Electronic Supplementary Information

Enhancement of thermoelectric properties of $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12}$ p-type skutterudite by tellurium addition

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1. EDS mapping analysis of $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12}$ and $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{11.9}Te_{0.1}$ sample

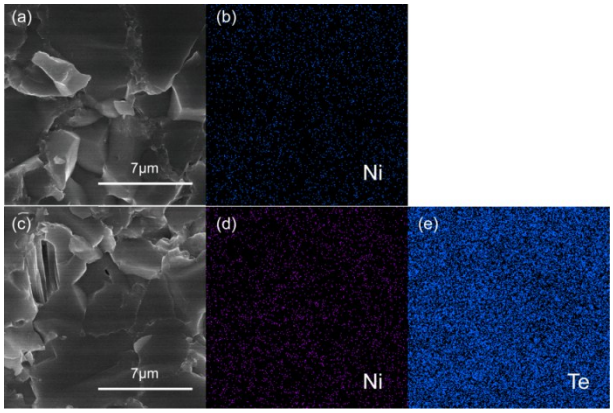

Figure S1 the microstructure and element distribution of the $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12}$ (a-b) and $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{11.9}Te_{0.1}$ (c-e) sample: (a, c) fractured surface images, and corresponding X-ray maps for Ni (b, d) and Te (e) by energy dispersive spectroscopy (EDS).

2. Rietveld refinements results

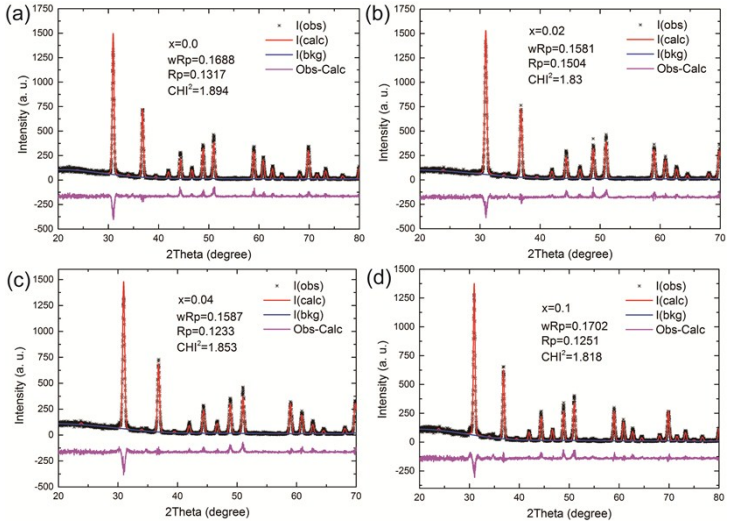

Figure S2 Rietveld refinements for $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12-x}Te_x$ samples. (a) x=0.00, (b) x=0.02, (c) x=0.04, (d) x=0.10

3. Calculation of effective mass and Lorentz number

The effective mass m* is estimated by the following equation [1]:

$$n = \frac{4}{\sqrt{\pi}}\left(\frac{2\pi m^* k_B T}{h^2}\right)^{\frac{3}{2}} F_{r+1}(\varphi)$$

Here, $F_n(\varphi)$ is the Fermi integration: $$F_n(\varphi) = \int_0^{\infty} \frac{x^n}{e^{(x-\varphi)}+1} dx$$, r is the scattering parameter (typical r=-1/2 for acoustic phonon scattering near room temperature) and is the reduced Fermi energy $\varphi = E_f/k_B T$ and which can be derived from the measured S on the basis of single parabolic band approximation:

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

In addition, the Lorenz number (L_0) is estimated by the following equation:

$$L_0 = \left(\frac{k_B}{e}\right)^2 \left(\frac{\left(r+\frac{7}{2}\right)F_{r+5/2}(\varphi)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\varphi)} - \left(\frac{\left(r+\frac{7}{2}\right)F_{r+3/2}(\varphi)}{\left(r+\frac{3}{2}\right)F_{r+1/2}(\varphi)}\right)^2\right)$$

The calculated Lorentz numbers of all the studied samples in this paper are shown in Figure S3.

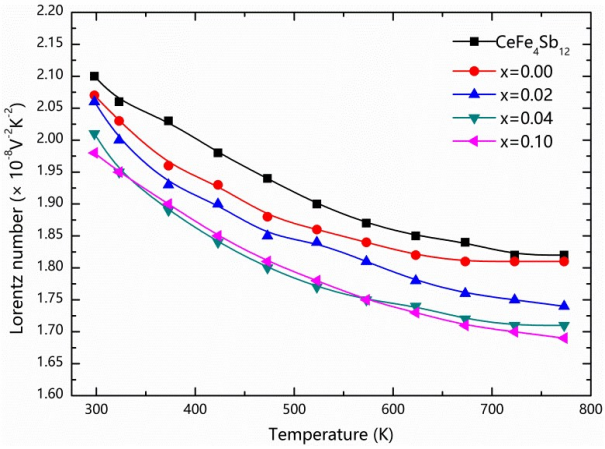

Figure S3 the calculated Lorentz number of all the $CeFe_4Sb_{12}$ and $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12-x}Te_x$ samples in this paper.

4. The temperature dependence of electronic thermal conductivity (κ_e) of

$Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12-x}Te_x$ samples

According to the Wiedemann-Franz law ($\kappa_e=L_0T/\rho$), the κ_e for all the samples in the whole measured temperature range is calculated based on the estimated Lorentz number L_0.

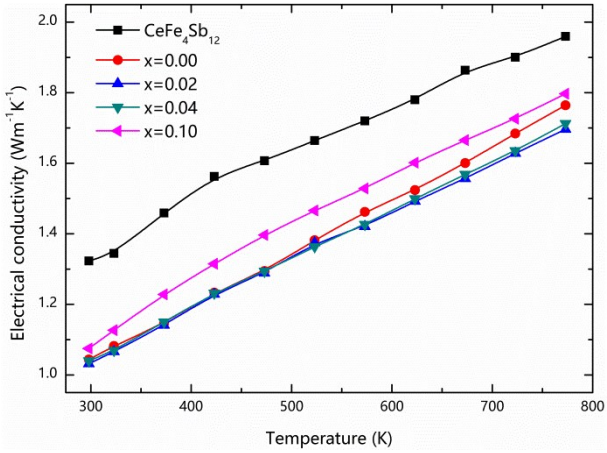

Figure S4 temperature dependence of electrical thermal conductivity of the $CeFe_4Sb_{12}$ and $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12-x}Te_x$ samples.

5. Calculation of κ_L and κ_{bp}

Above 673K, large amount of the electrons from the valence of p-type skutterudites are thermally activated to conduction band, which leads to the deleterious bipolar effect. The total thermal conductivity of p-type skutterudite in the range of intrinsic conduction is modified as this equation : $\kappa_{total} = \kappa_L + \kappa_e + \kappa_{bp}$, in which κ_{total}, κ_L, κ_e and κ_{bp} represent the total thermal conductivity, lattice thermal conductivity, electronic conductivity and bipolar thermal conductivity respectively. As suggested by Slack [2], the lattice thermal conductivity should follow the relationship $\kappa_L \propto T^{-1}$. At low temperature (below 673K) the bipolar effect is not obvious, the κ_{total}–κ_e follows that linear relationship quite well but it begins to deviate at temperature above 673K, as shown in Figure S5. The κ_L at high temperature is estimated by extrapolating the linear relationship of $\kappa_L \propto T^{-1}$ as shown by dashed line in Figure S5. So the κ_{bp} can be calculated by κ_{total} - κ_L - κ_e, as also shown in Figure S5.

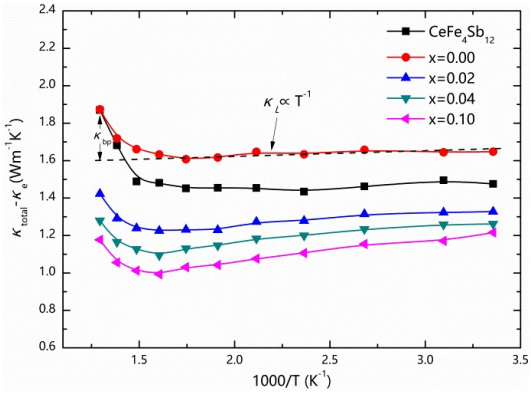

Figure S5 the total thermal conductivity minus electronic thermal conductivity as a function of temperature for the $CeFe_4Sb_{12}$ and $Ce_{0.9}Fe_{3.75}Ni_{0.25}Sb_{12-x}Te_x$ samples.

Reference

[1] R. H. Liu, P. F. Qiu, X. H. Chen, X. Y. Huang, L. D. Chen, Journal of Materials Research, 2011, 26, 1813-1820

[2]G. A. Slack, Solid State Physics, 1979, 34, 1-71