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Supplementary Information

Roles of AgSbTe₂ nanostructures in PbTe: Controlling thermal properties of chalcogenides

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Experimental Information

To avoid oxidation and homogeneous melting, experimental processes were performed in a rocking furnace with sealed quartz tubes evacuated 10^{-5} Torr and filled with high purity argon ambient gas. Fig. S1 shows images of the experimental processes and the rocking furnace. The sealed quartz tubes are fixed with stanchion in the rocking furnace.

(a) Materials

- ☑ Elements : Pb, Te, Ag, and Sb granule
- ☑ Compositions : $\text{AgPb}_m\text{SbTe}_{m+2}$ ($m=18$)

Process

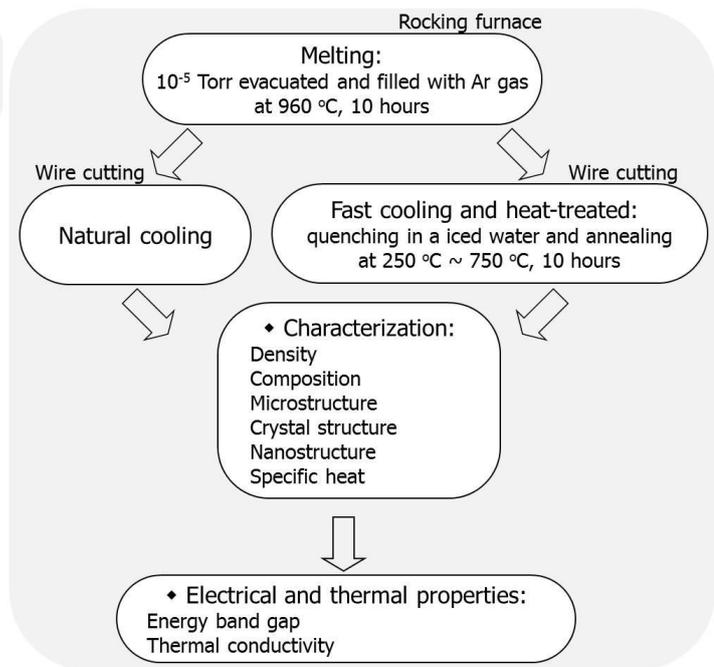
- ☑ High temperature melting
- ☑ Wire cutting, Grinding & Polishing
- ☑ Polishing

Characterization

- ☑ Density : Archimedes' principle
- ☑ Composition : EDS
- ☑ Microstructure : FE-SEM
- ☑ Crystal structure : XRD
- ☑ Nanostructure : STEM
- ☑ Specific heat : DSC

Electrical and thermal properties

- ☑ Energy band gap : FT-IR
- ☑ Thermal diffusivity : LFA-457



(b)

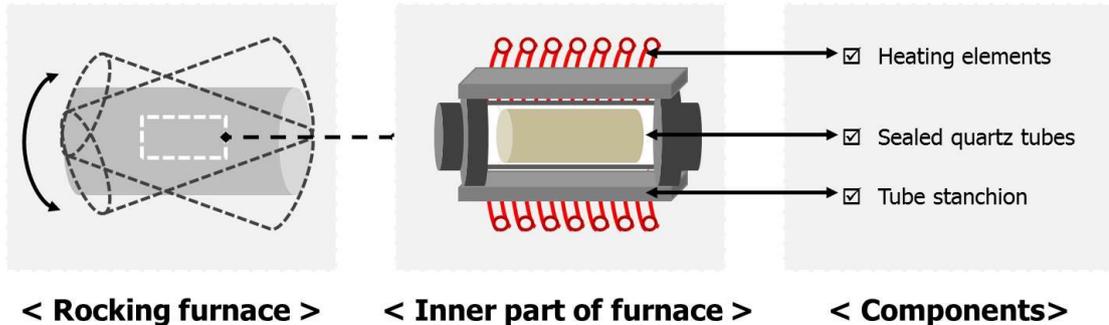


Fig. S1. Schematics of (a) the experimental processes and (b) the rocking furnace and components.

Schematics of the step of the nucleation, and growth and segregation of AgSbTe₂ nanostructures.

In order to investigate the formation and dispersion steps of AgSbTe₂ nanostructures, we estimate the sufficient thermal energies (q) that could be experienced during the heat-treated steps on the AgPb_mSbTe_{m+2} ($m=18$) compounds. At each step of this reaction, the nanostructures become controlled by heat-treated temperature (T_s) and phase transformations (P) from Ag-Sb-Te to Ag₂Te-Sb.

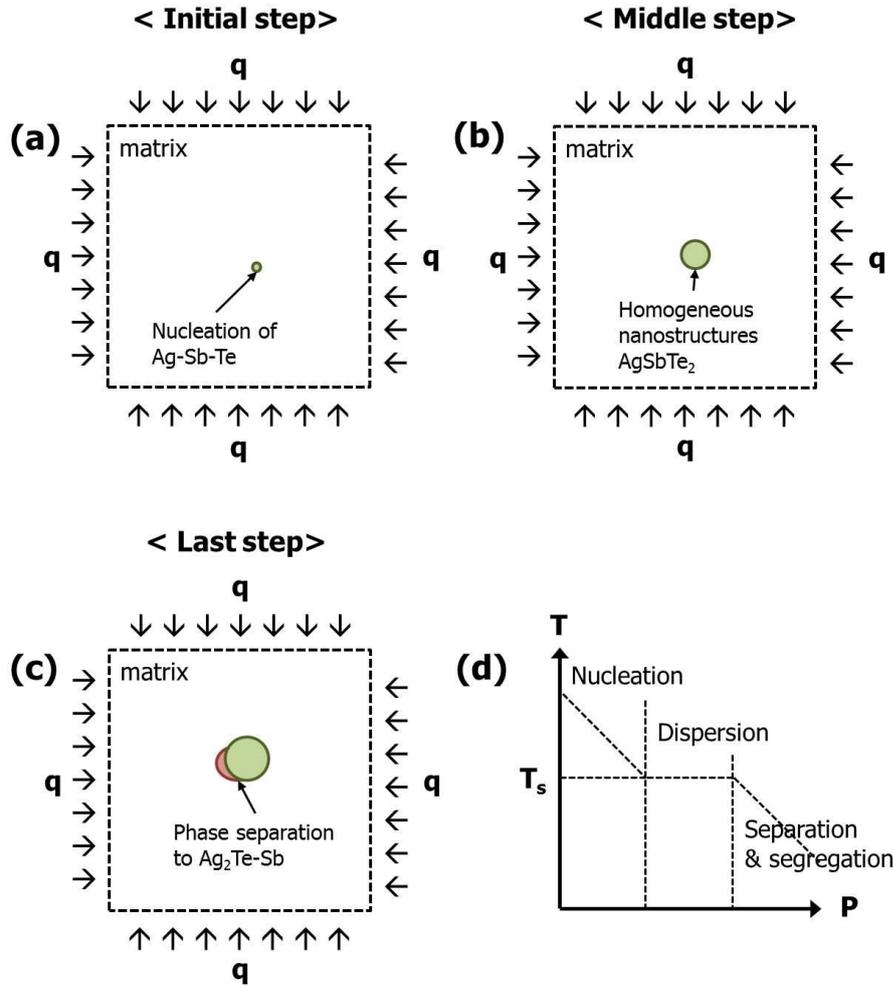


Fig. S2. Schematics of (a) the initial step of the nucleation Ag-Sb-Te nanostructures, (b) the middle step of the formation of homogeneous nanostructures of AgSbTe₂ and (c) the last step of the phase separation of AgSbTe₂ to Ag₂Te-Sb structure.

Thermoelectric properties as a function of temperature for $\text{AgPb}_{18}\text{SbTe}_{20}$ compounds.

The values of the Seebeck coefficient of the all samples are negative, which means that the major carriers are electrons. The absolute values of the Seebeck coefficient are increased in the temperature range from room temperature to 573 K. This region could be understood as an extrinsic region for the degenerate semiconductor. Assuming single-band conduction in the degenerate semiconductor, the Seebeck coefficient could be stated by following: $S = (\pi^2/3) * (k_B/e) * (r+3/2)/\eta$, where k_B is Boltzmann's constant, e is the carrier charge, r is the scattering parameter, η is the reduced Fermi energy ($=E_f/k_B T$), E_f is the Fermi energy. Therefore, the values of the Seebeck coefficient are in inverse proportion to Fermi energy. From this equation, it can be deduced that the values of absolute Seebeck coefficient increase as the temperature increases for the degenerate semiconductor, which is consistent with this study results in the temperature range from room temperature to 573 K. This behavior is identical with previously reported values for the PbTe related compounds.²¹⁻²⁴ The electrical conductivity of all samples is decreased from 323 K to 523 K, which means that these behaviors correspond to that of the degenerate semiconductor. The temperature dependence of the Seebeck coefficient for the all samples can be also understood as the behavior of the degenerate semiconductor.

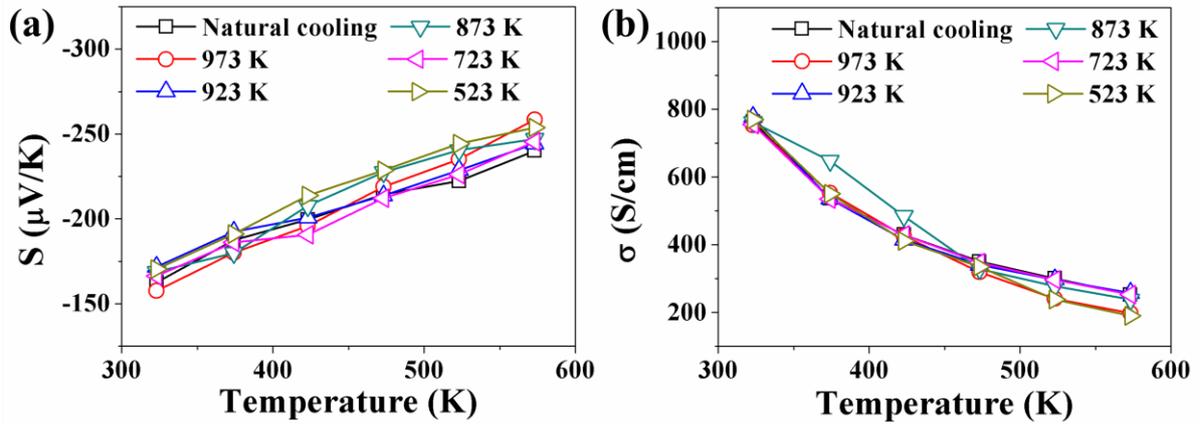


Fig. S3. Effect of temperature on the thermoelectric (TE) properties of $\text{AgPb}_{18}\text{SbTe}_{20}$ compounds: (a) Seebeck coefficient, (b) electrical conductivity.

Thermoelectric properties as a function of temperature for $\text{AgPb}_{18}\text{SbTe}_{20}$ compounds.

The nanostructural and compositional analysis were performed using scanning transmission electron microscopy. Fig. S4 presents the endotaxial nanostructure precipitates in PbTe matrix. The bright field images in Fig. S4 (a), (b), and (c) show that the nanostructure areas show hundreds nano sized grains around 200 ~ 500 nm. According to the STEM combined with EDS analysis, it was found that the nanostructure areas are in Ag-Te rich composition. The electron diffraction pattern of the Ag-Te rich grain exhibited that the Ag-Te rich are Ag_2Te phase (See Fig S4. (d)).

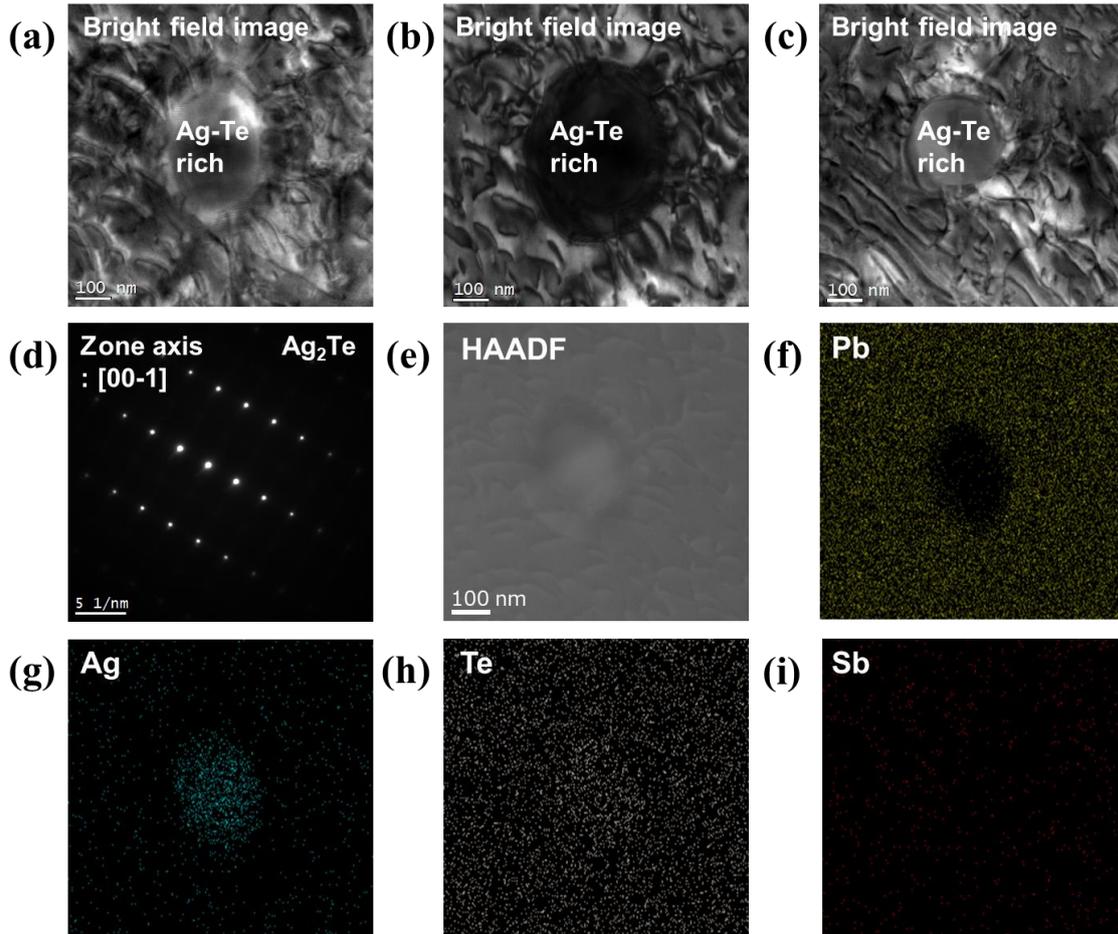


Fig. S4. STEM images of nanostructures of the sample heat-treated at 523 K. (a) The bright field image of one AgSbTe_2 , (b) the bright field image of another AgSbTe_2 , (c) the bright field image of the other AgSbTe_2 showing hundred nano sized grain in the PbTe matrix. The colored areas, (f) yellow is Pb, (g) sky blue is Ag, (h) grey is Te and (i) red is Sb of elements mapping, are drawn as a guide to the identification of phases of Pb, Te, Ag and Sb by STEM-EDS. The nanostructures were identified as Ag-Te rich area and Ag_2Te phase.

Lattice parameters of AgPb₁₈SbTe₂₀ compounds.

The calculated lattice parameters of all natural cooling (NC), the fast cooling and heat-treated AgPb₁₈SbTe₂₀ compounds (FC – heat-treated temperature) are shown in Table S1. Because the ionic radii of Ag (~1.60 Å), and Sb (~ 1.45 Å) are smaller than that of Pb (~ 1.80 Å), the lattice parameters of the all samples are reduced. Thus it might be conclude that Ag and Sb are well occupied in the Pb site in PbTe structure the same as NaCl structure.

Table S1. Comparison of relative lattice parameters of AgPb₁₈SbTe₂₀ compounds.

Compounds	NC	FC - 973	FC - 923	FC - 723	FC - 523
Lattice parameter (Å)	6.4432	6.4295	6.4386	6.4114	6.4137
Relative lattice parameter (%)	99.71	99.49	99.64	99.21	99.25

< Lattice parameter of PbTe : 6.4620 Å >