Supporting Information For:

High performance Na-doped PbTe – PbS thermoelectric materials: electronic density of states modification and shape-controlled nanostructures

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Sample Preparation for Thermoelectric Measurements

All cast ingots were cut using a low-speed diamond saw and subsequently polished using 400-grit SiC sandpaper mounted on a Buehler grinder/polisher. Average parallelepiped dimensions are 2 x 2 x 10 mm, coin dimensions 2 mm thick and 8 mm diameter. For high-temperature measurements, we coated the samples with a protective layer of boronitride (BN) powder applied from a commercially available aerosol spray to limit sample reactivity within the instrument. To facilitate in transport measurements, we applied tape to the sample surfaces to allow uncovered surfaces for lead attachment, Figure S1.

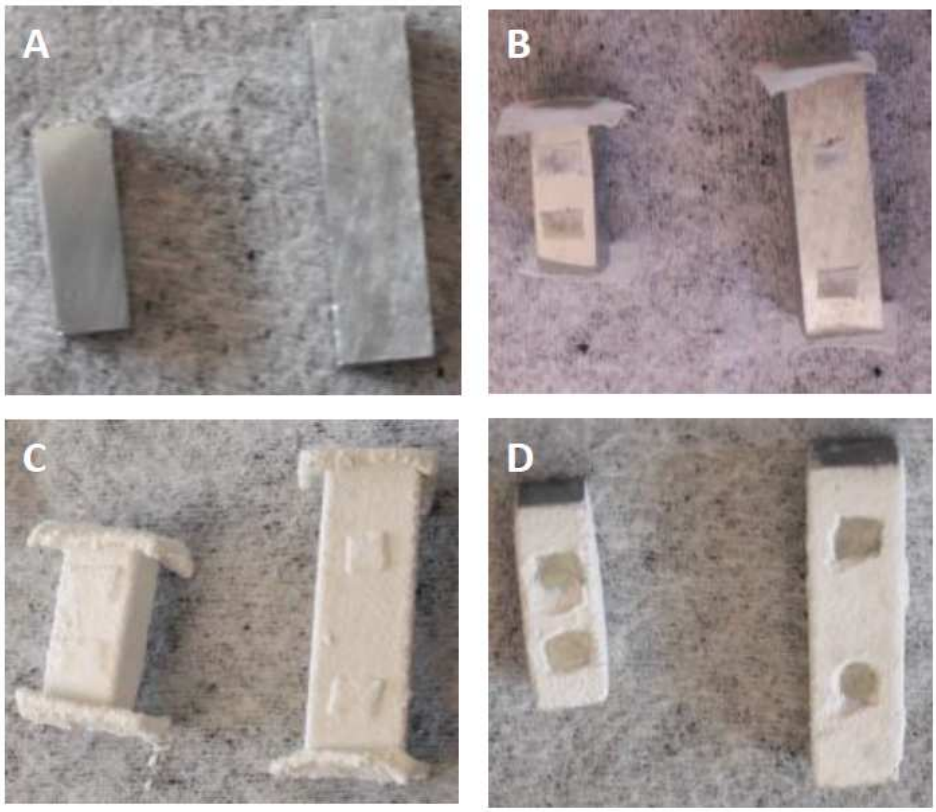

Figure S1. Photographs of application of boronitride coating, A) as-prepared samples, B) samples with tape applied to surfaces for electrical leads, C) samples coated with BN, D) tape removed and samples prepared for measurement.

The coin discs were also coated with BN and analyzed by laser-flash diffusivity. Because the BN layer reduces the thermal diffusivity, the samples were first measured without BN and then coated with BN and remeasured, Figure S2.

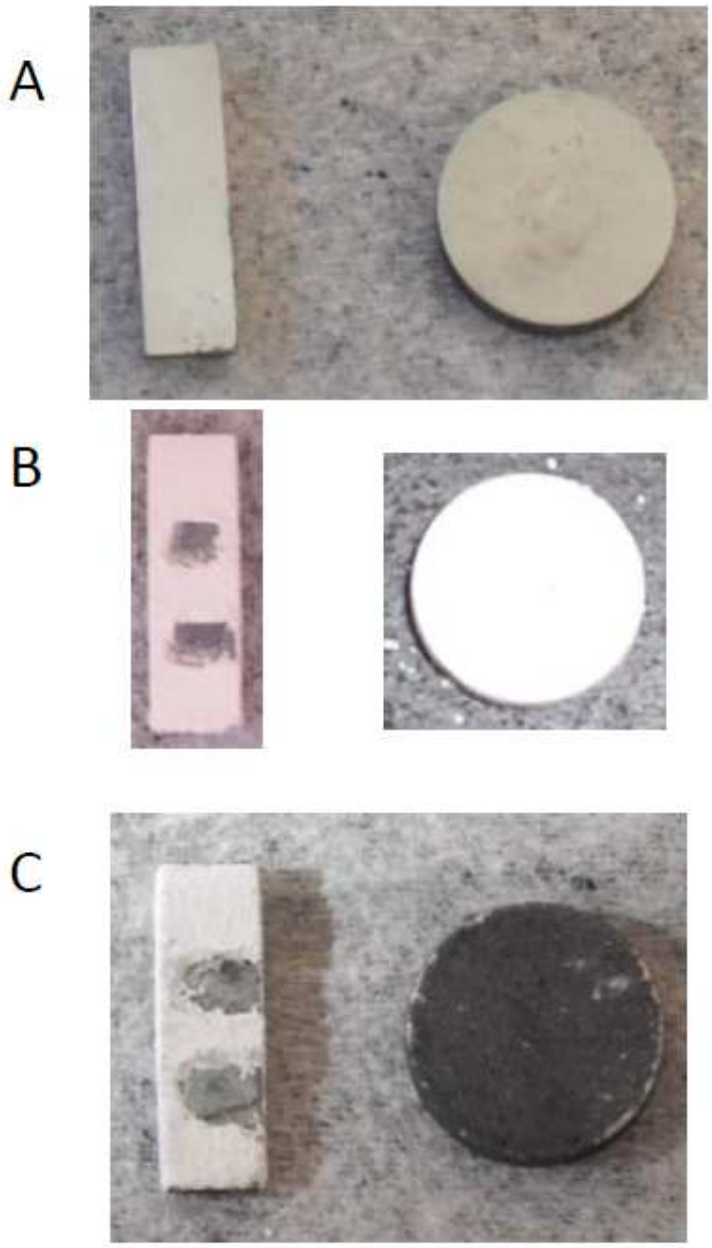

Figure S2. Photographs of BN-coated samples for measurement, A) as-prepared samples, B) samples prior to measurement, C) samples following measurement. The coin in C) has been coated with graphite to facilitate in black-body absorption/emission in the laser-flash technique.

Diffusivity Measurements

The measured diffusivities from the samples included in the study are shown in Figure S3.

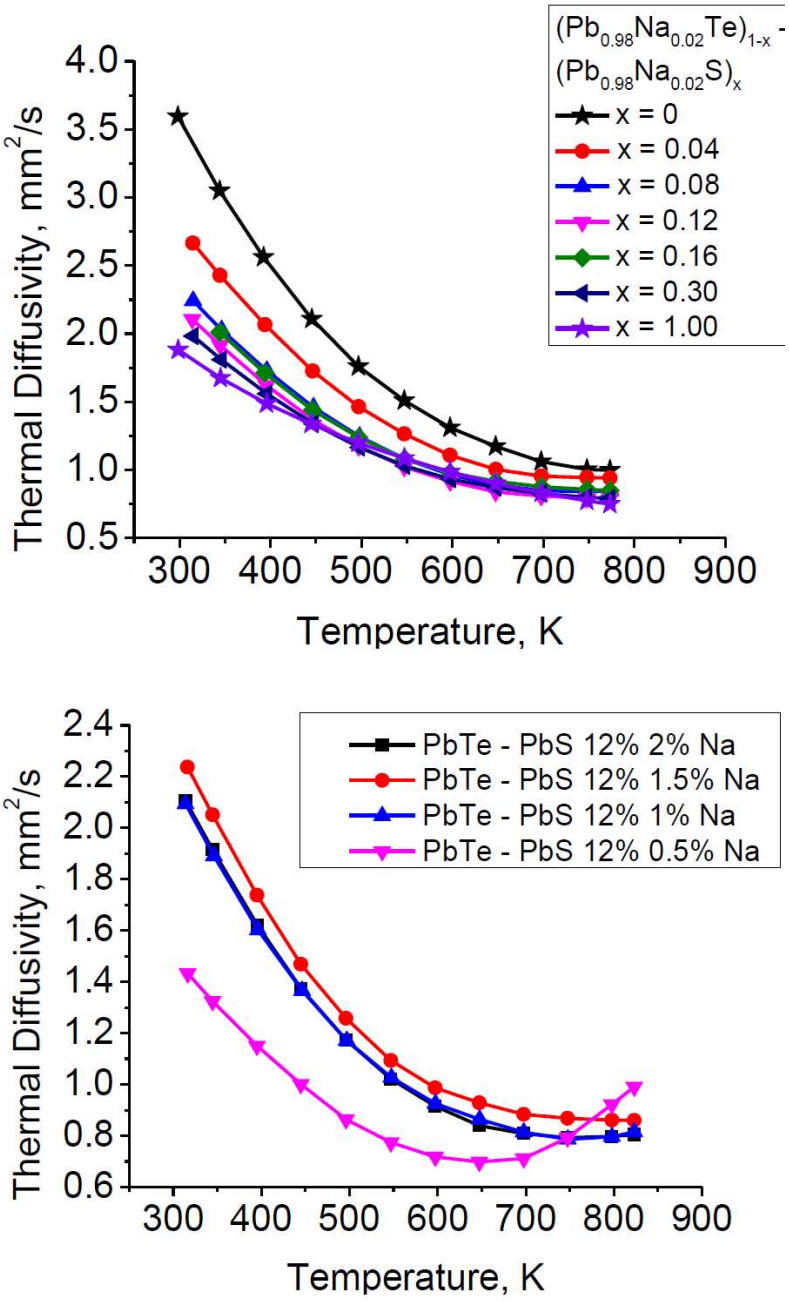

Figure S3. Measured thermal diffusivities for all samples included in the study.

For the high-temperature measurements, the diffusivity of the BN coated sample exhibited lower diffusivity. However, the temperature dependence (i.e. trend) of the diffusivities between measurements varied minimally. We translated the data for the BN coated sample as closely to the data for the non-BN coated sample, Figure S4.

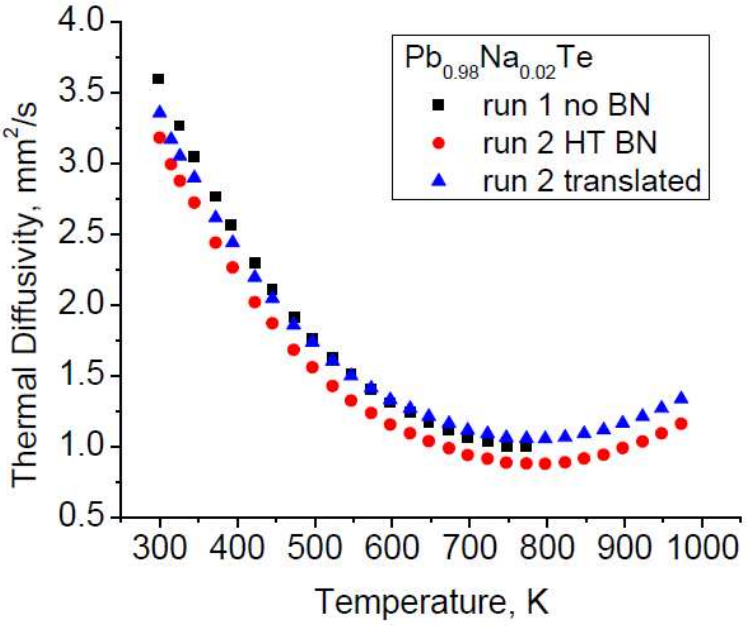

Figure S4. Plot of measured diffusivity for a high-temperature measurement of $Pb_{0.98}Na_{0.02}Te$. The sample was first measured without BN, then coated with BN and remeasured. The BN coated sample data was then translated to better represent the non-coated data.

Specific Heat

To estimate the specific heat of the samples, we utilized literature values of PbTe and PbS [1], 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 $PbTe_{1-x}S_x$ matrix, Figure S5. We did not include the incorporation of Na within the calculation.

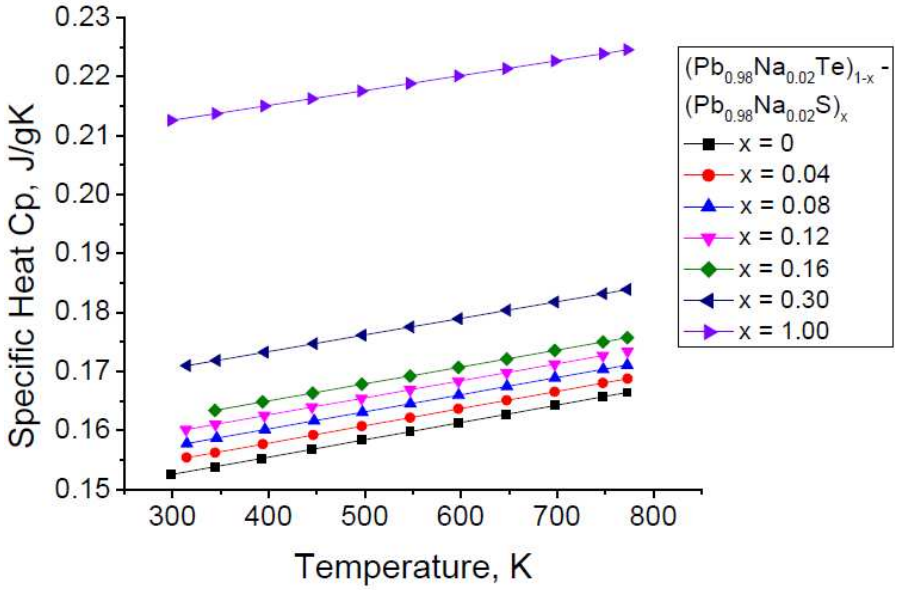

Figure S5. Values of specific heat used in the study.

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

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 S6 shows the obtained data for the samples examined in the report.

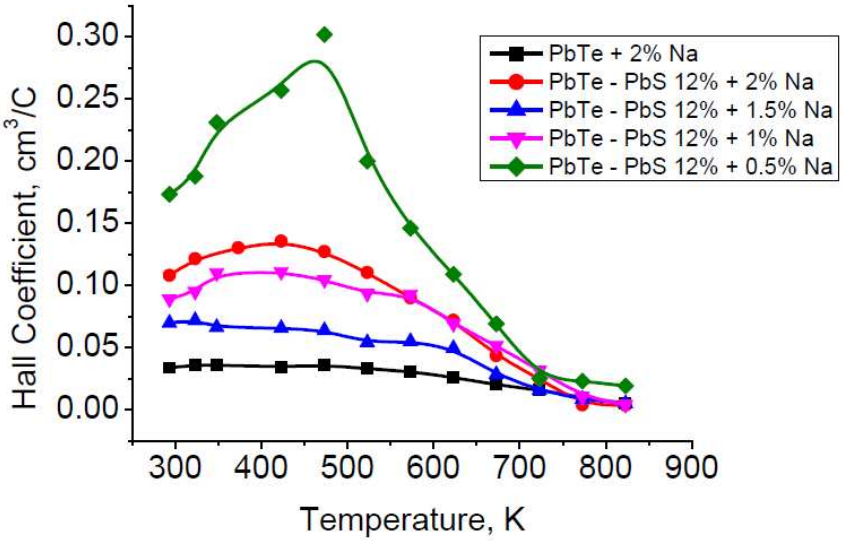

Figure S6. Measured Hall coefficient of samples included in the study. The Hall coefficient values were used to calculate sample hole concentrations and hole mobilities as described in the text.

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. Using established densities of PbTe of 8.242 g/cc and PbS of 7.597 g/cc [2,3], the theoretical density ρ(x) of the $PbTe_{1-x}S_x$ samples were calculated using the law of mixtures:

$$\rho(x) = (1-x)\rho_{PbTe} + (x)\rho_{PbS}$$

Because the Na alloys completely within the PbTe and PbS phases, we do not include Na doping in the final calculations of density. Table S1 shows sample densities for the samples in this report.

Composition	Measured Density g/cc	% Theoretical Density
PbTe + 2% Na	8.038	0.98
PbTe – PbS 4% + 2% Na	8.047	0.98
PbTe – PbS 8% + 2% Na	8.119	0.99
PbTe – PbS 12% + 2% Na	7.994	0.98
PbTe – PbS 12% + 1.5% Na	7.870	0.96
PbTe – PbS 12% + 1% Na	7.903	0.97
PbTe – PbS 12% + 0.5% Na	7.74	0.95
PbTe – PbS 16% + 2% Na	7.737	0.95
PbTe – PbS 30% + 2% Na	7.802	0.97
PbS + 2% Na	7.468	0.98

Table S1. Density of samples included in the study.

La Bail Refinement

Finely ground samples were placed in a CPS-120 Inel X-ray powder diffractometer using Ni-filtered Cu K_α radiation (λ = 1.54056 Å) in reflection geometry, equipped with a position sensitive detector and operating at 40 kV and 20 mA. Le Bail refinements were performed using the GSAS program. Table S2 shows the lattice parameters extracted from La Bail refinement from the powder X-ray diffraction data from Figure 6a, shown graphically in a plot in Figure 6b.

$Pb_{0.98}Na_{0.02}S_{1-x}Te_x$, x=	Lattice Parameter, Å	Error, ±Å
0	6.4732	.0001
0.04	6.4539	.0001
0.08	6.43967	.00007
0.12	6.4359	.0003
0.16	6.4493	.0002
0.3	6.4495	.0001
1	5.9392	.0001

Table S2. Lattice parameters and error for samples using Le Bail refinement.

References

(1) Blachnik, R.; Igel, R. *Z. Naturforsch. B* **1974**, *29*, 625.
(2) Madelung, O., Rössler, U., Schulz, M., Eds.; The Landolt-Börnstein Database, (SpringerMaterials, New York), Vol. 41C.
(3) Madelung, O., Rössler, U., Schulz, M., Eds.; The Landolt-Börnstein Database, (SpringerMaterials, New York), Vol. 41C.