Supplementary information

Record thermoelectric figure of merit in Bi_{1-x}Sb_x achieved by 1-D Landau level

quantization

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Supplementary Note I: Zero field transport for different crystals.

To study the thermoelectric properties of different doping levels, we synthesized three $Bi_{88}Sb_{12}$ single crystals with a variation in Te doping which is 0, 10, and 50 ppm, respectively. **Fig. S1**(a) shows the Seebeck coefficient of the 3 crystals as a function of temperature. Comparing the 3 samples, the Seebeck coefficients of the 10-ppm sample is close to that of the intrinsic $Bi_{88}Sb_{12}$, indicative of a low doping concentration introduced by Te. The 50-ppm doped sample shows much smaller Seebeck coefficients in the entire temperature range, as a signature of high doping. A turnover of the Seebeck coefficient is observed in all three sample near 100 K, as a result of thermal excitation. The identical trend has been observed in the resistivity measurement shown in **Fig. S1**(b). The undoped sample exhibits an intrinsic semiconductor behavior, with a resistivity turnover at 100 K, while the doped samples show metallic behavior. The thermal conductivities of three samples are shown in **Fig. S1**(c), with the variations arising from the electronic contributions and electron phonon scattering induced by the doped carriers. The calculated figure of merit *zT* is shown in **Fig.** Bi₈₈Sb₁₂, with the largest figure of merit reaching 0.8 at 160 K.



Figure S1 Zero field transport properties of the three crystals. (a) resistivity, (b) Seebeck coefficient, (c) thermal conductivity, and (d) the figure of merit zT among the 3 crystals with different doping levels of 0, 10, and 50 ppm Te.

Supplementary Note II: Additional transport properties for the 10-ppm crystal

The Hall resistivity of the 10-ppm Te doped crystal is shown in **Fig. S2**(a). The Hall slope gradually decreases with an increasing temperature as a consequence of increasing carrier concentration by thermal excitation, from which we calculated the Hall carrier concentration $n_{\rm H}$ shown in **Fig. 1**(d) in the main text. The high temperature magneto-Seebeck coefficient is shown in **Fig. S2**(b). The non-saturating Seebeck that is linear in field in the EQL and is shown in **Fig. 1**(f) starts to become marginally resolved above 6 T at 120 K and becomes unreachable in the fields available to us and above 140 K. This is because the EQL shifts up in field with temperature, due to the increase in n_{H} .



Figure S2 Hall and Seebeck coefficient of 10-ppm Te doped $Bi_{88}Sb_{12}$ crystal. (a) Hall resistivity. A negative Hall slope indicates the successful Te doping. The carrier concentration increases with temperature. (b) Temperature dependent mobility calculated from the Hall carrier concentration. (c) High field magneto-Seebeck coefficient above 120 K. The non-saturation behavior is invisible for 140 K and above.

Supplementary Note III: Full magneto-transport data of the three crystals.

Fig. S3 shows the magneto transport properties of the undoped $Bi_{88}Sb_{12}$, along with the calculated *zT* in field. For the intrinsic $Bi_{88}Sb_{12}$, we observe a large magnetoresistance as expected in an intrinsic semiconductor. At 20 K and 50 K, the sample turns into p-type at high field, confirmed by both Seebeck and Hall measurement. The Nernst curve shows a linear field dependence in field, as a signature for two-carrier Nernst effect. In the intrinsic sample, the thermal conductivity shows almost no field dependence at 20 K, where the heat is carried predominantly by the phonons. The best *zT* of the intrinsic $Bi_{88}Sb_{12}$ is 1.3 at 225 K, 2 T.

Fig. S4 summarizes the field dependent transport properties of the second 10-ppm doped $Bi_{88}Sb_{12}$ crystal, namely crystal b. All the transport signatures in crystal b is identical to that of the 10-ppm doped crystal a discussed in the main text, except for a slightly higher carrier concentration. The negative MR, oscillating Seebeck coefficient, and negative Hall slope are all reproduced, proving the robustness of the results. The highest *zT* obtained in crystal b is 2.3 at 100 K, which is slightly lower than crystal a as a result of slightly higher carrier concentration (n_{H} ~1.8×10¹⁷/cm³ by Hall measurement).

When 50 ppm Te is added to the $Bi_{88}Sb_{12}$ alloy, the doping concentration is high enough to push the sample into the metallic region, shown in **Fig. S5**. The field dependence of the transport properties show the signature of degenerately-doped semiconductors. The MR is suppressed to 200% at 2 T. The Seebeck coefficient slightly increases with field SdH oscillations are observed in *S* and ρ at 20 K. The Hall coefficient decreases with increasing temperature, and the Nernst thermopower has a classic single carrier Nernst shape. The *zT* achieved in the 50 ppm sample maxizes at 180 K with the peak value of 0.83. The lower *zT* is indicative of overdoping in this case.



Figure S3 Magneto transport data of the undoped $Bi_{88}Sb_{12}$ crystal. (a) resistivity, (b) Seebeck coefficient, (c) Hall resistivity, (d) Nernst thermopower, (e) thermal conductivity, and (f) *zT*. The intrinsic sample shows some signatures of the undoped semiconductor. The highest *zT* achieved is 1.3 at 225 K.



Figure S4 Magneto transport data of 10-ppm Te doped $Bi_{88}Sb_{12}$ doped crystal b. (a) resistivity, (b) Seebeck coefficient, (c) Hall resistivity, (d) Nernst thermopower, (e) thermal conductivity, and (f) zT. The 10-ppm sample b shows identical behavior for all the transport properties compared to 10-ppm crystal a. The sample to sample variation between a and b is from the slight difference in carrier concentration, with the carrier concentration of b to be 20% higher than crystal a.



Figure S5 Full transport data of 50-ppm Te doped $Bi_{88}Sb_{12}$ doped crystal. (a) resistivity, (b) Seebeck coefficient, (c) Hall resistivity, (d) Nernst thermopower, (e) thermal conductivity, and (f) *zT*. The 50-ppm doped sample shows the behavior of a heavily doped semiconductor. Since the sample is heavily doped, the max *zT* only reaches 0.8 at 180 K, much lower than the low-doping samples.

Supplementary Note IV: Crystal growth and sample characterization

Figure S6 shows the optical image of the zone melting grown single crystal. Centimeter size single crystal is obtained by this technique. The phase purity and crystal quality are examined by powder and single crystal X-ray diffraction, as illustrated in **Fig. S7**. The compositional homogeneity of the crystal is confirmed by SEM-EDX technique, as shown in **Fig. S8**. Figure S9 shows the STEM result on the crystal, in order to eliminate the possibility of any microstructure. The actual Te concentration is test by ICP and the results are summarized in Tab S1, with 50 ppm being the ICP detection limit.

Table S1 ICP detection for the Te concentration, HNO₃ is used for dissolving samples.

Te <0.005% <0.005% 0.0057±0.0009% 0.010		10	50	10	0	with Te in ppm
	±0.001%	6 0.010±0	0.0057±0.0009%	<0.005%	<0.005%	Te



Figure S6 Optical image of a typical zone melting grown crystal. Mirror like shiny cleavage plane can be clearly observed.



Figure S7 X-ray anlysis. XRD powder diffraction (a) and single crystal Laue diffraction (b). (c) and (d) Analysis results from the Laue diffraction.



Figure S8 Composition analysis. (a) SEM image of Te doped Bi₈₈Sb₁₂ crystal. A crack, along with several holes are observed from the image. The EDX spots are selected on different sides of the crack for better accuracy. (b) and (c) Bi and Sb composition scan of the image. According to the scan, the Bi is homogeneously distributed, while a slight compositional variation is tested on the Sb result. To quantify this inhomogeneity, 25 points are selected on different parts of the image, as shown in (d). The averaged results are shown in Table S2, with the compositional variation to be around 1%.

Spectrum	0	Bi	Sb	Spectrum	0	Bi	Sb	Spectrum	0	Bi	Sb
1	0	88.36	11.64	6	0	87.61	12.39	Mean	0	86.88	13.12
2	0	86.97	13.03	7	0	86.91	13.03	Sigma	0	0.74	0.74
3	0	86.35	13.65	8	0	86.37	13.63	sigmamean	0	0.24	0.24
4	0	87.14	12.86	9	0	85.98	14.02				
5	0	87.06	12.94	10	0	85.98	14.02				
Spectrum	0	Bi	Sb	Spectrum	0	Bi	Sb	Specturm	0	Bi	Sb

Table S2 EDX results on spots 1-25

11	0	86.63	13.37	16	0	86.69	13.31	21	0	87.40	12.60
12	0	86.66	13.34	17	0	88.08	11.92	22	0	88.93	11.07
13	0	87.84	12.16	18	0	87.00	13.00	23	0	87.79	12.21
14	0	87.91	12.09	19	0	87.99	120.1	24	0	88.71	11.29
15	0	87.27	12.73	20	0	87.96	12.04	25	0	88.21	11.79
Mean	0	87.26	12.74	Mean	0	87.54	12.46	Mean	0	88.21	11.79
Sigma	0	0.62	0.62	Sigma	0	0.65	0.65	Sigma	0	0.63	0.63
sigmamean	0	0.28	0.28	sigmamean	0	0.29	0.29	sigmamean	0	0.28	0.28

The EDX results show a general good homogeneity with the composition. The actual composition is approximately 87%±1%.



Figure S9 HAADF STEM result on Te doped $Bi_{88}Sb_{12}$ alloy. (a) cross-section of the Te doped Bi-Sb crystal, contrast variation is due to different sample thickness. (b) Zoomed in view for cross-sectional, which shows uniform HAADF-STEM contrast. (c) and (d) Atomic lattice structure is consistent with (210) projection of Bi R-3m. No signs of chemical ordering or segregation in HAADF-STEM contrast. (e) and (f) Second crystalline projection consistent with (841) R-3m projection also shows no signs of chemical ordering.

Supplementary Note V: Harman tests for the confirmation of zT

In this part we show the raw curve of the Harman test on sample b at different temperatures. **Fig. S10** (a)-(d) shows the Harman voltage responses as a function of time step and applied field. A clear saturation of the isothermal resistance can be observed at all fields. The zT of the sample is then determined by the formula of $zT = V_a/V_i - 1$.



Figure S10 Harman test results. (a)-(d) Harman voltage responses at different temperatures. The data are taken on sample b of 10-ppm Te doped $Bi_{88}Sb_{12}$. A stronger response is observed at higher field, because of the increasing resistivity with field.