## New Amide-Chloride Phases in the Li-Al-N-H-Cl System: Formation and Hydrogen Storage Behaviour

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**Table 1.** Phase abundance (weight %), corresponding crystallite sizes and cell parameters of the LiNH<sub>2</sub>-0.11AlCl<sub>3</sub> sample after different times of milling. All data have been obtained by Rietveld analysis using MAUD software on the patterns reported in Fig. 1.

Time of MA/ min	LiNH <sub>2</sub> (I-4)	Li₂NH-type (Fm∃m)	LiCl-type (Fm∃m)	AlCl <sub>3</sub> (C2/m:b1)	<d> Li<sub>2</sub>NH- type</d>	Lattice disorder Li <sub>2</sub> NH-type	<d> LiCl- type</d>	R <sub>wp</sub>
	Wt. % (±5%)	Wt. % (±5%)	Wt. % (±5%)	Wt. % (±5%)	Å (±5)	<&2> <sup>1</sup> / <sub>2</sub> (±0.0005)	Å (±5)	-
	Cell parameters, Å	Cell parameters, Å	Cell parameters, Å	Cell parameters.				
	(±0.005)	(±0.005)	(±0.005)	Å (±0.005)				
0	90			10				6 %
	<i>a</i> = 5.040 <i>c</i> = 10.257			a = 5.912 b = 10.315 c = 6.176 b = 108.428	-			
5	19	68	13	0 100.420	440	0.0025	720	7 %
	<i>a</i> = 5.045 <i>c</i> = 10.254	<i>a</i> = 5.251	<i>a</i> = 5.149					
15	13	71	16		290	0.0023	600	6 %
	<i>a</i> = 5.048 <i>c</i> = 10.264	<i>a</i> = 5.241	a = 5.153					
30	11	68	21		280	0.0029	650	4 %
	<i>a</i> = 5.048 <i>c</i> = 10.260	<i>a</i> = 5.238	<i>a</i> = 5.149					
60	13	71	16		240	0.0033	700	4 %
	<i>a</i> = 5.048 <i>c</i> = 10.249	a = 5.237	<i>a</i> = 5.148					
120	13	81	7		190	0.0042	700	5 %
	<i>a</i> = 5.072 <i>c</i> = 10.299	a = 5.237	<i>a</i> = 5.154					
300	8	92			180	0.0042	N.D.	4 %
	<i>a</i> = 5.072 <i>c</i> = 10.302	<i>a</i> = 5.231			-			

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## Table of Rietveld fit data obtained from XRPD patterns of Figure 1

Some comments are necessary for reading the table. The Wt% of each phase determination is subjected to strong correlations among various structural and non-structural parameters, so the data points must be contextualized in the solid state kinetic examined. Thus, data fluctuations from one specimen to the next must consider the error bar associated before claiming a true change.

Immediately soon after the milling of AlCl<sub>3</sub> and LiNH<sub>2</sub> we assist to a quick solid state reaction giving two FCC-type phases, one with lattice parameter *a* of ca. 5.25 Å (we call it Li<sub>2</sub>NH-type and must contain Al ions), the second with lattice parameter *a* of ca. 5.15 Å (we refer to it as LiCl-type given the presence of Cl<sup>-</sup> anions and the lattice parameter value known for LiCl crystals of 5.13(9) Å ). It emerges clearly that the imide-type phase Li<sub>2</sub>NH is going to dominate the long term process of ball milling, at expenses of the intermediated LiCl-type phase. Also the amide-like component (of tetragonal geometry) is disappearing slowly.

Reduction of the average crystallite size value and increase of lattice strain seems to occur unquestionably for the Li<sub>2</sub>NH-type phase. This is not so until 2 h for the LiCl-type remained phase. For such phase the lattice disorder value is not given because of poor numerical reliability, mainly related to its presence.

Other comments can be followed in the text.

## Information about the criteria for background contribution in the XRDP patterns

The green lines are the parametric representation of the background estimated on the ground of a parabolic term to which a broad halo simulating the contribution of the special holder to avoid any oxidation/hydrolysis process of the powders.



Figure S1. XRPD patterns of LA and LLA samples.



Figure S2. XRPD patterns of the  $LiNH_2$ -1.6LiH-0.11AlCl<sub>3</sub> sample after different times of milling.



Figure S3. EDS analysis from a general sector of: A) LA sample heated at 150 °C under argon; B) LA sample heated at 300 °C under 0.7 MPa of hydrogen.



Figure S4. A) Thermogravimetric (TG) and B) derivative thermogravimetric (DTG) curves of (I) LA and (II) LLA samples. The arrow indicates the corresponding y axis of heating ramp.



**Figure S5.** FTIR spectra measured in the same gas-cell. (a) 80 Pa of  $NH_3$ ; (b) gas collected during the heating of LA sample at 120 °C (560 Pa of  $NH_3$  in 35 MPa of total gas (approx.)); (c) gas collected during the heating of LLA sample at 300 °C. The  $NH_3$  spectrum showed are used during the calibration. Only the region of the main  $NH_3$  peaks is shown.

## Equations used to determine ammonia concentration in the desorbed gas up to 300 °C

To determine the ammonia concentration in the released gas, it is assumed that the desorbed gas from LA and LLA samples contains  $x_1$  mol H<sub>2</sub> and  $y_1$  mol NH<sub>3</sub>. As example, the following equations are used for LA sample, according to the data shown in Figs. 6A and 6B:

$$\frac{x_1 \times 2 + y_1 \times 17}{37.61} = 0.09$$

 $\frac{\frac{x_1}{f_1} + \frac{y_1}{f_2}}{37.61} = \frac{0.02}{2}$ 

where  $f_1=1$  and  $f_2=0.79$  are the conversion factors for hydrogen and ammonia, respectively.



**Figure S6.** FTIR spectra after non-isothermal heating up to 300 °C in volumetric equipment for: (I) LA and (II) LLA samples.



**Figure S7.** Hydrogen desorption and absorption of LLA sample at 300 <sup>o</sup>C (1<sup>st</sup> desorption: solid line; 1<sup>st</sup> absorption: dash line). Dehydrogenation curve of LiNH₂-LiH is shown as reference.