Chapter 3

Thermoelectric performance of Na-doped GeSe
Abstract

Recently, hole-doped GeSe materials have been predicted to exhibit extraordinary thermoelectric performance owing largely to extremely low thermal conductivity. However, experimental research on the thermoelectric properties of GeSe has received less attention. Here, we have synthesized polycrystalline Na-doped GeSe compounds, characterized their crystal structure and measured their thermoelectric properties. The Seebeck coefficient decreases with increasing Na content up to $x = 0.01$, due to an increase in the hole carrier concentration, and remains roughly constant at higher concentrations of Na, consistent with the electrical resistivity variation. However, the electrical resistivity is large for all samples leading to low power factors. Powder X-ray diffraction and scanning electron microscopy (SEM)/energy-dispersive spectrometry (EDS) results show the presence of a ternary impurity phase within the GeSe matrix for all doped samples, which suggests that the optimal carrier concentration cannot be reached by doping with Na. Nevertheless, the lattice thermal conductivity and carrier mobility of GeSe are similar to those of polycrystalline samples of the leading thermoelectric material SnSe, leading to quality factors of comparable magnitude. This implies that GeSe shows promise as a thermoelectric material if a more suitable dopant can be found.

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Thermoelectric performance of Na-doped GeSe

3.1 Introduction

Thermoelectric materials (TE) have been intensively investigated over the past decades due to their ability to convert waste heat to electricity, especially in view of the energy crisis and concern for the environment. The performance of a TE material is determined by its dimensionless figure of merit \((zT)\), defined as \(zT = (S^2\sigma T)/\kappa\), where \(S\) is the Seebeck coefficient, \(\sigma\) the electrical conductivity, \(\kappa\) the total thermal conductivity and \(T\) the absolute temperature. There is an ongoing search for new materials with high TE efficiency, especially using environmentally friendly and abundant elements, as well as the development of several approaches to improve the \(zT\) of existing materials via optimizing the parameters \(S\), \(\sigma\) and \(\kappa\). Chalcogenide compounds have been extensively studied and their TE performance has shown significant enhancement in recent years. High thermoelectric performance has recently been reported for single crystals of SnSe, largely due to their ultralow thermal conductivity. High \(zT\) values and low thermal conductivities are also reported in polycrystalline SnSe, but their power factor values are significantly lower than single crystals. Germanium telluride (GeTe) based materials have also been widely studied for their promising thermoelectric properties. However, germanium selenide (GeSe) has received little attention for thermoelectric applications despite its use in other applications such as optoelectronics, resistive memory cells, glass-forming materials for photonic devices with thin-film structures, photovoltaic applications, and resistive switching materials.

GeSe is a \(p\)-type narrow band gap semiconductor \((E_g = 1.1 - 1.2\) eV) which adopts a layered orthorhombic crystal structure (Figure 3.1a and b) at room temperature with space group \(Pnma\), isostructural with GeS, SnS and SnSe. Only a few reports have been published on the transport properties of GeSe; these mostly focus on the electrical conductivity with only two reports on the thermal conductivity of GeSe. Recently, a theoretical study predicted the thermoelectric performance of orthorhombic IV-VI compounds GeS, SnSe, SnS, and GeSe using density functional theory combined with Boltzmann transport theory. It is proposed that GeS, SnS and GeSe show comparable thermoelectric properties to SnSe, which makes them promising candidates for high efficiency thermoelectric applications.
modelling study using similar methods predicted extremely high thermoelectric performance in hole-doped GeSe crystals along the b- crystallographic direction, with a figure of merit ranging from 0.8 at 300 K to 2.5 at 800 K. This represents an even higher calculated figure of merit than that of hole-doped SnSe, which holds the current experimental record for high $zT$ among bulk systems.\textsuperscript{46} Thus, it is highly desired to experimentally explore the thermoelectric performance of GeSe-based materials. A recent study\textsuperscript{44} reports a maximum $zT$ of 0.16 at 700K for Ag-doped polycrystalline Ge$_{0.79}$Ag$_{0.01}$Sn$_{0.2}$Se by achieving carrier concentrations of $\sim$10$^{18}$ cm$^{-3}$. Better TE performance is predicted at higher carrier concentrations, which was impossible to obtain by silver doping.

In this study, we have fabricated polycrystalline pristine and Na-doped GeSe samples and measured their thermoelectric properties. We have found that the lattice thermal conductivity of our samples is significantly higher than the ultralow values predicted theoretically,\textsuperscript{46} but at $<$0.8 W m$^{-1}$ K$^{-1}$ above 550 K for the pristine sample is in good agreement with the previous experimental report in Ref. 44. Doping with 1% and 2% Na reduces $\kappa$ to $<$0.7 W m$^{-1}$ K$^{-1}$ and $\sim$0.5 W m$^{-1}$ K$^{-1}$ respectively in
the same temperature range. However, the power factors of the Na-doped samples are low due to the formation of Na-rich precipitates, which prevents optimal carrier concentrations from being reached. Nevertheless, the measured carrier mobility of GeSe is comparable with that of SnSe, thus GeSe may be a promising thermoelectric material if a more suitable dopant is identified.

3.2 Methods

3.2.1 Sample fabrication

Synthesis. Polycrystalline Ge$_{1-x}$Na$_x$Se samples with $x = 0.00, 0.01, 0.02$ and $0.04$ were synthesized using solid state reaction technique. Stoichiometric ratios of high purity elements, Ge (99.999%, Alfa Aesar), Se (99.999%, Alfa Aesar) and Na (99%, Aldrich), were weighed in an argon atmosphere glove box with a total mass of 10 g and loaded into carbon-coated quartz tubes. The tubes were sealed under vacuum, slowly heated to 1223 K and held at that temperature for 10 hours. The samples were then quenched in cold water, followed by annealing at 673 K for 72 hours. The ingots obtained were hand ground into fine powder using an agate mortar and pestle and loaded into a 12 mm diameter graphite die. The powders were then sintered using spark plasma sintering (SPS) at 623 K for 30 minutes under an axial pressure of 40 MPa in vacuum.

3.2.2 Materials Characterization

X-Ray diffraction. X-ray diffraction (XRD) measurements were performed using a GBC Scientific X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 25 mA) at room temperature. The structural parameters were extracted from the X-ray diffraction patterns by the Rietveld refinement method using the GSAS software suite.

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Electron microscopy analysis. The microstructures of the samples were studied using a high resolution scanning electron microscope (SEM), JEOL JSM-7001 equipped with an energy-dispersive X-ray spectrometer (EDS).

Transport properties measurements. The Hall coefficient \( R_H \) was measured by an in-house-built apparatus using the van der Pauw technique (perpendicular to the hot-pressing direction) in vacuum under magnetic fields of up to ±1.5 T. The Hall carrier concentration, \( n \), was obtained using \( n = 1 / e R_H \), where \( e \) is the elementary charge, and \( n, R_H \) and \( \sigma \) are the carrier concentration, Hall coefficient and electrical conductivity, respectively. Disc-shaped pellets with densities ~94% of the theoretical density, 12 mm diameter and 2 mm thickness were used for this measurement. The electrical conductivity (\( \sigma \)) and Seebeck coefficient (\( S \)) were measured simultaneously under 0.1 atm helium from room temperature to 573 K using a Linseis LSR-3 instrument. The samples for measurement were cut from pressed pellets and polished into a parallelepiped shape; measurements were performed in the in-plane direction. The thermal diffusivity, \( D \), was measured by the laser flash diffusivity method (Linseis LFA 1000) in the out-of-plane direction over the temperature range 300-573 K. The specific heat capacity \( (C_p) \) was calculated using the equation
\[
C_p(\text{GeSe, } 298.15-940 \text{ K}) = (46.777+15.099 \times 10^{-3}T - 0.0316 \times 10^{-6}T^2 - 1.231 \times 10^{-5}T^2) \text{ J.K}^{-1}\text{.mol}^{-1}.
\]
The thermal conductivity \( (\kappa) \) was calculated using \( \kappa = \rho D C_p \), where the density \( (\rho) \) of the pellets was calculated by measuring the mass and dimensions.

3.3 Results and discussion

Figure 3.2 shows the room temperature X-ray powder diffraction (XRD) patterns of the \( \text{Ge}_{1-x}\text{Na}_x\text{Se} \) compounds \((x = 0.00, 0.01, 0.02 \text{ and } 0.04) \). The main peaks of all samples could be indexed based on the orthorhombic \( \alpha \)-GeSe structure with the unit cell parameters \( a = 10.8419(9) \text{ Å}, b = 3.8389(6) \text{ Å} \) and \( c = 4.3951(7) \text{ Å} \) (space group, \( Pnma \)). Each primitive unit cell of \( \alpha \)-GeSe phase consists of eight atoms, which form two zig-zag double layers. Each atom is coordinated to three nearest neighbors within its own layer and three more distant neighbors in adjacent layers;
there is weak Van der Waals bonding between adjacent layers and strong covalent interactions within the layers.\textsuperscript{38,49,50} This phase is reported to transform to the high symmetry cubic rocksalt structure (\textit{Fm} \textit{3} \textit{m}, \( \beta \)-GeSe) at a temperature of 853 K (\( a = 5.73 \) Å).\textsuperscript{51-53} Table 3.1 lists the refined lattice parameters of the Ge\(_{1-x}\)Na\(_x\)Se (\( x = 0.00, 0.01, 0.02 \) and 0.04) compounds. There is no clear variation of lattice parameter with dopant concentration. X-ray diffraction analysis was performed on powders and pellets. For powder samples there is strong preferred orientation along the [100] direction (that is, the layer stacking direction in the crystallites tends to be perpendicular to the sample surface) which makes the [400] peak very strong. A similar degree of preferred orientation was observed in the x-ray diffraction patterns of the pellets, as shown in Figure 3.2b. This implies that the thermal conductivity was measured more along the \( a \)-direction, whereas the electrical resistivity and Seebeck coefficient measurements were performed largely in the \( bc \)-plane. Microstructural analysis of lightly and heavily doped GeSe samples was conducted by scanning electron microscopy (SEM). Figures 3.3a and b show representative back-scattered electron images (BSE) of Ge\(_{0.99}\)Na\(_{0.01}\)Se and Ge\(_{0.96}\)Na\(_{0.04}\)Se respectively. Precipitates are distributed in the GeSe matrix for both samples. The precipitates appear to vary in size and concentration with respect to the Na concentration. Precipitates of < 1 \( \mu \)m are most common in Ge\(_{0.99}\)Na\(_{0.01}\)Se, whereas those observed in Ge\(_{0.96}\)Na\(_{0.04}\)Se are typically 1-5 \( \mu \)m in size. The concentration of precipitates also appears to be increased for Ge\(_{0.96}\)Na\(_{0.04}\)Se.
Figure 3.2: (a) Room temperature XRD patterns of the powder Ge$_{1-x}$Na$_x$Se ($x = 0.00$, 0.01, 0.02 and 0.04) samples. The star indicates a graphite peak originating from the carbon-coated quartz tube and the circle at ~30 degrees indicates a peak from the sample holder. (b) Observed (black data points), fitted (red line) and difference (blue line) XRD profiles for the $x = 0.02$ sample. The fit used the March-Dollase preferred orientation model incorporated in the GSAS software. The green line represents the best fit obtained without any preferred orientation model. The inset shows a closer view of the fits; the symbols G and S indicate graphite and sample holder peaks, respectively.

Figure 3.3: BSE images of (a) Ge$_{0.99}$Na$_{0.01}$Se and (b) Ge$_{0.96}$Na$_{0.04}$Se. A secondary phase (darker grey) is observed in the GeSe matrix (lighter grey). (c) EDS characterization: BSE images of Ge$_{0.96}$Na$_{0.04}$Se showing a secondary phase within the GeSe matrix, with EDS elemental mapping for Ge, Se and Na. The secondary phase appears to be higher in Na and Se concentration and lower in Ge concentration than the surrounding GeSe matrix.
Table 3.1: Lattice parameters of Ge$_{1-x}$Na$_x$Se ($x = 0, 0.01, 0.02,$ and 0.04) compounds

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lattice parameter(Å)</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>GeSe</td>
<td>10.8419(8)</td>
<td>3.8390(6)</td>
<td>4.3950(7)</td>
</tr>
<tr>
<td>Ge$<em>{0.99}$Na$</em>{0.01}$Se</td>
<td>10.8437(4)</td>
<td>3.8389(7)</td>
<td>4.3978(8)</td>
</tr>
<tr>
<td>Ge$<em>{0.98}$Na$</em>{0.02}$Se</td>
<td>10.8455(2)</td>
<td>3.8463(3)</td>
<td>4.3880(4)</td>
</tr>
<tr>
<td>Ge$<em>{0.96}$Na$</em>{0.04}$Se</td>
<td>10.8398(2)</td>
<td>3.8376(8)</td>
<td>4.3966(7)</td>
</tr>
</tbody>
</table>

To probe the chemical composition of the secondary phase, energy dispersive X-ray spectroscopy (EDS) mapping was used. Figure 3.3c shows the EDS elemental map of precipitates within the GeSe matrix for the Ge$_{0.96}$Na$_{0.04}$Se sample. The precipitates are richer in Na and Se and poorer in Ge than the matrix, suggesting that sodium doping induces the formation of a ternary sodium germanium selenide as a secondary phase. The concentration of precipitates is too low to give rise to extra peaks in the XRD patterns, thus the phase could not be identified.

Figure 3.4a shows the total thermal conductivity, $\kappa$, of the Ge$_{1-x}$Na$_x$Se ($x = 0.00, 0.01, 0.02$ and $0.04$) compounds as a function of temperature in the range of 300-573 K. The thermal conductivity for all samples decreases with temperature. The thermal conductivity of the undoped sample is 1.57 W m$^{-1}$ K$^{-1}$ at 300 K which is reduced to 0.76 W m$^{-1}$ K$^{-1}$ at 573 K. This is significantly lower than the previously measured values in polycrystalline samples of 2.2 W m$^{-1}$ K$^{-1}$ and 1.3 W m$^{-1}$ K$^{-1}$ at 300 K and 573 K respectively in Ref. 43, but comparable to the values of 1.8 W m$^{-1}$ K$^{-1}$ and 0.8 W m$^{-1}$ K$^{-1}$ reported in Ref. 44 at the same temperatures. We note that the Dulong-Petit approximation of the specific heat capacity was used for GeSe in Ref. 44; if used for our samples, the thermal conductivity plotted in Figure 3.4a would be $\sim$10% lower at 573 K. Figure 3.4a also shows that the total thermal conductivity decreases with increasing dopant concentration and that samples with precipitates possess much lower thermal conductivity than lightly-doped samples. The lattice thermal conductivity, (Figure 3.4b), was obtained by subtracting the electronic contribution, $\kappa_e$, from the measured total thermal conductivity $\kappa = \kappa_{total} - \kappa_e$. The value of $\kappa_e$ can be estimated via the Wiedemann-Franz law, $\kappa_e = L\sigma T$, where $\sigma$ is the electrical conductivity and $L$ is the Lorenz number, which was calculated by using a single parabolic band model with the acoustic phonon scattering assumption.$^{54}$ These estimated lattice
thermal conductivities are compared with the previously predicted\textsuperscript{46} and measured\textsuperscript{44} values in Figure 3.4b. The results indicate that the lattice thermal conductivity is the predominant part of the total thermal conductivity in agreement with the low carrier concentration of $\sim 2 \times 10^{16}$ cm$^{-3}$ obtained by Hall effect measurement for the pristine sample at room temperature, and indicating that the electronic contribution to the total thermal conductivity is negligible ($\sim 10^{-6} - 10^{-5}$ W m$^{-1}$ K$^{-1}$). However, the lattice thermal conductivity of the undoped sample is higher than the extraordinarily low values of $\sim 0.6$ and $0.4$ W m$^{-1}$ K$^{-1}$ predicted for GeSe along the b axis\textsuperscript{46} at 300 K and 573 K respectively. The lattice thermal conductivity is reduced with Na content up to $x = 0.04$, for which we measure $\kappa_l = 0.44$ W m$^{-1}$ K$^{-1}$ at 573 K. This originates from the scattering of phonons at an increased density of interfaces and defects due to the distribution of precipitates within the matrix\textsuperscript{55,56}; such a decrease in $\kappa_l$ has also been observed for Ag-doped GeSe\textsuperscript{44} although the possible presence of precipitates was not investigated in that study.

In the calculations of thermal conductivity in Ref. 46, charge carrier concentrations of $4 \times 10^{19} - 6.5 \times 10^{19}$ cm$^{-3}$ were used since this range is predicted to yield optimal $zT$. The electronic component of the thermal conductivity for this range of carrier concentration $\kappa_e$ remains small, of the order of 0.2 W m$^{-1}$ K$^{-1}$ at 600 K, thus the calculations predict that the total thermal conductivity of GeSe should be even lower.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure3_4.png}
\caption{(a) Measured total thermal conductivity, $\kappa$, of Ge$_{1-x}$Na$_x$Se ($x = 0.00$, 0.01, 0.02 and 0.04) in the temperature range 300-573 K. (b) Calculated lattice thermal conductivity, $\kappa_l$, of Ge$_{1-x}$Na$_x$Se ($x = 0.00$, 0.01, 0.02 and 0.04) compared with theoretical values\textsuperscript{46} calculated along b axis and experimental values.\textsuperscript{44}}
\end{figure}
than that of SnSe. This would result in an extremely high predicted figure of merit of 2.1 at 600 K. However, our results suggest that the predicted values for thermal conductivity are underestimated unless the optimal carrier concentration can be reached while also maintaining a distribution of precipitates.

Table 3.2 compares the room temperature transport properties of Na-doped polycrystalline GeSe in our study compared to another recent experimental report in which pellets with comparable preferred orientation to our samples were measured using the same geometry. The thermal conductivities of the low-doped samples are very similar, but our study yields lower thermal conductivity for heavily doped samples. The electrical resistivity of our samples is much lower than the reported values in Ref. 44 for samples with the same composition (Ge$_{0.98}$Na$_{0.02}$Se and Ge$_{0.96}$Na$_{0.04}$Se).

Table 3.2: Transport properties of GeSe doped with Na at 300 K

<table>
<thead>
<tr>
<th>Composition</th>
<th>S(μVK$^{-1}$)</th>
<th>ρ(mΩcm)</th>
<th>κ (Wm$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{0.98}$Na$</em>{0.02}$Se$^{44}$</td>
<td>627</td>
<td>6.81×10$^5$</td>
<td>1.48</td>
</tr>
<tr>
<td>Ge$<em>{0.96}$Na$</em>{0.04}$Se$^{44}$</td>
<td>631</td>
<td>2.99×10$^7$</td>
<td>1.40</td>
</tr>
<tr>
<td>Ge$<em>{0.94}$Na$</em>{0.06}$Se$^{44}$</td>
<td>501</td>
<td>3.39×10$^7$</td>
<td>1.43</td>
</tr>
<tr>
<td>Ge$<em>{0.99}$Na$</em>{0.01}$Se (our work)</td>
<td>471</td>
<td>0.79×10$^6$</td>
<td>1.47</td>
</tr>
<tr>
<td>Ge$<em>{0.98}$Na$</em>{0.02}$Se (our work)</td>
<td>508</td>
<td>1.71×10$^6$</td>
<td>1.23</td>
</tr>
<tr>
<td>Ge$<em>{0.96}$Na$</em>{0.04}$Se (our work)</td>
<td>505</td>
<td>1.84×10$^6$</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The electrical resistivity of the Ge$_{1-x}$Na$_x$Se samples with x = 0.00, 0.01, 0.02 and 0.04 is shown as a function of temperature in the range 300-580 K in Figure 3.5a. The electrical resistivity decreases monotonically with temperature for all samples and remains roughly constant at temperatures above 450 K. At room temperature, sodium doping reduces the electrical resistivity of GeSe significantly from 1.0 × 10$^6$ mΩ cm for the undoped sample to 7.9 × 10$^4$ mΩ cm for x = 0.01, roughly by a factor of 12. However, further doping beyond x = 0.01 has no beneficial effect; the electrical resistivity of the x = 0.02 and x = 0.04 samples is slightly higher, probably because the doping limit is soon reached and additional sodium is incorporated into the precipitate phase. The Seebeck coefficients ($S$) of all samples as a function of the temperature are shown in figure 3.5b. The positive values over the entire
temperature range indicate that all samples are p-type semiconductors. The Seebeck coefficients increase with temperature over the whole temperature range except for the undoped sample which exhibits a maximum value at ~450 K. The samples show no sign of a bipolar effect over the temperature range in which the measurements were performed (300-580 K). We note that a bipolar effect was observed at temperatures above 600 K (above the selected range of the current study), in previous work.\textsuperscript{44} This effect is commonly observed in narrow band gap materials. The contribution of minority carriers to the transport properties of such materials increases with temperature due to thermal excitation of minority carriers across the band gap.\textsuperscript{57}

In the case of GeSe, since the band gap is wide (~1.1 eV\textsuperscript{35,36}), at temperatures below 600 K the probability of thermal excitation of the electrons to the conduction band is low, which results in suppression of the bipolar effect in this range of temperatures. Undoped GeSe shows the largest Seebeck coefficient ($S = 990 \mu V/K$) at 450 K. The Seebeck coefficient is smallest throughout the studied temperature range for the $x = 0.01$ sample, whereas the $x = 0.02$ and 0.04 samples exhibit similar and slightly larger values, which is consistent with the variation of the electrical resistivity since both the Seebeck coefficient and electrical resistivity are inversely proportional to the carrier concentration. This indicates that the carrier concentration increases with dopant concentration up to $x = 0.02$, beyond which it remains roughly constant. This

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.5.png}
\caption{(a) Logarithmic temperature dependence of the electrical resistivity of Ge\textsubscript{1-x}Na\textsubscript{x}Se ($x = 0.00, 0.01, 0.02$ and 0.04) in the temperature range 300-580 K. (b) Temperature dependence of the Seebeck coefficient of Ge\textsubscript{1-x}Na\textsubscript{x}Se ($x = 0.00, 0.01, 0.02$ and 0.04) in the temperature range 300-580 K.}
\end{figure}
result is in agreement with the SEM analysis where the concentration of precipitates is shown to increase with dopant concentration (Figure 3.3).

It was first proposed by Chasmar and Stratton\textsuperscript{58} that in order to achieve a higher figure of merit in a thermoelectric semiconducting compound, a material parameter known as the thermoelectric quality factor, $B$, must be improved. The quality factor can be used to evaluate the performance of a thermoelectric material through the combination of several fundamental parameters:\textsuperscript{58-63}

$$B = \frac{k_B^2}{e} \frac{2e(k_B T)^{3/2} N_V \mu_0 m_b^{3/2}}{(2\pi \hbar^3)^{3/2} \kappa_L} T$$

Here $k_B$ is the Boltzmann constant, $\hbar$ is the reduced Planck constant, $N_V$ is the band degeneracy, $m_b^*$ is the density of states effective mass of a single band, $\mu_0$ is the mobility at the non-degenerate limit, $T$ is the temperature, and $\kappa_L$ is the lattice thermal conductivity. The potential of doped GeSe compounds as good thermoelectric materials can be evaluated by comparing the quality factor of undoped GeSe with that of SnSe, assuming similar band structures. Table 3.3 shows the quality factors estimated for polycrystalline GeSe and SnSe at 580 K and the parameters used (or ranges of parameters in cases where a quantity has been reported in more than one study). Here we assume that the measured values of mobility correspond to $\mu_0$ at the non-degenerate limit, which has been shown for SnSe to be a valid approximation.\textsuperscript{15}

Taking into account the large uncertainty in these parameters, which are likely to be very sensitive to sample quality and small variations in stoichiometry, the two materials have similar quality factors. Therefore, it is likely that the thermoelectric performance of GeSe can be improved by choosing an effective dopant and by consequent band structure engineering.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$T$ (K)</th>
<th>$\kappa_L$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\mu_0$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe (n-type)</td>
<td>580</td>
<td>0.5-0.75\textsuperscript{14,15,64}</td>
<td>20\textsuperscript{15}*</td>
<td>$(28.54-42.81) \times 10^{45} \times m_b^{*3/2}$</td>
</tr>
<tr>
<td>GeSe</td>
<td>580</td>
<td>0.76</td>
<td>34.75</td>
<td>$48.94 \times 10^{45} \times m_b^{*3/2}$</td>
</tr>
</tbody>
</table>

*value measured at 750 K; $\mu_0 = 45$ cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K.
3.4 Conclusions

In summary, we have investigated the effect of Na doping on the thermoelectric performance of GeSe. We have synthesized Ge$_{1-x}$Na$_x$Se ($x = 0$-0.04) compounds and measured their thermoelectric properties. Our experimental results show that the substitution of Na for Ge in GeSe gives rise to the formation of Na-rich precipitates within the GeSe matrix and thus that Na is an unsuitable dopant for GeSe. Although the power factor of these samples is low because the optimal carrier concentration cannot be reached, GeSe could nevertheless be a promising thermoelectric material if suitably doped because it shows intrinsically low lattice thermal conductivity. The presence of Na-rich precipitates decreases the lattice thermal conductivity by around 50% to ~0.5 W m$^{-1}$ K$^{-1}$ at 500 K, thus a co-doping strategy may be a fruitful approach to optimizing the thermoelectric performance of GeSe. Furthermore, the carrier mobility of GeSe is similar to that of the leading thermoelectric material SnSe, giving a similar thermoelectric quality factor. Therefore, identifying an effective dopant might lead to significant improvement in the thermoelectric figure of merit in GeSe-based materials.
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