Supporting information

Structure and Failure Mechanism of the Thermoelectric CoSb$_3$/TiCoSb Interface

Guodong Li $^†$‡, Shiqiang Hao $^†$, Umut Aydemir $^‡$, Max Wood $^‡$, 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 and Engineering, Northwestern University, Evanston, Illinois 60208, USA.

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

$§$ITMO University, St. Petersburg, Russia

*Corresponding authors: jeff.snyder@northwestern.edu; zhangqj@whut.edu.cn
Explanation of four named interfacial structures

**Figure S1.** The upper$_{\text{CoSb}_3(100)}$/TiCoSb(111) interface. When the upper surface of CoSb$_3$(100) slab (upper$_{\text{CoSb}_3(100)}$) coheres with TiCoSb(111) to form the CoSb$_3$/TiCoSb interface, we name this interface as the upper$_{\text{CoSb}_3(100)}$/TiCoSb(111) interface.
Figure S2. The lower\_CoSb\(_{2}\)\(_{(100)}/\)TiCoSb\(\{111\}\) interface. When the lower surface of CoSb\(_{3}\)\(_{(100)}\) slab (lower\_CoSb\(_{3}\)\(_{(100)}\)) coheres with TiCoSb\(\{111\}\) to form the CoSb\(_{3}/\)TiCoSb interface, we name this interface as the lower\_CoSb\(_{2}\)\(_{(100)}/\)TiCoSb\(\{111\}\) interface.
Figure S3. The upper_CoSb$_3$(100)/TiCoSb(110) interface. When the upper surface of CoSb$_3$(100) slab (upper_CoSb$_3$(100)) coheres with TiCoSb(110) to form the CoSb$_3$/TiCoSb interface, we name this interface as the upper_CoSb$_3$(100)/TiCoSb(110) interface.
**Figure S4.** The lower$_{\text{CoSb}_3(100)}$/TiCoSb(110) interface. When the lower surface of CoSb$_3$(100) slab (lower$_{\text{CoSb}_3(100)}$) coheres with TiCoSb(110) to form the CoSb$_3$/TiCoSb interface, we name this interface as the lower$_{\text{CoSb}_3(100)}$/TiCoSb(110) interface.
Modeling possible coherent structures for the CoSb$_3$/TiCoSb interface

Along the lateral directions, we theoretically consider several possible coherent structures for each interface, as displayed in Figures S5-S8. Along the $c$ axis direction, we roughly estimate an initial bonding distance between the CoSb$_3$ and TiCoSb slabs for each interface. All the interfacial structures are fully optimized to rearrange the interfacial atoms using the gamma only $k$-point sampling. After relaxation, the calculated interfacial formation energies for all possible CoSb$_3$/TiCoSb interfacial structures are listed in Table 2, and the favorable CoSb$_3$/TiCoSb interfaces are shown in Figures 5-8 in the manuscript.
Figure S5. Considered possible coherent structures for the upper_CoSb$_3$(100)/TiCoSb(111) interface. Structures 1 and 2 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with an $a$ axis offset. Structures 3 and 4 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with a $b$ axis offset. Structures 5, 6 and 7 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with a diagonal offset. Structure 8 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together without any offset.
Figure S6. Considered possible coherent structures for the lower_CoSb$_3$(100)/TiCoSb(111) interface. Structures 1, 2 and 3 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with an $a$ axis offset. Structures 4, 5 and 6 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with a $b$ axis offset. Structures 7, 8 and 9 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together with a diagonal offset. Structure 10 represent the CoSb$_3$(100) slab and the TiCoSb(111) slab cohere together without any offset.
Figure S7. Considered possible coherent structures for the upper_CoSb$_3$(100)/TiCoSb(110) interface. Structures 1 and 2 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with an $a$ axis offset. Structures 3 and 4 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with a $b$ axis offset. Structures 5 and 6 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with a diagonal offset. Structure 7 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together without any offset.
Figure S8. Considered possible coherent structures for the lower_CoSb$_3$(100)/TiCoSb(110) interface. Structures 1, 2 and 3 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with an $a$ axis offset. Structures 4, 5 and 6 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with a $b$ axis offset. Structures 7, 8 and 9 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together with a diagonal offset. Structure 10 represent the CoSb$_3$(100) slab and the TiCoSb(110) slab cohere together without any offset.