Supporting Information

From the Ternary Phase $Ca_{14}Zn_{1+\delta}Sb_{11}$ ($\delta \approx 0.4$) to the Quaternary Solid Solutions $Ca_{14-x}RE_xZnSb_{11}$ (RE = La–Nd, Sm, Gd, $x \approx 0.9$). A Tale of Electron Doping via Rare-earth Metal Substitutions and the Concomitant Structural Transformations

*Sviatoslav Baranets and Svilen Bobev**

Department of Chemistry and Biochemistry, University of Delaware,
Newark, Delaware 19716, United States

Table S1. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.08}Ce_{0.92(1)}ZnSb_{11}$.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1/Ce1[b]	32*g*	0.04323(5)	0.0727(4)	0.17153(3)	0.0125(3)
Ca2/Ce2[b]	32*g*	0.02140(4)	0.37473(4)	0.00198(3)	0.0156(2)
Ca3/Ce3[b]	16*e*	0.35550(7)	0	1/4	0.0124(4)
Ca4/Ce4[b]	32*g*	0.34196(6)	0.07021(5)	0.09319(3)	0.0171(3)
Zn1	8*a*	0	1/4	3/8	0.0144(2)
Sb1	16*f*	0.13508(2)	0.38508(2)	1/8	0.01109(10)
Sb2	32*g*	0.36091(2)	0.25372(2)	0.05950(2)	0.01204(9)
Sb3	32*g*	0.12966(2)	0.02551(2)	0.04655(2)	0.01261(9)
Sb4	8*b*	0	1/4	1/8	0.01303(13)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

[b] Atomic occupancies according to the refinement: Ca1/Ce1 = 0.955(2)Ca + 0.045(2)Ce; Ca2/Ce2 = 0.854(2)Ca + 0.146(2)Ce; Ca3/Ce3 = 0.985(2)Ca + 0.015(2)Ce; Ca4/Ce4 = 0.970(2)Ca + 0.030(2)Ce.

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.11}Pr_{0.89(1)}ZnSb_{11}$.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1/Pr1[b]	32*g*	0.04327(5)	0.07264(5)	0.17156(3)	0.0124(3)
Ca2/Pr2[b]	32*g*	0.02158(4)	0.37466(4)	0.00247(3)	0.0150(3)
Ca3/Pr3[b]	16*e*	0.35546(7)	0	1/4	0.0123(4)
Ca4/Pr4[b]	32*g*	0.34226(6)	0.07026(5)	0.09311(4)	0.0167(3)
Zn1	8*a*	0	1/4	3/8	0.0140(2)
Sb1	16*f*	0.13512(2)	0.38512(2)	1/8	0.01094(10)
Sb2	32*g*	0.36103(2)	0.25371(2)	0.05929(2)	0.01163(9)
Sb3	32*g*	0.12952(2)	0.02543(2)	0.04658(2)	0.01262(9)
Sb4	8*b*	0	1/4	1/8	0.01271(13)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

[b] Atomic occupancies according to the refinement: Ca1/Pr1 = 0.939(2)Ca + 0.061(2)Pr; Ca2/Pr2 = 0.875(2)Ca + 0.125(2)Pr; Ca3/Pr3 = 0.980(3)Ca + 0.020(3)Pr; Ca4/Pr4 = 0.973(2)Ca + 0.0267(2)Pr.

Table S3. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.16}Nd_{0.84(1)}ZnSb_{11}$.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1/Nd1[b]	32*g*	0.04315(4)	0.07267(4)	0.17153(3)	0.0119(2)
Ca2/Nd2[b]	32*g*	0.02174(4)	0.37462(4)	0.00288(3)	0.0145(3)
Ca3/Nd3[b]	16*e*	0.35527(7)	0	1/4	0.0113(4)
Ca4/Nd4[b]	32*g*	0.34238(6)	0.07027(5)	0.09308(3)	0.0163(3)
Zn1	8*a*	0	1/4	3/8	0.0134(2)
Sb1	16*f*	0.13520(2)	0.38520(2)	1/8	0.01067(10)
Sb2	32*g*	0.36100(2)	0.25376(2)	0.05920(2)	0.01128(8)
Sb3	32*g*	0.12947(2)	0.02544(2)	0.04668(2)	0.01259(9)
Sb4	8*b*	0	1/4	1/8	0.01249(13)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

[b] Atomic occupancies according to the refinement: Ca1/Nd1 = 0.926(2)Ca + 0.074(2)Nd; Ca2/Nd2 = 0.901(2)Ca + 0.099(2)Nd; Ca3/Nd3 = 0.976(2)Ca + 0.024(2)Nd; Ca4/Nd4 = 0.975(2)Ca + 0.025(2)Nd.

Table S4. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.06}Sm_{0.94(1)}ZnSb_{11}$.

Atom	**Site**	***x***	***y***	***z***	$\boldsymbol{U_{eq}}$ [a] (Å^2)
Ca1/Sm1[b]	32*g*	0.04302(4)	0.07249(4)	0.17142(3)	0.0120(3)
Ca2/Sm2[b]	32*g*	0.02190(5)	0.37465(5)	0.00355(4)	0.0149(3)
Ca3/Sm3[b]	16*e*	0.35500(8)	0	1/4	0.0119(4)
Ca4/Sm4[b]	32*g*	0.34267(6)	0.07028(6)	0.09308(4)	0.0169(4)
Zn1	8*a*	0	1/4	3/8	0.0143(3)
Sb1	16*f*	0.13523(2)	0.38523(2)	1/8	0.01096(12)
Sb2	32*g*	0.36100(2)	0.25374(2)	0.05887(2)	0.01184(10)
Sb3	32*g*	0.12944(2)	0.02542(2)	0.04692(2)	0.01306(10)
Sb4	8*b*	0	1/4	1/8	0.01256(15)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

[b] Atomic occupancies according to the refinement: Ca1/Sm1 = 0.890(2)Ca + 0.110(2)Sm; Ca2/Sm2 = 0.925(2)Ca + 0.075(2)Sm; Ca3/Sm3 = 0.959(2)Ca + 0.041(2)Sm; Ca4/Sm4 = 0.969(2)Ca + 0.031(2)Sm.

Table S5. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.13}Gd_{0.87(1)}ZnSb_{11}$.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1/Gd1[b]	32*g*	0.04269(3)	0.07269(3)	0.17132(3)	0.0118(2)
Ca2/Gd2[b]	32*g*	0.02212(4)	0.37482(4)	0.00374(3)	0.0156(3)
Ca3/Gd3[b]	16*e*	0.35477(6)	0	1/4	0.0117(3)
Ca4/Gd4[b]	32*g*	0.34244(5)	0.07035(5)	0.09295(3)	0.0167(3)
Zn1	8*a*	0	1/4	3/8	0.0139(2)
Sb1	16*f*	0.13528(2)	0.38528(2)	1/8	0.01080(9)
Sb2	32*g*	0.36078(2)	0.25389(2)	0.05897(2)	0.01197(8)
Sb3	32*g*	0.12958(2)	0.02571(2)	0.04704(2)	0.01325(8)
Sb4	8*b*	0	1/4	1/8	0.01253(12)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

[b] Atomic occupancies according to the refinement: Ca1/Gd1 = 0.873(2)Ca + 0.127(2)Gd; Ca2/Gd2 = 0.953(2)Ca + 0.047(2)Gd; Ca3/Gd3 = 0.954(2)Ca + 0.046(2)Gd; Ca4/Gd4 = 0.979(2)Ca + 0.021(2)Gd.

Table S6. Selected interatomic distances (in Å) for $Ca_{14-x}RE_xZnSb_{11}$ (*RE* = Ce, Pr, Nd, Sm, Gd).

Bonds	**Ce**	**Pr**	**Nd**	**Sm**	**Gd**
Ca1/*RE*1–Sb1	3.2278(8)	3.2272(8)	3.2252(7)	3.2189(8)	3.2115(6)
Ca1/*RE*1–Sb2	3.1919(8) 3.2229(8)	3.1902(8) 3.2198(8)	3.1894(8) 3.2191(7)	3.1819(8) 3.2147(8)	3.1797(6) 3.2152(7)
Ca1/*RE*1–Sb3	3.2071(8) 3.2232(8)	3.2060(8) 3.2220(8)	3.2068(8) 3.2211(7)	3.2042(8) 3.2137(8)	3.2020(6) 3.2039(6)
Ca1/*RE*1–Sb4	3.2155(8)	3.2151(8)	3.2133(7)	3.2102(8)	3.2039(6)
Ca2/*RE*2–Sb1	3.3283(7)	3.3184(8)	3.3108(7)	3.2961(9)	3.2893(8)
Ca2/*RE*2–Sb2	3.1302(8) 3.6922(8)	3.1273(8) 3.6920(8)	3.1277(8) 3.6962(8)	3.1257(9) 3.6960(9)	3.1275(8) 3.7053(8)
Ca2/*RE*2–Sb3	3.1792(8) 3.2798(7)	3.1755(8) 3.2784(8)	3.1744(8) 3.2801(8)	3.1686(9) 3.2800(9)	3.1674(8) 3.2817(8)
Ca2/*RE*2–Sb4	3.4510(7)	3.4419(7)	3.4351(7)	3.4223(8)	3.4196(8)
Ca3/*RE*3–Sb1 × 2	3.3754(2)	3.3751(2)	3.3751(2)	3.3737(3)	3.3719(2)
Ca3/*RE*3–Sb2 × 2	3.2696(9)	3.2674(9)	3.2674(9)	3.2635(10)	3.2620(8)
Ca3/*RE*3–Sb3 × 2	3.1436(9)	3.1418(9)	3.1403(9)	3.1345(10)	3.1334(7)
Ca4/*RE*4–Sb1	3.1926(9)	3.1902(9)	3.1878(9)	3.1819(10)	3.1817(8)
Ca4/*RE*4–Sb2	3.1687(9) 3.4287(10)	3.1656(9) 3.4283(10)	3.1655(9) 3.4279(9)	3.1615(10) 3.4259(11)	3.1607(8) 3.4250(9)
Ca4/*RE*4–Sb3	3.7662(10) 3.2234(8)	3.7701(10) 3.2236(9)	3.7709(10) 3.2260(8)	3.7690(11) 3.2309(9)	3.2285(8) 3.2438(8)
Zn1–Sb2 × 4	2.7395(3)	2.7391(3)	2.7402(3)	2.7411(3)	2.7419(3)
Sb1–Sb4	3.1885(4)	3.1869(4)	3.1878(4)	3.1833(5)	3.1831(4)

Table S7. Selected crystallographic data for $Ca_{13.04}Sm_{0.96(1)}ZnSb_{11}$, obtained from Pb flux (T = 200(2) K, Mo K_α radiation, λ = 0.71073 Å).

Chemical formula	$Ca_{13.04}Sm_{0.96(1)}ZnSb_{11}$
fw/ g·mol^{-1}	2071.32
a/ Å	16.6479(10)
c/ Å	22.2117(15)
V/ Å^3	6156.0(8)
$\rho_{calc.}$/ g·cm^{-3}	4.47
μ_{MoK_α}/ cm^{-1}	142.0
R_1 (all data)[a]	0.0331
R_1 [$I>2\sigma(I)$][a]	0.0268
wR_2 (all data)[a]	0.0624
wR_2 [$I>2\sigma(I)$][a]	0.0602
$\Delta\rho_{max,min}$/ e·Å^{-3}	1.91, –1.12

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2F_o^2 + (0.0313\cdot P)^2 + (5.077\cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$

Table S8. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{13.04}Sm_{0.96(1)}ZnSb_{11}$, obtained from Pb flux.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1/Sm1[b]	32*g*	0.04306(4)	0.07251(4)	0.17144(3)	0.0117(3)
Ca2/Sm2[b]	32*g*	0.02189(5)	0.37463(5)	0.00354(4)	0.0138(3)
Ca3/Sm3[b]	16*e*	0.35495(8)	0	1/4	0.0118(4)
Ca4/Sm4[b]	32*g*	0.34272(6)	0.07044(6)	0.09307(4)	0.0159(3)
Zn1	8*a*	0	1/4	3/8	0.0134(2)
Sb1	16*f*	0.13521(2)	0.38521(2)	1/8	0.0105(1)
Sb2	32*g*	0.36102(2)	0.25378(2)	0.05892(2)	0.0114(1)
Sb3	32*g*	0.12946(2)	0.02542(2)	0.04689(2)	0.0126(1)
Sb4	8*b*	0	1/4	1/8	0.0121(1)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.
[b] Atomic occupancies according to the refinement: Ca1/Sm1 = 0.886(2)Ca + 0.114(2)Sm; Ca2/Sm2 = 0.924(2)Ca + 0.076(2)Sm; Ca3/Sm3 = 0.956(2)Ca + 0.044(2)Sm; Ca4/Sm4 = 0.972(2)Ca + 0.028(2)Sm.

Table S9. Selected crystallographic data for $Ca_{14}Zn_{1.41(1)}Sb_{11}$, obtained from Sn flux (T = 200(2) K, Mo K_α radiation, λ = 0.71073 Å).

Chemical formula	$Ca_{14}Zn_{1.41(1)}Sb_{11}$ [b]
fw/g·mol^{-1}	1992.79
a/ Å	16.7949(17)
c/ Å	21.998(2)
V/ Å^3	6205.0(14)
$\rho_{calc.}$/ g·cm^{-3}	4.27
μ_{MoK_α}/ cm^{-1}	127.9
R_1 (all data)[a]	0.0398
R_1 [$I>2\sigma(I)$][a]	0.0306
wR_2 (all data)[a]	0.0715
wR_2 [$I>2\sigma(I)$][a]	0.0682
$\Delta\rho_{max,min}$/ e·Å^{-3}	1.81, –0.85

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2F_o^2 + (0.0299\cdot P)^2 + (35.82\cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$

[b] Refined occupancy for the partially occupied interstitial Zn2 site: 0.104(3)

Table S10. Fractional atomic coordinates and equivalent isotropic displacement parameters U_{eq} for $Ca_{14}Zn_{1.41(1)}Sb_{11}$, obtained from Sn flux.

Atom	**Site**	***x***	***y***	***z***	U_{eq} [a] (Å^2)
Ca1	32*g*	0.04167(7)	0.07472(7)	0.17259(6)	0.0201(3)
Ca2	32*g*	0.02371(8)	0.37476(9)	0.00171(7)	0.0298(3)
Ca3	16*e*	0.35418(9)	0	1/4	0.0142(3)
Ca4	32*g*	0.34026(9)	0.07283(7)	0.09372(6)	0.0257(3)
Zn1	8*a*	0	1/4	3/8	0.0181(3)
Zn2 [b]	32*g*	0.4723(4)	0.0028(4)	0.0740(3)	0.014(2)
Sb1	16*f*	0.13614(2)	0.38614(2)	1/8	0.0145(1)
Sb2	32*g*	0.35864(2)	0.25635(2)	0.06222(2)	0.0173(1)
Sb3	32*g*	0.12860(3)	0.02817(2)	0.04522(2)	0.0205(1)
Sb4	8*b*	0	1/4	1/8	0.0231(1)

[a] U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.
[b] Partially occupied with site occupation factor 10.4(3)%.

Table S11. Interatomic distances (Å) involving the interstitial Zn atom in the structure of $Ca_{14}Zn_{1.37(1)}Sb_{11}$.

Atom pair	Distance
Zn2–Ca1	2.760(6)
Zn2–Ca2	2.685(6)
Zn2–Ca2	2.803(6)
Zn2–Ca4	2.531(6)
Zn2–Sb1	2.896(6)
Zn2–Sb2	3.085(6)
Zn2–Sb3	2.747(6)

Table S12. Selected parameters from the trial refinements of the $Ca_{14}Zn_{1.37(1)}Sb_{11}$ structure, confirming the site occupation factors (SOF).

		Occupancy factor set free for:				No SOF of Ca atoms refined[a]
		Ca1[b]	Ca2[b]	Ca3[b]	Ca4[b]	
Refined SOF		1.006(5)	0.995(6)	1.003(7)	1.008(5)	
U_{eq}[c]	Ca1	**0.019(1)**	0.019(1)	0.019(1)	0.019(1)	0.019(1)
	Ca2	0.028(1)	**0.027(1)**	0.028(1)	0.028(1)	0.028(1)
	Ca3	0.014(1)	0.014(1)	**0.014(1)**	0.014(1)	0.014(1)
	Ca4	0.024(1)	0.024(1)	0.024(1)	**0.025(1)**	0.024(1)
	Zn2[d]	0.016(2)	0.016(2)	0.016(2)	0.016(2)	0.016(2)
R_1 [$I>2\sigma(I)$][e]		0.0286	0.0286	0.0286	0.0286	0.0286
wR_2 [all data][e]		0.0694	0.0695	0.0694	0.0694	0.0694
$\Delta\rho_{max,min}$/e Å^{-3}		2.04, –1.50	2.04, –1.50	2.04, –1.50	2.06, –1.50	2.03, –1.50

[a] Except for the Zn2 site, no other sites have occupancies that are refined freely, as shown in Table 2 (main text);

[b] Refined while the occupancies of the other Ca atoms are kept unchanged;

[c] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor;

[d] Refined occupancy for the partially occupied interstitial Zn2 site remains 0.092(3) in all cases;

[e] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2F_o^2+(A\cdot P)^2+(B\cdot P)]$, and $P = (F_o^2+2F_c^2)/3$; *A, B* are the respective weight coefficients;

Table S13. Quantitative interpretation of the EDX measurements. The Sb:Zn ratio in the refined composition $Ca_{14}Zn_{1.37}Sb_{11}$ is 8.02. The hypothetical devoid of disorder and interstitial-free $Ca_{14}ZnSb_{11}$ has Sb:Zn ratio 11, and the previously put forth model for interstitial occupation by Sb, i.e., $Ca_{14}ZnSb_{11.2}$ requires Sb:Zn ratio of 11.2, respectively.

	Analysis #1 [a]	Analysis #2 [b]	Analysis #3 [c]	Analysis #4 [d]	Analysis #5 [e]	Analysis #6 [f]
Zn, at %	6.2	4.82	4.95	4.61	5.39	4.12
Sb, at %	40.71	41.19	42.44	39.55	42.33	42.48
Sb:Zn	**6.57**	**8.54**	**8.57**	**8.58**	**7.85**	**10.3**
Ca, at %	53.09	53.98	52.61	49.62	52.29	50.07
Pb, at %	< 0.5	< 0.5	< 0.5	6.23	< 0.5	< 0.5

[a] Single crystal from batch 1. Crystal surface (Figure S1 (a));

[b] Single crystal from batch 2. Averaged data from the cut (Figure S1 (b), (d));

[c] Single crystal from batch 3 (Figure S1 (e));

[d] Pellet (Figure S1- panels f), and g) area #1). A considerable amount of Pb flux is detected in that spot, yet the elemental ratio for Ca, Zn, and Sb is still in good agreement with the refined formula $Ca_{14}Zn_{1.37}Sb_{11}$;

[e] Pellet (Figure S1 - panels f), and g) area #2);

[f] Single crystal from batch containing La. No interstitial Zn is expected, based on the structure refinements from X-ray diffraction for $Ca_{14-x}La_xZnSb_{11}$.

Figure S1. (a) SEM image of the typical flux-grown single crystal of $Ca_{14}Zn_{1+\delta}Sb_{11}$. The presence of small lead particles on the crystal surface is seen; complete removal of the flux leftover is apparently very difficult. (b) SEM image of a freshly cut in half crystal of the $Ca_{14}Zn_{1+\delta}Sb_{11}$ phase, showing exposed clean surface. (c) Optical microscope image of a pellet made from the bulk $Ca_{14}Zn_{1+\delta}Sb_{11}$ material. (d) and (e) SEM images of the two different crystals taken at higher magnification. (f) SEM image of the pellet surface taken at higher magnification (note the presence of the Pb-flux particles in area labeled as #1). (g) and (h) EDX histograms gathered from the depicted areas in panel (f).

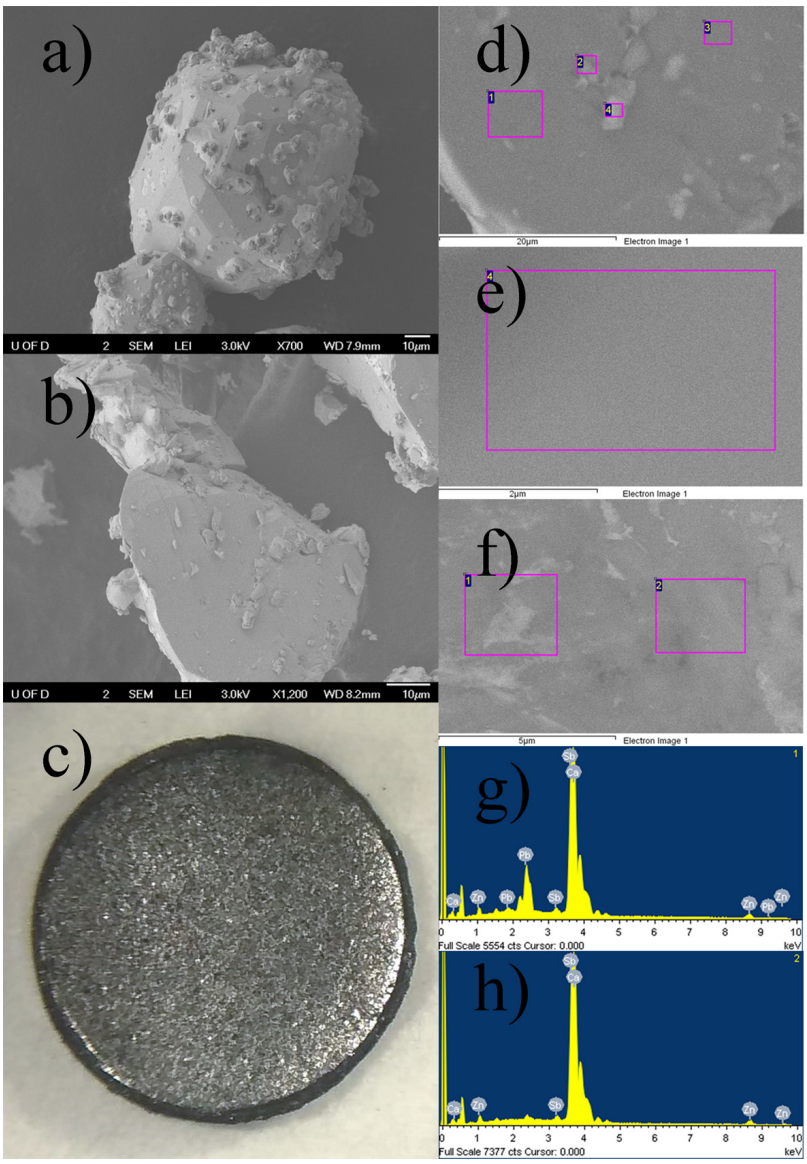

Figure S2. Calculated total density of states (DOS) (a) and partial density of states (PDOS) curves for the idealized, free of interstitial Zn compound $Ca_{14}ZnSb_{11}$. The Fermi level is chosen as the energy reference at 0 eV. The two PDOS plots show the partial contribution for Sb (b) and the s, p, and d bands contribution for Zn (c). The computation was done using TB-LMTO-ASA code within the local density approximation.

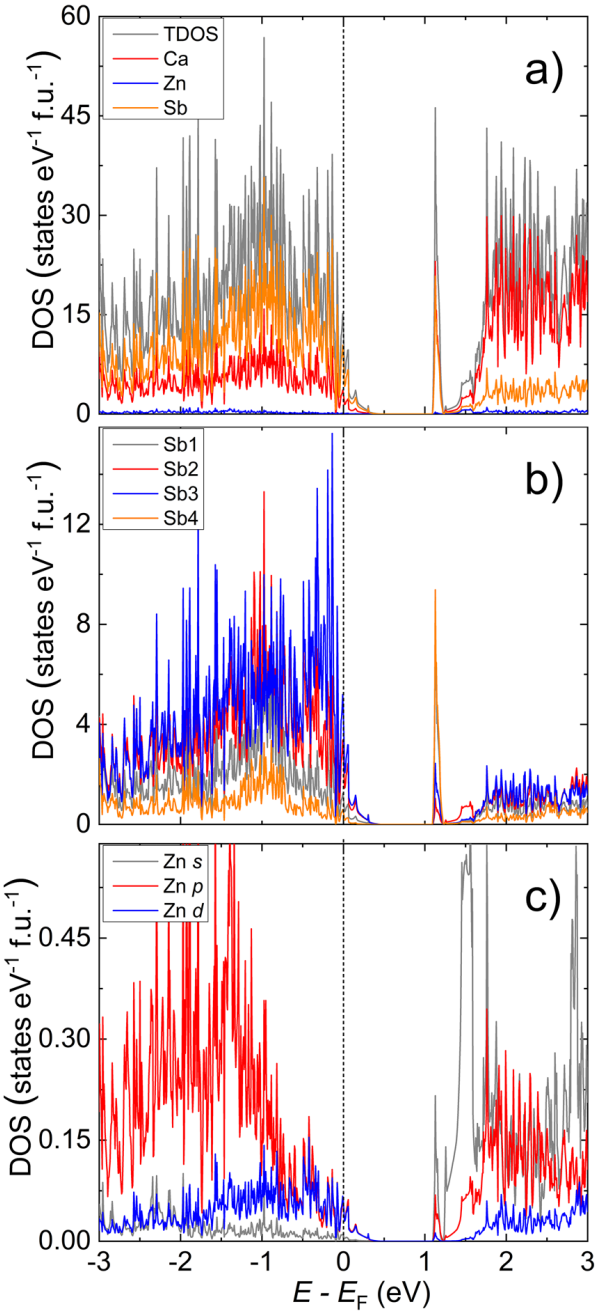

Figure S3. Temperature dependence of the electrical resistivity of $Ca_{13}LaZnSb_{11}$.