Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.


## Calculation of Lorentz constant

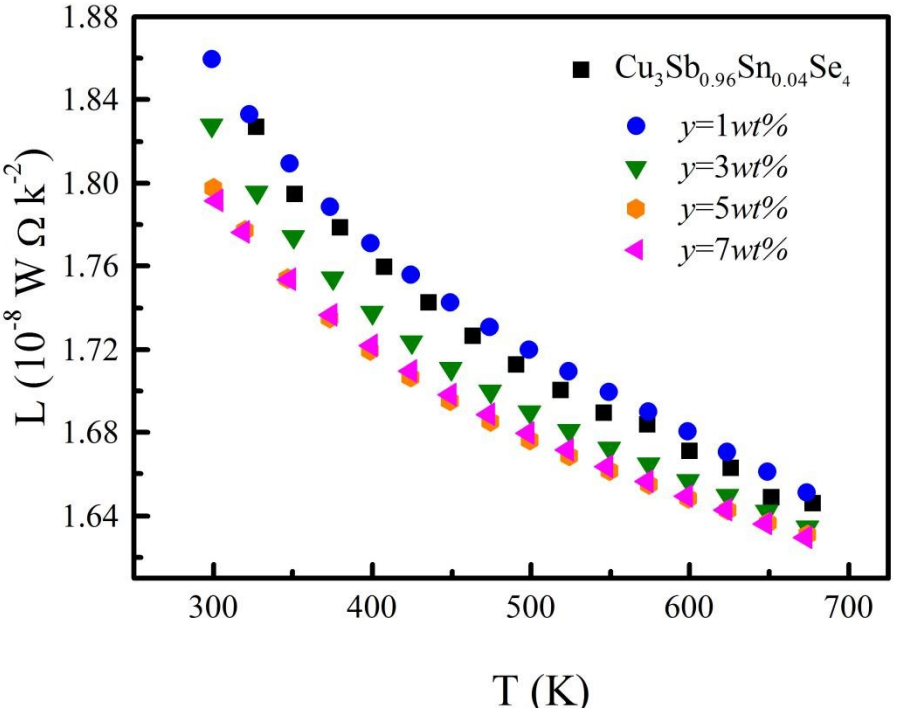


Figure S1. Temperature dependence of calculated Lorentz constant for $Cu_3Sb_{0.96}Sn_{0.04}Se_4$ bulk samples with y $AgSb_{0.98}Sn_{0.02}Se_2$ contents (y=1, 3, 5, 7wt%)

## Calculation of lattice thermal conductivity

In order to estimate the effects of different phonon scattering process, the lattice thermal conductivity was analyzed with Debye-Callaway model and the relaxation time $\tau$ can be calculated as the sum of different scattering process[1]:

$$\tau^{-1} = \tau_{PD}^{-1} + \tau_U^{-1} + \tau_N^{-1} + \tau_B^{-1}$$

Point defect phonon scattering:

$$\tau_{PD}^{-1} = \frac{\overline{V}\omega^4}{4\pi v^3}\Gamma$$

where $\overline{V}$ is average atomic volume of $Cu_3Sb_{0.96}Sn_{0.04}Se_4$, $\Gamma$ is point defect scattering parameter.

Umklapp scattering:

$$\tau_U^{-1} = \frac{\hbar\gamma^2\omega^2 T}{\overline{M}v^2\theta_D}\exp(-\theta_D/3T)$$

where $\overline{M}$ is average atomic volume of $Cu_3Sb_{0.96}Sn_{0.04}Se_4$, $\gamma$ is Gruneisen parameter.

Nanoparticles scattering:

$$\tau_N^{-1} = \frac{vV_P}{(2\pi R^2)^{-1} + \left[\frac{4}{9}\pi R^2(\frac{\Delta D}{D})^2(\frac{\omega R}{V})^4\right]^{-1}}$$

where $R$ is average size of grain, $D$ and $\Delta D$ are mass density of nanoparticles and difference value of mass density for nanoparticles and matrix.

Boundaries scattering:

$$\tau_B^{-1} = \frac{v}{L}$$

where $L$ is distance between nanoparticles. Here, $\tau_{PD}^{-1}$ and $\tau_N^{-1}$ are equations corresponding to $\omega^4$, so that we incorporate the scattering of nanoparticles into the scattering of point defect and simplify parameters to A. Similarly, the parameters in $\tau_U^{-1}$ can be replaced with B. Hence, $\tau^{-1}$ can be written as:

$$\tau^{-1} = A\omega^4 + B\omega^2 T\exp(-\theta_D/3T) + v/L$$

Table 1 calculated parameters of different phonon scattering process for matrix and composites samples.

| Sample | A($10^{-41}$ $s^3$) | B($10^{-41}$ $s^3$) | L(nm) |
|---|---|---|---|
| y = 0 | 0.15 | 3.83 | |
| y = 1wt% | 0.81 | 3.83 | 292 |
| y = 3wt% | 1.86 | 3.83 | 204 |
| y = 5wt% | 3.75 | 3.83 | 158 |
| y = 7wt% | 2.69 | 3.83 | 185 |

Table 2 Physical properties of $Cu_3Sb_{0.96}Sn_{0.04}Se_4$ used to calculate $\kappa_L$ based on different scattering process.

| Parameters | values |
|---|---|
| Debye temperature $\theta_D$ (K) | 131[2] |
| Longitudinal sound velocity $v_L$ ($ms^{-1}$) | 3643[3] |
| Transverse sound velocity $v_T$ ($ms^{-1}$) | 1485 |
| Sound velocity $v$ ($ms^{-1}$) | 1191.2 |
| Average atomic volume of $Cu_3Sb_{0.96}Sn_{0.04}Se_4$ $\overline{V}$ ($m^3$) | $2.27\times10^{-29}$ |
| Average atomic mass of $Cu_3Sb_{0.96}Sn_{0.04}Se_4$ $\overline{M}$ (kg) | $1.3\times10^{-25}$ |
| Gruneisen parameter $\gamma$ | 1.05[3] |
| Point defect scattering parameter Γ | 0.14[4] |

**Reference**

1. Skoug, E. J.; Cain, J. D.; Morelli, D. T., Structural effects on the lattice thermal conductivity of ternary antimony- and bismuth-containing chalcogenide semiconductors. *Appl Phys Lett* **2010,** *96* (18), 3.

2. Skoug, E. J.; Cain, J. D.; Morelli, D. T.; Kirkham, M.; Majsztrik, P.; Lara-Curzio, E., Lattice thermal conductivity of the Cu3SbSe4-Cu3SbS4 solid solution. *J Appl Phys* **2011,** *110* (2), 023501.

3. Zhang, Y. S.; Skoug, E.; Cain, J.; Ozolins, V.; Morelli, D.; Wolverton, C., First-principles description of anomalously low lattice thermal conductivity in thermoelectric Cu-Sb-Se ternary semiconductors. *Phys. Rev. B* **2012,** *85* (5), 6.

4. Morelli, D. T.; Heremans, J. P.; Slack, G. A., Estimation of the isotope effect on the lattice thermal conductivity of group IV and group III-V semiconductors. *Phys. Rev. B* **2002,** *66* (19).