Mechanochemical synthesis under deuterium gas in the Li-Mg-N-D system: a neutron diffraction study

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Fig. S1 shows the recorded IR spectrum of as-milled 2Li\textsubscript{3}+Mg powders after long-time milling (12 h). The characteristic bands lines of Mg(NH\textsubscript{2})\textsubscript{2} compound are identified at 3270 and 3328 cm\textsuperscript{-1}, very close to values reported by Linde and Juza\textsuperscript{1}: 3277 and 3329 cm\textsuperscript{-1}. In addition, a shoulder is detected at 3234 cm\textsuperscript{-1} which, based on PCI measurements, is tentatively assigned to intermediate compounds (LiNH\textsubscript{2} or Li\textsubscript{2}Mg\textsubscript{2}N\textsubscript{3}H\textsubscript{3} phases) due to incomplete D-uptake (reaction yield 87.5 \%).

![Infrared absorption spectrum](image)

Fig. S1: infrared absorption spectrum after long-time milling of 2Li\textsubscript{3}+Mg under deuterium gas for 12 h.

Fig. S2 shows the graphical output of the Rietveld refinement of NPD data for the long-time milled 2Li$_3$+Mg powder after thermal heating to 443 K. The as-milled amorphous Mg(ND$_2$)$_2$ phase crystallizes in the tetragonal unit cell ($I4_1/acd$ space group) with lattice parameters $a = 10.503$ and $c = 19.948$ Å at 443K.

Fig. S2: Rietveld refinement of the in-situ NPD diffraction pattern of long-time milled 2Li$_3$+Mg powder after thermal heating to 443 K. Observed (red dots), calculated (black solid line) and difference curves (blue solid line below) are shown. Vertical bars correspond to $(hkl)$ Bragg line positions for Mg(ND$_2$)$_2$, LiD and stainless-steel sample holder (SH1 and SH2) phases.
Fig. S3 shows the evolution of NPD patterns in the angular domain $2\theta = 25\text{-}70^\circ$ during step-wise deuteration of Li$_3$MgN$_2$D phase. As D incorporates in this phase to form a solid solution like Li$_{3-\delta-e}$Mg$_{1+\delta}$N$_2$D$_{1-\delta-e}$ phase, a diffraction peak gradually appears at $2\theta = 28.8^\circ$ revealing increasing atomic ordering as compared to the starting disordered cubic Li$_3$MgN$_2$D phase (S.G. = $Fm\bar{3}m$). The new diffraction peak can be indexed in the $P\bar{4}3m$ space group.

![Graphical representation of NPD patterns](image)

**Fig. S3.** Evolution of NPD patterns during Region AI with increasing deuterium pressure (from bottom to top). Diffraction lines for Li$_{3-\delta-e}$Mg$_{1+\delta}$N$_2$D$_{1-\delta-e}$ phase are indexed in S.G. $P\bar{4}3m$. Additional peaks from Li D phase and Fe-peaks from the sample holder (SH) are also marked.
Fig. S4 shows the graphical output of the Rietveld fit of NPD data acquired during the PCT desorption at 473 K for a D-content of 5.65 D/reactants. Beside diffraction peaks from the stainless steel sample holder, the fit comprises three phases: $\alpha$-Li$_2$MgN$_2$D$_2$ (blue), $\beta$-Li$_2$MgN$_2$D$_2$ (red) and LiD (green). The structure of $\alpha$ and $\beta$ polymorphs of Li$_2$MgN$_2$D$_2$ reported by Rijssenbeek et al. have been used. The refined lattice parameters are $a = 5.009$ Å, $b = 9.832$ Å and $c = 5.211$ Å for $\alpha$-Li$_2$MgN$_2$D$_2$ (S.G. Iba2) and $a = 5.050$ Å for $\beta$-Li$_2$MgN$_2$D$_2$ (S.G. P$\overline{3}$m).

Phase contents were evaluated as 29, 39 and 32 wt.% for $\alpha$-Li$_2$MgN$_2$D$_2$, $\beta$-Li$_2$MgN$_2$D$_2$ and LiD, respectively. This concurs with the desorption reaction:

$$\text{Mg (ND}_2)_2 + 6\text{LiD} \rightarrow \text{Li}_2\text{MgN}_2\text{D}_2 (66 \text{ wt.\%}) + 4\text{LiD (34 wt.\%)} + 2\text{D}_2$$

The unit cell volumes of $\alpha$ and $\beta$ polymorphs are 256 Å$^3$ ($Z = 4$) and 128.79 Å$^3$ ($Z = 2$) respectively. Note that the lattice parameter of the cubic imide compound $\beta$-Li$_2$MgN$_2$D$_2$ ($a = 5.050$ Å) on desorption is very close to that found for the novel imide phase at its maximum D-solubility limit on absorption ($a = 5.046$ Å). This supports that both imide structures are almost equivalent.

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2 J. Rijssenbeek, Y. Gao, J. Hanson, Q. Huang, C. Jones and B. Toby, *J. Alloys Compd.*, 2008, **454**, 233–244