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Supporting information:

Texturation Boosts the Thermoelectric Performance of BiCuSeO Oxyselenides

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Experimental details :

The samples with the composition of $Bi_{0.875}Ba_{0.125}CuSeO$ were synthesized by a two-step solid state reaction route. Stoichiometric mixture of Bi_2O_3 (4N), Bi (3N), Cu (3N), Se (5N) and BaO (4N) powders were mixed by ball milling process. Then the mixed powders were put in a graphite die followed by cold pressing, and sealed in vacuum quartz tubes which were sintered at 573 K for 15 h. The obtained bulks were ground into powder followed by cold pressing and heating at 1023 K for 24 h in vacuum in a hot pressing sinter. The as-synthesized bulks were reground into powders and then densified by hot press sintering under the axial compressive stress of 80 MPa in vacuum at 973 K for 30 min, resulting in cylinder-shaped samples of Ø15 mm × 50 mm. The hot-pressed Ø15 mm × 50 mm bulks were then charged into a Ø 20 mm graphite mould and were hot-pressed again at 983 K to obtain a textured bulk through the extra space. The obtained cylinder-shaped samples were then cut and polished, and followed by second times and third times hot-forging in larger diameter dies to obtain a textured bulk through the extra space, finally resulting in cylinder-shaped samples with thickness of 10mm. This hot-press processing includes four steps in order to get textured bulks. In order to express expediently in the text, the as-synthesized, the first hot-forged, the second hot-forged and the third hot-forged samples with textured microstructures were shortly named 0T, 1T, 2T and 3T, respectively. Correspondingly, the textured samples cut perpendicular and parallel to the pressing direction were named *x*T-⊥ (radial direction in a cylinder sample) and *x*T-// (axial direction in a cylinder sample, *x* is the number of hot-forging steps, *x*=0, 1, 2, 3), respectively. The sample photographs are shown in **Figure** S1.

The obtained textured pellets were cut perpendicularly and parallelly to the pressing direction into bars with dimensions about 10 mm × 3 mm × 3 mm that were

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used for simultaneous measurement of the Seebeck coefficient and the electrical conductivity using an Ulvac Riko ZEM-2 instrument (ZEM-2, ULVAC-RIKO, Japan) under a helium atmosphere from room temperature to 923 K. Heating and cooling cycles gave repeatable electrical properties, which indicates that the properties are thermally stable. Electrical properties obtained from different slices cut from the same pellets were similar, attesting the homogeneity of the samples. The uncertainty of the Seebeck coefficient and electrical conductivity measurements is 5 %. The textured pellets were polished into coins of Ø8mm×2mm for thermal diffusivity measurements. The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the material. The thermal conductivity was calculated from $\kappa=D\cdot C_p\cdot\rho$, where the thermal diffusivity coefficient (D) in the range room temperature to 923 K was measured using the laser flash diffusivity method in a Netzsch LFA427 (NETZSCH, LFA427, Germany). The thermal diffusivity data were analyzed using a Cowan model with pulse correction and heating and cooling cycles give reproducible values for each sample. The specific heat capacity (C_p) was determined by differential scanning calorimetry (NETZSCH DSC 404C Germany). The thermal diffusivity coefficient (D) and specific heat capacity (C_p) can be found in supporting information, **Figure** S4. The density (ρ) was determined by using the dimensions and mass of the sample, which was then reconfirmed using the Archimedes method. The relative density for all the samples is around 95 %. Thermal diffusivities obtained for different slices from the same pellet are also similar. The uncertainty of the thermal conductivity is estimated to be within 8%, considering the uncertainties for D, C_p and ρ. The combined uncertainty for all measurements involved in the calculation of ZT is less than 15 %. The Hall coefficients, R_H, of the samples were measured at room temperature using a physical properties measurement system (PPMS-9T, Quantum

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Design Inc, USA), and a magnetic field of 2T and electrical current of 30mA were applied. The carrier concentration (n_H) was calculated by $n_H=1/eR_H$, where e is the electronic charge. The carrier mobility (μ) was calculated by $\mu=\sigma R_H$, where σ is the electrical conductivity. Phase structure was analyzed by X-ray diffraction (XRD, CuKα, Bruker D8, Germany). Electron backscattering diffraction (EBSD) (Aztec) investigations were carried out in a scanning electron microscopy (SEM) microscope TESCAN MIRA 3 LMH operated at 30 kV. The thin SEM-EBSD specimens were prepared by conventional standard methods. The procedures include cutting, grinding, and polishing.

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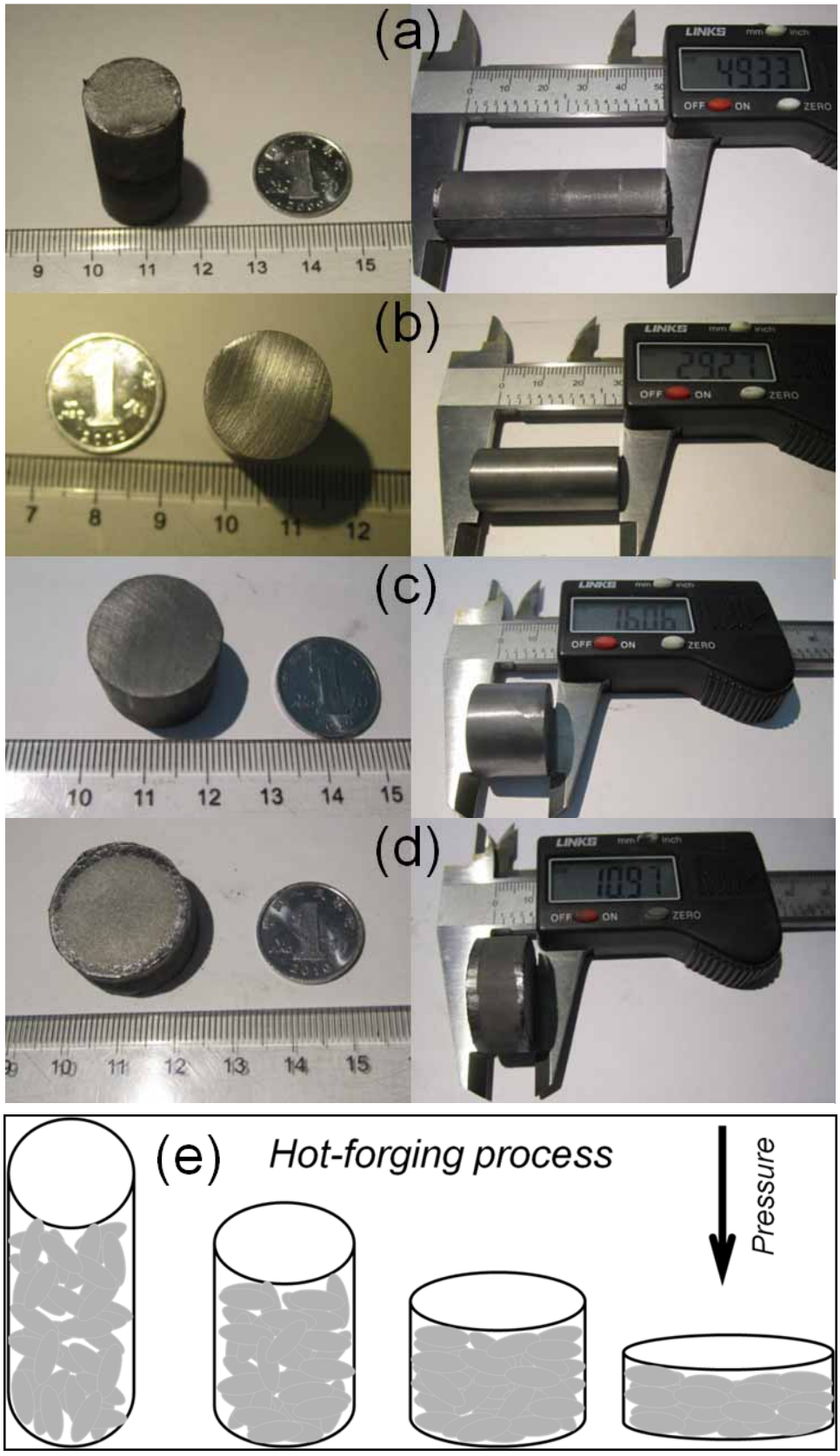

Figure S1: Typical samples used in this study: (a) As-synthesized sample (0T); (b) One step hot-forged sample (1T); (c) Two steps hot-forged sample (2T); (d) Three steps hot-forged sample (3T); (e) The scheme of hot-forging process.

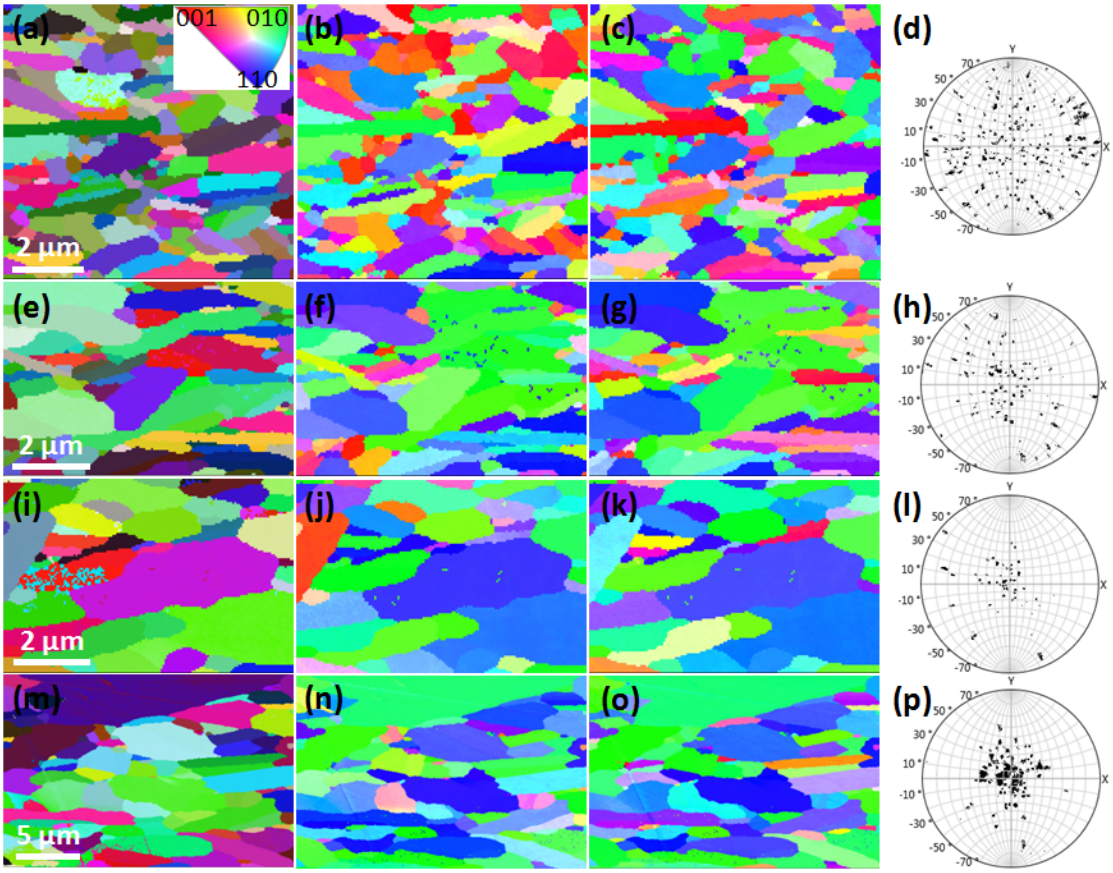

Figure S2: The micrographs are perpendicular to the pressure direction of textured $Bi_{0.875}Ba_{0.125}CuSeO$ samples before and after hot-forging: (a), (e), (i) and (m) all-Euler images of 0T-⊥, 1T-⊥ 2T-⊥ and 3T-⊥ samples, respectively; (b), (f), (j) and (n) X-Euler images of 0T-⊥, 1T-⊥ 2T-⊥ and 3T-⊥ samples, respectively; (c), (g), (k) and (0) Y-Euler images of 0T-⊥, 1T-⊥ 2T-⊥ and 3T-⊥ samples, respectively; (d), (h), (l) and (p) pole images of 0T-⊥, 1T-⊥ 2T-⊥ and 3T-⊥ samples, respectively.

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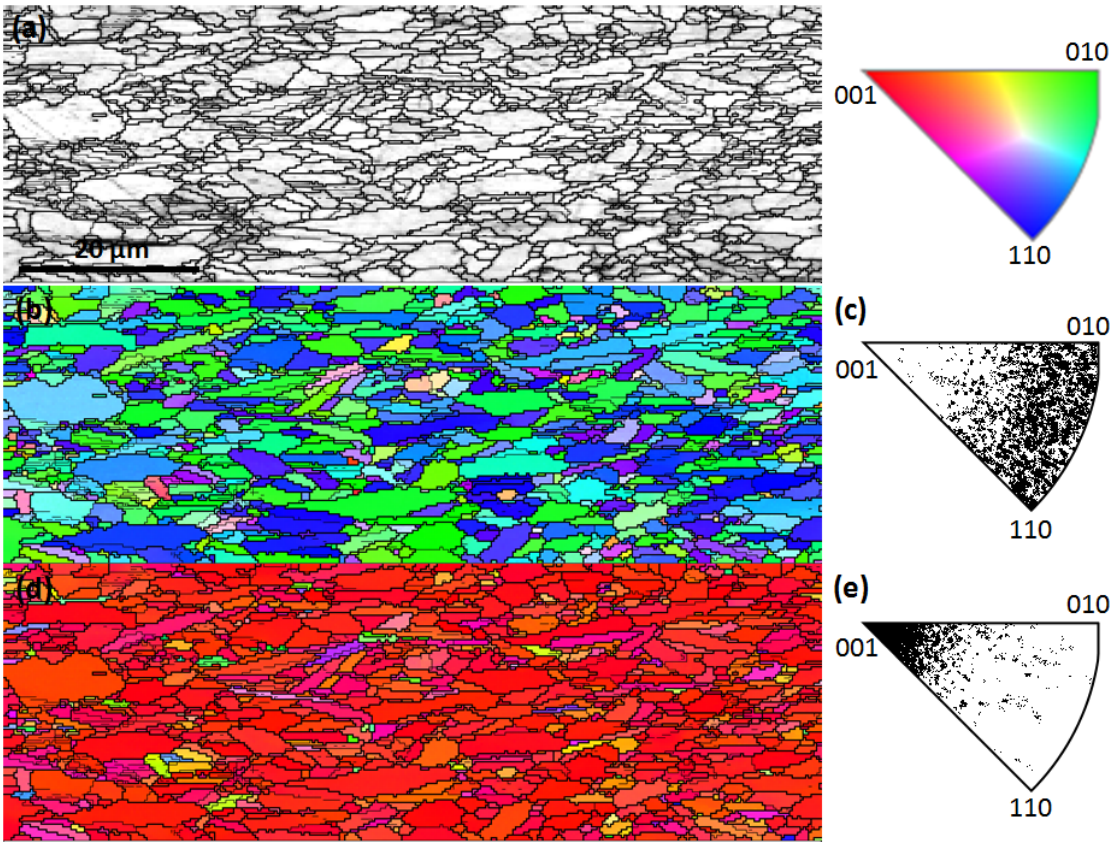

Figure S3: The micrographs are perpendicular to the pressure direction of $Bi_{0.875}Ba_{0.125}CuSeO$ (3T-⊥) sample after three hot-forging steps: (a) Band contrast image, (b) X-Euler image, (c) inverse pole image along X direction, (d) Z-Euler image, (e) inverse pole image along Z direction.

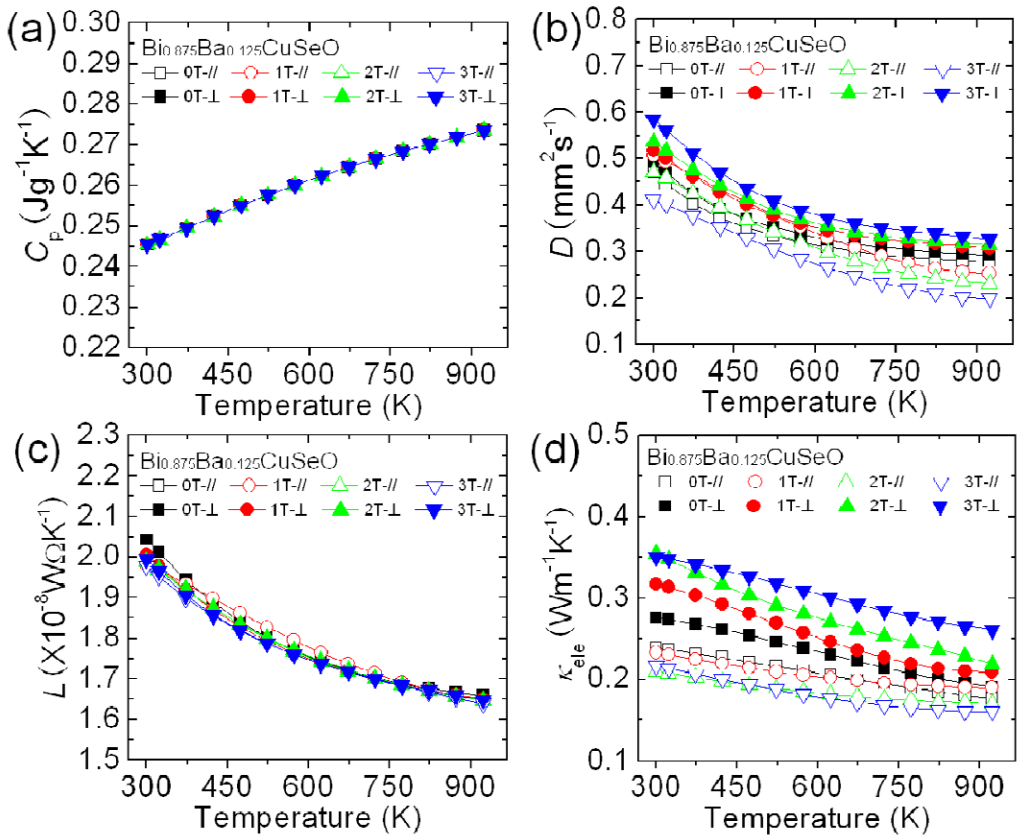

Figure S4: Thermoelectric properties as a function of temperature for textured $Bi_{0.875}Ba_{0.125}CuSeO$ samples: (a) Heat capacity; (b) Thermal diffusivity; (c) Lorenz number; (d) Electronic thermal conductivity