Supporting Information

Early Stage of the Single-Crystal Growth and Tipping Point of the Cationic Site-Preference in the Gd-doped Zintl Phase Thermoelectric Materials

Hayeon Sa,[1] Junsu Lee,[1] Yeongjin Hong,[1] Mi-Kyung Han,[2] Hongil Jo,[3] Dohyun Moon,[4] Kang Min Ok,[3] Sung-Jin Kim,[2] and Tae-Soo You[1,*]

[1]Department of Chemistry and BK21Four Research Team, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea

[2] Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Republic of Korea

[3] Department of Chemistry, Sogang University, Seoul 04107, Republic of Korea

[4] Beamline Department, Pohang Accelerator Laboratory, Pohang, Gyeongbuk 37673, Republic of Korea

CORRESPONDING AUTHOR FOOTNOTE

Email: tsyou@chungbuk.ac.kr

Phone: +82 (43) 261-2282

Fax: +82 (43) 267-2289

Table S1. Detailed Structural Information for Two Hypothetical Structure Models of $Ca_{11}Sb_{10}$ and $Ca_{10.5}Gd_{0.5}Sb_{10}$

chemical formula	$Ca_{11}Sb_{10}$	$Ca_{10.5}Gd_{0.5}Sb_{10}$
space group	*I*4/*mmm* (No. 139)	*P*2 (No. 3)
unit cell dimensions (Å)	a = 12.0180	a = 11.9850
		b = 17.2845
	c = 17.3090	c = 11.9850
volume (Å^3)	2499.98	2482.75

		atomic coordinates		
atom	Wyckoff site	x	y	z
		$Ca_{11}Sb_{10}$		
Ca1	16*n*	0	0.2526	0.3113
Ca2	16*n*	0	0.3393	0.1034
Ca3	8*h*	0.3378	0.3378	0
Ca4	4*e*	0	0	0.1665
Sb1	16*m*	0.2058	0.2058	0.1761
Sb2	8*j*	0.1543	1/2	0
Sb3	8*h*	0.1267	0.1267	0
Sb4	4*e*	0	0	0.3662
Sb5	4*d*	0	1/2	1/4
		$Ca_{10.5}Gd_{0.5}Sb_{10}$		
Ca1	2*e*	0	0.6890	0.2478
Ca2	2*e*	0.2478	0.1890	0
Ca3	2*e*	0.7478	0.6890	1/2
Ca4	2*e*	1/2	0.1890	0.2522
Ca5	2*e*	0	0.3110	0.7522
Ca6	2*e*	0.7522	0.8110	0
Ca7	2*e*	0.2522	0.3110	0.5
Ca8	2*e*	1/2	0.8110	0.7478
Gd	2*e*	0	0.8973	0.1625
Ca10	2*e*	0.1625	0.3973	0
Ca11	2*e*	0.6625	0.8973	1/2
Ca12	2*e*	1/2	0.3973	0.3375
Ca13	2*e*	0	0.1027	0.8375
Ca14	2*e*	0.8375	0.6027	0
Ca15	2*e*	0.3375	0.1027	1/2
Ca16	2*e*	1/2	0.6027	0.6625
Ca17	2*e*	0.1653	1/2	0.6653
Ca18	2*e*	0.6653	0	0.8347
Ca19	2*e*	0.1653	1/2	0.3347
Ca20	2*e*	0.3347	0	0.8347
Ca21	1*a*	0	0.8366	1/2
Ca22	1*d*	1/2	0.3366	0
Ca23	1*a*	0	0.1634	1/2
Ca24	1*d*	1/2	0.6634	0
Sb1	2*e*	0.2935	0.3241	0.7935
Sb2	2*e*	0.7935	0.8241	0.7065
Sb3	2*e*	0.2935	0.3241	0.2065
Sb4	2*e*	0.2065	0.8241	0.7065
Sb5	2*e*	0.2935	0.6759	0.7935
Sb6	2*e*	0.7935	0.1760	0.7065
Sb7	2*e*	0.2935	0.6759	0.2065
Sb8	2*e*	0.2065	0.1760	0.7065
Sb9	2*e*	0	1/2	0.8465
Sb10	2*e*	0.8465	0	0
Sb11	2*e*	0.3465	1/2	1/2

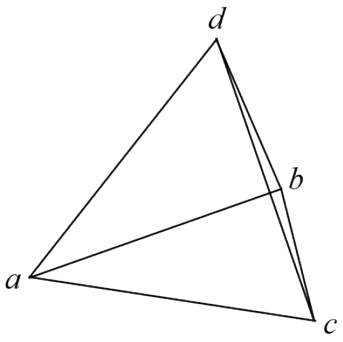
Sb12	2*e*	1/2	0	0.6535
Sb13	2*e*	0.3744	1/2	0.8744
Sb14	2*e*	0.8744	0	0.6256
Sb15	2*e*	0.3744	1/2	0.1256
Sb16	2*e*	0.1256	0	0.6256
Sb17	2*e*	0	0.6334	1/2
Sb18	2*e*	1/2	0.1334	0
Sb19	2*e*	0	0.3666	1/2
Sb20	2*e*	0	0.8666	0
Sb21	2*e*	0	1/4	0
Sb22	2*e*	0	3/4	0
Sb23	1*a*	1/2	1/4	1/2
Sb24	1*d*	1/2	3/4	1/2

Scheme S1. Calculations for the volumes of the cationic and anionic polyhedron:

1) Acquire the atomic coordinates of the vertices of each polyhedron from the SXRD data.

2) Divide the given polyhedron into smaller tetrahedra.

3) Calculate the volume (V) of each tetrahedron as followed.



a: (x_1, y_1, z_1), b: (x_2, y_2, z_2), c: (x_3, y_3, z_3), d: (x_4, y_4, z_4)

$$\mathrm{V} = \frac{|\,(a-d)\cdot((b-d)\times(c-d))\,|}{6}$$

4) The sum of the volumes of all tetrahedra is equal to the volume of the given polyhedron.

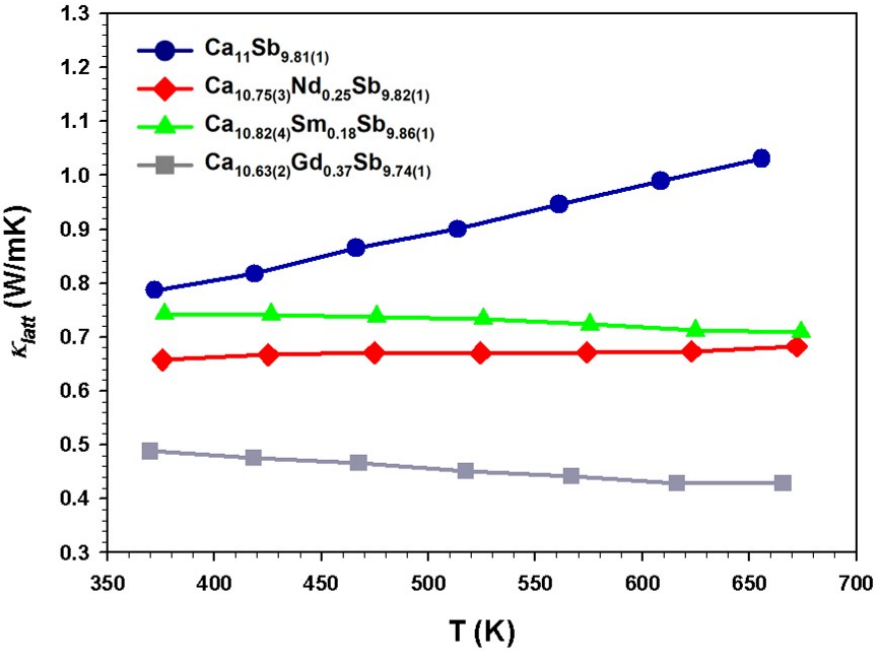


Fig. S1. Temperature-dependent lattice thermal conductivity κ_{latt} of $Ca_{10.63(2)}Gd_{0.37}Sb_{9.74(1)}$ measured between 372 and 674 K. The κ_{latt} of $Ca_{11}Sb_{9.81(1)}$, $Ca_{10.75(3)}Nd_{0.25}Sb_{9.82(1)}$, and $Ca_{10.82(4)}Sm_{0.18}Sb_{9.86(1)}$ from the literature are also plotted for the comparison purpose.