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$M_2(Si,Al)_4(N,C)_7$ (M = La,Y,Ca) carbonitrides
II. The crystal structure of $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

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Abstract

A new $(Ca,Y)Si_4(N,C)_7$ phase has been characterised lying between the two end-members $Y_2Si_4N_6C$ and $CaYSi_4N_7$. This phase is similar to $BaYbSi_4N_7$, which is made up of a network of $[N(SiN_3)_4]$ structural units linked together in a three-dimensional network, with the large cations located in the interstices, but $(Ca,Y)Si_4(N,C)_7$ is a disordered variant, with nitrogen atoms partially occupying two sets of equivalent sites related by the combined operations of rotation and tilt. The crystal of $(Ca,Y)Si_4(N,C)_7$ used for structure determination contained Ca and Y in the atomic ratio 2:3, the excess positive charge in the cation sites being balanced by the partial replacement of nitrogen by carbon in the central non-metal site of the $[N(SiN_3)_4]$ unit. Powder diffraction data are listed for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$, which is hexagonal with $a = 5.9874(4)$, $c = 9.7849(8)$ Å at ambient temperature. The crystal structure has been determined from single crystal data; $Z = 2$; S.G. $P6_3mc$ (no. 186); $R_{\text{int}} = 0.0274$, $R1 = 0.0384$, $wR2 = 0.0993$ for all data.

Keywords: Carbonitrides; Crystal structure; X-ray diffraction; $CaYSi_4(N,C)_7$

1. Introduction

Crystal structures of M–Si–Al–O–N oxynitrides have often previously been determined by powder X-ray and neutron diffraction because of the difficulty of producing crystals large enough in size to be analysed by single crystal techniques. However, the development of the small single crystal facility (Station 9.8)[1] at the CLRC Daresbury Laboratory in 1996 made it possible to mount crystals as small as 10–40 μm, thereby enabling crystal structures of "powder grains" to be determined, even in the case of phases existing as minor products in multiphase powder mixtures.

In the last few years, a group of compounds of the type $MYbSi_4N_7$ (M: = Ba, Sr,Eu),[2,3] have been prepared, which are hexagonal with unit cell dimensions $a \sim 6.0$, $c \sim 10.0$ Å. A characteristic feature of these compounds is four SiN_4 tetrahedra meeting at a common nitrogen atom, giving a building block of composition $[N(SiN_3)_4]$ (Fig. 1). The unit cell comprises four such units and the stacking arrangement is illustrated in Fig. 2. In each tetrahedron, three of the N–Si bonds are of normal length (∼1.7 Å), while the fourth (the bond involving the central nitrogen atom) is invariably longer (∼1.9 Å). The $[N(SiN_3)_4]$ structural units are linked together partly by the large cations, and also by Si–N–Si bonds between adjacent units.

The present paper describes the structure of a calcium yttrium derivative of this series, in which the central non-metal site in the $[N(SiN_3)_4]$ unit includes carbon; overall valency balance is preserved by the simultaneous partial substitution of yttrium for calcium in the large cation sites.

2. Experimental

The sample used in the present investigation was prepared by direct nitridation of a mixture of the component metals. Calcium was used in the form of BDH 99.9% calcium metal granules and silicon as Murex 99.9% powder. The calcium granules were initially flattened into thin sheets and cut into millimetre-sized pieces; on heating, these melted at relatively low temperatures (839 °C), generating pockets of

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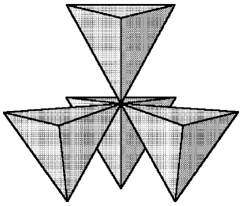

Fig. 1. The $[N(SiN_3)_4]$ structural unit in $M(II)M(III)Si_4N_7$ nitrides.

liquid which facilitated single crystal growth. Yttrium powder was supplied by Aldrich Chemicals in the form of the hydride, YH_2; this decomposed during the early stages of reaction, yielding a reactive yttrium powder. The starting mix of Ca, Si and YH_2 powders, in molar proportions 1:1:4, was dry mixed and uniaxially pressed into a pellet, which was nitrided in a graphite crucible at 1900 °C for 1 h in a carbon element furnace in nitrogen. No surrounding powder bed was used in order to facilitate good access of nitrogen to the metals in the sample. The resulting pellet comprised a grey sintered outer layer and a porous greyish-yellow inner region, with small single crystals clearly visible. The outer layer was rich in yttrium, due to the loss of calcium and was discarded, while the inner portion was gently crushed into a powder for analysis.

Powder X-ray diffraction was carried out using a Hägg–Guinier focusing camera; Cu $K\alpha_1$ radiation was used and an internal silicon standard added. Powder photographs were measured using an automatic line scanner (LS-20) and accompanying SCANPI and PIRUM software. EDX analysis was performed by means of a Hitachi 2400 electron microscope and analyser (Oxford Instruments Microanalysis ISIS-II), whilst NMR analysis was used to confirm the presence of carbon in the structure; the NMR results are reported fully in the first paper in this series.[4] A single crystal was selected from this sample and diffraction data collected on the Synchrotron Radiation Source at the CLRC Daresbury Laboratory (Station 9.8) using a Bruker SMART 1K CCD; structure solution and refinement were carried out using the SHELXTL suite of programs.[5] Structures have been plotted using ATOMS 4.1.

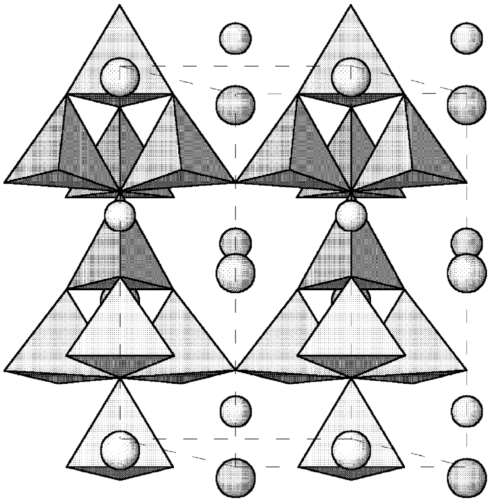

Fig. 2. Tetrahedral stacking arrangement of $MYbSi_4N_7$ (M: Ba,Sr,Eu) structures (after Huppertz and Schnick)[6,7]. Large circles represent M and smaller circles Yb.

3. Results

Powder X-ray diffraction analysis of the sample showed it to be single phase, the pattern indexing on a hexagonal unit cell of dimensions: $a = 5.9874(4)$, $c = 9.7849(8)$ Å; d-spacings and intensities are listed in Table 1. This

Table 1
Powder diffraction data for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

hkl	d_{calc} (Å)	d_{obs} (Å)	$2\theta_{obs}$	I_{obs}
1 0 0	5.1853	5.1833	17.093	3
0 0 2	4.8925	4.8954	18.107	<1
1 0 1	4.5817	4.5813	19.359	31
1 0 2	3.5585	3.5578	25.008	7
1 1 0	2.9937	2.9933	29.825	51
1 0 3	2.7609	2.7608	32.402	100
2 0 0	2.5926	2.5921	34.576	5
1 1 2	2.5536	2.5533	35.117	92
2 0 1	2.5062	2.5058	35.806	86
0 0 4	2.4462	2.4461	36.711	6
2 0 2	2.2909	2.2903	39.307	4
1 0 4	2.2124	2.2127	40.745	9
2 0 3	2.0296	2.0294	44.615	9
2 1 0	1.9598	1.9594	46.298	1
2 1 1	1.9217	1.9211	47.276	8
1 1 4	1.8943	1.8941	47.994	5
1 0 5	1.8309	1.8308	49.764	8
2 1 2	1.8193	1.8190	50.108	4
2 0 4	1.7793	1.7792	51.308	4
3 0 0	1.7284	1.7282	52.940	14
2 1 3	1.6799	1.6792	54.591	32
0 0 6	1.6308			
3 0 2	1.6297	1.6298	56.412	40
2 0 5	1.5620	1.5622	59.088	39
1 0 6	1.5557	1.5566	59.320	6
2 1 4	1.5295	1.5291	60.484	7
2 2 0	1.4969	1.4973	61.922	46
1 1 6	1.4321	1.4324	65.062	3
2 2 2	1.4314			
3 1 1	1.4228	1.4233	65.531	5
3 0 4	1.4116	1.4118	66.133	1
2 1 5	1.3848	1.3843	67.619	6
2 0 6	1.3804	1.3805	67.836	18
3 1 2	1.3798			
1 0 7	1.3497	1.3490	69.642	2
3 1 3	1.3159	1.3158	71.668	28
4 0 1	1.2851	1.2852	73.650	12
2 2 4	1.2768	1.2770	74.197	6
2 1 6	1.2536	1.2540	75.796	8
3 1 4	1.2398	1.2401	76.804	4
2 0 7	1.2304	1.2307	77.493	1
4 0 3	1.2047	1.2055	79.433	1
1 0 8	1.1904	1.1915	80.559	5
3 0 6	1.1862	1.1862	80.988	3

Hexagonal: $a = 5.9874(4)$, $c = 9.7849(8)$ Å diffraction pattern is similar to those of a number of $M^{III}{}_2Si_4(N,C)_7$, (M = Y,Ln) phases such as $La_2Si_4N_6C$, $Y_2Si_4N_6C$ and $LaYSi_4N_6C$, all of which have hexagonal or pseudo-hexagonal orthorhombic unit cells and contain a carbon atom at the centre of $[C(SiN_3)_4]$ tetrahedral groups[4]. Since the starting composition had the same stoichiometry and the large Ca and Y cations have atomic radii similar to the equivalent cations in the $(Ba,Sr,Eu)YbSi_4N_7$ series, it was expected that the compositions would be very similar. However, due to evaporation of the calcium metal, elemental analysis carried out by EDX on the powdered centre of the fired pellet showed the Ca:Y ratio to be not 1:1 but approximately 2:3, resulting in an overall Ca:Y:Si ratio of 0.8:1.2:4.0. With an excess of Y^{3+} relative to Ca^{2+}, the valencies would not balance if the compound was a pure nitride, and at the start of the work it was considered that this might be due to substitution of carbon for nitrogen. Confirmation of these assumptions was convincingly provided by the single crystal structure analysis, supplemented by ^{13}C NMR analysis carried out at the University of Durham[4].

Table 2
Crystallographic data for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

Identification code	kl075
Chemical formula	$C_{0.20}Ca_{0.80}N_{6.80}Si_4Y_{1.20}$
Formula weight	348.79
Temperature	150(2) K
Radiation, wavelength	Synchrotron, 0.6929 Å
Crystal system, space group	Hexagonal, $P6_3mc$
Unit cell parameters	$a = 5.9915(4)$ Å, $c = 9.7891(9)$ Å
Cell volume	304.33(4) Å^3
Z	2
Calculated density	3.806 g/cm^3
Absorption coefficient, μ	12.859 mm^{-1}
F (0 0 0)	335
Crystal colour and size	Pale blue, 0.04 mm × 0.02 mm × 0.02 mm
Reflections for cell refinement	1899 (θ range 3.82–29.22°)
Data collection method	Bruker SMART 1K CCD diffractometer ω rotation with narrow frames
θ Range for data collection	3.83–29.22°
Index ranges	h −8 to 6, k −6 to 8, l −13 to 13
Completeness to $\theta = 25.00°$	99.3%
Reflections collected	1952
Independent reflections	355 ($R_{int} = 0.0274$)
Reflections with $F^2 > 2\sigma$	348
Absorption correction	Semi-empirical from equivalents
Minimum and maximum transmission	0.60 and 0.81
Structure solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0667, 0.6788
Data/restraints/parameters	355/4/34
Final R indices [$F^2 > 2\sigma$]	$R1 = 0.0381$, $wR2 = 0.0990$
R indices (all data)	$R1 = 0.0384$, $wR2 = 0.0993$
Goodness-of-fit on F^2	1.176
Absolute structure parameter	0.355(17)
Largest and mean shift/su	0.000 and 0.000
Largest diffraction peak and hole	0.927 and −0.851e Å^{-3}

4. Crystal structure

Table 2 lists crystallographic data for the single crystal structure determination. Initial application of the SHELXS direct methods program identified the large cation sites and the basic distribution of tetrahedra, showing that the atomic arrangement was very similar to those of the $MYbSi_4N_7$ (M = Ba,Sr,Eu)[2,3] quaternary nitrides. In this structure (Fig. 2), groups of four $[SiN_4]$ tetrahedra are linked together at a central nitrogen atom to give a structural unit of overall

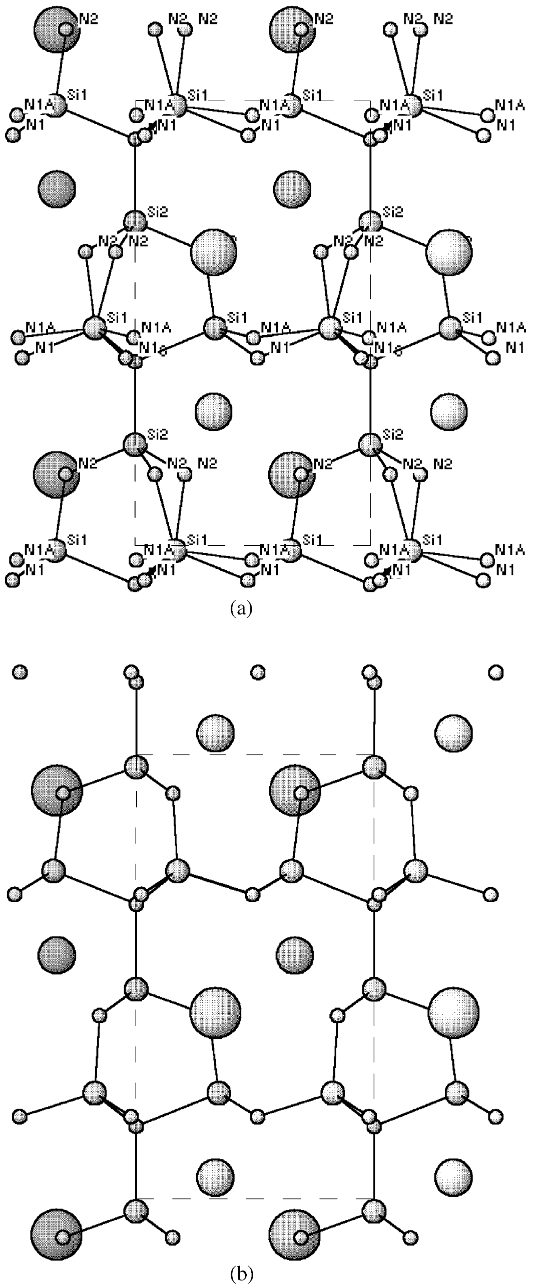

Fig. 3. Crystal structures perpendicular to [1 $\bar{1}$ 0] of $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$ and (b) $SrYbSi_4N_7$ (after Huppertz and Schnick[6]). (a) Large circles represent Ca and small circles Y; (b) circle size decreases in the order Sr, Yb, Si, N.

Table 3
Final atomic coordinates for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

Atom	Site/symmetry	*x*	*y*	*z*	Sof	U_{iso} (Å^2)
Y(1)	2*b*/3*m*	0.6667	0.3333	0.19909(8)	1.0	0.0086(3)
Ca(2)	2*b*/3*m*	0.6667	0.3333	−0.1594(3)	0.8	0.0211(6)
Y(2)	2*b*/3*m*	0.6667	0.3333	−0.1594(3)	0.2	0.0211(6)
Si(1)	6*c*/*m*	0.3406(3)	0.17031(14)	0.5111(2)	1.0	0.0086(5)
Si(2)	2*a*/3*m*	0.0000	0.0000	0.7732(4)	1.0	0.0074(6)
N(1)	6*c*/*m*	0.5202(12)	0.040(2)	0.5779(13)	0.5	0.0107(16)
N(1A)	6*c*/*m*	0.5027(11)	0.4973(11)	0.5329(14)	0.5	0.0107(16)
N(2)	12*d*/*1*	0.2952(14)	0.2115(15)	0.3396(7)	0.5	0.0091(15)
N(3)	2*a*/3*m*	0.0000	0.0000	0.5866(12)	0.8	0.016(3)
C(3)	2*a*/3*m*	0.0000	0.0000	0.5866(12)	0.2	0.016(3)

Table 4
Anisotropic displacement (Å^2) parameters for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Y(1)	0.0103(4)	0.0103(4)	0.0053(5)	0.000	0.000	0.00517(18)
Ca(2)	0.0197(8)	0.0197(8)	0.0238(13)	0.000	0.000	0.0098(4)
Y(2)	0.0197(8)	0.0197(8)	0.0238(13)	0.000	0.000	0.0098(4)
Si(1)	0.0059(9)	0.0100(7)	0.0086(9)	0.0003(4)	0.0006(8)	0.0029(4)
Si(2)	0.0077(8)	0.0077(8)	0.0069(13)	0.000	0.000	0.0038(4)
N(2)	0.007(3)	0.010(4)	0.008(3)	0.001(2)	0.001(3)	0.003(2)
N(3)	0.016(4)	0.016(4)	0.015(6)	0.000	0.000	0.0080(19)
C(3)	0.016(4)	0.016(4)	0.015(6)	0.000	0.000	0.0080(19)

Table 5
Bond lengths (Å) and angles (°) for $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$

Y(1)–N(1)	2.273(10)	[*x*3]	Ca(2)–N(1)	2.987(15)	[*x*3]
Y(1)–N(1A)	2.395(12)	[*x*3]	Ca(2)–N(1)	3.026(15)	[*x*3]
Y(1)–N(2)	2.399(8)	[*x*6]	Ca(2)–N(1A)	2.576(12)	[*x*3]
			Ca(2)–N(2)	2.620(9)	[*x*6]
Si(1)–N(1)	1.741(6)	[*x*2]	Si(2)–N(2)	1.707(8)	[*x*2]
Si(1)–N(1A)	1.710(6)	[*x*2]	Si(2)–N(2)	1.707(8)	[*x*2]
Si(1)–N(2)	1.738(7)	[*x*2]	Si(2)–N(2)	1.707(8)	[*x*2]
Si(1)–N(3)	1.916(6)		Si(2)–N(3)	1.827(13)	
N(2)–Si(2)–N(2)	107.8(4)	N(1)–Si(1)–N(1A)	109.1(10)		
N(2)–Si(2)–N(2)	107.8(4)	N(1)–Si(1)–N(2)	105.4(7)		
N(2)–Si(2)–N(2)	107.8(4)	N(1)–Si(1)–N(3)	109.7(4)		
N(2)–Si(2)–N(3)	111.1(4)	N(1A)–Si(1)–N(2)	112.4(7)		
N(2)–Si(2)–N(3)	111.1(4)	N(1A)–Si(1)–N(3)	112.3(5)		
N(2)–Si(2)–N(3)	111.1(4)	N(2)–Si(1)–N(3)	107.7(4)		

composition $[N(SiN_3)_4]$, in which the central nitrogen atom is in a regular sp^3 environment with respect to surrounding silicon atoms. These groups are linked to similar $[N(SiN_3)_4]$ groups at the circumferential nitrogen atoms to give "close-packed" layers, which are then stacked above one another vertically (but with a rotation of 60°) to build up the overall structure. In between the $[N(SiN_3)_4]$ units, the large cations occupy interstitial sites, and play the dual role of joining the anionic units together and also maintaining valency balance. In the initial refinement, one of the large cation sites was completely occupied by Y and the other by Ca; at this stage the *R*1 value was 0.044. In view of the excess of yttrium as determined by EDX, the Y(1) site was left fully occupied by Y, and the Ca(2) site was fixed as 80:20 Ca:Y. At the same time, 0.2 carbon atoms per formula unit were introduced into the central non-metal site of the $[N(SiN_3)_4]$ unit giving an overall composition of $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$. Continued refinement based on these changes resulted in further reduction of the *R*1 index to 0.038. However, at this stage, the isotropic displacement factors, U_{iso}, of the N(1) and N(2) atoms, were larger than expected. On allowing these to move off mirror planes into general positions, refinement showed that the tetrahedra tilted (i.e. the bases no longer remained perpendicular to the *c*-axis), and these gave two equivalent positions which the N(1) and N(2) atoms occupied statistically. This made no difference to the value of *R*1, but produced U_{iso} values of the same order of magnitude as the other atoms in the structure. These changes in the nitrogen atom positions might have been expected to generate some movement in the silicon atoms at the centre of the tetrahedra; however,

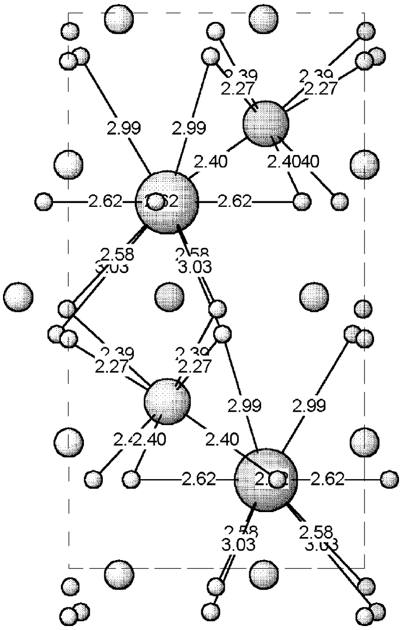

Fig. 4. Distribution of Ca (large circles)–N and Y(small circles)–N bond lengths (Å) in $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$ viewed perpendicular to $[1\ \bar{1}\ 0]$.

none was detected, and the U_{iso} values for these sites also retained sensible values. The refinement was terminated at this stage.

Fig. 3 shows the layout of the silicon-centred tetrahedra (a), compared to the similar arrangement in the compound $SrYbSi_4N_7$ (b), in which the N(1) and N(2) sites are fully occupied. It is believed that the cation non-stoichiometry in the present sample is responsible for this statistical occupation of N(1) and N(2) sites, which is probably more likely to be due to the Ca:Y ratio departing from 1:1 rather than the N:C ratio varying from 6:1; however, further work would be needed to confirm this. Final atomic coordinates and anisotropic temperature factors are listed in Tables 3 and 4.

Bond lengths and angles are shown in Table 5. N(1) and N(1A) lie in 6c sites and N(2) in 12d, all of which are 50% occupied; although the table lists all bonds, the Y(1) atoms have six neighbours, and the Ca,Y(2) atoms have a total of twelve neighbours. Six of the latter are shorter (∼2.6 Å) and the other six are longer (∼3.0 Å); see Fig. 4. This is consistent with the (Ba,Sr,Eu)$YbSi_4N_7$ series, where again the smaller cation (Yb) has six neighbours and the larger cation has twelve. Bond lengths from the central C,N(3) site are long, not necessarily due to the incorporation of carbon, because in the quaternary nitride phases this bond is also long, with a value similar to that in the present phases (∼1.9 Å). Clearly, this site is very suitable for occupation by carbon because the bonding is sp^3, almost identical to the environment of a carbon atom in silicon carbide. The nitrogen atoms on the circumference of the large $[(N,C)(SiN_3)_4]$ units are two-coordinated by silicon atoms and also two-coordinated by large cations, exactly as in other metal silicon nitrides such as $LaSi_3N_5$[6] and $Ln_3Si_6N_{11}$[7]. The whole anion network is three-dimensional, and therefore likely to display good refractoriness, a high modulus, and good hardness.[8]

$Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$ is a specific example of the wider group of covalently-bonded $M_2Si_4N_6C$ quaternary carbonitrides reported elsewhere (M: Ho,Tb)[9] and also in Part I of this series.[4] Other solid solution series exist in which carbon can be substituted by nitrogen, for example the series extending between AlN and SiC[10,11], the Al–C–N polytypes[12,13] and in fact most interstitial metal nitrides exhibit ranges of solid solution extending from the metal nitride to the metal carbide. However, in covalently bonded, silicon-containing ceramics, the simultaneous presence of nitrogen and carbon has generally not been observed, as typified by the fact that no ternary compounds exist in the SiC–Si_3N_4 system. Clearly in the present case, the additional cations allow further flexibility and also the unique feature of the $[N(SiN_3)_4]$ units, in having the central non-metal atom in an sp^3 environment, may be important in allowing the carbon to reside stably in the structure.

5. Conclusions

The crystal structure of a new quaternary carbonitride phase of composition $Ca_{0.8}Y_{1.2}Si_4N_{6.8}C_{0.2}$ has been determined. The unit cell is hexagonal, with dimensions $a = 5.9874(4)$ and $c = 9.7849(8)$ Å, similar to the series of quaternary metal silicon nitrides of the type (Ba,Sr,Eu)Si_4N_7. The main structural feature is the $[Si_4N_{12.8}C_{0.2}]$ units consisting of four tetrahedra linked together at a central non-metal atom, this site being the location of the carbon atoms. These units join together to form a three-dimensionally linked network of tetrahedra, with the large metal cations occupying interstices between them. In contrast to the (Ba,Sr,Eu)$YbSi_4N_7$ nitrides, the nitrogen atoms are split between two sets of equivalent positions, resulting in rotation and tilting of the silicon-centred tetrahedra. This is believed to occur because of the non-stoichiometric 0.8:1.2 ratio of Ca:Y in the present compound, compared with the 1:1 ratio in the quaternary nitrides.

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