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## **Li<sub>4</sub>Ca<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> and Li<sub>4</sub>Sr<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> - Quaternary Lithium Nitridosilicates with Isolated [Si<sub>2</sub>N<sub>6</sub>]<sup>10-</sup> Ions**

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**HAL Id: hal-00552476**

**<https://hal.science/hal-00552476v1>**

Submitted on 6 Jan 2011

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Zeitschrift für Anorganische und  
Allgemeine Chemie

**Li<sub>4</sub>Ca<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> and Li<sub>4</sub>Sr<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> - Quaternary Lithium  
Nitridosilicates with Isolated [Si<sub>2</sub>N<sub>6</sub>]<sup>10-</sup> Ions**

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|-------------------------------|--|
| Journal:                      | <i>Zeitschrift für Anorganische und Allgemeine Chemie</i>  |
| Manuscript ID:                | zaac.201000163.R1  |
| Wiley - Manuscript type:      | Communication  |
| Date Submitted by the Author: | 19-May-2010  |
| Complete List of Authors:     | Pagano, Sandro; LMU Munich, Chemistry<br>Lupart, Saskia; LMU Munich, Chemistry<br>Schmiechen, Sebastian; LMU Munich, Chemistry<br>Schnick, Wolfgang; LMU Munich, Chemistry |
| Keywords:                     | Lithium, Fluxing agent, Strontium, Nitridosilicate, X-ray diffraction  |
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13 **Li<sub>4</sub>Ca<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> and Li<sub>4</sub>Sr<sub>3</sub>Si<sub>2</sub>N<sub>6</sub> - Quaternary Lithium Nitridosilicates**  
14 **with Isolated [Si<sub>2</sub>N<sub>6</sub>]<sup>10-</sup> Ions**  
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23 **Sandro Pagano,<sup>[a]</sup> Saskia Lupart,<sup>[a]</sup> Sebastian Schmiechen,<sup>[a]</sup> and Wolfgang Schnick<sup>[a]\*</sup>**  
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## Abstract

The isotypic nitridosilicates  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  were synthesized by reaction of Sr or Ca with  $\text{Si}(\text{NH})_2$  and additional excess of  $\text{Li}_3\text{N}$  in weld shut tantalum ampoules. The crystal structure, which has been solved by single-crystal X-ray diffraction ( $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ :  $C2/m$ ,  $Z = 2$ ,  $a = 6.1268(12)$ ,  $b = 9.6866(19)$ ,  $c = 6.2200(12)$  Å,  $\beta = 90.24(3)^\circ$ ,  $wR2 = 0.0903$ ) is made up from isolated  $[\text{Si}_2\text{N}_6]^{10-}$  ions and is isotypic to  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ . The bonding angles and distances within the edge-sharing  $[\text{Si}_2\text{N}_6]^{10-}$  double-tetrahedra are strongly dependent on the Lewis acidity of the counter ions. This finding is discussed in relation to the compounds  $\text{Ca}_5\text{Si}_2\text{N}_6$  and  $\text{Ba}_5\text{Si}_2\text{N}_6$  which also exhibit isolated  $[\text{Si}_2\text{N}_6]^{10-}$  ions.

## Keywords

Lithium; Fluxing Agent; Strontium; Nitridosilicates; X-Ray diffraction

## Introduction

Recently, we have reported on the utilization of liquid lithium for the synthesis of quaternary lithium nitridosilicates. The ability of liquid lithium to dissolve a variety of metals, silicon and nitrogen allows for a controlled synthesis of group-type silicates, chain-like anions up to frameworks by simply adjusting the  $\text{Li}_3\text{N}$  content, the nitrogen pressure ( $\text{LiN}_3$ ) and the reaction temperature.<sup>[1]</sup> By adding an excess of  $\text{Li}_3\text{N}$  to the reaction mixture higher condensation of the  $[\text{SiN}_4]$ -tetrahedra network is suppressed and the lowest degree of condensation for nitridosilicates is observed. Orthosilicate-like isolated  $[\text{SiN}_4]^{8-}$  tetrahedra, which might occur in the compound  $\text{Li}_8\text{SiN}_4$  are not yet structurally verified.<sup>[2,3]</sup> Consequently, up to now group-type silicates made up from edge-sharing  $[\text{Si}_2\text{N}_6]^{10-}$  double-tetrahedra represent nitridosilicates with the lowest degree of condensation characterized by single-crystal X-ray diffractometry so far. Identical building blocks have already been reported for  $\text{Ba}_5\text{Si}_2\text{N}_6$  synthesized by *DiSalvo* et al. in a sodium flux and  $\text{Ca}_5\text{Si}_2\text{N}_6$  obtained via solid-state reaction of  $\text{Ca}_2\text{N}$  and Si.<sup>[4,5]</sup> In this contribution we report on synthesis and structural features of  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and on the isotypic Sr-phase.

## Results and discussion

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3  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  were synthesized from the corresponding metals,  $\text{Si}(\text{NH})_2$  and an  
4 excess of  $\text{Li}_3\text{N}$  in weld shut tantalum ampoules at 900 °C. Addition of Li metal as a fluxing  
5 agent was not essential for the synthesis of suitable single crystals. This might be due to  $\text{Li}_3\text{N}$   
6 acting as a flux as it melts above 815 °C under autogenous nitrogen pressure in closed  
7 systems.<sup>[6]</sup> The title compounds are not stable against air and moisture and were handled  
8 under inert gas atmosphere. The approximate atomic ratio of heavy elements (Ca/Sr and Si)  
9 was determined by energy dispersive X-ray microanalysis.  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$   
10 crystallize in the monoclinic space group  $C2/m$  with two formula units per unit cell (for  
11 details see Table 1).  
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20 The unit cell and coordination spheres of  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  are depicted in Figure 1 and Figure 2,  
21 respectively. The asymmetric unit consist of two Sr and N sites, one Si and Li site named  
22 according to Figure 2. The structure is built up from isolated  $[\text{Si}_2\text{N}_6]^{10-}$  ions and is isotypic to  
23 that of the nitridogermanate  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ .<sup>[7]</sup> Group-like  $[\text{Si}_2\text{N}_6]^{10-}$  ions have already been  
24 reported for  $\text{Ca}_5\text{Si}_2\text{N}_6$  and  $\text{Ba}_5\text{Si}_2\text{N}_6$ .<sup>[4,5]</sup> Due to the edge-sharing of  $[\text{SiN}_4]$  tetrahedra, the  
25 tetrahedra angels are distorted to values of 91 - 96° (N2-Si1-N2) for all compounds (cf. Table  
26 2). The corresponding Si1-N2 bonds are elongated from 1.74 Å to 1.81 – 1.85 Å, resulting in  
27 quite short Si1-Si1 distances ranging from 2.40(1) Å in  $\text{Ca}_5\text{Si}_2\text{N}_6$  to 2.556(7) Å in  
28  $\text{Ba}_5\text{Si}_2\text{N}_6$ .<sup>[4,5]</sup> The Si1-Si1 distances of  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  are ranging in between  
29 these values (cf. Table 2). Regarding the series of isolated  $[\text{Si}_2\text{N}_6]^{10-}$  ions one could assume  
30 that the distortion of the square built up from Si1 and N2 is dependent on the lewis acidity of  
31 the surrounding metal ions. The smaller ionic radius of  $\text{Ca}^{2+}$  compared to  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  leads  
32 to shorter N-metal distances and the higher lewis acidity results in a displacement of N2 from  
33 the ideal square built up from Si1 and N2. Consequently, the angels Si-N2-Si are increasing  
34 from 91.1(1)° in  $\text{Ba}_5\text{Si}_2\text{N}_6$ , 93.2(3)° in  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  to 96.7(1)° in  $\text{Ca}_5\text{Si}_2\text{N}_6$ .<sup>[4,5]</sup> Presumably,  
35 this effect is responsible for the decrease of the distances Si1-Si1 in the sequence  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  to  
36  $\text{Ca}^{2+}$  (Table 2). The distances N-EA (EA = alkaline earth) in  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  are  
37 in the typical range for alkaline earth nitrides.<sup>[8]</sup> In  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  both metal sites are  
38 coordinated by six N-atoms, whereas in  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  Sr1 exhibits a 6+2 coordination. The  
39 coordination spheres (cf. Figure 2) were assigned by lattice energy calculations (MAPLE;  
40 Madelung part of lattice energie).<sup>[9,10]</sup> In both compounds Li1 is coordinated by four N-atoms  
41 in distorted tetrahedral fashion (105-123°) with typical distances Li-N (values within the sum  
42 of the ionic radii).<sup>[9,11]</sup> The smaller lattice parameters of  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  also lead to significantly  
43 shorter Li-N distances (Li1-N1: 1.968(3), 2.072(3), 2.123(3) Å, Li1-N2: 2.259(3) Å). Edge-  
44 sharing of  $[\text{LiN}_4]$ -polyhedra along [100] causes chains of  $\text{Li}^+$ -ions with quite short Li1-Li1  
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3 distances ( $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$ : 2.213(6), 2.447(6)Å;  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ : 2.273(18), 2.487(19)Å). The Li-ion  
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5 conductor  $\text{Li}_2\text{SiN}_2$  exhibits comparable chains of  $[\text{LiN}_x]$ -polyhedra with analogues Li-Li  
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7 distances.<sup>[12]</sup> It may be noted that the addition of 1 % of Eu to the reaction mixture yielded red  
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9 single crystals, which, however showed no fluorescence under UV light at room temperature.

## 10 11 12 13 14 **Conclusion**

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16 In this contribution, we demonstrate that addition of an excess of  $\text{Li}_3\text{N}$  to the reaction mixture  
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18 of Ca/Sr and  $\text{Si}(\text{NH})_2$  suppresses the higher condensation of  $[\text{SiN}_4]$ -tetrahedra and a low  
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20 degree of condensation for nitridosilicates is achieved. The isotypic compounds  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$   
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22 and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  are the third and fourth example of nitridosilicates containing isolated  
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24  $[\text{Si}_2\text{N}_6]^{10-}$  ions, respectively. Presumably, the lengths of the distances Si-Si within the  
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26  $[\text{Si}_2\text{N}_6]^{10-}$  ions is dependent on the lewis acidity of the counter ions. It may be noted that the  
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28 presence of  $[\text{LiN}_4]$ -polyhedra chains along [100] might be an interesting feature for lithium  
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30 ion conductivity.

## 31 32 33 34 **Experimental Section**

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36 All manipulations were performed with rigorous exclusion of oxygen and moisture in flame-  
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38 dried Schlenk-type glassware on a Schlenk line interfaced to a vacuum ( $10^{-3}$  mbar) line or in  
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40 an argon-filled glove box (Unilab, MBraun, Garching,  $\text{O}_2 < 0.1$  ppm,  $\text{H}_2\text{O} < 0.1$  ppm).  $\text{Li}_3\text{N}$   
41  
42 was purchased from Alfa Aesar (99.4 %), Ca and Sr from Sigma-Aldrich (99.99 %) and  
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44  $\text{Si}(\text{NH})_2$  was synthesized according to the literature.<sup>[13]</sup>

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46 For the reactions, tantalum crucibles (wall thickness 0.5 mm, internal diameter 10 mm, length  
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48 300 mm) were cleaned in a mixture of  $\text{HNO}_3$  (conc.) and HF (40 %). They were arc-welded  
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50 under a pressure of 1 bar purified argon. The crucible holder was water cooled in order to  
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52 avoid decomposition reactions during welding.

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54 Single crystals of  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  were synthesized from 60 mg  $\text{Li}_3\text{N}$   
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56 (1.72 mmol), 50 mg  $\text{Si}(\text{NH})_2$  (0.86 mmol) and 34 mg Ca (0.86 mmol) / 75 mg Sr (0.86 mmol)  
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58 in closed tantalum crucibles placed in silica tubes. The silica tube (under argon) was placed in  
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60 the middle of a tube furnace. The temperature was raised to 900 °C (rate 180 °C h<sup>-1</sup>),  
maintained for 48 h, subsequently cooled to 500 °C (rate 5 °C h<sup>-1</sup>) and finally quenched to  
room temperature by switching off the furnace.

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3 **X-ray diffraction:** By inspection under a microscope integrated in a glove box, colorless  
4 single crystals of the title compounds were isolated from residual  $\text{Li}_3\text{N}$  and enclosed in glass  
5 capillaries. Single-crystal X-ray diffraction data were collected on a Stoe IPDS I for  
6  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and on an Oxford Diffraction XCalibur for  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  ( $\text{MoK}\alpha$  radiation). The  
7 program package SHELX97 was used for structure solution and refinement.<sup>[14]</sup> Further details  
8 of the crystal structure investigations can be obtained from the Fachinformationszentrum  
9 Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail:  
10 [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)) on quoting the depository number CSD-420675 ( $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$ ) and  
11 CSD-421259 ( $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ ), the names of the authors and citation of the publication.  
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19 **Microanalysis:** EDX spectra of selected crystals were obtained using a JSM 6500F scanning  
20 electron microscope (JEOL) equipped with an EDX detector 7418 (Oxford Instruments). The  
21 approximate molar ratio of the elements Ca : Si was found to be 22(2) : 14(2) (average from 3  
22 independent measurements) for  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and Sr : Si was found to be 19(2) : 13(2)  
23 (average from 3 independent measurements) for  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ .  
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### 30 **Acknowledgments**

31  
32 We thank Dr. Peter Mayer, **Thomas Miller** (single-crystal X-ray diffractometry) and Christian  
33 Minke (X-ray microanalysis). The authors gratefully acknowledge financial support from the  
34 Fonds der Chemischen Industrie (FCI) and the Deutsche Forschungsgemeinschaft (DFG),  
35 project SCHN 377/ 14-1.  
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**Table 1.** Crystallographic data of  $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$  and  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ .

| Formula  | $\text{Li}_4\text{Ca}_3\text{Si}_2\text{N}_6$                | $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ |
|--|--|---|
| Formula mass / $\text{g} \cdot \text{mol}^{-1}$                      | 288.24   | 430.86  |
| Crystal system   | monoclinic   |   |
| Space group  | $C2/m$ (no. 12)  |   |
| Cell parameters / $\text{\AA}, ^\circ$                               | $a = 5.7873(12)$   | $a = 6.1268(12)$                              |
|  | $b = 9.7045(19)$   | $b = 9.6866(19)$                              |
|  | $c = 5.9771(12)$   | $c = 6.2200(12)$                              |
|  | $\beta = 90.45(3)$   | $\beta = 90.24(3)$                            |
| Cell volume / $10^6 \text{ pm}^3$                                    | $V = 335.68(12)$   | $V = 369.14(12)$                              |
| Formula units / cell   | 2  |   |
| Crystal size / $\text{mm}^3$   | $0.08 \cdot 0.05 \cdot 0.02$                                 | $0.14 \cdot 0.12 \cdot 0.05$                  |
| $\rho_{\text{calcd.}} / \text{g} \cdot \text{cm}^{-3}$               | 2.852  | 3.876   |
| $\mu / \text{mm}^{-1}$   | 2.751  | 21.86   |
| $F(000)$   | 284  | 392   |
| Diffractometer   | Stoe IPDS I  | Oxford<br>Diffraction                         |
|  |  | XCalibur                                      |
| Temperature / K  | 295(2)   | 200(2)  |
| Radiation,<br>monochromator  | Mo- $K_\alpha$ , ( $\lambda = 71.073 \text{ pm}$ ), graphite |   |
| Absorption correction  | multi-scan   | numerical                                     |
| min. / max. transmission   | 0.726 / 0.946  | 0.0467 / 0.466                                |
| $\theta$ range / $^\circ$  | 2.3 – 30.5   | 3.89 – 29.99                                  |
| Measured reflections   | 1787   | 1221  |
| Independent reflections  | 505  | 539   |
| Observed reflections   | 450  | 456   |
| Refined parameters   | 36   | 36  |
| GoF  | 1.117  | 1.122   |
| $R$ indices ( $F_o^2 \geq 2\sigma(F_o^2)$ )                          | $R1 = 0.0219$  | $R1 = 0.0314$                                 |
|  | $wR2 = 0.0566$   | $wR2 = 0.0903$                                |
| $R$ indices (all data)   | $R1 = 0.0252$  | $R1 = 0.0370$                                 |
|  | $wR2 = 0.0572^{[a]}$   | $wR2 = 0.0935^{[b]}$                          |
| Max. / min. residual<br>electron density / $\text{e}\text{\AA}^{-3}$ | 0.512 / -0.457   | 1.816 / -1.741                                |

[a]  $w = [\sigma^2(F_o^2) + (0.0347 P)^2 + 0.00 P]^{-1}$  where  $P = (F_o^2 + 2 F_c^2) / 3$

[b]  $w = [\sigma^2(F_o^2) + (0.0595 P)^2 + 0.00 P]^{-1}$  where  $P = (F_o^2 + 2 F_c^2) / 3$



**Table 2.** Comparison of compounds exhibiting isolated  $[\text{Si}_2\text{N}_6]^{10-}$  ions.

|             | $\text{Ba}_5\text{Si}_2\text{N}_6$ <sup>[5]</sup> |                        | $\text{Ca}_5\text{Si}_2\text{N}_6$ <sup>[4]</sup> |                        | $\text{Li}_4\text{M}_3\text{Si}_2\text{N}_6$ |                        |
|-------------|---|------------------------|---|------------------------|--|------------------------|
|             | Na-Flux   | solid-state            | Ca  | Sr                     | Li-Flux                                      | Li-Flux                |
| Synthesis   | Na-Flux   | solid-state            | Li-Flux   | Li-Flux                | Li-Flux                                      | Li-Flux                |
| Space group | $P2_12_12_1$                                      | $C2/c$                 | $C2/m$  | $C2/m$                 | $C2/m$                                       | $C2/m$                 |
| X-ray T /K  | 293   | 293                    | 293   | 200                    | 293  | 200                    |
| Si-Si /Å    | 2.556(7)  | 2.40(1)                | 2.453(1)  | 2.540(4)               | 2.453(1)                                     | 2.540(4)               |
| Si-N2 /Å    | 1.83(2) <sup>[a]</sup>                            | 1.81(1) <sup>[a]</sup> | 1.83(1) <sup>[a]</sup>                            | 1.85(1) <sup>[a]</sup> | 1.83(1) <sup>[a]</sup>                       | 1.85(1) <sup>[a]</sup> |
| Si-N1 /Å    | 91.1(1) <sup>[a]</sup>                            | 96.7(1) <sup>[a]</sup> | 95.9(1)   | 93.2(3)                | 95.9(1)                                      | 93.2(3)                |
| Si-N2-Si /° | 1.75(2) <sup>[a]</sup>                            | 1.73(1) <sup>[a]</sup> | 1.711(2)  | 1.735(4)               | 1.711(2)                                     | 1.735(4)               |

[a] Averaged values because of more than one set of symmetry independent bonds/angles.

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7 **Figure 1.** Two unit cells of  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$  along [00-1]. Ellipsoids at 90 % probability level.  
8 [SiN<sub>4</sub>] units are depicted as closed gray tetrahedra, N atoms black, Sr ions white/black and Li  
9 ions gray.  
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15 **Figure 2.** Coordination spheres in  $\text{Li}_4\text{Sr}_3\text{Si}_2\text{N}_6$ . N atoms black, Sr ions white and Li ions gray.  
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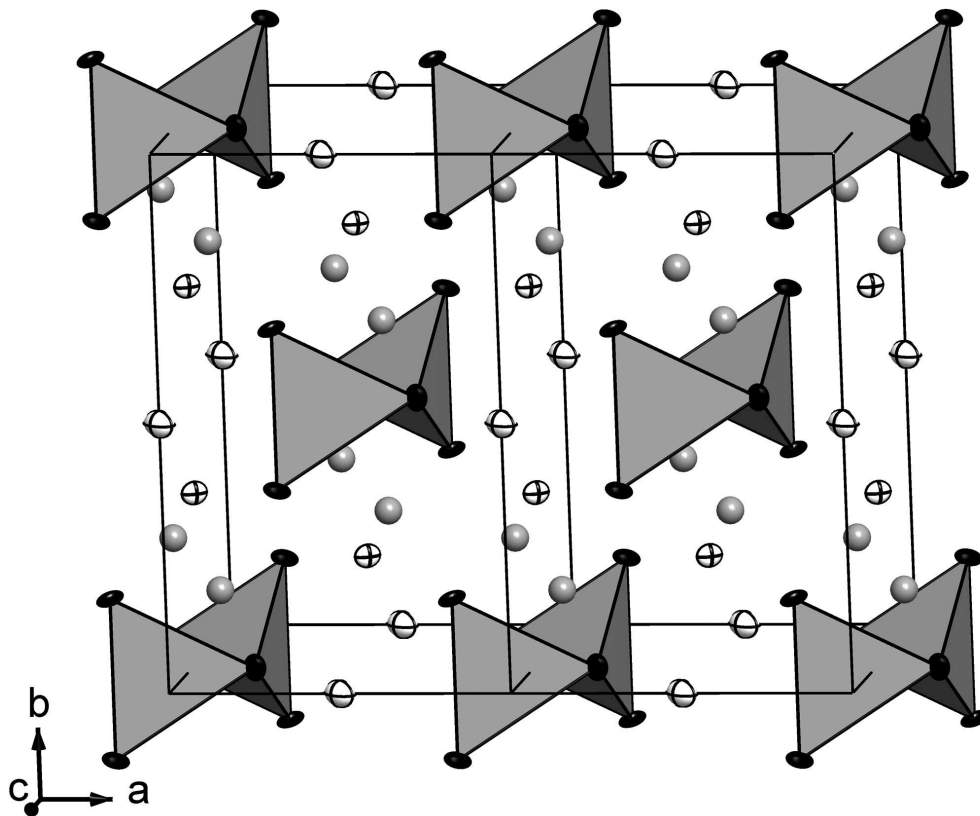


Figure1  
85x70mm (600 x 600 DPI)

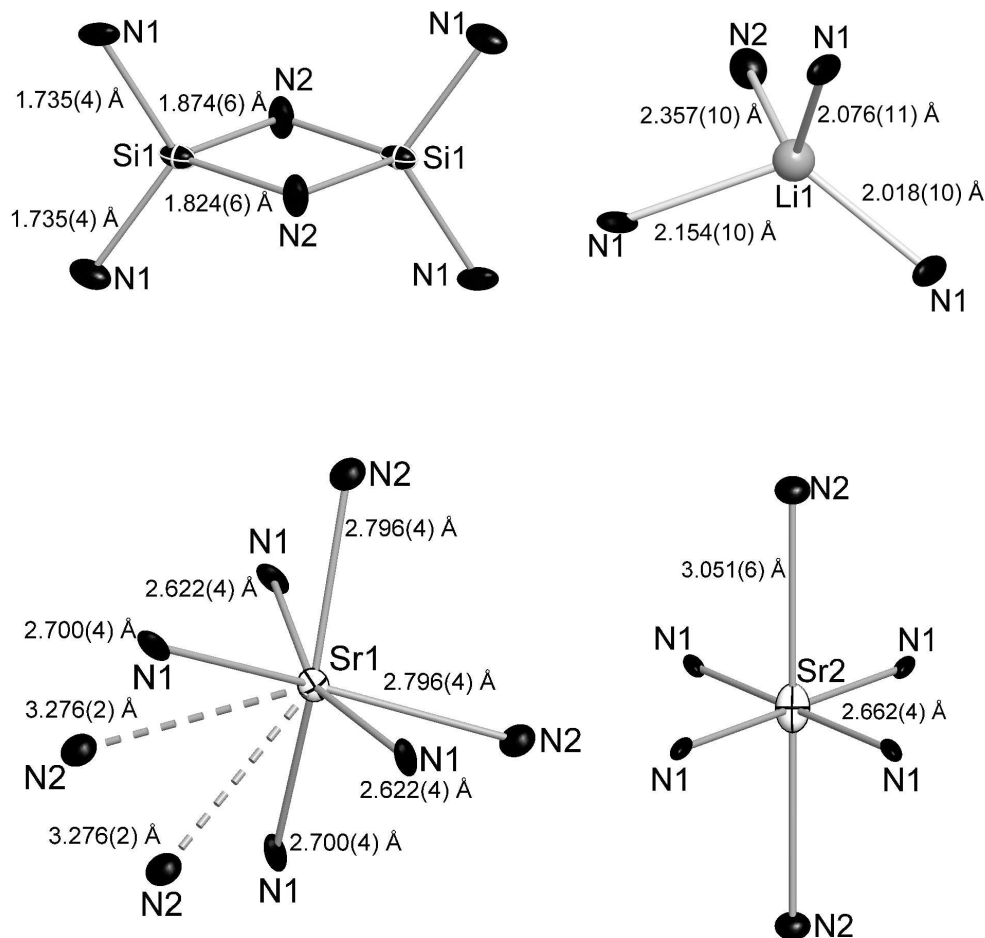


Figure2