Electronic Supplementary Information

Experimental details

The synthesis process started with element powders (Cu, 99.99% and S, 99.95%). Weighed powders were ball-milled at 425 rpm for 2, 4, and 8 h in a mixture atmosphere of high-purity argon (95%) and hydrogen (5%) gases using a planetary ball mill (QM-1SP2, Nanjing University, China). Stainless steel vessels and balls were used, and the weight ratio of the ball to powder was kept at 20:1. The ball-milled powders were sintered at 773 to 1173 K for 5 min in a Φ20 mm graphite moulds under a axial pressure of 40 MPa in a vacuum using the SPS system (Sumitomo SPS1050, Japan) with a heating rate of 100 K/min and soaking time of 5 min. Phase structure was analyzed by X-ray diffraction (XRD, CuKα, BrukerD8, Germany). The morphologies of fractographs and energy dispersive spectrum (EDS) of bulks were investigated by a field emission scanning electron microscopy (FESEM, SUPRATM 55, Germany). The differential thermal analysis (DTA) measurement was performed using a differential thermal analyzer (HCT-1, Beijing, China) in Ar atmosphere. The Thermoelectric properties were evaluated along the sample section perpendicular to the pressing direction of SPS. The Seebeck coefficient and electrical resistivity were measured at 323 to 673 K in a helium atmosphere using a Seebeck coefficient/electric resistance measuring system (ZEM-2, Ulvac-Riko, Japan). The thermal conductivity κ was calculated by the relationship of $\kappa = DC_pd$ with a specific heat C_p, which value is about 0.38 to 0.42 from room temperature to 673 K, measured by using a thermal analyzing apparatus (Dupont 1090B, USA), the density d and pore percentage of bulk samples were measured by the Archimedes method, and the thermal diffusivity D measured by a laser flash method (NETZSCH Laser Flash Apparatus LFA427, Germany).