

SUPPORTING INFORMATION

Intricate Li–Sn Disorder in Rare-earth Metal-
Lithium-Stannides. Crystal Chemistry of
 $RE_3Li_{4-x}Sn_{4+x}$ ($RE = \text{La–Nd, Sm}; x < 0.3$) and
 $Eu_7Li_{8-x}Sn_{10+x}$ ($x \approx 2.0$)

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Table S1. Selected crystal data and structure refinement parameters for $\text{Sr}_7\text{Li}_{8-x}\text{Sn}_{10+x}$.

empirical formula	$\text{Sr}_7\text{Li}_{5.76}\text{Sn}_{12.24(2)}$
fw, g mol ⁻¹	2106.08
λ , Å	0.71073
T , K	200(2)
Space group	<i>Cmmm</i> (No. 65), $Z = 2$
a , Å	7.6106(7)
b , Å	37.006(3)
c , Å	4.9211(4)
V , Å ³	1386.0(2)
ρ_{calcd} , g cm ⁻³	5.05
μ (Mo $K\alpha$), cm ⁻¹	241.3
GOF on F^2	1.086
R_1 [$I > 2\sigma(I)$] ^a	0.0368
wR_2 [$I > 2\sigma(I)$] ^a	0.0772
R_1 [all data] ^a	0.0492
wR_2 [all data] ^a	0.0835
$\Delta\rho_{\text{max,min}}/\text{e}\cdot\text{\AA}^{-3}$	5.44, -1.78

^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 $w = 1/[\sigma^2 F_o^2 + 0.0222P^2 + 62.3P]$, and $P = (F_o^2 + 2F_c^2)/3$;

^b The final difference Fourier map shows a residual peak, which is located 1.3 Å away from Sr4 and it was not possible to improve the structure refinement by including it to any reasonable model. We attribute this shortcoming to inadequate crystal quality, since for the isotypic $\text{Eu}_7\text{Li}_{6.01}\text{Sn}_{11.99(2)}$, the highest residual maxima and minima were 1.09 e·Å⁻³ and -1.54 e·Å⁻³, respectively. $\Delta\rho_{\text{max,min}}$ for the $\text{RE}_3\text{Li}_{4-x}\text{Sn}_{4+x}$ ($\text{RE} = \text{La-Nd, Sm}$) refinements are also generally not larger than 2 e·Å⁻³, except for the Sm-data. In this case, also due to problems with the crystal quality, the final difference Fourier map has a small peak of *ca.* 3 e·Å⁻³ located 0.8 Å away from Sm1, and a comparable in depth hole located 1.1 Å away from Sn1.

Table S2. Atomic coordinates and equivalent displacement parameters (U_{eq}^{a}) for $\text{Sr}_7\text{Li}_{5.76}\text{Sn}_{12.24(2)}$.

Atom	Site	x	y	z	$U_{\text{eq}}/\text{\AA}^2$
Sr1	4j	0	0.1618(1)	1/2	0.019(1)
Sr2	4j	0	0.2785(1)	1/2	0.012(1)
Sr3	4i	0	0.4450(1)	0	0.014(1)
Sr4	2a	0	0	0	0.016(1)
Sn1	8p	0.1866(1)	0.2141(1)	0	0.013(1)
Sn2	4j	0	0.3756(1)	1/2	0.016(1)
Sn3	4i	0	0.0937(1)	0	0.030(1) ^d
Sn4	4h	0.3110(2)	0	1/2	0.012(1)
Li1/Sn ^b	8q	0.1923(2)	0.0770(1)	1/2	0.014(1)
Li2/Sn ^c	8p	0.309(1)	0.1398(2)	0	0.017(3)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor;

^b Li1/Sn refers to the Li1 position, where the refinements show statistical mixing of Li and Sn atoms with a ratio 0.500:0.500(4);

^c Li2/Sn refers to the Li2 position, where the refinements show statistical mixing of Li and Sn atoms with a ratio 0.938:0.062(4);

^d The slight elongation of the anisotropic displacement parameter for Sn3 in this case is an artifact of the small Li/Sn disorder at the Li2 site. For the isotypic $\text{Eu}_7\text{Li}_{6.01}\text{Sn}_{11.99(2)}$, the Li2 position does not appear to be a subject of occupational disorder, while here, the close proximity of Sn3 to Li2/Sn may explain this small offset. We note that in $\text{RE}_3\text{Li}_{4-x}\text{Sn}_{4+x}$ ($\text{RE} = \text{La-Nd, Sm}$) too, the anisotropic displacement parameters for the RE2 and Sn2 atoms are slightly enlarged in one direction, and this elongation is more apparent when the degree of Li/Sn mixing is higher. Most likely, this is due to the Li/Sn disorder at the Li position, since both RE2 and Sn2 are close neighbors to the Li position.

Table S3. Important interatomic distances (Å) for $\text{Sr}_7\text{Li}_{5.76}\text{Sn}_{12.24(2)}$.

Atom pair	Distance (Å)	Atom pair	Distance (Å)
Sn1–Sn1	2.828(2)	Sr1–Sn1	$3.437(1) \times 4$
Sn1–Sn1	2.840(2)	Sr1–Sn3	$3.523(2) \times 2$
Sn4–Sn4	2.878(2)	Sr1–Li1	$3.463(2) \times 2$
Li1–Sn2	2.926(2)	Sr1–Li2	$3.499(7) \times 4$
Li1–Sn3	$2.929(1) \times 2$	Sr2–Sn1	$3.438(1) \times 4$
Li1–Sn4	2.989(2)	Sr2–Sn1	$3.709(1) \times 4$
Li2–Sn1	2.903(1)	Sr2–Sn2	3.592(1)
Li2–Sn2	$2.914(5) \times 2$	Sr3–Sn2	$3.556(2) \times 2$
Li2–Sn3	2.905(9)	Sr3–Sn4	$3.503(1) \times 4$
		Sr3–Li1	$3.493(1) \times 4$
		Sr3–Li2	$3.457(9) \times 2$
		Sr4–Sn3	$3.467(2) \times 2$
		Sr4–Sn4	$3.414(1) \times 4$

Table S4. Integrated COHP values of selected interactions in $\text{Sr}_7\text{Li}_6\text{Sn}_{12}$. The atom labels in this hypothetical model structure are derived from the experimentally determined $\text{Sr}_7\text{Li}_{8-x}\text{Sn}_{10+x}$ and the group-subgroup relationship within the Bärnighausen formalism between the two is presented in Figure S4.

Atom pair	Distance (Å)	$-i\text{COHP}$ (eV/ cell)
Li1–Sn4	2.926	0.045
Li1–Sn5	2.931	0.026
Li1–Sn6	2.989	0.033
Sn1–Sn4	2.926	0.147
Sn1–Sn5	2.931	0.141
Sn1–Sn6	2.989	0.137
Li2–Sn3	2.903	0.039
Li2–Sn4	2.914	0.039
Li2–Sn5	2.905	0.030
Li3–Sn3	2.903	0.039
Li3–Sn4	2.914	0.039
Li3–Sn5	2.905	0.030
Sn2–Sn5	2.828	0.169
Sn2–Sn5	2.840	0.164
Sn6–Sn6	2.878	0.151

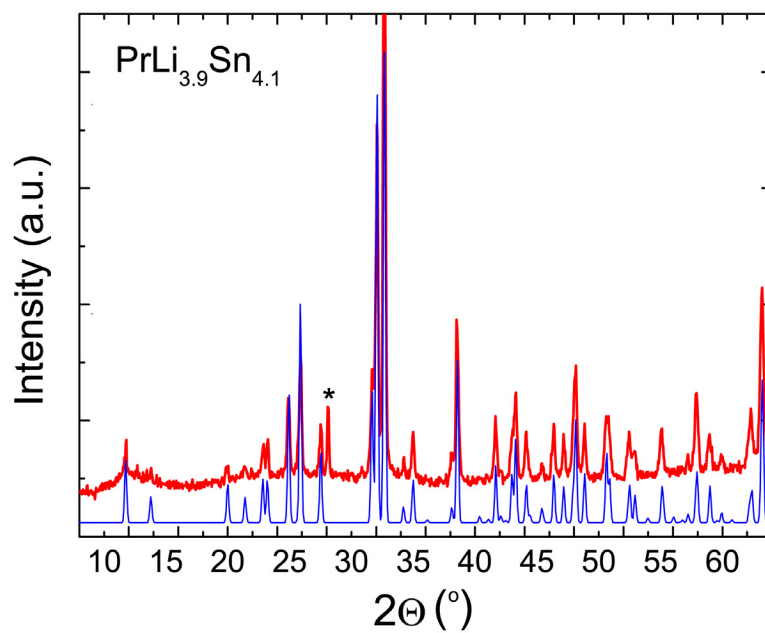


Figure S1. Experimental (red) and calculated (blue) powder X-ray diffraction pattern for Pr₃Li_{3.93}Sn_{4.07(1)}. The most intense peak corresponding to an impurity phase is denoted with the asterisk.

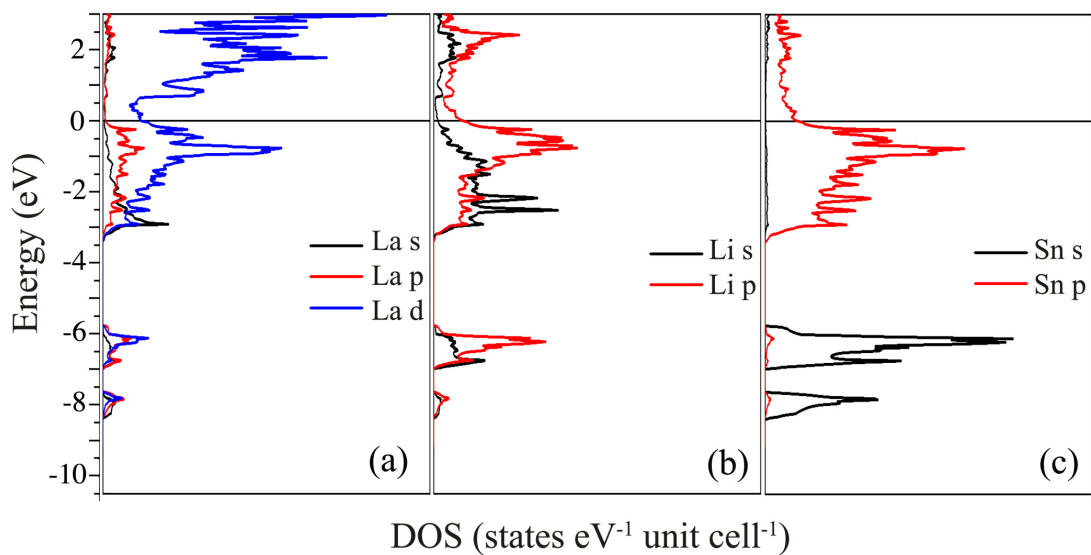


Figure S2. Calculated partial density of states (PDOS) curves for $\text{La}_3\text{Li}_4\text{Sn}_4$. The Fermi level is set at 0 eV as an energy reference. The PDOS plots show the s, p, and d bands for La (a), s and p bands for Li (b), and s and p bands for Sn (c).

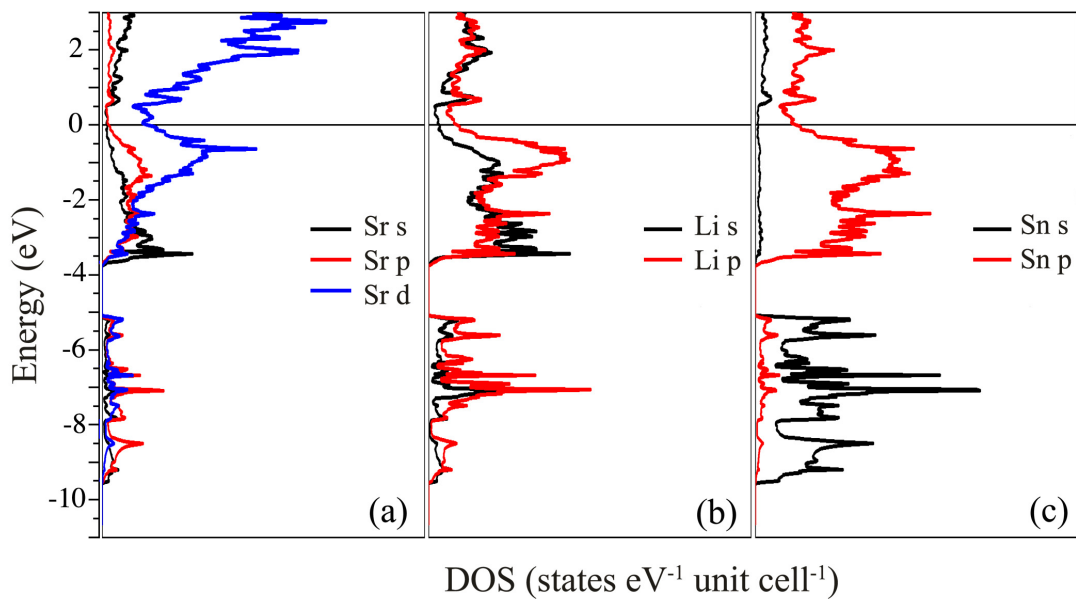


Figure S3. Calculated partial density of states (PDOS) curves for model $\text{Sr}_7\text{Li}_6\text{Sn}_{12}$ structure. The Fermi level is set at 0 eV as an energy reference. PDOS plots show the s, p, and d bands for Sr (a) Sr, s and p bands for Li (b), and s and p bands for Sn (c).

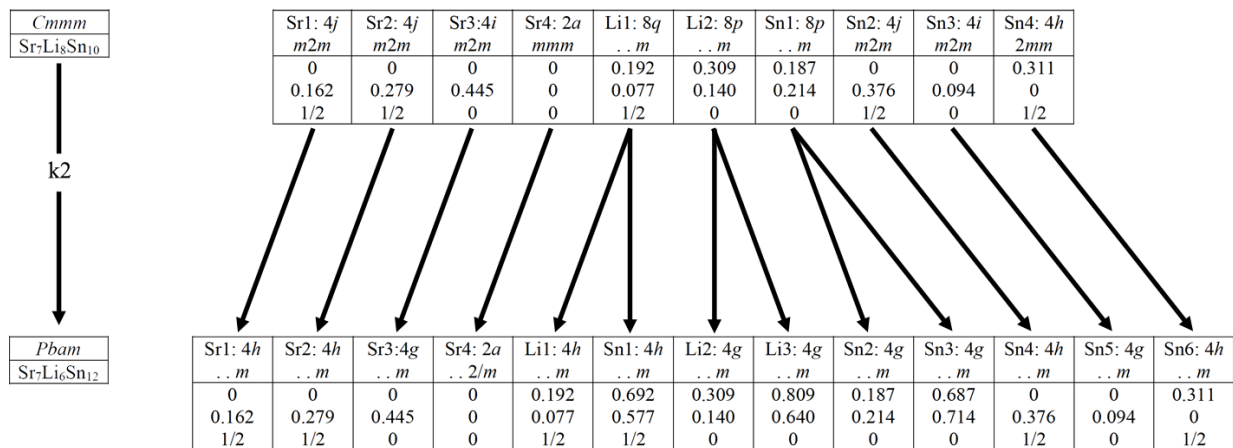


Figure S4. Group-subgroup relationship within the Bärnighausen formalism for the structures of $\text{Sr}_7\text{Li}_8\text{Sn}_{10}$ and the imaginary ordered model $\text{Sr}_7\text{Li}_6\text{Sn}_{12}$.