

Supplemental materials:

Experimental section

Commercial high purity Copper (99.9 mass%) and Sulfur (99.98 mass%) powders (Aldrich, UK) were used. The powders were weighed in a glove box to avoid reaction with moisture and oxygen in the air (Beta, Saffron, UK). The weighed powders were placed into a stainless steel (or WC) vessel with steel balls (or WC); the weight ratio of the steel balls to powders was 20:1 (50:1 for WC). The mixtures were ball-milled at 450 rpm for 3 hours in an atmosphere of high-purity argon gas using a planetary ball milling machine (QM-3SP2, Nanjin University, China). The powders were put into a graphite die (an inner diameter ~ 15 mm) and then sintered at 400 °C under 60 MPa with a heating rate of 50 K/min and holding time of 5 minutes in a spark plasma sintering furnace (SE-607, FCT System GmbH, Germany) in an argon environment.

We used two kinds of milling vessels and balls to prepare $\text{Cu}_{1.8}\text{S}$ powders. As shown in Fig. S1, the powders prepared using stainless steel balls/vessel are single phase (low temperature digenite), however, the powders prepared using WC balls/vessel are not single phase. There is some $\text{Cu}_{1.96}\text{S}$ inside and another, unidentified, impurity phase, which indicates that higher impact force is not helpful to synthesize pure digenite (the density of WC is 15.63 g/cm^3 , and the density of steel is 7.85 g/cm^3).

The samples were cut into $2.5 \times 2.5 \times 13$ mm bars for electrical conductivity (σ) and Seebeck coefficient (S) measurements using temperature differential and four point probe methods in a vacuum environment. The laser flash method (NETZSCH, LFA457, Germany) was used to measure the thermal diffusivity coefficient. The density of the samples was measured using the Archimedes method. The specific heat was determined using differential scanning calorimetry (NETZSCH DSC 404C Germany). The thermal conductivity (k) was obtained from the product of thermal diffusivity, specific heat and density. The zT value was calculated using the equation $zT = S^2 \sigma T / k$, where T is the absolute temperature. The crystal structure was characterised by X-ray diffraction (XRD) and the microstructure of samples was observed by scanning electron microscopy (SEM).

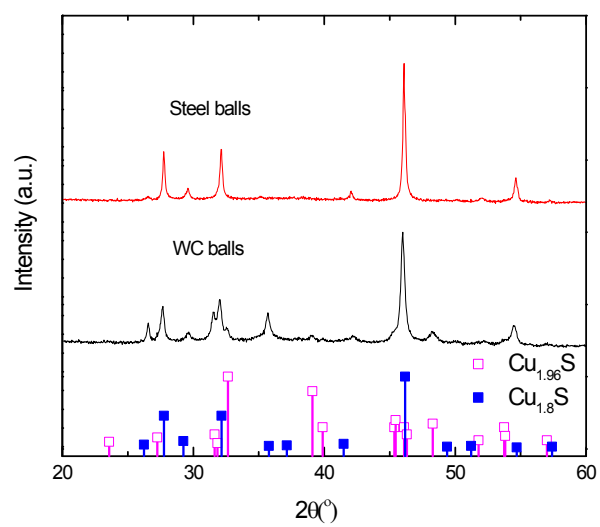


Fig. S1. XRD patterns of the powders ball milled from WC and stainless steel balls/vessels.

XPS was used to check the relative content of S^{2-} , Cu^{2+} , and Cu^{+} in $Cu_{1.75}S$ and $Cu_{1.8}S$ bulk samples. As shown in Fig. S2, they have similar spectra. This indicates that XPS is not useful for the quantification of composition or distinguishing between Cu^{1+} and Cu^{2+} .

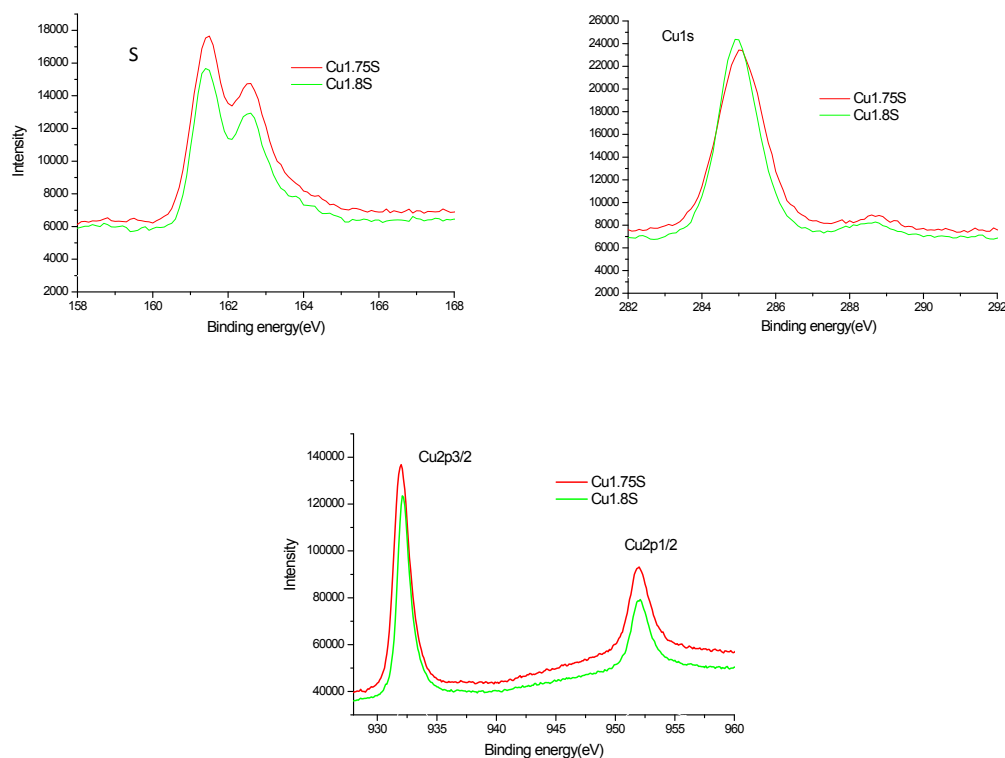


Fig. S2. XPS spectra of $Cu_{1.75}S$ and $Cu_{1.8}S$ bulk samples.

As shown in Fig. S3, for the $\text{Cu}_{1.8}\text{S}$ sample sintered at 400 °C, the grains did not grow significantly and the diameter was ~ 100 nm. For a sample sintered at 500 °C, some grains grew up to several micrometers. When the sintering temperature was increased to 600 °C, the density decreased because pores were produced because of the volatilization of S at higher temperature in a vacuum environment. All the compounds with different copper content had similar microstructures.

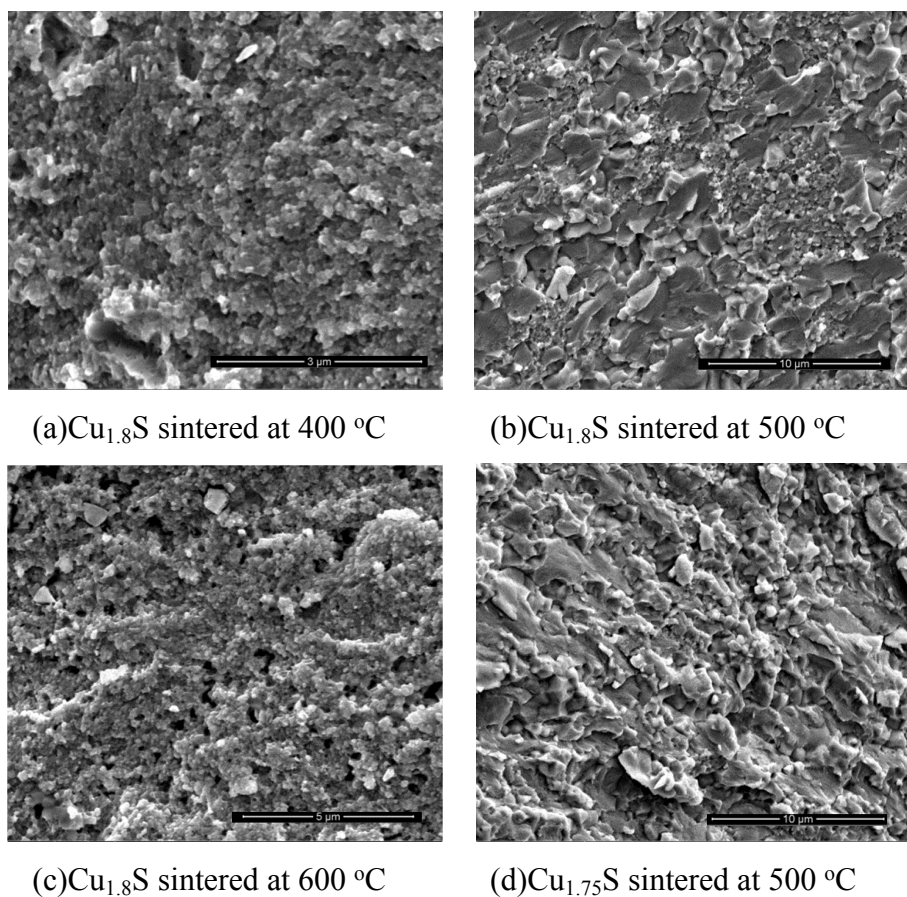


Fig. S3. SEM images of the samples sintered at different temperatures.

In the manuscript, the quoted ratio x of Cu/S is based the composition of the starting powder mixture. According to Fig. S1, there is no obvious volatilization of S after ball milling. The ratio of Cu/S after sintering is difficult to check because S is a light element. The SPS sintering of CuS involves rapid densification in several minutes in an argon environment (90 KPa). So the ratio x should be same as that of the starting powder mixture.

According to the measurement of Seebeck coefficient, the volatilization of S begins at ~ 400 °C. We tried to measure the thermoelectric properties at higher temperature (> 350 °C) as shown in Fig. S4. For $\text{Cu}_{1.8}\text{S}$, the maximum ZT is about 0.3 at 450 °C. However, the measurement could not be repeated because of the volatilization of sulfur. So in the paper we have only presented the repeatable measurements.

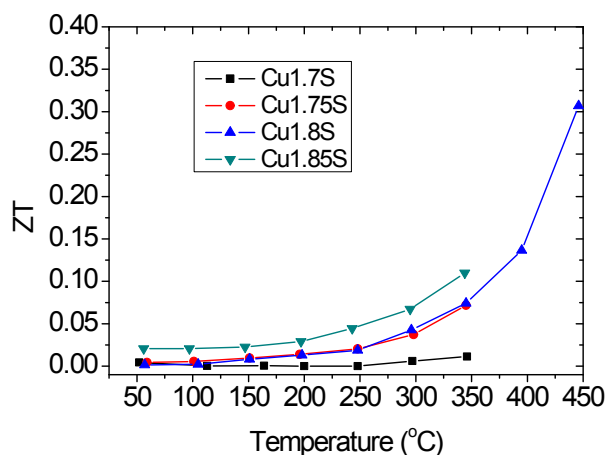


Fig. S4. Temperature dependence of zT value for Cu_xS