Supporting Information

Single parabolic band transport in p-type $EuZn_2Sb_2$ thermoelectrics

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Optical band gap (E_{opt}) involves a contribution due to the Burstein-Moss effect when the carrier concentration is high. According to $E_{opt} = E_g + (1 + \frac{m_c^*}{m_v^*})\xi$, where m_c^* and m_v^* are the conduction and valence band effective masses respectively, and ξ is the electrochemical relative to the valence band edge, E_{opt} increases by an additional term $(1 + \frac{m_c^*}{m_v^*})\,\xi$[1]. According to the SPB model, ξ for pristine $EuZn_2Sb_2$ here is about 0.065 eV at room temperature. This leads to an estimation of band gap (E_g) of ~0.45 eV if the effective masses for conduction and valence bands are identical.

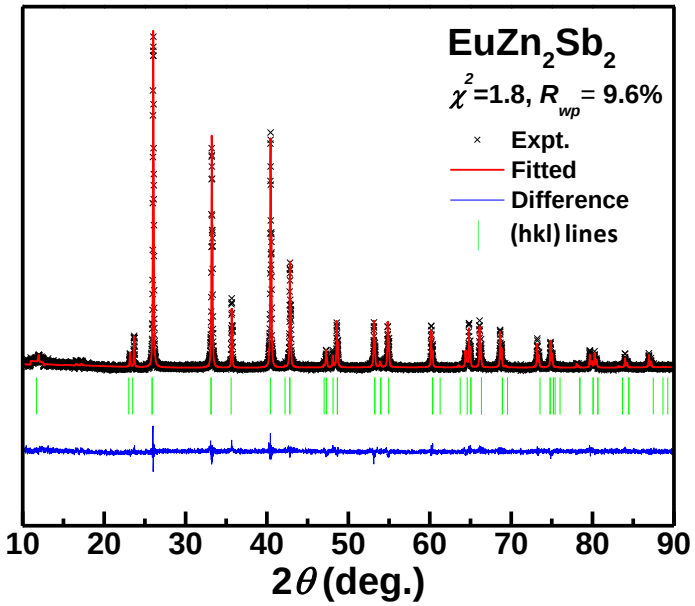

Fig. S1. XRD pattern with a Rietveld refinement for $EuZn_2Sb_2$ including profile fit, profile difference and profile residual (χ^2 and R_{wp}).

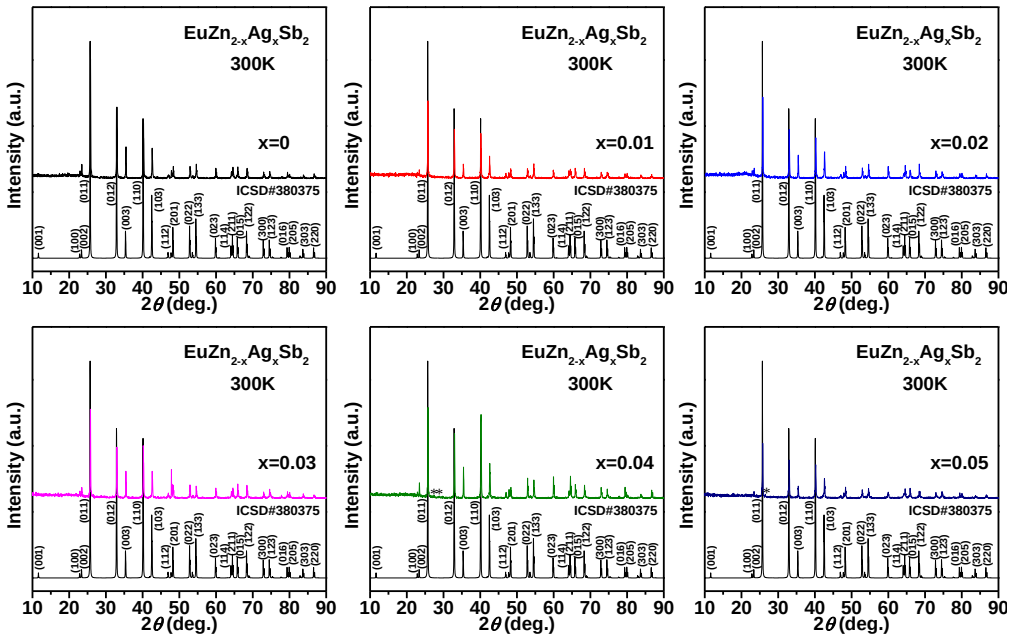

Fig. S2. XRD patterns for $EuZn_{2-x}Ag_xSb_2$ ($x \leq 0.05$)

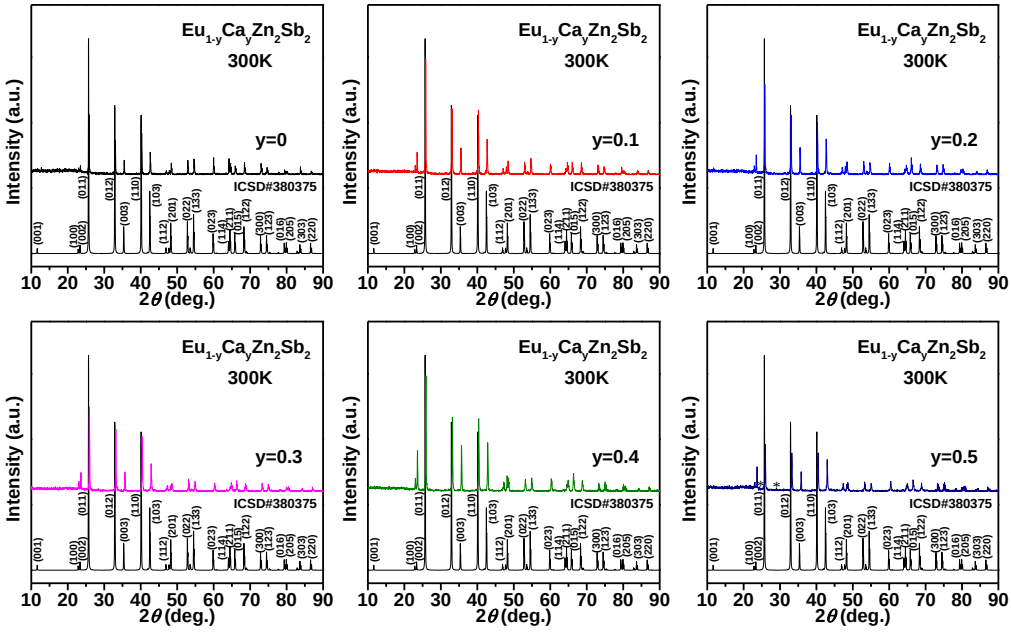

Fig. S3. XRD patterns for $EuZn_{2-x}Ag_xSb_2$ ($x \leq 0.05$)

To understand the lattice thermal conductivity (κ_L) for $EuZn_{2-x}Ag_xSb_2$, a point defect scattering model is developed using a pseudocubic approximation. In the solubility region ($x \leq 0.03$), the κ_L-reduction can be well understood by the model. With a further increase in x, a slight further reduction in κ_L is observed, presumably due to the existence of ZnSb secondary phase (Fig. S1 and S2).

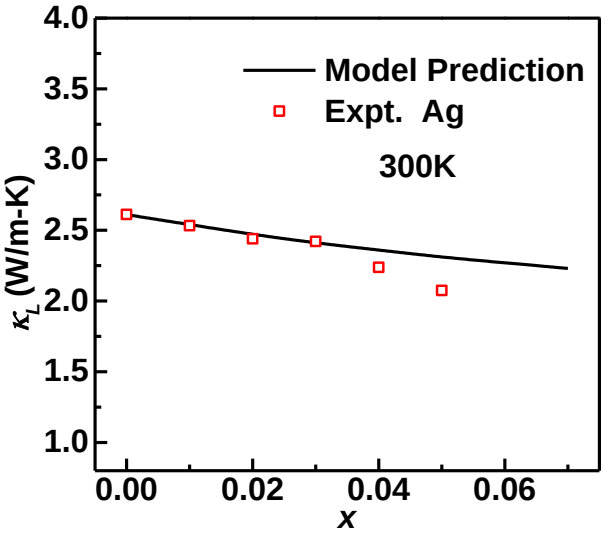

Fig. S4. Composition dependent lattice thermal conductivity for $EuZn_{2-x}Ag_xAb_2$ at room temperature

Below shows the details about the Debye-Callaway model. Phonon scattering by point defects relies on the mass $(\frac{\Delta M_i}{M})$ and strain $(\frac{\Delta \delta_i}{\delta})$ fluctuations between the host and guest atoms. Considering the crystal structure of $EuZn_2Sb_2$ is non-cubic, we model this material system by a pseudocubic approximation [as shown in equation (9)].

Table S1. The equations[2-4] used for the Debye-Callaway model in this work

$\frac{\kappa_L{}^{\mathrm{cal}}}{\kappa_L{}^{\mathrm{alloy}}} = \frac{\arctan(\mu)}{\mu}$	(1)
$\kappa_L{}^{\mathrm{alloy}} = y_i\kappa_L{}^{\mathrm{CaZn2Sb2}} + (1-y_i)\kappa_L{}^{\mathrm{EuZn2Sb2}}$	(2)
$\mu^2 = \frac{\pi^2\theta_D\Omega}{hv^2}\kappa_L{}^{\mathrm{alloy}}\Gamma_{\mathrm{exp}}$	(3)
$\Gamma_{\mathrm{exp}} = \sum_i y_i(1-y_i)[(\frac{\Delta M_i}{M})^2+\varepsilon(\frac{\Delta\delta_i}{\delta})^2]$	(4)
$\Delta M_i = M_{Eu} - M_{Ca}$	(5)
$M = y_i\ M_{Ca} + (1-y_i)\ M_{Eu}$	(6)
$\Delta\delta_i = \delta_{EuZn2Sb2} - \delta_{CaZn2Sb2}$	(7)
$\delta = y_i\ \delta_{CaZn2Sb2} + (1-y_i)\ \delta_{EuZn2Sb2}$	(8)
$\delta_{CaZn2Sb2} = (V_{CaZn2Sb2})^{1/3}; \delta_{EuZn2Sb2} = (V_{EuZn2Sb2})^{1/3}$	(9)
$\varepsilon = \frac{2}{9}[(G+6.5\gamma)\frac{1+r}{1-r}]^2$	(10)

where $\kappa_L{}^{\mathrm{alloy}}$, $\kappa_L{}^{\mathrm{cal}}$, $\kappa_L{}^{\mathrm{CaZn2Sb2}}$ and $\kappa_L{}^{\mathrm{EuZn2Sb2}}$ are the lattice thermal conductivity of alloy materials, the model prediction, intrinsic $CaZn_2Sb_2$ and $EuZn_2Sb_2$, respectively; θ_D is the Debye temperature; Ω is the volume per atom; h is the Planck constant; v is the average speed of sound; Γ_{exp} is the disorder parameter including the mass $(\frac{\Delta M_i}{M})$ and strain

($\frac{\Delta\delta_i}{\delta}$) components; M_{Eu} and M_{Ca} are respectively the host element mass and guest element mass; $\delta_{EuZn2Sb2}$ and $\delta_{CaZn2Sb2}$ are assumed to the lattice parameters of intrinsic $CaZn_2Sb_2$ and $EuZn_2Sb_2$ by a pseudocubic approximation, respectively; and ε is the strain parameter calculated by the shear moduli (G), Gruneisen parameter (γ) and poisson ratio (r).

References

1. Z. M. Gibbs, A. LaLonde and G. J. Snyder, *New Journal of Physics*, 2013, **15**, 075020.
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