Thermoelectric Silver-Based Chalcogenides

Si Yin Tee,* Daniel Ponsford, Chee Leng Lay, Xiaobai Wang, Xizu Wang, Darren Chi Jin Neo, Tianze Wu, Warintorn Thitsartarn, Jayven Chee Chuan Yeo, Guijian Guan, Tung-Chun Lee, and Ming-Yong Han*

Heat is abundantly available from various sources including solar irradiation, geothermal energy, industrial processes, automobile exhausts, and from the human body and other living beings. However, these heat sources are often overlooked despite their abundance, and their potential applications remain underdeveloped. In recent years, important progress has been made in the development of high-performance thermoelectric materials, which have been extensively studied at medium and high temperatures, but less so at near room temperature. Silver-based chalcogenides have gained much attention as near room temperature thermoelectric materials, and they are anticipated to catalyze tremendous growth in energy harvesting for advancing internet of things appliances, self-powered wearable medical systems, and self-powered wearable intelligent devices. This review encompases the recent advancements of thermoelectric silver-based chalcogenides including binary and multinary compounds, as well as their hybrids and composites. Emphasis is placed on strategic approaches which improve the value of the figure of merit for better thermoelectric performance at near room temperature via engineering material size, shape, composition, bandgap, etc. This review also describes the potential of thermoelectric materials for applications including self-powering wearable devices created by different approaches. Lastly, the underlying challenges and perspectives on the future development of thermoelectric materials are discussed.

1. Introduction

The concept of thermoelectricity dates from 1821, with the discovery of the Seebeck effect by T. J. Seebeck. This effect describes the creation of a voltage which arises from the temperature difference between two points of an electrically conducting material. In 1834, J. C. A. Peltier discovered the analogous reverse effect by generating heat flow with an electric current. Two decades later in 1854, W. Thomson demonstrated that reversible heating or cooling was possible under an electric current and in the presence of a temperature gradient. The combination of the Seebeck, Peltier, and Thomson effects define the field of thermoelectrics today, although it took almost a century for the initial discoveries to translate into an active field of research. In the early 20th century, thermoelectric materials were actively studied for use in valuable technologies, particularly for cooling and power generation applications in both civilian and military scenarios.

A. F. Ioffe developed the modern theory of semiconductor physics and enabled its applicability to thermoelectrics in 1949 by introducing the thermoelectric figure of merit, $zT = S^2 \sigma T / \kappa$, to evaluate thermoelectric performance, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the absolute temperature. It was found that thermoelectric materials with a high $zT$ are typically heavily doped semiconductors, the best-known examples being the tellurides of antimony, bismuth, and lead. In the 1950s, Goldsmid and...
Douglas demonstrated thermoelectric cooling to 0 °C with Bi₂Te₃.[⁴] the Soviet Union developed the first commercial thermoelectric generator using ZnSb.[³] and Chasmar and Stratton established a general strategy to quantify the thermoelectric performance of semiconductors depending on their effective mass, carrier mobility, doping, temperature, and thermal conductivity.[⁵] In 1995, Slack introduced a phonon-glass/electron-crystal strategy to disrupt phonon transport without affecting electron transport, opening up a new avenue for engineering thermoelectric materials with complex structures such as clathrates and skutterudites, which have large voids in their crystal structures. These developments have significantly broadened the commercial usage of devices capable of converting waste heat to electricity.[⁶]

The most widely investigated thermoelectric materials to date are metal chalcogenides based on Bi–Te/Sn–Se/Cu–Se, half-Heusler compounds, multicomponent oxides, GeTe/Pb/Te hybrids, and organic-inorganic composites.[⁷] Thermoelectric performance is generally assessed at low temperature (<300 K), near room temperature (300–500 K), medium temperature (500–800 K) and high temperature (>800 K). Bi–Te-based materials are perhaps those most commonly utilized with an optimal operation at near room temperature,[⁸,⁹] whereas (AgSbTe₂)ₓ(GeTe)₁₋ₓ are considered as the most prominent materials for applications at medium temperatures.[¹⁰,¹¹] SiGe is classically used in thermoelectric devices expected to operate at higher temperatures.[¹²,¹³]

Statistical data reveal that low-grade waste heat with temperatures of <100 °C (373 K) accounts for ≈63% of total waste heat worldwide.[¹⁴–¹⁶] Recent developments in room temperature thermoelectric materials promise to go some way to addressing this energy wastage problem. In particular, the excellent near room temperature thermoelectric performance of binary AgₓE (E = S, Se, Te) compounds and their multinary derivatives and hybrids is notable. These properties are attributed to the narrow bandgap, high electron mobility, and low electron effective mass required to achieve high electrical conductivity as well as relatively high Seebeck coefficient of such materials.[¹⁷] Moreover, Ag–Se-based materials are a desirable alternative to traditional Bi–Te materials because of the scarce availability of tellurium (0.001 ppm) in the Earth’s crust[¹⁸,¹⁹] and the toxicity of Bi–Te alloys.

Most recently, there has been a surge in research articles reporting on the development of silver-based chalcogenide thermoelectric materials, devices, and applications (Figure 1). This review aims to present a comprehensive survey of the developments in binary, multinary silver-based chalcogenides, as well as their hybrids and composites (Table 1). First, we introduce the preparative methodologies for silver-based chalcogenide materials and devices. Secondly, we review the advanced properties and aspects of structural design required for improving thermoelectric performance, by considering quantum confinement, nanostructuring/doping/alloying/vacancies, point defects/dislocations/interfaces/inclusions, and porosity (Figure 2a). Thirdly, we summarize the promising applications of these materials, including the development of flexible thermoelectric materials for wearable devices (Figure 2b). Last, we provide insights and perspectives on the work needed to leverage current successes and address future challenges in the field of silver-based chalcogenide thermoelectric materials.

Figure 1. Number of publications in a quadrennial period, as reported by the Web of Science when using the topic “silver thermoelectric” in the search engine.

2. Preparative Methodologies in Solid, Liquid, and Vapor Phases

Silver-based chalcogenides have been prepared via solid-state, liquid-state, and vapor-state reactions (Figure 3). The solid-state reaction methods include mechanical alloying, melt alloying, additive manufacturing, and crystal growth such as the Bridgman method or zone melting. The liquid-state reaction routes (also known as wet-chemical syntheses) comprise colloidal synthesis, hydrothermal or solvothermal precipitation, microwave- or ultrasound-assisted preparation, and template-assisted ion exchange reactions. The vapor-state preparation approaches encompass a variety of physical and chemical vapor deposition techniques.

2.1. Solid-State Preparation

Thermoelectric bulk materials can be prepared by blending two or more elements in stoichiometric quantities and then heating at a high temperature (500–2000 °C) in sealed quartz ampules. These solid-state reactions require a significant amount of heat to overcome the lattice energy, and enable the diffusion of cations and anions into various sites in products including Ag₄S,[²⁰] Ag₄Se,[¹⁹] Ag₃S₀·₈Te₀·₂,[²⁰] KAg₄Se₂,[¹⁷] and AgCu₀·₉₅Ni₀·₀₄Se.[²²] This traditional process is time-consuming and energy-intensive, and also presents difficulties for large-scale production. Meanwhile, the presence of trace impurities or secondary phases in products will greatly affect their thermoelectric properties. These effects arise when reactants are not present in exact stoichiometric proportions, and if unreacted residues remain following the reaction.[²¹] As the microstructures and properties of solidified ingots are strongly related to their liquid states,[²⁴] liquid-state sintering has been used to effectively optimize the microstructures to improve thermoelectric performance. This sintering method enables the rearrangement, dissolution, and recrystallization of grains.[²⁵–²⁷] Compared to conventional preparation routes of silver chalcogenides, a high-pressure preparation
Table 1. Summary of material preparation and thermoelectric characteristics of silver-based chalcogenides.

| Type | Silver-based chalcogenides | Preparation methods | \( \sigma [S \text{ cm}^{-1}] \) | \( S [\mu \text{V K}^{-1}] \) | \( \kappa [\text{W m}^{-1} \text{K}^{-1}] \) | Thermoelectrics \((zT, PF, PD, V, P, V_{oc})\) | Refs. |
|------|-----------------------------|---------------------|----------------|----------------|----------------|----------------|--------|
| Binary Ag\(_2\)S, Ag\(_2\)Se, Ag\(_2\)Te | Ag\(_2\)S | High pressure preparation | 240 | –150 | 0.45 | \(zT 0.62, 560 \text{ K} \) | [29] |
| | Ag\(_2\)Se | Melt alloying | 1988 | –133 | 1.0 | \(zT 0.96, 300 \text{ K} \) | [67] |
| | Ag\(_2\)Se | Melt alloying | 714 to 2500 | –90 to -160 | 0.8 to 2 | \(zT 1.0, 300 \text{ to } 375 \text{ K} \) | [19] |
| | Ag\(_2\)Se | Liquid-phase sintering | 2000 | –130 | 1.2 | \(zT 1.21, 389 \text{ K} \) | [68] |
| | Ag\(_2\)Se | Hydrothermal + SPS | 1500 | –120 | 1.1 | \(zT 0.6, 300 \text{ K} \) | [69] |
| | Ag\(_2\)Se | Aqueous synthesis + SPS | 981 | –146 | 0.77 | \(zT 0.8, 300 \text{ K} \) | [43] |
| | Ag\(_{1.975}\)Se\(_{1.025}\) | Mechanical alloying + pulse discharge sintering | 1000 | –145 | 0.8396 | \(zT 0.6, 300 \text{ K} \) | [37] |
| | Ag\(_{2.006}\)Se | Melt alloying + BM + HP | 1430 | –135 | 1.3 | \(zT 0.6, 300 \text{ K} \) | [70] |
| | Ag\(_2\)Se\(_{0.66}\) | Melt alloying + SPS | 1290 | –153 | 1.08 | \(zT 0.84, 300 \text{ K} \) | [71] |
| | Ag\(_2\)Se\(_{0.66}\) | Melt alloying + SPS | 1200 | –130 | 1.0 | \(zT 0.8, 300 \text{ K} \) | [72] |
| | Ag\(_2\)Se | Manual mixing + SPS | 1000 | –150 | 1.02 | \(zT 0.8, 390 \text{ K} \) | [73] |
| | Ag\(_2\)Se | Manual mixing + CP | 1700 | –132.5 | 0.9 | \(zT 1.2, 390 \text{ K} \) | [74] |
| | Ag\(_2\)Se | Aqueous synthesis + SPS | 6600 | –20 | 2.4 | \(zT 0.45, 323 \text{ K} \) | [51] |
| | Ag\(_2\)Se | Melt alloying + Zone melting | 1000 | –140 | 0.9 | \(zT 0.75, 300 \text{ K} \) | [39] |
| | Ag\(_2\)Se | Wet mechanical alloying + SPS | 900, 300K | –150, 300K | 0.83, 300K | \(zT 0.7, 300 \text{ K}; zT 0.9, 390 \text{ K} \) | [75] |
| | Ag\(_2\)Se | Cationic exchange | 750 | –90 | 0.53 | \(zT 0.46, 300 \text{ K} \) | [57] |
| | Ag\(_2\)Se | Melt alloying + SPS + pulsed laser deposition | 1000 | –120 | – | PF 1750 \(\mu \text{W m}^{-1} \text{K}^{-2}, 300 \text{ K} \) | [64] |
| | Ag\(_2\)Te | Colloidal synthesis +LBL dip coating | 13.5 | –110 | 0.045 | \(zT 0.32, 390 \text{ K} \) | [76] |
| | Ag\(_2\)Te | Solvothermal + SPS | 400 | –135 | 0.53 | \(zT 0.9, 623 \text{ K} \) | [44] |
| | Ag\(_2\)Ag\(_2\)Te | Solvothermal + SPS | 400 | –140 | 0.5 | \(zT 1.1, 623 \text{ K} \) | [44] |
| | S:Ag\(_2\)Te | Solvothermal + HP | 819.9 | –150 | 0.4 | \(zT 0.62, 550 \text{ K} \) | [77] |
| Ternary Ag-E\(_1\)E\(_2\)E = S, Se, Te | Ag\(_{1.975}\)Se\(_{1.025}\) | Melt alloying + SPS | 300 | –140 | 0.57 | \(zT 0.26, 300 \text{ K} \) | [20] |
| | Ag\(_{1.975}\)Se\(_{1.025}\) | Melt alloying + HP | 2000 | –178 | 0.7 | \(zT 1.08, 350 \text{ K} \) | [78] |
| | Ag\(_{2}\)Se | Colloidal synthesis + HP | 395 | –129 | 0.71 | \(zT 0.33, 355 \text{ K} \) | [45] |
| | Ag\(_2\)S\(_2\)Te\(_2\) | Melt alloying + HP | 800 | –83 | 0.78 | \(zT 0.2, 300 \text{ K} \) | [79] |
| | Ag\(_{2}\)S\(_2\)Te\(_2\) | Melt alloying + HP | 500 | –120 | 0.63 | \(zT 0.7, 573 \text{ K} \) | [79] |
| | Ag\(_{2}\)S\(_2\)Te\(_2\) | Melt alloying + SPS | 150 | –145 | 0.33 | \(zT 0.63, 450 \text{ K} \) | [20] |
| | Ag\(_{2}\)S\(_2\)Te\(_2\) | Melt alloying + SPS | 250 | –150 | 0.44 | \(zT 0.63, 450 \text{ K} \) | [20] |
| | Ag\(_{2}\)S\(_2\)Te\(_2\) | Melt alloying | 230 | –175 | 0.5 | \(zT 0.8, 600 \text{ K} V_{oc} 69.2 \text{ mV}, P 17.1 \text{ }\mu \text{W}, \Delta T 70 \text{ K} \) | [80] |
| Ternary Ag-M:Se/Se/Te M = Si, K, Cu, Ga, In, Sn, Sb, Au, Bi | KAg\(_3\)Se\(_2\) | Bridgman method | 0.1, RT | – | 0.4, RT | – | [21] |
| | Ag\(_{1.975}\)S\(_{1.025}\)Se | Chemical synthesis + SPS | 2130 | –115 | 0.88 | \(zT 0.9, 300 \text{ K} \) | [81] |
| | Ag\(_{1.975}\)Cu\(_{0.025}\)Se | Aqueous synthesis + SPS | 1778 | –120.1 | 0.83 | \(zT 1.2, 393 \text{ K} \) | [43] |

(Continued)
| Type                  | Silver-based chalcogenides          | Preparation methods | \( \sigma \) [S cm\(^{-1}\)] | \( S \) [\( \mu \)V K\(^{-1}\)] | \( \kappa \) [W m\(^{-1}\) K\(^{-1}\)] | Thermoelectrics (\( zT \), PF, PD, \( V \), \( P \), \( V_{OC} \)) | Refs. |
|----------------------|--------------------------------------|---------------------|--------------------------|--------------------------|--------------------------|-----------------------------------------------|-------|
| \( \text{Ag}_3\text{AuSe}_2 \) | Colloidal synthesis + HP             | 900                 | -130                     | 0.6                      | \( zT \geq 0.88, 390 \) K | \[46\]                                      |       |
| \( \text{Ag}_3\text{SiSe}_6 \) | Melt alloying + HP                   | 1000                | -130                     | 0.9                      | \( zT \geq 0.6, 300 \) K | \[82\]                                      |       |
| \( \text{AgSb}_{0.99}\text{Se}_2 \) | Melt alloying                        | 75                  | 300                      | 0.4                      | \( zT \geq 1.6, 10 \) K | \[83\]                                      |       |
| \( \text{AgInSe}_2 \) | Melt alloying + HP                   | 80                  | -295                     | 0.39                     | \( zT \geq 1.1, 900 \) K | \[84\]                                      |       |
| \( \text{AgCuSe} \) | Melt alloying + SPS                  | 1200                | -118                     | 1.01                     | \( zT \geq 0.6, 450 \) K | \[85\]                                      |       |
| \( \text{AgCuSe} \) | Aqueous synthesis + SPS             | 1050                | -90                      | 0.7                      | \( zT \geq 0.42, 323 \) K | \[86\]                                      |       |
| \( \text{AgCuSe} \) | Aqueous synthesis + SPS             | 100                 | 210                      | 0.3                      | \( zT \geq 0.9, 623 \) K | \[86\]                                      |       |
| \( \text{AgCuSe} \) | Colloidal synthesis + HP            | 100                 | -190                     | 0.25                     | \( zT \geq 0.68, 566 \) K | \[87\]                                      |       |
| \( \text{AgCuTe} \) | Melt alloying                        | 150                 | 240                      | 0.4                      | \( zT \geq 1.45, 700 \) K | \[88\]                                      |       |
| \( \text{AgCuS} \) | Chemical synthesis + CP + sintering  | 1.8                 | 400                      | 0.55                     | \( zT \geq 0.03, 380 \) K | \[89\]                                      |       |
| \( \text{AgBi}_2 \) | Chemical synthesis + CP + sintering  | 32                  | -195                     | 0.55                     | \( zT \geq 0.2, 810 \) K | \[90\]                                      |       |
| \( \text{AgBi}_2 \) | Melt alloying + SPS                  | 100                 | -235                     | 0.48                     | \( zT \geq 0.7, 823 \) K | \[91\]                                      |       |
| \( \text{AgSb}_{0.95}\text{Te}_2 \) | Melt alloying + CP + sintering       | 5                   | 375                      | 0.1                      | \( zT \geq 0.62, 814 \) K | \[92\]                                      |       |
| \( \text{AgSb}_{0.9} \text{Cl}_0.1 \text{Te}_2 \) | Melt alloying + SPS                | 13                  | 400                      | 0.2                      | \( zT \geq 1.87, 83 \) K | \[93\]                                      |       |
| \( \text{AgCuSe}_{0.95}\text{Te}_{0.05} \) | Melt alloying + SPS                 | 1000                | -115                     | 0.8                      | \( zT \geq 0.7, 450 \) K | \[94\]                                      |       |

Quaternary \( \text{Ag} \cdot \text{M}_{1} \cdot \text{M}_{2} \cdot \text{S/Se/Te} \)

\( M = \text{Na, Mg, Ca, Mn, Ni, Cu, Zn, Nb, Cd, Ga, In, Sn, Sb, Ba, Pb, Bi} \)
Table 1. (Continued).

| Type | Silver-based chalcogenides | Preparation methods (HP, CP, SPS, LBL, DC, BM) | $\sigma$ [S cm$^{-1}$] | $S$ [µV K$^{-1}$] | x [W m$^{-1}$ K$^{-1}$] | Thermoelectrics (zT, PF, PD, V, P, Voc, mV) | Refs. |
|------|-----------------------------|-----------------------------------------------|------------------------|-------------------|---------------------|----------------------------------------|------|
|      | $\text{Ag}_9\text{Bi}_{0.005}\text{Se}_{2}$ | Melt alloying + SPS | 125 | $-185$ | 0.5 | $zT = 0.7, 773$ K | [108] |
|      | $\text{AgPbBiSe}_3$ | Melt alloying | 70 | $-195$ | 0.52 | $zT = 0.43, 818$ K | [109] |
|      | $\text{AgS}_{0.7}\text{Bi}_{0.3}\text{Se}_{0.5}$ | Melt alloying + HP + annealing | 100 | $-200$ | 0.45 | $zT = 1.4, 800$ K | [110] |
|      | $\text{AgS}_{0.9}\text{Si}_{0.1}\text{Se}_{0.5}$ | Melt alloying | 250 | 264 | 0.4 | $zT = 2.6, 573$ K | [106] |
|      | $\text{AgS}_{0.9}\text{Si}_{0.1}\text{Se}_{0.5}$ | HP + annealing | 210 | 290 | 0.35 | $zT = 1.9, 584$ K | [112] |
|      | $\text{AgS}_{0.7}\text{Bi}_{0.3}\text{Se}_{0.5}$ | Melt alloying + SPS | 80 | 325 | 0.47 | $zT = 1.6, 850$ K | [113] |
|      | $\text{AgMnSbTe}_3$ | Melt alloying + SPS | 242 | 225 | 0.7 | $zT = 1.46, 823$ K | [114] |
|      | $\text{Ag}_{0.2}\text{Cu}_{0.89}\text{In}_{0.01}\text{Te}$ | Melt alloying | 1100 | 170 | 2.75 | $zT = 1.856, 298$ K | [115] |
|      | $\text{AgInSe}_2/\text{Ag}_2\text{Se}$ | Melt alloying + SPS | 50 | $-200$ | – | $zT = 0.9, 846$ K | [127] |
|      | $\text{Ag}_{5}\text{Bi}_{0.005}\text{Se}_{2}$ | Melt alloying + SPS | 150 | $-170$ | 0.45 | $zT = 0.8, 800$ K | [128] |
|      | $\text{Ag}_2\text{Se}/5\text{mol}\%\text{Te}$ | Colloidal synthesis + HP | 1000 | $-165$ | 0.7 | $zT$ up to 0.79, RT | [17] |

Other multinary: quinary, senary and septenary

| Type | Silver-based chalcogenides | Preparation methods (HP, CP, SPS, LBL, DC, BM) | $\sigma$ [S cm$^{-1}$] | $S$ [µV K$^{-1}$] | x [W m$^{-1}$ K$^{-1}$] | Thermoelectrics (zT, PF, PD, V, P, Voc, mV) | Refs. |
|------|-----------------------------|-----------------------------------------------|------------------------|-------------------|---------------------|----------------------------------------|------|
|      | $\text{Ag}_{0.985}\text{In}_{0.015}\text{BiSe}_2$ | Melt alloying | 125 | $-185$ | 0.5 | $zT = 0.7, 773$ K | [108] |
|      | $\text{Ag}_{0.96}\text{Zn}_{0.04}\text{Se}_2$ | Melt alloying | 240 | 225 | 0.7 | $zT = 1.46, 823$ K | [114] |
|      | $\text{Ag}_{0.2}\text{Cu}_{0.89}\text{In}_{0.01}\text{Te}$ | Melt alloying | 1100 | 170 | 2.75 | $zT = 1.856, 298$ K | [115] |
|      | $\text{Ag}_{2}\text{Se}/5\text{mol}\%\text{Te}$ | Colloidal synthesis + HP | 1000 | $-165$ | 0.7 | $zT$ up to 0.79, RT | [17] |
| Type | Silicon-based chalcogenides | Preparation methods | κ [W m\(^{-1}\) K\(^{-1}\)] | σ [μS cm\(^{-1}\)] | \(\mu\) [W m\(^{-1}\) K\(^{-1}\)] | Δ{T [K]} | \(\tau\) [s] | \(\Delta V\) [mV] | Power factor PF | Power density PD | References |
|------|-----------------------------|---------------------|-----------------|----------------|-----------------|-------------|-------|-------------|----------------|----------------|-----------------|
| Ag₂Se/paper | Solvothermal synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/PEDOT | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/PVDF | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyethylene | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyurethane | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyimide | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyamide | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyester | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polythiophene | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyethylene-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyacrylate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyurethane-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |
| Ag₂Se/polyvinylidene-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate-terephthalate | Chemical synthesis | 2.34 | 860 | 5.86 | 1.8 | 27K | 1.1 | 1000 | 0.12, 300K | 0.12, 300K | 134 |

\(\tau\): figure of merit; PF: power factor; PD: power density; V: output voltage; P: output power; V: open circuit voltage; ΔT: temperature difference; SPS: spark plasma sintering; HP: hot pressing; CP: cold pressing; LBL: layer-by-layer; DC: drop casting; BM: ball milling.
Figure 2. a) Schematic illustration of engineering strategies for optimizing silver-based chalcogenide thermoelectric materials. b) Schematic comparison of various binary, ternary, quaternary, hybrid, and composite silver-based chalcogenide thermoelectric materials for the applications of waste heat harvesting and their temperature range of operation.
Preparativemethodologiesofsilver-basedchalcogenidesbased
on solid-, liquid-, and vapor-state reaction. Solid-state reaction meth-
ods include mechanical milling, melt alloying, zone melting, Bridg-
man method, additive manufacturing, high-pressure preparation, and
spark plasma sintering. Liquid-state reaction preparations usually in-
volve wet-chemical routes in aqueous solutions/organicsolventsthrough
colloidsynthesis,hydrothermal/solvothermalprecipitation,microwave-
/ultrasound-assistedpreparationortemplate-assistedionexchangereac-
tions. Vapor-statereactionsencompassavarietyofphysicalandchemical
vapor deposition techniques.

2.2. Liquid-State Preparation

Providing enhanced control of stoichiometry, structure, and
phase purity, wet-chemical syntheses in the liquid phase have
become an increasingly important way to prepare a variety of
metal chalcogenides,[41] and their nanostructured derivatives.[42]
These syntheses present an energy-efficient strategy to syn-
these a wide variety of binary (Ag₂Se,[43]Ag₂Te,[44]) and
ternary (Ag₃SeS,[45]Ag₅AuSe₃[46]) silver-based chalcogenides and
their hybrids or composites.[47] In organic solvents, the col-
loidal synthesis of organic-coated chalcogenides often involves
the thermal decomposition of precursors in the presence of
surfactants,[45,48–50] which is unfavorable due to reduced elec-
trical conductivity and usually requires a prior ligand displace-
ment procedure.[17] Aqueous synthesis is preferred for the large-
scale production of chalcogenides (e.g., binary Ag₂Se, hybrid
Ag₆:Ag₂Se and ternary Cu⁺:Ag₂Se) at room temperature and
atmospheric pressure, as high temperatures and organic sol-
vents/surfactants are not required.[51]

Hydrothermal/solvothermal syntheses proceed in
aqueous/non-aqueous solutions in closed stainless steel au-
toclaves at high temperature and pressure.[44,51,52] Microwave-
assisted syntheses are carried out in solution and are enabled
by the friction and collisions between polar molecules under
an alternating electromagnetic field.[53–55] Alternatively, sono-
chemistry is used to produce inorganic particles via chemical
reaction under powerful ultrasound radiation between 20 kHz
and 15 MHz.[56] Ion exchange reactions are commonly used to
synthesize semiconductor nanocrystals, whereby guest cations

Photopolymerization-based processes can print high-quality sur-
face finishes at a fine resolution. However, the drawbacks of this
technique include a restricted choice of photoresists and a com-
plex curing process.[31] Powder bed fusion techniques employ se-
lective laser melting and selective laser sintering technology that
uses a heat source, such as a high power-density laser, to melt and
fuse regions of a powder bed,[32] while material jetting provides a
means to deposit materials in liquid or solid suspensions.[33] Owing
to the simplicity of the process, the extrusion of inks containing
inorganic particles is one of the most widely utilized printing
techniques for the production of inorganic thermoelectric mater-
ials with precise shape and dimension.[36]

Mechanical alloying (under wet or dry conditions) is com-
monly used to produce nano/microstructured silver-based
chalcogenides with reduced thermal conductivities.[37,38] A draw-
back of this technique is the extended and energy-intensive
milling process, which is required. Zone melting can directly
generate bulk Ag₂Se polycrystals without the need for additional
sintering processes, thus avoiding possible elemental inho-
mericity and the production of off-stoichiometric silver precipi-
tates or metastable phases, which arise from the migration of Ag⁺
and the volatilization of Se at high temperatures.[39] Alternatively,
the Bridgman method is used to grow AgBiSe₂ and Ge-doped
(GeSe)(AgBiSe₂)₁ₓ₋ₓ through directional solidification, by trans-
lating a melt from the hot zone to the cold zone in furnace.[40] As
reported, Bridgman-grown AgBiSe₂ possesses a low electrical re-
sistivity, likely ascribed to high packing density, high crystallinity
and presence of fewer grain boundaries.

Figure 3. Preparative methodologies of silver-based chalcogenides based
on solid-, liquid-, and vapor-state reaction. Solid-state reaction meth-
ods include mechanical milling, melt alloying, zone melting, Bridg-
man method, additive manufacturing, high-pressure preparation, and
spark plasma sintering. Liquid-state reaction preparations usually in-
volve wet-chemical routes in aqueous solutions/organicsolventsthrough
colloidsynthesis,hydrothermal/solvothermalprecipitation,microwave-
/ultrasound-assistedpreparationortemplate-assistedionexchangereac-
tions. Vapor-statereactionsencompassavarietyofphysicalandchemical
vapor deposition techniques.
are able to substitute with the host cations within the crystal lattice. A successful example of a cationic exchange transformation is the fabrication of polycrystalline Ag₂Se thin films, which was achieved by soaking Cu₁₋ₓSe films in a Ag⁺-rich solution.²⁵⁷

2.3. Vapor-Phase Preparation

Vapor condensation and surface reactions enable the formation of highly pure particles from individual atoms or molecules in the gas phase. The vapor-phase preparation process is highly susceptible to changes in vapor concentration, temperature, and pressure. Chemical and physical vapor phase deposition are two common methods for the fabrication of silver-based chalcogenide thin films. Chemical vapor deposition (CVD) is the formation of a thin film from the gaseous phase via the reaction and/or decomposition of volatile precursors on a substrate surface. Conventional CVD has been used for the growth of nanowire arrays in thermoelectric microgenerators,³⁵⁸ as well as the fabrication of β-Ag₂Se with unique hollow and layered branch-like morphology.³⁵⁹ Various modifications to traditional CVD processes also exist. Plasma-enhanced CVD utilizes plasma to catalyze the reaction of precursors at lower temperatures. Alternatively, atomic layer deposition is a CVD technique, which harnesses self-limiting and sequential reactions to produce ultrathin, conformal films with atomic-scale control over thickness and composition.⁶⁰,⁶¹ However, the atomic layer deposition of metal chalcogenide films is limited by the availability, reactivity, and toxicity of appropriate precursors.⁶²

In comparison, physical vapor deposition (PVD) involves only physical methods to deposit vaporized materials from solid targets onto substrates. For instance, a simple thermal evaporation route was used to prepare thin films of Ag₂Se with various thicknesses by using a heat source to evaporate bulk polycrystalline Ag₂Se in vacuo.⁶³ A related technique, pulsed laser deposition, is carried out by focusing a high-energy pulsed laser beam on a solid target material, such as Ag₂Se, inside a vacuum chamber. Using this method, the nonepitaxial growth of Ag₂Se thermoelectric thin films with desired phase and composition has been demonstrated.⁶⁴ Further iterations of PVD include reactive sputtering, in which compound films are deposited on substrates by introducing a reactive gas precursor, and magnetron sputtering, whereby magnetically confined plasma collides with an electrode or target in order to eject atoms for deposition on a substrate. Recently, pulsed hybrid reactive magnetron sputtering was used to develop a series of high-performance thermoelectric thin films at room temperature without the requirement for high-temperature post-treatment.⁶⁵,⁶⁶ Consequently, this method is particularly suitable for fabricating silver chalcogenide thin films with highly accurate stoichiometry on polymer substrates for applications such as wearable devices.⁶⁶

2.4. Densification of Powders

Generally, as-prepared thermoelectric materials are first sintered and then densified into pellets prior to characterization. The sintering process is critically important, since the microstructures formed during the process strongly influence the thermoelectric properties of the material. Applying pressure during the sintering process causes an increase in the driving force and kinetics of the densification. Spark plasma sintering (SPS) has become the most employed densification method, presenting significant advantages over conventional hot-pressing sintering, such as lower sintering temperatures and pressures, and shorter dwell times. As a result, coarsening and grain growth are minimized, and finer-grained dense structures and high relative densities can be achieved in a short time. Most importantly, nanosized powders can be sintered in this way without considerable grain growth.²³

3. Binary Silver Chalcogenides (Ag₂E)

Binary silver chalcogenides, Ag₂E (E = S/Se/Te), including silver sulfide, selenide, and telluride have emerged as promising candidate materials for heat energy harvesting at near room temperature (Table 1). Silver oxide (Ag₂O) has a larger bandgap (2.25 eV) than the rest of the silver chalcogenides (0.06–1 eV) and is not considered to be a good thermoelectric material. The optimal bandgap for maximizing the thermoelectric zT of a semiconductor material is found to be in the range of 6kBT/ℏ in kelvin.¹⁴⁹ According to this empirical rule, the narrow bandgaps of Ag₂S, Ag₂Se, and Ag₂Te semiconductors would indicate their potential for good thermoelectric performance.

3.1. Silver Sulfide (Ag₂S)

Ag₂S exists as three polymorphs: α-Ag₂S, β-Ag₂S, and γ-Ag₂S.¹⁵⁰ Monoclinic α-Ag₂S occurs at temperatures below ~450 K, while cubic β-Ag₂S exists in the temperature range 452–859 K, possessing a body-centered cubic (bcc) sublattice of S²⁻ with superionic properties. The γ-Ag₂S phase, with a face-centered cubic (fcc) sublattice of S²⁻, is stable from ~860 K up to melting temperature.¹⁵¹

Possessing a wider bandgap than Ag₂Se and Ag₂Te (~1 eV),¹⁵² Ag₂S exhibits a low electrical conductivity of approximately 10⁻¹ S m⁻¹, together with a low Seebeck coefficient and reasonably high electronic thermal conductivity; this combination of properties results in limited thermoelectric performance. To optimize the carrier concentration of Ag₂S, nonstoichiometric Ag₂₋ₓS was prepared by introducing Ag vacancies which enhance the electrical transport properties and prevent the loss of volatile sulfur through sublimation.²⁹,¹⁵³ Furthermore, the high-pressure approach used in this case promoted the formation of porous structures, which in turn reduced the lattice thermal conductivity, and thus a zT of 0.62 at 560 K was reached for the Ag₂₁.₈₆S system.

A high degree of ductility is commonly observed in metals and metal alloys, in contrast with semiconductors and ceramic materials. Owing to its wrinkled layer structure and weak Ag–S bonds, monoclinic Ag₂S exhibits unexpected ductility at room temperature (Figure 4a–d).²⁰,¹⁵₃,¹⁵₄ A study of the chemical bonding by Shi and co-workers found that silver diffusion results in the irregular distribution of Ag–Ag and Ag–S bonds, which suppresses the cleavage of Ag₂S, resulting in the high mechanical performance of the semiconductor.¹⁵₃ Stretchable thin films of Ag₂S have been produced according to a solution-processed synthesis on a stretchable substrate, which were capable of maintaining
Figure 4. Crystal structures for a) monoclinic Ag$_2$S and b) orthorhombic Ag$_2$Se. Reproduced under Creative Common CC BY 4.0 license.\cite{154} Copyright 2021, The Authors. Published by AAAS. c) Flexibility-$zT$ phase diagram for Ag$_2$S-Ag$_2$Se-Ag$_2$Te system. d) Twisted Ag$_2$S$_{0.5}$Se$_{0.5}$ and Ag$_2$S$_{0.8}$Te$_{0.2}$ samples in various shapes. e) Temperature dependence of $zT$ for Ag$_2$S$_{1-x}$Se$_x$ ($x$ = 0) (white), 0.1 (green), 0.3 (purple), and 0.5 (cyan), Ag$_2$S$_{0.8}$Te$_{0.2}$ (red), and Ag$_2$S$_{0.5}$Se$_{0.45}$Te$_{0.05}$ (yellow). f) Optical image of a six-couple flexible Ag$_2$S$_{0.5}$Se$_{0.5}$/Pt-Rh thermoelectric device. Reproduced with permission.\cite{20} Copyright 2019, Royal Society of Chemistry.
structural integrity at a tensile strain of 14.9%.\cite{155} Semiconducting Ag$_2$S is able to accommodate large amounts of Se (50%) or Te (20%) in ternary alloys which maintain the flexibility and ductility performance of pristine Ag$_2$S.\cite{154} The plastic deformations of monoclinic Ag$_2$S are accessible at room temperature; this enables the usage of Ag$_2$S in the creation of flexible and wearable thermoelectric devices (e.g., biosensors, smart watches and e-skins).\cite{156–160}

### 3.2. Silver Selenide (Ag$_2$Se)

Ag$_2$Se crystallizes in an orthorhombic structure (β-Ag$_2$Se) under ambient conditions and undergoes a polymorphic phase transition to a cubic structure (α-Ag$_2$Se) at an elevated temperature (409 K, 1 atm), which is stable until melting at 1170 K.\cite{161} The β-Ag$_2$Se phase exhibits semiconducting properties due to a narrow bandgap (0.15 eV), while the α-Ag$_2$Se phase displays metallic superionic properties, in which Ag$^+$ ions become mobile within a rigid sublattice of Se$_2^−$.\cite{162} Modulation of the electric transport properties of Ag$_2$Se near the phase transition boundary between the orthorhombic and cubic phases has provided a means to optimize thermoelectric properties.\cite{43} Ferhat and Nagao fabricated polycrystalline orthorhombic Ag$_2$Se ingots through the direct reaction of Ag and Se at 1273 K in an evacuated quartz tube, accomplishing a very high power factor of $\approx 3500 \, \mu W \, m^{-1} \, K^{-2}$ and a $zT$ value of 0.96 at 300 K, which is one of the highest power factor values reported at room temperature. This high performance was ascribed to the relatively low thermal conductivity and high carrier mobility of the material.\cite{167}

In recent years, numerous attempts have been made to finely tune the composition of nonstoichiometric Ag$_2$Se in order to control the concentration of free carriers and optimize thermoelectric properties. This tuning typically results in an increase of average $zT$ with temperature, and a decrease in electron concentration. These observations likely arise from the presence of Se in the Ag$_2$Se. A peak $zT$ was attained at 300 K by Aliev and co-workers, at an electron concentration of $n = 6.5 \times 10^{28}$ cm$^{-3}$.\cite{163} Lee et al. prepared Ag- and Se-rich Ag$_2$Se by mechanical alloying followed by pulse discharge sintering.\cite{17} It was found that excess Ag atoms or clusters increased the carrier concentration, but decreased the Hall mobility. A slight excess of Se was found to increase the Hall mobility, which had a strong effect on the increased $zT$ values. Huang and co-workers prepared bulk Ag$_2$Se by melting and chemical alloying.\cite{172} Hot-pressing was subsequently used to obtain pellets which featured Ag- and Se-rich nanoprecipitates and micropores with Se precipitation.

Fine-tuning the Ag/Se ratio to afford a slight excess of Se optimized the carrier concentration, resulting in an average $zT$ of 0.83 in the nominal composition of Ag$_{0.92}$Se$_{1.02}$ over the range of 300–380 K.

Day et al. used a single parabolic band model calculation to predict a high $zT$ of $\approx 1.0$ for Ag$_2$Se with a less-than-stoichiometric amount of Se.\cite{170} However, such high performance was not realized in their Ag-rich samples, Ag$_{2+x}$Se, because the optimum carrier concentration was not reached at these compositions. Conversely, Mi et al. used Se-rich Ag$_{2+y}$Se$_{1+x}$ to tune the carrier concentrations and electrical transport properties of Ag$_2$Se.\cite{164} The introduction of a small excess of Se (Ag$_2$Se$_{1.08}$) enabled a significant reduction in the carrier concentration towards the optimum value, resulting in an improved power factor and $zT$ value with a maximum of $\approx 1$ at 401 K. Li and co-workers demonstrated that an improvement in the power factor of polycrystalline Ag$_2$Se could be achieved when a liquid-phase sintering process was introduced.\cite{168} The greater power factor was associated with an increase in the Seebeck coefficient, resulting from an increase in the effective mass. In addition, a decreased carrier mobility was observed because of reduced electronic thermal conductivity, resulting in a $zT$ value of $\approx 1.21$ for the Ag$_2$Se.

Another effective strategy to improve thermoelectric performance is to diminish the lattice contribution to the total thermal conductivity. Chen et al. employed a method of wet mechanical alloying with spark plasma sintering to prepare hierarchically structured β-Ag$_2$Se.\cite{74} This structure was observed to promote strong phonon scattering and suppress lattice thermal conductivity. The low lattice thermal conductivity of $\approx 0.35 \, W \, m^{-1} \, K^{-1}$ at 300 K arises from the porous nature of hierarchical β-Ag$_2$Se structures, which also contain metastable phases, nanosized grains, semicoherent boundaries, high-density dislocations, and localized strains. The combination of these features contributed to high $zT$ values of $\approx 0.7$ at 300 K and $\approx 0.9$ at 390 K (Figure 5). The fast fusing process of Ag$_2$Se grains during sintering creates the porous structure, due to the high surface energy of nanosized Ag$_2$Se powders which have been produced by a wet mechanical alloying process.\cite{165} Comparatively, conventional melting-annealing-sintering processes\cite{70} and manual grinding methods\cite{70,74} generally yield highly densified Ag$_2$Se samples. Similar porous structures have also been observed in other silver chalcogenides produced by solution methods.\cite{17,44,166} Possibly due to the high surface energy of the nanosized powders.

A sequential manual mixing and spark plasma sintering method has been developed as a facile reaction process to synthesize silver chalcogenides from elemental powders directly.\cite{73,74} In the absence of a high-temperature annealing step, the alloying process is driven by the dissociative adsorption reaction of Se and Ag, and promoted by intermittent grinding under ambient conditions.\cite{74} In this case, a stoichiometric mixture of Ag and Se powders was reacted to form orthorhombic Ag$_2$Se. Even without grinding, phase-pure orthorhombic Ag$_2$Se was obtained after standing for 13 h under ambient conditions, as a consequence of a direct reaction between solid Ag and Se vapor. The subsequent cold-pressed stoichiometric Ag$_2$Se pellet featured multiscale nanostructures, whilst hot-pressed pellets produced by spark plasma sintering exhibited a larger average grain size, ranging from a few microns to tens of microns. In comparison with the hot-pressed Ag$_2$Se pellets, the cold-pressed pellets exhibited lower carrier concentrations (closer to the optimal carrier concentration in Ag$_2$Se), accounting for a lower electrical conductivity and a higher Seebeck coefficient. Cold-pressed Ag$_2$Se also displayed a larger weighted majority-to-minority carrier mobility ratio (electron/hole ratio) and lower thermal conductivity. The combination of these attributes resulted in a $zT$ value of 1.2 at 390 K for cold-pressed Ag$_2$Se prepared by the solventless synthesis process at room temperature.

Wang et al. developed an aqueous solution strategy to synthesize Ag$_2$E (E = S/Se/Te).\cite{166} By tuning the composition of precursors (Ag$^+/E^2$ ratios), the thermoelectric performance of silver chalcogenides could be effectively optimized, yielding...
Figure 5. a) Dark-field transmission electron microscopy (TEM) image of Ag$_2$Se showing the grain and pore distribution. b) Schematic view for the nanopore distribution at grain interfaces. c) High-resolution TEM image taken along the [101] zone axis and its fast Fourier transform (FFT) pattern. d) Enlarged image from the orange square area in (c) in which the “O” and “M” represent the orthorhombic phase and metastable phase of Ag$_2$Se, respectively. High-resolution TEM image showing e) high-density dislocations and f) nanosized grains with semi-coherent interfaces. g) Schematic illustration of Ag$_2$Se with hierarchical pore architectures consisting of high-density pores, a metastable phase, nanosized grains, semi-coherent grain boundaries, high-density dislocations, and localized strains, resulting in high thermoelectric performance at room temperature. Reproduced with permission.[75] Copyright 2020, American Chemical Society.

maximum $zT$ values of 0.84 at 380 K for Ag$_2$Se, 0.59 at 650 K for Ag$_2$Te and 0.27 at 540 K for Ag$_2$S. Chen et al. obtained thin polycrystalline films of Ag$_2$Se from Cu$_2$-xSe template films via a cation exchange process between Cu$^+$ and Ag$^+$ at room temperature (2Ag$^+$ + Cu$_2$Se → Ag$_2$Se + 2Cu$^+$).[57] These polycrystalline films exhibited a maximum power factor of 825 mW m$^{-1}$ K$^{-2}$ and a $zT$ value of 0.46 at room temperature. The Cu$_2$-xSe films, with an average thickness of 80 nm, exhibited an electrical conductivity of $\approx$2.39 $\times$ 10$^5$ S m$^{-1}$ at room temperature due to the high carrier concentration of holes (Cu vacancies). This value decreased significantly to $7.5 \times 10^4$ S m$^{-1}$ following the rapid diffusion of Ag$^+$ guest ions into both vacant and interstitial sites of Cu$_2$Se. As a result, the value of the Seebeck coefficient switched from positive to negative, indicating the phase transformation from p-type Cu$_2$Se to n-type Ag$_2$Se.

3.3. Silver Telluride (Ag$_2$Te)

Ag$_2$Te crystallizes in a monoclinic structure ($\beta$-Ag$_2$Te) under ambient conditions,[167] and undergoes a polymorphic phase transition to a cubic structure ($\alpha$-Ag$_2$Te) at 423 K.[167] The $\beta$-Ag$_2$Te
phase exhibits semiconducting behavior, having a narrow bandgap of 0.06 eV, while α-Ag₂Te displays metallic superionic properties, as Ag⁺ cations are able to easily move through the cubic sublattice of Te²⁻ at high temperatures.[160] The transition between these phases modifies the electrical transport properties and lattice volume of the material, which are closely related to its thermoelectric properties.

The presence of small molecules such as hydrazine, 1,2-ethanediol, and ethylenediamine, on the surface of Ag₂Te nanocrystal thin films has been demonstrated to alter the electrical transport properties of such films.[76] These effects vary with the strength of the binding affinity of the molecule to the surface, which derives from the number and type of functional groups present in the molecule. The small molecules serve to scatter phonons, thus reducing thermal conductivity and allowing for higher thermoelectric performance at room temperature.

Apart from size control and the surface binding of small molecules, thermoelectric performance can also be tuned via morphological control. Without using a surfactant, Chang et al. performed a solvothermal synthesis of phase-pure Ag₂Te nanowires under different heating conditions.[44] The initial reduction to form elemental silver was followed by the introduction of active Te in a dissolution step. The growth of the Ag₂Te nuclei occurs preferentially in one dimension due to the base facet size and surface tension, and an overall minimization of surface energy. In addition, higher growth temperatures were shown to increase the surface energy of nanowires, resulting in interconnected nanowires. As the temperature was increased even further, dendrites were obtained. Upon densifying the Ag₂Te nanowires to pellets, a maximum zT value of 0.9 was obtained at 630 K.

The introduction of holes in Ag₂Te can be achieved by doping with a metal to increase carrier concentration. Besides the enhancement of electrical properties, the reduction of lattice thermal conductivity is also an effective way to substantially improve thermoelectric properties. For instance, 1.63% of additional silver in Ag₂Te was shown to modulate the carrier density by affecting defects (e.g., completely ionized silver atoms at interstitial sites and vacancies), and creating both additional donor and acceptor levels.[44] Owing to the optimized carrier concentration and strengthened phonon scattering, the Ag-rich Ag₃Te (Ag₂₋ₓ,ₓTe) sample in this work exhibited a maximum zT value of 1.1 at 623 K, which is higher than the zT of the binary Ag₂Te equivalent (0.9 at 623 K).

4. Ternary Silver-Based Chalcogenides

Ternary silver-based chalcogenides can be created by reacting a silver precursor with two types of chalcogen precursors, or a silver precursor with another metal and a chalcogen precursor, resulting in products with the chemical compositions Ag₁₋ₓEₓ-E₂ (E = S/Se/Te) and Ag₉-M-E (M = Si/K/Cu/Ga/In/Sm/Sb/Au/Bi, E = S/Se/Te), respectively (Table 1). By tuning their chemical stoichiometries (i.e., atomic ratio of Ag/E or Ag/M), electronic properties including bandgap energy, crystal structure, carrier concentration, and even mechanical characteristics can be altered for the enhancement of thermoelectric performance.

4.1. Ag₁₋ₓEₓ-E₂ (E = S/Se/Te)

Ag₁₋ₓEₓ-E₂ (E = S/Se/Te) compounds have been reported to exhibit superior thermoelectric performance compared to their binary counterparts, which is typically ascribed to the effective scattering of short-wavelength phonons by the atomic defects, which are generated through alloying. As mentioned previously, regulating the semiconductor-supersonic phase transition, in conjunction with reduced grain size in solids, enables the balancing of electronic and thermal properties for optimized thermoelectric behavior. As a result, ternary silver-based chalcogenides, such as Ag₉Se₂S, also display lower thermal conductivities and higher zT values around the phase transition temperature.[45]

Jood et al. strived to enhance carrier mobility whilst simultaneously tuning carrier concentration.[19] Their study successfully optimized zT values by firstly revealing structural transformations in bulk stoichiometric Ag₉Se at room temperature, and secondly by stabilizing the main orthorhombic structure via the introduction of a slight excess of S or Se. The relationships between structural changes, carrier transport, and Ag₉Se ratio were established and used to optimize zT values in Ag₉Se. Consequently, a 40–70% enhancement in carrier mobility (2510 cm² V⁻¹ s⁻¹ at 300 K) was achieved for Ag₉SeₓE₀.₅ (₀ ≤ 0.01, E = Se or S), together with a low lattice thermal conductivity (0.2–0.1 W m⁻¹ K⁻¹ over 300–375 K), which resulted from the optimized defect structure. As a result, a room-temperature power factor of 3.2 mW m⁻¹ K⁻² and zT values of 0.9–1.0 between 300–375 K could be reached.

Recent work on ternary silver-based chalcogenides has revealed that S substitution at the Se sites of Ag₂Se can lower the phase transition temperature.[78] Following S substitution, a high zT of 1.08 was obtained at 350 K for the composition Ag₂S₀.₄Se₀.₆, which was 40 K lower than stoichiometric Ag₂Se, indicating that Ag₂Se-based solid solutions have great potential as near room temperature thermoelectric materials.

Alloying with Se in Ag₉S has been shown to lead to vast increases in electrical conductivity, e.g., a five-orders-of-magnitude increase from 0.1 S m⁻¹ for Ag₉S to 3 × 10⁴ S m⁻¹ for Ag₂S₀.₅Se₀.₅ at 300 K was recorded.[20] The considerably improved electrical conductivities are a consequence of the increasing carrier mobility which rises with increasing Se content in Ag₉S. Alloying Se at S-sites not only substantially reduces the bandgap, but also alters the shape of the conduction band minimum to yield a smaller carrier effective mass, which leads to higher carrier mobility. The alloying process also suppresses the lattice thermal conductivity by introducing point defects which scatter heat-carrying phonons. This effect also helps to improve zT of the material. Upon compositional optimization, a delicate balance was reached between high carrier mobility and power factor, and a zT of 0.26 for Ag₂S₀.₃Se₀.₇ at 300 K (Figure 4e) was achieved.

Apart from the ternary Ag₉–S–Se alloyed system, Chen et al. also prepared ternary Ag₉Se₁₋ₓTeₓ (₀ ≤ 1) microstructures via wet-mechanical alloying and spark plasma sintering.[168] Alteration of Te content, band structure, carrier concentration, and carrier mobility of Ag₉Se₁₋ₓTeₓ was observed to manipulate electronic transport properties. The dislocations, nanograins, high-density boundaries, Te substitutions, lattice distortions, and localized strain in Ag₉Se₁₋ₓTeₓ could strongly scatter phonons, and so a lattice thermal conductivity in the range of 0.21–0.31 W m⁻¹ K⁻¹ at 300 K was achieved.
Figure 6. a) Schematic aqueous synthesis of Ag₂Se at room temperature. b) Thermoelectric $zT$ as a function of temperature for Ag₂Se and $x\%$Cu⁺:Ag₂Se ($x = 1.0, 1.5$ and $2.0$) samples. Temperature dependent c) electrical conductivity ($\sigma$) and d) Seebeck coefficient ($S$) for Ag₂Se and Ag⁰:Ag₂Se pellets. Reproduced with permission. [43] Copyright 2022, American Chemical Society.

Zhou et al. solvothermally synthesized size-tunable Ag₂Te nanoparticles by using 1-dodecanethiol as both a surfactant, to confine the growth of particles, and a source of dopant sulfur.[77] Without the controlled doping of sulfur, quantum size effect resulted in an enlarged bandgap and decreased concentration of charge carriers. However, the quantum effect was not prevalent in S-doped Ag₂Te nanoparticles, due to undefined boundary distances among nanoparticles after hot pressing. The higher charge concentration of the nanoparticles was directly related to the increasing sulfur content. In addition, a higher Seebeck coefficient was also observed in the nanoparticles after hot pressing. The higher charge concentration of the nanoparticles was directly related to the increasing sulfur content. In addition, a higher Seebeck coefficient was also observed in the nanoparticles after hot pressing. A peak $zT$ value of ≈0.62 was obtained for 15 nm S-doped Ag₂Te particles at 550 K, which was 32% higher than the bulk Ag₂Te particles.

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4.2. Ag-M-E (M = Si/K/Cu/Sn/Sb/Au/Bi, E = S/Se/Te)

Another group of ternary silver-based chalcogenides, Ag-M-E (M = Cu/Sn/Sb/Au/Bi, E = S/Se/Te) have been extensively researched for potential improvements in thermoelectric performance. Li et al. demonstrated a one-pot solvothermal synthesis of Ag₂Se and Ag₁.₉Sn₀.₁Se granular structures with an average size of around 100 nm.[81] The Sn doping enhanced the thermoelectric performance of Ag₂Se, due to a reduced thermal conductivity and optimized power factor. The increase in electrical resistivity and Seebeck coefficient upon Sn doping was related to a decrease in electron concentration from 1.69 × 10¹⁹ cm⁻³ for Ag₂Se to 1.38 × 10¹⁹ cm⁻³ for Ag₁.₉Sn₀.₁Se at room temperature. A peak $zT$ of 0.7 was obtained at 317 K for Ag₂Se, and partial substitution of Ag by Sn yielded a higher $zT$ to 0.9 for Ag₁.₉Sn₀.₁Se at 300 K.

Recently, we have successfully synthesized binary Ag₂Se, hybrid Ag⁰:Ag₂Se, and ternary Cu⁺:Ag₂Se thermoelectric materials through aqueous solution-based approaches under ambient conditions (Figure 6a). This approach enables the control of the interior composition and the components of pure and doped Ag₂Se (as well as their phases), which can substantially influence their thermoelectric properties. In pure Ag₂Se, $zT$ values ranged from 0.8 to 1.1 between room temperature and 390 K. In comparison to pure Ag₂Se, Cu⁺ doping improved the $zT$ value to 0.9–1.2 between 300 and 393 K (Figure 6b). This increase was attributed to the enhanced electrical conductivity and the suppressed thermal conductivity which accompanies the incorporation of Cu⁺ into the lattice of Ag₂Se at very low concentrations ($x\%$Cu⁺:Ag₂Se, $x = 1.0, 1.5$, and $2.0$). On the other hand, the addition of Ag⁰ to Ag₂Se
drastically increased the electrical conductivity, leading to a more than 400% conductivity increase at 423 K. The presence of Ag⁺ in the Ag₂Se sample not only greatly increased its electrical conductivity, but also significantly decreased its Seebeck coefficient; the synergistic combination of these effects resulted in a lower power factor than that observed for pure Ag₂Se (Figure 6c,d).

Ternary AgCuSe nanoparticles synthesized under surfactant-free aqueous conditions were investigated for their thermoelectric properties in the temperature range of 3 to 623 K.[86] The nanoparticles exhibited strong metallic characteristics below 60 K, and exhibited n-type semiconductor properties as the temperature was increased. This property change was accompanied by a structural transformation from a pure tetragonal phase into a mixture of tetragonal and orthorhombic phases between 60 and 480 K. After a further transition to a cubic phase above 480 K, the nanoparticles displayed p-type semiconductor behavior. The cubic phase is comprised of a face-centered cubic lattice of Se²⁻ with randomly distributed Ag⁺ and Cu²⁺ ions amongst the tetrahedral sites, which enables the high mobility of the Ag⁺ and Cu²⁺ ions and results in superionic characteristics. Accordingly, the electrical conductivity of AgCuSe dropped from 1040 to 400 S cm⁻¹ as the temperature was elevated from 323 to 467 K, and further declined to 100 S cm⁻¹ after the phase transition, due to the drastically increased scattering of charge carriers by highly disordered Ag⁺ and Cu²⁺ ions. The Seebeck coefficient increased from ~90 μV K⁻¹ at room temperature to 226 μV K⁻¹ at 467 K and remained nearly constant in the cubic phase. As a result, zT values of 0.42 at 323 K and 0.9 at 623 K were achieved and exhibited good cycling stability. The temperature-dependent phase transition enables AgCuSe to act as either an n-type or a p-type thermoelectric material at different temperatures. Meanwhile, significant changes in the thermoelectric properties were observed in the presence of phase impurity-induced compound defects at high temperatures. As a result, the zT of AgCuSe continuously increased to 0.6 at 450 K, whereas nonstoichiometric AgCuSe showed a considerably lower zT with increasing temperatures, which was attributed to the contributions from both electrons and holes.[85]

Likewise, AgCuS is a superionic semiconductor that undergoes temperature-dependent p–n–p-type conduction switching during an orthorhombic to hexagonal structural transition.[169] Both the Ag vacancy concentration and Cu–S hybridized states are responsible for the p–n–p-type conduction switching in AgCuS. Upon creating extrinsic Ag/Cu nonstoichiometry in AgCuS, the p–n–p-type conduction switching diminishes and also results in enhanced thermoelectric properties. Particularly, the cation (Ag⁺ and Cu⁺) vacancies in AgCuS increase the p-type carrier concentration, which in turn improve the electrical transport. Both Ag₁₋ₓCuS and AgCu₁₋ₓS exhibit low thermal conductivity due to the low-energy cationic sublattice vibration caused by the movement of loosely bound Ag/Cu within the rigid anion sublattice. Ag₀.₉₅CuS yields a zT of ~0.15, which is considerably higher than that of pure AgCuS.

Ternary Ag₃AuSe₂ nanoparticles were synthesized from binary Ag₃Se nanoparticles via a colloidal approach.[46] The diffusion of Au⁺ into the β-Ag₃Se₂ lattice led to a phase transformation from orthorhombic β-Ag₃Se₂ to a cubic Ag₃AuSe₂ structure with a bandgap of ~0.2 eV.[170] The densified ternary powder displayed a two-fold decrease in electrical conductivity and 50% increase in Seebeck coefficient relative to pristine Ag₃Se, which translated into a higher power factor. This behavior originates from charge scattering and the corresponding energy filtering of carriers with lower energy, leading to a reduction in the bipolar effect induced by the phase transition.

Ternary I–V–V₂ AgME₂ compounds, such as AgBiS₂, AgSbSe₂, and AgBiSe₂, are very promising thermoelectric materials, possessing enhanced ionic and electronic mobilities, and low thermal conductivities. At room temperature, bulk AgBiS₂ crystallizes in a hexagonal phase and transforms to a cubic rocksalt structure at ≈473 K, with disordered Ag and Bi atoms. The anharmonicity in the Bi–E bond (E = S/Se/Te) originates from the electrostatic repulsion between the stereochemically active lone pair of bismuth and the valence bonding charge of the chalcogen. The magnitude of this repulsive force is expected to increase from tellurium to sulfur due to the increase in electronegativity up the chalcogen group.[171,172] Biswas et al. synthesized nanocrystals of the high-temperature rock-salt phase of AgBiS₂, in solution, which were kinetically stabilized at room temperature.[90] The presence of a notable order-disorder type transition in the Ag/Bi lattice, the high degree of anharmonicity in Bi–S bonds, and the nanoscale grain boundaries in AgBiS₂ gave rise to effective phonon scattering. This resulted in a minimal lattice thermal conductivity of 0.4–0.5 W m⁻¹ K⁻¹ between 290 and 830 K, and a zT value of ~0.2 at 810 K.

A greater zT value of ~0.7 at 820 K for AgBiS₂ has also been reported.[91] The high zT performance arose from the soft lattice vibration of (predominantly) Ag and the significant lattice anharmonicity from the local structural distortions along the [011] direction (Figure 7a,b), resulting from the stereochemical activity of the 6s⁻ lone pair of Bi. The soft lattice vibration of Ag and the anharmonicity from Bi also create low-lying optical phonons which strongly scatter the heat-carrying acoustic phonons (Figure 7c), thereby substantially suppressing the lattice thermal conductivity in cubic AgBiS₂ close to its theoretical minimum (Figure 7d). A significant improvement in the thermoelectric performance of AgSbSe₂ has also been observed upon the introduction of Sb deficiencies.[81] In this nonstoichiometric AgSbSe₂, an increased carrier concentration was observed without the need for additional doping, which in turn enhanced the electrical conductivity between 300 and 610 K. Additionally, AgSbSe₂ showed low thermal conductivity as a result of the phonon scattering which arises from bond anharmonicity and a disordered cation sublattice. The superior electronic transport coupled with a low thermal conductivity led to a peak zT of ~1 at 610 K for the AgSb₀.₉₉₂Se₂ and AgSb₁₋₀.₉₉₂Se₂ samples.

Other types of Ag-M-E compounds (M = K/Si, E = S/Se/Te) have also been prepared through alkali metal and nonmetal doping. As a dimensionally-reduced 2D derivative of 3D Ag₂Se (Figure 8a),[24] β-KAg₂Se₂ was prepared by solid-state reaction. The 2D derivative exhibited n-type semiconductor behavior with a ≈1 eV bandgap and high electron mobility at 300 K due to a highly disperse conduction band. The monolithic β-phase transformed to a hexagonal α-phase at 700 K through a first-order phase transition, which is ~300 K higher than the analogous transition temperature in the parent compound. An ultra-low thermal conductivity was observed in the β-phase due to the anharmonic motion of Ag ions, which impede the transport of phonons (even without extensive disordering). In this case, the dimensional reduction...
Figure 7. a,b) Crystal structure of AgBiS$_2$ in a cubic unit cell: a) undistorted and b) small distortions of central cations away from octahedral center. The gray, violet, and orange colors represent Ag, Bi, and S atoms, respectively. c) Atom-projected phonon density of states (PhDOS) for AgBiS$_2$. d) Temperature-dependent lattice thermal conductivity ($\kappa_{\text{lat}}$) of cubic AgBiS$_2$. The dashed line is the theoretical minimum of lattice thermal conductivity ($\kappa_{\text{min}} \approx 0.34 \text{ W m}^{-1} \text{ K}^{-1}$) of AgBiS$_2$. Reproduced with permission.[$^91$] Copyright 2019, American Chemical Society.

successively suppressed Type I phase transitions, though desirable electronic and thermal properties were retained.

In another case, polycrystalline Ag$_8$SiSe$_6$ exhibited a cubic structure above 370 K with a fully disordered cation sublattice and superionic conduction properties.[$^82$] Below 370 K, the localized cations bestowed exceptional stability against the migration of Ag$^+$ cations (Soret effect) under an applied temperature gradient. Electron mobilities as high as 1800 cm$^2$ (V s)$^{-1}$ were measured, with low thermal conductivity arising from Ag disorder and superstructure modulation, leading to $zT$ values of 0.6 to 0.8 at 300 to 350 K, respectively.

Ternary argyrodite-type Ag$_9$GaSe$_6$ is a newly recognized superior thermoelectric material due to its intrinsically low lattice thermal conductivity.[$^{110,173}$] However, liquid-like Ag atoms are believed to cause poor stability and performance irreproducibility. During a typical powder densification hot-pressing process, the high pressure induces the liquid-like Ag atoms to migrate to a position with a higher coordination number, giving rise to a metastable Ag distribution which carries a higher chemical potential and lower binding energy. In order to change such a high-pressure-induced high chemical potential state, an energy barrier has to be overcome, which can be realized by a subsequent annealing procedure to drive the high-energy metastable Ag atoms back to their original crystallographic sites (of lower chemical potentials). Remarkably, hot-pressed and annealed Ag$_9$GaSe$_6$ with low-chemical-potential Ag atoms was proven to be intrinsically stable, presenting a $zT$ of $\approx$1.4 at 800 K after multiple measurements in Ag$_{8.3}$Cu$_{0.7}$GaSe$_6$.[$^{110}$]

5. Quaternary Silver-Based Chalcogenides (Ag-M1-M2-E)

Quaternary silver-based chalcogenides, Ag-M1-M2-E (E = S/Se/Te, M = Na/Mg/Ca/Mn/Ni/Cu/Zn/Nb/Cd/Ga/In/Sn/Sb/Ba/Pb/Bi), are made up of four different atomic constituents, which significantly increases the opportunities to find candidates with suitable band structure, composition, and crystal structure to achieve higher thermoelectric performance (Table 1). For example, cubic I-V-VI$_2$ (where I = Cu/Ag/Au/alkali metals, V = As/Sb/Bi, VI = Se/Te) semiconductors are recognized for their intrinsically low lattice thermal conductivity (due to the strong anharmonic bonding arrangement in these compounds),[$^{172,174}$] rendering them promising thermoelectric materials in the intermediate temperature range (500–700 K).

5.1. Ag$_x$S + Se/Te

Alloying Ag$_x$S with Se and Te can substantially improve carrier mobility, and thus increase electrical conductivity. For example,
the electrical conductivity of Ag$_2$S$_{0.5}$Se$_{0.45}$Te$_{0.05}$ at 300 K was measured as $2.7 \times 10^{-4}$ S m$^{-1}$, five orders of magnitude greater than pristine Ag$_2$S (0.1 S m$^{-1}$). In this case, the optimized Ag$_2$S$_{0.5}$Se$_{0.45}$Te$_{0.05}$ composition found a balance between high carrier mobility and power factor to achieve a $zT$ value of 0.44 at 300 K (Figure 4e). Importantly, the significantly enhanced $zT$ values for Ag$_2$(S, Se, Te) were mostly attributed to the increase in Hall carrier concentration from $1.6 \times 10^{14}$ cm$^3$ for Ag$_2$S to $10^{18}$–$10^{19}$ cm$^3$ for Ag$_2$(S, Se, Te) at 300 K. Recently, Xie et al. demonstrated that a low concentration of excess Se ($\gamma$ = 0, 0.02, 0.03, 0.04, 0.05) may be added to reduce the carrier concentration and enhance the thermoelectric properties further. A $zT$ value of $\approx$0.3 for Ag$_2$S$_{0.4}$(Se$_{0.6}Te_{0.4})_{0.05}$ + 0.04Se at 300 K was recorded in this case, which was five times higher than Ag$_2$S$_{0.4}$(Se$_{0.6}Te_{0.4})_{0.05}$.

5.2. Ag$_2$S$_{0.7}$Se$_{0.3}$ + Cu

It is well established that the outstanding deformable and flexible thermoelectric materials (at room temperature) are Ag$_2$S-based semiconductor alloys, which exhibit n-type conduction behavior. The n-type semiconductor Ag$_2$S$_{0.7}$Se$_{0.3}$ exhibits good plasticity at room temperature with a monoclinic structure analogous to room-temperature Ag$_2$S. On the contrary, its copper counterpart, Cu$_2$S$_{0.7}$Se$_{0.3}$, adopts a hexagonal structure (analogous to the Cu$_2$S...
medium-temperature phase) with p-type conduction and poor plasticity. Upon alloying, the n-type conduction in Ag$_x$S$_{0.7}$Se$_{0.3}$ is switched into p-type conduction in (Ag$_{1-x}$Cu$_x$)$_2$S$_{0.7}$Se$_{0.3}$, with Cu doping when $x$ is above 0.6. Above this Cu concentration, hexagonal (Ag$_{1-x}$Cu$_x$)$_2$S$_{0.7}$Se$_{0.3}$ is similar to the hexagonal Cu$_2$S phase and exhibits p-type conduction behavior. At lower Cu concentrations, the monoclinic (Ag$_{1-x}$Cu$_x$)$_2$S$_{0.7}$Se$_{0.3}$ phase is similar to monoclinic Ag$_2$S, displaying n-type conduction properties. This Cu- and Ag-dependent conduction behavior is related to the dominant intrinsic defects inside the lattice, such as interstitial Ag sites and Ag vacancies. For instance, in monoclinic Ag$_2$S, the formation energy of an interstitial Ag site is smaller than that of a Ag vacancy, implying that the interstitial sites (electron donors) are easier to generate. Conversely, the formation energy of a Cu vacancy in hexagonal Cu$_2$S is smaller than that of an interstitial Cu site, suggesting that Cu vacancies (electron acceptors) are easier to generate.

In this study by Gao and co-workers, charged crystal defects were engineered so that both good plasticity and p-type conduction could be simultaneously realized in (Ag$_{1-x}$Cu$_x$)$_2$S$_{0.7}$Se$_{0.3}$ ($x$ = 0.7–0.8). At low Cu content ($x$ = 0, 0.1, and 0.2), the good plasticity in (Ag$_{1-x}$Cu$_x$)$_2$S$_{0.7}$Se$_{0.3}$ originates from the Ag$_2$S-like crystal structure. In this structure, there is a small slippage energy (Es) and a large cleavage energy (Ec) between the crystal planes, facilitating slipping without cleavage under an external stress. Unexpectedly, good plasticity was also observed in the Cu-rich (Ag$_{0.2}$Cu$_{0.8}$)$_2$S$_{0.7}$Se$_{0.3}$, as they displayed a comparable Ec/Es ratio to Ag$_2$S$_{0.7}$Se$_{0.3}$. During slipping, the increase in the total energy of Ag-based bonds is smaller than the Cu-based bonds, and so the energy barrier to slipping is lower. Thus, the Ag/Cu ratio accounts for the plasticity in Ag-containing (Ag$_{0.2}$Cu$_{0.8}$)$_2$S$_{0.7}$Se$_{0.3}$ and the brittleness in Ag-free Cu$_2$S$_{0.7}$Se$_{0.3}$, with the same crystal structure. Gao et al. observed a maximum $zT$ value of 0.42 at 800 K for p-type (Ag$_{0.2}$Cu$_{0.8}$)$_2$S$_{0.7}$Se$_{0.3}$, giving rise to p-type conduction behavior. Based on a first principle theoretical analysis, it was found that the soft vibrations of Ag and low-lying soft phonons both scatter heat-carrying acoustic phonon modes, thereby reducing the lattice thermal conductivity near room temperature. On the other hand, hexagonal AgCuTe also exhibits low lattice thermal conductivity near room temperature (despite its localized cations), suggesting the important role of intrinsic factors, such as structural complexity and the weak bonding characteristics of cations, in suppressing lattice thermal conductivity. Based on a first principles theoretical analysis, it was found that the soft vibrations of Ag and low-lying soft phonons both scatter heat-carrying acoustic phonon modes, thereby reducing the lattice thermal conductivity near room temperature. On the other hand, hexagonal AgCuTe also exhibits low lattice thermal conductivity near room temperature (despite its localized cations), suggesting the important role of intrinsic factors, such as structural complexity and the weak bonding characteristics of cations, in suppressing lattice thermal conductivity.

5.4. AgSbSe$_2$ + M2 (M2 = Na/Mg/Ca/Ba/Sn/Pb/Bi)

The p-type semiconductor AgSbSe$_2$, with a cubic rock-salt crystal structure, features disordered Ag/Sb positions and strong anharmonicity amongst the Sb–Se bonds, deriving from the Sb 5s$^2$ lone pair electrons. The intrinsically low concentration of holes in pristine AgSbSe$_2$ can be increased and optimized by doping with 2–4 mol% Pb$^{2+}$ or Bi$^{3+}$ via a solid-state reaction, resulting in enhanced electrical transport and a significant increase in power factor. Due to the synergy of optimized electrical transport and low thermal conductivity, $zT$ values of ≥1 and ≤1.15 at 680 K were recorded for AgSb$_0.96$Pb$_{0.04}$Se$_2$ and AgSb$_0.98$Bi$_{0.02}$Se$_2$, which were enhanced by 150% and 190% compared to that of pristine AgSbSe$_2$, respectively. Similarly, the hole concentration of pristine AgSbSe$_2$ can also be increased by doping with Ca$^{2+}$, which has two electrons in its valence shell and thus tends to increase the hole concentration when substitution takes place in the sublattice of Sb$^{3+}$. Moreover, the ionic radius of Ca$^{2+}$ dopant ions (≈99 pm) is comparable to that of the Sb$^{3+}$ host ions (≈92 pm), likely resulting in a larger solid solubility and higher hole concentration. A $zT$ value of 1.2 at 673 K was obtained for nanostructured AgSb$_{0.98}$Ca$_{0.02}$Se$_2$, due to the increased carrier concentration and the strengthened point-defect scattering of phonons.

Other doping studies have explored the substitution of Sb$^{3+}$ with monovalent Na$^+$, divalent Mg$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Sn$^{2+}$, and trivalent Bi$^{3+}$. For example, the substitution...
of Na+ in the sublattice of Sb3+ not only improved the carrier concentration (increasing the power factor), but also suppressed the thermal conductivity. Phonon scattering across multiple length scales was attributed to the existence of point defects, nanoscale stacking faults, and Na-rich precipitates. As a result of these factors, a zT value of 0.92 at 673 K was achieved for AgNa0.01Sb0.99Se2.[98] A zT value of 1.05 at 673 K for Mn2+-doped AgSbSe2 was obtained, and an average zT value of 0.63 from 300 to 673 K has been attained for AgSb0.99Mn0.01Se2.[101] In the case of AgSb0.99Sn0.01Se2, a zT value of 1.21 at 660 K was recorded, 363% higher than that of undoped AgSbSe2.[102]

5.5. AgBiSe2 + M2 (M2 = Nb/In) or X (X = Cl−/Br−/I−)

Similar to those materials mentioned in the previous section, n-type I-V-V1, AgBiSe2 features intrinsically low thermal conductivity due to the high degree of anharmonicity in the Bi–Se bond, and effective phonon scattering by the disordered Ag/Bi lattice. Recent efforts have been made to improve the electrical properties of the AgBiSe2 system, mostly focusing on elemental doping. For example, niobium doping enhanced the thermoelectric performance of AgBiSe2 by increasing the carrier concentration, which significantly boosted the zT value at 773 K from 0.5 for undoped AgBiSe2, to 1.0 for Ag0.96Nb0.04BiSe2.[107] In addition, indium doping at Ag sites has been shown to more than double thermoelectric performance, with a zT value of 0.7 at 773 K measured for Ag0.98In0.02BiSe2 compared to 0.3 for pristine AgBiSe2.[108] The thermoelectric enhancement is primarily attributed to the increased carrier concentration and the suppressed lattice thermal conductivity, which arises from the introduction of point defects as well as the increased anharmonicity of the chemical bonds due to In 5s2 lone pair electrons.

When AgBiSe2 was simultaneously doped with indium and hybridized with AgBiS2 through a mechanical alloying process, a peak zT of 0.9 was obtained at 773 K.[109] The introduction of the dopant tuned the carrier concentration, while hybridization with AgBiS2 significantly suppressed thermal conductivity as a result of phase boundary scattering. Moreover, the mechanical alloying process further reduced the lattice thermal conductivity, because of grain size reduction and enhanced alloy scattering from the S–Se substitution. Eventually, the ball milled 80% AgBiSe2,1In0.20 exhibited more than two times the zT value of pristine AgBiSe2.

The thermoelectric performance of AgSbSe2 can be also regulated by aliovalent doping. For example, the substitution of halide ions (Cl−/Br−/I−) into the Se2− sublattice was shown to significantly increase the n-type carrier concentration in AgBiSe2, giving rise to improved temperature-dependent electronic transport properties.[97] A peak zT value of 0.9 at 805 K was obtained for n-type AgBiSe2,0.98Cl0.2, due to an increased power factor and intrinsically low thermal conductivity.

6. Multinary Silver-Based Chalcogenides

Quinary silver-based chalcogenides, Ag-M1-M2-E1-E2 (E = S/Se/Te, M = Cu/Ge/Sn/Sb/Pb/Bi), are made up of five different atomic constituents, which generally exist in a solid solution containing different principle elements with individual concentrations in a molar ratio between 5 and 35, resulting in high configurational mixing entropy (Table 1).[100] The so-called high-entropy alloys have gained much attention in the field of thermoelectric materials owing to their increased phonon scattering, which arises from cation disorder and distorted lattices.[101]

An equimolar mixture of AgSbSe2 and SnSe forms a stable, cation-disordered cubic rock-salt p-type AgSbSnSe2 phase, in which Ag, Sn, and Sb cations are randomly distributed over the Na sites in the NaCl lattice (Figure 8b). AgSbSnSe2 was found to exhibit a low lattice thermal conductivity of 0.47 W m−1 K−1 at 673 K, due to the combined effects of cation disorder, phonon anharmonicity, low phonon velocity, and low-frequency optical modes.[116] To further improve the thermoelectric performance of AgSnSbSe2, a quinary NaCl-type solid solution, AgSnSbSe1.5Te1.5, was formed using high-entropy engineering methods. Te alloying on the Se sites introduced randomly disordered cations and anions, which simultaneously improved the electrical and thermal transport properties of AgSnSbSe2, as a result of strengthened phonon scattering. This heightened scattering arises from extra point defects and lattice dislocations, as well as a higher hole carrier concentration. As a consequence of these multiple effects, the highest zT value of 1.14 at 723 K and average zT of 1.0 (400–773 K) were achieved in AgSnSbSe1.5Te1.5, a high-entropy alloy (Figure 8c).

Similarly, Ag, Pb, and Bi cations in cubic rock-salt n-type AgPbBiSe2 remain statistically disordered in the Wyckoff position 4a, while the Wyckoff site 4b is occupied by Se anions. It was observed that AgPbBiSe2 exhibited a low intrinsic lattice thermal conductivity of 0.5 to 0.4 W m−1 K−1 in the temperature range 290–823 K.[109] Investigations into the phonon-transport processes of AgPbBiSe2 revealed a high degree of anharmonicity arising from the chemical disorder of cations. AgPbBiSe2 possesses bonding inhomogeneity, wherein Ag atoms are weakly bonded compared to Pb and Bi atoms in the lattice. The presence of 6s2 lone pairs in Pb and Bi induces strong variation in the chemical bonding of cations, and hence the lattice anharmonicity. Therefore, the fundamental origin of the phonon scattering process is the bonding heterogeneity and lattice anharmonicity arising from the 6s2 lone pairs of Bi and Pb. Further improvement of the thermoelectric properties was achieved by aliovalent halide doping, which increased the scattering of point defects, leading to a further reduction in the lattice thermal conductivity of AgPbBiSe2 to 0.23 W m−1 K−1 at 823 K. As a result, a doubling in zT value from 0.43 for pristine AgPbBiSe2 to 0.8 for AgPbBiSe2,0.95I0.05 at 818 K was observed.

Recently, Ag-doped GeTe together with Sb and Pb, simultaneously formed quinary Ge0.62Ag0.11Sb0.13Pb0.12Te, and exhibited a high zT value of 2.4 at 750 K, which is significantly greater than the value of 1.2 obtained for binary GeTe.[110] This research demonstrated that delocalized electrons resulting from increased crystal symmetry, and localized phonons from entropy-induced disorder could coexist in high-entropy GeTe-based materials after the alloying of Ag, Sb, and Pb. This provides the possibility of simultaneously optimizing the electrical and thermal transport properties of the material. In comparison, ternary Ge0.89Ag0.11Te and quaternary Ge0.77Ag0.11Pb0.12Te only showed very low zT values of 0.4, due to the presence of impurities such as PbTe and AgTe. When impurities such as Ag, Te and Sb, Te were not present, Ge0.77Ag0.11Sb0.13Te displayed a greatly improved zT value of ≈1.6 at 750 K. Upon further alloying
with a trace amount of Bi, senary Ge_{0.01}Ag_{0.12}Sb_{0.11}Pb_{0.11}Bi_{0.05}Te exhibited an even greater $zT$ value of $\approx 2.7$.\textsuperscript{[120]} When the number of the metal elements incorporated was increased to five or more by introducing Mn, Sn, or Cd (e.g., septenary Ge_{0.01}Ag_{0.12}Sb_{0.11}Pb_{0.11}Bi_{0.05}Mn_{0.05}Te with a $zT$ close to $\approx 2.7$), the second phases were eliminated in all of the samples, indicating that the stabilization phenomenon of the single-phase structure was dominated by increasing entropy.

Zhang et al. demonstrated that entropy engineering could be exploited to simultaneously yield both good thermoelectric performance and robust mechanical properties in quinary alloys (Ag_{x}Cu_{2−x}Te_{1−x}S_{x}Se_{x}).\textsuperscript{[119]} The coalloying of S/Se/Ag in Cu_{2}Te simultaneously stabilizes a high-symmetry hexagonal structure, extends the solubility limit of Ag, and reduces the phase transition temperature on account of increased configurational entropy. As a result, the carrier concentration is largely decreased while the effective mass is improved, contributing to a higher Seebeck coefficient and power factor. Meanwhile, the thermal conductivity is suppressed by one order of magnitude (measured as 0.29 W m$^{-1}$ K$^{-1}$ at room temperature), which predominantly arises from strong phonon scattering induced by lattice disorder. Notably, Cu_{1+x}Te_{1−x}S_{x}Se_{x} showed a maximum $zT$ value of 1.4 at 1000 K, which represents a 250% increase relative to that of pristine Cu_{2}Te ($zT = 0.4$). Upon introducing Ag to Cu_{1+x}Te_{1−x}S_{x}Se_{x}, the $zT$ value was further enhanced, reaching an average $zT$ of 0.74 within 300 to 1000 K for Ag_{x}Cu_{1+x}Te_{1−x}S_{x}Se_{x}. This represented an improvement of 470% over that of pristine Cu_{2}Te ($zT = 0.4$). More importantly, Ag alloying not only improved thermoelectric properties, but also contributed to the superior mechanical properties. The incorporation of Ag significantly reinforces the compressive stress and even induces a prominent plastic deformation in Ag_{0.1}Cu_{1.9}Te_{0.6}S_{0.2}Se_{0.2}, while the Ag-free alloys exhibit brittle fracture features. The enhancement of mechanical properties can be mainly ascribed to the severe lattice-distortion effect induced by high entropy alloying, which impedes dislocation movement and results in prominent solid solution strengthening.

Since the discovery of metal-like Ag–S-based materials, the design and exploitation of ductile thermoelectric semiconductors for high-performance flexible devices has received much attention.\textsuperscript{[131,182]} Semiconducting n-type Ag_{x}Se(S,Te)-based materials with both high thermoelectric performance and inherent ductility at room temperature have been developed, but their p-type counterparts remain uncommon. Yang et al. systematically developed a series of p-type ductile thermoelectric materials based on quinary AgCu_{x}Se(S,Te) pseudoternary solid solutions, through composition and structure modulation.\textsuperscript{[118]} Upon alloying with S, AgCuSe_{0.3−x}S_{x}Te_{0.7} ($x = 0.06$ and 0.08) exhibited good ductility, which originates from the increased amount of mult centered and diffused Ag–S bonds. These bonds induce a preference for slip over fracture in the material.

Beyond inherent ductility, AgCuSe_{0.3−x}S_{x}Te_{0.7} ($x = 0.06$ and 0.08) demonstrated p-type conduction and good thermoelectric performance. Introducing S resulted in an improved Seebeck coefficient, although the electrical conductivity was lowered due to the decreased hole concentration. Both the carrier thermal conductivity and lattice thermal conductivity decreased upon S alloying, yielding a reduced thermal conductivity. Resultantly, a $zT$ value of 0.31 at 300 K was recorded for AgCuSe_{0.3−x}S_{x}Te_{0.7} ($x = 0.06$ and 0.08). This value could be further increased to 0.45 at 300 K and 0.68 at 340 K in (AgCu)_{0.08}Se_{0.22}S_{0.08}Te_{0.7} by inducing a small degree of cation deficiency.

7. Hybridized Silver-Based Chalcogenides

The heterogeneous hybridization of silver-based chalcogenides with other types of semiconductors has attracted increasing attention as a method to synergistically combine the favorable properties of different material domains. Thermoelectric performance may be markedly altered by inserting a secondary foreign phase into the bulk matrix of a silver-based chalcogenide, particularly silver-based binary, and ternary selenides (Table 1). This technique is an efficient way to scatter heat-carrying phonons, improve Seebeck coefficients and stabilize crystal structures.

7.1. Hybridized Ag_{x}Se

Hybridized Ag_{x}Se was colloidaly prepared by introducing non-metal (Te or S) or metal (Cu) nanodomains into the host matrix of Ag_{x}Se,\textsuperscript{[17]} where an electron exchange took place at the interphase between the matrix and nano-inclusions. The n-type nano-hybrids with 5 mol% Te nano-inclusions displayed a $zT$ value of 0.79 at room temperature, which accounted for nearly a twofold enhancement compared to that of pristine Ag_{x}Se nanoparticles. The optimized thermoelectric performance was ascribed to electron filtering at interfaces, which improved the Seebeck coefficient without significantly compromising the electrical conductivity. In comparison, a similar loading of Cu nano-inclusions caused the opposite effect, increasing electrical conductivities and lowering Seebeck coefficients. When bulk Ag_{x}Se was mixed with 5 mol% nano-grained Cu_{x}Se powders, the resulting Cu_{x}Se/Ag_{x}Se hybrids possessed a $zT$ value of $\approx 0.45$ at 875 K, compared to $\approx 0.25$ at 300 K for bulk Ag_{x}Se.\textsuperscript{[184]} The thermal stability of Ag_{x}Se was greatly improved at high temperature after the incorporation of the Cu_{x}Se nano-inclusions. A positive trend in the electrical conductivity was observed with increasing the amount of nano-inclusions, due to the resulting increase in carrier density. In spite of the larger electrical conductivity, the thermal conductivity was reduced in the presence of nano-Cu_{x}Se inclusions.

7.2. Hybridized AgInSe_{2}

Among ternary chalcogenide semiconductors, I-III-VI\textsubscript{2} AgInSe_{2} is considered a potential material for thermoelectric applications due to its low lattice thermal conductivity, which originates from Ag–Se “cluster vibrations” at low phonon frequencies.\textsuperscript{[84]} However, the thermoelectric application of n-type AgInSe_{2} is limited by a bandgap of $\approx 1.24$ eV\textsuperscript{[185]} and a low carrier concentration of $\approx 1.3 \times 10^{11}$ cm$^{-3}$ at 300 K.\textsuperscript{[186]} In order to increase carrier concentration of AgInSe_{2}, Qiu et al. introduced off-stoichiometry by adding excess amounts of Ag to AgInSe_{2}, forming Ag_{1+x}InSe_{2}.\textsuperscript{[84]} The presence of excess Ag created interstitial Ag atoms, thereby increasing the electron density of the material. Moreover, the excess Ag (i.e., Ag_{1.02}InSe_{2}) increased the carrier concentration to
1.6 × 10^{26} \text{ cm}^{-3}, \text{ which accounted for 2–3 orders of magnitude enhancement relative to that of stoichiometric AgInSe}_2. \text{ As such, the increase in electronic transport properties, in conjunction with unchanged and low thermal conductivity, contributed to a } zT \text{ value of 1.1 at 900 K, which was a 62% increase compared to that of the stoichiometric AgInSe}_2 \text{ counterpart. }

Additionally, a trace amount of a secondary AgSe phase was found in the AgInSe$_2$ compound during solid-state reaction. As known, Ag$_x$Se$_y$ has a higher carrier concentration and superior electrical properties than AgInSe$_2$. In order to utilize the intrinsic properties of Ag$_x$Se$_y$, Zhong et al. prepared a AgInSe$_2$-based hybrid comprising a AgInSe$_2$ primary phase and a Ag$_x$Se secondary phase, Ag$_{1-x}$In$_x$Se$_{2-x}$ (x = 0–0.4).\textsuperscript{127} The in situ formation of Ag$_x$Se species in the AgInSe$_2$ matrix played the dual role of enhancing the carrier concentration/electrical properties, as well as promoting phonon scattering at the Ag$_x$Se/AgInSe$_2$ heterointerfaces (i.e., atomic scale lattice distortion and phase interfaces), thereby reducing the lattice thermal conductivity of the hybrid. Consequently, a zT value of ≈0.9 was reached at 846 K, a 2.7 times enhancement in thermoelectric performance compared to pristine AgInSe$_2$ (Figure 9a–d).

7.3. Hybridized AgInTe$_2$

Banik et al. demonstrated that co-doping of In and Ag in SnTe–AgInTe$_2$ (i.e., Ag$_y$In$_x$Sn$_{1-x}$Te$_2$) led to an improved thermoelectric performance over a broad temperature range (300–860 K).\textsuperscript{115} The co-dopants (In and Ag) play distinct and complementary roles in tuning the valence band structure of SnTe. Particularly, In doping creates resonance levels inside the valence bands, thereby improving the Seebeck coefficient at room temperature. On the other hand, the incorporation of Ag leads to an increase in the principal bandgap of SnTe, thus causing a decrease in the energy separation between two valence bands (light- and heavy-holes valence bands), also resulting in an improved Seebeck coefficient. Additionally, Ag doping boosts the p-type carrier mobility of SnTe. The synergistic effect of resonance level formation and the convergence of valence bands significantly improves the electronic transport properties of Ag$_y$In$_x$Sn$_{1-x}$Te$_2$, leading to a maximum zT of 1 at 856 K for Ag$_{0.025}$In$_{0.025}$Sn$_{1.05}$Te$_2$, which is substantially higher than that of undoped SnTe.

7.4. Hybridized AgBiSe$_2$

Ternary I-V-VI$_2$, AgBiSe$_2$ crystallizes in a hexagonal phase at room temperature, before undergoing structural phase transitions to a rhombohedral phase at 523 K and a cubic phase at 723 K. The abrupt changes in lattice constants and crystal structures during phase transitions can be stabilized between 300 and 800 K by alloying with PbSe in an entropy engineering process.\textsuperscript{128} The resultant (PbSe)$_{1-x}$(AgBiSe)$_x$ (x = 0.3) solid solutions with 1% Br possessed unique locally distorted cubic lattices that yielded low lattice thermal conductivities, approaching the glass limit between 300 and 800 K. Collectively, a peak zT value of 0.8 at 800 K and an average zT value of 0.42 were obtained for cubic n-type (PbSe)$_{0.7}$(AgBiSe)$_{0.3}$ solid solutions doped with 1% Br.

When AgBiSe$_2$ was doped with Ge, the resultant (GeSe)$_{0.03}$(AgBiSe)$_{0.97}$ compound exhibited a low thermal conductivity of 0.3 W m$^{-1}$K$^{-1}$, due to the formation of faceted rhombohedral Bi$_x$Se$_3$ (20–40 nm) embedded within the AgBiSe$_2$ matrix.\textsuperscript{40} The combined effects of Bi$_x$Se$_3$ nanoprecipitates and mass fluctuations/superlattice enhance phonon scattering and suppress thermal conductivity, resulting in a zT value of 1.05 for (GeSe)$_{0.03}$(AgBiSe)$_{0.97}$, which was 140% higher than that of pristine AgBiSe$_2$ (Figure 9e,f).

AgBiSe$_2$ can be introduced as an alloying material to tune the electronic structure and thermoelectric properties of orthorhombic and cubic SnSe.\textsuperscript{124} Upon AgBiSe$_2$ alloying, the layered orthorhombic phase is stabilized in (AgBiSe)$_x$(SnSe)$_{1-x}$ (0 ≤ x ≤ 0.28), which is typical for narrow bandgap semiconductors. With a further increase in the concentration of AgBiSe$_2$ (0.3 ≤ x ≤ 0.7), the bandgap closes and the high-pressure cubic rock-salt phase of SnSe is effectively stabilized at ambient temperature and pressure. The stabilization of the cubic structure arises from the increase in configurational entropy due to a higher atomic disorderliness in the system, resulting from the solid solution mixing of AgBiSe$_2$ and SnSe. Interestingly, pure cubic SnSe displayed a topological crystalline insulator phase, whereas cubic (AgBiSe)$_x$(SnSe)$_{1-x}$ (x = 0.33) exhibited a semi-metallic electronic structure with overlapping conduction and valence bands. Additionally, the cubic polycrystalline (AgBiSe)$_x$(SnSe)$_{1-x}$ (x = 0.30) showed n-type conduction at room temperature, while orthorhombic (AgBiSe)$_x$(SnSe)$_{1-x}$ (0 ≤ x ≤ 0.28) retained its p-type character. Notably, the p-type polycrystalline orthorhombic (AgBiSe)$_{0.22}$(SnSe)$_{0.78}$ yielded a zT value of 1.3 at 823 K due to the crystal and electronic structural optimizations.

7.5. Hybridized AgSbSe$_2$

The interdependent thermoelectric parameters of p-type AgSbSe$_2$ can be simultaneously improved by combining second-phase nanostructuring and carrier engineering approaches. Using these approaches, in combination with the intrinsically strong Sb–Se bond anharmonicity, a zT value of ≈1.1 at 635 K for 2 mol% ZnSe/AgSbSe$_2$ was recorded, which is 185% higher than that of pristine AgSbSe$_2$.\textsuperscript{125} In this instance, the concentration of ZnSe in AgSbSe$_2$ was varied, causing a transition from a solid solution system to a phase-separated structure, and significantly affecting the electronic and thermal transport properties. At a low concentration of <2 mol% ZnSe, a solid solution of AgSbSe$_2$/ZnSe was obtained, while a phase separation occurred between 2 and 8 mol% ZnSe, due to the formation of ZnSe nanostructures with different sizes and interfaces in the AgSbSe$_2$ matrix. A concentration of 2 mol% ZnSe was found to be the optimal amount for p-type doping in AgSbSe$_2$, increasing the hole concentration and thus boosting the electrical transport properties. In addition, nanoscale endotaxial ZnSe precipitates were understood to act as phonon scattering centers, contributing to a reduction in the lattice thermal conductivity. Overall, the concentration of dopants, size of precipitates, and the interfaces of precipitates in the matrix were crucial in determining the electronic transport properties. At the same time, secondary phase nanostructuring and the intrinsically strong Sb–Se bond anharmonicity (within a disordered cation sublattice) enabled effective phonon scattering, improving the thermoelectric performance of the AgSbSe$_2$/ZnSe system.
Figure 9. Temperature dependent a) Seebeck coefficient ($\alpha$), b) electrical conductivity ($\sigma$), c) lattice thermal conductivity ($\kappa_L$), d) thermoelectric $zT$ of Ag$_{1+x}$InSe$_{2+x}$ ($x = 0$–0.40). An inset in (c) is the total thermal conductivity. Reproduced with permission.[127] Copyright 2020, American Chemical Society. e) Temperature-dependent $zT$ and thermal conductivity of (GeSe)$_{0.03}$(AgBiSe$_2$)$_{0.97}$ and pristine AgBiSe$_2$ alloys. f) Backscattered electron image of AgBiSe$_2$ and inverse fast Fourier transform (FFT) image, showing the formation of Bi$_2$Se$_3$ nanoprecipitate embedded in the Ge-doped AgBiSe$_2$ matrix. Reproduced with permission.[40] Copyright 2017, Elsevier. g) Rock-salt cubic structure of (SnSe)$_0.5$(AgSbSe$_2$)$_0.5$. h) Magnitude of Se distortion along [111] direction with increasing temperature. Reproduced with permission.[126] Copyright 2021, American Chemical Society.
Structural transformations have a significant effect on thermal transport and thermoelectric properties. Typically, transformations occur from less symmetric structures to more symmetric structures with an increase in temperature. The change from a more symmetric to a less symmetric structure upon heating is rare, and this uncommon phenomenon is known as enneahedrism. Rock-salt (SnSe)_{2/3} (AgSbSe)_{2/3} exhibits rare enneahedric behavior due to the local distortion of Se along the [111] direction (Figure 9g,h).[126] Local off-centering of Se results in a local bonding hierarchy with three short and three long M-Se bonds (M = Sn/Ag/Sb) within the average rock-salt lattice, impeding phonon propagation and reducing lattice thermal conductivity. The presence of off-centering and consequent local bonding heterogeneity fosters a low lattice thermal conductivity in (SnSe)_{2/3} (AgSbSe)_{2/3}. After subsequent germanium doping to enhance electrical properties, a $\zeta T$ value of 1.05 was achieved for (SnSe)_{2/3} (AgSbSe)_{2/3} (x = 0.06) at 706 K.

7.6. Hybridized Ag$_2$Se and Ag$_2$AuSe$_2$

Hybridized nanoscale Ag–Au–Se systems, such as Au–Ag$_2$Se and Au–Ag$_2$AuSe$_2$, can be prepared from binary Ag$_2$Se nanoparticles with Au via a colloidal approach.[46] In this case, the presence of Ag and AuAuSe$_2$ resulted in a lower thermal conductivity; this decrease was due to more efficient scattering of phonons at grain boundaries, which was enhanced by the acoustic impedance mismatch of the Ag$_2$Se, Au, and Ag$_2$AuSe$_2$ domains. As a result, the occurrence of metallic Au and Ag$_2$AuSe$_2$ phases within a Ag$_2$Se matrix induced a sevenfold boost in thermoelectric performance, yielding a $\zeta T$ value of 0.88 at 390 K relative to 0.12 for the binary Ag–Se analog (Figure 10).

8. Composited Silver-Based Chalcogenides

Conventional inorganic nonmetal crystals exhibit poor flexibility due to strong ionic or covalent bonding. At low temperatures, monoclinic Ag$_2$S is known to display reasonable flexibility, although it exhibits the poorest thermoelectric performance amongst the silver chalcogenides. Conversely, orthorhombic Ag$_2$Se and monoclinic Ag$_2$Te lack mechanical flexibility, but display far better thermoelectric performance. For instance, orthorhombic Ag$_2$Se is a brittle material with a relatively small bandgap ($\approx 0.2$ eV), a high carrier mobility ($\approx 10^3$ cm$^2$ V$^{-1}$ S$^{-1}$) and good electrical conductivity ($\approx 10^3$ S m$^{-1}$) at room temperature. Upon compositional optimization, these silver chalcogenides reached a delicate balance between high carrier mobility, power factor, $\zeta T$ value and good mechanical flexibility, presenting $\zeta T$ values of 0.26 and 0.44 for Ag$_2$S$_{0.3}$Se$_{0.7}$ and Ag$_2$S$_{0.5}$Se$_{0.5}$Te$_{0.05}$ at 300 K, respectively (Figure 4c–f).[20]

Recent work found that amorphized Ag$_2$Te$_{1-x}$S$_x$ possesses both good flexibility and high thermoelectric performance.[79] The addition of S to Ag$_2$Te led to amorphization of Ag$_2$Te$_{1-x}$S$_x$ due to the small size and random dispersion of crystallites (Figure 11a). The unique disordered structure in Ag$_2$Te$_{0.4}$S$_{0.6}$ gives rise to exceptional flexibility, which is mainly ascribed to the formation and evolution of shear bands which account for the plasticity of bulk metallic glasses (Figure 11b). In comparison to ductile crystalline Ag$_2$S, which displays a lower carrier concentration ($\approx 10^{14}$ cm$^{-3}$) and poorer electrical conductivity,[153] amorphized Ag$_2$Te$_{0.4}$S$_{0.6}$ exhibits low lattice thermal conductivity due to its structural disorder, without a compromise in electrical transport properties. The Hall mobility and carrier concentration of Ag$_2$Te$_{0.4}$S$_{0.6}$ ($6.8 \times 10^{18}$ cm$^{-3}$) are an order of magnitude higher than other amorphous inorganic materials (Figure 11c). Accordingly, a $\zeta T$ value of 0.22 at room temperature and 0.70 at 573 K was achieved in flexible Ag$_2$Te$_{0.4}$S$_{0.6}$, glass.

Another ductile Ag-based thermoelectric material, Ag$_{20}$S$_7$Te$_3$, has been developed for its good shape conformability.[80] The outstanding shape conformability at room temperature derives from the low stacking fault energy in the (101)[010] slip system. Similarly to $\alpha$-Ag$_2$S, the three-point bending test revealed that Ag$_{20}$S$_7$Te$_3$ has a large bending strain above 15% without cracking.[153] Other semiconductors and ceramics are not able to withstand strains more than 3%.[185,186] The nano hardness and average Young’s modulus of Ag$_{20}$S$_7$Te$_3$ were determined to be 0.23 and 16.4 GPa, respectively. Both values are lower than the equivalent figures for $\alpha$-Ag$_2$S, which displays a nano hardness of 0.44 GPa and Young’s modulus of 27.1 GPa. Ag$_{20}$S$_7$Te$_3$ exhibits a Vicker’s hardness of 21.9 GPa, which is lower than $\alpha$-Ag$_2$S (30.7 GPa).[153] GaAs (750 GPa),[187] InP (510 GPa)[187] and InSb (250 GPa)[188] but similar to ductile metals such as Cu (50 GPa) and Au (25 GPa).[188]

Apart from the shape conformability, Ag$_{20}$S$_7$Te$_3$ also possesses a narrow bandgap of 0.29 eV (smaller than Ag$_2$S),[153] implying its potential as a thermoelectric material for near room temperature applications. The high carrier mobility and low lattice thermal conductivity observed in Ag$_{20}$S$_7$Te$_3$ give rise to a maximum $\zeta T$ of 0.80 at 600 K, which is comparable with commercial Bi$_2$Te$_3$-based alloys.[190]

Although silver-based chalcogenides exhibit good thermoelectric performance at near room temperature, they are still generally rigid or brittle, and hence are unsuitable for assembling flexible thermoelectric devices. Flexible thermoelectric materials derived from chalcogenide/polymer composites have emerged as promising candidates for future self-powering technology and battery-less sensors. Chalcogenide/polymer composites can simultaneously present both a high-power factor due to the inorganic filler, and a high flexibility and a low thermal conductivity originating from the polymer component (Table 1).

In order to increase flexibility without greatly compromising thermoelectric performance, a variety of polymers, such as poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), polyaniline (PANI), polypyrrole (PPy), and polyvinylidene fluoride (PVDF), have been investigated in flexible composite films. Preparation techniques have included physical mixing, drop casting, and vacuum-assisted filtration methods, but the thermoelectric performance is far from satisfactory so far in these instances.[191–191] In addition, various other substrates, including nylon,[47] cellulose,[140] polyimides,[194] and polyethylene naphthalates,[141] have also been examined in studies concerning flexible thermoelectrics.

8.1. Functional Polymers

Functional polymers possess excellent flexibility and low thermal conductivity, thus they are suitable for the production of
Figure 10. Schematic colloidal synthesis of alloyed and hybrid nanoparticles based on the Ag-Au-Se ternary system. Temperature dependent a) electrical conductivity ($\sigma$), b) Seebeck coefficient ($S$), c) thermal conductivity ($\kappa$), and d) thermoelectric $zT$ of binary Ag$_2$Se nanomaterial, Ag–Au–Se ternary nanocomposite, and Ag$_2$Se ingot reference (bulk Ag$_2$Se). Reproduced with permission.[46] Copyright 2016, American Chemical Society.

Composites with silver-based thermoelectric materials through a variety of solution processing methods or deposition techniques. A good degree of inherent flexibility enables these polymers to conform to the curvature of the host surface. A flexible Ag$_2$Se nanowires/PEDOT:PSS thermoelectric composite film was fabricated via a solution mixing and drop casting method, exhibiting a power factor of 178.59 μW m$^{-1}$ K$^{-2}$ at 300 K (at 80 wt% Ag$_2$Se nanowires).[139] In another study, an electron-conducting thin film comprised of β-Ag$_2$Te nanowires and poly[[N,N'−bis(2-oclyl)decyl]-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)] yielded a peak electrical conductivity of 0.61 S cm$^{-1}$ and a Seebeck coefficient of $-126$ μV K$^{-1}$, corresponding to a power factor of $\approx 1$ μW m$^{-1}$ K$^{-2}$ in the 85 wt% Ag$_2$Te film at room temperature.[146]
A freestanding and flexible Ag$_2$Se/PVDF composite film with a filler content of up to 90.5 wt% was prepared via the mixing of PVDF dendricolloids and Ag$_2$Se nanowires, followed by filtration and cold pressing. The electrical conductivity of the Ag$_2$Se/PVDF film increased from $\approx$6 to 206 S cm$^{-1}$ as the Ag$_2$Se/PVDF mass ratio was varied from 1:2 to 1:9.5. Meanwhile, a maximum Seebeck coefficient of $-115$ $\mu$V K$^{-1}$ was obtained at a mass ratio of 1:5, and a peak power factor value of $189$ $\mu$W m$^{-1}$ K$^{-2}$ was recorded at room temperature. The flexibility of the composite film was rationalized by the formation of a compact film with high density of the Ag$_2$Se film and the tuned orientation of Ag$_2$Se/Ag$_x$Se grains. Nevertheless, the optimal power factor of the Ag$_2$Se film is incomparable with that of bulk Ag$_2$Se (3500 $\mu$W m$^{-1}$ K$^{-2}$).

The addition of Cu to nylon films has also been investigated. A power factor of 2231.5 mW m$^{-1}$ K$^{-2}$ at 300 K was recorded, which was more than double that of the Ag$_2$Se film discussed above. The superior power factor results from the optimized carrier transport of the Ag$_2$Se/Ag/CuSe composite film (with a molar ratio of Ag/Cu/Se $= 4:1:3$), and the interfacial energy filtration effect. The carrier concentration was enhanced via the injection of electrons from Ag into the conduction band of the Ag$_2$Se and AgCuSe phases, while the energy filtering effect at the organic/inorganic heterointerface helped to maintain the magnitude of the Seebeck coefficient.

Ag$_2$Se/nylon composites were also prepared by the vacuum-assisted filtration of thick Ag$_2$Se nanowires or nanosheets. The nanowires were synthesized at 40 °C, in order to suppress the preferential growth of Ag$_2$Se grains along the (00l) direction which occurs at elevated temperatures. The change in morphology induced the formation of a compact film with $\approx$90% theoretical density after hot pressing. Collectively, the high density of the Ag$_2$Se film and the tuned orientation of Ag$_2$Se grains greatly enhanced the power factor to 1882 $\mu$W m$^{-1}$ K$^{-2}$ (with 90.7% retention after 1000 bending cycles) and $zT$ value of $\approx$0.8 was measured at 300 K, which is a $\approx$30% increase relative to the thin Ag$_2$Se nanowire film synthesized at room temperature.

Similarly, the wet chemical synthesis of Ag and Ag$_2$Se nanostructures was followed by vacuum-assisted filtration to form Ag/Ag$_2$Se composite films on nylon membranes, which were then hot pressed. A film with a molar Ag$_x$Se ratio of 3.5:1 exhibited a very high electrical conductivity of 3958 S cm$^{-1}$, due to the presence of a highly conducting Ag phase. The optimized composite film achieved a power factor of 1861 $\mu$W m$^{-1}$ K$^{-2}$ at room temperature and retained 93% of the original electrical conductivity after bending 1000 times (Figure 12a).

Ag/Ag$_2$Se nanodendrites have been successfully formed using a microwave-assisted synthesis method. Through tuning the molar ratios of Ag$_x$Se, the power factor was optimized to $\approx$2436 $\mu$W m$^{-1}$ K$^{-2}$ at room temperature (with a Ag$_x$Se molar ratio of 2.3:1). Apart from the excess Ag phase which significantly contributed to the high electrical conductivity of the composite film, the nanodendrites also have more contact points which can be welded together during the hot-pressing process. This results in a denser film with enhanced carrier transport. In addition, Ag has a lower work function value ($\approx$4.3 eV) compared to Ag$_2$Se ($\approx$6.79 eV), and therefore an ohmic contact could be established between the Ag and Ag$_2$Se phases, which enhanced the electrical conductivity of the film. After subject to a compressive force and a tensile force (1000 bending cycles), the Ag/Ag$_2$Se composite film retained 94% and 87% of the electrical conductivity, respectively.

Figure 11. a) High resolution TEM image of Ag$_2$Te$_{0.8}$S$_{0.4}$ showing a typical crystallite in the amorphous matrix. b) SEM image of the fracture surface showing crossing shear bands. c) Room temperature Hall mobility in comparison with other amorphous inorganic materials. Reproduced with permission. Copyright 2020, AAAS.
Figure 12. a) Thermoelectric performance of the flexible Ag/Ag$_2$Se/nylon composite film and the assembled thermoelectric generator (TEG). Reproduced with permission.$^{[130]}$ Copyright 2021, American Chemical Society. b) Schematic illustration of phonon scattering mechanisms in the PVP/Ag$_2$Se composite thermoelectric film. Reproduced with permission.$^{[131]}$ Copyright 2021, Elsevier.
8.1.3. Cellulose Papers

A series of Ag$_2$Se nanoparticles with Ag/Se molar ratios varying from 1.9 to 2.5 were synthesized via a solvothermal reaction and cold-pressed onto copy paper.\textsuperscript{[140]} The highest power factor value of 2450.9 $\mu$W m$^{-1}$ K$^{-2}$ at 303 K was achieved in the paper-supported Ag$_2$Se film after annealing in an inert atmosphere. A flexible paper-supported thermoelectric module was then assembled by series-connecting four pieces of annealed Ag$_2$Se nanowire film. This device achieved an output power density of 5.80 $W m^{-2}$ at a temperature difference of 25 K.

In a similar work, flexible n-type Ag$_2$Te nanowire films on paper substrates were constructed via a glass fiber-assisted cold pressing technique.\textsuperscript{[144]} By increasing the compressive stress, a continuous and dense thin film on a paper substrate was formed. This was accompanied by the disappearance of grain boundaries in the Ag$_2$Te nanowire film. As a result, the electrical conductivity of the paper-supported Ag$_2$Te nanowire film was improved, resulting in a maximum power factor of 192 $\mu$W m$^{-1}$ K$^{-2}$ at 468 K, while the power factor at room temperature was approximately half of this value. The film demonstrated good flexibility, with a 20% decline in power factor value after 500 bending cycles. A thermoelectric module assembled from ten legs of the paper-supported Ag$_2$Te nanowire film exhibited an open-circuit voltage of between 11 and 60 mV as temperature was raised from 20 to 80 K.

Zeng et al. attempted to improve the room-temperature thermoelectric performance of flexible Ag$_2$Te on filter paper by welding of Ag$_2$Te nanowires using vacuum filtration and drop-coating methods.\textsuperscript{[145]} The welded Ag$_2$Te nanowire film exhibited an electrical conductivity of 15335 S m$^{-1}$ at room temperature, which was twice as large as the nonwelded Ag$_2$Te nanowire film. This enhancement was ascribed to the interatomic bonding between the nanowires: closer physical connections increased the carrier mobility in the welded film compared to the non-welded film. A power factor of 152 $\mu$W m$^{-1}$ K$^{-2}$ at room temperature was obtained for the welded Ag$_2$Te nanowire film, which is nearly two times higher than Ag$_2$Te–glass fiber films.\textsuperscript{[144]} However, the electrical resistance increased by 30% after 1000 bending cycles, likely due to microcracking on the film after numerous bends.

8.2. Hybrid Polymer Substrates

A series of Ag$_2$Se/polymer composite films on nylon membranes were developed for their enhanced flexibility. The films were created by an in situ synthesis of polymer-coated Ag$_2$Se nanostructures, followed by vacuum-assisted filtration of the nanostructures onto a nylon membrane and a subsequent hot-pressing step. Polyvinylpyrrolidone (PVP) is typically used in these cases as a polymer adhesive to hinge Ag$_2$Se grains.\textsuperscript{[135]} In this instance, it was revealed that the PVP nanolayer impeded the sintering of Ag$_2$Se nanostructures, producing a porous microstructure composite film in which most Ag$_2$Se grains had coherent interfaces. The PVP/Ag$_2$Se composite film achieved a power factor of 1910 $\mu$W m$^{-1}$ K$^{-2}$ at room temperature and showed good flexibility, retaining 94.5% of the initial power factor after 1000 bending cycles. The intrinsically low thermal conductivity of PVP and its large number of nano/micro-pores, as well as the effect of PVP/Ag$_2$Se hetero-interfaces (which can scatter phonons with short- to long-wavelengths) (Figure 12b) resulted in a low thermal conductivity for the PVP/Ag$_2$Se composite films. A $\mu$T value of 1.1 at 300 K was obtained, an increase of 37.5% relative to the pristine Ag$_2$Se film in the absence of PVP. Likewise, a PANI-coated Ag$_2$Se nanowires/PVDF composite film displayed a maximum power factor of 196.6 $\mu$W m$^{-1}$ K$^{-2}$ at 300 K with 65 wt% Ag$_2$Se nanowires.\textsuperscript{[135]} Upon the assembly of a thermoelectric device with six legs of PVDF-based composite film, an output voltage of 15.4 mV and a power of 835.8 nW were generated at a temperature difference of 30 K.

An Ag$_2$Se/Ag/PEDOT composite film on a nylon membrane was engineered, which demonstrated a power factor of $\varepsilon$1442.5 $\mu$W m$^{-1}$ K$^{-2}$, an electrical conductivity of $\varepsilon$5957.3 S cm$^{-1}$ and a good flexibility.\textsuperscript{[118]} A 5.5% decline in electrical conductivity after 1000 bending cycles at room temperature was observed. The high electrical conductivity of the composite film was ascribed to the presence of an Ag phase, while the low thermal conductivity arose from PEDOT at the interface between Ag and Ag$_2$Se grains, and at the surface of Ag$_2$Se grains. The excellent flexibility was credited to the synergistic effects of the PEDOT layer and the nylon membrane, which enhanced the bonding between inorganic phases and the binding of the composite film onto the nylon.

An Ag$_2$Se/Se/PPy composite film was fabricated by the in situ polymerization of PPy at the surface of Ag$_2$Se nanostructures, and showed outstanding thermoelectric properties at room temperature.\textsuperscript{[134]} The composite film exhibited dense microstructures with nano- to sub-micrometer pores, which resulted from the in situ polymerization of PPy nanoshells. These nanoshells inhibited the sintering of Ag$_2$Se nanostructures at lower temperatures. Moreover, the well-developed crystalline Ag$_2$Se grains afforded the material a high electrical conductivity. Despite a lower Seebeck coefficient than was expected from the n-type Ag$_2$Se and p-type PPy, the energy-filtering effects at the heterointerfaces of Ag$_2$Se/Se and Ag$_2$Se/PPy in the film yielded a positive effect on the Seebeck coefficient, leading to a high-power factor of $\varepsilon$2240 $\mu$W m$^{-1}$ K$^{-2}$ at 300 K. The nano- to sub-micrometer pores and heterointerfaces in the composite film were able to scatter short- to long-wavelength phonons, leading to low thermal conductivity. These attributes resulted in a high $\mu$T value of 0.94 at 300 K, which was a 15% enhancement compared to that of the pristine Ag$_2$Se film without PPy. The Ag$_2$Se/Se/PPy composite film exhibited a decline of 6.5% in electrical conductivity after 1000 bending cycles.

9. Emerging Thermoelectric Applications

Typically, thermoelectric generators are based on the principle of the Seebeck effect and consist of dissimilar thermocouples (i.e., p-type and n-type semiconductors), which are connected electrically in series and thermally in parallel. With design simplicity, no moving parts, free maintenance, long lifetime and environmental friendliness without toxic byproducts, thermoelectric generators have become an attractive proposition in energy harvesting for a wide variety of applications in automobile engines,\textsuperscript{[196–201]} self-powered electronic devices,\textsuperscript{[202–205]} health monitoring and tracking systems,\textsuperscript{[206–208]} and aerospace systems.\textsuperscript{[209,210]} Various sizes of thermoelectric generators are needed to meet the
requirements of these applications, from large to micro-generators, which supply output powers ranging from several hundreds of watts to milliowatts across a vast range of temperature.\textsuperscript{[211,212]}

The Paris Climate Agreement on energy aims to substantially lower greenhouse gas emissions by at least 20% by 2030, compared to 1990 levels. The major sources of greenhouse gas emissions are power generation, manufacturing processes and transportation.\textsuperscript{[213]}

These activities generate numerous waste heat sources at low (<250 °C), medium (250–650 °C) and high (>650 °C) temperatures. In order to utilize this waste heat for appreciable power generation, thermoelectric generators have mostly been proposed as waste-heat recovery systems, capable of converting thermal energy into a useful DC power source.\textsuperscript{[10]}

9.1. High-Temperature Industrial Waste Heat Recovery/Conversion to Electric Power

A high proportion of the 33% of industrial energy used in manufacturing is dissipated directly into the atmosphere as industrial waste heat, which is sufficient to generate 0.9–2.8 TWh of clean energy per year via thermoelectric modules.\textsuperscript{[214]}

An electrical output of ≈214 W could be generated from high-temperature waste heat, using DC/AC inverters and a thermoelectric system attached to a carburizing furnace.\textsuperscript{[215]}

The energy harvested in this case could be used to power the factory housing the furnace, thereby greatly increasing its efficiency.

Energy-intensive steelmaking generates enormous quantities of waste heat, especially radiant heat from steel products. This heat can produce power thermoelectrically with an output of approximately 9 kW when continuously casting slab at ≈1188 K.\textsuperscript{[216,217]}

Likewise, energy-intensive cement manufacturing consumes a great amount of energy (3.2–6.3 GJ) per ton of clinker generated.\textsuperscript{[218]}

About 10–15% of the energy is lost as heat during the process. In this case, this energy could theoretically produce ≈211 kW of electrical power, whilst saving 3283 kW of energy.\textsuperscript{[219]}

Glass manufacturing processes involve the melting of glass pellets above 1500 °C. These processes could thermoelectrically generate 55.6 kW of electricity from the production of 500 tons of glass per day, based on a typical zT value of ≈1.1. This technology can recover up to 1.37 billion kWh of electricity annually throughout the glass processing factories in the United States, which is equivalent to annual savings of $112 million in the energy cost (or 7.71 × 10^6 kg of equivalent CO₂ emissions) for the production of 20 million tons of glass per year.\textsuperscript{[220]}

9.2. Medium-Temperature Automotive Waste Heat Recovery to Electric Power

Automotive industries are projecting a burgeoning interest in thermoelectric generators for turning the exhaust gas waste heat produced by internal combustion engines into electrical energy.\textsuperscript{[198]}

In a typical gasoline engine vehicle, approximately 20–30% of the combusted fuel is converted into useful energy for powering vehicles (about 30–45% for a diesel engine vehicle),\textsuperscript{[221,222]}

whereas the rest of the energy is lost as waste heat through the exhaust and cooling systems. Considering 6% of the exhaust waste heat could be converted into electrical energy, it would be possible to lower fuel consumption by up to 10%.\textsuperscript{[223]}

The study on waste energy recovery from exhaust gases in a diesel passenger car revealed the potential fuel savings ranged from 8% to 19%.\textsuperscript{[224]}

Major automobile manufacturers such as BMW,\textsuperscript{[225]} Renault,\textsuperscript{[226]} Honda,\textsuperscript{[227]} and Ford\textsuperscript{[228]} have started investing in thermoelectric generator-based waste heat harvesting systems for their new-generation vehicles. In 2013, Fiat and Chrysler announced the first commercial vehicle equipped with a thermoelectric generator, which achieved a 4% fuel economy improvement by harvesting electrical energy from its exhaust system.\textsuperscript{[229]}

Particularly, segmented thermoelectric materials such as TAGS \((\text{AgSbTe}_2)_x (\text{GeTe})_{1-x}\) have been used in the industry, due to their wide operational temperature range.\textsuperscript{[230]}

AgSbTe₂ is well known for its good thermoelectric properties in the medium temperature range (250–500 °C), as it possesses a large Seebeck coefficient and a low thermal conductivity.\textsuperscript{[171,231–234]}

The excellent thermoelectric performance of AgSbTe₂ indicates a great potential for usage in waste heat recovery applications in automotive exhausts. A high zT value of 1.59 was delivered at 673 K for AgSbTe₂, due to its low thermal conductivity (0.3 W m⁻¹ K⁻¹).\textsuperscript{[235]}

By optimizing the electronic transport via modulation of the disorder-induced localized electronic states, and simultaneous suppression of the lattice thermal conductivity (due to the formation of cation-ordered nanoscale domains), a maximum zT value of 2.6 was achieved in Cd-doped AgSbTe₂ at 573 K.\textsuperscript{[106]}

When substituting Sb with Zn in AgSbTe₂, the formation of intrinsic AgTe impurity phases was suppressed, which improved the thermal and mechanical stability, leading to a zT value of 1.9 at 584 K and a hardness value of ≈6.3 GPa for AgSb₉₀Zn₁₀Te₂.\textsuperscript{[112]}

Upon alloying with GeTe, p-type \((\text{AgSbTe}_2)_x (\text{GeTe})_{1-x}\) exhibited a zT value of 1.65 at 727 K with 2% neodymium doping.\textsuperscript{[262]}

Neboltixed growth AgPb₀.₉SbTe₃₋ₓ synthesized by combining AgSbTe₂ and PbTe was reported to exhibit a very high zT of 2.2 at 800 K.\textsuperscript{[237,238]}

9.3. Low-Temperature Body Heat Recovery to Electric Power

Generally, a human body generates ≈100 W of heat at rest and ≈525 W during physical activity.\textsuperscript{[239]}

Even with low-efficiency thermoelectric generators, the constant heat energy from the human body is still sufficient to be collected and converted into electrical power for driving small devices like wearable electronics. Flexible thermoelectric generators in wearable electronics should possess various features, including i) high thermoelectric performance at near room temperature, ii) compliant mechanical flexibility for curved or irregular skins, iii) high stretchability to accommodate strains induced by body motions, and iv) self-rescuing capabilities to heal mechanical damages in practical operation.

Jao et al. prepared a flexible thermoelectric generator (for use in a self-powered temperature sensor) by the physical mixing of Ag₁₋ₓTe nanowires with conductive PEDOT:PSS.\textsuperscript{[148]}

which demonstrated a Seebeck coefficient of 100 μV K⁻¹ and an output voltage of 2.6 mV at a temperature difference of 25 K. A recent study reported a self-powered flexible electronic device featuring a Ag₁₋ₓTe nanowire film,\textsuperscript{[145]}

which generated a stable output voltage of ≈0.52 mV at room temperature, as the contact resistance between Ag₁₋ₓTe nanowires had been decreased by welding.
A flexible thermoelectric module was assembled from four series-connecting four-leg Ag₂Te films and generated ≈4 mV at a temperature difference of 40° C. He et al. prepared a flexible thermoelectric generator by depositing Ag₃Se nanowires on a flexible nylon membrane, from which a four-leg assembly of binary Ag₃Se/nylon composite film was created, yielding a maximum power density of 2.3 W m⁻² at a temperature difference of 30 K. With the incorporation of Cu⁺, a power generator consisting of a six-leg flexible Ag₃Se/Ag/AgCuSe/nylon composite film produced an output voltage of 12.2 mV and a power density 5.42 W m⁻² at a temperature difference of 30K (Figure 13a).[132] A six-leg flexible thermoelectric generator featuring a Ag/Ag₃Se nanodendrites/nylon composite generated a voltage of 16.1 mV and a maximum power density of 13.56 W m⁻² at a temperature difference of 29.6 K.[131] Furthermore, the additional Ag phase in an eight-leg thermoelectric prototype with a Ag₂Se/Ag₃Se/nylon composite film generated a maximum power density of 8.74 W m⁻² at a temperature difference of 27 K.[130]

A four-leg thermoelectric generator was produced by assembling ternary Ag₂Se/Ag/PEDOT composite films on a nylon membrane, which produced an output voltage of 5.6 mV and a power density of ≈7.47 W m⁻² at a temperature difference of 27 K.[138] A Ag₂Se/PVP composite film assembled into a six-leg thermoelectric generator produced a maximum power of 4.16 μW and a maximum power density of 28.8 W m⁻² at a temperature difference of 29.1 K.[133] This work demonstrated that an insulating polymer could act as a suitable additive for improving both the thermoelectric properties and the flexibility of inorganic thermoelectric films.

A flexible thermoelectric generator composed of six legs of ternary Ag₂Se/Se/PPy composite films generated a voltage of 21.2 mV and a maximum power density of 37.6 W m⁻² at a temperature difference of 34.1 K.[134] Additionally, this flexible thermoelectric generator was successfully used to transform environmental low-grade waste heat into electricity. When the Ag₂Se/Se/PPy composite-based thermoelectric generator was put under a warm cell phone that just ended running a game program, an output voltage of 5.3 mV was generated from a temperature difference of ≈9.4 K between the cell phone and the ambient surroundings. This study also demonstrated the feasibility of preparing flexible composite films for applications in wearable electronics.

In order to form a device capable of harvesting human body heat, a four-leg thermoelectric generator was fabricated from Ag₂Se/nylon composite films.[129] The high density of Ag₂Se films and the tuned orientation of grains (by multisized Ag₂Se nanostructures) were expected to result in excellent thermoelectric performance. As a means to generate electricity from the temperature difference between the skin and the environment, one side of the thermoelectric generator was worn on the wrist and the other side was separated from the skin using a bubble film as a thermal insulator. The device demonstrated a maximum output power of 3.2 μW at a temperature difference of 30 K, corresponding to a maximum power density of 22.0 W m⁻² and a normalized maximum power density of 408 μW m⁻¹ K⁻² (Figure 13b). In comparison with the room-temperature thermoelectric properties of the flexible Ag₂Se hybrid films reported above, this value is almost ten times as high as that of the four-leg Ag₂Se/nylon device (2.3 W m⁻²) and four times as high as that of the six-leg
Ag2Se/Ag/AgCuSe/nylon device (5.42 W m−2) at the same temperature difference of 30 K.

Ductile semiconductors present a different approach for developing portable and sustainable flexible thermoelectrics. A series of room-temperature p-type ductile thermoelectric semiconductors, AgCu(Se, S, Te) p-sputter deposited solid solutions, with a zT value of 0.45 at 300 K was fabricated into flexible x-shaped thermoelectric devices with 0.3 mm in thickness. Specifically, p-type (AgCu)0.998Se0.21S0.06Te0.7 was coupled with n-type Ag20S7Te3 (connected electrically in series and thermally in parallel) between two polyimide-based flexible circuit boards. The six-couple (AgCu)0.998Se0.21S0.06Te0.7/Ag20S7Te3 legs produced an open circuit voltage of 3.7 mV and a maximum output power of 203 mW at a temperature difference of 1.5 K, generating a maximum normalized power density of up to 30 mW cm−2 K−2. This value is approximately four times higher than that of Bi2Te3-based thermoelectric generators and 10000 times greater than that of organic-based flexible thermoelectric generators.

A cross-plane x-shaped thermoelectric device with 31-couple (AgCu)0.998Se0.21S0.06Te0.7/Ag20S7Te3 was fabricated that effectively adhered to the curved surface of human skin. Under an ambient temperature of 298 K and when attached to a human’s wrist, the device produced an open circuit voltage of 0.7 V and maximum output power of 70 nW. The maximum normalized power density of this device was ≈11 mW cm−2 K−2.

Flexible thermoelectric components with complex shapes may be fabricated by 3D printing with additive manufacturing technologies. Thermoelectric inks are prepared by embedding the thermoelectric material in a passive matrix of additives and solvents. The resulting composite can then be printed by screen or ink-jet printing onto mechanically flexible substrates, which is typically followed by a sintering process. For instance, a UV-cured Ag2Se-based thermoelectric composite was fabricated using a 3D printer based on digital-light-processing techniques, achieving a power factor of ≈51.5 µW m−1 K−2 at room temperature. Mallick et al. reported a one-pot synthesis and processing of n-type Ag2Se-based screen-printed materials with mixed Ag and Se powder.[152] The targeted orthorhombic β-Ag2Se phase was formed via postprinting sintering at moderate temperature, thereby reducing the detrimental impacts of binder and solvent. A volatilized phase of Se was adsorbed dissociatively by Ag to create Ag2Se without defined grain boundaries and a high conductivity transport path. Consequently, the printed material exhibited a power factor of 17 m−1 K−2 and a zT value of ≈1 at room temperature, which was significantly higher than the zT of 0.6 for a printed Ag2Se film with silver paste and Se particle ink.[153] Furthermore, a printed thermoelectric generator with two thermocouples (Ag2Se-based material as the n-type leg and PEDOT:PSS as the p-type leg), achieved an output voltage of 17.6 mV with a high maximum power output of 0.19 µW at a temperature difference of 60 K.

Three flexible and shape-versatile thermoelectric generator prototypes (cuboid, cylindrical gear, and sawtooth) were successfully printed by stereolithography, a form of 3D printing, while an Ag2Se-based ink was prepared based on the stoichiometric ratio of Ag and Se powders in solvent and additive. [141] 3D-thermoelectric generators were then fabricated using Ag2Se-based ink as n-type legs and PEDOT as p-type legs on the surface of 3D-printed resin scaffolds of different shapes. The thermoelectric legs were connected electrically in series and thermally in parallel. The printed thermoelectric generators were then sintered to yield a β-Ag2Se phase in the n-type legs (Figure 13c). As for the thermoelectric performance, maximum power outputs of ≈0.4 µW or 7 µW were generated by the cuboid (4 thermocouples) and cylindrical gear (9 thermocouples) thermoelectric generators respectively, at a temperature difference of 70 K. Upon introducing the system to the skin, an open-circuit voltage of 4.2 mV at room temperature was achieved by the sawtooth-shaped 3D thermoelectric generator (8 thermocouples).

10. Conclusions and Perspective

This review outlines the recent achievements of emerging silver-based chalcogenides as thermoelectric materials in binary, ternary, quaternary, quinary, senary, and septenary compositions, which are prepared through various reactions, alloying, and doping processes. The potential of silver-based chalcogenides in flexible thermoelectric devices is an important factor in enabling the effective harvesting of heat at different scales. For instance, large quantities of heat are encountered in industrial settings, such as within the steel production industry and power stations, whilst intermediate levels of heat are generated in exhausts and alternators of cars, and microscale heat is created by the human body. Silver-based chalcogenides (including those which are doped, alloyed, hybridized, and composites) have been considered in the nascent stages of development for many thermoelectric materials, but a number of challenges have been encountered so far. For example, except for few of the widely studied silver-based chalcogenides, the synthesis of many of the multinary silver chalcogenides in a phase-pure form remains challenging, which hampers the study of the thermoelectric behavior of these materials. Often, the existence of a number of metastable phases leads to performance instability and irreproducibility. Such thermoelectric performance irreproducibility was frequently reported in liquid-like thermoelectric materials, likely due to the migration of liquid-like Ag atoms upon external stimulation (e.g., electric field or temperature gradient), which typically led to severe reductions in performance. Moving forward, ensuring that materials possess good stability and high zT under operating conditions is of vital importance for bridging the gap between fundamental materials science and practical applications, and for advancing thermoelectric technology towards commercial maturity.

Aside from those already studied, there remains a vast number of silver chalcogenide semiconductors, especially multinary compounds, that are yet to be examined for their thermoelectric potential. In the same way, sulfide counterparts also warrant more attention, as the majority of multinary compounds studied thus far are those of selenides and tellurides. Moreover, for a wider adoption of silver-based chalcogenides in thermoelectric applications, such materials are expected to acquire crystal behavior with respect to electrical conduction, and glass behavior with regard to thermal conduction. Therefore, a wide variety of material designs have been developed to offer various avenues for fine-tuning key
electronic properties and thermal transport parameters. Herein, we have reviewed a number of exemplary studies on silver-based chalcogenide thermoelectric materials which employ various engineering approaches, including quantum confinement, modulation doping, and energy filtering. These strategies seek to modify band structure and transport properties to either tune electrical conductivity and Seebeck coefficient independently, or increase them both simultaneously. Another fruitful strategy to increase $zT$ is to minimize the lattice thermal conductivity. This may be achieved via phonon engineering approaches which enhance phonon scattering and decrease lattice thermal conductivity, due to the incorporation of nanostructured precipitates, grain boundaries, multinary alloying, elemental doping, and point defect loading. Moreover, the inclusion of a second phase in heterogeneous thermoelectric hybrids is another route to achieving a high $zT$ value.

As estimated, a $zT$ value of $\approx 3$ is needed to realize practical thermoelectric applications and enable the large-scale applicability of waste-heat-recovery technologies. So far, it remains incredibly challenging to reach this value or greater, though a promising Ag-doped GeTe, together with Sb, Pb, and Bi (Ge$_{0.66}$Ag$_{0.11}$Sb$_{0.11}$Pb$_{0.02}$Bi$_{0.01}$Te$_{0.89}$), has been demonstrated to achieve a high $zT$ value of 2.7 at 750 K, and a high conversion efficiency of 13.3% at a temperature difference of 506 K, among the highest in the entire thermoelectric community. Particularly, a substantial enhancement in power factor is needed to raise $zT$ values, depending on further reductions in thermal conductivity and increases in electron conductivity. Apart from displaying high-quality thermoelectric properties, a good thermoelectric material should be scalable and cost-effective to facilitate mass production. Such a material should be able to form dense compacts for device integration and possess high thermal stability for extended periods. Refining the quantitative understanding of the relationship between structure or composition and the properties of these materials is essential before they may be rationally designed and prepared.

The large-scale applicability of waste-heat-recovery technologies also largely depends on the cost and environmental impact of thermoelectric materials, which are mainly based on alloys and compounds of bismuth, tellurium, and lead. Eventually, these elements should be replaced, due to their scarcity and toxicity. Driven by the growing demands of wearable and flexible electronic devices, there is an emerging research direction which focuses on methods to implement thermoelectric components into self-powered wearable devices which harvest microscale heat from the body. In enabling the widespread adoption of flexible thermoelectric devices, silver-based chalcogenide composites (including those which are film-, polymer-, and fiber-based) have great potential, because these materials can directly generate power from a temperature difference between the human body and the surrounding environment. In the urgent search for emerging green energy technologies, it is expected that silver-based chalcogenide thermoelectric materials will make a meaningful contribution to the minimization of fossil fuel usage in the near future. Silver-based chalcogenide thermoelectric materials in doped, alloyed, hybridized, and composited forms have already been utilized for a vast range of niche applications, and efforts to translate this technology to mainstream applications are ongoing.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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Si Yin Tee obtained her Ph.D. in Biomedical Engineering from National University of Singapore. Currently, she is working as a research scientist at the Institute of Materials Research and Engineering, A*STAR. Her research focuses on the development of functional metal and semiconductor nanostructures for biomedical, environmental and energy applications.

Ming-Yong Han worked with IBM and Indiana University, followed by time spent at the National University of Singapore as a faculty member, before his current appointments with the Institute of Materials Research and Engineering and Tianjin University. His research addresses problems at the interfaces of nanoscience, nanotechnology, biotechnology and energy/biomedical applications. He has published >220 papers and filed >100 patents including national entries, with >24000 citations and >300 research highlights. He is a Fellow of the Royal Society of Chemistry (FRSC) and a Web of Science/Scopus highly cited researcher.