Supporting Information

Experimental details

To synthesis the Ag_9GaSe_6 compound, high purity raw elements, Ag (shots, 99.999%, Alfa Aesar), Ga (shots, 99.999%, Alfa Aesar), and Se (pieces, 99.999%, Alfa Aesar) were weighted out in stoichiometric proportions and then sealed in silica tubes under vacuum. The tubes were heated to 1373 K and held at this temperature for 12 hours before quenching into cold water. Then, the quenched ingots were annealed at 873 K for 5 days. Finally, the products were ground into fine powders and sintered by Spark Plasma Sintering (Sumitomo SPS-2040) at 813–833 K under a pressure of 40 MPa for 10 minutes. High densities (> 99% of the theoretical density) were obtained for all samples.

Characterization methods

The phase purity and crystal structure were examined by the powder X-ray diffraction (PXRD) with Cu Kα radiation at 300 K. The electrical conductivity and Seebeck coefficient were measured by using ZEM-3 (ULVAC) from 300 to 800 K. The thermal conductivity was calculated from $\kappa = DC_p\rho$, where the thermal diffusivity (D) was obtained by using a laser flash method (Netzsch LFA 457), the specific heat (C_p) was measured by differential scanning calorimetric (Netzsch DSC 404F3), and the density (ρ) was measured by using the Archimedes method. Hall coefficient (R_H) was measured in a Physical Property Measurement System (Quantum Design) by sweeping the magnetic field up to 3 T in both positive and negative directions. Hall carrier concentration (p_H) and Hall mobility (μ_H) were estimated by $p_H = 1/eR_H$ and $\mu_H = \sigma R_H$, respectively. Measurements of the transverse and longitudinal sound velocities were performed on a sample with a diameter of 10 mm and a thickness of 2 mm using an Advanced Ultrasonic Measurement System (TECLAB).

Calculation details[1-5]

Average sound velocity (v_a) is calculated from the sound velocity

$$\frac{1}{\upsilon_a}=\left[\frac{1}{3}(\frac{1}{\upsilon_l^3}+\frac{2}{\upsilon_t^3})\right]^{1/3} , \qquad (1)$$

where ν_l is the longitudinal sound velocity and ν_t is the transverse sound velocity.

Young's modulus (E) is calculated by

$$E=\frac{\rho\nu_t^2(3\nu_l^2-4\nu_t^2)}{(\nu_l^2-\nu_t^2)} , \qquad (2)$$

where ρ is the sample density.

Poisson ratio (ν_p) is calculated by

$$\nu_p=\frac{1-2(\nu_t/\nu_l)^2}{2-2(\nu_t/\nu_l)^2} . \qquad (3)$$

Shear modulus (G) is calculated by

$$G=\frac{E}{2(1+\nu_p)} . \qquad (4)$$

The Gruneisen parameter (γ) is calculated by

$$\gamma=\frac{3}{2}(\frac{1+\nu_p}{2-3\nu_p}) . \qquad (5)$$

Debye temperature (θ_D) is calculated by

$$\theta_D=\frac{h}{k_B}(\frac{3N}{4\pi V})^{1/3}\nu_a , \qquad (6)$$

where h is Planck's constant, k_B is the Boltzmann constant, N is the number of atoms in the primitive unit cell (N = 64 for Ag_9GaSe_6) and V is the unit cell volume.

Phonon mean free path (l) is calculated by

$$\kappa_L=\frac{1}{3}C_V\nu_a l , \qquad (7)$$

where C_V is the heat capacity at constant volume.

Table S1 Sound velocities (longitudinal sound velocity ν_l, transverse sound velocity ν_t, average sound velocity ν_a) and lattice thermal conductivity κ_L of Ag_9GaSe_6. The elastic properties (Young's modulus E, Shear modulus G, Poisson ratio ν_p), the Grüneisen parameter γ, Debye temperature θ_D and phonon mean free path l are derived based on Eq. (1)-(7) based on the measured sound velocity.

T (K)	κ_L ($Wm^{-1}K^{-1}$)	v_l (ms^{-1})	v_t (ms^{-1})	v_a (ms^{-1})	E (GPa)	G (GPa)	v_p	γ	θ_D (K)	l (nm)
300	0.23	2865	1130	1281	26.25	9.321	0.408	2.72	137.1	0.28

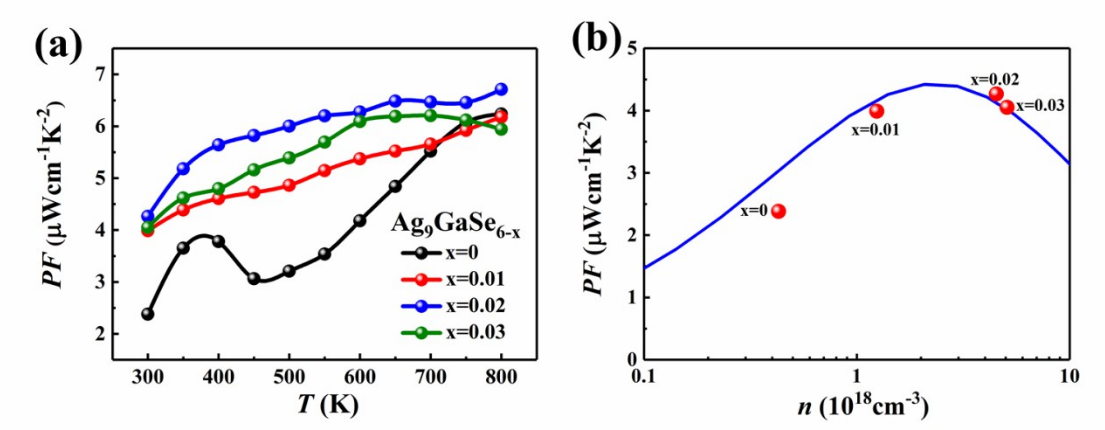

Fig. S1 (a) Temperature dependence and (b) Hall carrier concentration (*n*) dependence of *PFs* for Ag_9GaSe_{6-x}. The solid curve in Fig. S1b shows the calculated curve based on the single parabolic band (SPB) model with $m^* = 0.11m_e$ dominated by acoustic phonon scattering.

References

1 K. Kurosaki, A.Kosuga, H. Muta, M. Uno and S. Yamanaka, *Appl. Phys. Lett.*, 2005, **87**, 061919.

2 Y. L. Pei, J. Q. He, J. F. Li, F. Li, Q. J. Liu, W. Pan, C. Barreteau, D. Berardan, N. Dragoe and L. D. Zhao, *NPG Asia Mater.*, 2013, **5**, e47.

3 C. L. Wan, Z. X. Qu, Y. He, D. Luan and W. Pan, *Phys. Rev. Lett.*, 2008, **101**, 085901.

4 D. S. Sanditov and V. N. Belomestnykh, *Tech. Phys.*, 2011, **56**, 1619.

5 J. Y. Cho, X. Shi, J. R. Salvador, G. P. Meisner. J. Yang, H. Wang, A. A. Wereszczak, X. Zhou and C. Uher, *Phys. Rev. B*, 2011, **84**, 085207.