In-Situ Observation of the Continuous Phase Transition in Determining the High Thermoelectric Performance of Polycrystalline Sn$_{0.98}$Se

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ABSTRACT: We report a comprehensive in-situ phase-change study on polycrystalline Sn$_{0.98}$Se via high-temperature X-ray diffraction and in-situ high-voltage transmission electron microscopy from room temperature to 843 K. The results clearly demonstrate a continuous phase transition from Pnma to Cmcm starting from 573 to 843 K, rather than a sudden transition at 800 K. We also find that the thermal-conductivity rise at high temperature after the phase transition, as commonly seen in pristine SnSe, does not occur in Sn$_{0.98}$Se, leading to a high thermoelectric figure of merit. Density functional theory calculations reveal the origin to be the suppression of bipolar thermal conduction in the Cmcm phase of Sn$_{0.98}$Se due to the enlarged bandgap. This work fills the gap of in-situ characterization on polycrystalline Sn$_{0.98}$Se and provides new insights into the outstanding thermoelectric performance of polycrystalline Sn$_{0.98}$Se.

A typical IV–VI group semiconductor with a relatively narrow band gap value of ~0.9 eV, SnSe exhibits intriguing properties including ferroelectricity, superconductivity, the thermoelectric effect, and the photoelectric effect. In particular, SnSe has received extensive attention for applications in low-toxicity, cost-effective thermoelectric devices due to its ultralow thermal conductivity. Thermoelectric energy conversion efficiency can be defined by the dimensionless figure of merit $ZT = S^2σT/κ$, where $S$, $σ$, $κ$, and $T$ are the Seebeck coefficient, electrical conductivity, power factor, and absolute temperature, respectively. A high carrier concentration $n$ is key to achieving high $σ$ ($σ = neμ$) and to improving the thermoelectric efficiency. However, to improve $n$ in SnSe has been a challenge.

Historically, various methods have been explored to fabricate SnSe, such as single crystal growth, mechanical alloying, melting (include arc-melting), solid state reaction, and hydrothermal or solvothermal syntheses. On the basis of these methods, band engineering, including n-type and p-type doping, multiphase engineering, and vacancy engineering, have been widely used to modify the band structure and improve $n$. Compared to pristine SnSe, polycrystalline SnSe with a high Sn vacancy concentration (Sn$_{0.98}$Se) possesses much higher hole carrier concentration ($p$) and thus $σ$ as well as $σ^2κ$. After introducing ~2% Sn vacancies, the hole concentration is improved from ~2 x 10$^{17}$ cm$^{-3}$ to >1 x 10$^{19}$ cm$^{-3}$, further improving $σ$ from ~15 to ~150 S cm$^{-1}$ at room temperature (RT). Sn$_{0.98}$Se also possesses much lower $κ$ than pristine SnSe, which can be attributed to the strengthened phonon scattering at Sn vacancies as well as the lattice distortions and dislocations caused by the vacancies. Therefore, Sn vacancies have attracted much attention in recent years. Despite the good thermoelectric performance of

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Sn\textsubscript{0.98}Se, as a high-temperature thermoelectric material, a persistent question is whether its phase transition from \textit{Pnma} to \textit{Cmcn} occurs at 800 K, as has been found in pristine SnSe.\textsuperscript{3,4} In this paper, we report \textit{in situ} high-temperature X-ray diffraction (XRD) and \textit{in situ} high-voltage transmission electron microscopy (HVTEM) from room temperature (RT) to 843 K to investigate the phase change of polycrystalline Sn\textsubscript{0.98}Se. We found a continuous phase transition from \textit{Pnma} to \textit{Cmcn} starting from 573 to 843 K in polycrystalline Sn\textsubscript{0.98}Se.

We compare the main thermoelectric properties of polycrystalline Sn\textsubscript{0.98}Se and SnSe, including \( T \)-dependent \( \sigma \), \( T \)-dependent \( S \), \( T \)-dependent \( p \), \( T \)-dependent \( \mu \), \( T \)-dependent \( S' \sigma \), \( T \)-dependent \( \kappa \) with inset of \( T \)-dependent \( \kappa_l \), \( T \)-dependent \( ZT \), and \( p \)-dependent \( ZT \) (Figure 1h), respectively. The measured density of Sn\textsubscript{0.98}Se and SnSe were \( \sim 6.10 \) and \( \sim 5.99 \) g cm\(^{-3}\) by the Archimedes method.\textsuperscript{31} Compared with the theoretical density of SnSe (6.179 g cm\(^{-3}\)),\textsuperscript{14} our Sn\textsubscript{0.98}Se pellet has a very high relative mass density of \( \sim 98.7\% \), indicating a good sintering quality, which can exhibit intrinsic thermoelectric performance as evaluated. All properties were measured along the direction perpendicular to the sintering pressure (\( L \)). The green dashed lines indicate the theoretical phase-transition temperature of \( \sim 800 \) K. For the electrical transport performance, compared with pristine SnSe, the \( \sigma \) and \( S' \sigma \) of Sn\textsubscript{0.98}Se continue to rise after the theoretical phase-transition temperature of \( \sim 800 \) K, \( \mu \) follows the power law \( \mu \propto T^d \) with a slight deviation from \( d = -1.5 \) in a wide temperature range from 550 to 750 K, indicating that acoustic-phonon scattering is the main but not the only carrier scattering mechanism.\textsuperscript{3,4} With increasing temperature, the decrease of \( \kappa \) and \( \kappa_l \) for Sn\textsubscript{0.98}Se becomes much slower after \( \sim 550 \) K, and they do not show a sudden jump at \( \sim 800 \) K, being consistent with the observed continuous phase transition. The inset of 1000/\( T \)-dependent \( \kappa_l \) do not strictly follow a linear relationship for Sn\textsubscript{0.98}Se especially at higher temperature, indicating \textit{Cmcn} phase coexisted below 800 K.\textsuperscript{3,4} All this evidence justifies a conclusion that a continuous phase transition occurs in Sn\textsubscript{0.98}Se. The comparison of measured thermal diffusivity \( D \), calculated Lorenz number \( L \), determined electronic thermal conductivities \( (\kappa_e) \), and \( \kappa_e/\kappa_l \) ratio between polycrystalline Sn\textsubscript{0.98}Se and SnSe is shown in Figures S1 and S2 in the Supporting Information.

Before discussing the phase transition in Sn\textsubscript{0.98}Se, we first investigate the characterization of the RT \( \alpha \)-SnSe phase. For \( \alpha \)-SnSe, it has a typical orthorhombic structure with lattice parameters of \( a = 11.37 \) Å, \( b = 4.19 \) Å, and \( c = 4.44 \) Å and a space group of \( \text{Pnma} \) (\#62). Figure 2a–c shows the projected crystal structure of \( \alpha \)-SnSe viewed along the \( a \), \( b \), and \( c \)-axes, respectively. It is clearly seen that \( \alpha \)-SnSe possesses a typical double-layered structure.\textsuperscript{37} The adjacent Sn–Se layers are mainly bound to each other with a combination of van der Waals forces and long-range electrostatic attraction.\textsuperscript{38,39} The crystal structure of \( \beta \)-SnSe is also provided in Figure S3 for reference. Figure 2d is a spherical- aberration-corrected scanning-transmission-electron microscopy (Cs-corrected STEM) high-angle annular dark-field (HAADF) image taken from a laminar TEM specimen of Sn\textsubscript{0.98}Se as shown in the inset, viewed along the \( b \)-axis with overlays showing Sn atoms in light blue and Se atoms in red for the unit cell. The achieved image fits well with the crystal structure shown in Figure 2b without any discernible lattice defects viewed along the \( b \)-axis. Figure 2e also shows the results of the energy dispersive spectrometry (EDS) mappings of Sn, Se, and the overlap of Sn and Se. The real composition of Sn\textsubscript{0.98}Se is determined via both EDS and electron probe microanalyzer (EPMA). Both panels d and e of Figure 2 confirm that Sn\textsubscript{0.98}Se possesses the same crystal structure as SnSe.

In order to investigate the phase transition in our Sn\textsubscript{0.98}Se, \textit{in situ} XRD was conducted during the heating from RT to 843 K. Figure 3a shows the recorded XRD patterns of Sn\textsubscript{0.98}Se in a 2\( \theta \) range from 20\(^\circ\) to 70\(^\circ\). When \( T = \sim 303 \) K (RT), all the diffraction peaks can be exclusively indexed as an orthorhombic structured SnSe and a space group of \( \text{Pnma} \) (Standard Identification Card, JCPDS 48-1224).\textsuperscript{4,12,16,26,31,32,34} The 400* diffraction peak is the strongest peak, suggesting significant \( 100 \) surface. Figure 3b shows the magnified XRD patterns in...
θ range from 29° to 31.25°. A shift to lower diffraction angle during heating can be observed. It is obvious that the strongest 400* peak suddenly become much weaker when T > 573 K, indicating a variation of the surface derived from the phase transition. Figure 3c shows the magnified XRD patterns of Sn0.98Se at 303, 573, 813, and 843 K, respectively, in a 2θ range from 29° to 32°. Considering that the 400* peak for RT is significantly strong, the peak intensities for these patterns have been rescaled for better comparison. When T = 573 and 813 K (close to the theoretical phase-transition temperature of 800 K), both the Pnma phase (400* and 111* indexed, marked as blue) and the Cmcm phase (040* indexed, marked as pink) were found, indicating that both phases exist. When T = 843 K (>800 K), the Cmcm phase is the most significant, but there are still Pnma peaks that can be indexed. All these results indicate a continuous phase transition occurring in the Sn0.98Se. It should be noted that the left peak shift during heating is responsible for the lattice thermal expansion (marked in the figure). Both phase transition and thermal expansion/contraction result in the peak deviations.

To further study the continuous phase-transition behavior in our Sn0.98Se, in-situ HVTEM was performed during heating from RT to 843 K. Figure 4 shows a series of typical selected bright field (BF) TEM images and corresponding selected area electron diffraction (SAED) patterns with simulated selected area diffractions (SADs) for the same viewing area before heating (RT) and during heating at 573 K. From (a) to (b) in Figure 4, it is clearly seen that the low-temperature primitive orthorhombic Pnma structure is evident at RT transforming to the face centered orthorhombic phase around 573 K. The SAED patterns were acquired from approximately the same area of the sample. On the basis of the overlapping spots in the SAED pattern obtained at 573 K, an orientation relationship (OR) was found between SnSe Pnma (400) // SnSe Cmcm (040), suggesting that the sample has undergone a continuous structural phase transition. It should be noted that a weak ring pattern can be found and indexed as polycrystalline Se in the SAED pattern under RT, mainly derived from the high voltage of HVTEM which may slightly damage the ultrathin samples. Nevertheless, this small quantity of Se did not affect the results. After the heating process, the Sn0.98Se sample was then rapidly cooled to RT, from which only the Pnma phase can be indexed (as shown in Figure S4), no Cmcm phase was found, indicating that such a continuous phase transition is reversible. Considering that the Cmcm phase possesses much higher κ (mainly from κl; see Figure S1) than bright field (BF) TEM images and corresponding selected area electron diffraction (SAED) patterns with simulated selected area diffractions (SADs) for the same viewing area before heating (RT) and during heating at 573 K.

Figure 2. Confirmation of the Sn0.98Se Pnma phase. Crystal structure of α-SnSe along the (a) a-axis, (b) b-axis, and (c) c-axis. (d) Cs-corrected STEM HAADF image of Sn0.98Se sliced from the pellet (shown as inset), viewed along the b-axis with overlays showing Sn atoms in light blue and Se atoms in red and the unit cell and (e) corresponding EDS maps of Se, Sn, and overlap of Sn and Se.

Figure 3. In-situ XRD results of Sn0.98Se. (a) High-temperature XRD patterns of Sn0.98Se in a 2θ range from 20° to 70°. (b) Magnified XRD patterns of Sn0.98Se in a 2θ range from 29° to 31.25°. (c) Magnified XRD patterns of Sn0.98Se at 303, 573, 813, and 843 K in a 2θ range from 29° to 32°, the peak intensities for these patterns have been rescaled for better comparison.

Figure 4. In-situ TEM results of Sn0.98Se. Selected BF-TEM images and corresponding SAED patterns with SADs for the same viewing area (a) before heating and (b) during heating at 573 K.
the Pnma phase due to the difference of crystal structure, such a continuous phase transition explains why the decrease of $D$ and $k$ from Sn$_{0.98}$Se becomes much slower after $\sim$550 K with increasing temperature, and there is no sudden jump in $D$ and $k$ after $\sim$800 K.

From the above comprehensive and in-situ phase-change study on polycrystalline Sn$_{0.98}$Se via high-temperature SR-XRD and in-situ high-voltage TEM from RT to 843 K, we can conclude that a reversible and continuous phase transition from Pnma to Cmcm starting from 573 to 843 K exists in Sn$_{0.98}$Se. In order to understand the underlying physics behind the outstanding thermoelectric performance of Sn$_{0.98}$Se, we performed density-functional-theory (DFT) calculations. DFT is known to underestimate bandgaps, but it works well for the purpose of relative comparison. Figure 5a shows a comparison between the band structures of the Pnma and Cmcm phases for Sn$_{0.98}$Se. It shows that the Cmcm phase has a much smaller bandgap than the Pnma phase, explaining the experimentally observed high bipolar thermal conductivity when $T$ is above 800 K, as shown in Figure 1h. Figure 5b shows a comparison between the band structures of the Pnma and Cmcm phases for Sn$_{0.98}$Se, in which the Fermi level moves deeply into the valence band, indicating that Sn vacancies change SnSe into a degenerate p-type semiconductor with large hole concentration. It is noteworthy that the bandgap of Cmcm Sn$_{0.98}$Se is larger than that of Cmcm pristine SnSe, which indicates that the bipolar heat conduction of the former is much weaker than the latter. This result explains why the experimentally observed thermal conductivity of Sn$_{0.98}$Se does not rise after 800 K, which is commonly seen in pristine SnSe, and therefore explains the high thermoelectric figure of merit at high temperature. Figure 5c compares the density of states (DOS) of SnSe and Sn$_{0.98}$Se for both the Pnma and Cmcm phases, in which a clear difference between the bandgaps can be observed.

As shown in Figure 1h, there are several routes to further improve the $p$ value to achieve even higher ZT. One strategy is doping with other elements such as Na and Ag which exhibit $1^+$ valence state,$^{40,41}$ leading to higher $p$ and ZT by providing more holes in the system. Besides, alloying with other thermoelectric materials which have higher intrinsic $p$ values such as Cu$_2$Se and SnTe is also a good choice.$^{10,11,15,42,43}$ Furthermore, considering that our achieved Sn$_{0.98}$Se has a maximum Sn vacancy concentration of $\sim$2%, tuning the vacancy concentration to an even higher level is a potential way to achieve higher $p$ and ZT,$^{44}$ and an appropriate design of synthesis route such as solvent and vapor pressure control can achieve this goal.

In summary, we provide direct evidence that the continuous phase transition of Sn$_{0.98}$Se dominates its high electrical transport between 573 and 843 K using in situ high-temperature XRD and ultrahigh-voltage TEM. Furthermore, DFT calculations verify that the continuous phase transition plays a significant role in determining the outstanding thermoelectric performance in this temperature range. This work fills the gap of in-situ characterization on polycrystalline Sn$_{0.98}$Se, and provides a new perspective to explain the outstanding electrical transport performance in polycrystalline Sn$_{0.98}$Se.

## ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02818.

Plots of properties of polycrystalline Sn$_{0.98}$Se and SnSe, calculation details, thermal-transport performance, crystal structure, TEM characterizations, experimental details, and calculated stopping power of SnSe as a function of incident electron energy (PDF)

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### Notes

The authors declare no competing financial interest.

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