Roles of Thermal Disorder on High-*ZT* of PbTe

Theoretical treatments/computations are essential tools for understanding mechanisms of thermoelectric (TE) transport phenomena. Our theoretical treatment demonstrates that for PbTe, significant thermal disorder causes the maximum in *ZT*. Thermal atomic disorder leads to band convergence, i.e., some band peaks/valleys disappear. Disorder also creates a pseudo-amorphous structure which reduces the short and long-range acoustic phonon transport. Understanding of the thermal disorder provides an insight into design of improved TE chalcogenides.

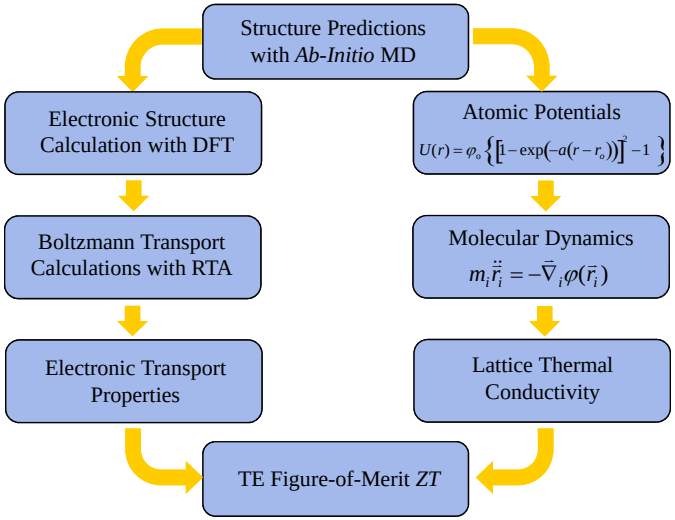

Figure 1. The diagram of calculation methodology. Our computational approach is three-fold, structure prediction, electronic properties calculations, and phonon properties calculations.

Temperature-Dependent Electronic Structures

Thermal-disordered configurations show anharmonic lattice vibrations and local electron orbital overlapping, affecting charge and phonon transports. Thermal disorder modifies the charge effective mass and suppress the phonon short- and long-range acoustic modes, resulting in high-*ZT* of PbTe.

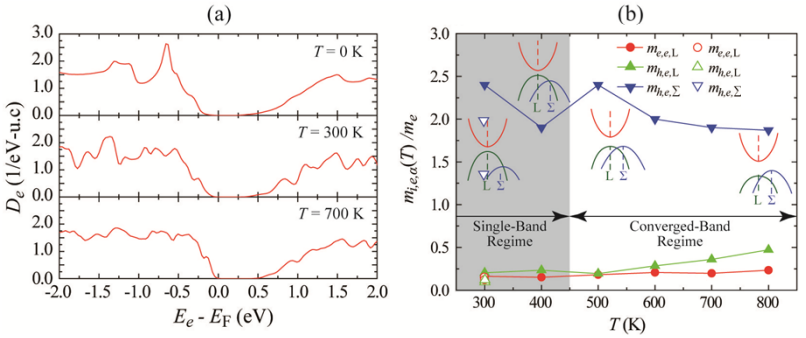

Figure 3. (a) Electronic DOS. (b) Temperature dependent DOS effective masses from AIMD [11]. .

Lattice Dynamics of Thermal-Disordered Structures

The high *ZT* of PbTe have not been explained through temperature-dependent electronic structure, lattice dynamics, and TE properties. Our simulations reproduce all reported lattice dynamics results of PbTe. From the orbital model perspective, the thermal disorder causes local orbital overlapping. It means the thermal disorder may be an evidence to explain its unique features.

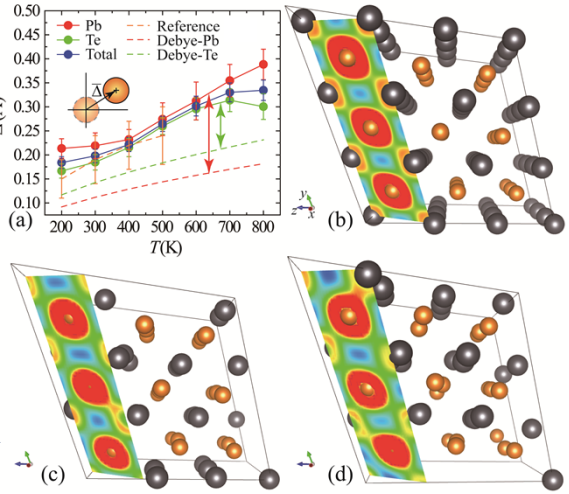

Figure 2. (a) Variation of the RMS atomic displacement. Debye model [7] is also shown. (b) – (d) Charge densities and atom positions for T = 0, 300, and 700 K. The charge density contours are for 0 (blue) to 0.289 (red) eÅ^{-3}.

TE Properties with Thermal-Disordered Structures

Combining all TE transport properties from DFT and MD/Green-Kubo calculations, the *ZT* of PbTe as a function of temperature is predicted. The results for thermal-disordered structures are in good agreement with the experiment. We verify our thermal-disorder model reveal the high-*ZT* PbTe behavior. Mechanism and physical understandings suggest a new route to control the effect of band convergence and pseudo-amorphous structure for achieving high *ZT*.

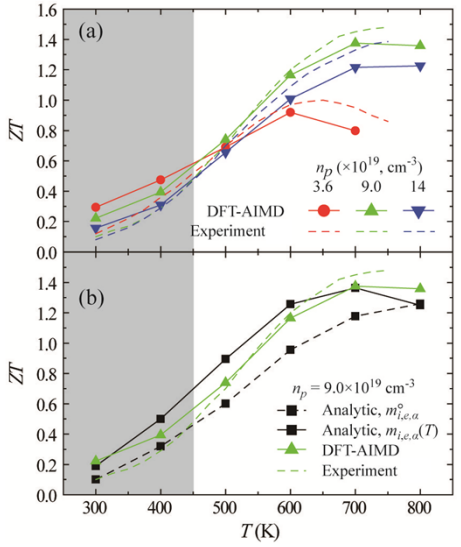

Figure 4 . (a) Variation of the DFT-AIMD predicted ZT as a function of temperature for the *p*-type PbTe. (b) Variation of *ZT* obtained from analytical model using constant $m_{i,e}$ and temperature dependent $m_{i,e}(T)$.