Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information For:

PbTe – $PbSnS_2$ thermoelectric composites: low lattice thermal conductivity from large microstructures

Steven N. Girard,[1] Thomas C. Hasapis,[2] Jiaqing He,[1,3] Xiaoyuan Zhou,[4] Euripides Hatzikraniotis,[2] Ctirad Uher,[4] Konstantinos M. Paraskevopoulos,[2] Vinayak P. Dravid,[3] and Mercouri G. Kanatzidis[1]*

[1]Department of Chemistry, Northwestern University, Evanston IL 60208, USA

[2] Physics Department, Aristotle University of Thessaloniki, GR- 54124, Thessaloniki, Greece

[3]Department of Materials Science and Engineering, Northwestern University, Evanston IL 60208, USA

[4]Department of Physics, University of Michigan, Ann Arbor MI 48109, USA

[*]To whom correspondence should be addressed

AUTHOR EMAIL m-kanatzidis@northwestern.edu

Kramers – Kronig transformation

In the Kramers-Kronig method the measured reflectivity *R(ω)* is transformed to calculate the phase angle *θ(ω)* between the reflected and incident wave:

$$\theta(\omega) = -\frac{2\omega}{\pi} P\int_0^{\infty} \frac{\ln r(\omega_i) - \ln r(\omega)}{\omega_i^2 - \omega^2} d\omega_i , \qquad \text{(S. 1)}$$

where ω is frequency in wavenumbers (cm^{-1}), $r(\omega) = (R(\omega))^{1/2}$ and *P* stands for the principal value of the Cauchy integral. The spectrum of *θ(ω)* is then utilized to obtain the real (*n(ω)*) and imaginary (*k(ω)*) parts of the complex refractive index ($\tilde{n}(\omega) = n(\omega) + ik(\omega)$) on the basis of the Fresnel formulas for normal incidence:

$$n(\omega) = \frac{1 - R(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)}\cos\theta(\omega)} \qquad \text{(S. 2)}$$

$$k(\omega) = \frac{2\sqrt{R(\omega)}\sin\theta(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)}\cos\theta(\omega)} \qquad \text{(S. 3)}$$

Computation of the real $\varepsilon_1(\omega)$ and imaginary parts $\varepsilon_2(\omega)$ of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is then straightforward:

$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega) \qquad \text{(S. 4)}$$

$$\varepsilon_2(\omega) = 2n(\omega)k(\omega) \qquad \text{(S. 5)}$$

The energy loss function Im(-1/ε), peaks of which are associated with the absorption of the longitudinal vibrations, is computed via:

$$\mathrm{Im}(-1/\varepsilon) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} = \frac{2n(\omega)k(\omega)}{(n^2(\omega) + k^2(\omega))^2} \qquad \text{(S. 6)}$$

Diffusivity Measurements

The measured diffusivities from the samples included in the study are shown in Figure S1.

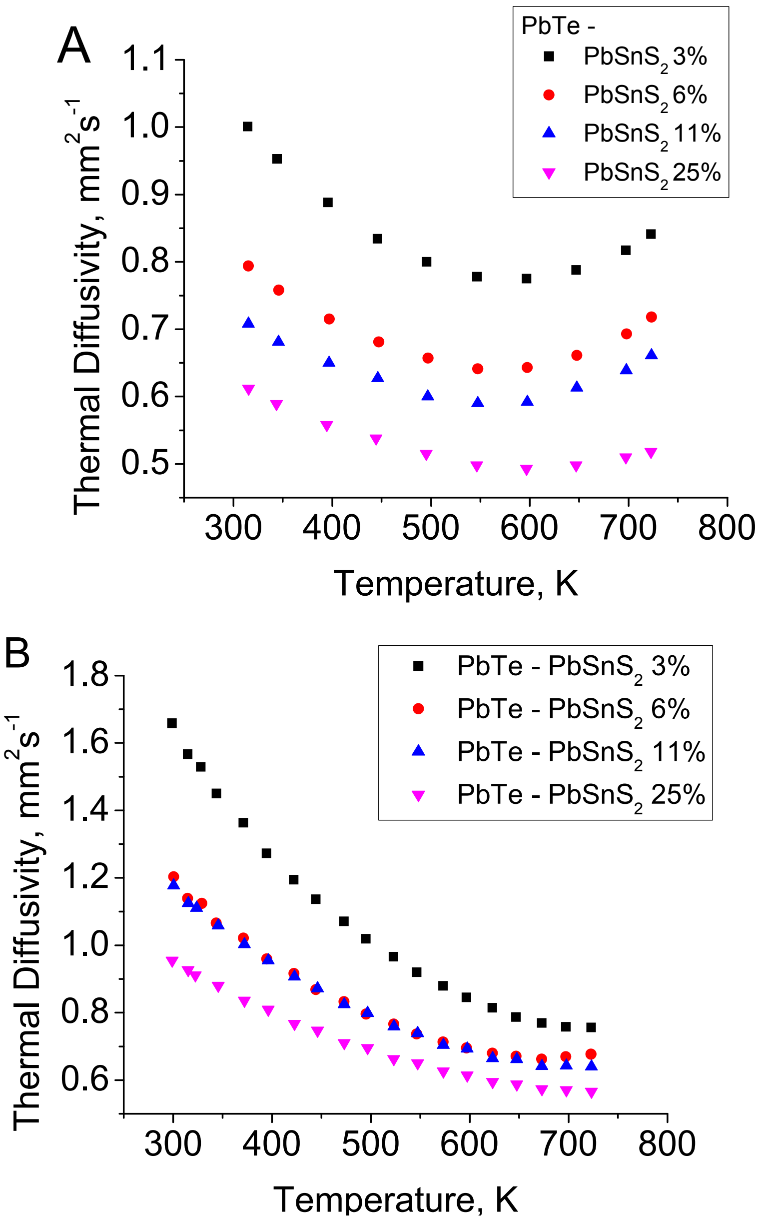

Figure S1. Measured thermal diffusivities for all samples included in the study: a) undoped PbTe – $PbSnS_2$ compositions, b) 0.055% PbI_2 – doped compositions.

Specific Heat

To estimate the specific heat of the samples, we utilized literature values of PbTe[1], and measured the specific heat using differential scanning calorimetry to 600 K for pure $PbSnS_2$ synthesized in our laboratory. Assuming that the thermal transport is determined predominately by the movement of phonons through the matrix, we assumed the law of mixtures from the nominal values of PbTe – $PbSnS_2$, Figure S2.

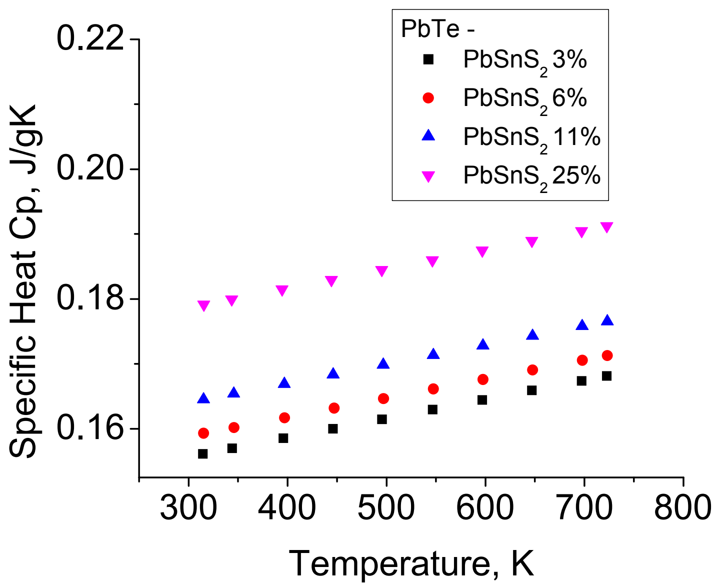

Figure S2. Values of specific heat used in the study.

We must note that in this calculation we assume a rule of mixtures from the atomic fraction of PbTe and $PbSnS_2$ only. We find a negligible difference in specific heat when volume fractions are used instead of atomic fraction.

Density

For coin-shaped samples analyzed for thermal diffusivity, sample densities were calculated using sample volume as measured using a digital caliper and mass measured on a 4 digit balance. Table S1 shows sample densities for the samples in this report.

Composition	**Measured Density g/cc**
PbTe – $PbSnS_2$ 3%	8.017
PbTe – $PbSnS_2$ 6%	8.068
PbTe – $PbSnS_2$ 11%	7.932
PbTe – $PbSnS_2$ 25%	7.424
PbTe – $PbSnS_2$ 3% + 0.055% PbI_2	8.062
PbTe – $PbSnS_2$ 6% + 0.055% PbI_2	7.746
PbTe – $PbSnS_2$ 11% + 0.055% PbI_2	7.871
PbTe – $PbSnS_2$ 25% + 0.055% PbI_2	7.513

Table S1. Density of samples included in the study.

Hall Effect

High temperature Hall effect measurements were carried out by an in-house high temperature/high magnetic field Hall apparatus. It consists of a nine Tesla air-bore superconducting magnet with a water-cooled oven inside the bore of the magnet, and a Linear Research AC bridge with 16 Hz excitation. Four-wire AC Hall measurements are performed on parallelepiped samples with the typical size of 1.5 x 3 x 10 mm to temperatures of 850 K under Argon atmosphere. Figure S3 shows the obtained data for the samples examined in the report.

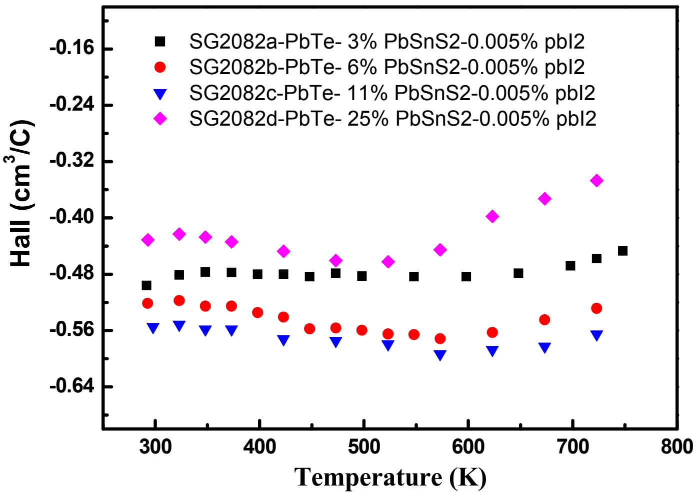

Figure S3. Measured Hall coefficient of samples included in the study. The Hall coefficient values were used to calculate sample electron concentrations and mobilities as described in the text.

References

(1) Blachnik, R.; Igel, R. *Z. Naturforsch. B* **1974**, *29*, 625.