Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 26 (2006) 3925–3931

www.elsevier.com/locate/jeurceramsoc

Time-of-flight Rietveld neutron structure refinement and quantum chemistry study of Y-α-sialon

L'ubomír Smrčok[a,*], David Salamon[a], Eva Scholtzová[a], James W. Richardson Jr.[b]

[a] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic
[b] Intense Pulsed Neutron Source Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, USA

Received 12 May 2005; received in revised form 9 November 2005; accepted 20 November 2005
Available online 18 January 2006

Abstract

A Y-α-sialon was prepared using a specially designed temperature regime supporting formation of α-sialon and the amount of non-crystalline phase was remarkably reduced by a chemical treatment. Chemical composition of the sample was determined by EDX analysis. Crystal structure of Y-α-sialon was refined using high quality time-of-flight neutron powder diffraction data taken with the General Purpose Powder Diffractometer (GPPD) at the IPNS, Argonne National Laboratory. Unrestrained structure refinement was done in the *P*31*c* space group. The list of simultaneously refined parameters included profile parameters, atomic coordinates, individual isotropic temperature parameters and the occupancy parameter of Y. The contents of Y in the cell refined to 0.38(1) and calculated Si–N distances in tetrahedra varied from 1.716(3) to 1.773(3) Å, but their distributions in the respective tetrahedra differ as in the parent structure of α-Si_3N_4. Anisotropic temperature parameters refinement, as well as constrained refinements of the occupancy parameters of Si–Al and N–O pairs, were also attempted, but they all ended with unphysical values. Variation of the background was analyzed using RDF formalism. Three peaks centered around 1.7 Å (with a shoulder at 2.2 Å), 2.8 Å and 3.5 Å proved that the composition of amorphous phase was close to that of crystalline. Ab initio cluster calculations performed at the B3LYP/6-31G** level of theory excluded configuration with O atoms bonded to three Si atoms and proved that the most probable is the configuration where an O atom is shared by three Al atoms.

Keywords: Powders-solid state reactions; Si_3N_4; Sialon; Rietveld refinement; Neutron diffraction

1. Introduction

Silicon nitride forms two groups of solid solutions based on α-Si_3N_4 and β-Si_3N_4, where Si could be replaced by Al and N for O. The term SiAlON was originally coined to describe materials containing Si, Al, O and N (and some other elements) of very wide compositions and crystal structures.[1] Nowadays the meaning of the word SiAlON has been more restricted towards solid-solution phases with the α- or β-Si_3N_4 crystal structures, colloquially named α- and β-sialons. It is generally accepted that α-sialons are isostructural with α-Si_3N_4 with **m** (Si–N) bonds replaced by **m** (Al–N) bonds and **n** (Si–N) bonds by **n** (Al–O) bonds, respectively. Because the crystal structure of α-sialons must be stabilized by an extra cation (M), their suggested chemical formula is $M_xSi_{12-m-n}\,Al_{m+n}O_nN_{16-n}$. The M in the formula symbolizes one of the cations as Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+} or rare earths. Some cations, however, could be accommodated in the sialon's structure only together with another cation,[2] or using quenching. The x value is in general less than or equal to two, but in practice it varies mostly between 0.3 and 1.0. It depends on the field of phase stability of α-sialons and on the stability area for different cations.[3] Another important factor influencing the final phase composition is the speed of cooling. Because of thermal instability of α-sialon, its amount significantly increases when the samples are fast cooled.[4] The rate of α-sialon formation also decreases with increasing ion radius of M, or when a high content of liquid phase is present.[5]

Inasmuch as it was until recently difficult to synthesize single crystals of M-α-sialons of a suitable size and quality (see for example ref. 6), powder structure refinements of their structures have been mostly reported. In the pioneering era of Rietveld refinement, when the method rather than the subject was many times of primary interest, Izumi et al.[7] used powder X-ray diffraction data to refine the structures of Y- and Ca-α-sialon.

---

* Corresponding author. Tel.: +421 2 5941 0435; fax: +421 2 5941 0444.
E-mail address: uachsmrk@savba.sk (L. Smrčok).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.11.006

Collected patterns were, however, contaminated by unidentified impurities, so that several 2Θ regions needed to be excluded from the refinements. Moreover, the structures were refined in multiphase Rietveld refinements (α-quartz admixture) with Si/Al–O/N distances constrained to lie "within a reasonable range". The only refined occupancy parameters were those of Y/Ca atoms and instead of individual only so-called group (Y, Si/Al, O/N) isotropic temperature parameters were used. The Si/Al and O/N ratios were kept fixed during refinements, the first ratio being based on EDAX data, and the O/N values were calculated from the Y/Ca, Si and Al amounts assuming that no vacancies were present in the structure. Due to application of the constraints, very similar Si/Al–/N/O distances were obtained from both refinements. Interestingly, despite the presence of different occupancies of Y and Ca (0.27, 0.34) there were no differences between Ca–N/O and Y–N/O distances, i.e. the nature of the modifying cation seemed to have no impact on its surrounding.

Cao et al.[8] presented a constant wavelength Rietveld neutron refinement of Y-α-sialon based on powder data collected using rather long wavelength (2.5718 Å), which seriously limited the number of Bragg diffractions in the pattern. No details either on the N versus O ratios used in the refinement or on chemical analysis were given, but due to the large difference in N/O scattering lengths, only N atoms were considered. The refinement on one hand showed site preferences in the Si/Al positions, but they were not reflected in Si/Al–N/O distances, i.e. highly questionable. Due to the high correlations between the site occupancies and individual temperature parameters during the refinement, only a so-called overall temperature parameter could be used.

The crystal structure of an oxygen rich sialon, α-$LiSi_9Al_3O_2N_{14}$ was refined in a multiphase refinement based on neutron TOF data.[6] In addition to the phase of interest, the pattern also contained β-sialon and α-eucryptite ($LiAlSiO_4$). Due to the low accuracy of the EDAX analysis, the chemical composition used in the refinement was based just on the starting composition. Refined isotropic thermal parameter for Li was remarkably larger than any other obtained from the same calculation and the Li position also deviated from the expected. The occupancies of Si/Al and N/O were not refined.

Although the available diffraction studies provided basic information on the structure of Y-α-sialon, it is obvious that they suffered from several drawbacks: application of restraints in combination with X-ray data, conflict between refined distances and site occupancies from CW neutron data, multiphase refinements principally providing less accurate data due to diffraction overlap, constrained or unexpected values of temperature parameters. Because we have developed and refined a method guaranteeing synthesis of very pure Y-α-sialon synthesis, we performed a TOF neutron diffraction and quantum chemistry study with the aim to investigate possible site preferences in this system. It was believed that the large number of Bragg peaks contained in a TOF pattern would provide information sufficient for determination of occupancies in all sites. In addition, a larger number of Bragg peaks was expected to provide better opportunity to get atom's occupancies and individual temperature parameters in a simultaneous refinement.

2. Experimental and calculation

Y-α-sialon was prepared using the starting powders: 71.95% α-Si_3N_4 (Permascand S95P, containing 1.4 wt.% O), 15.48% AlN (HC Starck Grade C, containing 1.6 wt.% O), 9.55% Y_2O_3 (HC Starck 99.99%), 3.02% La_2O_3 (Merck 99.5%). Theoretically calculated composition was $Y_{0.42}Si_{9.63}Al_{2.37}O_{1.12}N_{14.88}$. To calculate the expected composition the expected amounts of oxygen content in Si_3N_4 and AlN powders were also taken into account. Liquid phase was expected to contain 1.0 mol.% of Y_2O_3 and 0.4 mol.% La_2O_3. All starting powders were homogenized in isopropanol with Si_3N_4 balls for 12 h. The powders were dried and pressed into the cubic shape under the pressure of 100 MPa, followed by cold isostatic pressing at 250 MPa. Sintering was done in two independent steps. In the first step the sample was heated in a gas-pressure sintering furnace (GPS, KCE GmbH, Germany) at 1670 °C for 2 h in three MPa nitrogen and then cooled using fast cooling regime (>100 °C/min). In the second step 1750 °C/2 h/3 MPa/N_2 were used followed by a slow cooling regime (7 °C/min). The reason for this temperature regime was to avoid formation of kinetically promoted metastable phases. The final powder was chemically treated in hot H_3PO_4 to dissolve amorphous phase. Full details on the synthesis are described elsewhere.[9]

Scanning electron microscopy (SEM) and energy dispersive analysis (EDX) were used to observe the crystals' morphologies and to determine the amounts of the elements present in the sample. The EDX analysis was applied to five independent places using accelerating voltage of 15 kV and 100 s of counting time. The amounts of Si and N were determined with the help of Si_3N_4 standard, while Y, Al and O were determined by standardless methods.

The phase composition of sintered and chemically cleaned sample was analyzed by X-ray diffraction using transmission Stoe STADI P diffractometer with CoKα_1 radiation. Except for the dominant Y-α-sialon phase the sample contained a very small, though detectable amount of α-Si_3N_4. Time-of-flight neutron powder diffraction data were collected for 3 h using the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory.[10] For this measurement, the sample was sealed in a 5 cm^3 vanadium container. Time-focused and summed data in detector banks centered at $2\Theta = \pm 145°$, $\pm 125°$, $\pm 107°$, $\pm 90°$ and $+60°$ were available for Rietveld analysis.

The first step unrestrained structure refinement was done in the $P31c$ space group with the GSAS package[11,12] using all diffraction data. The list of simultaneously refined parameters included scale factor, four coefficients of Chebyshev polynomials used to approximate the backgrounds' variations, the lattice parameters, atomic coordinates, individual isotropic temperature parameters and occupancy parameter of Y. The initial positions of the atoms were taken from ref. 7.

When the refinement was completed, a graphical analysis of residuals revealed the possible presence of α-Si_3N_4. A new series of two-phase refinements was thus initiated using the crystallographic data from ref. 14. Unfortunately, similarity of the structures of the respective phases caused numerical difficulties resulting in some restrictions. First, only the data sets from the high-resolution data banks (±145° and ±125°) could be used. Second, it was not possible to refine also the atomic parameters of the less abundant phase, because such a refinement led to inaccurate interatomic distances and negative isotropic temperature parameters. Those parameters were thus kept fixed, but the lattice and profile parameters were relaxed. The amount of the second phase has formally refined to ∼13%, but it should be stressed, that this is a biased estimate and should be taken with caution. The main reason is similarity of the diffraction patterns which leads to "compensation" of inadequacies in the structural models.

Anisotropic temperature parameter refinement as well as constrained refinements of the occupancy parameters of Si–Al and N–O pairs were also attempted, but with a limited success (see below). The refinement was thus completed with isotropic temperature parameters using Y, Si and N scattering parameters only. The ab initio calculations were performed by GAUSSIAN98 program package[13] at the B3LYP/6-31G** level of theory. Hybrid DFT methods are more efficient than much more expensive multilevel correlated methods, while being much less computationaly expensive. The starting atomic coordinates were taken from the last refinement's cycle.

3. Results and discussion

The results of EDX analysis of the sintered sample are shown in Table 1. Theoretically calculated composition (expected) is very close to the composition calculated from EDX data using idealized α-sialon formula (Restricted). The composition directly calculated form the EDX data (Formula) has the x (**m**) values similar to Expected, but the **n** value is different. This difference most probably arises from a limited accuracy of the EDX method for analysis of "light" O and N. Assuming the idealized formula the composition of the sialon under study was estimated to be $Y_{0.4}Si_{9.66}Al_{2.34}O_{1.14}N_{14.86}$.

Refined atomic parameters and calculated interatomic distances are summarized in Tables 2–4. Profile fit for the highest resolution banks centered at $2\Theta = \pm 145°$ is shown in Fig. 1, the structure viewed along the c-axis is in Fig. 2a. Using the empirical equations[27] relating **m** and **n** to hexagonal lattice

Table 1
The results of EDX analysis

Composition	Y	Si	Al	O	N
Expected	0.42	9.63	2.37	1.12	14.88
EDX (mol.%)	1.15	27.6	6.76	7.43	57.06
Formula	0.40	9.65	2.36	2.60	19.95
Restricted	0.40	9.66	2.34	1.14	14.86

Expected—desired composition, EDX—as determined by EDX method, Formula—the formula calculated using the EDX data, Restricted—the composition renormalized using the idealized formula for α-sialon composition (see Section 1).

Table 2
Refined atomic positions and isotropic temperature parameters U_{iso} (Å^2) with estimated standard deviations in parenthesis

Atom	x	y	z	$U_{iso} \times 100$
Y	1/3	2/3	0.2602(15)	0.68(24)
Si(1)	0.5112(3)	0.0833(3)	0.2123(3)	0.88(3)
Si(2)	0.1693(2)	0.2517(2)	0.0051(4)	0.40(2)
N(1)	0	0	0.0031(5)	0.79(2)
N(2)	1/3	2/3	0.6480(4)	1.52(4)
N(3)	0.3430(1)	−0.0488(1)	−0.0140(3)	0.82(1)
N(4)	0.3180(1)	0.3178(1)	0.2489(4)	0.82(3)

The occupancy parameter of Y is 0.191(8), refined lattice parameters are $a = 7.81462(3)$ Å, $c = 5.69587(3)$ Å, cell volume = 301.236(3) Å^3 and calculated density $\rho = 3.281$ g cm^{-3}. The lattice parameters of the second phase, α-Si_3N_4 refined to 7.7448(2) Å and 5.6146(2) Å, respectively.

Table 3
Interatomic distances angles [Å, °] in the tetrahedron around Si(1)

	N(2)b	N(3)	N(3)c	N(4)a
N(2)b	1.744(2)	113.7(1)	112.1(1)	101.9(4)
N(3)		1.762(2)	111.8(1)	110.5(1)
N(3)c			1.768(2)	106.1(1)
N(4)a				1.766(2)

Symmetry operations are a: $-y+1, x-y, z$; b: $y, x, -1/2+z$; c: $x-y, -y, 1/2+z$. Si(1)–N distances are on the diagonal, off diagonal terms are the N′–Si(1)–N″ bond angles.

Table 4
Interatomic distances angles [Å, °] in the tetrahedron around Si(2)

	N(1)	N(3)a	N(4)	N(4)b
N(1)	1.737(1)	111.1(6)	111.3(1)	110.0(1)
N(3)a		1.769(2)	110.7(1)	104.0(1)
N(4)			1.716(3)	109.4(7)
N(4)b				1.773(3)

Symmetry operations are a: $-y, x-y, z$; b: $y, x, -1/2+z$. Si(2)–N distances are on the diagonal, off diagonal terms are the N′–Si(2)–N″ bond angles.

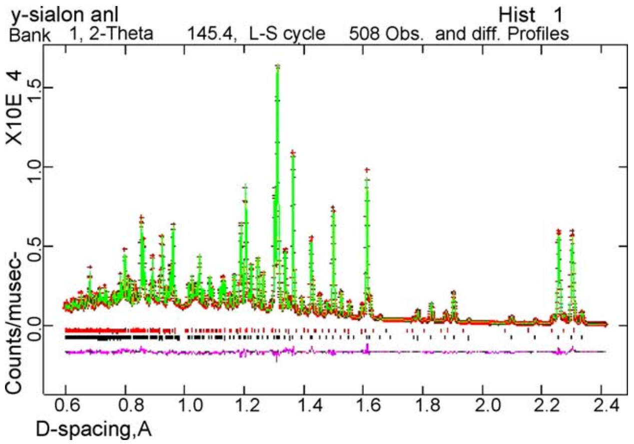

Fig. 1. Profile fit for the highest resolution banks centered at $2\Theta = \pm 145°$. Measured intensities are symbolized by crosses, calculated by the line overlaying them. The positions of Bragg peaks of individual phases (α-Si_3N_4 and Y-α-sialon, from top to bottom) are shown by vertical sticks, the difference curve is in the bottom. $R_{wp} = 0.04$, $R(F^{**}2) = 0.05$.

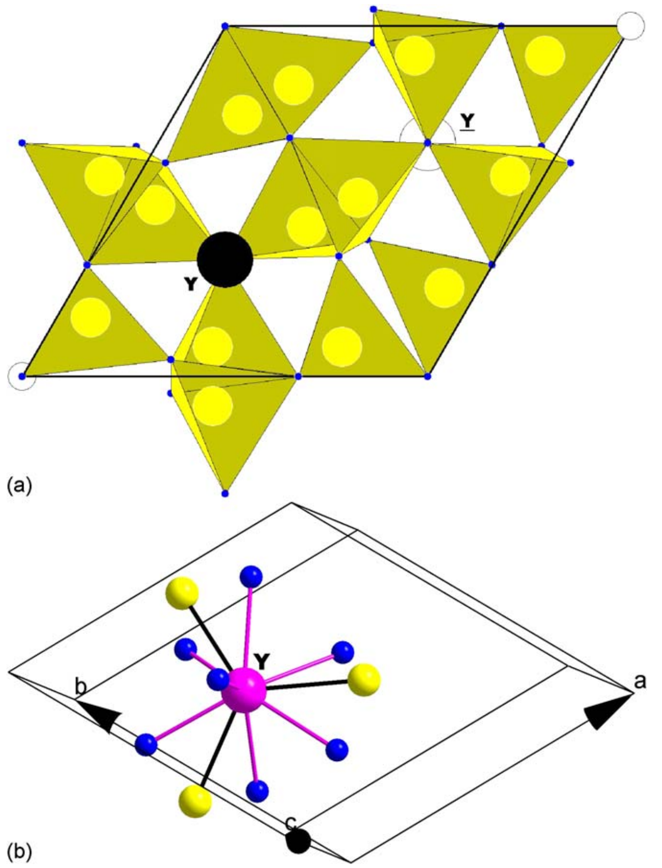

Fig. 2. (a) Polyhedral presentation of the structure of Y-α-sialon seen along *c*. Positions of Y-atoms are marked by large circles. (b) Space distribution of the atoms surrounding the Y-atom. N-dark small balls, Si-white large balls.

parameters *a* and *c* fairly small differences $\Delta a = 0.0016$ Å and $\Delta c = 0.0081$ Å were obtained.[1]

Final interatomic Si–N distances in [SiN_4] tetrahedra vary from 1.716(3) to 1.773(3) Å, but their distributions in the respective tetrahedra differ as in the parent structure of α-Si_3N_4 (Tables 3 and 4). Good agreement of these values with 1.72–1.78 Å reported for α-Si_3N_4[14] and/or 1.704–1.767 Å range[15] found for β-Si_3N_4 (both determined from X-ray single crystal data though of rather different quality) indicate no obvious ordering of N/O in the structure. The interval of refined values is on the other hand wider than the interval of Si–N interatomic distances found in the [SiN_3O] tetrahedra forming the Si_2N_2O structure[16]: <1.720–1.723> Å. This difference is most probably due to different structural motifs in those two structures. As far as the X-ray Rietveld refinement[7] is concerned, due to inherent limits in the data it has provided the distances to be too short (1.700(8) Å) or too long (1.80(1) Å) to be accurate. High quality Rietveld refinements of two un-doped sialons based on TOF data gave two different trends. Lindqvist et al.[17] obtained for O′-sialons ($Cmc2_1$) rather tight intervals of Si/Al–N distances centered around 1.72 Å, i.e. close to the values reported for Si_2N_2O. Similarity of the results was underlined also by the fact that one distance in the tetrahedron was found to be only ∼1.64 Å, which is with some little tolerance perfectly acceptable for an Si–O bond. In contrast the authors[18] reported for a β-sialon ($P6_3/m$) the distances limited at the low end by 1.73–1.74 Å, even though they obtained statistically significant occupancy parameters of oxygen atoms. The authors of a CW neutron diffraction study[24] tried to determine the N/O distribution in a β-sialon by modeling of cell's composition. To distinguish among different distribution models they used a crystallographic *R*-factor based on observed and calculated integrated intensities. Even though the *R*-factors space was rather flat, they preferred a model assuming ordered N/O distribution.

Although the isotropic temperature parameters are typically the weakest points of powder refinements, differences in the values refined for Si1 and Si2 as well as the out-of-line value for N2 (Table 2) point to the fact that the refinement done in the $P31c$ provides just an average structure. Larger values of U(Y) and U(N2) could be due to fewer degrees of freedom for the atoms in the special positions, if there were not a quite an acceptable value of U(N1). For the sake of comparison we note that Izumi's refinement,[7] gave incorrect order $B(\text{Si,Al}) > B(\text{Y}) > B(\text{N,O})$, and the study[6] which reported U(Li) more than 10 times larger than any other temperature parameter obtained for the structure.

A Y-atom is formally coordinated by seven N-atoms (Fig. 2b), but due to symmetry restraints imposed by the space group there are only three unequally populated groups of coordinating atoms: 3xN(3), 3xN(4) and 1xN(2), the Y–N distances being 2.687(6) Å, 2.669(1) Å and 2.209(11) Å, respectively. Cole et al.[19] studied the local environment of Er^{3+} stabilizing cation in a hot pressed α-sialon by EXAFS. Seven nearest neighbors were found to be in the distances of 2.257Å (2x) and 2.480 Å (5x), respectively. Inasmuch as their EXAFS analysis of Er_2O_3 gave six-fold coordination of Er with Er–O distance 2.265 Å they concluded, that Er^{3+} in the sialon was coordinated by O and N in the 2:5 ratio. Following the same reasoning they suggested, that in Y-α-sialon[7] the Y surrounding should be O:N = 1:6 despite the fact that Er^{3+} and Y^{3+} cations are of almost equal sizes and there is thus no obvious reason for very different coordination polyhedra.

As mentioned above an anisotropic refinement was also attempted, but the U_{ij} tensor of at least one Si atom was not positive definite. A calculation done just with Y atom anisotropic led to negligible drop of *R*-factors and the thermal ellipsoid was significantly (and unexpectedly) elongated along the *c*-axis. Such a shape could indicate such a distribution of Y atoms in the structure, which could point to the fact that the actual symmetry of the structure is lower than applied. All attempts to refine constrained Si/Al and/or O/N occupancies led to unphysical results: either to occupancy parameters >1 or to some negative isotropic temperature parameters. The Y content (∼0.38) is in very good agreement with the expected value, but the refinement of this value was a rather delicate procedure, because of the correlation

---

[1] Note, however, that the parameters p(m) and p(n) in the empirical equations are, though based on experimental data, reported without estimated uncertainities (variances). For instance, a regression calculation based on the compositions and the lattice parameters of the sialons summarized in ref. [27] gives the parameters, which are in fair agreement with those published, but the relative error of one of them is ∼100%. Moreover, the correlation coefficients relating **n** and Δa or Δc are insignificant, being only ∼0.4 or 0.5. These values contrast with ∼0.9 for **m** and Δa or Δc.

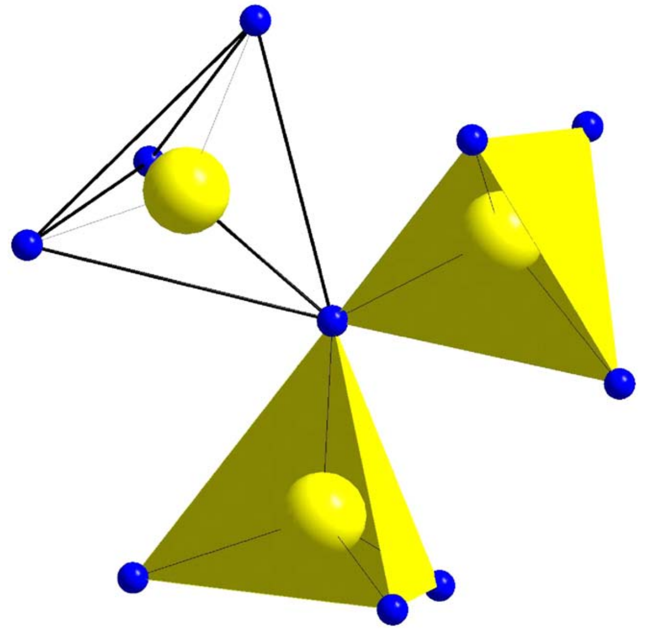

Fig. 3. A part of the structure of α-Si_3N_4 used for computational study. Terminating H-atoms were omitted for the sake of clarity.

between U(Y) and occ(Y) reaching ∼0.8, i.e. almost a linear dependence. The extremely large e.s.d. of U(Y) is obviously the price paid for the simultaneous refinement of the temperature and occupancy parameters for Y, and the value of the latter should be therefore taken with caution.

When the refinement was over variation of the background was analyzed using RDF formalism employing the data from the data bank centered at $2\Theta = \pm 145°$. Three rather broad peaks centered around 1.7 Å (with a shoulder at 2.2 Å), 2.8 Å and 3.5 Å, respectively, proved that the composition of amorphous phase was close to that of crystalline.

3.1. Ab intio study of local bonding conditions

Because the refinement provided only the information on the average composition of the basic building units (Fig. 3), a quantum chemistry study of local structural changes caused by Si–N by Al–O substitution in the structure of α-Si_3N_4 was done. Inasmuch as no fully quantitative description was required, the focus was mostly on the bonding condition of the atom shared by all three tetrahedra. The aim was to rank probable configurations assuming, that there were no vacancies in the structure. The bonding conditions in the basic structural motif of α-sialon were modeled with nine clusters (Fig. 4). To avoid dangling bonds, the atoms on the borders of the cluster were saturated by hydrogen atoms. The positions of all atoms were optimized until convergence was achieved.

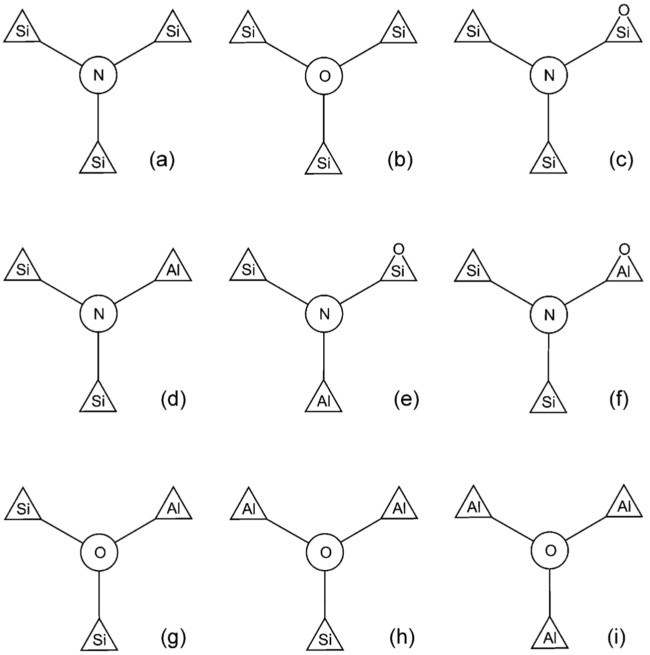

Fig. 4. A symbolic presentation of the cluster models. The letters in triangles mean the central atoms in tetrahedral. Large circles represent the atoms shared by all three tetrahedra.

Selected averaged optimized Si–N, Al–O, Si–O and Al–N bond lengths are presented in Table 5. To assess the accuracy of the method, several simple model tetrahedra were optimized first. The optimized average or individual interatomic distances in the respective polyhedra were as follows: $Si–(NH_2)_4 = 1.73$ Å, $Si–(OH)_4 = 1.64$ Å, $Si–(NH_2)_3OH = 3 \times 1.73$Å$/1 \times 1.67$ Å, $Al–(NH_2)_4 = 1.94$ Å, $Al–(OH)_4 = 1.78$ Å and

Table 5
Optimized bond lengths in the model clusters [Å]

Model		Center bonds				Border bonds			
		Si–N	Si–O	Al–O	Al–N	Si–N	Si–O	Al–O	Al–N
a	$[Si_3N_{10}H_{18}]$	1.756				1.736			
b	$[Si_3N_9H_{18}O_c]^{+1}$		1.799			1.704			
c	$[Si_3N_9H_{17}O_b]$	1.752				1.738	1.682		
d	$[Si_2AlN_{10}H_{18}]^{-1}$	1.715			1.917	1.759			1.879
e	$[Si_2AlN_9O_{Si}H_{17}]^{-1}$	1.734			1.926	1.752	1.705		1.872
f	$[Si_2AlN_9O_{Al}H_{17}]^{-1}$	1.712			1.923	1.759		1.804	1.862
g	$[Si_2AlN_9O_cH_{18}]$		1.752	1.977		1.713			1.842
h	$[SiAl_2N_9O_cH_{18}]^{-1}$		1.702	1.902		1.733			1.857
i	$[Al_3N_9O_cH18]^{-2}$			1.850					1.878

Mulliken Si–N, Si–O and Al–O bond populations (|e|) were within the following intervals: <0.32,0.39>, <0.17,0.24>, and <0.16,0.22>, respectively, indicating their decreasing covalent character.

Al–$(NH_2)_3OH$ = 3 × 1.88 Å/1 × 1.80 Å, respectively. These values are to be compared to the following reference values: Si–O = 1.61 Å, Al–O within 1.77–1.80 Å,[20] Al–N = 1.89 Å,[21] and Si–N within 1.704–1.767 Å range[15] as found for β-Si_3N_4 (see also above). Even though a rather conservative criterion for correspondence of the optimized and reference values ±0.05 Å was chosen, the overall accuracy of the method was found adequate. It is, however, evident, that at that level of accuracy the Si–N and Al–O distances are virtually indistinguishable.

To avoid ambiguities resulting from the limited sizes of the clusters in the following discussion only the center bond lengths (Table 5) were considered, while the border ones were reported just for the sake of completeness. A comparison of the optimized bond lengths with the reference values disqualified the models B, G and H with unrealistic Si–O bond lengths. Because all Si–N bond lengths obtained in these three models could be accepted, the configurations with a "three bonded" central O are highly improbable. Since both Si–O and Si–N are strong covalent bonds, such a result is in full accord with a chemical intuition.

Inasmuch as all the Al–N distances are near the upper limit of the acceptable values (1.89 + 0.05 Å), they are of no help in ranking the models. To give an example of a possible variability of calculated distances it is worth noticing that the authors[22] obtained from a solid state ab initio calculation avg(Al–N) only 1.84, i.e. near the lower edge of the interval of the acceptable values. Even shorter Al-to-surrounding atoms distances were found in the study[23] reporting an EXAFS analysis of two β-sialons: only 1.77–1.78 Å. The distribution peak was, however, so broad, that the reported values are misleading rather than informative. Slowly decreasing Al–O distance with increasing degree of Al for Si substitution in the line G–H–I shows, that while the G model is not acceptable due to long Si–O distance, the H is somehow on the border and the I is the only probable configuration with a central oxygen anion. The list of probable configurations thus contains only A, C, D, E, F and I. These results are in accord with ^{27}Al and ^{29}Si NMR study of a series of Li-sialons,[25] which have confirmed the general tendency for N to bond to Si and for O to coordinate to aluminium. Similarly, the authors[26] have recently by combination of experimental spectra and theoretical results showed, that in $Si_{6-x}Al_zO_zN_{8-z}$ the Al atoms are preferentially coordinated by O atoms.

4. Conclusions

Crystal structure of pure Y-α-sialon was, compared to previous studies, accurately refined without any constraints and/or supporting geometric restraints. Although all individual atomic parameters could have been refined simultaneously, no information on Si/Al and O/N distribution in tetrahedra was gained. The interatomic distances correspond to pure Si–N bonds or to a mixture of Si–N and Al–O bonds with the major share of the former. Ab intio calculation has effectively excluded configurations with O atoms bonded to three Si atoms and proved that the most probable is the configuration where an O atom is shared by three Al atoms. This suggests a direct correlation between the amounts of Al and O in sialons or formation of oxides on the surface.

An RDF analysis of the background proved that the composition of amorphous phase was close to that of crystalline.

Acknowledgements

The authors wish to express their thanks to Mrs. Marie Ptáčková from Brno University of Technology (Czech Republic) for EDX analyses. This work has benefited from the use of the Intense Pulsed Neutron Source at Argonne National Laboratory, the facility funded by the U.S. Department of Energy under Contract W-31-109-ENG-38. The study was also partially supported by the Slovak Grant Agency, project No. VEGA 2/4072/24 and grant ŠO 51/03R80600/03R0603.

References

1. Jack, K. H. and Wilson, W. I., Ceramics based on the Si-Al-O-N and related systems. *Nature (London) Phys. Sci.*, 1972, **238**, 28–29.
2. Mandal, H., Preparation of multiple-cation α-SiAlON ceramics containing lanthanum. *J. Am. Ceram. Soc.*, 1999, **82**, 229–232.
3. Rosenflanz, A. and Chen, I.-W., Phase relationships and stability of α-SiAlON. *J. Am. Ceram. Soc.*, 1999, **82**, 1025–1036.
4. Mandal, H. and Thomson, D. P., Reversible α ↔ β SiAlON transformation in heat-treated SiAlON ceramics. *J. Eur. Ceram. Soc.*, 1993, **12**, 421–429.
5. Camuscu, N., Thomson, D. P. and Mandal, H., Effect of starting composition type of rare earth sintering additive and amount of liquid phase on α ↔ β SiAlON transformation. *J. Eur. Ceram. Soc.*, 1997, **17**, 599–613.
6. Grins, J., Esmaeilzadeh, S. and Shen, Z., Structures of filled α-Si_3N_4 type $Ca_{0.27}La_{0.03}Si_{11.38}Al_{0.62}N_{16}$ and $LiSi_9Al_3O_2N_{14}$. *J. Am. Chem. Soc.*, 2003, **86**, 727–730.
7. Izumi, F., Mitomo, M. and Bando, Y., Rietveld refinement for calcium and yttrium containing α-sialons. *J. Mater. Sci.*, 1984, **19**, 3115–3120.
8. Cao, G. Z., Metselar, R. and Haije, W. G., Neutron diffraction study of yttrium α'-sialon. *J. Mater. Sci. Lett.*, 1993, **12**, 459–460.
9. Salamon, D., Šajgalík, P., Lenčéš, Z. and Křestan, J., The influence of La_2O_3 and Nd_2O_3 addition on aspect ratio of Y-α-sialon seeds. *Mater. Lett.*, 2005, **59**, 3201–3204.
10. Jorgensen, J. D., Faber Jr., J., Carpenter, J. M., Crawford, R. K., Haumann, J. R., Hitterman, R. L., Kleb, R., Ostrowski, G. E., Rotella, F. J. and Worlton, T. G., Electronically focused time-of-flight powder diffractometers at the intense pulsed neutron source. *J. Appl. Cryst.*, 1989, **22**, 321–333.
11. Larson, A. C., Von Dreele, R. B., General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748 (2000).
12. Tobby, B. H., EXPGUI, a graphical user interface for GSAS. *J. Appl. Cryst.*, 2001, **34**, 210–213.
13. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., and Cheeseman, J.R., *et al.* Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
14. Marchand, R., Laurent, Y. and Lang, J., Structure du nitrure de silicium α. *Acta Cryst.*, 1969, **B25**, 2157–2160.
15. Grűn, R., Structural and stability considerations between α-and β-Si_3N_4. *Acta Cryst.*, 1979, **B35**, 800–804.
16. Sjőberg, J., Helgesson, G. and Idrestedt, I., Refinement of the structure of Si_2N_2O. *Acta Cryst.*, 1991, **C47**, 2438–2441.
17. Lindqvist, O., Sjöberg, J., Hull, S. and Pompe, R., Structural changes in O′-sialons, $Si_{2-x}Al_xN_{2-x}O_{1+x}0.\ 04 \leq x \leq 0.\ 40$. *Acta Cryst.*, 1991, **B47**, 672–678.
18. Loong, Chun-Keung, Richardson Jr., J. W., Sukuzi, S. and Ozawa, M., Crystal structure and phonon densities of states of β'-sialon ceram-

ics, $Si_{6-z}Al_zN_{8-x}O_z$ ($0 \le z \le z4$). *J. Am. Ceram. Soc.*, 1996, **79**, 3250–3256.

19. Cole, M., O'Reilly, K. P. J., Redington, M. and Hampshire, S., EXAFS study of a hot pressed α'-sialon ceramic containing erbium as the modifying cation. *J. Mater. Sci.*, 1991, **26**, 5143–5148.
20. International Tables for X-ray Crystallography. Kynoch Press. Birmingham, England. III, 1962.
21. Schulz, H. and Thieman, K. H., Crystal structure refinement of AlN and GaN. *Solid State Commun.*, 1977, **22**, 815–819.
22. Fang, C. M. and Metselaar, R., First-principles calculations of the stability and local structure of α-sialon ceramics on the line Si_3N_4-1/2 Ca_3N_2:AlN. *J. Phys.: Condens. Mater.*, 2004, **16**, 2931–2939.
23. Sjőberg, J., Ericsson, T. and Lindqvist, O., Local structure of β'-sialons: an EXAFS study. *J. Mater. Sci.*, 1992, **27**, 5911–5915.
24. Khvatinskaya, D. Y., Em, V. T., Loryan, V. E. and Smirnov, K. L., A neutron-diffraction study on the structure of β'-SIALON. *Inorg. Mater.*, 1991, **27**, 1805–1807.
25. Kempgens, P., Harris, R. K., Yu, Z. and Thompson, D. P., Structural characterization of Li α-sialon ceramics by high-resolution ^{27}Al and ^{29}Si NMR spectroscopy. *J. Mater. Chem.*, 2001, **11**, 2507–2512.
26. Tatsumi, K., Mizoguchi, T., Yoshioka, S., Yamamoto, T., Suga, T., Sekina, T. and Tanaka, I., Distribution of solute atoms in- and spinel $Si_{6-x}Al_zO_zN_{8-z}$ by Al *K* β-edge X-ray absorption near-edge structure. *Phys. Rev.*, 2005, **B71** [article no. 033202].
27. Sun, W.-Y., Tien, T.-Y. and Yen, T.-S., Solubility limits of α'-SiAlON solid solutions in the system Si,Al,Y/N,O. *J. Am. Chem. Soc.*, 1991, **74**, 2450–2457.