Supporting Information

Crystal Structure, electronic structure and thermoelectric properties of β- and γ-Zn_4Sb_3 thermoelectrics: a (3+1)-dimensional superspace group approach

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The positional modulation function $\bar{u}$ of an atom is expressed as

$$\bar{u}(v) = \sum_{n=1}^{4}\{A_n \cos 2\pi n v + B_n \sin 2\pi n v\}, \quad \ldots(1)$$

where A_n and B_n are the cosine and sine components of the Fourier terms, and v is the fourth superspace coordinate. Figures S1(a), S1(b) and S1(c) show the positional modulations of the Zn(1), Zn_i, Sb(1) and Sb(2) atoms for β-Zn_4Sb_3 (723 K), γ-Zn_4Sb_3 (823 K) and β-Zn_4Sb_3 (long-heating), respectively, calculated by using the A_n and B_n values in Tables 2 and S2. Table S1 lists the Rietveld refinement results of β-Zn_4Sb_3 prepared under long-time heating for the SXRD measurement.

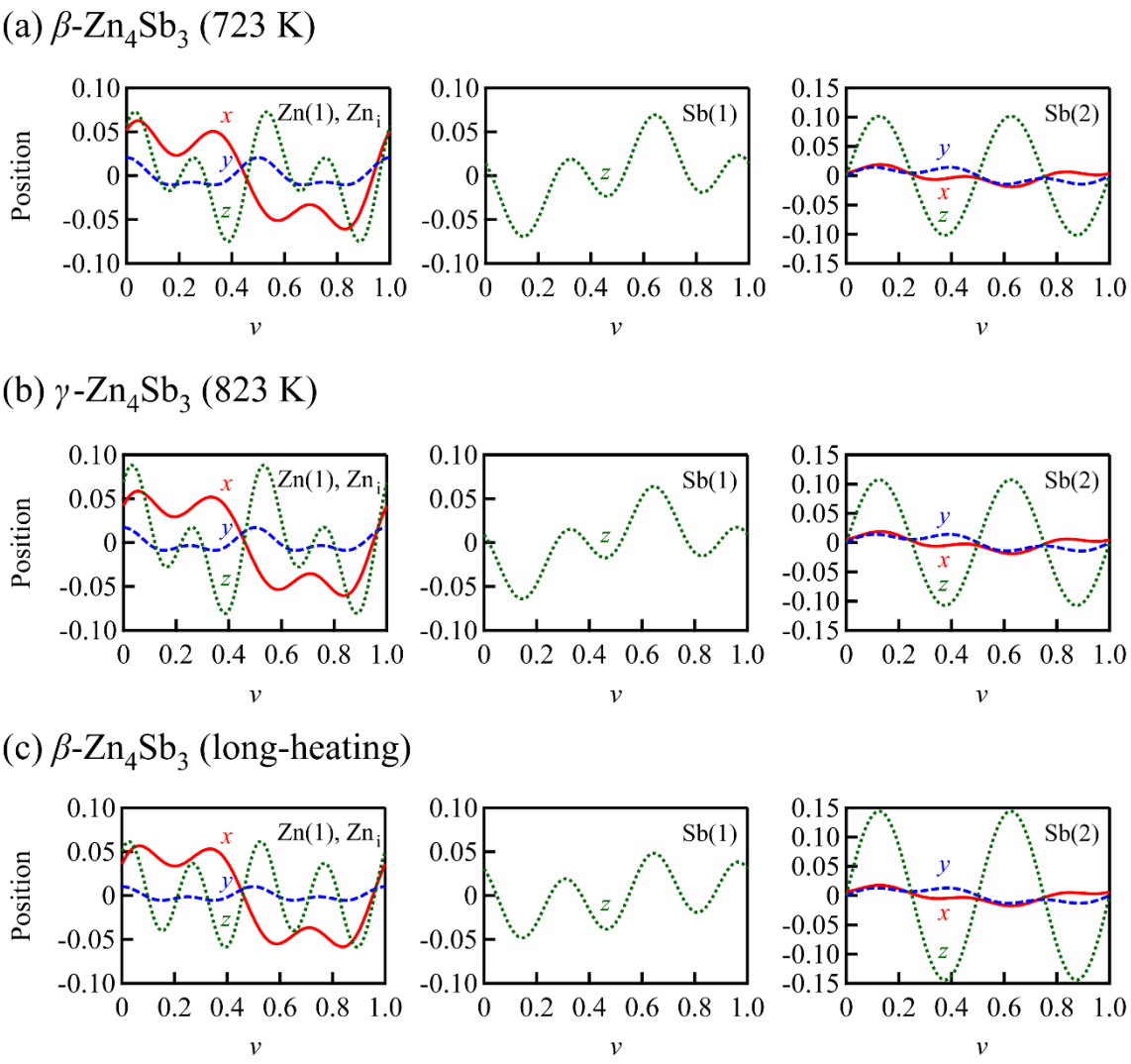

Fig. S1 Positional modulations of the Zn(1), Zn_i, Sb(1) and Sb(2) atoms for (a) β-Zn_4Sb_3 (723 K), (b) γ-Zn_4Sb_3 (823 K) and (c) β-Zn_4Sb_3 (long-heating).

Table S1 Reliability factors, lattice parameters and *c*-axis ratio *p* between the two subsystems of *β*-Zn_4Sb_3. The chemical formula is expressed as $[Zn_{3+\delta}Sb][Sb]_p$, prepared under long-time heating for the SXRD measurement. The Wyckoff positions, atomic coordinates, occupancies and equivalent isotropic displacement parameters U_{iso} for the fundamental structure are also listed.

β-Zn_4Sb_3	R_{wp} (%)		*gof*	*a* (Å)	c_1 (Å)	c_2 (Å)	*p*
	8.31		8.55	12.22058(10)	6.20821(8)	4.13418(5)	1.50168(7)
	Atom	Wyckoff	*x*	*y*	*z*	occ. (%)	U_{iso} (Å^2)
Subsystem 1							
$[Zn_{3+\delta}Sb]$	Zn	18*h*	0.21208(12)	= 2*x*	0.4765(3)	100	0.0206(9)
	Zn_i	18*h*	0.2190(15)	= 2*x*	0.118(6)	6.1(3)	= U_{iso}(Zn)
	Sb(1)	6*c*	0	0	0.2733(4)	100	0.0131(5)
Subsystem 2							
[Sb]	Sb(2)	6 sites	1/3	0	1/4	100	0.0083(4)

Table S2 Refined positional modulation wave components of β-Zn_4Sb_3 prepared under long-time heating for the SXRD measurement.

β-Zn_4Sb_3			x	y	z
Subsystem 1					
[$Zn_{3+\delta}Sb$]	Zn, Zn_i†	A_1	0.0151(17)	0	0
		B_1	0.0548(5)	0	0
		A_2	0.0029(7)	$= 2A_{2x}$	0.009(3)
		B_2	0‡	$= 2B_{2x}$	0.012(4)
		A_3	0.0159(13)	0	0
		B_3	0.0148(12)	0	0
		A_4	0.0022(7)	$= 2A_{4x}$	0.041(2)
		B_4	0‡	$= 2B_{4x}$	0.0267(18)
	Sb(1)	A_1	0	0	0
		B_1	0	0	0
		A_2	0	0	0‡
		B_2	0	0	-0.0170(17)
		A_3	0	0	0
		B_3	0	0	0
		A_4	0	0	0.0307(18)
		B_4	0	0	-0.017(2)
Subsystem 2					
[Sb]	Sb(2)	A_1	$= -\sqrt{3}B_{1x}$	0	0
		B_1	0.0114(3)	$= 2B_{1x}$	0
		A_2	$= \sqrt{3}B_{2x}$	0	0
		B_2	0.0063(4)	$= 2B_{2x}$	0
		A_3	0	0	0
		B_3	0	0	0.144(3)
		A_4	$= -\sqrt{3}B_{4x}$	0	0
		B_4	0.0028(4)	$= 2B_{4x}$	0

† Positional modulation wave components of Zn_i were set to be equal to those of Zn.

‡ The component was fixed at zero because it was not a significant value considering its standard deviation.

For the calculation of the electronic DOS of $Zn_{36}Sb_{30}$, $Zn_{37}Sb_{30}$, $Zn_{38}Sb_{30}$, $Zn_{39}Sb_{30}$, $Zn_{40}Sb_{30}$ and $Zn_{41}Sb_{30}$, the atomic coordinates of the Zn(1), Zn_i, Sb(1) and Sb(2) atoms listed in Table S3 are used. Considering that the 723 K sample has the commensurate crystal structure similar to the 823 K and long-heating samples, these atomic coordinates are generated based on the 723 K sample using the corresponding atomic coordinates (Table 2) and the positional modulations (Fig. S1(a)). The Zn(1), Zn_i, Sb(1) and Sb(2) atoms are in the unit cell of $a \times a \times 2c_{[Zn3+\delta Sb]}$ (i.e. the same size of the 3D-model): the lattice parameters are set at a (= b) = 12.23281 Å and $c = 2c_{[Zn3+\delta Sb]}$ = 12.42860 Å.

Table S3 Atomic coordinates of the Zn(1), Zn_i, Sb(1) and Sb(2) atoms for the calculation of the electronic DOS of $Zn_{36}Sb_{30}$, $Zn_{37}Sb_{30}$, $Zn_{38}Sb_{30}$, $Zn_{39}Sb_{30}$, $Zn_{40}Sb_{30}$ and $Zn_{41}Sb_{30}$.

Atom	Site	*x*	*y*	*z*	Atom	Site	*x*	*y*	*z*
Zn1	Zn(1)	0.17870116	0.41651457	0.24041439	Zn37†	Zn_i	0.18528114	0.45228243	0.53991115
Zn2	Zn(1)	0.23781342	0.82129884	0.24041439	Zn38†	Zn_i	0.54771757	0.81481886	0.03991115
Zn3	Zn(1)	0.58348543	0.76218658	0.24041439	Zn39†	Zn_i	0.88105091	0.39966538	0.87324449
Zn4	Zn(1)	0.73405879	0.56651457	0.26657628	Zn40†	Zn_i	0.79905090	0.85392255	0.25479930
Zn5	Zn(1)	0.83245578	0.26594121	0.26657628	Zn41†	Zn_i	0.21438424	0.14815219	0.70657782
Zn6	Zn(1)	0.43348543	0.16754422	0.26657628	Sb1	Sb(1)	0.00000000	0.00000000	0.13798853
Zn7	Zn(1)	0.90441949	0.74984791	0.40708106	Sb2	Sb(1)	0.00000000	0.00000000	0.33141470
Zn8	Zn(1)	0.84542842	0.09558051	0.40708106	Sb3	Sb(1)	0.66666667	0.33333333	0.30465520
Zn9	Zn(1)	0.25015209	0.15457158	0.40708106	Sb4	Sb(1)	0.66666667	0.33333333	-0.00191863
Zn10	Zn(1)	0.49906186	0.89984791	0.43324295	Sb5	Sb(1)	0.33333333	0.66666667	0.47132187
Zn11	Zn(1)	0.40078605	0.50093814	0.43324295	Sb6	Sb(1)	0.33333333	0.66666667	0.16474803
Zn12	Zn(1)	0.10015209	0.59921395	0.43324295	Sb7	Sb(1)	0.00000000	0.00000000	0.63798853
Zn13	Zn(1)	0.57108616	0.08318124	0.07374772	Sb8	Sb(1)	0.00000000	0.00000000	0.83141470
Zn14	Zn(1)	0.51209508	0.42891384	0.07374772	Sb9	Sb(1)	0.66666667	0.33333333	0.80465520
Zn15	Zn(1)	0.91681876	0.48790492	0.07374772	Sb10	Sb(1)	0.66666667	0.33333333	0.49808137
Zn16	Zn(1)	0.16572852	0.23318124	0.09990962	Sb11	Sb(1)	0.33333333	0.66666667	0.97132187
Zn17	Zn(1)	0.06745272	0.83427148	0.09990962	Sb12	Sb(1)	0.33333333	0.66666667	0.66474803
Zn18	Zn(1)	0.76681876	0.93254728	0.09990962	Sb13	Sb(2)	0.33318448	0.02407551	0.08333333
Zn19	Zn(1)	0.23775282	0.41651457	0.74041439	Sb14	Sb(2)	0.69089102	0.66681552	0.08333333
Zn20	Zn(1)	0.17876175	0.76224718	0.74041439	Sb15	Sb(2)	0.97592449	0.30910898	0.08333333
Zn21	Zn(1)	0.58348543	0.82123825	0.74041439	Sb16	Sb(2)	0.69086667	1.00000000	0.25000000
Zn22	Zn(1)	0.83239519	0.56651457	0.76657628	Sb17	Sb(2)	0.30913333	0.30913333	0.25000000
Zn23	Zn(1)	0.73411939	0.16760481	0.76657628	Sb18	Sb(2)	0.00000000	0.69086667	0.25000000
Zn24	Zn(1)	0.43348543	0.26588061	0.76657628	Sb19	Sb(2)	0.30928218	0.97592449	0.41666667
Zn25	Zn(1)	0.84536782	0.74984791	0.90708106	Sb20	Sb(2)	0.66664231	0.69071782	0.41666667
Zn26	Zn(1)	0.90448008	0.15463218	0.90708106	Sb21	Sb(2)	0.02407551	0.33335769	0.41666667
Zn27	Zn(1)	0.25015209	0.09551992	0.90708106	Sb22	Sb(2)	0.66651782	0.02407551	0.58333333
Zn28	Zn(1)	0.40072546	0.89984791	0.93324295	Sb23	Sb(2)	0.35755769	0.33348218	0.58333333
Zn29	Zn(1)	0.49912245	0.59927454	0.93324295	Sb24	Sb(2)	0.97592449	0.64244231	0.58333333
Zn30	Zn(1)	0.10015209	0.50087755	0.93324295	Sb25	Sb(2)	0.35753333	1.00000000	0.75000000
Zn31	Zn(1)	0.51203449	0.08318124	0.57374772	Sb26	Sb(2)	0.64246667	0.64246667	0.75000000
Zn32	Zn(1)	0.57114675	0.48796551	0.57374772	Sb27	Sb(2)	0.00000000	0.35753333	0.75000000
Zn33	Zn(1)	0.91681876	0.42885325	0.57374772	Sb28	Sb(2)	0.64261552	0.97592449	0.91666667
Zn34	Zn(1)	0.06739213	0.23318124	0.59990962	Sb29	Sb(2)	0.33330898	0.35738448	0.91666667
Zn35	Zn(1)	0.16578912	0.93260787	0.59990962	Sb30	Sb(2)	0.02407551	0.66669102	0.91666667
Zn36	Zn(1)	0.76681876	0.83421088	0.59990962					

† For the calculation of $[Zn_{37}Sb_{30}]$, $[Zn_{38}Sb_{30}]$, $[Zn_{39}Sb_{30}]$, $[Zn_{40}Sb_{30}]$ and $[Zn_{41}Sb_{30}]$, the [Zn37], [Zn37, Zn38], [Zn37, Zn38, Zn39], [Zn37, Zn38, Zn39, Zn40] and [Zn37, Zn38, Zn39, Zn40, Zn41] atoms were used, respectively.