Supporting Information

for *Adv. Electron. Mater.,* DOI: 10.1002/aelm.201400015

The Effects of Te^{2-} and I^- Substitutions on the Electronic Structures, Thermoelectric Performance, and Hardness in Melt-Quenched Highly Dense $Cu_{2-x}Se$

Lanling Zhao, Xiaolin Wang, Frank F. Yun, Jiyang Wang, Zhenxiang Cheng, Shixue Dou, Jun Wang, and G. Jeffrey Snyder*

Supporting Information

The effects of Te^{2-} and I^- Substitutions on Electronic structures, Thermoelectric Performance, and hardness in Melt-quenching Formed Highly Dense $Cu_{2-x}Se$

Lanling Zhao, Xiaolin Wang, Frank F. Yun, Jiyang Wang, Zhenxiang Cheng, Shixue Dou, Jun Wang, and G. Jeffery Snyder*

Figure S1. First Brillouin zone of the primitive cell for high temperature β-phase Cu_2Se. The blue lines indicate the Brillouin zone path used for the electronic band structure calculations.

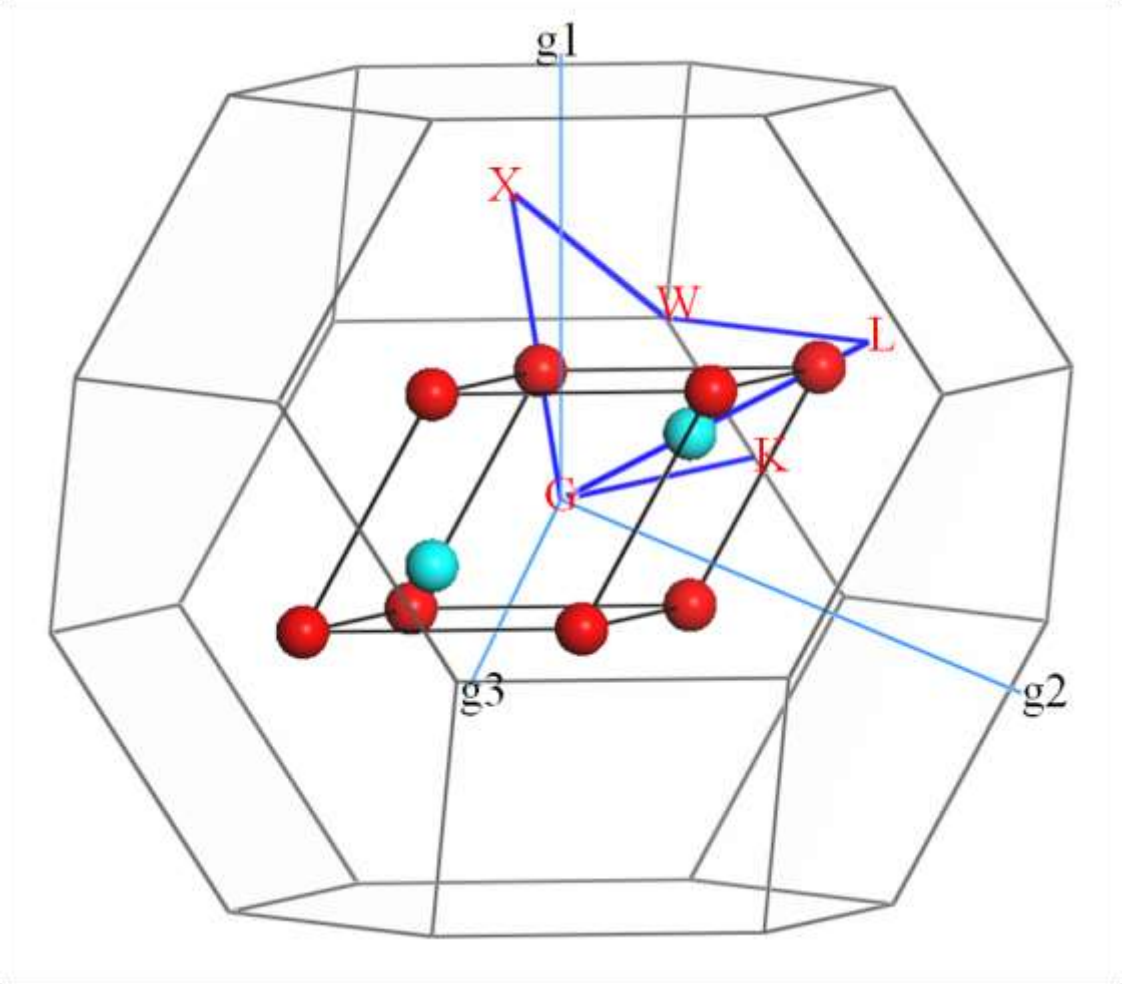

Table S1. Atomic positions for the as-prepared un-doped, and I-doped $Cu_{2-x}Se$ samples deduced from Rietveld refinements of XRD patterns.

Atom	$Cu_{2-x}Se$			$Cu_{2-x}I_{0.04}Se_{0.96}$			$Cu_{2-x}I_{0.08}Se_{0.92}$		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu1	0.3817(1)	0.0806(1)	0.3208(6)	0.3653(5)	0.0414(4)	0.2863(9)	0.3315(7)	0.0713(2)	0.3155(0)
Cu2	0.8910(1)	0.9160(0)	0.4405(1)	0.8902(6)	0.9224(3)	0.4375(0)	0.8921(0)	0.9182(4)	0.4420(5)
Cu3	0.8552(8)	0.2484(6)	0.3231(6)	0.9416(4)	0.2244(6)	0.3202(1)	0.8168(8)	0.2388(3)	0.3168(1)
Cu4	0.4343(0)	0.0708(9)	0.4510(8)	0.4064(9)	0.0858(3)	0.4601(5)	0.4090(0)	0.0676(6)	0.4595(1)
Cu5	0.1915(7)	0.1844(8)	0.3888(5)	0.2322(8)	0.2576(3)	0.3373(8)	0.2270(6)	0.2173(1)	0.3917(1)
Cu6	0.8995(0)	0.2488(2)	0.4353(7)	0.7967(3)	0.2843(3)	0.5169(0)	0.8970(4)	0.2645(2)	0.4515(7)
Cu7	0.6401(8)	0.9003(2)	0.3658(9)	0.6017(4)	0.8750(3)	0.3346(1)	0.6241(4)	0.9111(8)	0.3506(5)
Cu8	0.8215(6)	0.8998(6)	0.2931(9)	0.8508(3)	0.9101(0)	0.2897(6)	0.8560(0)	0.9164(6)	0.2890(8)
Cu9	0.4958(5)	0.2639(5)	0.3488(2)	0.5121(7)	0.2633(0)	0.3838(7)	0.5175(6)	0.2551(0)	0.3611(0)
Cu10	0.6836(2)	0.0858(8)	0.3915(5)	0.6656(5)	0.0716(6)	0.3946(6)	0.6718(7)	0.0809(6)	0.3972(5)
Cu11	0.9684(8)	0.0201(5)	0.3490(5)	0.9757(4)	0.0639(7)	0.3542(5)	0.9304(3)	0.0556(9)	0.3540(0)
Cu12	0.2703(5)	0.9276(9)	0.3977(7)	0.2407(2)	0.9280(2)	0.4041(2)	0.2402(9)	0.9255(0)	0.4024(7)
Se1	0.0677(9)	0.0700(6)	0.4470(3)	0.0532(7)	0.0707(9)	0.4448(0)	0.0604(2)	0.0874(8)	0.4346(5)
Se2	0.6782(6)	0.0867(6)	0.2995(7)	0.7039(4)	0.0762(1)	0.3074(3)	0.6845(1)	0.0783(7)	0.2988(9)
Se3	0.2013(4)	0.2442(1)	0.3140(3)	0.1793(6)	0.2157(0)	0.3148(2)	0.1776(5)	0.2301(1)	0.3030(5)
Se4	0.0720(9)	0.7441(4)	0.4425(1)	0.0780(4)	0.7560(3)	0.4489(5)	0.0889(3)	0.7526(7)	0.4470(5)
Se5	0.5669(2)	0.9032(1)	0.4389(3)	0.5714(5)	0.9040(4)	0.4426(6)	0.5660(5)	0.9086(6)	0.4371(1)
Se6	0.1927(0)	0.9177(8)	0.3103(2)	0.1633(8)	0.8951(2)	0.3194(1)	0.1886(3)	0.9024(4)	0.3039(8)
I	-	-	-	0.1885(4)	0.9051(7)	0.3064(9)	0.1977(3)	0.8943(8)	0.3154(5)
Te	-	-	-	-	-	-	-	-	-

Table S2. Atomic positions for the as-prepared Te-doped $Cu_{2-x}Se$ samples deduced from Rietveld refinements of XRD patterns.

Atom	$Cu_{2-x}Te_{0.02}Se$			$Cu_{2-x}Te_{0.08}Se_{0.98}$			$Cu_{2-x}Te_{0.16}Se_{0.84}$		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
Cu1	0.4116(4)	0.0832(9)	0.3272(0)	0.4354(2)	0.0089(6)	0.3289(1)	0.3772(1)	0.0860(7)	0.3120(5)
Cu2	0.8912(2)	0.9145(8)	0.4293(3)	0.8820(2)	0.9192(1)	0.4441(1)	0.9357(9)	0.9164(6)	0.4363(7)
Cu3	0.8714(6)	0.2481(1)	0.3035(5)	0.8738(6)	0.2643(1)	0.2996(5)	0.9118(3)	0.2268(3)	0.3214(5)
Cu4	0.4283(5)	0.0747(7)	0.4454(4)	0.4275(8)	0.0513(6)	0.4370(8)	0.3725(5)	0.0685(4)	0.4474(2)
Cu5	0.2264(0)	0.2055(2)	0.3962(5)	0.2280(4)	0.2387(6)	0.4058(5)	0.2160(5)	0.2277(4)	0.3984(8)
Cu6	0.9075(9)	0.2423(0)	0.4389(5)	0.8887(8)	0.2423(5)	0.4319(3)	0.9407(4)	0.2353(7)	0.4502(3)
Cu7	0.6125(4)	0.9103(1)	0.3686(0)	0.6647(0)	0.9292(9)	0.2697(8)	0.6073(6)	0.8647(5)	0.3492(2)
Cu8	0.8702(6)	0.9091(9)	0.2877(9)	0.8621(4)	0.9061(1)	0.2982(1)	0.9036(6)	0.9006(7)	0.2855(7)
Cu9	0.5734(4)	0.3094(9)	0.3915(1)	0.4424(9)	0.2128(3)	0.3373(5)	0.5310(2)	0.2157(2)	0.3381(3)
Cu10	0.6609(8)	0.0921(1)	0.3930(8)	0.6606(8)	0.1160(3)	0.3947(6)	0.7011(1)	0.0746(2)	0.3944(2)
Cu11	0.9354(5)	0.0590(5)	0.3566(1)	0.9928(7)	0.0545(1)	0.3551(6)	0.9346(5)	0.0687(4)	0.3622(9)
Cu12	0.2634(3)	0.9343(7)	0.3971(3)	0.2384(1)	0.9036(4)	0.4039(3)	0.2749(3)	0.9172(1)	0.4025(8)
Se1	0.0569(5)	0.0758(7)	0.4456(7)	0.0545(3)	0.0833(6)	0.4437(7)	0.0835(0)	0.0625(2)	0.4404(0)
Se2	0.6930(0)	0.0876(5)	0.3063(0)	0.7002(3)	0.0876(0)	0.3074(8)	0.6930(8)	0.0714(4)	0.3039(0)
Se3	0.2062(4)	0.2166(8)	0.3068(5)	0.1834(6)	0.2481(1)	0.3133(7)	0.1770(3)	0.2408(1)	0.2969(8)
Se4	0.0814(7)	0.7500(1)	0.4444(6)	0.0793(9)	0.7403(1)	0.4461(1)	0.0730(3)	0.7354(7)	0.4504(6)
Se5	0.5724(9)	0.8987(5)	0.4479(9)	0.5723(7)	0.9132(3)	0.4416(1)	0.5615(3)	0.9063(4)	0.4356(4)
Se6	0.2214(9)	0.9078(7)	0.3134(5)	0.1804(8)	0.9183(3)	0.3051(5)	0.6526(5)	0.9031(0)	0.2869(5)
I	-	-	-	-	-	-	-	-	-
Te	0.1660(8)	0.9510(7)	0.3156(1)	0.1831(2)	0.9104(7)	0.3123(0)	0.1912(0)	0.9036(9)	0.3046(2)

Table S3. Lattice parameters, R-factors for the as-prepared Te-doped $Cu_{2-x}Se$ samples deduced from Rietveld refinements of XRD patterns.

Sample \ Lattice parameter	*a* (Å)	*b* (Å)	*c* (Å)	*β*	*V* (Å^3)	*Rp*	*Rwp*
$Cu_{2-x}Se$	7.117(7)	12.358(6)	27.278(2)	94.112(6)	2392.0(1)	1.820	2.793
$Cu_{2-x}Te_{0.02}Se_{0.98}$	7.159(4)	12.249(1)	27.364(8)	94.556(2)	2392.2(1)	2.126	3.225
$Cu_{2-x}Te_{0.08}Se_{0.92}$	7.136(5)	12.361(6)	27.310(6)	94.572(7)	2401.6(3)	1.989	2.971
$Cu_{2-x}Te_{0.16}Se_{0.84}$	7.214(7)	12.345(2)	27.608(6)	94.789(3)	2450.4(3)	2.383	3.401
$Cu_{2-x}I_{0.04}Se_{0.96}$	7.115(1)	12.350(3)	27.306(5)	94.155(2)	2393.2(1)	2.668	3.606
$Cu_{2-x}I_{0.08}Se_{0.92}$	7.117(2)	12.368(1)	27.274(4)	94.033(4)	2394.9(2)	2.586	3.505

Figure S2. Typical cross-section FE-SEM images for the fabricated un-doped, Te-doped and I-doped $Cu_{2-x}Se$ bulks