Supporting Information

Lorenz number calculation in details:

In general, the total (κ) consists of the electronic thermal conductivity (κ_e) and lattice thermal conductivity (κ_L). The electronic part κ_{ele} is directly proportional to the electrical conductivity σ through the Wiedemann-Franz relation, $\kappa_e = L\sigma T$, where L is Lorentz number and its value is calculated by SPB model.[34] The Lorenz number can be given as:

$$L = \left(\frac{k_B}{e}\right)\left(\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)}\right]^2\right) \quad (1)$$

For the Lorenz number calculation, we should get reduced Fermi energy η firstly; the calculation of η can be derived from the measured Seebeck coefficients by using the following relationship:

$$S = \pm\frac{k_B}{e}\left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta\right) \quad (2)$$

where $F_n(\eta)$ is the $n-$th order Fermi integral,

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1+e^{\chi-\eta}}d\chi \quad (3)$$

where e is the electron charge, k_B is the Boltzmann constant, h is the Planck constant, r is the scattering factor. The scattering factor (r) is $-1/2$ since acoustic phonon scattering has been assumed as the main carrier scattering mechanism near room temperature (RT). Lorentz number can be obtained by combining equations (1), (2) and (3).

Table S1. Ba fraction determined by electron probe micro analysis (EPMA) for $Bi_{0.875}Ba_{0.125}Cu_{1-x}Ni_xSeO$.

samples	x=0	x=0.05	x=0.1	x=0.15	x=0.2
Ba fraction	0.076	0.108	0.085	0.112	0.084

Fig. S1. (a～e) elemental mapping of polished surface of $Bi_{0.875}Ba_{0.125}CuSeO$ sample.

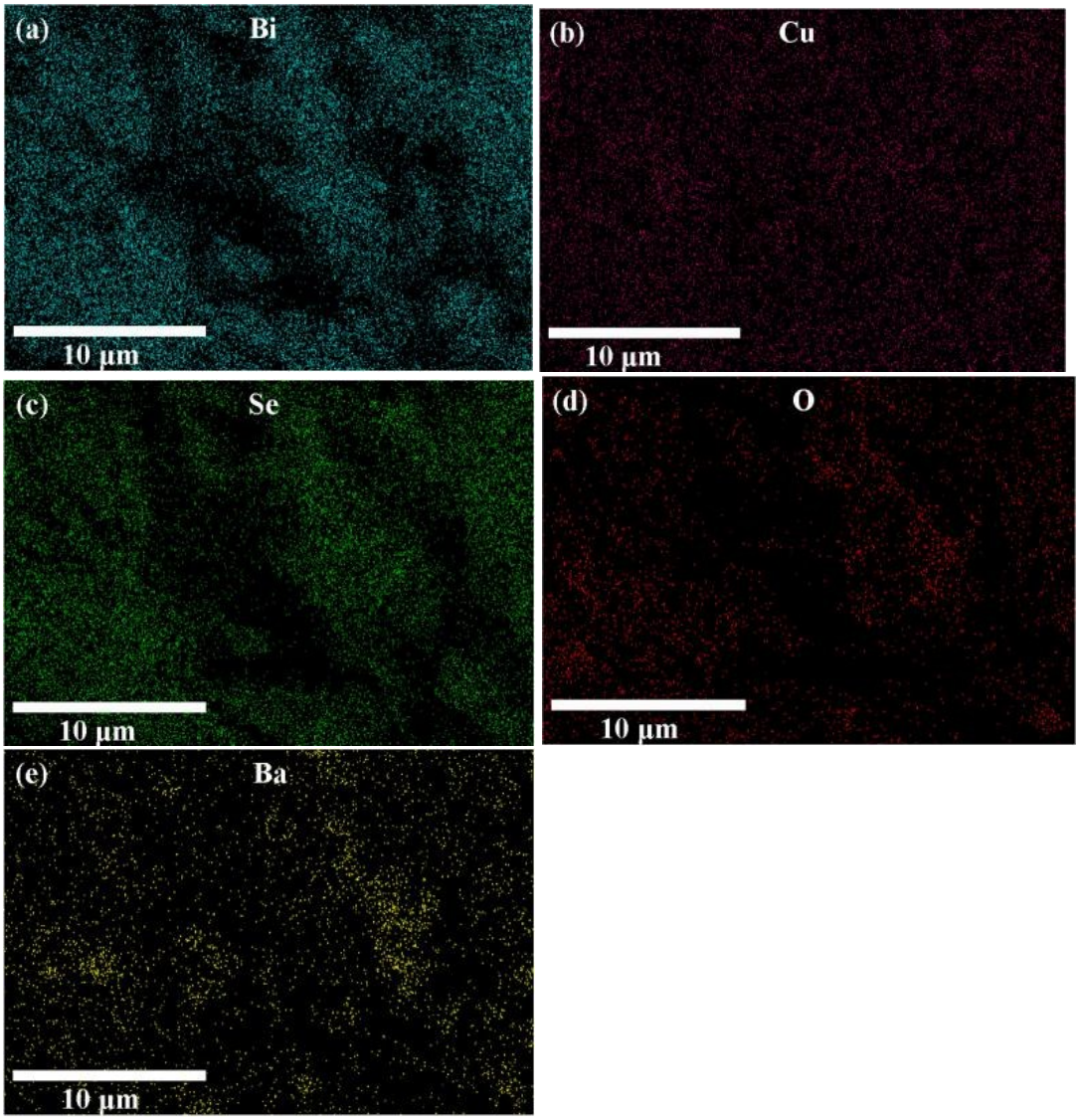


Fig. S2. (a～f) elemental mapping of polished surface of $Bi_{0.875}Ba_{0.125}Cu_{0.95}Ni_{0.05}SeO$ sample.

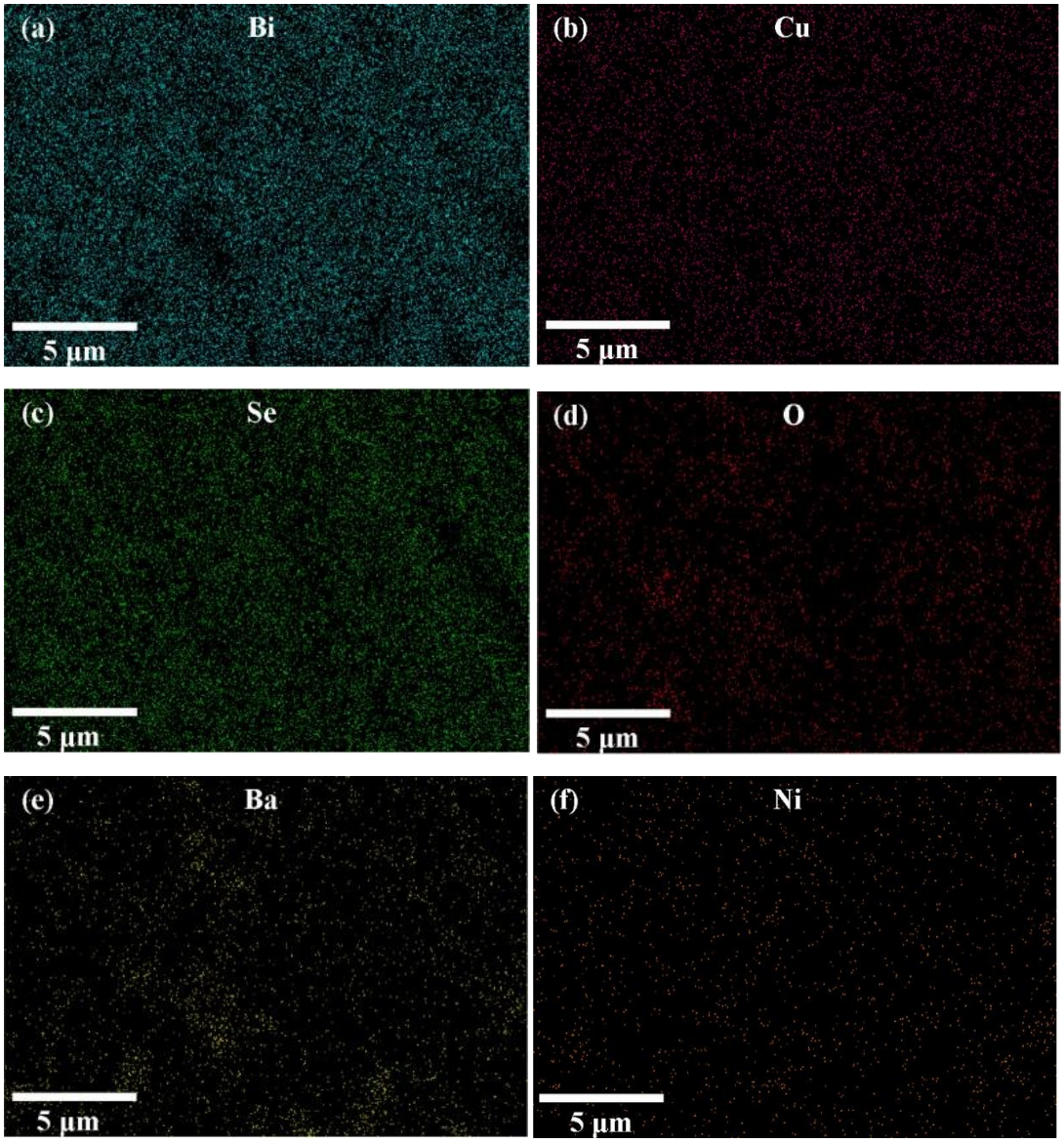


Fig. S3. (a～f) elemental mapping of polished surface of $Bi_{0.875}Ba_{0.125}Cu_{0.9}Ni_{0.1}SeO$ sample.

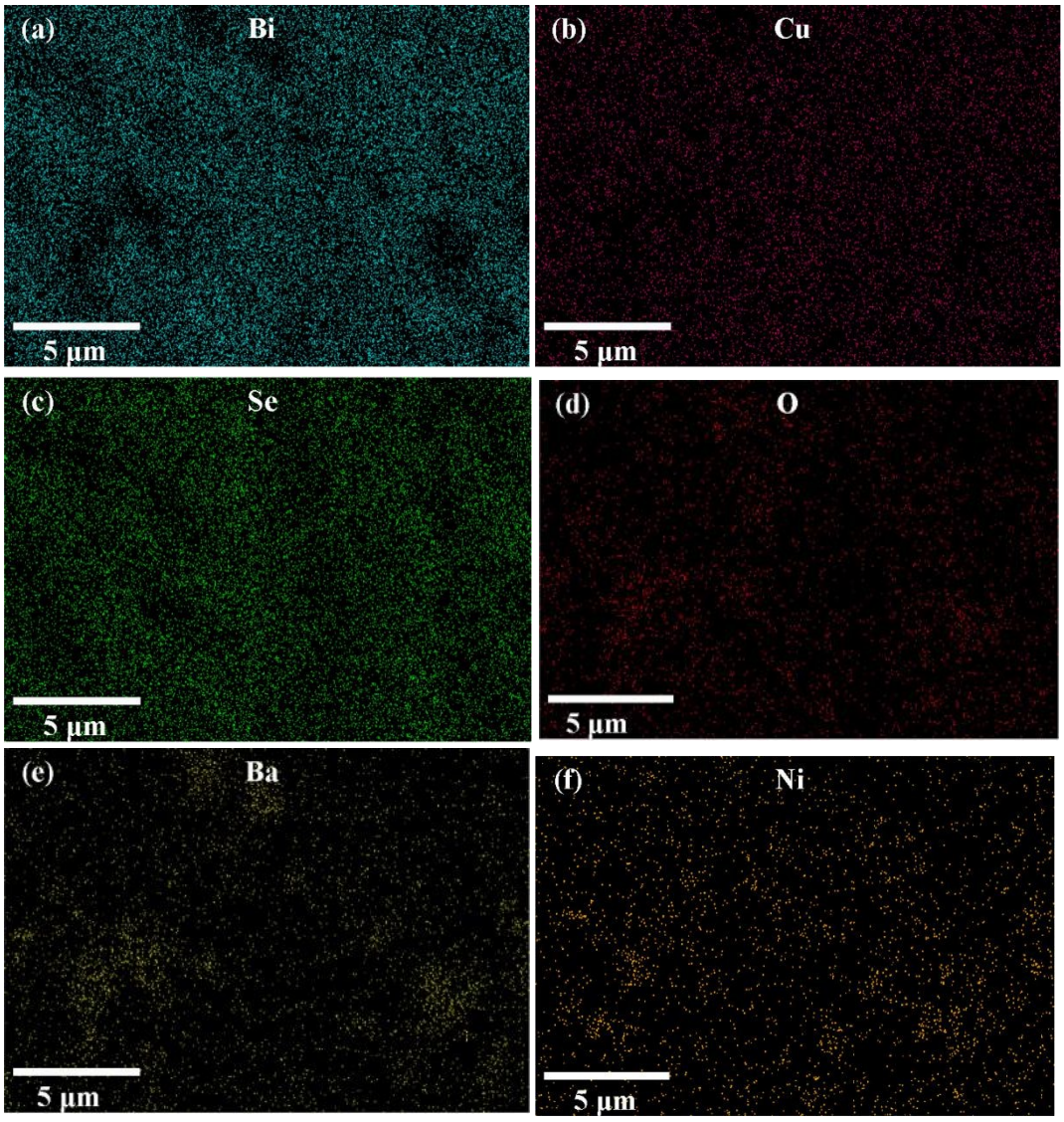


Fig. S4. (a～f) elemental mapping of polished surface of $Bi_{0.875}Ba_{0.125}Cu_{0.85}Ni_{0.15}SeO$ sample.

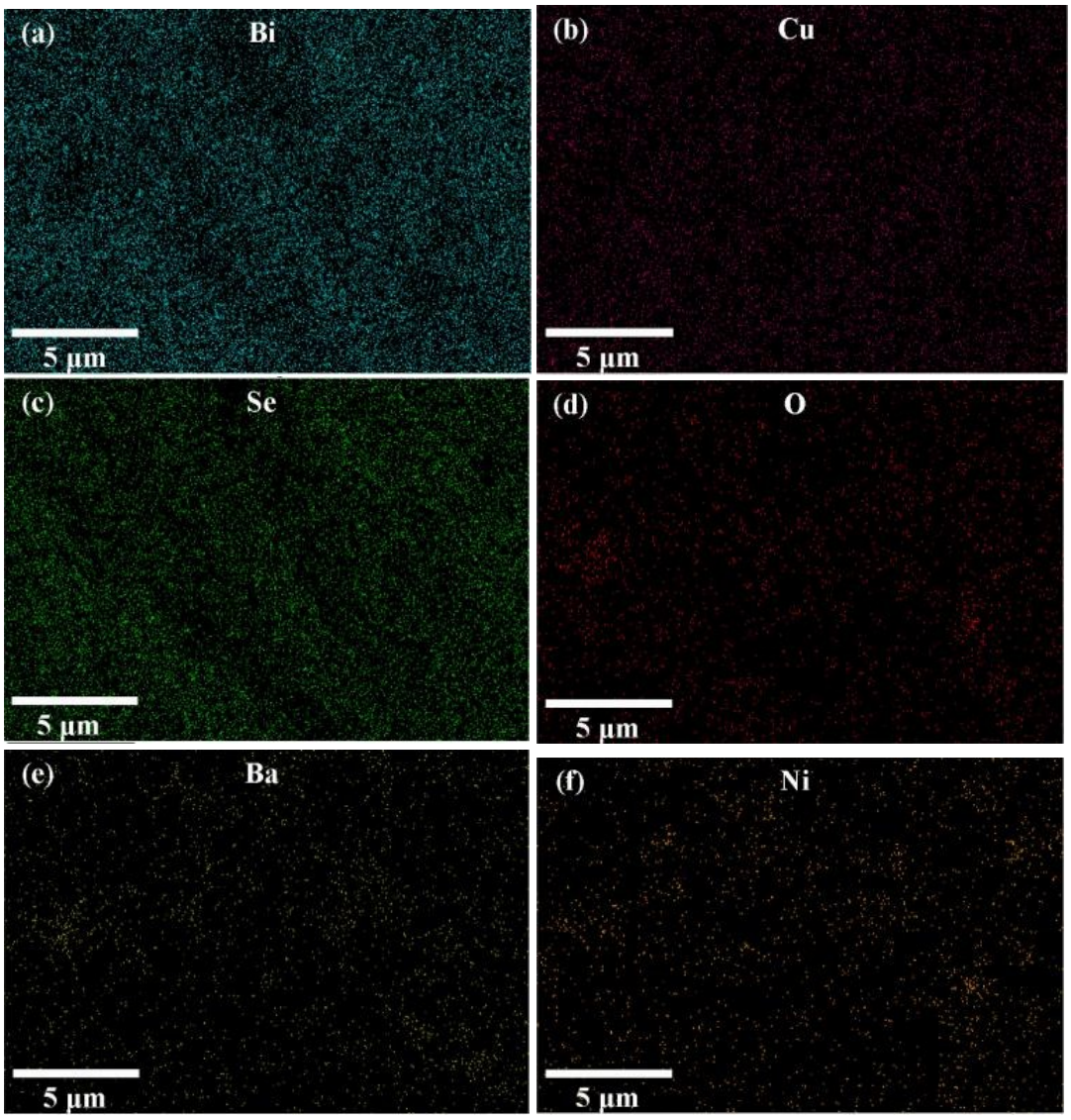


Fig. S5. (a~f) elemental mapping of polished surface of $Bi_{0.875}Ba_{0.125}Cu_{0.8}Ni_{0.2}SeO$ sample.

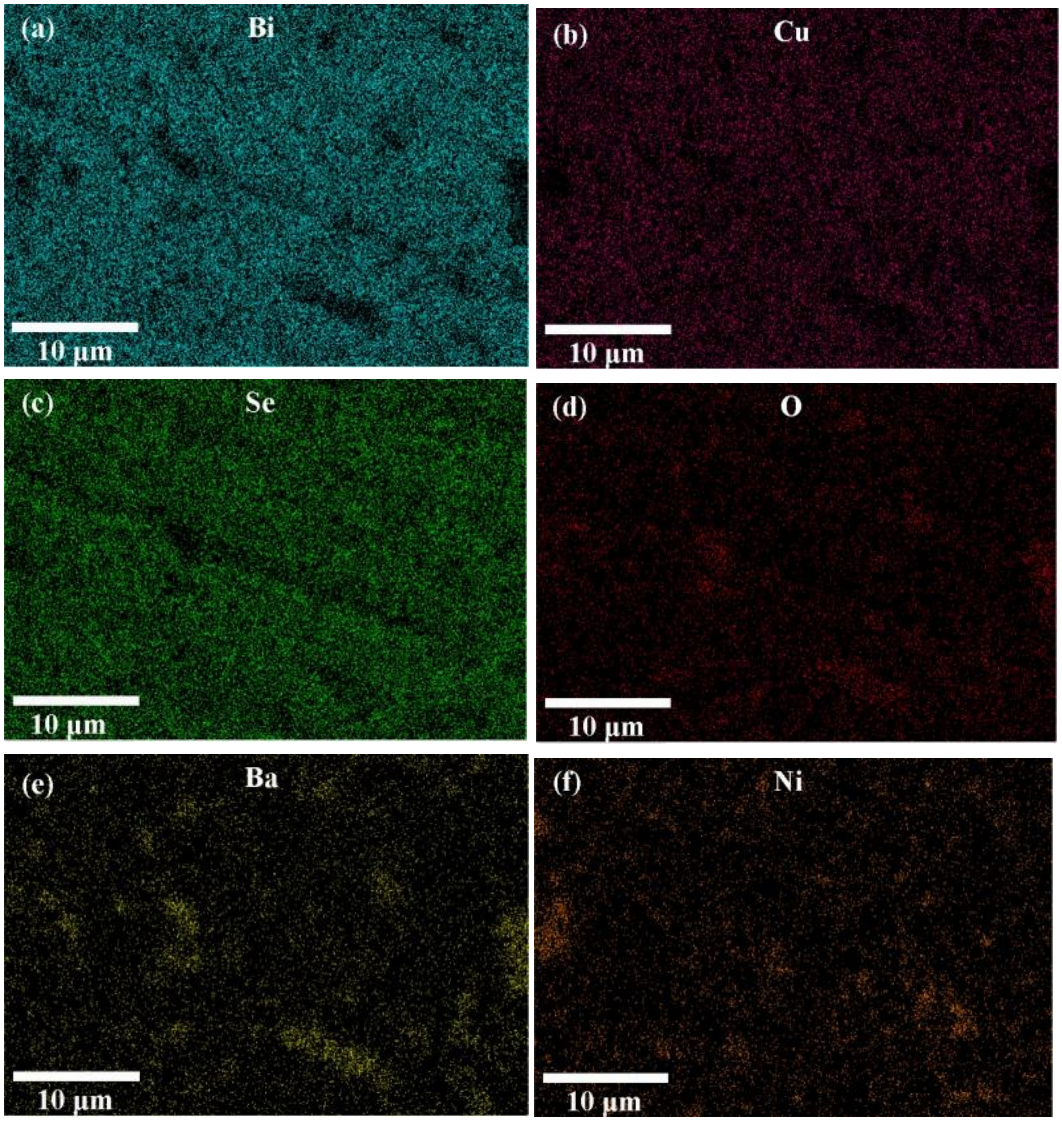


Fig. S6. SEM images of $Bi_{0.875}Ba_{0.125}CuSeO$ sample.

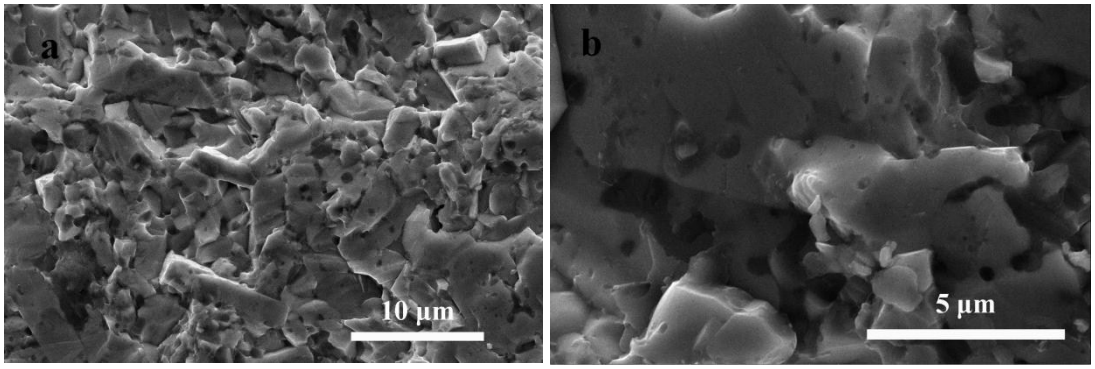


Fig. S7. Lorenz number as a function of temperature for $Bi_{0.875}Ba_{0.125}Cu_{1-x}Ni_xSeO$ and pristine BiCuSeO samples.

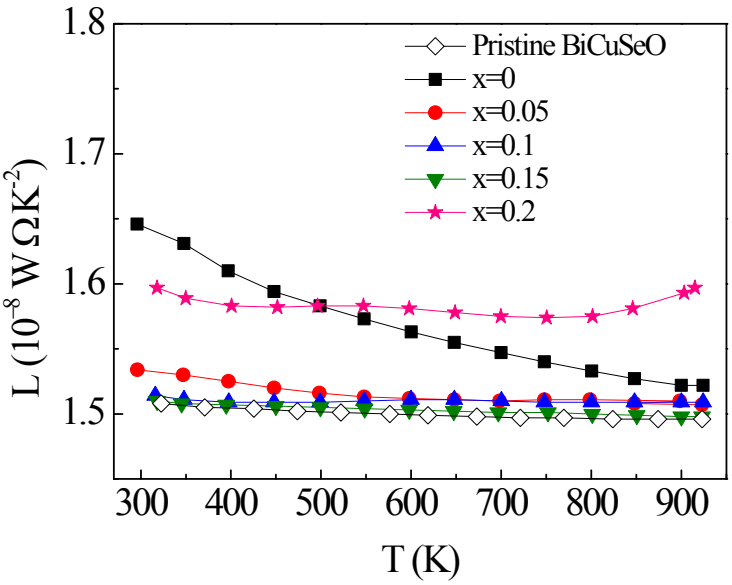


Fig. S8. Electronic thermal conductivity as a function of temperature for $Bi_{0.875}Ba_{0.125}Cu_{1-x}Ni_xSeO$ and pristine BiCuSeO samples.

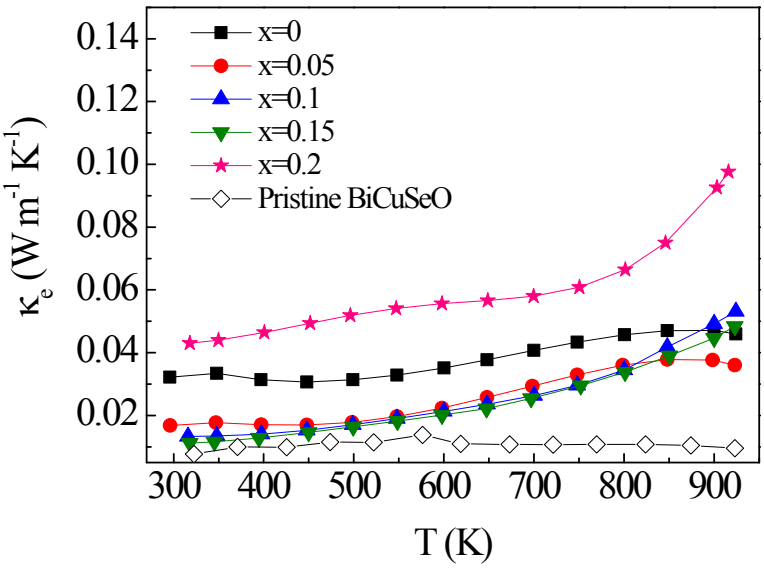


Fig. S9. The thermal diffusivity of $Bi_{0.875}Ba_{0.125}Cu_{1-x}Ni_xSeO$ and pristine BiCuSeO samples.

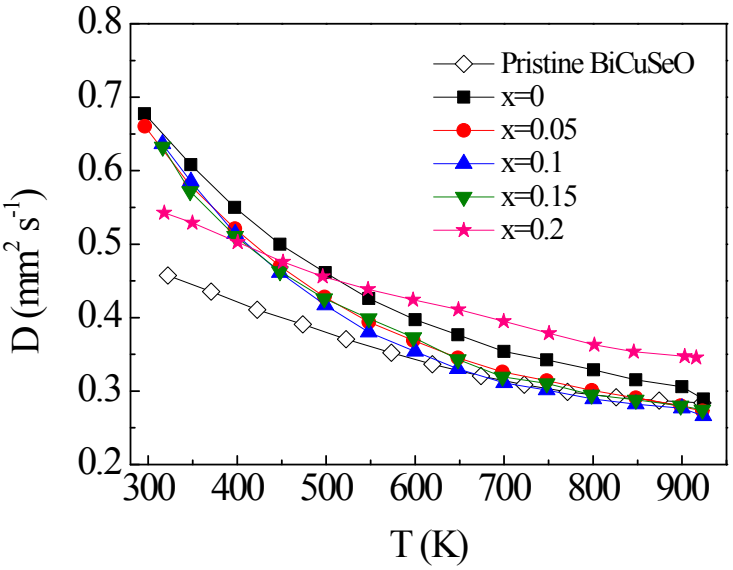
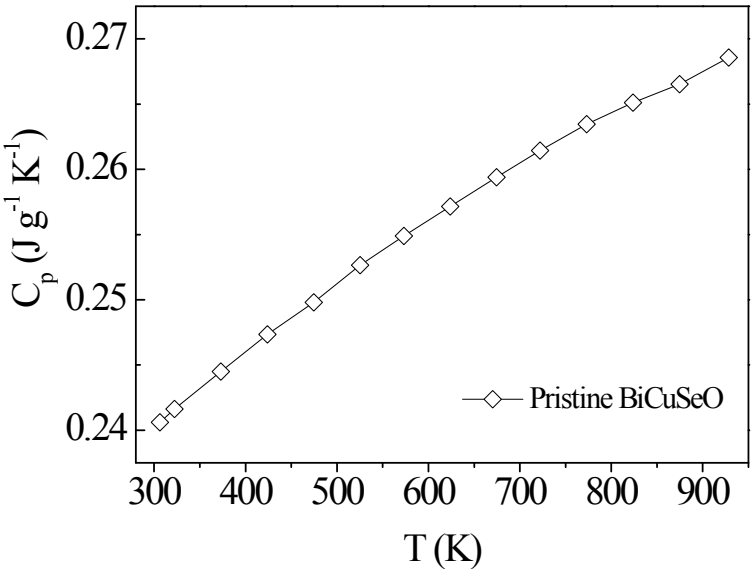


Fig. S10. The heat capacity of pristine BiCuSeO. We apply it for all samples, since the uncertainty among different samples could be negligible.[25,44,53]



Reference

[53] G. K. Ren, S. Y. Wang, Y. C. Zhu, K. J. Ventura, X. Tan, W. Xu, Y. H. Lin, J. H. Yang and C. W. Nan, Enhancing thermoelectric performance in hierarchically structured BiCuSeO by increasing bond covalency and weakening carrier-phonon coupling, *Energy Environ. Sci*. Published online, DOI: 10.1039/c7ee00464h.