Chapter 2
Superionic Phase Transition Optimizing Thermoelectric Performance in Silver Chalcogenide Nanocrystals

2.1 Motivation

On the basis of the conversion of heat into electricity, thermoelectric generators are today well recognized as viable renewable energy sources [1–4]. The heat can come from the combustion of fossil fuels, from sunlight, or as a byproduct of various processes (e.g., chemical reactions, nuclear decay, and so on). Accordingly, thermoelectric materials can play a role in both primary power generation and energy conservation. The performance of thermoelectric materials is quantified by a dimensionless figure of merit, $ZT$, which is defined as $\sigma \cdot S^2 T / \kappa$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $\kappa$ is the thermal conductivity of the material, and $T$ is the absolute temperature. The challenge to create high $ZT$ thermoelectric materials lies in achieving simultaneously high $\sigma$, high $S$, and low $\kappa$ in the same solid. However, there is a strong correlation of these three parameters according to the Wiedemann–Franz law, thus materials development schemes to achieving superior thermoelectric materials and for subsequent practical application are driven by the need to maximize the figure of merit, $ZT$, and to balance the competing requirements of high Seebeck coefficient, high electrical conductivity, and low thermal conductivity [5].

Occurrence of different polymorphic phases has often been observed in inorganic compounds, including natural and especially synthetic materials. Among them, many exhibit transformations from one crystal structure to another as the temperature or pressure is varied [6], which is the so-called phase transition. Besides such phase transitions involving changes in atomic configuration, many of the solids also undergo the orientation change of the electron clouds influencing the state of electron spin on passing through the phase transition, resulting in the widening/narrowing of the material band gap to form insulator or metal states; this reveals an intriguing route to control the carrier concentration by modulating related effects of electronic properties [7, 8]. Silver chalcogenides as typical materials with their intrinsic phase transition have attracted much interest as they, accompanied
with phase transition, undergo a reversible transformation between semiconductor and superionic conductor [9–11]. For example, Ag₂Se that crystallizes in the orthorhombic phase at room temperature is a narrow band-gap semiconductor with two crystallographically distinct silver atoms [12], while in the high-temperature cubic phase, α-Ag₂Se, selenium sublattice is ordered in a bcc lattice while silver atoms are statistically distributed over several interstitial sites [13–16], through which Ag⁺ cations can move easily and show superionic conductivity. As seen in Fig. 2.1, the calculated band gap is about 0.098 eV for orthorhombic Ag₂Se while 0 eV for cubic Ag₂Se, which is consistent with the experimental finding that the high-temperature phase of Ag₂Se shows metallic behavior in its electronic conductivity. These two compounds undergo a reversible first-order phase transition around 406 K with a remarkable change in its electronic property, which is presently giving a hint for the modulation of the electric properties at the phase transition temperature to optimize thermoelectric power factor. Thus, one may expect to obtain superior thermoelectric property in these materials vicinal their phase transition temperature.

In addition to the favorable electrical transport properties, a good thermoelectric material must also have low thermal conductivity (κ). A successful strategy to reduce the thermal conductivity has been applied to modify an already promising compound by reducing grain size to nanometer [17–19] that serves to introduce a large density of interfaces in which mid/long-wavelength phonons can be effectively scattered. Although mid/long-wavelength phonons are effectively scattered in nanocrystals, the short-wavelength phonons can propagate without significant scattering and thereby still contribute to heat conduction. Alloying is another successful strategy to reduce thermal conductivity due to mass fluctuations in the crystal lattice and thus increase the short-wavelength phonon scattering to reduce the lattice thermal conductivity [20–23]. So, as a result of alloying at nanoscale, a significant reduction in lattice thermal conductivity could be expected to achieve since phonons with an approximately even distribution of wavelengths can be effectively scattered.

Herein, nearly monodisperse silver chalcogenide quantum dots were successfully synthesized through a facile colloidal method, and their thermoelectric

![Fig. 2.1 Calculated band structure of orthorhombic (a) and cubic (b) Ag₂Se respectively](image)
property across the semiconductor–superionic conductor phase transition was systematically investigated. We put forward for the first time the general law that the optimized thermoelectric property could be achieved around the phase transition temperature. Furthermore, we first synthesized the Ag$_4$SeS quantum dots through the alloying of the Ag$_2$Se and Ag$_2$S quantum dots. Benefit from the alloy introduced point defects and atoms fluctuations, nearly full wavelength range of the phonons could be effectively scattered, which further reduced the thermal conductivity and improved the thermoelectric property.

### 2.2 Results and Discussion

Inspired by the above structural and electronic band structure analysis, we selected silver chalcogenides as examples for the investigation of phase transition with remarkable electronic property change on their thermoelectric property. Monodisperse silver chalcogenides nanocrystals with narrow size distribution were

![Figure 2.2](image-url)  
**Fig. 2.2** XRD pattern (a), TEM image (b), HRTEM image (c) and EDX spectrum (d) for as-prepared Ag$_2$Se nanocrystals.
synthesized through a simple colloidal method. The phase purity and crystal structure of the as-prepared products were examined by XRD and the results are shown in Fig. 2.2a. The XRD pattern of Ag$_2$Se match well with the standard orthorhombic Ag$_2$Se (space group: P2$_1$2$_1$2$_1$) with lattice constants $a = 4.333$ Å, $b = 7.062$ Å, and $c = 7.764$ Å (JCPDS 24-1041). The shape or morphology of pristine nanocrystals was examined by TEM and HRTEM. As shown in Fig. 2.2b, we can see the Ag$_2$Se nanocrystals sized in an average diameter of 10 nm with hexagonal shapes respectively. The TEM images also display the nearly monodisperse particle size distributions (see the insert of Fig. 2.2b). The HRTEM images (Fig. 2.2c) of one individual nanocrystal indicated the distances between the adjacent lattice fringes to be 2.655 Å which corresponds with the lattice spacing of the (1 1 2) d-spacing for orthorhombic Ag$_2$Se (2.673 Å, JCPDS 24-1041). Energy dispersive X-ray emission spectra (EDX) were measured to study the elemental composition and purity of these as-obtained products. The EDX results shown in Fig. 2.2d undoubtedly demonstrate that the chemical components only consisted of Ag and Se for the as-obtained nanocrystals. As shown in Fig. 2.2d, no other elemental species can be detected indicating the high purity of these samples (the other detected elements Cu and C are originated from the carbon-coated copper grid used for the TEM analysis).

The first-order phase transition usually involves a substantial entropy component, and our thermal analysis studies reveal the direct character of the first-order structural transition in solid materials. Typically, the appearance of endothermic (peak centered around 408 K) and exothermic (peak centered around 379 K) peaks in DSC curves (see in Fig. 2.3a) during the heating and cooling process clearly confirms the first-order transition of orthorhombic Ag$_2$Se. Detailed insight into the phase transition behavior of Ag$_2$Se nanocrystals was obtained from the temperature-dependent XRD. Results of the variable temperature XRD

![Graph](image)

**Fig. 2.3** DSC thermogram (a), temperature-dependent XRD patterns (b) of the as-prepared Ag$_2$Se nanocrystals, (c) Schematic representation of the structure phase transition between orthorhombic and cubic Ag$_2$Se
measurements for obtained products are shown in Fig. 2.3b. It can be seen that the as-prepared Ag₂Se samples clearly show the structural transition from the low-temperature orthorhombic phase to the high-temperature cubic phase. In fact, Ag₂Se is a narrow band-gap semiconductor and crystallizes in the orthorhombic phase at room temperature with two crystallographically distinct silver atoms [24, 25]: Ag(1) is coordinated tetrahedrally, whereas the coordination sphere of Ag (2) is almost triangular (Fig. 2.3c). In the high-temperature cubic phase, selenium sublattice is ordered in a bcc lattice while silver atoms are statistically distributed over several interstitial sites and delocalized in the channels along [100] consisting of octahedral and tetrahedral sites, through which Ag⁺ cations can move easily and show superionic conductivity [13–16]. Furthermore, as shown in Fig. 2.3d, the mixed orthorhombic and cubic phases existed in temperature ranges of 403–413 K which would attribute to the reduction of the lattice thermal conductivity.

It is well known that Ag₂Se is a narrow band-gap semiconductor and a promising candidate for the potential application of thermoelectric devices thanks to their high electrical conductivity and relatively high Seebeck coefficient. For the

Fig. 2.4 a XRD patterns of pristine, surface cleaned, and hot-pressed Ag₂Se nanocrystals respectively. b SEM image of the surface cleaned Ag₂Se nanocrystals. c SEM image of hot-pressed Ag₂Se nanocrystals
thermoelectric properties measurement, we have carefully removed the organic surfactants according to the procedure of previously reports and fabricated the hot-pressed bulk samples (the XRD patterns and SEM images of surface cleaned and hot-pressed bulk samples are shown in Fig. 2.4). As shown in Fig. 2.4a, there are no apparent changes in structure and purity of the samples detected after hydrazine treatment and hot-pressing compared to pristine nanocrystals. The SEM image (Fig. 2.4b) of Ag₂Se nanocrystals clearly showed that the size and shape were almost unchanged after hydrazine treatment, and also the bulk sample consisted of hot-pressed (Fig. 2.4c) Ag₂Se nanocrystals that are very dense with smooth surface.

Figure 2.5 shows the thermoelectric property of hot-pressed Ag₂Se sample. As shown in Fig. 2.5a, a pronounced increase in electric conductivity with temperature increasing to near 408 K clearly shows the typical electrical transition originated from the atom rearrangement and Ag⁺ disordering during the structural transition. As is known, the low-temperature Ag₂Se phase belongs to the orthorhombic system and has semiconducting properties with degenerating state of the electron gas, and then the low-temperature Ag₂Se phase changes to cubic type and exhibits superionic conductivity behavior as the temperature increases. Figure 2.5a also shows the Seebeck coefficient of these as-prepared nanocrystals. The negative sign of the Seebeck coefficient indicates that Ag₂Se nanocrystals are n-type semiconductors.

![Figure 2.5](image)

**Fig. 2.5** a Temperature dependence of the Seebeck coefficient (black) and the electrical conductivity (red) for Ag₂Se nanocrystals. b Evolution of the specific heat (black) and of the thermal diffusivity (red) of Ag₂Se nanocrystals as a function of temperature. c Temperature dependence of thermal conductivity for Ag₂Se nanocrystals. d Temperature dependence of the thermoelectric figure of merit ZT for Ag₂Se nanocrystals
and as temperature increased, the Seebeck coefficient (absolute value) dropped from 150 to 60 μV/K around 408 K. It is well known that the electrical conductivity is proportional to the charge carrier concentration, while the Seebeck coefficient decreases with increasing charge carrier concentration [26–29]. As a result, the metals usually display Seebeck coefficients of a few tens of μV/K, which are much lower than that of semiconductors. So, in this study, the larger Seebeck coefficient of low temperature phase and lower Seebeck coefficient of high temperature should be an inevitable result of the semiconductor–superionic conductor phase transition. Results revealing that the presence of structural phase transition concomitant with the abrupt increase in electrical conductivity by several orders of magnitude at elevated temperature affords the chance to balance the electronic and thermal properties around the transition temperature for achieving superior thermoelectric performance. Based on the regulation of electric transport property, a maximum power factor (\(\sigma \cdot S^2\)) is obtained around the phase transition temperature (see insert of Fig. 2.5a), which is a crucial step toward improving thermoelectric properties.

In addition to having favorable electrical transport properties, a good thermoelectric material must also have low thermal conductivity (\(\kappa\)). Figure 2.5c displays the temperature dependence of the thermal conductivity \(\kappa\). The exciting fact is that, the thermal conductivity of Ag2Se nanocrystals is much lower than those of many reported thermoelectric materials and covers the range of 0.78–0.89 W/mK over the temperature range of 300–480 K. A tiny peak in the thermal conductivity occurs, which is caused by the abrupt change in the silver ion mobility around orthorhombic–cubic phase transition temperature at 408 K. Although the increase in thermal conductivity is disadvantageous to obtaining a high figure of merit, the absolute value is still much lower compared to the previously reported values. The thermal conductivity was calculated by the following Eq. (1)

\[
\kappa = a \rho C_p
\]  

using the measured heat capacity \(C_p\), measured thermal diffusivity a, and density \(\rho\). A huge \(\lambda\)-shaped effect in the \(C_p\) curve (Fig. 2.5b) comes along with the phase transition at 408 K featuring a heat capacity of maximum 3.06 J/gK. Surprisingly, the thermal diffusivity (see in Fig. 2.5b) is low and covers the range of 0.098–0.35 mm²/s over the temperature range of 300–480 K. At the orthorhombic–cubic phase transition, a significant reduction of the thermal diffusivity to a very low value of 0.098 mm²/s at 408 K occurs that substantiated the huge mobility of the silver cations and the rearrangement of the anions during transition.

As is known, \(\kappa\) is the sum of two independent components, a lattice contribution \(\kappa_l\) and an electronic contribution \(\kappa_e\) equal to \(LT/\rho\) according to the Wiedemann–Franz law (L is the Lorenz constant and equal to \(2.45 \times 10^{-8}\) W Ω K⁻²). At low temperature, Ag2Se is a semiconductor with relatively low electrical conductivity and electrical contribution to the total thermal conductivity may be neglected, while the lattice thermal conductivity is also very low due to the reduction of grain size. Theoretically, reducing to nanometer of grain size serves to introduce a large density of interfaces in which phonons can be effectively scattered resulting in the
reduction of lattice thermal conductivity without having to compromise on carrier mobility values (see in Fig. 2.6) [26].

As temperature increased to 408 K, the orthorhombic to cubic phase transition appeared. Along with the phase transition, Ag$_2$Se began the change from semiconductor to superionic conductor and the electrical conductivity sharply increased. Although the electrical contribution to total thermal conductivity could not be neglected during phase transition, the lattice thermal conductivity dropped contrarily, but acutely. It is well known that during the phase transition, parent phase disappeared gradually while the secondary phase appeared. In our case, the in situ formed nanostructured Ag$_2$Se cubic phase evenly coexisting with the orthorhombic phase (which could be testified by the temperature-dependent XRD, as seen in Fig. 2.3d) makes our samples as in situ nanocomposites (see in Fig. 2.6b). The abundance of nano-interfaces effectively increases the phonon scattering and hence reduces the lattice thermal conductivity [30]. So, due to the combined contribution from electron and lattice, the total thermal conductivity gradually and slowly increases to 0.89 W/mK during the phase transition.

As the temperature further increases to above the phase transition region, the Ag$_2$Se crystallizes in the cubic phase. In the high-temperature cubic phase, anions sublattice is ordered in a bcc lattice while silver atoms are statistically distributed over several interstitial sites. It was found that the silver cations are delocalized in channels along [100] consisting of octahedral and tetrahedral sites, through which Ag$^+$ cations can move easily and show high conductivity. Due to disordering of Ag$^+$ cations in the lattice, the phonons could be effectively scattered, which preserve the low lattice thermal conductivity. So, although there is a slight increase in

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**Fig. 2.6** Schematic diagram illustrating various phonon scattering mechanisms in Ag$_2$Se nanocrystals. a Before phase transition. b During phase transition, and c after phase transition.
total thermal conductivity through the phase transition, the value still retains at a very low level over the investigated temperature range, which may be contributed by the Ag⁺ disordering and nanostructuring.

In Fig. 2.5d, the figures of merit for Ag₂Se nanocrystals calculated from the above data with the relationship \( \sigma \cdot S^2T/\kappa \), are shown. Of note, the Ag₂Se nanocrystals achieve a maximum \( ZT_{\text{max}} = 0.23 \) at the phase transition temperature around 408 K, which is reminiscent of the features of the temperature-dependent power factor curve. Our figure of merit behavior confirms the ability to achieve the thermoelectric materials with balanced electrical conductivity and lattice thermal conductivity through the intrinsic phase transition. Moreover, the optimized thermoelectric property obtained around phase transition temperature has confirmed as a general law rather than an individual case, as another example, 12 nm of monodisperse Ag₂S nanocrystals (details information of structural, size, and morphology see in Fig. 2.7) also possess a maximum \( ZT \) value of 0.12 around its semiconductor–superionic conductor phase transition temperature at 454 K.

Fig. 2.7 XRD pattern (a), TEM image (b), HRTEM image (c), and EDX spectrum (d) for as-prepared Ag₂S nanocrystals
To further lower the thermal conductivity, it is necessary to reduce the phonon mean free path. A successful strategy to reduce thermal conductivity is the design of alloys to create point defects that scatter heat carrying phonons. The introduction of randomness in the lattice by alloying often results in sufficient disorder or point defects to produce phonon scattering and is of great importance in the improvement of the performance of thermoelectric materials. So, the thermoelectric property of alloyed ternary silver chalcogenide compound, Ag₄SeS, was also investigated. In this study, monodisperse Ag₄SeS nanocrystals were successfully synthesized for the first time. All the diffraction peaks of XRD patterns in Fig. 2.8a can be exclusively indexed as the orthorhombic Ag₄SeS (space group: P2₁2₁2₁) with lattice constants $a = 4.33\ \text{Å}$, $b = 7.09\ \text{Å}$, and $c = 7.76\ \text{Å}$ (JCPDS 27-0620). No peaks attributable to impurities were observed, indicating the high purity of as-obtained products. The relatively broad peaks in the diffraction patterns were consistent with their small sizes. The shape or morphology of these three kinds of nanocrystals was examined by TEM and HRTEM. As shown in Fig. 2.8b, we can see the Ag₄SeS nanocrystals sized in an average diameter of 13 nm with hexagonal shapes. The TEM images also display the nearly monodisperse particle size distributions.

![Fig. 2.8 XRD pattern (a), TEM image (b), HRTEM image (c), and EDX spectrum (d) for as-prepared Ag₄SeS nanocrystals](image-url)
(see the insert of Fig. 2.8b). The HRTEM images (Fig. 2.8c) of one individual nanocrystal indicated the distances between the adjacent lattice fringes to be 2.428 Å which corresponds with the lattice spacing of the (0 1 3) d-spacing of Ag₄SeS (2.430 Å, JCPDS 27-0620). The EDX results shown in Fig. 2.8d undoubtedly demonstrate that the chemical components only consist of Ag, Se, and S with a Se to S atomic ratio nearly 1:1. No other elemental species can be detected indicating the high purity of these samples (the other detected elements Cu and C are originated from the carbon-coated copper grid used for the TEM analysis).

Compared to the binary silver chalcogenide compounds, the phase transition temperature of monodisperse alloyed ternary silver chalcogenide Ag₄SeS
nanocrystals was depressed to 355 K. It can be seen that the phase transition is indeed reversible in DSC curves (see in Fig. 2.9a): a dominant endothermic peak centered around 355 K during heating and an exothermic peak is centered at 331 K. The introduction of randomness in the lattice by alloying often results in sufficient disorder or defect (see in Fig. 2.10) to produce phonon scattering and is of great importance in the improvement of the performance of thermoelectric materials, and the scattering cross-section follows Rayleigh scattering as \( d^6/\lambda^4 \). Hence, short-wavelength phonons are effectively scattered in alloys. Our results (see in Fig. 2.11 and Table 2.1) strongly suggest that the atomic disorder between Se and S atoms connection with nanostructuring which scattering the mid/long wavelength phonons, should be responsible for the reduction of the lattice thermal conductivity in the Ag₄SeS solid solution alloy: the thermal conductivity maintains very low value and covers a range of 0.64–0.71 W/mK over a temperature range of 300–480 K. The figures of merit for Ag₄SeS nanocrystals calculated from the above data with the relationship \( \sigma \cdot S^2T/\kappa \), are shown. Of note, the Ag₄SeS nanocrystals achieve a maximum \( ZT_{\text{max}} = 0.33 \) at the phase transition temperature around 355 K.

![Fig. 2.11](image_url)

**Fig. 2.11** Temperature-dependence of the Seebeck coefficient (a); electrical conductivity (b); thermal conductivity (c) and thermoelectric figure of merit \( ZT \) (d) for Ag₂S, Ag₂Se and Ag₄SeS nanocrystals respectively.
2.3 Conclusion

In summary, nearly monodisperse silver chalcogenide nanocrystals were successfully synthesized through a facile colloidal method, and their thermoelectric property across the semiconductor–superionic conductor phase transition was systematically investigated for the first time. Our findings reveal that regulating the phase transition behavior coupled with reduced grain size in solids allows advances in balancing the electronic and thermal properties for optimal thermoelectric properties. As a consequence, a maximized $ZT$ was achieved around the temperature of the semiconductor–superionic conductor transition. Furthermore, along with the effective scattering of short-wavelength phonons by atomic defects created by alloying, the alloyed ternary silver chalcogenide compounds, Ag$_4$SeS shows much lower thermal conductivity and better $ZT$ value around the phase transition temperature, which is cooperatively contributed by semiconductor–superionic phase transition, reduction of grain size, and alloying. This work inspires us that taking advantage of the cooperative contribution of superionic phase transition, reduced grain size and alloying opens up a promising new approach to tailor materials for optimal thermoelectric performance.

References


Table 2.1 Summary of Seebeck coefficient, electrical conductivity, thermal conductivity and figure of merit $ZT$ at phase transition temperature for Ag$_2$S, Ag$_2$Se and Ag$_4$SeS nanocrystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transition temperature ($T_t$, K)</th>
<th>Seebeck coefficient at $T_t$ ($\mu$V/K)</th>
<th>Electrical conductivity at $T_t$ ($10^4$ Ω m)</th>
<th>Thermal conductivity at $T_t$ (W/mK)</th>
<th>$ZT$ at $T_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$S</td>
<td>454</td>
<td>−75.8</td>
<td>4.92</td>
<td>1.05</td>
<td>0.12</td>
</tr>
<tr>
<td>Ag$_2$Se</td>
<td>408</td>
<td>−108</td>
<td>4.41</td>
<td>0.89</td>
<td>0.23</td>
</tr>
<tr>
<td>Ag$_4$SeS</td>
<td>355</td>
<td>−129</td>
<td>3.95</td>
<td>0.71</td>
<td>0.33</td>
</tr>
</tbody>
</table>


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