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Rietveld refinements for calcium and yttrium containing α-sialons

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The crystal structures of calcium and yttrium containing α-sialons, $M_x(Si, Al)_{12}(N, O)_{16}$, were refined by the Rietveld analysis of their X-ray powder diffraction patterns. Rather low R factors obtained in the refinements provide conclusive evidence for a structural model proposed by the Newcastle group. In these α-sialons, the modifying cations occupy large closed interstices of the (Si, Al)–(N, O) network similar structurally to that in α-Si_3N_4; each cation is coordinated to seven (N, O) atoms with an average M–(N, O) length of ~ 0.26 nm. The (Si, Al)–(N, O) bonds range in distance from 0.17 to 0.18 nm (average 0.176 nm). The Rietveld method has been shown to give highly accurate occupation factors for the interstitial cations.

1. Introduction

Members of so-called α-sialon ceramics have received considerable interest in recent years because of their ease of preparation, thermal and chemical stability, low coefficient of thermal expansion, and electrical conductivity [1–7]. The general composition for α-sialon is $M_x(Si, Al)_{12}(N, O)_{16}$, where $x < 2$ and M is a modifying cation: M = Li^+, Mg^{2+}, Ca^{2+}, Y^{3+} or lanthanide ion other than La^{3+} and Ce^{3+} [5, 7]. As this formula indicates, the structures of α-sialon are derived from α-Si_3N_4 (trigonal, space group P31c [8]) by partial replacement of Si by Al and N by O; the modifying cations not only maintain electrical neutrality but also stabilize the trigonal α-Si_3N_4 structure. Crystallographic considerations suggest that these cations may occupy large closed interstices in the (Si, Al)–(N, O) network, i.e. 2(b) positions at $(1/3, 2/3, z)$ and $(2/3, 1/3, 1/2+z)$ [1, 4, 7].

Within the quasiternary systems Si_3N_4–AlN–CaO [9] and Si_3N_4–AlN–Y_2O_3 [6], α-Si_3N_4 forms limited solid solutions with CaO·3AlN and Y_2O_3·9AlN, respectively. The present investigation was undertaken to obtain the lattice and crystal-structural parameters of $Ca_x(Si, Al)_{12}(N, O)_{16}$ (Ca α-sialon) and $Y_x(Si, Al)_{12}(N, O)_{16}$ (Y α-sialon) from their angle-dispersive X-ray powder diffraction data. Although the structures of Ca α-sialons with x values of 1.0 and 1.83 have been determined by the Newcastle group [7], the details of the refinements have not yet been published to our knowledge.

The Rietveld method [10, 11] was applied for the above purpose because structure parameters calculated for the two samples from integrated diffraction intensities are not very accurate owing to the extensive overlap among reflections. This technique has now found wide spread application in the structure determination of compounds which are not available as single crystals. In Rietveld analysis the parameters in a structural model, plus necessary instrumental parameters, are adjusted in a computer calculation until the least-squares best fit is obtained between the entire calculated and observed powder patterns. Accordingly, the maximum amount of information can reliably be derived from the observed intensity data without any *a priori* assumptions.

We have already reported the Rietveld refinement of the Y α-sialon [12] using the XPD system [13, 14], a software package for the Rietveld analysis and simulation of X-ray diffraction patterns. However, the structure was refined by excluding those sections of data containing impurity peaks explicitly; this procedure is not complete enough to subtract all the contributions

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of impurity peaks to all the step-scanned intensity data.

The XPD system has recently been modified so as to deal with mixtures of two or more phases [15]. Rietveld refinements using this new version must, therefore, give more accurate parameters than those using the previous version. Furthermore, the XPD system makes it possible to include additional information such as known interatomic distances and angles as weighted constraints or to impose their expected ranges as boundary conditions. Such constrained refinements are needed in the present structural analyses because reflections from the α-sialons and impurities overlap to a great extent and a number of profile and structure parameters have to be refined.

2. Sample preparation and analyses

Starting materials for the preparation of the α-sialons were a mixture of $CaCO_3$*, Si_3N_4†, and AlN‡ (molar ratio $CaCO_3$, 1: Si_3N_4, 4: AlN, 3) and that of Y_2O_3§, Si_3N_4, and AlN (molar ratio Y_2O_3, 0.3: Si_3N_4, 3.1: AlN, 2.7). These mixtures were hot pressed for 1 h at 1700° C under a pressure of 19.6 MPa in a graphite die 50 mm in diameter (Ca α-sialon) or at 1750° C and 14.7 MPa in a graphite die of 15 mm diameter (Y α-sialon). The Ca α-sialon contained as impurities α-quartz and a trace amount of β-sialon, whereas the Y α-sialon contained α-quartz and a trace amount of an unknown compound.

The sintered materials were pulverized and submitted to X-ray powder diffraction. X-ray intensity data were collected with nickel-filtered Cu*K*α radiation for 40 sec at 0.04° intervals over the 2θ range 18 to 110° (Ca α-sialon) or at 0.05° intervals over the range 18 to 117.05° (Y α-sialon). The intensities in the angular ranges of 25.28 to 25.8°, 35.52 to 36.24°, 37.36 to 37.92°, 43.4 to 43.8°, 52.24 to 53°, 57.36 to 58.16°, and 66.2 to 67° for the Ca α-sialon and 28.05 to 29.75°, 31.6 to 32.2°, 35.55 to 35.95°, and 37.45 to 38.1° for the Y α-sialon were omitted from the subsequent refinements because, as described above, very weak peaks which could be assigned neither to the α-sialons nor α-quartz appeared in these regions.

The chemical compositions of the above α-sialons were determined by analytical electron microscopy (AEM). Samples for AEM were prepared by diamond cutting of thin sections, grinding and polishing to about 20 μm thick discs. They were then thinned down to some hundreds of nanometers by ion thinning using argon ions. They were then coated with a thin layer of carbon ~ 10 nm in thickness.

The sample was held in a beryllium-nosed specimen goniometer and analysed with a Philips EM-400 or a JEM-200CX analytical electron microscope equipped with an energy-dispersive X-ray spectrometer. The accelerating voltage was 100 kV, and the probe diameter at the specimen position was approximately 30 nm in a scanning transmission electron microscope mode. The counting time was 100 sec for each point analysis. Quantitative X-ray microanalysis of M, Si, and Al was performed on the basis of the thin-film approximation technique [16] using intensity data for more than 20 sampling points.

The composition was found to be $Ca_{0.67}Si_{10.0}Al_{2.0}N_{15.3}O_{0.7}$ for the Ca α-sialon and $Y_{0.5}Si_{9.3}Al_{2.7}N_{15.1}O_{0.9}$ for the Y α-sialon. The contents of N and O in these formulae were calculated from the analytical values of M, Si, and Al on the assumption that no vacancies are present at atomic positions other than those of the metal cations.

3. Structure refinements

The profile shape function adopted in this study is a modified pseudo-Voigt function [13], i.e. the sum of a Gauss function and a Lorentz function with unequal peak heights and full-widths at half maximum (FWHM):

$$g(2\theta_i - 2\theta_k) = \left(\frac{\gamma\pi^{1/2}H_k(\mathrm{G})}{c_0^{1/2}} + \frac{(1-\gamma)\pi H_k(\mathrm{G})}{c_1^{1/2}\delta}\right)^{-1} \times\left[\gamma \exp\left(\frac{-c_0(2\theta_i - 2\theta_k)^2}{H_k^2(\mathrm{G})}\right) + (1-\gamma)\left(1 + \frac{c_1(2\theta_i - 2\theta_k)^2\delta^2}{H_k^2(\mathrm{G})}\right)^{-1}\right] \quad (1)$$

where $2\theta_i$ is the scattering angle at the *i*th step, θ_k is the Bragg angle for the *k*th reflection, $c_0 = 4 \ln 2$, $c_1 = 4$, γ is the Gaussian fraction, $\delta = H_k(\mathrm{G})/H_k(\mathrm{L})$, and $H_k(\mathrm{G})$ and $H_k(\mathrm{L})$ are the FWHMs of the Gaussian and Lorentzian components, respectively. $H_k(\mathrm{G})$ in Equation 1 is given by

*Wako Pure Chemical Co., Japan. GR grade.
†H. C. Starck, West Germany. LC-10 grade. $\alpha/(\alpha + \beta) = 0.94$.
‡ Toshiba Ceramics Co., Japan. Al, 65 wt %; N, 32.3 wt %; Si, 0.2 wt %; O, 1.2 wt %.
§ Shin-etsu Chemical Co., Japan. 99.9% pure.

$$H_k(G) = U \tan^2\theta_k + V \tan\theta_k + W \quad (2)$$

where U, V and W are the FWHM parameters. With appropriate choices of γ, the above profile shape function can vary from Gaussian ($\gamma = 1$) to Lorentzian ($\gamma = 0$). The difference between the so-called pseudo-Voigt function [17, 18] and Equation 1 is that the value of δ is fixed at 1 in the former whereas δ is a variable parameter in the latter. Preliminary refinements showed that the use of Equation 1 led to more satisfactory fits than the use of the Gaussian, Lorentzian, modified Lorentzian, and intermediate Lorentzian functions [18]. Neither γ nor δ underwent large oscillations in the process of convergence. An asymmetric correction to the above symmetric profile shape function was just the same as described by Rietveld [10].

The background correction y_{bi} was modelled using the six-parameter function

$$y_{bi} = \sum_{j=0}^{5} b_j [2\theta_i/(\theta_{max} - \theta_{min}) - 1]^j \quad (3)$$

where b_0–b_5 are the background parameters, and θ_{max} and θ_{min} are respectively the maximum and minimum values of diffraction angles in step-scanned intensity data.

The X-ray powder diffraction patterns of the two samples were presumed to contain only the peaks of α-sialon and α-quartz. There were 43 variable parameters:

1. Global parameters
   - Z Zero-point shift for 2θ
   - b_0–b_5 Background parameters
2. Phase-dependent parameters
   - (a) α-Sialon
     - s Scale factor
     - U, V, W FWHM parameters
     - A Asymmetry parameter
     - γ Gaussian fraction
     - δ $H_k(G)/H_k(L)$
     - a, c Lattice parameters
     - g Occupation factor for the metal cation
     - x, y, z Fractional coordinates (14 parameters)
     - B Individual isotropic temperature factors for M, (Si, Al), and (N, O)
   - (b) α-Quartz
     - s Scale factor
     - U, V, W FWHM parameters
     - A Asymmetry parameter
     - γ Gaussian fraction
     - a, c Lattice parameters
     - Q Overall temperature factor

The z coordinate of the $(N, O)_1$ site was arbitrarily fixed at zero according to the description of Marchand *et al.* [8]. The value of δ for α-quartz was set at 1. The atomic coordinates in α-quartz were assumed to be just the same as those in the literature [19]. The atomic scattering factors used were calculated from the coefficients for their analytical approximations for neutral Y, Ca, Si, Al, N and O and collected for anomalous dispersion [20]. The range of data used for each peak was 11 times the FWHM on each side of the calculated Bragg position of the peak.

Some of (Si, Al)–(N, O) bond distances, which were calculated from atomic positional parameters refined in the absence of any constraints, were unrealistically large or small. In other words, the refinements converged towards false minima. The X-ray data were then supplemented with eight inequality constraints which restrict the (Si, Al)–(N, O) lengths within a reasonable range. Standard deviations of the resulting parameters were evaluated as described by Prince [21]. For further details of the refinement procedure, see Izumi [13, 14].

4. Results and discussion

Tables I and II list the final R factors and structure parameters for the α-sialons. The definition of the R factors in these tables is identical to that described by Young and Wiles [18]. Despite the marked overlap among the peaks from the α-sialons and α-quartz, the Rietveld refinements converged most satisfactorily, giving rather low R factors; the full powder patterns calculated from the refined parameters matched the experimental patterns very closely (Fig. 1). These results clearly support the ideas that the α-sialons have the expanded α-Si_3N_4 structure built up of $[(Si, Al)(N, O)_4]$ tetrahedra and that metal cations partially occupy the interstitial sites large enough to accommodate other cations [1, 4, 7] (Fig. 2).

Table III shows M–(N, O) and (Si, Al)–(N, O) tetrahedral bond lengths calculated by using UNICS III [22]. Each metal cation is coordinated to seven (N, O) atoms. The Ca–(N, O) bond lengths range from 0.236 to 0.269 nm, whereas

TABLE I Results of Rietveld refinements for Ca α-sialon*

Atom	Position	g	x	y	z	$B(\mathrm{nm}^2)$
Ca	2(b)	0.339(2)	1/3	2/3	0.228(1)	0.16(1)
$(Si, Al)_1$	6(c)	1	0.5090(2)	0.0820(1)	0.207(1)	0.0091(1)
$(Si, Al)_2$	6(c)	1	0.1681(1)	0.2512(1)	−0.003(1)	0.0091(1)
$(N, O)_1$	2(a)	1	0	0	0	0.0034(3)
$(N, O)_2$	2(b)	1	1/3	2/3	0.642(1)	0.0034(3)
$(N, O)_3$	6(c)	1	0.3477(3)	−0.0441(3)	−0.012(2)	0.0034(3)
$(N, O)_4$	6(c)	1	0.3164(3)	0.3150(3)	0.246(1)	0.0034(3)

*$R_{wp} = 6.9\%$, $R_p = 5.2\%$, $R_B = 4.9\%$. $a = 0.783832(7)$ nm, $c = 0.570327(6)$ nm. Numbers in parentheses here and elsewhere are estimated standard deviations in units of the last digit.

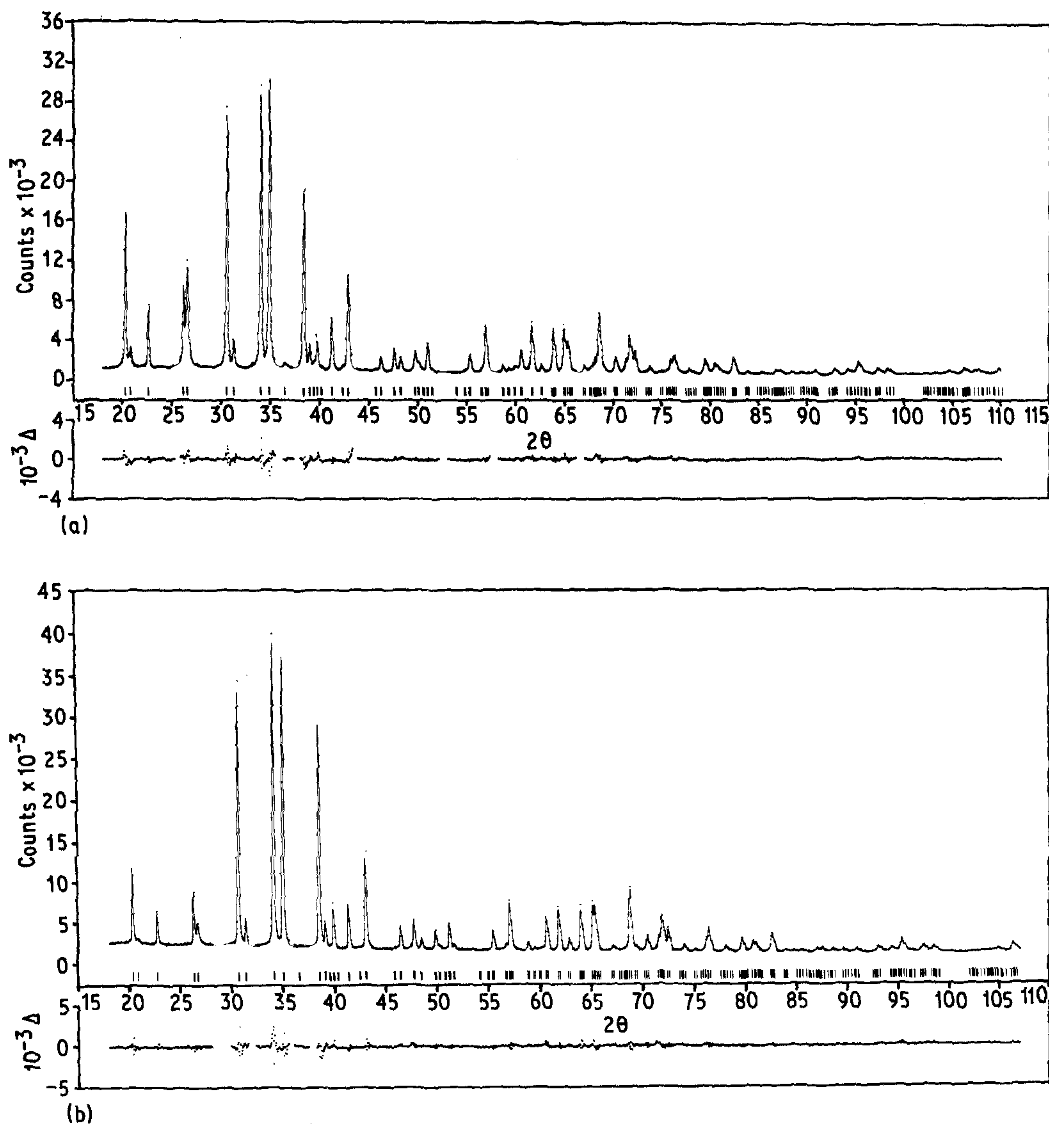

Figure 1 Rietveld refinement patterns for the (a) Ca and (b) Y α-sialons containing small amounts of α-quartz. In the upper portions, the observed data are indicated by the dots; the calculated pattern is shown as the solid line overlying them. The vertical markers in the central portions show positions calculated for $K\alpha_1$ and $K\alpha_2$ peaks. The lower portions are plots of Δ, the difference between the observed and calculated intensities.

TABLE II Results of Rietveld refinements for the Y α-sialon*

Atom	Position	g	x	y	z	$B(\text{nm}^2)$
Y	2(b)	0.272(2)	1/3	2/3	0.242(2)	0.0063(9)
$(\text{Si, Al})_1$	6(c)	1	0.5087(2)	0.0819(1)	0.213(1)	0.0092(2)
$(\text{Si, Al})_2$	6(c)	1	0.1706(2)	0.2533(2)	0.002(2)	0.0092(2)
$(\text{N, O})_1$	2(a)	1	0	0	0	0.0048(4)
$(\text{N, O})_2$	2(b)	1	1/3	2/3	0.653(2)	0.0048(4)
$(\text{N, O})_3$	6(c)	1	0.3458(3)	−0.0472(4)	−0.005(2)	0.0048(4)
$(\text{N, O})_4$	6(c)	1	0.3219(4)	0.3180(4)	0.246(2)	0.0048(4)

*$R_{\text{wp}} = 5.1\%$, $R_{\text{p}} = 3.8\%$, $R_{\text{B}} = 5.9\%$. $a = 0.782927(7)$ nm, $c = 0.570757(6)$ nm.

the Y–(N, O) bond lengths lie between 0.234 and 0.269 nm. The average M–(N, O) distances are almost the same for the two α-sialons: ~ 0.26 nm. The M–(N, O)_2 bond parallel to the c axis is much shorter than the other six M–(N, O) bonds. The three $(\text{N, O})_3$ atoms are pulled in towards the modifying cation relative to the three $(\text{N, O})_4$ atoms, forming stronger bonds with the cations than the latter. The modifying cations cannot be introduced into those channels in β-sialons which run parallel to the c direction; the strengthening of the three M–(N, O)_3 bonds and the presence of the strongest M–(N, O)_2 bond must stabilize the structure based on α-Si_3N_4 relative to that based on β-Si_3N_4.

Every (Si, Al) atom in this structure is surrounded tetrahedrally by (N, O) atoms, and each (N, O) atom has three (Si, Al) atoms as nearest neighbours. The (Si, Al)–(N, O) distances do not vary over a wide range; they lie between 0.170 and 0.180 nm with an average at 0.176 nm, which is slightly larger than the mean Si–N distance in α-Si_3N_4: 0.174 nm. The value of the maximum difference in the (Si, Al)–(N, O) distances, 0.01 nm, suggests that Al and O atoms do not segregate

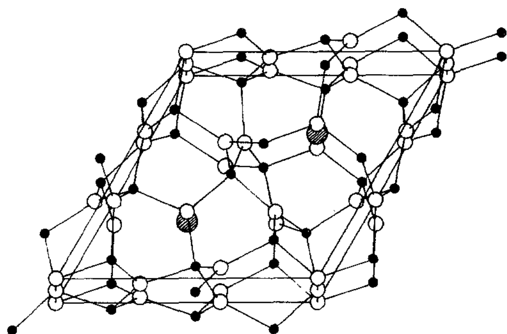

Figure 2 The structure of $M_x(\text{Si, Al})_{12}(\text{N, O})_{16}$ viewed along a direction which is nearly parallel to the c axis. Modifying cations are represented by shaded circles, (Si, Al) atoms by black spheres and (N, O) atoms by open circles.

appreciably in any of the Si and N positions respectively. The cell volume is 3.4% (Ca α-sialon) or 3.2% (Y α-sialon) greater than that of α-Si_3N_4 [8]. Park *et al.* [4] pointed out that the replacement of Si–N bonds by Al–N bonds primarily causes these increases in cell volume.

If the starting mixtures were thoroughly reacted to give only α-sialons, the values of x would be equal to 0.8 for the Ca α-sialon and 0.6 for the Y α-sialon. The metal contents calculated from the occupation factors for the interstitial sites were somewhat lower than those in the starting materials: $x = 0.678$ (Ca α-sialon) and $x = 0.544$ (Y α-sialon). These values are in good agreement with those determined by AEM: $x = 0.67$ (Ca α-sialon) and $x = 0.50$ (Y α-sialon). Minimum and maximum observed values of x are 0.5 and 1.6 for Ca α-sialons [7] and 0.33 and 0.67 for Y α-sialons [6]. The x values obtained for the present samples are within these solubility ranges. The standard

TABLE III M–(N, O) and (Si, Al)–(N, O) bond lengths for the Ca and Y α-sialons*

Bond	Ca α-sialon length (nm)	Y α-sialon length (nm)
M–(N, O)_2	0.236(1)	0.234(1)
$\text{M–(N, O)}_{3,\text{a}}$	0.2601(6)	0.2606(8)
$\text{M–(N, O)}_{3,\text{b}}$	0.2601(6)	0.2606(8)
$\text{M–(N, O)}_{3,\text{c}}$	0.2601(7)	0.2606(9)
M–(N, O)_4	0.2694(3)	0.2686(3)
$\text{M–(N, O)}_{4,\text{d}}$	0.2694(2)	0.2686(3)
$\text{M–(N, O)}_{4,\text{e}}$	0.2694(4)	0.2686(4)
$(\text{Si, Al})_1\text{–(N, O)}_{2,\text{f}}$	0.1764(2)	0.1758(3)
$(\text{Si, Al})_1\text{–(N, O)}_3$	0.1700(8)	0.170(1)
$(\text{Si, Al})_1\text{–(N, O)}_{3,\text{g}}$	0.180(1)	0.180(1)
$(\text{Si, Al})_1\text{–(N, O)}_{4,h}$	0.1794(4)	0.1754(5)
$(\text{Si, Al})_2\text{–(N, O)}_1$	0.1738(1)	0.1751(1)
$(\text{Si, Al})_2\text{–(N, O)}_{3,\text{b}}$	0.1798(4)	0.1786(5)
$(\text{Si, Al})_2\text{–(N, O)}_4$	0.1742(9)	0.173(1)
$(\text{Si, Al})_2\text{–(N, O)}_{4,\text{f}}$	0.1747(9)	0.177(1)

*Symmetry operations: (a) $x, 1+y, z$; (b) $-y, x-y, z$; (c) $1+y-x, 1-x, z$; (d) $1-y, 1+x-y, z$; (e) $y-x, 1-x, z$; (f) $y, x, -1/2+z$; (g) $x-y, -y, 1/2+z$; (h) $1-y, x-y, z$.

deviations of the occupation factors as low as 0.002 reflect the great sensitivity of X-ray intensities of some reflections to the metal content [4, 7].

As exemplified by this work, Rietveld analysis is a most excellent technique by which crystal structure parameters can be refined from powder diffraction data. It was originally devised for the analysis of neutron data but is now being used increasingly widely with X-ray data. Although Rietveld refinement has so far been applied to few ceramic materials, it will soon become an indispensable means of characterization. It will find wider applications in this field if some advanced features such as a multiphase capability and application of constraints are used.

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