## **Electronic Supplementary Information (ESI)**

## Engineering ferroelectric instability to achieve ultralow thermal conductivity and high thermoelectric performance in Sn<sub>1-x</sub>Ge<sub>x</sub>Te

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## Methods

**Reagents.** Tin (Alfa Aesar 99.99+ %), germanium (Aldrich 99.999%), tellurium (Alfa Aesar 99.999+ %) and antimony (Alfa Aesar 99.999+ %) were used for synthesis without further purification.

**Synthesis.** High quality polycrystalline ingots of  $Sn_{1-x}Ge_xTe$  (x = 0-0.5) have been synthesized by melting the stoichiometric amount of Sn, Ge and Te in vacuum sealed ( $10^{-5}$  Torr) quartz tube. The tubes were kept vertically in a box furnace and slowly heated to 900 °C over 12 hrs, then kept for 10 hrs, and cooled slowly (1.2 °C/min) to room temperature over a period of 12 hrs. Sb alloyed  $Sn_{1-x}Ge_xTe$  samples have been prepared via similar method. For the measurement of the electrical and thermal transport properties, ingots were cut and polished in the shape of bar and coin respectively.

To improve the thermoelectric properties, we have done spark plasma sintering (SPS) of the highest zT composition Sn<sub>0.57</sub>Sb<sub>0.13</sub>Ge<sub>0.3</sub>Te. The melt grown ingots were ground into fine powders using a mortar and pestle to reduce the grains size in an inert glove box. This powder was then pressed into cylindrical shape by SPS method (SPS-211LX, Fuji Electronic Industrial Co., Ltd.) at 773 K for 5 min in a 10 mm diameter graphite die under an axial pressure of 40 MPa in vacuum. Highly dense (~ 98% of theoretical density) disk-shaped pellets with ~10 mm diameter and ~10 mm thickness were obtained.

**Powder X-ray diffraction (PXRD).** Powder X-ray diffraction for all of the samples were recorded using a Cu K<sub> $\alpha$ </sub> ( $\lambda$  = 1.5406 Å) radiation on a Bruker D8 diffractometer.

**X-ray Pair Distribution Function:** Temperature dependent X-ray PDF data was collected using finely ground powder in beamline P02.1, PETRA III, DESY, Hamburg. Synchroton beam of fixed energy 59.83 keV and spot size 0.5 X 0.5 mm<sup>2</sup> was used to collect data. 2D image plate data was collected using a Perkin-Elmer detector which was processed using Fit2D<sup>1</sup> software to obtain the scattering intensities S(Q) in the Q-space. The pair distribution G(r) was then obtained by Fourier transformation of the scattering structure function F(Q) = Q[S(Q) - 1] using PDFgetX2<sup>2</sup> software. Finally, the modeling and refinement of G(r) was done using the software PDFgui.<sup>3</sup>

**Differential scanning calorimetry (DSC).** DSC data were collected by METTLER-TOLEDO Differential Scanning Calorimeter (DSC 822 e) with a heating/cooling rate of 1 K/min between 253 and 300 K in  $N_2$  atmosphere.

**Raman Spectroscopy.** Raman measurements were carried out using Horiba HR-Evolution spectrometer with 532 nm excitation laser. Ultra-low frequency filters were used to record the spectrum in the range of 18–200 cm<sup>-1</sup>. Frequency of local modes around Ge atoms can be represented as

$$\omega_0 = \omega_{TO}(SnTe) \left[ 1 + \frac{(M_{Ge} - M_{Sn})}{M_{Sn}} \right]^{-1/2} (1)$$

Where  $M_{\text{Ge}}$  and  $M_{\text{Sn}}$  are the atomic masses of Ge and Sn, respectively, and  $\omega_0$  is the frequency of the local modes around Ge. Frequency of local modes due to Ge atom doping is estimated to be ~ 24 to 27 cm<sup>-1</sup> which is in well agreement with the calculated and observed soft modes at ~ 19, 27 and 36 cm<sup>-1</sup>.

**Field emission scanning electron microscopy.** Backscattered electron imaging (BSE) mode field emission scanning electron microscopy (FESEM) experiments were performed using NOVA NANO SEM 600 (FEI, Germany) operated at 15 kV.

**TEM measurements.** TEM imaging was performed using an aberration corrected FEI TITAN cubed 80–300 kV transmission electron microscope operating at 300 kV. TEM samples were prepared by conventional mechanical thinning.

**Thermal conductivity.** Thermal diffusivity, *D*, was directly measured in the range 300–730 K by using laser flash diffusivity method in a Netzsch LFA-457 (Fig. S3a and S14). Coins with ~ 8 mm (or ~ 10 mm) diameter and less than 2 mm thickness were used in all of the measurements. Temperature dependent heat capacity,  $C_p$ , was derived using standard sample (pyroceram) in LFA-457, which is in good agreement with Dulong Petit  $C_p$  value (Fig. S3b). The total thermal conductivity,  $\kappa_{total}$ , was calculated using the formula,  $\kappa_{total} = DC_p\rho$ , where  $\rho$  is the density of the sample (Fig. 2a and S15a). The density of the pellets obtained was  $\geq 97\%$  of the theoretical density.  $\kappa_{el}$  (Fig. S4b and S15b) was determined based on Wiedemann-Franz Law, i.e.  $\kappa_{el} = L\sigma T$ , where *L* is the Lorenz number (Fig. S4a), estimated based on fitting of respective Seebeck *vs* temperature data following previous literature report.<sup>4</sup>

**Electrical transport.** Electrical conductivity ( $\sigma$ ) and Seebeck coefficients (*S*) were measured simultaneously under He atmosphere from room temperature to 721 K on a ULVAC-RIKO ZEM-3 instrument (Fig. 5 and S16). The typical sample for measurement had parallelepiped shape with the dimensions of ~ 2 × 2 × 8 mm<sup>3</sup>. The longer direction coincides with the direction in which the thermal conductivity was measured. Heating and cooling cycles give repeatable electrical properties for a given sample (Fig. S6). Low temperature range (< 300 K) of the resistivity was measured in a Quantum Design (QD) Physical Property Measurement System (PPMS).

**Hall measurement.** Carrier concentrations  $(n_{\rm H})$  were determined using Hall coefficient measurements at room temperature with a setup, designed by Excel instrument, where variable magnetic field (0–0.57 T) and fixed dc-current (100 mA) were used. Four-contact

Hall-bar geometry was used for the measurement. At 300 K, we estimated the carrier concentration,  $n_{\rm H}$ , from the formula:  $n_{\rm H} = 1/eR_{\rm H}$ , where *e* is the electronic charge,  $R_{\rm H}$  is hall coefficient.

**Estimation of**  $\kappa_{lat}$  **from Klemens model.** According to Klemens theory of disordered alloys,<sup>5</sup> the lattice thermal conductivity of a disordered alloy,  $\kappa_{lat}^d$  is determined by:

$$\kappa_{lat}^{d} = \frac{\tan^{-1}(u)}{u} \kappa_{lat}^{p}$$
(2)

Where  $\kappa_{lat}^p$  is the lattice thermal conductivity of a pure alloy and u can be expressed by

$$u^{2} = \frac{\pi^{2} \Theta_{D} \Omega}{h v^{2}} \kappa_{lat}^{p} \Gamma (3)$$

Here u is the disorder scaling parameter,  $\Theta_D$  is the Debye temperature ( $\Theta_D = 140$  K for SnTe<sup>6</sup>), h is the Plank constant, v is the sound velocity (v = 1800 m s<sup>-1</sup>, for SnTe<sup>6</sup>), and  $\Omega$  is the average volume per atom and  $\Gamma$  is the scattering parameter that combines the influences from mass, bonding force, and strain contrasts, described as

$$\Gamma = c(1-c)\left[\left(\frac{\Delta M}{M}\right)^2 + \varepsilon \left(\frac{\Delta a}{xa}\right)^2\right] (4)$$

where *c* is concentration of dopant,  $\varepsilon$  is a phenomenological parameter (163) related to the Grüneisen parameter  $\gamma$  (~ 2.1 for SnTe<sup>3</sup>), *M* and *a* are the molar mass and lattice constant of the alloy,  $\Delta M$  and  $\Delta a$  are the differences in mass and lattice constant between the two constituents.

**Computational details.** We used density functional theoretical (DFT) methods as implemented in QUANTUM ESPRESSO (QE) code,<sup>7</sup> taking into account only the valence electrons and replacing the potential of the ionic core with a pseudopotential. We used a generalized gradient approximation (GGA)<sup>8</sup> to the exchange-correlation energy functional as parameterized by Perdew, Burke, and Ernzerhof (PBE).<sup>9</sup> To describe the interactions between valence electrons and ions, we used Projected Augmented–Wave (PAW) potentials. Valence

and semi-core electronic states of Sn, Te and Ge were considered through the use of pseudopotentials (in  $4d^{10} 5s^2 5p^2$ ,  $4d^{10} 5s^2 5p^4$ , and  $3d^{10} 4s^2 4p^2$  configurations respectively). SnTe crystallizes in the rocksalt structure belonging to Fm-3m space group, with two atoms in the primitive unit cell and eight atoms in the conventional cubic unit cell. Pristine and Ge substituted SnTe were simulated using conventional cubic unit cell containing four SnTe. Electronic wave functions and charge density were represented in plane wave basis sets truncated with cut-off energies of 45 Ry and 400 Ry respectively. The Brillouin Zone (BZ) integrations were sampled on a uniform 20 x 20 x 20 mesh of k-points. The discontinuity in occupation numbers of electronic states was smeared using a Fermi-Dirac distribution function with broadening of  $k_BT = 0.003$  Ry. We determined lattice dynamical properties of SnTe and Sn<sub>0.75</sub>Ge<sub>0.25</sub>Te in their optimized structures obtained after vc-relaxation at the experimental lattice parameter. The PBE optimized lattice parameters of SnTe (a = b = c =6.37 Å) and Sn<sub>0.75</sub>Ge<sub>0.25</sub>Te (a = b = c = 6.28 Å) were considered for further calculations. Dynamical matrices were calculated within the Density Functional Perturbation Theory (DFPT) on a 2 x 2 x 2 q-points grid in the Brillouin Zone.<sup>10</sup> We Fourier interpolated these dynamical matrices to obtain the phonon dispersion along high symmetry lines ( $\Gamma$  - X - M -  $\Gamma$ - R - X - M - R) in the Brillouin zone. We estimated the measure of strain phonon coupling (couplings between acoustic and optical phonons) using a finite difference formula of  $\partial \omega_0^2(\epsilon)/\partial \epsilon$  having calculated squared phonon frequencies at strained structures. We used

scalar relativistic pseudopotentials (SOC = 0) in DFT-LR calculations of phonons. Moreover, to understand the role of Ge off-centering on the structural stabilization and the associated phase transition, we compared the energetics of Ge off-centering using DFT simulations. We off-centered Ge atoms along the <111> direction by 0.04 Å and varied the Ge concentration from  $Sn_{0.875}Ge_{0.125}Te$  to  $Sn_{0.75}Ge_{0.25}Te$ . We find that the reduction of total energies of the Ge off-centered  $Sn_{0.875}Ge_{0.125}Te$  and  $Sn_{0.75}Ge_{0.25}Te$  structures are -0.49 meV and -3.29 meV,

respectively, compared to that of the non-distorted counterparts. This shows the increasingly dominant role of Ge off-centering on the structural stabilization.

**Table S1.** Room temperature carrier concentration  $(n_{\rm H})$  and carrier mobility  $(\mu)$  of  ${\rm Sn}_{1-x}{\rm Ge}_x{\rm Te}$  (x = 0-0.3) and  ${\rm Sn}_{0.7-y}{\rm Sb}_y{\rm Ge}_{0.3}{\rm Te}$ . We have also compared our data with previously reported carrier concentration and mobility of SnTe based samples.

Sample	$n_{\rm H} (10^{19} {\rm cm}^{-3})$	$\mu \ (\mathrm{cm}^2 \ \mathrm{V}^{-1} \ \mathrm{s}^{-1})$
SnTe	33	170
$\mathrm{Sn}_{0.9}\mathrm{Ge}_{0.1}\mathrm{Te}$	11	370
$Sn_{0.8}Ge_{0.2}Te$	8.3	418
$Sn_{0.7}Ge_{0.3}Te$	8.9	421
$Sn_{0.66}Sb_{0.04}Ge_{0.3}Te$	5.44	300
$Sn_{0.57}Sb_{0.13}Ge_{0.3}Te$	4.5	310
Sn <sub>0.88</sub> Sb <sub>0.12</sub> Te (For comparison) <sup>6</sup>	15	130
SnTe-CdTe-CdS (For comparison) <sup>11</sup>	5.63	237
Sn <sub>0.97</sub> Bi <sub>0.03</sub> Te-3% SnSe (For comparison) <sup>12</sup>	8.5	355
$\frac{\text{Sn}_{0.97}\text{Bi}_{0.03}\text{Te}-3\% \text{ SnSe}}{(\text{For comparison})^{12}}$	8.7	344
Sn <sub>0.98</sub> Bi <sub>0.03</sub> Te-HgTe (For comparison) <sup>13</sup>	9.3	257

Table S2. Densities of all samples.

Composition	Density (g/cm <sup>3</sup> )	Composition	Density (g/cm <sup>3</sup> )
SnTe	6.26	Sn <sub>0.66</sub> Sb <sub>0.04</sub> Ge <sub>0.3</sub> Te	6.15
Sn <sub>0.9</sub> Ge <sub>0.1</sub> Te	6.2	$Sn_{0.6}Sb_{0.1}Ge_{0.3}Te$	6.12
Sn <sub>0.8</sub> Ge <sub>0.2</sub> Te	6.15	Sn <sub>0.57</sub> Sb <sub>0.13</sub> Ge <sub>0.3</sub> Te	6.09
Sn <sub>0.7</sub> Ge <sub>0.3</sub> Te	6.15	Sn <sub>0.57</sub> Sb <sub>0.13</sub> Ge <sub>0.3</sub> Te SPS	6.2



**Fig. S1** PXRD patterns of  $Sn_{1-x}Ge_xTe$  (x = 0-0.5) in log scale. Colored region indicates enhanced intensity of (111) reflection and apearance of rhobohedral phase x > 0.5 at room temperature. '\*' sign in  $Sn_{0.5}Ge_{0.5}Te$  indicates the presence of Ge- rich second phases. (b) DSC signal of  $Sn_{0.5}Ge_{0.5}Te$  sample.



**Fig. S2** (a) – (e) Temperature dependent resistivity of  $Sn_{1-x}Ge_xTe$  (x = 0 - 0.5). (f) Evolution of cubic to rhombohedral phase transition with Ge concentration in  $Sn_{1-x}Ge_xTe$  (x = 0 - 0.5) as inferred from resistivity and DSC studies.



**Fig. S3** (a) Temperature dependent thermal diffusivity (*D*) of  $Sn_{1-x}Ge_xTe$  (x = 0-0.3). (b) Typical temperature dependent heat capacity ( $C_p$ ) of  $Sn_{0.7}Ge_{0.3}Te$ .



**Fig. S4** Temperature dependent (a) Lorenz number (*L*) and (b)  $\kappa_{el}$  of Sn<sub>1-x</sub>Ge<sub>x</sub>Te (x = 0-0.3).



**Fig. S5** Temperature-dependent lattice thermal conductivity ( $\kappa_{lat}$ ) of Sn<sub>1-x</sub>Ge<sub>x</sub>Te (x = 0.3-0.5).



**Fig. S6** Heating and cooling cycle (a) electrical conductivity ( $\sigma$ ), (b) Seebeck coefficient (*S*) and (c) thermal conductivity ( $\kappa_{\text{total}}$ ) data of Sn<sub>0.7</sub>Ge<sub>0.3</sub>Te.



**Fig. S7** (a) & (b) Back scattered FESEM image and EDAX performed on  $Sn_{0.7}Ge_{0.3}Te$ . (c) Bright field TEM image of  $Sn_{0.7}Ge_{0.3}Te$ . Inset electron diffraction pattern is indexed to the rocksalt cubic SnTe structure. (d) High resolution TEM (HRTEM) image of  $Sn_{0.7}Ge_{0.3}Te$  showing (200) planes of  $Sn_{0.7}Ge_{0.3}Te$ .



Fig. S8 Comparison of phonon density of states of SnTe and Sn<sub>0.75</sub>Ge<sub>0.25</sub>Te.



**Fig. S9** Visualization of the atomic displacements of unstable phonons at the zone centre of (a) SnTe and (b)  $Sn_{0.75}Ge_{0.25}Te$ , Sn (Red in colour), Te (Blue in colour), and Ge (Pink in colour). There are equal and opposite displacements of Sn and Te atoms in (a) SnTe, whereas the displacements of Ge atoms completely dominate the lattice instability in (b)  $Sn_{0.75}Ge_{0.25}Te$ .



**Fig. S10** Global fit of x-ray PDF with (a) cubic structure and (b) rhombohedral distortion at room temperature in  $Sn_{0.7}Ge_{0.3}$ Te. Although, the global structure is well fitted with cubic phase, the local structure fits better with rhombohedral distortion.



Fig. S11 (a) – (f) Temperature evolution of local structure peak for the nearest neighbor atomic correlation in x-ray PDF and fits with rhombohedral distortion in  $Sn_{0.7}Ge_{0.3}Te$ .



**Fig. S12** Temperature dependence of thermal ADPs of Sn and Ge atoms obtained from X-ray PDF.



**Fig. S13** (a) Powder XRD patterns of  $Sn_{0.7-y}Sb_yGe_{0.3}Te$  (y = 0-0.15). (b) Powder XRD patterns of  $Sn_{0.57}Sb_{0.13}Ge_{0.3}Te$  sample before and after SPS-processing. (c) Lattice parameter (*a*) vs. Sb concentration (y) plot for  $Sn_{0.7-y}Sb_yGe_{0.3}Te$  (y = 0-0.15). Dashed line indicates the Vegard's law for solid solution.



**Fig. S14** Temperature dependent thermal diffusivity (*D*) of  $Sn_{0.7-y}Sb_yGe_{0.3}Te$  (y = 0-0.15).



**Fig. S15** Temperature-dependent (a) total thermal conductivity ( $\kappa_{total}$ ), (b) electronic thermal conductivity ( $\kappa_{el}$ ) and (c) lattice thermal conductivity ( $\kappa_{lat}$ ) of Sn<sub>0.7-y</sub>Sb<sub>y</sub>Ge<sub>0.3</sub>Te (y = 0-0.15) samples.



**Fig. S16** Temperature-dependent (a) electrical conductivity ( $\sigma$ ), (b) Seebeck coefficient (*S*) and (c) power factor ( $\sigma S^2$ ) of Sn<sub>0.7-y</sub>Sb<sub>y</sub>Ge<sub>0.3</sub>Te (y = 0–0.15).



**Fig. S17** Electronic absorption spectra of  $Sn_{1-x}Ge_xTe$  (x = 0-0.3).



**Fig. S18** Temperature-dependent zT of Sn<sub>0.7-y</sub>Sb<sub>y</sub>Ge<sub>0.3</sub>Te (y = 0-0.15) samples.

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