Solvothermal Synthesis and Thermoelectric Properties of Silver Selenide: A Postprint

Authors: Xie Zhengchuan, Gao Jie, Liu Chengyan, Cheng Yiran, Yu Zhonghai, Zhang Zhongwei, Li Jiahui, Miao Lei, Liu Chengyan

Date: 2022-10-26T16:53:38+00:00

Abstract

To prepare high-performance silver selenide (Ag2Se)-based thermoelectric materials using a low-energy-consumption and time-efficient method, silver nitrate (AgNO3) and elemental selenium (Se) were selected as raw materials, ethylenediamine was used as the solvent, and Ag2Se powders with different Ag/Se molar ratios (nAgNO3/nSe) were synthesized via a solvothermal method, followed by consolidation into bulk materials through spark plasma sintering (SPS). X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed for phase analysis and microstructural observation of the samples, a thermoelectric property measurement system was utilized to characterize the thermoelectric performance, and the performance was further verified through simulation calculations and actual output voltage testing of thermoelectric generator devices. The results indicate that as the nAgNO3/nSe ratio increases, the diffraction peaks of the second-phase elemental Ag in the silver selenide powder are enhanced, which is beneficial for optimizing the charge carrier transport properties of the samples. When the nAgNO3/nSe ratio is 2:1, the obtained sample exhibits optimal room-temperature thermoelectric properties, achieving a thermoelectric figure of merit (zT) of approximately 0.74 at 303 K. When the nAgNO3/nSe ratio is 1.9:1, the obtained sample reaches a maximum zT value of approximately 1.07 at 393 K, with an average zT value of approximately 0.82 between 303 and 393 K. Both simulation calculations and actual output voltage testing of thermoelectric generator devices demonstrate that the experimentally prepared silver selenide bulk material possesses the potential to replace N-type Bi2Te3-based thermoelectric materials.

Full Text

Abstract

Study on Solvothermal Preparation and Thermoelectric Properties of Silver Selenide

To prepare high-performance silver selenide-based thermoelectric materials using a low-energy-consumption and time-efficient method, we synthesized silver selenide powders with different silver-to-selenium molar ratios via a solvothermal method using ethylenediamine as the solvent. The powders were subsequently consolidated into bulk materials through spark plasma sintering (SPS). The thermoelectric properties of the samples were measured using a thermoelectric performance testing system, while phase analysis and microstructural observation were conducted through X-ray diffraction (XRD) and scanning electron microscopy (SEM). The performance was verified through simulation calculations and actual output voltage tests of thermoelectric generator devices.

The results demonstrate that the sample with $AgNO_3$/Se = 1.9:1 exhibits the optimal room-temperature thermoelectric performance. As the $AgNO_3$/Se ratio increases, the diffraction peaks of the elemental silver second phase in the silver selenide powder strengthen, which is beneficial for optimizing the carrier transport characteristics. A maximum thermoelectric figure of merit (zT) of 1.07 was achieved at 393 K for the $AgNO_3$/Se = 1.9:1 sample, with an average zT value of approximately 0.74 between 303–393 K. Both simulation calculations and actual output voltage measurements of thermoelectric generator devices confirm that the synthesized silver selenide bulk material has the potential to replace Bi_2Te_3-based thermoelectric materials.

Keywords: silver selenide; solvothermal method; thermoelectric materials; silver-selenium ratio; thermoelectric performance

---

1. Introduction

With the rapid development of human society and world population growth, energy demand continues to increase alongside accelerating industrialization. Regrettably, approximately 60% of energy is wasted as heat during the utilization of traditional fossil fuels such as coal, oil, and natural gas, while their combustion also causes environmental pollution. In conventional energy supply systems, about 80% relies on non-renewable fossil fuels. Developing clean energy alternatives to fossil fuels and building a sustainable society has become one of the global themes of the 21st century.

Thermoelectric conversion technology can directly achieve mutual conversion between thermal and electrical energy through the Seebeck and Peltier effects of thermoelectric materials. This technology can utilize industrial waste heat, automobile exhaust heat, and other low-grade thermal sources, as well as geothermal and solar energy, for thermoelectric power generation, or use electrical energy for solid-state refrigeration. As an effective way to cleanly utilize energy, thermoelectric materials have attracted increasing attention due to their advantages of easy miniaturization and flexibility, noiseless and pollution-free operation, and high stability. However, thermoelectric materials remain in a niche market stage, with the primary issue being insufficient energy conversion efficiency.

The energy conversion efficiency of thermoelectric materials is typically evaluated using the dimensionless thermoelectric figure of merit zT, defined as zT = $S^2\sigma T/$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and is the total thermal conductivity. A larger zT value indicates better thermoelectric performance and higher energy conversion efficiency. Since S, σ, and are coupled through carrier concentration, improving σ often leads to decreased S and increased . Therefore, enhancing thermoelectric performance requires synergistic optimization of these parameters to simultaneously achieve high S, high σ, and low .

Currently, the main commercially applied near-room-temperature thermoelectric material is Bi_2Te_3, which exhibits relatively excellent thermoelectric performance near room temperature. However, Bi_2Te_3-based thermoelectric materials suffer from scarce and toxic constituent elements, high prices, and typically require energy-intensive preparation methods such as melting, mechanical alloying, or prolonged high-temperature heat treatment. Silver selenide (Ag_2Se) is a narrow-bandgap semiconductor that undergoes a phase transition from orthorhombic β-Ag_2Se to cubic α-Ag_2Se with superionic characteristics near 406 K, featuring high σ and low . Its constituent elements are abundant in the earth's crust and have low toxicity, making it a promising near-room-temperature thermoelectric material with significant development potential.

Existing research on Ag_2Se-based thermoelectric materials often employs melting methods, mechanical alloying, or long-duration high-temperature treatments, which involve long cycles and high energy consumption. Wet chemical methods for preparing silver selenide often introduce external elements for doping during the synthesis stage with cumbersome experimental procedures. Most studies focus on optimizing the thermoelectric properties of silver selenide bulk materials, with few reports on the output performance of thermoelectric generator devices. In this work, we employed a low-temperature, short-duration solvothermal method using ethylenediamine as the solvent to synthesize Ag_2Se powders with different $AgNO_3$/Se molar ratios. After spark plasma sintering, we systematically investigated the phase composition, microstructure, and thermoelectric properties of the bulk materials, providing insights for further research and device applications of Ag_2Se-based thermoelectric materials.

2. Experimental Methods

2.1 Materials and Synthesis

The raw materials used in the experiments were silver nitrate ($AgNO_3$, $ 99.9 99*{2}Sebulkmaterialswithdifferent AgNO*{3}$/Se molar ratios is illustrated in [Figure 1: see original paper].

Stoichiometric amounts of $AgNO_3$ and Se powders were weighed according to molar ratios of 1.9:1, 2:1, and 2.1:1, and placed in a polytetrafluoroethylene (PTFE) liner. Ethylenediamine was then added to the liner containing Se powder, and the solution was slowly poured into the liner containing $AgNO_3$. The PTFE liner was placed on a magnetic stirrer for thorough mixing, then transferred to a stainless-steel autoclave. The sealed autoclave was placed in an electric heating oven for solvothermal reaction at 160°C for 12 hours. After cooling to room temperature, the product was collected and alternately washed with deionized water and anhydrous ethanol via centrifugation, then dried in a vacuum oven to obtain Ag_2Se powders with different $AgNO_3$/Se ratios. The powders were then sintered using spark plasma sintering (SPS) at 350°C to obtain bulk materials with different $AgNO_3$/Se ratios.

2.2 Characterization and Performance Testing

Phase analysis of the samples was performed using X-ray diffraction (XRD, D8-ADVANCE, Bruker). Microstructural observation was conducted using scanning electron microscopy (SEM, Quanta 450FEG). The Seebeck coefficient and resistivity were measured using a Seebeck coefficient/resistivity testing system (ZEM-3, Ulvac-Riko). The total thermal conductivity was calculated using the formula $= d \cdot D \cdot C$, where density d was measured by the Archimedes method, thermal diffusivity D was measured using a laser thermal conductivity meter (LFA467, NETZSCH), and specific heat C was calculated using the Dulong-Petit law. Carrier concentration and carrier mobility were measured using a Hall effect measurement system (8404, Shore). The output voltage of thermoelectric generator devices was tested using a digital multimeter (12E+, Fluke).

2.3 Device Simulation and Fabrication

The simulation optimization process for individual bulk dimensions was performed using multiphysics simulation software. A physical field of thermoelectric effect was constructed, and the thermoelectric performance parameters of the experimental Ag_2Se bulk and commercial $Bi_2Se_{0\cdot5}Te_{2\cdot5}$ bulk were input to simulate the output voltage of single bulk under a temperature difference of 50 K. The ambient temperature in the simulation field was set to 300 K. When the height of the thermoelectric bulk changed, the cold-side temperature remained consistent with the ambient temperature, while the hot-side temperature changed accordingly, and the cold-side temperature also changed with the variation in heat dissipation conditions.

The thermoelectric generator device fabrication process involved assembling the experimental Ag_2Se bulk and commercial $Bi_{0.5}Sb_{1.5}Te_3$ bulk into devices. The devices consisted of 2\$×2×\$4 thermoelectric legs connected electrically in series and thermally in parallel. Copper foils were used between bulk legs, with melted tin wire for soldering. Since the length and width of the bulks were set identically, only the height parameter was used to describe the working dimensions of the bulk.

---

3. Results and Discussion

3.1 Phase and Microstructure Analysis

The XRD patterns of Ag_2Se powders and bulk materials with different $AgNO_3$/Se ratios are shown in [Figure 2: see original paper]. All diffraction peaks of the synthesized powders correspond to orthorhombic β-Ag_2Se (PDF#01-071-2410) and cubic α-Ag_2Se (PDF#01-071-2410), indicating that β-Ag_2Se phase exists in all synthesized powders with different $AgNO_3$/Se ratios. As the $AgNO_3$/Se ratio increases, the diffraction peak intensity of elemental Ag second phase (PDF#01-089-3722) at 38.121° gradually strengthens. This may be due to incomplete reaction between selenium and silver sources during the solvothermal process, where unreacted selenium dissolves in ethylenediamine and is lost during centrifugal washing, while unreacted Ag^+ is reduced by ethylenediamine to elemental Ag that coexists with the synthesized Ag_2Se powder.

After sintering into bulk materials, the diffraction peak intensities of the second phase in the XRD patterns of Ag_2Se powders with different $AgNO_3$/Se ratios are all weakened to some extent. Notably, the $AgNO_3$/Se = 1.9:1 sample shows no elemental Ag diffraction peaks after sintering, possibly due to diffusion loss of Ag^+ during the sintering process.

The fracture surfaces of Ag_2Se bulk materials with different $AgNO_3$/Se ratios are shown in [Figure 3: see original paper]. White particles gradually appear in the images as the $AgNO_3$/Se ratio increases from 1.9:1 to 2.1:1, which may be elemental Ag precipitated from the second phase, confirming the existence of Ag second phase.

3.2 Thermoelectric Properties

The thermoelectric properties of Ag_2Se bulk materials with different $AgNO_3$/Se ratios are presented in [Figure 4: see original paper]. All samples exhibit negative Seebeck coefficients (S) across the tested temperature range, indicating n-type conduction with electrons as the majority carriers. The absolute value of S decreases gradually with increasing temperature for all samples. The resistivity ( ) also decreases gradually with temperature, decreasing from 1.17\$×10^{-5}\$

$\Omega \cdot$ m at 303 K to 0.313$×10^{-5}$ $\Omega \cdot$ m at 393 K for the $AgNO_3$/Se = 2.1:1 sample.

These changes may be related to carrier concentration. For degenerate semiconductors, S can be expressed as [24-26]:

S (π^2/3)(k_B^{2}T)/(eE_F)

where k_B is the Boltzmann constant, e is the electron charge, and E_F is the Fermi energy. Resistivity can be expressed as = 1/σ, with conductivity σ = ne , where n is carrier concentration and is carrier mobility. Both S and are inversely proportional to n. As the test temperature increases, intrinsic thermal excitation causes n to increase gradually, leading to decreases in both S and .

The carrier concentration of samples at room temperature shows an increasing trend with increasing $AgNO_3$/Se ratio, which may be caused by the second-phase metal Ag providing electrons. The power factor (PF = $S^2\sigma$) shows a trend of first increasing then decreasing with temperature, reaching its maximum for the $AgNO_3$/Se = 1.9:1 sample due to the combined effects of S and σ.

The thermal conductivity ( ) increases with temperature for all samples. For the $AgNO_3$/Se = 2.1:1 sample, increases from 0.647 $W \cdot m^{-1} \cdot K^{-1}$ at 303 K to 0.695 $W \cdot m^{-1} \cdot K^{-1}$ at 393 K. The of semiconductor materials is primarily contributed by electronic thermal conductivity (_e) and lattice thermal conductivity (_l). For Ag_2Se, _e contributes significantly to , which can be expressed by the Wiedemann-Franz law [28]:

_e = LσT

where L is the Lorenz constant. The increase in n caused by increasing second-phase Ag content leads to higher σ, thereby increasing _e and consequently the total .

The zT values of Ag_2Se bulk materials with different $AgNO_3$/Se ratios increase with temperature. The $AgNO_3$/Se = 1.9:1 sample exhibits the best room-temperature thermoelectric performance, achieving a maximum zT value of 1.07 at 393 K and an average zT value of 0.82 in the 303–393 K range.

3.3 Device Simulation and Performance

The relationship between simulated output voltage and bulk height for different widths is shown in [Figure 5: see original paper]. When the bulk width is the same, the simulated output voltage decreases with increasing width. When the bulk height is the same, the simulated output voltage increases with height. The variation pattern of simulated output voltage with height for Ag_2Se bulks with different widths is similar to that of commercial $Bi_2Se_{0 \cdot 5}Te_{2 \cdot 5}$ bulks. However, under the same conditions, the simulated output voltage of $AgNO_3$/Se = 1.9:1 Ag_2Se bulks is slightly lower than that of $Bi_2Se_{0 \cdot 5}Te_{2 \cdot 5}$ bulks.

The output voltage of thermoelectric generator devices at room temperature as a function of temperature difference is shown in [Figure 6: see original paper]. Devices assembled with experimental Ag_2Se bulks and commercial $Bi_0 \cdot_5 Sb_1 \cdot_5 Te_3$ bulks, as well as devices assembled with commercial $Bi_2Se_0 \cdot_5 Te_2 \cdot_5$ and $Bi_0 \cdot_5 Sb_1 \cdot_5 Te_3$ bulks, all show increasing output voltage with temperature difference, with little difference between them. This indicates that the synthesized Ag_2Se bulks have the potential to replace Bi_2Te_3-based thermoelectric materials.

---

4. Conclusion

In this study, Ag_2Se bulks with different $AgNO_3$/Se molar ratios were prepared using a low-energy-consumption, short-duration solvothermal method. By controlling the $AgNO_3$/Se ratio, the carrier transport properties of Ag_2Se bulks can be optimized, thereby tuning their thermoelectric performance. The $AgNO_3$/Se = 1.9:1 sample exhibits the best room-temperature thermoelectric performance, with a zT value of approximately 0.67 at 303 K and a maximum zT value of 1.07 at 393 K. The average zT value in the 303–393 K range is 0.74. Simulation calculations and thermoelectric generator device output voltage tests demonstrate that the synthesized Ag_2Se bulks have the potential to replace Bi_2Te_3-based thermoelectric materials, providing insights for further research and device applications of Ag_2Se-based thermoelectric materials.

References

[1] BISWAS K, HE J, BLUM I D, et al. High-performance bulk thermoelectrics with all-scale hierarchical architectures[J]. Nature, 2012, 489(7416): 414-418.

[2] YANG L, CHEN Z G, DARGUSCH M S, et al. High performance thermoelectric materials: progress and their advanced applications[J]. Advanced Energy Materials, 2017, 8(6): 1701797.

[3] SNYDER G J, TOBERER E S. Complex thermoelectric materials[J]. Nature Materials, 2008, 7(2): 105-114.

[4] IOFFE A F. Semiconductor Thermoelements and Thermoelectric Cooling[M]. London: Infosearch Limited, 1957: 1-13, 43-45.

[5] DRESSELHAUS M S, CHEN G, TANG M Y, et al. New directions for low-dimensional thermoelectric materials[J]. Advanced Materials, 2007, 19(8): 1043-1053.

[6] TAN G, ZHAO L D, KANATZIDIS M G. Rationally designing high-performance bulk thermoelectric materials[J]. Chemical Reviews, 2016, 116(19): 12123-12149.

[7] ZHU J, LIU Y, FU C, et al. Compromise and synergy in high-efficiency thermoelectric materials[J]. Advanced Materials, 2017, 29(14): 1605884.

[8] SHI X L, ZOU J, CHEN Z G. Advanced thermoelectric design: from materials and structures to devices[J]. Chemical Reviews, 2020, 120(15): 7399-7515.

[9] LIU W, JIE Q, KIM H S, et al. Advanced thermoelectrics governed by a single parabolic band: $Mg_2Si_{0}\cdot_5Sn_{0}\cdot_5$ solid solutions[J]. Advanced Energy Materials, 2015, 5(3): 1401640.

[10] ZHU B, LIU X, WANG Y, et al. Realizing record n-type Bi_2Te_3-based thermoelectric performance through synergistic optimization of carrier concentration and point defect scattering[J]. Energy & Environmental Science, 2020, 13: 2106-2114.

[11] LI S, WEI T, LIU W, et al. Magnetism-induced enhancement of room-temperature cooling performance in p-type BiSbTe alloys[J]. Energy & Environmental Science, 2020, 13: 535-544.

[12] ZHAO L D, TAN G, HAO S, et al. Low-cost, abundant binary sulfides as promising thermoelectric materials[J]. Materials Today, 2016, 19(4): 227-239.

[13] DALVEN R, GILL R. Energy bands in α-Ag_2Se[J]. Physical Review, 1967, 159(3): 645-649.

[14] JUNOD P, HEDIGER H, KILCHOR B, et al. Metal-non-metal transition in silver selenide[J]. Philosophical Magazine, 1977, 36(4): 941-958.

[15] FERHAT M, NAGAO J. Thermoelectric properties of Ag_2Se compounds[J]. Journal of Applied Physics, 2000, 88(2): 813-816.

[16] DAY T, DRYMIOTIS F, ZHANG T, et al. Evaluation of thermoelectric efficiency potential in silver selenide[J]. Journal of Materials Chemistry A, 2013, 1: 7568-7573.

[17] MI F, ZHANG L, QIU Y, et al. Thermoelectric transport in Ag_2Se: normal phases and phase transitions[J]. Applied Physics Letters, 2014, 104(13): 133906.

[18] DING F, QIU Y, CAI K, et al. High performance flexible thermoelectric power generator based on Ag_2Se film on nylon membrane[J]. Nature Communications, 2019, 10(1): 841.

[19] DRYMIOTIS F, DAY T W, BROWN D R, et al. Enhanced thermoelectric performance of $Ag_2Se_{0}\cdot_5Te_{0}\cdot_5$[J]. Applied Physics Letters, 2013, 103: 143906.

[20] LEE C, PARK H, HASHIMOTO H. Effect of non-stoichiometry on thermoelectric properties of n-type Ag_2Se alloy prepared by mechanical alloying process[J]. Journal of Applied Physics, 2007, 101(2): 645.

[21] CHEN J, SUN Q, BAO J, et al. Hierarchical structures in porous doped polycrystalline $SnSe_2$ toward ultra-high thermoelectric performance[J]. Journal of Materials Chemistry A, 2019, 7: 9761-9772.

[22] LU Y, QIU Y, CAI K, et al. Ultrahigh power factor flexible silver selenide-based thermoelectric devices[J]. Energy & Environmental Science, 2020, 13: 1240-1249.

[23] LI D, ZHANG X, LIU Y, et al. High thermoelectric performance Ag_2Se-based material prepared by chemical method[J]. Materials Chemistry Frontiers, 2020, 4(3): 875-880.

[24] CUTLER M, MOTT N F. Observation of Anderson localization in an electron gas[J]. Physical Review, 1969, 181(3): 1336-1340.

[25] LIU Y, LIU W, LI J, et al. Synergistically optimizing thermoelectric properties of polycrystal Sn through additional Ag_8SnSe_6 introducing[J]. CrystEngComm, 2020, 22: 248-256.

[26] WANG X, LIU Y, CHEN Y, et al. Dynamical Ag-intercalation in $AgSnSe_2$ with nano-precipitates[J]. ACS Applied Materials & Interfaces, 2020, 12: 51523-51529.

[27] SOOTSMAN J R, CHUNG D Y, KANATZIDIS M G. New and old concepts in thermoelectric materials[J]. Angewandte Chemie International Edition, 2009, 48(46): 8616-8639.

[28] LIANG Q, WANG Y, HUANG X, et al. Realizing n-type Mg_3Sb_2-based zintl compounds through codoping[J]. ACS Applied Materials & Interfaces, 2020, 12(19): 21799-21807.

[29] LIU W, JIE Q, KIM H S, et al. Advanced thermoelectrics governed by a single parabolic band: $Mg_2Si_{0 \cdot 5}Sn_{0 \cdot 5}$ solid solutions[J]. Advanced Energy Materials, 2015, 5(3): 1401640.

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv — Machine translation. Verify with original.