

First-principles calculations of the stability and local structure of α -sialon ceramics on the line
 $\text{Si}_3\text{N}_4\text{-}\frac{1}{2}\text{Ca}_3\text{N}_2\text{:3AlN}$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 2931

(<http://iopscience.iop.org/0953-8984/16/16/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 14:28

Please note that [terms and conditions apply](#).

First-principles calculations of the stability and local structure of α -sialon ceramics on the line $\text{Si}_3\text{N}_4 - \frac{1}{2}\text{Ca}_3\text{N}_2 : 3\text{AlN}$

C M Fang and R Metselaar

Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, The Netherlands

E-mail: R.Metselaar@tue.nl

Received 3 November 2003

Published 8 April 2004

Online at stacks.iop.org/JPhysCM/16/2931

DOI: 10.1088/0953-8984/16/16/016

Abstract

The atomic structures of calcium sialons $\text{Ca}_x\text{Si}_{12-m}\text{Al}_m\text{N}_{16}$ ($m = 0.5, 1, 2, 4$) with the α - or β - Si_3N_4 -type structure were calculated, using the *ab initio* DFT approach, including relaxations of both lattice parameters and positions of the atoms. For all m values the α - Si_3N_4 -type structure has a lower energy than the β -type. For $m = 1, 2$ and 4 the α -type structure is also stable against decomposition into the metal nitrides, in agreement with experimental data. For $m = 0.5$ stability becomes uncertain. Al ions prefer positions close to Ca. Rather strong structural relaxations occur around the Ca ion.

1. Introduction

Sialon ceramics have attracted attention for many years because of their high strength and hardness in combination with good chemical resistance. The main applications are presently as cutting tools. Recently it was shown that these materials are also of interest because of their optical properties, both because of their light absorption and because of their use as a host material for luminescent ions [1–4].

The first report on Si–Al–O–N ceramics was published in 1972 by Jack and Wilson [5]. They showed that the α - Si_3N_4 structure was expanded by about 3% by reaction of LiSi_2N_3 with Al_2O_3 . Five years later a report by Mitomo [6] that solid solutions of Si_3N_4 – Al_2O_3 – Y_2O_3 with the α structure could be prepared led to a rapid increase in the research of these so-called sialons [7, 8]. Sialons with either the α - or the β - Si_3N_4 structures can be made by suitable substitutions [8, 9]. Compounds with the α -structure have the general composition $\text{M}_x\text{Si}_{12-(m+n)}\text{Al}_{m+n}\text{O}_n\text{N}_{16-n}$, while those with the β -structure have the composition $\text{Si}_{12-z}\text{Al}_z\text{O}_z\text{N}_{16-z}$. M can be Li, Ca, Y or a rare-earth ion, with x being equal to m divided by the valency of the M ion. While the β -sialons form a continuous solid solution

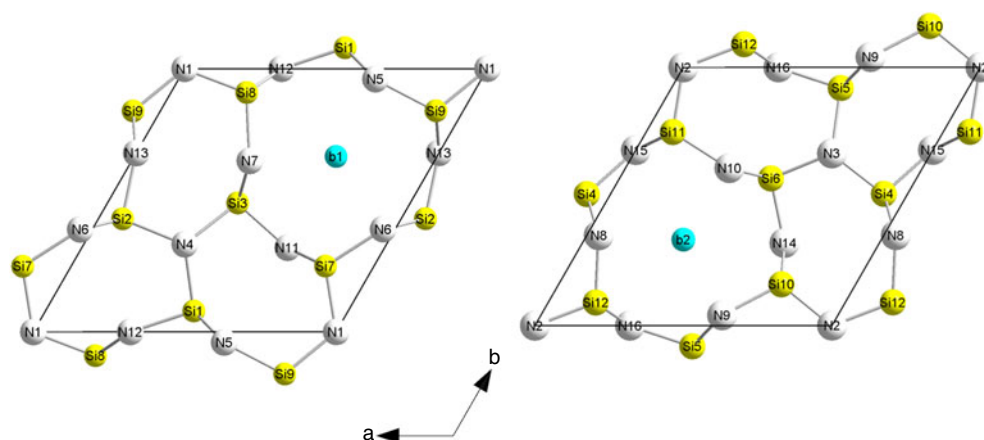


Figure 1. Projections on the (001) plane of the α - and β -sialon structures. (a) Atom configurations in the AB layers; (b) configuration of the CD layers. α consists of an ABCD stacking, whereas β consists of an AB stacking. The twelve-fold ring of atoms around position b1 at $1/3, 2/3$ in (a) forms continuous channels parallel to the z direction in the β -structure. In the α -structure two large interstices are formed at positions b1 $1/3, 2/3, z$ and b2 $2/3, 1/3, z+1/2$, with $z \approx 0.22$, which can accommodate metal ions. Positions shown are for the α -structure: the actual β -structure is less deformed than is shown here. The positions b are empty in the β -structure and can accommodate the M ions in the α -structure.

(This figure is in colour only in the electronic version)

in the range $0 \leq z \leq 4.2$, the α -structure is only stable for m values above about $m = 1$, depending on the M ion. It is not possible to substitute M ions in the β -structure.

In this paper we report the results of *ab initio* calculations on Ca- α -sialons with compositions along the line $\text{Si}_3\text{N}_4 - \frac{1}{2}\text{Ca}_3\text{N}_2 : 3\text{AlN}$ and we compare the total energies of these compounds with those of the hypothetical β -analogues. The calculations have also been performed for the binary nitrides, including α - and β - Si_3N_4 , AlN and Ca_3N_2 to estimate the relative stability of the sialons.

β - Si_3N_4 has the space group $P6_3/m$, with two molecules per unit cell. Of the 14 atoms, seven are in plane A with $z = 1/4$ and the other seven in plane B with $z = 3/4$ [10, 11] and the crystal consists of a stacking ABAB.... All six Si ions are on Wyckoff positions 6c in distorted SiN_4 tetrahedra. Each nitrogen atom links three SiN_4 tetrahedra (figure 1(a)). As shown in figure 1 this gives continuous channels parallel to the c axis. There has been some doubt whether the mirror plane is really present or that the space group is, in fact, $P6_3$ [9]. However, recently two *ab initio* calculations of the β -structure appeared [12], where it was shown that the $P6_3/m$ structure is recovered after relaxation of lattice parameters from an initial $P6_3$ structure.

The α -structure can be derived from the β -structure by alternating the AB layers shown in figure 1(a) with their mirror image CD shown in figure 1(b). This ABCD.... sequence leads to doubling of the c axis and a space group $P3_1c$ [5, 8, 13]. Due to the c -glide plane that connects the AB layers with the CD layers, instead of the continuous channels large interstices are now formed at sites 2b, with coordinates $(1/3, 2/3, z)$ and $(2/3, 1/3, z+1/2)$. The M ions are accommodated at these large interstices with $z \approx 0.22$. The approximate positions of the ions are given in table 1.

There are many theoretical simulations for the electronic structures of the binary nitrides. Xu and Ching [14, 15] performed band structure calculations for α - and β - Si_3N_4 using the

Table 1. Approximate coordinates of the atoms in the Ca- α -sialon (actual values depend on the m value). (Symmetry operations for 6(c): x, y, z ; $-y, x - y, z$; $y - x, -x, z$; $y, x, z + 1/2$; $x - y, -y, z + 1/2$; $-x, y - x, z + 1/2$.)

Atom	Wyckoff			
	position	x	y	z
Ca	2(b)	1/3	2/3	0.22
Si(1)	6(c)	0.51	0.08	0.20
Si(2)	6(c)	0.16	0.25	-0.01
N(1)	2(a)	0	0	0
N(2)	2(b)	1/3	2/3	0.64
N(3)	6(c)	0.35	-0.04	-0.03
N(4)	6(c)	0.32	0.32	0.23

self-consistent, orthogonalized linear combination of atomic orbitals (OLCAO) method [16]. They found that the electronic structures of α -Si₃N₄ and β -Si₃N₄ are similar and their results for β -Si₃N₄ are also in agreement with the calculations by Liu and Cohen using the first-principles pseudo-potential total energy approach within a localized orbital formalism [17]. The electronic structure of AlN has been calculated by Ching and Harmon [18]. Recently Orhan *et al* [19] performed band structure calculations for Ca₃N₂. Comparatively there are few reports on M- α -Si₃N₄-type compounds. Nakayasu *et al* [20, 21] performed first-principles molecular-orbital calculations for the electronic structure of Ln³⁺ (Ln: rare earth elements) α - and β -sialons using the discrete-variation X α cluster method. They discussed the electric field effects as well as the size effects of the Ln³⁺ ions on the local structures. However, in their calculations no structural relaxations have been taken into account.

2. Computational procedures

Structural optimizations and energy calculations were performed for the nitrides and sialons using the *ab initio* total-energy and molecular-dynamics program VASP [22–25] within the density functional theory (DFT). Vanderbilt-type ultra-soft pseudo-potentials (PP) [26, 27] were used. The Kohn–Sham orbitals were expanded in plane waves with a kinetic energy cut-off of 36 Ryd. Exchange and correlation were treated in the generalized gradient approximation (GGA) [25, 26].

To perform the structural optimizations and electronic energy calculations we used supercells for the Ca-sialons with dimensions $2a \times 2a \times 1c$ (a and c are the lattice parameters of the primitive cell) for the α -structures and supercells with dimensions $2a \times 2a \times 2c$ for the β -structures. The Brillouin zone (BZ) was sampled with a $4 \times 4 \times 8$, $4 \times 4 \times 4$, $4 \times 4 \times 4$ and $10 \times 10 \times 10$ Monkhorst–Pack grid [28] for β -Si₃N₄, α -Si₃N₄, Ca₃N₂ and AlN in the irreducible part, respectively. Correspondingly the Brillouin zone (BZ) was sampled with a $2 \times 2 \times 4$ Monkhorst–Pack grid, or 32 k -points in the irreducible part for the supercells.

3. Results and discussion

Calculations of the total energy were performed for the starting materials α - and β -Si₃N₄, Ca₃N₂ and AlN and for the compositions Ca _{$m/2$} Si_{12- m} Al _{m} N₁₆ with $m = 0.5, 1, 2$ and 4, as shown in tables 2 and 3. Note that these total energies are similar to cohesive energies, but they do not contain vibrational contributions and are dependent on the potential model used. This means that the absolute values are of little importance so only the energy differences

Table 2. Calculated energy differences for Ca- α -sialons with $m = 2$ for different positions of Al with respect to Ca (numbers refer to Si positions in figure 1).

Config. Nr.	Al positions	Ca–Al distances (nm)	Energy differences (eV)
1	11; 12	0.318; 0.318	0
2	6; 7	0.294; 0.399	0.066
3	7; 8	0.401; 0.459	0.098
4	4; 5	0.286; 0.292	0.000

Table 3. Calculated total energies for Ca-sialons $\text{Ca}_{m/2}\text{Si}_{12-m}\text{Al}_m\text{N}_{16}$ with different m values and α - or β - Si_3N_4 structure. E_{stab} gives the energy difference between the sialon and the sum of the energies of its constituents (see the text, equation (1)).

Composition or sialon m -value	Energy (eV)	E_{stab} (eV)
α - Si_3N_4	-57.801	
β - Si_3N_4	-57.804	
Ca_3N_2	-26.782	
AlN	-15.096	
α -sialon $m = 0.5$	-231.419	-0.056
β -sialon $m = 0.5$	-231.208	+0.155
α -sialon $m = 1$	-231.761	-0.250
β -sialon $m = 1$	-231.435	+0.251
α -sialon $m = 2$	-232.508	-0.708
β -sialon $m = 2$	-231.993	+0.193
α -sialon $m = 4$	-234.006	-1.646
β -sialon $m = 4$	-228.952	+3.406

matter. For the binary nitrides the calculated lattice parameters and bandgap values are in good agreement with the experimental values [5–10] and other calculations [13–18].

Both for the α - and the β -sialons the total energies were calculated for different possible atomic configurations of the aluminium ions with respect to the calcium ion. We consider in detail the results for $m = 2$. There is one Ca per unit cell so only one of the two available interstices is occupied. For the α -structure the Ca ion was placed on site b2 2/3, 1/3, 0.73 (these are the starting positions: after relaxation, small shifts may occur), while the b1 site at 1/3, 3/3, 0.23 was empty. There are nine nearest Si sites around the b sites, with Ca–Si distances varying between 0.29 and 0.32 nm. We calculated the energy for four configurations with different positions of the two Al ions. In configuration 1 the Al are on positions Si11 and Si12 in the cage of next-nearest neighbours around Ca (the position numbers can be found in figure 1). As shown in table 2 the Ca–Al distances are 0.32 nm and this configuration has the lowest energy. In configuration 3 the Al ions are on positions Si7 and Si8 at 0.40 and 0.45 nm, respectively, while the Al–Al distance is the same as in configuration 1. From table 2 one sees that the energy of configuration 1 is nearly 0.1 eV lower than of configuration 3. This is due to the fact that the repulsive energy of a $\text{Ca}^{2+}\text{--Al}^{3+}$ pair is lower than that of a $\text{Ca}^{2+}\text{--Si}^{4+}$ pair. In configuration 4 both Al ions are in the same plane as Ca, while in configuration 1 they are in a plane at $z/4$ below Ca, but the Ca–Al and Al–Al distances are about the same for both cases. This results in equal energies for cases 1 and 4. Finally in configuration 2 one Al is at 0.3 nm, as in configuration 1, while the other Al is at 0.4 nm from Ca. The Al–Al distance for case 2 is 0.53 nm instead of 0.6 nm for case 1, but the effect of a change in Al–Al interaction is covered by the effect of the increased Ca–Al distance, i.e. the increased Ca–Si repulsion, resulting in

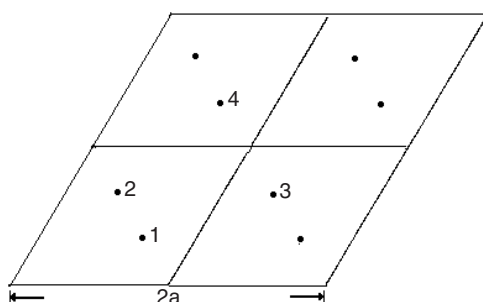


Figure 2. Schematic picture of the positions of the Ca ions for the $2a \times 2a \times c$ supercell of the Ca- α -sialon $\text{Ca}_4\text{Si}_{40}\text{Al}_{16}\text{N}_{64}$ ($m = 2$). The eight b sites are indicated: b sites 1–4 are occupied by Ca ions.

about 0.07 eV higher energy. From these results we conclude therefore that the lowest energy is obtained when the Al ions are close to the Ca ion.

For $m = 0.5$ or 1 we used a supercell with dimensions $2a \times 2a \times c$ corresponding to a composition $\text{CaSi}_{46}\text{Al}_2\text{N}_{64}$ for $m = 0.5$ and $\text{Ca}_2\text{Si}_{44}\text{Al}_4\text{N}_{64}$ for $m = 1$. For the latter case the two calcium ions were again placed in different positions with respect to each other. We also repeated the calculation for $m = 2$ with this supercell, i.e. for a composition $\text{Ca}_4\text{Si}_{40}\text{Al}_{16}\text{N}_{64}$. The four Ca ions in this cell were distributed as shown schematically in figure 2. The average total energy per unit cell is with -232.355 eV, which is 0.15 eV higher than for the other configurations. The influence of the Ca–Al distance is more difficult to see for the supercells since there are many Ca–Al distances involved. For $m = 1$ the configuration with smallest Ca–Al distances had about 0.01 eV lower energy. From the calculations for the supercells we found no indication for preferred Ca distributions.

Next we performed the same calculations assuming that the Ca-sialons had the β -structure. We used supercells with dimensions $2a \times 2a \times c$ or $2a \times 2a \times 2c$ for different positions of the Ca ion. After relaxation the z value for calcium was always about 0.22 or 0.72.

The results are summarized in table 3 for the configurations with lowest energy. Column 2 gives the total energy in electronvolts per formula unit of sialon with a given m value and either α - or β -structure. Column 3 gives the difference between the total energy and the sum of the energies of the constituents according to the formula:

$$E_{\text{stab}} = E(\text{Ca}_{m/2}\text{Si}_{12-m}\text{Al}_m\text{N}_{16}) - m/6E(\text{Ca}_3\text{N}_2) - (12 - m)/3E(\beta\text{-Si}_3\text{N}_4) - mE(\text{AlN}). \quad (1)$$

This calculation is, of course, neglecting entropy effects.

Table 3 shows the following results. In agreement with thermodynamic data the total energy of $\beta\text{-Si}_3\text{N}_4$ is slightly more negative than that of $\alpha\text{-Si}_3\text{N}_4$. The main conclusion from the table is that, for Ca-sialons, the α -structure is always more stable than the β -structure and that, at least for $m \geq 1$, the α -form is more stable than a mixture of the constituents, i.e. it will not decompose into the respective nitrides. The experimental work by Xie *et al* [29] shows that Ca- α -sialons with $m \lesssim 0.8$ are unstable. Our calculations show a stabilization energy for $m = 0.5$ of only 0.056 eV, which is less than kT at the preparation temperature of about 1700 K, which means that we cannot say if this composition is still stable.

Table 4 shows the calculated lattice constants, cell volumes and bandgap. In figure 3 the calculated lattice constants are compared with literature values from Shen and Nygren [30], which can be represented by the following equations (where $n = 0$ in our case):

$$a \text{ (\AA)} = 7.752 + 0.036m + 0.02n \quad (2a)$$

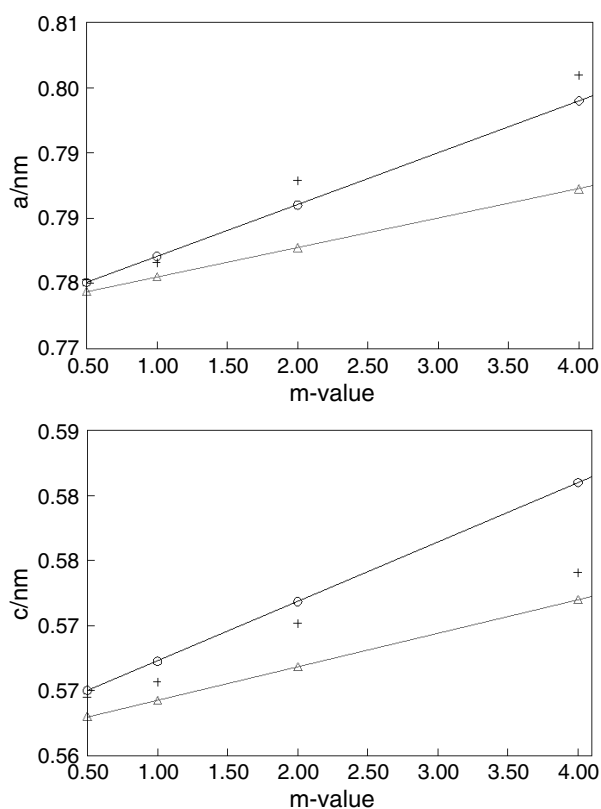


Figure 3. Calculated lattice parameters a and c for Ca- α -sialon in comparison with experimentally determined values using equations (2) and (3): + calculated, Δ equation (2), \circ equation (3).

$$c (\text{\AA}) = 5.620 + 0.031m + 0.04n \quad (2b)$$

and with literature values from Van Rutten [31] according to the equations:

$$a (\text{\AA}) = 7.749 + 0.0673m + 0.0023n \quad (3a)$$

$$c (\text{\AA}) = 5.632 + 0.0550m - 0.0054n. \quad (3b)$$

The calculated values fall within the range indicated by these literature data.

We have also calculated the partial and total electron density-of-states curves and electronic configurations. From these it follows that the sialons are basically ionic with N^{3-} , Si^{4+} , Al^{3+} and Ca^{2+} . The top of the valence band is dominated by N 2p states and the bottom of the conduction band by the empty s orbitals of the metals, mixed with some N 3s states. Values for the bandgap energy follow the expected trend of decreasing values for increasing substitution. We note that generally values calculated with DFT theory are too low: however, no experimental data are available yet.

From the viewpoint of crystal chemistry a closer look at the calculated atomic positions gives some very interesting results. We shall illustrate this by considering the results for the most stable configuration of an α -sialon with $m = 2$. As starting positions for the calculations we used the data obtained by Rietveld refinement of x-ray powder diffraction measurements by Izumi *et al* [32]. Allowing the ions to relax from the original positions we find that slight changes occur. This becomes most evident when we look at the atomic distances around the

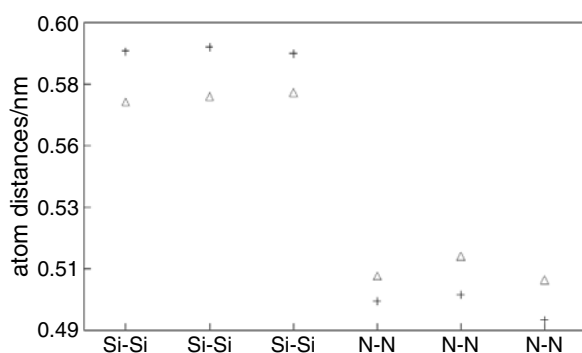


Figure 4. Distances for Ca- α -sialon with $m = 2$ between opposite Si-Si and N-N pairs in the cage around the empty b site at 1/3, 2/3, 0.22 (triangles) and around the Ca ion at 2/3, 1/3, 0.72 (+ signs).

Table 4. Calculated lattice parameters, cell volume, c/a ratio and value of the bandgap energy for Ca-sialons $\text{Ca}_{m/2}\text{Si}_{12-m}\text{Al}_m\text{N}_{16}$ with different m values and α - or β - Si_3N_4 -structure.

Composition or sialon m value	a (nm)	c (nm)	c/a	V (nm)	E_{gap} (eV)
α - Si_3N_4	0.7794	0.5648	0.725	0.2971	4.1
β - Si_3N_4	0.7648	0.2920	0.383	0.1479	4.6
Ca_3N_2	1.4454			1.5027	1.0
AlN	0.3117	0.4996	1.603	0.0420	3.4
α -sialon $m = 0.5$	0.7784	0.5654	0.726	0.2965	4.0
β -sialon $m = 0.5$	0.7648	0.5823	0.761	0.2949	—
α -sialon $m = 1$	0.7806	0.5668	0.726	0.2990	4.0
β -sialon $m = 1$	0.7681	0.5823	0.758	0.2977	—
α -sialon $m = 2$	0.7906	0.5722	0.724	0.3101	3.1
β -sialon $m = 2$	0.7797	0.5868	0.752	0.3083	—
α -sialon $m = 4$	0.8036	0.5769	0.718	0.3229	2.3
β -sialon $m = 4$	0.7953	0.6019	0.757	0.3324	—

2b sites. In our calculation Ca is at the site b2 2/3, 1/3, 0.72 (in plane D), while site b1, with coordinates 1/3, 2/3, 0.22 (plane B), is empty. These b sites have seven nitrogen atoms as nearest neighbours, viz one N atom at the b site with $z = 0.14$ or 0.64 , three with about the same z value as the b site and three N atoms about $0.23c$ below the b site (planes A or C). The Si (or Al) atoms are next-nearest neighbours of Ca; six of them are positioned in the ring and three are in a plane about $0.47c$ higher than the b site. If we calculate the distances from the b sites to N and Si we find that the distances from the nitrogen to the empty b site are, on average, 7.3 pm larger than to Ca, while the silicon distances are about 7.8 pm smaller to the empty site than to the site occupied by calcium. This is illustrated clearly in figure 4, where we have plotted the distances between atoms on opposite positions in the cage around the b site. This behaviour can, of course, be understood from the electrostatic forces between the atoms, but it is demonstrated here for the first time because diffraction measurements always give values averaged over several unit cells.

Diffraction measurements show that there is a wide distribution in Si-N bond lengths; in Ca- and Y- α -sialons, values between 0.170 and 0.180 nm are observed [33]. According to Hampshire *et al* [34] the average length for Si-N is 0.174 nm and for Al-N 0.187 nm. These

Table 5. Bond lengths in nanometres of the SiN₄ and AlN₄ tetrahedra around the b site occupied by Ca (rows 1–6) or the empty b site (rows 7–12). Data are for a Ca- α -sialon with $m = 2$; atom numbers correspond with those in figure 1.

Si6 to:	N3-0.1723	N14-0.1762	N10-0.1742	N7-0.1776
Si10 to:	N2-0.1650	N9-0.1806	N14-0.1780	N11-0.1764
Si5 to:	N3-0.1724	N16-0.1727	N9-0.1792	N5-0.1772
Si5 to:	N3-0.1720	N15-0.1723	N8-0.1744	N6-0.1789
Al on Si11 to:	N2-0.1783	N10-0.1910	N15-0.1849	N13-0.1832
Al on Si12 to:	N2-0.1789	N8-0.1885	N16-0.1858	N12-0.1850
Si9 to:	N1-0.1763	N5-0.1785	N13-0.1698	N15-0.1738
Si2 to:	N4-0.1817	N13-0.1704	N6-0.1787	N8-0.1748
Si7 to:	N1-0.1744	N6-0.1771	N11-0.1748	N14-0.1793
Si3 to:	N4-0.1798	N11-0.1749	N7-0.1773	N10-0.1745
Si8 to:	N1-0.1762	N7-0.1796	N12-0.1707	N16-0.1749
Si1 to:	N4-0.1800	N5-0.1713	N12-0.1778	N9-0.1785

values correspond closely to the average values from our calculations: 0.1756 nm for Si–N and 0.1844 nm for Al–N. However, a consequence of the potential differences between the occupied and the empty b sites is that bond lengths of corresponding tetrahedra will also be different. This is illustrated in table 5. The bond length in the first of the four columns is the one for the Si–N bond in the radial direction with respect to the b site. For the tetrahedron around Ca this bond is nearly always the shortest of the four bonds, in contrast with those around the empty site, where it is one of the longest. Moreover the bond lengths in the first column of the second group are longer than those of the first group.

4. Summary and conclusions

First-principles calculations based on the DFT theory, including relaxation, were applied to compounds with compositions Ca_{*m*/2}Si_{12–*m*}Al_{*m*}N₁₆ for $m = 0.5, 1, 2$ and 4. It was shown that Ca-doped sialons with the α -Si₃N₄-type structure have a lower energy than those with the β -Si₃N₄-type structure, in agreement with experimental results. However, for a Ca- α -sialon with $m = 0.5$ the calculated value of the stabilization energy becomes so small that stability is uncertain. The experimentally determined phase diagram shows instability for m values below about 0.8. Configurations with the aluminium ions as close as possible to the Ca ion have the lowest energy. The influence of the electrostatic forces induced by the substitution of Ca on a b site has been investigated in detail. Around the Ca ion a structural relaxation occurs, leading to changes in Ca–Si and Ca–N bond lengths in comparison with those around an empty b site. The calculated results are in good agreement with the known experimental data.

References

- [1] Shen Z, Nygren M and Hälenius U 1997 *J. Mater. Sci. Lett.* **16** 263
- [2] Karunaratne B S B, Lumby R J and Lewis M H 1996 *J. Mater. Res.* **11** 2790
- [3] Van Krevel J W H, Hintzen H T, Metselaar R and Meijerink A 1998 *J. Alloys Compounds* **268** 272
- [4] Van Krevel J W H, Van Ruten J W T, Mandal H, Hintzen H T and Metselaar R 2002 *J. Solid State Chem.* **165** 19
- [5] Jack K H and Wilson W I 1972 *Nature (Phys. Sci.)* **238** 28
- [6] Mitomo M 1977 *Yogyo-Kyokai-Shi* **85** 50
- [7] Cao G Z and Metselaar R 1991 *Chem. Mater.* **3** 242
- [8] Metselaar R 1994 *Pure Appl. Chem.* **66** 1815

- [9] Riley F L 2000 *J. Am. Ceram. Soc.* **83** 245
- [10] Grün R 1979 *Acta Crystallogr. B* **35** 800
- [11] Goodman P and O'Keeffe M 1979 *Acta Crystallogr. B* **36** 2891
- [12] Belkada R, Koyama M, Shibayanagi T and Naka M 2002 *Phys. Rev. B* **65** 092104
- [13] Belkada R, Shibayanagi T, Naka M and Koyama M 2000 *J. Am. Ceram. Soc.* **83** 2449
- [14] Xu Y N and Ching W Y 1995 *Phys. Rev. B* **51** 17379
- [15] Xu Y N and Ching W Y 1988 *Mater. Res. Soc. Symp. Proc.* **105** 181
- [16] Ching W Y and Lin C C 1975 *Phys. Rev. B* **12** 5536
- [17] Liu A Y and Cohen M L 1990 *Phys. Rev. B* **41** 10727
- [18] Ching W Y and Harmon B N 1986 *Phys. Rev. B* **34** 5305
- [19] Orhan E, Jobic S, Brec R, Marchand R and Saillard J-Y 2002 *J. Mater. Chem.* **12** 2475
- [20] Nakayasu T, Yamada T, Tanaka I, Adachi H and Goto S 1997 *J. Am. Ceram. Soc.* **79** 2527
- [21] Nakayasu T, Yamada T, Tanaka I, Adachi H and Goto S 1997 *J. Am. Ceram. Soc.* **80** 2525
- [22] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** 558
- [23] Kresse G and Hafner J 1994 *Phys. Rev. B* **49** 714251
- [24] Kresse G and Furthmüller J 1996 *Comput. Mater. Sci.* **6** 15
- [25] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [26] Kresse G and Hafner J 1994 *J. Phys.: Condens. Matter* **6** 8245
- [27] Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
- [28] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [29] Xie R-J, Mitomo M, Xu F-F, Uheda K and Bando Y 2001 *Z. Metallk.* **92** 8
- [30] Shen Z J and Nygren M 1997 *J. Eur. Ceram. Soc.* **17** 1639
- [31] Van Rutten J W T 2000 *PhD Thesis* Eindhoven University of Technology, Eindhoven
- [32] Izumi F, Mitomo M and Bando Y 1984 *J. Mater. Sci.* **19** 3115
- [33] Cao G Z, Metselaar R and Haye W G 1993 *J. Mater. Sci. Lett.* **12** 459
- [34] Hampshire S, Park H K, Thompson D P and Jack K H 1978 *Nature* **274** 880