Supporting information

Brittle Failure Mechanism in Thermoelectric Skutterudite $CoSb_3$

Guodong Li [§,†,‡], Qi An [§,⊥], Wenjuan Li [†,‡], William A. Goddard III [*,⊥], Pengcheng Zhai [†], Qingjie Zhang [*,†], and G. Jeffrey Snyder [*,‡]

[†]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.

[‡]Department of Materials Science, Northwestern University, Evanston, Illinois 60208, USA.

[⊥]Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125, USA.

[§]These authors contributed equally to this work

[*]Corresponding authors: jeff.snyder@northwestern.edu; wag@wag.caltech.edu; zhangqj@whut.edu.cn

Shear failure mode of $CoSb_3$ along the (001)/<110> slip system

Figure S1-S2 show the partial atomic configurations and the average bond lengths (Sb1-Sb2, Sb3-Sb4, Co1-Sb3) along the (001)/<110> slip system. The system (Co-Sb frameworks and Sb-rings) continuously stretches with increasing strain until the strain of 0.254. With further strain, the Sb1-Sb2 bond weakens due to quickly increased Sb1-Sb2 bond length, suggesting the softening of Sb-rings, thus leading to the gradually decreased stress. However, the Co-Sb frameworks deform uniformly because of the slightly stretched Co1-Sb3 bond length. At 0.358 strain, the failure of short Sb3-Sb4 bond leads to deconstruction of Sb-rings and collapse of Co-Sb frameworks, resulting in a sudden dropped stress as shown in figure 1. Prior to failure strain of 0.358, the Sb1-Sb2, Sb3-Sb4 and Co1-Sb3 bonds stretch from 3.03, 2.90, and 2.53 Å to 3.78, 3.06 and 2.64 Å, with an increase of 24.75%, 5.52% and 4.35%, respectively.

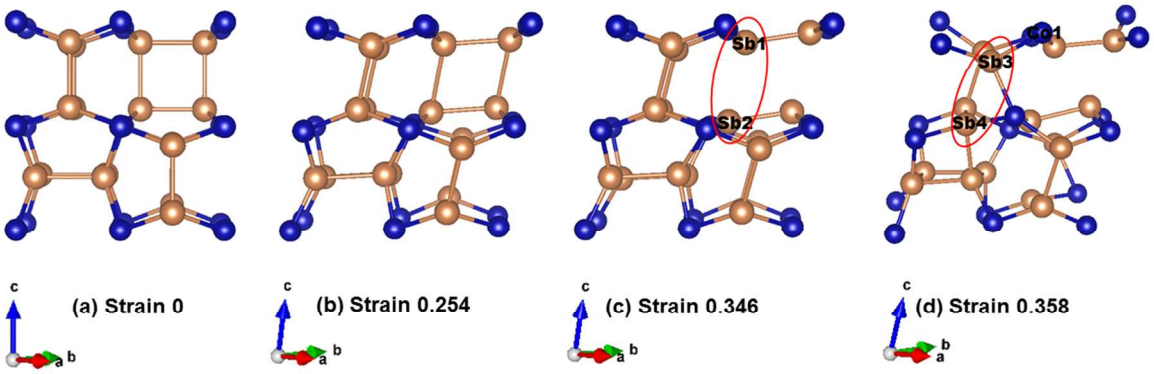

Figure S1. The partial atomic configurations shearing along the (001)/<110> slip system: (a) strain 0 corresponds to the initial stage, (b) strain 0.254 corresponds to the ideal strength, (c) strain 0.346 before failure strain, (d) failure strain 0.358.

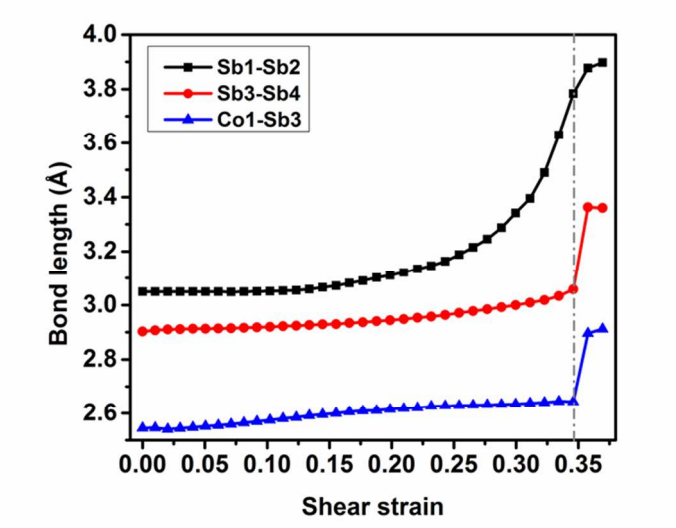

Figure S2. The average bond lengths (Sb1-Sb2, Sb3-Sb4, and Co1-Sb3 bonds marked in figure S1) with the increasing shear strain along the (001)/<110> slip system. The gray dash line represents the strain before failure.

Shear failure mode of $CoSb_3$ along the (111)/<1-10> slip system

Figure S3 shows the partial atomic configurations for shearing along the (111)/<1-10> slip system, and figure S4 shows the average bond lengths (Sb1-Sb2, Sb3-Sb4, Sb5-Sb6, Co1-Sb7) with increasing shear strain. As the strain increases to 0.243, the model continuously deforms. At 0.243 strain corresponding to the ideal strength, the Sb5-Sb6 bond is compressed to a critical length 2.86 Å, but the Sb-rings remain the rectangular shape as shown in figure S3(b). With further strain, the Sb5-Sb6 bond begins to stretch, and the Sb-rings change to a rhombus shape, suggesting the Sb-rings has started to soften, leading to the gradually decreased stress as shown in figure 1, even though all average bond lengths grow slowly. At 0.346 strain, the deconstruction of Sb-rings caused by the Sb3-Sb4 bond failure results in the structural collapse and the sudden decreased stress. Prior to the failure strain of 0.346, the Sb1-Sb2, Sb3-Sb4 and Co1-Sb7 bond lengths change from 3.03, 2.90, and 2.53 Å to 3.22, 3.08 and 2.72 Å, with an increase of 6.27%, 6.21% and 7.51%, respectively.

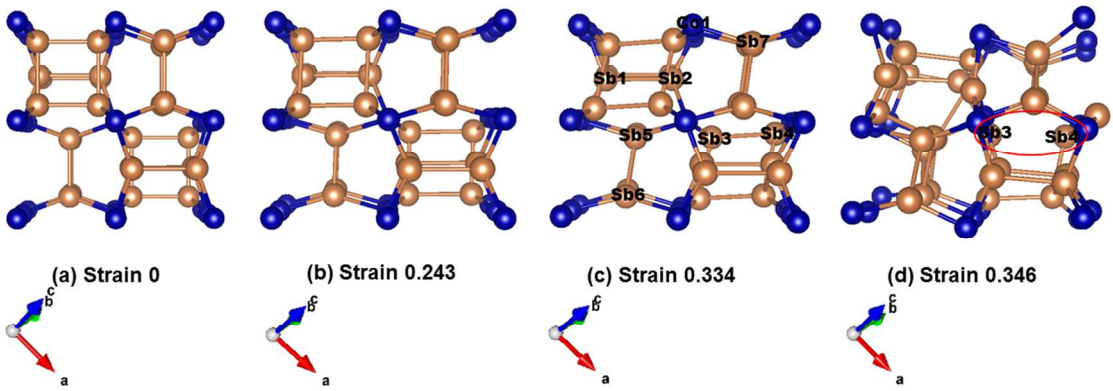

Figure S3. The partial atomic configurations shearing along the (111)/<1-10> slip system: (a) strain 0 corresponds to the initial stage, (b) strain 0.243 corresponds to the ideal strength, (c) strain 0.334 before failure strain, (d) failure strain 0.346.

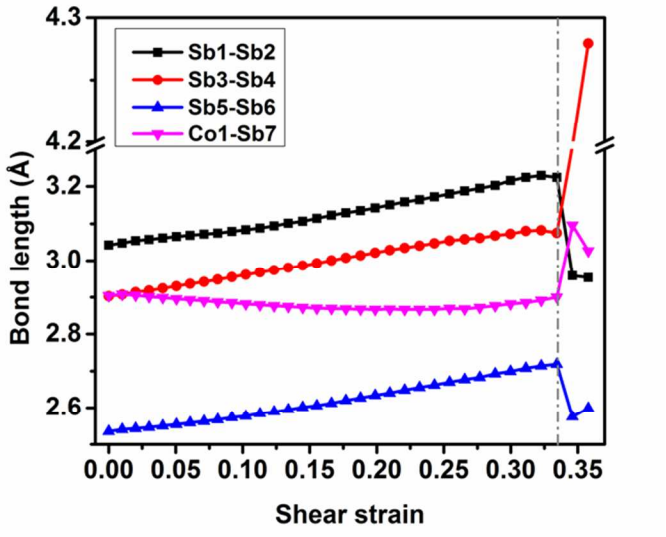

Figure S4. The average bond lengths (Sb1-Sb2, Sb3-Sb4, Sb5-Sb6, and Co1-Sb7 bonds marked in figure S3) with the increasing shear strain along the (111)/<1-10> slip system. The gray dash line represents the strain before failure.

Tensile failure mode of $CoSb_3$ along the [1-10] tension system

Figure S5-S6 plot the partial atomic structures and bond lengths along [1-10] tension system respectively. With the strain increased to 0.173, the Sb1-Sb2 bond stretches uniformly, then weakens rapidly, leading to the rapid softening of Sb-rings. At 0.184 strain, the Sb3-Sb4 bond failure and Sb1-Sb2 bond reconstruction are responsible for the deconstruction of Sb-rings, leading to the stress relaxation and structural rearrangement. With further tension, the Co1-Sb5 bond failure indicates the collapse of Co-Sb framework, hence resulting in totally structural failure and the stresses dropping to ~0 GPa. Prior to the failure strain of 0.184, the Sb1-Sb2, Sb3-Sb4 and Co1-Sb5 bond lengths change from 3.03, 2.90, and 2.53 Å to 3.43, 3.10, and 2.72 Å, with an increase of 13.20%, 6.90% and 7.51%, respectively.

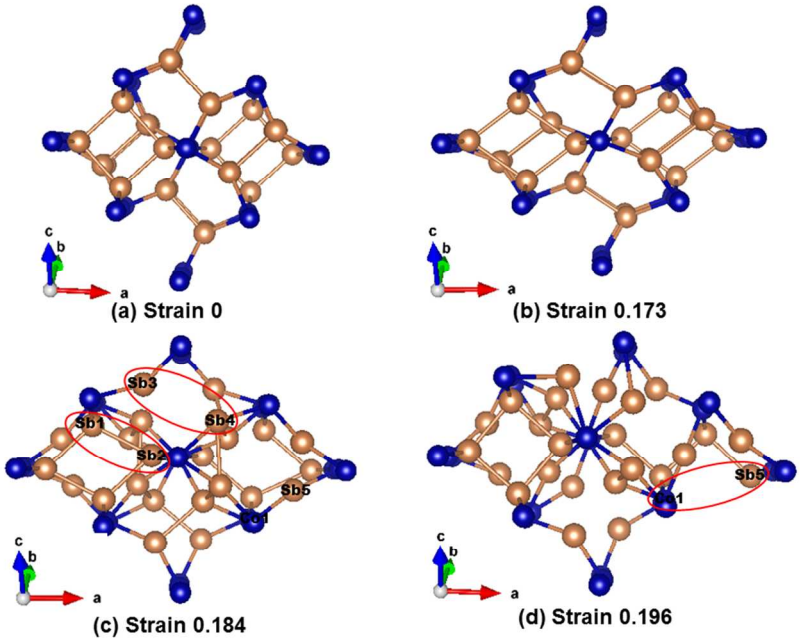

Figure S5. The partial atomic structures along the [1-10] tension system: (a) strain 0% corresponds to the initial stage, (b) strain 17.25% corresponds to the ideal strength, (c) failure strain 18.43%, (d) strain 19.61% corresponds to the Co1-Sb5 bond failure.

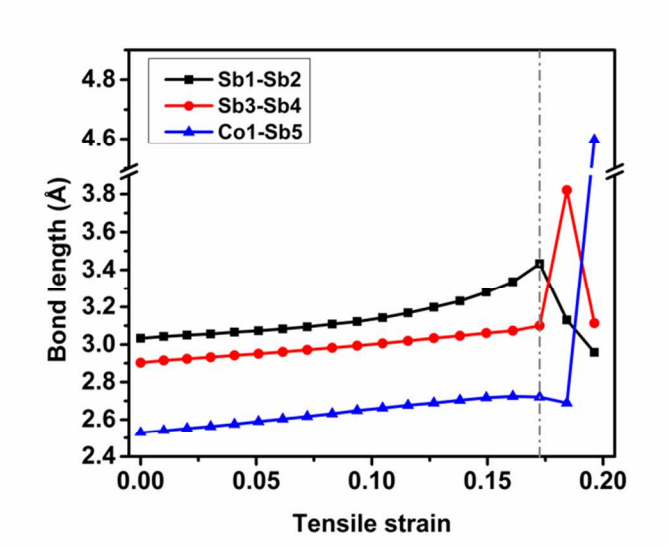

Figure S6. The average bond lengths (Sb1-Sb2, Sb3-Sb4, and Co1-Sb2 bonds marked in figure S5) with the increasing tensile strain along the [1-10] tension system. The gray dash line represents the strain before failure.

Tensile failure mode of $CoSb_3$ along the [111] tension system

Figure S7-S8 plot the partial structural patterns and bond lengths along [111] tension system. With the strain increased to 0.196, the Sb1-Sb2 and Sb3-Sb4 bonds deform slowly, the lengths change from 3.03 to 3.16 Å and from 2.90 to 3.02 Å, with an increase of 4.29% and 4.14% respectively. The small deformation suggests that the Sb-rings do not soften much. The Co1-Sb4 bond expands rapidly, and the length changes from 2.53 to 2.98 Å, with an increase of 17.79%, indicating the Co-Sb framework expands highly. At 0.220 strain, the deconstruction of Sb-rings caused by the Sb-Sb bond failure leads to the collapse of Co-Sb frameworks and stress relaxation.

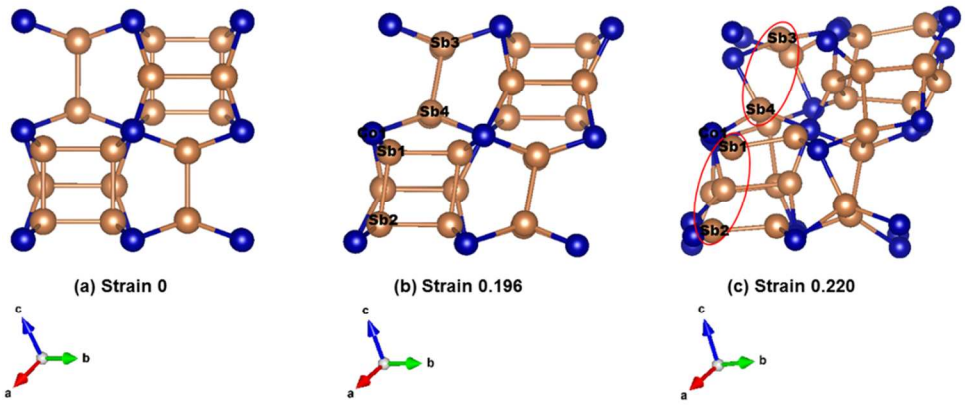

Figure S7. The partial atomic configurations along the [111] tension system: (a) strain 0 corresponds to the initial stage, (b) strain 0.196 corresponds to the ideal strength, (c) failure strain 0.220.

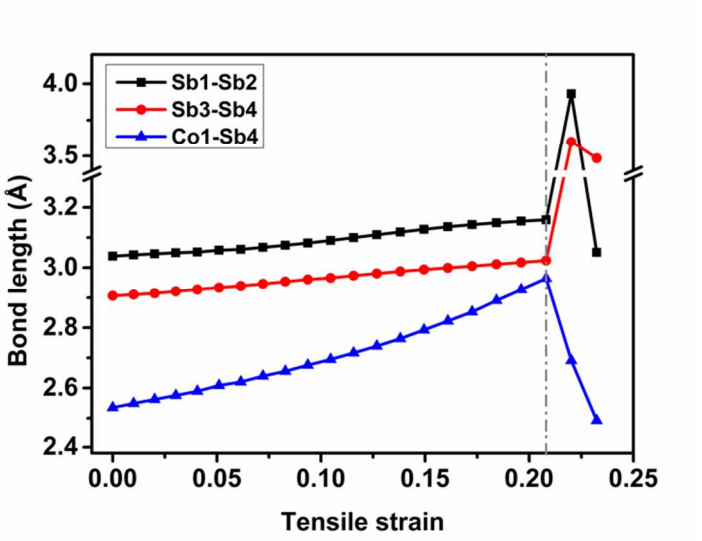

Figure S8. The average bond lengths (Sb1-Sb2, Sb3-Sb4, and Co1-Sb4 bonds marked in figure S7) with the increasing tensile strain along [111] tension system. The gray dash line represents the strain before failure.