Electronic Supplementary Information

$Bi_{0.33}(Bi_6S_9)Br$ compositing in Bi_2S_3 bulk materials forwards high thermoelectric properties

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Materials and method

Materials synthesis: Bismuth nitrate pentahydrate ($Bi(NO_3)_3·5H_2O$, 99.9%) and thiourea (CN_2H_4S, 99.99%), thioglycolic acid ($C_2H_4O_2S$, 98%) were purchased from Aladdin. All of them were used as the starting materials without further purification. In the fabrication procedure, three steps were mentioned.

Step one: synthesis of Bi_2S_3 nano-powders

0.761 g CN_2H_4S was dissolved into 80 mL deionized water and stirred at 100 ^oC for 5 min, then 1.4344 g $Bi(NO_3)_3·5H_2O$ also add to the solution and stirred for 5 min more. After that, 1 mL thioglycolic acid was dropped into the mixed solution. Finally, the solution was transferred to Teflon stainless steel and reacted at 140 ^oC for 16 h. The black Bi_2S_3 (BS) powders were obtained after centrifuging and drying at 3500 r and 70 ^oC, respectively.

Step two: synthesis of $Bi_{0.33}(Bi_6S_3)Br$ nano-powders

The synthesis procedure of $Bi_{0.33}(Bi_6S_9)Br$ (BSBr) powders are similar to that of the Bi_2S_3 powders. The only one different is that 1 mL hydrobromic acid was dropped into the mixed solution before transferring it to Teflon stainless steel.

Step three: preparation of Br-doped Bi_2S_3 bulks

The BSBr were added to Bi_2S_3 nano-powders according to the weight ratio of Bi_2S_3 + *x* wt % BSBr (*x* = 0, 3, 5, 7). The mixed powders were dispersed in ethyl alcohol by ultrasonic for 10 min to ensure homogeneous mixing. Then, the mixing solution were centrifuged at 3500r for 3 min, and dried at 70 ^{o}C for 12 h. The composite nano-powders were further densified by SPS technology at 673 K for 5 min under the pressure of 40 MPa using the SPS machine purchased from Japan (Sumitomo SPS632LX).

Characterization: The phase structure was performed by X-ray diffraction (XRD) Miniflex600. The field emission scanning electron microscopy (FE-SEM) was used to observe the morphologies of all samples. The elemental distribution of the sintered bulk samples was determined by energy dispersive spectroscopy and electron probe micro-analysis (EPMA, Shimadzu 1730H). Hall measurement system (HMS 7000) was used to measure the Hall coefficient (RH) at room temperature by the van der Pauw method. The transverse and longitudinal acoustic velocities were measured using an UMS Advanced Ultrasonic Modulus measurement system.

TE performance characterization: The fabricated bulks were cut and polished into square-shape of 6 mm $\times$ 6 mm $\times$1 mm and strip-shapes of 2 mm $\times$ 2 mm $\times$ 10 mm for the measurement of thermal diffusivity coefficient and electrical properties, respectively. The Seebeck coefficient/electrical resistance measuring system was used for the measurement of Seebeck coefficient and electrical resistivity. The thermal conductivity κ was calculated by the relationship of κ = DCpd, C_p was obtained from

ref. 24, *d* measurements based on the Archimedes method and *D* measured by a laser flash method. All TE properties obtained in this work were measured along the perpendidular to the pressure direction.

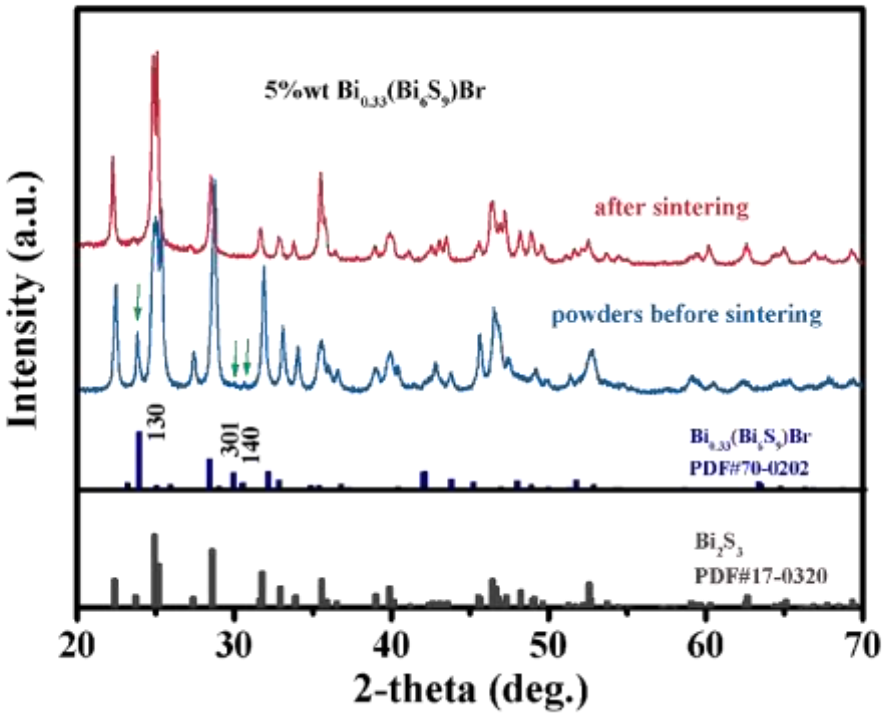

Fig. S1 XRD patterns of the Bi_2S_3 + 5% $Bi_{0.33}(Bi_6S_9)Br$ before and after sintering

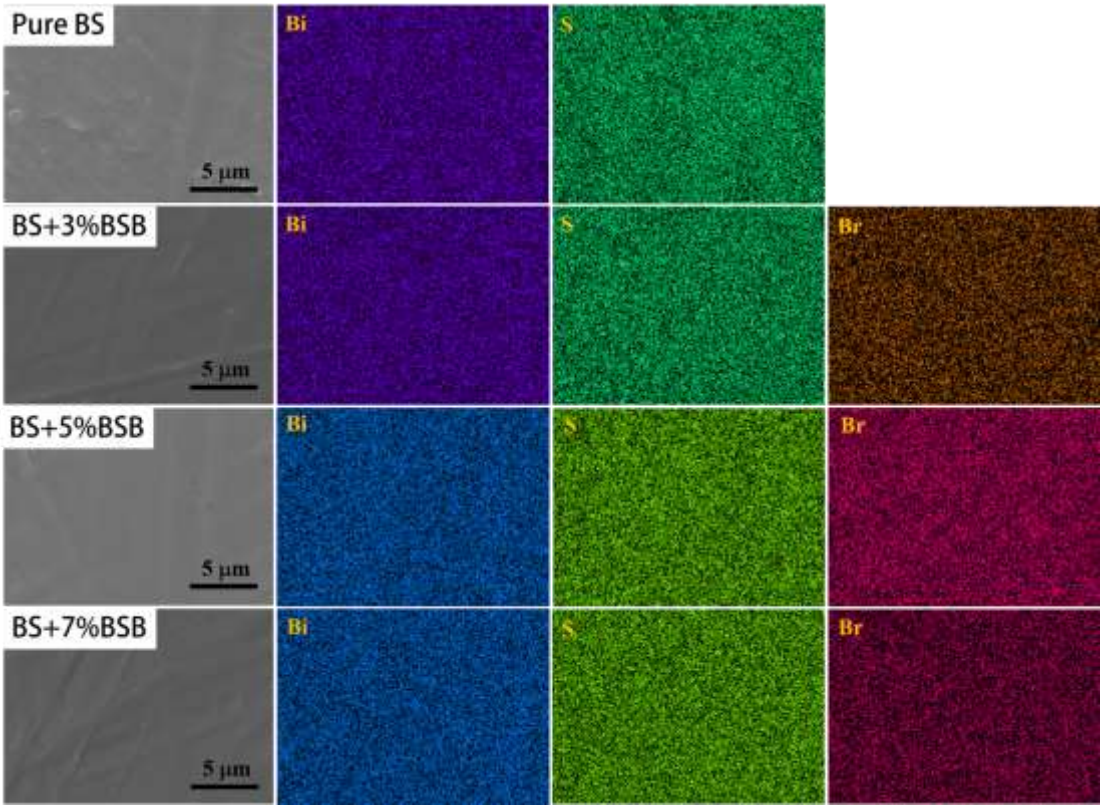

Fig. S2 the back-scattered electron (BSE) images of Bi_2S_3 + *x* wt % $Bi_{0.33}(Bi_6S_9)Br$ (*x* = 0, 3, 5, 7) samples and corresponding elemental dispersive spectrums (EDS) mapping.

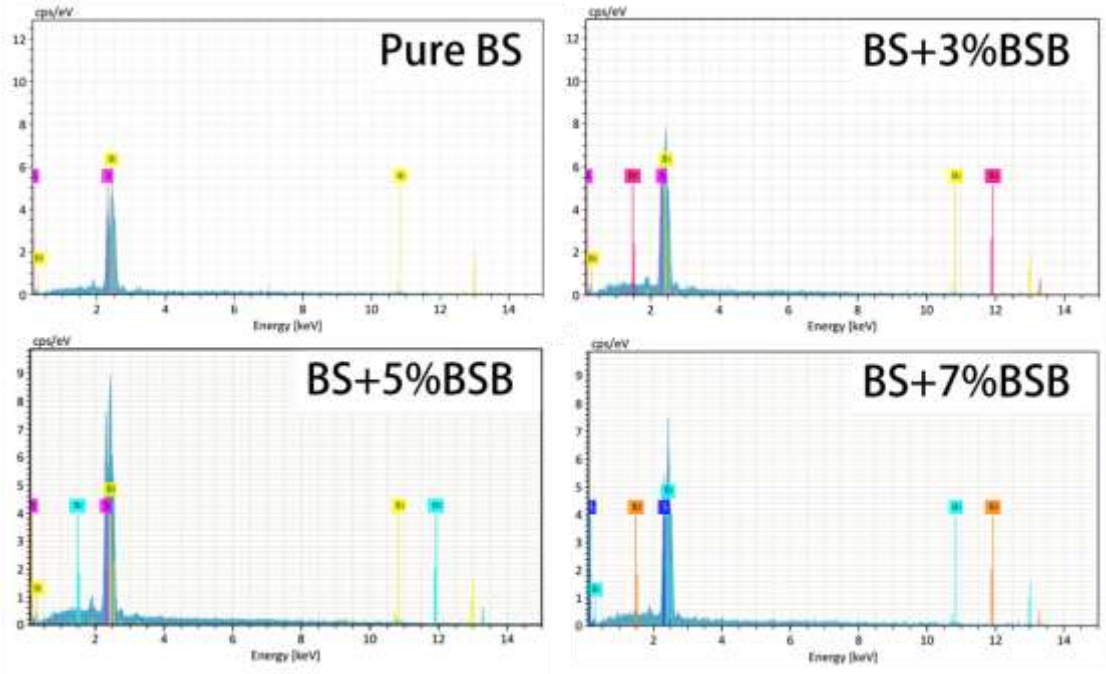

Fig. S3 the spot-scattered spectra of Bi_2S_3 + *x* wt % $Bi_{0.33}(Bi_6S_9)Br$ (*x* = 0, 3, 5, 7) samples

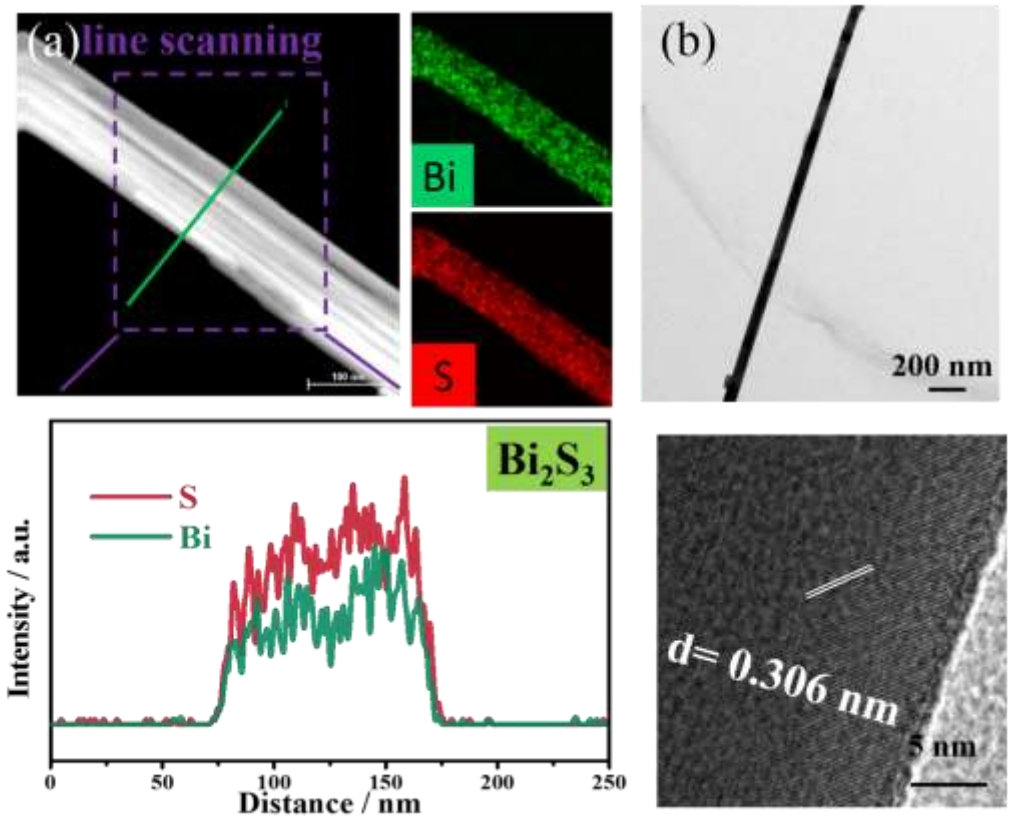

Fig. S4 (a) TEM image of Bi_2S_3 rod and corresponding mapping and line scanning, (b) a low resolution TEM image and corresponding high resolution TEM image

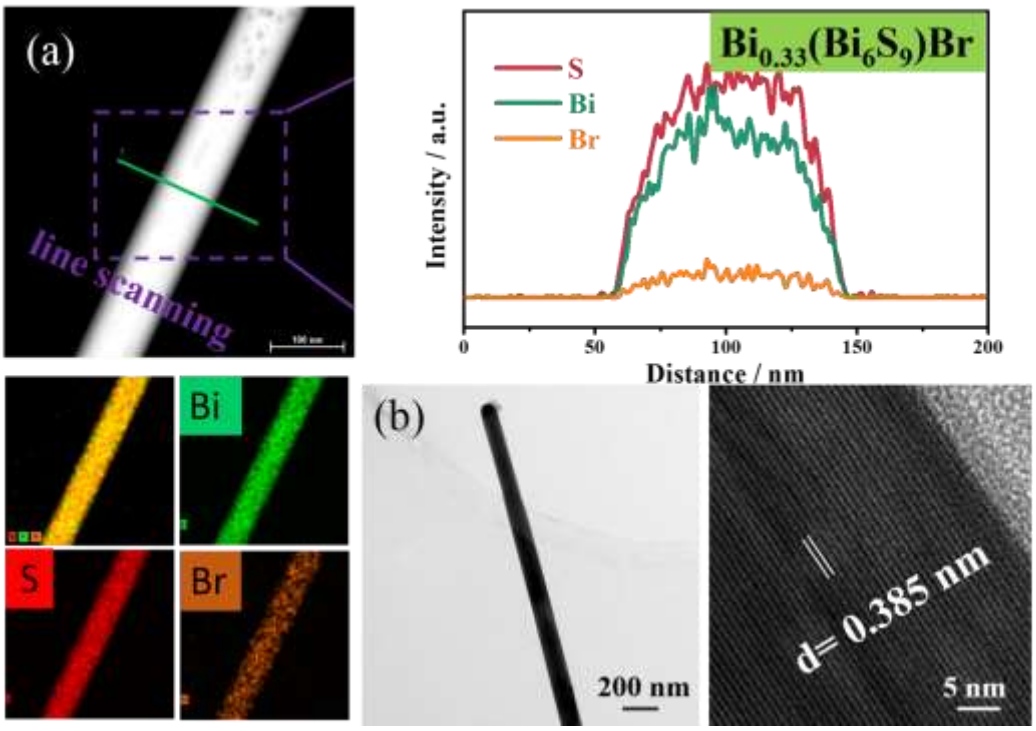

Fig. S5 (a) TEM image of $Bi_{0.33}(Bi_6S_9)Br$ rod and corresponding mapping and line scanning, (b) a low resolution TEM image and corresponding high resolution TEM image

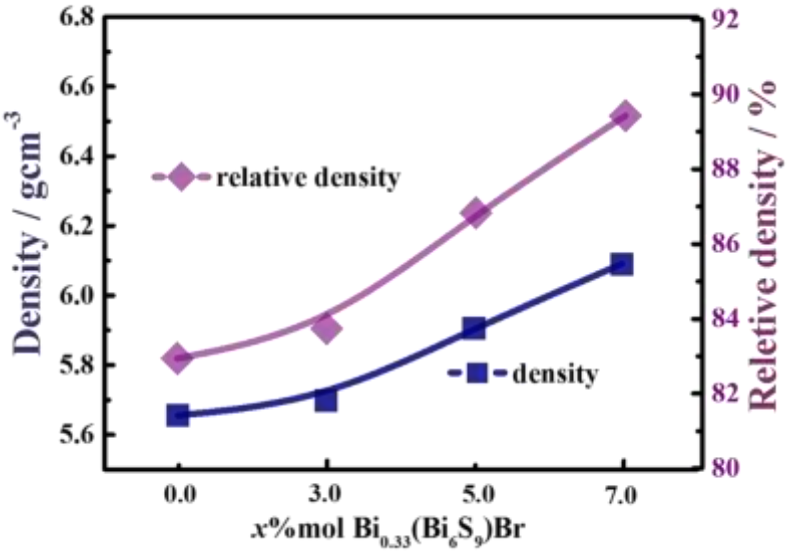

Fig. S6 the density and relative density of Bi_2S_3 + *x* wt % $Bi_{0.33}(Bi_6S_9)Br$ (*x* = 3, 5, 7) samples

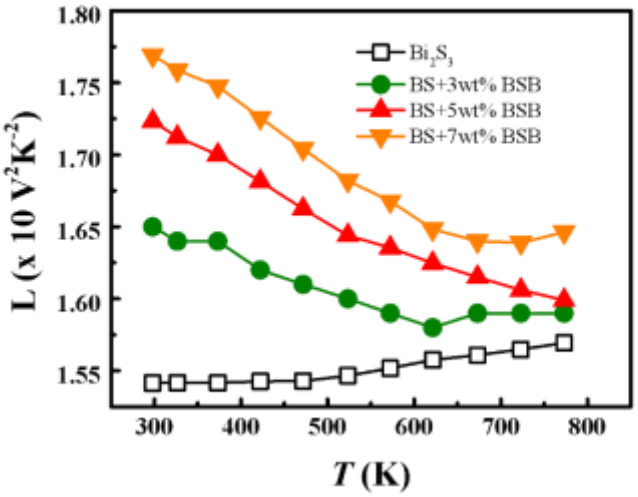

Fig. S7 Lorenz number as a function of temperature

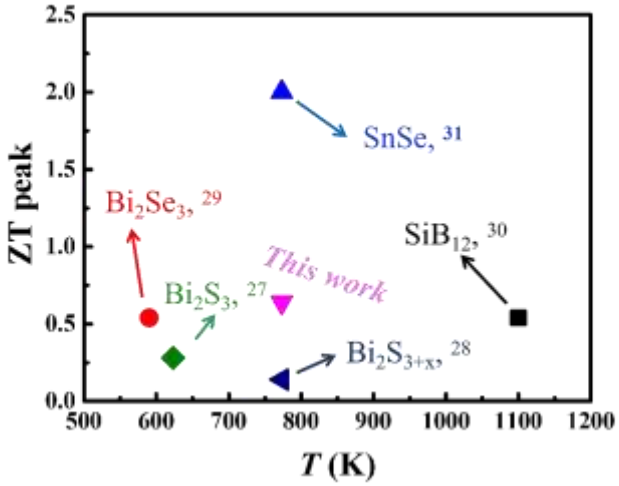

Fig. S8 ZT comparison of this work with other thermoelectric materials