Prediction of thermodynamically stable Li–B compounds at ambient pressure†

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To clarify controversial structures and phase stability in the Li–B system, we predicted energetically favorable compounds and crystal structures of the Li–B binary system at ambient pressure, mainly including Li6B5, LiB2, and LiB3, from ab initio evolutionary structure simulations and further investigated physical properties of stable Li–B compounds using first-principles methods. Metallic Li4B6, predicted in our simulations, has trigonal symmetry with space group R32 and contains linear B chains, but its superconducting Tc is low according to the electron–phonon coupling calculations. Orthorhombic LiB2 (Pnma) and tetragonal LiB3 (P4/mmb) are zero-gap semiconductors; LiB2 is a Dirac semimetal, and both LiB2 and LiB3 are promising thermoelectric materials.

Introduction

Atoms of light elements have simple electronic structures, but can form complex compounds possessing extraordinary properties. Boron is electron-deficient and boron-based compounds being likely to form multicenter bonds1–2 are often accompanied by complicated crystal structures and stoichiometries. After the discovery of high-Tc superconductivity in MgB2,3 borides of light metals have attracted much attention. Compounds of the lightest metals have attracted much attention. Compounds of the lightest metals have attracted much attention.

Many investigations have been carried out to explore possible compositions in the Li–B system, but only a few compounds are well characterized. Nesper et al. have confirmed tetragonal LiB14 (1A2d)4 and successfully prepared dark red transparent crystals of LiB14 (P4/mmb).5 Lithium borides close to the stoichiometric ratio 1:1 have been intensively studied. Wang et al. reported the preparation of LiB and claimed that the compound is Li5B4 with a rhombohedral crystal structure.6,7 Similar stoichiometries, e.g., LiB and Li1.06B8,9 were reported later. Liu et al. experimentally studied LiB10 by X-ray diffraction and found that the stoichiometric LiB has hexagonal symmetry with space group P63/mmc. Theoretical results from Rosner et al.11 showed that the electron–phonon coupling effect in hexagonal LiB is rather small. Recently, based on the X-ray and neutron powder diffraction data, Wörle and Nesper concluded that LiB (0.82 < x < 1.0) has an extraordinary crystal structure which contains linear carbyne-like boron chains with strong covalent bonds between boron atoms.12 However, more detailed structural information on this compound is still absent and the corresponding physical properties need to be studied systematically. Here we present a theoretical study of the Li–B system, clarifying stable compositions, crystal structures and physical properties of lithium borides by first-principles methods.

Computational details

The ab initio evolutionary structure prediction method as implemented in the USPEX (Universal Structure Predictor: Evolutionary Xtallography) code13,14 was employed to determine the energetically favorable compositions and structures in the Li–B system at ambient pressure. USPEX has been widely used to predict the lowest-enthalpy structures without any experimental data.13–16 Especially, besides the traditional fixed-composition search (FCS), the recently developed variable-composition search (VCS) in the USPEX code17,18 allows one to predict stable stoichiometries. Structure relaxations and total energy calculations were performed...
within density functional theory as implemented in the Vienna Ab Initio Simulation Package (VASP). The projector augmented wave (PAW) method was used to describe the interaction between electrons and cores, and the generalized gradient approximation functional of Perdew, Burke, and Ernzerhof was used to treat the exchange–correlation energy. In the PAW potentials, electronic configurations $1s^22s^1$ and $2s^22p^1$ were treated as valence for Li and B, respectively. A cutoff energy of 540 eV for plane wave basis sets and dense $\Gamma$-centered $k$-point meshes with a reciprocal-space resolution of $2\pi \times 0.03 \text{ Å}^{-1}$ were used for all the structures to ensure sufficient convergence of the energy, forces and stress tensor. For the predicted stable crystal structures, the GW approximation was used for obtaining more accurate electronic structures.

Lattice dynamics were calculated using the frozen phonon method as implemented in the Phonopy package. Force constant matrices were determined using the $2 \times 2 \times 2$, $2 \times 2 \times 2$, and $2 \times 2 \times 3$ supercells for LiB$_2$, LiB$_3$, and LiB$_5$, respectively. In addition, to investigate the possibility of superconducting state in LiB$_5$, electron–phonon coupling (EPC) calculations were carried out using density-functional perturbation theory, as implemented in the Quantum Espresso (QE) package. For self-consistent calculations in QE, Vanderbilt-type ultrasoft pseudopotentials with a kinetic cutoff energy of 180 Ry for wave functions and a $16 \times 16 \times 16$ MP $k$-point grid with a Gaussian smearing of 0.05 Ry were used, together with a $6 \times 6 \times 6$ $q$-mesh, which ensures that the electron–phonon matrix elements are well converged.

Thermoelectric properties of Li–B compounds were calculated using Boltztrap, within semi-classical Boltzmann theory and the rigid-band approximation. The thermoelectric figure of merit $ZT$ is

$$ZT = \frac{S^2\sigma T}{k}$$

where $\kappa$ is the total thermal conductivity ($\kappa = \kappa_L + \kappa_E$, with $\kappa_L$ and $\kappa_E$ being the lattice thermal conductivity and electronic thermal conductivity, respectively). In this work, instead of $ZT$, we computed the parameter $S^2\sigma$, known as the power factor.

### Results and discussion

#### Stable Li–B compounds at ambient pressure

Stability of compounds in multicomponent systems can be evaluated from the thermodynamic convex hull construction. The calculated convex hull of the Li–B system at ambient pressure is mainly built from the results of VCS using USPEX. At a few selected chemical compositions, the structures of assumed lithium borides were also predicted using the FCS method. In addition, we also calculated the enthalpies of formation of some Li–B compounds like LiB, LiB$_2$, LiB$_3$, LiB$_4$, Na$_2$B$_{20}$-type, Na$_2$B$_{25}$-type, and NaB$_{15}$-type structures based on previous theoretical or experimental structural data and compiled them in Fig. 1. In the VCS and FCS, the ambient-pressure phases of Li and B, with space groups $Im\overline{3}m$ and $R\bar{3}m$, respectively, can be reproduced readily. It can be found from Fig. 1 that besides the experimentally determined Li$_6$B$_5$, three newly found phases can coexist with solid Li and B in the ground state. Their optimized lattice parameters are listed in Table 1. Especially, stoichiometric LiB based on the previous structure models is always metastable and lies above the tie line joining Li$_6$B$_5$ and LiB$_2$, which is consistent with the computational study by Kolmogorov and Curtarolo and clearly indicates that stoichiometric LiB is less stable than nonstoichiometric LiB ($0.8 \leq \chi \leq 1$). The recent high-pressure synchrotron powder data combined with first-principles calculations also confirmed that LiB remains metastable at ambient pressure, which is in agreement with our prediction. Moreover, high pressure above 20 GPa can drive the occurrence of the transition from non-stoichiometric LiB$_{y}$ (down to $y = 0.75$) to 2D-layered stoichiometric LiB. However, it must be pointed out that high-pressure stabilization of Li–B compounds is beyond the scope of current work. Crystal structures of Li$_6$B$_5$, LiB$_2$, and LiB$_3$ are shown in Fig. 2. Their detailed physical properties are discussed in the following sections. Structural data of some

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice parameters (Å, deg.)</th>
<th>Atomic position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_6$B$_5$ (R32)</td>
<td>$a = 4.778$, $a = 92.2$</td>
<td>Li: 3d</td>
<td>x: 0.0000, y: 0.6676, z: 0.3324</td>
</tr>
<tr>
<td>LiB$_2$ (Pnma)</td>
<td>$a = 6.160$, $b = 4.452$, $c = 7.133$</td>
<td>Li: 4c, 4b</td>
<td>x: 0.4076, y: 0.2500, z: 0.0511, 0.2080, 0.7500, 0.1818</td>
</tr>
<tr>
<td>LiB$_3$ (P4/mmb)</td>
<td>$a = 5.978$, $c = 4.158$</td>
<td>Li: 4g, 4b</td>
<td>x: 0.3164, y: 0.8164, 0.0000, 0.0000, 0.2061</td>
</tr>
</tbody>
</table>

Fig. 1: Enthalpies of formation ($\Delta H$, in meV per atom) with respect to bcc Li and LiB$_2$ ($R\bar{3}m$) for the Li–B system at ambient pressure.
low-energy metastable phases found in our simulations are listed in ESL.†

**Li$_6$B$_5$: a metallic phase containing carbyne-like boron chains**

Li$_6$B$_5$ in our electronic structure search has a trigonal structure with space group R32. In the R32 structure as shown in Fig. 2a, B atoms occupy the 1b and 2c atomic sites and form the linear boron chains which are encapsulated in the channels formed by Li atoms. It must be pointed out that trigonal Li$_6$B$_5$ is consistent with the structure described by Wörle and Nesper for LiB$_0$ (0.82 < x < 1.0).11 B–B, Li–B, and Li–Li distances and mass densities of Li$_6$B$_5$, along with metastable phases Li$_6$B$_4$ (Immm), Li$_6$B$_3$ (Cc), and LiB (P6$_3$/mmc) also predicted from our FCS simulations, are listed in Table 2. It can be found that the calculated values of Li$_6$B$_5$ are in good agreement with the experimental data for the nonstoichiometric LiB.10

Now we can give our interpretation of the initially mysterious facts – (1) non-stoichiometric formula LiB$_{1-x}$, and its precise composition, (2) incommensurability and (3) metallicity of this phase. The structure, when viewed along the threefold axis, can be described as consisting of straight –B–B– and –Li–Li– chains in a 1 : 2 ratio. If B–B and Li–Li distances were the same, the stoichiometry would be Li$_2$B. However, the sizes of Li and B are very different – their atomic radii are in a Li : B = 1.85 ratio, which would bring the “ideal” ratio of Li and B atoms to 2.0/1.85 = 1.08 (corresponding to stoichiometry Li$_{1.08}$B = Li$_{0.92}$B$_{1.32}$). This composition, with extra lithium atoms compared to the ideal Zintl–Klemm compound LiB, should be metallic. In metals, all ionic interactions (repulsive between Li$^+$ particles) are very efficiently screened, enabling Li atoms to come closer (2.649 Å in Li$_6$B$_5$, compared with 2.785 Å in LiB – see Table 2) and making the composition even more Li-rich and increasing the density of the compound. Incommensurability of the structure and disorder in the vertical position of B-chains are direct consequences of these factors and are reflected in the existence of essentially degenerate structures of Li$_6$B$_5$: R3, P31m, C2/m. Our R32-Li$_6$B$_5$ phase is the best small-cell approximate of the real incommensurate LiB$_{1-x}$ compound.

Fig. 3 presents the calculated electronic band structure and density of states (DOS) of the R32 phase of Li$_6$B$_5$. Two bands marked in Fig. 3 cross the Fermi energy level (EF), indicating metallic character of this phase. The total DOS at EF is about 1.71 states per eV per f.u., which is mainly contributed by B-2p states. Fig. 3b shows the calculated electron localization function (ELF) of R32-Li$_6$B$_5$. The maximum value of ELF between B atoms is about 0.9, indicating strong covalent bonds between B atoms in the linear boron chain. At the same time, there is no ELF peak between the linear B chain and Li atoms, suggesting no covalent bonding between them.

Fig. 4 shows the calculated phonon dispersion curves, phonon DOS, and Eliashberg spectral function $\tilde{\chi}^2F(\omega)$ of Li$_6$B$_5$. Two phonon bands between 15.8 and 35.7 THz can be assigned to the bending vibrations of the linear B chain. The highest-frequency bands above 35.7 THz are ascribed to the symmetric and antisymmetric stretching vibrations of B atoms. The integral of the EPC parameter $\tilde{\chi}(\omega)$ is only about 0.21. Vibrations below 16.5 THz contribute about 65.9% of the total $\tilde{\chi}$ value. The contribution from the bending vibrations of the B chain is negligible.

### Table 2

<table>
<thead>
<tr>
<th>Phase</th>
<th>Li–B distances (Å)</th>
<th>Li–B densities (ρ) (g cm$^{-3}$)</th>
</tr>
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<tbody>
<tr>
<td>Li$_6$B$_5$</td>
<td>1.589–1.590</td>
<td>1.559</td>
</tr>
<tr>
<td>LiB$<em>{0.92}$B$</em>{1.32}$</td>
<td>2.649–2.658</td>
<td>2.785–3.118</td>
</tr>
<tr>
<td>Li$_6$B$_3$</td>
<td>2.301–2.314</td>
<td>2.436</td>
</tr>
<tr>
<td>Li$_6$B$_4$</td>
<td>1.46</td>
<td>1.25</td>
</tr>
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</table>

*Note: Values in parentheses indicate experimental data.*
The stretching vibrations between B atoms above 35.7 THz contribute about 34.1% of the total $\lambda$. The calculated logarithmic average frequency $\omega_{\text{log}}$ is about 325.6 K. The corresponding critical superconductivity temperature $T_c$, obtained from the Allen–Dynes equation using commonly accepted Coulomb pseudopotential $\mu^* = 0.10$, is only about 0.32 K. This value of $T_c$ is somewhat lower than that of the pure metallic Li ($<1.3$ K).

**LiB$_2$: a new stable phase with distinctive band structure**

The crystal structure of LiB$_2$ predicted from our evolutionary simulations has orthorhombic symmetry with space group $Pnma$. B atoms form edge-sharing pentagonal pyramids connected into a network, and Li atoms are located in its tunnels. It must be pointed that the crystal structure of LiB$_2$ is very similar to that of MgB$_4$ which has the same symmetry (space group $Pnma$). The most significant structural difference between LiB$_2$ and MgB$_4$ is that there are twice as many Li ions in the tunnels of the boron framework in LiB$_2$ as Mg atoms in MgB$_4$. This relationship is easily understood, considering their chemical formulas as $(\text{Li}^+)_2\text{B}_4$ vs. $(\text{Mg}^{2+})\text{B}_4$.

Fig. 5 shows the calculated band structure of $Pnma$-LiB$_2$. There is a crossing of valence and conduction bands at one point in the $\Gamma$–$Z$ line, which is also confirmed by the GW quasiparticle calculation. The density of states at $E_F$ is zero, and here we have a pair of touching Dirac cones, which means that $Pnma$-LiB$_2$ is a Dirac semimetal. A similar behavior appears in the band structure of graphene and theoretically predicted 2D layered $Pmmn$-boron. The 3D structure of $Pnma$-LiB$_2$ allows it to hold Dirac quasiparticles in the bulk and this feature can lead to many exciting physical properties, such as extraordinary transport behavior.

We further evaluated the thermoelectric properties of LiB$_2$ based on the semi-classical Boltzmann theory. Fig. 6a shows the carrier concentration as a function of chemical potential at 300 K. Fig. 6b shows the calculated Seebeck coefficient ($S$) as a function of temperature at different chemical potentials ($\mu$). The $S$ of undoped LiB$_2$ is only 56.68 $\mu$V K$^{-1}$, but the thermoelectric properties change with the doping level. For n-type doping, the thermopower increases dramatically as the chemical potential of the electron increases, and can reach $S = 95$ $\mu$V K$^{-1}$ at $\mu = 0.30$ eV.
-160.72 μV K⁻¹ at μ = 0.004 eV at 300 K. For p-type doping, the thermopower increases to about 157.85 μV K⁻¹ at μ = -0.002 eV at 300 K. The calculated power factor $S^2 \sigma / \tau$ of LiB₂ is depicted in Fig. 6c. Both n-type and p-type doping can increase the power factor. For p-type doping, the maximum value of $S^2 \sigma / \tau$ occurs at μ = 0.038 eV, and for n-type doping the maximum value of the power factor is 1.94 x 10¹¹ W m⁻¹ K⁻² s⁻¹ at μ = -0.019 eV.

Fig. 7 shows the calculated phonon dispersion curves along the high-symmetry directions in the Brillouin zone and projected phonon DOS for Pnma-LiB₂. Low-frequency vibrations below 20 THz mainly come from Li atoms, but coupled Li–B translational motions are also not negligible. In the higher-frequency region between 20 and 28 THz, the phonon spectrum is mainly due to the librational motions of B atoms. The flat bands at around 32 THz can be assigned to the stretching vibrations of B atoms.

LiB₃: a semimetal with a high thermoelectric power factor

LiB₃ found in our simulations has a tetragonal structure with space group P4/mmb. As shown in Fig. 2c, B atoms form B₆-octahedra linked into a network, with Li atoms occupying the channels in it. In fact, this structure is identical to the crystal structure of LiB₃ reported by Nesper.⁵

Fig. 8 presents the calculated electronic band structure and DOS of the P4/mmb phase of LiB₃. Like LiB₂, it is a zero-gap semimetal. The valence and conduction bands touch at the Z point and form massive (e.g., non-massless) Dirac cones. The bands near $E_F$ are more dispersive than in LiB₂, which results in a smaller carrier concentration, disadvantageous for thermoelectric properties. However, there is a section of flat valence bands along the Γ–Z path very close to the Fermi level. This may be favorable for thermopower after doping.

From Fig. 9a, we can see that for increasing carrier concentration, n-type doping is more efficient than p-type doping for LiB₃, because of the flat band along the Γ–Z direction in LiB₃. The calculated $S$ as a function of temperature at different chemical potentials depicted in Fig. 9b shows that pure LiB₃ has a negligible thermopower and is insensitive to the change of temperature.

Under room temperature, the p-type doping can increase the thermopower up to ~89.21 μV K⁻¹ at μ = 0.006 eV. Especially, minor n-type doping has a good effect on the thermopower.
At room temperature, the maximum value of $S$ is 86.86 $\mu$V K$^{-1}$ at $\mu = -0.007$ eV, but when the chemical potential $\mu$ is increased a little further, $S$ starts to go up with increasing temperature. The value of $S$ reaches 141.37 $\mu$V K$^{-1}$ at 800 K when $\mu = -0.022$ eV. As shown in Fig. 9c, the change in the power factor $S^2\sigma/\tau$ with the chemical potential of LiB$_3$ is obviously different from that of LiB$_2$ (see Fig. 6c). The value of $S^2\sigma/\tau$ reaches $3.69 \times 10^{11}$ W m$^{-1}$ K$^{-2}$ s$^{-1}$ when $\mu$ is $-0.035$ eV for n-type doping, which is 7 times higher than the maximum value for p-type doping ($0.51 \times 10^{11}$ W m$^{-1}$ K$^{-2}$ s$^{-1}$) at $\mu = 0.109$ eV. The traditional thermoelectric material Bi$_2$S$_3$ has an obviously larger maximum $S$ of 300 $\mu$V K$^{-1}$, and it also has larger $S^2\sigma/\tau$ of $1.2 \times 10^{12}$ W m$^{-1}$ K$^{-2}$ s$^{-1}$. However, the calculated power factor of LiB$_3$ is comparable to the value of another environment-friendly thermoelectric material, Sn doped Mg$_2$Si ($0.87 \times 10^{11}$–$5.2 \times 10^{11}$ W m$^{-1}$ K$^{-2}$ s$^{-1}$). As a result, although LiB$_3$ has a smaller $\mu$ than LiB$_2$, the higher value of $S^2\sigma/\tau$ resulting from minor n-type doping makes LiB$_3$ a more promising thermoelectric material than LiB$_2$.

Fig. 10 shows the calculated phonon dispersion curves and phonon density of states (PDOS) projected on Li and B atoms for the P4/mmb structure of LiB$_3$ at ambient pressure.

**Conclusion**

From the global ab initio evolutionary search for stable compounds and crystal structures, we built the complete thermodynamic convex hull for the Li–B binary system at ambient pressure, and determined the crystal structures of stable Li–B compounds including Li$_6$B$_5$, LiB$_3$, and LiB$_2$. Li$_6$B$_5$, the first structure found in our work has space group R32, and this metallic phase contains the characteristic linear B chains surrounded by Li atoms. Our electron–phonon coupling calculations indicate that Li$_6$B$_5$ cannot be a good superconductor. The predicted orthorhombic LiB$_2$ (Pnma) and tetragonal LiB$_3$ (P4/mmb) are semimetals, with promising thermoelectric properties (especially LiB$_3$). In addition, LiB$_2$ is a 3D-solid with massless Dirac fermions.

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