

Crystal structure and mechanical properties of SrSi₇N₁₀

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1. Introduction

Nitridosilicates, oxonitridosilicates and oxonitridoaluminosilicates are well known to exhibit interesting physical properties such as high strength, good wear resistance, high decomposition temperature, good oxidation resistance, excellent thermal-shock properties and resistance to corrosive environments. Such materials have traditionally been developed for specific applications such as cutting tools, burners, welding nozzles, heat exchangers and engine applications. During the last decades, a rapid development has been made in new synthesis methods.

With more than 1000 crystalline structures, oxosilicate chemistry [1] appears to be very rich and versatile. Typical building units of silicates are SiO₄ tetrahedrons with the oxygen atoms being connected to one (O^[1]) or two (O^[2])

neighboring Si⁴⁺. Contrarily, nitrogen atoms in nitridosilicates can be connected to one (N^[1]), two (N^[2]), three (N^[3]) and even four (N^[4]) silicon atoms [2–6]. Thus nitridosilicates and oxonitridosilicates exhibit a much higher variety of structural features, especially in terms of connectivity of the tetrahedral networks. The crystal chemistry of silicates has become much richer by introducing nitrogen atoms as anionic network formers, instead of or additionally to oxygen. The main obstacle for development in this field has been the lack of appropriate synthesis methods, which has been solved to some extent by using high-temperature furnaces and electropositive metals, the synthesis route used in this work.

In this article, we report on the synthesis, crystal structure determination and single-crystal hardness properties of the phase SrSi₇N₁₀ (isostructural with its barium equivalent, BaSi₇N₁₀ [7]). Within the group of all known nitridosilicates, SrSi₇N₁₀ and BaSi₇N₁₀ represent the most highly condensed ternary framework structures. The Si : N molar ratio of 1 : 1.43 reaches almost the value for binary Si₃N₄ (1 : 1.33).

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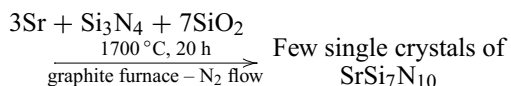
2. Experimental

2.1. Synthesis of SrSi₇N₁₀

Initially, a single crystal of SrSi₇N₁₀ was obtained by the reaction of a mixture of strontium (70 mg, 0.80 mmol) with silicon diimide (101 mg, 2 mmol) in a radio-frequency furnace using tungsten crucibles (heating from RT to 900 °C within 5 min, then holding the temperature for 25 min, heating to 1600 °C within 2 h, holding the temperature for 10 h, slowly cooling to 1000 °C within 48 h, then quenching to room temperature).

More and larger single crystals of SrSi₇N₁₀ were obtained by the following two different ways of synthesis:

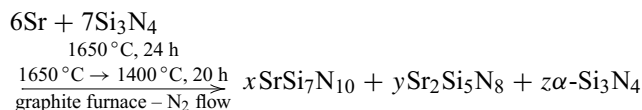
- (i) 309.1 mg of Sr metal (3.519 mmol), 164.6 mg of Si₃N₄ powder (1.173 mmol) and 493.5 mg of SiO₂ powder (8.21 mmol) were mixed together under argon atmosphere in a glove box and transferred into a niobium tube. The reaction mixture was heated in a graphite furnace under nitrogen flow to 1700 °C within 2 h and maintained at that temperature for 20 h; the sample was then quenched to room temperature. Few single crystals of SrSi₇N₁₀ were obtained as colorless and transparent needles.



- (ii) Sr metal and Si₃N₄ powder were heated together in a niobium tube at 1650 °C in a graphite furnace under N₂ flow. For that purpose a mixture of Sr metal (ChemPur, under argon, 98%, stoichiometric excess of 50%: 2.36 mmol; 155.4 mg) and Si₃N₄ (2.8 mmol; 386.3 mg) was mixed together under argon atmosphere in a glove box and transferred into a niobium tube. The latter was positioned in a graphite furnace. Under a nitrogen atmosphere the reaction mixture was heated to 650 °C within 1 h and to 1650 °C within another 24 h, maintained at that temperature for 12 h, and then slowly cooled to 1400 °C within 20 h. Finally, the product was quenched to room temperature. X-ray powder diffraction performed on the resulting powder confirmed that this process led to the formation of SrSi₇N₁₀, but the sample contained also some secondary phases (Sr₂Si₅N₈ and α-Si₃N₄). So far, we have not been able to prepare a monophasic SrSi₇N₁₀ sample. As compared to the synthesis of BaSi₇N₁₀, it seems to be specifically harder to yield a single-phase product.

Energy dispersive spectrometry (EDS) analyses were performed on several selected colorless, transparent single crystals using a scanning electron microscope. The following atomic metal composition was found: 13.1(3)% Sr and 86.9(3)% Si. The theoretical composition calculated for SrSi₇N₁₀ is 12.5% Sr and 87.5% Si. In the experimental conditions used, the nitrogen content determination was

not performed, however the metal composition determined in combination with crystallographic data, unequivocally shows that this phase is a pure nitride.



2.2. Crystal structure determination

2.2.1. Data collection

A single-crystal X-ray diffraction data collection was performed at room temperature with an Image Plate STOE Diffractometer. Experimental details are given in Table 1. Data processing was carried out with the IPDS analysis software [8] and the lattice parameters were refined by a least-squares refinement. A semi-empirical absorption correction was applied to the data sets by the program MULTISCAN [9].

2.2.2. Structure solution and refinement

The nitridosilicate SrSi₇N₁₀ crystallizes monoclinic. Among the possible space groups, the refinement procedure allowed to retain the non-centrosymmetric space group *Pc* (No. 7) for this compound, the same space group in which BaSi₇N₁₀ is described [7].

Table 1
Crystallographic data^a for SrSi₇N₁₀ (e.s.d.s in parentheses)

	(1)
Refined formula	SrSi ₇ N ₁₀
Formula weight (g·mol ⁻¹)	424.3
Crystallographic system	monoclinic
Lattice parameters:	
<i>a</i> (Å)	6.868 (1)
<i>b</i> (Å)	6.694 (1)
<i>c</i> (Å)	9.614 (2)
β (°)	105.98 (2)
<i>V</i> (Å ³)	424.9 (1)
Space group	<i>Pc</i> (No. 7)
<i>Z</i>	2
<i>T</i> (K)	293
Density (g·cm ⁻³)	3.32
μ (mm ⁻¹)	7.33
θ range (°)	3.04; 25.98
Index range	
<i>h</i>	–8; 8
<i>k</i>	0; 8
<i>l</i>	–10; 10
<i>R</i> ^b	0.0412
<i>R</i> _w ^c	0.0387
<i>S</i>	0.97
Δρ _{max} (e ⁻ ·Å ⁻³)	1.63
Δρ _{min} (e ⁻ ·Å ⁻³)	–2.07
No. of reflections used	1434
No. of parameters	163
Flack parameter	0.006 (8)

^a All data collected with Mo Kα radiation (λ = 0.71069 Å).

^b $R = \sum(|F_o - F_c|) / \sum|F_o|$.

^c $R_w = \{\sum[w(|F_o - F_c|)^2] / \sum[w|F_o|^2]\}^{1/2}$.

Table 2
Atomic positions and equivalent thermal displacement parameters for SrSi₇N₁₀ (e.s.d.s in parentheses)

Atom	Wyckoff position	x	y	z	U(iso) _{eq.}
Sr1	2a	0.9570	-0.06277(6)	0.1695	0.0282
Si1	2a	0.5402(2)	-0.9742(2)	0.3284(1)	0.0071
Si2	2a	0.3540(2)	-0.0271(2)	0.5165(1)	0.0069
Si3	2a	0.1089(2)	-0.3940(2)	0.5733(1)	0.0070
Si4	2a	0.6665(2)	-0.3653(2)	0.4930(2)	0.0063
Si5	2a	0.8499(2)	-0.6238(2)	0.3093(1)	0.0070
Si6	2a	0.2968(2)	-0.6191(2)	0.3841(1)	0.0065
Si7	2a	0.4841(2)	-0.3707(2)	0.1880(2)	0.0069
N1	2a	0.7462(6)	-0.8433(6)	0.3305(5)	0.0132
N2	2a	0.5671(6)	-0.1317(6)	0.4763(4)	0.0080
N3	2a	0.3177(6)	-0.8696(6)	0.3649(4)	0.0094
N4	2a	0.1532(6)	-0.1642(5)	0.5181(4)	0.0105
N5	2a	0.2860(5)	-0.5003(6)	0.2239(4)	0.0095
N6	2a	0.4467(6)	-0.1165(5)	0.1721(5)	0.0092
N7	2a	0.8876(5)	-0.3852(5)	0.6329(4)	0.0062
N8	2a	0.0791(5)	-0.5792(5)	0.4386(4)	0.0085
N9	2a	0.7040(5)	-0.4135(5)	0.3258(4)	0.0066
N10	2a	0.4973(5)	-0.5394(5)	0.5241(4)	0.0078

Thermal displacement parameters for SrSi₇N₁₀ (e.s.d.s in parentheses)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Sr1	0.0310(3)	0.0198(3)	0.0417(4)	-0.0060(2)	0.0232(2)	-0.0059(2)
Si1	0.0081(6)	0.0083(6)	0.0053(7)	0.0015(4)	0.0027(5)	-0.0007(4)
Si2	0.0105(6)	0.0073(6)	0.0037(7)	-0.0011(4)	0.0036(4)	0.0009(4)
Si3	0.0088(6)	0.0085(5)	0.0040(7)	0.0000(4)	0.0021(4)	0.0002(4)
Si4	0.0065(6)	0.0075(6)	0.0044(6)	-0.0002(4)	0.0010(4)	0.0006(4)
Si5	0.0070(6)	0.0086(6)	0.0054(7)	-0.0011(4)	0.0018(5)	-0.0008(4)
Si6	0.0073(5)	0.0073(5)	0.0054(7)	0.0000(4)	0.0025(5)	-0.0007(4)
Si7	0.0082(6)	0.0077(5)	0.0051(6)	-0.0004(4)	0.0026(4)	0.0008(4)
N1	0.015(2)	0.016(2)	0.011(2)	0.001(2)	0.008(2)	-0.00(1)
N2	0.010(2)	0.005(2)	0.009(2)	0.001(1)	0.002(2)	0.002(1)
N3	0.011(2)	0.014(2)	0.004(2)	0.003(1)	0.003(1)	0.001(1)
N4	0.010(2)	0.007(2)	0.015(2)	-0.005(2)	0.004(2)	-0.003(1)
N5	0.010(2)	0.014(2)	0.006(2)	0.002(1)	0.002(1)	-0.001(1)
N6	0.012(2)	0.009(1)	0.008(2)	-0.002(2)	0.005(1)	0.001(2)
N7	0.010(2)	0.009(2)	0.002(2)	0.002(1)	0.004(1)	0.004(1)
N8	0.008(2)	0.012(2)	0.005(2)	0.001(1)	0.002(2)	0.000(1)
N9	0.009(2)	0.006(2)	0.006(2)	0.000(1)	0.003(1)	0.002(1)
N10	0.009(2)	0.009(2)	0.006(2)	0.002(1)	0.002(1)	-0.003(1)

The unit cell, crystal system, space group and refinement results are summarized in Table 1.

The structure was solved by direct methods (program SIR97 [10]) combined with Fourier difference syntheses and refined against F using reflections with $[I/\sigma(I) > 3]$ (program CRYSTALS [11]).

All atoms were refined anisotropically. A refinement of the occupancy factors confirmed the composition SrSi₇N₁₀ and according to this refinement each crystallographic site is fully occupied. Atomic positions, equivalent thermal factors, and selected interatomic distances are given in Tables 2 and 3, respectively.

2.3. Hardness measurements

A common technique to determine the hardness of small single crystals ($0.5 * 0.05 * 0.05 \text{ mm}^3$) is the Vickers method.

Isolated colourless and transparent single crystals have been stuck with a fine layer of epoxy on a glass support. Then the samples were analyzed on a nanoindenter Nano Indenter IIs, MTS Systems Corp., Oak Ridge, TN, USA [12]; 25 mN (2.5 g) as test load as suitable parameter was chosen.

3. Results

The empirical formula deduced from the single-crystal X-ray diffraction refinement, SrSi₇N₁₀, is in good agreement with the EDS analyses. The bond lengths within the SiN₄ tetrahedrons range from 1.660(4) Å to 1.801(4) Å. The effective ionic radii in nitrides [13,14] for the present atoms are N³⁻ = 1.44 Å and Si⁴⁺ = 0.29 Å, yielding an expected interatomic distance of 1.73 Å for a Si–N bond. The Si–N

Table 3
Selected interatomic distances (Å) for SrSi₇N₁₀ (e.s.d.s in parentheses)

Anionic framework					
Si–N bond lengths					
Si1–N1	1.660(4)	Si1–N2	1.739(4)	Si1–N6	1.745(4)
Si1–N3	1.801(4)				
Si2–N4	1.660(4)	Si2–N6	1.745(4)	Si2–N2	1.759(4)
Si2–N3	1.760(4)				
Si3–N4	1.682(4)	Si3–N5	1.763(4)	Si3–N8	1.763(4)
Si3–N7	1.767(4)				
Si4–N2	1.696(4)	Si4–N9	1.728(4)	Si4–N10	1.729(4)
Si4–N7	1.734(4)				
Si5–N1	1.669(4)	Si5–N8	1.742(4)	Si5–N9	1.760(4)
Si5–N7	1.786(4)				
Si6–N3	1.697(4)	Si6–N5	1.716(4)	Si6–N10	1.724(4)
Si6–N8	1.735(4)				
Si7–N10	1.712(4)	Si7–N6	1.721(3)	Si7–N5	1.727(4)
Si7–N9	1.736(4)				
Si–Si distances					
Si1–Si2	2.511(1)	Si1–Si2	2.918(1)	Si1–Si7	2.954(2)
Si1–Si6	3.037(2)	Si1–Si4	3.059(2)	Si2–Si6	2.993(2)
Si2–Si3	3.110(2)	Si2–Si7	3.130(2)	Si2–Si4	3.170(2)
Si3–Si6	2.912(2)	Si3–Si6	2.922(2)	Si3–Si4	2.928(2)
Si3–Si7	2.962(2)	Si3–Si5	3.080(2)	Si3–Si5	3.248(2)
Si4–Si7	2.855(2)	Si4–Si5	2.955(2)	Si4–Si5	2.988(2)
Si4–Si6	2.995(2)	Si4–Si7	3.082(2)	Si5–Si6	2.953(2)
Si5–Si7	2.988(2)	Si6–Si7	2.851(2)	Si6–Si7	3.051(2)
Sr ²⁺ environment					
Sr1–N4	2.706(4)	Sr1–N1	2.808(4)	Sr1–N3	2.962(4)
Sr1–N7	3.041(3)	Sr1–N2	3.094(4)	Sr1–N1	3.242(4)
Sr1–N4	3.321(4)	Sr1–N6	3.376(4)	Sr1–N9	3.497(4)
Sr1–N8	3.522(4)	Sr1–N6	3.530(4)	Sr1–N5	3.648(4)
Sr1–N7	3.730(3)				

bond lengths are in the typical range for Si–N^[2] (see Table 3).

In the case of N atoms participating in corner and edge-sharing between tetrahedrons the Si–N bond lengths are considerably longer (1.745(8) Å and 1.765(6) Å, respectively) than those observed for N^[2] (1.660(4) Å). This situation is in accordance with the structural data of Ba₅Si₂N₆, where discrete anions [Si₂N₆]^{10–} have been identified, representing pairs of edge-sharing tetrahedrons [15]. The observed edge-sharing of SiN₄ tetrahedrons in SrSi₇N₁₀ causes significantly smaller Si···Si distances (2.511(2) Å) as compared to corner-sharing tetrahedrons (2.918(2) Å). The non-bonding distance N···N between the two N atoms of the common edge are significantly shorter (2.480(5) Å) than the other observed distances N···N in the structure (ranging from 2.801(6) Å to 3.056(6) Å, average 2.86 Å).

SrSi₇N₁₀ is iso-structural with BaSi₇N₁₀. It is built up by a three-dimensional Si–N framework with Sr²⁺ in the voids of the network structure. The unit cell volumes of both alkaline earth nitridosilicates are surprisingly similar, 423.0(1) Å³ and 426.63(3) Å³ for SrSi₇N₁₀ and BaSi₇N₁₀, respectively, even though the ionic radii of the cations Sr²⁺ and Ba²⁺ are quite different (1.44 Å and 1.61 Å for ^{XII}Sr²⁺ and ^{XII}Ba²⁺, respectively). This observation may be interpreted by a very high rigidity of the highly condensed [Si₇N₁₀]^{2–} network, which is only slightly affected by exchanging Ba²⁺ by Sr²⁺. An analogous rigidity has also been observed for oxonitridosilicates and sialons such as the so-called S-phases [16]. Presumably, the Ba²⁺ ions fit perfectly into the cavities of the [Si₇N₁₀]^{2–} network, while the Sr²⁺ are almost too small, giving rise to the much easier synthetic approach to single-phase samples of BaSi₇N₁₀ as compared to SrSi₇N₁₀. This size effect is also reflected in the rather large thermal displacement parameter of Sr.

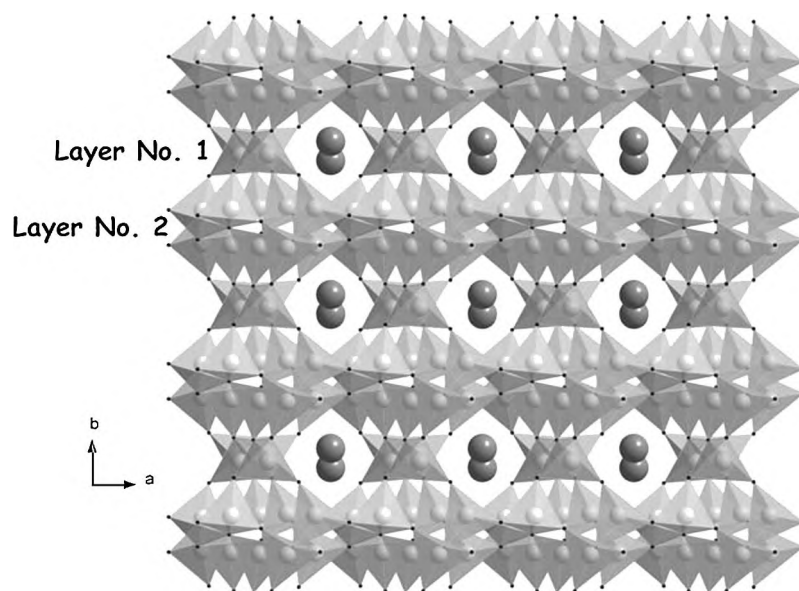


Fig. 1. Projection of the structure of SrSi₇N₁₀ approximately along [001] and illustration of the two types of layers building the framework structure.

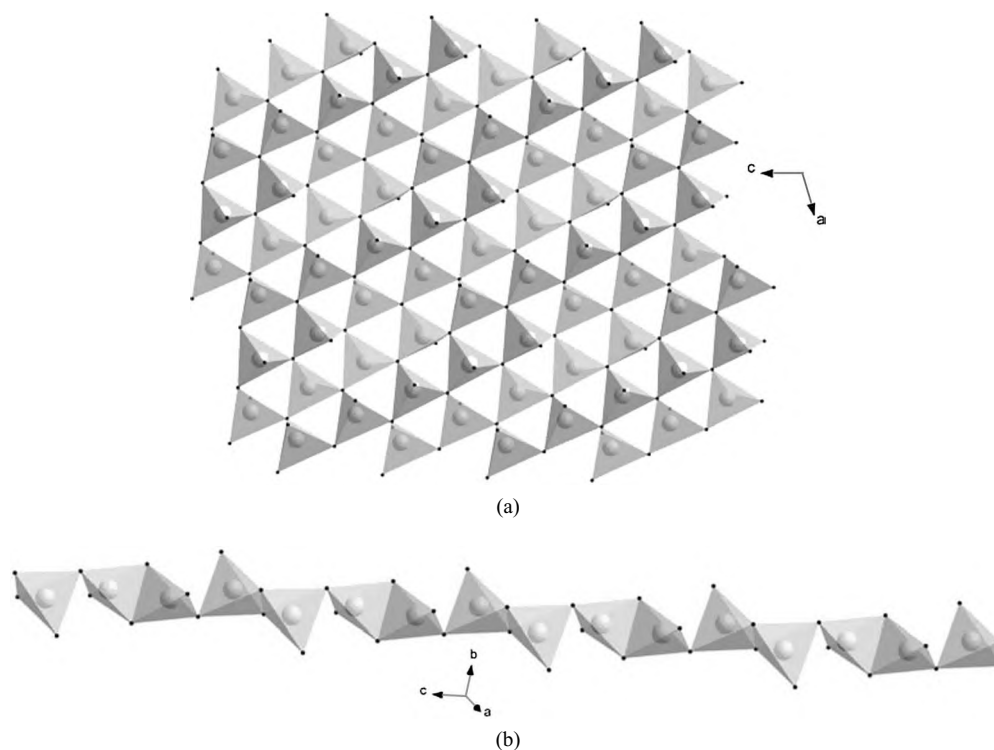


Fig. 2. (a) Projection of layer No. 2 in the (a, c) plane of the unit-cell. (b) Projection of layer No. 1: infinite chains along the c axis of the unit-cell.

The structure of $\text{SrSi}_7\text{N}_{10}$ can be described as a 3-D network built from a regular succession of two different layers along the b axis of the unit cell (Fig. 1). Nearly coplanar and corrugated layers of type 2 (Fig. 2(a)), which are oriented perpendicular to $[010]$, are assembled by condensed Dreier-rings made up of corner-sharing SiN_4 tetrahedrons. All tetrahedrons within these layers are exclusively connected by triply bridging N^{3-} . As it has been noted for $\text{BaSi}_7\text{N}_{10}$, similar planar and corrugated layers of Dreier-rings also exist in $\text{Si}_2\text{N}_2\text{NH}$ [17] and $M_2\text{Si}_5\text{N}_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) [18, 19] although the configuration pattern of the SiN_4 tetrahedrons within the layers is different in each compound, i.e., the respective layers differ topologically by the specific sequence of their tetrahedron vertices pointing upwards (U) and downwards (D) with respect to the layer plane. Very re-

cently, a novel type of layer silicate, namely $\text{CaSi}_2\text{O}_2\text{N}_2$, has been described, that exclusively contains comparable layers of Dreier-rings that are not connected to each other [20]. In $\text{Si}_2\text{N}_2\text{NH}$ [21] and $M_2\text{Si}_5\text{N}_8$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) [18,19] these highly condensed layers are connected by further SiN_4 tetrahedrons, while in $\text{SrSi}_7\text{N}_{10}$ and $\text{BaSi}_7\text{N}_{10}$ these layers are condensed by layers of type 1 (Fig. 2(b)), that are composed of parallel Vierer single-chains running along $[001]$. Within these chains, corner-sharing and edge-sharing SiN_4 tetrahedrons are alternating.

The strontium counter-ions are coordinated by thirteen nitrogen atoms (Fig. 3) within a distance of $2.706(4)$ – $3.730(3)$ Å, which is an environment close to that observed for Ba^{2+} in the $\text{BaSi}_7\text{N}_{10}$ phase. Since Sr^{2+} is much smaller than Ba^{2+} , the shortest distances $\text{Sr}-\text{N}$ are as expected

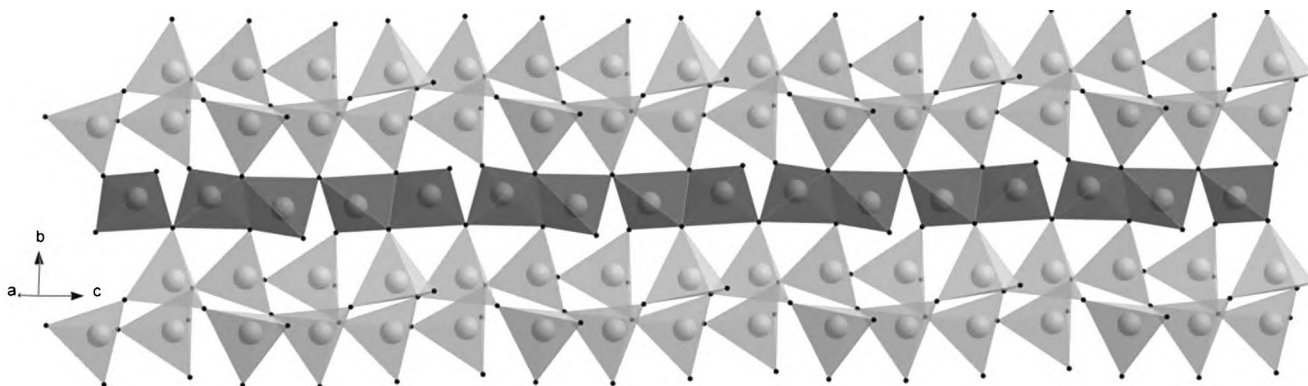


Fig. 3. Illustration of the connection between layer No. 1 and layer No. 2.

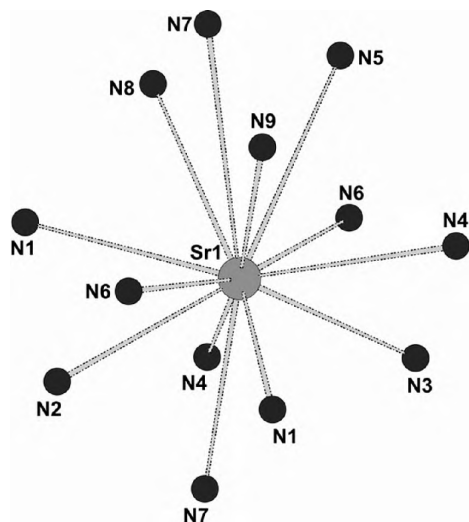


Fig. 4. Presentation of the Sr^{2+} environment.

shorter (2.706(4) Å vs. 2.913(3) Å). Due to the rigidity of the network the largest coordination distances Sr–N are even longer than the longest Ba–N distances (3.730(3) Å vs. 3.529(3) Å), so that in summary the spread of coordination distances is significantly larger in the strontium compound compared with $\text{BaSi}_7\text{N}_{10}$.

The hardness investigations (nine independent nanoindentations) exhibit an average Vickers hardness for $\text{SrSi}_7\text{N}_{10}$ of 16.1(5) GPa ($E = 115(2)$ GPa). The measured hardness value for $\text{SrSi}_7\text{N}_{10}$ is close to the highest reported values for sintered polycrystalline α -sialons [22–25] and α - Al_2O_3 [26] (in the range of 21–22 GPa). This high value can be explained by the presence of the 3-D network for this structure combined with a very high condensation degree of the SiN_4 tetrahedrons.

4. Conclusion

In this article, we have reported the high-temperature solid state synthesis, the crystal structure and the single-crystal hardness properties of $\text{SrSi}_7\text{N}_{10}$. This phase is one of the very few examples of a compound having a 3-D network structure which exhibits edge-sharing and at the same time corner-sharing SiN_4 tetrahedrons. Moreover, this phase presents very interesting hardness properties. Again, we have confirmed that, in combination with a given metal, nitridosilicates exhibit a by far larger range of condensation degrees than oxosilicates. Within the group of the known

ternary nitridosilicates, $\text{SrSi}_7\text{N}_{10}$ and $\text{BaSi}_7\text{N}_{10}$ appear to be the most highly condensed examples.

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