Supporting Information

High thermoelectric performance in rhombohedral GeSe ingots achieved by alloying Pb

Yang Jin[1], Denzheng Gao[1], Yixuan Hu[1], Pengpeng Chen[1], Yuting Qiu[2]*, Li-Dong Zhao[1]*

1. School of Materials Science and Engineering, Beihang University, Beijing 100191, China.

2. Engineering Practice and Innovation Center, Beihang University, Beijing 100191, China

Corresponding authors' email: qyt2014@buaa.edu.cn; zhaolidong@buaa.edu.cn

1. Experiment details

1.1 Sample synthesis

Ge shot (99.999%), Se shot (99.999%), Ag shot (99.999%), Bi shot (99.99%), Te bar (99.999%) and Pb bar (99.999%) were weighted according to $(Ge_{1-x}Pb_xSe)_{0.9}(AgBiTe_2)_{0.1}$ (x=0-0.06) compositions. Then, GeSe ingots were synthesized using a sealed-vacuum technique in silica tubes (pressure < ~10^{-4} Torr) *via* a multi-stage heating program. This process comprised melting at 1273 K for 10 h, a subsequent 10 h soak for homogenization, and a controlled cooling stage of 1 K/h from 1273 K down to 853 K. Then, the crystals are cooled in the furnace to ambient temperature.

1.2 Structural characterization

The phase identification was conducted by powder XRD (LANScientific, China) with Cu Kα radiation (λ =1.5418 Å) operating at 20 mA and 40 kV.

1.3 Electrical and thermal transport properties

The attained ingots were processed into bars (10×3×3 mm^3) through polishing and cutting. The Seebeck coefficient and electrical resistivity were then measured simultaneously from 303 K to 723 K using a Cryoall CTA instrument under a helium atmosphere. The attained ingots were processed into square pieces (8×8×1 mm^3) for testing thermal diffusivity (D) employing a Netzsch LFA457 instrument. And the thermal conductivity was determined based on the relation $\kappa = D \cdot C_p \cdot \rho$. In this equation, the specific heat capacity (C_p) was derived from the Dulong-Petit law,[1] while the density (ρ) was determined from the specimen's dimensions and mass.

1.4 Hall measurements

The acquired ingots were processed into slices (6×6×0.7 mm^3) for testing carrier density and mobility employing a Lake Shore 8400 Series measurement system (Model 8404, USA) at 303 K.

1.5 Sound velocity tests

The attained ingots were processed into bulks with parallel upper and lower surfaces. The longitudinal and transverse sound velocities were measured using an ultrasonic instrument (Ultrasonic Pulser/Receiver Model 5058 PR, Olympus, USA), which can be derived from $2d/t$, where d is the thickness of the samples and t is the travel time.

1.6 Distortion parameters calculation

v_a is average sound velocity, which can be obtained as:[2]

$$v_a = \left[\frac{1}{3}\left(\frac{1}{v_l^3}+\frac{2}{v_s^3}\right)\right]^{-1/3} \qquad \text{* MERGEFORMAT (1)}$$

where v_l and v_s denote longitudinal and transverse sound velocities, respectively. Γ, the imperfection scaling parameter is a weighted sum of the mass fluctuation Γ_M and strain field fluctuation Γ_S and can be written as $\Gamma = \Gamma_M + \varepsilon\Gamma_S$. And ε denotes a phenomenological adjustable parameter related to the Poisson ratio (v_p) and Grüneisen parameter (γ).[3] v_p and γ can be written as:[2]

$$\varepsilon = \frac{2}{9}\left[\left(G+6.4\gamma\right)\frac{1+v_P}{1-v_P}\right]^2 \qquad \text{* MERGEFORMAT (2)}$$

$$v_p = \frac{1-2\left(v_s/v_l\right)^2}{2-2\left(v_s/v_l\right)^2} \qquad \text{* MERGEFORMAT (3)}$$

$$\gamma = \frac{3}{2}\left(\frac{1+v_P}{2-3v_P}\right) \qquad \text{* MERGEFORMAT (4)}$$

where G is a ratio between the relative change of bulk modulus and banding length, here $G = 3$ for lead chalcogenides.[4] As for the parameter Γ in this work, Pb occupies Ge sites. Thus, Γ is defined as:[5]

$$\Gamma_{Ge_{1-x}Pb_xSe} = \frac{1}{2}\left(\frac{M_{(Ge,Pb)}}{\overline{M}_{(Ge,Pb)}}\right)^2 \Gamma_{(Ge,Pb)} \qquad \text{* MERGEFORMAT (5)}$$

$$\overline{M}_{(Ge,Pb)} = \frac{1}{2}\left(M_{Ge}+M_{Pb}\right) \qquad \text{* MERGEFORMAT (6)}$$

$$\Gamma_{(Ge,Pb)} = \Gamma_{M(Ge,Pb)} + \varepsilon\Gamma_{S(Ge,Pb)} \qquad \text{* MERGEFORMAT (7)}$$

$$\Gamma_{M(Ge,Pb)} = x(1-x)\left(\frac{\Delta M_{(Ge,Pb)}}{M_{(Ge,Pb)}}\right)^2 \qquad \text{* MERGEFORMAT (8)}$$

$$\Gamma_{S(Ge,Pb)} = x(1-x)\left(\frac{\Delta r_{(Ge,Pb)}}{r_{(Ge,Pb)}}\right)^2 \qquad \text{* MERGEFORMAT (9)}$$

where $M_{(Ge,Pb)} = (1 - x)M_{Ge} + xM_{Pb}$, $\Delta M = M_{Ge} - M_{Pb}$ and $r_{(Ge, Pb)} = (1 - x)r_{Ge} + xr_{Pb}$, $\Delta r = r_{Ge} - xr_{Pb}$.

1.7 Thermoelectric power generation tests

The single-leg module is manufactured by $(Ge_{0.99}Pb_{0.01}Se)_{0.9}(AgBiTe_2)_{0.1}$ ingot with dimensions 2.787 mm × 2.878 mm × 9.4 mm. Ni as a barrier layer was galvanized using a commercial nickelplating solution. Cu sheet, as the electrode, was connected with conductive silver paste. The output power and conversion efficiency of the device were characterized employing a TE conversion efficiency measurement system (Mini-PEM UlvacRiko, Japan). The theoretical resistance was calculated based on sample geometry and resistivity, and was compared with the measured device resistance. The resistance introduced by the interfaces is approximately 700 μΩ cm^2 at 353 K, which is much higher than others literatures.[6, 7] Therefore, it is speculated that this interface resistance not only includes the interface between the barrier layer and GeSe-based matrix, but also the resistance of the interfaces between the barrier layer material and the conductive silver paste, as well as between the conductive silver paste and the Cu electrode.

2. Figure caption

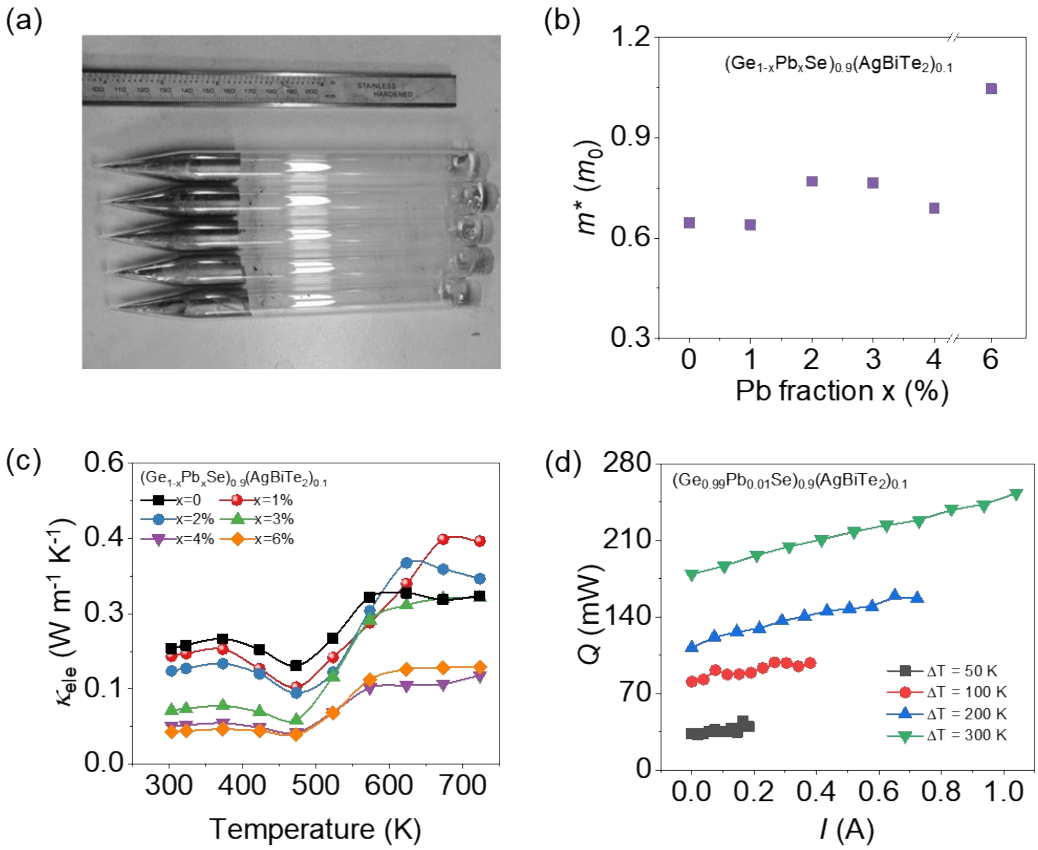

Fig. S1 (a) The images of high quality $(Ge_{1-x}Pb_xSe)_{0.9}(AgBiTe_2)_{0.1}$ (x=0-0.06) ingots, (b) DOS mass, (c) electronic thermal conductivity, and (d) heat flow of the single-leg device fabricated by $(Ge_{0.99}Pb_{0.01}Se)_{0.9}(AgBiTe_2)_{0.1}$.

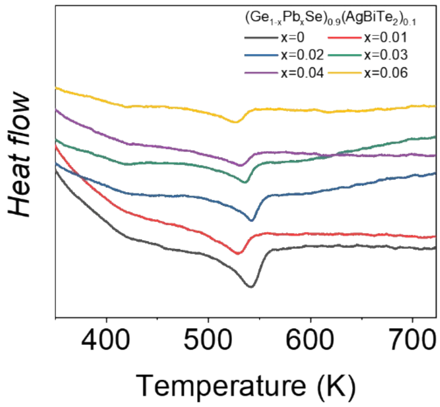

Fig. S2. The differential scanning calorimetry (DSC) measurements of $(Ge_{1-x}Pb_xSe)_{0.9}(AgBiTe_2)_{0.1}$ (x=0-0.06) ingots.

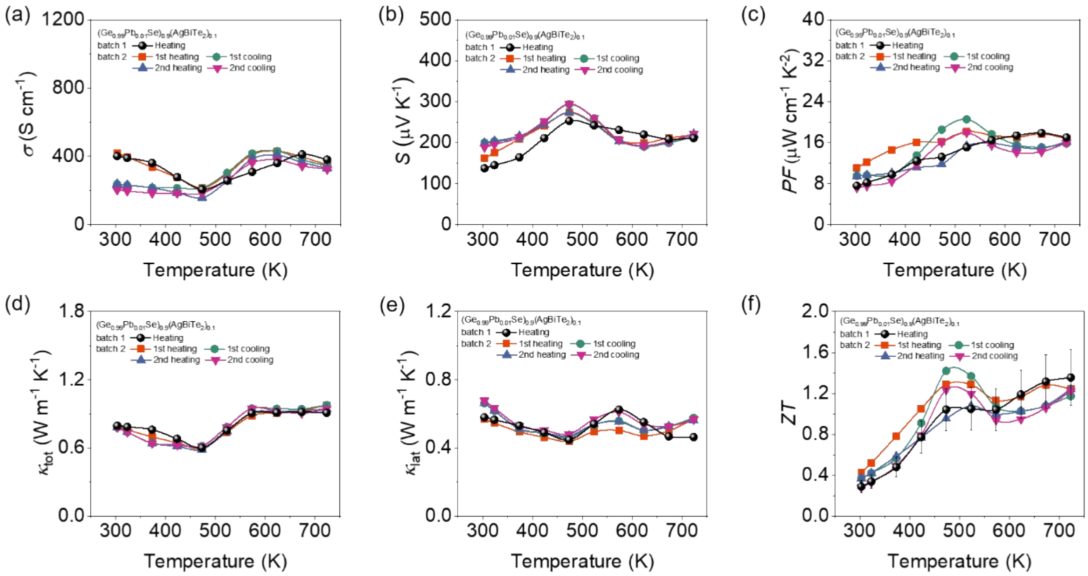

Fig. S3. The heating and cooling measurements for high performance $(Ge_{0.99}Pb_{0.01}Se)_{0.9}(AgBiTe_2)_{0.1}$ ingot, indicating good thermal stability in this study. (a) Electrical conductivity, (b) Seebeck coefficient. (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity, and (f) *ZT* values.

3. Table caption

Tab. 1 The density of $(Ge_{1-x}Pb_xSe)_{0.9}(AgBiTe_2)_{0.1}$ (x=0-0.06) samples.

$(Ge_{1-x}Pb_xSe)_{0.9}(AgBiTe_2)_{0.1}$	x=0	x=0.01	x=0.02	x=0.03	x=0.04	x=0.06
Density (g/cm^{-3})	5.87	5.90	5.87	5.97	6.10	6.11

References

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