Supplementary Information

Facile Synthesis of N-type Hexagonal $(Bi(Bi_2S_3)_9)I_3)_{0.667}$ as a Promising Thermoelectric Compounds

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Experimental procedure

1.1 sample synthesis

All the reagents used in this process are of analytical purity without further purification. A simple synthesis procedure is described in the following: 1.234 g Bi(NO)3.5H2O and 0.761 g CS(NH2)2 were dissolved into 80 ml deionized water and stirred at 80 °C for 5 min, followed by respectively adding 1 ml of thioglycolic acid and hydroiodic acid to the yellow solution. After 5 min more, the mixed canary yellow solution was transferred to a 100 ml Teflon-lined autoclave, then sealed and maintain at 140 °C for 16 h. The final black products were collected and washed by water three times and alcohol three times more, then dried at 70 °C overnight. The sample was centrifuged at 3500 rpm.

1.2 phase and microstructure characterization

X-ray diffraction (XRD) patterns were measured via a Miniflex600 operating at 40 kV and 15 mA using monochromated Cu Kα1 radiation (λ=1.541 Å, step size=0.01°, 10°min^{-1} from 20 to 70). The morphologies of the fractured surface of all samples were characterized by FE-SEM (FESEM;

Zeiss Merlin, Germany). The absorption spectra and diffuse-reflectance spectrum of the samples were found using a UV-vis-NIR spectrophotometer (UV-3600 plus). Focused Ion Beam (FIB, FEI Helios600i) with the in-situ lift-out technique was utilized to prepare the TEM samples. A Pt layer was sputtered on the full sample to protect the sample surface before the ion milling. This cap material also solve the charging problem in FIB. The major milling progress was regulated with the SEM and the milling was done with a 30 kV Ga ion beam. To reduce the damage layer on the samples, the final milling was measured with 5 kV followed by 2 kV Ga ion beam.

1.3 Thermogravimetric analysis, differential scanning calorimetry measurements.

Thermogravimetric (TG), differential scanning calorimetry (DSC) were performed on *Netzsch* STA 404 Germany. Small amount of (~8 mg) broken bulk were placed in Al2O3 crucible. For DSC and TG, they were heated from about 298 K to 973 K (10 K/min).

1.4 Thermoelectric observation

To obtain the optimized thermoelectric properties, the bulk sample was measured along the perpendicular section to the pressure direction of SPS. The electrical transport properties were measured from 323 to 673 K using a Seebeck coefficient/electrical resistance measuring instrument (ZEM-3, Ulvac-Riko, Japan) under a helium atmosphere protection. The thermal conductivity κ was obtained according to the relevance of $\kappa = DC_p d$, thermal diffusivity coefficient (D), measured via a laser flash method (LFA457, Netzsch, Germany), specific heat (C_p), measured via thermal analysis-based (STA449, Netzsch, Germany), density of samples (d), measured according to the Archimedes principle. The Hall coefficients (RH) of the samples were measured at room temperature using a Photonic Hall Effect Measurement instrument (HMS-7000) with a magnetic field of 1T and an electrical current of 20 mA applied. The carrier concentration (n) was

calculated using $n=1/eR_H$, where e is the charge. Besides, the mobility (μ) was calculated as $\mu=R_H\sigma$.

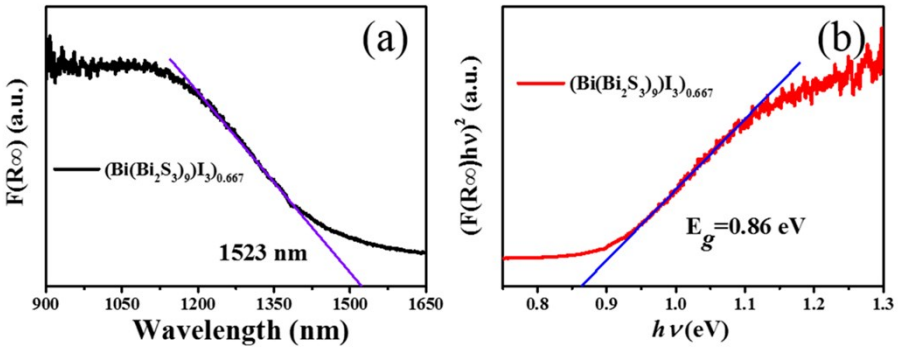

Fig. S1 (a) UV-vis absorption spectra and (b) diffuse-reflectance spectrum of $(Bi(Bi_2S_3)_9)I_3)_{0.667}$ powders

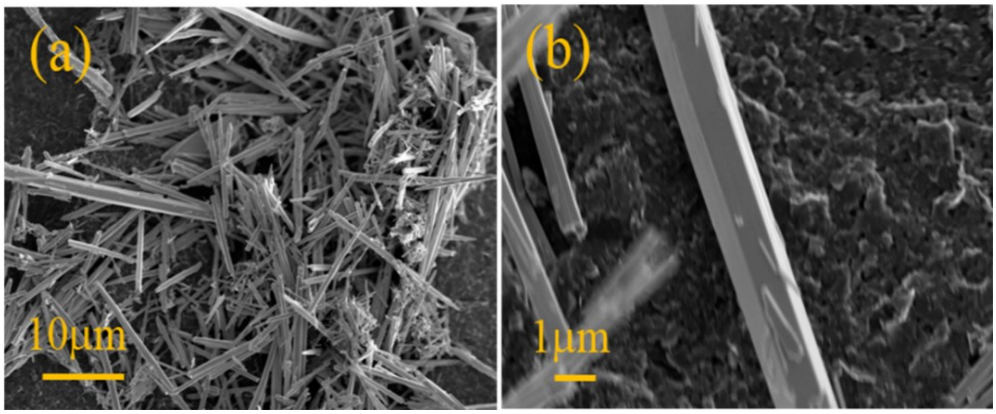

Fig. S2 SEM images of synthesized $(Bi(Bi_2S_3)_9)I_3)_{0.667}$ powder (a) low magnified image; (b) high magnified image

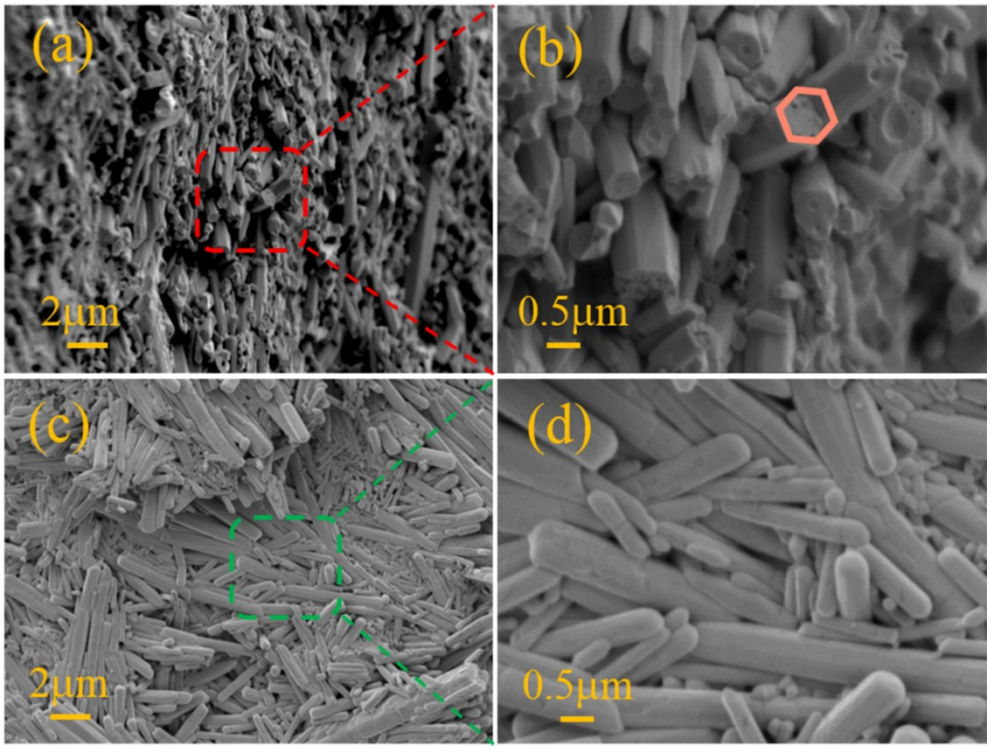

Fig. S3 The freshly fractured surfaces of $(Bi(Bi_2S_3)_9)I_3)_{0.667}$ bulk (a-b) parallel, (c-d) perpendicular to the pressure direction

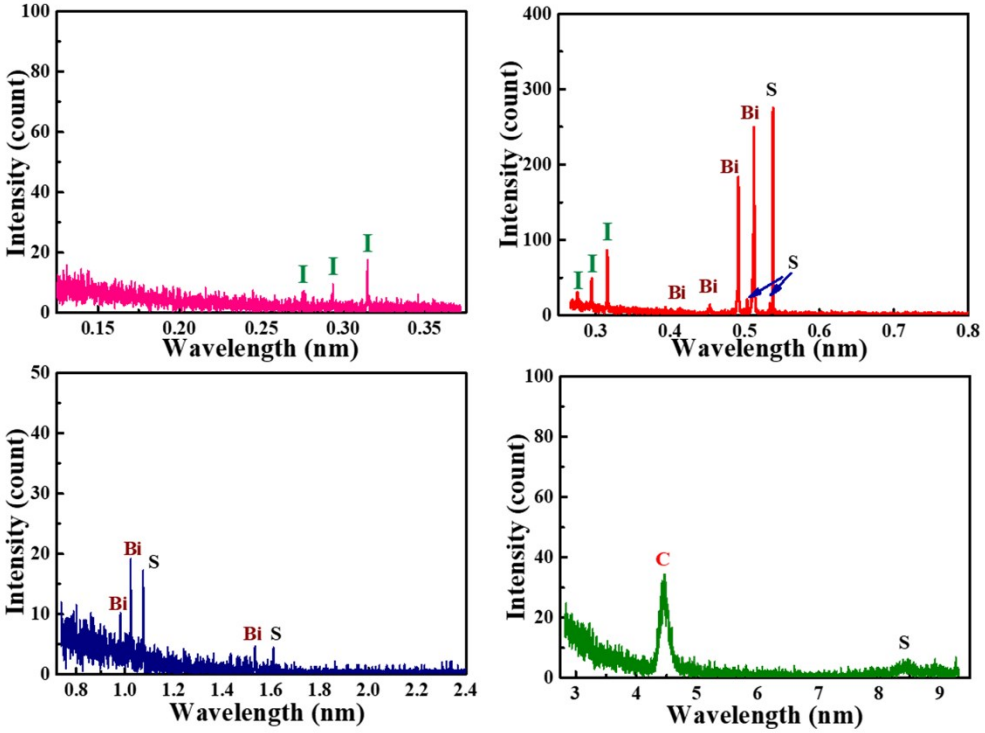

Fig. S4 EPMA spot spectra of the polished $(Bi(Bi_2S_3)_9)I_3)_{0.667}$ in the whole measured band range