Supporting Information (SI)

Enhanced thermoelectric performance in topological crystalline insulator *n*-type $Pb_{0.6}Sn_{0.4}Te$ by simultaneous tuning of the band gap and chemical potential

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EXPERIMENTAL DETAILS

Reagents. Tin (Sn, Alfa Aesar 99.99+ %), tellurium (Te, Alfa Aesar 99.999+ %), lead (Pb, Alfa Aesar 99.99+ %) and tellurium iodide (TeI_4, Alfa Aesar99%) were used for synthesis without further purification.

Synthesis. Ingots (~6 g) of $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$ (x = 0.0, 0.005, 0.01, 0.02, 0.03) were synthesized by mixing stoichiometric ratios of high-purity elemental Sn, Pb, Te and TeI_4 in quartz tubes. The tubes were sealed under vacuum (10^{-5} Torr) and slowly heated to 723 K over 12 h (58 K/hr), then heated up to 1323 K in 5 h (120 K/hr), annealed for 5 h (0 K/hr), and cooled down to 1023 K over 2 h (150 K/hr) and annealed for 4 h (0 K/hr), then slowly cool down to room temperature over a period of 18 h (55 K/hr).

In order to achieve homogeneity in the samples without any surface crack or defects, we have taken two step annealing strategies. First, we have given 5 hrs annealing time at 1323 K during synthesis and shaken the tubes several times and secondly, we have given 4

hrs annealing time at 1023 K to get good quality (high density, ~ 97 %) ingot samples. We have executed thermoelectric measurements for all samples as synthesized ingot from melt.

Powder X-ray diffraction. Powder X-ray diffraction of ground samples were recorded using a Cu K_α (λ = 1.5406 Å) radiation on a Bruker D8 diffractometer at room temperature.

Band gap measurement. To estimate optical band gap of the as synthesized samples diffuse measurement has been done with finely ground powder at room temperature using FT-IR Bruker IFS 66V/S spectrometer in a wave-number range 4000-400 cm^{-1} with 2 cm^{-1} resolution and 50 scans. Absorption (α/S) data were calculated from reflectance data using Kubelka-Munk equation: $\alpha/S=(1-R)^2/(2R)$, where R is the reflectance, α and S are the absorption and scattering coefficient, respectively. The energy band gaps were obtained from α/S vs E_g (eV) plot.

Electrical transport. Electrical conductivity and Seebeck coefficients were measured simultaneously under He atmosphere from room temperature to 723 K on a ULVAC-RIKO ZEM-3 instrument. The sample for measurement had a parallelepiped shape with the typical dimensions of ~2×2×8 mm^3. The longer direction coincides with the direction in which the thermal conductivity was measured.

Hall measurement. For determining the carrier concentrations, Hall measurements were carried out on the rectangular samples in four-contact geometry in a magnetic field of 0.57 T at room-temperature in custom-built equipment developed by Excel Instruments.

Thermal transport. Thermal diffusivity, D, was directly measured in the range 300–723 K by using a laser flash diffusivity method in a Netzsch LFA-457 instrument (Figure S4, SI). Coins with ~ 8mm diameter and less than 2 mm thickness were used for the measurements. The temperature dependent heat capacity, C_p, was derived using a standard sample (pyroceram) in LFA-457. The total thermal conductivity, κ_{total}, was calculated using the

formula, $\kappa_{total} = DC_p\rho$, where ρ is the density of the sample. The density of the pellets obtained was in the range ~97% of the theoretical density. Thermal conductivity was measured in the same direction of electronic transport measurement.

Kelvin probe force microscopy. To investigate the relative position of the Fermi level, Kelvin probe force microscopy has been done with coins (~ 8 mm diameter and ~1 mm thickness) at room temperature using Bruker's dimension icon atomic force microscopy (AFM) system. A Pt-Ir coated Si cantilever (SCM-PIT-V2 from Bruker) with 25 nm radius was used for KPFM measurement.

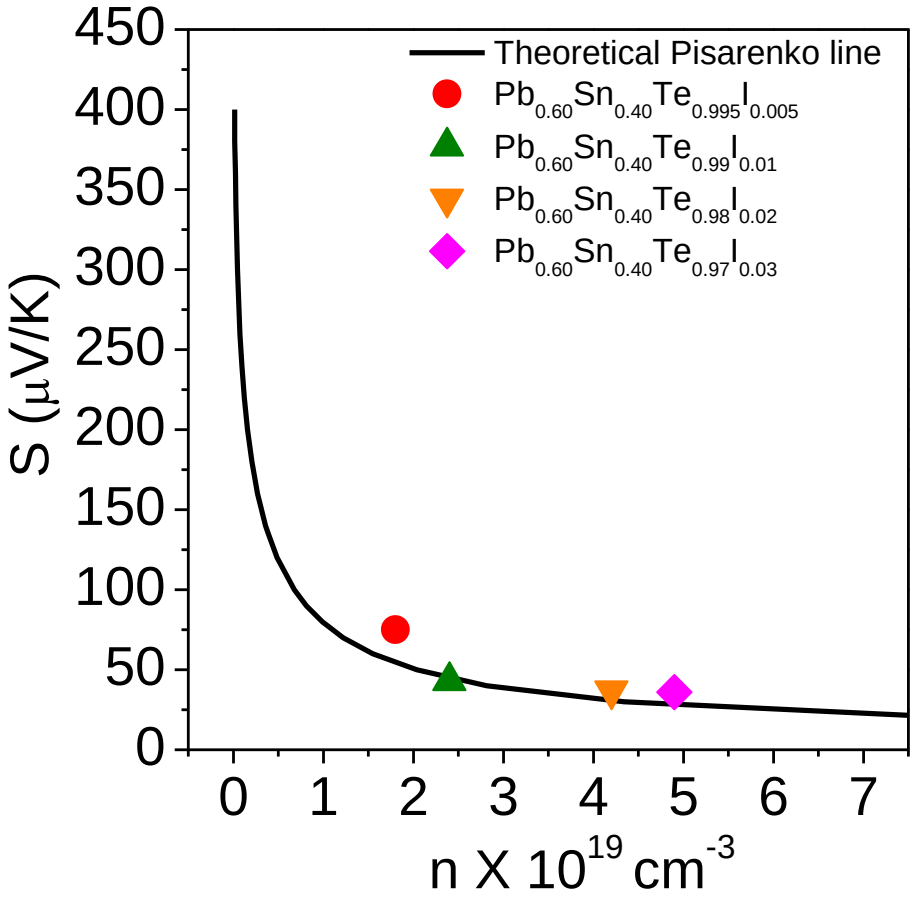

Figure S1. Seebeck coefficient (S) as a function of carrier concentration (n) (Pisarenko plot) at T=300 K for $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$ (x = 0.005, 0.01, 0.02 and 0.03) samples.

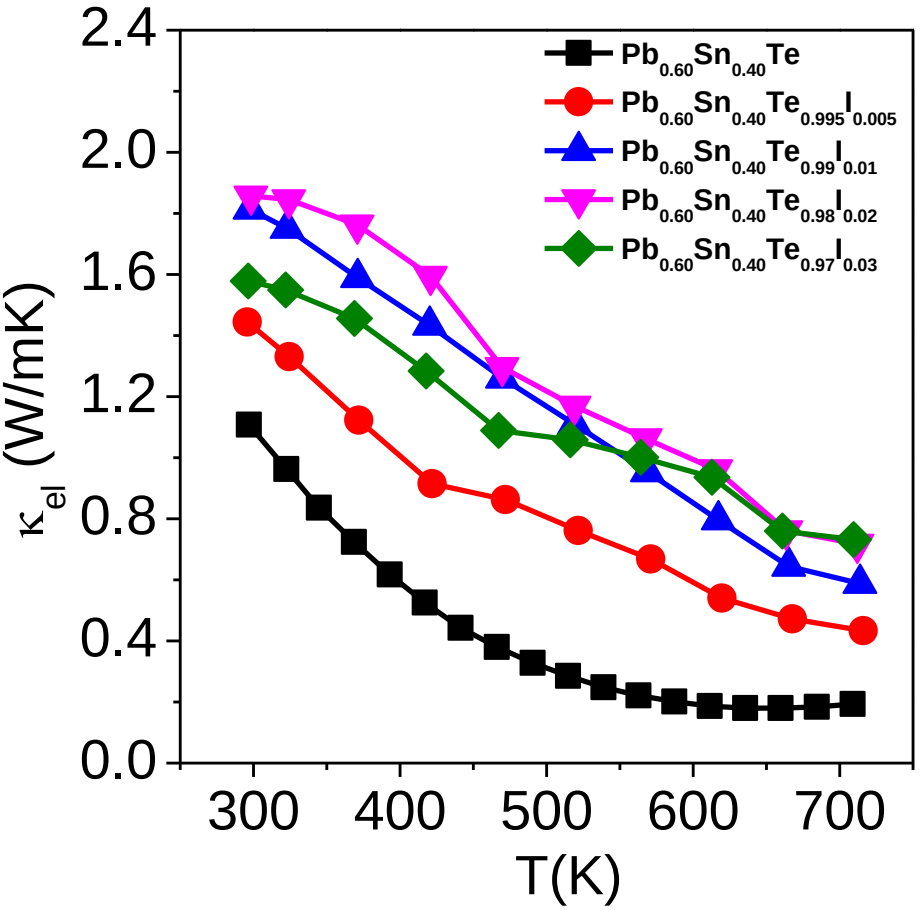

Figure S2. Temperature dependent electrical thermal conductivity (κ_{el}) for $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$ (x = 0, 0.005, 0.01, 0.02 and 0.03) samples.

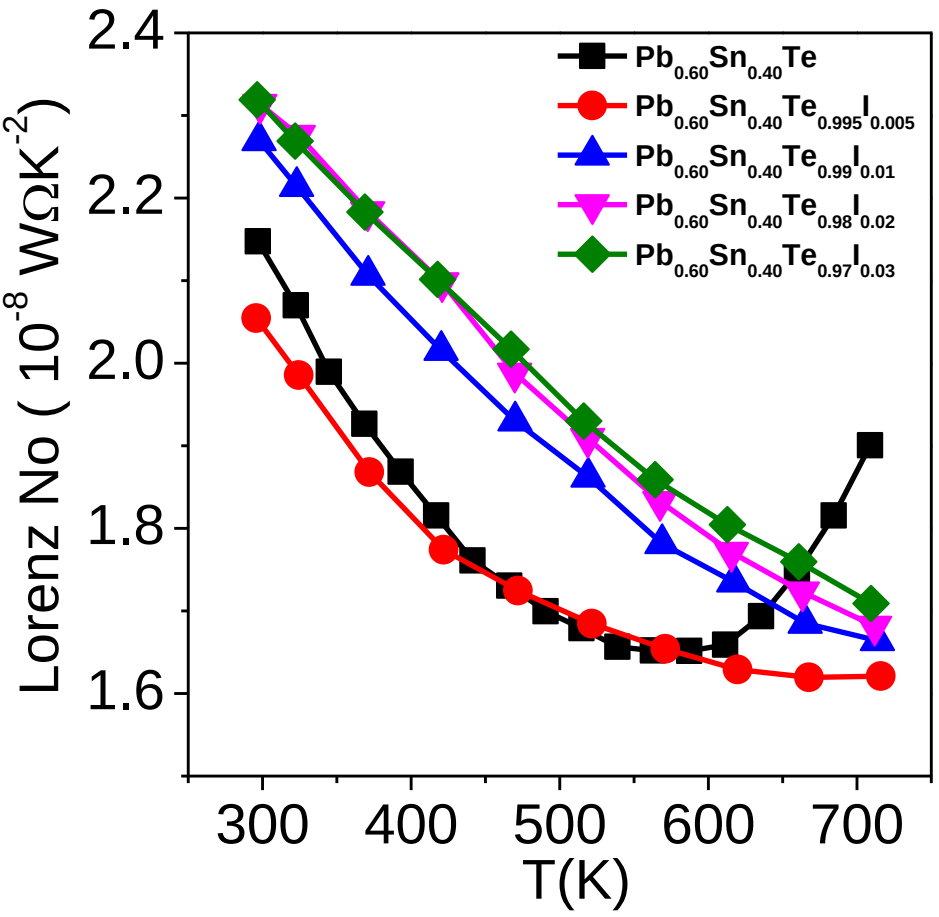

Figure S3. Temperature dependent Lorenz number (L) for $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$(x = 0, 0.005, 0.01, 0.02 and 0.03) samples.

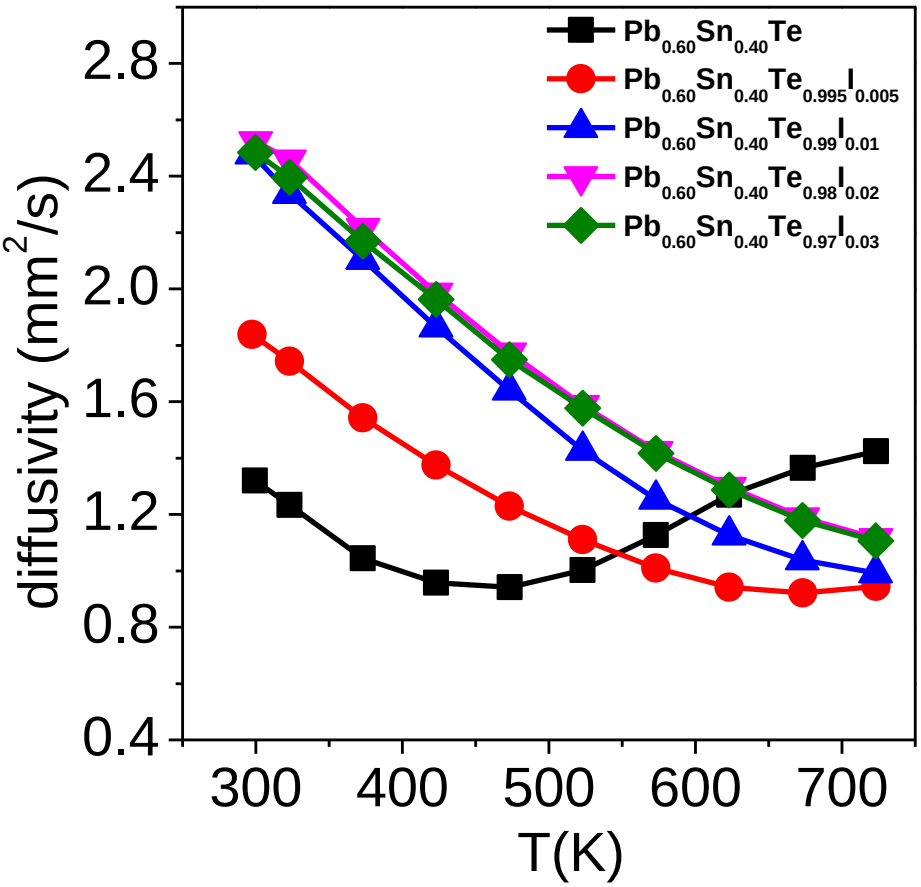

Figure S4. Temperature dependent diffusivity (D) for $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$(x = 0, 0.005, 0.01, 0.02 and 0.03) samples.

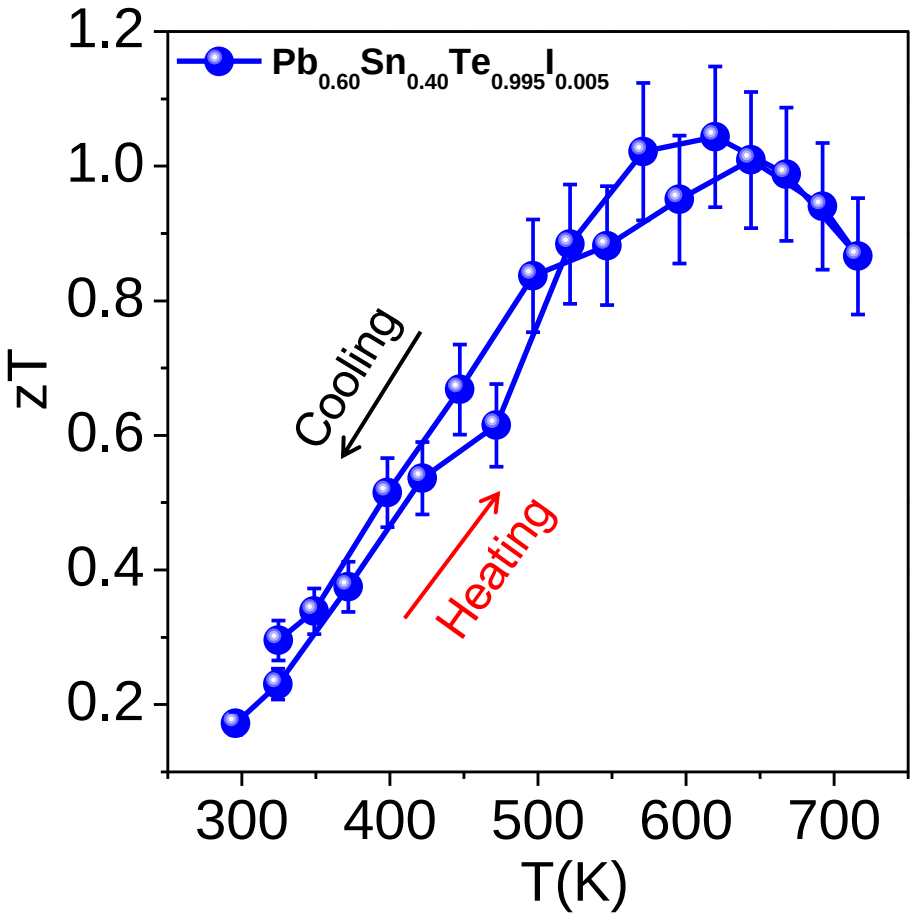

Figure S5. Temperature dependent thermoelectric figure of merit of $Pb_{0.60}Sn_{0.40}Te_{0.995}I_{0.005}$ sample with 10 % error bar, representing the stability of the sample against high temperature measurements and reproducibility of the measurements.

Table S1. Contact potential difference (CPD) of highly ordered pyrolytic graphite (HOPG) and $Pb_{0.60}Sn_{0.40}Te_{1-x}I_x$ (x = 0, 0.005 and 0.02) samples at room temperature.

Sample	CPD_{HOPG} (eV)	CPD_{Sample} (eV)
$\mathbf{Pb_{0.60}Sn_{0.40}Te}$	0.23	0.463
$\mathbf{Pb_{0.60}Sn_{0.40}Te_{0.995}I_{0.005}}$	0.23	0.496
$\mathbf{Pb_{0.60}Sn_{0.40}Te_{0.98}I_{0.02}}$	0.23	0.514