Electronic Supplementary Information (ESI)

Mechanochemistry of lithium nitride under hydrogen gas

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Figure S1 shows the XRD patterns of Li_3N after milling for 15 and 30 min under hydrogen gas. The patterns are compared to a simulated diffraction pattern of Li_4NH according to its reported crystal structure.[27] The milled samples do not contain the intermediary Li_4NH phase. Note that the main peak of Li_4NH phase (located at ~ 20°) is not present in milled samples.

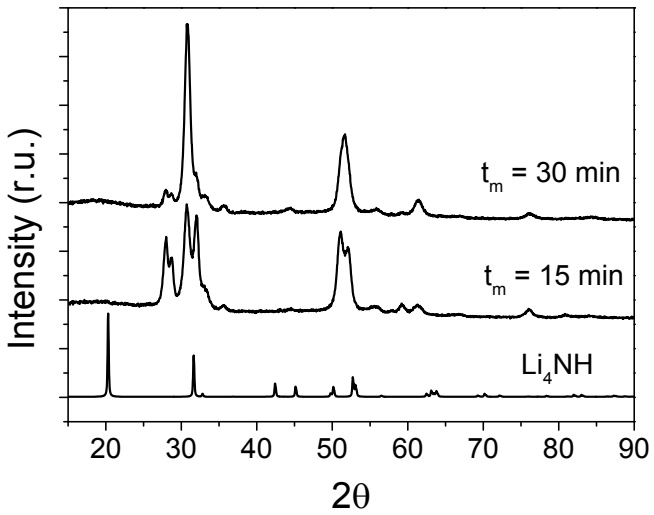

Fig S1. XRD patterns of samples milled for 15 and 30 min under hydrogen gas compared with a simulated pattern for the Li_4NH compound.[27]

Figure S2 shows the recorded IR spectrum of Li_3N after milling for 180 min under hydrogen gas. The characteristic bands lines of Li_2NH compound are observed.

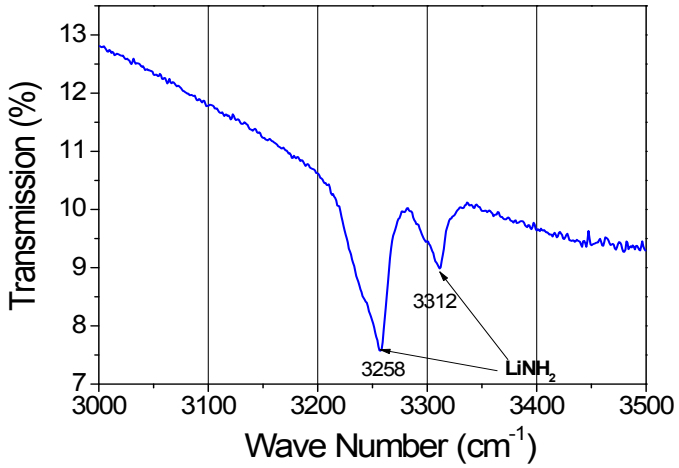

Figure S2: infrared absorption spectrum after milling of Li_3N under hydrogen gas for t = 180 min.

Table S1 : Crystallographic data of Li_3N samples milled at different times, *t*, under 9 MPa of hydrogen pressure. Phase identification, space group (S.G.), cell parameters, crystallite size (D_v), strain and content are given for each detected phase. Standard deviations refereed to the last digit are given in parenthesis for refined parameters. Rietveld agreement factors (R_b, R_{wp} and χ^2) are also given.

Sample, *t* (min)	Phase	S.G.	Cell parameters			D_v	Strain	Content	R_b	R_{wp}	χ^2
			a (Å)	*b* (Å)	*V* (Å^3)	(nm)	(%)	(wt.%)	(%)	(%)	
0	α-Li_3N	*P6/mmm*	3.651(1)	3.879(1)	44.79(1)	42(9)	0.5(1)	51(3)	2.7	10.3	1.99
	β-Li_3N	*P6$_3$/mmc*	3.573(1)	6.352(2)	70.24(2)	23(2)	0.5	44(3)	7.1		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	5(1)	6.0		
15	β-Li_3N	*P6$_3$/mmc*	3.566(1)	6.345(3)	69.90(2)	14(1)	0.5(1)	58(3)	3.2	5.5	2.4
	Li_2NH	*Fm□m*	4.999(2)		125.0(1)	8(1)	0.8	34(2)	1.8		
	LiH	*Fm□m*	4.084		68.12	10	0.1	2(2)	23.5		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	6(2)	3.7		
30	β-Li_3N	*P6$_3$/mmc*	3.570(1)	6.343(3)	70.01(2)	16(2)	0.5	18(2)	3.5	4.6	1.7
	Li_2NH	*F□3m*	4.993(1)		124.4(1)	11(1)	0.8	71(2)	1.9		
	LiH	*Fm□m*	4.084		68.12	10	0.1	5(2)	12.6		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	6(2)	2.6		
60	Li_2NH	*F□3m*	4.986(1)		124.0(1)	10(2)	0.8(1)	77(3)	2.3	6.6	1.5
	LiH	*Fm□m*	4.084		68.12	10	0.1	19(2)	8.0		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	4(2)	3.8		
90	Li_2NH	*F□3m*	4.996(2)		124.7(2)	14(2)	0.8	33(3)	1.5	5.1	1.8
	$LiNH_2$	*I□*	5.013(6)	10.08(3)	253.0(6)	6(1)	0.8	29(2)	2.1		
	LiH	*Fm□m*	4.086(1)		68.20(3)	9(2)	0.1	33(2)	3.7		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	5(2)	0.9		
120	Li_2NH	*F□3m*	5.016(6)		126.2(2)	8	0.2	4(3)	0.3	4.9	1.9
	$LiNH_2$	*I□*	5.060(3)	10.05(1)	257.3(3)	10(1)	0.8	48(3)	1.2		
	LiH	*Fm□m*	4.086(1)		68.24(3)	10(2)	0.1	41(3)	3.6		
	Li_2O	*Fm□m*	4.649(2)		100.5(1)	6	0.5	7(2)	1.1		
180	$LiNH_2$	*I□*	5.061(2)	10.08(1)	258.3(3)	12(2)	0.8(1)	50(2)	1.7	4.5	3.0
	LiH	*Fm□m*	4.084(1)		68.12(3)	10(2)	0.1(1)	46(3)	2.8		
	Li_2O	*Fm□m*	4.650		100.5	6	0.5	4(2)	2.9		