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Electronic Supplementary Information (ESI)

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 $2Li_3$+Mg powders after long-time milling (12 h). The characteristic bands lines of $Mg(NH_2)_2$ compound are identified at 3270 and 3328 cm^{-1}, very close to values reported by Linde and Juza[1]: 3277 and 3329 cm^{-1}. In addition, a shoulder is detected at 3234 cm^{-1} which, based on PCI measurements, is tentatively assigned to intermediate compounds ($LiNH_2$ or $Li_2Mg_2N_3H_3$ phases) due to incomplete D-uptake (reaction yield 87.5 %).

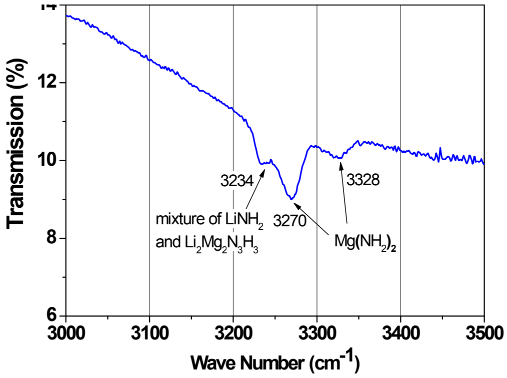

Fig. S1: infrared absorption spectrum after long-time milling of $2Li_3$+Mg under deuterium gas for 12 h.

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[1] G. Linde and R. Juza, *Z. Für Anorg. Allg. Chem.*, 1974, **409**, 199–214

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.

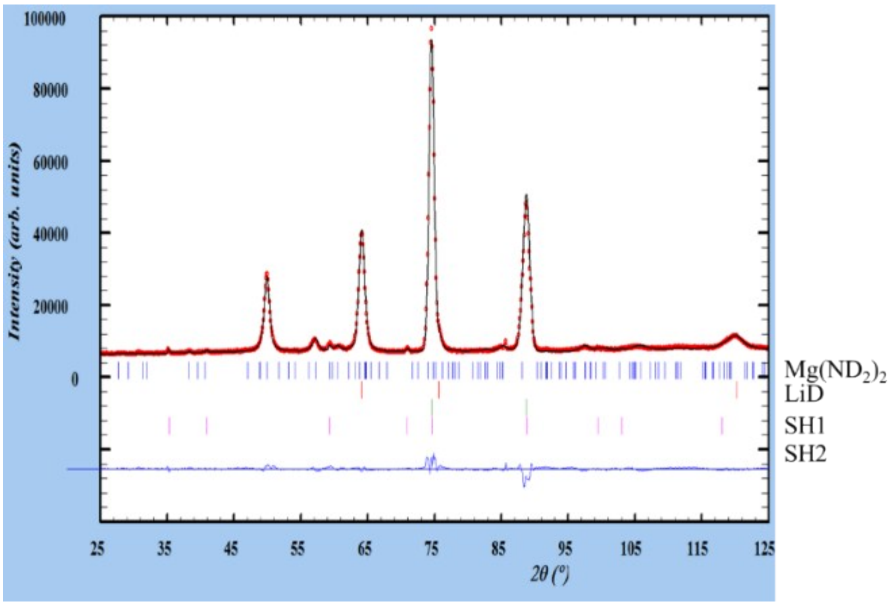

Fig. S2: Rietveld refinement of the in-situ NPD diffraction pattern of long-time milled $2Li_3$+Mg powder after thermal heating to 443 K. Observed (red dots), calculated (black solid line) and difference curves (blue solid line below) are shown. Vertical bars correspond to (*hkl*) Bragg line positions 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 2θ = 25-70° during step-wise deuteration of Li_3MgN_2D phase. As D incorporates in this phase to form a solid solution like $Li_{3-\delta-\varepsilon}Mg_{1+\delta}N_2D_{1-\delta+\varepsilon}$ phase, a diffraction peak gradually appears at 2θ = 28.8° revealing increasing atomic ordering as compared to the starting disordered cubic Li_3MgN_2D phase (S.G. = *Fm□m*). The new diffraction peak can be indexed in the *P□3m* space group.

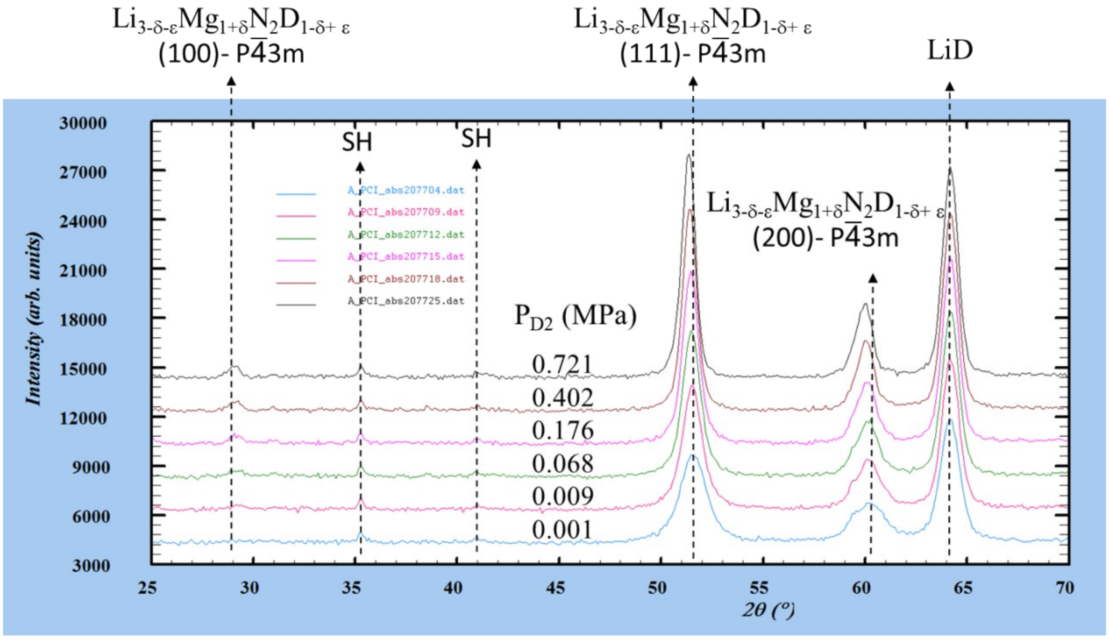

Fig. S3. Evolution of NPD patterns during Region AI with increasing deuterium pressure (from bottom to top). Diffraction lines for $Li_{3-\delta-\varepsilon}Mg_{1+\delta}N_2D_{1-\delta+\varepsilon}$ phase are indexed in S.G. *P*□3*m*. Additional peaks from Li D phase and Fe-peaks from the sample holder (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: α-$Li_2MgN_2D_2$ (blue), β-$Li_2MgN_2D_2$ (red) and LiD (green). The structure of α and β polymorphs of $Li_2MgN_2D_2$ reported by Rijssenbeek et *al*. have been used.[2] The refined lattice parameters are a = 5.009 Å, b = 9.832Å and c = 5.211 Å for α-$Li_2MgN_2D_2$ (S.G. *Iba*2) and a = 5.050 Å for β-$Li_2MgN_2D_2$ (S.G. *P*□3*m*).

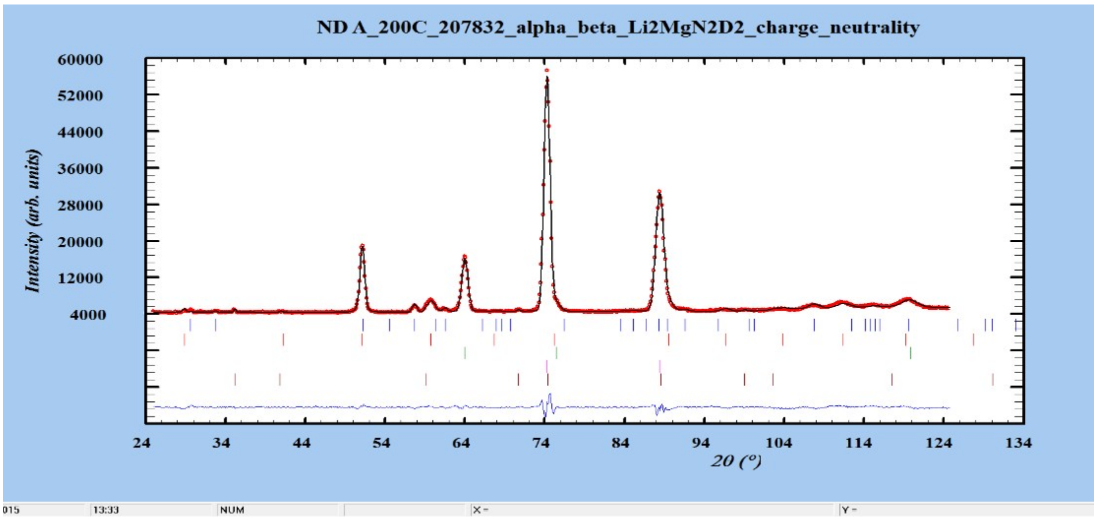

Fig. S4. Rietveld refinement of the sample at D-content of 5.65 D/reactants during desorption PCT isotherm (473 K). Observed (dots), calculated (black solid line) and difference curves (blue solid line below) are shown. Vertical bars correspond to (*hkl*) Bragg line positions for α-$Li_2MgN_2D_2$ (blue), β-$Li_2MgN_2D_2$ (red), LiD (green) and sample holder (pink and brown).

Phase contents were evaluated as 29, 39 and 32 wt.% for α-$Li_2MgN_2D_2$, β-$Li_2MgN_2D_2$ and LiD, respectively. This concurs with the desorption reaction:

$Mg(ND_2)_2 + 6LiD \rightarrow Li_2MgN_2D_2(66\ wt.\%) + 4LiD\ (34\ wt.\%) + 2D_2$

The unit cell volumes of α and β 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 β-$Li_2MgN_2D_2$ (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