Supporting Information

Crystal structure and thermoelectric properties of novel quaternary $Cu_2MHf_3S_8$ (M – Mn, Fe, Co, Ni) thiospinels with low thermal conductivity

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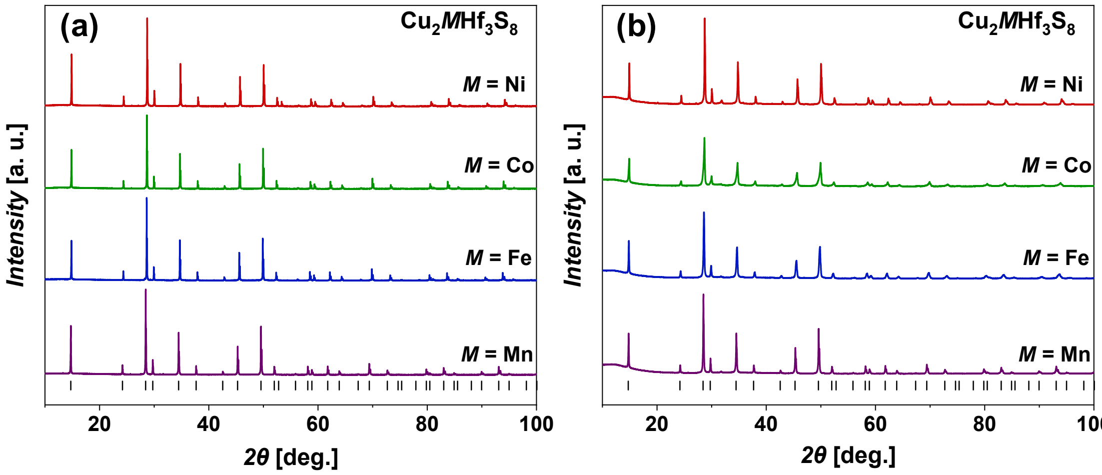

Figure S1. Powder XRD patterns of $Cu_2MHf_3S_8$ samples after synthesis (a) and pellets after measurements (b).

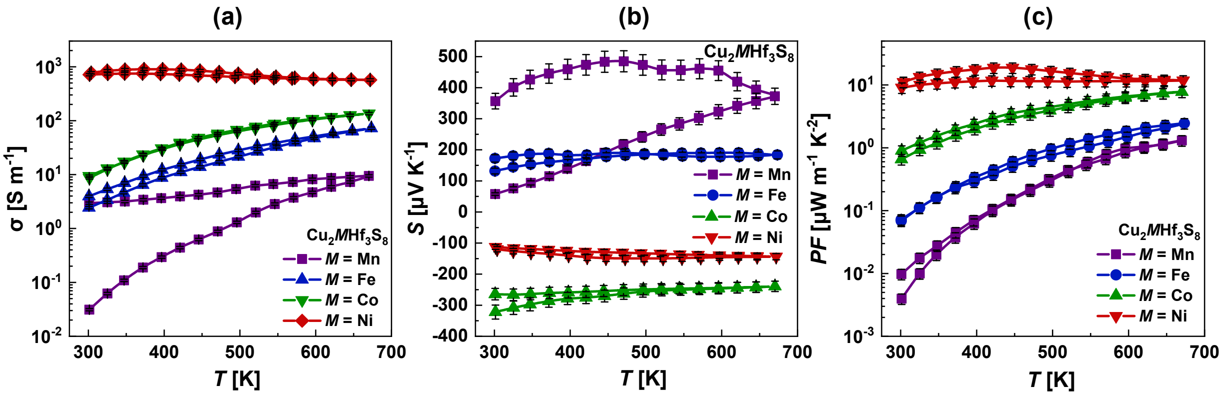

Figure S2. Heating and cooling data of electrical conductivity (a), Seebeck coefficient (b), and thermoelectric power factor *PF* (c) for $Cu_2MHf_3S_8$.

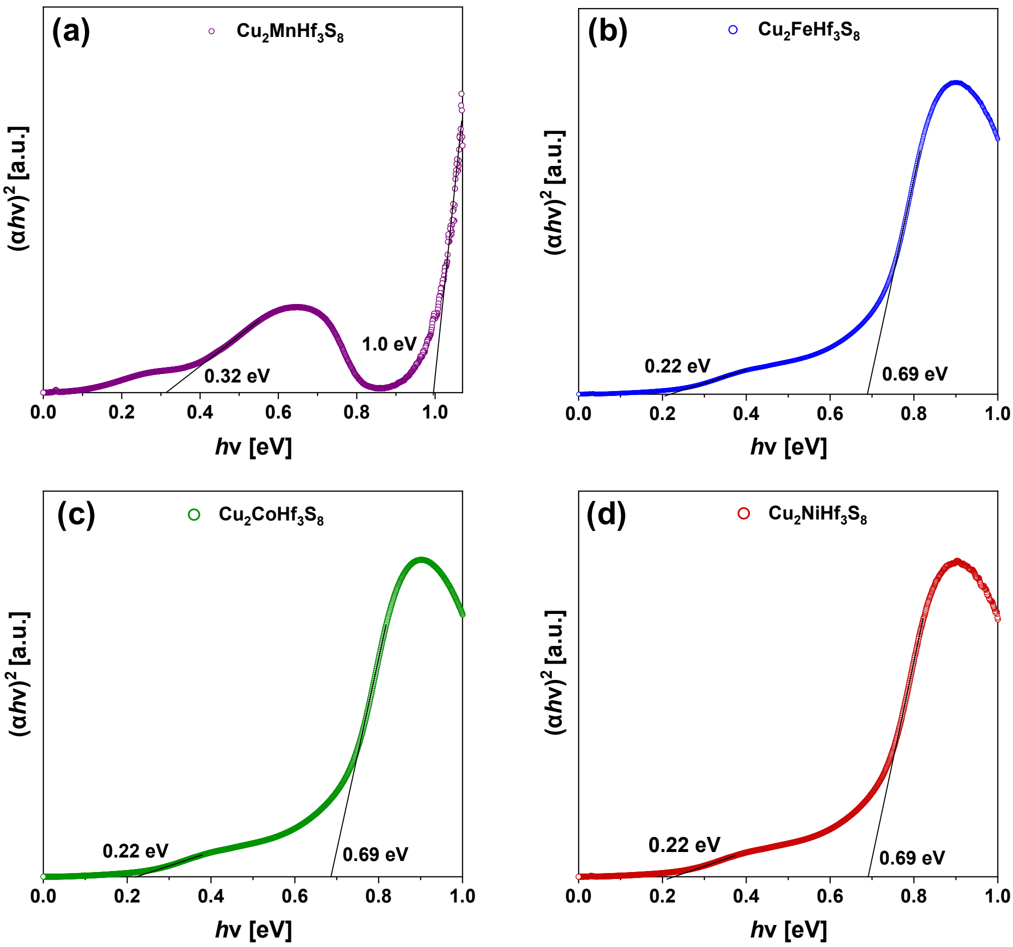

Figure S3. The optical absorption spectra versus photon energy of $Cu_2MHf_3S_8$ (M=Mn, Fe, Co, and Ni) thiospinels at room temperature.

Elastic properties

The bulk modulus was calculated using the following equation [1-3]:

$$B = \rho\left(\upsilon_L^2 - \frac{4}{3}\upsilon_T^2\right). \tag{S1}$$

where ρ is the material density.

The shear modulus was calculated as:

$$G = \upsilon_T^2 \rho. \tag{S2}$$

The Young's modulus is calculated as:

$$E = \frac{9BG}{3B+G}. \tag{S3}$$

The Poisson's ratio is calculated as:

$$\nu = \frac{E-2G}{2G}. \tag{S4}$$

The Debye temperatures were calculated using the following expression [4]:

$$\Theta_D = \frac{h}{k_B}\left[\frac{3n}{4\pi}\left(\frac{N_A\rho}{M}\right)\right]^{1/3} v_m, \tag{S5}$$

where h is Planck's constant, k_B is Boltzmann's constant, N_A is Avogadro's number, M is the molecular weight, n is the number of atoms in the molecule, and v_m is the averaged wave velocity integrated over several crystal directions [5]:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3}+\frac{1}{v_l^3}\right)\right]^{-1/3}, \tag{S6}$$

where v_l and v_t are the longitudinal and transverse sound velocities.

Effect of the difference between the longitudinal and transverse speed of sound on the Grüneisen parameter

Grüneisen parameters γ were calculated using the following equation [5]:

$$\gamma = \frac{3}{2}\left(\frac{1+\nu}{2-3\nu}\right). \tag{S7}$$

where ν is the Poisson ratio. The square of the ratio of the longitudinal and transverse speed of sound $\left(\frac{v_l}{v_t}\right)^2$ can be found using the following equation [5]:

$$\left(\frac{v_l}{v_t}\right)^2 = \left(\frac{2-2\nu}{1-2\nu}\right) \tag{S8}$$

Let us consider that $\alpha = \left(\frac{v_l}{v_t}\right)^2$. Then α is greater if the ratio v_L:v_S is greater. After solving the system of equations (S7) and (S8), we obtain: $\gamma = \frac{\frac{3}{2} + \frac{\frac{3}{2}(2-\alpha)}{2-2\alpha}}{2 - \frac{3(2-\alpha)}{2-2\alpha}}$. After plotting the derivative $\frac{d\gamma}{d\alpha}$ and analyzing this dependence we have found that it is an increasing function over the interval (1; 10) ($\alpha < 1$ is not considered because it would mean that $v_L < v_T$, the values of $\alpha > 10$ were not considered as $v_L > \sqrt{10}\, v_T$ is very unlikely). The performed analysis indicates that γ increases with increasing α, therefore γ increases with increasing $\frac{v_l}{v_t}$ ratio.

Thermal transport properties

From the kinetic theory, the lattice thermal conductivity is expressed as [6]:

$$\kappa_{lat} = \frac{1}{3} C_V v_m l_{ph} \tag{S9}$$

where κ_{lat} is experimental lattice thermal conductivity, C_V is the specific heat at constant volume, v_m is the average sound velocity. Considering this, the phonon mean free path can be calculated using the following equation [7]:

$$l_{ph} = \frac{3\kappa_{lat}}{C_V v_m} \tag{S10}$$

For the calculation of l_{ph} at 298 K, the κ_{lat} was assumed equal to the measured κ due to very low electrical conductivity ($\sigma < 10$ S/cm), specific heat capacity was estimated using the Dulong-Petit approximation, and average sound velocity was obtained from the acoustic data of longitudinal v_l and transverse v_t sound velocities using Equation S9.

References

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