Li4Ca3Si2N6 and Li4Sr3Si2N6 - Quaternary Lithium Nitridosilicates with Isolated [Si2N6]10- Ions

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Li$_4$Ca$_3$Si$_2$N$_6$ and Li$_4$Sr$_3$Si$_2$N$_6$ - Quaternary Lithium Nitridosilicates with Isolated [Si$_2$N$_6$]$^{10-}$ Ions

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Abstract

The isotypic nitridosilicates $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ were synthesized by reaction of Sr or Ca with $Si(NH)_2$ and additional excess of Li_3N in weld shut tantalum ampoules. The crystal structure, which has been solved by single-crystal X-ray diffraction ($Li_4Sr_3Si_2N_6$: *C2/m*, *Z* = 2, *a* = 6.1268(12), *b* = 9.6866(19), *c* = 6.2200(12) Å, *β* = 90.24(3)°, *wR*2 = 0.0903) is made up from isolated $[Si_2N_6]^{10-}$ ions and is isotypic to $Li_4Sr_3Ge_2N_6$. The bonding angles and distances within the edge-sharing $[Si_2N_6]^{10-}$ double-tetrahedra are strongly dependent on the lewis acidity of the counter ions. This finding is discussed in relation to the compounds $Ca_5Si_2N_6$ and $Ba_5Si_2N_6$ which also exhibit isolated $[Si_2N_6]^{10-}$ 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 Li_3N content, the nitrogen pressure (LiN_3) and the reaction temperature.[1] By adding an excess of Li_3N to the reaction mixture higher condensation of the $[SiN_4]$-tetrahedra network is suppressed and the lowest degree of condensation for nitridosilicates is observed. Orthosilicate-like isolated $[SiN_4]^{8-}$ tetrahedra, which might occur in the compound Li_8SiN_4 are not yet structurally verified.[2,3] Consequently, up to now group-type silicates made up from edge-sharing $[Si_2N_6]^{10-}$ 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 $Ba_5Si_2N_6$ synthesized by *DiSalvo* et al. in a sodium flux and $Ca_5Si_2N_6$ obtained via solid-state reaction of Ca_2N and Si.[4,5] In this contribution we report on synthesis and structural features of $Li_4Ca_3Si_2N_6$ and on the isotypic Sr-phase.

Results and discussion

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$Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ were synthesized from the corresponding metals, $Si(NH)_2$ and an excess of Li_3N in weld shut tantalum ampoules at 900 °C. Addition of Li metal as a fluxing agent was not essential for the synthesis of suitable single crystals. This might be due to Li_3N acting as a flux as it melts above 815 °C under autogenous nitrogen pressure in closed systems.[6] The title compounds are not stable against air and moisture and were handled under inert gas atmosphere. The approximate atomic ratio of heavy elements (Ca/Sr and Si) was determined by energy dispersive X-ray microanalysis. $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ crystallize in the monoclinic space group *C*2/*m* with two formula units per unit cell (for details see Table 1).

The unit cell and coordination spheres of $Li_4Sr_3Si_2N_6$ are depicted in Figure 1 and Figure 2, respectively. The asymmetric unit consist of two Sr and N sites, one Si and Li site named according to Figure 2. The structure is built up from isolated $[Si_2N_6]^{10-}$ ions and is isotypic to that of the nitridogermanate $Li_4Sr_3Ge_2N_6$.[7] Group-like $[Si_2N_6]^{10-}$ ions have already been reported for $Ca_5Si_2N_6$ and $Ba_5Si_2N_6$.[4,5] Due to the edge-sharing of $[SiN_4]$ tetrahedra, the tetrahedra angels are distorted to values of 91 - 96° (N2-Si1-N2) for all compounds (cf. Table 2). The corresponding Si1-N2 bonds are elongated from 1.74 Å to 1.81 – 1.85 Å, resulting in quite short Si1-Si1 distances ranging from 2.40(1) Å in $Ca_5Si_2N_6$ to 2.556(7) Å in $Ba_5Si_2N_6$.[4,5] The Si1-Si1 distances of $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ are ranging in between these values (cf. Table 2). Regarding the series of isolated $[Si_2N_6]^{10-}$ ions one could assume that the distortion of the square built up from Si1 and N2 is dependent on the lewis acidity of the surrounding metal ions. The smaller ionic radius of Ca^{2+} compared to Sr^{2+} and Ba^{2+} leads to shorter N-metal distances and the higher lewis acidity results in a displacement of N2 from the ideal square built up from Si1 and N2. Consequently, the angels Si-N2-Si are increasing from 91.1(1)° in $Ba_5Si_2N_6$, 93.2(3)° in $Li_4Sr_3Si_2N_6$ to 96.7(1)° in $Ca_5Si_2N_6$.[4,5] Presumably, this effect is responsible for the decrease of the distances Si1-Si1 in the sequence Ba^{2+}, Sr^{2+} to Ca^{2+} (Table 2). The distances N-EA (EA = alkaline earth) in $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ are in the typical range for alkaline earth nitrides.[8] In $Li_4Ca_3Si_2N_6$ both metal sites are coordinated by six N-atoms, whereas in $Li_4Sr_3Si_2N_6$ Sr1 exhibits a 6+2 coordination. The coordination spheres (cf. Figure 2) were assigned by lattice energy calculations (MAPLE; Madelung part of lattice energie).[9,10] In both compounds Li1 is coordinated by four N-atoms in distorted tetrahedral fashion (105-123°) with typical distances Li-N (values within the sum of the ionic radii).[9,11] The smaller lattice parameters of $Li_4Ca_3Si_2N_6$ also lead to significantly shorter Li-N distances (Li1-N1: 1.968(3), 2.072(3), 2.123(3) Å, Li1-N2: 2.259(3) Å). Edge-sharing of $[LiN_4]$-polyhedra along [100] causes chains of Li^+-ions with quite short Li1-Li1

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distances ($Li_4Ca_3Si_2N_6$: 2.213(6), 2.447(6)Å; $Li_4Sr_3Si_2N_6$: 2.273(18), 2.487(19)Å). The Li-ion conductor Li_2SiN_2 exhibits comparable chains of $[LiN_x]$-polyhedra with analogoues Li-Li distances.[12] It may be noted that the addition of 1 % of Eu to the reaction mixture yielded red single crystals, which, however showed no fluorescence under UV light at room temperature.

Conclusion

In this contribution, we demonstrate that addition of an excess of Li_3N to the reaction mixture of Ca/Sr and $Si(NH)_2$ suppresses the higher condensation of $[SiN_4]$-tetrahedra and a low degree of condensation for nitridosilicates is achieved. The isotypic compounds $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ are the third and fourth example of nitridosilicates containing isolated $[Si_2N_6]^{10-}$ ions, respectively. Presumably, the lengths of the distances Si-Si within the $[Si_2N_6]^{10-}$ ions is dependent on the lewis acidity of the counter ions. It may be noted that the presence of $[LiN_4]$-polyhedra chains along [100] might be an interesting feature for lithium ion conductivity.

Experimental Section

All manipulations were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware on a Schlenk line interfaced to a vacuum (10^{-3} mbar) line or in an argon-filled glove box (Unilab, MBraun, Garching, O_2 < 0.1 ppm, H_2O < 0.1 ppm). Li_3N was purchased from Alfa Aesar (99.4 %), Ca and Sr from Sigma-Aldrich (99.99 %) and $Si(NH)_2$ was synthesized according to the literature.[13]

For the reactions, tantalum crucibles (wall thickness 0.5 mm, internal diameter 10 mm, length 300 mm) were cleaned in a mixture of HNO_3 (conc.) and HF (40 %). They were arc-welded under a pressure of 1 bar purified argon. The crucible holder was water cooled in order to avoid decomposition reactions during welding.

Single crystals of $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$ were synthesized from 60 mg Li_3N (1.72 mmol), 50 mg $Si(NH)_2$ (0.86 mmol) and 34 mg Ca (0.86 mmol) / 75 mg Sr (0.86 mmol) in closed tantalum crucibles placed in silica tubes. The silica tube (under argon) was placed in the middle of a tube furnace. The temperature was raised to 900 °C (rate 180 °C h^{-1}), maintained for 48 h, subsequently cooled to 500 °C (rate 5 °C h^{-1}) and finally quenched to room temperature by switching off the furnace.

X-ray diffraction: By inspection under a microscope integrated in a glove box, colorless single crystals of the title compounds were isolated from residual Li_3N and enclosed in glass capillaries. Single-crystal X-ray diffraction data were collected on a Stoe IPDS I for $Li_4Ca_3Si_2N_6$ and on an Oxford Diffraction XCalibur for $Li_4Sr_3Si_2N_6$ ($Mo_{K\alpha}$ radiation). The program package SHELX97 was used for structure solution and refinement.[14] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-420675 ($Li_4Ca_3Si_2N_6$) and CSD-421259 ($Li_4Sr_3Si_2N_6$), the names of the authors and citation of the publication.

Microanalysis: EDX spectra of selected crystals were obtained using a JSM 6500F scanning electron microscope (JEOL) equipped with an EDX detector 7418 (Oxford Instruments). The approximate molar ratio of the elements Ca : Si was found to be 22(2) : 14(2) (average from 3 independent measurements) for $Li_4Ca_3Si_2N_6$ and Sr : Si was found to be 19(2) : 13(2) (average from 3 independent measurements) for $Li_4Sr_3Si_2N_6$.

Acknowledgments

Table 1. Crystallographic data of $Li_4Ca_3Si_2N_6$ and $Li_4Sr_3Si_2N_6$.

Formula	$Li_4Ca_3Si_2N_6$	$Li_4Sr_3Si_2N_6$
Formula mass / g · mol⁻¹	288.24	430.86
Crystal system	monoclinic	
Space group	$C2/m$ (no. 12)	
Cell parameters / Å, °	$a = 5.7873(12)$ $b = 9.7045(19)$ $c = 5.9771(12)$ $\beta = 90.45(3)$	$a = 6.1268(12)$ $b = 9.6866(19)$ $c = 6.2200(12)$ $\beta = 90.24(3)$
Cell volume / 10^6 pm³	$V = 335.68(12)$	$V = 369.14(12)$
Formula units / cell	2	
Crystal size / mm³	$0.08 \cdot 0.05 \cdot 0.02$	$0.14 \cdot 0.12 \cdot 0.05$
$\rho_{calcd.}$ / g · cm⁻³	2.852	3.876
μ / mm⁻¹	2.751	21.86
$F(000)$	284	392
Diffractometer	Stoe IPDS I	Oxford Diffraction XCalibur
Temperature / K	295(2)	200(2)
Radiation, monochromator	Mo-K$_\alpha$, ($\lambda = 71.073$ pm), graphite	
Absorption correction	multi-scan	numerical
min. /max. transmission	0.726 / 0.946	0.0467 / 0.466
θ range / °	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))	$R1 = 0.0219$ $wR2 = 0.0566$	$R1 = 0.0314$ $wR2 = 0.0903$
R indices (all data)	$R1 = 0.0252$ $wR2 = 0.0572$[a]	$R1 = 0.0370$ $wR2 = 0.0935$[b]
Max. / min. residual electron density/ eÅ⁻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 $P= (F_o^2 + 2\ F_c^2)\ /3$

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Table 2. Comparison of compounds exhibiting isolated $[Si_2N_6]^{10-}$ ions.

| | $Ba_5Si_2N_6$[5] | $Ca_5Si_2N_6$[4] | $Li_4M_3Si_2N_6$ | |
			Ca	Sr
Synthesis	Na-Flux	solid-state	Li-Flux	Li-Flux
Space group	$P2_12_12_1$	$C2/c$	$C2/m$	$C2/m$
X-ray T /K	293	293	293	200
Si-Si /Å	2.556(7)	2.40(1)	2.453(1)	2.540(4)
Si-N2 /Å	1.83(2)[a]	1.81(1)[a]	1.83(1)[a]	1.85(1)[a]
Si-N1 /Å	91.1(1)[a]	96.7(1)[a]	95.9(1)	93.2(3)
Si-N2-Si /°	1.75(2)[a]	1.73(1)[a]	1.711(2)	1.735(4)

[a] Averaged values because of more than one set of symmetry

independent bonds/angles.

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Figure 1. Two unit cells of $Li_4Sr_3Si_2N_6$ along [00-1]. Ellipsoids at 90 % probability level. [SiN_4] units are depicted as closed gray tetrahedra, N atoms black, Sr ions white/black and Li ions gray.

Figure 2. Coordination spheres in $Li_4Sr_3Si_2N_6$. N atoms black, Sr ions white and Li ions gray.

References

[1] S. Pagano, S. Lupart, M. Zeuner, W. Schnick, *Angew. Chem.* **2009**, *121*, 6453-6456; *Angew. Chem., Int. Ed.* **2009**, *48*, 6335-6338.

[2] J. Lang, J.-P. Charlot, *Rev. Chim. Miner.* **1970**, *7*, 121-131.

[3] H. Yamane, S. Kikkawa, M. Koizumi, *Solid State Ionics* **1987**, *25*, 183-191.

[4] F. Ottinger, R. Nesper, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1597-1602.

[5] H. Yamane, F. J. DiSalvo, *J. Alloys Compd.* **1996**, *240*, 33-36.

[6] R. P. Elliot, *Constitution of Binary Alloys*, McGraw-Hill Book Company, New York, **1965**.

[7] D. G. Park, Z. A. Gál, F. J. DiSalvo, *J. Solid State Chem.* **2003**, *172*, 166-170.

[8] P. Hoehn, S. Hoffmann, J. Hunger, S. Leoni, F. Nitsche, W. Schnelle, R. Kniep, *Chem. Eur. J.* **2009**, *15*, 3419-3425.

[9] R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Found. Crystallogr.* **1976**, *32*, 751-767.

[10] R. Hübbenthal, Programm zur Berechnung des Madelunganteils der Gitterenergie, Vers. 4; Universität Gießen **1993**.

[11] H. Baur, *Crystallogr. Rev.* **1987**, *1*, 59-83.

[12] S. Pagano, M. Zeuner, S. Hug, W. Schnick, *Eur. J. Inorg. Chem.* **2009**, 1579-1584.

[13] H. Lange, G. Wötting, G. Winter, *Angew. Chem.* **1991**, *103*, 1606-1625; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1579-1597.

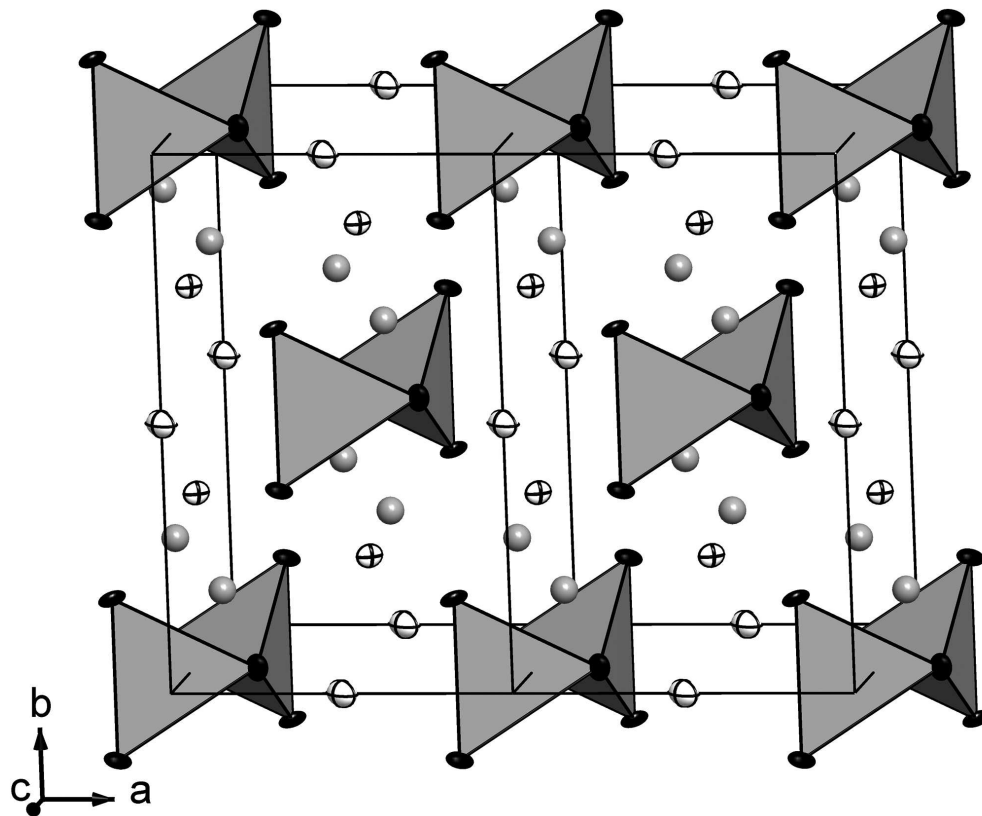[14] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112-122.
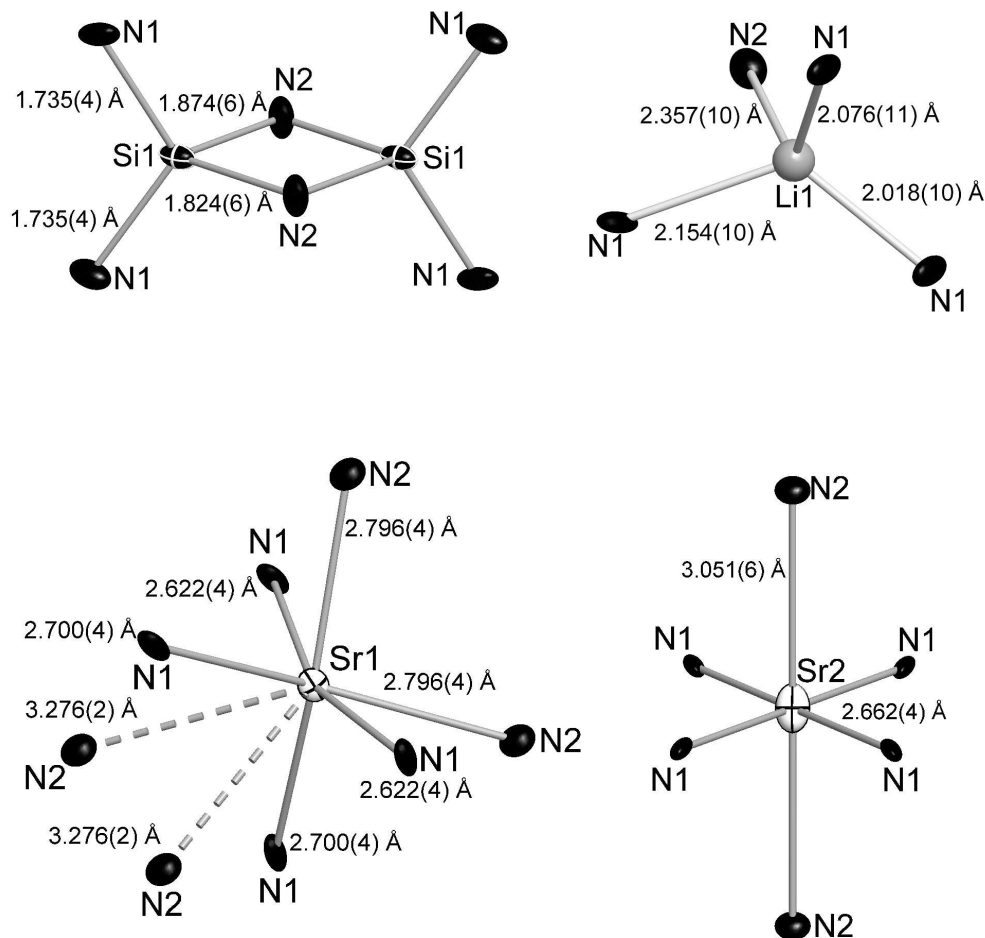
Figure1
85x70mm (600 x 600 DPI)

Figure2