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Eu₂Si₅N₈ and EuYbSi₄N₇. The First Nitridosilicates with a Divalent Rare Earth Metal

HUBERT HUPPERTZ AND WOLFGANG SCHNICK

Laboratorium für Anorganische Chemie, Universitätsstrasse 30, D-95440 Bayreuth, Germany. E-mail: wolfgang.schnick@uni-bayreuth.de

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Abstract

The crystal structures of dieuropium pentasiliconoctanitride, Eu₂Si₅N₈, and europium ytterbium tetrasiliconheptanitride, EuYbSi₄N₇, are based on three-dimensional networks of corner-sharing SiN₄ tetrahedra. Eu₂Si₅N₈ is isotypic with the previously reported Sr and Ba analogues; EuYbSi₄N₇ is isotypic with SrYbSi₄N₇ and BaYbSi₄N₇.

Comment

Recently, we developed a novel synthetic approach to multinary nitridosilicates by reacting alkaline earth or rare earth metals with silicon diimide in a specially developed high-frequency furnace (Huppertz & Schnick, 1997*b*). These reactions may be interpreted as the dissolution of an electropositive metal in a nitrido-analogous polymeric acid accompanied by the evolution of hydrogen.

SiO₄ and SiN₄ tetrahedra are characteristic structural elements in oxo- and nitridosilicates, respectively. These tetrahedra are commonly connected through corner shar-

ing to give network structures. Additionally, in nitridosilicates, edge sharing has been observed (Ba₅Si₂N₆; Yamane & DiSalvo, 1996) as well as vertex sharing together with edge sharing of SiN₄ tetrahedra (BaSi₇N₁₀; Huppertz & Schnick, 1997*a*). In contrast to oxygen in oxosilicates, nitrogen in nitridosilicates shows a greater flexibility. Whereas the structural chemistry of oxosilicates is limited to terminal O atoms and simple bridging O^[2] atoms, the nitridosilicates extend this range, exhibiting terminal N^[1] atoms, and N^[2], N^[3] and N^[4] atoms, connected to two, three and even four neighbouring Si tetrahedral centres, respectively. These structural variabilities in nitridosilicates provide a significant extension of the conventional silicate chemistry.

Until now nitridosilicates have only been obtained in combination with divalent alkaline earth metals (*e.g.* Ca₂Si₅N₈; Schlieper & Schnick, 1995), divalent transition metals (*e.g.* MnSiN₂; Maunaye, Marchand, Guyader, Laurent & Lang, 1971), or trivalent lanthanides (*e.g.* Ce₃Si₆N₁₁, BaYbSi₄N₇; Huppertz & Schnick, 1996*a,b*). The title compounds Eu₂Si₅N₈ and EuYbSi₄N₇ represent the first nitridosilicates containing a divalent rare earth metal.

The structure of Eu₂Si₅N₈ is based on a network of corner-sharing SiN₄ tetrahedra and is isotypic with Sr₂Si₅N₈ and Ba₂Si₅N₈ (Schlieper, Milius & Schnick, 1995). In this network half of the N atoms connect two, and the other half three, Si atoms. The N^[3] atoms are arranged in corrugated sheets perpendicular to [100] (Fig. 1). The Eu²⁺ ions, which are mainly coordinated by N^[2] atoms (Eu—N: 2.60–3.25 Å), are situated in channels along [100] formed by Si₆N₆ rings.

The Si–N network structure in EuYbSi₄N₇ is built up from star-shaped [N(SiN₃)₄] building blocks (Fig. 2),

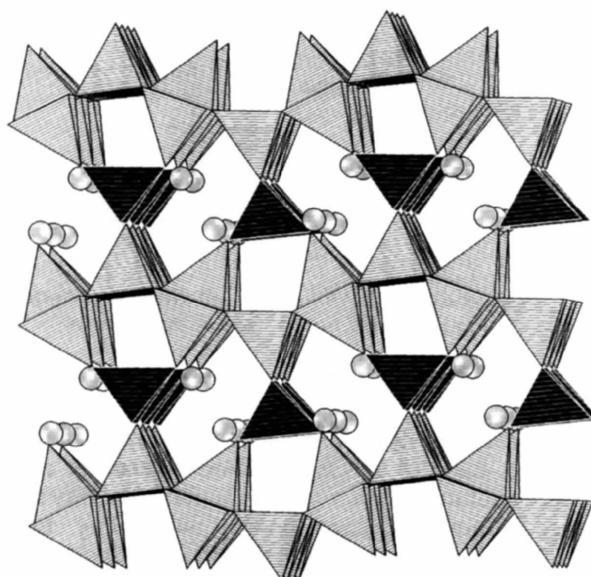


Fig. 1. Crystal structure of Eu₂Si₅N₈, viewed along [100].

where the central N atoms simultaneously bridge four Si tetrahedral centres. By connecting these groups through common N^[2] atoms, a stacking variant of the wurtzite-analogous aluminium nitride structure is formed. Systematic elimination of tetrahedra from this arrangement along [100] leads to the formation of Si₆N₆-ring channels, containing Eu²⁺ and Yb³⁺ ions. The Eu²⁺ and Yb³⁺ ions show anticuboctahedral and octahedral coordination, respectively, by N atoms of the Si₄N₇ network. The Eu—N and Yb—N contact distances (2.93–3.06 and 2.27–2.28 Å, respectively) approximately correspond to the sum of the ionic radii (Baur, 1987). The bond lengths to the N^[4] atoms are significantly longer (Si—N: 1.87–1.94 Å) than those to the N^[2] atoms (Si—N: 1.69–1.72 Å).

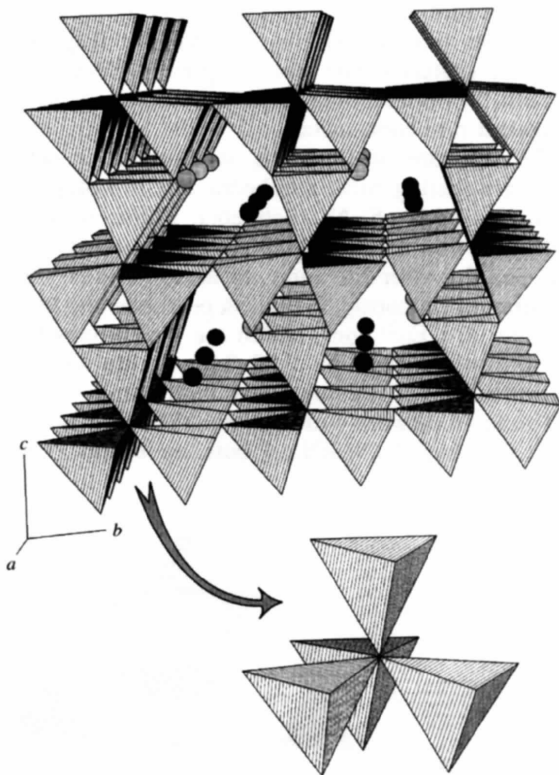


Fig. 2. Crystal structure of EuYbSi₄N₇, viewed along [100]. The Eu²⁺ ions are shown as grey and the Yb³⁺ ions as black spheres.

The reaction of pure metals with silicon diimide [Si(NH)₂] provides a straightforward preparative route to nitridosilicates. These compounds possess highly condensed network structures showing outstanding chemical, thermal and mechanical stabilities, which are a direct consequence of the high stability of the chemical bonding between the constituent elements.

Experimental

For the synthesis of Eu₂Si₅N₈, metallic europium (136.8 mg, 0.90 mmol) and silicon diimide (116.2 mg, 2 mmol) were mixed thoroughly under argon in a glove box and transferred to a tungsten crucible positioned in a high-frequency furnace. The reaction mixture was heated to 923 K and directly to 1923 K within 2 h, maintained at that temperature for 3 h, and then quenched to room temperature. This process led to the formation of Eu₂Si₅N₈ as a single-phase coarsely crystalline red solid.

For EuYbSi₄N₇, the metals Eu and Yb (1 mmol) were mixed with Si(NH)₂ (2 mmol) under inert gas atmosphere and transferred in a tungsten crucible to the high-frequency reactor. Under nitrogen atmosphere the reaction mixture was slowly heated up to 1923 K, maintained at that temperature for 48 h, and then quenched to room temperature.

Eu₂Si₅N₈

Crystal data

Eu₂Si₅N₈
M_r = 556.45
 Orthorhombic
*Pmn*2₁
a = 5.7094 (4) Å
b = 6.8207 (4) Å
c = 9.3291 (6) Å
V = 363.29 (4) Å³
Z = 2
D_x = 5.087 Mg m⁻³
D_m not measured

Mo Kα radiation
 λ = 0.71073 Å
 Cell parameters from 33 reflections
 θ = 5.14–17.44°
 μ = 17.896 mm⁻¹
T = 293 (2) K
 Prism
 0.10 × 0.08 × 0.08 mm
 Red

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction:
 empirical via ψ scans
 [XSCANS (Siemens, 1994)
 and SHELXTL (Sheldrick,
 1994)]
T_{min} = 0.218, *T_{max}* = 0.278
 1811 measured reflections
 1727 independent reflections

1609 reflections with
I > 2σ(*I*)
R_{int} = 0.0101
 θ_{max} = 34.99°
h = -9 → 9
k = -11 → 11
l = -15 → 15
 3 standard reflections
 every 97 reflections
 intensity decay: 0.89%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.047
S = 1.122
 1727 reflections
 83 parameters
w = 1/[σ²(*F_o*²) + (0.0168*P*)²
 + 1.8337*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.16 e Å⁻³
 Δρ_{min} = -1.11 e Å⁻³

Extinction correction:
 SHELXTL (Sheldrick,
 1994)
 Extinction coefficient:
 0.0293 (7)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)
 Absolute configuration:
 Flack (1983) parameter
 = 0.17 (3)

Table 1. Selected geometric parameters (Å, °) for Eu₂Si₅N₈

Eu1—N1 ⁱ	2.529 (8)	Si1—N6 ^{iv}	1.768 (6)
Eu1—N3 ⁱⁱ	2.724 (5)	Si1—N4 ⁱⁱⁱ	1.769 (4)
Eu1—N2	2.8931 (14)	Si2—N1 ⁱ	1.710 (10)

Eu1—N4 ⁱⁱⁱ	2.975 (4)	Si2—N2 ^{vii}	1.718 (9)	Si2 ^{vi} —N1—Si2	113.0 (2)	Si1 ^{viii} —N3—Si2	112.07 (11)
Eu1—N3 ⁱⁱⁱ	3.158 (6)	Si2—N3 ^{viii}	1.719 (4)	Si1—N2—Si2 ^{viii}	116.9 (2)	Si2—N3—Si2 ^{ix}	106.75 (12)
Eu1—N6 ^{iv}	3.246 (6)	Si3—N2	1.668 (8)	Symmetry codes: (i) $x, 1 + y, z$; (ii) $x - y, x, \frac{1}{2} + z$; (iii) $y, -x + y, \frac{1}{2} + z$;			
Eu2—N2 ⁱⁱ	2.554 (9)	Si3—N5 ^{ix}	1.735 (6)	(iv) $1 + x, y, z$; (v) $1 - x, -y, \frac{1}{2} + z$; (vi) $1 - y, 1 + x - y, z$; (vii) $1 - x, -y, z - \frac{1}{2}$;			
Eu2—N3 ⁱⁱ	2.589 (5)	Si3—N4	1.765 (4)	(viii) $x - 1, y, z$; (ix) $-y, x - y, z$.			
Eu2—N1 ^{iv}	2.8902 (12)	Si4—N3	1.682 (3)	The directions of the polar axes were determined using reflections of the sign ranges hkl for $\text{Eu}_2\text{Si}_5\text{N}_8$ and $\bar{h}\bar{k}\bar{l}$ for $\text{EuYbSi}_4\text{N}_7$ together with all corresponding Friedel pairs $\bar{h}\bar{k}\bar{l}$ and $\bar{h}\bar{k}\bar{l}$ for $\text{Eu}_2\text{Si}_5\text{N}_8$ and $\text{EuYbSi}_4\text{N}_7$, respectively. The complete spheres implied by the index ranges in the tables were not recorded. The origins were fixed by the method of Flack & Schwarzenbach (1988).			
Eu2—N5 ^v	2.902 (6)	Si4—N5	1.752 (3)	Our experience in crystal structure determination of rare earth compounds indicates that a significant residual electron density may occur despite an absorption correction. Accordingly, the appreciable residual electron density located in the neighbourhood of some heavy atoms in $\text{EuYbSi}_4\text{N}_7$ is not unusual.			
Eu2—N4 ^{vi}	3.235 (4)	Si4—N6	1.759 (4)	The displacement factors for N2 in both compounds are strongly anisotropic. This might be caused by disorder, residual absorption errors or actual marked anisotropy. However, in the absence of other evidence we cannot distinguish these possibilities. The light-atom U values are necessarily imprecise in the presence of heavy atoms.			
Si1—N1	1.672 (8)	Si4—N4	1.782 (4)	For both compounds, data collection: <i>XSCANS</i> (Siemens, 1994); cell refinement: <i>XSCANS</i> ; data reduction: <i>SHELXTL</i> (Sheldrick, 1994); program(s) used to solve structures: <i>SHELXTL</i> ; program(s) used to refine structures: <i>SHELXTL</i> ; molecular graphics: <i>KPLOT</i> (Hundt, 1979); software used to prepare material for publication: <i>SHELXTL</i> .			
Si3—N4—Si1 ^x	126.2 (3)	Si4—N5—Si4 ^{xii}	110.4 (3)	Financial support by the Deutsche Forschungsgemeinschaft (project SCHN 377/6-1, 377/6-2 and Gottfried Wilhelm Leibniz program) and the Fonds der Chemischen Industrie is gratefully acknowledged.			
Si3—N4—Si4	116.5 (2)	Si4—N6—Si4 ^{viii}	107.2 (3)	Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1226). Services for accessing these data are described at the back of the journal.			
Si1 ^x —N4—Si4	117.3 (2)	Si4—N6—Si1 ^{xiii}	117.5 (2)				
Si3 ^{xi} —N5—Si4	124.0 (2)	Symmetry codes: (i) $x, y - 1, z$; (ii) $\frac{x}{2} - x, -y, z - \frac{1}{2}$; (iii) $x - 1, y, z$; (iv) $\frac{x}{2} - x, 1 - y, z - \frac{1}{2}$; (v) $x - 1, y, z - 1$; (vi) $x - \frac{1}{2}, 1 - y, z - \frac{1}{2}$; (vii) $\frac{x}{2} - x, -y, \frac{1}{2} + z$; (viii) $3 - x, y, z$; (ix) $\frac{x}{2} - x, 1 - y, z - \frac{1}{2}$; (x) $1 + x, y, z$; (xi) $\frac{x}{2} - x, 1 - y, \frac{1}{2} + z$; (xii) $4 - x, y, z$; (xiii) $\frac{x}{2} - x, 1 - y, \frac{1}{2} + z$.					

EuYbSi₄N₇*Crystal data*EuYbSi₄N₇ $M_r = 535.43$

Hexagonal

 $P6_3mc$ $a = 5.9822 (3) \text{ \AA}$ $c = 9.7455 (4) \text{ \AA}$ $V = 302.03 (2) \text{ \AA}^3$ $Z = 2$ $D_x = 5.887 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 62 reflections

 $\theta = 5.74\text{--}17.48^\circ$ $\mu = 26.406 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Prism

 $0.20 \times 0.10 \times 0.10 \text{ mm}$

Brown

Data collection

Siemens P4 diffractometer

 ω scans

Absorption correction:

empirical via ψ scans[*XSCANS* (Siemens, 1994)and *SHELXTL* (Sheldrick,

1994)]

 $T_{\min} = 0.56, T_{\max} = 0.71$

4996 measured reflections

1378 independent reflections

1250 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.0439$ $\theta_{\max} = 52.48^\circ$ $h = -12 \rightarrow 12$ $k = -13 \rightarrow 13$ $l = -21 \rightarrow 21$

3 standard reflections

every 97 reflections

intensity decay: 1.36%

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.021$ $wR(F^2) = 0.049$ $S = 1.068$

1378 reflections

32 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.1496P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 1.69 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -4.21 \text{ e \AA}^{-3}$

Extinction correction:

SHELXTL (Sheldrick,

1994)

Extinction coefficient:

0.0436 (13)

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute configuration:

Flack (1983) parameter

 $= -0.013 (11)$ Table 2. Selected geometric parameters (\AA , $^\circ$) for $\text{EuYbSi}_4\text{N}_7$

Yb1—N1	2.267 (3)	Si1—N2	1.694 (3)
Yb1—N2 ⁱ	2.280 (3)	Si1—N3 ⁱⁱ	1.865 (4)
Eu1—N1	2.925 (3)	Si2—N2 ^v	1.713 (3)
Eu1—N2 ⁱⁱ	2.9947 (2)	Si2—N1	1.7189 (15)
Eu1—N1 ⁱⁱⁱ	3.058 (3)	Si2—N3	1.941 (2)

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