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The Synthesis and Structural Investigation of Mixed Lithium / Sodium Amides

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Supplementary Information

System II

A typical refinement from synchrotron X-ray powder diffraction data for System II samples are shown in Figure S1. The lattice parameters for $Li_3Na(NH_2)_4$ and $LiNa_2(NH_2)_3$ formed in System II are summarised in tables ST1, ST2 and ST3.

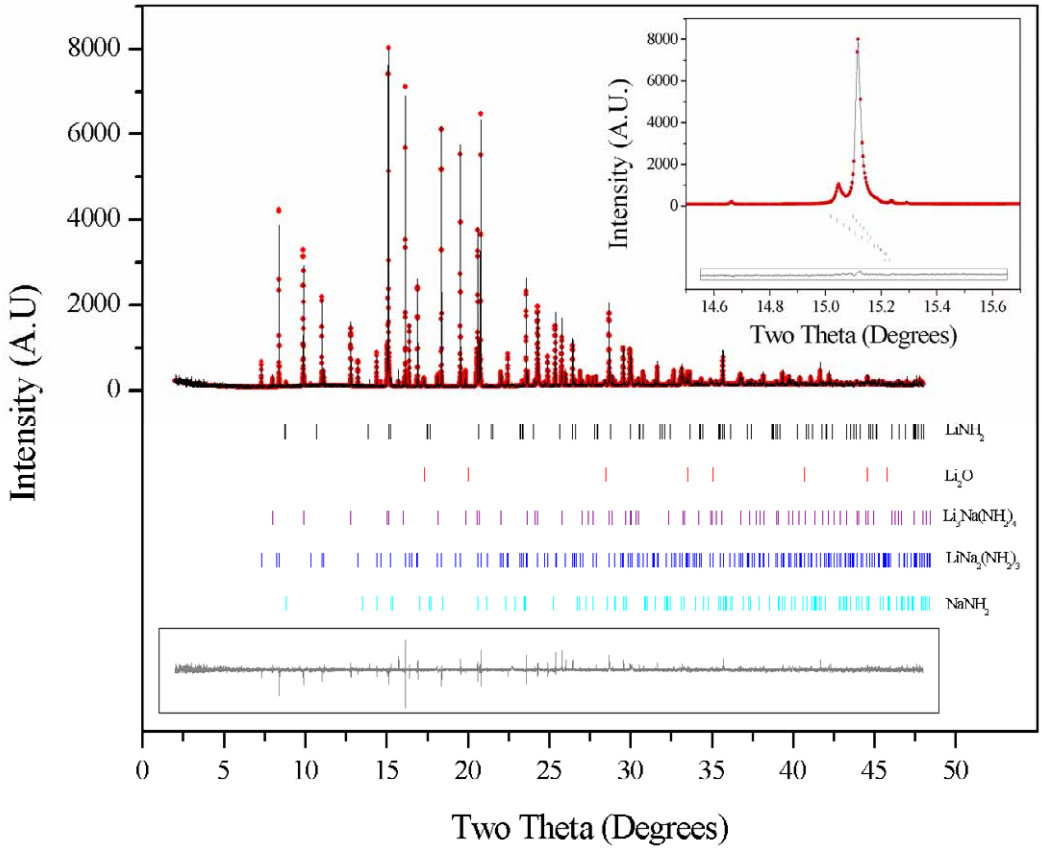

Figure S1: The observed (red dots), calculated (black line) and difference (Y_{obs}-Y_{calc}, solid line in box) plots for the structure refinement of the products of the System II reaction between $0.583LiNH_2$ and $0.417NaNH_2$ from X-ray synchrotron diffraction data. The Bragg peak positions for $LiNH_2$, $NaNH_2$, $LiNa_2(NH_2)_3$, Li_2O and $Li_{3+y}Na_{1-y}(NH_2)_4$ are all shown by the vertical tick marks. Insert: two theta region of the (013) and (112) Bragg peaks for $Li_3Na(NH_2)_4$ highlighting the increased complex microstructure and two-theta dependent strain broadening in these data.

$LiNa_2(NH_2)_3$

Atom	Site	*x/a*	*y/b*	*z/c*	occupancy	B_{iso} (Å^2)
Na1	4i	0.50	0.0	0.14216	1	2.0
Na2	2a	0.0	0.0	0.0	1	2.0
Na3	2f	0.50	0.50	0.25	1	2.0
Li1	4j	0.35356	0.36094	0.0	1	2.0
N1	4j	0.66317	0.27595	0.0	1	2.0
N2	8k	0.20732	0.27336	0.15765	1	2.0
H1	8k	0.73697	0.29827	0.056	1	2.0
H2	8k	0.16362	0.18116	0.21186	1	2.0
H3	8k	0.10362	0.32316	0.14126	1	2.0

a = b = 6.28325(1) Å, c = 11.14942(2) Å

Table ST1 . Summary of refined structural parameters for $LiNa_2(NH_2)_3$ (space group $P4_2/m$, n. 84) generated in System II.

$Li_3Na(NH_2)_4$

Atom	Site	*x/a*	*y/b*	*z/c*	occupancy	B_{iso} (Å^2)
Na1	2c	0.0	0.50	0.25	oNa_n	2.0
Li1	2c	0.0	0.50	0.25	1-oNa_n	2.0
Li2	2a	0.0	0.0	0.0	1	2.0
Li3	4f	0.0	0.5	0.0087	1	2.0
N1	8g	0.250(1)	0.248(2)	z_N	1	2.0
H1	8g	0.365	0.29	0.11	1	2.0
H2	8g	0.233	0.139(6)	0.168(3)	1	2.0

a = b = 5.08111(7) Å, c = 11.5078(3) Å

Table ST2. Summary of refined structural parameters for $Li_3Na(NH_2)_{4\ 4}$ (space group I-4, n. 82) generated in System II.

						Cell Parameters	
Phase Name	Refined Stoichiometry Formula	Scale Factor	Occupancy Na	z_N	Na-N bond length	*a* (Å)	*c* (Å)
$Li_3Na(NH_2)_4$_00	$Li_{3.040(6)}Na_{0.960(6)}(NH_2)_4$	0.0000023(2)	0.960(6)	0.1012(2)	2.4899(5)	5.0830(4)	11.5349(1)
$Li_3Na(NH_2)_4$_01	$Li_{3.061(7)}Na_{0.939(7)}(NH_2)_4$	0.000087(1)	0.939(7)	0.1012(3)	2.4870(5)	5.0813(4)	11.5110(2)
$Li_3Na(NH_2)_4$_02	$Li_{3.082(9)}Na_{0.918(9)}(NH_2)_4$	0.0000140(7)	0.918(9)	0.1012(3)	2.4841(6)	5.0796(4)	11.4871(3)
$Li_3Na(NH_2)_4$_03	$Li_{3.10(1)}Na_{0.90(1)}(NH_2)_4$	0.0000036(5)	0.90(1)	0.1012(4)	2.4812(6)	5.0780(3)	11.4632(3)
$Li_3Na(NH_2)_4$_04	$Li_{3.12(1)}Na_{0.88(1)}(NH_2)_4$	0.0000023(4)	0.88(1)	0.1012(4)	2.4783(6)	5.0763(3)	11.4392(4)
$Li_3Na(NH_2)_4$_05	$Li_{3.15(1)}Na_{0.85(1)}(NH_2)_4$	0.0000009(4)	0.85(1)	0.1012(5)	2.4754(6)	5.0746(3)	11.4153(4)
$Li_3Na(NH_2)_4$_06	$Li_{3.17(1)}Na_{0.83(1)}(NH_2)_4$	0.0000017(4)	0.83(1)	0.1012(5)	2.4725(6)	5.0729(3)	11.3914(5)
$Li_3Na(NH_2)_4$_07	$Li_{3.19(2)}Na_{0.81(2)}(NH_2)_4$	0.0000003(3)	0.81(1)	0.1012(6)	2.4696(7)	5.0713(3)	11.3675(5)
$Li_3Na(NH_2)_4$_08	$Li_{3.21(2)}Na_{0.79(2)}(NH_2)_4$	0.0000002(3)	0.79(2)	0.1012(6)	2.4667(7)	5.0696(2)	11.3436(6)
$Li_3Na(NH_2)_4$_09	$Li_{3.23(2)}Na_{0.77(2)}(NH_2)_4$	0.0000001(3)	0.77(2)	0.1012(7)	2.4638(7)	5.0679(2)	11.3196(6)
$Li_3Na(NH_2)_4$_10	$Li_{3.25(2)}Na_{0.75(2)}(NH_2)_4$	0.0000001(2)	0.75(2)	0.1012(8)	2.4609(8)	5.0662(2)	11.2957(7)

Table ST3. Summary of the refined formulae, (0, ½, ¼) site occupancies, scale factors, nitrogen z-coordinates and a and b lattice parameters of the eleven modelled phases of the $Li_{3+y}Na_{1-y}(NH_2)_4$ formed in System II.

Non-stoichiometry in the $LiNH_2$ phase is not observed in System II reactions, nor in the precursor $LiNH_2$ (Figure S2). No asymmetry of the Bragg peaks associated with $LiNa_2(NH_2)_3$ was observed, which is consistent with the presence of a stoichiometric phase.

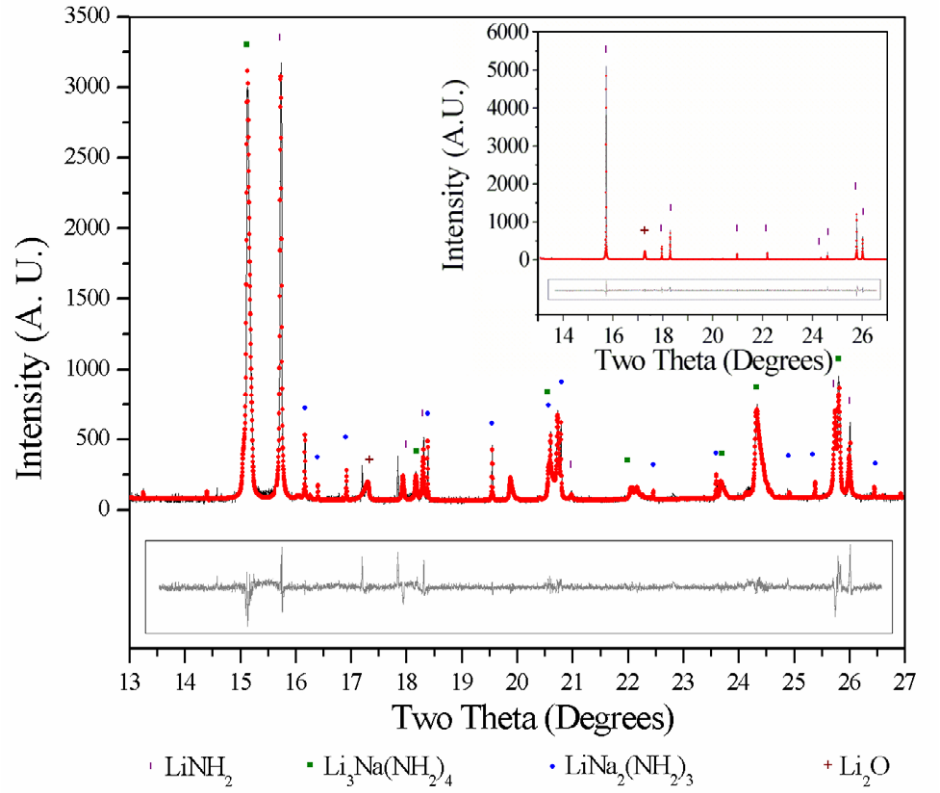

Figure S2 The two theta region of 13 - 27° in of the pattern of $0.833LiNH_2 + 0.167NaNH_2$ from System II, highlighting the symmetry of the $LiNH_2$ peaks compared to the asymmetrical $Li_3Na(NH_2)_4$ peaks. Insert: Two theta range of 13 - 27° in the pattern of the $LiNH_2$ precursor material.