) phase of 1L-ZrTeSe$_4$.

4. FPMD simulations for 1L-ZrTeSe$_4$ at 500 K, 700 K, 900 K, and 1200 K

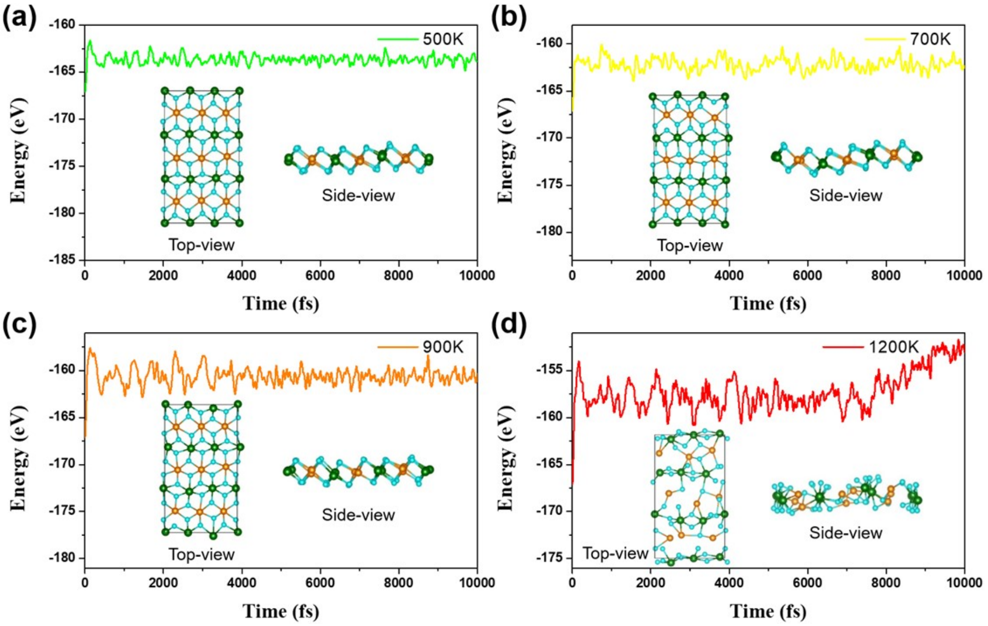

Figure S4. Energy fluctuations as a function of time in FPMD simulation at (a) 500 K, (b) 700 K, (c) 900 K, and

(d) 1200 K. The insets in each panels show the snaptshots at the end of the FPMD simulation.

5. Radial distribution function for 1L-$ZrTeSe_4$

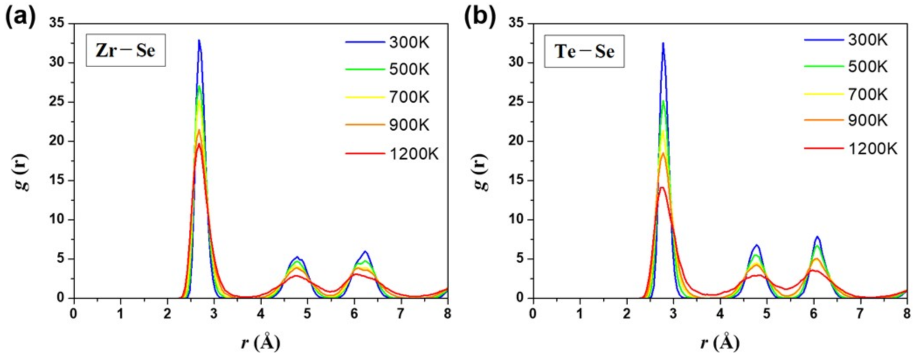

Figure S5. (a) Zr−Se and (b) Te−Se radial distribution function $g(r)$ as function of radius r for 1L-$ZrTeSe_4$ from FPMD simulation.

6. Calculations of Debye temperature and Grüneisen parameter of 1L-$ZrTeSe_4$

For further discussion of the low lattice thermal conductivity of 1L-$ZrTeSe_4$, we have done the additional calculation of the elastic properties which are widely used to evaluate inter-atomic bonding strength and lattice vibration anharmonicity in a crystal lattice. In general, the lower Young's modulus (Y_S) and Debye temperature (Θ_D) indicate a low lattice thermal conductivity. Note that the equations for the Θ_D and Grüneisen parameter (γ) based on the elastic constants of a 2D material can be found elsewhere.[S1]

Consequently, we obtained $Ys = 44$ N m^{-1} and $\Theta_D = 407$ K for 1L-$ZrTeSe_4$. They are comparable to good thermoelectric materials. In addition, the γ is also used to characterize the intensity of phonon anharmonic scattering. A larger γ of a material indicates more anharmonic. It results in low thermal conductivity. As a result, based on the obtained elastic constants of 1L-$ZrTeSe_4$, the γ is calculated to be 2.307. Hence, the value is comparable to thermoelectric materials, such as lead chalcogenides (1.67-1.69)[S2] and 2D group-IV materials (silicene and germanene) (1.84-1.86).[S3]

7. Issue of the polar optical phonon effect on thermoelectric properties

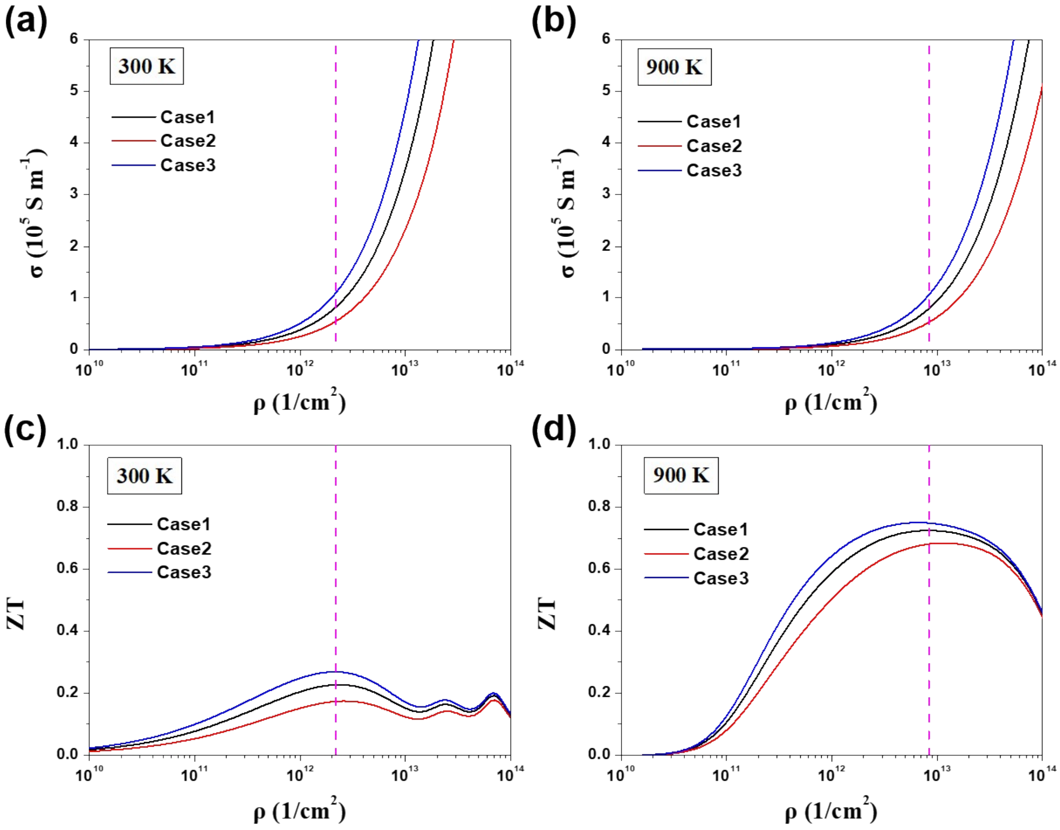

Figure S6. The calculated electric conductivities σ of Case1, Case2, and Case3 at (a) 300K (b) 900K. The calculated thermoelectric figure of merit ZT of Case1, Case2, and Case3 at (c) 300K and (d) 900 K. In each panel, the vertical dashed line indicates optimal carrier concentration.

Recently, Wang et al.[S4] calculated the polar optical phonon relaxation time (τ_{OP}) of $SiTe_2$ and $SnTe_2$ monolayers using the equation proposed by Ridley.[S5] However, since our system ($ZrTeSe_4$) is a novel two-dimensional (2D) material, the parameters (the high frequency and static dielectric constants) are not reported experimentally and theoretically. Thus, it is challenging to know the polar optical phonon relaxation time of 1L-$ZrTeSe_4$. On the other hand, for both $SiTe_2$ and $SnTe_2$ monolayers, the difference between all the calculated relaxation times (τ_{AP}, τ_{OP}, and τ_{Total}) is less than 10 times, namely, they are of the same order of magnitude (several 10^{-14} s).[S4]

Taking this into account, let's apply it to our considered system. After Boltzmann transport calculation, we can obtain the relaxation time (τ) dependent electric conductivity (σ/τ). Then, we multiply this quantity with the available τ value (including τ_{OP} and acoustic phonon relaxation time τ_{AP}). Therefore, to investigate the effect of temperature-dependent optical phonon relaxation time on thermoelectric properties of 1L-$ZrTeSe_4$, here we assume three possible cases, that is, $\tau_{OP} = \tau_{AP}$ (Case1),

$\tau_{OP} = 0.5\tau_{AP}$ (Case2), and $\tau_{OP} = 2\tau_{AP}$ (Case3) at different temperatures (300K and 900K). According to the Matthiessen rule, the total relaxation times (τ_{Total}, which is already included the contribution of both τ_{OP} and τ_{AP}) are calculated to be 5.28×10^{-14} s (1.76×10^{-14} s), 3.52×10^{-14} s (1.17×10^{-14} s), and 7.04×10^{-14} s (2.35×10^{-14} s) for Case1, Case2, and Case3 at 300 K (900K), respectively.

As shown in Fig. S6, for the calculated σ at both temperatures (300 and 900 K), Case2 decreased by 33.33%, while Case3 increased by 33.33%, compared to Case1. This is because the calculated electrical conductivity (σ/τ) using the BoltzTraP is simply multiplied by the τ_{Total}. Subsequently, considering the optimal concentration at 300 K (900 K), the thermoelectric figure of merit (ZT) of Case2 decreased by 22.96% (6.01%), while the ZT of Case3 increased by 17.51% (3.30%), compared to the ZT of Case1. Therefore, we may conclude that the effect of polar optical phonon could not significantly affect the thermoelectric ZT at high temperatures.

References

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