

Preparation and Crystal Structures of the Rare Earth Nitrido-Oxosilicates and Nitridosilicates with the General Formula $R_{6+x/3}Si_{11}N_{20+x}O_{1-x}$ and the Ideal Compositions $R_6Si_{11}N_{20}O$ and $R_{6.33}Si_{11}N_{21}$, Respectively ($R = Y$ and Gd–Lu)

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The nine title compounds were prepared by reaction of multiple-phase rare earth silicide oxide powders with nitrogen. Single crystals of the erbium compound were isolated from a sample, which had been melted in a high-frequency furnace. Two slightly different trigonal crystal structures ($P31c$, $Z=2$) were established from single-crystal X-ray diffractometer data. Two fully occupied erbium sites were found for a crystal with the composition $Er_6Si_{11}N_{20}O$: $a=977.3(1)$ pm, $c=1059.7(1)$ pm, $R=0.021$ for 1531 structure factors and 68 variable parameters. A third erbium site was refined with partial occupancy for another crystal with the composition $Er_{6.254(3)}Si_{11}N_{20.762(9)}O_{0.238(9)}$: $a=978.5(1)$ pm, $c=1064.4(1)$ pm, $R=0.023$ for 884 F values and 71 variables. The presence and the location of the oxygen atoms in these transparent crystals are based on structure-chemical arguments. For a crystal without oxygen the third erbium site should have an occupancy of 33%, corresponding to the formula $Er_{6.33}Si_{11}N_{21}$. The two fully occupied erbium sites are coordinated by six, the partially occupied erbium site is coordinated by seven nitrogen (oxygen) atoms. The silicon atoms have four nitrogen (oxygen) neighbors in tetrahedral arrangement. Some nitrogen atoms are bonded to only one silicon atom, but most are linking two SiN_4 tetrahedra via common corners. The compounds may therefore be considered essentially as framework nitridosilicates. In contrast to normal oxosilicates, where the oxygen atoms have one or two silicon neighbors, the structures of these nitrido-silicates also contain nitrogen atoms which link three or even four SiN_4 tetrahedra. © 1997 Academic Press

INTRODUCTION

Nitridosilicates of the rare earth elements were first prepared with the compositions $LaSi_3N_5$ (1) and $Sm_3Si_6N_{11}$ (2). We have recently reported about the preparation of the corresponding isotopic compounds $LnSi_3N_5$ ($Ln = Ce, Pr,$

Nd) and $Ln_3Si_6N_{11}$ ($Ln = La, Ce, Pr, Nd$) (3). The crystal structures of these compounds were determined for $LaSi_3N_5$ (1), $CeSi_3N_5$ (4), $Sm_3Si_6N_{11}$ (3), $Ce_3Si_6N_{11}$ (5), and $Pr_3Si_6N_{11}$ (6). In searching for isotopic nitridosilicates of the heavier rare earth elements we obtained the compounds reported here. The oxygen was first incorporated accidentally. It is required to balance the charge of these transparent crystals. Subsequently the compounds were also prepared from stoichiometric mixtures. The general formula for these compounds is $R_{6+x/3}Si_{11}N_{20+x}O_{1-x}$. Thus, the ideal formulas for the end members of this solid solution series are $R_6Si_{11}N_{20}O$ and $R_{6.33}Si_{11}N_{21}$. The two structure determinations for the new compounds reported here correspond to the formulas $Er_6Si_{11}N_{20}O$ and $Er_{6.254(3)}Si_{11}N_{20.762(9)}O_{0.238(9)}$.

SAMPLE PREPARATION

Starting materials were ingots of the rare earth elements with nominal purities $> 99.9\%$. Filings were prepared under dried paraffine oil. Subsequently the oil was washed out with dry n -hexane. High-purity silicon powder was used, and a small amount of oxygen was eventually added in the form of the lanthanoid oxides Ln_2O_3 . Multiphase samples of the overall composition $Ln:Si:O = 6:11:1$ were prepared by arc-melting cold pressed pellets. The resulting buttons were crushed to a fine powder and reacted in a molybdenum boat with nitrogen under normal pressure at $1500^\circ C$ for one week. The products were essentially single phase.

The single-crystals of the erbium compound were prepared in a different way. An equimolar mixture of erbium filings and α - Si_3N_4 powder ($> 99.9\%$) was pressed to a pellet and prereacted by arc-melting. The resulting multiphase sample was then sealed in an evacuated silica tube and annealed for five hours in a high-frequency furnace. The excess silicon is needed to raise the electrical conductivity of

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the multiple-phase sample. The sample temperature was raised at least initially above the melting temperature of the main phase. To reduce the attack on the sample tube, the tube was cooled on the outside by a stream of cold water. The resulting ingot was then crushed to powder in a steel mortar and treated with boiling *aqua regia* to further separate the crystals.

LATTICE CONSTANTS AND PROPERTIES

The samples were characterized by their Guinier powder patterns using $\text{CuK}\alpha_1$ radiation and α -quartz as a standard ($a = 491.30$ pm, $c = 540.46$ pm). The lattice constants (Table 1) were obtained by least-squares fits. The plot of the cell volumes (Fig. 1) shows the yttrium compound to have a volume, which is in between those of the corresponding dysprosium and holmium compounds. This is in agreement with the fact that in carbides the cell volumes of the yttrium compounds fit between those of the terbium and holmium compounds, and in oxides the volumes of the yttrium compounds are in between those of the dysprosium and erbium compounds (7).

The polycrystalline samples were gray; however, this is not their intrinsic color, since the single crystals of the erbium compound were transparent with a pink hue. The compounds are stable in air and not attacked by aqueous solutions as is demonstrated by their stability in hot *aqua regia*. Their melting points are well beyond 1500°C .

STRUCTURE DETERMINATION AND REFINEMENTS

The structure of the new compounds was determined by single-crystal diffractometer data of the erbium compound. Two single crystals, which turned out to have slightly different compositions, were isolated from the heterogeneous sample, prepared in the high-frequency furnace as described

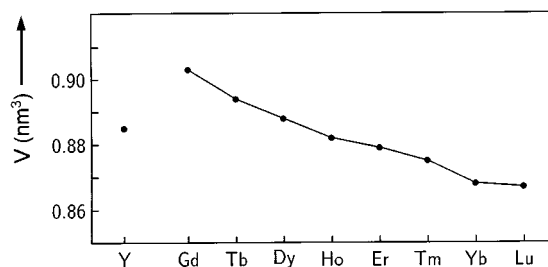


FIG. 1. Cell volumes of the compounds $R_6\text{Si}_{11}\text{N}_{20}\text{O}$ with $R = \text{Y}$ and Gd-Lu .

above. Intensity data were recorded with a four-circle diffractometer, using graphite-monochromated $\text{MoK}\alpha$ radiation and a scintillation counter with pulse-height discrimination. Background counts were measured at both ends of each $\theta/2\theta$ scan. Absorption corrections were made from psi scan data. The values for the lattice constant a found for the two crystals on the four-circle diffractometer (Table 2) were in good agreement with the corresponding lattice constant as refined from the Guinier powder data (Table 1). The lattice constant c as determined for crystal 2 on the single-crystal diffractometer is slightly larger. This suggests that most of the sample had a composition as found for crystal 1 with the ideal composition $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$.

Both data sets had the Laue symmetry $\bar{3}m$, and the systematic extinctions led to the two space groups $P31c$ (No. 159) and $P\bar{3}1c$ (No. 163), of which the noncentrosymmetric group $P31c$ eventually was found to be correct during the structure determination. The positions of the erbium atoms were established by the Patterson method and the light atoms were located by subsequent difference Fourier syntheses. The structures were refined by a full-matrix least-squares program using atomic scattering factors (8), corrected for anomalous dispersion (9). The weighting scheme accounted for the counting statistics, and a factor correcting for isotropic secondary extinction was optimized as a least-squares parameter. It turned out that the two data sets originated from two crystals with opposite polarity, and in order to make the results of the two refinements comparable, one data set was converted by replacing the labels hkl with the labels $\bar{h}\bar{k}\bar{l}$. All positional parameters were eventually standardized with the program STRUCTURE TIDY (10).

The data from the crystal with the ideal composition $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ (crystal 1) were refined first, assuming all positions of the light atoms to be occupied by nitrogen atoms. This, however, results in a formula with imbalanced oxidation numbers: $[\text{Er}_6]^{+18}[\text{Si}_{11}]^{+44}[\text{N}_{21}]^{-63}$, i.e., 62 positive formal charges cannot be balanced by 63 negative ones. Since the compound is transparent (both crystals) and since the environments of the sites now called O1a/O1b

TABLE 1
Lattice Constants of the Compounds $R_{6+x/3}\text{Si}_{11}\text{N}_{20+x}\text{O}_{1-x}$
with $R = \text{Y}$ and Gd-Lu^a

R	a (pm)	c (pm)	c/a	V (nm ³)
Y	981.3(5)	1061.2(7)	1.081	0.8850
Gd	987.6(3)	1068.4(3)	1.082	0.9025
Tb	983.9(2)	1066.1(2)	1.084	0.8936
Dy	982.0(3)	1063.2(4)	1.083	0.8879
Ho	979.8(2)	1061.1(2)	1.083	0.8822
Er	978.7(2)	1059.1(3)	1.082	0.8786
Tm	976.0(2)	1060.7(5)	1.087	0.8750
Yb	974.2(4)	1057.0(5)	1.085	0.8688
Lu	972.6(2)	1058.6(2)	1.088	0.8672

^a Standard deviations in the place values of the least significant digits are given in parentheses throughout the paper.

TABLE 2
Some Data and Results of the Structure Determinations of the Two Crystals with the General Composition $\text{Er}_{6+x/3}\text{Si}_{11}\text{N}_{20+x}\text{O}_{1-x}$

	Crystal 1: $x = 0$	Crystal 2: $x = 0.762(9)$
Formula	$\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$	$\text{Er}_{6.254(3)}\text{Si}_{11}\text{N}_{20.762(9)}\text{O}_{0.238(9)}$
Space group	$P31c$ (Nr. 159)	$P31c$ (Nr. 159)
Lattice constants (single-crystal) (pm)	$a = 977.3(1)$ $c = 1059.7(1)$	$a = 978.5(1)$ $c = 1064.4(1)$
Cell volume (nm^3)	$V = 0.8765$	$V = 0.8826$
Formula units per cell	$Z = 2$	$Z = 2$
Formula mass	1608.6	1649.6
Calculated density (g/cm^3)	6.10	6.21
Crystal size (μm^3)	$20 \times 20 \times 20$	$20 \times 20 \times 40$
Scan range	$4^\circ < 2\theta < 70^\circ$	$4^\circ < 2\theta < 70^\circ$
Range in hkl	$\pm 15, \pm 15, \pm 16$	$\pm 15, \pm 15, 0-16$
Highest/lowest transmission	1.36	1.97
Total no. of reflections	12870	8070
Data after averaging	2340	1460
Inner residual (on F values)	$R_i = 0.038$	$R_i = 0.048$
Reflections with $I_0 > 3\sigma(I_0)$	1531	884
Number of variables	67	71
Extinctions corr. value g^a	$5.6(3) \times 10^{-8}$	$2.67(3) \times 10^{-7}$
Conventional residual	$R = 0.021$	$R = 0.023$
Weighted residual	$R_w = 0.022$	$R_w = 0.027$
Highest residual density ($e/\text{\AA}^3$)	4.8	1.6

^a The extinction correction value g is defined by corr. factor = $1/(1 + g \cdot I_c)$.

and N9/O1, respectively, differed in the two crystals, in correspondence with the unoccupied or partially occupied Er3 site, we decided these sites to be occupied with oxygen (O1a/O1b) in crystal 1 and with mixed occupancy (N9/O1) in crystal 2. This makes it possible to completely balance the oxidation numbers according to the formulas $[\text{Er}_6]^{+18}[\text{Si}_{11}]^{+44}[\text{N}_{20}]^{-60}[\text{O}]^{-2}$ and $[\text{Er}_{6.254}]^{+18.762}[\text{Si}_{11}]^{+44}[\text{N}_{20.762}]^{-62.286}[\text{O}_{0.238}]^{-0.476}$. No residual electron density (greater than $1.5 e/\text{\AA}^3$, the electron density of the 20th strongest residual peak) was found for the Er3 position of crystal 1, whereas in crystal 2 this site is occupied by 25.4(3)% with erbium atoms. This site is not suited for silicon atoms, because the surrounding light atoms are too far away and also it refined to an occupancy of 140(2)% when silicon atoms were placed on this position. An energy dispersive X-ray fluorescence analysis of crystal 2 in a scanning electron microscope, carried out after the X-ray data collection, did not show any impurity elements heavier than sodium.

The erbium atoms were refined with ellipsoidal, the other with isotropic displacement parameters. Since the space group $P31c$ is polar, we also refined the crystal structures in the settings with the other polarity. This resulted in the residuals $R = 0.037$ and 0.028 for the crystals 1 and 2, respectively, as compared to the residuals 0.021 and 0.023 for the settings with the correct polarity. The final results are listed in the Tables 2 and 3. The anisotropic displacement

parameters and the structure factor tables are deposited (11). The interatomic distances (Table 4) were calculated with the lattice constants as obtained from the powder data (Table 1). Thus, the differences in the interatomic distances of two refinements are only due to the differences of the positional parameters. Parallel projections of the structure of $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ are presented in Fig. 2 and stereoplots of both structures are shown in Fig. 3.

DISCUSSION

The compounds described in the present report are new. They should have large band gaps, because they are transparent, and they should be pyroelectric, since they crystallize with the polar point group $3m$. We have found two slightly different crystal structures for the erbium compound. They correspond to the ideal compositions $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ and $\text{Er}_{6.33}\text{Si}_{11}\text{N}_{21}$. The crystal 1 practically has the ideal composition $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$, while the crystal 2, $\text{Er}_{6.254(3)}\text{Si}_{11}\text{N}_{20.762(9)}\text{O}_{0.238(9)}$, has gone three-fourths of the way to the ideal composition $\text{Er}_{6.33}\text{Si}_{11}\text{N}_{21}$. It seems likely that all of these compounds with the general composition $\text{R}_{6+x/3}\text{Si}_{11}\text{N}_{20+x}\text{O}_{1-x}$ have homogeneity ranges, which may extend to the two limiting compositions $\text{R}_6\text{Si}_{11}\text{N}_{20}\text{O}$ and $\text{R}_{6.33}\text{Si}_{11}\text{N}_{21}$. As already discussed above, the oxygen content is a theoretical requirement. It results from the necessity to balance the charges of these

TABLE 3
Atomic Parameters of $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ and $\text{Er}_{6.254(3)}\text{Si}_{11}\text{N}_{20.762(9)}\text{O}_{0.238(9)}^a$

Atom	<i>P31c</i>	Occup.	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B_{\text{iso}}$
Er1	6 <i>c</i>	0.993(1)	0.12677(4)	0.26088(3)	0.32642(4)	0.382(6)
	6 <i>c</i>	0.997(1)	0.12912(8)	0.26272(5)	0.32630(6)	0.382(7)
Er2	6 <i>c</i>	1.003(1)	0.20647(4)	0.40963(4)	0	0.536(6)
	6 <i>c</i>	0.998(2)	0.20118(7)	0.40089(6)	0	0.688(8)
Er3	—	—	—	—	—	—
Si1	2 <i>b</i>	0.254(3)*	1/3	2/3	0.7851(3)	0.31(5)
	6 <i>c</i>	0.962(7)	0.1292(2)	0.5723(2)	0.4924(2)	0.17(3)
Si2	6 <i>c</i>	0.994(9)	0.1314(3)	0.5733(4)	0.4932(3)	0.21(4)
	6 <i>c</i>	0.958(6)	0.3408(2)	0.1580(2)	0.1427(2)	0.27(3)
Si3	6 <i>c</i>	0.945(8)	0.3398(4)	0.1582(4)	0.1435(3)	0.28(5)
	6 <i>c</i>	0.974(7)	0.5359(2)	0.0103(2)	0.2546(2)	0.29(3)
Si4a	6 <i>c</i>	0.976(9)	0.5321(3)	0.0043(4)	0.2545(3)	0.30(4)
	2 <i>b</i>	0.358(9)*	1/3	2/3	0.1849(9)	0.16(8)*
Si4b	2 <i>b</i>	0.82(1)*	1/3	2/3	0.1775(7)	0.5(1)*
	2 <i>b</i>	0.642*	1/3	2/3	0.2529(5)	0.16*
Si5	2 <i>b</i>	0.18*	1/3	2/3	0.265(3)	0.5*
	2 <i>a</i>	1.07(1)	0	0	0.0639(4)	0.1
N1	2 <i>a</i>	0.95(1)	0	0	0.0695(7)	0.29(7)
	6 <i>c</i>	1.06(2)	0.0087(8)	0.4300(7)	0.3865(6)	0.5(1)
N2	6 <i>c</i>	0.98(2)	0.012(1)	0.429(1)	0.3837(9)	0.4(1)
	6 <i>c</i>	1.03(2)	0.0131(8)	0.1749(7)	0.1233(6)	0.3(1)
N3	6 <i>c</i>	0.96(2)	0.011(1)	0.172(1)	0.1281(9)	0.5(1)
	6 <i>c</i>	1.11(2)	0.3153(8)	0.4882(7)	0.2146(6)	0.4(1)
N4	6 <i>c</i>	0.99(2)	0.310(1)	0.487(1)	0.2146(9)	0.5(2)
	6 <i>c</i>	1.13(2)	0.3652(7)	0.2776(7)	0.0141(6)	0.3(1)
N5	6 <i>c</i>	0.97(2)	0.366(1)	0.278(1)	0.0139(9)	0.3(1)
	6 <i>c</i>	1.02(2)	0.3657(7)	0.2578(7)	0.2846(6)	0.3(1)
N6	6 <i>c</i>	1.10(3)	0.374(1)	0.264(1)	0.2872(9)	0.3(1)
	6 <i>c</i>	1.07(2)	0.4807(8)	0.0990(7)	0.1365(6)	0.4(1)
N7	6 <i>c</i>	0.97(2)	0.474(1)	0.092(1)	0.138(1)	0.9(2)
	2 <i>b</i>	1.12(3)	1/3	2/3	0.452(1)	0.5(2)
N8	2 <i>b</i>	0.84(4)	1/3	2/3	0.463(2)	0.7(3)
	2 <i>a</i>	1.00(3)	0	0	0.405(1)	0.3(2)
O1a } O1b }	2 <i>a</i>	1.09(4)	0	0	0.407(2)	0.4(2)
	2 <i>b</i>	0.358*	1/3	2/3	0.020(2)	0.4(2)*
N9/O1	2 <i>b</i>	0.642*	1/3	2/3	0.980(1)	0.4*
	2 <i>b</i>	0.89(4)	1/3	2/3	0.008(2)	1.7(4)

^a Each atom is listed with two sets of parameters corresponding to the structure refinements of crystals 1 and 2 with the compositions $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ and $\text{Er}_{6.254(3)}\text{Si}_{11}\text{N}_{20.762(9)}\text{O}_{0.238(9)}$, respectively. The first line of any set stands for crystal 1, the second line for crystal 2. The split position O1a/O1b was refined only for the first data set, the N9/O1 position only for the second (crystal 2). The Er3 position was found to be occupied only in the second crystal. The occupancy parameters listed in the third column were obtained in separate least-squares cycles. In the final refinements all atomic positions were assumed to be fully occupied with the exception of those occupancy values, which are marked by an asterisk. Those parameters listed without a standard deviation were constrained to be equal to the corresponding parameters with a standard deviation. In the final cycles the N9/O1 position of crystal 2 was refined with the mixed occupancy 0.762/0.238 corresponding to the Er3 occupancy of 0.254 ($3 \times 0.254 = 0.762$). In the last column, the isotropic and equivalent isotropic (Er1, Er2) *B* values ($\times 10^{-4}$, in units of pm^2) of the displacement parameters are given. The displacement parameter of the Si5 atom of crystal 1 was fixed at the indicated value, because of its tendency to refine to a negative value. The parameter *z* of the Er2 positions was held constant to define the origin of this polar space group.

transparent crystals. The identification of the site with the mixed occupancy N9/O1 (respectively the O1a/O1b site) was made mainly on the basis of its proximity to the Er3 site, which was found to be entirely unoccupied in $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ (crystal 1); it should be occupied to one-third in a crystal containing no oxygen, corresponding to the

formula $\text{Er}_{6.33}\text{Si}_{11}\text{N}_{21}$. For details concerning the differences between the two structures the reader is referred to the Tables 3 and 4 and also to Fig. 4.

The Si4 site had to be refined with a split position for both data sets. Its occupancy values Si4a/Si4b of 0.358(9)/0.642(9) and 0.82(1)/0.18(1) for crystals 1 and 2, respectively,

TABLE 4
Interatomic Distances in the Two Crystals of $\text{Er}_{6+x/3}\text{Si}_{11}\text{N}_{20+x}\text{O}_{1-x}$ ^a

		$x = 0$	$x = 0.762(9)$			$x = 0$	$x = 0.762(9)$			$x = 0$	$x = 0.762(9)$		
Er1:	1 N8	236.3(4)	238.6(7)	Si1:	1 N1	171.6(7)	176(1)	N2:	1 Si2	172.7(4)	171.1(7)		
	1 N2	237.5(6)	235.7(9)		1 N6	171.9(7)	176(1)		1 Si5	176.7(6)	174.3(9)		
	1 N3	237.7(6)	234(1)		1 N4	172.5(6)	172.0(8)		1 Er1	237.5(6)	235.7(9)		
	1 N4	238.0(6)	237.9(9)		1 N7	178.5(3)	174.1(4)		1 Er2	249.4(6)	248.6(9)		
	1 N5	239.5(4)	242.5(6)		1 Er2	334.5(1)	337.2(1)		N3:	1 Si4a	169.5(6)	170.1(9)	
	1 N1	252.8(5)	248.3(7)		1 Er1	340.9(2)	340.0(3)			1 Si4b	171.4(6)	174(1)	
	1 Si3	305.6(2)	302.3(2)		1 Er2	346.2(2)	347.1(3)			1 Si3	174.0(4)	173.7(6)	
	1 Si2	316.4(2)	317.5(3)		Si2:	1 N2	172.7(6)		171.1(8)	1 Er1	237.7(6)	234(1)	
	1 Si5	334.9(3)	341.3(6)			1 N4	173.2(7)		174(1)	1 Er2	246.5(6)	248.4(9)	
	1 Si2	336.1(2)	334.4(3)			1 N6	173.4(4)		173.4(6)	N4:	1 Si1	172.5(6)	172.0(8)
	1 Si1	340.9(2)	340.0(3)		1 N5	174.2(7)	178(1)		1 Si2		173.2(7)	174(1)	
	1 Si2	341.8(2)	344.0(3)		1 Er3	—	315.4(3)		1 Er1		238.0(7)	237.9(9)	
	1 Si4b	352.7(1)	348.3(6)		1 Er1	316.4(2)	317.5(3)		1 Er2	247.2(4)	244.8(6)		
	1 Er2	353.5(1)	349.9(1)		1 Er1	336.0(2)	334.4(3)		N5:	1 Si2	174.2(7)	178(1)	
	1 Er2	357.8(1)	352.7(1)		1 Er1	341.8(2)	344.0(3)			1 Si3	177.7(7)	176(1)	
	1 Er2	368.0(1)	366.5(1)		1 Er2	346.7(2)	342.7(3)			1 Er1	239.5(4)	242.5(6)	
	Er2:	2 Er1	383.0(1)		385.4(1)	Si3:	1 N3		174.0(6)	174(1)	1 Er2	242.0(6)	239.6(9)
		1 O1a	218.9(3)		—		1 N1		174.3(6)	173.6(9)	1 Er3	—	258.9(6)
1 O1b		219.0(2)	—	1 N6	175.5(6)		175(1)	N6:	1 Si1	171.9(7)	176(1)		
1 N9/O1		—	225.2(1)	1 N5	177.7(5)	175.8(7)	1 Si2		173.4(4)	173.4(7)			
1 N5		242.0(6)	239.6(9)	1 Er1	305.6(2)	302.3(2)	1 Si3		175.5(6)	175(1)			
1 N3		246.5(6)	248.4(9)	1 Er3	—	282.1(3)	1 Er3	—	267(1)				
1 N4		247.2(4)	244.8(6)	1 Er2	345.2(2)	350.7(3)	N7:	3 Si1	178.5(3)	174.1(4)			
1 N1		247.6(5)	249.7(7)	Si4a:	1 Si4b	[72(1)]		[93(3)]	1 Si4b	210(1)	211(4)		
1 N2		249.4(6)	248.6(9)		3 N3	169.5(6)		170.1(6)	N8:	1 Si5	168(1)	173(2)	
1 Si4a		292.9(7)	293.9(5)		1 O1a	174(3)	—	3 Er1		236.3(4)	238.6(7)		
1 Er3		—	320.9(3)	1 N9/O1	—	181(3)	O1a:	1 O1b		[44(4)]	—		
1 Si1		334.5(1)	337.2(1)	1 O1b	[218(2)]	—		1 Si4a	174(3)	—			
1 Si3		345.2(2)	350.7(3)	3 Er2	292.9(7)	293.9(5)		3 Er2	218.9(3)	—			
1 Si4b		345.3(4)	360.5(3)	Si4b:	1 Si4a	[72(1)]	[93(3)]	1 Si4b	[246(3)]	—			
1 Si1		346.2(1)	347.1(2)		3 N3	171.4(4)	174(1)	O1b:	1 O1a	[44(4)]	—		
1 Si5		353.7(2)	347.5(2)		1 N7	210(1)	211(4)		1 Si4a	[218(2)]	—		
1 Si2		346.8(2)	342.7(3)	1 O1a	[246(3)]	—	3 Er2		219.0(2)	—			
1 Er1		353.5(1)	349.9(1)	1 O1b	290(2)	—	1 Si4b	290(2)	—				
1 Er1	357.8(1)	352.7(1)	3 Er2	345.3(4)	360.5(3)	N9/O1:	1 Si4a	—	181(3)				
1 Er1	368.0(1)	366.5(1)	3 Er1	352.7(1)	348.3(6)		3 Er2	—	225.2(1)				
2 Er2	377.4(1)	389.9(1)	Si5:	1 N8	168(1)		173(2)	1 Er3	—	237(3)			
Er3:	1 N9/O1	—		237(3)	3 N2	176.7(6)	174.3(9)						
	3 N5	—		258.9(6)	3 Er1	334.9(3)	341.3(6)						
	3 N6	—	267(1)	3 Er2	353.7(2)	347.5(2)							
	3 Si3	—	282.1(2)	N1:	1 Si1	171.6(7)	175(1)						
	3 Si2	—	315.4(3)		1 Si3	174.3(7)	174(1)						
	3 Er2	—	320.9(3)		1 Er2	247.6(6)	249.7(9)						
			1 Er1	252.8(5)	248.3(7)								

^a For these calculations the lattice constants as obtained from the Guinier powder data were used. For both refinements, all distances shorter than 400 pm (Er–Er), 350 pm (Er–Si), 300 pm (Er–N, Er–O, Si–O), 250 pm (Si–Si, N–N), and 220 pm (Si–N) are listed. Interatomic distances enclosed in brackets do not need to occur, since the corresponding sites are not fully occupied.

do not seem to be related to the different compositions of the crystals, nor are they intimately connected with the polarity of the crystals: the occupancy values for the Si4a/Si4b positions were not found to be significantly different when the crystal structures were refined with the reverse polarity. This polarity is already fixed by the groupings of

the other atoms, as can readily be seen from the orientation of the SiN_4 tetrahedra located at the trigonal axis 00z (Fig. 3). The split position O1a/O1b, on the other hand, is a result of the split Si4a/Si4b position: the O1a position is occupied, when the Si4a position is occupied. The distance Si4a–O1a of 174(3) pm is close to the range of

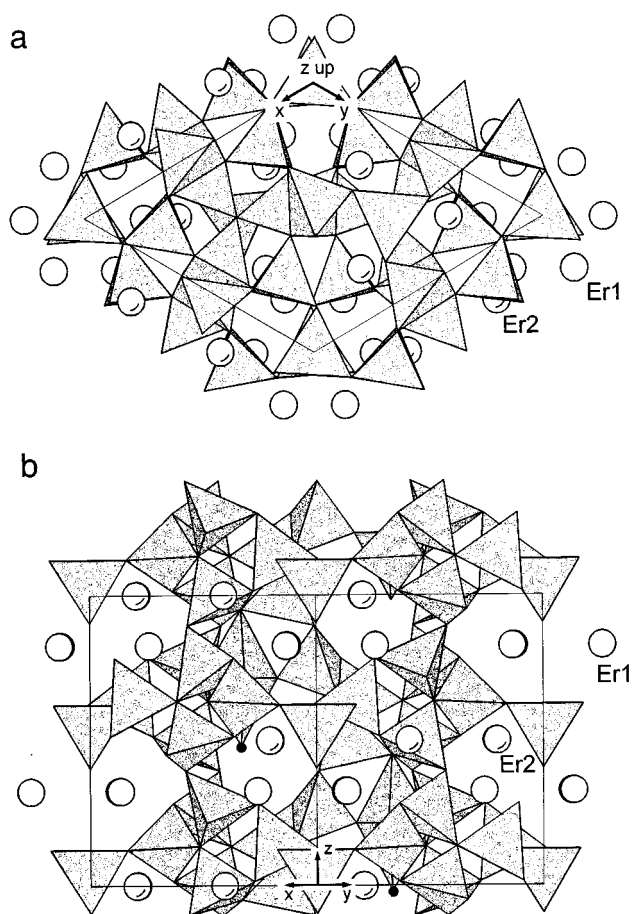


FIG. 2. The structure of $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ as projected along the trigonal axis (a) and perpendicular to the (110) plane (b). The silicon atoms within the SiN_4 tetrahedra are not shown. The black dots represent the positions of the O1b atoms.

Si–O distances between 157 and 172 pm found for well-refined silicate structures (12). The O1b position is occupied, when the silicon atoms occupy the Si4b positions. The Si4b–O1b distance of 290(2) pm is certainly a nonbonding distance. Thus, the O1b atoms are coordinated by three Er2 atoms at the relatively short distance of 219.0(2) pm in nearly trigonal-planar coordination. The N9/O1 position (crystal 2) is also expected to be split, as can be concluded from its relatively large isotropic displacement parameter; however, the data set was not accurate enough to allow such a refinement.

The two fully occupied erbium positions Er1 and Er2 are both coordinated by six light atoms in trigonal prismatic and octahedral coordination, respectively, both very distorted. For the Er1 positions the light atoms are all nitrogen atoms at average distances of 240.3 and 239.5 pm for the crystals 1 and 2, respectively.

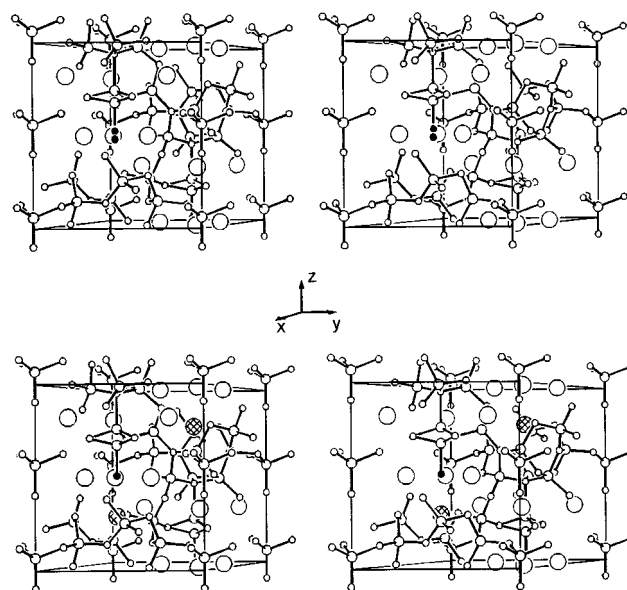


FIG. 3. Stereoplots of the crystal structures with the ideal compositions $\text{Er}_6\text{Si}_{11}\text{N}_{20}\text{O}$ (top) and $\text{Er}_{6.33}\text{Si}_{11}\text{N}_{21}$ (bottom). For details concerning the occupancy of the split position O1a/O1b (top) and the position with the mixed occupancy N9/O1 (bottom), marked with black dots, see Fig. 4. The Er3 position is hatched.

For the Er2 atom of crystal 1 one light atom is the oxygen atom O1a/O1b at the rather short distance of 219 pm. However, the average distance of 241.9 pm from the Er2 atom of crystal 1 to the six light atoms is similar to the corresponding distances of the Er1 atom. In crystal 2 the Er2 atom is coordinated to the N9/O1 position at the distinctly greater bond distance of 225 pm, even though the N9/O1 site was not refined as a split position. Thus, its occupancy by mainly nitrogen atoms makes a difference. The average Er–N distance of 242.7 pm, however, is again close to the average distance of the other erbium atoms to the light atoms.

The Er3 site is not occupied in crystal 1, and in crystal 2 its occupancy is 25.4(3)%. It is coordinated by seven light atoms in a capped octahedral arrangement with the average distance of 259.2 pm. This distance is much greater than the overall average Er–N(O) distance of 241.1 pm for the other erbium atoms. In part this can be rationalized by the higher coordination number of the Er3 atom, and in part also by the fact that the Er3 site is not fully occupied. The nitrogen (and oxygen) atoms surrounding this site carry partial negative charges, which repel each other. Quite generally it is observed, that the average distance to a partially occupied site in an essentially ionic compound is greater than the distance to a fully occupied site, as is convincingly demonstrated in the structure of $\text{Re}_{1.16}\text{O}_3$ (13). The reverse is true for typically intermetallic phases.

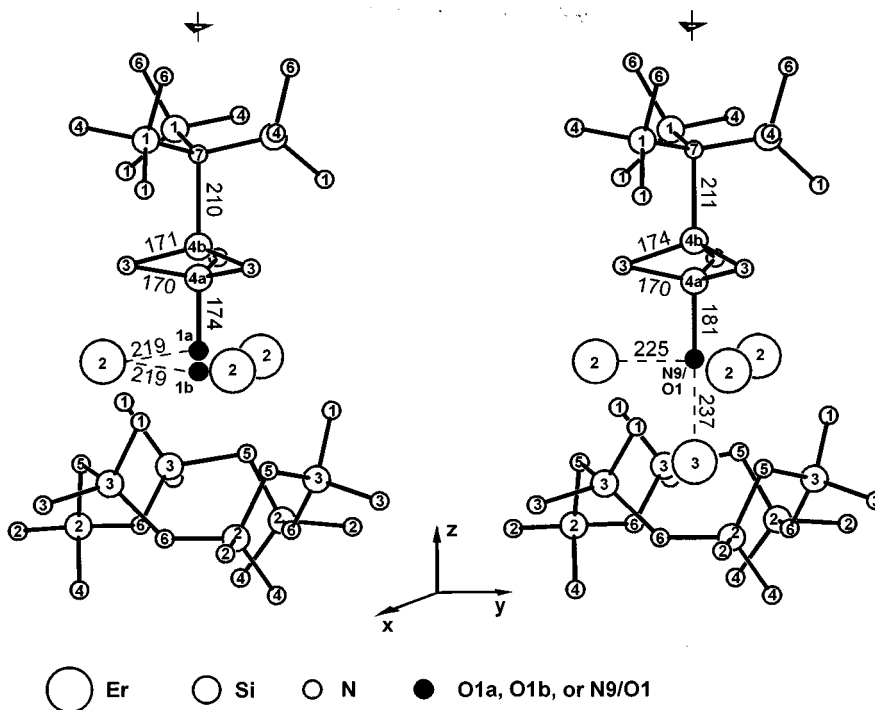


FIG. 4. The atomic arrangement around the split O1a/O1b positions (left) and the position with the mixed occupancy N9/O1 (right). The Si4a position has the same occupancy as the O1a position. The data for crystal 2 were not accurate enough to allow a refinement of the site N9/O1 with split occupancy. The nitrogen/oxygen ratio of this site depends on the occupancy of the Er3 site. For the ideal composition $\text{Er}_{6.33}\text{Si}_{11}\text{N}_{21}$ the Er3 site has an occupancy of 33.3%, and the N9/O1 site is then occupied to 100% by nitrogen atoms.

The silicon atoms of both crystals have four light neighbors in tetrahedral arrangement. The N–Si–N(O) angles vary between $97.5(3)$ and $115.3(3)^\circ$ for crystal 1, and between $99.3(4)$ and $116.7(4)^\circ$ for crystal 2. The average Si–N distances for crystal 1 (in pm units with the corresponding distances for crystal 2 in parentheses) of 173.6 (174.5), 173.4 (174.1), 175.4 (174.6), 174.5 (174.0) for the Si1, Si2, Si3, Si5 atoms are all slightly longer than the corresponding distance of 170.6 (172.8) pm of the Si4a site, which is occupied to 35.8% (82%). The argument, mentioned above, concerning bond lengths from occupied and nonoccupied sites, does not apply in this case, since the Si4a site is quite close to the Si4b site, and both together are fully occupied. The Si4b site, however, does have an unusual coordination in that the N7 atoms in crystals 1 and 2 are at the rather large distances of 210(1) and 211(4) pm, respectively. For that reason the average Si4b–N distances of 181.0 and 183.2 pm are also rather large.

We conclude with some remarks about the linking of the SiN_4 tetrahedra. Most of the nitrogen atoms in the two closely related structures link two SiN_4 tetrahedra. The N8 atoms may be called terminal nitrogen atoms, since they belong to only one silicon atom, and this seems to be a novel feature for nitridosilicates. Terminal oxygen atoms, on the

other hand, are quite common in oxosilicates. In contrast, the N6 and some N7 atoms are shared by three SiN_4 tetrahedra. This is frequently observed for nitridosilicates (3–6), whereas in oxosilicates the oxygen atoms never belong to more than two SiO_4 tetrahedra (12). The remaining N7 atoms (64 and 18% in crystals 1 and 2, respectively) even have four silicon neighbors, albeit the fourth silicon atom, Si4b, is further away at 210(1) and 211(4) pm in the crystals 1 and 2, respectively (Fig. 4).

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