Structural study of ball-milled sodium alanate under high pressure

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ABSTRACT

Ball-milled NaAlH₄ was studied up to 15 GPa in a diamond anvil cell (DAC) by X-ray diffraction using a synchrotron radiation source. Lattice parameters were determined from the X-ray diffraction data at various pressures up to 6.5 GPa. Intensity of the powder diffraction patterns decreased with increasing pressure. Amorphisation started at a pressure of ~6.5 GPa and completed at 13.5 GPa. Reversible phase transformation from amorphous phase to the tetragonal phase was observed. A fit to the pressure–volume data equation of state was obtained using the Birch–Murnaghan equation of state and the bulk modulus was found to be 52.16 ± 0.9 GPa which is twice higher than the unmilled NaAlH₄.

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1. Introduction

NaAlH₄ has been proposed as a viable hydrogen storage media capable of supplying hydrogen at moderate temperatures and at rates required for fuel cell applications. These favorable characteristics, particularly the reversibility of NaAlH₄ as a hydrogen storage media, were reported first by Bogdanovich et al. [1] and was immediately followed by extensive study of related complex metal hydrides by a number of researchers [2–6]. Reversibility and enhanced desorption kinetics were clearly demonstrated for NaAlH₄ when doped with titanium and other transition metals [1–5]. Phase transitions and crystal structure modifications have been studied during the thermal decomposition of NaAlH₄ [7,8]. Enhanced desorption kinetics were clearly demonstrated for NaAlH₄ doped with Ti and/or Zr catalyst [9–11]. *Ab initio* calculations by projected augmented plane wave method indicate that NaAlH₄ undergoes a phase transformation from tetragonal structure with space group *I*4₁/a, i.e., SrMgH₄-type structure to the β -orthorhombic (*Cmc*2₁) structure at 6.43 GPa with a 45% volume contraction [12]. It was also suggested that the β -NaAlH₄

stores more hydrogen volumetrically than the α -phase and would, if stabilized at ambient conditions, be an interesting candidate for further studies with regard to hydrogen absorption/desorption efficiency. Recently Talyzin and co-worker [13] performed high pressure Raman measurements up to 17 GPa on NaAlH₄. They reported two possible phase transformations: one at ~3 GPa which was less obvious as a structural transformation, and a second at ~12 GPa to the orthorhombic structure. Our previous X-ray measurements on commercially available NaAlH₄ showed the phase transformation to β -NaAlH₄ phase with orthorhombic structure which is in agreement with the predicted structure by Vajeeston et al. [12] followed by amorphisation at ~13.6 GPa [14].

In comparison, the related hydride LiAlH₄ has a monoclinic structure at ambient conditions with space group *P*2₁/*c* and undergoes a slow phase transition from an α -cubic to a β -phase. This transformation has been reported to occur between 2.2 and 3.5 GPa [15]. Alternatively, NaBH₄ under pressure shows a phase transformation from α -cubic to β -tetragonal structure starting at 5.4 GPa with an orthorhombic phase stabilized at pressures above 8.9 GPa [16]. An electronic structure study by *ab initio* calculation indicated that the primary change corresponds to a narrowing of the band gap in α -NaBH₄, caused by broadening of sodium antibonding states in the conduction band [17]. In case of ammonia borane complex (NH₃BH₃), two pressure-induced structural transitions were observed in this solid, in contrast to the temperature behavior where a single transition occurs. Raman spectra of NH₃BH₃ was

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studied up to 4 GPa and it was found that the vibrational modes involving the NH_3 group show negative pressure dependences, but the vibrations of the BH_3 group have a positive dependence supporting the existence of the dihydrogen bond [18].

It has been shown that ball milling improves the hydrogen storage properties of hydrides including NaAlH_4 [2–5,19,20]. The enhanced hydrogen sorption properties of hydrides, in general, after ball milling has been attributed to: (i) the formation of a large amount of oxide-free surface, (ii) the reduction in grain size, and (iii) the introduction of lattice defects [21]. Milling essentially results in increasing the surface to bulk ratio, increasing grain and fault boundary densities that assist diffusion and the rate of H_2 sorption. Therefore, it would be of great interest to study mechano-chemically milled NaAlH_4 to understand the effect of milling on the structural behaviour using high-pressure methods. In this paper, micro X-ray diffraction measurements were carried out using a synchrotron source under pressure up to 15 GPa.

2. Experimental

NaAlH_4 (99% purity from Sigma–Aldrich) was ball-milled for 60 min in a Spex 8000 ball mill vial with 6.35 mm and 12.7 mm stainless steel balls at room temperature under a dry argon atmosphere. Milling typically resulted in a reduction of particle size without decomposition. The crystal structure and purity of the milled alanate were checked by X-ray powder diffraction using $\text{Cu K}\alpha$ radiation.

The high-pressure X-ray powder diffraction experiments were performed at beamline 16-IDB, HPCAT (High Pressure Collaborative Access Team) of APS (Advanced Photon Source) at Argonne National Laboratory. The monochromatic beam of wavelength 0.45657 Å was focused to approximately $100\text{ }\mu\text{m}^2$ and the data was recorded by a Mar345 image plate. The sample was loaded with mineral oil in a Mao–Bell diamond anvil cell (DAC). A stainless steel gasket of thickness 50 μm and hole size 200 μm served as the sample chamber with a few grains of platinum metal loaded with the sample as a pressure marker. X-ray diffraction (XRD) analysis of the ball-milled sample shows single phase NaAlH_4 having tetragonal structure with space group $I4_1/a$ identical to the unmilled sample. Lattice parameters were determined from Rietveld structure refinement using GSAS with GUI interface [22–24].

In order to determine particle size, lanthanum hexaboride (LaB_6) crystals of particle size 2 μm were used as the standard. XRD pattern of NaAlH_4 (both as-received and ball-milled) and LaB_6 were recorded at the same conditions. Rietveld structure refinement was performed on the angle dispersive X-ray diffraction (ADXRD) pattern of the above-mentioned materials, using GSAS software. Refined value of Lorentzian–Scherrer broadening term in GSAS profile function of LaB_6 was used as an instrumental broadening. This value was subtracted from the corresponding broadening term of the NaAlH_4 samples to determine diffraction line broadening related to the particle size effect.

3. Results and discussion

Lattice parameters of unmilled and milled samples are given in Table 1. Gomes et al. [20] reported decreasing of the unit cell volume and c/a ratio after ball milling which is in agreement with our results. These observations can be attributed to the increase of surface to volume ratio in the particles.

Particle size was determined by substituting ‘X’ in the relation [24]:

$$P(\text{\AA}) = \frac{18,000B\lambda}{\pi X}, \quad (1)$$

where B is the Scherrer constant (0.9), λ is the X-ray radiation wavelength, and X is the Lorentzian–Scherrer broadening term in GSAS profile function. From the above equation, particle size of as-received and ball-milled NaAlH_4 samples were found to be

Table 1
Comparison of lattice parameters of the milled and unmilled NaAlH_4

NaAlH_4	a (Å)	c (Å)	c/a	V (Å ³)
Unmilled	5.0428(3)	11.400(1)	2.2606	289.91(2)
Milled	5.0253(3)	11.354(1)	2.2593	286.74(3)

Fig. 1. Comparison of the ADXRD data collected for ball-milled NaAlH_4 for various pressures at room temperature. Note the disappearance of the peaks at 13.5 GPa.

1.08 μm and 715 nm, respectively. It was found that ball milling of the NaAlH_4 decreases the particle size by $\sim 30\%$. Fig. 1 shows the ADXRD pattern of NaAlH_4 collected at various pressures up to 13.5 GPa. Amorphisation of the sample was observed between 12 and 13.5 GPa.

The variation of lattice parameters with pressure up to 6.8 GPa is shown in Fig. 2. It is observed that a and c lattice parameters decrease with increasing pressure with a c/a ratio of ~ 2.2 maintained. It was observed that the amorphisation of the ball-milled sample occurred at approximately 1.5 GPa above that of unmilled NaAlH_4 . Above 6.8 GPa the structural fit could not be obtained due to the broadening and disappearance of all Bragg reflections other than (013) and (112) peaks. This is an indication of the onset of amorphisation of milled NaAlH_4 .

The experimental data were fitted with a third order Birch–Murnaghan equation of state (EOS) [25]:

$$P = \frac{3}{2} K_{300,0} \left[\left(\frac{V_{300,0}}{V} \right)^{7/3} - \left(\frac{V_{300,0}}{V} \right)^{5/3} \right] \times \left[1 - \frac{3}{4} (4 - K'_{300,0}) \left(\frac{V_{300,0}}{V} \right)^{2/3} - 1 \right] \quad (2)$$

where $K_{300,0}$, $K'_{300,0}$, and $V_{300,0}$ are the bulk modulus, its pressure derivative and volume of unit cell at zero pressure and

Fig. 2. Lattice parameters variation with pressure for the ball-milled NaAlH_4 up to 6.8 GPa.

Fig. 3. Birch–Murnaghan equation of state fit obtained for ball-milled NaAlH₄ with K' set to 4.

300 K, respectively. Experimental P – V data were fitted using the Marquardt–Levenberg least square fitting procedure with a commercial sigma plot (SPSS) program. Fig. 3 shows the behavior of relative volume with pressure, where the EOS fit was obtained using the Birch–Murnaghan equation of state with K' constrained to 4. The bulk modulus of ball-milled NaAlH₄ increased from 25.3 ± 1.3 GPa [14] to 52.16 ± 0.9 GPa, which is a surprisingly large positive effect.

4. Conclusion

Lattice parameters were determined by Rietveld refinement and found to be: $a = 4.827(2)$ Å; $c = 10.650(3)$ Å; $c/a = 2.206(3)$; $V = 248.2(2)$ Å³. The intensity of the powder diffraction pattern decreased with increasing pressure. Amorphisation of the sample started at a pressure of ~ 6.5 GPa and was completed at 13.5 GPa. The structure was found to be reversible when the pressure was released. The new phase observed before amorphisation in the case of the unmilled sample (i.e., β -NaAlH₄) [26,14] was absent in the ball-milled sample. A recent report on the X-ray diffraction study of NaAlH₄ indicates a phase transformation to the monoclinic β -phase which corresponds to the amorphisation pressure in our observation. This pressure-induced amorphisation must have been influenced by the presence of mineral oil, which can be explained by the variation of the hydrostatic conditions [27]. We report the absence of high-pressure phases in the ball-milled samples concluded from both the X-ray and Raman experiments. This could be due to the surface state domination of the phase transformation. The increase in the surface area (with strong stress effects) to bulk volume ratio, resulting from ball milling could have forced the system to an amorphous phase, as an easier path during the phase transformation [28,29]. The experiment was repeated two times to check the amorphisation pressure and presence of the high-pressure phase. It was concluded that the ball milling caused changes in the phase transformation pressure by 1.5 GPa and decreased the compressibility by almost a factor of 2. This is caused by the size-induced pressure effect due to larger surface area in the nanophase materials when compared to their bulk. [30,31].

To study the size effect with pressure, milled NaAlH₄ was loaded with mineral oil and the XRD pattern was recorded up to 11.45 GPa.

The pressure was then released to 2 GPa and once again increased to 13.5 GPa in order to observe any changes in the size effect. No high-pressure phase was observed prior to amorphisation contrary to the unmilled NaAlH₄. Hence, we conclude that pressurising the sample to 11 GPa did not have any effect on the particle size.

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References

- [1] B. Bogdanovich, R. Brand, A. Marjanovich, M. Schickardi, M.J. Tolle, J. Alloys Compd. 302 (2000) 36–58.
- [2] C.M. Jensen, R.A. Zidan, N. Mariels, A.G. Hee, C. Hagen, Int. J. Hydrogen Energy 24 (1999) 461.
- [3] R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen, J. Alloys Compd. 285 (1999) 119.
- [4] A. Zaluska, L. Zaluska, J.O. Strom-Olsen, J. Alloys Compd. 298 (2000) 125–134.
- [5] D.L. Anton, J. Alloys Compd. 356–357 (2003) 400–404.
- [6] S. Satyapal, J. Petrovich, C. Read, G. Thomas, Catal. Today 120 (2007) 246–256, therein.
- [7] R.K. Ahluwalia, Int. J. Hydrogen Energy 32 (2007) 1251.
- [8] E.C. Ashby, P. Kobetz, Inorg. Chem. 5 (1966) 1615.
- [9] M.P. Balogh, G.G. Tibbetts, F.E. Pinkerton, G.P. Meisner, C.H. Olk, J. Alloys Compd. 350 (2003) 136–144.
- [10] K.J. Gross, S. Guthrie, S. Takara, G. Thomas, J. Alloys Compd. 297 (2000) 270–281.
- [11] K.J. Gross, G.J. Thomas, C.M. Jensen, J. Alloys Compd. 330–332 (2002) 683–690.
- [12] P. Vajeeston, P. Ravindran, R. Vidy, H. Fjellva, A. Kjekshus, Appl. Phys. Lett. 82 (14) (2003).
- [13] A.V. Talyzin, B. Sundqvist, High Pressure Res. 26 (September (3)) (2006) 165–173.
- [14] R. Selva Vennila, L. George, V. Drozd, S.K. Saxena, Materials Letters (2008) to submit.
- [15] R.S. Chellappa, D. Chandra, S.A. Gramsch, R.J. Hemley, J. Lin, Y. Song, J. Phys. Chem. B 110 (2006) 11088–11097.
- [16] R.S. Kumar, A.L. Cornelius, Appl. Phys. Lett. 87 (2005) 261916.
- [17] C. Moysés Araújo, R. Ahuja, A.V. Talyzin, B. Sundqvist, Phys. Rev. B 72 (2005) 054125.
- [18] S. Trudel, D.F.R. Gilson, Inorg. Chem. 42 (2003) 2814–2816.
- [19] G.P. Meisner, G.G. Tibbetts, F.E. Pinkerton, C.H. Olk, M.P. Balogh, J. Alloys Compd. 337 (2002) 254–263.
- [20] S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M.P. Sulic, C.M. Jensen, J. Alloys Compd. 390 (2005) 305–313.
- [21] R.A. Dunlap, Z.H. Cheng, G.R. MacKay, J.W. O'Brien, D.A. Small, Hyperfine Interact. 130 (2000) 109–126.
- [22] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2000.
- [23] B.H. Toby, J. Appl. Crystallogr. 34 (2001) 210–221.
- [24] A.C. Larson, R.B. Von Dreele, GSAS Manual, Los Alamos National Laboratory, 1985, <http://ftp.lanl.gov/public/gsas>.
- [25] N. Funamori, T. Yagi, T. Uchida, Geophys. Res. Lett. 23 (1996) 953.
- [26] R.S. Kumar, E. Kim, O. Tschauner, A.L. Cornelius, Phys. Rev. B 75 (2007) 174110.
- [27] L.C. Ming, S.R. Shieh, A. Jayaraman, S.K. Sharma, Y.H. Kim, J. Phys. Chem. Solids 60 (1999) 69–81.
- [28] S. Klotz, G. Hamel, J.S. Loveday, R.J. Nelmes, M. Guthrie, A.K. Soper, Phys. Rev. Lett. 89 (2002) 285502–285506.
- [29] Pon, J.M. Leger, J. Haines, L.S. De Oliveira, C. Chateau, A. Le Sauze, R. Marchand, S. Hull, J. Phys. Chem. Solids 2 (60) (1999) 145–152.
- [30] R. Selva Vennila, S.R. Kulkarni, S.K. Saxena, H.P. Liermann, S. Sinogeikin, Appl. Phys. Lett. 89 (2006) 261901–261903.
- [31] Z. Wang, Y. Zhao, D. Schiferl, C.S. Zha, R.T. Downs, T. Sekine, Appl. Phys. Lett. 83 (2003) 3174–3176.