The Lesser-Known B-Ln (Boron-Lanthanide) Systems: B-Dy (Boron-Dysprosium), B-Ho (Boron-Holmium), B-Lu (Boron-Lutetium), B-Pr (Boron-Praseodymium), B-Tm (Boron-Thulium), and B-Yb (Boron-Ytterbium)

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Equilibrium Diagram

In a series of previous assessments, phase equilibria in the binary systems featuring B and several Ln elements have been reviewed. A common element of these reviews has been the paucity of experimental results on which the assessed diagrams were based. Experimental data for the seven B-Ln systems not assessed to date is scarcer still; as a result, a more general review of the available information for these systems is preferred to a formal assessment. The boride compounds of these seven elements are similar to those in other B-Ln systems [76Spe, 77Spe], and the estimated phase diagrams are also comparable with others previously described [96Lia1, 96Lia2, 96Lia3]. This review presents an update of information previously described by [76Spe, 77Spe], which the reader is encouraged to consult.

The B-Ln systems have several common features, likely shared by these six systems. These include (1) negligible solubility ranges in the terminal solid solutions, (2) complete miscibility in the liquid, and (3) a series of high-melting-point boride compounds, most with minimal solubility ranges. The boride compounds have a finite number of compositions, including:

- LnB_2: Stable AlB_2-type diborides have been reported for Sc, Y, and the lanthanide elements Gd through Lu [76Spe]. Five of the six elements discussed here fall into this category. DyB_2, HoB_2, LuB_2, TmB_2, and YbB_2 all decompose peritectically in favor of the tetraboride, with YbB_2 decomposing to Yb vapor rather than a lanthanide-rich liquid. None of the diborides have a significant composition range.
- Ln_2B_5: Compounds of this stoichiometry have been reported for Gd, Nd, and Sm [76Spe], but do not exist for heavier lanthanide elements. A lower boride of praseodymium produced by [72Fis] may have this stoichiometry, but this has not been confirmed.
- LnB_4: Stable tetraborides exist in all of the B-Ln systems with the exception of Eu [76Spe]. The tetraborides are highly stable, and become more so as the atomic number of the lanthanide element increases. PrB_4 decomposes peritectically in favor of the hexaboride, while DyB_4, HoB_4, LuB_4, and TmB_4 all apparently melt congruently [72Eto1]. The decomposition of YbB_4 to a Yb-rich vapor phase and the hexaboride is an anomaly (as is the Yb-B system in general). Lanthanide tetraborides may have a small solubility range [96Lia3], but this has not been measured in most cases.
- LnB_6: The CaB_6-type hexaborides are the best-known of the lanthanide boride compounds and exist in stable form for all but the heaviest lanthanide elements. They all have very high decomposition temperatures and a considerable solubility range in the B-rich direction. PrB_6 melts congruently, while DyB_6 and HoB_6 melt peritectically in favor of the tetraboride. YbB_6 decomposes to a Yb-rich vapor phase and a B-rich liquid. Stable Lu and Tm hexaborides do not exist [63Prz, 64Stu], although impurity-stabilized metastable compounds have been reported [68Mor].
- LnB_{12}: Stable UB_{12}-type dodecaborides have been reported for the heavier lanthanides, including DyB_{12}, HoB_{12}, LuB_{12}, TmB_{12}, and YbB_{12} [76Spe, 94Pad]. These compounds have a minimal solubility range and decompose peritectically, in favor of either the hexaboride (Dy, Ho, Yb) or the tetraboride (Lu, Tm). The results of [86Shi] again suggest that these compounds may have a nonnegligible solubility range, but this has otherwise not been confirmed.
- "LnB_{66}": YB_{66}-type hectoborides also exist only for the heavier lanthanide compounds, including Dy, Ho, Lu, Tm, and Yb [72Sch, 72Spe]. They may have a considerable solubility range, though these have never been accurately determined. All five hectoborides decompose peritectically in favor of the dodecaborides.

The high decomposition temperatures of the lanthanide boride compounds, as well as difficulty in preparing these compounds

Table 1 Reported Lanthanide Boride Decomposition/Melting Temperatures

Phase	Type of decomposition	Temperature, K	Reference
DyB_6	Peritectic	2473	[69Tim, 74Spe]
	Congruent melting	2573	[68Mor]
DyB_{66}	Peritectic	2298	[74Spe]
HoB_6	Congruent melting	2453	[68Mor]
LuB_6	Congruent melting	2443	[68Mor]
PrB_6	Congruent melting	2883	[68Mor]
YbB_6	Congruent melting	2643	[68Mor]

Table 2 Lanthanide Boride Crystal Structure Data

Phase	Composition, at.% B	Pearson symbol	Space group	Strukturbericht designation	Prototype	Elements forming compound
LnB_2	66.7	*hP*3	*P*6/*mmm*	*C*32	AlB_2	Dy, Ho, Lu, Tm, Yb
LnB_4	80	*tP*20	*P*4/*mbm*	$D1_e$	ThB_4	Dy, Ho, Lu, Pr, Tm, Yb
LnB_6	85.7 to 89.6	*cP*7	$Pm\bar{3}m$	$D2_1$	CaB_6	Dy, Ho, Pr, Yb
LnB_{12}	92.3	*cF*52	$Fm\bar{3}m$	$D2_f$	UB_{12}	Dy, Ho, Lu, Tm, Yb
LnB_{66}	80	*cF*1880	$Fm\bar{3}c$	…	ThB_{66}	Dy, Ho, Lu, Tm, Yb
Metastable Phase						
LnB_6	…	*cP*7	$Pm\bar{3}m$	$D2_1$	CaB_6	Lu, Tm

in a pure form, have made accurate determination of their decomposition or melting temperatures difficult. Table 1 lists the currently available experimental values for these temperatures; other than these, no reported liquidus temperatures have been found. The phase transformation temperatures of the lanthanide elements and B are listed in [Massalski2].

Metastable Phases

The Lu and Tm hexaborides reported by [68Mor] are apparently stable only when impurities, particularly C, are present. Other than these hexaborides, no metastable boride compounds of any of these six elements have been reported.

Crystal Structures and Lattice Parameters

The typical crystal structures of LnB_2, LnB_4, LnB_6, LnB_{12}, and LnB_{66} compounds are listed in Table 2. Insufficient data are available for the tentative "Pr_2B_5" phase reported by [72Fis] to include this phase in Table 2. Tables 3 to 7 list previously reported composition and room-temperature lattice parameter data for the stable boride compounds, categorized by compound stoichiometry. Determinations of coefficients of thermal expansion for these compounds include:

- HoB_4, LuB_4, and YbB_6, 273 to 1073 K [58Ste]
- HoB_{12}, 298 to 625 K [61LaP]
- DyB_{12}, HoB_{12}, LuB_{12}, TmB_{12}, and YbB_{12}, 78 to 1300 K [71Pad]
- PrB_6 and YbB_6, 298 to 1000 K [72Dut, 73Dut]
- DyB_4, HoB_4, PrB_4, and TmB_4, 298 to 1273 K [74Pad]
- DyB_{12}, HoB_{12}, LuB_{12}, TmB_{12}, and YbB_{12}, 77 to 1200 K [80Moi]

Thermodynamics

The available thermodynamic data for these six systems are limited to the solid boride compounds and are quite limited at that. Heat-capacity measurements have been reported for PrB_4 and LuB_{12} (low temperature) and for PrB_4 and PrB_6 (high temperature) [84Pad, 88Mur, 93Bol1, 93Bol2, 93Mur]. Experimental determinations of enthalpy of formation have been made at 1473 K for PrB_4 (–265.5 kJ/mol), PrB_6 (–569.1 kJ/mol), and for LuB_2 (–89.4 kJ/mol) [95Mes1, 95Mes2]. Using the experimentally obtained thermodynamic data for PrB_4 [93Bol2, 93Mur, 95Mes1], it is possible to derive expressions for the enthalpy and Gibbs energy of formation of the tetraboride. For the reaction αPr + 4 βB $\leftrightarrow$ PrB_4 (298 to 1068 K):

$$\Delta_f H^0 = -267\,083 + 21.311\,T - 12.623 \times 10^{-3}\,T^2 + 1\,063\,436/T \text{ J/mol}$$

$$\Delta_f G^0 = -267\,083 - 21.311\,T \ln T + 12.623 \times 10^{-3}\,T^2 + 575\,218/T + 118.17\,T \text{ J/mol}$$

For the reaction βPr + 4 βB – PrB_4 (1068 to 1204 K):

$$\Delta_f H^0 = -255\,782 + 0.293\,T - 1.208 \times 10^{-3}\,T^2 + 851\,916/T \text{ J/mol}$$

Table 3 Lanthanide Diboride Lattice Parameter Data

Phase	Composition, at.% B	Lattice parameters, nm *a*	*c*	Comment	Reference
DyB_2	66.7	0.3285	0.3835	…	[64Pos]
		0.3291	0.3847	Dy-saturated	[74Spe]
		0.3287	0.3847	B-saturated	[74Spe]
		0.3287	0.3845	…	[78Wil]
		0.32874	0.38393	…	[90Kle]
HoB_2	66.7	0.327	0.381	…	[64Pos]
		0.3281	0.3811	…	[73Bau]
		0.3279	0.3811	…	[77Can]
		0.3281	0.3813	…	[78Wil]
		0.32835	0.38186	…	[90Kle]
LuB_2	66.7	0.3246	0.3704	…	[63Prz]
		0.32442	0.37061	…	[90Kle]
TmB_2	66.7	0.3261	0.3755	…	[72Cas]
		0.3250	0.3739	…	[73Bau]
		0.3258	0.3745	…	[77Can]
		0.32573	0.37473	…	[90Kle]
YbB_2	66.7	0.3250	0.3731	…	[74Bau]

Table 4 Lanthanide Tetraboride Lattice Parameter Data

Phase	Composition, at.% B	Latttice parameters, nm *a*	*c*	Comment	Reference
PrB_4	80	0.720	0.411	…	[56Pos]
		0.7241	0.4119	…	[72Fis]
		0.7235	0.4116	…	[76Ber]
		0.7236	0.4119	…	[93Bol1, 93Mur]
DyB_4		0.7101	0.40174	…	[59Eic]
		0.7102	0.4017	…	[72Fis]
		0.70974	0.40166	Dy-saturated	[74Spe]
		0.70946	0.40174	B-saturated	[74Spe]
		0.7021	0.3972	…	[76Sch]
		0.7097	0.4016	…	[76Ber]
		0.7097	0.4016	…	[79Eto]
		0.70882	0.40207	…	[90Kle]
HoB_4	80	0.7064	0.4000	…	[58Ste]
		0.7086	0.40079	…	[59Eic]
		0.7087	0.4008	…	[72Fis]
		0.7085	0.4004	…	[79Eto]
		0.70753	0.40097	…	[90Kle]
LuB_4	80	0.6997	0.3938	…	[58Ste]
		0.716	0.4053	…	[58Nes]
		0.7036	0.3974	…	[72Fis]
		0.70384	0.39714	…	[90Kle]
TmB_4	80	0.705	0.399	…	[61Pad]
		0.7057	0.3987	…	[72Fis]
		0.70504	0.39851	…	[90Kle]
	79.3	0.70550	0.39870	…	[94Oka2]
YbB_4	80	0.701	0.400	…	[56Pos]
		0.7064	0.3989	…	[72Fis]
		0.7055	0.4004	…	[76Ber]
		0.70612	0.39893	…	[94Oka1]

Table 5 Lanthanide Hexaboride Lattice Parameter Data

Phase	Composition, at.% B	Lattice parameter (a), nm	Comment	Reference
(PrB_6)	85.7	0.4121	…	[32Sta]
		0.4129	…	[56Pos]
		0.412	…	[60Sam]
		0.4123	…	[63Sam]
		0.41316	…	[64Bli]
		0.4130	…	[67Shu]
		0.4129	…	[68Mor]
		0.4133	…	[70Lee]
		0.4131	…	[71Hac]
	85.7	0.41329	Pr-saturated	[71Yaj]
	89.7	0.41355	B-saturated	[71Yaj]
		0.4148	…	[72Dut]
(DyB_6)	85.7	0.41020	…	[59Eic]
		0.414	…	[58Nes]
		0.4097	…	[68Mor]
		0.4097	…	[68Tim]
		0.40969	Dy-saturated	[74Spe]
		0.41008	B-saturated	[74Spe]
(HoB_6)	85.7	0.413	…	[58Nes]
		0.4096	B-saturated	[59Eic]
		0.4098	…	[59Tvo]
		0.4091	Ho-saturated	[68Mor]
(LuB_6)	85.7	0.412	Metastable	[58Nes]
		0.4100	Metastable	[68Mor]
(TmB_6)	85.7	0.411	Metastable	[61Pad]
(YbB_6)	85.7	0.413	…	[32All]
		0.4140	…	[56Pos]
		0.4145	…	[58Ste]
		0.41468	…	[59Eic]
		0.4142	…	[68Mor]
		0.4124	…	[72Dut]
		0.4149	…	[80Tar]
		0.41474	…	[93Oka]
		0.4138	…	[61Zhu]

$$\Delta_f H^0 = -255\,782 + 0.293\,T - 1.208 \times 10^{-3}\,T^2 + 851\,916/T \text{ J/mol}$$

$$\Delta_f G^0 = -255\,782 - 0.293\,T \ln T + 1.208 \times 10^{-3}\,T^2 + 425\,958/T - 30.75\,T \text{ J/mol}$$

For the reaction Pr (L) + 4 βB – PrB_4 (1204 to 2300 K):

$$\Delta_f H^0 = -257\,229 - 4.228\,T - 1.208 \times 10^{-3}\,T^2 + 851\,916/T \text{ J/mol}$$

$$\Delta_f G^0 = -257\,229 + 4.228\,T \ln T + 1.208 \times 10^{-3}\,T^2 + 425\,958/T - 57.46\,T \text{ J/mol}$$

Measurements of high-temperature compound decomposition vapor pressures have been reported for PrB_6 and HoB_4 [75Ame], which presumably could be used to calculate Gibbs energies of formation. However, there is some doubt about the decomposition mechanism. [75Ame] claim that PrB_6 decomposes congruently at high temperatures to a stoichiometric mixture of Pr (G) and B (G):

$$PrB_6 \leftrightarrow Pr\ (G) + 6\ B\ (G)$$

Based on the measured vapor pressure, the enthalpy and entropy change for this reaction (3 488 900 J/mol and 927.8 J/mol · K at 2285 K, respectively) were determined. However, if the standard enthalpies and Gibbs energies of formation for Pr (G) and B (G) extrapolated from the tabulation of [82Pan] are applied to these calculated enthalpy and entropy of decomposition values, the standard enthalpy and Gibbs energy of formation from the elements at 2285 K of PrB_6 turn out to equal

Table 6 Lanthanide Dodecaboride Lattice Parameter Data

Phase	Composition, at.% B	Lattice parameter (a), nm	Comment	Reference
DyB_{12}	92.3	0.7501	…	[61Lap]
		0.7499	…	[71Pad]
		0.74989	…	[72Sch]
		0.74992	Dy-saturated	[74Spe]
		0.75001	B-saturated	[74Spe]
		0.75002	…	[91Pad]
HoB_{12}	92.3	0.7492	…	[61Lap]
		0.7491	…	[71Pad]
		0.74916	…	[91Pad]
(LuB_{12})	92.3	0.7464	…	[61Lap]
		0.7464	…	[71Pad]
		0.7464	…	[85Iga]
		0.74644	…	[91Pad]
	92.3	0.74631	Lu-saturated	[86Shi]
	92.8	0.74629	B-saturated	[86Shi]
TmB_{12}....................................	92.3	0.7476	…	[61Lap]
		0.7474	…	[71Pad]
		0.74760	…	[91Pad]
YbB_{12}	92.3	0.7469	…	[63Lap]
		0.7468	…	[71Odi, 71Pad]
		0.7469	…	[85Iga]
		0.7462	…	[64Smi]

Table 7 Lanthanide Hectoboride Lattice Parameter Data

Phase	Composition, at.% B	Lattice parameter (a), nm	Comment	Reference
(DyB_{66})..................................	98.5	2.3422	…	[72Spe]
		2.3466	Dy-saturated	[72Spe]
		2.3419	B-saturated	[72Spe]
		2.3441	…	[72Sch]
(HoB_{66})..................................	98.5	2.3441	B-saturated	[72Sch]
(LuB_{66})	98.5	2.3412	B-saturated	[72Sch]
(TmB_{66})	98.5	2.3433	B-saturated	[72Sch]
(YbB_{66})..................................	98.5	2.3422	B-saturated	[72Sch]
		2.3415	B-saturated	[72Spe]

+107 600 and +64 500 J/mol, respectively. Furthermore, the vaporization experiments reported by [72Eto2] and [79Gor] show that PrB_6 decomposes to Pr vapor and a B-rich liquid. As a result, the thermodynamic data for PrB_6 calculated by [75Ame] should be disregarded.

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*Indicates key paper.
#Indicates presence of a phase diagram.

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