

Supplementary Information for:

**Band engineering via biaxial strain for enhanced thermoelectric
performance in stannite-type $\text{Cu}_2\text{ZnSnSe}_4$**

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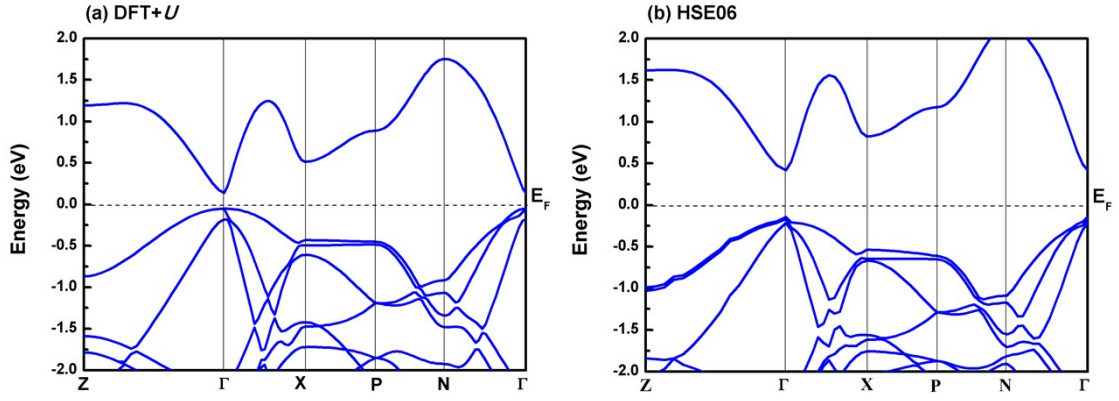


Fig. S1 Calculated band structures near the Fermi energy of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ using different methods. (a) DFT+ U , (b) HSE06. The Fermi levels are set to zero.

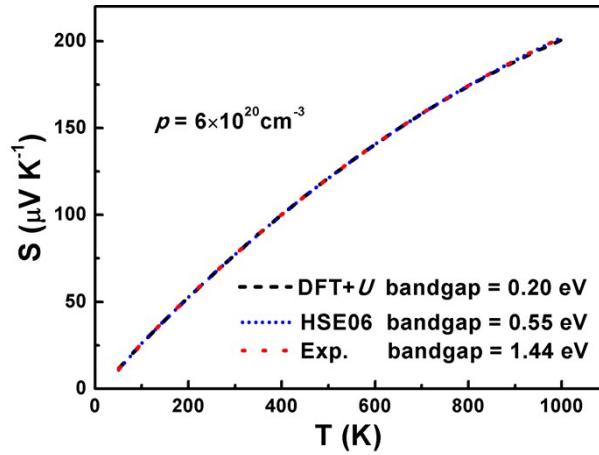


Fig. S2 Calculated Seebeck coefficients of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ using the rigid band approach. The band gaps are set to 0.20 eV, 0.55 eV and 1.44 eV for DFT+ U , HSE06 and experimental value, respectively.

We tested the DFT+ U and HSE06 as the exchange-correlation functional in band structure calculation of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$, as shown in Fig. S1. The results show that the band gaps are 0.19 eV and 0.55 eV for DFT+ U and HSE06 methods, respectively, and the HSE06 method gives a band gap more close to experiment value (1.44 eV). The magnitude of Seebeck coefficients can decrease at high temperature and low doping when the band gap is too small, namely, bipolar transport. Here, we only estimated the highly doped $\text{Cu}_2\text{ZnSnSe}_4$ ($p = 6 \times 10^{20} \text{ cm}^{-3}$). Based on the rigid band approach, we calculated the Seebeck coefficients of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ using different band gaps (see Fig. S2), and the results show that the Seebeck coefficients are irrelevant to the band gaps under this doping concentration, indicating the bipolar transport can be avoided for the doping levels and temperatures that we consider here. On the other hand, we can see from Fig. S1 that the valence band edge structures in the DFT+ U and HSE06 methods are very similar. Based on Semi-classic Boltzmann transport theory, thermoelectric properties of semiconductors are determined by the band edge features. In addition, the DFT(GGA) approach have been used to calculating the transport properties of $\text{Cu}_2\text{ZnSnSe}_4$ in Refs [17,18]. So, it is reasonably to choose DFT+ U method for electrical transport calculations.

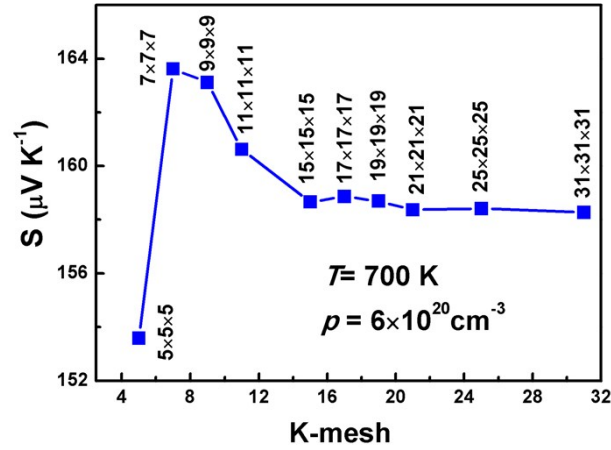


Fig. S3 k -mesh convergence of calculated Seebeck coefficients of unstrained stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ at 700 K with the hole-concentration $p = 6 \times 10^{20} \text{ cm}^{-3}$.

As we can see in Fig. S3, the Seebeck coefficient reaches the convergence precision when the VASP eigenvalues are calculated on a k -grid of $21 \times 21 \times 21$. So, the k -mesh of $31 \times 31 \times 31$ used in the text is dense enough to secure convergence for the doped $\text{Cu}_2\text{ZnSnSe}_4$.

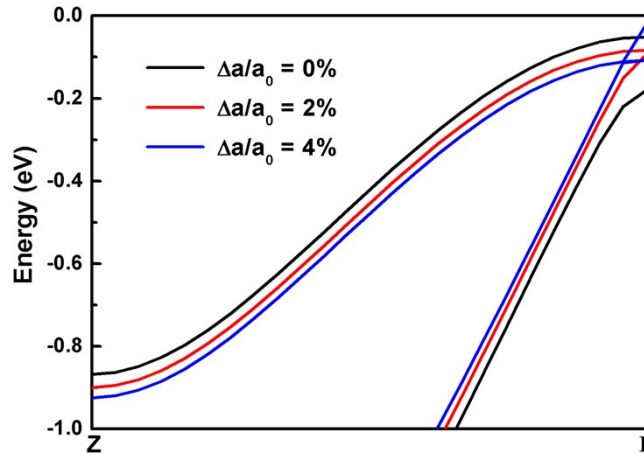


Fig. S4 Calculated band structures along $Z(0.5 \ 0.5 \ -0.5) - \Gamma(0 \ 0 \ 0)$ near the Fermi energy of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ under three typical strains. The Fermi levels are set to zero.

The thermoelectric performance of $\text{Cu}_2\text{ZnSnSe}_4$ is related to degeneracy and the effective mass of electrons. The effective mass is determined by the curvature of the band dispersion. As can be seen from Fig. S4, the curvature of the band dispersion appears to have almost no change under strains, suggesting that the effective mass does not change with strain. Based on Semi-classic Boltzmann transport theory, the thermoelectric properties of $\text{Cu}_2\text{ZnSnSe}_4$ are mainly determined by the band features, not by the band gaps. So, the enhancement of thermoelectric performance of $\text{Cu}_2\text{ZnSnSe}_4$ under strain is mainly determined by the convergence of heavy- and

light-hole bands near the Fermi level, and such phenomena are also discovered in other thermoelectric materials (Refs. [19-24]).

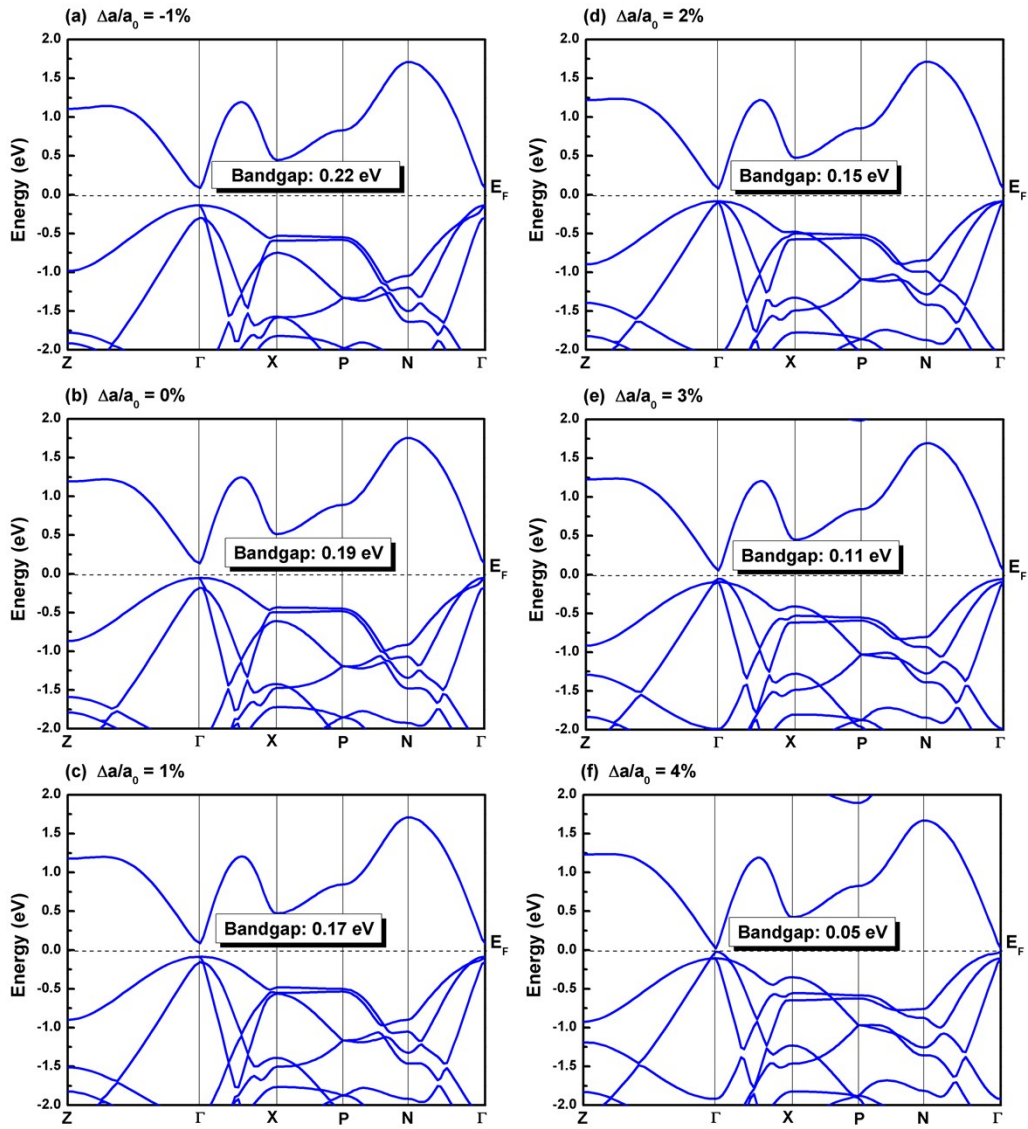


Fig. S5 Calculated band structures near the Fermi energy of stannite-type $\text{Cu}_2\text{ZnSnSe}_4$ under different strains. The Fermi levels are set to zero.