JOURNAL OF MATERIALS SCIENCE 16 (1981) 2263–2268

A neutron diffraction investigation of some β′-sialons

L. GILLOTT, N. COWLAM, G. E. BACON
Department of Physics, University of Sheffield, Sheffield, UK

Neutron diffraction measurements have been made on β′-sialons having chemical compositions $Si_{6-Z}Al_ZO_ZN_{8-Z}$, where $Z = 2.0$, 2.9 and 4.0. The powder diffraction patterns have been recorded for sample temperatures of 300 K and 4.2 K, and the profile refinement method has been used in the data analysis. The unit-cell dimensions and the atomic co-ordinates were found to vary in a regular way with composition. The values of scattering amplitude per atomic site obtained using the refinement method provide evidence of a preferential replacement of nitrogen by oxygen on specific crystallographic sites, and an indication of a small vacancy concentration on the metal-atom sites.

---

1. Introduction

The structure of β-Si_3N_4 [1, 2] is described by the hexagonal space group $P6_3/m - C^2_{6h}$, No. 176 in which the silicon atoms occupy 6h positions $(x, y, \frac{1}{4})$, with $x = 0.1733$ and $y = -0.2306$, and the nitrogen atoms occupy both 6h positions, with $x' = 0.3323$ and $y' = 0.0314$, and 2c positions $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. Alternatively, the existence of small departures from the ideal co-ordinate of the 6h sites, $z/c = \frac{1}{4}$, may indicate that $P6_3$ is a more accurate choice of space group [3]. The structure is based on tetrahedral atomic groupings. Tetrahedra of nitrogen atoms are joined by sharing corner atoms, so that each nitrogen is common to three tetrahedra. These tetrahedra are orientated with one edge parallel to the c-axis, so that the joining of neighbouring tetrahedra and the vertical repetition of unit cells produces parallel chains of tetrahedra along the c-axis. In every unit cell two of the eight nitrogen atoms are situated in special positions (2c) at the centre of an equilateral triangle of silicon atoms in the basal plane. The vertical sequence of these triangles, whose spacing is half the unit cell dimension, is such that these silicon atoms also form less-regular triangles normal to the basal plane, and the nitrogen atoms in the 6h sites are slightly displaced from the centre of these. As a result of this there are three distinct Si–N nearest neighbour distances. In the β′-sialons [4] aluminium replaces some of the silicon, and oxygen replaces some of the nitrogen. This replacement need not occur randomly on the 6h and 2c sites and, for example, there can be a small percentage of voids on the different sites or, if the replacement occurred in a regular way, the possibility of a superlattice formation. The aim of the present experiments was to obtain values of the unit cell dimensions and atomic co-ordinates for the three different chemical compositions chosen, and to investigate the occupancy of the 6h and 2c sites.

2. Neutron diffraction experiments

β′-sialons with the general formula $Si_{6-Z}Al_ZO_ZN_{8-Z}$ and having $Z = 2.0$, 2.9, and 4.0, were prepared from mixtures of Si_3N_4 and Al_2O_3, in the form of fine powders, for the neutron diffraction experiments.* The neutron diffraction measurements were performed using the D2 diffractometer at the Institute Laue–Langevin. In each experiment a range of scattering angles, θ, where $5° < 2\theta < 120°$ was investigated in steps of 0.1° with a count time of 2 min per step. The total scan time was approximately 40 h. Experiments were performed with the specimens at room temperature (300 K) and in a cryostat at 4.2 K. In each case the powder samples were contained in a thin-walled vanadium cylinder and the cryo-

---

*Samples prepared and supplied by Professor K. H. Jack of the University of Newcastle-upon-Tyne.

0022–2461/81/082263–06$02.60/0

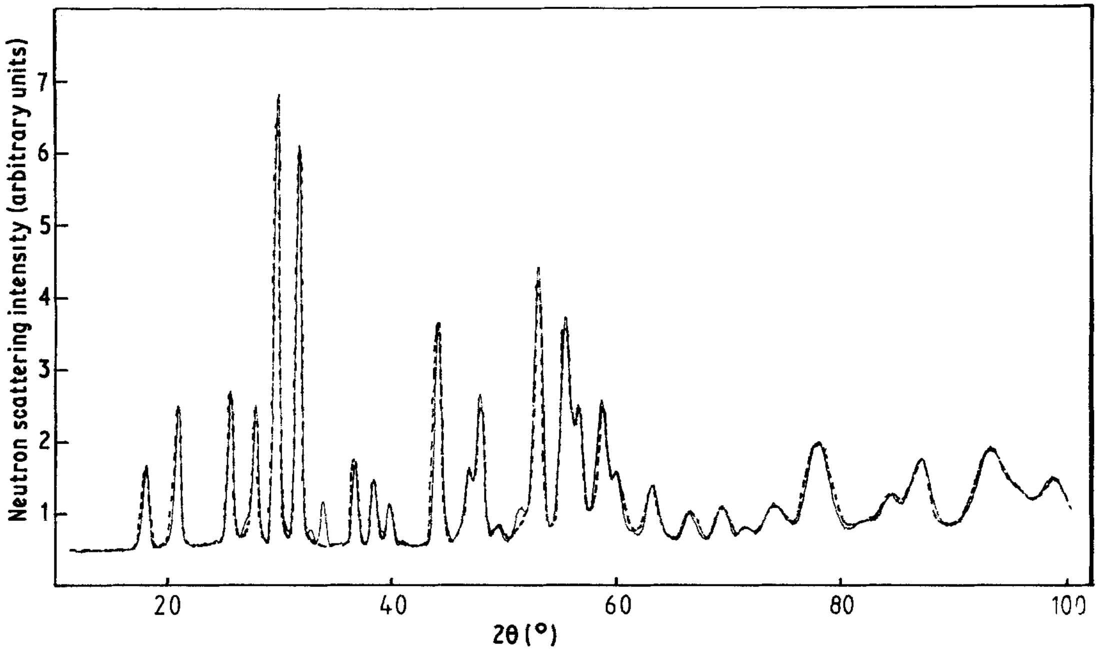

Figure 1 The neutron diffraction pattern of the β'-sialon $Si_2Al_4O_4N_4$ measured at 4.2 K. Continuous line: experimental data; broken line: the fitted profile, with a reliability factor of $R = 9.3\%$.

stat had a vanadium and aluminium tail. A typical diffraction pattern is shown in Fig. 1. In this diagram the Bragg diffraction peaks are well resolved for 2θ values below about 30°, but at higher angles, considerable overlap of adjacent Bragg diffraction peaks occurs. In fact, for $2\theta \approx 100°$ analysis has shown that as many as 25 individual reflections may be contributing to the intensity at any given angle. The profile refinement method [5] was developed to obtain structural information in exactly these circumstances. In this method, the whole of the experimental diffraction pattern is fitted by a calculated curve based on the parameters describing the expected structure of the specimen and the parameters describing the neutron diffractometer itself. The values of these parameters of both kinds can be adjusted to provide the best fit between the observed and calculated diffraction patterns by means of a least-squares fit refinement; the quality of fit is monitored by a reliability factor, R. However, a particular problem with this approach is the difficulty of estimating the true back-ground scattering levels at high angle, as can be seen from Fig. 1. This uncertainty limits the information which can be obtained with regard to the thermal motion of the atoms, and consequently this work has been concentrated at present on a detailed analysis only of the low-temperature data.

3. Data analysis

The neutron diffraction intensity data were analysed using the EDINP profile refinement computer program [6]. This program was used in the conventional way, refining the parameters of the neutron diffractometer first before proceeding to refine the unit-cell dimensions and the parameters describing the site positions and their occupancies. A typical diffraction pattern, together with its fitted profile (shown by the broken line), is given in Fig. 1; the reliability factor for this particular fit was $R = 9.3\%$, and similar values for R were obtained with the other specimens. The diffraction pattern shown in Fig. 1 has a small number of weak impurity peaks, which were not fitted by the calculated profile. It was not possible to identify these peaks as being due to the formation of a superlattice, to the existence of minority phases of α'-sialons [2] or to the existence of the sialon X-phase [4]. Some contamination from minority phases, both crystalline and glassy [7, 8], may be expected in β'-sialons produced by the reaction of Si_3N_4 with Al_2O_3. Additional diffraction peaks produced by this contamination have the effect of slightly increasing the value of the R-factor obtained. These impurity peaks from minor crystallographic phases cannot be expected to have any systematic effect, either on the profile

TABLE I Values of the unit-cell dimensions of β'-sialons at room temperature (300 K) and 4.2 K, as determined using the profile refinement method.

Temperature (K)	Unit cell dimension of $Si_{6-Z}Al_ZO_ZN_{8-Z}$					
	$Z = 2.0$		$Z = 2.9$		$Z = 4.0$	
	a (Å)	c (Å)	a (Å)	c (Å)	a (Å)	c (Å)
300 (room temperature)	7.649(3)	2.950(3)	7.668(3)	2.966(3)	7.695(a)	2.995(4)
4.2	7.643(4)	2.945(3)	7.664(3)	2.963(3)	7.692(a)	2.990(3)

refinement procedure or on the values of the parameters obtained. Additional scattering from a minority glassy phase, on the other hand, could possibly influence the values of the thermal vibration parameters obtained, particularly if the scattering provided a uniform back-ground level at large 2θ values.

The values of unit-cell dimensions obtained from the analysis at both sample temperatures of 300 K and 4.2 K are given in Table I. These values are not corrected for any systematic errors which may occur in the neutron diffraction measurements [9]. It is in fact possible to make such corrections by extrapolation methods in conjunction with the profile refinement method, but, in the present case, the absence of resolved peaks at high enough Bragg angles excluded this possibility. However the unit-cell dimensions at 300 K (Table I) agree reasonably with values determined from X-ray measurements [4]. Since the experimental uncertainties in the unit-cell dimensions are commensurate with the actual difference in the values between 4.2 K and 300 K, an accurate calculation of the coefficient of thermal expansion cannot be made. There appears to be an increase of approximately 0.1 % in both the a and c unit-cell dimensions between 4.2 K and 300 K, and this agrees favourably with the results from measurements at higher temperatures [4].

Having established the unit-cell dimensions, the atomic structure of β-Si_3N_4 was then used as a basis for the structure of the β'-sialons, and a refinement of the atomic structure was made using the low temperature data. The values of the atomic co-ordinates of the 6h and 2c sites determined using the profile refinement technique are given in Table II for all three specimens. The value of the scattering amplitude from any particular site is dependent on the occupancy of that site. When more than one species of atom may occupy a site, the precision with which the occupancy can be determined experimentally depends on the difference between the scattering amplitudes of the various atoms which can occupy the site. A particular advantage of neutron diffraction analysis, when applied to β'-sialons, is that the difference in the scattering amplitudes of nitrogen and oxygen atoms is greatly enhanced. This can be seen from a comparison of the ratio of atomic numbers (7:8) which determines the ratio of the X-ray scattering amplitude with the ratio of the neutron diffraction scattering amplitudes (0.94×10^{-12} cm: 0.580×10^{-12} cm) of the two elements. The atomic occupation of the 6h and 2c sites was determined by allowing the scattering amplitudes of all the sites to be variables in the refinement procedure, subject to the constraint that the total scattering amplitude from all the sites remained constant at a level determined by the composition. The atomic occupation of these sites was then determined by finding the combination of atoms which when present could account for the experimental values of the average

TABLE II Values of the atomic positional co-ordinates of β'-sialons at 4.2 K, as determined from the profile refinement method.

Atomic sites	Atomic co-ordinates for $Si_{6-Z}Al_ZO_ZN_{8-Z}$								
	$Z = 2.0$			$Z = 2.9$			$Z = 4.0$		
	x	y	z	x	y	z	x	y	z
6 Si in 6h	0.1698(5)	−0.2341(7)	0.250	0.1686(4)	−0.2355(6)	0.250	0.1678(4)	−0.2365(5)	0.250
6 N1 in 6h	0.3335(6)	0.0307(2)	0.250	0.3320(6)	0.0301(2)	0.250	0.3321(5)	0.0290(2)	0.250
2 N2 in 2c	0.333	0.667	0.250	0.333	0.667	0.250	0.333	0.667	0.250

TABLE III Values of the site occupancy for oxygen and nitrogen atoms on the 6h and 2c sites, determined from the scattering amplitudes per site at 4.2 K, together with the values expected from a random site occupation, and the experimentally-determined vacancy concentrations, C_{vac}, for the metal-atom 6h sites.

Composition	Site	Site occupancy in $\mathrm{Si}_{6-Z}\mathrm{Al}_Z\mathrm{N}_{8-Z}\mathrm{O}_Z\mathrm{N}_{8-Z}$				
		Oxygen and nitrogen sites				Metal-atom sites
		Observed occupation		Random occupation		Vacancy concentration on 6h sites, C_{vac}
		⟨O atoms⟩	⟨N atoms⟩	⟨O atoms⟩	⟨N atoms⟩	
$Z = 2.0$	6h	1.1	4.9	1.5	4.5	3%
	2c	0.9	1.1	0.5	1.5	
$Z = 2.9$	6h	1.8	4.2	2.2	3.8	5%
	2c	1.1	0.9	0.7	1.3	
$Z = 4.0$	6h	2.5	3.5	3.0	3.0	5%
	2c	1.5	0.5	1.0	1.0	

scattering lengths of each of the crystallographic sites. It was found that the uncertainties in the values of site occupation obtained could be minimized by allowing there to be a small concentration of vacancies on the 6h sites. The atomic occupations and the vacancy concentrations, C_{vac}, deduced from this process, are given in Table III, together with values appropriate to a random site-occupation. In assessing the possible errors in these values of site occupation and vacancy concentration, it was borne in mind that there is some correlation between these two values and also further correlation between them and the overall scale factor between the observed and calculated diffraction profiles. However, it appears from the calculations that uncertainties of 10% in the occupation parameters, and up to 30% in the vacancy concentrations, represent reliable estimates of the errors involved.

4. Discussion

The values of the parameters given Tables I and II can be seen to vary with composition in a broadly linear way, and their values are in good agreement with values obtained from X-ray diffraction experiments [10]. It is convenient to summarize the compositional variations of the parameters obtained here in graphical form. These diagrams can then form the basis of a discussion of the structural changes observed in going from β-$\mathrm{Si_3N_4}$ [1, 2] to the β'-sialon with $Z = 4$. All the percentage differences given below refer to differences between these two compounds. The variation in the *a* and *c* unit-cell dimensions are shown in Fig. 2a and b; there is a 1.1% change in *a*, and a 2.9% change in *c*, respectively. The change in unit-cell volume (5%) is smaller than the 11% change in the total volume of the atoms present (based on tetrahedral covalent radii) as the larger

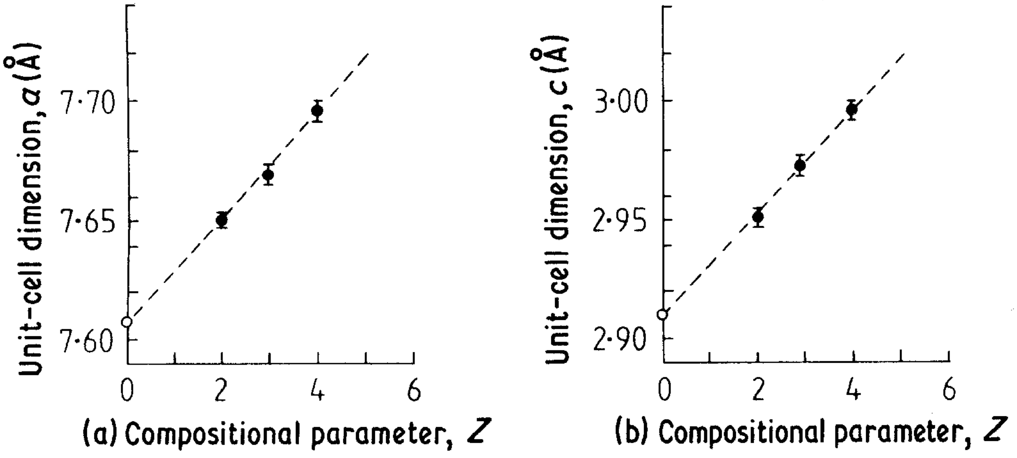

Figure 2 Compositional variations of the unit-cell dimensions (a) *a* and (b) *c* for $\mathrm{Si}_{6-Z}\mathrm{Al}_Z\mathrm{O}_Z\mathrm{N}_{8-Z}$ obtained using the profile refinement method.

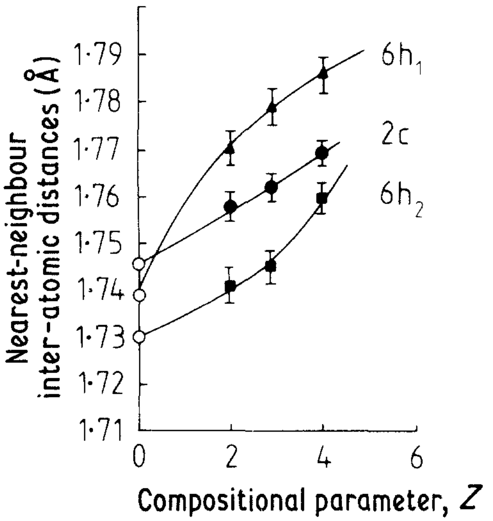

Figure 3 Compositional variations of the (Si, Al) → (O, N) nearest-neighbour inter-atomic distances for $Si_{6-Z}Al_ZO_ZN_{8-Z}$ obtained using the profile refinement method.

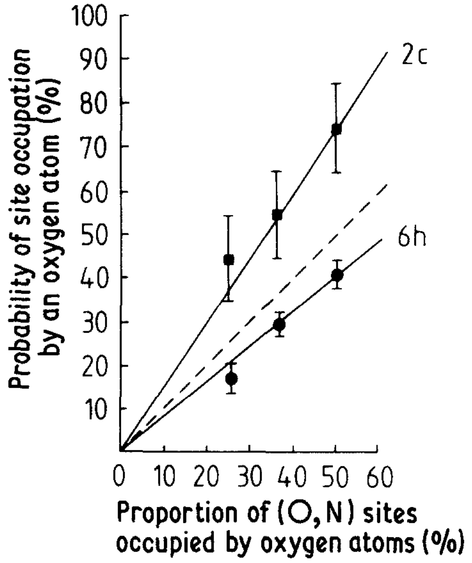

Figure 4 Probability of site occupation by an oxygen atom plotted against the percentage of oxygen atoms among the (O, N) atoms for $Si_{6-Z}Al_ZO_ZN_{8-Z}$ obtained using the profile refinement method.

aluminium and smaller oxygen atoms replace silicon and nitrogen atoms, respectively. It may be expected, however, that structural adjustments can be relatively easily accomodated in β-Si_3N_4, which has a rather open structure (see Fig. 2 of [2]), and some indication of these changes is given in terms of the nearest neighbour Si–N distances, represented in Fig. 3, which are derived from Tables I and II. In the case of β-Si_3N_4 the largest Si–N distance is from the triangle of silicon atoms in the basal plane to the nitrogen atoms in the 2c special positions. Fig. 3 shows that this distance has the smallest increase (1.3 %), consistent with it being preferentially filled with the smaller oxygen atoms. The two slightly shorter and different Si–N distances to the nitrogen atoms in the 6h sites increase by 1.8 % and 2.7 % indicating a significant further distortion of the silicon–nitrogen triangle normal to the basal plane for the β'-sialons.

The nature of the preferential site occupation for the oxygen and nitrogen atoms can be seen most easily by deriving the probabilities of site occupation from the results given in Table III. The probabilities that the 6h and 2c sites are occupied by oxygen atoms are plotted against the percentages of oxygen in Fig. 4. The magnitude of the error bars in this diagram are derived from the errors in the scattering amplitudes per site derived using the profile refinement process (see Section 3). The broken line in Fig. 4 represents the variation expected for a random site occupation, and it is clear that the results indicate a linear trend away from this possibility. Any preferential occupation by the silicon atoms of their 6h sites would cause a change of symmetry in the structure, and the appearance of new Bragg reflections, and these have not been observed. However, the difference in the scattering amplitudes of silicon and aluminium atoms is not as favourable as that for oxygen and nitrogen atoms: seven times less favourable for neutron scattering, and four times less favourable for X-ray scattering (where the contrast is already weak). This experimental inability to distinguish between the metalloid atoms must limit our understanding of the rather complex changes in bond distance and structural distortion that are implied to take place by Fig. 3. However, it has been possible to obtain some information about vacancy concentrations, C_{vac}, on the metalloid sites, as described above, and it was found that the most consistent values of site occupation for the 6h sites occupied by (Si, Al) were $C_{vac} = 3\,\%$ for $Z = 2$, $C_{vac} = 5\,\%$ for $Z = 2.9$ and $C_{vac} = 5\,\%$ for $Z = 4$.

It has been pointed out by Jack [11] that these values of vacancy concentration may provide some information relevant to the correct chemical description of β'-sialons. The description $Si_{6-Z}Al_ZO_ZN_{8-Z}$ used throughout this account is one representation of the chemical composition which may be associated with the method of preparation, namely that of reacting Si_3N_4 with

$Al_2O_3 + AlN$ according to the equation

$$\left(2-\frac{Z}{3}\right)Si_3N_4+\frac{Z}{3}(Al_2O_3+AlN) = Si_{6-Z}Al_ZO_ZN_{8-Z}. \qquad (1)$$

This method of preparation has been developed experimentally [9] as a means of avoiding the minority-phase contamination which can occur when preparing β'-sialons by the reaction of Si_3N_4 and Al_2O_3 alone [8]. According to this *latter* method it can be seen that for every nitrogen atom in Si_3N_4 replaced by an oxygen atom, then three-quarters of a silicon atom is replaced by two-thirds of an aluminium atom. The composition may then be given as $Si_{6-3/4x}\,Al_{2/3x}\,O_x\,N_{8-x}\,\square_{x/12}$, where $\square$ represents a vacancy. This discription can be found in earlier literature (for example, Fig. 13 of [10]). This latter composition requires a concentration of vacancies of $x/12$ on the 6h metal-atom sites, as indicated. The three β'-sialons measured here are described according to this latter chemical composition by the values, $x = 2$, $x = 3$ and $x = 4$, and for these three compounds the percentage of vacancies on the metal-atom 6h sites is predicted to be 2.8%, 4.2% and 5.5%, respectively. The experimental values of 3%, 5% and 5% given above are in good agreement with these figures, which, as described earlier, arise solely from the values of the scattering amplitudes per site obtained using the profile refinement method and not from any preconceived model. However, whilst these neutron diffraction experiments provide reasonable evidence for the existence of site vacancies in β'-sialons, some care must be taken in interpreting these figures as there is not yet a clear identification of all the minority phases present in the samples and the influence these may have on the composition of the β'-sialon matrix.

5. Conclusions

The profile refinement method has been applied to the analysis of the neutron diffraction data for β'-sialons. The diffracton patterns were fitted with a reliability factor close to 9%, and the crystallographic parameters obtained are seen to vary linearly with sialon composition. There is good contrast between the oxygen atom and nitrogen atom when using neutron diffraction methods, and the results obtained indicate a definite trend towards a preferential occupation by oxygen atoms of the 2c crystallographic sites and an indication of the presence of a small vacancy concentration on the metal-atom sites.

Acknowledgements

The authors would like to thank Professor K. H. Jack for the provision of the β'-sialon samples and for his helpful comments on the manuscript, particularly on the matter of the vacancy concentrations in β'-sialons. The neutron experiments were performed on the D2 diffractometer at ILL, Grenoble, under financial support from the Science Research Council.

References

1. D. HARDIE and K. H. JACK, *Nature* **180** (1957) 332.
2. S. WILD, P. GRIEVESON and K. H. JACK, *Spec. Ceram.* **5** (1972) 385.
3. R. GRUN, *Acta Cryst.* **B35** (1979) 800.
4. K. H. JACK, *J. Mater. Sci.* **11** (1976) 1135.
5. H. M. RIETVELD, *Acta Cryst.* **2** (1969) 65.
6. G. S. PAWLEY, G. A. MACKENZIE and O. W. DIETRICH, *ibid.* **A33** (1977) 142.
7. P. DREW and M. H. LEWIS, *J. Mater. Sci.* **9** (1974) 1833.
8. M. H. LEWIS, B. D. POWELL, P. DREW, R. J. LUMBY, B. NORTH and A. J. TAYLOR, *J. Mater. Sci.* **12** (1977) 61.
9. G. E. BACON, N. COWLAM and A. G. SELF, *Acta Cryst.* **A33** (1977) 46.
10. K. H. JACK, *Trans J. Brit. Ceram. Soc.* **72** (1973) 376.
11. *Idem*, private communication.

Received 13 November 1980 and accepted 11 February 1981.