

Supporting Information

The Power of Aluminum: Optimizing Thermoelectric Properties of the Intermetallic Phase, $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$

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Experimental

Synthesis of Binary Precursors

The polycrystalline synthesis of $\text{Eu}_{11}\text{Sb}_{10}$ and AlSb was made in 5 g batches through ball milling of the elements, followed by annealing. The starting materials for the binary precursors were handled in an argon-filled glove box with oxygen levels below 0.5 ppm. The elements used were Eu pieces (Ames Laboratory, 99.999%), Sb shot (Alfa Aesar, 99.999%, 6 mm), and Al shot (4-8 mm (0.2-0.3 in), Puratronic™, 99.999% (metals basis)). The Eu metal was arc-melted under argon to remove oxides and then cleaned with a wire brush under argon to remove any residual surface oxides. Stoichiometric amounts of the elements (total 5 gm) were loaded into a 65 cm³ stainless-steel grinding vial with two 12.7 mm diameter balls (SPEX) for each binary. The stainless-steel grinding vials were sealed in Mylar bags inside the glove box before milling with an 8000M SPEX high energy mill for two rounds of 1 hr with 20-minute scrapes in between to achieve homogenous powder. The powders were removed from the grinding vial and transferred to Ta or Nb tubes that were welded shut on both ends under an inert atmosphere in an Ar(g) arc-welder. The Ta or Nb tubes containing the binary powders were sealed in a quartz tube under a vacuum below a pressure of 50 mTorr. The reaction vessels were placed in a furnace, heated to 800 °C at 100 °C/h, dwelled for 24 hrs, and cooled to room temperature before being removed from the furnace. Powder X-ray diffraction analysis was performed for each binary, and purity was confirmed.

Synthesis of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ ($x = 0.00, 0.08$ and $y = 0.30, 1.00$)

$\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ ($x = 0.00, 0.08$ and $y = 0.30, 1.00$) was synthesized by ball milling the binary precursors of $\text{Eu}_{11}\text{Sb}_{10}$, AlSb , and with stoichiometric amounts of Eu and Al metals for the intended composition in an

argon-filled glove box with oxygen levels below 0.5 ppm. To make the 5g polycrystalline sample, molar ratios of $5+x$ Eu: $3+y$ Al: 6 Sb ($x = 0.00$ and 0.08 , $y = 0.30$ and 1.00) were calculated from the binary precursors and stoichiometric amounts of metals, then they were loaded into a 65 cm³ stainless-steel grinding vial with 2 12.7 mm diameter balls (SPEX). Each round of ball milling consisted of 4 1-hr mills with 20-minute scrapes in between to achieve homogeneity. The homogenized black powders were transferred to a 12.7 mm internal diameter graphite die (Cal Nano) inside the glove box sealed with 10 pieces of grafoil on each side of the die's openings and graphite plungers. The sample was transferred into a Spark Plasma Sintering (SPS) instrument (Dr. Lab Sinter Jr., Fuji Corp.), and the chamber was evacuated to less than 13 Pascals. The chamber was refilled with Ar (g) to 50,000 Pa, and the die was cold pressed with a pressure of 6.5 kN before heating. The samples were heated to 923.15 K for 9 min and dwelled at this temperature for 30 min. After dwelling at 923.15 K for 30 minutes, the temperature was increased to 1,073.15 K over 3 minutes and held for 30 minutes for consolidation. The pressure at the first temperature of 923.15 K was kept at 6.5 kN and increased to 10.5 kN once the temperature increased to 1,073.15 K. Once the sintering process was complete, the resultant black pellet was cleaned of any graphite foil using sandpaper. The cleaned black pellet was sliced into multiple pellets with an Isomet Low-Speed Cutter diamond saw (Buehler) with cutting fluid to analyze via PXRD and measure thermo transport properties. The corresponding pellets had a density >95% of their theoretical value, which was determined using the Archimedes method.

Powder X-ray Diffraction (PXRD)

PXRD data were collected with a Bruker D8 Advance Eco Diffractometer using Cu K α radiation from $2\theta = 20^\circ$ — 80° with a step size of 0.02° and scan rate of 1 s/step at room temperature in air. The polycrystalline samples were ground inside an Ar-filled glove box and plated on a zero-background holder with isopropanol. The diffraction patterns were refined using Topas5 software.

Thermogravimetric (TG)/Differential Scanning Calorimetry (DSC)

Melting point studies of aluminum excess were done on polished pellet pieces of Eu_{5,x}Al_{3,y}Sb₆ using TG/DSC (STA 449 F3 Jupiter, Netzsch) from room temperature up to 800°C with a heating rate of 10K/min under a 50 mL/min flow of Ar. A piece of Aluminum metal (Aluminum shot, approx. 4-8mm (0.2-0.3in), Puratronic™, 99.999% (metals basis)) was used as a reference.

Compositional Analysis

Fragments of the polycrystalline pellet were embedded in epoxy and subsequently sanded for analysis. Energy dispersive X-ray spectroscopy data was collected with an FEI Scios DualBeam SEM/FIB with a window-less Oxford Instrument X-max50, 50 mm² silicon drift detector.

Thermal Conductivity

Thermal Diffusivity (D) was measured on thin (1.19 to 1.2 mm thick) slices of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ pellets using a Netzsch LFA 457 Microflash under a flow of high purity Ar with a polished piece of Zr ribbon wrapped around the sample holder to act as an oxygen catcher. The thermal conductivity (κ) was determined from the equation: $\kappa = D \times \rho \times C_p$. The heat capacity value, C_p , is $3R/\text{atom}$ (R = gas constant). All the pellets' density (ρ) was measured multiple times using the Archimedes method using toluene as the liquid. All samples were > 95% of their theoretical crystallographic densities, calculated using the Arrhenius method.

The lattice thermal conductivity in **Fig. S6** was calculated by subtracting the electronic thermal conductivity, κ_e , from that of the total thermal conductivity, which was calculated using the Wiedemann-Franz law, $\kappa_e = L\rho T$, where L is the Lorenz number, ρ is the electrical resistivity, and T is the absolute temperature. The Lorenz number was calculated using the following equation and by assuming a parabolic band and acoustic phonon scattering:

$$L = 1.5 + \exp\left[-\frac{|S|}{116}\right]$$

Where S is the Seebeck coefficient.¹

Transport Measurements

A Linseis LSR-3 instrument was used to measure resistivity and Seebeck coefficient employing the four-probe method from 350K to 800K under He atmosphere. The sample geometries were bar-shaped (10.5mm x 4mm x 2mm) using 8 mm probes and polished before measurements. Multiple samples were measured to ensure reproducibility, and the data was cross-checked using measurements at JPL and Northwestern. The Seebeck coefficient was measured using a light pulse technique as described above using W/Nb thermocouples. Electrical resistivity (ρ) was measured using the van der Pauw (VDP) technique with a current of 10 mA.

Electrical resistivity and Hall effect data were measured using a home-built Hall effect instrument for the samples measured at Northwestern.² This set-up utilizes a four-point Van der Pauw resistivity measurement with molybdenum leads and a current of 100 mA. Seebeck coefficient data was collected using a home-built two-probe Seebeck instrument with chromel/Nb thermocouples.²

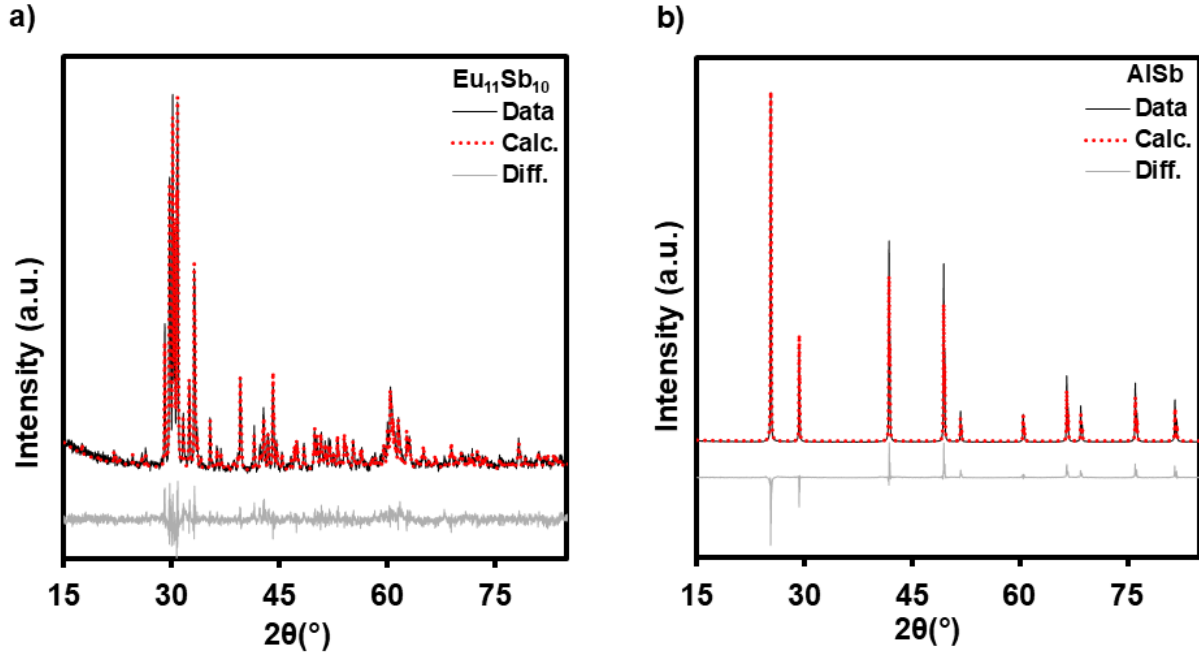


Fig. S1. Rietveld refinements for powder x-ray diffraction of the starting materials: a) $\text{Eu}_{11}\text{Sb}_{10}$ and b) AlSb .

Table S1. Lattice Parameters and Rietveld Refinement Parameters and Selected Statistics for $\text{Eu}_{11}\text{Sb}_{10}$ and AlSb

Composition	* $\text{Eu}_{11}\text{Sb}_{10}$	$\text{Eu}_{11}\text{Sb}_{10}$	* AlSb	AlSb
Unit cell dimensions	$a = 12.325(2) \text{ \AA}$	$a = 12.3313 (7) \text{ \AA}$	$a = 6.138 \text{ \AA}$	$a = 6.13840 (12) \text{ \AA}$
	$b = 12.325(2) \text{ \AA}$	$b = 12.3313 (7) \text{ \AA}$	$b = 6.138 \text{ \AA}$	$b = 6.13840 (12) \text{ \AA}$
	$c = 18.024(4) \text{ \AA}$	$c = 18.0041 (10) \text{ \AA}$	$c = 6.138 \text{ \AA}$	$c = 6.13840 (12) \text{ \AA}$
	$\alpha=\beta=\gamma=90^\circ$	$\alpha=\beta=\gamma=90^\circ$	$\alpha=\beta=\gamma=90^\circ$	$\alpha=\beta=\gamma=90^\circ$
Volume (\AA^3)	2737.95	2737.7 (3)	231.25	231.295 (14)
Rwp (%)	—	12.84	—	14.30
Rp (%)	—	10.04	—	11.17

GoF	—	1.46	—	1.78
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*From references 3,4

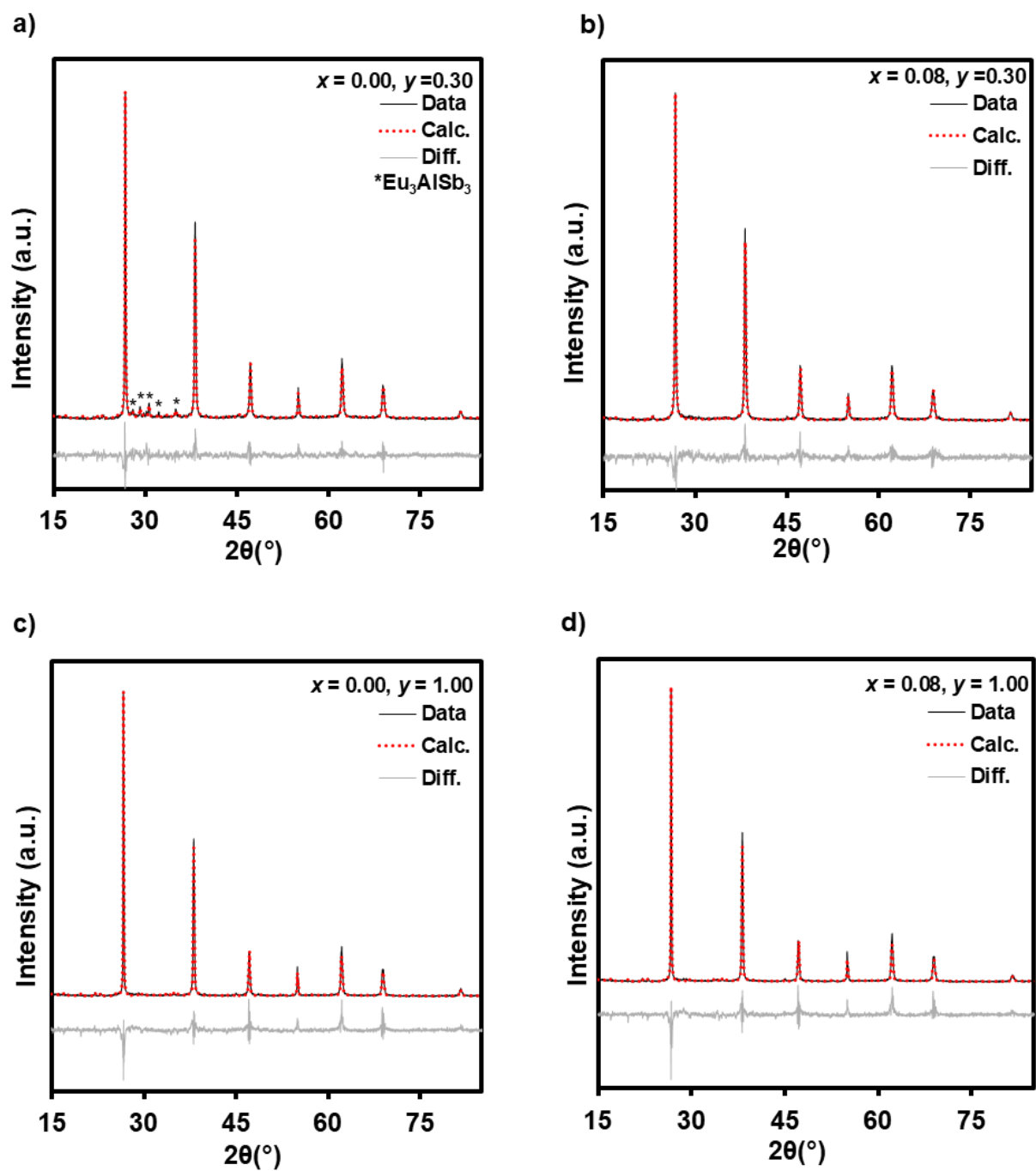


Fig. S2. Rietveld refinement of the powder diffraction of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$.

Table S2. Selected Rietveld Refinement Statistics of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ ($x = 0.00, 0.08$ and $y = 0.30, 1.00$)

Composition	$\text{Eu}_{5.08}\text{Al}_{3.3}\text{Sb}_6$	$\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$	$\text{Eu}_5\text{Al}_{3.3}\text{Sb}_6$	$\text{Eu}_5\text{Al}_4\text{Sb}_6$
Temperature	Room Temperature			
Radiation	Cu K_α			
Wavelength	1.54 Å			
Rwp (%)	10.98	14.11	11.11	13.98
Rp (%)	8.04	10.84	8.35	10.77
GoF	1.55	1.69	1.55	1.70
$\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ (wt %)	100	100	97.51	100
Eu_3AlSb_3 (wt %)	0	0	2.49	0

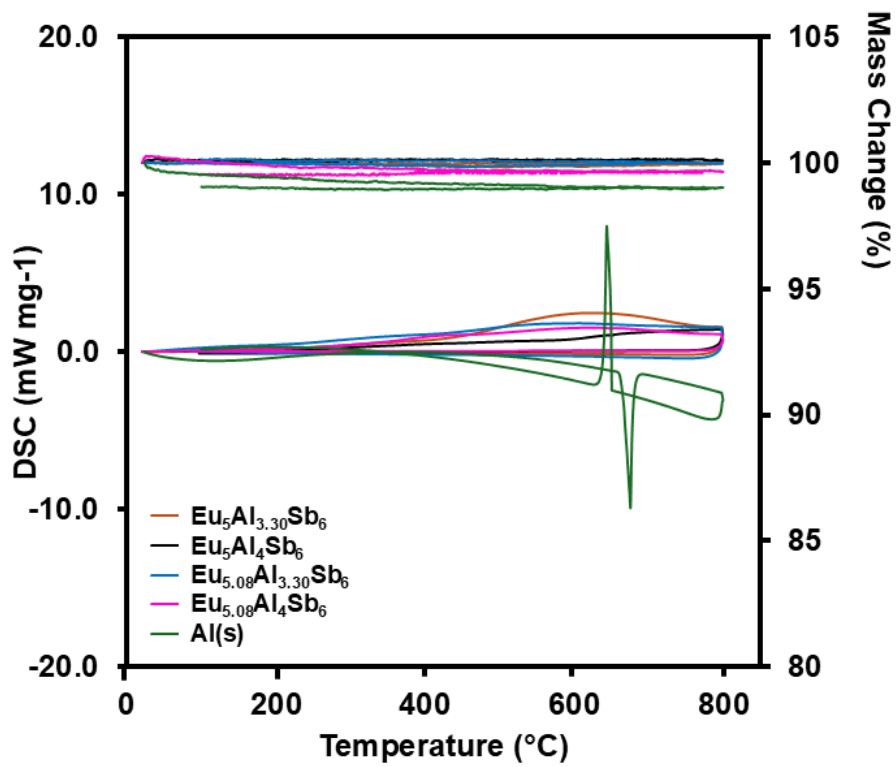


Fig. S3. TG (top right axis) and DSC (bottom left axis) of polished pieces of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ from room temperature (25 °C) to 800 °C under the flow of 50 mL/min of Argon. The TG/DSC trace of Al(s) shot as a reference is dark green.

Table S3. Polycrystalline Loading and EDS (Energy Dispersive Spectroscopy) Determined Compositions

Nominal Composition	Experimental Eu (x) and Al (y) content	EDS Analysis
$\text{Eu}_{5.08}\text{Al}_{3.30}\text{Sb}_6$	$x = 0.08, y = 0.30$	$\text{Eu}_{4.9(2)}\text{Al}_{3.3(3)}\text{Sb}_{6.0(4)}$
$\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$	$x = 0.08, y = 1.00$	$\text{Eu}_{4.9(6)}\text{Al}_{4.0(7)}\text{Sb}_{6.1(4)}$
$\text{Eu}_5\text{Al}_{3.30}\text{Sb}_6$	$x = 0.00, y = 0.30$	$\text{Eu}_{4.8(2)}\text{Al}_{3.4(3)}\text{Sb}_{5.9(2)}$
$\text{Eu}_5\text{Al}_4\text{Sb}_6$	$x = 0.00, y = 1.00$	$\text{Eu}_{4.8(4)}\text{Al}_{4.1(8)}\text{Sb}_{6.2(5)}$

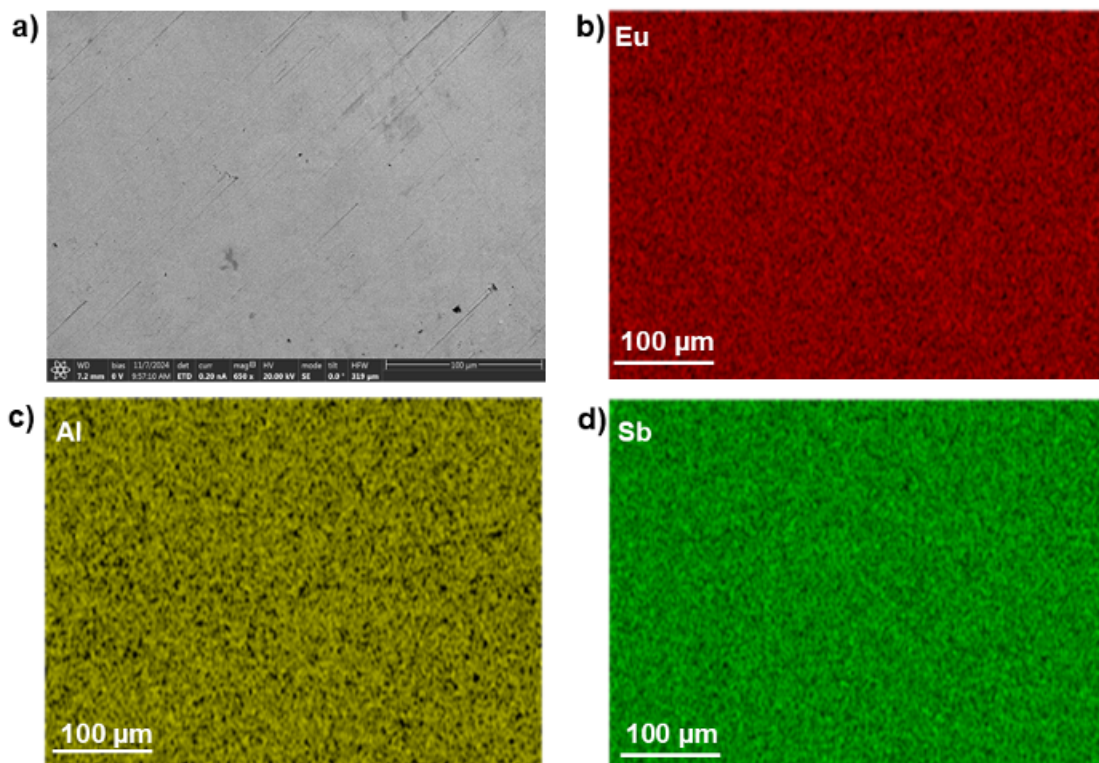


Fig. S4. (a) Secondary electron image collected with a 20 KV electron beam on the pellet $\text{Eu}_{5.08}\text{Al}_{3.30}\text{Sb}_6$. (b-c) EDS elemental maps for $\text{Eu}_{5.08}\text{Al}_{3.30}\text{Sb}_6$.

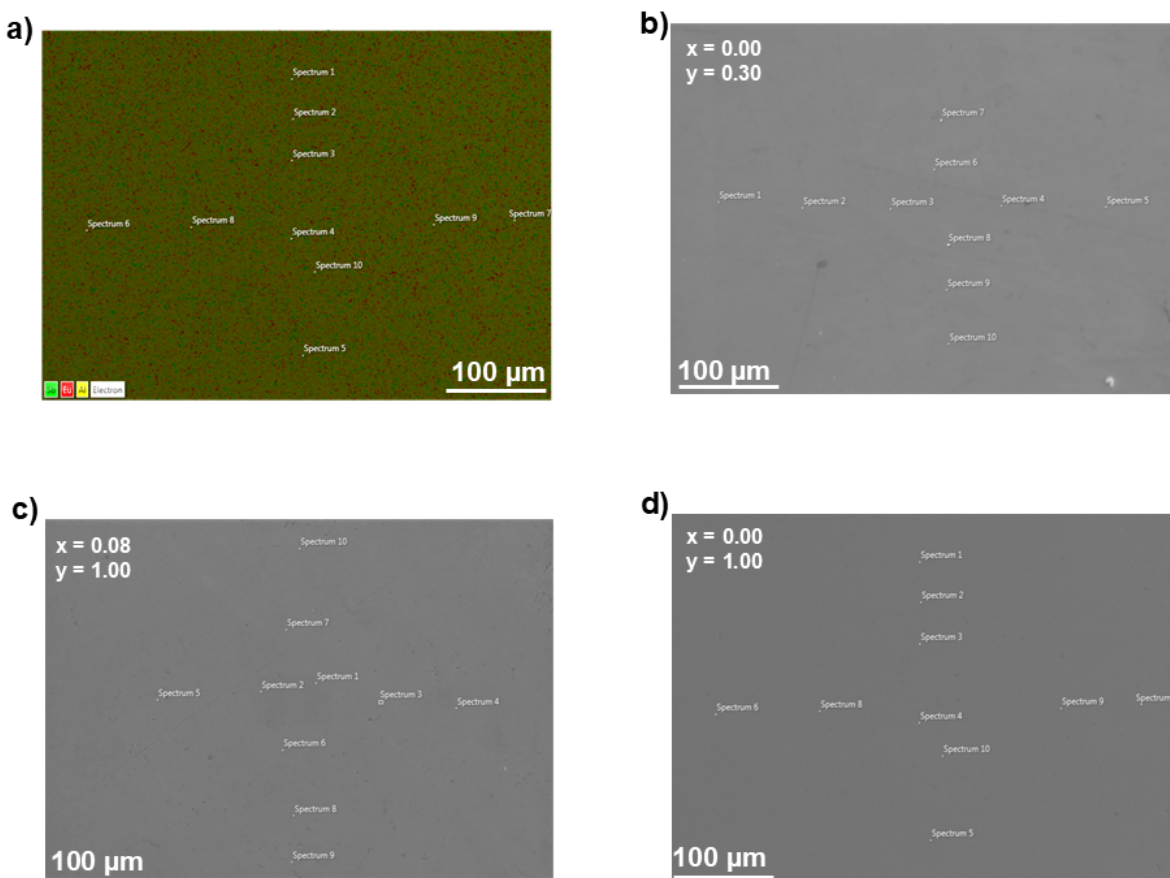


Fig. S5. Elemental map of $\text{Eu}_5\text{Al}_4\text{Sb}_6$ (Elements Sb, Eu, and Al are indicated by the colors, green, red, and yellow) and secondary electron images of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$. Nominal values of x and y for each sample are provided.

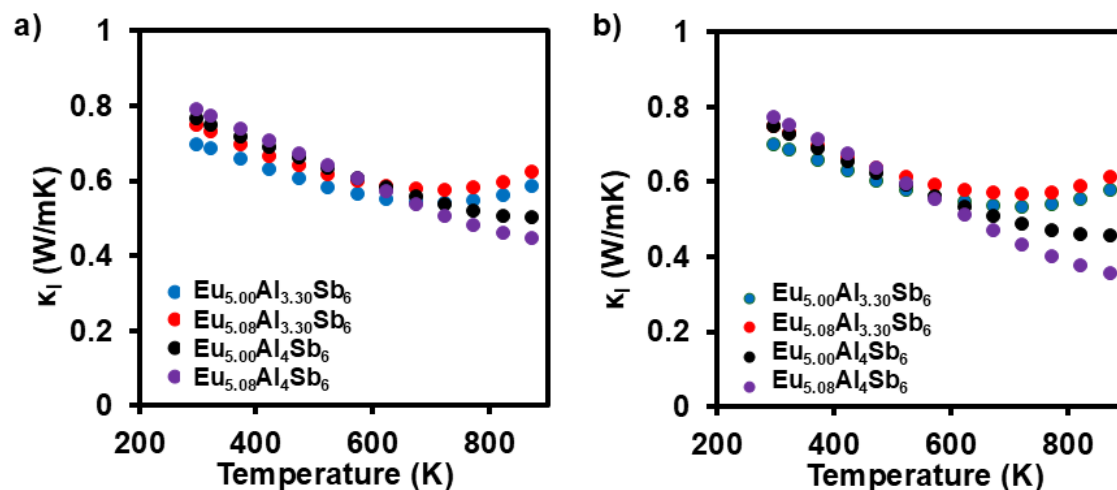


Fig. S6. Calculated lattice thermal conductivity for $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ ($x = 0.00, 0.08$ and $y = 0.30, 1.00$). Employing the Lorenz number for a) degenerate semiconductors and b) for metallic systems.

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