Electronic Supplementary Material (ESI)

High-Performance Electron-doped $GeMnTe_2$: Hierarchical Structure and Low Thermal Conductivity

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Density of $Pb_xGe_{1-x}MnTe_2$

Table S1 Sample Density

Composition	x = 0.00	x = 0.02	x = 0.04	x = 0.06	x = 0.08	x = 0.10
Density(g/cm^3)	6.02	6.02	6.05	6.05	6.11	6.09

Electrical transport properties of $Pb_xGe_{1-x}MnTe_2$

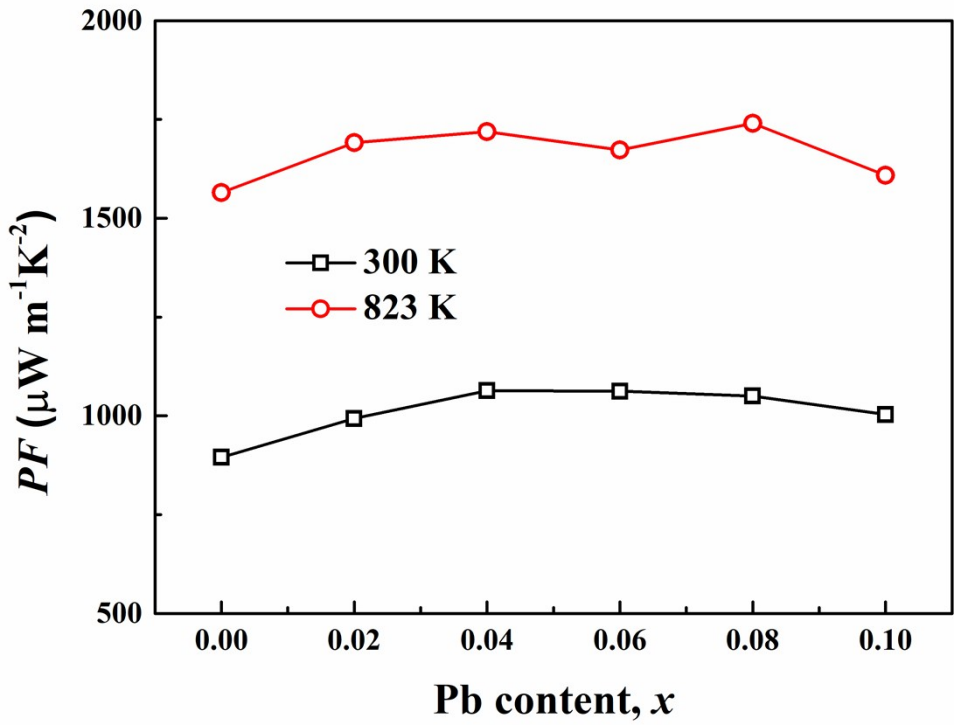

Fig. S1 PF of $Pb_xGe_{1-x}MnTe_2$ at room temperature and 823 K.
The PF is maintained or even increased when Pb is alloyed, meaning that electrical transport properties are not much affected.

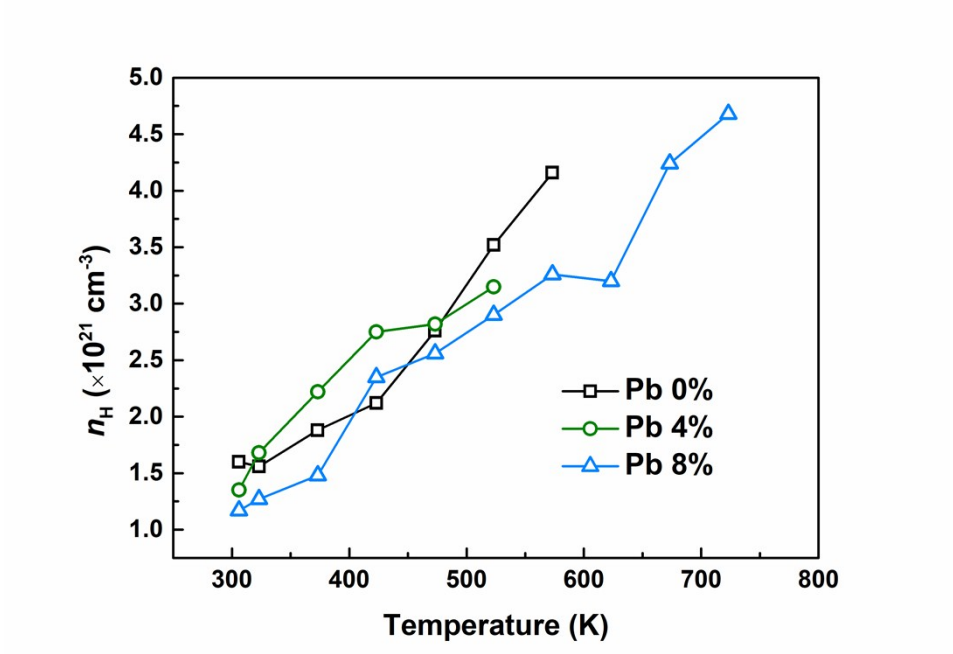

Fig. S2 Temperature dependence of carrier concentration.

Stability of samples

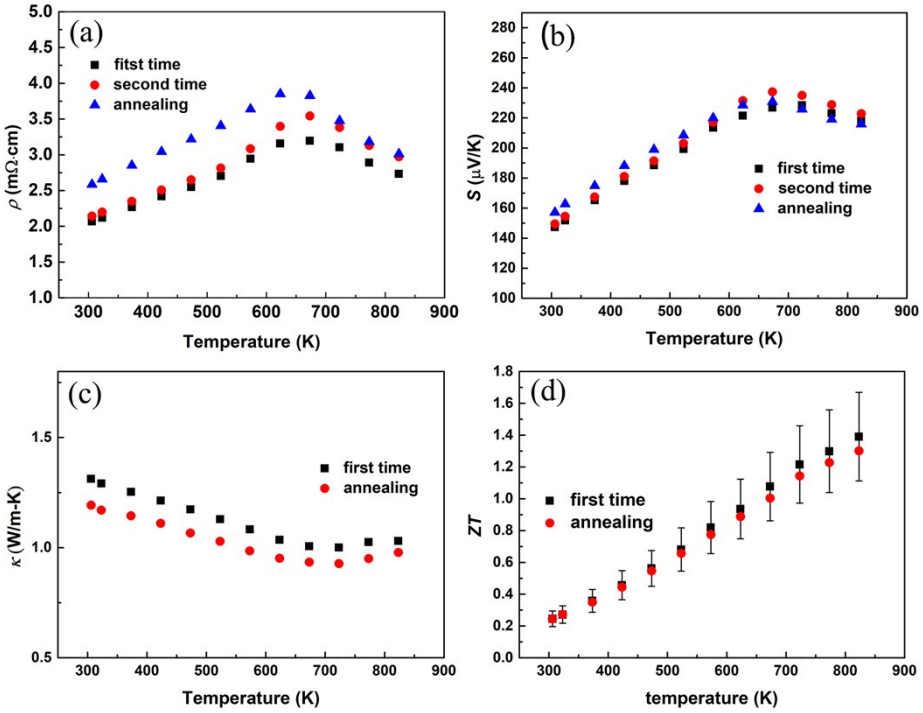

Fig. S3 (a) electrical resistivity and (b) Seebeck coefficient of repeat measurement of the same sample, the results of annealed samples are included. (c) thermal conductivity and (d) *ZT* values of annealed samples.

Due to the nano-inclusion and low thermal conductivity, stability of the samples should be tested. The repeat measurement shows similar electrical resistivity and Seebeck coefficient. Again, the sample with a composition of $Pb_{0.08}Ge_{0.92}MnTe_2$ was vacuum sealed in the glass tubes and annealed at 823 K for 24 h. From the results, the low thermal conductivity was also maintained as well as a comparable *ZT*.

FTIR spectroscopy analysis of samples

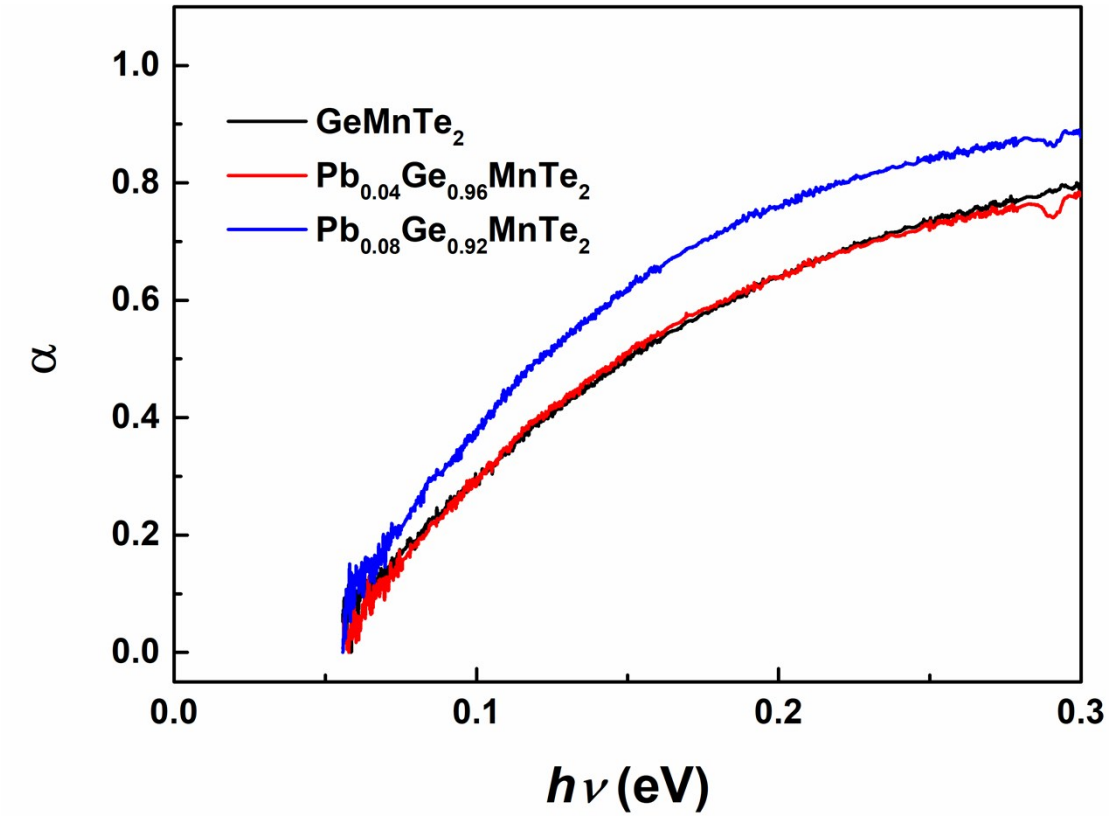

Fig. S4. The absorbancy (α) versus photon energy ($h\nu$) of samples.

The FTIR spectroscopy was applied to study the band gap of synthesized samples. Due to the high carrier concentration (~ 10^{21} cm^{-3}), the free carriers absorption is strong that makes it hard to determine the real band gap of these samples.

Measured Cp of samples

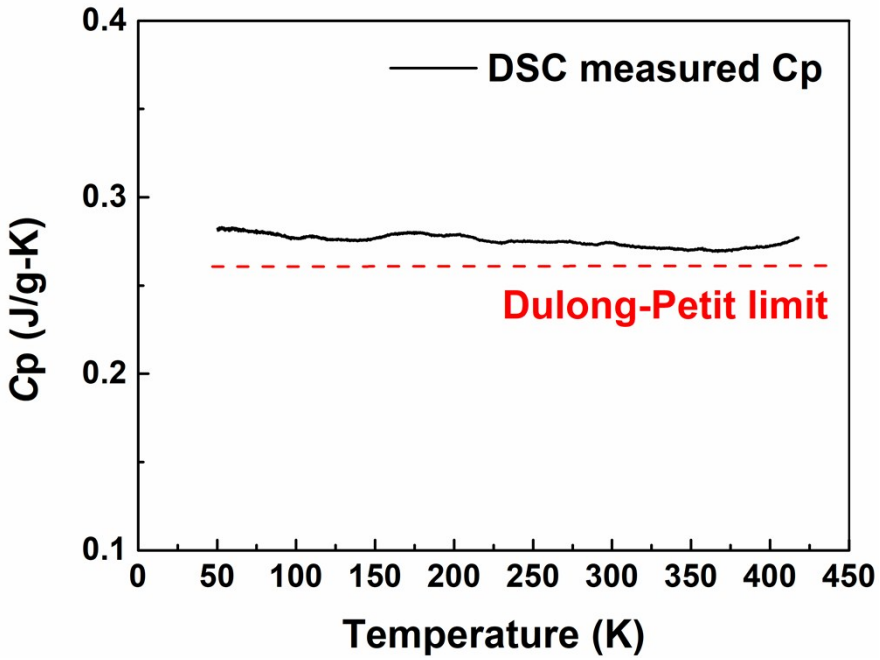

Fig. S5. Measured Cp value of $Pb_{0.08}Ge_{0.92}MnTe_2$ sample.

The experimental Cp value was collected by DSC measurement, which is close to the Dulong-Petit limit value. For good compare with the literature value, we applied a Dulong-Petit limit value to calculate the thermal conductivity in this work.

Lattice thermal conductivity modelling

The lattice thermal conductivity could be expressed as the following equations [1]

$$\kappa_{\mathrm{L}}=\frac{1}{3}\int_0^{\omega_{\max}} C_{\mathrm{s}}(\omega,T)\tau(\omega,T){v_{\mathrm{g}}}^2(\omega)\mathrm{d}\omega \tag{S1}$$

When at high temperatures, the heat capacity is

$$C_{\mathrm{s}}(\omega)=\frac{3k_{\mathrm{B}}\omega^2}{2\pi^2 v_{\mathrm{g}} v_{\mathrm{p}}^2} \tag{S2}$$

where $v_g = d\omega/dk$ is the phonon group velocity, $v_p = \omega/k$ is the phase velocity.

The relaxation time for phonon-phonon scattering (τ_{pp}), grain boundary scattering (τ_{GB}) and point defect scattering (τ_{PD}) could be estimated as the following expression, respectively. [2-4]

$$\tau_{\mathrm{pp}}^{-1}=\mathrm{A}\frac{\omega^2 T}{v_{\mathrm{g}} v_{\mathrm{p}}^2} \tag{S3}$$

$$\tau_{\mathrm{GB}}^{-1}=v_{\mathrm{g}}/d \tag{S4}$$

$$\tau_{\mathrm{PD}}^{-1}=\mathrm{B}\frac{\omega^4}{v_{\mathrm{g}} v_{\mathrm{p}}^2} \tag{S5}$$

Where A and B are material-dependent parameters, d is the average grain size.

Then the total relaxation time is calculated by

$$\tau^{-1}=\tau_{\mathrm{pp}}^{-1}+\tau_{\mathrm{GB}}^{-1}+\tau_{\mathrm{PD}}^{-1} \tag{S6}$$

With Eqs. S5 and S6, Eqs. S1 becomes:

$$\kappa_{\mathrm{L}}=\frac{k_B}{2\mathrm{A}\pi^2}\int_0^{\omega_{\max}}\frac{v_{\mathrm{g}}^2}{1+\frac{\mathrm{B}\omega^2}{\mathrm{A}T}+\frac{v_{\mathrm{g}}\omega^4}{\mathrm{A}Td}}d\omega \tag{S7}$$

It should be noted that

$$\frac{k_B}{2\mathrm{A}\pi^2}\int_0^{\omega_{\max}} v_{\mathrm{g}}^2 d\omega=\frac{k_{\mathrm{B}}k_{\max}}{\mathrm{A}\pi^3}v_{\mathrm{s}}^3 \tag{S8}$$

Where Born von Karman approximation of the phonon dispersion relation is used

$$\omega=\frac{2}{\pi}v_{\mathrm{s}}k_{\max}\sin(\frac{\pi}{2}\frac{k}{k_{\max}}) \tag{S9}$$

From Eqs. S7 and S8, we could conclude that the real expression of the lattice thermal conductivity may contain v_s^5 parts if we use the taylor expansion to solve the integral. So a v_s^3 law would overestimate the reduction of lattice thermal conductivity. It also worth noting that more accurate simulation could be carried out with Eqs. S7, but due to the lack of the material-dependent parameter, a simplified model is used here.

Reference

[1] M.Kaviany, Heat transfer Physics, 1st ed., Cambridge University Press, New York 2008.

[2] M. Roufosse, P. G. Klemens, *Phys. Rev. B* **1973**, *7*, 5379.

[3] C. A. Ratsifaritana, P. G. Klemens, *Int. J. Thermophys.* **1987**, *8*, 737.

[4] G. Tan, S. Hao, R. C. Hanus, X. Zhang, S. Anand, T. P. Bailey, A. J. E. Rettie, X. Su, C. Uher, V. P. Dravid, G. J. Snyder, C. Wolverton, M. G. Kanatzidis, *ACS Energy Lett.* **2018**, *3*, 705.