Supplementary Information

$Mg_3(Bi,Sb)_2$ single crystals towards high thermoelectric performance

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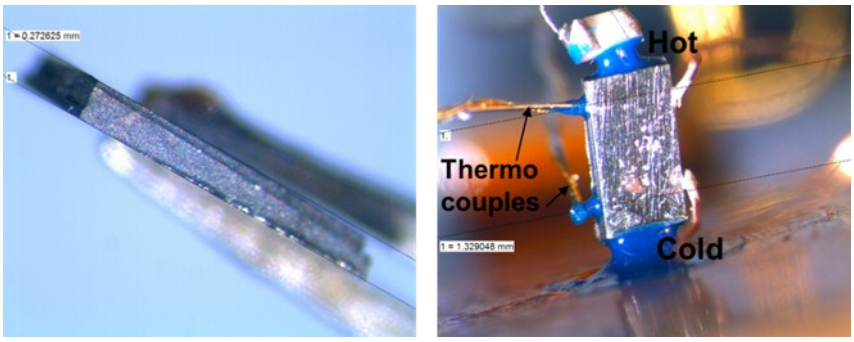

Fig. S1 Sample setup for thermal conductivity measurement by steady state method. Thermal gradient is along the *ab* plane direction (parallel to the layered plane of the single crystals).

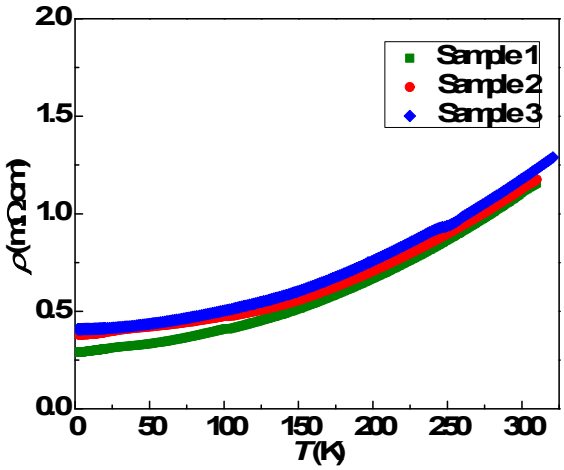

Fig. S2 Temperature dependence of the resistivity for three samples from the same batch of Y-doped $Mg_3Bi_{1.25}Sb_{0.75}$ single crystals.

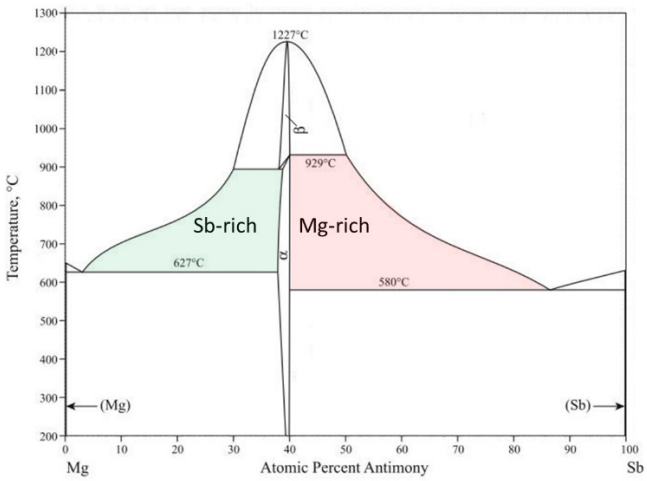

Fig. S3 Phase diagram of Mg-Sb.

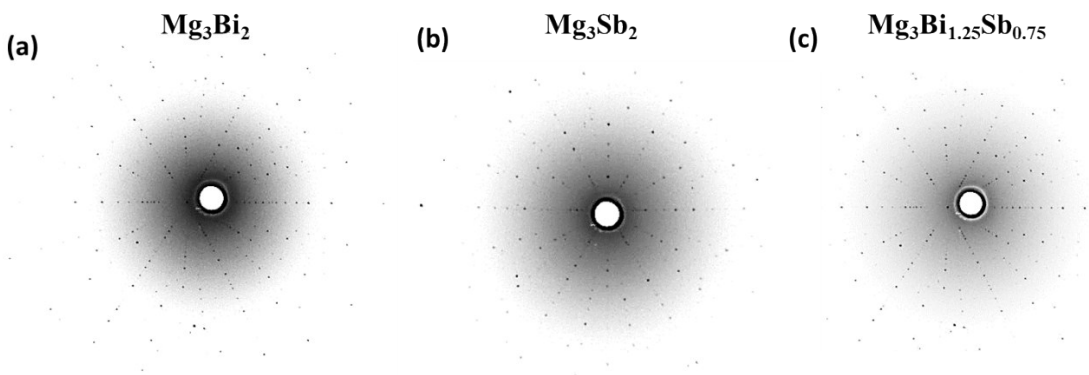

Fig. S4 (a)-(c) Laue XRD pattern of Mg_3Bi_2, Mg_3Sb_2 and $Mg_3Bi_{1.25}Sb_{0.75}$, respectively.

For all three single crystals, the backscattering Laue XRD diffraction patterns show clear diffraction spots, and no impurity dots are found, indicating the high quality and crystallinity of the as-grown single crystals.

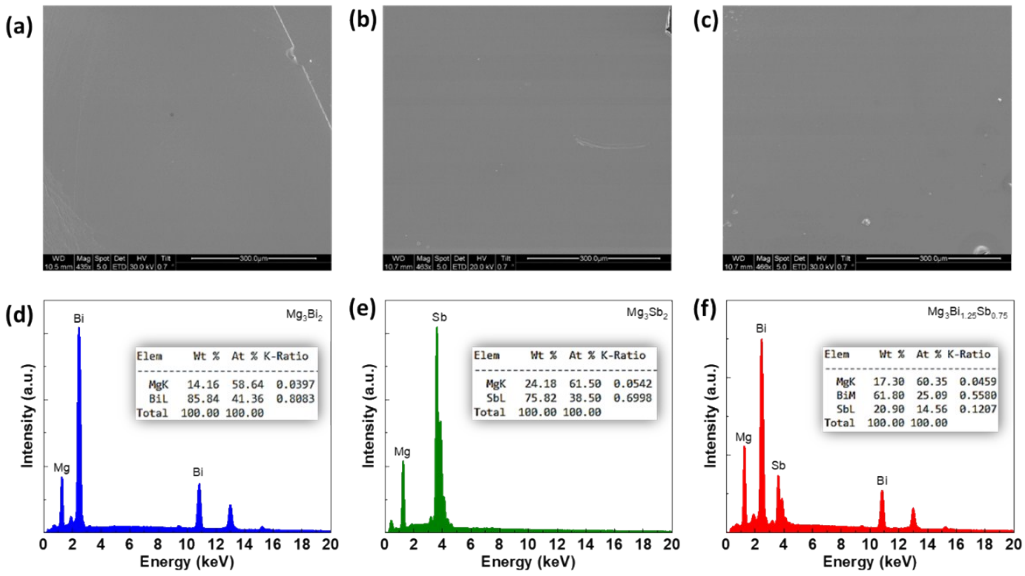

Fig. S5 (a)-(c) SEM images and (d)-(f) EDX patterns of Mg_3Bi_2, Mg_3Sb_2 and $Mg_3Bi_{1.25}Sb_{0.75}$, respectively.

SEM with EDX analysis demonstrates the chemical compositions of Mg_3Bi_2 and Mg_3Sb_2 agree well with the stoichiometric compositions (**Fig. S5**). The ternary compound is revealed to be $Mg_3Bi_{1.25}Sb_{0.75}$ according to the EDX analysis. It is worth noting that the compositions of the single crystals are very close to the Mg : X = 3 : 2 relation (X = Bi, Sb) without an uncontrollable large amount of excess Mg as in polycrystalline samples.

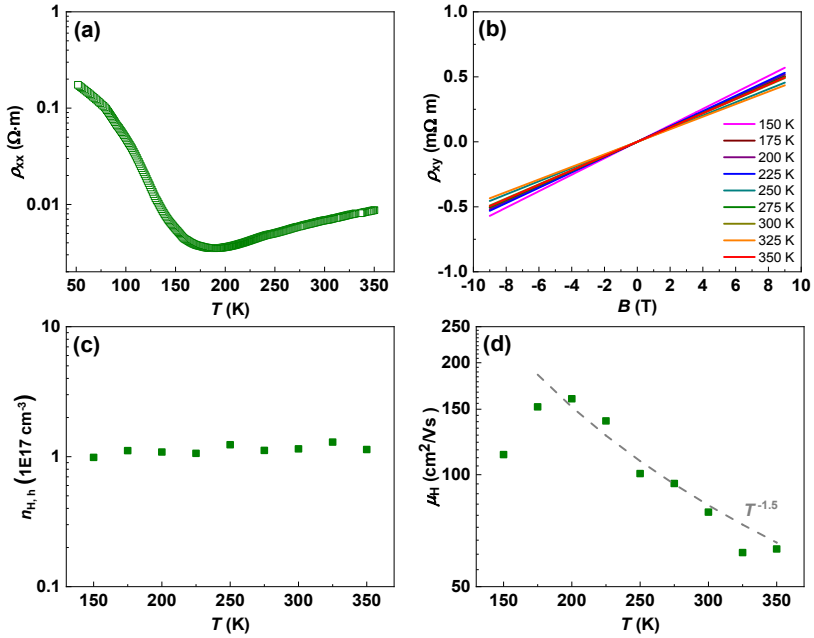

Fig. S6 Electrical transport properties of Mg_3Sb_2. (a) Temperature dependence of resistivity, (b) magnetic field dependence of Hall resistivity, (c) Hall carrier concentration, (d) Hall mobility.

Pure Mg_3Sb_2 show a semiconducting behavior with a first decrease and then increase resistivity with increasing temperature, as shown in **Fig. S6**(a). As a semiconductor, the pure Mg_3Sb_2 sample show very high resistivity, demonstrating the high quality of the single crystal. Linear magnetic field dependence of the Hall resistivity with a positive slop indicates the p-type transport behavior of the sample. The hole concentration is pretty low and hardly changes in the whole temperature range. The mobility shows a $T^{-1.5}$ dependence which implies the dominant scattering as phonon scattering. Although Mg_3Sb_2 shows a p-type behavior, the single crystals can be doped into n-type since they are rich of Mg.

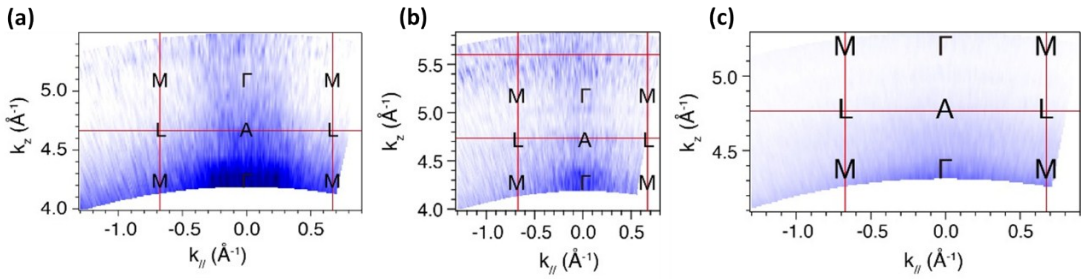

Fig. S7 ARPES intensity at different kz. (a) Mg_3Bi_2, (b) $Mg_3Bi_{1.25}Sb_{0.75}$, (c) Mg_3Sb_2.

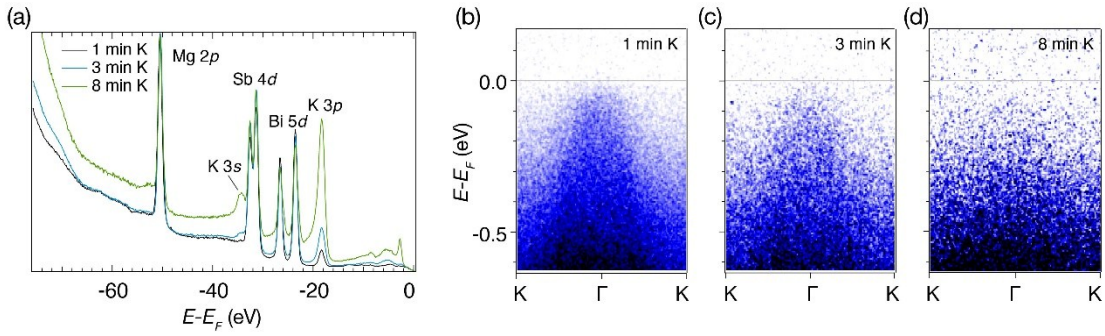

Fig. S8 K-doped $Mg_3Bi_{1.25}Sb_{0.75}$ photoemission. (a) K-doped $Mg_3Bi_{1.25}Sb_{0.75}$ core-level spectra, obtained with hν = 95 eV. (b)-(d) Series of ARPES intensity plots along Γ-K.

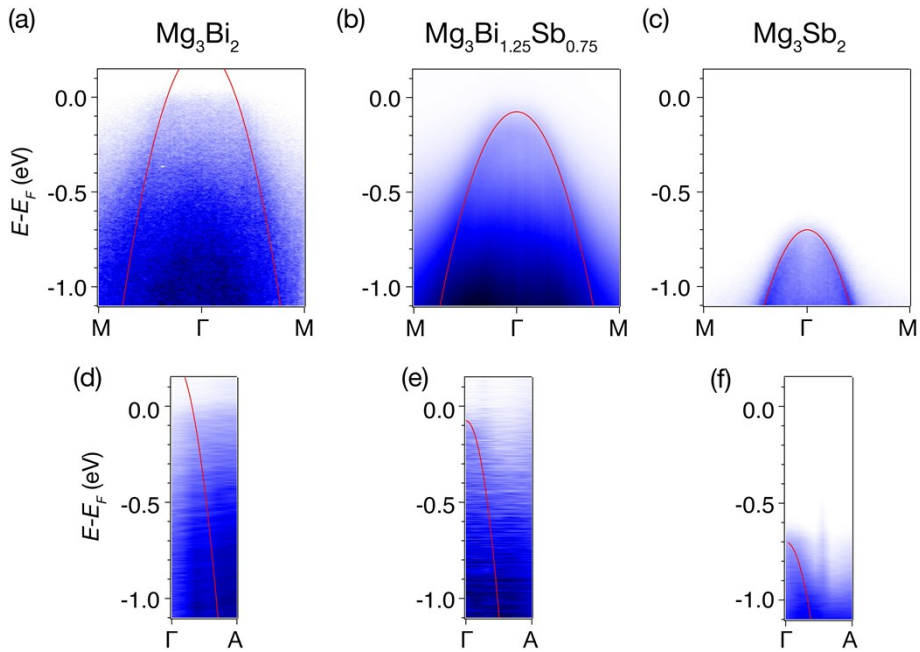

Fig. S9 ARPES intensity plots of three compounds along high symmetry directions, (a)-(c) Γ-M, (d)-(f) Γ-A. The red lines are parabolic fitting lines.

The effective mass can be calculated by fitting the band dispersions with parabola. As shown in **Fig. S9**, we fit the hole bands of the three compounds along the Γ-M and Γ-A directions. Effective mass values of Mg_3Bi_2 are 0.72 m_e and 0.24 m_e along in-plane (Γ-M) and cross-plane (Γ-A) directions, respectively. Mg_3Sb_2 shows 0.9 m_e and 0.16 m_e and $Mg_3Bi_{1.25}Sb_{0.75}$ shows 0.72 m_e and 0.24 m_e along in-plane and cross-plane directions, respectively.