n-type SnSe, Oriented-Nanoplate Based Pellets for High Thermoelectric Performance

Yubo Luo, Yun Zheng, Zhongzhen Luo, Shiqiang Hao, Chengfeng Du, Qinghua Liang, Zhong Li, Khiam Aik Khor, Kedar Hippalgaonkar, Jianwei Xu, Qingyu Yan*, Chris Wolverton, Mercouri G. Kanatzidis*

Dr. Y. Luo, Dr. Y. Zheng, Dr. Z. Luo, Dr. C. Du, Dr. Q. Liang, Prof. Q. Yan
School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
E-mail: AlexYan@ntu.edu.sg

Dr. Y. Luo, Dr. Z. Luo, Prof. M. G. Kanatzidis
Department of Chemistry, Northwestern University, Evanston, IL 60208, USA.
E-mail: m-kanatzidis@northwestern.edu

Dr. S. Hao, Prof. C. Wolverton
Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA.

Dr. Z. Li, Prof. K. A. Khor
School of Mechanical and Aerospace Engineering Nanyang Technological University 50 Nanyang Avenue, Singapore 639798, Singapore

Dr. K. Hippalgaonkar, Prof. J. W. Xu
Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research) 2 Fusionopolis Way, Innovis, 138634, Singapore

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We report that electron doped n-type SnSe\textsubscript{2} nanoplates show promising thermoelectric (TE) performance at medium temperatures. After simultaneous introduction of Se deficiency and Cl doping, the Fermi level of SnSe\textsubscript{2} shifts towards the conduction band, resulting in two orders of magnitude increase in carrier concentration and a transition degenerate transport behaviour. In addition, all-scale hierarchical phonon scattering centres, such as point defects, nanograin boundaries, stacking faults and the layered nanostructures cooperate to produce very low lattice thermal conductivity. As a result, an enhanced in-plane ZT\textsubscript{max} of 0.63 was achieved for 1.5 at\% Cl doped SnSe\textsubscript{1.95} pellet at 673 K, which is much higher than the corresponding in-plane ZT of pure SnSe\textsubscript{2} (0.08).

1. Introduction

With the rising demands for energy consumption and the depletion of the fossil fuels, thermoelectric (TE) solid-state energy conversion technology\textsuperscript{[1]} has attracted great attention in reducing the energy consumption and enhancing the energy utilization efficiency, due to their capability to direct convert waste heat into electricity.\textsuperscript{[2]} The thermoelectric performance is evaluated by the dimensionless figure of merit ZT of the materials, as $ZT=S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, $\kappa$ is the thermal conductivity, respectively.\textsuperscript{[3]} Over the past decades, substantial progress has been made to develop high performance TE materials by adopting advanced processing techniques,\textsuperscript{[4]} new material design concepts\textsuperscript{[5]} and band engineering\textsuperscript{[6]}
to traditional TE materials. In addition, pursuing new materials with unique micro/nanostructure\textsuperscript{[7]} and/or special crystal structure\textsuperscript{[8]} also has proven successful in yielding high TE performance.\textsuperscript{[9]}

For practical applications, developing earth-abundant, low cost TE materials with high $ZT$ values is highly desired. In this regard, Pb-free Sn based compounds such as SnSe\textsuperscript{[10]}, SnTe\textsuperscript{[11]}, Mg$_2$Sn\textsuperscript{[12]} and TiNiSn\textsuperscript{[13]} based compounds are considered to be promising for medium temperature TE applications. Recently, the CdI$_2$-type dichalcogenide semiconductor SnSe$_2$ has drawn a lot of interest due to its unique layered structure (Figure S1, Supporting Information), in which the intralayer Sn and Se atoms are covalently bonded in the $ab$ planes and the layers are held together by interlayer van der Waals interactions along the $c$ axis. Thus SnSe$_2$ shows anisotropic electronic and optoelectronic properties.\textsuperscript{[14]} More importantly, theoretical studies\textsuperscript{[15]} have predicted that SnSe$_2$ could be a promising n-type TE material with a predicted high $ZT$ value of 2.95 along the $a$ axis, while a low $ZT$ of 0.68 along $c$ axis at 800 K with a carrier concentration of $10^{20}$ cm$^{-3}$ due to the anisotropic electrical and thermal transport properties.\textsuperscript{[16]} This indicates that the orientation and carrier concentration are the key factors for high TE performance. However, only few experimental studies on SnSe$_2$ have been reported, the low carrier concentration ($\sim$10$^{17}$ cm$^{-3}$) and random-oriented grains still result in low power factor ($\sim$150 $\mu$Wm$^{-1}$K$^{-2}$) and $ZT$ ($\sim$0.2).\textsuperscript{[16b]}

Herein, we employ a defect chemistry approach\textsuperscript{[17]} by simultaneously introducing selenium (Se) deficiency and chlorine (Cl) doping in SnSe$_2$ nanoplate-based pellets, in which the nanoplates show preferable orientation of the (001) planes along the primary surface of the pellet (in-plane). This yields a sharp increase in the in-plane electrical conductivity and power factor. The Se deficiency and chlorine doping is chosen because of their electron donor nature as :
As a result, the 1.5 at% Cl doped SnSe_{1.95} sample exhibits an in-plane power factor of 799.2 \mu Wm^{-1}K^{-2} at room temperature. This value is much higher than that of the pure SnSe_{2} (26.8 \mu Wm^{-1}K^{-2}). Meanwhile, the samples exhibit low lattice thermal conductivity resulting from a wide-frequency phonon scattering by different structural features (e.g. layered nanostructure, stacking faults, nano-sized grains and rich grain boundaries). As a consequence, an enhanced in-plane ZT of 0.63 at 673 K has been obtained for 1.5 at% Cl doped SnSe_{1.95} samples, while the corresponding cross-plane ZT is only 0.38, and the in-plane ZT of pristine SnSe_{2} is only 0.08.

2. Results and discussion

2.1. Phase and microstructure

The SnSe_{2} nanoplate-based pellets were synthesized through a two-step process: (1) the preparation of precursor bulk ingots by a vacuum-sealed high temperature melting process, followed by ball-milling grinding of the ingots; (2) obtaining the nanoplate-based pellets through the recrystallization of grinded precursors in a spark plasma sintering (SPS) process. (See Experimental Section in the Supporting Information for details). The crystal structure and phase of the as-obtained pellets were confirmed with X-ray diffraction (XRD) as illustrated in Figure 1a. The XRD peaks of all samples can be well indexed as the layered SnSe_{2} (JCPDF no. 04-003-1275) without detectable peaks from impurities. This indicates that the Se deficient and Cl/ I doped SnSe_{1.95} samples retain the hexagonal close packed (hcp) crystal structure. In addition, the zoom-in high angle XRD patterns show that the diffraction peaks of the Cl doped SnSe_{1.95} shift to higher 2\theta values as compared to the undoped SnSe_{1.95}, while the diffraction peaks of the I doped SnSe_{1.95} shift to lower 2\theta values comparing to the
undoped SnSe$_{1.95}$ (Figure S2, Supporting Information). It indicates that Cl and I atoms entered into the crystal structure of SnSe$_{1.95}$ and resulted in lattice parameter change because of the difference in radius of Cl$^-$ (1.81 Å)/ I$^-$ (2.20 Å) and Se$^{2-}$ (1.98 Å).

The field emission scanning electron microscopic (FESEM) images (Figure 1b) of the fractured cross section of the samples reveal that the pellets are composed of closely stacked nanoplates. These nanoplates show lateral sizes of about 100-400 nm along their primary surfaces with thicknesses of 20-60 nm. Given that ball-milled powders are randomly oriented submicron-sized grains (Figure S3, Supporting Information), the observed preferential growth along the $ab$ plane of the layered SnSe$_2$ structure arises during SPS. To identify the preferred crystal orientation of the stacked nanoplates, ultrasonic exfoliation was employed to get individual SnSe$_2$ nanoplates (Figure 1c). The corresponding high resolution transmission electron microscopy (HRTEM) image of the nanoplates (Figure 1d) suggests that it is single crystalline and its primary surface exposes the (001) facets, which is confirmed by the selected area electron diffraction (SAED) pattern (Figure 1d inset).

Accordingly, we measured the XRD patterns of the samples along two directions (Figure S4, Supporting Information): (1) the scattering vector$^{[18]}$ of the x-ray is perpendicular to the primary surface of the pellets (cross-plane; parallel to the direction of applied pressure); (2) the scattering vector of the x-ray is parallel to the primary surface of the pellets (in-plane; perpendicular to the applied pressure). The orientation factors $F$ were calculated using the Lotgering method.$^{[19]}$ ($F=0$: randomly oriented; $F=1$ perfectly oriented) of the (0 0 l) planes in the XRD patterns measured along the two directions for these pellet samples (Table S1, Supporting Information). It is noted that the Se deficiency and Cl/I doping do not change the
value of F obviously rather the orientation of the sample in the XRD measurements matters. The F values of these pellets are estimated to be ~0.65 and ~0.15 for samples measured with the x-ray scattering vector parallel and perpendicular to the applied pressure, respectively.

This indicates that the nanoplates in the pellet tend to orient their primary surface (e.g. (001) facets) parallel to in-plane of the pellets. This orientation is perpendicular to the pressing directions and is favorable for the electrical and thermal transport properties.

A detailed TEM analysis was carried out on a representative sample of 1.5 at% Cl doped SnSe$_{1.95}$ pellet. The low magnification TEM image (Figure 2a) displays that the pellet sample is composed of nanograins, and some of them with sizes up to a few hundreds of nanometers. Similar microstructures can be observed for other batches of samples (Figure S5, Supporting Information). The further HRTEM analysis of the 1.5 at% Cl doped SnSe$_{1.95}$ pellet shows many structural features, e.g. the crystal grain along (001) (Figure 2b), the grain boundaries (Figure 2c), twin crystals (Figure 2d), stacking faults (Figure 2e) and the layered nanostructures (Figure 2f). Such wide-size-ranged nano-structural features are known to enhance the scattering of phonons with different wavelengths.

2.2. Electrical transport properties

The electrical resistivities ($\rho$) and Seebeck coefficients ($S$) of these nanoplate-based pellets along in-plane of the pellet were measured in the temperature range from 298-773 K. As depicted in Figure 3a, the $\rho$ of the Se deficient and halogen-doped pellets are much lower than that of the pristine SnSe$_2$ over the entire temperature range. For instance, the room temperature $\rho$ of the SnSe$_2$, SnSe$_{1.95}$, 0.5 at% Cl, 1.0 at% Cl, 1.5 at% Cl and 1.5 at% I doped SnSe$_{1.95}$ pellets are 0.9, 0.08, 0.007, 0.006, 0.0046 and 0.036 $\Omega$cm, respectively. The room-temperature Hall measurement (Table 1)
indicates the increase in carrier concentration as a consequence of electronic doping, which further supports the conclusion that the Cl/I have entered into the SnSe$_{1.95}$ crystal structure as electron donors. In addition, it should be noted that the carrier concentration of 1.5 at% Cl doped SnSe$_{1.95}$ is much higher than that of 1.5 at% I doped SnSe$_{1.95}$, which may be attributed to that the smaller Cl is more easily to be doped into SnSe$_{1.95}$ lattice than the much larger I. Similar results were observed in halogen doped In$_2$Se$_3$ compounds.[20]

In addition, the $\rho$ vs. $T$ curves of these pellets show a transition from semiconducting to metallic/heavily-doped-semiconducting characteristics when introducing the Se deficiency and the Cl/I doping. Analysis of the Log $\sigma$ vs. 1000/$T$ curve of SnSe$_2$ (Figure 3b) suggests two thermally excitable shallow energy levels ($E_1$, $E_2$) and a deep energy level ($E_3$). The estimated activation energies of $E_1$, $E_2$ and $E_3$ are 0.078eV ($E_{a1}$), 0.097eV ($E_{a2}$) and 0.247eV ($E_{a3}$), respectively. However, only a single thermally excitable deep energy level is obtained for the SnSe$_{1.95}$ (Figure S6a, Supporting Information) and I doped SeSn$_{1.95}$ sample (Figure S6b, Supporting Information), and no thermally excitable deep energy level for Cl doped sample (Figure S6c, Supporting Information). It indicates the Fermi level is shifted very close to the conduction band of SnSe$_2$ (Figure S6d).

Accordingly, calculations of the electronic band structure (Figure 3c) based on density functional theory (DFT)[3a,16] further supports that the Fermi level ($E_F$) gradually moves toward the conduction band with increasing carrier concentration. The electronic absorption spectra (Figure 3d) indicates a bandgap of ~1.0 eV for all samples indicating that the Se deficient and Cl/I doping has negligible effects on the bandgap.

The in-plane Seebeck coefficients are depicted in Figure 3e. Owing to the increased carrier concentration, the absolute Seebeck coefficient of the Se deficient and Cl/I doped pellets are lower.
than in pristine SnSe$_2$. The room temperature Seebeck value of the SnSe$_2$, SnSe$_{1.95}$, 0.5 at% Cl, 1.0 at% Cl, 1.5 at% Cl and 1.5 at% I doped SnSe$_{1.95}$ pellets are -493.1, -443.1, -239.3, -219.2, -200.8 and -373.7μVK$^{-1}$, respectively. Furthermore, by fitting the Seebeck coefficients with the well-established Pisarenko relation$^{[3a,13]}$ (Figure 3f), we obtain a higher effective mass m$^*$ for the Cl/I doped SnSe$_{1.95}$ sample than the pure SnSe$_2$. This should result from the increase of the electronic DOS near the Fermi level, as described by the following equation.$^{[3a]}

\[ N(E) = 4\pi \frac{(2m^*)^{3/2}}{\hbar^2} (E - E_\text{F})^{1/2} \] (2)

Where $N(E)$ is the density of states, $\hbar$ is the plank constant, $E_\text{F}$ is the energy of the conduction band.

As a result of the higher electrical conductivities, the in-plane power factors (Figure 57, Supporting Information) increase significantly for the Se deficient and Cl/I doped pellets. A nearly quadruple power factor is achieved for 1.5 at% Cl doped SnSe$_{1.95}$ at 773 K compared to the pure SnSe$_2$ pellet, which indicates that Cl-doping is highly effective in improving the thermoelectric properties of SnSe$_2$.

Because of the anisotropic characteristic of the samples, we measured the resistivities (Figure 4a) and Seebeck coefficients (Figure 4b) along the in-plane and cross-plane directions for the 1.5 at% Cl doped SnSe$_{1.95}$ pellets. The in-plane resistivity is much lower than cross-plane value over the whole temperature range. This is expected because the preferred orientation of nanoplate perpendicular to the pressing direction essentially reflects transport along the ab planes of the SnSe$_2$ structure (Figure 4c).$^{[16c]}$ The in-plane Seebeck coefficient is close to the cross-plane value as expected since it is typically an isotropic quantity.$^{[16d]}$ Consequently, the in-plane power factor (Figure 4d) is much higher than the cross-plane one owing to its lower resistivity over the entire temperature. It means that oriented nanoplates have their best electrical transport properties along the in-plane direction.
2.3. Thermal transport properties

The temperature dependent thermal conductivities $\kappa$ of the series of pellets along the in-plane direction are shown in Figure 5a. The in-plane $\kappa$ shows slight change when introduce the Se deficiency and Cl/I doping. For example, the in-plane $\kappa$ of SnSe$_2$, SnSe$_{1.95}$, 0.5 at% Cl, 1.0 at% Cl, 1.5 at% Cl and 1.5 at% I doped SnSe$_{1.95}$ pellets are 0.76, 0.78, 0.79, 0.79, 0.78 and 0.86 Wm$^{-1}$K$^{-1}$ at 773 K. The thermal conductivity $\kappa$ is composed of the electronic thermal conductivity $\kappa_e$ and the lattice thermal conductivity $\kappa_l$. The $\kappa_e$ of the samples can be estimated by the Wiedemann–Franz law $\kappa_e = LT$,\textsuperscript{[21]} where $L$ is the Lorenz number (Figure S8, Supporting Information) and estimated using a single parabolic band (SPB) model because it is a rather complex process to obtain the precise $L$ value in the multiple band materials (such as SnSe, PbTe and SnSe$_2$) due to the complex electronic band structure and the possible interband interaction.\textsuperscript{[22]} By subtracting $\kappa_e$ from $\kappa$, it is clear that the in-plane $\kappa_l$ (Figure 5b) of Se deficient and Cl doped samples is slightly lower than that of the pure SnSe$_2$ owing to the extra phonon scattering by atomic scale point defects (V$_{Se}^2$, Cl$_{Se}^+$) and the enhanced electron-phonon coupling. More interestingly, it should be noted that the in-plane $\kappa_l$ is much lower than the predicted in-plane theoretical value of SnSe$_2$ and the experimental value of single-crystal counterpart. Overall, the observed low $\kappa_l$ of the Cl doped SnSe$_{1.95}$ comparing to that of the single-crystal SnSe$_2$ may be ascribed to the all-scale phonon scattering by hierarchical structural features as schematically shown in Figure 5c, which are expected to scatter phonons over a wide-frequency range. The calculation of phonon relaxation time vs. frequency for each scattering mechanism based on the Callway model\textsuperscript{[3a]} is plotted in Figure S9 of Supporting Information. Thus, preparing polycrystalline SnSe$_2$ with orientated nanoplates is an effective method to reduce the $\kappa_l$ of SnSe$_2$. In addition, the measured $\kappa$ along in-plane and cross-plane directions of the 1.5 at% Cl doped

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SnSe$_{1.95}$ pellet (Figure 5d) shows that the in-plane $\kappa$ and $\kappa_\parallel$ are higher than the cross-plane $\kappa$ and $\kappa_\perp$, which is mainly due to the smaller group velocities along the $c$ axis of SnSe$_2$ crystal than that along the $a$ axis.$^{[16a]}$

2.4. Thermoelectric performance

Figure 6a presents the temperature dependent in-plane thermoelectric figure of merits $ZT$ of the pellets. The sharp increase in power factor and reduction in lattice thermal conductivity in the Se deficient and the Cl doped pellets lead to greatly increased $ZT$ values in the whole measurement temperature range. A sharply enhanced in-plane $ZT_{\text{max}}$ of 0.63 was achieved for 1.5 at% Cl doped SnSe$_{1.95}$ comparing to the pure SnSe$_2$ (0.08) at 673 K, which is higher than that of the cation Ag doped Sn$_{0.99}$Ag$_{0.01}$Se$_2$ polycrystalline sample ($ZT \approx 0.4$ at 773 K)$^{[23]}$ and the hot-pressed Cl doped SnSe$_2$ with random orientated grains ($ZT \approx 0.2$ at 610 K)$^{[16b]}$. In addition, the in-plane $ZT_{\text{max}}$ is also much higher than the corresponding cross-plane $ZT_{\text{max}}$ (0.38) as shown in Figure 6b. More importantly, it should be noted that both the in-plane and cross-plane $ZT$ values of the 1.5 at% Cl doped SnSe$_{1.95}$ sample are slightly higher than that of the corresponding p-type polycrystalline SnSe sample in the temperature range of 300 K~773 K (Figure 6b). Therefore, the present work indicates that both the anion Cl doping and orientation regulation are effective to enhance the thermoelectric performance of SnSe$_2$ compounds.

3. Conclusion

We conclude that electron doping and grain orientation are essential to enhance the TE performance of SnSe$_2$. The preferential orientation of (00l) facets of SnSe$_2$ during the SPS process results is key to the highly increased performance. Enhanced power factors along the preferred
orientation direction were achieved via simultaneously introducing Se deficiency and Cl doping, which control the carrier concentration and results in very low lattice thermal conductivity. The latter occurs because of the strong phonon scattering occurring through the all-scale hierarchical nanostructural and microstructural features. Eventually, an enhanced in-plane $ZT$ of 0.63 was obtained for 1.5 at% Cl doped SnSe$_{1.95}$ at 673 K, which is much higher than the corresponding $ZT$ (0.38) along cross-plane direction, and much higher than the in-plane $ZT$ (0.08) of undoped SnSe$_2$. Finally, we have demonstrated that the SnSe$_2$ can be a promising n-type TE material at medium temperatures with low cost, nontoxicity and earth abundancy. Considering that the orientation factor $F$ of these samples is only ~0.65 for the (001) planes along the primary surface, further development aimed to achieve better aligned nanoplates should result in additional performance enhancements (e.g. increase $F$ to 0.99).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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References


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Figure 1. (a) XRD patterns of the sintered SnSe$_2$, SnSe$_{1.95}$, 1.5 at% Cl doped SnSe$_{1.95}$ and 1.5 at% I doped SnSe$_{1.95}$. (b) The cross-plane fracture morphology of the SnSe$_2$ nanoplates. (c) The low magnification TEM image, (d) high resolution TEM (HRTEM) image and (inset) selected area electron diffraction (SAED) of the exfoliated individual SnSe$_2$ nanoplate.
Figure 2. TEM characterization of the typical microstructure of the 1.5 at% Cl doped SnSe_{1.95} pellet, (a) the low magnification TEM image of the sample, HRTEM of (b) individual grain and (c) grain boundaries of adjacent grains, HRTEM of structural features (d) twin crystal, (e) stacking faults and (f) layered nanostructures.
Figure 3. (a) Temperature dependent electrical resistivities of the pellets, (b) the Log $\sigma$ of SnSe$_2$ and SnSe$_{1.95}$ as a function of 1000/T, (c) the band structure of SnSe$_2$, the horizontal dashed lines at 0.63, 0.88, and 1.05 eV are corresponding to the carrier concentration of $1 \times 10^{17}$, $5 \times 10^{18}$, and $5 \times 10^{19}$ cm$^{-3}$, respectively. (d) Electronic absorption spectra of the SnSe$_2$, SnSe$_{1.95}$, Cl doped SnSe$_{1.95}$ and I doped SnSe$_{1.95}$ samples, respectively. (e) The temperature dependent Seebeck coefficients of the pellets. (f) Fitting of Seebeck coefficients with carrier concentration based on Pisarenko relationship.
Figure 4. Temperature dependent in-plane and cross-plane (a) electrical resistivities and (b) Seebeck coefficients of the 1.5 at% Cl doped SnSe\textsubscript{1.95} sample, (c) the crystal structure of SnSe\textsubscript{2}, (d) temperature dependent in-plane and cross-plane power factors of the 1.5 at% Cl doped SnSe\textsubscript{1.95} sample.
Figure 5. In-plane (a) thermal conductivities and (b) lattice thermal conductivities of the pellets as a function of temperature, (c) the schematic illustration of the wide-frequency phonon scattering by hierarchical architecture phonon scattering centers, (d) temperature dependent in-plane and cross-plane thermal conductivities and lattice thermal conductivities of the 1.5 at% Cl doped SnSe$_{1.95}$ pellet.

Figure 6. (a) Temperature dependent In-plane ZT values of the samples, (b) temperature dependent in-plane and cross-plane ZT values of the 1.5 at% Cl doped SnSe$_{1.95}$ sample and p-type polycrystalline SnSe sample (Ref. 22a).

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Table 1. The carrier concentrations $n_e$, Hall mobilities, electrical resistivities and Seebeck coefficients of the samples at room temperature.

<table>
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<th>$n_e$ ($\times 10^{17}$ cm$^{-3}$)</th>
<th>$\mu_H$ (cm$^2$/V$^{-1}$S$^{-1}$)</th>
<th>$\rho$ (Ωcm)</th>
<th>$S$ (μVK$^{-1}$)</th>
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<tr>
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A novel eco-friendly n-type SnSe\textsubscript{2} oriented-nanoplate based thermoelectric material is demonstrated. A high power factor is achieved through defect chemistry approach and a low thermal conductivity is achieved by all-scale hierarchical phonon scattering. Eventually, an enhanced in-plane ZT\textsubscript{max} of 0.63 was achieved for 1.5 at\% Cl doped SnSe\textsubscript{1.95} pellet at 673 K, which is much higher than the corresponding in-plane ZT of pure SnSe\textsubscript{2} (0.08).

**Keyword:** SnSe\textsubscript{2}, thermoelectric, nanoplate orientation, Se deficiency, chlorine doping


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