

Supporting Information

Multifaceted Sn–Sn bonding in the solid state. Synthesis and structural characterization of four new Ca–Li–Sn compounds

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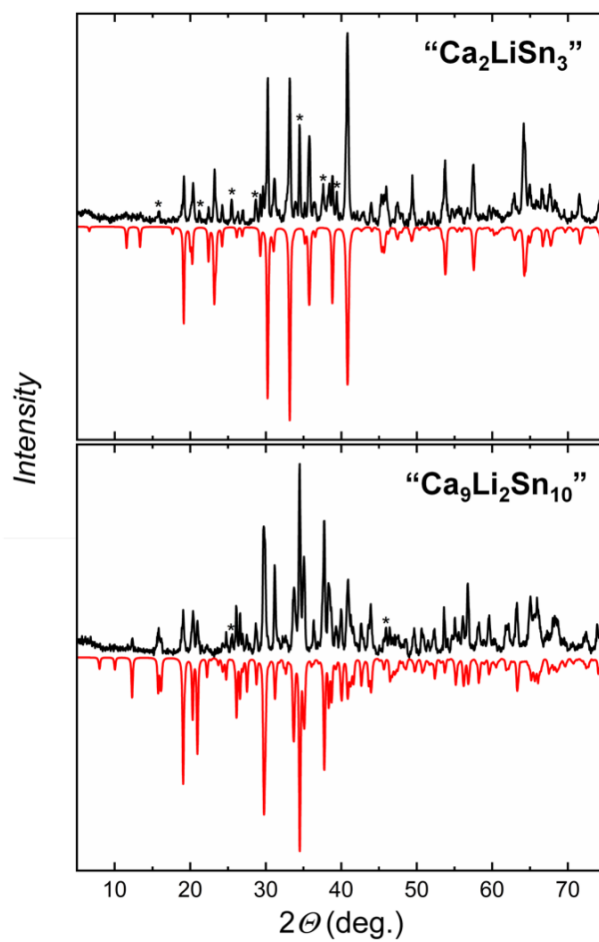


Fig. S1 PXRD patterns of the samples with nominal compositions Ca_2LiSn_3 (top) and $\text{Ca}_9\text{Li}_2\text{Sn}_{10}$ (bottom). Experimental patterns are shown in black. Theoretical simulations based on the refined crystal structures of Ca_2LiSn_3 and $\text{Ca}_{9-x}\text{Li}_2\text{Sn}_{10}$ ($x \approx 0.16$), respectively, are shown in red. Bragg peak positions of the most intense impurity reflections are marked with asterisks.

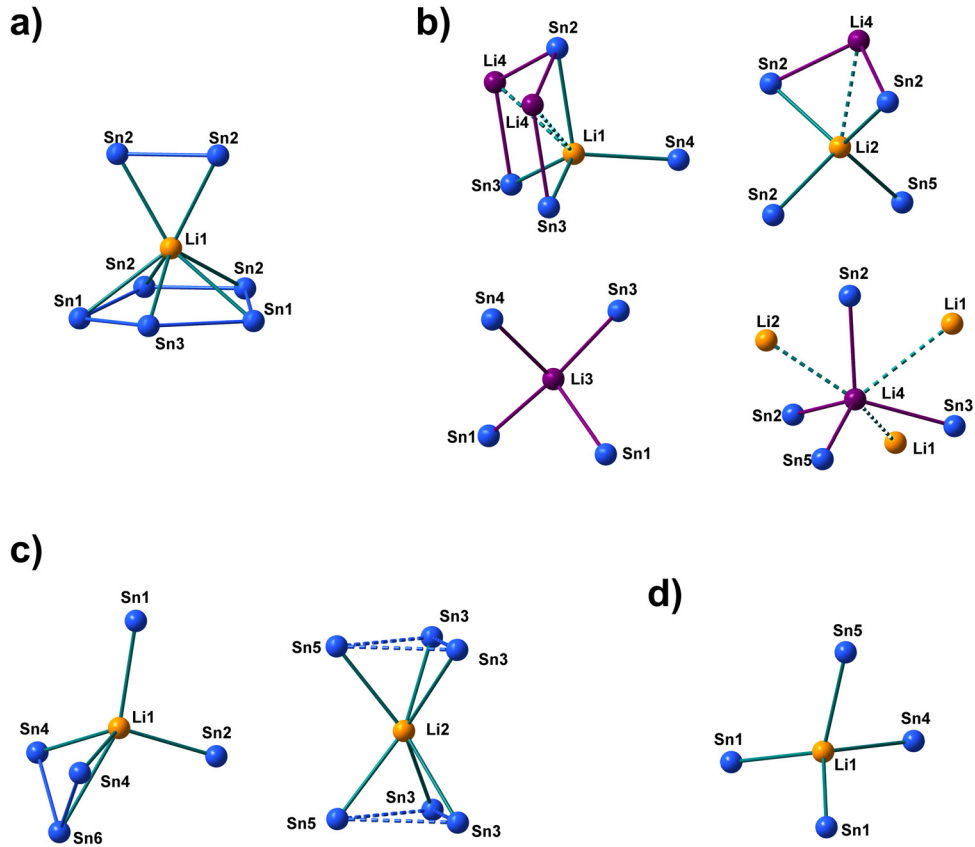


Fig. S2 Local coordination of the Li atoms in the structures of Ca_4LiSn_6 (a), $\text{Ca}_9\text{Li}_{6+x}\text{Sn}_{13-x}$ ($x \approx 0.28$) (b), Ca_2LiSn_3 (c), and $\text{Ca}_{9-x}\text{Li}_2\text{Sn}_{10}$ ($x \approx 0.16$) (d). Li, Sn, and mixed Li/Sn sites are shown in orange, blue, and purple, respectively.

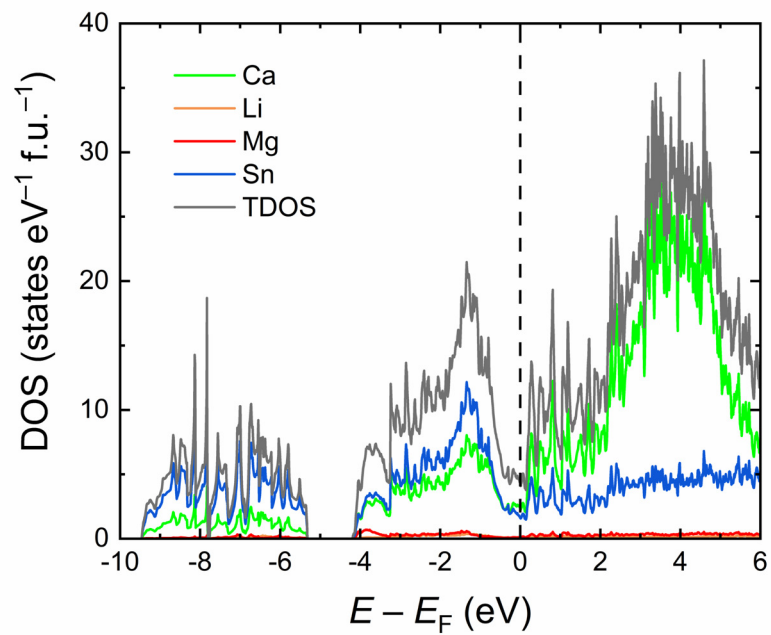


Fig. S3 Total and projected electronic densities of states (DOS) for the hypothetical compound $\text{Ca}_9\text{LiMgSn}_{10}$.

Table S1 Selected interatomic distances (Å) for Ca₄LiSn₆

Atoms	Distance	Atoms	Distance
Ca1 —Sn4	3.1598(8)	Ca3 —Sn2 × 2	3.1678(3)
—Sn1	3.2380(8)	—Sn4	3.224(1)
—Sn2	3.2435(7)	—Sn2 × 2	3.3133(3)
—Sn3	3.3189(8)	—Sn1 × 2	3.3515(7)
—Sn3	3.3620(8)	—Sn1 × 2	3.5648(6)
—Sn1	3.4329(8)	Li1 —Sn2 × 2	2.891(8)
—Sn4	3.5139(8)	—Sn2 × 2	2.895(8)
—Sn1	3.6310(7)	—Sn3	2.899(9)
Ca2 —Sn1 × 2	3.3641(8)	—Sn1 × 2	3.096(6)
—Sn2 × 2	3.376(1)	Sn1 —Sn2	2.9346(3)
—Sn3	3.385(1)	—Sn3	2.9633(3)
—Sn3	3.392(1)	—Sn4	2.9981(3)
—Sn2 × 2	3.569(1)	Sn2 —Sn2	2.7971(5)
—Sn4 × 2	3.8952(4)	—Sn1	2.9347(3)
		Sn3 —Sn1 × 2	2.9634(3)
		Sn4 —Sn1 × 2	2.9982(3)

Table S2 Selected interatomic distances (Å) for Ca₉Li_{6+x}Sn_{13-x} (x ≈ 0.28)

Atoms	Distance	Atoms	Distance
Ca1 —Sn1	3.196(2)	Li1 —Sn3 × 2	2.82(1)
—Sn4 × 2	3.212(2)	—Sn4	2.87(2)
—Sn3	3.245(2)	—Sn2	2.89(2)
—Sn6 × 2	3.369(2)	—(Li/Sn)4 × 2	3.28(1)
—Sn1	3.498(2)	Li2 —Sn2 × 2	2.78(1)
—(Li/Sn)3 × 2	3.825(2)	—Sn5	2.84(2)
Ca2 —Sn5 × 2	3.311(2)	—(Li/Sn)4	2.88(2)

	—Sn3 × 2	3.331(2)		—Sn2	2.90(2)
	—(Li/Sn)4 × 2	3.339(2)	(Li/Sn)3	—Sn3	2.862(2)
	—Sn4 × 2	3.342(2)		—Sn4	2.877(2)
	—(Li/Sn)3 × 2	3.373(2)		—Sn1 × 2	2.9036(9)
Ca3	—Sn1	3.168(2)	(Li/Sn)4	—Sn5	2.797(2)
	—Sn3 × 2	3.228(2)		—Sn3	2.806(2)
	—Sn1 × 2	3.235(2)		—Sn2 × 2	2.853(1)
	—Sn6	3.605(2)	Sn1	—(Li/Sn)3 × 2	2.9036(9)
	—(Li/Sn)3 × 2	3.632(2)		—Sn6 × 2	3.2390(6)
	—(Li/Sn)3	3.748(2)	Sn2	—(Li/Sn)4 × 2	2.853(1)
Ca4	—Sn5 × 2	3.323(2)	Sn3	—(Li/Sn)4	2.806(2)
	—Sn4 × 2	3.337(2)		—(Li/Sn)3	2.862(2)
	—Sn2 × 2	3.371(2)	Sn4	—Sn5	2.865(1)
	—(Li/Sn)4	3.480(3)		—(Li/Sn)3	2.877(2)
	—Sn2	3.815(2)	Sn5	—(Li/Sn)4	2.797(2)
Ca5	—Sn5 × 4	3.2296(6)		—Sn4	2.865(1)
	—Sn2 × 2	3.4188(8)	Sn6	—Sn1 × 4	3.2390(6)
	—(Li/Sn)4 × 4	3.945(2)			

Table S3 Selected interatomic distances (Å) for Ca₂LiSn₃

Atoms	Distance	Atoms	Distance
Ca1	—Sn2 × 2 3.239(3)	Li2	—Sn5 × 2 2.99(6)
	—Sn4 3.276(5)		—Sn3 × 4 3.03(3)
	—Sn1 × 2 3.294(3)	Sn1	—Sn6 2.986(2)
	—Sn3 × 2 3.421(3)		—Sn3 3.028(2)
	—Sn6 × 2 3.655(3)	Sn2	—Sn5 2.951(2)
Ca2	—Sn2 × 2 3.257(3)		—Sn3 2.971(3)
	—Sn1 × 2 3.278(3)	Sn3	—Sn2 2.971(3)
	—Sn3 × 2 3.578(4)		—Sn1 3.028(2)
	—Sn5 × 2 3.595(4)		—Sn3 3.287(3)
Ca3	—Sn2 × 4 3.357(2)		—Sn5 3.363(3)
	—Sn5 × 2 3.439(5)	Sn4	—Sn6 × 2 2.974(3)

	—Sn3 × 4	3.582(5)	Sn5	—Sn2 × 2	2.951(2)
Ca4	—Sn4	3.195(9)		—Sn3 × 2	3.363(3)
	—Sn1 × 4	3.219(2)	Sn6	—Sn4 × 2	2.974(3)
	—Sn6 × 2	3.481(5)		—Sn1 × 2	2.986(2)
Li1	—Sn2	2.82(5)			
	—Sn1	2.9(1)			
	—Sn4 × 2	3.01(4)			
	—Sn6	3.25(9)			

Table S4 Selected interatomic distances (Å) for $\text{Ca}_{9-x}\text{Li}_2\text{Sn}_{10}$ ($x \approx 0.16$)

Atoms	Distance	Atoms	Distance		
Ca1	—Sn1	3.2113(8)	Ca5	—Sn4 × 4	3.3381(3)
	—Sn3 × 2	3.2683(6)		—Sn5 × 4	3.4356(3)
	—Sn4 × 2	3.2888(6)	Li1	—Sn5	2.852(7)
	—Sn3 × 2	3.4874(6)		—Sn4	2.883(6)
Ca2	—Sn3 × 2	3.2546(6)		—Sn1 × 2	2.909(4)
	—Sn2 × 2	3.2703(6)	Sn1	—Sn2	2.9160(4)
	—Sn5 × 2	3.3680(6)	Sn2	—Sn1	2.9160(4)
	—Sn4 × 2	3.4207(6)		—Sn5	2.9437(4)
Ca3	—Sn1	3.2699(8)	Sn3	—Sn3	2.8823(5)
	—Sn5 × 2	3.3011(6)		—Sn4	2.9247(4)
	—Sn1 × 2	3.3449(6)	Sn4	—Sn5	2.9198(4)
	—Sn2 × 2	3.5068(6)		—Sn3	2.9246(4)
Ca4	—Sn3	3.2427(8)	Sn5	—Sn4	2.9198(4)
	—Sn2 × 2	3.2873(6)		—Sn2	2.9437(4)
	—Sn2	3.3008(9)			
	—Sn1 × 2	3.3624(6)			
