Supplementary Information:

Contrasting roles of small metallic elements M (M=Cu, Zn, Ni) in enhancing the thermoelectric performance of n-type $PbM_{0.01}Se$

Xin Qian,[a] Dongyang Wang,[a] Yang Zhang,[b] Haijun Wu,[b,*] Stephen J. Pennycook,[b] Lei Zheng,[a,*] Pierre F. P. Poudeu,[c,*] Li-Dong Zhao[a,**]

[a] *School of Materials Science and Engineering, Beihang University, Beijing 100191, China.*

[b] *Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore*

[c] *Laboratory for Emerging Energy and Electronic Materials, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, USA.*

Corresponding authors: wu.haijun@u.nus.edu, zhenglei@buaa.edu.cn, ppoudeup@umich.edu, zhaolidong@buaa.edu.cn

Density functional theory (DFT) calculations: First-principles calculation performed using the projector-augmented wave (PAW) method[1], which was implemented in the Vienna Ab-initio Simulation Package (VASP)[2]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)[3] was adopted to describe the exchange-correlation functional. The lattice parameters and atomic coordinates were optimized until the convergence of total energy and interatomic residual force smaller than 10^{-7} eV and 10^{-2} eVÅ^{-1}, respectively. A 4 × 4 × 4 supercell (128 atoms) was constructed to modeling pure and Cu doped PbSe.

The formation energy of the defect is calculated by:[4, 5]

$$\Delta H^f(\alpha,q) = E(\alpha,q) - E(host) + \sum_i n_i(E_i + \mu_i) + q(E_V + E_f + \Delta V) \quad \text{(S1)}$$

where E (α, q) and E(host) refers to the total energy of defect α and charge state q contained supercell and the undoped supercell, respectively. μ_i is the atomic chemical potential of constituent i and E_i is the average energy of element in its most stable crystal. n_i is the number of the component atom i added to ($n_i < 0$) or taken from ($n_i > 0$) the supercell. $q(E_V+E_f+\Delta V)$ is a function of E_f. E_V is the energy level of valence band maximum (VBM) in pristine PbSe. E_f is Fermi level reference to VBM and varies from 0 to band gap (E_g). ΔV is the correction term to align the reference potential between pure and defect contained supercell. This value is acquired by the difference of core energy level between the farthest from defect and the responding atom in pristine PbSe supercell.

References

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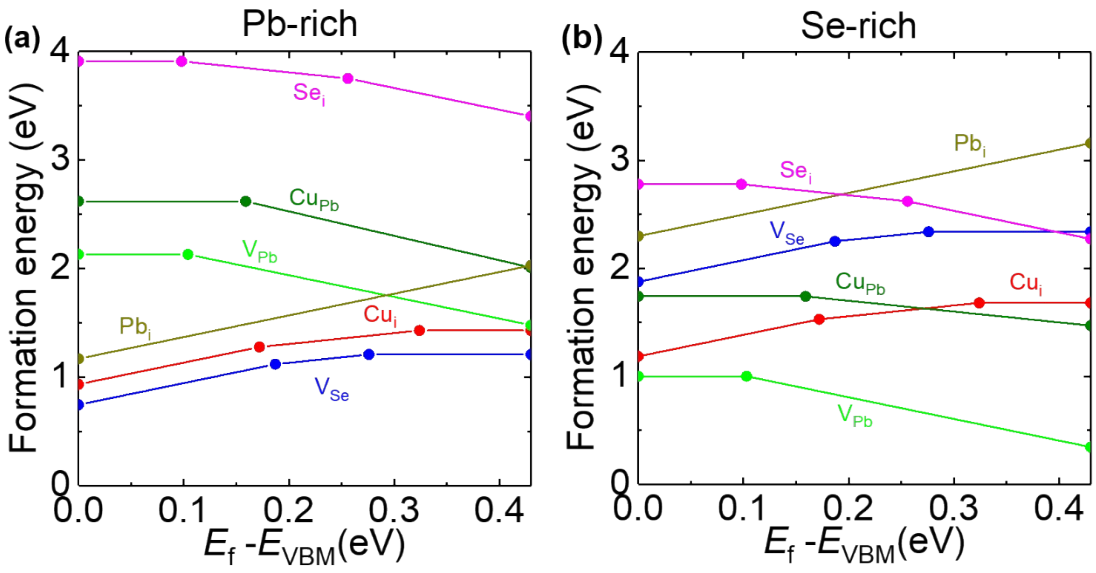

Fig. S1 Formation energies for charged and neutral points defect in PbSe under Pb- and Se-rich conditions. The energy level is reference to the valence band maximum (VBM) of the host. Kinks in the curves refer to the transition energy levels between the different charge states.