Supplementary Information (SI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2025

## Decoupling Electrical Conductivity and Seebeck Coefficient via Isoelectronic Alloying in 9-4-9-type $Ca_{9-\nu}Eu_{\nu}Zn_{4,7}Sb_{9}$ ( $0 \le y \le 5.0$ ) Zintl Phase

Wenhua Xue, <sup>a,b</sup> Chen Chen, <sup>c</sup> Pengfei Nan, <sup>d</sup> Youwen Long, <sup>a</sup> Binghui Ge, <sup>\*d</sup> Qian Zhang <sup>\*b</sup> and Yumei Wang <sup>\*ae</sup>

- <sup>a</sup> Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
- <sup>b</sup> School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen 518055, China
- <sup>c</sup> School of Physical Sciences, Great Bay University, Dongguan, 523000, China
- <sup>d</sup> Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China
- <sup>e</sup> Beijing Branch of Songshan Lake Materials Laboratory, Beijing 100190, China

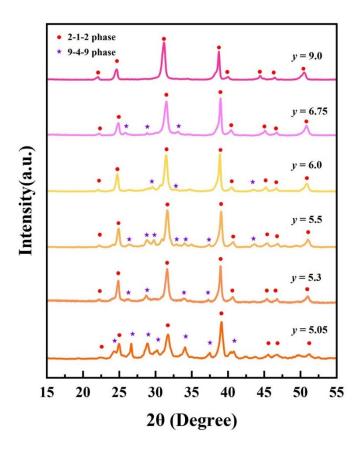


Fig. S1. The XRD patterns for the  $Ca_{9-y}Eu_yZn_{4.7}Sb_9$  (y = 5.05, 5.3, 5.5, 6.0, 6.75) and  $Ca_{9-y}Eu_yZn_{4.41}Sb_9$  (y = 9.0) samples.

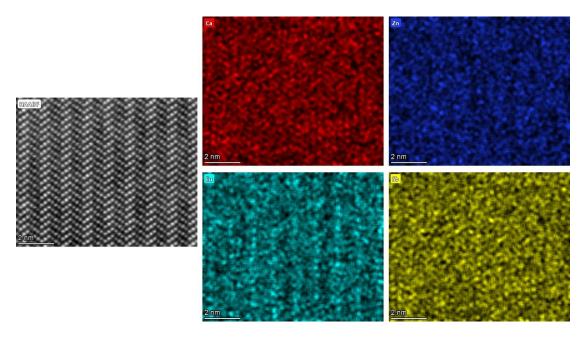


Fig. S2. The EDS mapping of the "intergrowth" structure in  $Ca_{9-y}Eu_yZn_{4.7}Sb_9$  (y = 5.05).

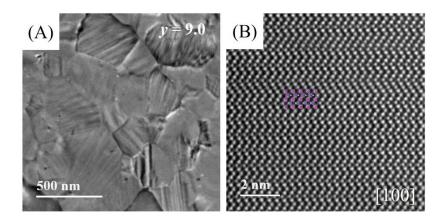


Fig. S3. (a) Low-magnification TEM image and (b) corresponding HAADF-STEM image for  $Ca_{9-y}Eu_yZn_{4.41}Sb_9$  (y = 9.0).