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

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

(1)

where \( \Theta_D \) 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 Grüneisen parameter, which is a direct measure of the anharmonicity of the bonds in a solid,\(^2\) can be estimated through the relationship\(^3\)

\[ \kappa_L = A \frac{M_{\text{avg}} \Theta_D^2 \delta}{\gamma^2 n^{2/3} T} \]  

(2)

where \( \kappa_L \) is the lattice thermal conductivity, \( M_{\text{avg}} \) is the average mass of the atoms in the crystal, \( \delta \)\(^3\) is the volume per atom, \( n \) is the number of atoms in the primitive unit cell (\( n = 10 \) for Cu₅FeS₄), and \( A \) is a collection of physical constants (\( A = 3.1 \times 10^{-6} \) if \( \kappa \) is in Wm⁻¹K⁻¹, \( M_{\text{avg}} \) in amu, and \( \delta \) in Angstroms).
Figure S1. DSC scan profile for bornite Cu$_5$FeS$_4$ 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. $ln(\sigma)$ 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$_2$Te$_3$, PbTe, and SiGe as well as the reported sulfides such as TiS$_2$, PbS, CuFeS$_2$, Cu$_{12}$Sb$_4$S$_{13}$, and $\alpha$-Cu$_2$S.
Figure S5. XRD diffraction patterns of $0.5\text{Cu}_8\text{S}_4-0.5\text{Cu}_5\text{Fe}\square_2\text{S}_4$ 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 $\text{Cu}_5\text{FeS}_4$ and tetragonal $\text{Cu}_{1.96}\text{S}$. These two phases gradually transfer to cubic phase when increasing temperature. The diffraction peaks at 673 K for $0.5\text{Cu}_8\text{S}_4-0.5\text{Cu}_5\text{Fe}\square_2\text{S}_4$ solid solution shift to the low angle as compared with those for high cubic phase of $\text{Cu}_5\text{FeS}_4$ (PDF-#24-0050) because the lattice parameter of $\text{Cu}_2\text{S}$ (~5.707 Å) is larger than that of $\text{Cu}_5\text{FeS}_4$ (~5.5 Å).
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Figure S6. Temperature dependence of power factor ($PF = S^2\sigma$) for $m$Cu$_8$S$_4$-(1-$m$)Cu$_5$Fe□$_2$S$_4$ ($m = 0, 0.2, 0.5, 0.8$).

References


