Supporting Information

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Thermally Controlled Charge-Carrier Transitions in Disordered PbSbTe Chalcogenides

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Figure S1: DOS for Pb$_2$Sb$_2$Te$_5$. The shift of the valence band (left side) towards the Fermi energy as well as the reduction of the conduction-band tail are observed. The samples annealed at 240 °C show signs of trap states, with distinct peaks in the conduction and valence band.
Table S1: Measured XRD peak positions compared to the positions for an ideal cubic system. Small deviations indicate a slight deviation from the perfect rock-salt-like structure.

| hkl   | PbSb₂Te₄ Data (°) | PbSb₂Te₄ Theory (°) | Pb₂Sb₂Te₅ Data (°) | Pb₂Sb₂Te₅ Theory (°) |
|-------|------------------|---------------------|--------------------|----------------------|
| (0 0 2) | 28.48            | 28.38               | 28.17              | 28.12                |
| (0 2 2) | 40.43            | 40.54               | 39.97              | 40.20                |
| (2 2 2) | 50.05            | 50.22               | 49.43              | 49.76                |
| (0 0 4) | 59.03            | 58.62               | 58.26              | 58.12                |
| (0 2 4) | 66.58            | 66.42               | 65.80              | 65.80                |
| (2 2 4) | 73.92            | 73.66               | 72.93              | 73.00                |
Figure S2: XRD spectra after annealing. a) Additional peaks not associated with the rock-salt-like phase can be identified for highest annealing temperatures in Pb$_2$Sb$_2$Te$_5$. b) At 300 °C, for both PbSb$_2$Te$_4$ and Pb$_2$Sb$_2$Te$_5$, the lattice separates into the constituents with peaks associated with the cubic phase of PbTe in red and peaks associated with the hexagonal phase of Sb$_2$Te$_3$ in blue.
Figure S3: a) Regions of stability for disordered Pb$_2$Sb$_2$Te$_5$ (with configurational entropy) with respect to the stoichiometrically closest phases. The coordinates in the box are the chemical potentials of Pb, Sb, and Te (expressed as $\Delta \mu_i$) at the four limiting points. The regions of stability just touch each other, in accordance with the corresponding phase-formation energies lying on a straight line in Figure 3a. b) Regions of stability for ordered Pb$_2$Sb$_2$Te$_5$ with respect to the stoichiometrically closest phases. The areas just do not overlap.
As for PbSb$_2$Te$_4$, in the disordered, cubic phase, Sb$_{Pb}$, Pb$_{V}$, and Sb$_{V}$ are the most favorable defects, leading to n-doping. On the contrary, Pb$_{Sb}$ has the lowest formation energy in the ordered structure, yielding p-doping. In the ordered structure, defects on Te sites occur three times each due to inequivalent lattice sites (Te$_1$: next to vacancy layer; Te$_2$: between Sb and Pb layers; Te$_3$: between two Pb layers).
Remark on band-gap corrections in GST and PST

In disordered, cubic GeSb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$, our recent DFT study\cite{1} reveals the point defects Sb$_{\text{V}}$, Ge$_{\text{V}}$, and Sb$_{\text{Ge}}$ associated with n-doping to have the smallest formation energies. It was noted that misplaced band edges, which are common in DFT calculations, could erroneously lower the true formation energies, especially for defects associated with n-doping. Comparing the DFT gap to the experimental gap in GST, we found that a band-edge correction via shifting the conduction-band minimum lifts these defects by about 0.25 eV for each electron that is introduced into the bulk system. The formation energies of the n-type defects would then become comparable to those of certain p-type defects in the low-energy regime; thus, neither n- or p-doping is clearly suggested by the simulations alone. Combined with the experimentally observed p-type conduction, the Ge$_{\text{Sb}}$ defect was identified to probably play the most important role for explaining p-doping in this material.\cite{1}

In the present study of PbSb$_2$Te$_4$ and Pb$_2$Sb$_2$Te$_5$, an analogous argument proves more difficult because of the lack of studies reporting the corresponding experimental band gaps. Given the available values of 0.42 eV for nano-crystallites of disordered, cubic Pb$_2$Sb$_2$Te$_5$\cite{2} and 0.48 eV for stable, hexagonal PbSb$_2$Te$_4$\cite{3} a rough estimate on the order of 0.5 eV seems appropriate. Comparing this with the HOMO-LUMO gap estimated as 0.25 eV for a disordered model of PbSb$_2$Te$_4$ leads to a band-gap correction of n-type defects of around 0.25 eV, i.e., similar to GST. However, in PST, the difference in energy between the lowest n-type defect and the lowest p-type defect is about 0.1–0.15 eV larger compared with GST, supporting the predominance of n-type defects even after band-edge corrections. We furthermore note that the upward shift of 0.25 eV is an upper limit for the correction of n-type defects; if a downward shift of the valence-band edge were considered to recover the true band gap, p-type defects would instead be lifted. Finally, the experiments presented here strongly support the finding that additional Pb and Sb atoms are the main defects in the disordered phase. This situation is drastically different from GST compounds, where an excess of cations is not experimentally observed.

References

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