Supporting Information for

A Cu-based Cu_{8-x}Ge(S, Te)₆ Argyrodite: the Widespan Cubic-Phase Region and Ultralow Lattice Thermal Conductivity

Yi-Fen Tsai[†], Charlotte L. Stern[‡], Bo-Chia Chen[†], G. Jeffrey Snyder[⊥]*, and Hsin-Jay Wu[†]*

[†]Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan

[⊥]Department of Materials Science and Engineering, Northwestern University, Evanston 60208, US

Email: jeff.snyder@northwestern.edu ; ssky0211@nycu.edu.tw

1. EXPERIMENTAL METHODS

Sample synthesis. The argyrodite $Cu_{8-x}GeS_{4.36}Te_{1.64}$ alloys were prepared from the high-purity pure elements Ge (99.999%), Te (99.999%), S₈ (99.998%) and pre-mixed Cu₂S powder (< 99.5%) stoichiometrically. Placed the weighted precursors in a carbon-coated quartz tube with a diameter of 12.7 mm and then sealed under the degree of vacuum ~ 10^{-3} pascal. Heated the sealed ampules from 300 K to 1323 K for 11 hours and then soaked under 1323 K for 2 hours in a vertical furnace equipped with a proportion integration differentiation (PID) temperature controller. Rocked the ampules to homogenize and slightly tapped the ampules' bottom to condense the melts several times simultaneously. The homogenized alloys were furnace cooled by 75 K per hour and post-annealed at 723 K for 72 hours. The annealed $Cu_{8-x}GeS_{4.36}Te_{1.64}$ alloys were cooled to room temperature by the PID controller and underwent the transport properties' assessment and the material analysis after the appropriate treatment.

Structural characterization. The structural identification was accomplished by single crystal *x*-ray diffraction (SCXRD) and high-resolution powder *x*-ray diffraction (HRPXRD). In SCXRD, single crystals of $Cu_{8-x}GeS_{4.36}Te_{1.64}$ were supplied. A single crystal with a size of 0.05mm was hand-picked from the sharp tip of the synthesized alloy, and the crystal was mounted on a MITIGEN holder in paratone oil on an XtaLAB Synergy R, DW system, and HyPix diffractometer. The crystal was kept at 99.98(11) K during data collection. Using Olex2¹, the structure was solved with the SHELXT² structure solution program using Intrinsic Phasing and refined with the XL³ refinement package using Least Squares minimization. The refinement details for Cu2 and Cu3 were restrained e.s.d. (0.01) that their U_{ij} components approximate to isotropic. The HRPXRD was operated by synchrotron radiation under the energy of 20 KeV, and the insert wavelength was 0.61992 Å. The powder sample was prepared by a 500-mesh screen to get the fine particle (< 25 µm). The data collection ranged from 100 K to 450 K with a cooling/heating rate of 10 K per minute, scanned once every 5 K, and collected for 60 seconds. The experimental data reflects the measured temperature, diffraction angle, and intensity for Cu_{8-x}GeS_{4.36}Te_{1.64} alloy.

TE properties assessments. The ingot $Cu_{8-x}GeS_{4.36}Te_{1.64}$ alloy was gently polished into a flat disk ($\emptyset = 12.7 \text{ mm}$) for electrical and thermal transport property measurement. For the temperaturedependent electrical conductivity σ , Hall carrier concentration n_{H} , and Hall mobility μ_{H} were simultaneously measured by the home-build high-temperature Hall system, where the Hall

measurement was designed based on the Van der Pauw method. The thermopower, Seebeck coefficient S, were determined by a home-build Seebeck system with the delta-T (ΔT) is 10 K between two electrodes. The relationship between electrical conductivity σ , carrier concentration $n_{\rm H}$, and mobility $\mu_{\rm H}$ can be described by the given formula $\sigma = e n_{\rm H} \mu_{\rm H}$, where $e = 1.6 \times 10^{-19} C$. The thermal conductivity $\kappa = D_T C_p d$ comprised three parameters, where D_T is the thermal diffusivity, $C_{\rm p}$ is the specific heat, and d is the density of the alloy. A Simultaneous Thermal Analysis (STA, Netzsch) under the N₂ atmosphere measured the phase transition behavior. The specific heat C_p was measured by the differential scanning calorimeter (Netzsch DSC 3500 Sirius) with the sapphire as the standard comprehension. The density d was evaluated by the density balance (JA-2003J), and the thermal diffusivity $D_{\rm T}$ was obtained by the laser flash method from the commercial apparatus (Netzsch LFA-457). According to the Wiedemann-Franz law, the lattice thermal conductivity can be estimated where the total thermal conductivity is contributed by a lattice (κ_L) and electrical thermal conductivity (κ_e) as the given equation $\kappa = \kappa_L + \kappa_e$. The electrical thermal conductivity (κ_e) is converted by the relationship between electrical conductivity (σ), Lorentz factor (L), and temperature (T) in a formula of $\kappa_e = \sigma LT$ where the Lorentz factor is based on the single parabolic (SPB) model, in which the Lorentz factor $L = \{1.5 + \exp\left[-\frac{|S|}{116}\right] \times 10^{-8} V^2 K^{-2}$ was

used⁴.

Speed of sound measurement. The sound velocities were measured on the Cu_{8-x}Ge(S, Te)₆ by pulse-echo method at room temperature. A transducer with a center frequency of 5 MHz in longitudinal (v_L) and transverse (v_T) while the glue was used as a couplant between the pellet sample and the ultrasonic transducers. The waveform was recorded by a digital oscilloscope (TBS 1072B-EDU, Tektronix), and the pulse parameters, such as PRF (Hz), energy, damping, and gain (dB), were manipulated by the ultrasonic pulse receiver (5072PR, Panametrics). The transducer sends the pulse and then receives the reflected ultrasound. To calculate the speed of sound ($v = 2dt_d^{-1}$), the delayed-time t_d , between reflections and the sample thickness *d* were considered.



Figure S1 The temperature dependence heat capacity



Figure S2 PXRD of synthesized Cu₈GeS₆.

Table S1 Room temperature electrical properties of synthesized Cu_8GeS_6 and $Cu_{8-x}GeS_{4.36}Te_{1.64}$

Compound	$\rho(m\Omega cm)$	$\sigma(10^3 Sm^{-1})$	<i>n</i> _H (cm ⁻³)	
Cu ₈ GeS ₆	314.0	0.319	7.4 x 10 ¹⁵	
Cu _{8-x} GeS _{4.36} Te _{1.64}	32.5	3.08	2.0 x 10 ¹⁸	

Formula weight	930.19			
Temperature (K)	99.98(11)			
Crystal system	Cubic			
Space group	F43m			
a, b, c (Å)	10.09100(10), 10.09100(10), 10.09100(10)			
α, β, γ (°)	90, 90, 90			
Volume (Å ³)	1027.55(3)			
Z	4			
$\rho_{\rm calc} ({\rm mgmm^{-3}})$	6.013			
μ (mm ⁻¹)	64.779			
F(000)	1677			
Crystal size (mm ³)	$0.067\times0.043\times0.016$			
2θ range for data collection	15.208 to 156.116°			
Index ranges	$-12 \le h \le 12, -12 \le k \le 12, -12 \le l \le 12$			
Reflections collected	5696			
Independent reflections	142 [R(int) = 0.0484]			
Data / restraints / parameters 142 / 12 / 27				
Goodness-of-fit on F ²	1.175			
Final R indexes $[I > 2\sigma (I)]$	$R_1 = 0.0324, wR_2 = 0.0855$			
Final R indexes [all data]	$R_1 = 0.0326, wR_2 = 0.0856$			
Largest diff. peak / hole (eÅ-3) 1.044 / -1.006			

Table S2 Crystal data and structure refinement for $Cu_{8-x}GeS_{4.36}Te_{1.64}$.

						~	~
Atom	x	У	z	Occupancy	U	Site	Symmetry
Te1	0.75000	0.25000	0.75000	0.640	0.039	4c	43m
Te2	0.50000	0.50000	0.50000	1.000	0.019	4b	43 <i>m</i>
Ge1	0.75000	0.25000	0.25000	1.000	0.008	4d	43 <i>m</i>
Cu1	0.56350	0.25120	0.56350	0.450	0.033	48h	<i>m</i>
Cu2	0.50000	0.25900	0.50000	0.100	0.016	24f	2.mm
Cu3	0.63000	0.27600	0.55800	0.083	0.066	96i	1
S1	0.62400	0.12400	0.37600	1.000	0.009	16e	.3m
S2	0.75000	0.25000	0.75000	0.360	0.039	4c	43 <i>m</i>

Table S3 Structure parameters for $Cu_{8-x}GeS_{4.36}Te_{1.64}$.

2. REFERENCES

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.

- 2. G. M. Sheldrick, Acta Crystallogr. A: Found. Adv., 2015, 71, 3-8.
- 3. G. M. Sheldrick, Acta Crystallogr. A: Found. Adv., 2008, 64, 112-122.
- 4. H. S. Kim, Z. M. Gibbs, Y. Tang, H. Wang and G. J. Snyder, APL Mater., 2015, 3, 041506.