Supplemental Information for Impact of Bi substitution on the mobility and figure of merit in Eu₂ZnSb_{2-x}Bi_x alloys

Microprobe:

The chemical composition of the target phases was determined by electron probe micro-analysis (EPMA) with wavelength dispersive X-ray spectroscopy (WDS) using a JEOL JXA-8200 system. EPMA results are shown in Figure SI.1. Results suggest significant agreement with nominal compositions. It is important to take the results in Table SI.1 with a grain of salt as the slight deviations from the nominal charge-balanced composition do not agree with the defects per unit cell (u.c.) reflected in the carrier concentration ($2.3x10^4$ for Eu₂ZnSb₂ and 0.028 defects/u.c. for Eu₂ZnBi₂).

Table SI.1. Microprobe compositions normalized to Sb or Bi = 2.

Nominal composition	WDS composition
Eu ₂ ZnSb ₂	$Eu_{2.08(8)}Zn_{0.99(2)}Sb_2$
Eu ₂ ZnBi ₂	$Eu_{2.13(9)}Zn_{0.98(8)}Bi_2$

Powder X-ray diffraction patterns:

The powder XRD patterns of the $Eu_2ZnSb_{2-x}Bi_x$ series, shown in Figure SI.1, suggests that the samples are single phase, with the exception of small impurity peaks (< 5%) identified as $EuZn_2Pn_2$. Shifts to lower angles observed in the major peaks for Bi containing samples suggests Bi is substituting onto the Sb-site.



Figure SI.1. Powder X-ray diffraction patterns of $\text{Eu}_2\text{ZnSb}_{2-x}\text{Bi}_x$ (x = 0, 0.25, 1, 2) samples show the increasing unit cell volume. Very small peaks belonging to EuZn_2Pn_2 (Pn = Sb, Bi) were observed, most prominently in the sample with x = 0.25 at ~34 degrees.

Pair Distribution Function Analysis:

Powder Eu₂ZnSb_{2-x}Bi_x samples with x = 0.25, 1.00, and 2.00 were measured at beamline 11-ID-C at the Advanced Photon source using X-rays with a wavelength of 0.1174 Å. Scattered intensities were recorded with a 2D detector up to a wave vector of q = 25 Å⁻¹. The experimental diffraction patterns were converted into the atomic pair distribution functions (PDFs) illustrated in Figure SI.2.



Figure SI.2. Powder X-ray diffraction patterns of $Eu_2ZnSb_{2-x}Bi_x$ (x = 0.25, 1, 2) samples were collected at APS and converted into atomic pair distribution functions (circle markers). The fits shown in red utilize the nominal structure with space group $P6_3/mmc$. This structure model provides a reasonable fit to the experimental PDFs but fails to capture features that can be observed in Figure 2b-c in the main text.

Structure models:

DFT calculations were used to relax the atomic positions in several candidate super structures with ordered Zn vacancies, including the *Pmma* structure suggested by Bobev et al. in ref.¹ Note: there is no evidence of *long range* ordering in this structure, which means that none of the proposed ordering schemes in Figure SI.3 represent the long range periodic structure of Eu_2ZnPn_2 . However, the reduced symmetries allow for variation in atomic positions, and thus bond length and angle distortions, which help explain the local disorder that can be observed in the PDF data.

The structure in Figure SI.3a) assumes all Zn atoms reside in alternating layers. This yields the worst agreement with the PDF data, and the energy of this structure was above the convex hull, indicating that it is not a stable structure. The other three models SI.3b-d) have energies below the convex hull, which suggests that they are more stable. After relaxing the atomic positions in these structure models, we found that there is very little variation in the Zn-Bi bond lengths, but the Zn-Bi bond angles within the hexagonal layers (nominally 120 degrees) vary significantly. Ultimately, the model shown in Figure SI.3d) agrees best with the experimental PDF data because the lower symmetry also allows the planar hexagonal layers to corrugate slightly, leading to variation of the out-of-plane Zn-Bi distances.



Figure SI.3. Comparison of structure models for Eu_2ZnBi_2 with ordered Zn vacancies. The Zn atoms are shown in cyan, Bi orange, and Eu dark teal. The energy of the structure in a) lies above the convex hull, while the three structures shown in b-d) have energies below the convex hull, indicating higher stability.

Lattice Thermal conductivity of Eu₂ZnBi₂:

The SPB generated Lorenz number (L_{SPB}), which is used to calculate the electronic thermal conductivity (κ_e) via the Weidman-Franz law, results in unrealistic negative lattice thermal conductivity (κ_L) values when subtracting κ_e from the experimental total thermal conductivity ($\kappa = \kappa_e + \kappa_L$). Though it is still unclear what a valid model for *L* would be in the case of Eu₂ZnBi₂, if we take the Cahill κ_{min} to be a reasonable estimate for κ_L , Figure SI.4 suggests *L* is nearly the average of the intrinsic limit and L_{SPB} .



Figure SI.4. The total experimental thermal conductivity of Eu₂ZnBi₂ is shown by the symbols. The three solid curves show the values of κ_L that are obtained under different assumptions for the Lorenz number (*L*). We tested the intrinsic and metallic limits ($L = 1.5 \times 10^{-8}$ and 2.44 $\times 10^{-8}$ W/K² respectively) as well as the values obtained from an SPB model.

Bibliography

 Wilson, D. K.; Saparov, B.; Bobev, S. Synthesis, Crystal Structures and Properties of the Zintl Phases Sr2ZnP2, Sr2ZnAs2, A2ZnSb2 and A2ZnBi2 (A = Sr and Eu). *Zeitschrift für Anorg. und Allg. Chemie* 2011, 637 (13), 2018–2025.