Self-Doping Enables Flexible Ag_2Se Bulks for Room-Temperature Thermoelectric Generators and Coolers

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Experimental details

Synthesis of materials

A total of ten grams of high-purity elements of Ag (99.99%, Alfa Aesar) and Se (99.99%, Alfa Aesar) were accurately weighed according to the predetermined composition listed in **Table S2** and sealed in quartz tubes under vacuum (~10^{-3} torr). The quartz tubes were slowly heated to 1323 K, held at this temperature for 2 hours to ensure homogenization, and rapidly quenched in water. After pretreatment, the quartz tubes were heated to 1273 K at a controlled rate of 1.5 K min^{-1}, held for 6 hours to facilitate heating of the homogeneous quartz tubes, and cooled to room temperature at the same rate.

Room temperature compression

To evaluate the mechanical properties of the specimens, compression examinations were conducted at room temperature (296 ± 2 K) under ambient. In this examination, the specimens possessing a pillar structure (about 5 mm × 5 mm × 10 mm) were subjected to a compressive stress along the long-side of the specimen (i.e., stress was parallel to the 10 mm side) using a universal testing machine (AG-Xplus 50kN, Shimadzu). To ensure a stable compression process, a small pre-stress was applied prior to the commencement of compression test. The compression was terminated until the failure of the specimens with an initial compressive strain rate of 0.05 mm min^{-1}. This examination is denoted as "RT Stress-Strain (*S*-*S*) measurement" and the obtained curve is suggested as *S*-*S* curve in the following sections unless otherwise mentioned.

Stress-Temperature (S-T) measurement

Besides to the aforementioned RT compression examinations, to evaluate the mechanical properties of the specimens under phase transformation, the specimens were scanned in a specific temperature range including the phase transformation temperature under a constant compressive stress of 2 MPa using a universal testing machine (AG-Xplus 50kN, Shimadzu). This examination is denoted as "Stress-Temperature (*S*-*T*) measurement" and the obtained curve is suggested as *S*-*T* curve unless otherwise mentioned.

Temperature was controlled using a temperature controller (SSR-PG TC K, Sakaguchi) and the heating process was manipulated from RT to ~423 K with a heating rate of 5 K min^{-1} followed by an air-cooling process to RT. During the heating process, to avoid the oxidation of the specimens, a high purity N_2 atmosphere (purity 99.99%) was dynamically flowed into the chamber of furnace. To accurately record the temperature of the specimens, they were placed on the center of stage of the testing machine equipped with a thermocouple, which was very close to the specimens.

Prior to the commencement of the *S*-*T* measurement, a small pre-stress was introduced to the specimens to obtain a stable compression process. Additionally, to rule out any displacement brought about from the thermal expansion of the system, instead of reading the cross-head of the universal testing machine, the displacement of the specimens was recorded using an *in-situ* high-resolution camera system during the temperature scanning under a 2 MPa compressive stress. Lastly, the collected data (i.e., temperature read by a thermal couple and the strain read by a high-resolution camera system) was analyzed using DIPP-Motion V2D software.

TE properties Measurement

The solidified alloys were then cut and ground into specific shapes: columns 4 mm × 4.3 mm × 12 mm and pellets with 6 mm diameter and 2 mm thickness. These samples were further ground on # 4000 SiC paper (Buehler) in preparation for thermoelectric measurements. The electrical resistivity ρ and Seebeck coefficient S were measured by a commercial instrument

(ZEM-3, ULVAC) under the helium-filled atmosphere. In the thermal properties, the thermal conductivity κ comprised three factors according to the equation $\kappa = D \times C_p \times d$. The thermal diffusivity D was measured by a commercial instrument (LFA-467, Netzsch), the specific heat capacity C_p was measured by DSC (DSC 3500 Sirius, Nertzch), while the density d was obtained by Archimedes' method (JA-2003J, Chrom Tech), respectively. The DSC samples of Ag_2Se-based alloy (50 mg) were carefully loaded into crucibles. The samples were then subjected to a heating process, gradually reaching a temperature of 470 K, followed by a controlled cooling phase down to 303 K, with a heating/cooling rate of 10 K min^{-1}, all within a nitrogen-filled atmosphere. The lattice thermal conductivity could be estimated by $\kappa_L = \kappa - \kappa_e$, where the electronic thermal conductivity κ_e was calculated using the Wiedemann-Franz law $\kappa_e = LT\rho^{-1}$. Note that the Lorentz factor L correlates with the S via the equation $L = \left\{1.5 + exp\left[-\frac{|S|}{116}\right]\right\} \times 10^{-8} V^2 K^{-2}$. [20] The carrier concentration (n_H) and mobility (μ_H) were obtained by Hall measurement (ECOPIA, HMS-3000) under the magnetic field of 0.49T.

Characterization

Mechanical grinding and polishing were applied on the Ag_2Se-based alloy, using SiC paper (#400 to #4000) and Al_2O_3 powder with particle sizes of 1.0 μm and 0.05 μm, respectively, and were followed by further metallographic observation and compositional analysis (JEOL JXA-8530F). The Ag_2Se-based alloys were crushed into powder, sieved through 500 mesh, and placed into the capillaries. The in-situ synchrotron-radiation powder X-ray analysis at the TPS-19A beamline of the National Synchrotron Radiation Research Center (NSRRC, Taiwan), with the wavelength of 0.61992 Å. The microstructure of the Ag_2Se and $SeAg_2Se$ were analyzed using field-emission transmission electron microscopy (FETEM, Talos F200X G2) at an accelerating voltage of 200 kV. Sample preparation for this analysis utilized a focused ion beam (FIB, Hitachi NX2000) with a Ga^+ ion source.

TE conversion efficiency and Z-meter measurement:

TEG (Mini-PEM): The Ag_2Se-based samples were shaped into rectangular dimensions of 4.0 mm (depth) × 4.3 mm (width) × 12.0 mm (height). Copper wires with a diameter of 0.45 mm were used as conducting leads. During assembly, one type of solder paste, Sn-Bi solder (138°C, Shenmao), was utilized. First, the copper wires were soldered to the electrodes using Sn-3Ag-0.5Cu (491 K, SAC). Next, the electrodes were connected to the single-leg thermoelectric device using SAC solder wire. The assembled single-leg device was then placed into a commercial instrument (Mini-PEM, ULVAC). To minimize thermal contact resistance between the copper blocks and electrodes, a 200 μm thick graphite sheet (Grafoil) was applied to the hot and cold sides with thermal grease (KS-613, Shin-Etsu Silicone).

TEC (Z-meter): Using a high-performance Ag_2Se alloy for the *n*-type material, a thermoelectric pellet was fabricated to estimate the cooling performance. First, the nickel wires were joined to the measuring holder using Sn-Bi solder (411 K, Shenmao). The Ag_2Se alloy was shaped into a $2 \times 3 \times 4$ mm^3 pellet, which was then printed with liquid-metal layers to serve as conductors for two nickel wires. The assembled holder was then placed into a commercial instrument (DX4091, TEC Microsystems). The obtained result of ΔT_{max} of the thermoelectric pellet was shown in Figure S5.

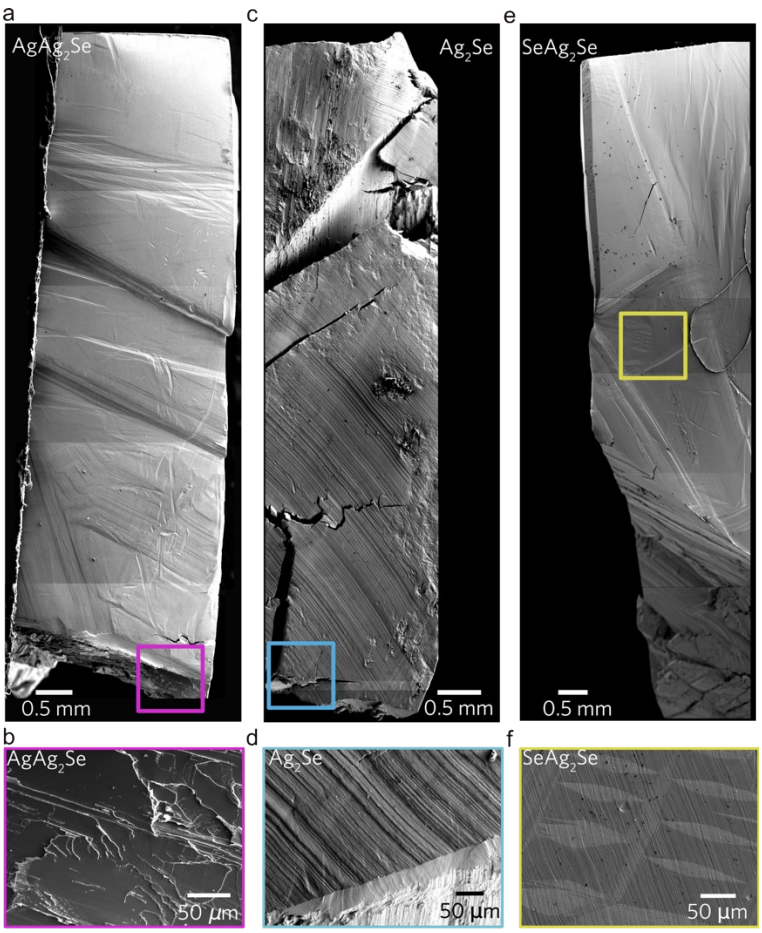

Figure S1. The cross-sectional SEM images of the (a,b) $AgAg_2Se$, (c,d)Ag_2Se, and (e,f) $SeAg_2Se$ specimens.

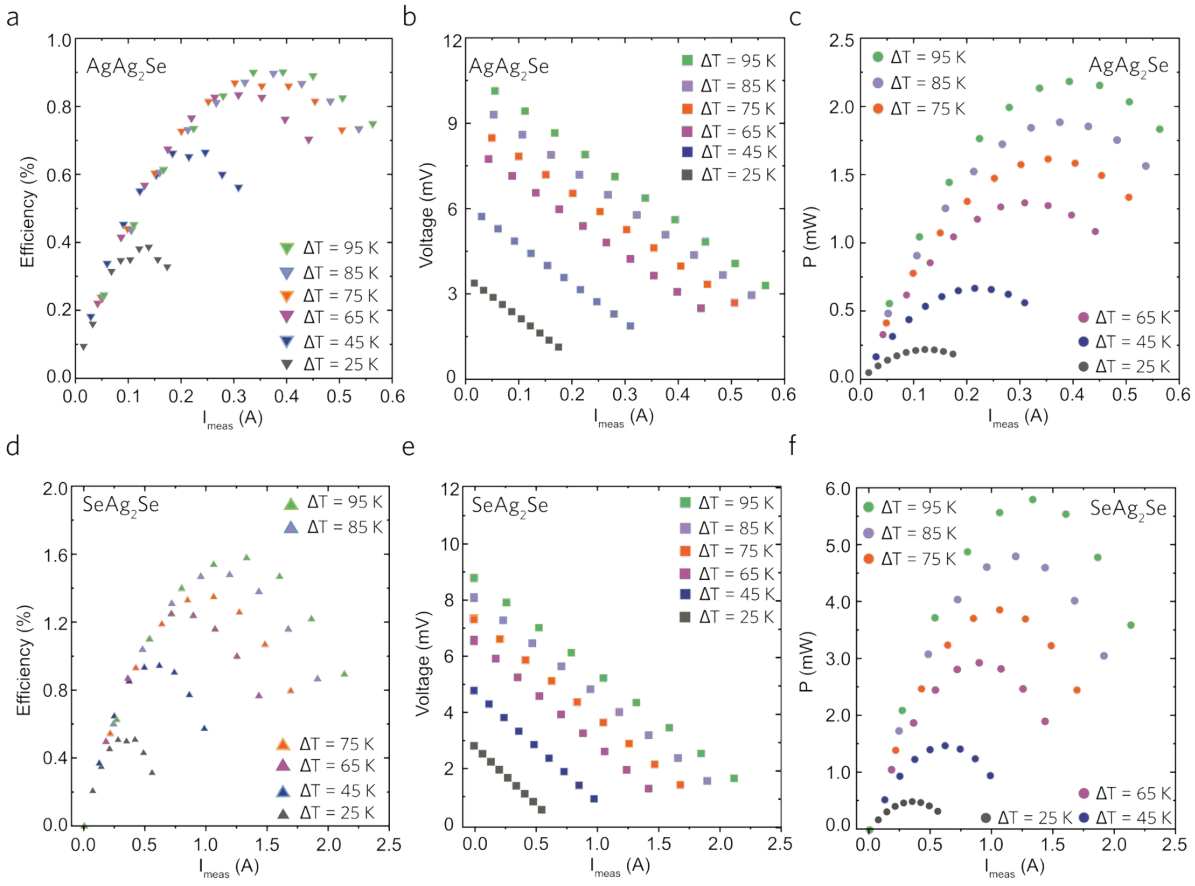

Figure S2. The single-leg mini-PEM measurement result includes a, d) conversion efficiency η. b, e) terminal voltage V. c, f) output power P_{out} with the current of the single legs of $AgAg_2Se$, Ag_2Se, and $SeAg_2Se$ alloy as a function of temperature gradient ΔT.

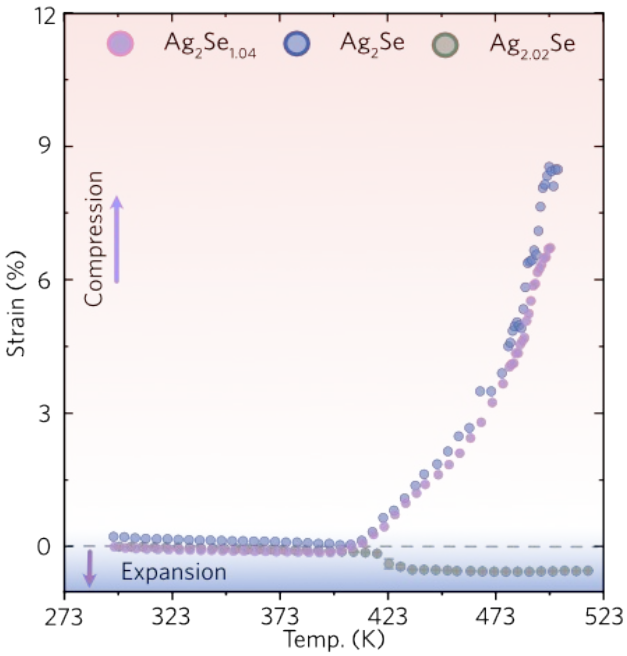

Figure S3 Temperature-dependent strain curves of Ag_2Se, Se-rich $Ag_2Se_{1.04}$, and Ag-rich $Ag_{2.02}Se$ recorded heating up from room temperature RT to 500 K.

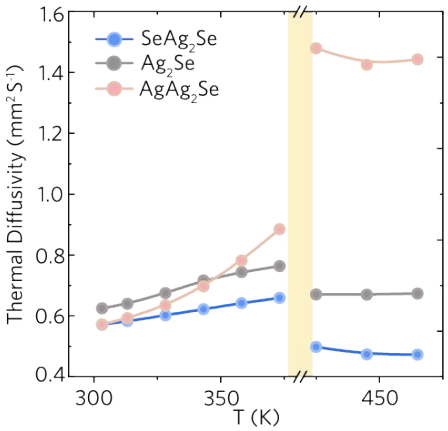

Figure S4 Temperature dependence of the thermal diffusivity.

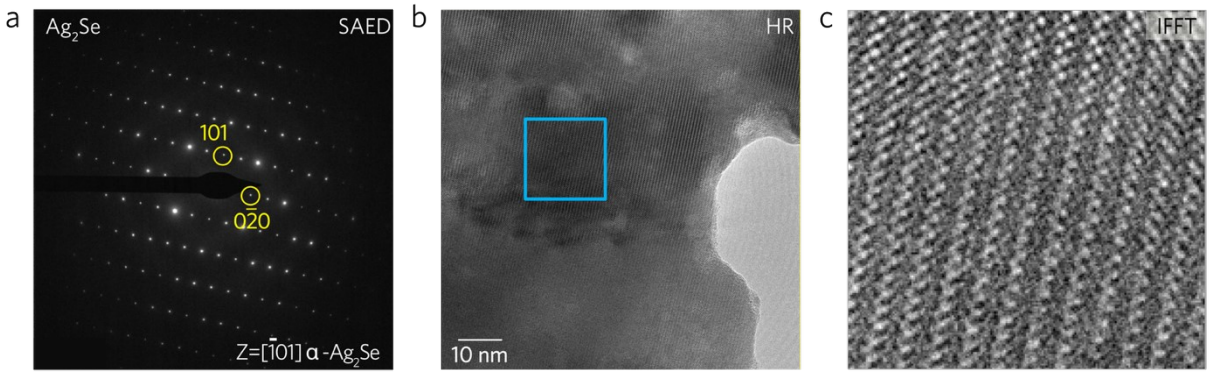

Figure S5 (a–c) Lattice-resolved HRTEM image of Ag_2Se with corresponding SAED pattern along the $[\bar{1}01]$zone axis and IFFT reconstruction.

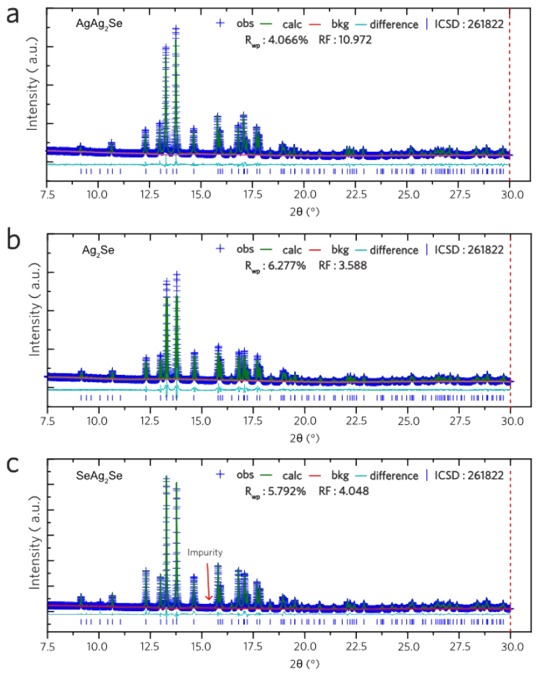

Figure S6 (a, b) Powder XRD patterns of $AgAg_2Se$, Ag_2Se, and $SeAg_2Se$ at room temperature (synchrotron radiation source: TPS-19A).

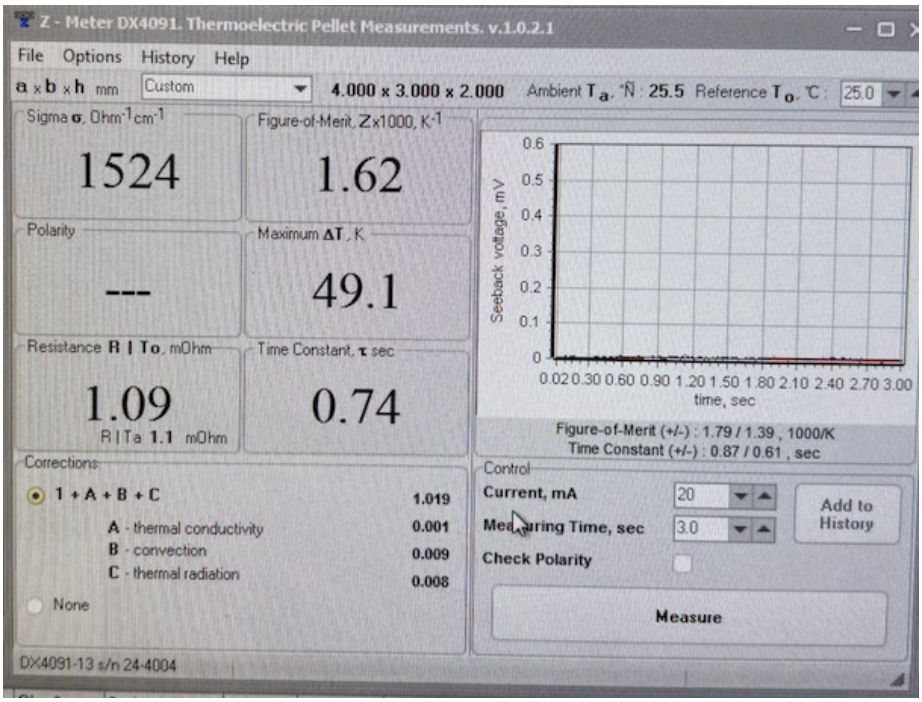

Figure S7 The thermoelectric cooling performance of the as-fabricated thermoelectric pellet.

Table S1. Thermal and electrical transport properties of Ag-Se based alloys at room temperature.

Sample	σ [S*cm]	S [μVK^{-1}]	κ [Wm^{-1}K^{-1}]	zT_{peak}	μ_H [cm^{2}V^{-1}s^{-1}]	n_H [10^{18}cm^{-3}]
$SeAg_2Se$	1501	-139	1.34	0.84	1988±14	-3.57±0.03
Ag_2Se	2932	-89.8	1.58	0.58	2050±32	-4.34±0.06
$AgAg_2Se$	3322	-88.4	1.92	0.53	1895±56	-4.87±0.10

Table S2. The nominal composition of Ag_2Se-based samples.

Sample	**Ag (*at%*)**	**Se (*at%*)**
$SeAg_2Se$	65.79	34.21
Ag_2Se	66.66	33.34
$AgAg_2Se$	66.89	33.11

Table S3. The lattice parameters of Ag-Se based alloys by Rietveld refinement.

Sample	***a* (Å)**	***b* (Å)**	***c* (Å)**
$SeAg_2Se$	4.33290	7.07333	7.78654
Ag_2Se	4.33518	7.06906	7.77369
$AgAg_2Se$	4.33589	7.06756	7.76896

Table S4. EPMA analysis for the $SeAg_2Se$ sample.

Sample	**Region**	**Ag (*at%*)**	**Se (*at%*)**	**wt (%)**
$SeAg_2Se$	Light	64.94±0.32	35.06±0.32	99.91±0.53
	Dark	64.70±0.38	35.30±0.38	99.74±0.14