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One Cation makes a difference: Structure–Thermoelectric Interplay in Pseudo–Rock Salt Intermetallic $\text{Eu}_{5-x}\text{A}_x\text{Al}_3\text{Sb}_6$ (A = Sr and Yb)

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Abstract:

Polar intermetallics are an emerging class of thermoelectric materials whose electronic properties can be finely tuned by cation chemistry. Single crystals of $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5-x}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$ were synthesized by flux methods and their structures determined by single-crystal X-ray diffraction, confirming monoclinic $C2/m$ symmetry and an electron count near $3.5 e^-$ per atom, consistent with polar intermetallic classification. The Al content in these phases can be increased from 3 to 4, and a comparative study of polycrystalline synthesized $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and its Sr- and Yb-substituted solid solutions, along with the pseudo-quinary phase $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$, is presented. Substituting Eu^{2+} with the more ionic Sr^{2+} enhances mobility and increases the magnitude of the Seebeck coefficient, while more covalent Yb^{2+} drives the system metallic, lowering Seebeck values but improving zT to 0.8 at 873 K. The quinary phase further suppresses bipolar conduction, delaying the high-temperature downturn observed in both ternary solid solutions. Across all compositions, thermal conductivities remain exceptionally low ($<1 \text{ W m}^{-1} \text{ K}^{-1}$), enabling promising figures of merit. These results highlight how ionic versus covalent A-site substitution can serve as a powerful lever to control scattering, band overlap, and transport in polar intermetallics, opening design pathways parallel to those of the benchmarked half-Heuslers phases and PbTe.

Introduction:

Intermetallics are a distinct class of compounds formed from metals or metalloid elements in precise compositions, often adopting complex, sometimes unpredictable crystal structures that give rise to unique physical properties.^{1,2} Intermetallic compounds can generally be divided into three categories · based on their valence electron-to-atom ratio (e/a). Hume–Rothery phases occur when $1 \leq e/a \leq 2$; polar intermetallics span from $1.2 \leq e/a \leq 4$; and Zintl phases have $e/a \geq 4$.^{2–4} Hume–Rothery phases form stable alloys when the substituent elements in a solid solution

share similar crystal structures, atomic sizes, valences, and electronegativities.^{5,6} The Zintl concept uses an electron-counting rule that links the number of valence electrons available to each anion for covalent bond formation, driven by electrons supplied by the cation.⁷ Polar intermetallics are especially interesting due to their structural and electronic complexity, combining features of both Hume–Rothery and Zintl phases. These combined features make electron counting, oxidation-state assignment, and crystal-structure prediction particularly difficult.^{1,4,8} The wide range of possible compositions in intermetallics leaves many areas unexplored, providing opportunities to discover exciting physical properties.

Zintl phases have become cornerstone thermoelectric materials owing to their predominantly semiconducting nature and inherent structural complexity. These thermoelectric materials can convert heat into electricity, making them especially valuable for energy storage and harvesting. Thermoelectric research is focused on optimizing the dimensionless figure of merit, zT , which governs the performance of these materials.^{7,9} The dimensionless figure of merit zT (eqn(1)), shown below, encapsulates the interplay among thermal conductivity, κ (W/m·K), electrical resistivity, ρ ($\Omega\cdot\text{m}$), the Seebeck coefficient, S (V/K), and an absolute temperature, T (K).

$$zT = \frac{\alpha^2 T}{\rho \kappa} \quad \text{Eqn (1)}$$

The higher the zT , the more effective a thermoelectric material is at converting heat into electricity. The hurdle in achieving a high zT lies in the interdependence of thermal conductivity, electrical resistivity, and the Seebeck coefficient on carrier concentration, such that improving one parameter often compromises another. Although this interdependence of carrier concentration makes optimizing zT challenging, Zintl phases stand out for their large and complex unit cells, which suppress lattice thermal conductivity, and for their high band degeneracy, which enhances the Seebeck coefficient, making them excellent candidates for thermoelectric materials.^{7,9,10}

Zintl phases are not the only intermetallics with thermoelectric potential: Heusler and half-Heusler phases, which adopt face-centered cubic structures, are also actively studied.^{11–13} Half-Heusler phases, including XNiSn and XCoSb (where $\text{X} = \text{Ti, Zr, or Hf}$), have emerged as pivotal low-toxicity thermoelectric materials, exhibiting band degeneracy and high thermopower.¹⁴ Like their metallic counterparts, Heusler and half-Heusler phases generally exhibit high thermal

conductivity, and current research is focused on reducing it.¹⁴ Additionally, half-Heuslers phases exhibit rich chemistry, leading to other phenomena such as magnetism and half-metallicity. Many of the same bonding and doping concepts developed for Zintl compounds aid in explaining and rationalizing their structure and bonding.¹⁴ Therefore, gaining deeper insight into these intermetallic subclasses is key to advancing thermoelectric materials.

Recent studies have highlighted $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$, a rare-earth intermetallic distinguished by its simple yet complex crystal structure, intriguing magnetism, and promising thermoelectric properties.^{3,15,16} The (e/a) ratio of ~ 3.5 places $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ between polar intermetallic and Zintl phases. Mössbauer and Al K-edge XANES are consistent with Eu^{2+} , Sb^{3+} , and Al^{3+} ; Zintl electron counting indicates that $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ should have an excess of 1 e^- .^{3,15} Single-crystal X-ray diffraction of $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$, along with high-resolution TEM of $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ revealed a pseudo-rock salt-like “ASb” framework ($\text{A} = \text{Eu}, \text{Sr}, \text{Al}_3$) with monoclinic $C2/m$ space group (No. 12, $Z = 2$), **Figure 1**. Structural analysis reveals that in the $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ series, either an Eu/Sr atom partially occupies the A(1) site or Al in the form of an Al_4 tetrahedron, with the occupancy pattern varying with the Sr substitution. At low Sr content ($x = 0.62$ and 0.72), Sr occupies the A(1) site at 2.6 and 5.8% respectively. As Sr content increases to $x = 1.37, 2.44$, and 4.00 , the A(1) site is occupied by the Al cluster. This indicates that the aluminum content fluctuates depending on the presence of an A(1) cation. Al K-edge XANES indicates Al $3p$ –Eu $4f/5d$ interactions but shows little sensitivity to Sr substitution.³ The disorder of the Al_4 cluster is modeled structurally as a dual tetrahedron and behaves electronically like an alkaline-earth cation, analogous to Al_{14} units in iodide salts or any Al cluster.^{3,15,17,18} $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ orders antiferromagnetically below 10 K.¹⁵ Resistivity and heat capacity confirm a transition at this temperature, and Curie–Weiss fitting yields a Eu^{2+} moment of $7.80\text{ }\mu_B$.¹⁵ As Sr is substituted into the solid solution, it introduces competing antiferromagnetic (AFM) and ferromagnetic (FM) interactions.³ The composition $x = 0.30$ shows transitions at 10 and 6 K,³ while the fully substituted Sr analogue ($x = 5.03$) is diamagnetic.³

The polycrystalline synthesis of $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$ was optimized for thermoelectric studies, revealing an n-type semimetal with low thermal conductivity ($<0.9\text{ W m}^{-1}\text{ K}^{-1}$) and large negative Seebeck coefficients.¹⁶ These characteristics arise from the compound’s pseudo-rock salt structure, disorder, and multi-valley band degeneracy. Structural disorder at the A(1) site,

where either Eu cations or Al clusters can reside, contributes to phonon scattering, while fine-tuning the Eu and Al content (e.g., $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$) improves phase purity and enhances the zT .^{3,15,16} For $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ and $\text{Eu}_5\text{Al}_4\text{Sb}_6$, maximum zT values of 0.8 at 873 K and 0.6 at 773 K, respectively, were achieved.¹⁶

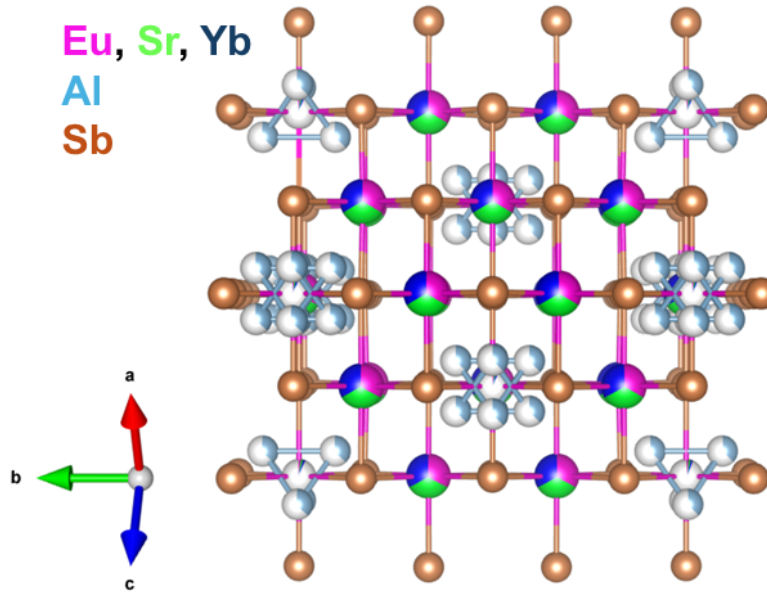


Figure 1. A view of the unit cell of $\text{A}_{5.08}\text{Al}_3\text{Sb}_6$ ($\text{A} = \text{Eu}, \text{Sr}, \text{Yb}$) showing the rock salt-like framework with the corresponding atoms Eu pink, Sr green, Yb dark blue, Al light blue, and Sb in bronze (occupancy and mixed sites are indicated with filled sections on the spheres).

In this study, we prepare both single crystals and polycrystalline samples. Single crystals of the Eu–Yb solid solution and the pseudo-quinary Eu–Sr–Yb–Al–Sb compound $(\text{Eu}/\text{Yb}/\text{Sr})_{5+x}\text{Al}_3\text{Sb}_6$ were grown from Sn flux to further investigate the crystal structure and magnetic properties of this structure type. Polycrystalline samples with composition $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) were prepared with the Al content of 4 according to an optimized polycrystalline synthesis previously applied to $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$.¹⁶ Substitution of Eu with Sr or Yb in polycrystalline $\text{Eu}_5\text{Al}_4\text{Sb}_6$ offers an opportunity to probe how changes in cation chemistry influence thermoelectric behavior. The Sr cation is close in size to Eu but is significantly less electronegative, while Yb is smaller and has a similar electronegativity. Given the electronic and size differences, different thermoelectric properties are expected to emerge from replacing the Eu with Sr or Yb, despite the structural similarities.

Experimental:

Synthesis of $\text{Eu}_{5.08-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5-x}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$ Single Crystals

Starting materials and elements were handled in an argon-filled glovebox with oxygen levels <0.5 ppm. The elements used for the $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ solid solution were Eu pieces (Stanford Advanced Materials, 99.99%), Sb shots (Alfa Aesar, 99.999%, 6 mm), Yb pieces (Stanford Materials, 99.99%), Al shot 4–8 mm (0.2–0.3 in), Puratronic™, 99.999% (metal basis), and Sn shot (Alfa Aesar, 99.99%, 1–3 mm). Eu and Yb metal pieces were arc-melted under argon to remove surface oxides, and any remaining residues were further cleaned with a wire brush inside an argon-filled glovebox. The synthesis of these single crystals was carried out similarly to the previously reported synthetic route for $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$, using a Sn metallic flux.^{3,15} In brief, the compositions of the solid solution were loaded according to $3-y\text{Eu}/y\text{Yb}/5\text{Al}/3\text{Sb}/15\text{Sn}$ ($y = 0.25, 0.50, 1.00$, and 1.25) and as $3-x-y\text{Eu}/x\text{Sr}/y\text{Yb}/5\text{Al}/3\text{Sb}/15\text{Sn}$ ($x = 2.00$ and $y = 1.00$) into a clean 2.5 mL Al_2O_3 crucible, as part of the Canfield crucible set.^{19,20} For single-crystal growth, the flux is added first, followed by the constituent elements in order of increasing melting point. The Canfield crucible set, containing the elemental constituents, was placed in a fused silica tube with one end sealed. Quartz wool was placed at both ends of the crucible set to provide padding. The fused silica ampule was sealed under vacuum below a pressure of 50 mTorr. The sealed ampule was placed in a Thermo Scientific™ Thermolyne™ Muffle Furnace and heated to 1050 °C at 100 °C/h, where it dwelled for 12 h, then slowly cooled at 2 °C/h until it reached the spin-off temperature of 750 °C.²¹ Once the furnace reached 750 °C, the ampule was removed, inverted, and centrifuged to remove the Sn flux from the crystals. After the ampules were centrifuged, they were opened inside a nitrogen-filled glovebox. The crystals from each batch were placed in uncapped vials and exposed to air for about a week, following the same procedure used for the $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ solid solution.³ Unlike their Sr counterparts, which are air-sensitive, the Yb-rich crystals remained intact for a week in air without any visible signs of tarnishing or degradation. Although the batches of single crystals showed no visible tarnishing, they were stored in a nitrogen-filled glovebox before measurements to minimize air exposure.

Bulk Synthesis of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ (A = Sr: $x = 0.5, 2.5, 5$; A = Yb: $x = 0.5, 1, 1.5, 2, 5$) and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$

Bulk samples of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) were prepared by a synthetic route that produced polycrystalline products in 3-gram batches. The elements used for $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) were Eu pieces (Stanford Advanced Materials, 99.99%), Sr metal pieces (Alfa Aesar, 99.99%), Sb shot (Alfa Aesar, 99.999%, 6 mm), Yb pieces (Stanford Materials, 99.99%), and Al flakes (Aldrich, 1 mm, 99.99% metal basis). Eu, Sr, and Yb metal pieces were arc-melted under argon to remove surface oxides, and any remaining residues were further cleaned with a wire brush inside an argon-filled glovebox. Eu, Sr, Yb, Al, and Sb in stoichiometric amounts were loaded into a 65 cm³ stainless-steel grinding vial with two 12.7 mm diameter balls (SPEX). Each round of ball milling consisted of four 1-hour cycles, with 20-minute intervals for scraping, to ensure thorough homogenization of the elements. The resulting black powder was sieved to obtain a uniform particle size before transfer to a 12.7 mm internal graphite die (Cal Nano). In an argon-filled glovebox, the ball-milled powder was loaded into a graphite die, with ten Grafoil sheets placed on each opening before inserting the plungers. Once the sample was loaded into the graphite die, it was transferred into the chamber of a Spark Plasma Sintering (SPS) instrument (Dr. Lab Sinter Jr., Fuji Corp.) and evacuated to a pressure of less than 13 Pascals. Then, the chamber was filled with Ar (g) to 50,000 Pa, and the die was cold-pressed to a pressure of 6.5 kN before heating. All samples, except $\text{Yb}_5\text{Al}_4\text{Sb}_6$, underwent sintering and consolidation under the same conditions as for the published $\text{Eu}_{5+x}\text{Al}_{3+y}\text{Sb}_6$.¹⁶ The heating profile consisted of ramping to 923 K over 9 minutes, holding for 30 minutes, and then increasing to 1073 K with an additional 30-minute dwell, while the applied load was increased from 6.5 kN to 10.5 kN. To avoid competing phases for the $\text{Yb}_5\text{Al}_4\text{Sb}_6$ compound, a modified temperature profile was set to 873 K for 9 minutes, followed by a 30-minute dwell, then increased to 923 K with an additional 30-minute dwell under the same maximum load of 10.5 kN. After sintering, the black pellets were cleaned of graphite foil, sectioned using a diamond saw (Buehler) for Powder X-ray Diffraction (PXRD) and thermotransport measurements, and found to have a density greater than 95% of their theoretical density by the Archimedes method.

PXRD Analysis

PXRD data were collected at room temperature in air on ground single crystals and bulk powders of both solid solutions using a Bruker D8 Advance Eco diffractometer with Cu K α radiation, 1000W (40kV, 25mA), over $2\theta = 15\text{--}85^\circ$, with a step size of 0.02° , and a scan rate of 1 s per

step. Polycrystalline samples and ground single crystals were prepared on a zero-background holder using isopropanol. All the diffraction patterns were refined using Topas5 software.²²

Single-Crystal X-ray Diffraction

Shiny, black, plate-like crystals from the $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$ reactions (with the loading compositions y noted above) were selected under Paratone oil, mounted on a MiTeGen MicroLoop, and cooled in a nitrogen stream. Single-crystal X-ray data were measured under a nitrogen cold stream, at 90 K (-183°C), with a Bruker APEX Duo diffractometer, employing Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Preliminary unit-cell determinations were carried out on each crystal prior to overnight data collection. The diffraction symmetry confirmed a monoclinic C -centered lattice with parameters closely matching those of $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$.^{3,15} Four ω -scan data frame series were collected (Mo $K\alpha$) with 0.3° wide scans, 20 seconds per frame, and 606 frames collected per series at varying ϕ angles ($\phi = 0^\circ, 90^\circ, 180^\circ, 270^\circ$). The crystal-to-detector distance was 5.15 cm. Data were processed with SAINT (version 8.38a) to correct for Lorentz and polarization effects, and absorption corrections were applied using Blessing's method as implemented in SADABS. XPREP indicated that the centrosymmetric space group $C2/m$ (No. 12) applies to all crystals, based upon system symmetry, systematic absences, and intensity statistics. Structural modulation was evaluated in JANA using the monoclinic cell, but no evidence of modulation was detected.²³ The SHELXTL program package was used to perform the structural refinements. The reported $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ model served as the starting point for the refinement.^{3,15,24} Following the approach used in the $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ study, Yb atoms were introduced onto all four crystallographically distinct Eu sites (Eu1–Eu4), with atomic positions and thermal parameters restrained while occupancies were refined freely.³ For the mixed-cation system containing Eu, Yb, and Sr, all three atoms were placed on the unique Eu sites and refined in the same manner. The occupancies of all Al and Sb atoms were also refined without constraints. After the total Al occupancy converged to a stable value, it was fixed for the subsequent refinements.^{3,15} The **Supporting Information (SI)** summarizes atomic coordinates and selected bond distances from single-crystal refinements in **Tables S1 and S2**. Single crystals were ground into a powder for Rietveld refinement and provided in **SI, Figure S1**.

Thermogravimetric (TG)/Differential Scanning Calorimetry (DSC)

Melting point studies of aluminum excess were conducted on polished pellet pieces of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Yb}$ and Sr) using a TG/DSC (STA 449 F3 Jupiter, Netzsch) from room temperature to 800°C with a heating rate of $10\text{K}/\text{min}$ under a $50\text{ mL}/\text{min}$ flow of Ar. A piece of Aluminum metal (Aluminum shot, approx. 4-8mm (0.2-0.3in), Puratronic™, 99.999% (metal basis)) was used as a reference.

Compositional Analysis

Single-crystal samples were placed flat on carbon tape, and fragments of the polycrystalline pellet were embedded in epoxy and polished for analysis. Energy-dispersive X-ray spectroscopy (EDS) was performed on an FEI Scios DualBeam SEM/FIB equipped with a windowless Oxford Instruments X-max50 (50 mm^2) silicon drift detector. For each composition, ten EDS point analyses were collected to calculate averages and standard deviations of the elemental atomic percentages. A secondary-electron image of a selected crystal (20 kV, 1.6 nA) and elemental maps for a $\text{Eu}_{4.24}\text{Yb}_{0.84}\text{Al}_3\text{Sb}_6$ crystal are provided in the **SI, Figure S2**.

Thermal Conductivity

Thermal Diffusivity (D) was measured on thin (1.19 to 1.2 mm thick) slices of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) 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 using the equation: $\kappa = D \times \rho \times C_p$. The Dulong-Petit heat capacity value, C_p , is calculated from $3R/\text{atom}$ ($R = \text{gas constant}$). All the pellets' density (ρ) was measured in replicate using the Archimedes method using toluene as the liquid. All samples were $> 95\%$ of their theoretical crystallographic densities, calculated using the Arrhenius method.

Electrical Resistivity and Seebeck

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 instrument was calibrated with a constantan standard before use. The sample geometries were bar-shaped ($10.5\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$) and were polished before measurements using 8 mm probes. Multiple samples were measured to ensure reproducibility, and the data were cross-checked with measurements taken at Northwestern University. At Northwestern, electrical resistivity and Hall effect data were

measured using a home-built Hall instrument.²⁵ This set-up utilizes a four-point van der Pauw resistivity measurement with molybdenum leads and a current of 100 mA. Seebeck coefficient data were collected using a home-built two-probe Seebeck instrument with chromel/Nb thermocouples.²⁵

Results and Discussion:

Synthesis

The flux composition for Yb substitution into $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ was adapted from that used for crystal growth of the parent $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and the Sr solid solution $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ compounds.^{3,15} Single-crystal growth and structural characterization were performed for $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ and selected $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$ compositions; the Sr-containing series ($\text{Eu}_{5-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$) has been studied in prior work and is referenced for context.³ The $\text{Eu}_{5.08-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ solid solution and $\text{Eu}_{5-x-y}\text{Sr}_y\text{Yb}_x\text{Al}_3\text{Sb}_6$ compounds are referred to by the value of x , which corresponds to the refined Yb content, and y corresponds to Sr for the pseudo-quinary Eu–Sr–Yb–Al–Sb compound obtained from single-crystal structure refinement. As seen in Figure 2, the crystals typically adopt a plate-like morphology, similar to that observed for both $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$. The reaction yield is approximately 85% of the expected product, assuming Sb as the limiting reagent.^{3,15} With increasing Yb content, the crystals become less air sensitive and do not tarnish overnight.

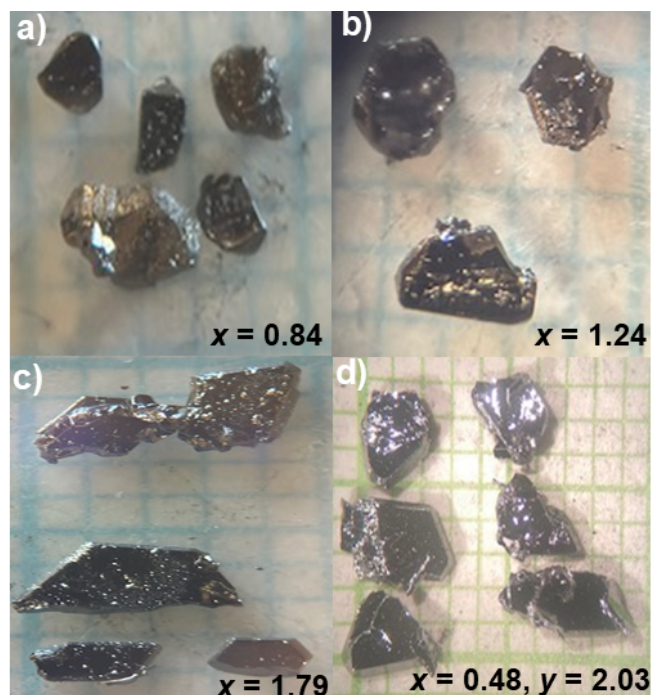


Figure 2. Representative single crystals of the $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$ solid solutions grown from Sn flux, shown on a 1 mm x 1 mm square grid. Refined compositions: (a) $x = 0.84$, (b) $x = 1.24$, (c) $x = 1.79$ for $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$; (d) $x = 0.50$, $y = 2.03$ for $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$.

Crystal Structure

Single crystals were initially examined by PXRD after flux reactions with increasing Yb content. The full Yb phase, $\text{Yb}_5\text{Al}_4\text{Sb}_6$, could not be prepared as a single crystal following the same flux procedure, so it was prepared as a polycrystalline powder. Data from single crystal samples will be indicated by the nominal composition Al_3 , and polycrystalline samples by Al_4 . Crystals from each batch were ground into powders for diffraction measurements, and the data were collected in ambient air. As shown in **Figure 3a**, the PXRD patterns confirmed phase-pure solid solutions, with no secondary crystalline phases and only minor traces of Sn detected. A systematic shift in intensities toward higher 2θ values indicates lattice contraction as Yb is incorporated into Eu sites. Selected bond distances from Rietveld refinement of the X-ray powder diffraction for the polycrystalline $\text{Yb}_5\text{Al}_4\text{Sb}_6$ sample are provided in **SI, Table S3**. Rietveld refinement plots of ground single crystals of $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ are provided in **SI, Figure S1**. Rietveld parameters for the refinement of the powder diffraction pattern of ground single crystals of $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ are provided in **SI, Table S4**. **Figure 3 (b–d)** displays the powder diffraction patterns of the polycrystalline Sr, Yb, and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ samples, while the

corresponding lattice parameters, Rietveld refinements, and statistics are summarized in SI, Table S4.

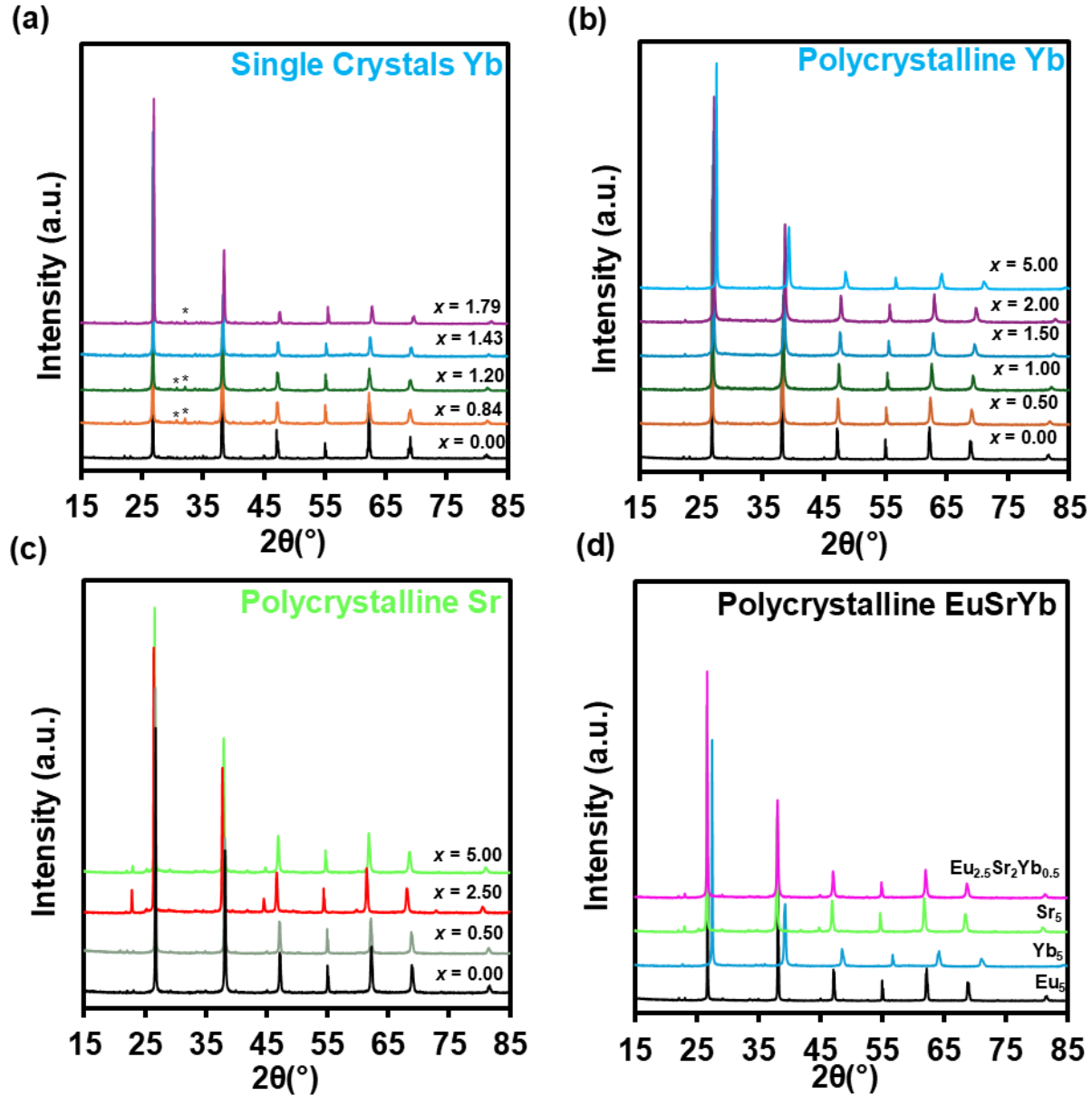


Figure 3. Stacked PXRD patterns for $\text{Eu}_{5-x}\text{A}_x\text{Al}_2\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) single crystals ($z \sim 3$) ground into powder and synthesized polycrystalline samples ($z = 4$). (a) $\text{Eu}_{5-x}\text{A}_x\text{Al}_3\text{Sb}_6$ ($\text{A} = \text{Yb}$) single crystals ground into powder, with x indicated, and asterisks indicate small amounts of the Sn metal from the flux. (b-c) Patterns for the polycrystalline synthesized $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) samples. (d) Diffraction pattern of polycrystalline synthesized sample of the pseudo-quinary compound, $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_4\text{Sb}_6$ ($x = 2.0$ and $y = 0.5$), compared to the powder diffraction patterns for $\text{A}_5\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Eu}, \text{Sr}, \text{and Yb}$).

Single-crystal X-ray diffraction confirmed that all members of the solid solution crystallize in a monoclinic crystal system with a $C2/m$ space group. **Table 1** summarizes selected crystal data collection and refinement parameters for four $\text{Eu}_{5.08-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ crystals and $\text{Eu}_{2.57}\text{Sr}_{2.03}\text{Yb}_{0.48}\text{Al}_{2.63}\text{Sb}_6$. Incorporation of Yb leads to a systematic decrease in the single-crystal lattice parameters of the solid solution, $\text{Eu}_{5-x}\text{A}_x\text{Al}_3\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb), and the pseudo-quinary Eu-Sr-Yb-Al-Sb compound, $\text{Eu}_{5-x-y}\text{Sr}_x\text{Yb}_y\text{Al}_3\text{Sb}_6$, which hosts a mixed Eu/Sr/Yb A-site, while the β angle remains unchanged within standard deviations. As with $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$, where x is determined by single-crystal refinement, the compounds are referred to by their nominal compositions $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$, since slight deviations are observed in the Eu and Al contents.³ Although slight deviations are observed in both the total cations occupying the A-sites and the Al content, a clear correlation exists between A(1) site occupancy and Al content. When the refined Al content exceeds 3 per formula unit, the A(1) cation site refines to zero occupancy, yielding a total A-site composition of 5 per formula unit.^{3,15} When a small fraction of a cation occupies the A(1) site, the Al content refines to between 2.5 and 3, and the total A-sites cations exceed 5. When no cation is present on the A(1) site, the Al content refines to a value above 3. This is consistent with our hypothesis that the Al cluster serves as a pseudo-atom in the structure. **Table 2** presents the compositions determined from single-crystal X-ray refinements alongside those obtained by SEM/EDS analysis. An SEM image of a representative crystal ($\text{Eu}_{4.24}\text{Yb}_{0.84}\text{Al}_3\text{Sb}_6$) with EDS elemental maps is provided in **SI, Figure S2**.

Table1. Selected Crystal Data Collection and Refinement Parameters for 4 Members of $\text{Eu}_{5.08-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ and $\text{Eu}_{2.57}\text{Sr}_{2.03}\text{Yb}_{0.48}\text{Al}_{2.63}\text{Sb}_6$

Single Crystal Composition	* $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$	$\text{Eu}_{4.24(1)}\text{Yb}_{0.84(1)}\text{Al}_3\text{Sb}_6$	$\text{Eu}_{3.8(2)}\text{Yb}_{1.2(1)}\text{Al}_{3.29}\text{Sb}_6$	‡ $\text{Eu}_{3.33(1)}\text{Yb}_{1.79(1)}\text{Al}_{2.62}\text{Sb}_6$
CCDC #	2272573 ¹⁵	2498312	2498314	2498315
Temperature	90 K			
Wavelength	0.71073 Å ³			
Space Group	$C2/m$			
Z	2			
Unit cell dimensions	$a = 8.151(1)$ Å	$a = 8.1441(5)$ Å	$a = 8.1378(4)$ Å	$a = 8.0895(2)$ Å
	$b = 14.181(2)$ Å	$b = 14.1542(8)$ Å	$b = 14.1351(7)$ Å	$b = 14.0321(5)$ Å
	$c = 8.145(1)$ Å	$c = 8.1304(5)$ Å	$c = 8.1213(4)$ Å	$c = 8.0740(3)$ Å

	$\beta = 109.577(2)^\circ$	$\beta = 109.628(4)^\circ$	$\beta = 109.545(3)^\circ$	$\beta = 109.517(2)^\circ$
Volume	887.1(2) Å ³	882.76(11) Å ³	880.35 Å ³	863.84(5) Å ³
Θ-range for data collection	2.654 to 27.546°	2.660 to 27.485°	2.661 to 27.492°	2.676 to 27.521°
Unique Reflections collected	4066	3473	3454	3421
Completeness to Θ = 25.242°	100.0%	100.0%	100.0%	100.0%
Density	5.93 g/cm ³	6.02 g/cm ³	6.05 g/cm ³	6.25 g/cm ³
Absorption coefficient	26.751 mm ⁻¹	28.302 mm ⁻¹	28.787 mm ⁻¹	31.192 mm ⁻¹
Goodness-of-fit	1.126	1.081	1.066	1.145
Highest Peak	-	1.453	1.935	3.187
Deepest Hole	-	-1.649	-1.953	-2.277
Final R indices [I>2σ(I)]	R ₁ = 0.0292 wR ₂ = 0.08078	R ₁ = 0.0282 wR ₂ = 0.0597	R ₁ = 0.0328 wR ₂ = 0.0657	R ₁ = 0.0326 wR ₂ = 0.0753
Final R indices [all data]	R ₁ = 0.0341 wR ₂ = 0.0922	R ₁ = 0.0367 wR ₂ = 0.0646	R ₁ = 0.0431 wR ₂ = 0.0717	R ₁ = 0.0346 wR ₂ = 0.0782
Single Crystal Composition	[‡] Eu _{3.74(2)} Yb _{1.43(1)} Al _{2.62} Sb ₆		Eu _{2.57(1)} Sr _{2.03(1)} Yb _{0.48(3)} Al _{2.63} Sb ₆	
CCDC #	2498316		2498317	
Temperature	90 K			
Wavelength	0.71073 Å ³			
Space Group	C2/m			
Z	2			
Unit cell dimensions	$a = 8.0857(5) \text{ Å}$ $b = 14.0401(9) \text{ Å}$ $c = 8.0766(5) \text{ Å}$ $\beta = 109.584(4)^\circ$		$a = 8.1298(4) \text{ Å}$ $b = 14.1274(7) \text{ Å}$ $c = 8.1290(4) \text{ Å}$ $\beta = 109.520(3)^\circ$	
Volume	863.85(10) Å ³		879.98(8) Å ³	
Θ-range for data collection	2.677 to 27.662°		2.658 to 27.554°	
Reflections collected	3477		3471	
Completeness to Θ = 25.242°	100.0%		100.0%	
Density	6.21 g/cm ³		6.02 g/cm ³	

Absorption coefficient	30.273 mm ⁻¹	28.302 mm ⁻¹
Goodness-of-fit	1.126	1.086
Highest Peak	1.846	2.211
Deepest Hole	-2.198	-1.766
Final R indices [I>2σ(I)]	R ₁ = 0.0324 wR ₂ = 0.0748	R ₁ = 0.0336 wR ₂ = 0.0805
Final R indices [all data]	R ₁ = 0.0365 wR ₂ = 0.0789	R ₁ = 0.0430 wR ₂ = 0.0902

* From Published CIF

† Crystals from independent syntheses of the same nominal composition

Table 2. Single Crystal and EDS (Energy Dispersive Spectroscopy) Determined Compositions and Cation Totals for Eu_{5-x}Yb_xAl₃Sb₆ and Eu_{5-x}Sr_xYb_yAl₃Sb₆ from Single Crystal Structure Determination

(A site) cation total	Single Crystal Composition	EDS Composition
5.08	Eu _{4.24(1)} Yb _{0.84(1)} Al ₃ Sb ₆	Eu _{4.1(2)} Yb _{0.5(1)} Al _{3.7(2)} Sb _{5.7(2)}
5.00	Eu _{3.8(2)} Yb _{1.2(1)} Al _{3.29} Sb ₆	Eu _{3.8(1)} Yb _{0.8(2)} Al _{3.6(2)} Sb _{5.7(1)}
5.17	Eu _{3.74(2)} Yb _{1.43(1)} Al _{2.62} Sb ₆	Eu _{3.0(1)} Yb _{1.5(2)} Al _{3.8(4)} Sb _{5.7(3)}
5.09	Eu _{3.33(1)} Yb _{1.79(1)} Al _{2.62} Sb ₆	Eu _{3.2(6)} Yb _{2.4(8)} Al ₃₍₁₎ Sb _{5.9(3)}
5.24	Eu _{2.57(1)} Sr _{2.03(1)} Yb _{0.48(3)} Al _{2.63} Sb ₆	Eu _{1.5(3)} Sr _{1.9(5)} Yb _{1.3(2)} Al _{3.8(6)} Sb _{5.7(5)}

Figure 4 illustrates the solid-solution structures of Eu_{5-x}Sr_xAl₃Sb₆ ($x = 0, 0.30$) and Eu_{5-x}Yb_xAl₃Sb₆ ($x = 0.84$), with all crystallographic sites labeled by both atom type and site number. Both the Yb-substituted solid solution and the mixed-cation phase adopt the same structure as the parent Eu_{5.08}Al₃Sb₆, preserving the rock-salt-like Eu/Sr/Yb–Sb framework in which each Eu/Sr/Yb atom is octahedrally coordinated by six Sb atoms. Within the unit cell, the octahedral centers at the corners and *C*-face positions host an Al₄ cluster, modeled as two overlapping tetrahedra with about 37.5% occupancy distributed across the Al(1), Al(2), and Al(3) sites. These sites may also be partially occupied (0–24%) by a Eu, Sr, or Yb atom at the Eu/Sr/Yb(1) position.^{3,15} In addition, the electron density around the Sb(2) site in the octahedron exhibits slight disorder, as indicated by the Sb(2B) position. In the Yb solid solution, the corners and face-centered *C* positions of the unit cell are occupied either by Eu atoms or by disordered Al₄

tetrahedra, with no Yb detected at the A(1) site. Previously, refinements treated Eu and Sr as sharing the same sites with freely refined occupancies, since their similar Shannon radii did not indicate a strong site preference. In this work, Figure 4b and c show apparent selectivity, with Sr favoring the larger Eu(2) site, Eu favoring the Eu(1) site, and Yb occupying the smaller Eu(3) and Eu(4) sites.^{3,15,26} This site preference shifts in the mixed-cation compound $\text{Eu}_{2.73}\text{Sr}_{2.03}\text{Yb}_{0.48}\text{Al}_{2.57}\text{Sb}_6$, where all three cations are introduced simultaneously.

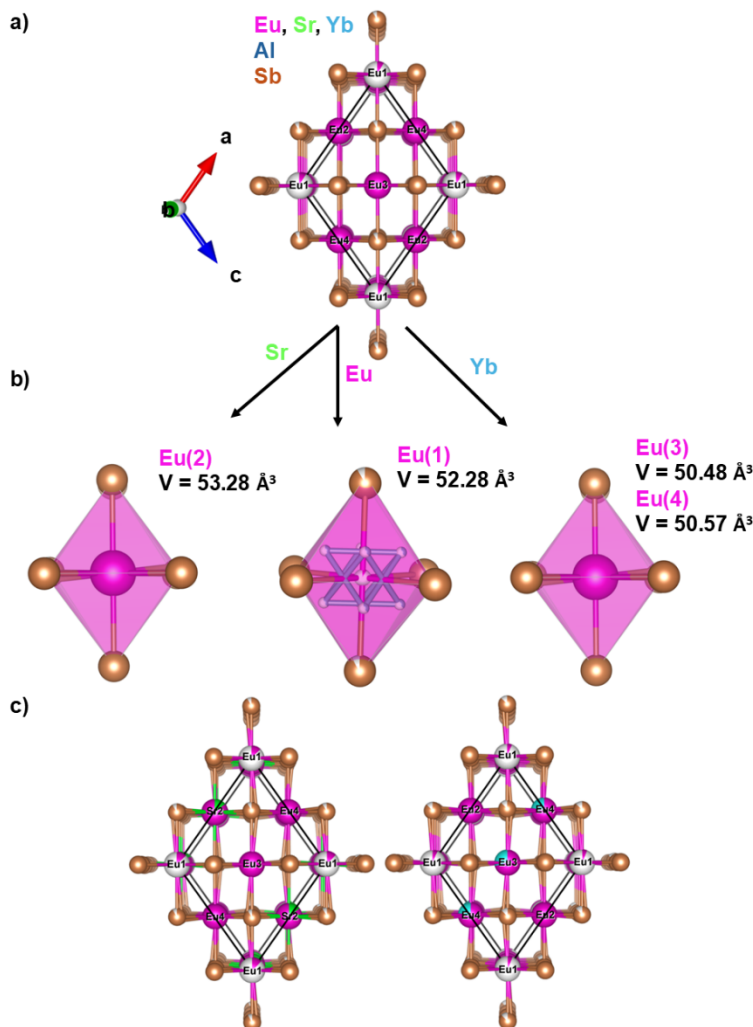


Figure 4. (a) Pseudo-rock salt-like framework of $\text{Eu}_{5-x}\text{A}_x\text{Al}_3\text{Sb}_6$ (A = Sr, Yb) shown without Al atoms for visual clarity. Colored wedges indicate occupancy for the respective atom. (b) Coordination polyhedra of the four distinct Eu sites, highlighting their relative volumes. (c) Visual representation of site preferences: Sr occupies the largest Eu(2) polyhedron ($x = 0.30$),³ Eu favors the Eu(1) site, and Yb tends toward the smaller Eu(3) and Eu(4) sites ($x = 0.84$).

To further probe how multiple cations compete for specific sites, we examined the triple-cation compound $\text{Eu}_{2.73}\text{Sr}_{2.03}\text{Yb}_{0.48}\text{Al}_{2.57}\text{Sb}_6$, shown in **Figure 5**. When all three cations are present in the system, Sr shows a strong preference for the Eu(2–4) sites, with the highest occupancy at Eu(3) (66.7%), followed by Eu(4) (37.8%) and Eu(2) (30.4%). Yb, on the other hand, is distributed over the Eu(1–3) sites, with occupancies of 8% at Eu(1), 4.6% at Eu(2), and a maximum of 31% at Eu(3). According to Figure 4b, Yb is expected to favor the Eu(3) site with the lowest polyhedral volume, and this trend is at least reflected in its partial occupancy there, even though it also appears at Eu(1) and Eu(2). Importantly, Eu(2) and Eu(3) sites incorporate all three cations, Eu(4) contains only Sr and Eu, while Eu(1) is occupied exclusively by Yb. Key bond distances and angles for the $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$ crystals are listed in **SI, Table S2**. In the Yb solid solution, only the composition with $x = 1.20$ refines to a full cation total of 5, with an Al content of 3.29 corresponding to about 41% occupancy of the Al_4 tetrahedron. For the other compositions ($x = 0.84, 1.43, 1.79$), the Al content vacillated between 2.6 and 3, with the Eu1 site occupied exclusively by Eu. At these compositions, the Eu1 occupancies refine to 8% for $x = 0.84$, 17% for $x = 1.43$, and 9% for $x = 1.79$. These trends can be understood through the Pauling electronegativity principle, where Al (with Pauling electronegativity of 1.61) adjusts its occupancy to compensate for the presence of the A(1) cation. In particular, the difference is greatest for Yb (1.06), compared with Eu (1.20) and Sr (0.95), which explains the observed adjustments in Al content.²⁷

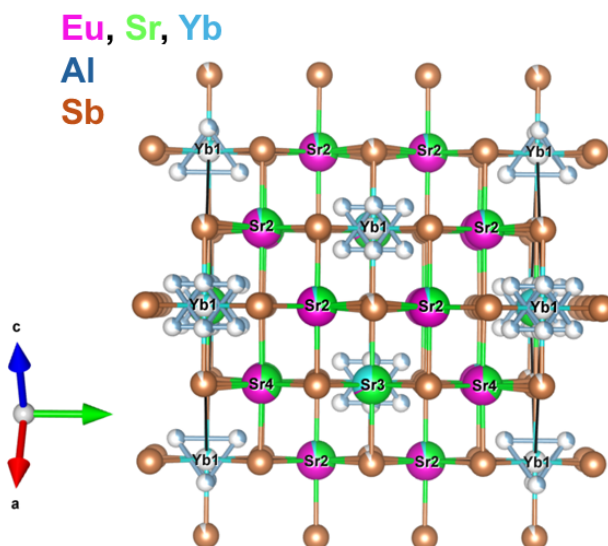


Figure 5. View of the $\text{Eu}_{2.73}\text{Sr}_{2.03}\text{Yb}_{0.48}\text{Al}_{2.57}\text{Sb}_6$ structure, showing the pseudo rock salt framework with Eu, Sr, Yb, Al, and Sb atoms shown in pink, green, light blue, navy blue, and bronze, respectively. The A(1) site is mainly occupied by Yb, the A(2) site is primarily Eu and Sr, and the A(3) site is mainly Sr and Yb. Colored wedges indicate occupancy for the respective atom.

To gain deeper insight into the structure and bonding in the Yb solid solution, **Figure 6** presents the volumes of the A–Sb₆ octahedra and Al₄ tetrahedra as a function of Yb content, along with the average A–Sb bond distances versus Yb content (x) and the Al₄ volume as a function of A(1) site occupancy. With the incorporation of Yb, there is a decrease in polyhedral volume for all A-site polyhedra with similar Eu/Yb–Sb bond distances. The incorporation of Yb results in shorter A–Sb bond distances and reduced polyhedral volumes, consistent with an increase in covalent character in the bonding framework. **Figure 6b** shows that the average distance for Eu/Yb–Sb decreases systematically with increasing x . As shown in **Figure 6c**, the average Al–Al bond length in the Yb solid solution remains nearly constant with only minor fluctuations, following the overall trend. The dual tetrahedra refine to an average Al–Al distance of 2.63 Å, comparable to 2.64 Å in the parent $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and similar to what was observed in the $\text{Eu}_{5-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ solid solution.^{3,28} The average Eu/Yb–Sb bond distances refine to 3.36(2) Å for Eu/Yb(2), 3.26(3) Å for Eu/Yb(3), and 3.27(3) Å for Eu/Yb(4), values that fall within the typical Yb–Sb range of 3.00–3.30 Å reported for compounds such as $\text{Yb}_{11}\text{Sb}_{10}$, Yb_4Sb_3 , YbSb , Yb_5Sb_3 , and YbSb_2 .²⁹ Rare-earth antimonides show comparable behavior, with both volumes and average bond distances shifting when a more electronegative or significantly less electronegative element is introduced into the structure.^{30,31} As mentioned earlier, $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ is considered a polar intermetallic, with a total valence electron count of 49.16 e[−].^{3,4,15} In simple electron counting terms, each Eu or Yb gives 2 electrons, Al gives 3, and Sb gives 5, and in some cases, large Al clusters like Al₁₄ can act like alkaline earth metals.^{3,4,15,17,32} For the Yb solid solution, the total valence electron count stays close to 49, and when divided by the number of atoms per formula unit, the ratio comes out to about 3.5. That ratio, along with the phase width, is what places these compounds in the polar intermetallic family. Altogether, the electron counting, site occupancies, and bonding trends show that both the Yb solid solution and the Eu–Sr–Yb triple-cation phase preserve the polar intermetallic character of $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$, with subtle adjustments in Al content and cation distribution maintaining the overall electronic balance. The Yb analogue proved challenging to obtain as single crystals due to the presence of competing side phases;

however, it was successfully prepared as a polycrystalline sample, and its properties are discussed in the bulk property measurement sections.

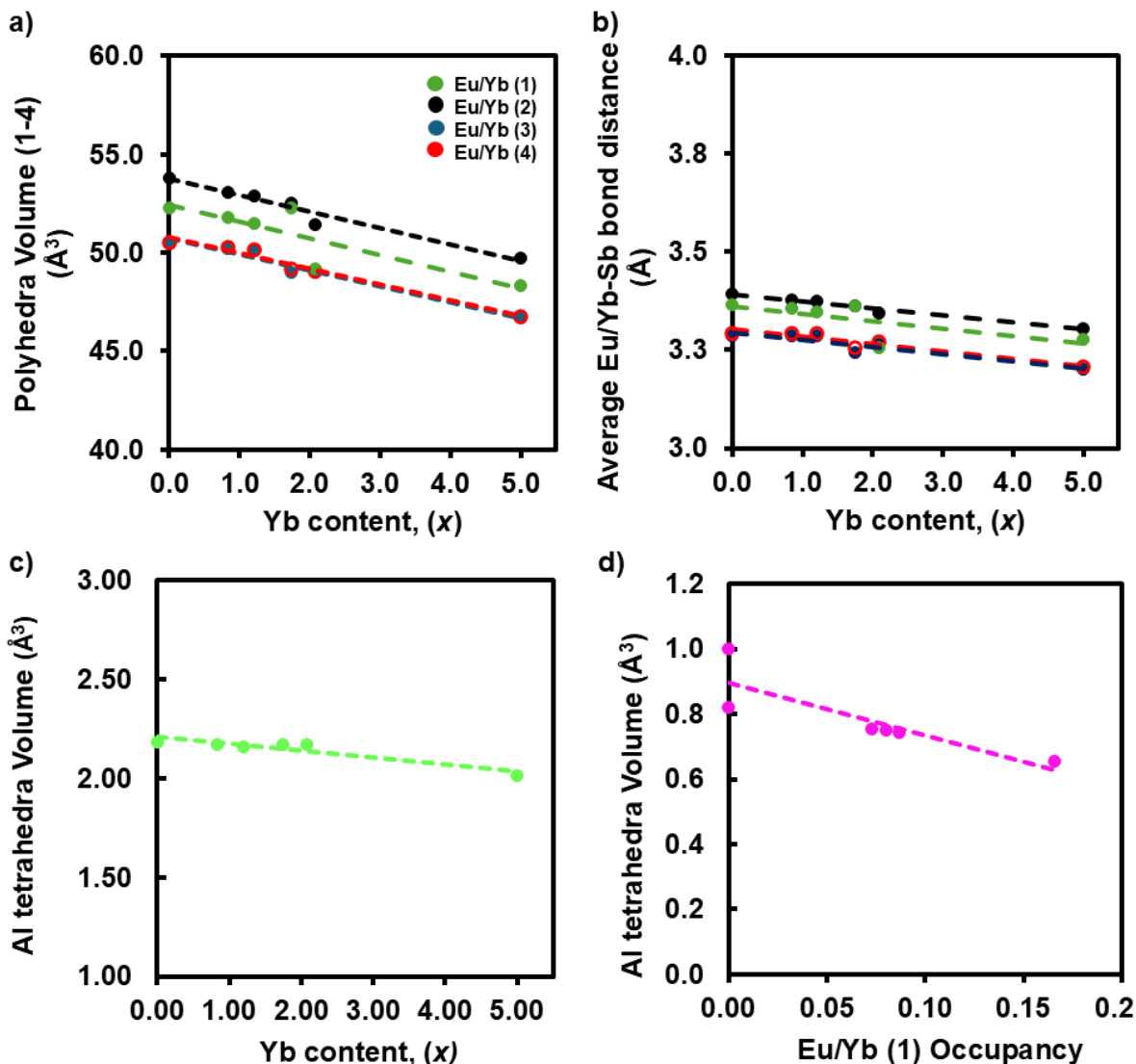


Figure 6. Average Eu/Sr–Sb bond distance and corresponding polyhedral volume as a function of Yb content (x) for $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Yb}$). (a) Polyhedral volume, (b) average Eu/Yb–Sb bond distance, (c) Al_4 tetrahedra volume, and (d) Al_4 tetrahedra volume versus Eu/Yb(1) occupancy.

Polycrystalline Synthesis

Polycrystalline samples were prepared and optimized using metallurgical synthesis. Similar to the polycrystalline synthesis previously reported for $\text{Eu}_5\text{Al}_4\text{Sb}_6$,¹⁶ the nominal compositions were set with the A-site cation total fixed at 5 and the Al content at 4. For the Sr solid solution, three

representative compositions were selected at $x = 0.5, 2.5, \text{ and } 5.0$. For the Yb series, all single-crystal compositions ($x = 0.5, 1.0, 1.5, 2.0, \text{ and } 5.0$) were converted into bulk powders. In addition, the triple-cation phase $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ was prepared. Powder diffraction patterns are shown in **Figure 3b-d**, showing the phase purity of the $\text{A}_5\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) series and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ compared to that of the parent compound $\text{Eu}_5\text{Al}_4\text{Sb}_6$. Phase purity was further examined through Rietveld refinement to obtain lattice parameters and refinement statistics, as well as by EDS to determine nominal compositions; these results are summarized in **Tables 3 and 4**, respectively. Rietveld refinement plots for the synthesized polycrystalline powders are shown in **SI, Figures S3** (Yb) and **S4** (Sr). An SEM image and EDS maps of a piece of the $\text{Eu}_{4.5}\text{Sr}_{0.5}\text{Al}_4\text{Sb}_6$ pellet, with the EDS spectra for both $\text{Eu}_{4.5}\text{Sr}_{0.5}\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{4.5}\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ pellets, are presented in **SI, Figure S5 and S6**. **Figure 7** compares the lattice parameters and unit-cell volumes obtained from single-crystal X-ray diffraction with those from bulk polycrystalline samples of the solid solutions ($\text{A} = \text{Yb}, \text{Sr}$). The values from single-crystal and bulk measurements are in good agreement. As expected, the Sr solid solution shows a linear increase in both lattice parameters and unit-cell volume, while the Yb compounds display a linear decrease relative to the parent $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$. In addition to the solid solutions, the full Yb analogue could only be synthesized as a bulk polycrystalline sample with the composition $\text{Yb}_5\text{Al}_4\text{Sb}_6$. **Figure 8** shows a ternary diagram illustrating the proximity of the Yb–Al–Sb phases in composition space, where attempts to grow $\text{Yb}_5\text{Al}_4\text{Sb}_6$ as single crystals were hindered by competing phases such as $\text{Yb}_5\text{Al}_2\text{Sb}_6$, Yb_3AlSb_3 , $\text{Yb}_{11}\text{AlSb}_9$, and $\text{Yb}_{14}\text{AlSb}_{11}$.^{33–35} With $\text{Yb}_5\text{Al}_4\text{Sb}_6$ synthesized as a polycrystalline sample, the lattice parameters were refined to provide structural details. The refined lattice parameters of $\text{Yb}_5\text{Al}_4\text{Sb}_6$ are $a = 7.92(1) \text{ \AA}$, $b = 13.81(1) \text{ \AA}$, $c = 7.95(1) \text{ \AA}$, $\beta = 109.61(1)^\circ$, with a unit-cell volume of $820.0(1) \text{ \AA}^3$. This lattice contraction, illustrated in **Figure 7**, is consistent with both the size and the increased covalent character of Yb relative to Eu and the more ionic Sr.^{3,15,29}

Table 3. Lattice Parameters of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) Synthesized as Polycrystalline Solids and Selected Rietveld Refinement Statistics

Composition	* $\text{Eu}_5\text{Al}_4\text{Sb}_6$	$\text{Eu}_{4.5}\text{Sr}_{0.5}\text{Al}_4\text{Sb}_6$	$\text{Eu}_{2.5}\text{Sr}_{2.5}\text{Al}_4\text{Sb}_6$	$\text{Sr}_5\text{Al}_4\text{Sb}_6$
Temperature	Room Temperature			
Radiation	Cu K_α			

Wavelength	1.5405 Å			
Unit cell dimensions	$a = 8.1618(6)$ $b = 14.108(1)$ $c = 8.1780(5)$ $\beta = 109.356(7)$	$a = 8.1957(4)$ $b = 14.178(1)$ $c = 8.1677(4)$ $\beta = 109.398(5)$	$a = 8.196(4)$ $b = 14.243(1)$ $c = 8.250(4)$ $\beta = 109.470(1)$	$a = 8.2645(13)$ $b = 14.342(2)$ $c = 8.2523(11)$ $\beta = 109.574(8)$
Volume	888.5(1)	894.7(1)	907.9(1)	921.6(1)
Rwp (%)	14.11	14.36	13.38	13.05
Rp (%)	10.84	10.76	10.79	10.36
GoF	1.70	1.80	1.80	1.89
Composition	Eu _{4.5} Yb _{0.5} Al ₄ Sb ₆	Eu _{4.0} Yb _{1.0} Al ₄ Sb ₆	Eu _{3.5} Yb _{1.5} Al ₄ Sb ₆	Eu _{3.0} Yb _{2.0} Al ₄ Sb ₆
Unit cell dimensions	$a = 8.1392(7)$ $b = 14.1517(13)$ $c = 8.1547(7)$ $\beta = 109.578(6)$	$a = 8.1339(16)$ $b = 14.064(3)$ $c = 8.1438(15)$ $\beta = 109.361(9)$	$a = 8.1302(15)$ $b = 14.047(3)$ $c = 8.0928(14)$ $\beta = 109.502(8)$	$a = 8.0782(18)$ $b = 14.038(3)$ $c = 8.0899(17)$ $\beta = 109.576(8)$
Volume	884.9(14)	878.9(3)	871.2(3)	864.4(3)
Rwp (%)	12.46	13.40	12.76	12.48
Rp (%)	9.52	10.49	10.25	9.82
GoF	1.60	1.76	1.83	1.75
Composition	Yb ₅ Al ₄ Sb ₆		Eu _{2.5} Sr ₂ Yb _{0.5} Al ₄ Sb ₆	
Unit cell dimensions	$a = 7.9247(5)$ $b = 13.8103(8)$ $c = 7.9545(5)$ $\beta = 109.617(7)$		$a = 8.2062(9)$ $b = 14.1566(13)$ $c = 8.1916(7)$ $\beta = 109.346(5)$	
Volume	820.0(1)		897.91(15)	
Rwp (%)	12.99		12.77	
Rp (%)	9.53		9.79	
GoF	2.24		1.70	

Table 4. Polycrystalline Loading and EDS (Energy Dispersive Spectroscopy) Determined Compositions of Pressed Pellets of Polycrystalline Synthesized Eu_{5-x}A_xAl₄Sb₆ (A = Sr and Yb) Samples

Nominal Composition	Experimental A (Sr(x)) or (Yb(y))	EDS Analysis
Eu_{4.5}Sr_{0.5}Al₄Sb₆	$x = 0.50$	Eu_{4.5(4)}Sr_{0.5(1)}Al_{3.9(1)}Sb_{6.1(4)}
Eu_{2.5}Sr_{2.5}Al₄Sb₆	$x = 2.50$	Eu_{2.5(2)}Sr_{2.4(2)}Al_{4.1(6)}Sb_{6.0(4)}
Sr₅Al₄Sb₆	$x = 5.00$	Sr_{5.1(3)}Al_{4.1(7)}Sb_{5.8(4)}
Eu_{4.5}Yb_{0.5}Al₄Sb₆	$x = 0.50$	Eu_{4.3(7)}Yb_{0.6(1)}Al₄₍₁₎Sb_{5.9(8)}
Eu_{4.0}Yb_{1.0}Al₄Sb₆	$x = 1.00$	Eu_{3.8(3)}Yb_{1.0(1)}Al_{4.2(8)}Sb_{5.8(4)}
Eu_{3.5}Yb_{1.5}Al₄Sb₆	$x = 1.50$	Eu_{3.3(3)}Yb_{1.4(2)}Al₄₍₁₎Sb_{5.8(6)}
Eu_{3.0}Yb_{2.0}Al₄Sb₆	$x = 2.00$	Eu_{2.9(2)}Yb_{1.9(2)}Al_{4.2(6)}Sb_{5.9(4)}
Yb₅Al₄Sb₆	$x = 5.00$	Yb_{4.3(3)}Al₄₍₁₎Sb_{5.5(6)}
Eu_{2.5}Sr_{2.0}Yb_{0.5}Al₄Sb₆	$x = 2.00$ and $y = 0.50$	Eu_{2.4(4)}Sr_{1.9(2)}Yb_{0.5(1)}Al₄₍₁₎Sb_{5.9(7)}

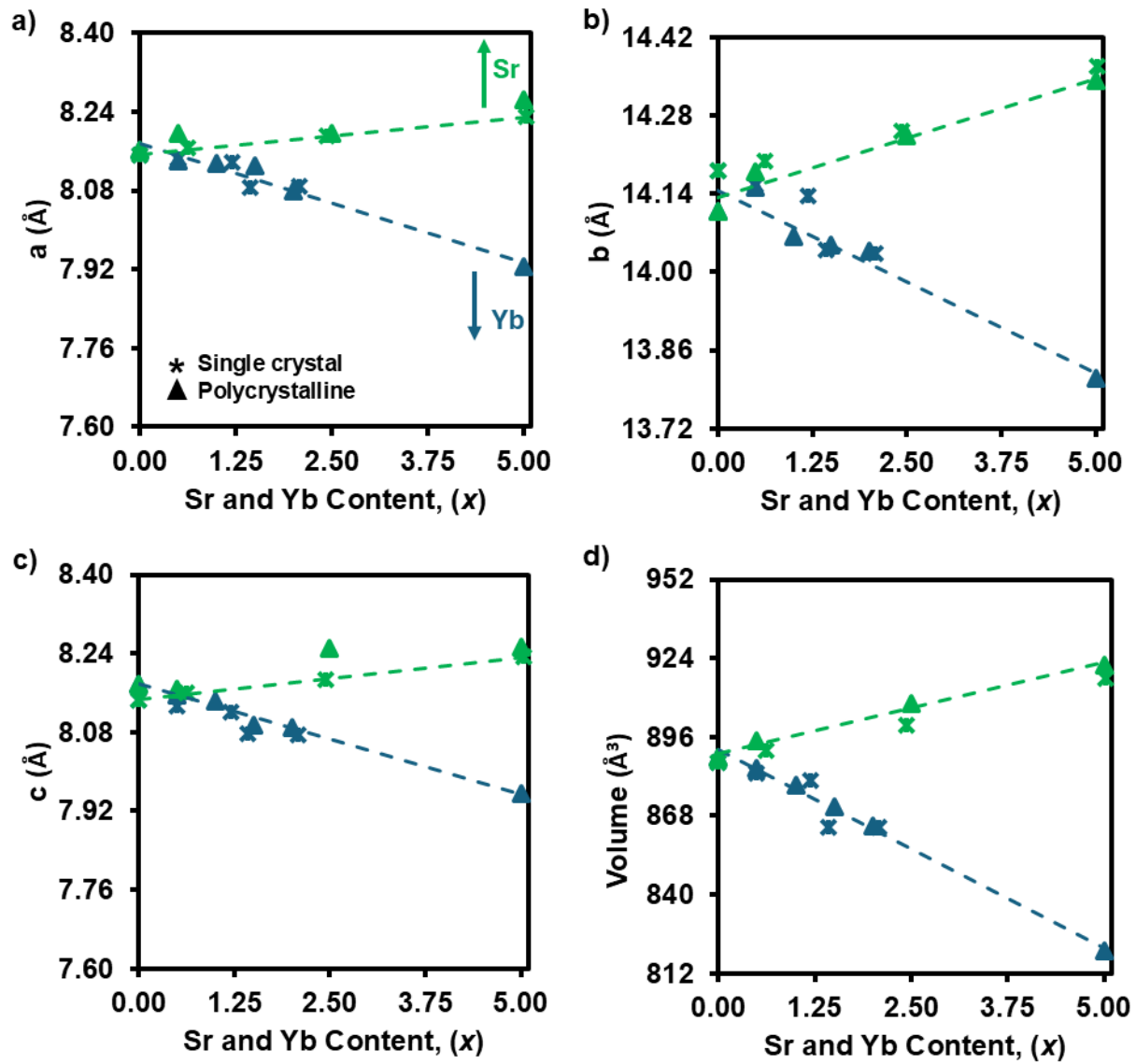


Figure 7. (a–c) Lattice parameters (Å) and (d) volume (Å³) from single-crystal $\text{Eu}_{5-x-y}\text{Yb}_x\text{Sr}_y\text{Al}_3\text{Sb}_6$ and polycrystalline synthesized powders from powder X-ray diffraction versus refined Yb and Sr content (x) for $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($A = \text{Sr}$ and Yb).

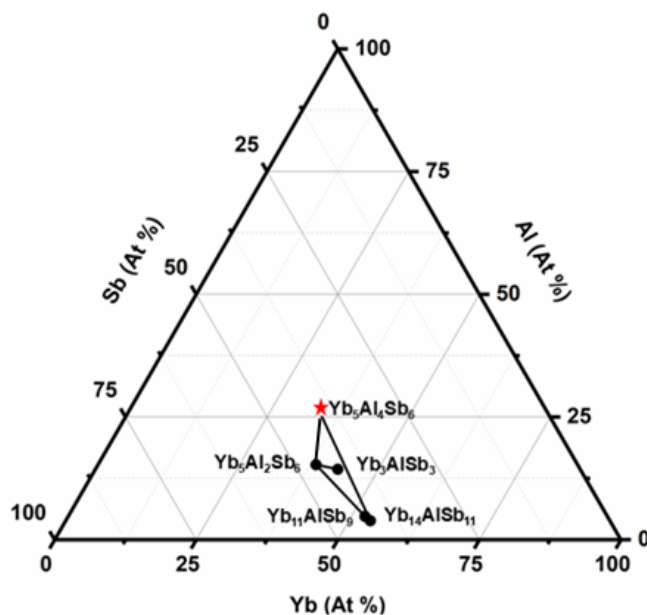


Figure 8. Ternary phase diagram of Yb–Al–Sb Zintl phases. The newly identified $\text{Yb}_5\text{Al}_4\text{Sb}_6$ phase is indicated by a red star, while previously reported thermodynamically stable phases are shown as black circles.^{33,34,36,37}

Complementing the lattice parameter refinements, EDS measurements were performed to verify the nominal compositions of the Sr and Yb-substituted polycrystalline solid solutions. Secondary electron imaging and elemental analysis confirmed the phase purity and homogeneity of the Sr and Yb polycrystalline pellets. The nominal compositions of these samples, compared with those calculated from EDS, are summarized in **Table 4**. The slight increase in Al content is consistent with the EDS results. For the $\text{Sr}_5\text{Al}_4\text{Sb}_6$ and $\text{Yb}_5\text{Al}_4\text{Sb}_6$ polycrystalline samples, EDS and TG-DSC (**Figure 9**) were used to probe possible excess Al at grain boundaries; Al shot was measured as a reference for Al-related signals. No excess Al was detected within the sensitivity of these methods. In SEM-EDS, practical detection limits are on the order of 0.1 to 0.5 wt %, and the effective spatial resolution is governed by the electron interaction volume, which is submicrometer to micrometer at typical accelerating voltages.³⁸ In TG-DSC, no Al melting endotherm is observed near 660 °C. A simple mass balance shows that one Al atom per $\text{Eu}_5\text{Al}_4\text{Sb}_6$ formula unit corresponds to about 1.7 wt % free Al; smaller amounts (for example, ≤ 0.5 Al per formula unit, ≤ 0.8 wt %) approach the practical detectability of heat-flux DSC at the sample masses used and would not be expected to yield a resolvable peak. Taken together, these measurements indicate no detectable excess Al in the Sr and Yb end-member pellets.^{16,38–40} By

confirming phase purity and homogeneity and ruling out aluminum at the grain boundaries, we establish a solid basis to explore the thermal transport properties of these solid solutions.

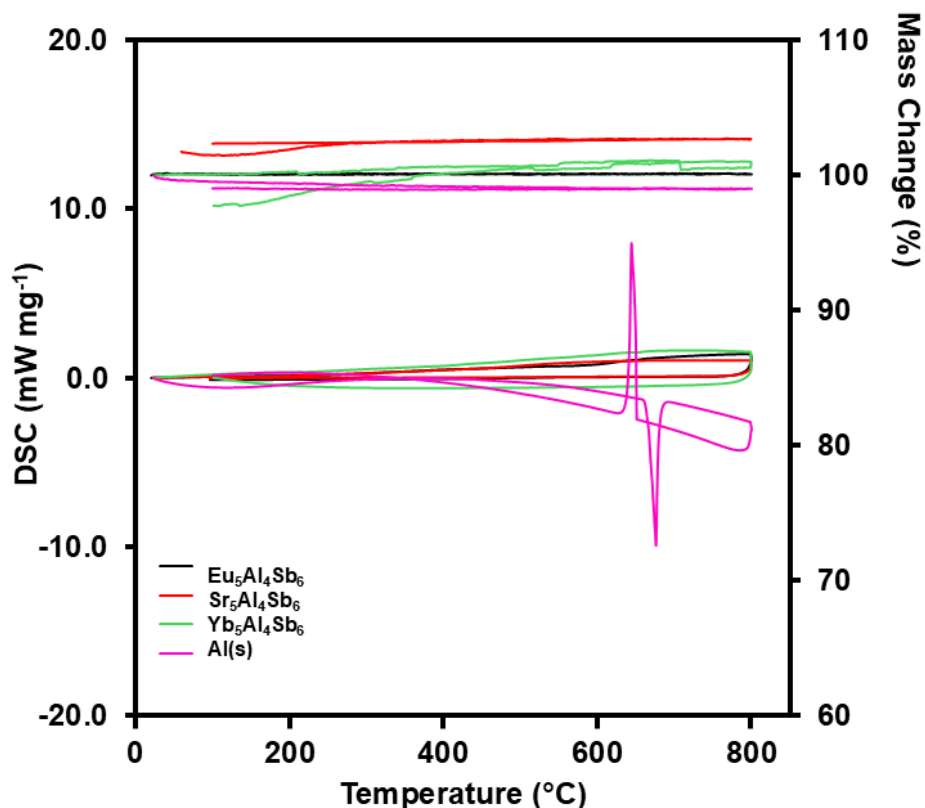


Figure 9. TG (top right axis) and DSC (bottom left axis) of polished pieces of $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$ and Yb) from room temperature (25 °C) to 800 °C under the flow of 50 mL/min of Argon. The TG/DSC trace of Al(s) is shown as a reference and appears bright pink.

Thermal Transport Properties:

Polycrystalline samples of the semimetallic systems $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ were examined for their thermal and electrical transport properties. Both compounds exhibit low thermal conductivity, with values below $1 \text{ W m}^{-1} \text{ K}^{-1}$.¹⁶ The thermal transport properties can be linked to structural features of the material. Disorder within the Al cluster, along with associated vacancies and Eu-site substitutions, may serve as a source of point defects that scatter phonons and suppress thermal conductivity. In contrast, the favorable electrical properties arise from the high symmetry of the pseudo-rock salt framework and the presence of multi-valley band degeneracy. In this study, Sr- and Yb-substituted $\text{Eu}_5\text{Al}_4\text{Sb}_6$ solid solutions are used to directly test how the A-site chemistry impacts transport behavior. Research on Zintl phases, such as $\text{A}_5\text{Al}_2\text{Sb}_6$ and

AZn₂Sb₂ (where A = Sr, Ca, Yb, Eu), has demonstrated that the choice of A-site cation can tune carrier concentrations by influencing intrinsic defects.^{41–43} These ideas suggest that differences in electronegativity between Eu, Sr, and Yb tune the balance between covalency and ionicity, which in turn affects band dispersion. As illustrated in **Figure 10**, this may appear as a pseudogap-like feature for the Sr solid solution, while Yb incorporation drives the semimetallic state toward a more metallic character.^{42,44–46}

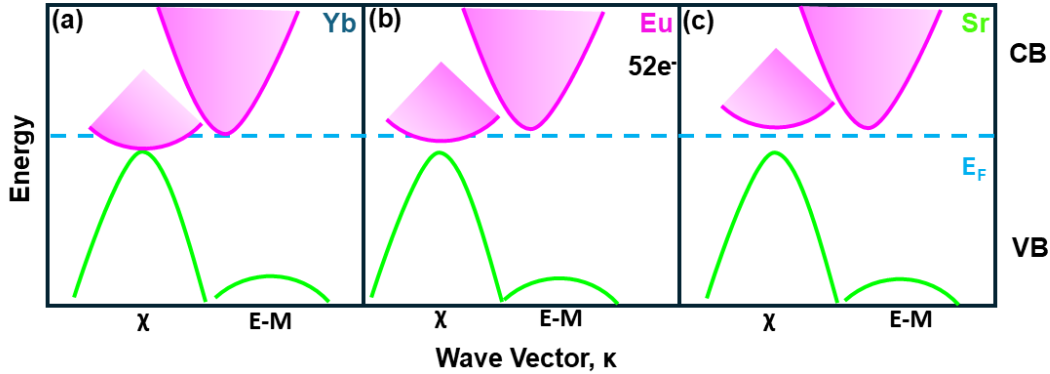


Figure 10. Cartoon illustration of the band structure for the hypothetical Eu₅Al₄Sb₆ compound.¹⁵ The bands show semimetallic behavior for the Yb-containing phase and semiconducting behavior for the Sr-containing phase with at least two conduction valleys close to the Fermi level ($E = 0$ eV), one at the X point and another along the E–M path. (a) Yb solid solution, (b) Eu₅Al₄Sb₆ as reference, and (c) Sr solid solution.

Total thermal conductivity values are shown in **Figure 11** for both the Sr and Yb solid solutions. Similar to Eu₅Al₄Sb₆ and Eu_{5.08}Al₄Sb₆, both the Yb and Sr solid solutions exhibit low thermal conductivity values (<1 W m⁻¹ K⁻¹). **Figure 11** shows the total thermal conductivity values for both the Sr and Yb solid solutions. The Sr- and Yb-substituted samples also exhibit low thermal conductivity, remaining below 1 W m⁻¹ K⁻¹, similar to Eu₅Al₄Sb₆ and Eu_{5.08}Al₄Sb₆.¹⁶ Low thermal conductivity is expected for both solid solutions, arising from structural disorder together with intrinsic defects such as point-defect phonon scattering and possible aluminum at grain boundaries, which sets them apart from the much higher values typically observed in metals (>10 W m⁻¹ K⁻¹) and also differentiates them from half-Heusler phases (~ 4 – 10 W m⁻¹ K⁻¹).^{12,47} Several notable features stand out in these solid solutions. In the Sr solid solution, the total thermal conductivity systematically decreases with increasing Sr content, with the full Sr analogue showing the lowest value (**Figure 11a**). At 800 K, the Sr solid

solution shows total thermal conductivity values of 0.61, 0.56, and 0.52 W m⁻¹ K⁻¹ for $x = 0.5$, 2.5, and 5.0, respectively.

A similar trend is observed in other A–Al–Sb systems (A = Ca, Sr), such as the 3-1-3 and 5-2-6 phases, where replacing Ca with the less electronegative Sr reduces thermal conductivity.^{35,41,48} This parallels the Sr solid solution, where increasing Sr content enhances the ionic character and leads to systematically reduced thermal conductivity. In contrast, the Yb solid solution exhibits the opposite trend, with thermal conductivity increasing as Yb is incorporated. The lowest values are reached at 800 K, measuring 0.62, 0.65, and 0.79 W m⁻¹ K⁻¹ for $x = 0.5$, 1.0, and 1.5, while the full Yb analogue shows a similar minimum of 0.79 W m⁻¹ K⁻¹ at 673 K. The increase in thermal conductivity can be linked to the stronger bonding character that arises from the more covalent nature of Yb compared to Eu. A similar effect has been observed in skutterudite systems with minor electronegativity differences, such as CoSb₃ and IrSb₃. A high degree of covalent bonding favors efficient electronic transport but also raises the lattice thermal conductivity by stiffening the framework. The extracted κ_l and κ_e are shown in **SI, Figures S6 and S7**.⁹ In contrast, two notable features stand out in the Yb₅Al₄Sb₆ and Eu₃Yb₂Al₄Sb₆ phases. For Yb₅Al₄Sb₆, minority carrier contributions appear at a lower temperature (~600 K) compared to Eu₅Al₄Sb₆, where they emerge closer to 800 K, as indicated by the upturn in Figure 11b. Meanwhile, Eu₃Yb₂Al₄Sb₆ shows the lowest thermal conductivity within the Yb solid solution. This may be attributed to enhanced phonon scattering from mass and strain disorder associated with the mixed Eu/Yb occupancy, an effect well described by alloy-scattering models.⁴⁹ According to the Klemens mass difference model, mixing atoms of different masses, such as Eu and Yb, enhances phonon scattering, which in turn lowers the lattice thermal conductivity.⁴⁹ This effect is most pronounced near a 50/50 composition, where disorder is maximized, as observed in systems such as Mg₃Sb₂–Mg₃Bi₂.^{49,50} Motivated by this, we targeted the mixed composition Eu_{2.5}Sr₂Yb_{0.5}Al₄Sb₆ and measured its thermal transport to assess the impact of further alloy disorder. The triple-cation sample closely follows Eu_{2.5}Sr_{2.5}Al₄Sb₆, with a total thermal conductivity of 0.76 W m⁻¹ K⁻¹ at room temperature, decreasing to 0.49 W m⁻¹ K⁻¹ at 873 K. The lattice thermal conductivity and electronic contribution are plotted for both solid solutions and the pseudo-quinary Eu_{2.5}Sr₂Yb_{0.5}Al₄Sb₆ compound and shown in **SI, Figures S6 and S7**. Similar to the Eu₅Al₄Sb₆ and Eu_{5.08}Al₄Sb₆ lattice thermal conductivity, using the Wiedemann-Franz subtraction, κ_l for all compounds is approximately the same regardless of

whether a degenerate or metallic Lorenz number is used.⁵¹ After subtracting the lattice part from the total thermal conductivity, we examine the electronic term (κ_e) across the series. In **SI**, **Figure S8**, κ_e grows with temperature and is most pronounced for $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, while it remains smaller for $\text{Eu}_5\text{Al}_4\text{Sb}_6$. This is consistent with $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ being more metallic, with bands of higher degeneracy than in $\text{Eu}_5\text{Al}_4\text{Sb}_6$, and with the Fermi level sitting deeper in the conduction band pockets.^{15,16} In the Sr-containing solid solution, the lattice term dominates, and with increasing Sr content, the electronic contribution drops below about $0.1 \text{ W m}^{-1} \text{ K}^{-1}$, becoming negligible. The same behavior holds for the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$. In contrast, the Yb-containing solid solution exhibits a sizable electronic contribution at high temperatures, consistent with the hypothesis that increasing Sr content in the solid solution facilitates a transition toward a pseudogap. Whereas Yb substitution drives the bands towards a more metallic state, as illustrated by the band diagram cartoon in **Figure 10**. Concerning heat transport, the lattice term governs both the Sr solid solution and the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ compound, whereas the electronic term becomes more significant in the Yb series. Since the choice of cation directly affects the balance between lattice and electronic contributions, we further investigate how these substitutions influence the electronic transport properties.

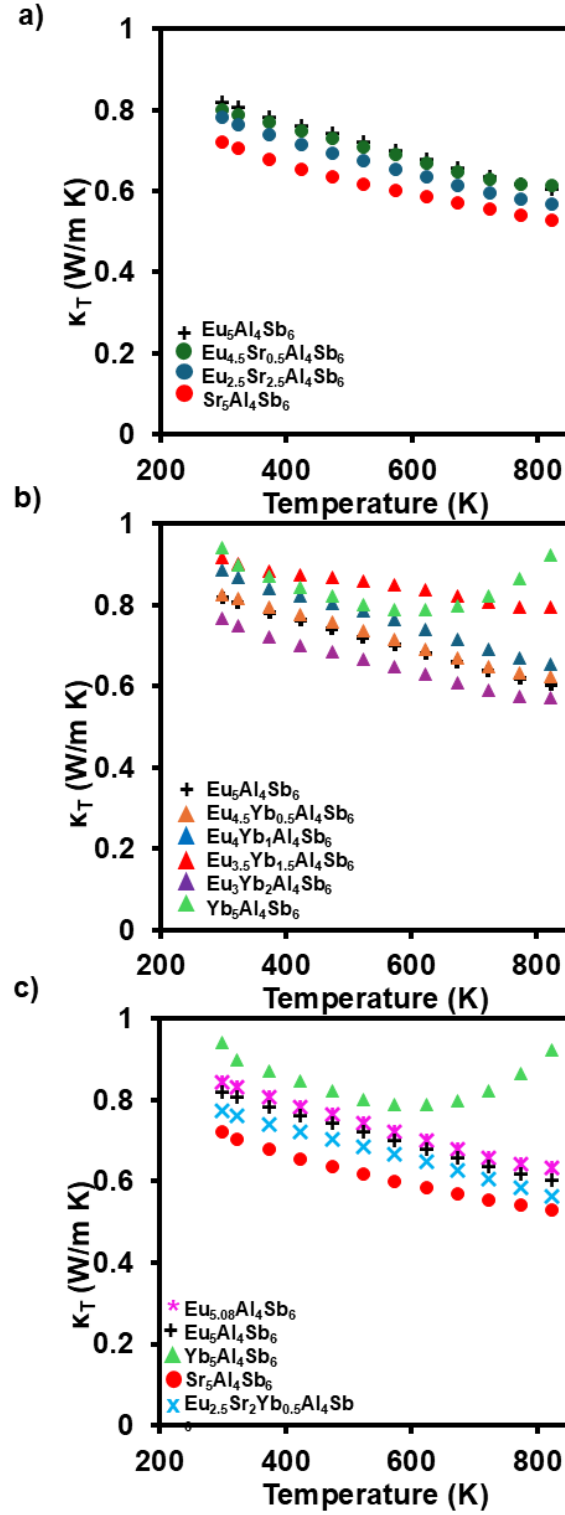


Figure 11. Temperature-dependent total thermal conductivity from 300 to 800 K for $\text{Eu}_5\text{Al}_4\text{Sb}_6$ compared with (a) $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}$), (b) $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Yb}$) and (c) $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, $\text{A}_5\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Eu}, \text{Yb}, \text{Sr}$) and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$.

Electronic Transport Properties

Temperature-dependent electronic transport properties are shown in **Figure 12**. In semi-metallic systems, such as the NiTZ half-Heusler phases, improvements in thermoelectric performance have been linked to the coexistence of heavy and light bands.⁵² The heavy bands sustain large Seebeck coefficients, while the light bands provide the mobility needed for strong electrical transport.^{9,44,53,54} A similar picture may apply here, where the balance of heavy and light bands could shift with cation choice, with Yb driving the system more metallic, Sr favoring a pseudogap, and the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_{2.5}\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ compound, falling in between. As shown in **Figure 12b**, introducing Sr drives the system toward more semiconducting behavior. At room temperature, $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ have nearly the same resistivities of 9.0 and 10.0 m Ω cm, respectively. With Sr substitution, $x = 2.5$, the room-temperature resistivity increases by nearly fourfold to ~ 54 m $\Omega \cdot \text{cm}$; at $x = 5.0$, it reaches $\sim 1.6 \times 10^3$ m $\Omega \cdot \text{cm}$. Notably, the $\text{Sr}_5\text{Al}_4\text{Sb}_6$ end member shows a decreasing resistivity with increasing temperature, a semiconducting-like trend consistent with a pseudo-gap; this behavior is in line with the more ionic character of Sr^{2+} , which may push the electronic structure toward a pseudo-gap. Compared to some reported Sr-Al-Sb families, the resistivities of $\text{Eu}_{5-x}\text{Sr}_x\text{Al}_4\text{Sb}_6$ at compositions $x = 2.5$ and 5.0 are quite high. For example, in the 5-2-6, 14-1-11, and 3-1-3 systems, $\rho(300 \text{ K})$ are about 1.4, ~ 0.4 , and $\sim 0.7 \Omega \cdot \text{cm}$, respectively.^{42,55,56} In both the Yb and Sr solid solutions, signs of bipolar conduction emerge above 600 K, indicating the activation of minority carriers. This is significant because, even though $\text{Sr}_5\text{Al}_4\text{Sb}_6$ shows much higher resistivities than the Eu-rich compounds, the onset of bipolar transport indicates that the system remains semimetallic or small-gap in nature rather than a wide-gap semiconductor. For the Sr solid solution with $x = 0.5$, the room-temperature resistivity is about 9.5 m $\Omega \cdot \text{cm}$, which lies between those of $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, and increases gradually with temperature. In the Sr solid solution ($x = 0.5$), the room-temperature resistivity is 9.5 m $\Omega \cdot \text{cm}$, between that of $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, and it increases gradually with temperature. The mobility (**Figure 13b**) is higher and coincides with a modest increase in the Hall carrier density (**Figure 13a**), which we ascribe to a slight shift of E_F away from E_F pseudo-gap and/or a change in the Hall factor. The $\text{Eu}_{2.5}\text{Sr}_{2.5}\text{Al}_4\text{Sb}_6$ sample shows a lower carrier concentration than either $\text{Eu}_5\text{Al}_4\text{Sb}_6$, $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, or $\text{Eu}_{4.5}\text{Sr}_{0.5}\text{Al}_4\text{Sb}_6$, likely due to the system approaching a pseudo-gap regime.

In contrast, the Yb solid solution shows the opposite behavior, with all Yb-containing phases being less resistive than $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$, exhibiting room-temperature resistivity values in the range of 4–6 $\text{m}\Omega\cdot\text{cm}$. For the Yb solid solution, the anomaly lies with the $\text{Yb}_5\text{Al}_4\text{Sb}_6$ compound, whose resistivity at room temperature is about 20 $\text{m}\Omega\cdot\text{cm}$, roughly three times higher than EuAl_4Sb_6 . This value also exceeds that of other Yb–Al–Sb phases, such as $\text{Yb}_5\text{Al}_2\text{Sb}_6$ (0.91 $\text{m}\Omega\cdot\text{cm}$) and Yb_3AlSb_3 (4.35 $\text{m}\Omega\cdot\text{cm}$).^{34,37} The high resistivity in the $\text{Yb}_5\text{Al}_4\text{Sb}_6$ system may be linked to several factors. Across the compositions of $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_4\text{Sb}_6$, the full Yb analogue shows the lowest weighted mobility (**Figure 13f**). Single-crystal refinements indicate that Yb preferentially occupies the smaller Eu(3)/Eu(4) sites (**Table S1**), which increases Yb–Sb covalency and modifies the local bonding environment.⁵⁷ The Seebeck coefficients for the Sr and Yb series provide a complementary perspective on the electronic transport properties and how changes in cation chemistry significantly influence the thermopower. As shown in **Figure 12a,c,e**, the Seebeck coefficient remains negative over the measured temperature range, indicating n-type transport. The magnitude is comparable to established half-Heuslers phases such as $\text{TiCo}_{0.85}\text{Fe}_{0.15}\text{Sb}_{1-x}\text{Sn}_x$ and $\text{Zr}_{1-x}\text{Nb}_x\text{NiSn}$.^{58,59} In the half-Heuslers phases, the enhanced Seebeck response was attributed to band convergence, where heavy bands provide high Seebeck coefficients. In the Sr solid solution, the magnitude of the Seebeck coefficient increases (or becomes more negative) as more Sr is substituted into the structure. At approximately 800 K, the Seebeck coefficients reach $-245\text{ }\mu\text{V K}^{-1}$ for $x = 0.5$, $-325\text{ }\mu\text{V K}^{-1}$ for $x = 2.5$, and $-538\text{ }\mu\text{V K}^{-1}$ for $x = 5.0$, reflecting a significant enhancement in thermopower with increasing Sr substitution. **Figures 13b** and **13d** show that the Hall and weighted mobilities for $x = 0.5$ remain higher than those for $x = 2.5$ across the measured temperature range. This difference may be due to increased alloy disorder in the $x = 2.5$ composition, where greater Eu–Sr site mixing introduces additional scattering that partially offsets the transport gains from Sr substitution.⁴⁹ In $\text{Sr}_5\text{Al}_4\text{Sb}_6$, the increase in weighted mobility with temperature may reflect the activation of higher-mobility conduction pathways as the system transitions further into a pseudo-gap regime. As impurity scattering becomes less dominant, intrinsic band transport becomes more evident, consistent with the enhanced Seebeck effect and the gradual suppression of semimetallic behavior shown in the schematic band structure (**Figure 10**).^{15,16,60}

In contrast to Sr substitution, Yb substitution lowers the Seebeck magnitude across most compositions (**Figure 12c**): at 800 K, $|S|$ is 227, 211, 237, and 220 $\mu\text{V K}^{-1}$ for $x = 0.5, 1.0, 1.5,$

and 3.0. The $\text{Yb}_5\text{Al}_4\text{Sb}_6$ end member, however, shows roughly the same magnitude in Seebeck values similar to that of $\text{Eu}_5\text{Al}_4\text{Sb}_6$ (Figure 12c and 12e). The weighted mobility is about the same for the $x = 0.5$ to 1.5 for the Yb solid solution, while the $x = 5.0$ shows the lowest weighted mobility. The higher resistivity of $\text{Yb}_5\text{Al}_4\text{Sb}_6$ may be explained by stronger carrier scattering in the Yb–Sb framework and by the Yb site preference noted above. EDS shows small Yb and Sb deficiencies (Table 4), introducing A-site and Sb-vacancy defects that add scattering. As a result, $\text{Yb}_5\text{Al}_4\text{Sb}_6$ has higher resistivity and lower weighted mobility than both the Yb solid-solution compositions and $\text{Eu}_5\text{Al}_4\text{Sb}_6$. The Seebeck remains similar because the reduced Fermi level is comparable. A possible explanation is that features in the density of states near the Fermi level, such as the position of Yb versus Eu 4*f* states, may impact the Seebeck without any change in valence.^{57,61–63} For the quaternary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$, the Seebeck coefficient reaches $-301 \mu\text{V K}^{-1}$ at 800 K. At the same time, the room temperature resistivity is $53 \text{ m}\Omega\cdot\text{cm}$, highlighting its distinct transport behavior compared to the solid solution end members. The power factor trends for the Eu, Sr, Yb, and Eu/Sr/Yb triple-cation systems are shown in **Figure 13**. Across the series, values range from approximately 0.3 to $5 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for the Sr compounds, 1 to $6 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for the Yb compounds, and about $2.89 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ at 800 K. In comparison, other thermoelectric families typically show power factors of about $5\text{--}20 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for Zintl phases, less than $1 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for metals, and $20\text{--}50 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for half-Heuslers phases.^{64–66} The $\text{A}_5\text{Al}_4\text{Sb}_6$ compounds ($\text{A} = \text{Yb}$ and Sr) display a promising power factor and their performance shows potential to rival half-Heuslers phases, which are often considered the benchmark materials for high power factors in thermoelectrics. Unlike half-Heuslers phases, however, these compounds benefit from low thermal conductivity, below $1 \text{ W m}^{-1} \text{ K}^{-1}$, giving them an inherent advantage in maximizing efficiency. Ongoing substitutional studies targeting the Al site with Ga or In are being pursued to tune the band structure further while reducing A-site cation disorder.^{67,68} Reproducibility was evaluated using replicate samples of $\text{Eu}_{2.5}\text{Sr}_{2.5}\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ and by repeating transport cycles; the resulting resistivity and Seebeck curves overlap closely, as shown in **SI, Figure S9**. These strategies not only highlight pathways for enhancing power factor but also set the stage for evaluating overall thermoelectric efficiency through the figure of merit zT .

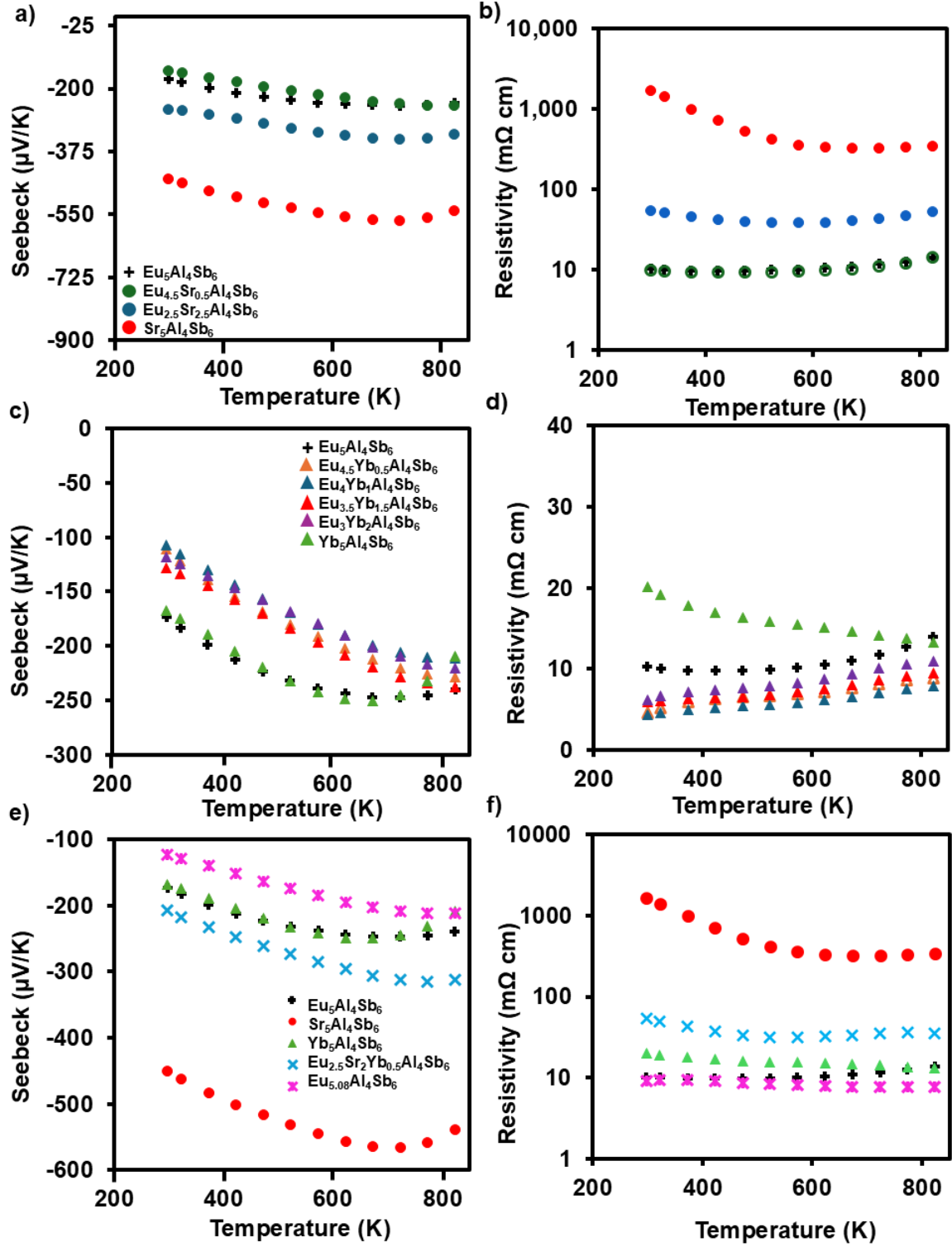
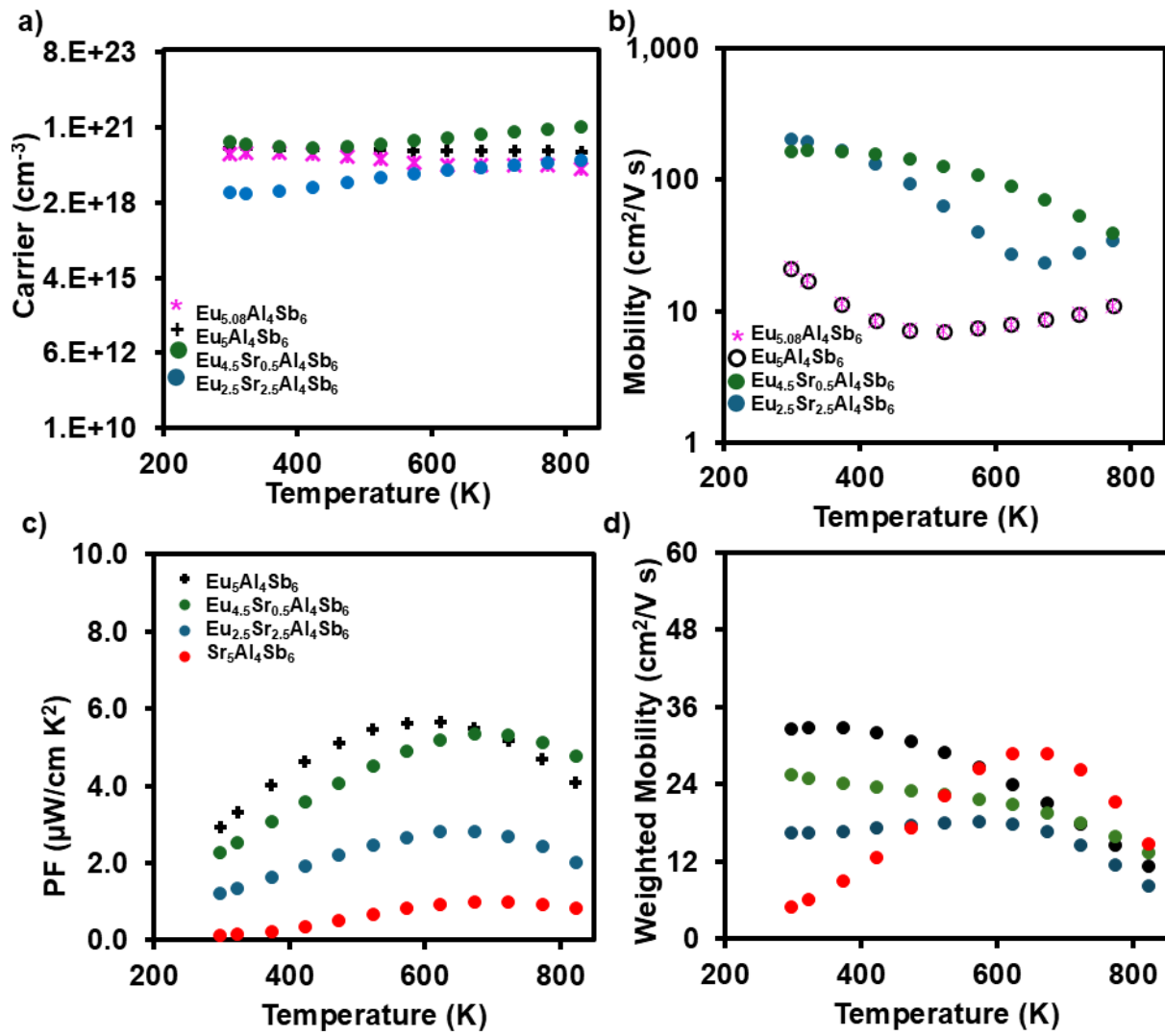


Figure 12. Temperature-dependent electronic transport properties. The left panels show the Seebeck coefficient, and the right panels show the electrical resistivity as a function of temperature. Panel sets are arranged as follows: (a, b) Sr series, (c, d) Yb series, and (e, f) Eu/Sr/Yb comparison.



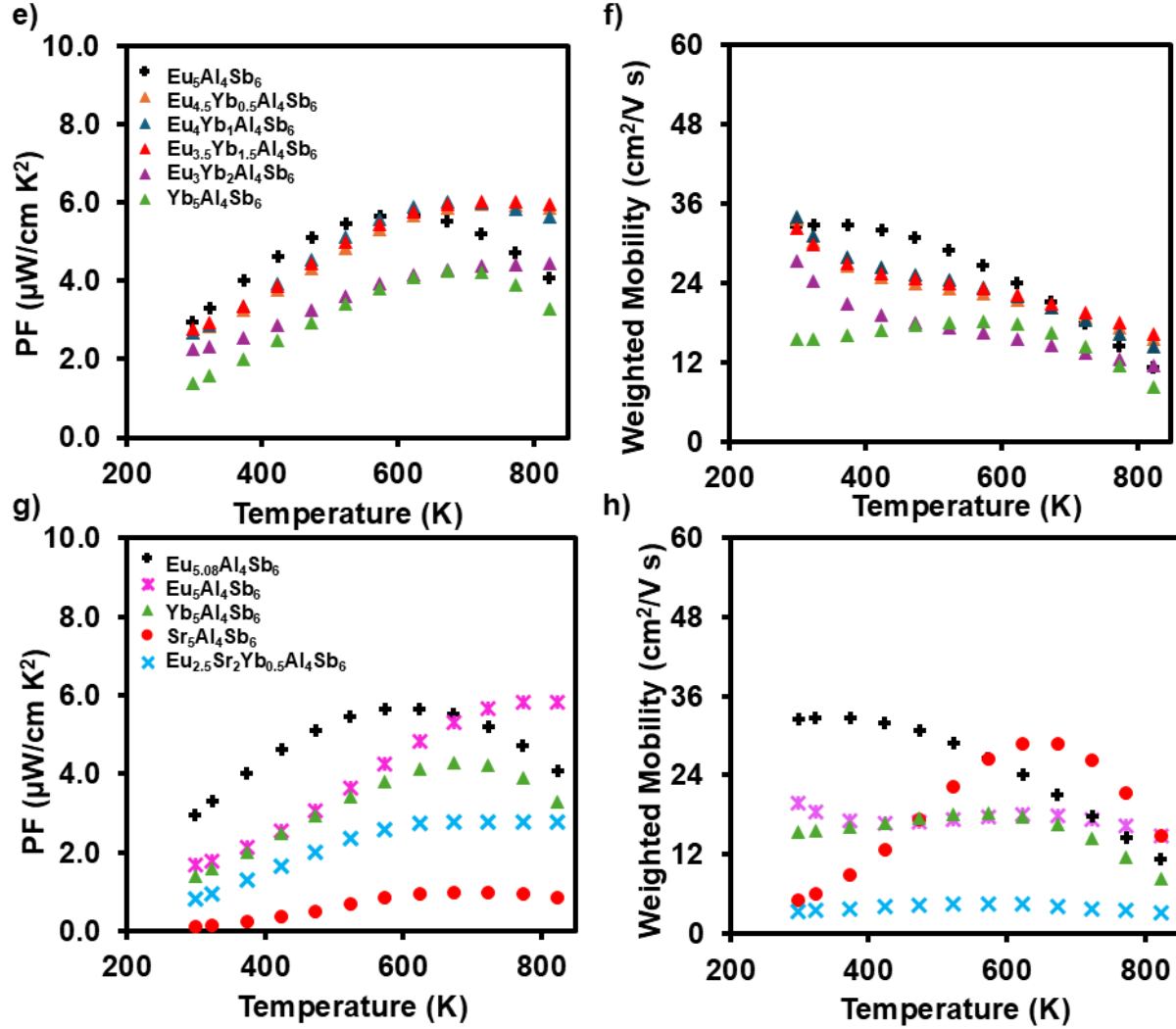


Figure 13. Temperature-dependent electronic transport properties of $\text{A}_5\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Eu}, \text{Sr}, \text{Yb}$) and the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ system. (a) Carrier concentration of the Sr solid solutions ($x = 0.5, 2.5$) compared to $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$. (b) Hall mobility of the Sr solid solutions ($x = 0.5, 2.5$) compared to $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$. (c, e, g) Power factor for the Sr, Yb, and $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$, respectively. (d, f, h) Weighted mobility for the Sr, Yb, solid solutions and the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$, respectively.

Figure of Merit:

The thermoelectric figure of merit, zT , for the $\text{A}_5\text{Al}_4\text{Sb}_6$ compounds and the Eu/Sr/Yb triple-cation system provides a direct measure of how their transport properties combine to determine overall performance. In **Figure 14**, the relative figure of merit (zT) values for the Sr- and Yb-substituted solid solutions, as well as the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ compound, are

compared. **Figure 14d** highlights the compositions that exhibit the most promising performance. As reported previously, $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ reached zT values of 0.6 at 773 K and 0.8 at 873 K, respectively.¹⁶ For the Sr solid solution, zT generally decreases as the series progresses toward the Sr-rich end member $\text{Sr}_5\text{Al}_4\text{Sb}_6$. However, the $x = 0.5$ composition stands out, achieving a zT of 0.62 at 773 K. This improvement is attributed to a slightly higher carrier concentration, which enhances electrical transport. At the same time, Sr substitution reduces lattice thermal conductivity through alloy scattering. Together, these effects preserve the Seebeck and resistivity values while reducing the overall thermal conductivity, resulting in an improved zT . In contrast, the Yb solid solution displays the opposite trend relative to its Sr-substituted counterpart. In the Yb solid solution, zT initially increases across compositions from $x = 0.5$ through $x = 2$, reaching values at 873 K of 0.80 and 0.68, respectively. These values all surpass the 0.6 observed for $\text{Eu}_5\text{Al}_4\text{Sb}_6$ at 773 K, highlighting the beneficial effect of partial Yb substitution at elevated temperatures. Above 873 K, most Yb-containing samples show a characteristic downturn in zT . The fully substituted analogue $\text{Yb}_5\text{Al}_4\text{Sb}_6$ reaches a maximum zT of 0.3 near 600 K—lower than the partially substituted compounds but still indicative of potential for further optimization. In contrast, the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ phase benefits from the small Yb addition, which reduces bipolar conduction and shifts the onset of the downturn from 773 K to a higher temperature of 873 K. This compound achieves a maximum zT of 0.5 at 873 K, and its ability to avoid the high-temperature downturn highlights its potential stability and competitiveness for thermoelectric applications at elevated temperatures. Overall, the results demonstrate that targeted substitution with either the more ionic Sr or the more covalent Yb significantly influences transport and thermoelectric behavior.

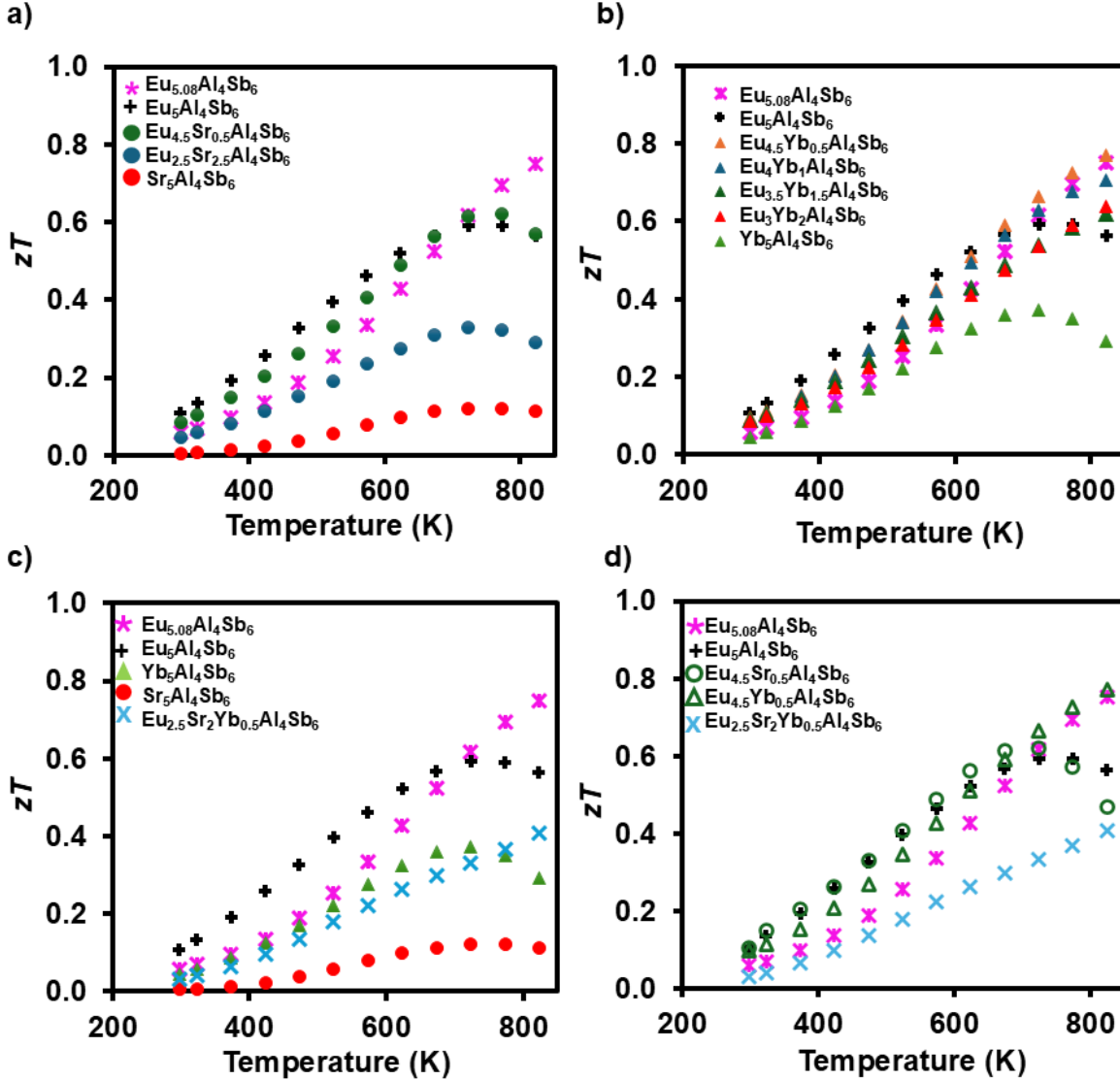


Figure 14. Temperature-dependent thermoelectric figure of merit (zT) for $A_5Al_4Sb_6$ ($A = \text{Eu}, \text{Sr}, \text{Yb}$) and the Eu/Sr/Yb triple-cation system. (a) Sr solid solution, (b) Yb solid solution, and (c) $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ triple-cation compound. (d) Comparison of the most promising zT values with $\text{Eu}_5\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$.

Summary

Single crystals of the Eu–Yb solid solution were successfully grown using Sn flux according to the stoichiometry $\text{Eu}_{5-x}\text{Yb}_x\text{Al}_3\text{Sb}_6$. Polycrystalline synthesis was necessary to obtain the full Yb analog of $\text{Eu}_5\text{Al}_3\text{Sb}_6$ due to competing ternary phases. Single-crystal X-ray diffraction revealed that these compounds crystallize in the monoclinic crystal system with a $C2/m$ space group, consistent with the parent $\text{Eu}_{5.08}\text{Al}_3\text{Sb}_6$ and previously reported $\text{Eu}_{5.08-x}\text{Sr}_x\text{Al}_3\text{Sb}_6$ solid

solutions.^{3,15} Bulk polycrystalline synthesis enabled measurement of transport properties for $\text{Eu}_{5-x}\text{A}_x\text{Al}_4\text{Sb}_6$ ($\text{A} = \text{Sr}; x = 0.5, 2.5, 5.0$; $\text{A} = \text{Yb}; x = 0.5, 1.0, 1.5, 2.0, 5.0$) and the pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ phase. All compositions exhibit low total and lattice thermal conductivity ($<1 \text{ W m}^{-1} \text{ K}^{-1}$), with a clear trend of decreasing values in the Sr series and increasing values in the Yb series. Sr substitution (more ionic) shifts the system toward a pseudo-gap regime, increasing resistivity while boosting the Seebeck coefficient; Yb substitution (more covalent and smaller cation) yields a more metallic response with lower $|S|$. Power factors show promise with values of $0.3\text{--}5 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for the Sr series, $1\text{--}6 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for the Yb series, and around $3 \mu\text{W cm}^{-1} \text{ K}^{-2}$ for the quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ compound. More importantly, the figure of merit (zT) reveals clear advantages based on the choice of A-site cation. The Sr $x = 0.5$ composition reaches a zT of 0.62 at 773 K, comparable to $\text{Eu}_5\text{Al}_4\text{Sb}_6$ ($zT = 0.6$ at 773 K), while the Yb solid solution improves zT across $x = 0.5\text{--}2$, attaining 0.80, 0.71, 0.64, and 0.68 at 873 K.¹⁶ Notably, Yb $x = 0.5$ is similar to $\text{Eu}_{5.08}\text{Al}_4\text{Sb}_6$ (0.8 at 873 K).¹⁶ The pseudo-quinary $\text{Eu}_{2.5}\text{Sr}_2\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ phase further reduces the downturn in zT seen in the ternary and quaternary analogs, reaching 0.5 at 873 K without signs of saturation. The choice of A-site cation plays a crucial role in fine-tuning the balance between electronic transport, scattering mechanisms, and thermal transport. Further efforts are needed to better understand how substitutions impact the properties of $\text{Eu}_5\text{Al}_4\text{Sb}_6$. A goal is to further improve the power factor, aiming to match the thermoelectric performance of established half-Heuslers phases while maintaining the much lower thermal conductivity.

Supporting Information

Tables of X-ray data-collection and refinement parameters; Rietveld plots from powdered crystals; Table of Rietveld refinement for polycrystalline $\text{Eu}_{4.5}\text{Yb}_{0.5}\text{Al}_4\text{Sb}_6$ and $\text{Eu}_{4.5}\text{Sr}_{0.5}\text{Al}_4\text{Sb}_6$ samples, Table of bond distances of $\text{Yb}_5\text{Al}_4\text{Sb}_6$, SEM/EDS maps for a $\text{Eu}_{4.24}\text{Yb}_{0.84}\text{Al}_3\text{Sb}_6$ single crystal; lattice thermal-conductivity data, and plots of reproducibility of electrical and Seebeck transport measurements (PDF).

Accession Codes:

Deposition Numbers 2498312, 2498314, 2498315, 2498316, and 2498317 ($x = 0.84, 1.42, 1.79$, and 1.2) and ($x = 0.48, y = 2.03$) contain the supplementary crystallographic data for this paper.

These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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