Equations for the Debye-Callaway model

We applied the Debye-Callaway model for the thermal conductivity, including all the possible scattering mechanisms [7–9] **in the form:**

$$\kappa_l = \frac{1}{3}\int_0^{\omega_{max}} C_s(\omega) v_g(\omega)^2 \tau(\omega) d\omega$$

Where the maximum phonon frequency is given by

$$\omega_{max} = \left(\frac{6\pi^2}{V}\right)^{1/3} v_{sound}$$

Being V the volume of the unit cell, and v_{sound} the average speed of sound between longitudinal and transverse modes. Here, the phonon group velocity is approximated as the speed of sound, i.e., $v_g(\omega) = v_{sound}$. At high temperatures, the spectral heat capacity ($C_s(\omega)$) can be approximated as:

$$C_s(\omega) = \frac{3k_B\omega^2}{2\pi^2 v_{sound}^3}$$

k_B is the Boltzmann constant. The phonon relaxation time is modelled by a combination of Umklapp (τ_U), grain-boundary (τ_{GB}), and point defects (τ_{PD}) in the form

$$\tau^{-1} = \sum_i \tau_i^{-1}$$

Umklapp scattering models the phonon scattering by the following frequency dependency:

$$\tau_U(\omega) = \frac{(6\pi^2)^{1/3}}{2} \frac{\bar{M} v_{sound}^3}{k_B V^{1/3} \gamma^2 \omega^2 T}$$

Where $\bar{M}$ is the average atomic mass and γ the Gruneisen parameter. Grain-boundary scattering is governed by the following relaxation time:

$$\tau_{GB} = \frac{d}{v_{sound}}$$

Where d is the SEM or XRD particle/domain size.

Point defects are modelled with both mass (m_i) and atomic radius (r_i) fluctuations residing on site with average mass and radius $\bar{m}$ and $\bar{r}$, respectively:

$$\tau_{PD} = \frac{V\omega^4}{4\pi v_{sound}^3}\left[\sum_i f_i\left(1 - \frac{m_i}{\bar{m}}\right)^2 + \sum_i f_i\left(1 - \frac{r_i}{\bar{r}}\right)^2\right]$$

The fluctuation is modelled by the occupancy fraction f_i. Because the EDS data shows sulphur loss, we decided to model just the effect of vacancies as point defects. We neglect other point

defects (such as Cu-Zn disordered) since their scattering potential is smaller than that of vacancies. In this case, the effects of strain given by the second summation in the equation above are therefore considered null. Since the mass of the vacancies is zero ($m_i = 0$), the equation can be reduced to:

$$\tau_{PD} = \frac{V\omega^4}{4\pi v_{sound}^3}\left[\sum_i f_i\right]$$

This methodology was implemented in a simple Python code. In order to fit the results, an additional scaling factor was used to multiply the lattice thermal conductivity and was freely adjusted to a better fit.

Debye-Callaway modelling

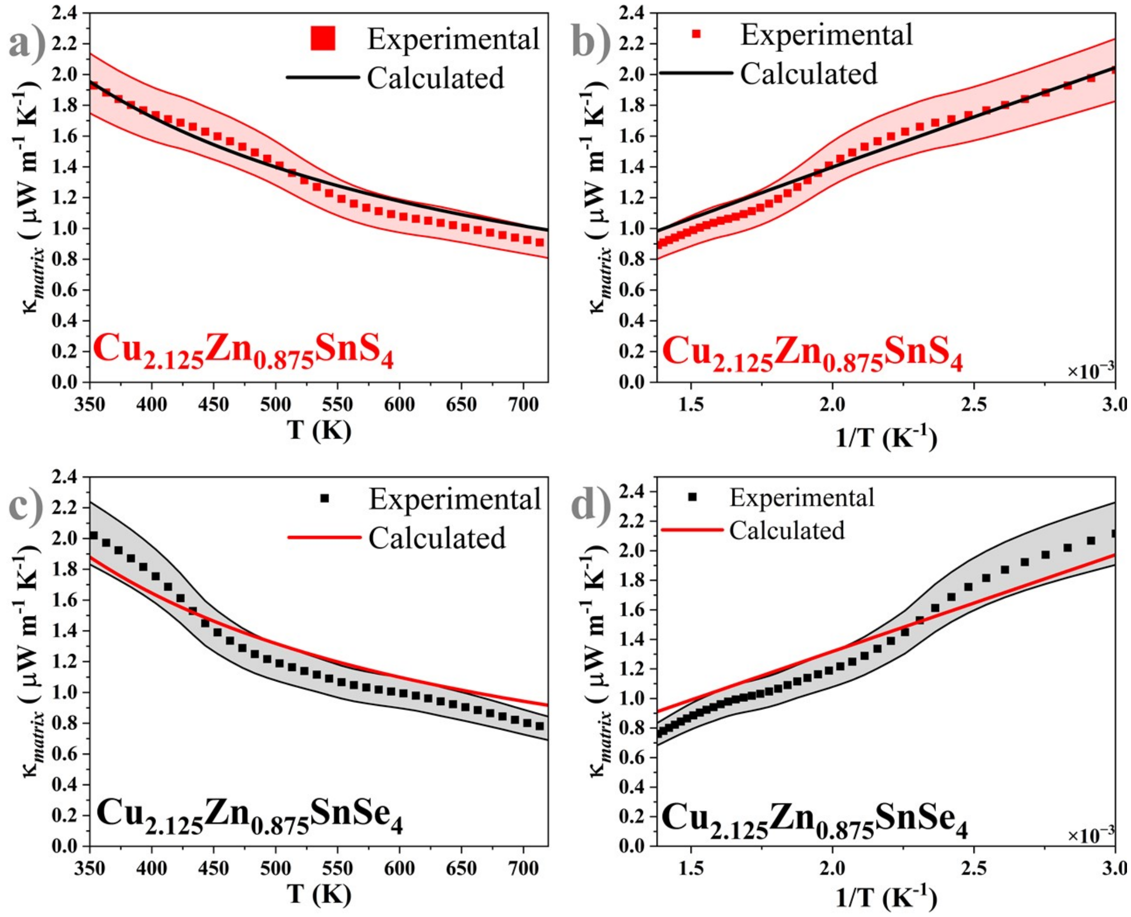

Figure R 1. Matrix thermal conductivity as a function of temperature (a) and inverse temperature (b) for CZTSe. The same is true for the CZTSe sample, in items (c) and (d). The symbols correspond to the experimental data, and the solid lines are the Debye-Callaway model. Continuous lines around the experimental values correspond to the errors in the measurement.

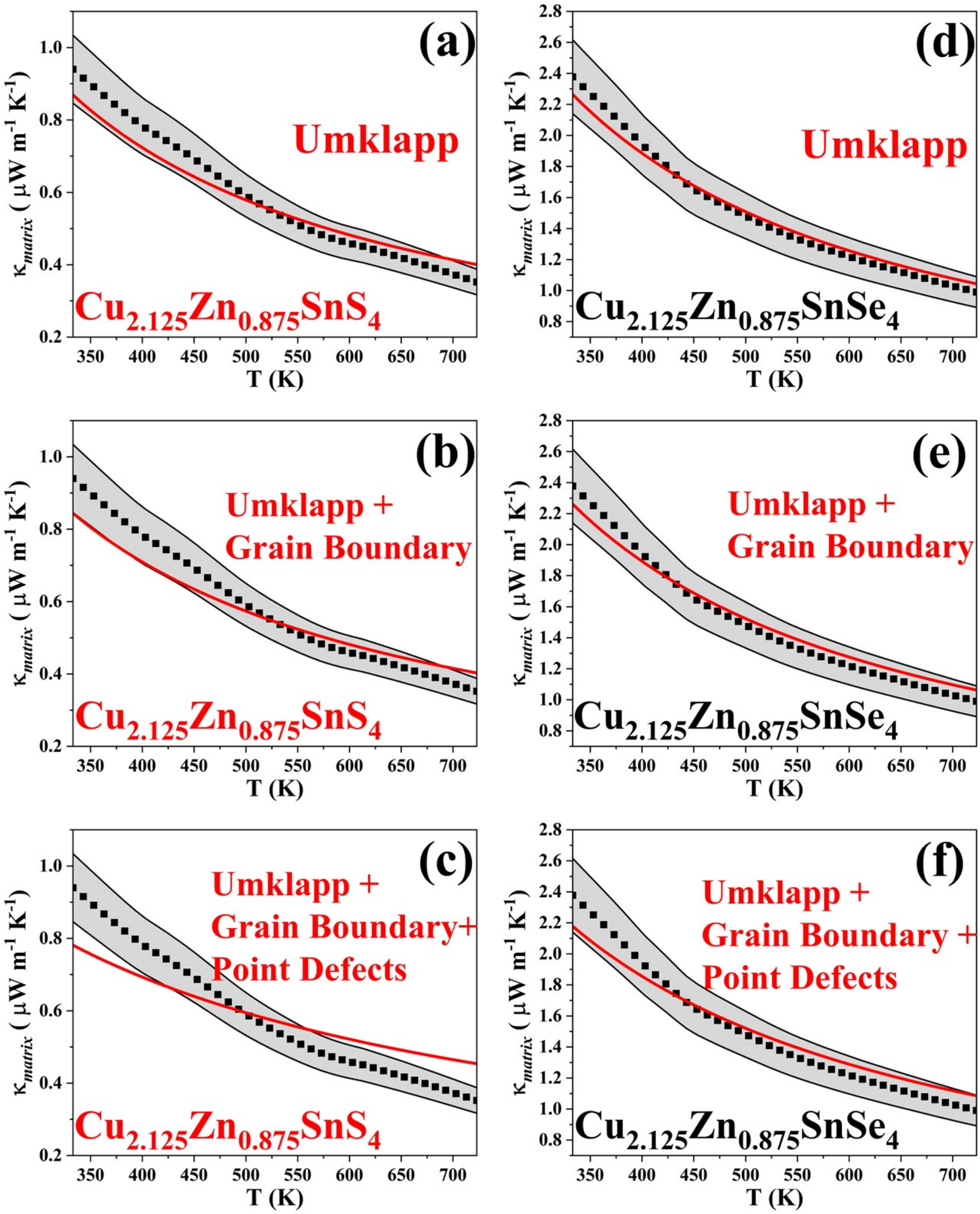

Figure R 2. Matrix thermal conductivity as a function of temperature for CZTS (a-c) and CZTSe (d-f). The models used to fit the Debye-Callaway model are given in red within the plots.