High-pressure phase of $NaBH_4$: Crystal structure from synchrotron powder diffraction data

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The ambient pressure fcc phase of $NaBH_4$ transforms into a tetragonal P-42_1c near 6 GPa and then into an orthorhombic *Pnma* phase above 8 GPa. While the structures of the cubic and tetragonal phases are known, the structural information for the orthorhombic phase was limited to the space group and cell parameters. Here, we present synchrotron powder diffraction data for $NaBH_4$ collected in a diamond anvil cell up to 11.2 GPa. A $BaSO_4$-type structure of the orthorhombic high-pressure phase was solved *ab initio* from diffraction data and refined by the Rietveld method. Both tetragonal and orthorhombic phases show pronounced preferred orientation of crystallites with respect to the compression direction.

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Alkali metal alanates and borohydrides are promising materials for hydrogen storage due to their rather high gravimetric hydrogen contents. Interest in structural studies of these materials has therefore increased significantly during recent years. High-pressure studies of alanates were largely initiated by theoretical prediction of a large volume collapse in high-pressure phases of $LiAlH_4$ and $NaAlH_4$.[1,2] Experimental high-pressure studies confirmed the existence of high-pressure phase transitions in these materials, but failed to confirm the theoretically predicted structures.[3–7] A similar situation seems to prevail as well for high-pressure studies of alkali metal borohydrides: all attempts to predict high-pressure phases theoretically[8–10] were so far unsuccessful, since the predicted structures were not confirmed experimentally.[11–13] The reason for such poor agreement is not quite clear at the moment. Therefore, knowledge of the high-pressure structures of borohydrides could help improve current theoretical methods. Here, we focus our attention on the crystal structure of high-pressure polymorphs of technologically important sodium borohydride.

Sodium borohydride ($NaBH_4$) exhibits a cubic structure (α-$NaBH_4$) under ambient conditions. Experimental studies have shown that it has either the *Fm*-3*m* (Ref. 14) or the *F*43*m* (Refs. 15 and 16) space group. The two models are essentially identical; therefore, the higher symmetry space group *Fm*-3*m* has been commonly accepted for α-$NaBH_4$.[13,14] At low temperature, it shows a phase transition into a tetragonal P-42_1c phase (β-$NaBH_4$).[17] This phase transition is of the first order and occurs at ~186–190 K.[18] According to NMR data, this phase transition is of the order-disorder type.[19] High-pressure studies of $NaBH_4$ were recently reported in several papers. The first study included experimental data on Raman spectroscopy which revealed a phase transition at about 10 GPa, and a theoretical prediction of a monoclinic $P2_1/c$ high-pressure phase.[6,11] This prediction was not confirmed in the subsequent x-ray diffraction study (XRD) by Kumar and Cornelius,[13] who reported two phase transitions: the first one at about 6 GPa into the tetragonal β-$NaBH_4$ phase and the second into an orthorhombic *Pnma* phase at ~8.9 GPa (γ-$NaBH_4$). A later thermal conductivity study further helped map the *P*-*T* boundary between the cubic and tetragonal phases of $NaBH_4$ at low temperature.[20] The transition from cubic into tetragonal phase was also observed in a study by Sihachakr *et al.* at 6.3 GPa, but they could not detect any other phase transition up to 85 GPa.[21] The structure of the γ-$NaBH_4$ phase has remained unknown. In this study, we report the structure of the *Pnma* γ-$NaBH_4$ phase solved *ab initio* from synchrotron powder diffraction data.

The powder of $NaBH_4$ (98% purity) was purchased from Sigma-Aldrich. The sample was loaded into a 200 μm hole drilled in a stainless steel gasket and placed into a Merril-Bassett modified diamond anvil cell with flat culets of diameter 600 μm. All manipulations were done under a high purity argon atmosphere. Ruby was used for pressure calibration. No pressure-transmitting medium was used due to the high reactivity of the sample material. Pure $NaBH_4$ provided good quasihydrostatic conditions up to 10 GPa, as could be seen from the very small broadening of the ruby fluorescence peaks and the narrow diffraction lines of $NaBH_4$. XRD patterns were recorded at the Swiss-Norwegian Beam Lines (SNBL) of ESRF at the wavelength $\lambda = 0.711\,36$ Å using a MAR345 image plate detector.

Our preliminary XRD data recorded upon compression confirmed the study of Kumar and Cornelius.[13] Therefore, in this work the low-pressure range was omitted and the experiment was started from 8.8 GPa. At this pressure, a mixture of tetragonal and orthorhombic phases was observed. The pressure was further increased in a few steps up to 11.2 GPa. The XRD pattern from the pure orthorhombic phase was recorded at 11.2 GPa and analyzed in detail. All the diffraction peaks are consistent with the *Pnma* space group. The high quality of the diffraction data allowed us to solve the structure *ab initio* using FOX (Ref. 22) starting from Na atoms and rigid BH_4 tetrahedra as building blocks. For the successful solution of the structure, it was absolutely essential to model a texture, including one parameter (March-Dollase model) in the global optimization. The three main axes of the orthorhombic cell were tested as directions of the preferred orientation. The structure was solved with most *a* axes approximately aligned with the compression direction. The structure was refined by the Rietveld method with FULLPROF (Ref. 23) using 72 reflections, 18 intensity-dependent refined parameters, and 7 soft restraints defining an approximately tetrahedral BH_4 geometry. The Na^+ ion was refined anisotropically.

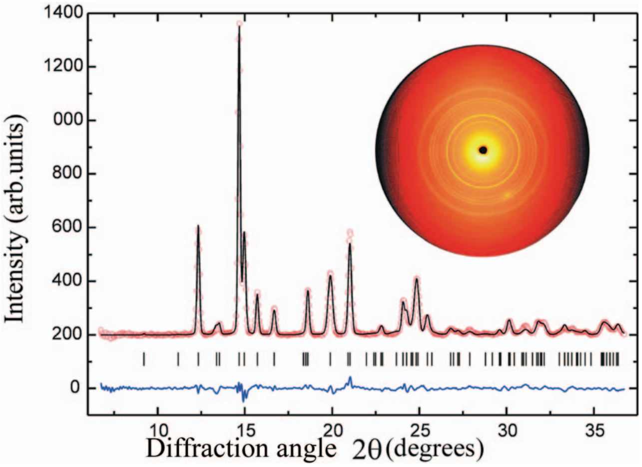

FIG. 1. (Color online) Background-subtracted Rietveld refinement profile for the *Pnma* phase of $NaBH_4$ at 11.2 GPa. A raw two-dimensional image is shown in the inset. $\lambda = 0.711\,36$ Å.

The preferred orientation was refined in the March-Dollase model to 1.61(1). Anisotropic line broadening was modeled by two-parameter orthorhombic strain in the *ab* plane. During the refinement, the background was modeled by interpolated points (the highest peak-to-background ratio was about 1), but for the presentation purposes (see Fig. 1), it has been subtracted. The refinement converged at $R_B = 7.9\%$, $R_F = 6.0\%$, $R_p = 13.3\%$, and $R_{wp} = 8.82\%$. Atomic and cell parameters are listed in Table I, and the fit to the experimental data is shown in Fig. 1. Elimination of the correction for the preferred orientation leads to an increase in R_B from 7.9% to 45%. That means that not only the structure solution but also the refinement would fail if we did not take the texture into account. It is worth noting that elimination of hydrogen atoms increases R_B from 7.9% to 17%, thus showing that their contribution to x-ray diffraction intensities is sufficient for localization of H atoms even from high-pressure synchrotron data.

The *Pnma* phase has a $BaSO_4$-type structure (see Fig. 2). This structure type rarely occurs in the family of light metal hydrides. It has been found only for ambient pressure phases of $KAlD_4$ and $KGaD_4$.[24] Neither the $BaSO_4$-type structure nor the tetragonal $NaBH_4$ polymorph has been predicted by theory.[11] Instead, a transition from cubic to monoclinic α-$LiAlH_4$-type structure ($P2_1/c$) was predicted at 19 GPa, and then to orthorhombic $LiBH_4$-type structure (*Pnma*) at 33 GPa.[11] These two structures have not been observed experimentally. Moreover, the latter structure type is unlikely to appear even at higher pressures, since the coordination number (CN) for the Na atom would be smaller than in the lower-pressure phase (4 in the $LiBH_4$ type structure against 6 in *Fm*-3*m*, P-42_1c, and *Pnma* phases); usually, increased pressure favors phases with higher CN. It is important to note that orthorhombic $LiBH_4$ is sometimes erroneously attributed to the $KGaH_4$ ($BaSO_4$) structure type.[25] These two structure types have the same symmetry and Wyckoff sequence and similar unit cell volumes. Nevertheless, they differ significantly with respect to the coordination numbers of the cations' and the anions' sites (CN=6 with octahedral coordination for the $BaSO_4$-type structure and CN=4 with tetrahedral coordination in $LiBH_4$).

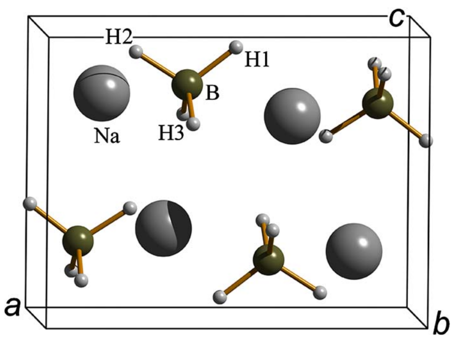

FIG. 2. (Color online) Crystal structure of γ-$NaBH_4$, space group *Pnma*.

In the orthorhombic γ phase, the Na atom is surrounded by six borohydride anions at Na-B distances of 2.763(3)–2.849(3) Å. They are slightly shorter than Na-B distances in the P-42_1c β phase at 10 K (2.93–3.06 Å) and in the cubic $NaBH_4$ α phase at ambient conditions (3.07 Å).[16] H2 and H3 atoms form nine short contacts Na-H at 2.09–2.35 Å and H1 atom forms three longer contacts at 2.48–2.52 Å. Thus, with respect to hydrogen atoms, CN for Na is 12, and BH_4 units are connected to Na^+ cations via tetrahedra edges. The same CN is observed in the tetragonal and cubic structures (Na-H, 2.44–2.59 and 2.58 Å, respectively). The BH_4 units are very close to the tetrahedral geometry, with B-H distances centered on 1.17 Å. The shortest H...H distance between BH_4 anions is 2.31 Å.

Decompression data were recorded from 11.2 down to 0.7 GPa. Figure 3 shows that the high-pressure phase transitions in $NaBH_4$ system are completely reversible. At 6.7 GPa, the pattern corresponds to a mixture of orthorhom-

TABLE I. Experimental structural parameters for the high-pressure polymorph of $NaBH_4$.

Structure	Atom	*x*	*y*	*z*	*B* (Å^2)
$BaSO_4$ structure type	Na	0.1540(5)	$\frac{1}{4}$	0.2107(3)	1.96(2)
Pnma, *Z*=4	B	0.5924(3)	$\frac{1}{4}$	0.7841(5)	2.46(15)
a=7.2970(11), *b*=4.1166(5)	H1	0.4676(7)	$\frac{1}{4}$	0.9161(11)	0.5(4)
c=5.5692(7) Å at 11.2 GPa	H2	0.7298(6)	$\frac{1}{4}$	0.8926(12)	0.5(4)
	H3	0.4135(9)	0.9825(8)	0.3363(9)	0.5(4)

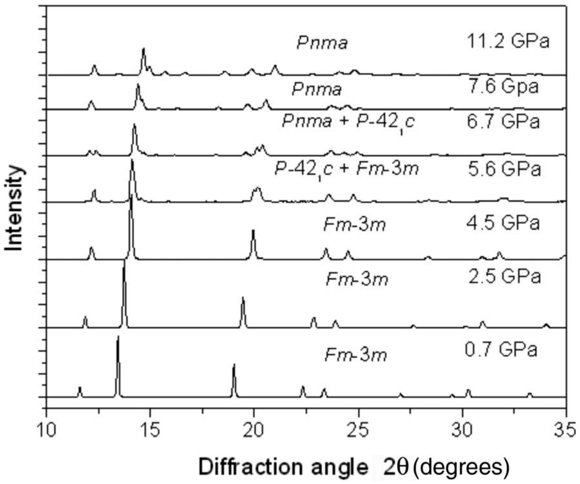

FIG. 3. XRD patterns recorded upon decompression of $NaBH_4$.

bic [43%, a=7.669(3), b=4.1752(7), c=5.7084(8) Å] and tetragonal [57%, a=4.0628(2), c=5.591(1) Å] phases. At 5.6 GPa, the tetragonal $P\text{-}42_1c$ phase was observed as a major component [64%, a=4.0951(2), c=5.6300(9) Å], in coexistence with the cubic phase [36%, a=5.7441(4) Å]. A pure *Fm*-3*m* phase was recovered at 4.5 GPa and lower pressures. Upon a pressure increase, the tetragonal phase appears at 6.3 GPa,[13] suggesting that the corresponding hysteresis should be quite narrow. The coexistence of the two phases confirms the first order character of the cubic to tetragonal phase transition, albeit no discernible volume change has been observed from our data and in Ref. 13. We observed a small volume increase of ~1% upon a transition from *Pnma* to $P\text{-}42_1c$ phase. This is somewhat in contradiction with the volume change by 5.3%, calculated using the experimental equation of state for the *Pnma* phase.[13]

Finally, we comment on the structure of the tetragonal $NaBH_4$ phase. The $P\text{-}42_1c$ structure has not been refined from high-pressure data, but only from low temperature ambient pressure diffraction data.[16] However, another tetragonal structure with $P4_2/nmc$ symmetry has been discussed as a possible high-pressure modification of $NaBH_4$.[25] This structure was reported for KBH_4 at low temperature[26] and may therefore be a prototype structure for $NaBH_4$. Although the $P\text{-}42_1c$ model is generally accepted for β-$NaBH_4$, it is hardly possible to distinguish the two very similar models from diffraction data. We used the $P\text{-}42_1c$ model to fit the data from the two-phase samples and found that the tetragonal phase is also strongly textured: its c axis is preferentially aligned with the compression direction, and the refined texture parameter varies between 1.34(1) and 1.361(7) in the two samples. This may explain why the tetragonal $NaBH_4$ phase has not been refined earlier from high-pressure diffraction data.

In conclusion, high quality synchrotron powder diffraction data were recorded for the orthorhombic high-pressure phase of γ-$NaBH_4$ at 11.2 GPa. Its structure has been solved *ab initio* from diffraction data using a global optimization algorithm. γ-$NaBH_4$ has a $BaSO_4$-type structure, which was already found in light hydrides for the ambient pressure $KAlH_4$. The *Pnma* structure displays a very pronounced in-plane uniaxial texture in which most a axes are approximately aligned with the compression direction. The quality of the diffraction data collected using synchrotron radiation is, therefore, sufficient for both the structure solution and refinement of light borohydrides. This opens up the possibility of further diffraction experiments with finer pressure sampling, where the microscopic mechanism of phase transformations and the pressure dependence of the corresponding order parameters could be evaluated.

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