Supporting Information

Experimental details

To synthesis the Ag$_9$GaSe$_6$ 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 K$\alpha$ 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 ($\rho$) 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 ($\mu_H$) 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 ($v_o$) is calculated from the sound velocity
where $v_l$ is the longitudinal sound velocity and $v_t$ is the transverse sound velocity.

Young’s modulus ($E$) is calculated by

$$E = \frac{\rho v_l^2 (3v_t^2 - 4v_l^2)}{(v_t^2 - v_l^2)},$$  \quad (2)

where $\rho$ is the sample density.

Poisson ratio ($\nu_p$) is calculated by

$$\nu_p = \frac{1 - 2(v_t/v_l)^2}{2 - 2(v_t/v_l)^2}. \quad (3)$$

Shear modulus ($G$) is calculated by

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

The Gruneisen parameter ($\gamma$) is calculated by

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

Debye temperature ($\theta_D$) is calculated by

$$\theta_D = \frac{h}{k_B} \left( \frac{3N}{4\pi V} \right)^{1/3} v_a,$$  \quad (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$_9$GaSe$_6$) and $V$ is the unit cell volume.

Phonon mean free path ($l$) is calculated by

$$\kappa_L = \frac{1}{3} C_V v_a l,$$  \quad (7)

where $C_V$ is the heat capacity at constant volume.

Table S1 Sound velocities (longitudinal sound velocity $v_l$, transverse sound velocity $v_t$, average sound velocity $v_a$) and lattice thermal conductivity $\kappa_L$ of Ag$_9$GaSe$_6$. The elastic properties (Young’s modulus $E$, Shear modulus $G$, Poisson ratio $\nu_p$), the Gruneisen parameter $\gamma$, Debye temperature $\theta_D$ and phonon mean free path $l$ are
derived based on Eq. (1)-(7) based on the measured sound velocity.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\kappa_l$ (Wm$^{-1}$K$^{-1}$)</th>
<th>$\nu_l$ (ms$^{-1}$)</th>
<th>$\nu_i$ (ms$^{-1}$)</th>
<th>$\nu_a$ (ms$^{-1}$)</th>
<th>$E$ (GPa)</th>
<th>$G$ (GPa)</th>
<th>$\nu_F$</th>
<th>$\gamma$</th>
<th>$\theta_0$ (K)</th>
<th>$l$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
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<td>2865</td>
<td>1130</td>
<td>1281</td>
<td>26.25</td>
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<td>0.408</td>
<td>2.72</td>
<td>137.1</td>
<td>0.28</td>
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</tbody>
</table>

Fig. S1 (a) Temperature dependence and (b) Hall carrier concentration ($n$) dependence of $PF_s$ for Ag$_9$GaSe$_{6-x}$. 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