Structural Behavior of Li₂B₁₀H₁₀

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Supporting Information

ABSTRACT: On the basis of X-ray and neutron powder diffraction, first-principles calculations, and neutron vibrational spectroscopy, $\text{Li}_2\text{B}_{10}\text{H}_{10}$ was found to exhibit atypical hexagonal symmetry to best stabilize the ionic packing of the relatively small Li^+ cations and large ellipsoidal $\text{B}_{10}\text{H}_{10}^{2-}$ anions. Moreover, differential scanning calorimetry and neutron-elastic-scattering fixed-window scans suggested that $\text{Li}_2\text{B}_{10}\text{H}_{10}$, similar to its polyhedral cousin $\text{Li}_2\text{B}_{12}\text{H}_{12}$, undergoes an order–disorder phase transition near 640 K. These results provide valuable structural information pertinent to understanding the potential role that $\text{Li}_2\text{B}_{10}\text{H}_{10}$ plays during LiBH_4 dehydrogenation–rehydrogenation as well as its prospects as a superionic Li^+ cation conductor.

■ INTRODUCTION

Polyhedral boron-hydrogen compounds containing the relatively stable decahydro-closo-decaborate $(B_{10}H_{10}^{2-})$ and dodecahydro-closo-dodecaborate $(B_{12}H_{12}^{2-})$ anions have been studied more intensely in recent years because of their possible formation and persistence as side-products during the dehydrogenation of tetrahydroborate-based hydrogen-storage materials,¹⁻¹¹ as well as for their own potential as host materials for ammonia and indirect hydrogen storage.¹²⁻¹⁵ Of particular interest are the lighter alkali- and alkaline-earth-metal congeners containing Li, Na, Mg, and Ca because the incorporation of these elements yields storage materials with larger hydrogen mass fractions. More recently, polyhedral boron-hydrogen compounds of Na and potentially Li have also shown great promise as superionic electrolytes for next-generation, solid-state rechargeable batteries.^{16–20} $Na_2B_{10}H_{10}$ is noteworthy for displaying an exceptional conductivity of about 0.01 S cm⁻¹ at 383 K.²⁰ The high conductivities for these types of compounds are made possible in part because of the spacious cation diffusion corridors that exist within the sublattice of overly large, quasispherical anions.

The crystal structures of all alkali-metal dodecahydro-*closo*dodecaborates are now known.^{3,16,17,21–25} In contrast, although the alkali-metal decahydro-*closo*-decaborates of Na, K, and Rb have been found to possess structures with monoclinic symmetry,²⁶ the crystal structures of the remaining heavier Cs and lighter Li congeners have not yet been determined. The latter $Li_2B_{10}H_{10}$ is of particular importance because it is directly associated with LiBH₄, one of the most widely studied borohydrides for hydrogen storage. It is important to know the structural behavior of this polyhedral salt in order to develop a



more complete thermodynamic picture of the potential LiBH₄ decomposition–recomposition pathways. In addition, as shown recently for Na₂B₁₀H₁₀,²⁰ such information is also desirable for evaluating its potential as a superionic conductor material.

Here, we report the structure of $Li_2B_{10}H_{10}$ based on Rietveld structural analyses of X-ray powder diffraction (XRPD) and neutron powder diffraction (NPD) data combined with first-principles calculations and corroborated by neutron vibrational spectroscopy. Moreover, on the basis of differential scanning calorimetry (DSC) and neutron-elastic-scattering fixed-window scans, we suggest that a second, high-temperature structure forms.

EXPERIMENTAL DETAILS

Aqueous lithium decahydro-*closo*-decaborate $(Li_2B_{10}H_{10})$ was formed by first preparing $(H_3O)_2B_{10}H_{10}$ from $B_{10}H_{14}$ (Sigma-Aldrich²⁷) and triethylamine by a procedure described in detail elsewhere,²⁰ then neutralizing the $(H_3O)_2B_{10}H_{10}$ with 0.1 M LiOH until pH 7 was reached. Finally, anhydrous $Li_2B_{10}H_{10}$ was obtained using a rotary evaporator at 323 K to form a hydrated solid followed by complete dehydration under vacuum at 433 K for 16 h. The isolated yield of $Li_2B_{10}H_{10}$ was 74% based on the starting amount of $B_{10}H_{14}$. For neutron inelastic scattering measurements, isotope-enriched $^7Li_2{}^{11}B_{10}H_{10}$ was prepared in a similar fashion starting from ${}^{11}B_{10}H_{14}$ (Katchem) and later substituting 7LiOH (Cambridge Isotope Laboratories, 99.9+ % 7Li) for LiOH in the cation-exchange step. (N.B., both ⁶Li and ¹⁰B present in natural Li and B are strong neutron absorbers.)

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A portion of this material was further modified by exchange of H with D to form a ⁷Li₂¹¹B₁₀D₁₀ sample for NPD measurements. (N.B., H has a very large incoherent neutron scattering cross section which leads to an undesirably high NPD background.) This was accomplished by four sequential exchange treatments adapted from Muetterties et al.,²⁸ each one comprised of the dissolution and stirring for several or more days of 1 g of ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}(\text{H}_{x}\text{D}_{1-x})_{10}$ in 25 mL of D₂O (Cambridge Isotope Laboratories, 99.9% D) slightly acidified by adding approximately 50 μ L of a saturated solution of deuterochloric (DCl) acid in D_2O . The final dried sample was fully deuterated (>99%) as verified from model refinement of the NPD pattern at 7 K. Moreover, this was corroborated by the neutron vibrational spectrum at 4 K, which was absent of any anomalous H-related perturbations to the expected phonon density of states of otherwise isotopically pure ${}^{7}\text{Li}{}^{11}\text{B}_{10}\text{D}_{10}$.

Li₂B₁₀H₁₀ was first structurally characterized by XRPD using a Rigaku Ultima III X-ray diffractometer with a Cu K α source $(\lambda = 1.5418 \text{ Å})$. Differential scanning calorimetry measurements were made with a Netzsch (STA 449 F1 Jupiter) thermogravimetric analysis DSC instrument under He flow with Al sample pans. Neutron scattering measurements were performed at the National Institute of Standards and Technology Center for Neutron Research. NPD patterns for ⁷Li₂¹¹B₁₀D₁₀ were measured on the BT-1 High-Resolution Powder Diffractometer²⁹ at 7 and 295 K using the Cu(311) monochromator ($\lambda = 1.5398(2)$ Å). Horizontal divergences of 60', 20', and 7' of arc were used for the in-pile, monochromatic-beam, and diffracted-beam collimators, respectively. The sample was contained in a 6 mm diameter V can inside a He closed-cycle refrigerator. Neutron vibrational spectroscopy (NVS) measurements of both 7Li211B10H10 and 7Li211B10D10 at 4 K were performed on the Filter-Analyzer Neutron Spectrometer (FANS)³⁰ using the Cu(220) monochromator with pre- and post-collimations of 20' of arc, yielding a full-width-at-half-maximum (fwhm) energy resolution of about 3% of the neutron energy transfer. Neutronelastic-scattering fixed-window scans for ⁷Li₂¹¹B₁₀H₁₀ were measured between 250 and 680 K at 0.25 K min⁻¹ on the High-Flux Backscattering Spectrometer (HFBS)³¹ using 6.27 Å wavelength neutrons, with a resolution of 0.8 μ eV fwhm. All neutron data were analyzed using the DAVE software package.³⁷

To assist the structural refinements, first-principles calculations were performed within the plane-wave implementation of the generalized gradient approximation to density functional theory (DFT) using a Vanderbilt-type ultrasoft potential with Perdew–Burke–Ernzerhof exchange correlation.³³ A cutoff energy of 544 eV and a $2 \times 2 \times 1$ k-point mesh (generated using the Monkhorst–Pack scheme) were used and found to be sufficient for the total energy to converge within 0.01 meV/atom. For comparison with the NVS measurements, the phonon densities of states (PDOSs) were calculated from the DFT-optimized structure using the supercell method ($2 \times 2 \times 1$ cell size) with finite displacements^{34,35} and were appropriately weighted to take into account the H, D, ⁷Li, and ¹¹B total neutron scattering cross sections.

All structural depictions were made using the VESTA (Visualization for Electronic and STructural Analysis) software.³⁶ For all figures, standard uncertainties are commensurate with the observed scatter in the data, if not explicitly designated by vertical error bars.

RESULTS AND DISCUSSION

The XRPD pattern of $Li_2B_{10}H_{10}$ was indexed to a hexagonal structure with lattice parameters of approximately a = 7.037 Å



Figure 1. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) XRPD profiles for $\text{Li}_2\text{B}_{10}\text{H}_{10}$ at room temperature (Cu K α radiation). Vertical bars indicate the calculated positions of the Bragg peaks. $R_{wp} = 0.0948$, Rp = 0.0862, $\chi^2 = 1.480$.



Figure 2. Experimental (circles), fitted (line), and difference (line below observed and calculated patterns) NPD profiles ($\lambda = 1.5398(2)$ Å) for ⁷Li₂¹¹B₁₀D₁₀ at (bottom panel) 7 K ($R_{wp} = 0.0406$, Rp = 0.0331, $\chi^2 = 1.121$) and (top panel) 295 K ($R_{wp} = 0.0427$, Rp = 0.0356, $\chi^2 = 1.177$). Vertical bars indicate the calculated positions of the Bragg peaks.

and c = 14.922 Å. Assessment of the extinction symbol associated with the space group of the new phase indicated the most probable to be $P6_422$ (no. 181). The crystal structure was

$Li_2B_{10}H_{10}$			T = 295 K	XRPD (Cu K α) (λ = 1.5418 Å)			
a = 7.042(1) Å	c = 1	4.931(2) Å	<i>V</i> = 64	1.3(3) Å ³	Z = 6		
atom	site	x	у	z	$U_{\rm iso}$ (Å ²)	Occ.	
Lil	6f	1/2	1/2	0.428(1)	0.0574	1	
B1	6 <i>i</i>	0.6969(8)	0.3484(8)	1/3	0.0215	1	
B2	12k	0.8720(8)	0.6070(4)	0.3680(4)	0.0215	1	
B3	12k	0.8844(8)	0.369(1)	0.4109(4)	0.0215	1	
H1	6 <i>i</i>	0.500(1)	0.250(1)	1/3	0.0215	1	
H2	12k	0.811(2)	0.724(1) 0.4006(8)		0.0215	1	
H3	12k	0.817(2)	0.265(2)	0.4788(5)	0.0215	1	
$^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{1}$	10		T = 295 K		NPD Cu(311) ($\lambda = 1.5398(2)$ Å)		
a = 7.0363(2) Å	c = 1	4.9154(6) Å	V = 639.	52(4) Å ³	Z = 6		
atom	site	x	у	z	$U_{\rm iso}~({ m \AA}^2)$	Occ.	
Li1	6f	1/2	1/2	0.422(1)	0.042(4)	1	
B1	6 <i>i</i>	0.6960(4)	0.3480(2)	1/3	0.0207(4)	1	
B2	12k	0.8760(3)	0.6081(3)	0.3662(2)	0.0207(4)	1	
B3	12k	0.8777(3)	0.3693(3)	0.4136(1)	0.0207(4)	1	
D1	6 <i>i</i>	0.4998(7)	0.2499(4)	1/3	0.0373(6)	1	
D2	12k	0.8193(6)	0.7314(6)	0.3960(3)	0.0373(6)	1	
D3	12k	0.8071(6)	0.2701(6)	0.4824(2)	0.0373(6)	1	
$^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$			T = 7 K	NPD Cu(311) ($\lambda = 1.5398(2)$ Å)			
a = 7.0119(1) Å	c = 1	c = 14.8008(5) Å		21(3) Å ³	Z = 6		
atom	site	x	у	z	U_{iso} (Å ²)	Occ.	
Li1	6f	1/2	1/2	0.4249(6)	0.010(2)	1	
B1	<i>6i</i>	0.6968(3)	0.3484(2)	1/3	0.0082(2)	1	
B2	12k	0.8756(3)	0.6084(3)	0.3666(1)	0.0082(2)	1	
B3	12k	0.8774(2)	0.3683(2)	0.4145(1)	0.0082(2)	1	
D1	6i	0.4999(5)	0.2500(3)	1/3	0.0190(3)	1	
D2	12k	0.8187(4)	0.7324(4)	0.3968(2)	0.0190(3)	1	
D3	12k	0.8062(4)	0.2682(4)	0.4836(2)	0.0190(3)	1	
^{<i>a</i>} For each, the anion cen	ter of mass is loc	ated at 3c (1/2, 0, 0).					

then partially solved using direct space methods under this space group. First-principles DFT calculations were then performed to optimize the $B_{10}H_{10}^{2-}$ configuration, particularly the H positions. Rietveld structural refinement³⁷ on the DFT-relaxed structural model was performed using the GSAS package³⁸ on the XRPD data. The $B_{10}H_{10}^{2-}$ was kept as a rigid body. The $B_{10}H_{10}^{2-}$ rigid body together with Li atom coordinates and lattice parameters were refined, yielding the agreement factors of $R_{\rm wp} = 0.0948$, Rp = 0.0862, and $\chi^2 = 1.480$. The Rietveld fit to the XRPD pattern is shown in Figure 1. Refined lattice parameters of Li₂B₁₀H₁₀ are a = 7.042(1) Å and c = 14.931(2) Å. Crystallographic details can be found in Table 1 and in the CIF file in the Supporting Information.

Additional structural measurements were performed by NPD on the ⁷Li₂¹¹B₁₀D₁₀ sample at 7 and 295 K. The ⁷Li₂¹¹B₁₀D₁₀ crystal structure was successfully refined from the NPD data based on the XRPD-derived Li₂B₁₀H₁₀ structural model. No phase transition was observed in the measured temperature range. All the atomic coordinates of ⁷Li, ¹¹B, and D were refined freely without any restraints or rigid bodies. The thermal factors of like atoms were constrained to be the same. The Rietveld fits to the NPD patterns are shown in Figure 2. Refined lattice parameters of ⁷Li₂¹¹B₁₀D₁₀ are a = 7.0119(1) Å and c = 14.8008(5) Å at 7 K and a = 7.0363(2) Å and c = 14.9154(6) Å at 295 K. As expected, the lattice parameters for ⁷Li₂¹¹B₁₀D₁₀ are slightly smaller (by $\approx 0.1\%$) than those for Li₂B₁₀H₁₀. Again, crystallographic details can be found in Table 1 and in the CIF files in the Supporting Information.

The $Li_2B_{10}H_{10}$ crystal structure is shown in Figure 3. The $B_{10}H_{10}^{2-}$ anions are packed in a nominally hexagonal-closepacked fashion, with the anions in each ab plane identically orientationally aligned with their apical axes lying within the plane. In each successive ab plane, the apical axes are rotated 120° with respect to the previous plane. Li⁺ cations are situated in trigonal planar interstitial positions defined by three anions from two neighboring ab planes. Figure 4 depicts the trigonal planar coordination in more detail, using the 7 K NPD results for ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$. Each cation is coordinated most closely to two D atoms from each of the three surrounding anions, with three different Li-D distances of 2.028, 2.044, and 2.216 Å. The distances between the cations and anion centers of mass are 3.578 and 3.759 Å. Moreover, Figure 5 shows that each anion is coordinated to six near-neighbor cations, with the two apical D atoms each associated with two cations and the remaining eight equatorial D atoms each associated with one cation.

It is of interest to compare the cation–anion coordinations and Li–D distances with those in $Pa\overline{3}$ -symmetric Li₂B₁₂H₁₂.³ The latter possesses similar near-trigonal-planar coordination for Li⁺ and two near-neighbor H atoms from each of the three surrounding anions, but with two different Li–H distances of 2.077 and 2.216 Å. In addition, each anion is likewise coordinated to six near-neighbor cations, but each of the twelve H atoms are associated with only one cation. Coordination similarities reflect the similarities in the sizes and shapes of the B₁₀H₁₀^{2–} and B₁₂H₁₂^{2–} anions, whereas some difference in geometric

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Figure 3. Crystal structure of $Li_2B_{10}H_{10}$. Red, green, and white spheres denote Li, B, and H atoms, respectively.



Figure 4. Trigonal planar coordination of the Li⁺ cation in ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$ from a perspective perpendicular to both the plane and the *c*-axis. The distances at 7 K between Li and the nearest D atoms, and between Li and the centers of the nearest $B_{10}D_{10}{}^{2-}$ anions, are indicated.

details reflect the inherent differences in the number of B and H atoms comprising the two anions.

We point out that the Li⁺/anion size ratio of 0.164 for $\text{Li}_2\text{B}_{10}\text{H}_{10}$, as determined from an extrapolated Shannon radius³⁹ for 3-fold-coordinated Li⁺ of ≈ 0.52 Å and an approximate anion radius of ≈ 3.18 Å, derived from the average cation—anion distance of ≈ 3.70 Å (from Figure 4), favors the observed 3-fold coordination based on simple geometric packing criteria.^{16,40} To maximize its cohesive energy, it is clear that the relatively small size of the Li⁺ cation leads to the atypical hexagonal structural arrangement with the surrounding $\text{B}_{10}\text{H}_{10}^{2-}$ anions in contrast to the heavier alkali-metal monoclinic congeners.



Figure 5. 6-fold coordination of the $B_{10}D_{10}^{2-}$ anion in ${}^7Li_2{}^{11}B_{10}D_{10}$ from two orthogonal perspectives perpendicular to the *c*-axis.



Figure 6. Neutron vibrational spectra (black) of ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ and ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$ at 4 K compared to the simulated one-phonon (gray) and one+two-phonon (red) densities of states from first-principles phonon calculations of the optimized hexagonal structure. (N.B., 1 meV \approx 8.066 cm⁻¹).

The neutron vibrational spectra for both ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ and ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$ at 4 K are shown in Figure 6 and are compared with the simulated PDOSs based on the DFT-optimized structure. Because of the relatively large neutron scattering cross-section for H atoms compared to ${}^{7}\text{Li}$ or ${}^{11}\text{B}$ atoms, the ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ spectrum is dominated by the optical vibrational modes involving H atom displacements, whereas for ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$, the relatively smaller D atom cross section leads to somewhat more spectral contributions from the other constituent



Figure 7. Sequential heating–cooling DSC scans for $Li_2B_{10}H_{10}$ (5 K min⁻¹) as designated by the legend. Arrows denote heating and cooling segments.

atoms. The agreement between the experimental and simulated spectra for both ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ and ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$ is noteworthy and helps to corroborate the derived hexagonal structure. It has been shown previously for the $\text{B}_{12}\text{H}_{12}{}^{2-}$ -anion-based, alkalimetal salts that the PDOS is sensitive to the crystal structure arrangement.⁴¹ Further information about the character, symmetry, and energies of the different phonon modes contributing to the simulated PDOSs can be found in the Supporting Information.

Figure 7 shows a set of three sequential heating-cooling DSC scans (5 K min⁻¹) for $Li_2B_{10}H_{10}$ between 300 and 675 K. During the first heating scan, there is an endothermic feature occurring without noticeable mass loss at an onset temperature of around 640 K. This feature is reminiscent of that corresponding to the entropically driven order–disorder phase transition for ${\rm Li}_2B_{12}{H_{12}}^{16}$ and suggests that some type of order-disorder transition is also occurring for Li₂B₁₀H₁₀. The subsequent DSC cooling scan indicates a substantially hysteretic exothermic event commencing near 540 K, signaling the return to the low-temperature phase, but the intensity is diminished with respect to the previous endothermic event. Moreover, the endothermic events associated with the second and third heating scans, now shifted downward by more than 30 K, are becoming significantly less intense with each cycle progression, and likewise for the corresponding exothermic events. Hence, similar to the thermal behavior of the disordered Li₂B₁₂H₁₂ phase,¹⁶ these DSC scans suggest the occurrence of some type of slow thermal transformation or degradation of the proposed high-temperature Li₂B₁₀H₁₀ phase. Thus, as for Li₂B₁₂H₁₂, any consideration of Li₂B₁₀H₁₀ as a practical superionic electrolyte in the future may strongly depend on being able to lower its transition temperature significantly through appropriate modifications.

Finally, to further probe the nature of the transformation observed in Figure 7, we performed a preliminary assessment of its anion reorientational mobility up to 680 K via neutronelastic-scattering fixed-window scans (see Figure 8), which can detect anion reorientational jump frequencies $\geq 10^8 \text{ s}^{-1}$, as signaled by a sudden drop in neutron elastic scattering intensity. Similar to the rapid $B_{10}H_{10}^{2-}$ anion reorientational jump frequencies on the order of $3 \times 10^{10} \text{ s}^{-1}$ observed at 375 K for disordered $\text{Na}_2^{11}\text{B}_{10}\text{H}_{10}^{20}$ there is clear evidence of anion reorientational motions above the 10^8 s^{-1} threshold frequency for the spectrometer above about 650 K upon heating, which persist until about 550 K upon cooling. This is consistent with the hysteretic phase-change behavior observed by DSC in Figure 7 and corroborates the reversible, highly mobile, and disordered nature of the high-temperature phase. The structural nature of this disordered phase (possibly multiphase) region is



Figure 8. Neutron-elastic-scattering fixed-window scans for ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ measured at a momentum transfer of 0.87 Å⁻¹ on HFBS, compared with that for Na $_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ (adapted from ref 20). N.B., the two data sets were normalized so as to have equal intensities at 270 K. Arrows denote heating and cooling segments.

difficult to determine by diffraction methods, but attempts are underway.

SUMMARY

The structure of Li₂B₁₀H₁₀ was determined by X-ray and neutron powder diffraction methods in combination with firstprinciples computations and corroborated by neutron vibrational spectroscopy. Unlike its heavier alkali-metal monoclinic congeners, it displays P6422 symmetry with a nominally hexagonal-close-packed arrangement of $B_{10}H_{10}^{2-}$ anions and a trigonal planar coordination of the Li⁺ cations. Differential scanning calorimetry and neutron-elastic-scattering fixedwindow scans indicate a transition starting near 640 K to an unknown disordered structure region. This new structural information is a valuable addition to what is already known about the Li-B-H phase diagram and should be incorporated into any future analyses of LiBH₄ reaction pathways related to dehydrogenation-rehydrogenation as well as considered when attempting to design a potential Li₂B₁₀H₁₀-based fast-ion conductor.

ASSOCIATED CONTENT

S Supporting Information

CIF files for XRPD- and NPD-refined structures; instructions and datafiles to generate animations of all vibrational modes contributing to the simulated PDOSs; tables of DFT-generated phonon symmetries and energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

The Structural Behavior of $Li_2B_{10}H_{10}$

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How to view phonon animations using the V Sim software*

The Li2B10H10_phonons.xyz and Li2B10D10_phonons.xyz files contain the information needed to view the animated (gamma-point) phonon normal modes from the DFT-optimized 0 K ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ and ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{D}_{10}$ structures, respectively, following the steps below:

- Get the V Sim software (It is free, and there is no need to install).
- Go to the following webpage and download the Win32 binaries: http://www-drfmc.cea.fr/L Sim/V Sim/download.html
- Unzip the zip file to wherever you want to put the software.
- Click "~V_Sim\bin\V_sim.exe" to start the V_Sim program, then open the **Li2B10H10_phonons.xyz** or **Li2B10D10_phonons.xyz** file to view the phonon animations.
- To build bonds in the structure, check the box on the left side of the "Pairs" button, and click the "Pairs" button.
- Highlight a pair and click the "Auto set" button to allow bonding.
- Adjust the "Link parameters," if desired.
- Adjust the element color, radius, etc. on the "Elements" tab, if desired.
- Go to the "Phonons" tab, highlight a phonon mode, and click the "Play" button to view a phonon animation.

* N.B., the use of this software does not imply its recommendation or endorsement by NIST.

Table S1. List of phonon symmetries and the corresponding phonon energies at the gamma point from the DFT-optimized ${}^{7}\text{Li}_{2}{}^{11}\text{B}_{10}\text{H}_{10}$ structure at 0 K. The number before the symmetry symbol denotes the degeneracy. (N.B.: Infrared-active modes = A2, E1 and Raman-active modes = A1, E1, E2.) Modes below 300 cm⁻¹ possess translational and/or librational character.

Phonon	Energy	Energy	2E2	81.3	656.05	2E2	113.4	915.14
Symm.	(meV)	(cm^{-1})	A2	81.4	656.85	A1	113.6	916.46
B1	4.4	35.81	2E1	82.8	667.98	B1	114.1	920.78
2E1	8.9	71.43	B2	83.3	671.91	2E1	114.4	922.89
B2	9.9	79.99	2E2	84.0	677.96	2E2	115.3	930.12
2E1	12.9	103.74	A1	84.3	680.09	A1	115.4	931.08
2E2	14.9	120.25	B1	84.5	681.35	B1	116.0	935.73
B2	15.3	123.38	2E1	84.8	683.83	2E1	116.4	938.81
2E1	15.9	128.48	2E1	87.2	703.11	A2	116.5	940.23
A2	15.9	128.66	A1	87.7	707.42	2E2	116.6	940.62
B1	17.2	138.42	2E2	87.8	708.12	2E1	121.3	978.22
2E2	17.9	144.75	B2	88.0	710.28	B1	121.5	980.44
B1	22.9	184.37	B1	89.8	724.49	B2	121.7	982.09
2E1	25.5	205.66	2E1	90.9	733.70	2E1	122.1	985.11
2E2	28.0	226.29	B2	91.1	735.01	A2	123.1	993.36
A2	28.4	229.08	2E1	91.7	739.63	2E2	123.5	996.59
2E1	28.7	231.84	A2	92.9	749.58	A2	126.1	1017.05
A1	28.9	232.99	2E2	93.7	756.14	2E2	126.3	1019.06
B2	29.7	239.85	2E2	95.2	768.14	2E2	129.1	1041.28
B1	33.2	267.78	A1	95.8	773.01	A1	129.1	1041.43
2E1	34.0	274.57	A2	100.1	807.71	B1	130.5	1052.57
2E1	36.4	293.91	2E2	100.5	810.63	2E1	130.7	1054.55
2E2	37.0	298.71	2E1	100.6	811.21	2E1	134.9	1088.41
B2	37.1	299.58	B2	101.4	818.06	B2	135.1	1090.17
2E2	57.3	462.30	B1	102.4	825.98	2E1	310.7	2506.74
A1	57.7	465.65	2E1	102.4	826.26	A1	311.0	2508.89
2E1	59.0	476.18	2E1	102.9	829.88	2E2	311.1	2509.69
B1	59.1	477.01	B2	103.3	833.04	A2	311.1	2509.96
A2	59.6	481.00	2E2	103.9	838.50	B1	311.3	2511.27
2E2	59.7	481.44	A1	104.8	845.41	B2	311.3	2511.42
A2	66.5	536.35	B1	105.4	850.20	2E2	311.3	2511.63
2E2	66.7	538.13	2E1	105.5	851.24	2E1	311.3	2511.77
B1	66.8	538.72	2E2	106.9	862.07	B1	313.1	2526.01
2E1	66.9	539.36	A1	107.0	863.60	2E1	313.4	2528.07
A2	71.2	574.57	A2	108.0	871.05	B2	313.4	2528.41
2E2	71.8	579.58	2E2	108.4	874.28	A1	313.5	2529.21
B1	72.0	581.21	A2	109.3	881.97	A2	313.7	2530.56
2E1	72.3	583.59	2E2	109.5	883.05	2E1	313.8	2531.42
2E2	76.0	613.32	B1	109.9	886.90	2E2	314.1	2533.72
A1	76.4	616.47	2E1	110.0	887.26	2E1	314.4	2536.74
2E1	76.7	619.09	2E1	110.3	889.45	B2	314.6	2538.42
B2	76.8	619.30	B2	110.5	891.51	2E2	315.1	2542.37
2E2	77.0	621.09	A2	113.2	913.23	2E2	316.2	2551.11
A1	77.3	623.45	2E2	113.3	913.77	A1	316.4	2552.77

Table S2. List of phonon symmetries and the corresponding phonon energies at the gamma point from the DFT-optimized $^{7}Li_{2}^{11}B_{10}D_{10}$ structure at 0 K. The number before the symmetry symbol denotes the degeneracy. (N.B.: Infrared-active modes = A2, E1 and Raman-active modes = A1, E1, E2.) Modes below 300 cm⁻¹ possess translational and/or librational character.

94.2

760.19

760.63

760.99

763.50

771.77

771.96

789.73

790.45

860.45

861.25

866.27

868.21 892.48

892.49

895.88

896.26

920.20

920.32

922.21

922.90 971.90

972.19

982.82

983.27

1853.51

1854.75

1856.10

1857.22

1858.16

1858.40

1858.65

1858.75

1868.82

1868.96

1869.68

1872.70

1873.09

1873.74

1876.47

1880.79

1886.91

1887.60

1898.16

1898.70

Symm. (meV) (cm ⁻) 2E1 67.4 543.77	A2	94.3
B1 4.3 34.37 A2 70.1 565.34	2E2	94.3
2E1 8.5 68.75 2E2 70.6 569.21	A1	94.6
B2 9.4 76.23 2E1 70.8 571.48	A1	95.7
2E1 11.7 94.65 B2 71.0 572.80	2E2	95.7
B2 14.1 113.60 2E2 71.3 575.04	B2	97.9
2E2 14.3 115.61 A1 71.5 577.18	2E1	98.0
A2 14.7 118.27 B1 72.1 581.74	B1	106.7
2E1 14.7 118.43 2E1 73.3 591.23	2E1	106.8
B1 15.8 127.56 2E2 75.2 606.58	A2	107.4
2E2 16.6 133.61 A1 75.3 607.48	2E2	107.6
B1 22.6 182.57 B1 77.0 621.49	2E2	110.6
2E1 25.2 203.27 2E2 77.1 622.05	A2	110.6
2E2 28.0 225.73 2E1 77.2 623.20	2E1	111.0
A2 28.2 227.39 A1 77.4 624.49	B1	111.1
2E1 28.4 229.40 2E1 77.6 626.17	A2	114.1
A1 28.8 232.68 B2 78.0 629.19	2E2	114.1
B2 29.5 238.18 A2 79.7 643.17	B1	114.3
B1 33.0 266.07 2E2 79.9 644.81	2E1	114.4
2E1 33.8 272.92 2E1 82.3 664.11	A1	120.5
2E1 36.3 292.55 B2 82.4 664.94	2E2	120.5
2E2 36.9 297.38 2E2 82.8 667.65	2E1	121.8
B2 37.0 298.26 A1 83.0 669.20	B2	121.9
2E2 52.0 419.63 A2 83.9 676.62	2E1	229.8
A1 52.5 423.56 2E2 84.2 678.97	A1	229.9
2E1 53.2 429.27 A1 85.9 692.93	2E2	230.1
B1 53.3 430.06 2E2 85.9 693.10	A2	230.2
A2 54.2 436.92 2E1 86.4 696.72	2E2	230.3
2E2 54.2 437.43 B2 86.6 698.64	B2	230.4
A2 57.7 465.73 B2 87.2 703.41	B1	230.4
2E2 58.5 471.58 B1 87.3 704.68	2E1	230.4
B1 59.0 475.97 2E1 87.4 705.06	B2	231.6
2E1 59.4 479.46 2E1 87.5 705.85	B1	231.7
2E1 60.2 485.82 2E2 89.4 721.40	2E1	231.8
B1 60.4 487.33 A2 89.4 721.45	2E1	232.1
A2 61.2 493.44 2E2 89.9 725.49	A2	232.2
2E2 61.4 495.22 B1 90.0 726.11	A1	232.3
2E1 64.1 517.52 A1 90.0 726.17	2E2	232.6
2E2 64.3 518.77 2E1 90.5 729.92	2E2	233.1
A1 65.0 524.62 2E1 91.2 735.92	2E1	233.9
B2 65.1 524.88 B2 91.4 737.44	B2	234.0
2E2 65.4 527.81 2E1 92.9 749.10	2E2	235.3
A2 65.5 528.16 B1 93.2 751.66	A1	235.4