Electron density distribution and crystal structure of 27R-SiAlON, Si$_{3-x}$Al$_{6+x}$O$_x$N$_{10-x}$ ($x \sim 1.9$)

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The 27R-SiAlON crystal with the general formula Si$_{3-x}$Al$_{6+x}$O$_x$N$_{10-x}$ (Z = 3) was characterized using laboratory X-ray powder diffraction (Cu Kα) and energy dispersive X-ray spectroscopy. The [Si:Al] molar ratios were determined to be [0.12(1):0.88(1)], corresponding to $x = 1.9(1)$. The Si$_{12}$Al$_{36}$O$_{46}$N$_{50}$ (centrosymmetric) compound is trigonal with space group $R3m$ (centrosymmetric). The hexagonal unit-cell dimensions are $a = 0.30591(4)$ nm, $c = 7.1454(1)$ nm and $V = 0.57940(1)$ nm$^3$. The structural parameters of the initial model were taken from those of 27R-AlON (Al$_9$O$_3$N$_7$), which were subsequently refined by the Rietveld method. The final structural model showed the positional disordering of two of the five types of (Si,Al) sites. The maximum-entropy method-based pattern fitting method was used to confirm the validity of the split-atom model, in which conventional structure bias caused by assuming intensity partitioning was minimized. The disordered crystal structure was successfully described by overlapping five types of domains with ordered atom arrangements. The distribution of atomic positions in one of the five types of domains can be achieved in the space group $R3m$. The atom arrangements in the four other domains are noncentrosymmetric with the space group $R3m$. Two of the four types of domains are related by a pseudo-symmetry inversion, and the two remaining domains also have each other the inversion pseudo-symmetry. The very similar domain structure was also reported for 27R-AlON.

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1. Introduction

Silicon aluminium oxynitride (SiAlON) compounds are technically important materials for high temperature engineering applications. In the quaternary system Si$_3$N$_4$–SiO$_2$–Al$_2$O$_3$–AlN, there are six SiAlON polytypoids (8H, 15R, 12H, 21R, 27R and 2H) established so far at the compositions between β-SiAlON and AlN.1) In the notation of Ramsdell,2) the polytypoids with the general formula (Si,Al)$_{16}$O$_m$(N$_{1+m}$)$_{m+1}$ are denoted as 2mH (m even) and 3mR (m odd). For aluminium oxynitride (AlON) polytypoids with the general formula Al$_m$O$_n$(N$_{m+n}$)$_{m+n-3}$, the crystal structure of 27R (n = 9) has been successfully determined using the recent analytical techniques for X-ray powder diffraction (XRPD) data and as described below. The crystal structure has shown positional disordering of two of the five types of Al sites. This disordered structure with space group $R3m$ has been considered to be a statistical average of the five types of structural configurations with ordered atom arrangements. The distribution of atomic positions in one of the structural configurations can be achieved in the space group $R3m$ (centrosymmetric). The atom arrangements in the four other configurations are noncentrosymmetric with the space group $R3m$.

Recent advances in the field of crystal-structure analysis from XRPD data have enabled us to investigate unknown structures as well as complex structures, including positional disordering of atoms. To begin with initial structural models, the structural parameters of which are subsequently refined using the Rietveld method.3) A combined use of the Rietveld method, the maximum-entropy method (MEM)4) and the MEM-based pattern fitting (MPF) method5) has enabled us to disclose new structural details. MEM is capable of estimating structure factors of unobserved reflections and improving those of overlapped reflections, which give MEM advantages over the classical Fourier method. However, the Rietveld method and MEM have a drawback in determining the electron-density distributions (EDDs) because the observed structure factors, $F_{o}$(Rietveld), are biased toward the structural model assuming intensity partitioning. On the other hand, the MPF method can minimize the structural bias. Thus, the MEM and MPF analyses are alternately repeated (REMEDY cycle) until the reliability indices reach minima.6) Crystal structures can be seen clearly from EDDs determined by MPF.

In the present study, we have investigated the crystal structure of 27R-SiAlON by XRPD; the initial structural model, being isomorphous with that of 27R-AlON (Al$_9$O$_3$N$_7$), has been refined by the Rietveld method. The validity of the final structural model has been confirmed by the three-dimensional EDDs determined by the MPF method. The general formula of Si$_{6-x}$Al$_{12+x}$O$_{28-2x}$N$_{20-2x}$ ($z = 4–5.5$) was used for 27R-SiAlON.1) However, the number of formula unit (Z) in the hexagonal unit cell is non-integral (=1.5) for this formula. Thus, we have adopted a modified general formula of Si$_{3-x}$Al$_{6+x}$O$_x$N$_{10-x}$ ($x = 2–2.75$) with Z = 3.

2. Experimental

The reagent-grade chemicals of Si$_3$N$_4$ (99.9%, KCL Co., Ltd., Saitama, Japan), Al$_2$O$_3$ (99%, Kishida Chemical Co., Ltd., Osaka, Japan), AlN (99.9%, KCL Co., Ltd., Saitama, Japan) and SrCO$_3$ (99.5%, Mitsua Chemical Co., Ltd., Kanagawa, Japan) were mixed in molar ratios of [Si$_3$N$_4$:Al$_2$O$_3$:AlN:SrCO$_3$] = [1:2.8:1.375], corresponding to [Si:Al:Sr] = [0.183:0.733:0.084]. The well-mixed chemicals were heated under a nitrogen pressure of 0.1 MPa at 2023 K for 1 h, followed by cooling to ambient temperature by cutting furnace power. The reaction product was a
sintered material consisting of platelet crystals of 27R-SiAlON and interstitial liquid phase (now amorphous phase at ambient temperature). A part of the sintered specimen was finely ground to obtain powder specimen, and a polished section was prepared for the other part of the specimen.

A diffractometer (X’Pert PRO Alpha-1, PANalytical B.V., Almelo, the Netherlands), equipped with an incident-beam Ge(111) Johannson monochromator to obtain CuK$_\alpha$ radiation and a high-speed detector was used in the Bragg–Brentano geometry. The X-ray generator was operated at 45 kV and 40 mA. An automatic divergence slit was used to keep a constant illuminated length of 5 mm on the specimen surface. Other experimental conditions were: continuous scan, experimental 2$\theta$ range from 5.01 to 141.19°, 8150 total data points and 7.7h total experimental time. The entire experimental diffraction pattern was employed for the crystal-structure analysis. Structural parameters were refined by the Rietveld method using the computer program RIETAN-FP. The crystal-structure models, equidensity isosurfaces of EDDs and two-dimensional EDD map were visualized with the computer program VESTA.

The microtexture on the polished-section surface was observed using a scanning electron microscope (SEM; JSM-6010LA, JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray analyzer (EDX; JED-2300, JEOL Ltd., Tokyo, Japan). Spot analyses were made on the polished surface to determine the molar ratios of Si, Al and Sr. The correction for intensities was made using the ZAF routines, which use fundamental factors to correct for the effects of atomic number (Z), absorption (A) and fluorescence (F). The derived [Si:Al] molar ratios must be accurate and reliable because the unreliability induced mainly by the Z correction would be minimized for the adjacent elements of Si and Al in the third period of the periodic table. On the other hand, the analytical results on the lighter elements of O and N would be inferior in quantitativeness for the EDX analysis.

3. Results and discussion

3.1 Chemical composition

The platelet crystals of 27R-SiAlON in Fig. 1 were uniformly distributed within the matrix of liquid phase that is now amorphous at ambient temperature as evidenced by XRPD. The regions of the former were darker in contrast to the latter. The EDX spectrum shows the existence of Si, Al, O and N atoms and absence of Sr atoms in the crystal [Fig. 2(a)]. The molar ratios of [Si:Al] were quantitatively determined for 9 crystal fragments (27 measurement points) to be [0.12(1):0.88(1)], where the numbers in parentheses indicate standard deviations. Thus, the x-value of the general formula Si$_{3-x}$Al$_x$O$_x$N$_{10-x}$ would be 1.9(1) for the present 27R-SiAlON, corresponding to the chemical formula Si$_{111/4}$Al$_{1/4}$O$_{1/4}$N$_{81/4}$ (Z = 3). The chemical composition of the liquid phase was found to be rich in Sr content. We determined the average [Si:Al:Si] molar ratios by examining ten points randomly in the liquid-phase region to be [0.23(2):0.60(6):0.17(4)] [Fig. 2(b)]. In the Si–Al–Sr triangular diagram (Fig. 3), the average composition of the starting mixture almost lie on the tie line connecting those of 27R-SiAlON and interstitial liquid phase, which indicates that the sample is composed exclusively of the two phase (crystalline 27R-SiAlON and liquid).

3.2 Structure refinement

All of the diffraction peaks in Fig. 4 were successfully indexed with a rhombohedral unit cell with hexagonal axes of $a \approx 0.306$ nm and $c \approx 7.145$ nm. We constructed the initial structural model with the space group $R3m$, the structural parameters of which...
were taken from those of 27R-AlION (Al₉O₃N₇). In this model, there are 12 independent sites in the unit cell: 7 (Si,Al) sites at Wyckoff positions 3a (Si,Al)1 and 6c (Si,Al)2, (Si,Al)3, (Si,Al)4A, (Si,Al)4B, (Si,Al)5A and (Si,Al)5B and 5 (O,N) sites at 6c. The cation-site pair of (Si,Al)4A and (Si,Al)4B and that of (Si,Al)5A and (Si,Al)5B are the split sites of the same symmetry sites of 6c.

The structural parameters of all atoms were refined by the Rietveld method using the computer program RIETAN-FP. A Legendre polynomial was fitted to background intensities with twelve adjustable parameters. The split Pearson VII function was used to fit the peak profile. The O and N atoms were assumed to be randomly distributed over the same sites in the crystal structure, although there might be the site preference of these atoms; the occupancies (g) of O and N atoms in each (O,N) site were fixed at g(O) = 0.19 and g(N) = 0.81. The isotropic displacement (U) parameters for (O,N) sites were constrained to be equal. The distribution of (Si,Al) atoms between (Si,Al)4A and (Si,Al)4B sites, and that between (Si,Al)5A and (Si,Al)5B sites were determined by imposing the linear constraints of g((Si,Al)-4A) + g((Si,Al)4B) = 1 and g((Si,Al)5A) + g((Si,Al)5B) = 1. The parameters U((Si,Al)4A) and U((Si,Al)4B) were constrained to be equal, and so the parameters U((Si,Al)5A) and U((Si,Al)5B).

Because the g-values and corresponding U parameters were strongly correlated, they were refined alternately in successive least-squares cycles. The subsequent Rietveld refinement resulted in the satisfactory U parameters for all the sites with R indices of $R_{wp} = 5.36\%$ ($S = 1.24$), $R_B = 4.22\%$, $R_B = 8.64\%$ and $R_F = 7.02\%$, indicating that the disordered arrangements of both (Si,Al)4 and (Si,Al)5 sites can be represented adequately with the split-atom model in Fig. 5. The separation distances of these split sites are 0.072(1) nm for (Si,Al)4A-(Si,Al)4B and 0.073(1) nm for (Si,Al)5A-(Si,Al)5B. Crystal data are given in Table 1, and the final atomic positional and U parameters are given in Table 2. The selected interatomic distances, together with their standard deviations, are listed in Table 3. It should be noted that the g-values of (Si,Al)4A, (Si,Al)4B, (Si,Al)5A and (Si,Al)5B are, respectively, nearly equal to 5/6, 1/6, 7/12 and 5/12. These g-values of the split sites are in fair agreement with those of 27R-AlION (g((Si,Al)4A) = 0.83, g((Si,Al)4B) = 0.17, g((Si,Al)5A) = 0.59 and g((Si,Al)5B) = 0.41). The similarity in corresponding g-values between 27R-SiAlO and 27R-AlION will eventually cause almost the same abundance of domains with ordered structures, which will be mentioned later.

The MPF method was subsequently used to confirm the validity of the split-atom model. The EDDs with 30 × 30 × 716 pixels in the unit cell, the spatial resolution of which is ca. 0.010 nm, were obtained from the MPF method using the computer programs RIETAN-FP and Dysnomia. After one REMEDY cycle, $R_B$ and $R_F$ further decreased to 3.55 and 2.47%, respectively ($R_{wp} = 5.34\%$, $S = 1.23$ and $R_B = 4.17\%$). Subtle EDD changes as revealed by MPF significantly improve the $R_B$ and $R_F$. The decreases in $R$ indices demonstrate that the crystal structure can be seen more clearly from EDD instead of from the conventional structural parameters reported in Table 2. Observed, calculated, and difference XRPD patterns for the final MPF are plotted in Fig. 4. The EDDs determined by MPF are in reasonably good agreement with the atom arrangements (Fig. 6). For example, the three-dimensional EDDs at the (Si,Al)4 and (Si,Al)5 sites were elongated along the c-axis, the equidensity iso-surfaces of which are in harmony with the atom arrangements. The 2D EDD map at the height of (Si,Al)4 and (Si,Al)5 sites shows that the positions of split (Si,Al) sites are successfully disclosed by the EDDs (Fig. 7). We found the peak positions of EDDs from the 3D pixel data and compared them with the coordinates of all atoms that were determined by the Rietveld
method. The positional deviations of all atoms in the unit cell were found to be necessarily less than 0.002 nm, which is within the resolution limit of the 3D EDDs. We therefore concluded that, as long as the crystal structure was expressed by a ball-and-stick model, the present split-atom model would be satisfactory.

The two types of crystals, 27R-SiAlON and 27R-AlON, have been found to be isostructural to each other. The marked difference is their unit-cell dimensions; both the \(a\)- and \(c\)-dimensions were shorter for 27R-SiAlON (\(a = 0.30599(4)\) nm and \(c = 7.1454(1)\) nm) than for 27R-AlON (\(a = 0.30656(2)\) nm and \(c = 7.2008(3)\) nm).

### 3.3 Structure description

The crystal structure is made up of the coordination elements of one \([\text{Si},\text{Al})(\text{O},\text{N})_6\] octahedron and six types of \([\text{Si},\text{Al})(\text{O},\text{N})_4\] tetrahedra. The ionic radii of Si\(^{4+}\) and Al\(^{3+}\) in the sixfold

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**Table 1. Crystal data for Si\(_{1.1}\)Al\(_{7.9}\)O\(_{1.9}\)N\(_{8.1}\)**

| Chemical composition | \(\text{Si}_{1.1}\text{Al}_{7.9}\text{O}_{1.9}\text{N}_{8.1}\) |
|----------------------|----------------------------------|
| Space group          | \(R3m\) (No. 166)                |
| \(a/\text{nm}\)       | 0.30599(4)                       |
| \(c/\text{nm}\)       | 7.1454(1)                        |
| \(V/\text{nm}^3\)     | 0.57940(1)                       |
| \(Z\)                | 3                                |
| \(D_0/\text{Mg}\text{m}^{-1}\) | 3.336                           |

**Table 2. Structural parameters and isotropic atomic displacement parameters for Si\(_{1.1}\)Al\(_{7.9}\)O\(_{1.9}\)N\(_{8.1}\)**

| Site | Wyckoff position | \(g\) | \(x\) | \(y\) | \(z\) | \(10^4 \times U/\text{nm}^2\) |
|------|------------------|-------|-------|-------|-------|-----------------------------|
| \([\text{Si},\text{Al})\text{1}\] | 3a    | 1     | 0     | 0     | 0     | 1.47(13)                    |
| \([\text{Si},\text{Al})\text{2}\] | 6c    | 1     | 0     | 0     | 0.29478(4) | 0.69(8)                    |
| \([\text{Si},\text{Al})\text{3}\] | 6c    | 1     | 0     | 0     | 0.07423(4) | 1.07(8)                    |
| \([\text{Si},\text{Al})\text{4A}\] | 6c    | 0.811(8) | 0  | 0     | 0.22450(7) | 1.04(10)                   |
| \([\text{Si},\text{Al})\text{4B}\] | 6c    | 0.189 | 0     | 0     | 0.2142(3)  | 1.04                        |
| \([\text{Si},\text{Al})\text{5A}\] | 6c    | 0.577(8) | 0 | 0     | 0.1433(19) | 1.03(13)                   |
| \([\text{Si},\text{Al})\text{5B}\] | 6c    | 0.424 | 0     | 0     | 0.1555(1)  | 1.03                        |
| \([\text{O},\text{N})\text{1}\] | 6c    | 1     | 0     | 0.31962(8) | 1.34(9)                   |
| \([\text{O},\text{N})\text{2}\] | 6c    | 1     | 0     | 0.0470(1)  | 1.34                        |
| \([\text{O},\text{N})\text{3}\] | 6c    | 1     | 0     | 0.2513(1)  | 1.34                        |
| \([\text{O},\text{N})\text{4}\] | 6c    | 1     | 0     | 0.11570(9) | 1.34                        |
| \([\text{O},\text{N})\text{5}\] | 6c    | 1     | 0     | 0.1839(1)  | 1.34                        |

Site occupancies: \([\text{Si},\text{Al})\] sites: 12.2% Si and 87.8% Al; \([\text{O},\text{N})\] sites: 19.0% O and 81.0% N.

**Table 3. Selected bond lengths (nm) for Si\(_{1.1}\)Al\(_{7.9}\)O\(_{1.9}\)N\(_{8.1}\)**

| Bond | \(d/\text{nm}\) |
|------|-----------------|
| \([\text{Si},\text{Al})\text{1}-(\text{O},\text{N})\text{1}\] | 0.2020(3) |
| \([\text{Si},\text{Al})\text{2}-(\text{O},\text{N})\text{1}\] | 0.1773(5) |
| \([\text{Si},\text{Al})\text{2}-(\text{O},\text{N})\text{2}\] | 0.1866(2) |
| \([\text{Si},\text{Al})\text{3}-(\text{O},\text{N})\text{2}\] | 0.184 |
| \([\text{Si},\text{Al})\text{4A}-(\text{O},\text{N})\text{3}\] | 0.1918(8) |
| \([\text{Si},\text{Al})\text{4A}-(\text{O},\text{N})\text{4}\] | 0.1836(2) |
| \([\text{Si},\text{Al})\text{4A}-(\text{O},\text{N})\text{5}\] | 0.186 |
| \([\text{Si},\text{Al})\text{4B}-(\text{O},\text{N})\text{4}\] | 0.1781(2) |
| \([\text{Si},\text{Al})\text{4B}-(\text{O},\text{N})\text{5}\] | 0.217(2) |
| \([\text{Si},\text{Al})\text{5A}-(\text{O},\text{N})\text{4}\] | 0.197(1) |
| \([\text{Si},\text{Al})\text{5A}-(\text{O},\text{N})\text{5}\] | 0.1816(2) |
| \([\text{Si},\text{Al})\text{5B}-(\text{O},\text{N})\text{5}\] | 0.218(1) |
| \([\text{Si},\text{Al})\text{5B}-(\text{O},\text{N})\text{6}\] | 0.179(2) |

Fig. 5. Crystal structure of 27R-SiAlON (\(\text{Si}_{1.1}\text{Al}_{7.9}\text{O}_{1.9}\text{N}_{8.1}\)). All the atoms are expressed as solid spheres. Because the occupancies of (Si,Al)4A, (Si,Al)4B, (Si,Al)5A and (Si,Al)5B sites are less than unity, the (Si,Al) atoms occupying there are displayed as blue circle graphs for occupancies. Red and yellow bicolor balls are for oxygen (red) and nitrogen (yellow) sites. Atom numbering corresponds to that given in Table 2.
coordinates \[ \tau(\text{Si}^{4+}(6)) = 0.0400 \text{ nm}, \quad \tau(\text{Al}^{3+}(6)) = 0.0535 \text{ nm}, \quad \tau(\text{O}^{2-}(4)) = 0.138 \text{ nm} \] and \[ \tau(\text{N}^{3-}(4)) = 0.146 \text{ nm} \] predicts the interatomic distance of 0.178 nm for Si–O, 0.186 nm for Si–N, 0.192 nm for Al–O and 0.200 nm for Al–N. Thus, (Si,Al)–(O,N) distances in [(Si,Al)(O,N)6] octahedron (=0.2020 nm in Table 3) is comparable to the Al–O and Al–N distances, strongly suggesting the preferred occupation of Al atoms at the octahedral site. The tetrahedrally coordinated Si and Al normally have the interatomic distances of 0.162 nm for Si–O, 0.175 nm for Al–O and 0.187 nm for Al–N. \[ \text{Thus, the average interatomic distances of } [(\text{Si,Al})(\text{O,N})4] \text{ tetrahedral in } \text{Si}_{1.1}\text{Al}_{7.9}\text{O}_{1.9}\text{N}_{8.1}, \text{ ranging from 0.184 to 0.189 nm (Table 3), indicate that the (O,N) sites would be actually occupied by both O and N atoms. There is a possibility of site preference of O and N in the (O,N) sites. However, the information available at present on atom distances is insufficient for the significant results.} \]

In our previous study, we have speculated that the disordered crystal structure of 27R-AlON is made up of the five types of domains with the ordered atom arrangements \[ \text{[8]. One of the most plausible explanations to interpret the disordered crystal structure of } \text{Si}_{1.1}\text{Al}_{7.9}\text{O}_{1.9}\text{N}_{8.1} \text{ is to, in a similar manner, consider the structure to be a statistical average of several structural configurations. From the parent disordered structural model as shown in Fig. 5, we have successfully extracted five types of ordered atom arrangements, which are termed I, II, III, VI and V (Fig. 8).} \]

All of the ordered models are free from the neighboring cations of (Si,Al)4B and (Si,Al)5A, because the interatomic distance of (Si,Al)4B–(Si,Al)5A (=0.249 nm) is unusually short as compared with those of (Si,Al)4A–(Si,Al)5B (=0.364 nm), (Si,Al)4A–(Si,Al)5A (=0.302 nm) and (Si,Al)4B–(Si,Al)5B (=0.3026 nm). The atom arrangement in the unit cell of model I is centrosymmetric with the space group \[ R3m; \text{ the number of each (Si,Al) atom in the unit cell } (N) = \frac{N(\text{Si,Al}1)}{3} = \frac{N(\text{Si,Al}2)}{6} = \frac{N(\text{Si,Al}3)}{3}, \text{ and } \frac{N(\text{Si,Al}5A)}{6} \text{ and } \frac{N(\text{Si,Al}5B)}{6} \text{ are all equal to three. The number of each (Si,Al) site in the unit cell of the ordered models are summarized in Table 4.} \]

The five types of atom arrangements of II, III, VI and V are noncentrosymmetric with the space group \[ R3m. \text{ When the center of symmetry is removed from the space group } R3m, \text{ the resulting space group is } R3m. \text{ The two structural configurations of II and III and those of VI and V (Fig. 8) are therefore related by a pseudo-symmetry inversion. Both of the atomic configurations of II and III are free from the (Si,Al)4B site. With the models IV and V, the } N(\text{Si,Al}4A)+N(\text{Si,Al}4B)+N(\text{Si,Al}5A)-N(\text{Si,Al}5B) \text{-values are all equal to three. The number of each (Si,Al) site in the unit cell of the ordered models are summarized in Table 4.} \]

The similar domain structures have been also proposed for oxycarbides, oxycarbonitrides and AlON. \[ (19-25) \]

The five types of atom arrangements of II, III, VI and V are composed of three types of basic building elements. They are (i) the sheet of \[ [(\text{Si,Al})(\text{O,N})6] \text{ octahedra (the octahedral sheet),} \]

(ii) the sheets of \[ [(\text{Si,Al})(\text{O,N})4] \text{ tetrahedra (the tetrahedral sheet),} \]

where \[ M(\text{O,N})i \text{-values are all equal to three. The number of each } (\text{Si,Al}) \text{ site in the unit cell of the ordered models are summarized in Table 4.} \]

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where \[ M(\text{O,N})i \text{-values are all equal to three. The number of each } (\text{Si,Al}) \text{ site in the unit cell of the ordered models are summarized in Table 4.} \]
A disordered structural model is given by $\{A(d_m)\}^{N(M)} m$, where $N(M)m$ is the number of cation $M$ in the unit cell of the ordered model $m$. The most simple and plausible $A(d_m)$-values ($A(d_m) = 1$) which satisfy both equations of $[\Sigma(A(d_m) \times N(A14A)_m)]:[\Sigma(A(d_m) \times N(A14B)_m)]=[5/6:1/6]$ and $[\Sigma(A(d_m) \times N(A15A)_m)]:[\Sigma(A(d_m) \times N(A15B)_m)]=[7/12:5/12]$ are $A(d_{I})=A(d_{II})=A(d_{III})=A(d_{IV})=A(d_{V})=1/6$ and $A(d_{VI})=A(d_{VII})=1/4$. This implies that the formation abundance of domains II and III is 1.5 times larger than that of the other domains; $[A(d_{I}):A(d_{II}):A(d_{III}):A(d_{IV}):A(d_{V})]=[2:3:3:2:2]$.

The size of the five types of domains probably distributes between those of the unit cell and the wavelength of X-rays. These domains would be combined randomly in order to form the whole disordered structure. In the resultant structure, there are vacant sites between the two $(O,N)$ layers, which correspond to the vacant cation sheet of the ordered models. The present
domain structure could be formed during crystal growth or high-low phase transformation during cooling. With 27R-AION (Al$_2$O$_3$N$_7$) in our previous study, we have derived exactly the same domain abundance of $[A(d_1):A(d_2):A(d_3):A(d_4):A(d_5)] = [2:3:2:2:2]$. The more detailed examination would be necessary to clarify the formation mechanism of the disordered structures of 27R-SiAlION and 27R-AION.

4. Conclusion

We clarified the disordered crystal structure of 27R-SiAlION (Si$_{1.1}$Al$_{7.5}$O$_{15}$N$_{3.1}$O$_{1.5}$), which was satisfactorily represented by the split-atom model with the space group R$ar{3}$m. The validity of the structural model was confirmed by the EDDs determined by MFP. The disordered crystal structure was interpreted to be a statistical average of the five types of ordered atom arrangements. One of them was centrosymmetric with the space group R$ar{3}$m, and the four others were noncentrosymmetric with the space group R$ar{3}$m. We speculated the disordered crystal structure to be made up of the five types of domains with ordered atom arrangements. The very similar domain structure was also reported for 27R-AION in our previous study.

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