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Synthesis and Crystal Structure of Lithium Beryllium Deuteride Li_2BeD_4

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Single-phase ternary deuteride Li_2BeD_4 was synthesized by a high-pressure high-temperature technique from LiD and BeD_2. The crystal structure of Li_2BeD_4 was solved from X-ray and neutron powder diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 7.06228(9)$ Å, $b = 8.3378(1)$ Å, $c = 8.3465(1)$ Å, $\beta = 93.577(1)°$, and $Z = 8$. Its structure contains isolated BeD_4 tetrahedra and Li atoms that are located in the structure interstices. Li_2BeD_4 does not undergo any structural phase transitions at temperatures down to 8 K.

Introduction

Recent developments in hydrogen power engineering have resulted in a revival of interest in the chemistry of covalent and ionic complex hydrides of light nontransition metals. Special interest is being paid to the compounds with high hydrogen content, which is necessary for its extraction and further use in chemical reactions or for combustion in the fuel elements.[1] A hydrogen capacity which determines the amount of available energy is the second critical value for proposed materials in addition to a cycling performance. From this point of view, the lithium beryllium hydrides are good candidates for hydrogen storage. The hydrogen capacities for the proposed $LiBeH_3$ and Li_2BeH_4 compounds are 15.9 and 15.0 wt %, respectively. Only two known hydrides, namely, BeH_2 and $LiBH_4$, have higher capacities (18.3 and 18.5 wt %, respectively). Although the lightest ternary hydrides could hypothetically be formed in the Li−Be−H system, the synthetic problems and especially difficulties in their structure characterization make this class of compounds extremely hard for investigation.

Different authors reported a formation of four compounds in the Li−Be−H system: Li_2BeH_4, $LiBeH_3$, $LiBe_2H_5$, and Li_3BeH_5.[2,3] However, even the composition of the reported compounds in some cases is an open issue. For example, the X-ray diffraction pattern of $LiBeH_3$, which was first reported by Bell and Coates, has later been attributed to the $\{LiBeH_3\_0.25(C_2H_5)_2O\}$ composition.[3] The formation of $LiBe_2H_5$ and Li_3BeH_5 was not confirmed in any later investigations. The recent systematic investigation of the Li−Be−H system was carried out by Zaluska et al.[4] They claimed the existence of the $Li_3Be_2H_7$ compound; however, no structural confirmation for this conclusion has been given.

A number of attempts to index and solve the crystal structure of Li_2BeH_4 have been undertaken in the past. They all were using either two rather poor quality X-ray powder diffraction data sets published earlier[2,3] or the theoretical calculations based on the same data.[5−7] None of the suggestions for indexing of the X-ray patterns published either by Bell et al. or Ashby et al. were satisfactory.[8] These results often led to the unrealistic values of calculated density for Li_2BeH_4; even a superconductivity at room temperature was

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proposed based on one of these values.[7] The investigations aiming to find a superconductivity in these hydrides are active until now.[9] The first satisfactory lattice determination was presented by our group a few years ago based on X-ray powder data obtained for the Li_2BeD_4 sample placed in the sealed capillary and the $P2_1/c$ space group was proposed based on systematic extinctions.[10] However, at that time we could not find any proper crystal structure solution.

The main problem of the X-ray structural analysis for the compounds with low atomic numbers is their poor scattering ability for the incident X-rays. The intensity of coherently diffracted X-rays is proportional to the square of the atomic number and falls dramatically with a decrease of this value. In our case, all three elements constituting the compound are very light. This causes severe problems for the casual X-ray experiment; in particular, it requires the counting times on the order of days even for the poorest statistics. The natural way out of this complication is the use of neutron diffraction as a complementary technique with another set of scattering lengths of the elements. The scattering lengths[11] of Li, Be, and D for thermal neutrons are as follows: −1.90 fm (i.e., is negative) and 7.79 and 6.67 fm (1 fm = 10^{-15} m); thus, in contrast to the X-ray case, both Be and D are good enough scatterers to easily find them in the structure. The problem of locating the lithium ions is then a final step to be done with the use of an X-ray data set with known positions of beryllium and deuterium atoms.

In this work, we present the crystal structure determination for the Li_2BeD_4 from the combined X-ray and neutron powder diffraction data analysis.

Experimental Section

General Procedures. All complex hydrides, $BeCl_2$, LiH, and their mixtures, are very sensitive to the presence of oxygen, moisture, and vapors of organic compounds. They are readily hydrolyzed and may even flare up when contacting with moist air. Moreover, fine-dispersed beryllium compounds are extremely toxic. Therefore, all synthesis and intermediate manipulations with initial reagents, mixtures, and final products including specimen preparation for the X-ray and neutron investigations were carried out in the glovebox under the atmosphere of dry argon. Phase transformations and exchange reactions were investigated using the hydraulic press under applied force of up to 2000 tons with two Bridgmen-type anvils in a high-pressure (HP) apparatus of the "lens"-type made of lithographic stone.[12]

X-ray powder diffraction (XPD) data were collected on an automated STADI/P diffractometer (Cu Kα_1 radiation, Ge monochromator, Debye−Scherrer mode, scintillation counter). Powder was ground in an agate mortar and placed into the Ar-filled and sealed glass capillary with internal diameter of 1.0 mm. The capillary was mounted on the goniometer head and rotated during the data collection. Experimental data were collected for 7 days because of the low scattering properties of elements. Neutron powder diffraction (NPD) experiment was performed with a high-resolution Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor in Dubna with the instrumental resolution close to $\Delta d/d = 0.0015$.[13] Indexing of the XPD pattern was performed with the Treor[14] program. EXPO[15] and FOX[16] programs were used for structure model construction. The refinement of the crystal structure parameters was carried out with the MRIA[17] and GSAS[18] programs. In the latter case both XPD and NPD data sets were used simultaneously for a fitting procedure. IR spectra were obtained with the Specord-75 spectrophotometer in Nujol and in the KBr pellets. Experimental density of synthesized hydrides and deuterides was determined by the gas bottle method in helium[19] or by a common bottle technique in octane.

Syntheses. Starting materials, LiH and LiD (>98% purity), were purchased from the "Khimreaktiv" company, and preparation of single-phase $BeCl_2$ and $BeH(D)_2$ is described below.

$BeCl_2$ was obtained by treatment of metallic Be by gaseous Cl_2.[20]

$BeH(D)_2$ hydride (deuteride) was synthesized by an exchange reaction between $BeCl_2$ and LiH(D) according to the procedure described in ref 21.

$$BeCl_2 + 2LiH(D) \rightarrow BeH(D)_2 + 2LiCl$$

After this reaction, the products were developed by 5% HCl solution at 0−5 °C for 2−4 h to eliminate chlorides followed by drying in a vacuum at 30−40 °C. Hydrogen content in the BeH_2 was controlled by the volumetric method (hydrolysis of the sample in 10% solution NaOH). In all samples, the determined H(D) content was more than 98% of the theoretically calculated value.

The **$Li_2BeH(D)_4$** compounds were synthesized by two different techniques.

Method 1. The direct interaction between binary hydrides or deuterides was realized:

$$2LiH(D) + BeH(D)_2 \rightarrow Li_2BeH(D)_4$$

The stoichiometric mixture of LiH and BeH_2 (2:1) or corresponding deuterides with an overall sample mass of 5−6 g was intimately ground in a hermetic ball mill for 8−10 h. A powder was pressed into pellets (∼0.5 g) and placed in stainless steel containers. Reaction was carried out at 600 °C for 1 h under 3 GPa pressure as described in ref 22. The phase composition of every

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synthesized sample was checked by X-ray powder diffraction. Ten individual batches with the same XPD patterns were combined, giving totally about 4 g of Li_2BeD_4 for subsequent XPD, NPD, and IR study.

Method 2. Li_2BeH_4 was synthesized by an exchange reaction at the same condition:

$$BeCl_2 + 4LiH(D) \rightarrow Li_2BeH(D)_4 + 2LiCl$$

The starting mixture was treated by the same procedure as in Method 1. In this case, an admixture of lithium chloride was present in the samples.

Results and Discussion

Structure Solution and Refinement. The XPD pattern of Li_2BeD_4 is shown in Figure 1. It was indexed in a monoclinic cell with lattice parameters $a = 7.0969(9)$ Å, $b = 8.374(2)$ Å, $c = 8.384(2)$ Å, $\beta = 93.69(1)°$, $V = 497.2(1)$, and $Z = 8$.[10] No visible admixture peaks were observed. Since the only $h0l$: $l = 2n$ and $0k0$: $k = 2n$ extinction conditions could be deduced from the peak list obtained by pattern fitting, the $P2_1/c$ space group was chosen for structure solution. The correctness of the found indexing solution is confirmed by good agreement of the calculated 0.72 g/cm^3 and measured 0.71 g/cm^3 (for Li_2BeH_4) densities. One should note that the X-ray patterns of Li_2BeD_4 and Li_2BeH_4 are almost identical and the lattice parameters remained unchanged regardless of the starting composition and phases present.

The existence of the $Li_2BeH(D)_4$ hydride was confirmed by our other syntheses in the Li−Be−H system. All samples with this stoichiometry prepared by different synthetic techniques from hydrides or deuterides contained $Li_2BeH(D)_4$ as a main or single phase. The main difference of the present work from the earlier ones was a specimen preparation for X-ray study. We prepared our specimens in an Ar-filled glovebox followed by placement of them in a sealed glass capillary. One should note that samples placed between scotch or foils demonstrated other phase compositions, indicating the decomposition or interaction processes in the substance. Thus, the specimen preparation procedure may be a reason for the discrepancies in the XPD data published earlier by different authors. Indeed, some researchers that investigated earlier the Li−Be−H system did observe the diffraction patterns such as that shown in Figure 1 but the authors did not attribute them to the Li_2BeH_4 compound.[4,23] We did not observe any of the earlier reported $LiBeH_3$, $LiBe_2H_5$, or Li_3BeH_5 compounds. However, some samples with different compositions contained well reproducible peaks which were not attributed to any phases described in the literature. Unfortunately, we failed to identify these unknown phases. In addition to Li_2BeH_4, our preliminary investigation revealed at least three new compounds existing in the Li−Be−H system; some of them actually may be other polymorphs of the Li_2BeH_4 hydride. However, indexing and structure determination for these phases demand a separate study.

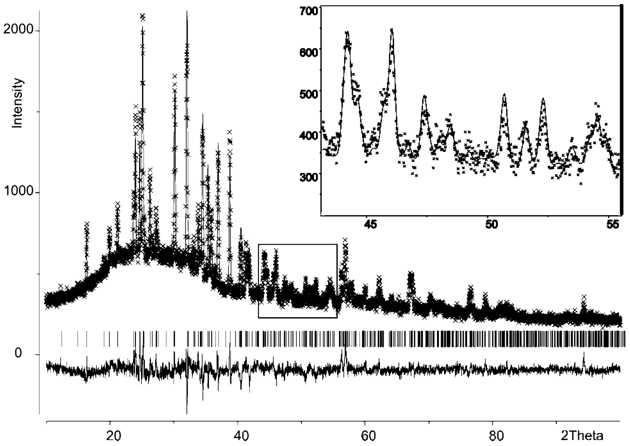

Figure 1. The observed, calculated, and difference XPD patterns for Li_2BeD_4.

Although the X-ray pattern of Li_2BeD_4 was successfully indexed, we failed to find the crystal structure solution using only the XPD data. Therefore, the neutron diffraction data set was collected in order to assess the crystal structure details. Li_2BeD_4 sample of ~3 g mass was prepared by Method 1 for the neutron diffraction experiment. The use of deuterium instead of hydrogen for neutron diffraction study is more suitable because of its much smaller incoherent scattering ($\sigma_{inc,D} \approx 2$ b, while $\sigma_{inc,H} \approx 80$ b), leading to the very high background in diffraction patterns.

The direct methods implemented in the EXPO program complex in application to the neutron diffraction data set were utilized at the beginning of the structure solution process. An intermediate step was converting the HRFD time-of-flight neutron diffraction spectrum into the artificial one in the 2θ scale, as none of the structure solution routines available so far could treat the TOF data. One should note that such a "transformation" is more complicated than just a simple substitution of variables. The crucial point is the proper assignment of the weights to the point-by-point intensities. This "artificial" diffraction pattern was in fact used as a powder pattern in EXPO. The extraordinary resolution of HRFD allowed the program to immediately and reliably locate the BeD_4 tetrahedra in the structure. Similar tetrahedra with the average Be−H separation about 1.4 Å were found in the BeH_2 structure.[24]

The attempt to locate the lithium atoms by direct methods with the neutron diffraction data set was, however, unsuccessful—due to the relatively weak scattering ability of lithium atoms for neutrons. On the other hand, Li atoms are in a comparatively better contrast in the X-ray diffraction case, especially if the BeH_4 tetrahedra are already located in the structure. The next step, therefore, was the use of the ab initio global optimization algorithm implemented in the FOX program and applied to the X-ray data set. The BeD_4 tetrahedra found in the first step were incorporated in the Li_2BeD_4 unit cell and their positions and orientations were fixed. The positions of four lithium atoms were then found, starting from a completely random configuration.

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Table 1. Summary of Crystallographic Information for Li_2BeD_4

composition	Li_2BeD_4	
formula weight	30.95	
crystal system	monoclinic	
space group	$P2_1/c$ [14]	
a (Å)	7.06228(9)	
b (Å)	8.3378(1)	
c (Å)	8.3465(1)	
β,°	93.577(1)	
volume (Å^3)	490.52(1)	
Z	8	
D_{calc}, g·cm^{-3}	0.838	
Color	white	
μ (cm^{-1})	0.66	
temperature, K	293	
	Data Set	
	XPD	NPD
radiation, wavelength (Å)	Cu Kα_1, 1.5406	
diffractometer	STADI/P, Stoe	HRFD in Dubna
data collection mode	Debey-Scherrer	TOF
2θ (deg) and d-range (Å) used for refinement	10−100	0.8−2.8
number of points	4500	6131
refinement type	Full Profile	
R_{wP}, R_P	0.0669, 0.0530	0.0471, 0.0629
R_{wP}, R_P, χ^2 totals	0.0514, 0.0624, 2.420	

Table 2. Atomic Positions and Displacement Parameters for Li_2BeD_4

atom	x	y	z	100 × U_{eq}, Å^2
Be(1)	0.9652(5)	0.0681(4)	0.7018(4)	1.53(4)
Be(2)	0.4859(5)	0.2090(4)	0.0630(4)	1.53
Li(1)	0.6879(11)	0.0777(10)	0.4405(9)	3.16(8)
Li(2)	0.1219(9)	0.2136(9)	0.4176(8)	3.16
Li(3)	0.8461(10)	0.0776(10)	0.0923(9)	3.16
Li(4)	0.4128(10)	0.9263(10)	0.2073(10)	3.16
D(1)	0.2122(10)	0.0046(7)	0.3508(8)	3.32(2)
D(2)	0.9714(8)	0.0947(7)	0.8671(7)	3.32
D(3)	0.6432(8)	0.2002(7)	0.9656(7)	3.32
D(4)	0.4379(8)	0.1277(6)	0.5920(8)	3.32
D(5)	0.0018(8)	0.2137(7)	0.6197(7)	3.32
D(6)	0.5421(8)	0.1331(7)	0.2102(7)	3.32
D(7)	0.9030(9)	0.0585(7)	0.3311(6)	3.32
D(8)	0.3326(8)	0.1255(7)	0.9808(7)	3.32

Table 3. Main Interatomic Distances (Å) for Li_2BeD_4

atoms	distance	atoms	distance
Be(1)−D(1)	1.435(7)	Li(2)−D(1)	1.949(10)
Be(1)−D(2)	1.396(7)	Li(2)−D(2)	1.950(9)
Be(1)−D(5)	1.426(7)	Li(2)−D(5)	1.935(9)
Be(1)−D(7)	1.445(7)	Li(2)−D(7)	2.108(9)
Be(2)−D(3)	1.419(7)	Li(2)−D(8)	2.049(9)
Be(2)−D(4)	1.427(6)	Li(3)−D(2)	2.131(9)
Be(2)−D(6)	1.417(7)	Li(3)−D(2)	1.946(10)
Be(2)−D(8)	1.426(7)	Li(3)−D(3)	2.007(9)
Li(1)−D(1)	1.962(10)	Li(3)−D(5)	2.063(10)
Li(1)−D(3)	1.893(10)	Li(3)−D(7)	2.015(9)
Li(1)−D(4)	2.274(10)	Li(3)−D(8)	2.176(10)
Li(1)−D(4)	1.940(10)	Li(4)−D(1)	2.019(10)
Li(1)−D(6)	2.173(9)	Li(4)−D(3)	1.811(10)
Li(1)−D(7)	1.827(10)	Li(4)−D(4)	1.974(10)
		Li(4)−D(6)	1.950(10)

The Rietveld refinement of the Li_2BeD_4 crystal structure was carried out simultaneously for the XPD and the room-temperature NPD (TOF) data sets. Thermal parameters were constrained to equality within the different atom types. The resulting crystallographic parameters, atomic coordinates, and main interatomic distances are given in Tables 1, 2, and 3, respectively. The observed, calculated, and difference NPD patterns for Li_2BeD_4 are shown in Figure 2. The NPD patterns for Li_2BeD_4 taken at 293 K (a = 7.06228(9) Å, b = 8.3378(1) Å, c = 8.3465(1) Å, β = 93.577(1)°, and V = 490.52(1) Å^3) and 8 K (a = 7.0220(1) Å, b = 8.3099(1) Å, c = 8.2751(1) Å, β = 93.260(2)°, and V = 482.09(2) Å^3) are very similar. A refinement of the found structure model with the data set obtained at 8 K confirmed that the structure is kept down to this temperature.

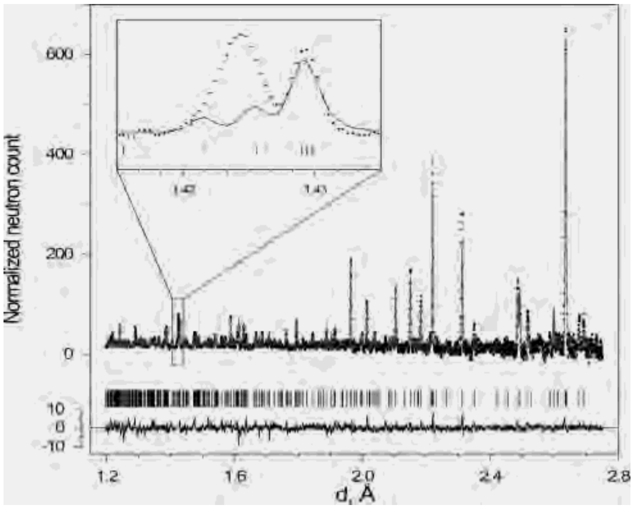

Figure 2. The observed, calculated, and difference NPD patterns for Li_2BeD_4. An insert demonstrates an enlargement of the region where the maximal admixture peak is present. Difference curve is shown in the I/ESD scale.

The fitting of the NPD data revealed a presence of five diffraction peaks belonging to an unknown phase. Therefore, one region containing the maximal intensity peak of admixture was excluded from the NDP data set during the refinement. This strongest peak belonging to the unknown phase is shown in the insert in Figure 2. Four other peaks are less than 10% of the maximal one. However, no admixture peaks were detected on the XPD pattern of the same sample and we could not estimate an amount of this foreign phase. This fact also allows us to suggest that the real amount of the admixture is rather small. Taking into account small d-values and poor statistics of the NPD experiment, these 5 peaks could not be indexed with good reliability. Use of the full NPD data set results only in minor changes of the refined values for the atomic coordinates and in the increase of the reduced χ^2 value from 2.42 to 3.2.

Crystal Structure of Li_2BeD_4. The crystal structure of Li_2BeD_4 is shown in Figure 3. It contains the isolated BeD_4 tetrahedra and Li atoms are situated in the structure interstices. All tetrahedra are close to regular with the Be−D bond lengths of 1.396−1.445 Å. These separations are close to those found in the BeH_2 structure.[24] The rather small splitting of the absorption bands for the Be−H(D) bond vibration on IR spectra for Li_2BeH_4 (1630 and 1700 cm^{-1}) and for Li_2BeD_4 (1180 and 1230 cm^{-1}) indicates the weak distortion of the $BeH(D)_4$ tetrahedra and confirms the correctness of structure solution. A BVS calculation[25] yields a valence of about +2.0 for both Be atoms. Our result

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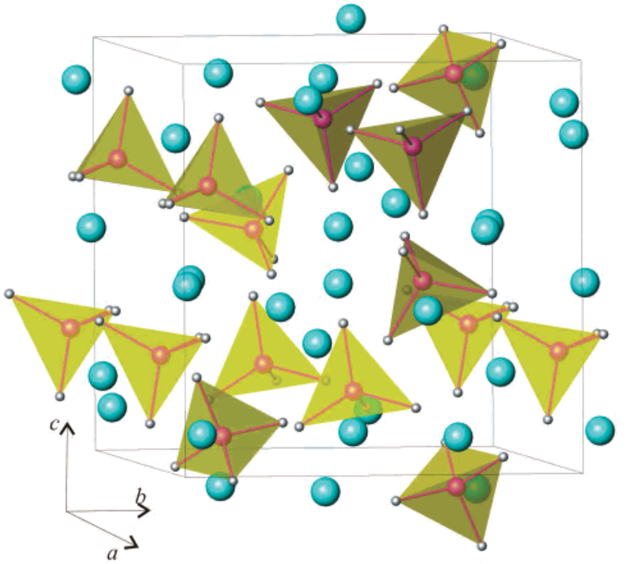

Figure 3. Crystal structure of Li_2BeD_4. Cyan spheres represent Li atoms. Be atoms (red) are situated in the tetrahedra formed by deuterium atoms (gray).

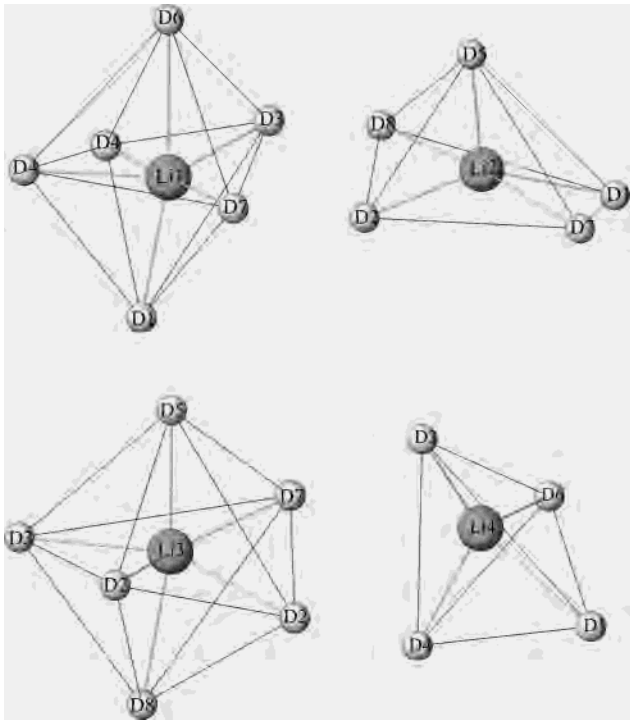

Figure 4. Coordination polyhedra for Li atoms in the Li_2BeD_4 structure.

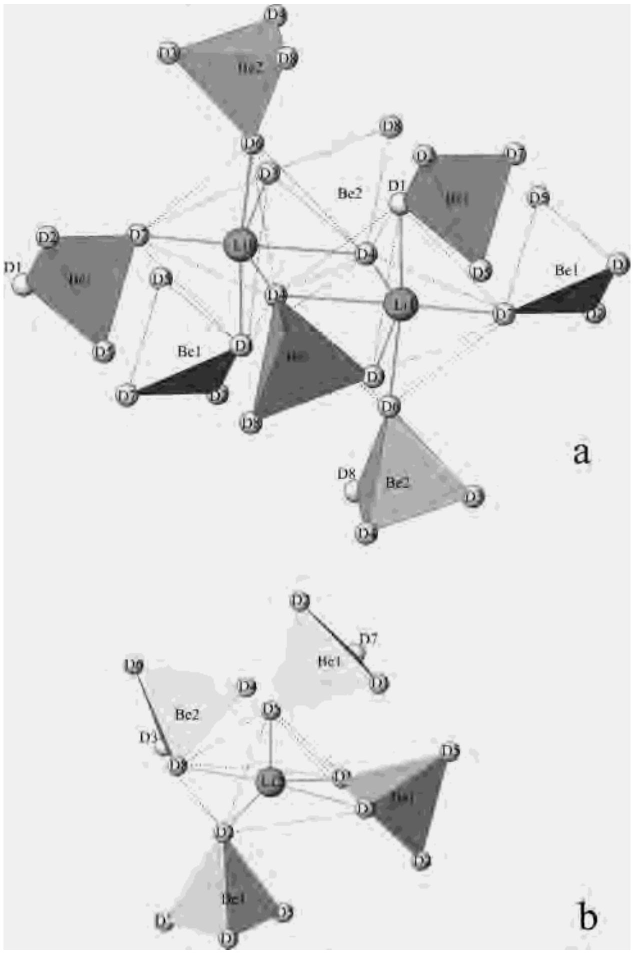

Figure 5. Connections of Li(1) (a) and Li(2) (b) coordination polyhedra with BeD_4 tetrahedra.

confirms a conclusion made by Zaluska et al. that only one type of the Be−H bonding exists in the compound.[4]

Electron localization function[26] (ELF) distribution analysis allows suggestion of the covalent Be−H bonding inside the $[BeH_4]^{2-}$ anions. This bond is undoubtedly highly polarized, similar to that found in molecular BeH_2.[27] No evidence for covalent Li−H interaction was found; therefore, Li^+−$[BeH_4]^{2-}$ bonding is simply ionic.

Coordination polyhedra for lithium atoms are shown in Figure 4. Li(1) and Li(3) are situated in strongly distorted octahedra. The Li−D distances in the $Li(1)D_6$ octahedron are in a range of 1.83−2.27 Å. Two neighboring $Li(1)D_6$ octahedra share the D(4)−D(4) edge, thus forming the Li_2D_{10} dimer (Figure 5a). Six BeD_4 tetrahedra are connected to this dimer via the corners. Additionally, two $Be(2)D_4$ tetrahedra are connected to the same Li_2D_{10} dimer by edge sharing, these edges being formed by D(3) and D(4) atoms. A similar arrangement is realized for the Li(3) atoms. In this case, the octahedra are even more distorted, although the difference in the Li(3)−D separations is noticeably smaller, 1.95−2.18 Å. The $Be(1)D_4$ octahedron shares the D(2)−D(7) edge with the $Li(3)D_6$ octahedron whereas six other tetrahedra are connected via corners. The Li(2) atom is situated in the strongly distorted tetragonal pyramid (Figure 5b). All five Li(2)−D distances are close to each other: 1.94−2.11 Å. One of four BeD_4 groups has common D(7)−D(1) edge with the $Li(2)D_5$ pyramid whereas the other three tetrahedra are sharing corners with it. The tetrahedron with the Li−D distances in the range of 1.81−2.02 Å is the coordination polyhedron for the Li(4) atom. The $Li(4)D_4$ tetrahedron shares all four corners with the BeD_4 tetrahedra.

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Based on the ionic radii ratio, one may expect that the Li_2BeH_4 crystal structure may be close to that of magnesium silicate Mg_2SiO_4. However, the orientation of the SiO_4 tetrahedra and the distribution of the Mg atoms in Mg_2SiO_4 is different.[28] Recently, Toraya and Yamazaki reported the structure of a new modification of calcium silicate Ca_2SiO_4.[29] This structure ($a = 8.2127(5)$ Å, $b = 9.7930(4)$ Å, $c = 9.7954(5)$ Å, $\beta = 94.848(5)°$, $Z = 8$, S.G. $P2_1/c$) is similar to that of Li_2BeD_4. The motif of the silicate groups placement in the unit cell of x-Ca_2SiO_4 is similar to an arrangement of the beryllium hydride groups in Li_2BeD_4. However, the distribution and coordination arrangement of the Ca and Li atoms in these two structures are essentially different. Namely, the pentagonal bipyramid and tetragonal antiprizm are realized for calcium atoms in the silicate structure whereas the octahedron is the maximal coordination for lithium atoms in the structure of the hydride. Nevertheless, in both structures a connection of the tetrahedral group with the A-cation polyhedra via a common edge is present.

Conclusions

The presented crystal structure determination of Li_2BeD_4 is the first reliable result of structure solution for a ternary hydride in the Li−Be−H system. This example demonstrates the power of modern software for the direct structure determinations from powder diffraction data and the advantages of the simultaneous use of neutron and X-ray diffraction data for the structural characterization of compounds in the lightest ternary system, even when the quality of diffraction data is not very high. A painstaking maintenance of synthetic and specimen preparation conditions allowed obtaining the reproducible X-ray diffraction data for Li_2BeH_4 and other investigated compositions.

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Supporting Information Available: Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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