

# Novel layered lithium nitridonickelates; effect of Li vacancy concentration on N co-ordination geometry and Ni oxidation state

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**New compounds in which nickel is substituted for lithium in lithium nitride show evidence of high lithium vacancy concentrations and an ordering of these vacancies to form new structural variants.**

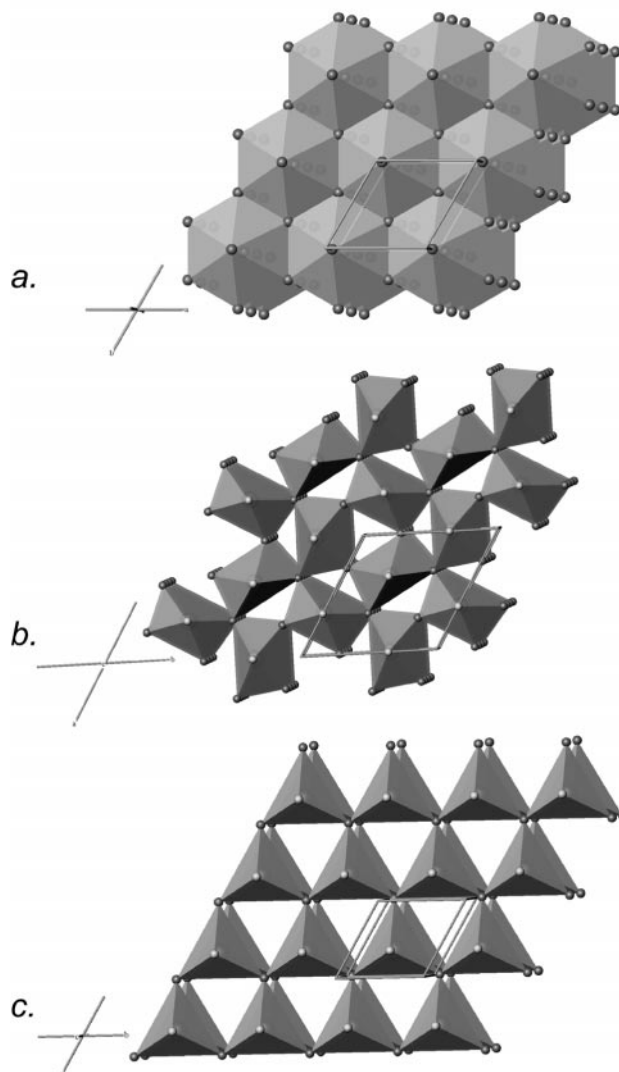
The chemistry of transition metal ternary nitrides has recently been the subject of intense study.<sup>1</sup> However, the reactions of lithium nitride with the first row transition elements were first studied over fifty years ago.<sup>2–4</sup> A number of different compositions and structures are observed for the resulting lithium nitridometallates, some of the most common being based either on an antiferroite structure<sup>2</sup> or on a modification of the lithium nitride structure itself.<sup>3</sup> Late first row transition nitridometallates such as those formed with Co, Ni and Cu favour this latter structure type. The transition metal (M), in these compounds, partially substitutes for lithium between Li<sub>2</sub>N planes to form Li<sub>3–x</sub>M<sub>x</sub>N but the limit of substitution, *x*, is below unity. The parent binary nitride, Li<sub>3</sub>N, is a lithium ion conductor.<sup>5</sup> Control of *x* has implications both structurally and in terms of the conductivity of materials. We report here the synthesis and structure of two new layered nitridonickelates.

New ternary lithium nitrides were synthesised by reaction of excess lithium nitride with nickel foil under a positive pressure of nitrogen gas. All manipulations were carried out in an argon or nitrogen-filled evacuable glove box. Lithium nitride (Li<sub>3</sub>N) was prepared by reaction of gaseous nitrogen with cleaned lithium metal (5–6 g) dissolved in liquid sodium at 650 °C.<sup>6</sup> Ternary nitrides were prepared by reaction of Li<sub>3</sub>N with a nickel foil (99.9% BDH) dissolved in liquid sodium at 650 °C.<sup>6</sup> The tube was placed inside a stainless steel vessel under a positive pressure of nitrogen (*ca.* 2 atm) and heated to 750 °C for 24 h. The vessel was cooled and opened in a nitrogen filled glove box. The reaction yielded a gold coloured coating of crystalline product on the nickel foil. The air-sensitive crystals were isolated, loaded and sealed in capillaries.

Structure solution and refinement reveals two distinct products with compositions Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> and LiNiN.<sup>7</sup> Both compounds have structures closely related to Li<sub>3</sub>N, with alternate layers of Li–N sheets and metal ions stacked perpendicular to the *c*-axis. The proposed structures of both compounds exhibit lithium vacancy ordering not seen in lithium nitride or the previously reported Li<sub>3–x</sub>M<sub>x</sub>N compounds. Furthermore, Li ion vacancy concentrations in these lithium nitridometallates are well above the 1–2% level usually observed in Li<sub>3</sub>N. This Li vacancy ordering enforces changes in space group with vacancy concentration and the approximate doubling of the Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> *a*-parameter relative to the Li<sub>3</sub>N unit cell dimensions. It was almost impossible to discriminate between ordered and disordered models for the LiNiN structure by X-ray diffraction.<sup>8</sup>

It is useful to compare and contrast the structures of the nitridonickelates and the parent compound, Li<sub>3</sub>N in terms of the nitrogen coordination environment. Lithium nitride, Li<sub>3</sub>N is composed of layers of N-centred hexagonal bipyramids which stack along the *c*-axis. [Li<sub>2</sub>N] planes (where each N is surrounded by a 'graphitic-like' hexagon of six Li atoms) are

interconnected by Li atoms between layers (in the apical positions of the hexagonal bipyramids) [Fig. 1(a)].<sup>†</sup> In the nitridonickelates, Ni replaces Li in these 'apical' sites between layers additionally creating Li vacancies in the [Li<sub>2</sub>N] planes. Hence there is an evolution of nitrogen co-ordination geometry with vacancy concentration. In Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> [Fig. 1(b)] the nitrogen coordination is effectively reduced to '6 + 1' (distorted pentagonal bipyramidal). Within the Li–N planes, nitrogen is now surrounded by five lithium ions. In reality, the in-plane Li(1)–N(1) distance [2.42(4) Å] is much larger than the sum of



**Fig. 1** Structure of (a) Li<sub>3</sub>N, showing edge sharing of N(Li<sub>3</sub>) polyhedra in the *ab* plane (b) Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub>, showing vertex sharing of N(Li<sub>4</sub>Ni<sub>2</sub>) polyhedra in the *ab* plane and creation of Li vacancies (c) LiNiN, showing vertex sharing of N(Li<sub>3</sub>Ni<sub>2</sub>) polyhedra in the *ab* plane and creation of Li vacancies.

the ionic radii<sup>9</sup> and the nitrogen coordination is closer to distorted octahedral than pentagonal bipyramidal. Li coordination within planes is both three- and two-fold. The N-centred polyhedra are linked by vertices both in the *ab* plane and along *c*. In the proposed structure of LiNiN [Fig. (1c)], the nitrogen coordination is reduced further to five (trigonal bipyramidal). The N coordination and the *intra*-layer linking in this compound are akin to that in the high-pressure form of Li<sub>3</sub>N ( $\beta$ -Li<sub>3</sub>N, with the Na<sub>3</sub>As structure),<sup>10</sup> although the stacking of layers is altered. As in Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub>, the N-centred polyhedra are linked by vertices in three dimensions. The lithium coordination in the Li–N planes in LiNiN is exclusively trigonal planar as in the Li<sub>3</sub>N parent structure. In both nitridonickelates, Li–N planes are linked *via* infinite, perpendicular N–Ni–N chains. In LiNiN, as in Li<sub>3</sub>N, these chains are straight whereas in Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> they are slightly bent.

The Li–N bond lengths in both Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> [mean distance: 2.086(5) Å, excluding the interaction at 2.42(4) Å] and LiNiN [2.1697(6) Å] are of the same order as those observed in the parent binary nitride (2.130 Å).<sup>11</sup> The interplane Ni–N distances [1.777(1) Å in Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> and 1.7700(5) Å in LiNiN] are considerably shorter than the equivalent Li(2)–N distance in Li<sub>3</sub>N (1.939 Å).<sup>11</sup> The Ni–N bond lengths are similar to those (Li,Ni)–N distances derived from *c*-parameters of Li<sub>3–x</sub>Ni<sub>x</sub>N solid solution members<sup>2</sup> and are only marginally shorter than those observed in other nitridonickelate(I) species such as CaNiN (1.7904 Å)<sup>12</sup> and SrNiN [average: 1.81(4) Å].<sup>13</sup> These distances indicate the likely significant covalent ( $\pi$ ) character of the Ni–N bond in nitridonickelates. Besides the Li<sub>3–x</sub>M<sub>x</sub>N compounds, perhaps the most closely related structure to Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> and LiNiN is that of Li<sub>4</sub>FeN<sub>2</sub>, also a defect variant of Li<sub>3</sub>N. In the nitridoferrate, however, metal vacancies occur *between* [Li<sub>2</sub>N] planes (*i.e.* on iron positions) and the structure can be described by the formulation Li<sub>2</sub>(Fe<sub>0.5</sub>□<sub>0.5</sub>)N (where □ is a vacancy). The equivalent interplanar metal–nitrogen (Fe–N) distance in Li<sub>4</sub>FeN<sub>2</sub> is 1.86(1) Å; longer than those observed in the nickel nitrides.

The nitridonickelates can be regarded as vacancy-ordered layer compounds, Li<sub>3–x–y</sub>Ni<sub>x</sub>□<sub>y</sub>N. In these examples, *x* = 1, *y* = 0.333 in Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> and *x* = 1, *y* = 1 in LiNiN. Besides affecting the nitrogen coordination environment, the other consequence of removing lithium is to increase the nickel valency and oxidation states above one become possible. Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> contains Ni<sup>I</sup>/Ni<sup>II</sup> (Ni<sup>1.33+</sup>) whereas LiNiN contains exclusively divalent nickel. During the course of this study, the related nitridonickelate Li<sub>5.69</sub>Ni<sub>2.31</sub>N<sub>3</sub> was reported which also adopts the *P62m* structure isotopic with Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub>.<sup>14</sup> In this case, *x* = 0.77, *y* = 0.3333 and Ni has an oxidation state of 1.43.

Bond valence calculations<sup>15</sup> performed for the nitridonickelates yielded the following values: (a) LiNiN: Li = 0.7, Ni = 1.9, N = –2.6; (b) Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub>: Li(1) = 0.7, Li(2) = 0.8, Ni = 1.9, N = –3.0. While the Li and N site valences compare well with Li<sub>3</sub>N, perhaps more interesting is the magnitude of the Ni valences. These would suggest that Ni is present as predominantly Ni(II). Calculations performed on original Li<sub>3–x</sub>Ni<sub>x</sub>N compositions, with (Li,Ni)–N bond lengths derived from *c*-parameters, produce similar values. In some cases, these absolute values may be artificially high since  $\pi$ -bonding contributions in transition metal nitrides lead to bonds shorter than anticipated from ‘purely ionic’ contributions. However, the inference is that regardless of the Li/Ni distribution on the interplanar site, creation of Li vacancies in the [Li<sub>2</sub>N] plane is inevitable to maintain charge balance. There is a striking paucity of reliable structural data for the earlier reported Li<sub>3–x</sub>M<sub>x</sub>N compounds. The increase in *a*-parameters with increasing *x* in these compounds suggests that substitution of transition metals for lithium *between* [Li<sub>2</sub>N] planes also engenders structural change *within* those planes (albeit in a *disordered* manner). Neutron diffraction is a crucial tool in determining the site occupancy of light elements. Only ‘Li<sub>2.5</sub>Cu<sub>0.5</sub>N’ has been examined by powder neutron diffraction (PND) and this compound was found to contain *ca.* 15% Li

vacancies in the [Li<sub>2</sub>N] plane (giving a refined composition Li<sub>2.2</sub>Cu<sub>0.5</sub>N).<sup>16</sup>

The ionic and electronic conductivity and the magnetic behaviour of Li<sub>3–x</sub>M<sub>x</sub>N (M = Co, Ni) nitrides have been examined previously.<sup>17</sup> We are preparing Li<sub>3–x–y</sub>Ni<sub>x</sub>□<sub>y</sub>N materials in bulk to investigate their electronic and magnetic properties. The effect of increased Li<sup>+</sup> ion vacancies and nickel oxidation states may have exciting implications for conductivity and magnetism in these lithium ternary nitrides.

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## Notes and references

† Colour versions of Fig. 1 along with an additional figure showing the structure of Li<sub>3</sub>N, Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub> and LiNiN connected by vertices along the *c*-axis can be accessed electronically (see <http://www.rsc.org/suppdata/cc/1999/1187>).

- See, for example: D. H. Gregory, *J. Chem. Soc., Dalton Trans.*, 1999, 259; R. Niewa and F. J. DiSalvo, *Chem. Mater.*, 1998, **10**, 2733.
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- Cleaned, pure lithium was added to an excess of molten sodium contained in a stainless-steel crucible at 250 °C. The cooled crucible was sealed inside a stainless-steel distillation vessel which was evacuated and filled with nitrogen gas (*ca.* 2 atm). The vessel was heated to 650 °C with the nitrogen pressure monitored using a pressure transducer. Excess Na was removed by vacuum distillation at 350 °C for 12 h.
- Crystal data*: Li<sub>5</sub>Ni<sub>3</sub>N<sub>3</sub>, *M* = 252.9, hexagonal space group *P62m* (no. 189), *a* = 6.475(3), *c* = 3.555(2) Å, *Z* = 1, *V* = 129.1(3) Å<sup>3</sup>, *D<sub>c</sub>* = 3.253 g cm<sup>–3</sup>,  $\mu$  = 10.67 mm<sup>–1</sup>, 868 reflections measured at 293(2) K, 109 independent (*R<sub>int</sub>* = 0.0712). Data collected on a Rigaku R-Axis II area detector diffractometer with graphite monochromated Mo- $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods with SHELXS-86<sup>a</sup>, and refined by least squares within SHELXL-93.<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.59P]$  where  $P = (F_o^2 + 2F_c^2)/3$  *R*1 = 0.0351, *wR*2 = 0.0884.  
LiNiN, *M* = 79.66, hexagonal space group *P6m2* (no.187), *a* = 3.758(1), *c* = 3.540(1) Å, *Z* = 1, *V* = 43.30(2) Å<sup>3</sup>, *D<sub>c</sub>* = 3.055 g cm<sup>–3</sup>.  $\mu$  = 10.606 mm<sup>–1</sup>, 1440 reflections measured at 297(2) K, 171 independent (*R<sub>int</sub>* = 0.024). Data collected on a Stadi-4 diffractometer with Mo- $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by direct methods with SHELXL-86<sup>a</sup> and refined by least squares within SHELXL-93.<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ . *R*1 = 0.0374, *wR*2 = 0.0803. (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467; (b) G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Gottingen, Gottingen, Germany, 1993.  
CCDC 182/1262. See <http://www.rsc.org/suppdata/cc/1999/1187/> for crystallographic files in .cif format.
- The alternative disordered model was refined in space group *P6/mmm* with an *R*1 factor higher by 0.01 (0.046). The key differences compared to the *P6m2* model are the partial occupancy of the interplane site by Li (Li:Ni = 0.23:0.87) and disordered Li vacancies in the Li–N planes giving a Li(2) site partial occupancy (0.55).
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