# High thermopower and ultra low thermal conductivity in Cd-based Zintl phase compounds

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#### **1 PBE band structures:**



Figure S1: PBE band structures for (a) CdSb, (b) CaCd<sub>2</sub>Sb<sub>2</sub>, (c) SrCd<sub>2</sub>Sb<sub>2</sub>, and (d) BaCd<sub>2</sub>Sb<sub>2</sub>.

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## 2 Orbital decomposed density of states:

Figure S2: Orbital decomposed density of states for CdSb, CaCd<sub>2</sub>Sb<sub>2</sub>, SrCd<sub>2</sub>Sb<sub>2</sub>, and BaCd<sub>2</sub>Sb<sub>2</sub>.

#### Anisotropy in thermopower:



Figure S3: Anisotropy in thermopower as a function of carrier concentration for (a) CdSb, (b)  $CaCd_2Sb_2$ , (c)  $SrCd_2Sb_2$ , and (d)  $BaCd_2Sb_2$  at 300 K. The solid and doted lines denote results for *p*- and *n*-type charge carriers.



### **4** Temperature dependence of thermopower at fixed doping levels:

Figure S4: Thermopower as a function of temperature at optimised fixed doping levels for (a) CdSb, (b)  $CaCd_2Sb_2$ , (c)  $SrCd_2Sb_2$ , and (d)  $BaCd_2Sb_2$  under *p* and *n*-type doping.

### 5 Effect of ionic radii on thermoelectric properties



Figure S5: Transport coefficient (a)  $\sigma/\tau$ , (b) S, and, (c)  $S^2\sigma/\tau$  as a function of temperature for CaCd<sub>2</sub>Sb<sub>2</sub>, SrCd<sub>2</sub>Sb<sub>2</sub>, and BaCd<sub>2</sub>Sb<sub>2</sub> at a fixed doping level of  $1 \times 10^{19}$  cm<sup>-3</sup>. The direction of arrows in Fig. (a) and (b) represent the increasing ionic radii.

### 6 Temperature dependence of power factor at fixed doping levels:



Figure S6: Calculated power factor as a function of temperature at optimised fixed doping levels for (a) CdSb, (b)  $CaCd_2Sb_2$ , (c)  $SrCd_2Sb_2$ , and (d)  $BaCd_2Sb_2$  under *p* and *n*-type doping.

#### 7 Electronic structure and transport for PbTe and PbSe:

The electronic structure calculations were performed within density functional theory (DFT) using the linearised augmented plane-wave (LAPW) method with local orbitals (1, 2) as implemented in the WIEN2k code (3). The LAPW sphere radii were set 2.5 for all the elements. In addition  $Rk_{max} = 9.0$ , is used to ensure the well convergence of basis set where, R and  $k_{max}$  are the smallest LAPW sphere radius and interstitial plane-wave cutoff, respectively. The Brillouin zone was sampled by taking 5000 **k**-points for all crystal structures. In order to obtain an accurate band gap we employ modified Becke Johnson functional (4, 5) of Tran and Blaha (TB-mBJ). The transport calculations were done using Boltzmann transport theory (6) within the constant scattering time approximation. We used BoltzTraP code (7) for transport calculations by taking 40000 **k**-points in the irreducible Brillouin zone.



Figure S7: The band structure of PbTe (a) and PbSe (b) calculated with the TB-mBJ potentials. For both band structures the energy zero is set to the valence band maximum. The calculated bandgap are in excellent agreement with the experimental values. These results were further used in transport calculation in order to compare with Zintl phase. (See Figure 6 of the manuscript)

#### 8 Dependence of lattice thermal conductivity on anharmonic scattering rates and total scattering phase space



Figure S8: (a) Anharmonic scattering rates of CdSb and ACd<sub>2</sub>Sb<sub>2</sub> (A=Ca,Sr, and Ba) at 300 K vs angular frequency  $\omega$ . (b) Three phonon scattering phase space for ACd<sub>2</sub>Sb<sub>2</sub> (A=Ca,Sr, and Ba). Note that BaCd<sub>2</sub>Sb<sub>2</sub> exhibits highest scattering rate followed by CdSb, CaCd<sub>2</sub>Sb<sub>2</sub>, and SrCd<sub>2</sub>Sb<sub>2</sub>. This is similar to the trend observed in Grüneisen parameters ( $\gamma$ ).

# 9 Calculation of lattice thermal conductivity by Debye-Callaway model:

The Debye-Callaway model (8, 9, 10) approximates the lattice thermal conductivity as a function of Debye temperatures ( $\Theta_D$ ), phonon group velocities (v) and Grüneisen parameters ( $\gamma$ ). Next we use these above mentioned quantities to parametrize the Debye-Callaway model and calculate the lattice thermal conductivity. The resulting thermal conductivities are shown in Figure S9. When compared with the  $\kappa_l$  obtained from iterative solution of Boltzmann transport equation (BTE) these values are quite over estimated. This is because Debye Callaway model severs as a upper limit to lattice thermal conductivity. This phenomenon is agreement other theoretical studied (11). The theoretically calculated thermal conductivity for CdSb and CaCd<sub>2</sub>Sb<sub>2</sub> captures the experimental trend an follows the order BaCd<sub>2</sub>Sb<sub>2</sub> < CdSb < CaCd<sub>2</sub>Sb<sub>2</sub> < SrCd<sub>2</sub>Sb<sub>2</sub> which, is same as the trend obtained from BTE. The disagreement between experimental and theoretical values can be attributed to the approximations inherent in the Debye-Callaway formalism.



Figure S9: Lattice thermal conductivity of CdSb and  $ACd_2Sb_2$  (where A = Ca, Sr, Ba) as obtained by Debye Callaway model. The diamond, triangle and cross denote experimental values of CdSb,  $CaCd_2Sb_2$  and PbTe, respectively. The points represent the calculated values.

#### References

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