

Magnesium borohydride : synthesis and crystal structure

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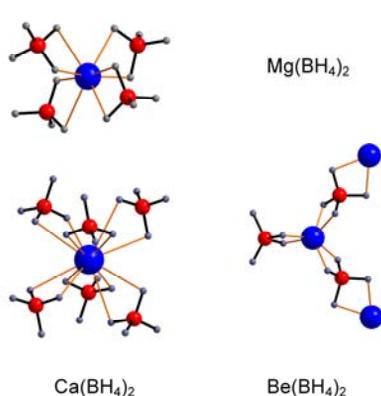


Figure 1. Structural comparison of the $M(\text{BH}_4)_2$ series' members. M (in blue) = Mg and Ca: 3-d framework; Be: 1-d polymer. Coordination of Mg5 is shown for $\text{Mg}(\text{BH}_4)_2$.

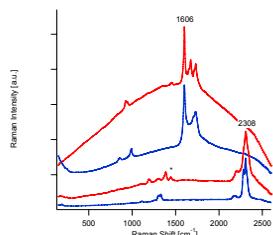


Figure 2. Raman spectra of $\text{Mg}(\text{BH}_4)_2$ (in red) and LiBH_4 (in blue). Upper curves: deuteride, lower curves: hydride. The asterisk indicates a band resulting from residual diethyl-ether.

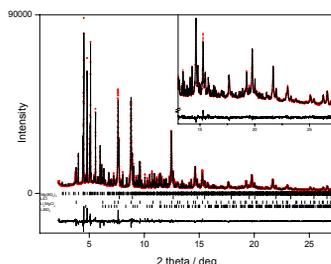


Figure 3. Observed (red), calculated (black) and difference (bottom) synchrotron powder diffraction patterns for $\text{Mg}(\text{BD}_4)_2$, $\lambda = 0.40008 \text{ \AA}$. The Bragg positions for individual phases are shown with ticks.

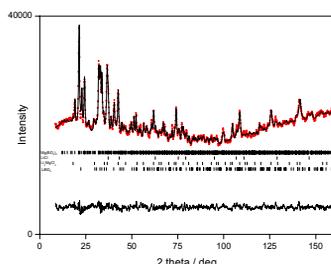


Figure 4. Observed (red), calculated (black) and difference (bottom) neutron powder diffraction patterns for $\text{Mg}(\text{BD}_4)_2$, $\lambda = 1.8857 \text{ \AA}$. The Bragg positions for individual phases are shown with ticks.

$\text{Mg}(\text{BD}_4)_2$ at 20°C:
 $P6_1$, $a = 10.3182(1)$, $c = 36.9983(5) \text{ \AA}$, $V = 3411.3(1) \text{ \AA}^3$

Five symmetry independent Mg^{2+} ions and ten symmetry-independent $[\text{BD}_4]^-$ ions. The Mg^{2+} and $[\text{BD}_4]^-$ ions are connected into a novel three-dimensional framework. All Mg^{2+} cations have similar atomic environments.

BD_4 tetrahedra as semirigid bodies with ideal tetrahedral bond angles and a common refined BD distance of 1.18(1) \AA .

Each Mg^{2+} ion is surrounded by four $[\text{BD}_4]^-$ tetrahedra arranged in a deformed tetrahedron (Mg-B 2.31(3)–2.53(2) \AA ; B-Mg-B 83(2)–131(2) deg). Each $[\text{BD}_4]^-$ ion is approximately linearly coordinated by two Mg^{2+} ions (Mg-B-Mg 148(1)–177(2)deg).

The orientation of the $[\text{BD}_4]^-$ tetrahedra is such that each Mg^{2+} ion is coordinated by tetrahedral edges only (μ_2 - D_2 bridges), resulting in an unusual eightfold, relatively irregular hydrogen coordination environment.

Mg-D distances in the range of 1.81(4)–2.25(5) \AA , with the exception of one longer distance of 2.46(8) \AA .

The increase of the hydrogen coordination number from six (for Be^{2+}) to eight (for Mg^{2+}) and twelve (for Ca^{2+}) suggests that cation size is one of the reasons that $\text{Mg}(\text{BD}_4)_2$ does not adopt one of the simpler structures of its alkaline-earth analogues.

The structure of $\text{Mg}(\text{BD}_4)_2$ differs from those of its beryllium and calcium analogues, as well as from those predicted by theory [1,2].

The structure is one of the most complex atom arrangements solved from powder diffraction data so far.

	LiBD_4	LiBH_4	$\text{Mg}(\text{BH}_4)_2$	$\text{Mg}(\text{BD}_4)_2$
$\nu_1 + \nu_2$	1730	2321sh	2334sh	1733
B-H(D) stretching +Fermi resonance	1705	2275	2283sh	1716
	1603	2301	2308vs	1674
				1654
				1606
$\nu_2 + \nu_4$	989	1316	1388	946
	856	1286	1310	924
	838sh	1235	1268	830
		1099	1205	802
		1090	1190	775
			1126w	
			1088w	
			1039w	
Lattice modes	673	285	670	
	366	255	248	
	245	189	204	
			195	
			172	

Table 1. Observed Raman shifts (in cm^{-1}) for lithium and magnesium borohydride at room temperature (see Figure 2) vs = very strong, sh = shoulder, w = weak.

Synchrotron X-ray and neutron diffraction:

A powder synchrotron X-ray diffraction (S) pattern for $\text{Mg}(\text{BD}_4)_2$ was measured over 24 h at room temperature using synchrotron radiation ($\lambda = 0.400080(1) \text{ \AA}$) at the Swiss–Norwegian Beam Line BM1B of the ESRF (Grenoble).

A powder neutron diffraction (N) pattern was measured for the same sample at 100°C using neutron radiation ($\lambda = 1.8857 \text{ \AA}$) on the HRPT at the Swiss Spallation Source (SINQ) of the PSI (Viligen).

The S data were indexed in a hexagonal cell by using Dicolv96. The structure was solved jointly from the S and N data by direct-space methods (program FOX [4]) in space group $P6_1$.

Five magnesium atoms and ten BD_4 groups were refined jointly on the S and N data by using TOPAS Academic [5]. The BD_4 tetrahedra were kept as semirigid bodies with ideal tetrahedral bond angles and a common refined BD distance.

In the final cycle, 186 parameters were refined, yielding the agreement factors of $R_{\text{wp}} = 0.048$, $R_{\text{Bragg}}(\text{main phase}) = 0.034$, and $\chi^2 = 16$ for the S data, and of $R_{\text{wp}} = 0.018$, $R_{\text{Bragg}}(\text{main phase}) = 0.008$, and $\chi^2 = 7.45$ for the N data.

Nine S patterns were collected over the temperature range 100–200°C to check for the phase transition reported in reference [6]. A transition to a HT phase was indeed observed at approximately 180°C. The HT phase is possibly unstable above this temperature. Its diffraction peaks were not consistent with a hypothetical cubic Cu_2O -type metal substructure nor with a face-centered cubic structure ($a \sim 15.5 \text{ \AA}$) as reported in reference [6].

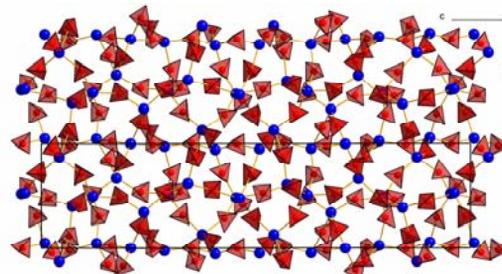


Figure 5. Structure of $\text{Mg}(\text{BH}_4)_2$ viewed along the hexagonal b axis, showing two unit cells. Red (partially transparent) tetrahedra are BH_4^- units; Mg atoms in blue. Considering the cations as A and the tetrahedral anions as B, the resulting three-dimensional framework, in which each tetrahedron AB₄ shares all of its vertices with another tetrahedron, resembles the frameworks of oxides and aluminosilicates, which generally display nearly linear A-B-A fragments.

Synthesis:

Commercial LiBH_4 or LiBD_4 (2 g, 91.8 mmol; and anhydrous MgCl_2 (4 g, 42 mmol) were introduced into a 500-ml flask containing dry diethyl ether (300 ml). The mixture was heated under reflux for 3 days in a nitrogen atmosphere, and ether was repeatedly added to compensate for evaporation losses. The reaction mixture was allowed to cool for 1 h. Then the liquid phase was removed using a syringe equipped with a small filter and collected in a new flask. The ether was removed under vacuum (10^{-2} – 10^{-3} mbar, liquid-nitrogen trap) at room temperature, leaving a white paste of solvated $\text{Mg}(\text{BH}_4)_2$ or $\text{Mg}(\text{BD}_4)_2$ and other compounds.

Upon careful drying under vacuum at increasing temperatures (50, 70, 90, 110, 130, and 145°C) over 3 or 10 days (in two different experiments), a dry solid was obtained. X-ray analysis revealed the presence of some LiCl , Li_2MgCl_4 , and LiBH_4 or LiBD_4 , in addition to the main phase $\text{Mg}(\text{BH}_4)_2$ or $\text{Mg}(\text{BD}_4)_2$ (yield ca. 30%). Above 150°C, the sample started to decompose.

For samples heated to only 120°C, ether was detected in the Raman spectrum; these samples were not sufficiently well-crystallized for high-resolution diffraction studies.

Raman spectra:

In the BH stretching region (around 2300 cm^{-1}), the spectra of $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 are similar, while those of the corresponding deuterides are more complex.

In the bending region (1000–1400 cm^{-1}), the spectra of the hydrides and the deuterides show significant differences.

By correlating the BD stretching frequency with the BD bond length, as was done for the cubic alkali-metal borohydrides [3], a frequency of 1605 cm^{-1} suggests a bond length of 1.17 \AA .

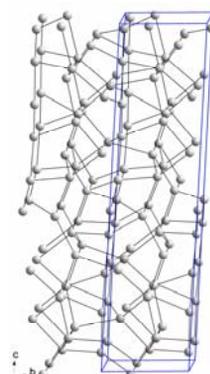


Figure 6. Considering the cations (A) only, the Mg^{2+} network ($\text{Mg}-\text{Mg} > 4.6 \text{ \AA}$) resembles an amorphous state on a local level. Four-connected Mg nodes are shown.

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