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Baseline Studies on the Effect of Gaseous Impurities on Long-Term Thermal Cycling and Aging Properties of Complex Hydrides for Hydrogen Storage

Low Temperature Neutron Diffraction and High Pressure Experiments on Li – Based Complex Hydrides

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Abstract

Complex alkali hydrides such as $LiAlH_4$ are particularly attractive as potential candidates for hydrogen storage, as $LiAlH_4$ with a very high theoretical hydrogen content of 10.5 wt. %. The reversibility and kinetics of hydrogen absorption/desorption is aided by addition of suitable catalysts [1,2]. Recent a*b initio* calculations [3] have predicted that $LiAlH_4$ transforms from an ambient pressure (α-$LiAlH_4$) monoclinic (*$P2_1/C$*) structure [4] to a high pressure (β-$LiAlH_4$) tetragonal structure (*I41/a*) above 2.6 GPa with a high volume reduction (17%). This phase transformation has been observed experimentally [8] by in-situ high pressure Raman spectroscopy studies is.

In this work, the pressure induced transformation of LiAlH4 have been studied in considerable detail using in-situ high pressure Raman spectroscopy in a Diamond Anvil Cell (DAC) from 0 to 6 GPa. The wavenumber shifts associated with pressure increase suggest a phase transformation at ~3 GPa. For the first time, it is demonstrated that the high pressure phase can be retained at lower pressures (~1 GPa) by "pressure quenching" the sample. However, the current results suggest that the retention of the high pressure phase is favored if the initial pressure increase were performed in step-wise manner.

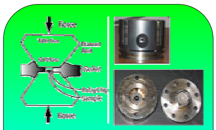
Currently, we are performing baseline studies on the understanding crystal structure behavior starting compounds, such as Li_3N and $LiAlD_4$ using neutron diffraction methods. We have determined the lattice expansions in Li_3N in the range of 10 – 573 K. Lattice expansions in the $LiAlH_4$ have also been determined in the range of 10-300 K.

Experimental

High Pressure In-situ Raman Spectroscopy: Diamond Anvil Cell (DAC) is an apparatus that is used to generate high pressures. The elegant design of the DAC allows for easy modifications to be adapted for in-situ spectroscopy or crystal structure measurements. Raman measurements were performed using the 514.5 nm green lines of an Argon ion laser (Coherent Innova 90). The imaging spectrograph (ISA HR460) with 460 mm focal length f/5.3 and Charge Coupled Device (CCD) detector provided a resolution of 1800 grooves/mm grating. The Raman scattering wavelength was calibrated using Ne lines. The pressure increase was monitored using ruby flourescence shifts using the calibration described by Mao et al.

Material: Pure LiAlH4 powder (95%) was obtained from Aldrich. The powder form was preferred since the sample loading was performed in a glove box (Argon atmosphere) without any pressure transmitting medium. It is not possible to use a volatile pressure transmitting medium such as 4:1 methanol:ethanol inside a glove box. The complete vibrational mode assignment for LiAlH4 was performed and was found to be in close agreement with the literature [5,6].

Experiment No.1 (Step-wise Pressure Increase and Rapid "Pressure Quenching"): The first experiment was to increase the pressure in steps by turning the allen screws. The Raman spectra was obtained after waiting for about 30 minutes after each step increase in pressure to allow the stabilization of pressure. Once a maximum pressure of 5 or 6 GPa was reached, the pressure was decreased rapidly to about ~1.2GPa. The sample was allowed to sit for 3 hours before obtaining the spectra. Three sample runs were performed and for one sample run the quenched sample was held at a constant load for about 6 days.

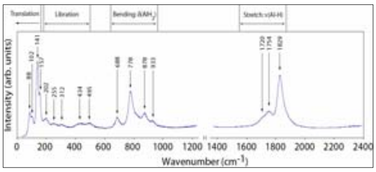


A simplified schematic of the gasketed DAC assembly and the actual DAC that was used to perform high pressure experiments on pure LiAlH4 is shown above. The experiments were performed at the Geophysical Laboratories, Carnegie Institution of Washington DC, a Carnegie-DOE Alliance Center (CDAC).

Experiment No.2 (Rapid Pressure Increase Followed by "Pressure Quenching"): The second experiment was to rapidly increase the pressure to a maximum pressure of about 5 GPa. The Raman spectra was obtained after waiting for about 2 hours after this step. Then the pressure was decreased rapidly in two steps. First it was decreased to about ~1.5GPa and spectra was obtained after 30 mins. In the second step (performed inside the glove box), the pressure was decreased down to ambient pressure. After 30 mins, the spectra was obtained.

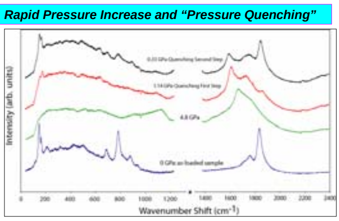
$LiAlH_4$ High Pressure Raman Spectroscopy Results

Raman Spectra of As-loaded $LiAlH_4$ Sample



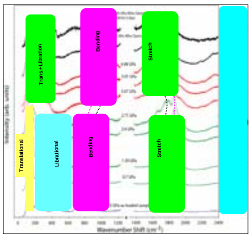
- The resolution of Raman spectra is excellent and low wavenumber translational and librational modes can be observed in the as-loaded sample.
- The complete vibrational mode assignment for ambient pressure α-$LiAlH_4$ is based upon Bureau et al. [7].

Rapid Pressure Increase and "Pressure Quenching"



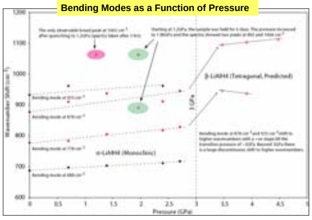
- The sample was pressurized rapidly to 4.8 GPa and then quenched in two steps; first to 1.14GPa and then to 0.33GPa.
- The translational and librational modes are reappearing in the quenched sample. The Al-H stretch modes reappear with broadening (with relative intensity changes) suggesting a reversible transition from β-$LiAlH_4$ to ambient pressure α-$LiAlH_4$ phase.

Step-wise Pressure Increase and "Pressure Quenching"

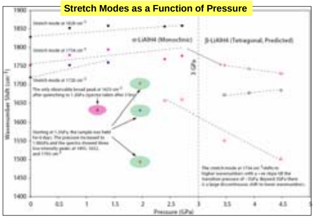


- The Raman Spectra of LiAlH4 as a function of pressure is shown above. Along with the bending modes, the translational and librational modes of LiAlH4 were monitored as a function of pressure.
- Talyzin and Sundquist [7] were unable to monitor the effect of pressure on these low wavenumber modes in their high pressure Raman experiments.
- The librational modes exhibit changes in intensities until 2.4GPa before merging into a broad close to the transformation pressure of 3GPa.At pressures beyond 3GPa, the translational and librational modes merge to form a broad peak.
- This characteristic is retained in the quenched β-LiAlH4 phase;1.2GPa spectra taken after 3 hours and 1.96GPa spectra taken after 6 days (DAC stored in glove box). The increase in pressure of the quenched sample is due to the inherent relaxation of DAC.

Bending Modes as a Function of Pressure



Stretch Modes as a Function of Pressure



- The wavenumber shift as a function of pressure is shown above. Large discontinuities in the slope (dν/dP) suggest a phase transition around 3GPa. It noted though that new peaks belonging to β-LiAlH4 begin to appear around 2.4GPa.
- The results from one sample run are shown here. Analysis of Raman spectra from other sample runs are in progress

Summary

- **The in-situ high pressure Raman spectroscopy studies have been conducted on pure $LiAlH_4$. For the first time, the translational and librational modes of $LiAlH_4$ have been monitored as a function of pressure.**
- **The analysis of the Raman spectra reveals a phase transition at 3GPa corroborating the results previous high pressure experiments.**
- **For the first time, the effect of "pressure quenching" of the high the pressure β-LiAlH4 phase has been studied. The pressure to which the sample was quenched is relatively high (~1.2GPa) due to concerns about air leak into the sample.**
- **The Raman spectra of the quenched b-LiAlH4 phase at 1.2GPa (obtained after 3 hours) and 1.96GPa (obtained after 6 days) retains the characteristics of the high pressure phase.**
- **It is noted that the retention of the high pressure phase is favored if a "step-wise pressure increase followed by quenching" is performed rather than a "rapid pressure increase followed by quenching". The slow pressure transition kinetics of LiAlH4 could be a plausible explanation for this behavior.**
- **In contrast to Talyzin and Sundquist [7], the spectra of β-LiAlH4 displays only two stretch modes suggesting that tetragonal phase is a possibility. However, raw data from recent x-ray diffraction experiments by Pitt et al. [8] suggests a different structure.**
- **The experiments discussed in this work were repeated and preliminary analysis of other sample runs indicate a reproducibility of the retention of the high pressure phase after "pressure quenching".**

References

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4.B.C. Hauback, H.W. Brinks, H. Fjellvag, J. Alloys Compd. 346 (2002) 184.
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7.A.V. Talyzin, B. Sundquist, Phys. Rev. B 70 (2004) 180101.
8.M.P. Pitt, W.G. Marshall, D. Blanchard, H. Fjellvåg, B.C. Hauback "http://www.xray.cz/epdic/abstracts/326.htm"

Neutron Scattering Studies on $LiAlD_4$

Lithium aluminum deuteride sample (LiAlD4, >98% D and chemical assay > 95%) was obtained from Sigma-Aldrich in the form of a powder, and stored under argon atmosphere. Time-of-flight (TOF) neutron powder diffraction (NPD) data was collected for $LiAlD_4$ sample using the General Purpose Powder Diffractometer (GPPD) at Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. Diffraction data were collected on all detector banks. The sample was initially loaded in the cylindrical vanadium sample holder (with an aluminum top and utilizes an indium seal) in a helium-filled recirculating glovebox. Data taken from 10 K to 300 K by the Displex Refrigerator cooling system.

Rietveld refinements were performed using the General Structure Analysis System (GSAS) [1-2] Starting model was taken as the structure published by Sklar et al. [3] and Hauback et al. [4] with monoclinic structure (space group P21/c).

References:
[1] A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000).
[2] B. H. Toby, *EXPGUI*, a graphical user interface for *GSAS, J. Appl. Cryst.* 34, 210-213 (2001).
[3] N. Sklar and B. Post, *Inorg. Chem,* 6, 669 (1967).
[4] B.C. Hauback, H.W. Brinks and B. H. Fjellvag, *J. Alloy and Compounds,* 346, 184 (2002).

General Purpose Powder Diffractometer (GPPD)

Low Temperature Displex Refrigerator 10 K - RT

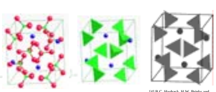
Refined Cell of $LiAlD_4$ @ 300 K

Monoclinic - $P2_1/c$

a = 4.82403(6) b = 7.80155(8) c = 7.89613(7)

β = 112.2657(8)

Li	0.5658(11)	0.4685(6)	0.8250(6)
Al	0.1336(5)	0.20637(26)	0.93093(28)
D1	0.1860(4)	0.09853(24)	0.77015(19)
D2	0.3534(4)	0.37102(22)	0.97830(17)
D3	0.2402(4)	0.08827(21)	0.11513(21)
D4	0.8024(5)	0.26120(21)	0.86714(27)



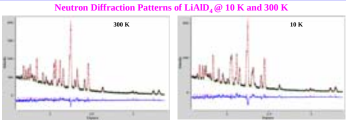
Made By CrystalMaker Program (This Study)

[4] B.C. Hauback, H.W. Brinks and B. H. Fjellvag, *J. Alloy and Compounds,* 346, 184 (2002).

Lattice Parameters of $LiAlD_4$ from 10 K – 300 K

Temp (K)	a	b	c	β	Volume
10	4.81782	7.79719	7.84064	112.2424	272.621
40	4.81656	7.79813	7.82595	112.2344	272.088
70	4.81646	7.79815	7.82418	112.2334	272.023
100	4.81660	7.79772	7.82632	112.2352	272.086
130	4.81693	7.79702	7.83119	112.2369	272.247
160	4.81763	7.79678	7.83863	112.2418	272.527
190	4.81858	7.79693	7.84779	112.2455	272.897
220	4.81989	7.79752	7.85870	112.2507	273.362
250	4.82130	7.79846	7.87118	112.2556	273.900
280	4.82288	7.80010	7.88544	112.2606	274.533
300	4.82403	7.80155	7.89613	112.2657	275.012

Neutron Diffraction Patterns of $LiAlD_4$ @ 10 K and 300 K



Atomic Coordinates @ Different Temperatures

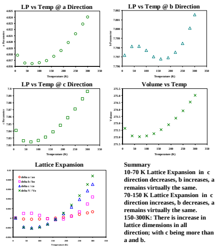
10 K and 300 K (This Study)

T (K)	Atom	x	y	z
300	Li	0.5658(11)	0.4685(6)	0.8250(6)
	Al	0.1336(5)	0.20637(26)	0.93093(28)
	D1	0.1860(4)	0.09853(24)	0.77015(19)
	D2	0.3534(4)	0.37102(22)	0.97830(17)
	D3	0.2402(4)	0.08827(21)	0.11513(21)
	D4	0.8024(5)	0.26120(21)	0.86714(27)
10	Li	0.5680(10)	0.4650(5)	0.8276(5)
	Al	0.1342(4)	0.20655(23)	0.93196(26)
	D1	0.18242(27)	0.09855(18)	0.76727(14)
	D2	0.35765(28)	0.36911(17)	0.97938(15)
	D3	0.24156(28)	0.08518(17)	0.11452(17)
	D4	0.80375(40)	0.26210(17)	0.87048(22)

8 K and 295 K (Hauback et al. [4])

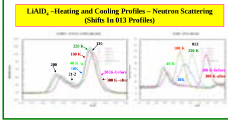
T (K)	Atom	x	y	z
295	Li	0.5601(12)	0.4657(6)	0.8236(6)
	Al	0.1428(2)	0.2013(1)	0.9311(1)
	D1	0.1902(10)	0.0933(8)	0.7710(6)
	D2	0.3526(10)	0.3726(7)	0.9769(6)
	D3	0.2384(11)	0.0840(7)	0.1141(7)
	D4	0.8024(14)	0.2644(7)	0.8689(8)
8	Li	0.5703(24)	0.4656(11)	0.8266(11)
	Al	0.1386(11)	0.2033(6)	0.9302(6)
	D1	0.1826(6)	0.0958(4)	0.7643(3)
	D2	0.3524(6)	0.3713(4)	0.9749(4)
	D3	0.2425(6)	0.0806(3)	0.1148(4)
	D4	0.7994(7)	0.2649(4)	0.8724(4)

Lattice Expansion of LiAlD4 from 10 K to 300 K

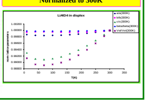


Summary
10-70 K Lattice Expansion in c direction decreases, b increases, a remains virtually the same.
70-150 K Lattice Expansion in c direction increases, b decreases, a remains virtually the same.
150-300K: There is increase in lattice dimensions in all direction; with c being more than a and b.

LiAlD$_4$ –Heating and Cooling Profiles – Neutron Scattering (Shifts In 013 Profiles)



Lattice Parameter and Volume Changes Normalized to 300K



Summary

- **Total lattice expansions at a direction is 0.13%, b is 0.06%, c is 0.71% and volume is 0.88%. Hauback et al. reported that lattice expansions at c direction is 1.0%, and the a and b directions are less than 0.2% [4].**
- **Neutron diffraction data show the 013 peak are shifted when temperature increase from 10 K to 300 K, and the 200, 21-2 and 130 peaks are remained the same.**

Acknowledgement
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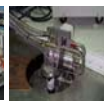
Neutron Scattering Studies on Li_3N

Lithium nitride sample (Li_3N, 80mesh) was obtained from Sigma-Aldrich in the form of a powder. Time-of-flight (TOF) neutron powder diffraction (NPD) data was collected for Li_3N sample using the General Purpose Powder Diffractometer (GPPD) at Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. Diffraction data were collected on all detector banks. The sample was initially loaded in the cylindrical vanadium sample holder (with an aluminum top and utilizes an indium seal) in a helium-filled recirculating glovebox. Data taken from 10 K to 300 K by the Displex Refrigerator cooling system and heated by the coffee can furnace from room temperature to 573 K.

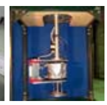
Rietveld refinements were performed using the General Structure Analysis System (GSAS) [1-2] Starting model was taken as the structure of α phase published by Rabenau et al. [3] and Duncan et al. [4] with hexagonal structure (space group P6/mmm) and Beister et al. [5] with hexagonal structure (space group P63/mmc).

References:
[1] A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (2000).
[2] B. H. Toby, *EXPGUI*, a graphical user interface for *GSAS, J. Appl. Cryst.* 34, 210-213 (2001).
[3] A. Rabenau and H. Schulz, *J. less-Common Met.*, 50, 155 (1976).
[4] H. Duncan et al., *Chem. Mater.*, 14, 2063 (2002).
[5] H. J. Beister et al., *Angew. Chem. Int. Ed. Engl*, 27, 1101 (1988).

General Purpose Powder Diffractometer (GPPD)

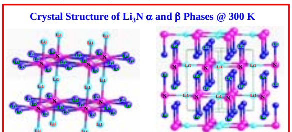


Low Temperature - Displex Refrigerator - 10 K - RT



High Temperature - Coffee Can Furnace - RT - 350°C

Crystal Structure of Li_3N α and β Phases @ 300 K



Li_3N α Phase
Hexagonal - P6/mmm (191)
a = 3.64651 c = 3.87306

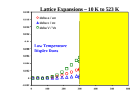
Li1	0	0	1/2
Li2	1/3	2/3	0
N	0	0	0

Li_3N β Phase
Hexagonal - P63/mmc (194)
a = 3.56868 c = 6.34040

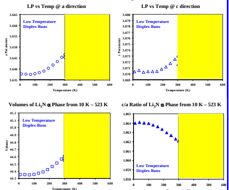
Li1	0	0	1/2
Li2	1/3	2/3	0.578259
N	0	0	0.25

Lattice Parameters of Li3N α Phase from 10 K to 523 K

Temp (K)	a	c	Volume
10	3.63761	3.87037	44.3523
40	3.6375	3.8706	44.3522
70	3.63745	3.8703	44.3476
100	3.63769	3.87041	44.3546
130	3.63826	3.87041	44.3686
160	3.63897	3.87044	44.3863
190	3.64025	3.87079	44.4215
220	3.64177	3.87117	44.4628
250	3.64339	3.87175	44.5092
280	3.6453	3.87245	44.5638
300	3.64651	3.87306	44.6004
300	3.645223	3.871559	44.55044
323	3.646633	3.872334	44.59383
373	3.650596	3.873486	44.70411
423	3.654231	3.875166	44.81261
473	3.65879	3.87629	44.93752
523	3.663158	3.878628	45.07205

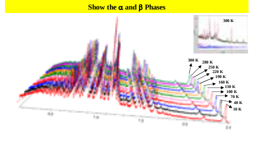


Lattice Expansion and c/a Ratio of Li_3N α Phase from 10 K to 523 K

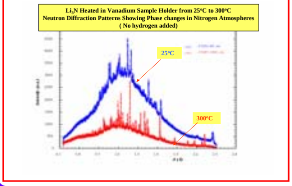


Summary:
- **Lattice expansion at a direction (0.7%) is larger than at c direction (0.2%) (10-253 K)**
- **Total volume expansion is 1.6% from 10 K to 523 K**
- **c/a ratio are decreasing from 1.064 to 1.059 at 10-523 K temperature range**

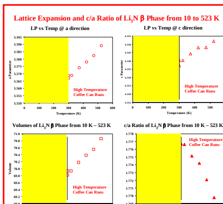
Neutron Diffraction Patterns of Li3N form 10 K to 300 K Show the α and β Phases



Li_3N Heated in Vanadium Sample Holder from 25°C to 300°C Neutron Diffraction Patterns Showing Phase changes in Nitrogen Atmospheres (No hydrogen added)



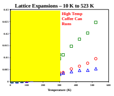
Lattice Expansion and c/a Ratio of Li_3N β Phase from 10 K to 523 K



Summary
- **Lattice expansion at a and c direction are almost same from 10 K to 300 K**
- **Total volume expansion is 2.46% from 10 K to 523 K**
- **c/a ratio remained the same form 10 K to 300 K, and decreased from 1.7767 to 1.7698 at 300-523 K temperature range**

Lattice Parameters of Li_3N β Phase from 10 K to 523 K

Temp (K)	a	c	Volume
10	3.55525	6.318	69.159
40	3.55543	6.318	69.167
70	3.55551	6.3184	69.173
100	3.55615	6.3194	69.209
130	3.5572	6.3214	69.273
160	3.55844	6.3225	69.333
190	3.55997	6.3265	69.436
220	3.56199	6.33	69.554
250	3.5642	6.3343	69.687
280	3.56688	6.3375	69.827
300	3.56868	6.3404	69.929
300	3.566776	6.337244	69.81842
323	3.568756	6.340397	69.93073
373	3.573973	6.344316	70.17869
423	3.577968	6.348033	70.37687
473	3.582383	6.348253	70.55311
523	3.589169	6.352007	70.86253



Summary

- **Neutron diffraction data of Li_3N sample show two phases, α and β, from 10 K to 523 K.**
- **Detail lattice parameters, volumes, c/a ratio and lattice expansions for α and β phase are obtained.**
- **Total volume expansions of Li_3N β phase (2.46%) are larger than α phase (1.6%) form 10 K to 523 K.**
- **Neutron diffraction data show there is a phase transition between 523 K and 573 K.**