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Observation of novel phases during deuteration of lithium nitride from *in situ* neutron diffraction

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Abstract

We report on *in situ* neutron diffraction measurements during the deuteration of Li_3N. A number of novel observations are described: The presence of cubic 'quasi-imide' phases with composition-dependent lattice parameters, the identification of Li_4ND and the suppression of LiD formation at low deuterium content. On the basis of these observations, it is proposed that the quasi-imide phase is intermediate between Li_4ND and Li_2ND, having a composition $Li_{2+y}ND$. Charge balance is accomplished in this compound by the inclusion of both, formally, D^- and D^+, the latter species being present in the imide ion, $(ND)^{2-}$.

1. Introduction

The report by Chen et al. that Li_3N could reversibly store hydrogen in excess of the US Department of Energy's long-term target of 9 wt% produced a step-change in thinking in the hydrogen storage research community. A two-stage reaction was initially proposed [1]

$$Li_3N + H_2 \rightleftharpoons Li_2NH + LiH \tag{1}$$

$$Li_2NH + H_2 \rightleftharpoons LiNH_2 + LiH. \tag{2}$$

Despite a significant amount of subsequent research [2–6], there remains no clear agreement in the literature regarding the decomposition mechanism in this system. Two principle viewpoints have emerged: Chen et al. proposed a molecule–molecule reaction, with H_2 produced via redox of H^+ and H^-. However, thermal desorption measurements with a $Li_2NH + 2LiD$ mixture produced mainly H_2 in addition to HD and D_2, seemingly contrary to their hypothesis [2]. An additional puzzling feature was that, upon further cycling with H_2, $LiND_2$ was formed, suggesting an HD exchange mechanism in the original $LiNH_2$ [2]. An alternative decomposition pathway involving an ammonia-mediated reaction has been discussed by several authors [3–5]. This picture can be understood as the decomposition of the $LiNH_2$ to Li_2NH and NH_3, with the latter reacting with LiH to produce fresh $LiNH_2$ and H_2.

There are some indications that the reaction pathways are more complex than the forms suggested in (1) and (2). In particular, a number of reports have been given of non-stoichiometric phases forming from decomposition reactions. Chen et al. reported a Li-rich 'imide-like phase with a shrunken lattice' in the thermal desorption product of a 1:2 molar ratio mixture of $LiNH_2$ and LiH [2]. These authors tentatively ascribed the stoichiometry Li_yNH_{3-y} ($y > 2$) to this compound. More recently, David et al. have reported a series of non-stoichiometric phases with compositions $Li_{2-y}NH_{1+y}$ in the decomposition product of hydrogenated Li_3N [6]. In the present work, it is shown that a non-stoichiometric cubic 'quasi-imide' phase is produced in the deuterium *absorption* reaction at low pressure, with a composition-dependent lattice parameter.

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2. Experimental

Neutron diffraction measurements were performed on the OSIRIS instrument [7] at the ISIS facility, UK. The starting material of Li_3N (99.5%, Alfa Aesar Ltd.) was transferred to a purpose-built steel pressure cell under an Ar atmosphere. The can is designed to take advantage of the back-scattering geometry of OSIRIS, with a vanadium window coated with 2 μm of Al_2O_3 to act as a permeation barrier to hydrogen and its isotopes [8]. A boron-nitride back-plate is used to absorb neutrons that have passed through the sample, to prevent scattering from the rear of the can. Deuterium gas (99.5%, BOC Ltd.) is used in preference to hydrogen, as the large incoherent cross section of the latter isotope renders diffraction impractical. Loading of deuterium was performed *in situ* by the Sievert's method. All measurements were performed at 250 °C. A series of diffraction patterns were recorded in the range $0 < x < 2$, where x is the molar ratio of *atomic* deuterium to the starting compound of Li_3N, i.e. corresponding to the regime of reaction (1). In a separate measurement, we have determined that the $LiND_2$ phase forms at pressures in excess of ~0.5 bars [9]; in order to suppress its formation, the experimental conditions were determined such that this pressure was not exceeded. Rietveld profile refinement of diffraction data, corrected for wavelength dependent effects, was performed using the GSAS software [10]. The model for the quasi-imide phase, discussed in Section 3.1 is based on the $F\bar{4}3m$ anti-fluorite type structure for Li_2NH [11]. The fcc positions (4a) were refined with mixed partial occupancy of N^{3-} and H^- ions, with the total occupancy constrained to unity. In addition, the D partial occupancy on the 16e positions was refined. No constraint on the Li to N ratio was imposed.

3. Results and discussion

The measured diffraction patterns indicate a number of marked differences from reaction (1). By way of example, Fig. 1 shows the diffraction pattern for $x = 0.4$, the most significant features of which are

(1) The complete absence of LiD.
(2) A minority phase of Li_4ND.
(3) At least two cubic 'quasi-imide' phases.

A minority phase of Li_2O, not present in the starting compound, remained passive during deuteration; this phase is assumed to have formed due to the out-gassing of H_2O from the porous boron-nitride back-plate during heating to 250 °C. A trace amount of imide phase formed on heating the sample, before having being exposed to deuterium; it is possible that this is correlated with the production of Li_2O in a reaction such as $2Li_3N + H_2O \rightarrow 2Li_2NH + Li_2O$.

The choice of the name 'quasi-imide' arises from the structural similarity with the imide phase, Li_2ND. In the present work, the quasi-imide phase is assigned the composition $Li_{2+y}ND$ (see Section 3.1 for details). The quasi-imide lattice parameter exhibits distinctly different behavior above and below $x \sim 0.7$ (Fig. 2a): At low deuterium content, at least two cubic phases are observed, both with lattice parameters *decreasing* with deuterium up-take. It is possible that the phase with the larger lattice parameter results from the presence of the imide phase at $x = 0$. A minimum in the lattice parameter occurs at $x \sim 0.7$; above this value, the data are consistent with a single-phase, the lattice parameter of which is found to *increase* linearly with deuterium content.

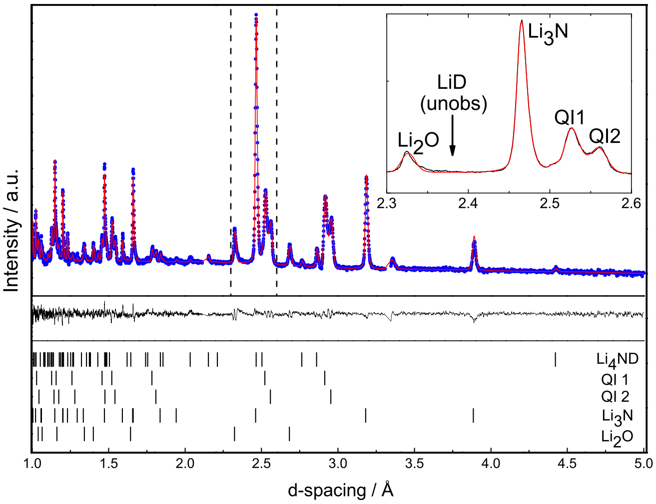

Fig. 1. Observed and calculated neutron diffraction pattern for $x = 0.4$. Two cubic 'quasi-imide' phases (QI1 and QI2) are observed in addition to Li_4ND, Li_3N and some Li_2O. Low-intensity reflections from the boron-nitride back-plate are also present, the most prominent of which is at 3.14 Å. The inset (corresponding to area in dotted lines on main plot) shows the region where the LiD (1 1 1) reflection would occur (2.38 Å).

Based on the molar phase fractions (Fig. 2b), conversion of Li_3N to $Li_{2+y}ND$ is the sole reaction at low D content. At around $x = 0.2$, Li_4ND is seen to form, the phase fraction of which reaches a maximum at about $x = 0.6$, correlated with the appearance of LiD. The composition of the quasi-imide phase, inferred from Rietveld refinement, is found to remain relatively constant ($0.85 < y < 1$). Here, the Li_3N phase is consumed in the reaction at a significantly more rapid rate than suggested by (1). Above $x \sim 0.7$, the phase fraction of LiD grows as the fraction of Li_4ND decreases. In this range, the composition of the quasi-imide phase changes markedly from $Li_{2.8}ND$ to $Li_{2.35}ND$.

To the authors' knowledge, the observation of Li_4ND produced from the reaction of D_2 with Li_3N is unprecedented. The synthesis of Li_4NH from the reaction of Li_3N and LiH has been reported previously by Marx [12].

$$Li_3N + LiH \rightarrow Li_4NH. \tag{3}$$

Combination of (1) and (3) gives a net reaction of

$$2Li_3N + H_2 \rightarrow Li_4NH + Li_2NH. \tag{4}$$