

Supporting Information

Extraordinary role of Zn in enhancing thermoelectric performance of Ga-doped n-type PbTe

Zhong-Zhen Luo,^{1,2,3,4} Songting Cai,^{4,5} Shiqiang Hao,⁵ Trevor P. Bailey,⁶ Yubo Luo,^{3,4,7}
Wenjun Luo,^{2,8} Yan Yu,^{1,2} Ctirad Uher,⁶ Christopher Wolverton,⁵ Vinayak P. Dravid,⁵
Zhigang Zou,^{1,2,8,*} Qingyu Yan,^{3,*} Mercouri G. Kanatzidis^{4,*}

¹Key Laboratory of Eco-materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou, 350108, China

²Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou, Fujian 350108, P. R. China

³School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue 639798, Singapore

⁴Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

⁵Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

⁶Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, United States

⁷State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China

⁸Eco-materials and Renewable Energy Research Center, College of Engineering and Applied Sciences, Nanjing University, Nanjing, 210093, China

EXPERIMENTAL SECTION

Synthesis. The starting materials, Pb wire (99.99%, American Elements, USA), Te shot (99.999%, 5 N Plus, Canada), Zn shot (99.999%, Sigma-Aldrich, USA), and Ga shots (99.99%, Sigma-Aldrich, USA) were weighed according to the nominal compositions of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-x\%\text{ZnTe}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) and loaded into 13 mm diameter quartz tubes. The Ga-free $\text{PbTe}-x\%\text{ZnTe}$ ($x = 0, 0.5, 1, 2$ and 3) samples (~ 2 g in mass for each) were prepared to investigate the solid solubility and optical band gap. The tubes were evacuated and then flame-sealed under a pressure of $\sim 2 \times 10^{-3}$ torr. The samples were heated to 1373 K over a period of 11 h, then soaked there for 6 h, and finally water quenched to room temperature. For a typical sample, the following amounts were used: Pb (9 g, 43.4 mmol), Te (5.6992 g, 44.7 mmol), Zn (0.0073 g, 0.1 mmol), and Ga (0.0779 g, 1.1 mmol) to prepare a ~ 15 g ingot of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.25\%\text{ZnTe}$.

Densification. The resultant ingots were hand crushed into a fine powder using a mechanical mortar and pestle and then sintered using the Spark Plasma Sintering (SPS) technique (SPS-211LX, Fuji Electronic Industrial Co. Ltd.) at 773 K for 5 min under an axial pressure of 40 MPa in a vacuum. Highly dense (relative densities $\sim 95\%$) disk-shaped pellets, with a thickness of ~ 12 mm and diameter ~ 12.7 mm, were obtained.

Powder X-ray Diffraction (PXRD) Characterization. The PXRD patterns of samples were recorded at room temperature using a Rigaku Miniflex powder X-ray diffractometer with Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation operating at 40 kV and 15 mA. The measurement 2θ range and scan increments are $20\text{--}80^\circ$ and 0.02° , respectively.

Band Gap Measurements. The diffuse optical reflectance for $\text{PbTe}-x\%\text{ZnTe}$ finely ground powder samples was determined at room temperature. The spectra were recorded in the mid-IR region ($400\text{--}4000 \text{ cm}^{-1}$) using a Nicolet 6700 FT-IR spectrometer. The band gap was calculated using the Kubelka-Munk equation: $\alpha/S' = (1-R)^2/(2R)$, where R , α and S' are the reflectance coefficient, absorption coefficient, and scattering coefficient, respectively.¹

Electronic Transport Properties. The electrical conductivity and Seebeck coefficient were measured simultaneously from 300 K to 873 K using an Ulvac Riko ZEM-3 system under a low-pressure He atmosphere. For the test, sintered pellets were cut and polished to the dimensions of $\sim 11 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$. The uncertainties are $\sim 5\%$ for the electrical conductivity and 3% for the Seebeck coefficient, respectively.²

Hall Measurements. Specimens of size $\sim 1 \text{ mm} \times 3 \text{ mm} \times 8 \text{ mm}$ were surrounded by pressure contacts for the measurement of the Hall effect at room temperature and up to $\approx 813 \text{ K}$ for select samples. An AC 4-probe method in a homemade system was implemented with excitation fields of $\pm 0.5 \text{ Tesla}$ to counteract any probe misalignment. The homemade system uses an air-bore, helium-cooled superconducting magnet to generate the field within a high temperature oven that surrounds the Ar-filled sample probe. The estimated error for the Hall coefficient, R_H , is based on the standard deviation of several data points at a single temperature, and is approximately 5-10%. The carrier concentration was calculated from the Hall coefficient assuming a single carrier, i.e., $n = 1/(e|R_H|)$, where e is the electron charge.

Thermal Conductivity. The thermal diffusivity, D , was measured from 300 K to 873 K using the laser flash method (Netzsch LFA457) under a continuous nitrogen flow. The SPS sintered samples were cut to squared shape pellets with the dimensions of $\sim 6 \times 6 \times 1.5 \text{ mm}^3$, then coated with a thin layer of graphite to minimize errors from the emissivity of the material for the measurement. The experimental results were analyzed using a Cowan model with pulse correction. The total thermal conductivity (κ_{tot}) was calculated from $\kappa_{\text{tot}} = D \cdot C_p \cdot \rho$, where C_p and ρ are the specific heat capacity and the density, respectively. The C_p was obtained from the following formula: $C_p/k_B \text{ per atom} = 3.07 + 4.7 \times 10^{-4} (T/\text{K} - 300)$.³⁻⁵ Last, the ρ was determined using the mass and dimensions of the samples. With the uncertainties from D ($\sim 5\%$), ρ ($\sim 5\%$), and C_p ($\sim 15\%$), the combined uncertainty for all measurements involved in ZT determination is around 20%.

Electron Microscopy. Scanning/transmission electron microscopy (S/TEM) and STEM energy dispersive spectroscopy (EDS) experiments were carried out using a JEOL ARM300F microscope operated at 300 kV. The electron-beam transmitted TEM

specimens were prepared by conventional methods, including cutting, grinding, and Ar-ion milling (3.5 kV for ~1 hour until a hole is formed, followed by ion cleaning with 0.3 kV for 1 hour) under low temperature (liquid nitrogen stage).

Density Functional Theory (DFT) Calculations. We use Density Functional Theory (DFT) to calculate total energies and relaxed geometries within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof exchange correlation functional with Projector Augmented Wave potentials.⁶ We used periodic boundary conditions and a plane wave basis set as implemented in the Vienna ab initio simulation package.⁷ The total energies were numerically converged to approximately 3 meV/cation using a basis set energy cutoff of 500 eV and dense k -meshes corresponding to 4000 k -points per reciprocal atom in the Brillouin zone. We used a 54 atom cell for the electronic band structure calculations. The dopant concentration of Zn in the cell of $\text{Pb}_{27}\text{Te}_{27}$ is thus 3.7%. For the off-center configuration calculations, we compare the regular Zn substitution Pb site and three shifted Zn substitution along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively. For the Ga-doped and Zn alloyed PbTe, we examined multiple configurations of Zn and Ga in the Pb sublattice to determine the most favorable structure.

Density Functional Theory (DFT) for Phonon Dispersion Calculations. For phonon dispersion calculation, the total energies and relaxed geometries were calculated by DFT within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof the exchange correlation functional with Projector Augmented Wave potentials.⁶ We use periodic boundary conditions and a plane wave basis set as implemented in the Vienna ab initio simulation package.⁷ The total energies were numerically converged to approximately 3 meV/cation using a basis set energy cutoff of 450 eV and dense k -meshes corresponding to 4000 k -points per reciprocal atom in the Brillouin zone.

To quantitatively explore the origin of the κ_{lat} at the atomic level, we used the Debye-Callaway model to evaluate the κ_{lat} of Zn doped PbTe. It is known that the relationship between phonon frequency and crystal volume change is characterized by Grüneisen parameters, which allow us to estimate the lattice anharmonicity and better

understand the physical nature of κ_{lat} . We calculated the phonon and Grüneisen dispersions within the quasi-harmonic approximation. The phonon dispersions are calculated on a 128 atom cell at two volumes, one is the equilibrium volume V_0 and another one is the isotropically compressed volume $0.985V_0$.

The Debye-Callaway formalism⁸ has been shown to produce accurate values of κ_{lat} , compared to experiment, for low-conductivity thermoelectric compounds.⁹⁻¹¹ The κ_{lat} can be written as a sum over one longitudinal κ_{TA} and two transverse κ_{TA} and κ_{TA} acoustic phonon branches: $\kappa_{\text{lat}} = \kappa_{\text{TA}} + \kappa_{\text{LA}} + \kappa_{\text{TA}}$. The partial conductivities κ_i (i corresponds to TA, TA' and LA modes) are given by:

$$\kappa_i = \frac{1}{3} C_i T^3 \left\{ \int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{(e^x - 1)^2} dx + \frac{\left[\int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{\tau_N^i (e^x - 1)^2} dx \right]^2}{\int_0^{\Theta_i/T} \frac{\tau_c^i(x) x^4 e^x}{\tau_N^i \tau_U^i (e^x - 1)^2} dx} \right\} \quad (1)$$

In this expression, Θ_i is the longitudinal (transverse) Debye temperature, $1/T_N^i$ is the scattering rate for normal phonon processes, $1/T_R^i$ is the sum of all resistive scattering processes, and $1/T_C^i = 1/T_N^i + 1/T_R^i$, $x = \omega/k_B T$, and $C_i = k_B^4/2\pi^2 v_i$, here, $\hbar$ is the Planck constant, k_B is the Boltzmann constant, ω is the phonon frequency, and v_i is the longitudinal or transverse acoustic phonon velocity.

In our case, the resistive scattering rate includes the scattering rates due to Umklapp phonon-phonon scattering ($1/T_U^i$), and normal phonon scattering ($1/T_N^i$). The normal phonon scattering and Umklapp can be written as,

$$\frac{1}{\tau_N^{LA}(x)} = \frac{k_B^5 \gamma_{LA}^2 V}{M \hbar^4 v_{LA}^5} x^2 T^5 \quad (2)$$

$$\frac{1}{\tau_N^{TA/TA'}(x)} = \frac{k_B^5 \gamma_{TA/TA'}^2 V}{M \hbar^4 v_{TA/TA'}^5} x T^5 \quad (3)$$

$$\frac{1}{\tau_U^i(x)} = \frac{k_B^2 \gamma_i^2}{M \hbar v_i^2 \Theta_i} x^2 T^3 e^{-\Theta_i/3T} \quad (4)$$

where γ , V , and M are the Grüneisen parameter, the volume per atom, and the average mass of an atom in the crystal, respectively. The Grüneisen parameter can be defined as, $\gamma_i = -\frac{V \partial \omega_i}{\omega_i \partial V}$, characterizing the relationship between phonon frequency and volume change.

X-ray photoelectron spectroscopy (XPS) measurement. XPS measurement of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.25\%\text{ZnTe}$ was performed on a Thermo Scientific ESCALAB 250 Xi spectrometer. The measurement was carried out with a monochromatic Al K_{α} X-ray source (1486.6 eV) under an ultrahigh vacuum ($< 10^{-8}$ mbar). The peaks were calibrated with the C 1s peak binding energy at 284.7 eV (carbon tape) and fitted using the Advantage software.

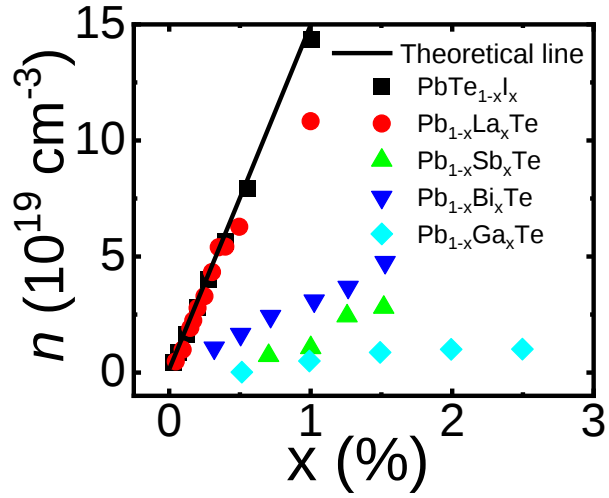


Figure S1. Comparison of n values for n-type PbTe thermoelectric materials with different n-type dopants Ga,¹² I,¹³ La,¹⁴ Sb,¹⁵ and Bi.¹⁵

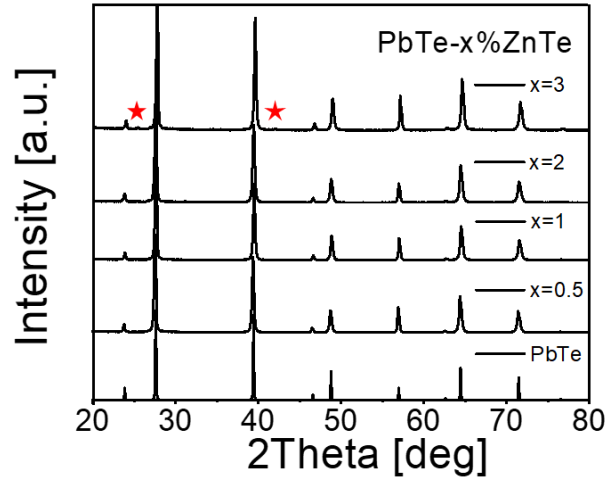


Figure S2. PXRD patterns of PbTe–x%ZnTe ($x = 0, 0.5, 1, 2$ and 3) samples, with all peaks indexed by the PbTe cubic phase (JCPDS #06-0354). The red stars display the second phase of ZnTe. The solubility limit of ZnTe in PbTe is less than 3%.

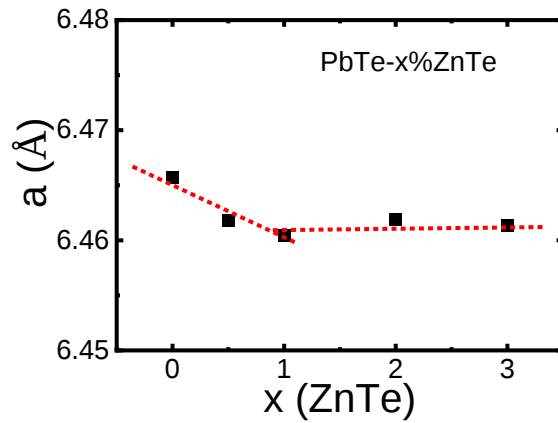


Figure S3. Refined lattice parameters for PbTe–x%ZnTe samples as a function of ZnTe content. The red dash line is a guide to the eye.

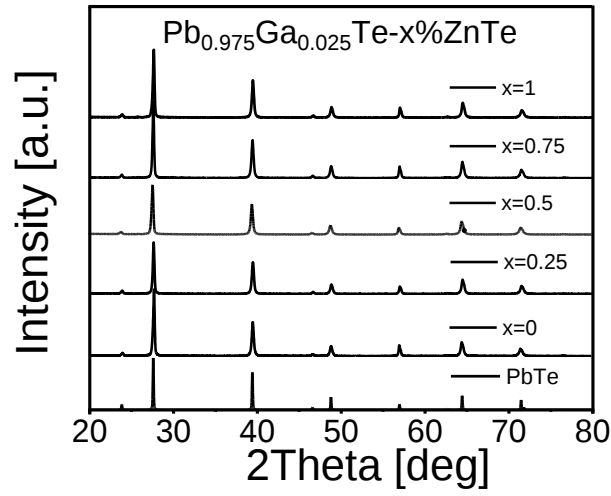


Figure S4. PXRD patterns of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-x\%\text{ZnTe}$ ($x = 0, 0.25, 0.5, 0.75$, and 1) samples, with all peaks indexed by the PbTe cubic phase (JCPDS #06-0354).

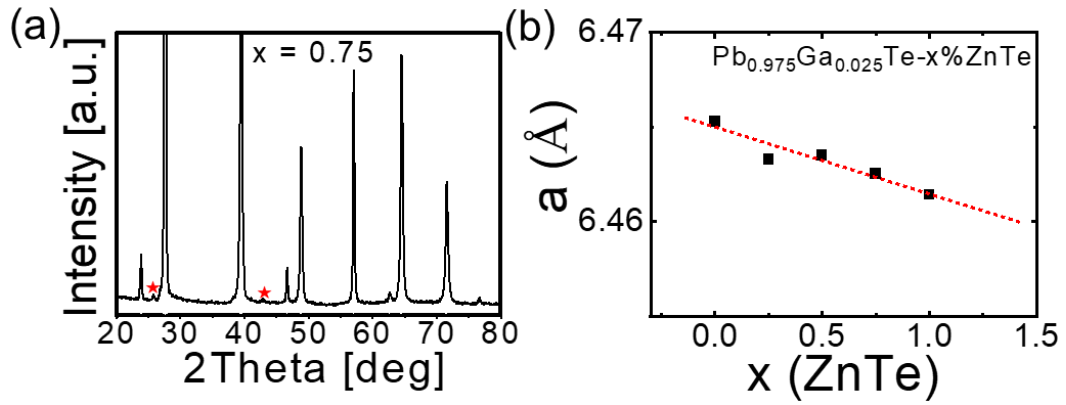


Figure S5. (a) The zoomed-in view of the PXRD pattern of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.75\%\text{ZnTe}$, revealing that a trace amount of Ga_2Te_3 second phase can be detected (marked by red stars); (b) Refined lattice parameters of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-x\%\text{ZnTe}$ samples as a function of ZnTe content. The red dash line is a guide to the eye.

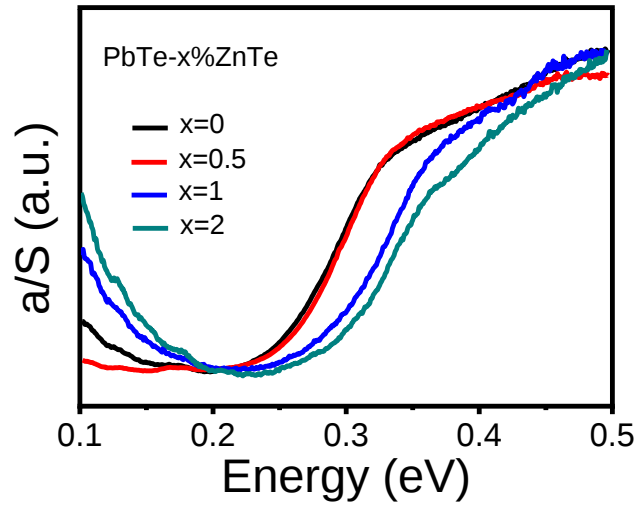


Figure S6. Electronic absorption spectra obtained from diffuse reflectance infrared spectroscopy measurements on PbTe-x%ZnTe samples (without Ga doping to avoid spectroscopic interference from free carriers) show the increasing band gap with increasing ZnTe content.

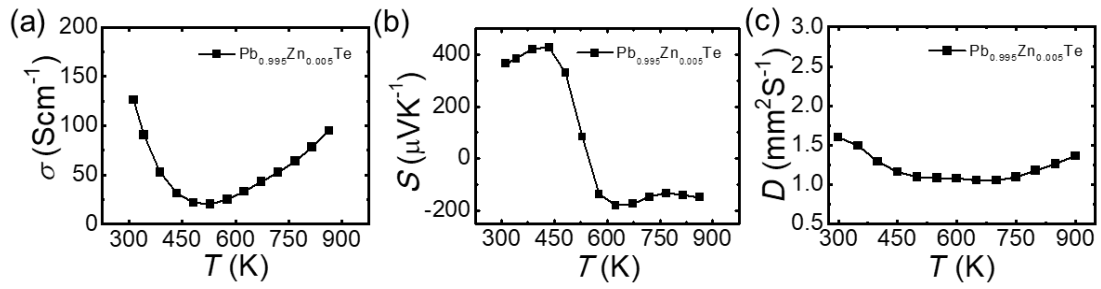


Figure S7. Thermoelectric properties as a function of temperature for Pb_{0.995}Zn_{0.005}Te, (a) Electrical conductivity, σ ; (b) Seebeck coefficient, S and (c) Thermal diffusivity, D . The result indicates that the ZnTe alloying can not improve the σ of PbTe without Ga-doping.

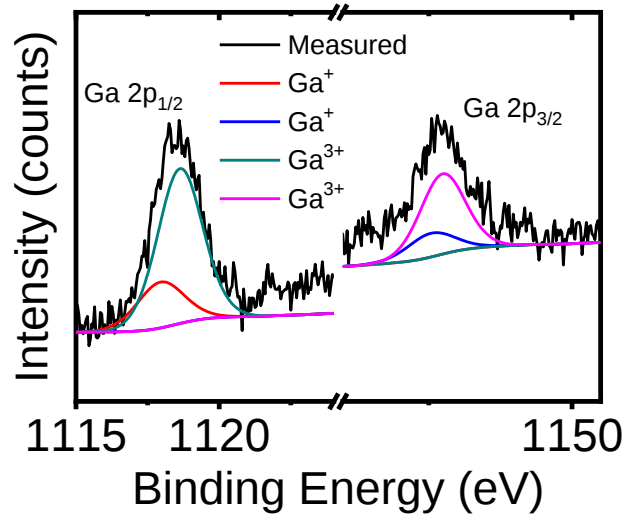


Figure S8. The X-ray photoelectron spectra (XPS) of Ga $2p_{1/2}$ and $2p_{3/2}$ core states in $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.25\%\text{ZnTe}$ samples. The spectra indicate that Ga as an amphoteric dopant has Ga^{3+} and Ga^+ states in the PbTe matrix. The Ga^+ state will offer extra free electrons by thermally activated behavior at high temperatures.^{16, 17}

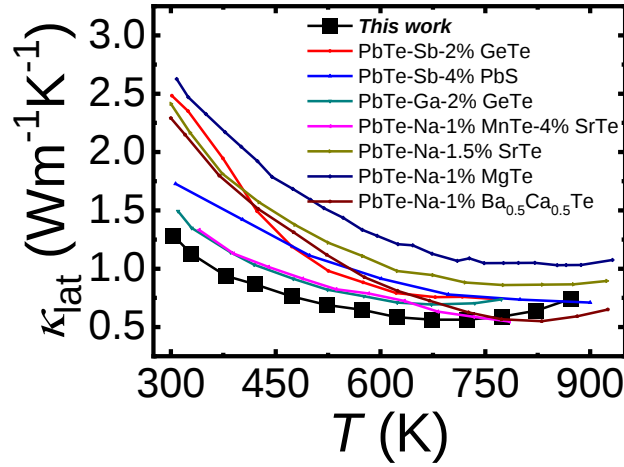


Figure S9. Comparison of κ_{lat} values for n- and p-type PbTe-based thermoelectric materials with relatively low alloying content.^{15, 18-23}

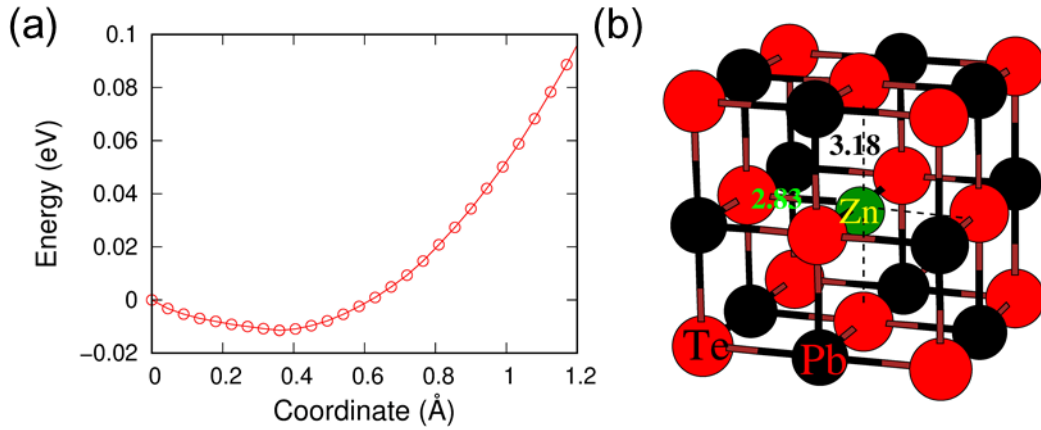


Figure S10. (a) The energy profile of ZnTe-alloyed PbTe as a function of coordinates with Zn replacing Pb in the octahedral site along the [111] direction. The energy profile from the regular Zn site to the off-centered site from 0 to 0.4 Å was calculated by Nudged Elastic Bands method.²⁴ However, for the coordinate from 0.4 to 1.2 Å, the energy profile is evaluated by the static calculation without considering the atomic configuration relaxation. (b) Illustration of the Zn off-centered PbTe structure model with typical bond lengths of Zn–Te (2.83 Å) and Pb–Te (3.18 Å). The regular bond lengths of Pb–Te and Zn–Te are 3.275 and 2.674 Å for pure PbTe and ZnTe, respectively.

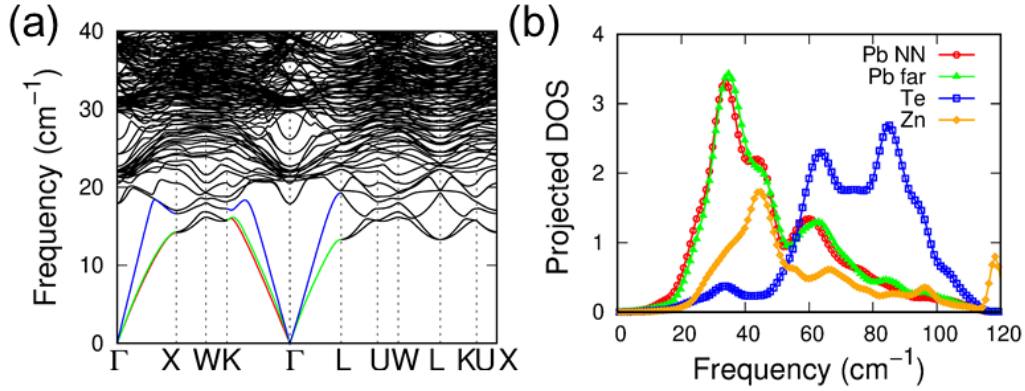


Figure S11. (a) Phonon dispersion curves (green and red curves for the transverse and blue curves for the longitudinal acoustic branches) and (b) the projected phonon density of states (DOS) for discordant Zn-alloyed PbTe.

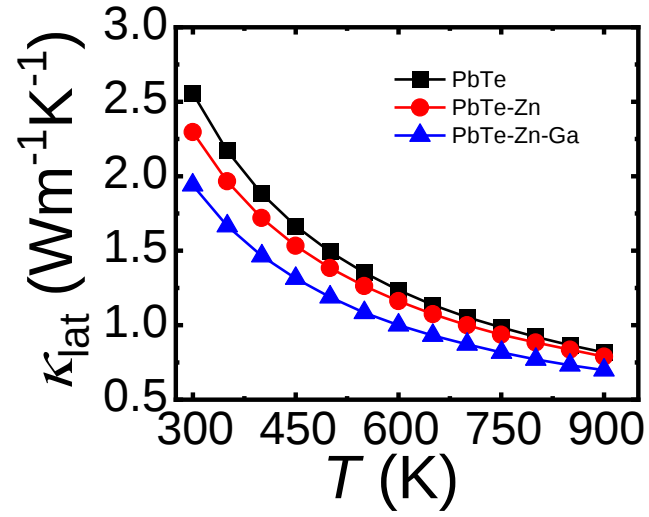


Figure S12. The κ_{lat} comparison of pure PbTe, Zn-alloyed PbTe, and Ga-doped and Zn-alloyed PbTe as a function of temperature, calculated from the DFT phonon dispersion curves and Debye–Callaway formalism.

Table S1. Room temperature densities of $\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-x\%\text{ZnTe}$ ($x = 0, 0.25, 0.5, 0.75$, and 1) samples

Composition	Measured Density, g/cm^3	Theoretical Density, %
$\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}$	7.94	97.4
$\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.25\%\text{ZnTe}$	7.80	95.8
$\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.5\%\text{ZnTe}$	7.82	96.1
$\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-0.75\%\text{ZnTe}$	7.90	97.2
$\text{Pb}_{0.975}\text{Ga}_{0.025}\text{Te}-1\%\text{ZnTe}$	7.87	96.9

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