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Electron density distribution and disordered crystal structure of 15R-SiAlON, SiAl₄O₂N₄

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ABSTRACT

The crystal structure of SiAl₄O₂N₄ was characterized by laboratory X-ray powder diffraction (CuKα₁). The title compound is trigonal with space group *R*3*m*. The hexagonal unit-cell dimensions (*Z*=3) are *a*=0.301332(3) nm, *c*=4.18616(4) nm and *V*=0.3291825(5) nm³. The initial structural model was successfully derived by the charge-flipping method and further refined by the Rietveld method. The final structural model showed the positional disordering of one of the three (Si,Al) sites. The maximum-entropy method-based pattern fitting (MPF) 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 reliability indices calculated from the MPF were *R*_{wp}=5.05%, *S* (= *R*_{wp}/*R*_e)=1.21, *R*_p=3.77%, *R*_B=1.29% and *R*_f=1.01%. The disordered crystal structure was successfully described by overlapping three types of domains with ordered atom arrangements. The distribution of atomic positions in one of the three types of domains can be achieved in the space group *R*3*m*. The atom arrangements in the other two types of domains are noncentrosymmetrical with the space group *R*3*m*. These two structural configurations are related by the pseudo-symmetry inversion.

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1. Introduction

Silicon aluminum oxynitride (SiAlON) compounds are technically important materials for high temperature engineering applications. In the quaternary system Si₃N₄–SiO₂–Al₂O₃–AlN, there are six SiAlON polytypoids (8*H*, 15*R*, 12*H*, 21*R*, 27*R* and 2*H*) established far at the compositions between β-SiAlON and AlN [1]. In the notation of Ramsdell [2], the polytypoids with the general formula (Si,Al)_{*m*}(O,N)_{*m*+1} are denoted as 2*mH* (*m* even) and 3*mR* (*m* odd). With 15*R* (*m*=5), the structural model with the space group *R*3*m* has been derived from the X-ray powder diffraction (XRPD) data by Thompson [3]. In the structural model, there are eleven independent sites in the unit cell; five (Si,Al) sites at Wyckoff positions 3*a* and six (O,N) sites at 3*a*. One of the (Si,Al)–(O,N) distances (=0.2793 nm) was unusually long as compared with the interatomic distances in [(Si,Al)(O,N)₄] tetrahedra. Bando et al. have investigated the crystal structure as well as the chemical composition of 15*R*-SiAlON (SiAl₄O₂N₄) using the high-resolution transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer and electron energy loss spectrometer [4]. The convergent beam electron diffraction (CBED) patterns showed the possible space groups to be *R*3*m* and *R*3̄*m*.

Since the mirror plane normal to the *c*-axis was absent for the structure image that was obtained from the square area of about 6.3 nm on each side, they proposed the disordered structural model with the space group *R*3*m*. Their structural model is characterized by the splitting of two of the five independent (Si, Al) sites at 3*a*.

For aluminum oxynitride (AlON) polytypoids with the general formula Al_{*n*}O₃N_{*n*-2} [5–9], the crystal structures of 21*R* (*n*=7) [10] and 27*R* (*n*=9) [11] have been successfully determined using the recent analytical techniques for XRPD data as described below. The crystal structures have shown positional disordering of two of the four types of Al sites for 21*R* and two of the five types of Al sites for 27*R*. Each disordered structure with the space group *R*3*m* 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 *R*3̄*m* (centrosymmetrical). The atom arrangements in the four other configurations are noncentrosymmetrical with the space group *R*3*m*.

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 are required, which may be determined by, for example, the charge-flipping method [12]. The structural parameters are subsequently refined using the Rietveld method [13]. A combined use of the Rietveld method, the

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maximum-entropy method (MEM) [14] and the MEM-based pattern fitting (MPF) method [15] 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 [16]. Crystal structures can be seen clearly from EDDs determined by MPF.

In the present study, we have determined the crystal structure of 15R-SiAlON ($\text{SiAl}_4\text{O}_2\text{N}_4$) from XRPD data. The initial structural model has been derived using powder charge-flipping method and further modified into the split-atom model. The validity of the structural model has been confirmed by the three-dimensional EDDs determined by the MPF method.

2. Experimental

The reagent-grade chemicals of Si_3N_4 (99.9%, KCL Co., Ltd., Saitama, Japan), Al_2O_3 (99%, Taimei Chemicals Co. Ltd., Nagano, Japan) and AlN (99.9%, KCL Co., Ltd., Saitama, Japan) were mixed in molar ratios of $[\text{Si}_3\text{N}_4:\text{Al}_2\text{O}_3:\text{AlN}] = [1:2:8]$, corresponding to $[\text{Si}:\text{Al}:\text{O}:\text{N}] = [1:4:2:4]$. 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 slightly sintered polycrystalline material consisting exclusively of $\text{SiAl}_4\text{O}_2\text{N}_4$.

The sintered material was finely ground to obtain powder specimen and introduced into a glass capillary tube of internal diameter of approximately 0.4 mm. The XRPD intensities were collected on a diffractometer in the Debye–Scherrer geometry (SmartLab, Rigaku Co., Tokyo, Japan), which was equipped with an incident-beam $\text{Ge}(111)$ Johansson monochromator to obtain $\text{CuK}\alpha_1$ radiation and a high-speed detector (Rigaku D/teX). The X-ray generator was operated at 45 kV and 200 mA. Other experimental conditions were: continuous scan, experimental 2θ range from 3.0° to 158.0° and a scan speed of $0.2^\circ/\text{min}$, 15,501 total data points and 12.9 h total experimental time. No preferred

orientation could be seen in the diffraction pattern which was collected with the specimen rotating. We corrected the X-ray absorption using the μr value (μ : linear absorption coefficient; r : sample radius) of the sample and capillary tube, which was determined by the transmittance of direct incident beam. The structure data were standardized according to rules formulated by Parthé and Gelato [17] using the computer program STRUCTURE TIDY [18]. The crystal-structure models, equidensity isosurfaces of EDDs, and two-dimensional EDD map were visualized with the computer program VESTA [19].

3. Results and discussion

3.1. Crystal structure determination and refinement

All of the diffraction peaks in Fig. 1 were successfully indexed with a hexagonal unit cell of $a \approx 0.301$ nm and $c \approx 4.19$ nm. The unit-cell parameters and integrated intensities were refined by the Pawley method [20] using the computer program PDXL (Rigaku Co., Tokyo, Japan). The observed diffraction peaks were examined to confirm the presence or absence of reflections. Systematic absences $h-k+l \neq 3n$ for $hkil$ reflections were found, which implies that the possible space groups are $R3$, $R\bar{3}$, $R32$, $R3m$ and $R\bar{3}m$.

All the possible space groups were tested by the powder charge-flipping method [12] using the computer program Superflip [21] for crystal structure determination. Because the atomic scattering factors of Si and Al and those of O and N are nearly the same, a unit-cell content of $[15\text{Al } 18\text{N}]$ was used as input data for the search of an initial structural model. A promising structural model was successfully obtained for the space group $R\bar{3}m$. There are seven independent sites in the unit cell; four (Si,Al) sites at Wyckoff positions $3a$ ((Si,Al)1) and $6c$ ((Si,Al)2A, (Si,Al)2B and (Si,Al)3) and three (O,N) sites at $6c$. Because of the unusually short distance of (Si,Al)2A – (Si,Al)2B (≈ 0.085 nm), these $6c$ sites (point symmetry $3m$) can be regarded as the split sites of the same symmetry site of $6c$.

The structural parameters of all atoms were subsequently refined by the Rietveld method using the computer program RIETAN-FP [22]. A Legendre polynomial was fitted to background intensities with twelve adjustable parameters. The split pseudo-Voigt function [23] was used to fit the peak profile. The Si and Al atoms as well as the O and N atoms were assumed to be randomly

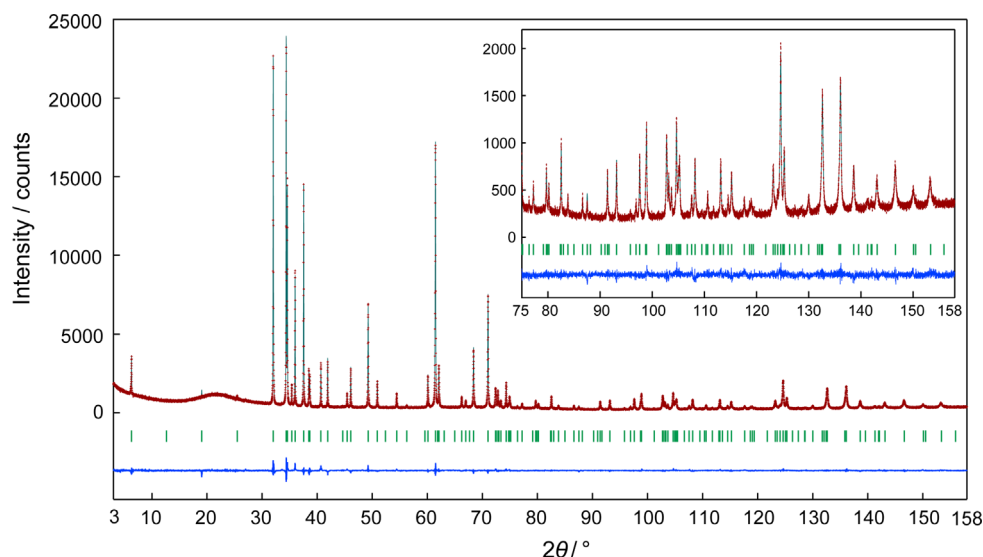


Fig. 1. Comparison of the observed diffraction patterns of $\text{SiAl}_4\text{O}_2\text{N}_4$ (symbol: +) with the corresponding calculated pattern (upper solid line). The difference curve is shown in the lower part of the diagram. Vertical bars indicate the positions of possible Bragg reflections.

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