The B-Li (Boron-Lithium) System

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Equilibrium Diagram

No equilibrium phase diagram for the B-Li system is available. Some obscure B-rich compounds were detected by [57Mar], [62Sec1], and [62Sec2]. Subsequently, several compounds possibly occurring in the system were proposed by many investigators (Table 1). The stability, homogeneity, and temperature ranges of each phase are quite uncertain. It appears that, as for pure B, many metastable B-Li phases form readily.

B Terminal Phase

The rhombohedral modification (βB) is the equilibrium phase. The melting point of B is 2092 °C [Melt]. The solubility of Li in (B) could not be detected by change in the lattice parameter [62Sec1, 62Sec2].

$B_{12}Li$

Presence of $B_{12}Li$ [62Sec2] or $B_{10.85 \pm 0.35}Li$ [67Sec] was suggested based on chemical and X-ray analyses of alloys with nominal compositions ranging from 9 to 55 at.% Li. [67Sec] considered the $B_{10.85}Li$ composition (8.4 at.% Li) to represent the low-B side of a region of solid solubility. The B-rich end of this phase is probably metastable tetragonal B. The formula $B_{12}Li$ (7.7 at.% Li) is listed tentatively in Tables 1 and 2.

In the composition range where $B_{12}Li$ was found by [67Sec] (9 to 55 at.% Li), a few additional compounds

Table 1 B-Li Crystal Structure Data

Phase(a)	Composition, at.% Li	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(βB)	0	*hR*108	$R\bar{3}m$	...	...	[77Cal]
B	0	*tP*196	$P4_1$	...	...	[60Tal]
$B_{12}Li$	~8.4	*tP***	...	...	...	[63Sec2]
B_6Li	14.3	...	...	...	...	[50Kie]
$B_{14}Li_3$	17.6	...	...	...	...	[84Mai]
B_4Li	20	*c***	...	...	...	[65Cas]
$B_{19}Li_6$	24	...	...	...	...	[84Mai]
B_3Li	25	...	...	...	...	[79Dal]
B_2Li(b)	33.3	...	...	...	...	[76Sch]
BLi	50	*t***	...	...	...	[77Sor]
B_6Li_7 or B_6Li_5	53.8	*hR*10	*R*3*m*	...	...	[78Wan]
BLi_3	75	*c***	...	...	...	[78Mit]
(βLi)	100	*cI*2	$Im\bar{3}m$	*A*2	W	[King1]
(αLi)	100	*hP*2	$P6_3/mmc$	*A*3	Mg	[King2]

Note: For pure B, only the phases mentioned in text are listed.
(a) All phases may not be stable. (b) High pressure phase?

Table 2 B-Li Lattice Parameter Data

Phase	Composition, at.% Li	Lattice parameters, nm *a*	*c*	Comment	Reference
(βB)	0	1.0139	...	α = 65.20°	[77Cal]
B	0	1.014	1.417	...	[79Vla]
$B_{12}Li$	~8.4	1.016	1.428	...	[67Sec]
B_4Li	20	0.720	...	...	[65Cas]
BLi	50	1.391	0.815	...	[77Sor]
B_6Li_7	55.6(a)	0.493	...	α = 90.0°	[78Wan]
(βLi)	100	0.35093	...	...	[King1]
(αLi)	100	0.3111	0.5093	...	[King2]

Note: Phases with unknown lattice parameters are not listed (see Table 1). For pure B, only the phases mentioned in text are listed.
(a) Measured at the composition of B_4Li_5.

(below) have been observed. It has not been determined if these phases are related to each other, forming a continuous phase field, or if there are several stable compounds separated by two-phase fields.

B_6Li

[32And] prepared B_6Li by electrolysis. [50Kie] proposed the same formula, based on analogy with other alkali hexaborides, and [74Rup] confirmed its existence by X-ray analysis of a single crystal. The homogeneity range is unknown.

B_4Li

B_4Li, with cubic symmetry, was patented by [65Cas]. This compound was also found as a product in an anode made of B-Li mixture discharged in a LiCl-KCl eutectic melt [79Dev].

B_3Li

This stoichiometry was obtained in an alloy formed by a direct reaction of Li(L) and B(s) on heating between 300 and 450 °C [79Dal].

B_2Li

B_2Li is a high-pressure phase existing above 1400 °C [76Sch]. B_2Li was also found by [76Jam] in a B-Li alloy anode discharged in a LiCl-KCl eutectic melt. The composition of compounds found in alloys with 9 to 55 at.% Li was predominant at 32 at.% Li [62Sec1, 62Sec2], close to B_2Li.

BLi

[77Sor] claimed that BLi forms on heating by an exothermic reaction of the elements at ~360 °C.

B_4Li_5 or B_6Li_7

On the basis of X-ray and neutron diffraction data, [78Wan] determined the structure of B_4Li_5 (see "Crystal Structures and Lattice Parameters" section). Density, electrical resistivity, and Hall coefficient measurements on 40 to 100 at.% Li alloys [78Mit] indirectly supported the presence of B_4Li_5. On the other hand, B_6Li_7 stoichiometry was obtained by direct reaction of Li(L) and B(s) on heating between 480 and 650 °C [79Dal] and by the analysis of the anodic discharge behavior of B-Li alloys [79Dev]. In Tables 1 and 2, it is assumed that B_4Li_5 (55.6 at.% Li) is the same as B_6Li_7 (53.8 at.% Li).

BLi_3

Density studies by [78Mit] (see above) indicated the existence of BLi_3. However, thermal analysis of 50 to 90 at.% Li alloys did not reveal its presence [79Dal].

(βLi) and (αLi) Terminal Solid Solutions

The melting point of βLi and the βLi ↔ αLi allotropic transformation temperature are 180.6 °C [Melt] and −193 °C [Hultgren,E], respectively. No solubility of B in either form of Li is known.

Other Phases

[84Mai] synthesized $B_{14}Li_3$, $B_{19}Li_6$, and B_3Li in Mo-lined Nb ampules. The first two compounds have uncommon stoichiometries.

Crystal Structures and Lattice Parameters

Crystal structure and lattice parameter data for B-Li phases are given in Tables 1 and 2, respectively. Pure B may have as many as nine allotropic forms [Pearson3]. Only the data for the phases discussed above are listed.

The crystal structure and lattice parameters of $B_{12}Li$ are similar to those of metastable tetragonal B (Tables 1 and 2). Probably, $B_{12}Li$ is within the solid solubility range of metastable B. The structure of B_4Li_5 is rhombohedral, with a = 0.493 nm and α = 90.0°, but it is disordered in such a way that its long-range symmetry is bcc, with a = 0.493 nm [78Wan]. B_4Li_5 may be B_6Li_7 (see "Equilibrium Diagram").

Thermodynamics

Little information is available on the thermodynamic properties of the B-Li system. The enthalpy of formation of B_3Li at 320 to 450 °C and B_6Li_7 at 520 to 650 °C from Li(L) and B(s) are approximately −13.5 and −12.9 kJ/g-atom, respectively [79Dal].

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* Indicates key paper.

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The Cs-Li (Cesium-Lithium) System

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Equilibrium Diagram

The assessed Cs-Li phase diagram (Fig. 1) is a simple system that exhibits virtually complete immiscibility in both the liquid and solid states. At higher temperatures, the diagram is dominated by the vapor phase protruding from the Cs side.

The diagram is similar to the K-Li, Li-Na, and Li-Rb systems. The extent of immiscibility is expected to be the most pronounced in this system, because Li and Cs have the smallest and largest alkali-metal atomic diameters, respectively.

As reported by [Shunk] and [Hansen], the Cs-Li system has been investigated by [39Boh] (thermal analyses) and by [62Cue] (solubility measurements). More recently, density measurements of Cs in Li have been reported by [70Nov]. The crystal structures of the pure elements are listed in Table 1.

Table 2 lists data of [62Cue] for the solubility of Cs in Li corresponding to two experimental runs. Applying a regression analysis to the data, the following expression for the solubility of Cs in Li as a function of temperature, in K, can be calculated:

$$\log (\text{at.\% Cs}) = 4.43 - 6594/T \qquad \text{(Eq 1)}$$

A comparison of the measured and smoothed data is also given in Table 2.

[70Nov] reported density measurements in the range 25 to 1100 °C and calculated a solubility of 7.5 wt.% Cs (42.2 at.% Cs) in Li at 1100 °C. It is unlikely that solubility is extensive at this temperature. At 1100 °C, the vapor pressure of Cs is approximately 11.3 atm, and at 1 atm a Cs-Li liquid alloy with 42.2 at.% Cs would be unstable. [70Nov] did not report the total pressure.

In Fig. 1, the Li(L_2) portion of the phase diagram up to 1100 °C was taken from Eq 1. Transition temperatures were taken from [83Cha], [King1], and [King2]. The

Table 1 Cs-Li Crystal Structure and Lattice Parameter Data

Phase	Composition, at.% Li	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm a	c	Comment
(Cs)	0.00	*cI2*	$Im\bar{3}m$	*A2*	W	0.6141	...	25 °C
(αLi)	100.00	*hP2*	$P6_3/mmc$	*A3*	Mg	0.3111	0.5093	<75 K
(βLi)	100.00	*cI2*	$Im\bar{3}m$	*A2*	W	0.35093	...	25 °C