Supporting Information

Fabrication and thermoelectric properties of n-type $CoSb_{2.85}Te_{0.15}$ using selective laser melting

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1. Introduction of the SLM apparatus

The SLM apparatus used in our experiment is a customized system developed by our group. Figure S1 shows the schematic diagram of the SLM instrument. The apparatus comprises a vacuum chamber, a substrate on a lifting stage, a scraper to spread the powder on the substrate, a fiber laser with oscillating mirrors along x- and y-axis, a computer to control the lifting stage, the output power and scanning path of the laser beam. The SLM processing used a commercial fiber laser (MFSC-100W), with the maximum output power of 100 W, laser wavelength of 1064 nm, and the focal spot size of about 100 μm. The laser passes through the window on the top of chamber to reach the sample. The material of the window where the laser passes through is fused silica with coatings for a reinforced transmissivity to 1064nm IR laser.

During the fabrication process, the slurry was spread on the substrate with a blade, when the ethanol evaporates, a flat powder bed layer of 30-40 μm thickness on the substrate is ready for further laser processing. A laser beam is controlled to scan across the powder bed via the two oscillating mirrors above the fused silica window. The substrate will move down with lifting device by certain thickness after each scan. And the slurry is then spread on this layer with the blade. This process repeats until the sample is fabricated.

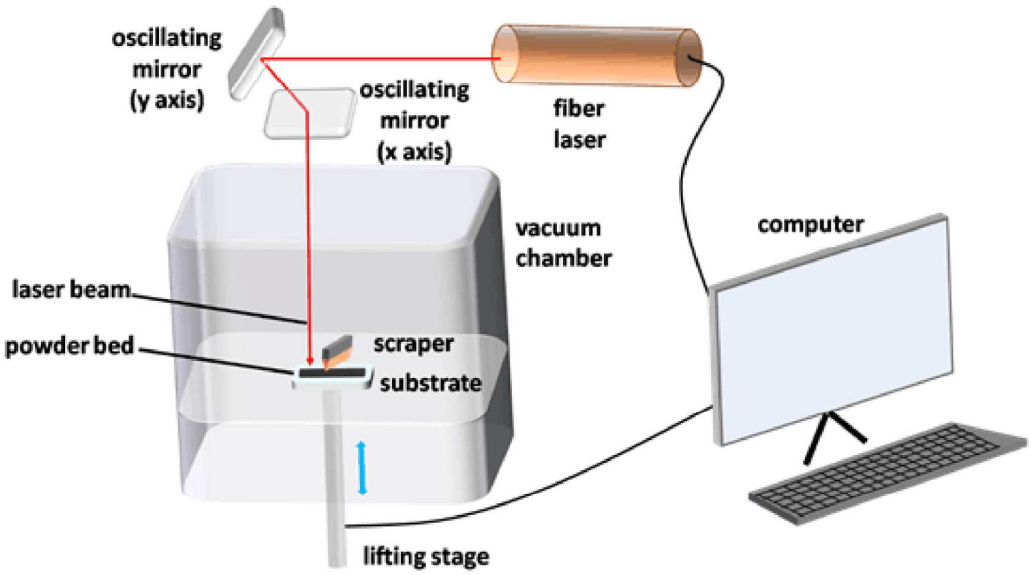

Figure S1: The schematic diagram illustrates the customized apparatus used for the SLM experiments. The apparatus comprises a vacuum chamber, a substrate on a lifting stage, a scraper to spread the powder on the substrate, a fiber laser with oscillating mirrors along x- and y-axis, a computer to control the lifting stage, the output power and scanning path of the laser beam.

2. Laser power density E_V dependence of the weight loss percentage of each layer

During the SLM process, we can observe some smoke occurring when the laser melts the powder bed. We used conductive tapes to collect a small amount of particles from the smoke. The tapes with the collected particles were then characterized by SEM and EDS to observe the morphology and confirm its composition. Figure S2 (a)-(d) shows the SEM images of vaporized particles. The vaporized particle usually possess spherical or ellipsoid shapes with a diameter typically around 10~30 μm. The composition of these particles are Co-Sb compounds.

When the laser energy density E_V=58~130 J/mm^3, the layer quality is good. Therefore, we select a series of laser parameters in this range to test the weight loss percentage of $CoSb_{2.85}Te_{0.15}$ in the process of SLM surface forming. SHS prepared $CoSb_{2.85}Te_{0.15}$ powder was sintered by SPS at 650 ℃ for 8 minutes under 40 MPa to obtain a cylinder with the diameter of 20 mm, which served as a substrate in this part of the experiment. Using an electronic balance to weigh the substrate mass m_1. The slurry was spread on the substrate, when the ethanol evaporates, weigh the total mass of substrate and powder bed m_2. After laser processing, weigh the total mass of substrate

and forming surface m_3. Therefore, m_2-m_1 is the mass of powder bed, m_3-m_1 is the mass of single layer, m_2-m_3 is the mass of weight loss during SLM processing. And the weight loss percentage of each layer is (m_2-m_3)/(m_2-m_1). The weight loss percentage as a function of laser energy density E_V is given in figure S2(e). The weight loss percentage is around 2% to 10%, and it obviously shows a positive correlation with E_V.

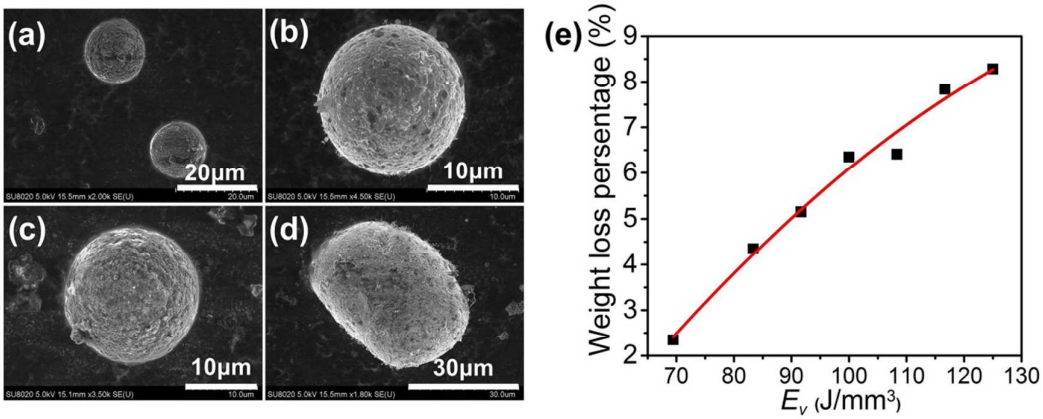

Figure S2: (a)-(d) SEM images of vaporized particle; (e) laser power density E_V dependence of the weight loss percentage of each layer

3. Exploration of annealing process parameter

We annealed the SLM-prepared samples in vacuum under different conditions and check the phase of samples by XRD. First, the SLM-prepared samples were annealed in vacuum for 60 min at different temperatures from 150 ℃ to 520 ℃. Figure S3 shows the XRD patterns of these samples. The result shows that the transition temperature of $CoSb_2$ to $CoSb_3$ is at about 400 ℃, and the samples annealed at 450 ℃ and 480 ℃ show almost single phase except a small amount of $CoSb_2$. However, when the annealing temperature increase further, $CoSb_3$ start to decompose due to the sublimation of Sb and second phases start to increase. Then, we fixed the annealing temperature at 450 ℃ and varied the annealing duration from 30 minutes to 360 minutes. Figure S4 shows the XRD patterns of these samples annealed for different durations and that of the as-prepared sample. The sample annealed for 30 minutes comprises of mainly $CoSb_3$ with second phases $CoSb_2$ and Sb still detectable. With the annealing temperature increased to 120 minutes, Sb almost disappears although

$CoSb_2$ is still visible. When the annealing duration increases to 240 minutes, $CoSb_2$ content is further reduced. Further increasing the annealing duration did not help eliminate $CoSb_2$ from the sample. So we chose to anneal the sample at 450 ℃ for 4 hours in our research.

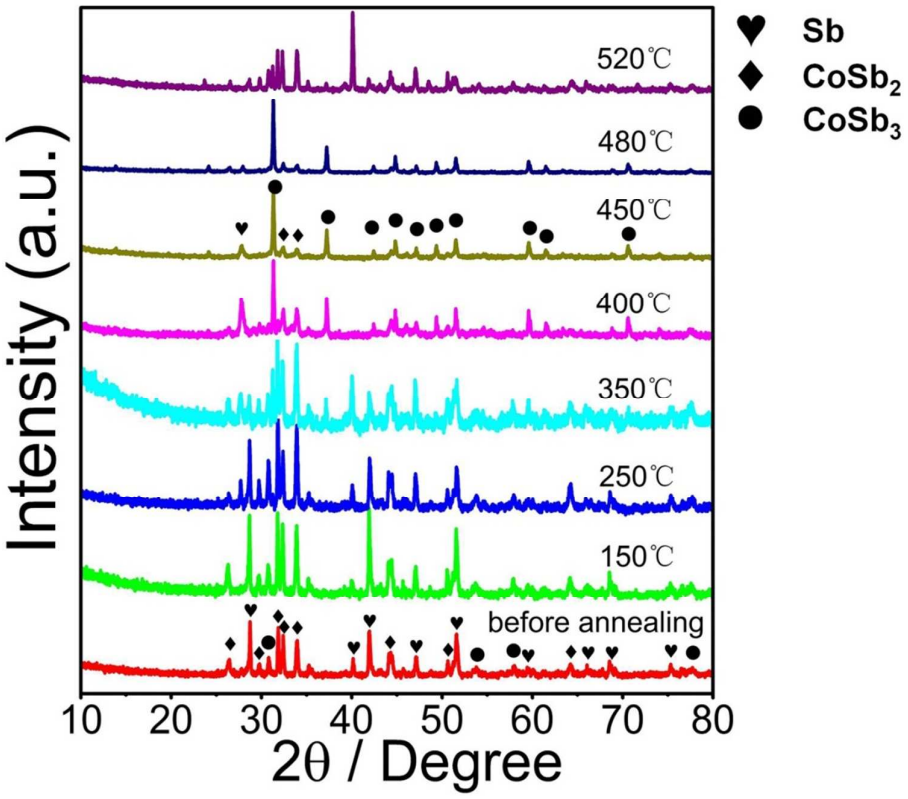

Figure S3: XRD patterns of the SLM-prepared samples were annealed in vacuum for 60 minutes at different temperatures from 150 ℃ to 520 ℃.

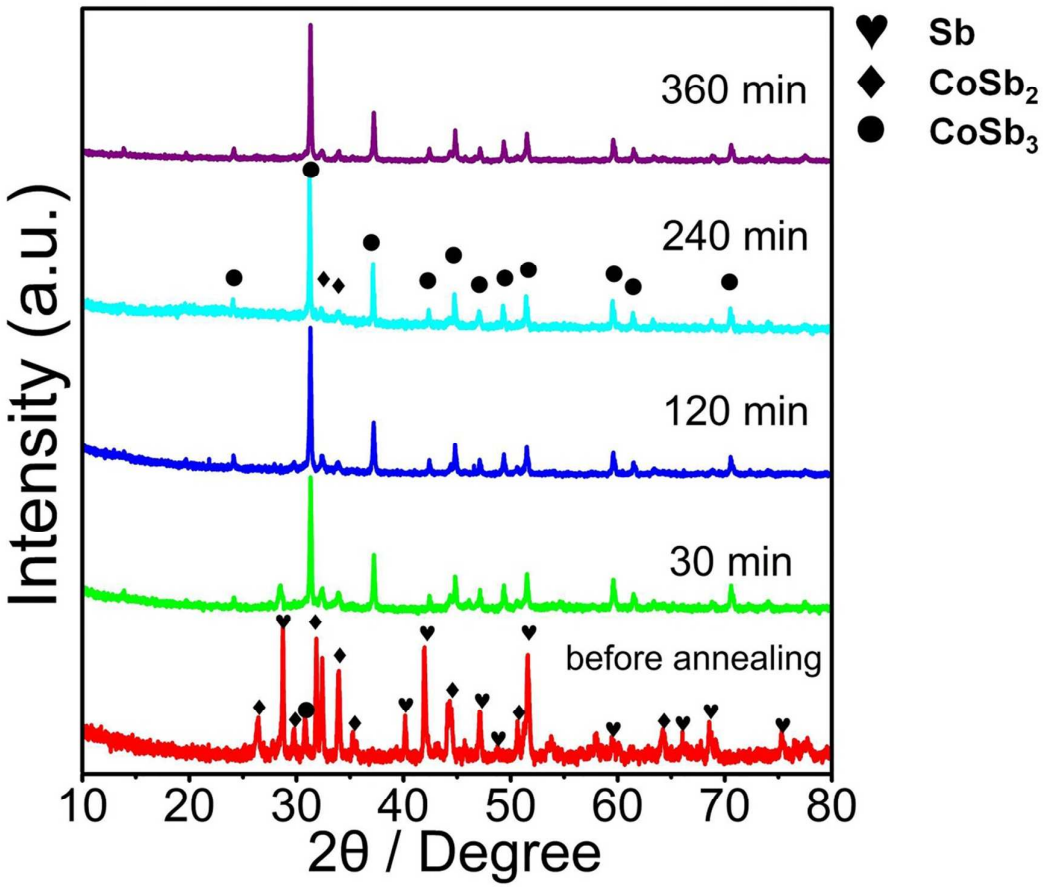

Figure S4: XRD patterns of the SLM-prepared samples were annealed in vacuum at 450 ℃ for different annealing duration from 30 minutes to 360 minutes.