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Review

The chemistry of ternary and higher lithium nitrides

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Contents

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ABSTRACT

Lithium, as the lightest metallic element, forms a wide range of compounds of increasing importance as functional materials. This is especially true in an energy storage and conversion context, for example, where high energy density and high lithium ion mobility provide the drivers behind technologies such as rechargeable batteries and hydrogen storage. As a small, monovalent, mobile cation, Li^+, is amenable structurally to a variety of coordination environments and its ability to readily occupy vacancies and interstitial positions lends it to a rich insertion and intercalation chemistry and the flexibility to form a myriad of structure types across a large stoichiometric range. This flexibility is as prevalent in nitrides as in oxides and other inorganic solids and lithium forms a larger number of ternary and higher compounds with nitrogen than any other single metal. Nevertheless, there are clear trends in the crystal chemistry of lithium nitrides and patterns to the bonding within these structures; key structure types and motifs dominate. Hence, not only does it become possible to anticipate composition–structure relationships in the synthesis of new nitrides, but also materials design and prescribed properties from magnetism through semiconducting and optical properties to superionic conductivity becomes a realistic prospect. This review presents a comprehensive account of the crystal chemistry of ternary and higher lithium nitrides across the periodic table and highlights the opportunities for materials design from the emerging understanding of structure–property relationships in these compounds.

1. Introduction

Undoubtedly nitride chemistry has enjoyed a renaissance over the last 20 years; a period in which first the number of newly discovered compounds has increased many-fold and second our enriched understanding of structure–property relationships has enabled the design of increasingly complex nitride materials with useful functionality. This dramatic progress has been charted periodically in several review papers and books. Central to solid state and materials chemistry more generally, is to be able to make the all-important links between composition, structure and properties. For oxide chemistry, this has taken place over many decades to the point where many of the fundamental relationships among key families of materials are routinely known and accepted, with ubiquitous examples and case studies that form the bedrock of inorganic solid-state chemistry in textbooks at undergraduate level. Nitride chemistry is still at an early stage in its development relatively speaking, but spurred by contemporary technological and environmental drivers and the socio-economic requirement to progress new materials to market more rapidly, substantial developments in key application areas have been made over a short space of time. Further, rather than impede fundamental inorganic and physical chemistry as result, these drivers have provided opportunities for furthering knowledge at all levels.

Hence, since DiSalvo's prophetic article in 1990 [1] and Brese and O'Keeffe's seminal review of nitride crystal chemistry in 1992 [2] ternary and higher nitrides have begun a gradual maturity towards interesting and valuable materials. In the last 20 years since the latter of the two articles above, the chemistry of the nitrides has been reviewed periodically (for example: [3–6]). This contribution considers the complex nitrides of only one metal, yet it is testament to the tremendous growth of the area that the size of this review resembles many of the more general discussion written in the previous two decades. We focus here on lithium nitrides since lithium has become, in recent times, highly topical and pertinent in terms of energy materials in particular. Its high mobility as an ion (Li^+) coupled with its light weight lends itself to high energy density applications. Further, however, the size and mobility of the cation gives rise to a rich insertion and intercalation chemistry which proves to be important not only in the storage of charge in batteries but also in the design of modified materials with tailored electronic structures. In this review, therefore, we consider the ternary and higher nitride compounds of lithium across the periodic table, discussing (briefly) the synthesis of such compounds, their crystal structures and, where relevant, pertinent physical (and/or chemical) properties. Necessarily in the interests of brevity we restrict our focus to those compounds containing only nitride anions rather than combinations of N^{3-} with other anionic species. Needless to say, such anionic combinations offer further opportunities still to tune the structures and properties of the nitridic compounds of lithium and present the inorganic materials chemist with a vast array of unusual and enticing possibilities for innovative materials design.

2. Lithium nitrides of the s-block elements

Lithium ternary nitrides of the s-block elements are relatively few in number. To date, no lithium ternary nitrides of the alkali metals have been reported. This can be due partly to the extraordinary synthetic conditions that the heavier binary alkali metal nitrides require for formation and indeed, only the existence of Na_3N and K_3N (other than Li_3N) is certain among the alkali metals [7–10]. In fact, Hartree–Fock calculations have predicted the existence of two stable phases in the Li–Na–N system, namely $Li_2Na_4N_2$ and $Li_4Na_2N_2$ [11], that would hypothetically have the Li_3N-type structure seen for the lithium nitridometallates of the late-transition metals (Section 4). These have yet to be realised experimentally. By contrast, combinations of lithium with alkaline-earth metals are well known in nitrides. The majority of these ternary nitrides tend to be ionic in nature. A summary of this group of lithium ternary nitrides with metals from the lightest element to the heaviest follows below. Additional information is available in reference [10].

2.1. Beryllium

Lithium beryllium nitride, LiBeN, was first reported by Brice et al. in 1969 from the reaction between Li_3N and either Be_3N_2 or the metal in a nitrogen atmosphere at 853 K [12]. These authors defined the structure of LiBeN as orthorhombic. Later, Somer and coworkers re-evaluated the structure of LiBeN using crystals grown from the reaction between Li_3N and Be (1:1 ratio) at 1273 K. LiBeN crystallises in the monoclinic space group $P2_1/c$ with $a = 4.540(1)$ Å, $b = 4.760(1)$ Å, $c = 5.807(1)$ Å and $\beta = 124.90(1)^\circ$ [13]. The structure consists of 2D infinite nets of BeN_3 triangles parallel to the (1 0 0) plane (with Be–N distances of 1.625 Å, 1.674 Å and 1.683 Å) that are held by lithium atoms that form distorted tetrahedra with nitrogen (d(Li–N) = 2.079–2.23 Å). These infinite 2D layers have been previously reported in EuPdGe [14]. Recent *ab-initio* calculations on the optical properties of LiBeN suggest that the compound is a wide bandgap semiconductor [15].