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Nitridosilicates

Tuning the Dimensionality of Nitridosilicates in Lithium Melts**

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Owing to their large scope of materials properties, such as luminescence, lithium ion conductivity, and nonlinear optical properties, nitridosilicates have attracted broad academic and industrial interest.[1–6] In particular, doping of alkaline earth metal nitridosilicates (e.g., $M_2Si_5N_8$, $MSi_2N_2O_2$; M = Ca, Sr, Ba) with Eu^{2+} has pushed the borders of luminescent materials industrially used in phosphor-converted warm-white LEDs.[7–10] The majority of hitherto-investigated nitridosilicates are three-dimensional framework silicates, obtained by high-temperature reactions starting from the respective metals and silicon nitride or silicon diimide ($Si(NH)_2$).[2,11,12] Introduction of oxygen into nitridosilicates seems to favor layerlike oxonitridosilicates (e.g., $MSi_2N_2O_2$,[7,13] $Ba_3Si_6N_4O_9$).[14] However, there is still a significant lack of less condensed or even metal-rich nitridosilicates. In this context $RE_5Si_3N_9$ (RE = La, Ce) is the only chain-type[15] and $Pr_9Se_6[Si_3N_9]$ the only ring-type[16] nitridosilicate reported so far. The predominance of highly condensed Si/N substructures may be a consequence of the high-temperature reactions that have been mostly employed for the synthesis of nitridosilicates. Under such conditions, highly condensed nitridosilicates seem to be energetically or kinetically favored over less condensed substructures. Accordingly, it is not surprising that the first group-type nitridosilicate, namely, $Ba_5Si_2N_6$, was synthesized in sodium melts at surprisingly low temperature (760 °C).[17] This synthetic approach employing liquid sodium as a flux and decomposition of sodium azide as nitrogen source has also afforded structurally elucidated $MSiN_2$ (M = Ca, Sr, Ba).[18]

During our search for a complementary approach and low-temperature routes to less condensed nitridosilicates, we targeted a series of precursor compounds[19,20] and flux methods,[21] ending up with the idea to utilize liquid lithium, which has been effectually used for the synthesis of borides and carbides.[22–24] Interest in liquid lithium incipiently stems from its proposed use as a tritium breeder and/or primary coolant in several designs of the deuterium/tritium-fuelled thermonuclear reactor.[25] Thus, substantial knowledge is available about the reactivity of lithium melts with silicon and/or nitrogen.[26] According to these investigations silicon and nitrogen dissolve to a comparable extent in lithium at elevated temperatures.[26] Systematic investigations in the system Li/Si/N already have afforded a number of ternary lithium nitridosilicates with interesting material properties, for example, lithium ion conductivity.[3,26–28] These findings distinguish nitride chemistry in lithium from nitride chemistry in sodium, in which silicon and nitrogen are only sparingly soluble. The nitrogen uptake of liquid sodium is improved if alkaline earth metals are added, as reported by Simon and coworkers during their studies on subnitrides (e.g., $NaBa_3N$).[29] In an investigation of the reaction between liquid lithium containing dissolved alkaline earth metals and low nitrogen contents, a homogenous solution of Li/M/N (M = Ca, Sr, Ba) was found.[30] In summary, applicable solubility has been reported in the systems Li/Si/N and Li/M/N. Thus, it was intriguing to combine these systems and utilize the solubilities for the synthesis of quaternary lithium alkaline earth nitridosilicates. Although the addition of Li to sodium melts has led to quaternary phases in the field of nitridogallates and -germanates (e.g., $LiCaGaN_2$,[31] $Li_4Sr_3Ge_2N_6$),[32] no lithium alkaline earth metal nitridosilicates are known so far.

Our experiments were conducted in closed tantalum crucibles, heated to 900 °C under argon atmosphere, and used $Si(NH)_2$ as reactive Si precursor, Ca or Sr metal, LiN_3 or Li_3N as additional nitrogen source, and Li as flux (detailed experimental data for the synthesis of single crystals and bulk samples are given in the Supporting Information). Systematic investigations in this system led to the discovery of novel compounds covering the whole range of dimensionality of $[SiN_4]$ building blocks from group-type ions through chains and sheets up to frameworks. The diversity known for oxosilicate chemistry, which has also been reported for nitridometalates,[33,34] is now accessible for nitridosilicates. Three new nitridosilicates are briefly presented to illustrate the structural variety accessible by the lithium-flux method and new structural features resulting from the incorporation of Li^+ or Li_2O.

The compound with the less condensed $[SiN_4]$ building blocks is $Li_4Ca_3Si_2N_6$ (**I**).[35] It consists of edge-sharing "bow-tie" $[Si_2N_6]^{10-}$ units and is isotypic with $Li_4Sr_3Ge_2N_6$.[32] The grouplike silicate $[Si_2N_6]^{10-}$, known from $Ba_5Si_2N_6$ and $Ca_5Si_2N_6$ has the lowest degree of condensation of structurally characterized nitridosilicates.[17,36] By adding sufficient Li_3N to the reaction mixture higher condensation of the $[SiN_4]$ network can be suppressed and **I** is isolated. Hitherto-unknown intermediates such as double-chain-like silicates can be obtained when an appropriate amount of Li_3N is added to the reaction mixture. $LiCa_3Si_2N_5$ (**II**) exhibits two zweier single-chains, connected through common edges along [001] (Figures 1 and 2).[37] The formula $[Si_2N_5]^{7-}$ could be indicative

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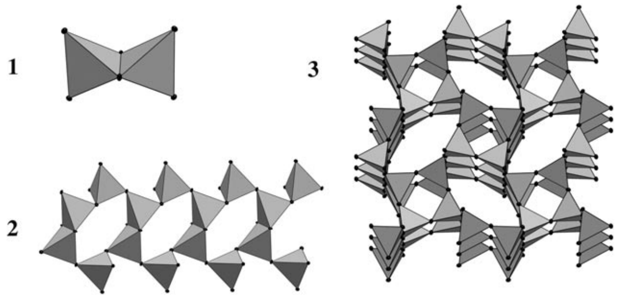

Figure 1. $[SiN_4]$ substructures: double tetrahedra (**1**) in **I** ($Li_4Ca_3Si_2N_6$), double-chain (**2**) in **II** ($LiCa_3Si_2N_5$), and framework (**3**) in **III** ($Li_2Sr_4Si_4N_8O$).

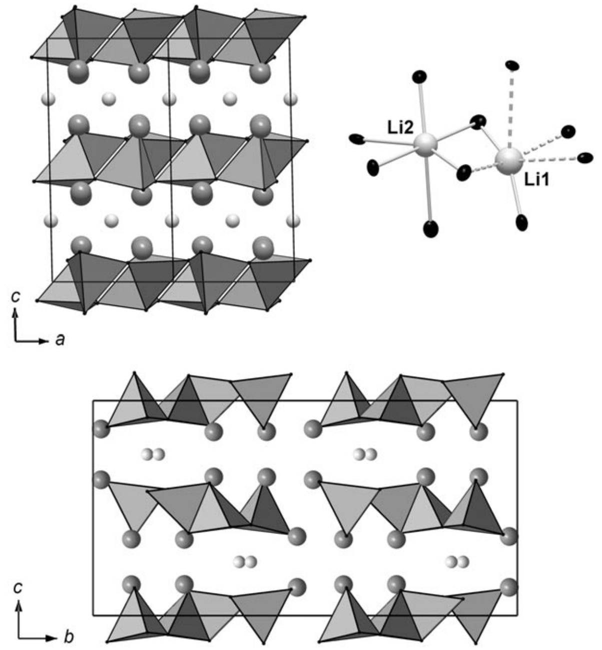

Figure 2. Unit cell of $LiCa_3Si_2N_5$ (**II**) along [010] (top) and along [100] (bottom). Coordination spheres of the Li^+ ions in **II** (top right, ellipsoids at 90% probability). $[SiN_4]$ units are depicted as filled gray tetrahedra, N atoms black, Ca ions dark gray, and Li ions light gray.

of a layer silicate, but due to edge sharing of the $[SiN_4]$ tetrahedra, which is unprecedented for oxosilicates, **II** is the first double-chain-like nitridosilicate. Interestingly, the structure exhibits an infinite chain of Li^+ ions running along the *a* axis (Figure 2). The structure contains two crystallographically independent Li^+ positions, and the coordination spheres of the lithium ions were assigned by lattice energy calculations (MAPLE: Madelung part of lattice energy).[38,39] Accordingly, Li2 is octahedrally coordinated by nitrogen, whereas Li1 exhibits only two close nitrogen contacts relevant to the lattice energy and four elongated Li–N distances. If both lithium polyhedra are interpreted in terms of distorted octahedra, as illustrated in Figure 2, the polyhedra share one edge, and Li^+ ion conductivity along the *a* axis seems likely. This assumption is supported by our observation that the line width at half-maximum (FWHM) of the ^7Li solid-state MAS NMR of **II** at room temperature is halved compared to **I**, although **I** exhibits solely one crystallographically independent lithium position. The ^7Li solid-state NMR spectra of **I** and **II** (see Supporting Information) consist of an intense isotropic peak centered at 2.0 ppm (FWHM: 7.9 ppm) for **I** and 2.7 ppm (FWHM: 2.9 ppm) for **II**. The chemical shifts are comparable to those of $LiSi_2N_3$ (1.3 ppm) and Li_2SiN_2 (1.7 ppm).[20,40] The applicability of **II** as Li^+ ion conductor is currently being investigated.

From a series of new Sr compounds, we present $Li_2Sr_4Si_4N_8O$ (**III**) exemplarily, as it exhibits a zeolite-analogous $[SiN_2]^{2-}$ framework incorporating Li_2O.[41] It was synthesized from Li_2O, Sr, $Si(NH)_2$, and LiN_3 in liquid lithium. As **III** is resistant to oxygen and water, the colorless crystals can be isolated from side products by washing with EtOH. Compound **III** can be formulated as $Li_2O@[SrSiN_2]_4$, as oxygen is located in channels together with the Li^+ ions along [001] and is not bound to any silicon atoms (Figure 3). The $[SiN_2]^{2-}$ framework is made up exclusively of vertex-sharing vierer rings, condensed analogously to the BCT zeolite framework type.[42] Characteristic for the BCT structure are vierer ring and achter ring channels along [001] and sechser ring channels along [100] and [010], respectively (Figure 1 and Figure 3). In contrast to the BCT-type structures reported so far, the achter rings are distorted and evocative of the layer silicate apophyllite.[43] Therefore, the structure could also be described by the condensation of apophyllite-like layers along

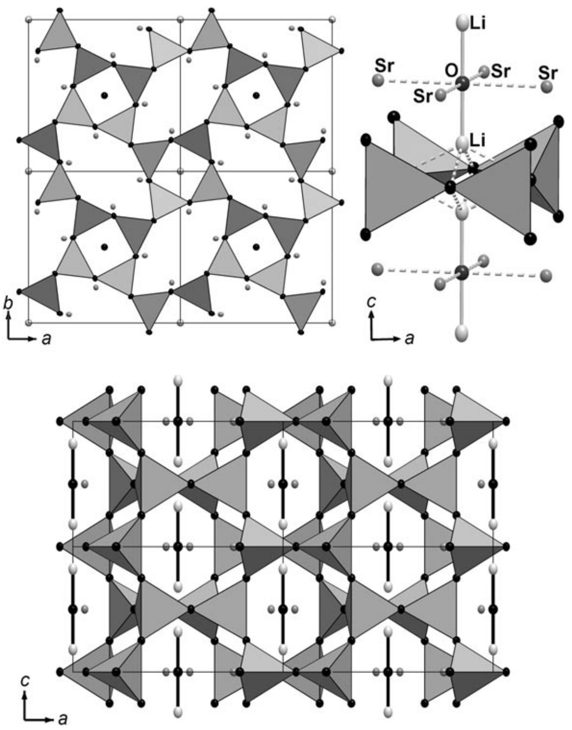

Figure 3. 2×2×2 unit cell of $Li_2Sr_4Si_4N_8O$ along [001] (top left) and along [010] (bottom, Li_2O illustrated by black bonds). Top right: Li_2O unit in $Li_2Sr_4Si_4N_8O$. $[SiN_4]$ units are depicted as filled gray tetrahedra, N/O atoms black, Sr ions dark gray and Li ions light gray. Ellipsoids at 50% probability.

[001]; especially the rather rare space group $P4/mnc$ is typical for this mineral. The Sr^{2+} ions are centered in the sechser ring channels, whereas Li_2O is positioned in a strandlike fashion in the vierer ring channels (Figure 3, top right). The Li–O and Sr–O distances are significantly shorter than the Li–N and Sr–N distances and correspond well to the data found in the literature.

Compound **III** underlines the wide structural variety for nitridosilicates with a molar ratio Si:N = 1:2 (c.f. $MSiN_2$, Li_2SiN_2).[18,20] Interestingly, **III** has the lowest framework density[44] (16.7) and additionally it is the first nitridosilicate having a zeolite-type framework, which already has been found in oxosilicate chemistry. This may arise from Li_2O, if it is interpreted in terms of a molecule-like inorganic template. A template effect of Li_2O has already been discussed for the compound $Li_6B_{18}(Li_2O)_x$, where Li_2O was essential for formation of the zeolite-analogous boride framework.[22] This observation is consistent with our finding that other lithium strontium nitridosilicates are formed if no Li_2O is present. Inclusion of Li_2O is supported by ^7Li solid-state MAS NMR spectroscopy and Raman measurements (see Supporting Information).

The ability of liquid lithium to dissolve a variety of metals, inorganic salts, and even complex anions (e.g., CN_2^{2-})[25] opens the door to a plethora of new nitridosilicates. Preliminary experiments with lanthanides or other alkali metal salts as templates point in this direction.

In summary, the lithium-flux method allows control of the dimensionality of $[SiN_4]$ substructures, from group-type silicates through chainlike anions to frameworks, by simply adjusting the Li_3N content, the nitrogen pressure (LiN_3), and the reaction temperature. Furthermore, chemical screening of suitable materials for lithium ion conductivity or luminescence can now be facilitated by this versatile synthetic approach.

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