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Structural Changes in O'-Sialons, $Si_{2-x}Al_xN_{2-x}O_{1+x}$, $0·04 \leq x \leq 0·40$

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Abstract

Structural changes in the aluminium silicon nitride oxide $Si_{2-x}Al_xN_{2-x}O_{1+x}$, O'-sialon, due to gradually varying stoichiometry, have been studied by Rietveld analysis of time-of-flight powder diffraction data from a pulsed neutron source. Refinements were based on the orthorhombic space group $Cmc2_1$ with cell dimensions, depending on composition, in the ranges $a = 8·8807$ (13)–8·9254 (5), $b = 5·4965$ (4)–5·4988 (7) and $c = 4·8550$ (6)–4·8596 (2) Å. $V = 237·00$ (6)–238·45 (2) Å³, $Z = 4$, $D_x = 2·81$ (1) g cm⁻³, $M_r = 100·22$–100·54. Neutrons with time-of-flight from 2000 to 20000 μs for a total flight path of 12 m and detectors placed at 130–158° (2θ), averaged to 145°, were used for data acquisition at room temperature under vacuum ($< 10^{-4}$ Pa). Final R_I values (for intensities) vary from 0·038 to 0·070 and R_p values (for profile) from 0·045 to 0·086. Only the (Si,Al)—O(2) bond length is significantly influenced by the change in composition, whereas the Si—O(2)—(Si,Al) bond angles, connecting the puckered layers of Si,Al and N,O(1), remains unchanged. The change in (Si,Al)—O(2) bond length is related to the change in occupancies of Si and Al in the tetrahedral site, *i.e.* to the change in x, and is in agreement with the expression $(1 - x/2)1·62$ Å + $(x/2)1·77$ Å, which has been determined for layered silicates. No ordering of the replacing atoms has been observed for the range of O'-sialons studied. The JCPDS File Nos. for the samples are: for $x = 0·40$, No. 42-1490; for $x = 0·16$, No. 42-1491; and for $x = 0·04$, No. 42-1492.

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Introduction

In most aluminium silicon nitride oxide phases, generally denoted as sialons, replacement of atoms occurs, forming regions of varying stoichiometry, where aluminium atoms can occupy tetrahedral sites (Jack, 1983). In aluminium silicates, where aluminium can also be found in tetrahedral coordination, corner sharing or edge sharing between two aluminium-containing tetrahedra has not been observed, except for a limited number of structures *cf.* Loewenstein's rule (Liebau, 1985; Loewenstein, 1954). This seems not to be the case in compounds where the coordination sphere contains not only oxygen but also nitrogen, *e.g.* AlN has a wurtzite structure. This is obvious for $Si_{6-z}Al_zN_{8-z}O_z$, the β'-sialon phase, where the Al/Si ratio can exceed unity with all the aluminium atoms remaining in tetrahedral coordination (Ekström, Käll, Nygren & Olsson, 1989, and references therein). However, for $Si_{2-x}Al_xN_{2-x}O_{1+x}$, the O'-sialon phase, the maximum aluminium content is much smaller and the structural details are not clear.

The structure of O'-sialon has been determined by single-crystal X-ray diffraction using an Si_2N_2O crystal (Idrestedt & Brosset, 1964), which corresponds to a composition with $x = 0$. The space group was determined as $Cmc2_1$ belonging to the orthorhombic system. The structure of O'-sialon has four formula units in the unit cell with three atoms in the asymmetric unit; Si/Al and N/O(1) in general positions and O(2) in a special position, $4(a)$.* The structure of

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* Double notation is used for sites in which replacement occurs. In expressing the Si—O(2)—(Si,Al) angle, however, single notation is used for one of the metal-atom sites since replacement is not believed to take place in two adjacent tetrahedra.
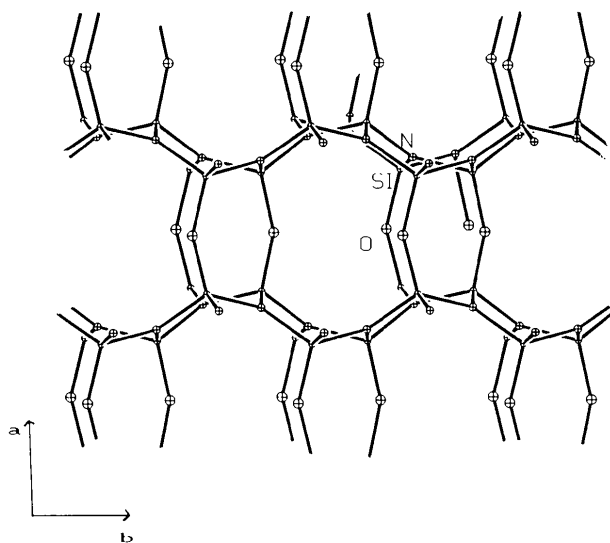

Fig. 1. Structure of O'-sialon viewed down the *c* axis.

Si_2N_2O can be considered as composed of puckered Si—N layers linked by Si—O—Si bridges, Fig. 1. Within the range of solid solubility available, on increasing the aluminium and oxygen content, the unit-cell edge *a* perpendicular to the Si—N planes increases, while no significant change is seen for the other unit-cell edges (Trigg & Jack, 1987). As with other sialons, Si is considered to be replaced by Al in its tetrahedral position while N is simultaneously replaced by O, thereby maintaining charge neutrality (Jack, 1983). The occupancies are thus fixed by the total composition. The reported maximum replacement of Si and N in O'-sialon varies from $x = 0.05$ (Land, Wimmer, Burns & Choudhury, 1978) to $x = 0.60$ (Jack, 1976).

The subject of this work is to study changes in the structural details of O'-sialons as the composition is altered. The use of neutron diffraction allows site occupancies to be calculated, since there is a large difference in scattering lengths for the elements occupying the same crystallographic positions. The analysis of the powder profile was carried out using the Rietveld (1969) method for profile refinement.

Experimental

The samples were prepared by mixing α-Si_3N_4, SiO_2 xerogel and Al_2O_3 powders. Mixing/milling was carried out in an agate ball mill with ethanol and pressing agents. The dried powder mixture was then formed, cold isostatically pressed at 275 MPa and the remaining ethanol and pressing agents were driven off at 573 K. The powder compacts were fired at 2093 K for 30 min under a protective powder (pre-oxidized Si_3N_4). The sintered samples were crushed to powder and etched in hot sodium hydroxide solution (1 *M*) and hot *aqua regia* to remove remaining glass and metal impurities and finally washed in hot deionized water. Five samples, 1, 2, 3, 4 and 5, were prepared in this way with different proportions of the three starting powders, giving calculated *x* values of 0.04, 0.10, 0.16, 0.24 and 0.40, respectively. Since it has been shown that it is possible to increase the range of solid solubility by using Y_2O_3 as a sintering aid (Sjöberg, O'Meara & Pompe, 1191), two samples, 6 and 7, with additions of 5 wt% Y_2O_3 were also prepared. The calculated *x* values for these samples were 0.30 and 0.40, respectively, and they were fired at 1923–1973 K for 2.5 h.

The positions of the diffraction peaks were determined by the Hägg–Guinier film technique in combination with optical line scanning, using programs *SCAN*3 and *SCANPI*7 (Johansson, Palm & Werner, 1980). Least-squares refinement of the lattice parameters was carried out with the program *PIRUM* (Werner, 1969). For consistency in the calculations, the same reflections were used for all

samples. In addition, secondary phases were identified by X-ray powder diffraction. Here, a 2θ powder diffractometer was used as a complement to the film technique.*

Neutron diffraction data for samples 2, 3, 4, 6 and 7 were collected at the pulsed neutron source ISIS, Rutherford–Appleton Laboratory (RAL), England, using the Polaris medium-resolution diffractometer (Hull & Mayers, 1989), which received neutrons from a 316 K H_2O moderator. The time-of-flight data were collected in ten resolution-focussed ^3He gas detectors placed at 130–158° in 2θ at a total distance of 12 m from the moderator, covering a range in d (Å) of 0·2–3·2 with a resolution of about 5 $\times 10^{-3}$. The samples were placed in a vanadium

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* X-ray powder patterns and primary digital neutron diffraction data, including error estimation for each point, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54181 (198 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. Three of the X-ray patterns have also been deposited with the JCPDS: for $x = 0.40$ as No. 42-1490; for $x = 0.16$ as No. 42-1491; and for $x = 0.04$ as No. 42-1492.
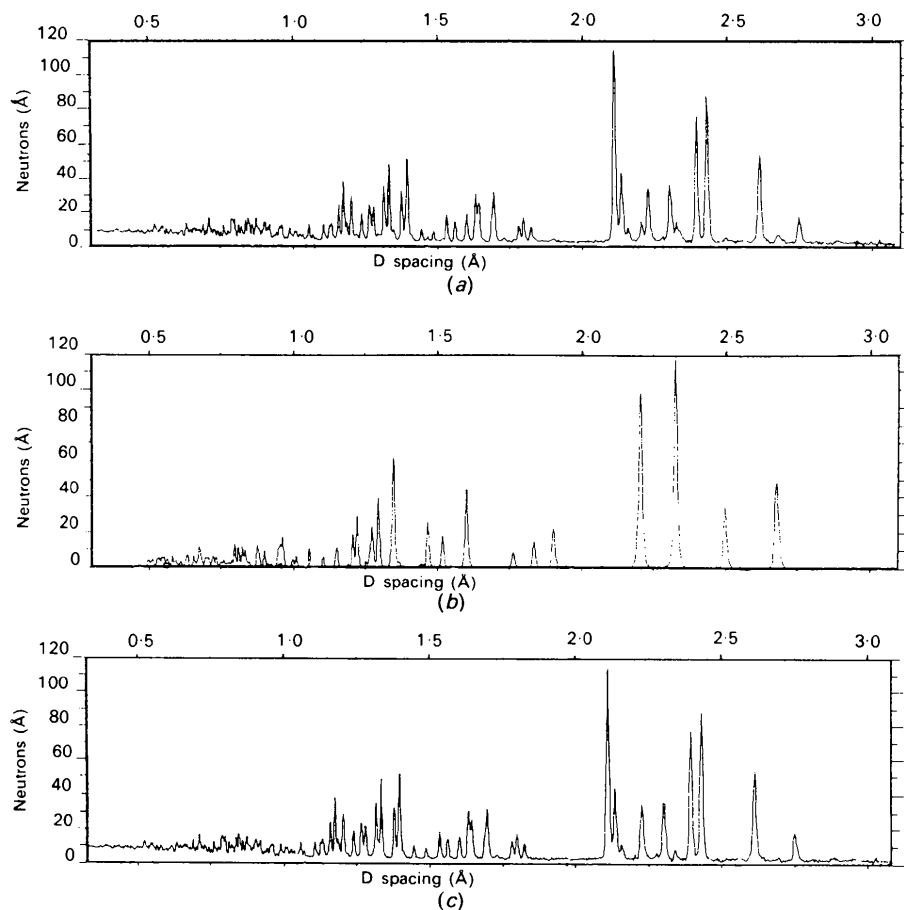
cylinder of 9 mm diameter, which was filled up to 35–38 mm. The data were collected over a period of 2 h at ambient temperature in vacuum ($< 10^{-4}$ Pa), and subsequently focussed, normalized and corrected analytically for attenuation.

Analysis of the diffraction profiles

Programs for least-squares profile refinement for time-of-flight diffraction data, *TF12LS* and *TF15LS* (David, Akporiaye, Ibberson & Wilson, 1988), were used to extract crystallographic information. These programs were developed at RAL, based on the principles for Rietveld refinement, to include expressions for the peak shape obtained from the spallation source. The scattering lengths used for Si, Al, N and O were 4·1490, 3·4460, 9·3000 and 5·0201 fm, respectively. The refinement included an overall intensity scale factor, five background parameters, zero-point and three peak-shape parameters, three lattice parameters, seven atomic coordinates, one site-occupancy factor and three isotropic temperature factors. The weighting scheme used in the minimized equation was $1/\sigma^2$. No preferred orientation was

Fig. 2. Subtraction of secondary phase from raw data. (a) Raw data. (b) Secondary phase diffractogram, β'-sialon. (c) Raw data minus contribution from β'-sialon.

assumed. The peak shape was described by a convolution of the Ikeda–Carpenter function with the Voigt function. Refinements included background between reflection positions. The background was represented by a Chebyschev polynomial with five parameters. Occupancies for the Si/Al and N/O(1) sites were related by strict constraint. Structural model and initial values for crystallographic parameters were taken from a high-temperature neutron diffraction experiment on Si_2N_2O (Billy, Labbe, Selvaraj & Roult, 1980).

At the time of experimentation no multiphase versions of the refinement programs were available, so the problem of separating overlapping reflections, arising from the secondary phases which were invariably present, had to be dealt with by partial refinement and subsequent subtraction of the contribution from these phases to the corrected raw data.
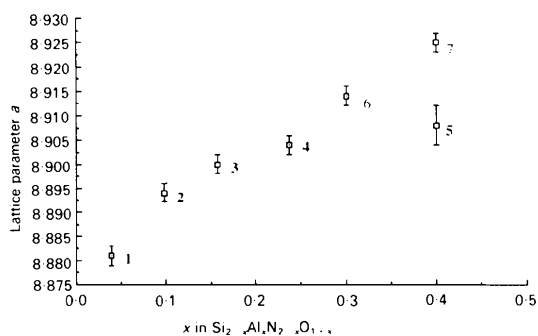
Table 1. *Lattice parameters determined by Hägg–Guinier film technique*

Sample	a (Å)	b (Å)	c (Å)	V (Å^3)
1	8·8807 (13)	5·4973 (10)	4·8550 (6)	237·00 (6)
2	8·8934 (6)	5·4984 (8)	4·8579 (4)	237·56 (4)
3	8·8997 (9)	5·4988 (7)	4·8588 (4)	237·60 (4)
4	8·9052 (7)	5·4982 (6)	4·8582 (3)	237·86 (4)
5	8·9112 (16)	5·4976 (6)	4·8596 (4)	237·93 (5)
6	8·9137 (8)	5·4965 (4)	4·8565 (2)	238·01 (3)
7	8·9254 (5)	5·4974 (3)	4·8593 (3)	238·45 (2)

Single-phase refinement was then carried out on the remaining profile. This procedure was possible using the interactive graphics program *GENIE* (David et al., 1986) developed at ISIS, Fig. 2. A reference test on a mixture of two well known phases, α-Si_3N_4 and β-Si_3N_4, provided confidence for this method.

For one of the minor phases, β'-sialon, the composition was expected to vary due to the different amounts of Al_2O_3 present in the sample. The composition of β'-sialon was estimated by determining the lattice parameters and using their dependence on composition (Ekström, Käll, Nygren & Olsson, 1989). Oxygen was assumed to be distributed over the two nitrogen positions according to refinements made by van Dijen, Metselaar & Helmholdt (1987) on neutron diffraction data for β'-sialons. For one of the impurity phases, the 'sialon X-phase', $Si_3Al_6N_2O_{12}$, present in sample 7, adequate structure information is not available, so it was necessary to exclude a number of regions from the refinement for this sample where remaining contributions from this phase might have been present.
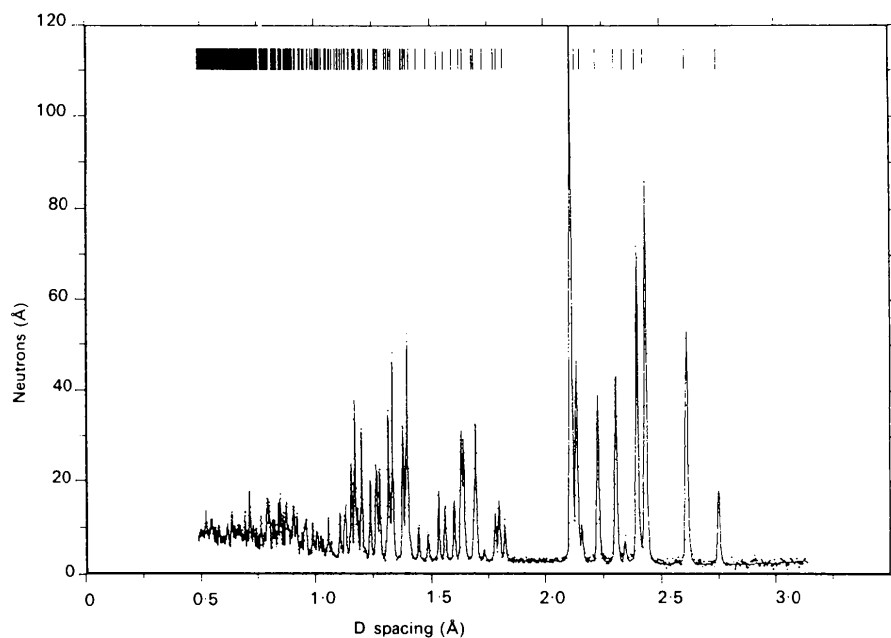

Fig. 3. Lattice parameter a versus composition.

Fig. 4. Results of Rietveld refinement, sample 3.

O'-SIALONS

Table 2. Results from Rietveld refinements

(x, y, z) are the atom coordinates, ITF the isotropic temperature factors, Site [fr] the site occupancy in fractions and Site [x] the site occupancy as x in the O'-sialon formula. $R_p = [\sum(Y_i^{obs} - Y_i^{calc})/\sum Y_i^{obs}]$, $R_{wp} = [\sum(Y_i^{obs} - Y_i^{calc})^2/\sum w_i(Y_i^{obs})^2]^{0.5}$, $R_I = [\sum(I_k^{obs} - I_k^{calc})/\sum I_k^{obs}]$, $R_{wi} = [\sum(I_k^{obs} - I_k^{calc})^2/\sum w_k(I_k^{obs})^2]^{0.5}$, $R_E = [(N - C + P)/\sum w_i(Y_i^{obs})^2]^{0.5}$, $\chi^2 = (R_{wp}/R_E)^2$.

	Sample 2				Sample 3				Sample 4			
(x, y, z), ITF (Å²)												
Si Al	0·1769 (2)	0·1504 (3)	0·2810 (5)	0·29 (2)	0·1771 (2)	0·1506 (4)	0·2808 (6)	0·33 (3)	0·1775 (2)	0·1496 (4)	0·2809 (7)	0·31 (3)
N O(1)	0·2182 (1)	0·1244 (2)	0·6268 (4)	0·37 (1)	0·2182 (1)	0·1246 (2)	0·6270 (5)	0·40 (1)	0·2181 (1)	0·1246 (2)	0·6270 (5)	0·31 (2)
O(2)	0·0000	0·2133 (3)	0·2300	0·51 (4)	0·0000	0·2136 (4)	0·2300	0·60 (4)	0·0000	0·2133 (4)	0·2300	0·66 (5)
Site [fr]												
Si N, Al O(2)	0·92 (3)	0·08 (3)			0·90 (3)	0·10 (3)			0·81 (3)	0·19 (3)		
Site [x]	0·17 (6)				0·20 (6)				0·38 (6)			
	$R_p = 4·50$	$R_{wp} = 3·56$	$R_I = 3·84$	$R_{wi} = 0·20$	$R_p = 4·73$	$R_{wp} = 3·32$	$R_I = 3·89$	$R_{wi} = 0·24$	$R_p = 5·48$	$R_{wp} = 4·26$	$R_I = 4·17$	$R_{wi} = 0·21$
χ^2	2·3				2·1				3·7			
Observations	1862				1862				1704			
Reflections	1111				1111				1113			
Regions used (μs)	3015 20000				3015–20000				3530–20000			

	Sample 6				Sample 7			
(x, y, z), ITF (Å²)								
Si Al	0·1781 (3)	0·1495 (5)	0·2803 (9)	0·21 (4)	0·1783 (3)	0·1497 (6)	0·2803 (9)	0·22 (4)
N O(1)	0·2183 (1)	0·1243 (2)	0·6276 (7)	0·26 (2)	0·2182 (2)	0·1240 (3)	0·6270 (7)	0·32 (3)
O(2)	0·0000	0·2134 (5)	0·2300	0·66 (7)	0·0000	0·2131 (6)	0·2300	0·65 (8)
Site [fr]								
Si N, Al O(1)	0·80 (4)	0·20 (4)			0·72 (4)	0·28 (4)		
Site [x]	0·40 (8)				0·56 (8)			
	R_p 8·63	R_{wp} 3·62	R_I 6·11	R_{wi} 0·34	R_p 5·70	R_{wp} 4·48	R_I 6·97	R_{wi} 0·40
χ^2	4·5				2·5			
Observations	1614				1489			
Reflections	1116				534			
Regions used (μs)	3860 20000				3860 7353, 7582 7902, 8019–8749, 8874–9026, 9281 13425, 13665 13875, 14165 19000			

Results

Only the lattice parameter a, perpendicular to the Si—N planes, shows any significant variation, Table 1 and Fig. 3. For samples 1–5 the increase in a reached a limit at $x \simeq 0·2$, in perfect agreement with earlier work (Trigg & Jack, 1987). Thus, the calculated x value for sample 5 ($=0·40$) has not been reached. For samples 6 and 7, containing yttrium oxide, higher values of a were found, indicating higher x values, which may be a consequence of the difference in composition of the melt from which the O'-sialon is formed, and the lower temperature of synthesis.

In all samples, minor amounts of β'-sialon and α-Si$_3$N$_4$ were present, the β'-sialon being formed along with the O'-sialons, while α-Si$_3$N$_4$ is the unreacted starting material. The 'sialon X-phase', Si$_3$Al$_6$N$_2$O$_{12}$, (Thompson & Korgul, 1983) was present in samples 5 and 7 and possibly also in sample 6.

The results of the refinement are summarized in Table 2. Definitions of the various R factors are also given as well as the regions used for refinement. The parameter χ^2 is a measure of precision of the fit of the model to the experimental data, and should be close to unity in an ideal case. It is calculated as (weighted profile R factor/expected R factor)^2. The refinement was most successful for samples 2 and 3,

Table 3. Bond angles (°) and bond lengths (Å) calculated from Rietveld refinement results

Sample	Si'—O(2)—(Si/Al)"	(Si,Al)—O(2)	Si,Al—N,O(2)		
2	149·7 (2)	1·630 (2)	1·726 (3)	1·726 (2)	1·721 (2)
3	149·8 (2)	1·633 (2)	1·728 (4)	1·725 (2)	1·720 (2)
4	149·7 (2)	1·638 (2)	1·726 (4)	1·721 (3)	1·722 (3)
6	149·8 (3)	1·644 (3)	1·730 (5)	1·718 (4)	1·716 (4)
7	150·0 (3)	1·647 (3)	1·728 (6)	1·720 (4)	1·717 (4)

Fig. 4. The results are also satisfactory for samples 4, 6 and 7. Table 3 contains relevant bond lengths and bond angles calculated from the refined structure parameters for samples 2, 3, 4, 6 and 7. In addition to the parameters given in Table 3, it should be noted that no changes could be observed in the bond angles to atoms of the nearest coordination sphere around the Si/Al or the N,O(1) sites.

Discussion

It is clear from Table 3 that the only significant change is that seen in the (Si,Al)—O(2) bond length. The Si—O(2)—(Si,Al) bond angle does not change, in contrast to when pure Si$_2$N$_2$O is exposed to high temperatures (Billy, Labbe, Selvaraj & Roult, 1980) or pressure (Srinivasa, Cartz, Jorgensen, Worlton, Beyerlein & Billy, 1977). The N/O(1) site remains in the plane of the surrounding Si/Al atoms, even when

a considerable number of nitrogen atoms have been replaced by oxygen. Thus, oxygen also coordinates the metal atoms in a planar fashion. The correlation of bond lengths to x values, calculated from initial powder compositions, is shown in Fig. 5. The average bond length calculated for the (Si,Al)—O(2) bond is introduced as a dotted line, using the bond lengths for Si—O and Al—O, as given by Smith & Bailey (1963) for layered silicate structures, 1·62 and 1·77 Å. The agreement of the experimental data with the calculated line is good. Within the puckered layers, some Si—N bonds are replaced by Al—O bonds and equal numbers of Al—N and Si—O bonds occur. As the Al—O bonds are almost of the same length as the Si—N bonds, as is the average of Si—O and Al—N bonds (Shannon & Prewitt, 1969), no change in bond lengths within the puckered planes should be expected.

Occupancy factors obtained from the refinements of the O'-sialons clearly show that the amount of aluminium and oxygen in the structure increases as the cell parameter a increases. The replacement is found to be larger than the maximum given by Trigg & Jack (1987), if yttria is added to the powder mixtures. A discrepancy between the refined occupancy factors along with their corresponding estimated standard deviations and the compositions of the powder mixtures used for preparation is observed, although the general trend is maintained. Losses during sintering and material remaining as glass could be part of the explanation, but this effect is not believed to be of importance for the samples studied. There are strong correlations of site occupancy to the overall intensity scale factor and to the isotropic temperature factors. The full variance–covariance matrix is used in the estimation of standard deviations, which are thus properly calculated (Prince, 1982), but in Rietveld refinements they generally tend to become underestimated. Since the scale factor is almost the same for all samples, as are the correlation elements given in the variance–covariance matrices, the occupancy factors can be expected to
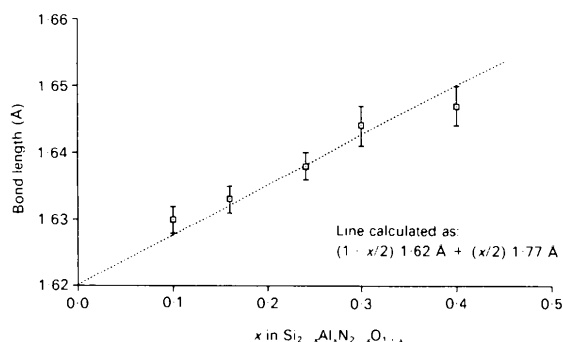
be accurate on a relative scale. They also seem to be within reasonable absolute limits if larger – and more correct – estimated standard deviations are anticipated.

The possibility of vacancies in the structure has been ignored in the calculations. The concentration of vacancies in related silicate structures is considered to be low, and hence, if present in the O'-sialons, vacancies would not contribute significantly to the calculated occupancy factors. The same applies to inclusion of impurities in the structure, since contaminating elements are believed to have been avoided through the choice of starting materials and preparation procedure. The possible presence of yttrium atoms in the structure in samples 6 and 7 will be dealt with in a separate report (Sjöberg, O'Meara & Pompe, 1991). Apart from refinements based on X-ray data, energy-dispersive analyses of elements in TEM for isolated small-angle single crystals have been made. Whereas the presence of yttrium in the crystals cannot be concluded from X-ray work, the TEM–EDX study indicated yttrium amounts at the level of 1 at %. It does not seem, therefore, that the possible presence of yttrium would affect the results of the calculations based on neutron diffraction data.

Neutron diffraction studies on β'-sialons (Gillot, Cowlam & Bacon, 1981; van Dijen, Metselaar & Helmholdt, 1987) provide some limited data for comparison. The tendencies indicated are similar to those given above for O'-sialons, although the atomic coordinates calculated for the neutron diffraction data from the β'-sialons are probably not fully correct since these refinements are based on the space group $P6_3/m$ rather than $P6_3$, which is the space group accepted for β'-sialons as determined by single-crystal X-ray diffraction on β-Si$_3$N$_4$ (Grün, 1979; Bando, 1983).

Refinements for the O'-sialon samples using a space group with lower symmetry, monoclinic Cc, to detect possible ordering of the tetrahedra, were also tried. No indication of ordering could be observed, although the results a have rather high degree of uncertainty owing to strong correlations between parameters. In analogous silicates, ordering is necessary usually at atomic ratio Si/Al = 1, but this is not the case for β'-sialons (Gillot, Cowlam & Bacon, 1981; van Dijen, Metselaar & Helmholdt, 1987), which can accommodate more aluminium in tetrahedral coordination. Consequently, even at (hypothetical) $x = 1$ in O'-sialon, ordering might not be necessary. Recently, a domain structure in the β'-sialons was proposed, based on MAS NMR studies (Dupree, Lewis & Smith, 1988). If correct, this model might also be applied to O'-sialons. However, this model is not in agreement with Loewenstein's rule, nor with the neutron diffraction experiments on β'-sialons.

Fig. 5. Bond length (Si,Al)—O(2) *versus* composition.

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Energy-Minimized Hydrogen-Atom Positions of Kaolinite

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Abstract

The H-atom positions within fixed non-H-atom structures of kaolinite have been determined using energy-minimization procedures. Our model treats all H-atom interactions as electrostatic except the intramolecular hydroxyl term which is described using a coulombic subtracted offset Morse potential. All inner-surface hydroxyl groups are found to point almost perpendicular to the layers and therefore appear to be involved in interlayer hydrogen bonding. The orientation of the inner hydroxyl is found to be directed towards the octahedral vacancy.

1. Introduction

The neutral 1:1 layers of kaolinite are held together by long-range interlayer hydrogen bonds. Although the crystal structure of the material, excepting the hydrogen positions, has been known reasonably well for a number of years from X-ray powder diffraction (Brindley & Nakahira, 1958; Brindley & Robinson, 1945, 1946) and electron diffraction techniques (Zvyagin, 1960), the positions of the H atoms are somewhat uncertain and remain controversial. It is this uncertainty which provided the motivation to study kaolinite using our energy-minimization techniques.

2. Historical background

A number of techniques have been used to locate the H atoms and understand the hydrogen bonding in kaolinite. First, infrared absorption spectroscopy has been widely employed in studying the orientations of