Electronic Supplementary Information

Sulfide bornite thermoelectric material: natural mineral with ultralow thermal conductivity

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Physical parameters calculation details:

The average sound velocity is calculated by

$$v_{avg} = \frac{2\pi\Theta_D k_B}{h(6\pi^2 n)^{1/3}} \qquad (1)$$

where Θ_D is the Debye temperature, k_B is the Boltzmann constant, h is the Planck constant, and n is the number of atoms per unit volume.[1] The Grűneisen parameter, which is a direct measure of the anharmonicity of the bonds in a solid,[2] can be estimated through the relationship[3]

$$\kappa_L = A\frac{M_{avg}\Theta_D^3 \delta}{\gamma^2 n^{2/3} T} \qquad (2)$$

where κ_L is the lattice thermal conductivity, M_{avg} is the average mass of the atoms in the crystal, δ^3 is the volume per atom, n is the number of atoms in the primitive unit cell ($n = 10$ for Cu_5FeS_4), and A is a collection of physical constants ($A = 3.1\times 10^{-6}$ if κ is in $Wm^{-1}K^{-1}$, M_{avg} in amu, and δ in Angstroms).
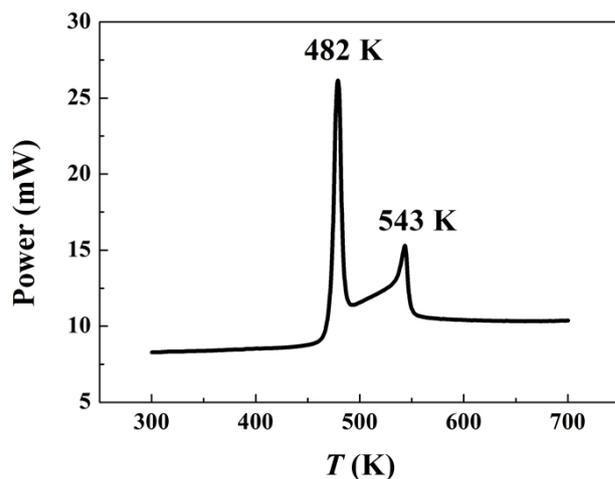
Figure S1. DSC scan profile for bornite Cu_5FeS_4 between 300 and 700 K. The two exothermic

peaks at the temperature of 482 K and 543 K imply the existence of two phase transitions over
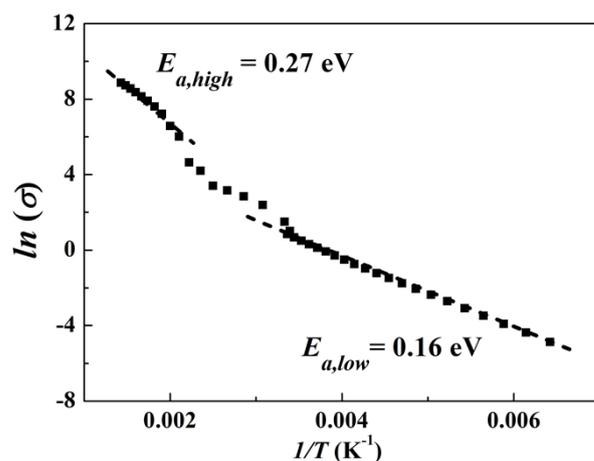
the measured temperature range.

Figure S2. *ln(σ)* as a function of 1/*T* for Bornite. The dashed lines represent the fitting curves

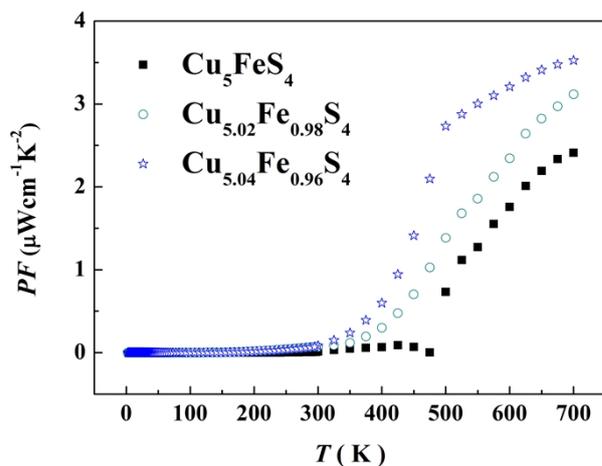using the empirical relation, $\sigma \sim \exp(-E_a/k_BT)$.

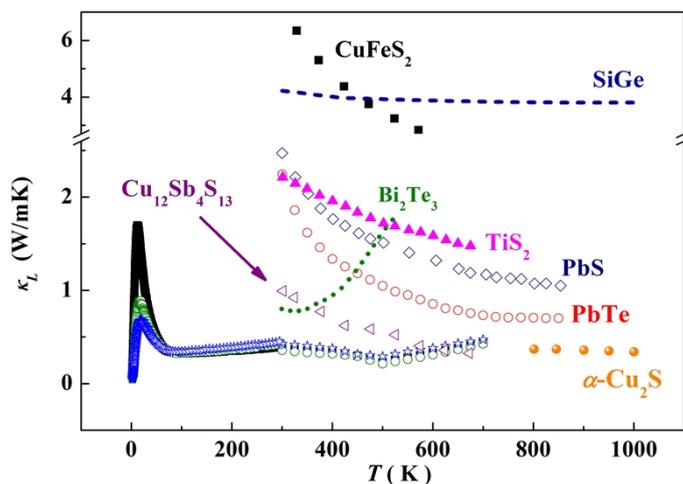Figure S3. Temperature dependence of power factor ($PF = S^2\sigma$) for bornite samples.

Figure S4. Temperature dependence of lattice thermal conductivities of bornite and some state-of-the-art TE materials such as Bi_2Te_3,[4] $PbTe$,[5] and $SiGe$[6] as well as the reported sulfides such as TiS_2,[7] PbS,[8] $CuFeS_2$,[9] $Cu_{12}Sb_4S_{13}$,[10] and α–Cu_2S.[11]
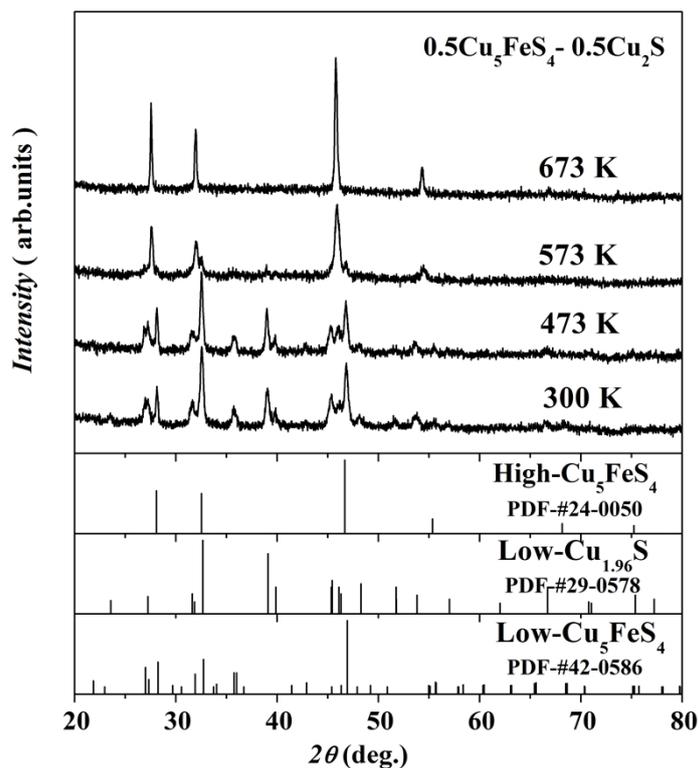
Figure S5. XRD diffraction patterns of $0.5Cu_8S_4$-$0.5Cu_5Fe\square_2S_4$ solid solution collected at 300 K, 473 K, 573 K, and 673 K. At 300 K, the solid solution sample consists of two phases, orthorhombic Cu_5FeS_4 and tetragonal $Cu_{1.96}S$. These two phases gradually transfer to cubic phase when increasing temperature. The diffraction peaks at 673 K for $0.5Cu_8S_4$-$0.5Cu_5Fe\square_2S_4$ solid solution shift to the low angle as compared with those for high cubic phase of Cu_5FeS_4 (PDF-#24-0050) because the lattice parameter of Cu_2S (~ 5.707 Å) is larger than that of Cu_5FeS_4 (~ 5.5 Å).

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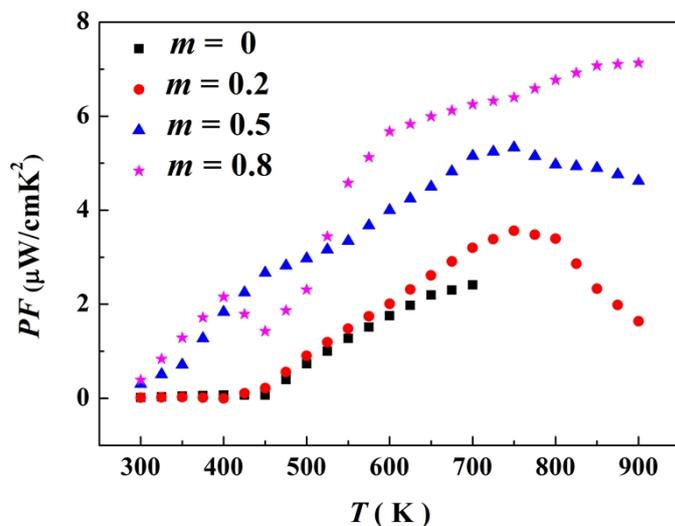
Figure S6. Temperature dependence of power factor ($PF = S^2\sigma$) for mCu$_8$S$_4$-(1-m)Cu$_5$Fe$\square_2$S$_4$ (m = 0, 0.2, 0.5, 0.8).

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