The Li-Sn (Lithium-Tin) System

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Equilibrium Diagram

The assessed Li-Sn phase diagram is given in Fig. 1, and a detailed section of this diagram is shown in Fig. 2. Special points of the diagram are presented in Table 1.

The phase diagram has been investigated by thermal analysis over the entire composition range [10Mas, 32Bar, 34Gru] and in a restricted composition range [79Bai]. Liquidus data have been obtained also by emf measurements [66Fos, 81Wen] and solubility measurements [82Dad].

Four eutectics have been reported for this system. The Li-side eutectic temperature was found to be 175 °C [10Mas], 179 °C [34Gru], or 183.3 °C [82Dad]. The eutectic composition was reported by all investigators [10Mas, 34Gru, 82Dad] to be ≈0 at.% Sn. In the most recent and precise determination [82Dad], there was no detectable difference (+/– 0.1 °C) between the Li freezing point and the eutectic temperature. The solubility of Sn in Li was measured in the range 306 to 472 °C [82Dad], who reported the following expression for the solubility:

$$\ln X_{Sn} = 4.742 - 6794/T \qquad \text{(Eq 1)}$$

$$579 \leq T(\text{K}) \leq 745$$

Extrapolation of this equation gives a eutectic composition of approximately 0.004 at.% Sn at the freezing point of Li. On the assumption of zero solid solubility at this point, a simple thermodynamic calculation indicates that the eutectic temperature lies 0.02 K below the Li freezing point.

The second, high-temperature eutectic was reported to be 752 °C, 20.5 at.% Sn [34Gru]. The third, intermediate eutectic was reported to be 458 °C, 37 at.% Sn [10Mas]; 458 °C, 35 at.% Sn [32Bar]; 470 °C, 43 at.% Sn [34Gru]; 469 °C, 43 at.% Sn [79Bai]; and 470 °C, 43 at.% Sn [81Wen]. The Sn-side eutectic was reported to be 214 °C, 95 at.% Sn [10Mas]; 214 °C, 94 at.% Sn [32Bar]; and 222 °C, 95 at.% Sn [34Gru].

The solubility of Li in solid Sn was determined at 200 °C from hardness curves and other methods [38Jen] and was reported to be less than 0.1 at.% (this is consistent with the fact that electric conductivity measurements of an alloy of 99 at.% Sn [34Gru] showed a distinct change of slope at 220 °C, that is, the eutectic temperature). On the assumption of zero solid solubility, the theoretical liquidus compositions would be: at 214 °C, 94 at.% Sn; at 222 °C, 96.6 at.% Sn. The liquidus data near this eutectic [10Mas, 32Bar, 34Gru] are too scattered to locate the eutectic more precisely. Thus, a mean value of 218 °C, 95 at.% Sn was chosen for the assessed phase diagram.

The reasons for the locations of the phase boundaries in the assessed phase diagram are given after the following discussion of intermediate compounds.

$Li_{22}Sn_5$ was prepared by direct reaction of the elements [64Gla] and was characterized by its powder x-ray pattern [64Gla]. Its range of homogeneity at 415 °C was found to be 1.2 at.% Sn, from 17.9 to 19.1 at.% Sn [80Wen, 81Hug] from emf/coulometric titration measurements. Its congruent melting point, deduced from the liquidus data of [34Gru] is 758 °C (Fig. 2).

"Li_4Sn" was thought to melt congruently at 684 °C [32Bar] or 765 °C [34Gru]. It is probable that "Li_4Sn" (20 at.% Sn) was mistaken for $Li_{22}Sn_5$ (18.5 at.% Sn).

Li_7Sn_2 was prepared by direct reaction of the elements [34Gru, 75Fra2] and melts congruently at 783 °C [34Gru]. It was characterized by its x-ray single-crystal pattern [75Fra2]. According to emf/coulometric titration measurements [80Wen, 81Hug], its homogeneity range at 415 °C is 1.4 at.% from 21.5 to 22.9 at.% Sn. Thermal analysis data [34Gru, 79Bai] establish the high-temperature homogeneity range; at 715 °C, it extends as far as 24 at.% Sn (Fig. 2).

$Li_{13}Sn_5$ was prepared from direct reaction of the elements [75Fra3] and was characterized by its x-ray single-crystal pattern [75Fra3, 81Wen]. Its range of homogeneity at 415 °C is 0.5 at.% [80Wen, 81Hug] as determined by emf/coulometric titration measurements. It melts incongruently at 716 °C at a peritectic composition of 30 at.% Sn [79Bai].

Li_5Sn_2 was prepared by direct combination of the elements [75Fra1] and was characterized by its x-ray single-crystal pattern [75Fra1]. It melts incongruently at 720 °C [34Gru] or 698 °C [79Bai], at a peritectic composition of 28 at.% Sn [34Gru] or 31 at.% Sn [79Bai]. Its range of homogeneity at 415 °C is 1.0 at.% [80Wen, 81Hug], according to emf/coulometric titration measurements.

Li_7Sn_3 was prepared by direct reaction of the elements [74Mul] and characterized by the x-ray single-crystal pattern [74Mul]. It melts incongruently at 500 °C [79Bai]. A peritectic at 502 °C, 58.3 at.% Sn observed by [34Gru] and attributed by them to "Li_2Sn," probably corresponds to Li_7Sn_3.

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Table 1 Special Points of the Assessed Li-Sn Phase Diagram

Reaction	Compositions of the respective phases, at.% Sn			Temperature, °C	Reaction type
L ↔ (βLi)		0		180.6	Melting
L ↔ (βLi) + $Li_{22}Sn_5$	0	0	18.5	180.6	Eutectic
L ↔ $Li_{22}Sn_5$		18.5		758	Congruent
L ↔ $Li_{22}Sn_5$ + (Li_7Sn_2)	20.3	18.5	22.2	752	Eutectic
L ↔ Λι$_7$Sn$_2$		22.2		783	Congruent
L + (Li_7Sn_2) → $Li_{13}Sn_5$	29.5	24.0	27.8	716	Peritectic
L + $Li_{13}Sn_5$ → Li_5Sn_2	31.1	27.8	28.6	698	Peritectic
L + Li_5Sn_2 → Li_7Sn_3		28.6	30.0	502	Peritectic
L ↔ Li_7Sn_3 + LiSn	43	30	50	470	Eutectic
L ↔ ΛιΣν		50		487	Congruent
L + LiSn → Li_2Sn_5		50	71.4	320	Peritectic
L ↔ Λι$_2$Sn$_5$ + (βSn)	95	71.4	100	214	Eutectic
L ↔ (βSn)		100		231.9681	Melting

Table 2 Li-Sn Crystal Structure Data

Phase	Composition, at.% Sn	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(αLi)(a)	0	*hP*2	$P6_3/mmc$	*A*3	Mg	[Massalski2]
(βLi)	0	*cI*2	$Im\bar{3}m$	*A*2	W	[Massalski2]
($Li_{22}Sn_5$)	17.9 to 19.1	*cF*432	*F*23	…	$Li_{22}Pb_5$	[64Gla]
(Li_7Sn_2)	22.2 to 24.0	*oC*36	*Cmmm*	…	Ge_2Li_7	[75Fra2]
($Li_{13}Sn_5$)	27.5 to 28.0	*hP*18	$P\bar{3}m1$	…	$Li_{13}Sn_3$	[75Fra3]
(Li_5Sn_2)	28.1 to 29.1	*hR*7	$R\bar{3}m$	*D*8*g*	B_5Mo_2	[75Fra1]
(Li_7Sn_3)	29.7 to 30.3	*mP*20	$P2_1/m$	…	Li_7Sn_3	[74Mul]
LiSn	49.5 to 50.5	*mP*6	*P*2/*m*	…	LiSn	[73Mul]
Li_2Sn_5	71.4	*tP*14	*P*4/*mbm*	…	Hg_5Mn_2	[69Han]
(αSn)(c)	100	*cF*8	$Fd\bar{3}m$	*A*4	C(b)	[Massalski2]
(βSn)	100	*tI*4	$I4_1/amd$	*A*5	Sn	[Massalski2]

(a) <72 K. **(b)** At 415 °C [80Wen, 81Hug]. **(c)** <18 °C.

"Li_3Sn_2" was thought to melt congruently at 465 °C [10Mas] or 483 °C [32Bar]. This compound was not reported in other work [34Gru, 79Bai] and was shown not to be present at 415 °C [81Wen] as shown by emf/coulometric titration measurements. It is probable that the reported "melting points" of this compound [10Mas, 32Bar] were misinterpretations of the intermediate eutectic (458 to 470 °C).

LiSn was prepared by direct combination of the elements [34Gru, 73Mul, 79Bai] and was characterized by its single-crystal x-ray pattern [73Mul]. Its congruent melting point was reported to be 485 °C [34Gru], 488 °C [81Wen], and 486 °C [79Bai]. Its homogeneity range at 415 °C is 1.9 at.% [80Wen, 81Hug], as measured by emf/coulometric titration.

Li_2Sn_5 was prepared by direct reaction of the elements [69Han] and was characterized by its single-crystal x-ray pattern [69Han]. It was reported to melt incongruently at 319 °C [10Mas], at a peritectic composition of 76.5 at.% Sn. Peritectics observed at 320 °C, 79 at.% Sn [32Bar] and 326 °C, 78 at.% Sn [34Gru] were incorrectly assigned to "$LiSn_4$" and "$LiSn_2$," respectively.

The general shape of the liquidus in Fig. 1 is based on the data of [34Gru], while the number and identity of intermediate compounds are based on the more recent evidence. The Li-side liquidus is not well defined. It is drawn to respect the results of solubility measurements [82Dad] rather than those of thermal analysis [32Bar, 34Gru], but the position of the boundary is in doubt. In the interval 24 to 32 at.% Sn, the diagram is drawn with greater weight given to the most recent data [79Bai].

Crystal Structures and Lattice Parameters

The crystal and lattice parameter data are summarized in Tables 2 and 3.

$Li_{22}Sn_5$ is isostructural with fcc $Li_{22}Pb_5$ [64Gla] with 16 formula units in the unit cell [Pearson3]. Li_7Sn_2 is orthorhombic, isostructural with Li_7Ge_2 and similar to Li_7Pb_2 [75Fra2]. $Li_{13}Sn_5$ is trigonal, with an ordered bcc derivative structure [75Fra3]. Li_5Sn_2 is trigonal/rhombohedral, similar to idealized trigonal/rhombohedral Li_2Si and hexagonal Li_9Ge_4 [75Fra1].

Li_7Sn_3 is monoclinic, a variant of the bcc structure [74Mul]. LiSn is monoclinic and is not isostructural with LiGe or LiPb [73Mul]. Li_2Sn_5 is tetragonal, isostructural with Hg_5Sn_2; the basic building unit of this structure is a pentagonal prism with two atoms at the extended poles [69Han].

Thermodynamics

Earlier data on liquid Li-Sn solutions were reviewed by [75Smi]. The excess chemical potential of Li in solution has been determined by emf measurements in the overall ranges 0

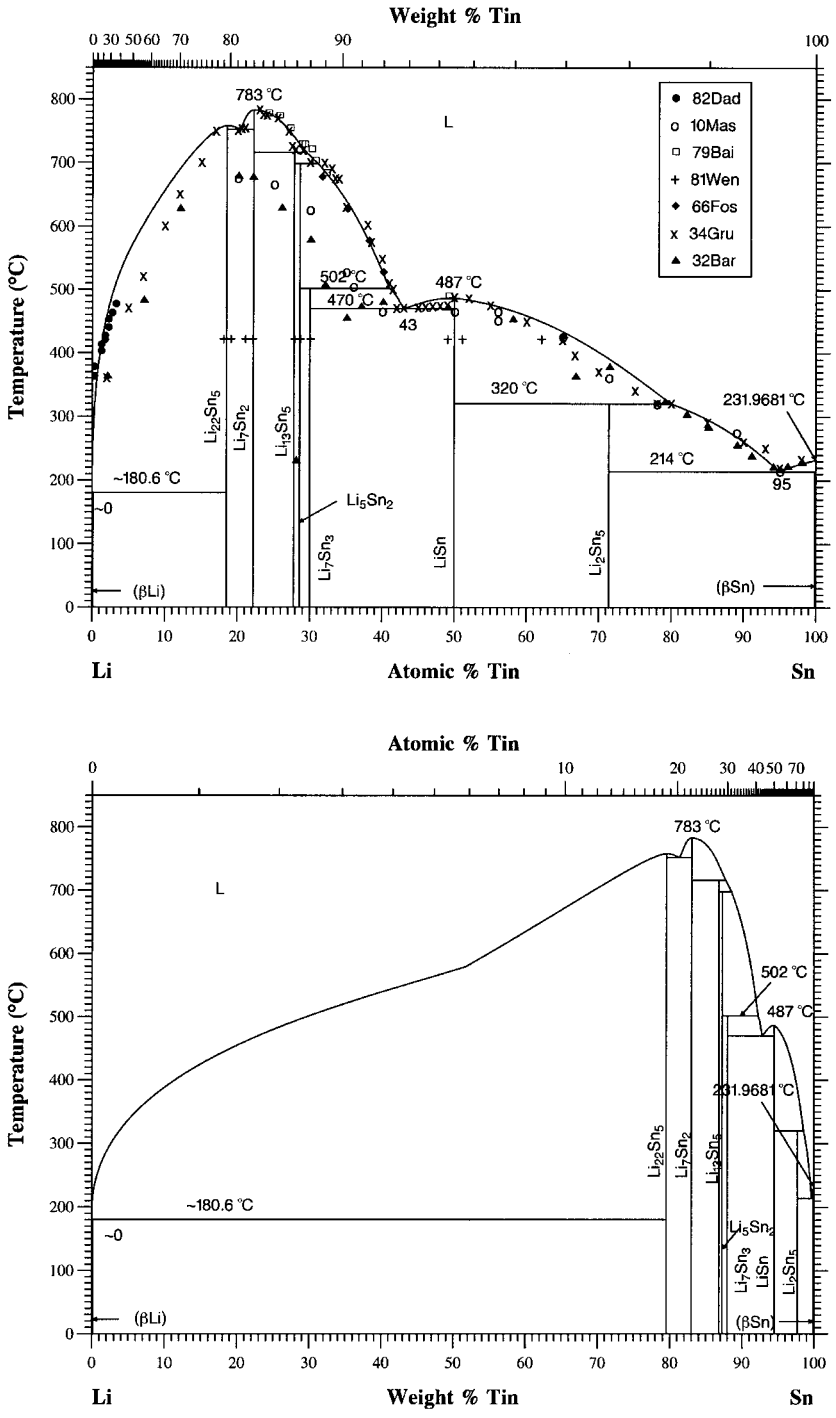

Fig. 1 Assessed Li-Sn phase diagram. Although ranges of homogeneity have been reported for some of the intermediate phases, the ranges refer to a single temperature and are neglected in this diagram.

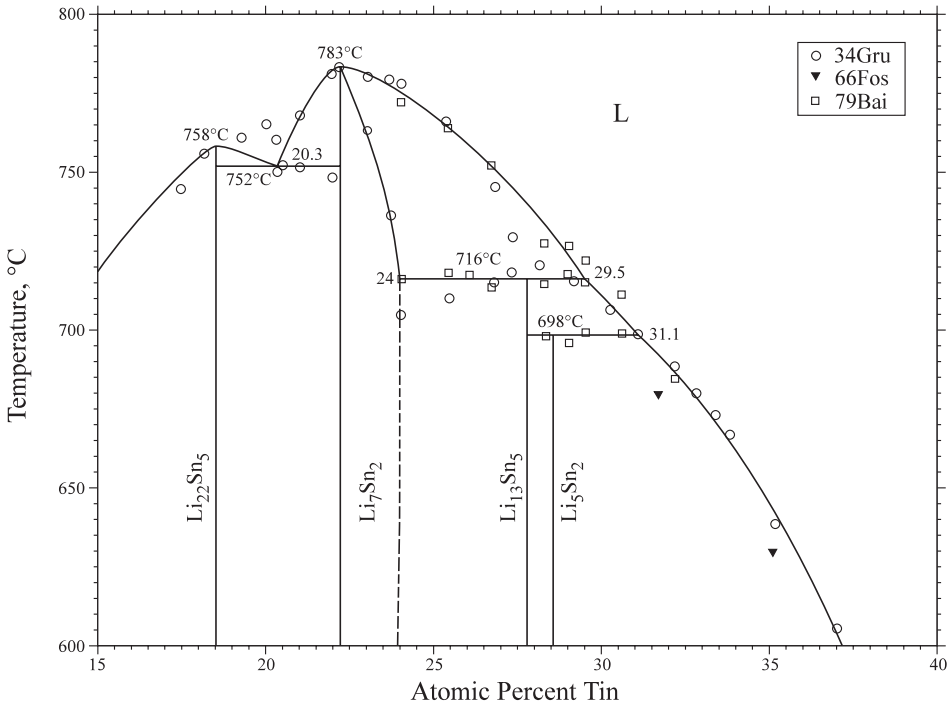

Fig. 2 Detail of assessed Li-Sn phase diagram.

to 100 at.% Sn and 360 to 850 °C [66Fos, 72Mor, 77Sab, 79Yat, 81Wen, 86Mos]. The vapor pressure of Li-Sn solutions was determined by the transpiration method at 1200 °C [72Fis] and by the Knudsen effusion method at 700 and 850 °C [71Bar]. The enthalpy of mixing of Li-Sn solutions was measured by direct high-temperature calorimetry in the interval 418 to 665 °C [86Mos]. All results indicate that both ΔH and G^E of liquid Li-Sn solutions are strongly negative and highly skewed toward the Li extreme (Fig. 3). This suggests strong Li-Sn interaction in the solution, and this is corroborated by neutron diffraction [84Alb] and electrical resistivity [82Mar] measurements.

Standard thermodynamic properties of formation of Li-Sn compounds have been determined from emf measurements [66Fos, 81Wen], by solution calorimetry [82Som], and by direct calorimetry [38Kub, 56Kub]. The most recent emf-derived data [81Wen] are probably the most reliable and are summarized in Table 4. The other data [38Kub, 56Kub, 66Fos, 82Som] are in fair agreement with those of [81Wen].

Cited References

10Mas: G. Masing and G. Tammann, "Behavior of Li toward Na, K, Sn, Cd, and Mg," *Z. Anorg. Chem., 67*(2), 183-199 (1910) in German. (Equi Diagram; Experimental; #)

32Bar: A. Baroni, "Alloys of Li. Thermal and X-Ray Analysis of the System Li-Sn," *Atti Rend. Accad. Lincei, Roma, 16*(6), 153-158 (1932) in Italian. (Equi Diagram; Experimental; #)

34Gru: G. Grube and E. Meyer, "Electrical Conductivity and Phase Diagram of Binary Alloys. 16. The System Li-Sn," *Z. Elektrochem., 40*(11), 771-777 (1934) in German. (Equi Diagram; Experimental; #)

38Jen: E. Jenckel and L. Roth, "The Solubility of Several Metals in Sn and Their Influence on the Recovery Temperature," *Z. Metallkde., 30*, 135-144 (1938) in German. (Equi Diagram; Experimental)

38Kub: O. Kubaschewski and W. Seith, "Heats of Formation of Nonferrous Alloys," *Z. Metallkde., 30*, 7-9 (1938) in German. (Thermo; Experimental)

56Kub: O. Kubaschewski and J.A. Catterall, "Thermochemical Data of Alloys," Pergamon Press, London, 13-14 (1956). (Thermo; Review)

64Gla: E.I. Gladyshevskii, G.I. Oleksiv, and P.I. Kripyakevich, "New Examples of the Structural Type $Li_{22}Pb_5$," *Kristallografiya, 9*(3), 338-341 (1964) in Russian; TR: *Sov. Phys. Crystallogr., 9*(3), 269-271 (1964). (Equi Diagram, Crys Structure; Experimental)

66Fos: M.S. Foster, C.E. Crouthamel, and S.E. Wood, "Thermodynamics of Binary Alloys. II. The Li-Sn System," *J. Phys. Chem., 70*(10), 3042-3045 (1966). (Equi Diagram, Thermo; Experimental; #)

69Han: D.A. Hansen and L.J. Chang, "Crystal Structure of Li_2Sn_5," *Acta Crystallogr. B, 25*(11), 2392-2395 (1969). (Equi Diagram, Crys Structure; Experimental)

71Bar: P. Baradel, A. Vermandé, I. Ansara, and P. Desré, "Thermodynamic Investigation of Liquid Li-Sn Alloys," *Rev. Int. Hautes Temp. Refract., 8*(3-4), 201-204 (1971) in French. (Thermo; Experimental)

72Fis: A.K. Fischer and S.A. Johnson, "Liquid-Vapor Equilibria and Thermodynamics of Li-Sn System," *J. Chem. Eng. Data, 17*(3), 280-283 (1972). (Thermo; Experimental)

72Mor: A.G. Morachevskii, L.N. Gerasimenko, A.I. Demidov, and O.A. Drozdova, "Thermodynamic Properties of Molten Li-Sn Alloys," *Elektrokhimiya, 8*(11), 1622-1624 (1972) in Russian; TR: Sov. *Electrochem., 8*(11), 1578-1580 (1972). (Thermo; Experimental)

73Mul: W. Müller and H. Schäfer, "The Crystal Structure of LiSn," *Z. Naturforsch. B, 28*(5-6), 246-248 (1973) in German. (Crys Structure; Experimental)

74Mul: W. Müller, "Preparation and Crystal Structure of Li_7Sn_3," *Z. Naturforsch. B, 29*(5-6), 304-307 (1974) in German. (Equi Diagram, Crys Structure; Experimental)

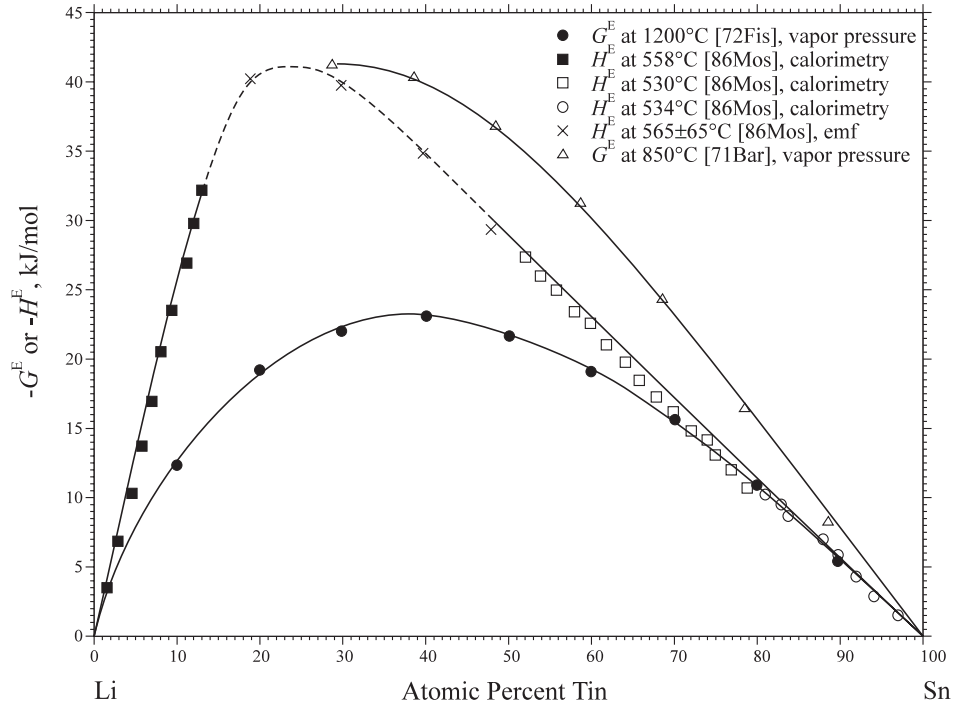

Fig. 3 Excess thermodynamic properties of liquid Li-Sn solutions.

Table 3 Li-Sn Lattice Parameter Data at 25 °C

Phase	Composition, at.% Sn	Lattice parameters, nm *a*	*b*	*c*	β or γ	Reference
αLi(a)	0	0.3111	…	0.5093	…	[Massalski2]
βLi	0	0.35093	…	…	…	[Massalski2]
($Li_{22}Sn_5$)	18.5	1.978	…	…	…	[64Gla]
(Li_7Sn_2)	22.2	0.980	1.380	0.475	…	[75Fra2]
($Li_{13}Sn_5$)	27.8	0.470	…	1.712	…	[75Fra3]
(Li_5Sn_2)	28.6	0.474	…	1.983	…	[75Fra1]
(Li_7Sn_3)	30.0	0.945	0.856	0.472	105.95° (γ)	[74Mul]
(LiSn)	50.0	0.517	0.774	0.318	104.5° (β)	[73Mul]
(Li_2Sn_5)	71.4	1.0274	…	0.3125	…	[69Han]
αSn(b)	100	0.64892	…	…	…	[Massalski2]
βSn	100	0.58318	…	0.31818	…	[Massalski2]

(a) <72 K. **(b)** <18 °C.

75Fra1: U. Frank, W. Müller, and H. Schäfer, "The Crystal Structure of Li_5Sn_2," *Z. Naturforsch. B, 30*(1-2), 1-5 (1975) in German. (Equi Diagram, Crys Structure; Experimental)

75Fra2: U. Frank, W. Müller, and H. Schäfer, "The Crystal Structure of Li_7Sn_2," *Z. Naturforsch. B, 30*(1-2), 609 (1975) in German. (Equi Diagram, Crys Structure; Experimental)

75Fra3: U. Frank and W. Müller, "Preparation and Crystal Structure of $Li_{13}Sn_5$ and the Structural Relations between the Phases of the Systems Li-Sn and Li-Pb," *Z. Naturforsch. B, 30*(3), 316-322 (1975) in German. (Equi Diagram, Crys Structure; Experimental)

75Smi: J.F. Smith and Z. Moser, "Thermodynamic Properties of Binary Li Systems. A Review," *J. Nucl. Mat., 59*(2), 158-174 (1976). (Thermo; Review; #)

Table 4 Standard Thermodynamic Formation Data of Li-Sn Compounds at 415 °C [81Wen]

Formula	$\Delta_f H$, kJ	$\Delta_f S$, kJ
$Li_{22}Sn_5$	–1100	–0.378
Li_7Sn_2	–394	–0.126
$Li_{13}Sn_5$	–825	–0.264
Li_5Sn_2	–318	–0.099
Li_7Sn_3	–453	–0.143
LiSn	–70	–0.026

$\Delta_f G^0 = \Delta_f H^0 - T\Delta_f S^0$ kJ per gram-formula weight

77Sab: M.-L. Saboungi and M. Blander, "Activity Coefficients of Dilute Solutions of Li in Liquid Al-Sn Alloys: Electromotive Force Measurements and Interpretation," *J. Electrochem. Soc., 124*(1), 6-13 (1977). (Thermo; Experimental)

79Bai: D.M. Bailey, W.H. Skelton, and J.F. Smith, "Li-Sn Phase Relationships between Li_7Sn_2 and Li-Sn," *J. Less-Common Met., 64*(2), 233-240 (1979). (Equi Diagram; Experimental; #)

79Yat: S.P. Yatsenko and E.A. Saltykova, "Thermodynamic Properties of Alloys of the Li-Sn System," *Khim. Thermodin. Termokhim.*, 190-191 (1979) in Russian. (Thermo; Experimental)

80Wen: C.J. Wen and R.A. Huggins, "Chemical Diffusion in Intermediate Phases in the Li-Sn System," *J. Solid State Chem., 35*(3), 376-384 (1980). (Equi Diagram, Crys Structure; Experimental)

81Hug: R.A. Huggins, "Use of Molten Salt Electrochemical Cells to Determine Thermodynamic and Kinetic Properties of Solids," *Chemical Metallurgy—A Tribute to Carl Wagner,* N.A. Gokcen, Ed., American Institute of Mining Metallurgical and Petroleum Engineers, New York, 339-360 (1981). (Crys Structure; Experimental)

81Wen: C.J. Wen and R.A. Huggins, "Thermodynamic Study of the Li-Sn System," *J. Electrochem Soc., 128*(6), 1181-1187 (1981). (Equi Diagram, Thermo; Experimental; #)

82Dad: A.T. Dadd, P. Hubberstey, and P.G. Roberts, "Solutions of Group IV Elements in Liquid Li," *J. Chem. Soc. Faraday Trans. I, 78*(9), 2735-2741 (1982). (Equi Diagram; Experimental)

82Mar: C. van der Marel, A.B. van Oosten, W. Geertsma, and W. van der Lugt, "The Electrical Resistivity of Liquid Li-Sn, Na-Sn and Na-Pb Alloys: Strong Effects of Chemical Interactions," *J. Phys. F, 12*(10), 2349-2361 (1982). (Thermo; Experimental)

82Som: F. Sommer, B. Fischer, and B. Predel, "Determination of the Formation Enthalpies of Na Alloys of Li with In, Tl, Sn, Pb and Bi," *Material Behavior and Physical Chemistry in Liquid Metal Systems,* H.U. Borgstedt, Ed., Plenum Press, New York, 395-400 (1982). (Thermo; Experimental)

84Alb: B.P. Alblas, W. van der Lugt, J. Dijkstra, and C. van Dijk, "Structure of Li-Sn Alloys," *J. Phys. F, 14*(9), 1995-2006 (1984). (Thermo; Experimental)

86Mos: Z. Moser, W. Gasior, F. Sommer, G. Schwitzgebel, and B. Predel, "Calorimetric and emf Studies on Liquid Li-Sn Alloys," *Metall. Trans. B, 17*(4), 791-796 (1986). (Thermo; Experimental; #)

# Indicates presence of a phase diagram.

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