An extended high pressure-temperature phase diagram of NaBH₄

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We have studied the structural stability of NaBH₄ under pressures up to 17 GPa and temperatures up to 673 K in a diamond anvil cell and formed an extended high P - T phase diagram using combined synchrotron x-ray diffraction and Raman spectroscopy. Even though few reports on phase diagram of NaBH₄ are found in current literature, up to our knowledge this is the first experimental work using diamond anvil cell in a wide pressure/temperature range. Bulk modulus, its temperature dependence, and thermal expansion coefficient for the ambient cubic phase of NaBH₄ are found to be 18.76(1) GPa, -0.0131 GPa K⁻¹, and $12.5 \times 10^{-5} + 23.2 \times 10^{-8}$ T/K, respectively. We have also carried out Raman spectroscopic studies at room temperature up to 30 GPa to reinvestigate the phase transitions observed for NaBH₄. A comparative symmetry analysis also has been carried out for different phases of NaBH₄. © 2009 American Institute of Physics. [DOI: 10.1063/1.3211081]

I. INTRODUCTION

The structural investigation on metal borohydrides or alanates is interesting because of their high gravimetric hydrogen content. Sodium borohydride, NaBH₄, is a potential hydrogen storage material and has a theoretical hydrogen storage capacity of 10.6 wt %. Li *et al.*,¹ demonstrated NaBH₄ slurry as an efficient way of application and generated hydrogen by the simple reaction $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$. Due to strong covalent and ionic bonding nature, dissociation temperatures of borohydrides are very high. The improvement of the hydride properties by catalytic addition requires better understanding of the phases and its phase stability. It is found that hydrogen desorption in NaBH₄ can be enhanced by addition of Pt or Ru.² Under ambient conditions the NaBH₄ has a cubic structure with space group $Fm\bar{3}m$.^{3,4} At low temperatures, below 190 K, NaBH₄ exists in a tetragonal structure.^{5,6} The well investigated high-pressure phases of NaBH₄ at room temperature are of tetragonal- $P\bar{4}2_1c$ and orthorhombic- $pnma$ structure which appears above 6.3 and 8.9 GPa, respectively.⁴ The previous reports suggest that the orthorhombic phase is stable in the pressure range of 8.9–30 GPa. Lee *et al.*⁷ studied the *ab initio* structural stability of cubic and tetragonal phases of NaBH₄ up to 30 GPa and 4000 K but an experimental phase diagram is lacking in the current literature in these ranges. A low temperature phase diagram of NaBH₄ was reported by Sundqvist and Andersson⁶ in the P - T plane of 0–2 GPa and 100–300 K. In the phase diagram reported by Sundqvist *et al.*,⁸ tetragonal to orthorhombic phase boundary of NaBH₄ is marked in the range of 9–11 GPa.

Even though there are many reports on high pressure phase transitions some of them failed to observe a phase transition above 10.8 GPa.⁸ The *ab initio* calculations by

Araujo *et al.*⁹ showed a cubic to monoclinic transition at 19 GPa and to orthorhombic at 33 GPa. Through Raman spectroscopic studies, the same group observed a phase transition in the range of ~ 10.8 –14.8 GPa and a completely new phase was formed above 15 GPa. However the x-ray diffraction (XRD) experiments reported cubic to tetragonal transition at 6.3 GPa and to orthorhombic at 8.9 GPa.^{4,10,11} Because of these inconsistencies in reported transition pressures and phases, we have carried out *in situ* high P - T structural measurements on NaBH₄ both by XRD and Raman spectroscopy using diamond anvil cell (DAC) to obtain further understanding of its stability. Investigation of structural stability under elevated pressure and temperature can assist in the design of suitable storage materials with desired thermodynamic properties.

The high pressure structural behavior of alkali and alkaline earth metal borohydrides is widely investigated. The ambient phase of LiBH₄ which has an orthorhombic ($Pnma$) structure transforms initially into a tetragonal ($Ama2$) at 1.2 GPa and then to a cubic ($Fm\bar{3}m$) phase at 10 GPa.^{12,13} KBH₄ exhibits structural phase transitions from a cubic ($Fm\bar{3}m$) to a tetragonal ($P\bar{4}2_1c$) phase at 3.8 GPa and to an orthorhombic ($Pnma$) phase at 6.8 GPa.¹⁴ High pressure phase transitions of alkali-metal borohydrides are found to be first order and fully reversible. In alkaline earth metal borohydrides, Ca(BH₄)₂ has an orthorhombic structure ($F2dd$) and Mg(BH₄)₂ has a complex hexagonal unit cell with space group $P6_1$ and both of them exhibit polymorphism.^{15,16} Therefore it is interesting to study the structural behavior of metal borohydrides under various conditions of pressures and temperatures.

Filinchuk *et al.*¹¹ found that texture has much influence in the structure refinement of NaBH₄. Theoretically predicted structures of borohydrides (Refs. 17 and 18) are found to be different from that of the experimentally observed ones.^{4,9,15,19} More theoretical and experimental investigations

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are required to explain the inconsistencies in these results. In this work we extend the P - T plane of the experimental NaBH_4 phase diagram from ambient to 17 GPa and 673 K using combined XRD and Raman spectroscopy studies. A comparative symmetry analysis also has been carried out for various phases of this hydride. We also present the results of Raman spectroscopic studies of NaBH_4 up to ~ 30 GPa.

II. EXPERIMENTAL DETAILS

NaBH_4 of 99% purity purchased from Sigma Aldrich was used for the study. All sample handlings were carried out in an argon atmosphere. Mao-Bell-type DAC with diamonds of 0.4 mm culets and steel gasket of 0.18 mm hole was used. For heating experiments resistive ring heater and specially designed K-type thermocouples were employed around diamond culets. For accurate pressure measurement, NaCl and ruby chips were added to the sample. We have conducted experiment with and without mineral oil, a pressure transmitting medium and observed highly nonhydrostatic behavior above 12 GPa in both cases. In the heating experiments no pressure transmitting medium was used.

High temperature compression data at each pressure were collected in various steps between 0.2 and 17 GPa. The high pressure/temperature XRD measurements were conducted at station B2 of Cornell High Energy Synchrotron Source (CHESS) in Cornell University with facilitating radiation of wavelength $\lambda = 0.49594$ Å. Some part of the high P - T diffraction studies was carried out at X17B2 beamline of National Synchrotron Light Source in Brookhaven National Laboratory (energy dispersive, $2\theta = 6.4762^\circ$). The two-dimensional diffraction patterns obtained were integrated using FIT2D software and refined with Rietveld method implemented in GSAS-EXPGUI software package.²⁰ The energy dispersive x-ray spectra were analyzed with PLOT85. Raman spectroscopy experiments were carried out with an argon ion (Ar^+) laser system (Spectra Physics, model 177G02) of $\lambda = 514.5$ nm. Backscattered Raman spectra were collected by high throughput holographic imaging spectrograph (Kaiser Optical Systems, model HoloSpec $f/1.8i$) with volume transmission grating, holographic notch filter, and thermoelectrically cooled charge coupled device detector (Andor Technology). The Raman system has a spectral resolution of 4 cm^{-1} and the spectra were collected at an exposure of 600 s.

III. RESULTS AND DISCUSSION

A. *In situ* high pressure-temperature x-ray diffraction

The synchrotron diffraction patterns of NaBH_4 were refined with Rietveld analysis and the obtained lattice parameter for the ambient phase $a = 6.107(0.2)$ Å ($V = 227.83$ Å³) at 0.2 GPa is in agreement with the reported value.⁴ Figure 1 shows the indexed synchrotron XRD pattern of cubic NaBH_4 with the results of Rietveld analysis. In the cubic phase the Na atoms occupy $4a$ sites at (0,0,0) and B atoms at $4b$ (0.5,0.5,0.5) positions, whereas the H atoms occupy $32f$ sites with coordinates $x = 0.400264$. The orientationally disordered $(\text{BH}_4)^-$ tetrahedral units are octahedrally surrounded by Na^+ cations facilitating ionic nature for the

FIG. 1. Synchrotron XRD pattern of the cubic phase of NaBH_4 collected at 0.8 GPa and room temperature with the results of Rietveld analysis. The peak positions marked as “a” (green) correspond to that of NaBH_4 and those marked as “b” (pink) are of NaCl.

compound. Figure 2 shows the selected XRD patterns collected at different pressures/temperatures. The cubic structure is stable below 6.5 GPa and further increase in pressure causes splitting of (200), (220), and (311) lines which indicate a transition to tetragonal phase. XRD pattern collected at 9 GPa shows appearance of many new peaks which correspond to an orthorhombic phase. The tetragonal phase at 6.5 GPa transformed back to cubic phase when temperature was increased to 373 K and the compression increases this transformation temperature.

For the cubic- NaBH_4 , the pressure-volume-temperature (P - V - T) data were fitted with the third order Birch-Murnaghan equation of state (EOS) using EOSFIT (Ref. 21) and the value of the bulk modulus (K_0) is found to be 18.76(1) GPa with its pressure derivative $K'_0 = 3.48(0.3)$ and equilibrium unit cell volume $V_0 = 231.817(0.9)$ Å³. We have also determined the temperature derivative of bulk modulus and thermal expansion coefficient for the ambient phase and the obtained values are $dK/dT = -0.01307$ GPa K⁻¹ and $\alpha = 12.5 \times 10^{-5} + 23.21 \times 10^{-8}$ T/K, respectively. Figure 3 shows a comparison of P - V data at 298 and 573 K with the previously reported data at room temperature by Kumar and Cornelius.⁴ At low pressures below 2 GPa our data show a slight deviation from the latter which can be due to an error in pressure determination due to a buildup of anisotropic stress.⁶ The obtained value of K_0 for cubic phase is in agreement with the 19.9 GPa reported by Kumar and Cornelius.⁴ They also reported that the bulk modulus of orthorhombic- NaBH_4 is 31.1 GPa. The ambient cubic phase of NaH and its high pressure phase have a bulk modulus of 19.4 and 28.3 GPa, respectively.²² It suggests that the boron addition to NaH does not have much influence on its compressibility. The calculated values of K_0 for cubic and tetragonal phase of NaBH_4 are 20.6 and 30.9 GPa, respectively, at 0 K.¹⁰ First principles calculations by Vajeeston *et al.*²³ show a K_0 of 7.6 GPa for the NaBH_4 , which is much lower than all other reported values. The bulk modulus of several other borohydrides also has been investigated and among that

FIG. 2. Selected XRD patterns of NaBH_4 : (a) the cubic (3.4 GPa), tetragonal (6.5 GPa), and orthorhombic (9 GPa) phases at room temperature (b) at various temperatures and 6.5 GPa. Between 323 and 373 K, tetragonal to cubic phase transition occurs. Peaks marked as * are of NaCl, which was used to determine pressure in the experiment.

LiBH_4 has bulk modulus in the range of 14.4–26 GPa for three different phases.¹³ For KBH_4 which exhibits high pressure phase transitions similar to that of NaBH_4 , the K_0 is found to be 16.8 GPa.¹⁴ The $\alpha\text{-Ca}(\text{BH}_4)_2$ and the high pressure phase of $\text{Mg}(\text{BH}_4)_2$ have bulk modulus of 22.9 and 10.16 GPa, respectively.^{24,15} It is interesting to note that all these borohydrides have bulk modulus in the same range and they are highly compressible.

We have noted the transition points for NaBH_4 at various

FIG. 3. Pressure dependence of the unit cell volume (circles) for the high-pressure phase of cubic NaBH_4 during compression at room temperature and at 573 K fitted with third order Birch–Murnaghan EOS (line) in comparison with the P - V data reported by Kumar and Cornelius (Ref. 4) (asterisks).

pressures and temperature to form a P - T phase diagram. Figure 4 shows the phase diagram of the NaBH_4 in the pressure range of 0–17 GPa and temperature range of 175–673 K. The phase boundaries are obtained by heating at almost constant pressure. The cubic phase is found to be stable up to 673 K and ~ 6 GPa. On increasing pressure at room temperature, the cubic- NaBH_4 transforms to tetragonal phase at

FIG. 4. P - T phase diagram of NaBH_4 investigated through DAC technique using combined XRD and Raman spectroscopic measurements (circles) including the results of low temperature study of Sundqvist and Andersson (Ref. 6) (asterisks). The phase regions marked as C, T, O, and M are cubic, tetragonal, orthorhombic, and monoclinic respectively. The “?” mark implies that the structure is not confirmed.

FIG. 5. Selected Raman spectra of NaBH_4 (a) at different pressures, and the spectrum marked as “?” corresponds to the appearance of a new phase, and (b) at 9.5 GPa and at various temperatures in comparison with a spectrum at 3 GPa. The peak marked as * is due to impurities of diamond in DAC.

6.5 GPa and back transforms to cubic at 373 K [Fig. 2(b)]. The phase transitions observed in NaBH_4 are found to be reversible with increase in temperature or decrease in pressure with some hysteresis. We have incorporated the available low temperature P - T data from Sundqvist and Andersson⁶ in our phase diagram, which is compatible with the current results. The cubic to tetragonal structural transition with a narrow phase boundary compared to that of tetragonal to orthorhombic transition implies that entropy of cubic phase is comparable to that of tetragonal phase. A large slope observed for the cubic-tetragonal phase boundary thus can be correlated with a significant volume change according to Clapeyron equation, $dT/dP = \Delta V/\Delta S$. The molar volumes of cubic, tetragonal, and orthorhombic phases are found to be 34.3, 28.14, and 26.11 cm^3/mol , respectively, and suggest a larger slope for the cubic-tetragonal than the tetragonal-orthorhombic phase boundary.

In the cubic- NaBH_4 , bond lengths are found to be 1.208–1.709, 1.047, 3.03, and 2.57 Å for H–H, B–H, Na–B, and Na–H, respectively, at 0.8 GPa. Except Na–H bonds all the other bonds are highly compressive. On increasing pressure from 0.8–3.8 GPa, Na–H and B–H bonds exhibit 1.45% and 22% compression, respectively. Hence we may expect that the distortion in $(\text{BH}_4)^-$ tetrahedra can cause the phase transitions. The H–B–H and B–H–H bond angles remain unchanged in this pressure range while Na–H–B and H–Na–H

angles diverge/converge. The coordination number and geometry of coordination polyhedra vary with pressure and temperature leading to phase transition.

B. In situ high pressure Raman spectroscopy

Figure 5 shows the Raman spectra of NaBH_4 at some selected pressures and temperatures in the B–H stretching region (2100 – 2500 cm^{-1}). B–H bending modes (1100 – 1300 cm^{-1}) overlap with the Raman peak due to diamond in DAC and hence we have excluded them from further analysis. According to our Raman spectroscopy results phase transitions occur at ~ 6.3 and 8.3 GPa to tetragonal and orthorhombic structures, respectively. No new Raman peaks emerged in the cubic to tetragonal transition except a slope change in some Raman modes. There is a new peak appearing at ~ 8.3 GPa indicating tetragonal to orthorhombic phase transition. The cubic-tetragonal transition is an order-disorder transition which was also observed at ~ 190 K.⁶ Again a new phase starts to appear above 14 GPa and form a completely new phase at 17 GPa and it is stable up to 30.4 GPa [Fig. 6(a)]. At each pressure, a rise in temperature reversed the transition, as can be observed from Figs. 5(b) and 6(b). It may be possible that the new phase is not distinguishable in XRD patterns as above 14 GPa the XRD patterns are much broader and weak, which makes it difficult to identify any splitting of peaks. Above 14 GPa the

FIG. 6. Some selected Raman spectra of NaBH_4 (a) during compression in the range of 14–30.4 GPa, (b) at 14 GPa and various temperatures, and (c) during decompression.

relative intensities of the peaks change to that of a monoclinic $\alpha\text{-LiAlH}_4$ ($P2_1/c$)-type phase.²⁵ We have not observed any anomalies in Raman shift below 3 GPa as reported by Araujo *et al.*⁹ Figure 6(c) shows Raman spectra collected at various pressures during decompression. A large hysteresis (~ 3 GPa) is observed in the reverse transition of orthorhombic phase at room temperature. The experimentally observed B–H stretching mode frequencies for all the four phases of NaBH_4 are presented in Table I. The Raman mode present at 754 cm^{-1} in the spectra of cubic phase was not present in that of the high pressure phases. We could not accurately determine the B–H bending mode of $\sim 1278\text{ cm}^{-1}$ at high pressures because of its overlap with the Raman peak of diamond from DAC.

The observed transitions are much clear from the plot of Raman shift with pressure (Fig. 7). It is found that the pressure induced shift in Raman peaks arises from the bond compression and the energy storage exerted by compressive stress.²⁶ Raman modes increase/stiffen the vibration with compression of bond under pressure, whereas the bond expansion softens the vibration. There is a correlation between B–H stretching frequencies and B–H bond length and energy. In the tetragonal phase the stiffening of bond due to compression is absent, whereas all other phases have shift in Raman mode frequency. This can be related to the bond re-ordering under pressure accompanied with the transition of an orientationally disordered cubic to an orientationally ordered tetragonal phase. For a hydrogen bonded B–H stretch-

TABLE I. The observed B–H stretching Raman modes in cm^{-1} (sh—shoulder) for different phases of NaBH_4 .

0 GPa		6.3 GPa		9.1 GPa		17.2 GPa	
Cubic		Tetragonal		Orthorhombic		Monoclinic	
2205.77		2286.62		2311.57		2368.12	sh
2236.77		2335.59	sh	2356.74	sh	2408.61	sh
2331.7	sh	2384.34	sh	2407.54		...	
...		...		2436.89		2452.84	sh
2335.66		2426.13	sh	2450.44	sh	...	
2350.73		2430.05		2475.74	sh	2491.05	
...		...		2492.85		2534.12	sh
2461.91	sh	2512.4		2533.68	sh	2613.65	sh
...		...		2591.52	sh	2671.24	sh

FIG. 7. The Raman shift vs pressure obtained by peak fitting of B–H stretching modes at each pressure (a) during compression and (b) decompression. Pressures that correspond to phase transition are marked with grid lines parallel to the y axis.

ing mode, a positive pressure dependence may be explained by H–H repulsion under compression.²⁷ A change in slope of at least three peaks and an appearance of a new peak during compression confirm the transition of orthorhombic to another high pressure phase observed in the range of 14–17 GPa. The decompression data [Fig. 7(b)] show that the phase

transitions that occurred are reversible with a hysteresis, which supports the observation of Sundqvist *et al.*⁸ We could not distinguish an orthorhombic to tetragonal transition from the decompression data which can be due to the hysteresis on the reverse transition of orthorhombic phase. Table II gives the change in slopes of Raman shift versus pressure during compression, which indicates that there are four high pressure phases of NaBH₄ which exist in the range of 0–30 GPa at room temperature. First principles calculations by Araujo *et al.*⁹ found a cubic to monoclinic ($P2_1/c$) phase transition at 19 GPa while their experimental Raman spectra at 14 GPa are very similar to that of the orthorhombic phase as observed in our Raman studies. Calculations of Kim *et al.*¹⁰ and experiments of Kumar and Cornelius⁴ found that orthorhombic phase is stable up to 30 GPa. The compression data of Araujo *et al.*⁹ show a complete transition to an orthorhombic phase at 14.8 GPa which reverse transform to low pressure phase at 7 GPa on decompression. This result deviates from our observations of transition pressures of 8.3 and 5 GPa for forward and reverse transitions of orthorhombic phase, respectively. The difference in the measured pressures might be the reason why they have missed the phase transition above 14 GPa in their Raman spectroscopic study up to 16.2 GPa.

C. Correlation of site group to factor group and Raman activity

To identify the Raman active vibrational modes of different phases of NaBH₄ we have carried out factor group analysis.^{28,29} The total irreducible representation of cubic (Oh^5) phase of NaBH₄ is found to be $\Gamma_{\text{tot}} = A_{1g} + A_{2u} + E_u + E_g + T_{2u} + 2T_{2g} + 4T_{1u} + T_{1g}$ which suggests that it has 30 degrees of vibrational freedom among which T_{1u} is an acoustical mode and A_{1g} , E_g , and T_{2g} are Raman active modes. Therefore there should be four fundamental vibrational modes in the Raman spectra of cubic phase of NaBH₄. Tetragonal (D_{2d}^4) phase with $\Gamma_{\text{tot}} = 3A_1 + 3A_2 + 5B_1 + 5B_2 + 10E$ has 36 degrees of vibrational freedom among which B_2 and E are acoustical modes and A_1 , B_1 , B_2 , and E are Raman active modes. This implies that there should be 21 fundamental vibrational modes in the Raman spectra of tetragonal phase of NaBH₄. Further the orthorhombic phase of (D_{2h}^{16}) NaBH₄ has $\Gamma_{\text{tot}} = 9A_g + 6A_u + 6B_{1g} + 9B_{1u} + 9B_{2g} + 6B_{2u} + 6B_{3g} + 9B_{3u}$ and 60 degrees of vibrational freedom among which B_{1u} , B_{2u} , and B_{3u} are acoustical modes and A_g , B_{1g} , B_{2g} , and B_{3g} are Raman active modes. It gives 30 fundamental vibrational modes in the Raman spectra of orthorhombic phase of

TABLE II. The pressure derivative of Raman shift for NaBH₄ at different pressure ranges.

ν (cm ⁻¹)	Compression $d\nu/dp$ (cm ⁻¹ GPa ⁻¹)			Decompression $d\nu/dp$ (cm ⁻¹ GPa ⁻¹)	
	0–6.3 GPa	8.3–17 GPa	17.5–28 GPa	5.2–13.6 GPa	14.2–26 GPa
2200	11.51(1)	8.2(7)	7.56(3)	9.9(0.5)	6.23(0.4)
2300	13.82(2)	8.88(2)	11.45(8)	12.97(0.8)	6.05(0.7)
2340	15.93(1)	13.32(3)	11.97(9)	14.66(0.6)	...
2400	...	10.39(1)	...	16.04(2)	6.07 (0.6)

NaBH₄. If we assign a monoclinic $P2_1/c$ structure (C_{2h}^5) to the NaBH₄ phase which appeared above 14 GPa in comparison with the theoretical prediction of Araujo *et al.*,⁹ it has 24 degrees of vibrational freedom ($\Gamma_{\text{tot}}=3A_g+9A_u+3B_g+9B_u$) and among which A_u and B_u are acoustical modes and A_g and B_g are Raman active modes. Therefore there should be six fundamental vibrational modes in the Raman spectra of monoclinic phase of NaBH₄. The observed Raman spectra are in agreement with the results of the factor group analysis which shows an increment in degrees of vibrational freedom and number of Raman active modes with pressure from cubic to tetragonal and to orthorhombic phase transitions and then a drop at the formation of a new phase. Therefore we conclude that the high pressure phase observed above 14 GPa can be of monoclinic structure with space group $P2_1/c$ as showed by calculations of Araujo *et al.*⁹ The theoretically predicted monoclinic phase is observed through Raman spectroscopy unlike in XRD because of its ability to distinguish small traces of various local phases coexisting in a compound.³⁰

IV. CONCLUSIONS

Phase diagram of NaBH₄ has been constructed to an extended pressure and temperature range with combined synchrotron XRD and Raman spectroscopy. It can be concluded that at room temperature there are four different phases of NaBH₄ that exist in the pressure range studied. The phase observed above 14 GPa may be a monoclinic phase as reported by theoretical calculations. P - V - T data of the ambient phase was fitted with third order Birch–Murnaghan EOS and the value of bulk modulus is found to be $K_o=18.76(1)$ GPa with its pressure derivative $K'_o=3.48(0.3)$ and equilibrium unit cell volume $V_o=231.817(0.9)$ Å³. The temperature derivative of bulk modulus for the ambient phase of NaBH₄ is $dK/dT=-0.013\ 07$ GPa K⁻¹ and its thermal expansion coefficient is $\alpha=12.5\times 10^{-5}+23.21\times 10^{-8}$ T/K.

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