Electronic Supplementary Information

CsBi$_4$Te$_6$: A New Facile Synthetic Method and Mid-temperature Thermoelectric Performance

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Experimental Section

Syntheses

All acquired elements were stored inside an Ar-filled glovebox (moisture and oxygen levels less than 0.1 ppm), and loading manipulations were carried out in the glovebox. Reactants RE (3N or higher) were purchased from Huhhot Jinrui Rare Earth Co.,Ltd., Bi (5N), and Te (5N) were purchased from Alfa Aesar, and CsCl (4N) was purchased from Sinopharm Chemical Reagent Co., Ltd. The mixture of RE, Bi, Te and CsCl were placed in a silica tube (diameter, 15 mm). The silica tube was then evacuated, sealed, and placed perpendicularly inside a temperature controlled furnace. The sample was heated to 1173K in 30h, and annealed at 1173 K for 2 days followed by cooling to 573 K at 5 K/h before switching off the furnace. The products were washed and dried with ethanol, and target crystals of CsBi$_4$Te$_6$ formed in 5–95% yield (based on RE).

The resulting target crystals were ground into a fine powder and subsequently hot pressed around 673 K under a pressure of 100 MPa for 1 h. The obtained pellets had relative densities no less than 98% of the theoretical value (7.18 g/cm^3).

Crystal Structure Determinations

The data collection was performed on a Rigaku Saturn 70 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The Lorentz and polarization correction were done. The absorption correction was performed by the multiscan method.[1] The structure was solved by the direct method and refined by the full-matrix least-squares fitting on F^2 by SHELX-97.[2] All atoms were refined with anisotropic thermal parameters. The coordinates were standardized using *STRUCTURE TIDY*.[3]

Powder X-ray Diffraction (PXRD)

The PXRD patterns were taken at room temperature on a Rigaku DMAX 2500 powder X-ray diffractometer by using Cu Kα radiation.

Elemental Analysis

The semiquantitative microprobe elemental analysis was performed on a field emission scanning electron microscope (JSM6700F) equipped with an energy-dispersive X-ray (EDX) spectroscope (Oxford INCA). The Ultima-2 inductively coupled plasma (ICP) optimal emission spectrometer was used for quantitative determination of the composition of single crystals.

Magnetic susceptibility measurements

The direct current magnetic susceptibility was measured using a Quantum Design PPMS-9T magnetometer at a field of 1000 Oe in the temperature range of 2–300 K.

Thermoelectric Property Measurements

The electrical resistivity and Seebeck coefficient were measured simultaneously in a helium atmosphere using a ULVAC-RIKO ZEM-3 instrument system. The thermal diffusivity (*D*) was directly measured by the laser flash diffusivity method with the aid of a Netzsch LFA-457

instrument. The total thermal conductivity was calculated via $\kappa = D \cdot C_p \cdot d$, where C_p was estimated using the Dulong-Petit approximation ($C_p = 3k_B$ per atom), d was the measured density, which was determined using the dimensions and mass of the sample and then reconfirmed by measurements using Archimedes' principle on a home-built device.

References

(1) *CrystalClear*, version 1.3.5; Rigaku Corp.: The Woodlands, TX, 1999.

(2) G. M. Sheldrick, *SHELXTL*, version 5.1; Bruker-AXS: Madison, WI, 1998.

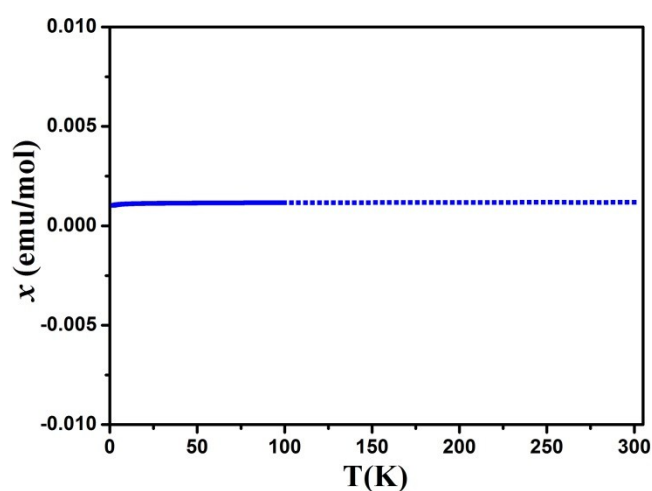(3) L. M. Gelato and E. Parthe, *J. Appl. Crystallogr.*, 1987, **20**, 139–143.

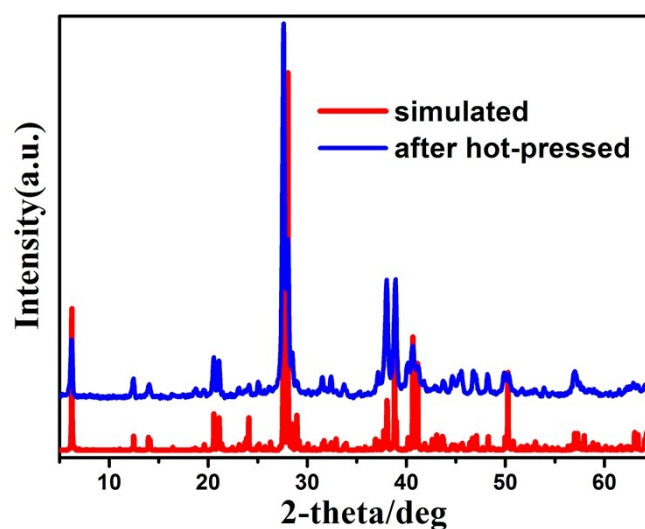**Figure S1.** Molar susceptibilities of $CsBi_4Te_6$ as a function of temperature.

Figure S2. Simulated (red) and after hot-pressed (blue) PXRD patterns of the as-synthesized $CsBi_4Te_6$.