

High-Purity Amorphous Boron Synthesis from Boron Trifluoride and Lithium Hydride

Paata Nikoleishvili[✉], Gigla Tsurtsunia, Tina Lezhava, Nana Koiava, Rusudan Kurtanidze, Nunu Jokhadze

R. Agladze Institute Inorganic Chemistry and Electrochemistry, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia
Email: nikoleishvili@gmail.com

How to cite this paper: Nikoleishvili, P., Tsurtsunia, G., Lezhava, T., Koiava, N., Kurtanidze, R. and Jokhadze, N. (2026) High-Purity Amorphous Boron Synthesis from Boron Trifluoride and Lithium Hydride. *Journal of Materials Science and Chemical Engineering*, 14, 52-69.
<https://doi.org/10.4236/msce.2026.1410002>

Received: September 14, 2026

Accepted: October 9, 2026

Published: October 12, 2026

Copyright © 2026 by author(s) and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).
<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Ultrapure amorphous elemental boron was prepared via a two-stage route starting from boron trifluoride diethyl etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) and lithium hydride. In the first stage, LiBH_4 was synthesized in tetrahydrofuran at 50°C - 55°C using an optimized $\text{LiH}:\text{BF}_3$ molar ratio of 4.7:1, yielding 93% isolated product at $>99\%$ ^{11}B NMR purity, fluoride-free and with negligible diborane emission. In the second stage, the isolated LiBH_4 was thermally decomposed in a horizontal tube furnace under argon at 650°C , with thermal events consistent with decomposition via a $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate. Staged ethanolysis and dilute acid purification yielded amorphous nanostructured boron of 98.7% purity, with primary particle size ~ 60 nm, specific surface area $45 \text{ m}^2 \cdot \text{g}^{-1}$.

Keywords

High Purity Boron, Boron Trifluoride, Borohydride Thermal Decomposition

1. Introduction

Ultrapure amorphous elemental boron is a material of considerable technological importance for aerospace engineering, nuclear technologies, and high-energy-density fuels, but its direct synthesis from the elements is impractical. The direct reaction of lithium, boron, and hydrogen to form LiBH_4 —a necessary intermediate for elemental boron production—requires extreme conditions (150 bar H_2 , 650°C), and the subsequent thermal decomposition of this intermediate to release elemental boron is itself a multi-step process requiring temperatures above 600°C . Moreover, elemental boron is not cheaply available, so indirect routes via lithium borohydride are used instead [1] [2]. The wet-chemical route through the reaction of lithium hydride with boron trifluoride in ethereal solvents has therefore be-

come the dominant industrial method for the synthesis of lithium borohydride, with the LiBH_4 subsequently decomposed thermally to release amorphous boron.

Lithium borohydride was first synthesized in 1940 by Schlesinger and Brown [1] by the reaction of ethyllithium with diborane but attempts to prepare it via the alternative reaction of LiH with BF_3 in ethereal solvents began somewhat later. Elliott, Boldebeck and Roedel [3] first reported the reaction of LiH with boron trihalide ether complexes—including $\text{BF}_3 \cdot \text{Et}_2\text{O}$ —to generate diborane, using $\text{LiH}:\text{BF}_3$ molar ratios between 2:1 and 3.7:1; their experimental focus was diborane yield and purity, and no concrete data on LiBH_4 formation or yield were given. Fedneva [4] subsequently investigated the mechanism of this reaction in detail and concluded that LiBH_4 is not formed directly and stably in a single step, contrary to Elliott's assumption. Instead, diborane forms first as the primary boron-containing product

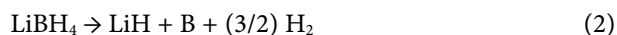


and is only subsequently able to react further with excess LiH in a second step to build up lithium borohydride. A follow-up communication by Fedneva [4] examined the reaction at a 4:1 $\text{LiH}:\text{BF}_3$ molar ratio near 0°C and found that, owing to the comparatively high solubility of LiF under these conditions, a large amount of lithium fluoroborate (LiBF_4) forms as a competing byproduct while very little LiBH_4 is actually produced—demonstrating that stoichiometry alone is insufficient for good yield, and that reaction temperature, LiF solubility, and reagent addition order are all critical variables [4].

These mechanistic constraints were resolved industrially by Hauk and Wietelmann [5] (Chemetall GmbH), who patented a process specifying a $\text{LiH}:\text{BF}_3$ molar ratio greater than 4.1:1 (particularly preferably $>4.4:1$), finely divided LiH (mean particle size $d_{50} \leq 0.2 - 0.5 \text{ mm}$), a small LiBH_4 seed charge (0.5 - 10 mol%) to reliably initiate the exothermic reaction, and reaction in a higher-boiling ethereal solvent—tetrahydrofuran, 2-methyltetrahydrofuran, tetrahydropyran, or 1,2-dimethoxyethane—at $10^\circ\text{C} - 70^\circ\text{C}$, preferably $30^\circ\text{C} - 70^\circ\text{C}$, in “semi-batch” mode with LiH suspended first and BF_3 metered in [2] [6]. Under these conditions the patent reports LiBH_4 yields $\geq 90\%$ (based on BF_3) with purity $>95\%$ by ^{11}B -NMR, essentially free of fluoride and with negligible diborane emission; worked examples achieved 93% and $\sim 95\%$ isolated yield in THF and dimethoxyethane, respectively, versus only 46% yield and heavy $\text{LiB}_2\text{H}_7/\text{BH}_3$ contamination when the $\text{LiH}:\text{BF}_3$ ratio fell to 4.08:1 [5]. More broadly, alongside mechanochemical ball-milling routes from borate precursors, the reaction of BF_3 with LiH in ethereal solvents remains one of the principal industrial methods by which LiBH_4 is produced today.

Once synthesized, LiBH_4 can be thermally decomposed to release elemental boron. LiBH_4 is a salt-like, hygroscopic crystalline material adopting the orthorhombic Pnma space group at room temperature ($a = 7.173 \text{ \AA}$, $b = 4.434 \text{ \AA}$, $c = 6.798 \text{ \AA}$, $\rho = 0.669 \text{ g}\cdot\text{cm}^{-3}$) and undergoing a polymorphic transformation to a disordered high-temperature hexagonal phase near 108°C , melting near $268^\circ\text{C} - 270^\circ\text{C}$

[1] [7]. The overall decomposition reaction



was long recognized to proceed through several intermediate steps rather than in one clean transition, with 13.8 wt% hydrogen released only when heated to 900°C [1]. Orimo *et al.* [8] provided early spectroscopic evidence for this complexity: room-temperature Raman measurements on LiBH_4 heated above 430°C revealed spectral signatures corresponding to both an intermediate $\text{Li}_2\text{B}_{12}\text{H}_{12}$ phase and amorphous boron as coexisting decomposition products, and combined with first-principles phase-stability calculations this work established $\text{Li}_2\text{B}_{12}\text{H}_{12}$ as the thermodynamically most stable intermediate compound on the pathway to elemental boron, proposing two competing reactions with distinct mass losses (≈ 10 wt%, 56 kJ/mol H_2 via the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ route; a further ≈ 4 wt%, 125 kJ/mol H_2 toward $\text{LiH} + \text{B}$). Hwang *et al.* [9] gave direct ^{11}B MAS/CPMAS NMR confirmation of this intermediate: the spectral signature of partially decomposed LiBH_4 closely matched the closo-borane reference compound $\text{K}_2\text{B}_{12}\text{H}_{12}$, confirming $[\text{B}_{12}\text{H}_{12}]^{2-}$ as a genuine intermediate species rather than earlier-hypothesized substoichiometric “ $\text{LiBH}_3/\text{LiBH}_2/\text{LiBH}$ ” phases, while MQMAS NMR further isolated a distinct spectral component matching amorphous elemental boron as the terminal product [9].

The chemical origin of this intermediate was clarified by Friedrichs, Remhof, Hwang and Züttel [7], who demonstrated via in-situ XRD and NMR that $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (together with an amorphous $\text{Li}_2\text{B}_{10}\text{H}_{10}$ phase) forms when LiBH_4 reacts with gaseous diborane released during early decomposition at 200°C—a self-reinforcing mechanism whereby the closo-borate intermediate delays release of free elemental boron until it itself decomposes at higher temperature, a behavior the authors suggest generalizes to other borohydrides [7]. Yan *et al.* [10] subsequently showed that the balance between the direct decomposition pathway and the indirect $\text{Li}_2\text{B}_{12}\text{H}_{12}$ pathway is jointly controlled by temperature and hydrogen back-pressure: at low pressure (0.1 - 10 bar, 800 - 873 K) both pathways proceed concurrently, whereas elevated H_2 pressure (50 bar at 873 K, or 10 bar at 700 K) forces decomposition exclusively through $\text{Li}_2\text{B}_{12}\text{H}_{12}$ [10]. Pitt, Paskevicius, Brown, Shepard and Buckley [11] mapped this system comprehensively up to 600°C using DTA/TGA, TPD-MS, XRD, and FTIR: isothermal desorption above the melting point first yields LiH plus a $\gamma\text{-Li}_2\text{B}_{12}\text{H}_{12}$ polymorph, which converts to a substoichiometric $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$ phase persisting largely unchanged up to 600°C under vacuum with no further LiH formation; only by 650°C does this residual closo-borate finally decompose, releasing amorphous boron (with some dissolved Li) as the true end product, with prolonged isothermal treatment also generating Li-B alloy side phases. Complementary in-situ evidence comes from Reed and Book [12], whose temperature-resolved Raman spectroscopy (80°C - 600°C, flowing argon) directly tracked LiBH_4 's phase transition, melting, and decomposition in real time: $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was observed forming at $\sim 350^\circ\text{C}$ - 356°C , with amorphous boron appearing shortly after at $\sim 380^\circ\text{C}$ - 385°C , and both phases persisted within the

melt and remained detectable after cooling to room temperature.

At the atomistic level, Hoang and Van de Walle [13] proposed via first-principles DFT calculations of native point defects in LiBH_4 that decomposition is mediated by mass transport of specific defect species: negatively charged hydrogen interstitials (H_i^-) act as the nucleation site for LiH formation and constitute the rate-limiting diffusing species with a self-diffusion activation energy of 1.65 eV, while boron-vacancy defects ($V^+_{\text{BH}_4}$, $V^0_{\text{BH}_3}$) mediate transport of $(\text{BH}_4)^-/\text{BH}_3$ units toward the surface, where elemental boron is ultimately released, and highly mobile lithium vacancies and interstitials (formation energies as low as 0.50 eV, migration barriers $\sim 0.29 - 0.30$ eV) maintain local charge neutrality throughout. Beyond mechanistic characterization, recent patent literature by Sanchez *et al.* [14] has addressed the practical challenge of converting borohydride decomposition into genuinely high-purity, high-surface-area boron: heating an alkali borohydride together with a molten inorganic alkali halide salt (80 - 99.9 wt%) under inert atmosphere at $600^\circ\text{C} - 1000^\circ\text{C}$ —sufficient both to decompose the borohydride and to keep the salt fully molten so as to disperse the resulting boron particles—yields boron nanoparticle aggregates ≤ 25 nm (preferably 2 - 10 nm) at $>90 - 98$ mol% purity and specific surface areas up to $\sim 900 \text{ m}^2\cdot\text{g}^{-1}$, a substantial improvement over the $\sim 10 - 20 \text{ m}^2\cdot\text{g}^{-1}$ characteristic of conventional micrometric amorphous boron produced by magnesiothermic reduction of boron oxide.

It should be noted that the thermal decomposition of LiBH_4 has been extensively studied in the context of hydrogen storage, where the primary objective is reversible hydrogen release and uptake. In those studies, the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate is often regarded as an obstacle because it raises the decomposition temperature and limits reversibility [7] [10]. In contrast, the present work focuses on the same decomposition process with a different objective: maximizing the yield of ultrapure amorphous elemental boron from LiBH_4 , which is itself synthesized from LiH and $\text{BF}_3\cdot\text{Et}_2\text{O}$. This shift in perspective means that the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate, rather than being an impediment, is simply a necessary stage on the pathway to elemental boron, and the reaction conditions are optimized accordingly.

2. Experimental

2.1. Materials and Reagent Preparation Reagents

All reagents used in this work were of analytical or synthesis grade and were purchased from established international chemical suppliers. The complete list of materials, together with their formulae, purities, suppliers, and catalogue numbers, is given below.

Lithium hydride (LiH) was obtained from Sigma-Aldrich (Merck KGaA, Germany, catalogue no. 201049) as a powder of $\geq 97\%$ purity with a particle size of ≤ 0.2 mm. Boron trifluoride (BF_3) gas of $\geq 99.5\%$ purity, supplied anhydrous in a lecture bottle, was also purchased from Sigma-Aldrich (catalogue no. 292532).

The ethereal solvents used as reaction media were all sourced from Sigma-Al-

drich (Merck KGaA, Germany): anhydrous diethyl ether ($(\text{C}_2\text{H}_5)_2\text{O}$) of $\geq 99.7\%$ purity, containing BHT as stabilizer (catalogue no. 296082); anhydrous tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) of $\geq 99.9\%$ purity, inhibitor-free (catalogue no. 401757); and anhydrous 1,2-dimethoxyethane ($\text{C}_4\text{H}_{10}\text{O}_2$) of $\geq 99.5\%$ purity, inhibitor-free (catalogue no. 259527).

Inert gases used throughout the work were high-purity argon (Ar, 99.999% grade 5.0, O_2 and $\text{H}_2\text{O} < 3$ ppm) and high-purity nitrogen (N_2 , 99.999% grade 5.0), both supplied by Air Liquide (France) and Messer.

Because lithium hydride, boron trifluoride, and lithium borohydride all react rapidly and exothermically with atmospheric moisture and oxygen, all reagents were opened, stored, and handled exclusively inside an argon-filled glove box (MBraun LABstar or equivalent) in which O_2 and H_2O levels were continuously monitored and maintained below 1 ppm. Solid reagents were transferred to and from the glove box in tightly sealed Schlenk vessels flushed with argon.

Drying and Deoxygenation of Solvents

The ethereal solvents used both as reaction media (diethyl ether, THF, 1,2-dimethoxyethane) and as scrubbing media required rigorous removal of water and dissolved oxygen prior to use. Even trace moisture hydrolyzes BF_3 , releases HF, deactivates LiH, and destroys any LiBH_4 formed; trace oxygen leads to formation of oxidized boron species (BO_3 , BO_4) detectable by ^{11}B NMR. The solvents were therefore dried by a two-stage procedure.

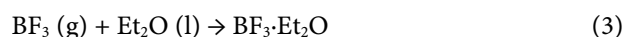
In the first stage, the commercial anhydrous solvent (typically supplied at < 50 ppm H_2O) was pre-dried by standing over freshly activated 4 Å molecular sieves for a minimum of 48 h. The molecular sieves themselves had been activated by heating at 300°C under dynamic vacuum ($\leq 10^{-2}$ mbar) for 12 h and then cooled and stored under argon before use. This step reduced the residual water content to < 10 ppm as verified by Karl Fischer titration (Metrohm 831 KF Coulometer).

In the second stage, the pre-dried solvent was transferred to a solvent still under argon and refluxed over freshly cut sodium metal in the presence of benzophenone as an indicator. The characteristic deep-blue-to-purple color of the sodium benzophenone ketyl radical confirmed the absence of both moisture and oxygen. Solvents were freshly distilled from the still directly into oven-dried Schlenk flasks under argon flow immediately before use; solvent standing in storage for more than 48 h after distillation was re-distilled. For diethyl ether specifically, dissolved peroxides were first removed by passage over an activated basic alumina column prior to sodium/benzophenone distillation, since peroxides in ether pose a serious explosion hazard and interfere with subsequent BF_3 complexation.

For 1,2-dimethoxyethane, which is less amenable to sodium/benzophenone drying because of its higher boiling point (85°C) and coordinating character, the procedure was modified: after pre-drying over 4 Å sieves, the solvent was refluxed for 6 h over CaH_2 under argon, then distilled onto fresh molecular sieves and stored under argon in a Schlenk flask sealed with a Teflon stopcock.

2.2. Synthesis of Boron Trifluoride Diethyl Etherate (BF₃·Et₂O)

Although BF₃·Et₂O is commercially available, in-house synthesis affords higher purity and allows precise control of the BF₃/Et₂O molar ratio, which is critical for the subsequent LiBH₄ synthesis step. The complex was prepared by direct complexation of gaseous BF₃ with rigorously dried diethyl ether according to:



The reaction was carried out in a jacketed glass reactor (500 mL, PTFE-sealed) fitted with a mechanical stirrer, a gas-inlet dip tube reaching below the liquid surface, a reflux condenser, and an exhaust line vented through a scrubber filled with 5 M aqueous NaOH to trap any unreacted BF₃. The entire apparatus was oven-dried at 130°C for 12 h, assembled hot, and purged with high-purity argon for at least 30 min before use.

Freshly distilled, anhydrous diethyl ether (200 mL, ~1.9 mol) was charged to the reactor under argon flow and cooled to 0°C - 5°C in an ice/water bath. Gaseous BF₃ was then introduced slowly (~50 mL·min⁻¹, measured by a calibrated mass-flow controller) through the dip tube under vigorous stirring (400 rpm). The reaction is strongly exothermic; the jacket temperature was maintained at 0°C - 10°C throughout the addition to prevent evaporation of the ether and to keep the growing BF₃·Et₂O complex in solution. A slight molar excess of BF₃ over Et₂O (BF₃:Et₂O ≈ 1.05:1) was used to ensure complete conversion.

Excess BF₃ was then purged from the reactor with dry argon for 30 min. The crude BF₃·Et₂O was fractionally distilled under argon through a short Vigreux column, collecting the main fraction at 125°C - 127°C (lit. b.p. 126°C) as a colorless-to-pale-yellow liquid. The distilled complex was analyzed by ¹¹B NMR (single sharp signal at +0.5 ppm relative to BF₃·Et₂O reference) and by density measurement (1.125 g·mL⁻¹ at 25°C), both consistent with high-purity BF₃·Et₂O. Because the complex hydrolyzes rapidly in humid air with release of HF, the product was stored in a tightly sealed, PTFE-stoppered Schlenk flask under argon at 4°C, away from light, and used within four weeks of preparation.

2.3. Synthesis of Lithium Borohydride (LiBH₄)

LiBH₄ was prepared by the reaction of finely divided, pre-dried LiH with BF₃·Et₂O in a higher-boiling ethereal solvent (THF), following the optimized process reported by Hauk and Wietelmann [5]:



The reaction was carried out in a 500 mL jacketed glass reactor fitted with a mechanical stirrer (300 - 400 rpm), a pressure-equalizing dropping funnel, a reflux condenser, and an argon inlet/outlet system with an exhaust scrubber filled with dry acetone to trap any diborane emissions. All glassware was oven-dried at 130°C for 12 h and assembled hot under argon flow.

Freshly purified LiH powder (42.4 g, 5.34 mol, LiH:BF₃ = 4.73:1) was suspended in 300 g of freshly distilled anhydrous THF inside the glove box and transferred

to the reactor under argon. A small seed charge of commercial LiBH_4 (1.1 g, ~ 4 mol% of the BF_3 to be added) was added to reliably initiate the exothermic reaction. The $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (158.1 g, 1.13 mol total, $\approx 48\%$ BF_3 w/w) was diluted with anhydrous THF (1:1 v/v) in the dropping funnel and metered dropwise ($1 - 2$ drops $\cdot \text{s}^{-1}$) into the stirred LiH suspension. The internal temperature was initially raised to 53°C to trigger the reaction and then maintained at $50^\circ\text{C} - 55^\circ\text{C}$ by jacket cooling (jacket at 45°C) throughout the ~ 90 min addition. Onset of reaction was confirmed by a rapid rise in internal temperature ($53^\circ\text{C} \rightarrow 59^\circ\text{C}$ within 5 min) and a corresponding increase in solution conductivity (from 0.03 to $0.10 \text{ mS} \cdot \text{cm}^{-1}$).

After the $\text{BF}_3 \cdot \text{Et}_2\text{O}$ addition was complete, the mixture was maintained under reflux (66°C) for a further 90 min to drive the reaction to completion, monitored by the cessation of H_2 evolution and stabilization of internal temperature and conductivity. The reaction mixture was then cooled to room temperature and filtered under a slight positive argon pressure through a Schlenk glass frit (porosity 4) to remove the LiF precipitate. The filter cake was washed twice with 100 mL portions of anhydrous THF to recover any entrained LiBH_4 . The combined THF filtrates yielded 390 g of a clear, colorless LiBH_4 solution (5.9 wt% LiBH_4 , corresponding to 22.9 g isolated, 93% yield based on BF_3).

For isolation of solid LiBH_4 , the filtered solution was concentrated on a rotary evaporator ($30^\circ\text{C} - 40^\circ\text{C}$, $10 - 20$ mbar) under an argon blanket, and the resulting white crystalline solid was dried under high vacuum (10^{-2} mbar) at $60^\circ\text{C} - 80^\circ\text{C}$ for 4 - 6 h to remove coordinated THF. The product was analyzed by ^{11}B NMR, showing a single dominant signal at -41.3 ppm ($>99\%$ of total signal, characteristic of $[\text{BH}_4]^-$) and a very minor signal at -30 ppm ($\sim 0.5\%$, trace secondary product), with fluoride content below detection limit ($<0.005 \text{ mmol} \cdot \text{g}^{-1}$) and no boron detected in the acetone scrubber ($<0.005 \text{ mmol} \cdot \text{g}^{-1}$, confirming negligible diborane emission). The isolated LiBH_4 was stored under argon in a sealed Schlenk flask at 4°C in the dark.

2.3.1. Effect of LiH:BF₃ Molar Ratio on LiBH₄ Yield

To establish the optimum stoichiometry for LiBH_4 formation, a series of eight parallel reactions was carried out at fixed reaction conditions (THF as solvent, addition temperature $50^\circ\text{C} - 55^\circ\text{C}$, reflux time 90 min, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ metered into LiH suspension over 90 min, 4 mol% LiBH_4 seed charge), varying only the LiH:BF₃ molar ratio from a substoichiometric 3.5:1 up to a large excess of 5.0:1. In each experiment, the amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was held constant at 1.13 mol, and the mass of LiH was adjusted accordingly. LiBH_4 yield was determined gravimetrically after filtration, solvent removal, and vacuum drying, and cross-checked by quantitative ^{11}B NMR against a calibrated internal standard. The results are summarized in **Table 1**.

The yield increased markedly between 4.1:1 ($46\% \pm 2\%$) and 4.3:1 ($71\% \pm 2\%$), consistent with the $>4.1:1$ threshold specified in the Hauk & Wietelmann patent [5]. At sub stoichiometric and near-stoichiometric ratios (Entries 1 - 4, 3.5:1 to 4.1:1), LiBH_4 yields remained low ($32\% - 46\%$), and the ^{11}B NMR spectra of the

crude product were heavily contaminated with LiBF_4 (–1 ppm), LiB_2H_7 (–25 ppm), and BH_3 residues (–15 to +5 ppm). This is consistent with Fedneva's original observation that, at ratios of 4:1 or below, the good solubility of LiF in the reaction medium favors formation of LiBF_4 as a competing thermodynamic sink, effectively consuming boron before it can be reduced to $[\text{BH}_4]^-$. At 4.7:1 the yield reached a plateau ($93\% \pm 2\%$); a further increase to 5.0:1 gave no significant improvement ($94\% \pm 2\%$, $p > 0.05$). Product purity, as measured by ^{11}B NMR, followed the same trend, reaching 99% for entries 7 and 8, with essentially no detectable LiBF_4 or diborane-related species. A ratio of 4.7:1 was therefore selected as the lowest ratio providing the maximum yield and purity.

Table 1. Influence of $\text{LiH}:\text{BF}_3$ molar ratio on LiBH_4 yield and product purity. Conditions: 1.13 mol $\text{BF}_3\cdot\text{Et}_2\text{O}$ in THF, addition at 50°C - 55°C , 90 min addition + 90 min reflux, 4 mol% LiBH_4 seed.

Entry	$\text{LiH}:\text{BF}_3$ (mol/mol)	LiH mass (g)	LiBH_4 yield (%)*	Purity by ^{11}B NMR (%)	Main byproducts detected
1	3.5:1	31.4	32	61	LiBF_4 , LiB_2H_7 , BH_3
2	3.8:1	34.1	41	68	LiBF_4 , LiB_2H_7 , BH_3
3	4.0:1	35.9	44	72	LiB_2H_7 , BH_3 , traces LiBF_4
4	4.1:1	36.8	46	74	LiB_2H_7 , BH_3
5	4.3:1	38.6	71	88	LiB_2H_7 (traces)
6	4.5:1	40.4	87	94	Traces LiB_2H_7
7	4.7:1	42.2	93	99	None detected
8	5.0:1	44.9	94	99	None detected

*Yield based on BF_3 charged. All experiments were performed in triplicate ($n = 3$); values are given as mean $\pm$ SD, with $\text{SD} \leq 2\%$.

2.3.2. Effect of Reaction Temperature on LiBH_4 Yield

Having fixed the $\text{LiH}:\text{BF}_3$ ratio at the optimum value of 4.7:1, a second series of five reactions was performed to establish the influence of reaction temperature on LiBH_4 yield and purity. All other conditions were held constant (THF as solvent, $\text{LiH}:\text{BF}_3 = 4.7:1$, 90 min $\text{BF}_3\cdot\text{Et}_2\text{O}$ addition, 90 min post-addition reflux, 4 mol% LiBH_4 seed). The internal reaction temperature during the $\text{BF}_3\cdot\text{Et}_2\text{O}$ addition and subsequent hold was varied from 25°C (well below the THF reflux temperature) up to 66°C (reflux of THF). Results are summarized in **Table 2**.

The temperature series shows a clear dependence of yield on reaction temperature. At 25°C (Entry 9), the reaction between LiH and $\text{BF}_3\cdot\text{Et}_2\text{O}$ proceeded far too slowly: internal temperature and conductivity measurements indicated that only ~50% of the BF_3 had reacted by the end of the 90 min hold, and analysis of the isolated product showed substantial residual LiBF_4 , reflecting incomplete reduction. Raising the temperature to 35°C (Entry 10) accelerated conversion significantly but not sufficiently for complete reaction within the given hold time, and traces of LiB_2H_7 remained detectable. At 45°C (Entry 11) the reaction pro-

ceeded smoothly to $85\% \pm 2\%$ yield with 94% purity. At 55°C (Entry 12) the yield increased significantly to $93\% \pm 2\%$ ($p < 0.01$), with 99% ^{11}B NMR purity and no detectable fluoride or diborane species—consistent with the reaction being fast enough to consume all BF_3 within the addition period, while remaining well below the reflux temperature of THF, so that diborane (which is only sparingly soluble in THF) remains dissolved and reacts further with excess LiH rather than escaping.

Table 2. Influence of reaction temperature on LiBH_4 yield and product purity. Conditions: $\text{LiH}:\text{BF}_3 = 4.7:1$, THF solvent, 90 min addition + 90 min hold, 4 mol% LiBH_4 seed.

Entry	Reaction temperature ($^\circ\text{C}$)	LiBH_4 yield (%) [*]	Purity by ^{11}B NMR (%)	Notes/observations
9	25	42	74	Very slow reaction; incomplete BF_3 consumption after hold; residual LiBF_4 detected
10	35	68	87	Reaction proceeds smoothly but slowly; some LiB_2H_7 still present
11	45	85	94	Good conversion; only trace LiB_2H_7
12	55	93	99	Optimum: full conversion, clean ^{11}B NMR, no fluoride
13	66 (reflux)	89	96	Slight loss to volatile diborane observed in scrubber ($0.04 \text{ mmol B}\cdot\text{g}^{-1}$)

^{*}Yield based on BF_3 charged. All experiments were performed in triplicate ($n = 3$); values are given as mean $\pm$ SD, with $\text{SD} \leq 2\%$.

At the highest tested temperature of 66°C (Entry 13, reflux), the yield was lower ($89\% \pm 2\%$). Although this difference is close to the experimental uncertainty ($p \approx 0.07$), a small but detectable amount of boron ($0.04 \text{ mmol B}\cdot\text{g}^{-1}$ solution equivalent) was captured in the acetone scrubber only at this temperature, indicating partial loss of the boron budget as gaseous diborane escaping the reaction mixture before it could react with the surrounding LiH . Additionally, ^{11}B NMR of the crude product at this temperature showed a small peak at -25 ppm attributable to trace LiB_2H_7 , consistent with incomplete second-step reduction. A reaction temperature of $50^\circ\text{C} - 55^\circ\text{C}$ was therefore selected for all subsequent syntheses: it is sufficiently high to ensure full kinetic conversion of $\text{BF}_3\cdot\text{Et}_2\text{O}$ within the addition/hold window, but low enough to retain any transiently formed diborane in solution long enough for its complete conversion to LiBH_4 .

2.4. Thermal Decomposition of LiBH_4 to Amorphous Elemental Boron Apparatus

Thermal decomposition of the isolated LiBH_4 was carried out in a horizontal high-temperature tube furnace (Carbolite Gero model STF 16/450, Carbolite Gero Ltd., Hope Valley, UK) equipped with a maximum operating temperature of 1600°C and a heated zone of 450 mm length. The furnace was fitted with a dense recrys-

tallized alumina (Al_2O_3 , $\geq 99.7\%$ purity) work tube (outer diameter 60 mm, inner diameter 50 mm, total length 900 mm), sealed at both ends with water-cooled stainless-steel vacuum flanges equipped with Viton O-rings and Swagelok gas-inlet and gas-outlet ports.

Temperature control and programming were provided by a Eurotherm 3216P1 PID controller integrated with the furnace, capable of programmable multi-segment heating and cooling ramps with a control accuracy of $\pm 1^\circ\text{C}$. The sample temperature was independently monitored by a Type-S (Pt/Pt-10%Rh) thermocouple positioned in direct contact with the sample crucible via a closed-end alumina thermowell inserted through the outlet flange, with temperature data logged at 5-second intervals to a PC.

The gas-handling system consisted of: (i) an inlet line supplying high-purity argon (99.999%, Messer, Georgia) passed sequentially through an oxygen trap (Agilent OT3-4, <15 ppb O_2 output) and a moisture trap (Agilent MT200-4, <15 ppb H_2O output) to remove residual contaminants; (ii) a calibrated mass-flow controller regulating argon flow through the tube; and (iii) an outlet line vented through a bubbler filled with silicone oil (to prevent back-diffusion of air) followed by a scrubber containing 5 M aqueous NaOH to neutralize any escaping acidic gases. A turbomolecular pumping station (base pressure $\sim 10^{-5}$ mbar) was connected to the outlet flange through a UHV-compatible bellows valve, allowing evacuation of the tube prior to argon backfilling. Pressure was monitored by a combined gauge mounted on the outlet flange.

The sample crucibles were of stainless steel (grade 316L, wall thickness 1 mm, internal dimensions $60 \times 20 \times 15$ mm).

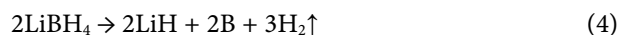
2.4.1. Sample Preparation and Loading

All sample handling was carried out inside the argon-filled glove box. A weighed portion of freshly prepared LiBH_4 (typically 5.0 g, corresponding to a theoretical elemental boron yield of 2.48 g assuming complete decomposition according to Equation (3) below) was transferred as a fine powder into a pre-cleaned, oven-dried (130°C , 12 h) 316L stainless-steel crucible. The crucible was loaded no more than half-full to allow for the volume expansion accompanying melting ($\sim 15\%$) and to provide sufficient headspace for the escape of evolved H_2 gas.

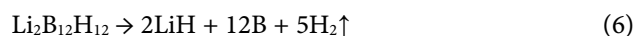
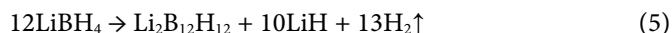
The loaded crucible was placed inside a purpose-built stainless-steel transfer container fitted with a gas-tight O-ring seal and sealed under argon. The transfer container was removed from the glove box and connected directly to a modified port on the furnace outlet flange, and the crucible was slid into the center of the alumina work tube (i.e., the isothermal zone) via a stainless-steel push rod under a continuous positive argon flow (100 sccm) that prevented ingress of air. Once the crucible was correctly positioned within ± 5 mm of the thermocouple tip, the transfer port was closed and the furnace tube sealed.

2.4.2. Decomposition Procedure

The overall decomposition reaction targeted is:



but proceeds in practice through the intermediate $\text{Li}_2\text{B}_{12}\text{H}_{12}$ borate phase:



so that reaching 600°C - 650°C is essential to fully decompose the persistent $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate and release amorphous elemental boron.

The furnace tube was first evacuated to a base pressure of $\sim 10^{-4}$ mbar using the turbomolecular pump, held for 30 min to remove any residual atmosphere, and then backfilled with high-purity argon to slightly above atmospheric pressure (1.05 bar). This evacuation-backfill cycle was repeated three times to ensure a rigorously oxygen- and moisture-free atmosphere in the work tube. During the entire decomposition run, a continuous slow argon flow (100 sccm) was maintained through the tube to sweep out evolved H_2 and any volatile byproducts (traces of diborane), keeping the interior atmosphere inert and preventing back-diffusion of air through the outlet.

The decomposition thermal program consisted of five segments:

- **Segment 1—Warm-up ($25^\circ\text{C} \rightarrow 200^\circ\text{C}$, $5^\circ\text{C}\cdot\text{min}^{-1}$, 35 min).** The furnace was heated at a moderate ramp rate to dry the sample and desorb any weakly adsorbed species without inducing premature decomposition.
- **Segment 2—Pre-melt hold (200°C , 30 min).** An isothermal hold was applied to allow any final moisture desorption and to equilibrate the temperature across the sample.
- **Segment 3—Melting and initial decomposition ($200^\circ\text{C} \rightarrow 350^\circ\text{C}$, $3^\circ\text{C}\cdot\text{min}^{-1}$, 50 min).** The slow ramp rate through the melting region (LiBH_4 m.p. $\approx 280^\circ\text{C}$) allowed controlled melting without excessive foaming from the accompanying H_2 evolution. Onset of hydrogen release was indicated qualitatively by a rise in outlet pressure (~ 1.1 - 1.3 bar) despite the continuous argon purge, consistent with formation of the $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate and initial amorphous boron nuclei according to Equation (5).
- **Segment 4—High-temperature decomposition ($350^\circ\text{C} \rightarrow 650^\circ\text{C}$, $5^\circ\text{C}\cdot\text{min}^{-1}$, 60 min).** The furnace was ramped to the target dwell temperature of 650°C , chosen to lie above the reported $\sim 600^\circ\text{C}$ stability limit of $\text{Li}_2\text{B}_{12}\text{H}_{12}$, ensuring full decomposition of the closo-borate intermediate to elemental boron and LiH per Equation (5).
- **Segment 5—Isothermal dwell (650°C , 4 h).** The sample was held isothermally at 650°C for 4 h to drive the reaction to completion. The outlet pressure was used only for qualitative monitoring of hydrogen evolution; no calibration to H_2 flow was performed. The fixed 4 h dwell was chosen to exceed the point at which no further pressure change was observed over a 30 min window.

After the dwell, the furnace was cooled slowly to room temperature at $5^\circ\text{C}\cdot\text{min}^{-1}$ under continuous argon flow to prevent thermal shock to the alumina tube and to avoid re-oxidation of any exposed boron surfaces. Once the internal temperature had dropped below 40°C , the outlet flange was opened under argon

flow, the sample crucible was transferred back to the sealed transfer container while still under argon protection, and the container was returned to the glove box for product recovery.

2.5. Purification of Amorphous Elemental Boron Rationale

The dark grey/black solid recovered from the tube furnace after thermal decomposition of LiBH_4 is not pure boron. It consists of amorphous elemental boron intimately mixed with several coproducts and residual intermediates that must be systematically removed to reach the target purity of >98.5%. The principal contaminants are:

- **Lithium hydride (LiH)**—the stoichiometric coproduct of LiBH_4 decomposition (Equation (3)), present in molar equivalence to boron;
- **Residual $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$** —small amounts of the persistent substoichiometric closeborate intermediate that may survive if any portion of the sample experienced local under-heating;
- **Trace lithium metal**—formed by partial thermal decomposition of LiH at the highest dwell temperatures;
- **Surface oxide/hydroxide layer (B_2O_3 , $\text{B}(\text{OH})_3$)**—formed rapidly on freshly exposed boron surfaces by reaction with atmospheric moisture and oxygen during any brief handling excursion outside the glove box;
- **Metallic contaminants from the crucible**—traces of Fe, Cr, and Ni that may have leached from the 316L stainless-steel crucible during the isothermal dwell at 650°C .

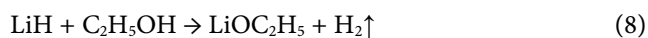
Each contaminant class requires a specific purification strategy exploiting differences in solubility, reactivity, and chemical stability between it and elemental boron. The purification protocol described below proceeds in five sequential stages, each targeted at removing a specific contaminant class while preserving the amorphous boron matrix intact.

Stage 1—Controlled Ethanolysis of Lithium Hydride

The most abundant contaminant, LiH, is highly reactive and reacts violently with water according to:



Direct addition of water to the crude powder would therefore cause vigorous, potentially incendiary H_2 evolution, thermal shock, and mechanical disruption of the amorphous boron particles. To avoid this, LiH is first hydrolyzed in a controlled manner using absolute ethanol as a milder proton source:



The reaction of LiH with ethanol proceeds smoothly at 0°C , with H_2 evolution rate low enough to be safely managed by an argon purge and a mineral oil bubbler.

Stage 2—Aqueous Quench and Acid Wash

Once the LiH was fully converted to soluble lithium ethoxide, distilled water (100 mL) was added dropwise to the suspension over 30 min, again with cooling

in an ice/water bath. This hydrolyzed the ethoxide to lithium hydroxide and simultaneously dissolved any residual water-soluble Li-containing species. Critically, $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and its substoichiometric derivative $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$ are highly water-soluble ($>50 \text{ g}/100 \text{ mL H}_2\text{O}$ at 25°C) and pass into the aqueous phase at this stage, while amorphous elemental boron is completely insoluble in water and remains suspended as a dark solid.

Following aqueous quenching, dilute hydrochloric acid (2 M HCl, 100 mL) was added slowly to the suspension with continued stirring, bringing the medium to $\text{pH} \approx 1$. The acidic conditions dissolve:

- residual LiOH, forming soluble LiCl;
- any surface $\text{B}_2\text{O}_3/\text{B}(\text{OH})_3$ oxide layer, converting it to soluble boric acid (H_3BO_3);
- traces of Fe, Cr, and Ni leached from the crucible, converting them to soluble metal chlorides;
- any remaining $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$, which decomposes acidolytically.

Amorphous boron itself does not react with dilute HCl at room temperature and survives this treatment unchanged. The acid-treated suspension was stirred at room temperature for a further 3 h to allow complete dissolution of the contaminants.

Stage 3—Filtration and Neutral Washing

The acid-treated suspension was filtered under a slight positive argon pressure through a Büchner funnel fitted with a POR-4 sintered glass frit (porosity 10 - 16 μm), retaining the fine amorphous boron powder as a dark cake while allowing all dissolved contaminants to pass through with the filtrate. The filter cake was washed sequentially: With distilled water ($5 \times 50 \text{ mL}$ portions), until the filtrate pH reached neutral ($\text{pH } 6.5 - 7.0$), with absolute ethanol ($3 \times 30 \text{ mL}$ portions), to displace residual water from the porous boron structure and to accelerate subsequent drying, with acetone ($3 \times 30 \text{ mL}$ portions), to further reduce residual solvent content and prevent aggregation of the fine particles during drying.

Stage 4—Vacuum Drying

The washed cake was transferred, still on the sintered glass filter, into a vacuum oven and dried at $80^\circ\text{C} - 100^\circ\text{C}$ under reduced pressure ($<10 \text{ mbar}$) for 6 h.

3. Result and Discussion

3.1. Thermal Decomposition of LiBH_4 —Derivatographic Analysis

Simultaneous TG/DTA/DSC (Netzsch STA 449 F5 Jupiter, alumina crucible, argon flow $60 \text{ mL}\cdot\text{min}^{-1}$, heating rate $5^\circ\text{C}\cdot\text{min}^{-1}$, from 30°C to 800°C) of a 25 mg sample of the isolated LiBH_4 produced a derivatogram (Figure 1) showing four distinct thermal events:

- 1) $\sim 116^\circ\text{C}$ —a small, sharp endothermic peak with negligible mass loss ($<0.1 \text{ wt}\%$), corresponding to the orthorhombic $\rightarrow$ hexagonal polymorphic transition of solid LiBH_4 .
- 2) $\sim 278^\circ\text{C}$ —a sharp endothermic peak with a small associated mass loss of ~ 0.4

wt%, corresponding to the melting of LiBH_4 accompanied by a minor initial hydrogen desorption from the liquid.

3) $320^\circ\text{C} - 450^\circ\text{C}$ (peak at $\sim 385^\circ\text{C}$)—a broad endothermic feature with major mass loss of ~ 7.8 wt%, corresponding to the first significant decomposition stage in which LiBH_4 decomposes to $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and LiH (Equation (4)) with release of H_2 . The mass loss agrees well with the theoretical value of 8.0 wt% expected for stoichiometric conversion of 12LiBH_4 to $\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH} + 13\text{H}_2$.

4) $500^\circ\text{C} - 680^\circ\text{C}$ (peak at $\sim 600^\circ\text{C}$)—a second broad endothermic feature with a further mass loss of ~ 4.6 wt%, corresponding to decomposition of the $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$ intermediate to $\text{LiH} + \text{amorphous B} + \text{H}_2$ (Equation (5)). Beyond 680°C , no further mass loss was detected up to 800°C , confirming that the LiH coproduct is stable in this temperature range, consistent with its literature decomposition temperature of $\sim 900^\circ\text{C}$.

The total measured mass loss up to 680°C was 12.8 wt%, in reasonable agreement with the theoretical value of 13.8 wt% for full conversion of LiBH_4 to $\text{LiH} + \text{B} + (3/2) \text{H}_2$ (Equation (3)), with the ~ 1 wt% shortfall attributable to a small loss of boron budget as trace diborane during the intermediate stage, consistent with the observations of Friedrichs *et al.* [7] and of Reed & Book [12]. The clear separation between the two hydrogen-release events in the derivatogram (peaks at $\sim 385^\circ\text{C}$ and $\sim 600^\circ\text{C}$) is consistent with the two-step decomposition pathway via a persistent $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate, as proposed by Orimo *et al.* [8] and mapped in detail by Pitt *et al.* [11].

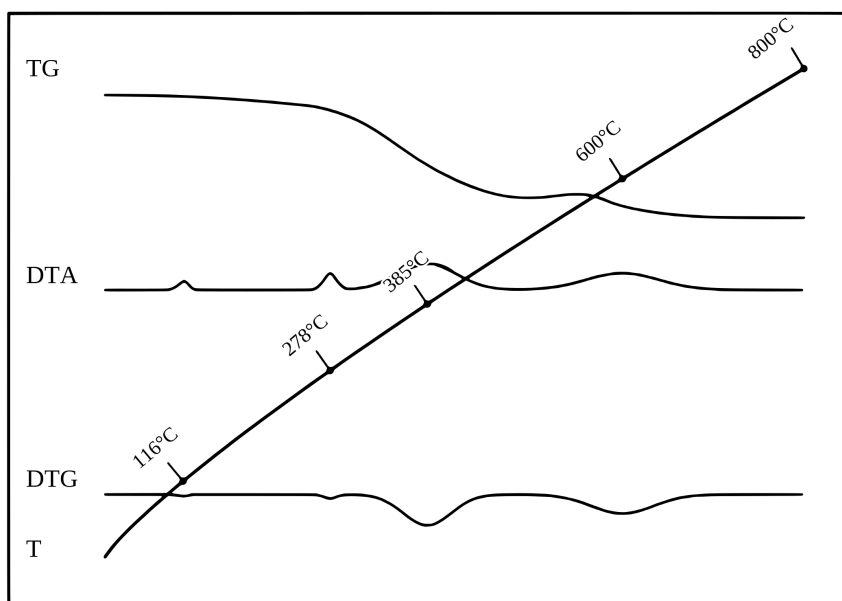


Figure 1. Derivatogram (TG/DTA/DSC) of the thermal decomposition of LiBH_4 .

3.2. Confirmation of Amorphous Boron Formation

The purified end-product of the tube-furnace decomposition was extensively characterized to confirm both its amorphous nature and its elemental identity.

XRD of the purified powder (Bruker D8 Advance, Cu K α , $2\theta = 10^\circ - 80^\circ$, air-tight sample holder) showed no crystalline reflections attributable to LiH, LiF, Li₂B₁₂H₁₂, LiBH₄, or any crystalline polymorph of boron. Instead, only two very broad diffuse halos were observed (**Figure 2**), centered at $2\theta \approx 20^\circ$ and $\sim 35^\circ$ (FWHM $\sim 10^\circ$ and $\sim 15^\circ$, respectively), characteristic of the short-range order of amorphous elemental boron. This pattern matched closely with the reference XRD trace of commercial amorphous boron (ABCR, 95% - 97% purity) and with the pattern reported by Sanchez *et al.* [14] for their nanostructured amorphous boron.

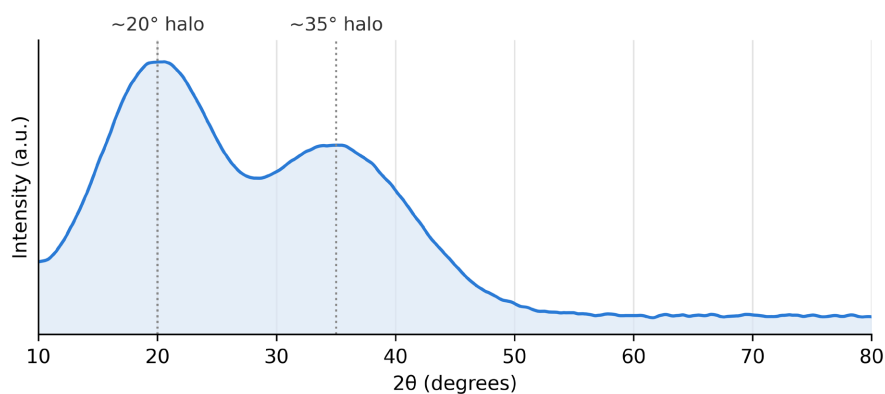


Figure 2. XRD pattern of the purified amorphous boron powder, showing broad diffuse halos characteristic of amorphous elemental boron.

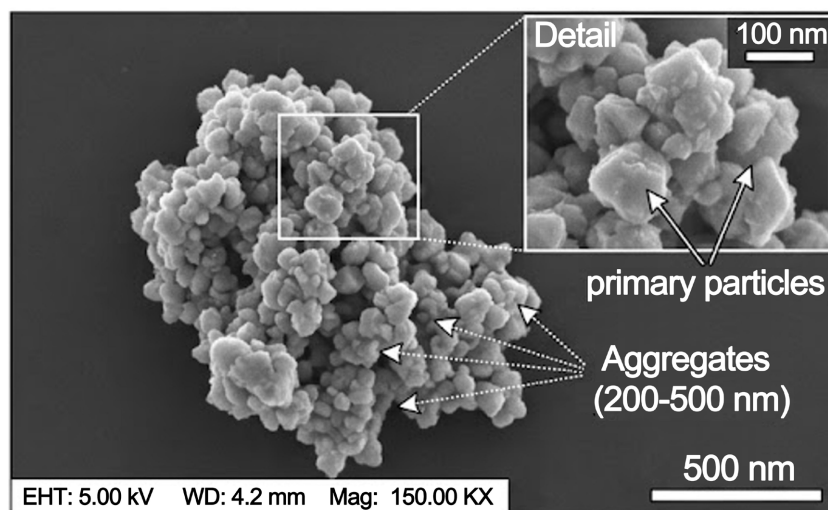


Figure 3. SEM image of the purified amorphous boron powder: primary particles of 40 - 100 nm aggregating into 200 - 500 nm clusters.

SEM-EDX revealed a nanoparticulate morphology (**Figure 3**) consisting of aggregates of primary particles in the 40 - 100 nm range, with the larger aggregates reaching 200 - 500 nm. EDX elemental mapping showed a uniform boron distribution with only trace oxygen signal (~ 1.5 at% O), and no detectable Li, F, or transition metal signals above the noise floor (~ 0.1 at%). This indicates both the

compositional purity of the product and the complete removal of the LiF/LiCl residuals from the acid-washing stages.

ICP-OES elemental assay after microwave-assisted acid digestion (concentrated HNO_3/HF , CEM MARS 6) gave an elemental boron content of $98.7\% \pm 0.2\%$, with Li = 32 ppm, F below detection limit (<10 ppm), Fe = 45 ppm, Cr = 15 ppm, Ni = 8 ppm, and Al below detection limit (<10 ppm). The total metallic contamination remained below 100 ppm, meeting the specification for high-purity amorphous boron. The boron content (98.7 wt%, determined by [method]) reflects the bulk composition. The oxygen detected by EDX (~ 1.5 at%) arises from a thin B_2O_3 surface layer formed on air exposure of the high-surface-area boron during sample handling, which EDX, as a surface-sensitive method, overrepresents. The remaining ~ 1.3 wt% is attributed mainly to oxygen, hydrogen, and carbon.

FTIR (PerkinElmer Frontier, ATR mode) of the purified boron powder (**Figure 4**). showed complete absence of the B-H stretching bands at $2400 - 2600 \text{ cm}^{-1}$ that would signal residual borohydride or closo-borate species, confirming the completeness of the thermal decomposition. Only weak broad absorption near $1350 - 1450 \text{ cm}^{-1}$ was observed, attributable to the trace surface BO_3 groups already identified by ^{11}B NMR.

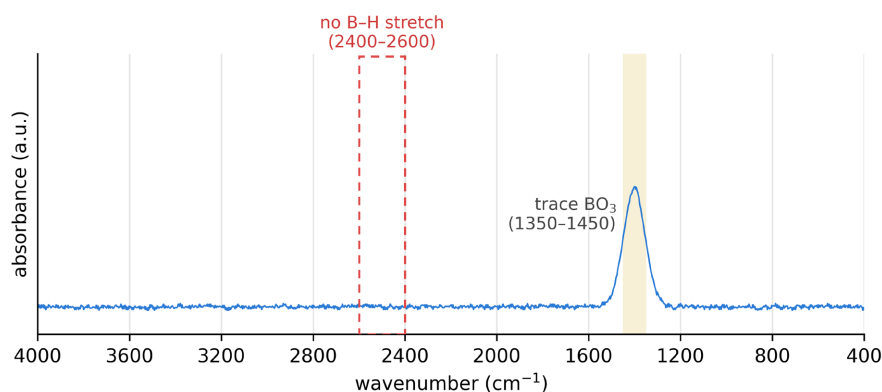


Figure 4. FTIR spectrum of the purified boron powder: no B-H stretch ($2400 - 2600 \text{ cm}^{-1}$), weak trace BO_3 band ($1350 - 1450 \text{ cm}^{-1}$).

4. Conclusions

This work has demonstrated that ultrapure amorphous nanostructured boron can be reliably prepared through a two-stage laboratory-scale route based on well-established but often overlooked chemistry: synthesis of lithium borohydride from lithium hydride and boron trifluoride diethyl etherate in tetrahydrofuran, followed by controlled thermal decomposition of the isolated LiBH_4 in a horizontal tube furnace under argon at 650°C , and a staged aqueous purification (ethanolysis of LiH followed by dilute HCl washing) to remove all residual lithium- and halide-containing species.

Systematic variation of the $\text{LiH}:\text{BF}_3$ molar ratio and reaction temperature identified an optimum at $\text{LiH}:\text{BF}_3 = 4.7:1$ and $50^\circ\text{C} - 55^\circ\text{C}$, delivering LiBH_4 in 93%

isolated yield and >99% ^{11}B NMR purity, in close quantitative agreement with the industrial process patented by Hauk & Wietelmann. Thermal decomposition proceeded in two steps, with sequential mass losses at $\sim 385^\circ\text{C}$ and $\sim 600^\circ\text{C}$ matching the theoretical values for Equations (4) and (5), consistent with the pathway via a $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate reported in the literature [8] [11]. The final purified product was characterized as amorphous elemental boron of 98.7% purity, with primary particle size ~ 60 nm, specific surface area $45\text{ m}^2\cdot\text{g}^{-1}$.

The two-stage LiH/BF_3 -based route therefore represents a practical, scalable, and reproducible pathway to nanostructured amorphous boron from readily available industrial reagents—well suited to producing precursor material for metal borides, high-energy-density additives, and other advanced boron-based applications where reactivity and purity outweigh the need for the ultrafine morphologies achievable only by molten-salt-mediated methods.

Author Contributions

Paata Nikoleishvili: Conceptualization, Methodology, Writing - original draft, Writing - review & editing—formulation of the main idea of the work and the research strategy; preparation of the manuscript.

Gigla Tsurtsumia: Supervision, Project administration, Investigation—supervision and execution of the project.

Tina Lezhava: Investigation—study of the lithium borohydride synthesis processes.

Nana Koiava: Investigation—study of the lithium borohydride decomposition processes.

Rusudan Kurtanidze: Investigation—analytical characterization.

Nunu Jokhadze: Investigation—analytical characterization.

All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Schlesinger, H.I. and Brown, H.C. (1940) Metallo Borohydrides. III. Lithium Borohydride. *Journal of the American Chemical Society*, **62**, 3429-3435. <https://doi.org/10.1021/ja01869a039>
- [2] Wietelmann, U. and Hauk, D. (2004) Process for Preparing Lithium Borohydride. European Patent EP1440934 (A1). Chemetall GmbH.
- [3] Elliott, J.R., Boldebuck, E.M. and Roedel, G.F. (1952) Preparation of Diborane from Lithium Hydride and Boron Trihalide Ether Complexes. *Journal of the American Chemical Society*, **74**, 5047-5052. <https://doi.org/10.1021/ja01140a017>
- [4] Fedneva, E.M. (1959) The Influence of Temperature on the Reaction of Lithium Hydride with Boron Trifluoride Etherate. *Russian Journal of Inorganic Chemistry*, **4**, 124-125.
- [5] Hauk, D. and Wietelmann, U. (2005) Process for the Preparation of Lithium Boro-

- hydride. US Patent Application US2005/0074385.
- [6] Wietelmann, U., Hauk, D., Majdalani, A. and Lischka, U. (2004) Method for Producing Alkali Metal Monohydridoborates and Monohydridoaluminates. US Patent 6,713,642 B2. Chemetall GmbH.
 - [7] Friedrichs, O., Remhof, A., Hwang, S.J. and Züttel, A. (2010). Role of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ for the Formation and Decomposition of LiBH_4 . *Chemistry of Materials*, **22**, 3265-3268. <https://doi.org/10.1021/cm100536a>
 - [8] Orimo, S.I., Nakamori, Y., Eliseo, J.R., Züttel, A. and Jensen, C.M. (2007) Complex Hydrides for Hydrogen Storage. *Chemical Reviews*, **107**, 4111-4132. <https://doi.org/10.1021/cr0501846>
 - [9] Hwang, S.J., Bowman, R.C., Reiter, J.W., Rijssenbeek, J., Soloveichik, G.L., Zhao, J.C., Kabbour, H. and Ahn, C.C. (2008) NMR Confirmation for Formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ Complexes during Hydrogen Desorption from Metal Borohydrides. *The Journal of Physical Chemistry C*, **112**, 3164-3169. <https://doi.org/10.1021/jp710894t>
 - [10] Yan, Y., Remhof, A., Hwang, S.J., Li, H.W., Mauron, P., Orimo, S.I. and Züttel, A. (2012) Pressure and Temperature Dependence of the Decomposition Pathway of LiBH_4 . *Physical Chemistry Chemical Physics*, **14**, 6514-6519. <https://doi.org/10.1039/c2cp40131b>
 - [11] Pitt, M.P., Paskevicius, M., Brown, D.H., Sheppard, D.A. and Buckley, C.E. (2013) Thermal Stability of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and Its Role in the Decomposition of LiBH_4 . *Journal of the American Chemical Society*, **135**, 6930-6941. <https://doi.org/10.1021/ja400131b>
 - [12] Reed, D. and Book, D. (2011) In-Situ Raman Study of the Thermal Decomposition of LiBH_4 . *MRS Proceedings*, **1216**, Article No. 605. <https://doi.org/10.1557/proc-1216-w06-05>
 - [13] Hoang, K. and Van de Walle, C.G. (2012) Native Point Defects in LiBH_4 : A First-Principles Study. *International Journal of Hydrogen Energy*, **37**, 5825-5832.
 - [14] Sanchez, C., Gervais Stary, C., Portehault, D. and Gouget, G. (2018) Nanostructured Amorphous Boron Material. US Patent Application US 2018/016962.