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Disordered crystal structure of 20*H*-AlON, $Al_{10}O_3N_8$

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ABSTRACT

The disordered crystal structure of 20*H*-AlON ($Al_{10}O_3N_8$) was determined by combined use of X-ray powder diffraction and transmission electron microscopy. The title compound is hexagonal with space group $P6_3/mmc$ ($Z=2$) and the unit-cell dimensions are $a=0.307082(5)$ nm, $c=5.29447(8)$ nm and $V=0.432376(12)$ nm^3. The structural model showed the positional disordering of three of the six Al sites in the unit cell. The reliability indices calculated from the Rietveld method were $R_{wp}=6.97\%$, S ($=R_{wp}/R_e$)$=1.68$, $R_p=5.45\%$, $R_B=5.13\%$ and $R_F=4.56\%$. We interpreted the disordered structure of 20*H*-AlON as a statistical average of six different types of ordered structural configurations, which are composed of an octahedral [Al(O, N)$_6$] layer and tetrahedral [Al(O, N)$_4$] layers. We demonstrated the high correlations between the hexagonal unit-cell dimensions and the octahedral layer concentrations for AlON and SiAlON polytypoids.

1. Introduction

In the region close to aluminum nitride of the AlN–Al_2O_3 phase diagram, three different kinds of aluminum oxynitride (AlON) polytypoids with the general formula $Al_mO_3N_{m-2}$ are established; they are 27*R* with $m=9$ ($Al_9O_3N_7$), 21*R* with $m=7$ ($Al_7O_3N_5$) and 12*H* with $m=6$ ($Al_6O_3N_4$) [1–6]. The notation was given by Ramsdell as 2*mH* (*m* even) or 3*mR* (*m* odd) [7]. In our previous studies, we have already reported the crystal structures of 27*R*- and 21*R*-AlON [8,9]. The 12*H*-AlON should be isostructural with 12*H*-silicon aluminum oxynitride (SiAlON) in the quaternary system Si_3N_4–SiO_2–Al_2O_3–AlN. The crystal structure of 12*H*-SiAlON has been, together with those of 8*H*-, 15*R*- and 27*R*-SiAlON, determined in our previous studies [10–13]. In addition to the AlON polytypoids of 27*R*, 21*R* and 12*H* as already established, Bartram and Slack (1979) [2] and Sakai (1978) [3] have reported, respectively, 20*H*-AlON ($Al_{10}O_3N_8$) and 16*H*-AlON ($Al_8O_3N_6$). These crystal structures as well as their phase stability in the relevant binary phase diagram are still uncertain.

We reported in our previous studies that the crystal structures of AlON and SiAlON polytypoids necessarily showed positional disordering of some of the cation sites, and hence they were expressed by the split-atom models. In the present study, we prepared the 20*H*-AlON polycrystal and clarified the disordered atom arrangements in the crystal structure. The ordered structural model was initially derived from the X-ray powder diffraction (XRPD) data using the direct methods and it was further modified into the disordered (split-atom) model.

2. Experimental

2.1. Material

The reagent-grade chemicals of Al_2O_3 (99%, Taimei Chemicals Co. Ltd., Nagano, Japan) and AlN (99.9%, KCL Co., Ltd, Saitama, Japan) were weighed in molar ratios of [Al_2O_3:AlN]=[1:8], corresponding to [Al:O:N]=[10:3:8]. In our preliminary experiment, the heat treatment under a nitrogen pressure of 1.0 MPa at 2173–2323 K failed to synthesize 20*H*-AlON. Thus, we used a hot isostatic press (HIP, KOBELCO Dr. HIP, Kobe Steel, Ltd., Kobe, Japan) for the successful synthesis at higher temperatures and pressures. The well-mixed chemicals were heated in the HIP at 2673 K for 2 h under a nitrogen pressure of 178 MPa, and then cooled to ambient temperature by cutting the furnace power. We obtained a marginally sintered polycrystalline sample, which was composed of not only 20*H*-AlON but also AlN, 27*R*-AlON, 21*R*-AlON and 12*H*-AlON. With AlON polytypoids, the oxygen content with respect to nitrogen content (i.e., O/N molar ratio) steadily increases from 20*H* (O/N=0.375), 27*R* (O/N=0.429), 21*R* (O/N=0.6) to 12*H* (O/N=0.75).

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2.2. Characterization

We ground a part of the multi-phase sample and obtained the fine powder specimen. The XRPD intensities in the 2θ range of 3.0–148.6° (Cu$K\alpha_1$ operated at 45 kV and 40 mA) with 8714 total data points were collected on a diffractometer in the Bragg-Brentano geometry (X'Pert PRO Alpha-1, PANalytical B.V., Almelo, the Netherlands). We used a computer program VESTA [14] to visualize the structural models.

We prepared the thin specimen from the other part of the sample by argon ion beam milling (Model 695 PIPSII, Gatan Inc., CA, U.S.A.), which was subsequently examined using a transmission electron microscope (TEM, JEM 2010, JEOL ltd., Tokyo, Japan) operated at 200 kV. We obtained the selected-area electron diffraction (SAED) patterns, together with lattice images, to derive the proper unit-cell dimensions.

3. Results and discussion

3.1. Structure determination and modification of the structural model

The SAED patterns of 20*H*-AlON were indexed with a hexagonal unit cell of $a \approx 0.31$ nm and $c \approx 5.30$ nm (Fig. 1), which were readily distinguishable from those of the other AlON compounds with different hexagonal *c*-axis dimensions of ~7.20 nm for 27*R*-AlON [8], ~5.72 nm for 21*R*-AlON [9] and ~3.28 nm for 12*H*-AlON [10]. The lattice image indicates that 20*H*-AlON is generated by stacking layers with the periodicity of ~5.3 nm along the *c*-axis. The presence of 16*H*-AlON, the *c*-axis length of which is ~4.31 nm [3], was not confirmed in the sample.

The XRPD pattern in Fig. 2 was made up of the diffraction intensities peculiar to 20*H*-AlON, AlN, 27*R*-AlON, 21*R*-AlON and 12*H*-AlON. We refined the unit-cell dimensions and integrated intensities of 20*H*-AlON by the Le Bail method [15] using a computer program RIETAN-FP [16]. The structural models of AlN [17], 27*R*-AlON [8], 21*R*-AlON [9] and 12*H*-AlON [10] were included in the refinement as the coexisting phases. We subsequently derived the initial structural model by the direct methods [10] using a program package EXPO2014 [18]. We adopted the space group $P6_3/mmc$ for 20*H*-AlON, because the AlON and SiAlON compounds with the hexagonal Bravais lattice were necessarily of this space group. Because the atomic scattering factors are nearly the same between O and N, we used a unit-cell composition of [20Al and 22N] as input data and derived the initial structural model. The resulting structure data were standardized according to the rules formulated by Parthé and Gelato [19] using a computer program STRUCTURE TIDY [20]. There were thirteen crystallographic sites in the unit cell; seven Al sites at Wyckoff positions 2*a* (Al1), 4*e* (Al3, Al5A and Al5B) and 4*f* (Al2, Al4 and Al6), and six (O, N) sites at 2*b* [(O, N)6], 4*f* [(O, N)1, (O, N)3 and (O, N)5] and 4*e* [(O, N)2 and (O, N)4]. Because the Al5A–Al5B distance (≈ 0.079 nm) was unusually short, we regarded that the corresponding sites (point symmetry $3m$) were the split sites of the same symmetry site of 4*e*. The site occupancy (*g*) of Al6 (point symmetry $3m$) was fixed at 1/2, indicating that it was the split site of the higher symmetry site of 2*b* (point symmetry $\bar{6}m2$).

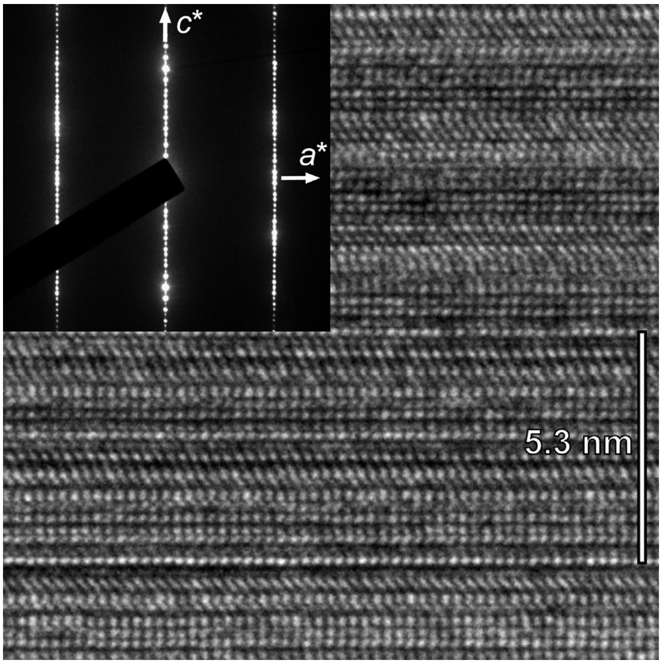

Fig. 1. Selected-area electron diffraction pattern and corresponding lattice image. Incident electron beam is almost in parallel with the hexagonal *a*-axis.

The structural and profile parameters were refined using the Rietveld method [21] on the computer program RIETAN-FP [16]. Each (O, N) site of the structural model was assumed to be necessarily composed of 27.27% oxygen and 72.73% nitrogen, corresponding to [O:N]=[3:8] in molar ratios. We constrained the isotropic displacement (*U*) parameters for all (O, N) sites to be equal. We imposed the linear constraint for *g*-values of Al5A and Al5B as $g(\text{Al5A})+g(\text{Al5B})=1$. The refinement results were, however, unsatisfactory due to the relatively high reliability (*R*) indices [22] ($R_{\text{wp}}=8.04\%$, $S=1.93$, $R_{\text{p}}=6.10\%$, $R_{\text{B}}=6.11\%$ and $R_F=5.35\%$) as well as the relatively large *U*-value of Al4 ($=1.64(10) \times 10^{-2}$ nm^2), which promoted us to split the Al4 site, in addition to the Al5 and Al6 sites, in the modified structural model.

In the modified model, we split the Al4 site into two independent positions of Al4A and Al4B with the same crystallographic site 4*f* and imposed the linear constraint of $g(\text{Al4A})+g(\text{Al4B})=1$. The XRPD patterns that are obtained by observation and calculation for the final Rietveld refinement, together with their difference, are plotted in Fig. 2. The resulting *U* parameters for all the sites were satisfactory with *R* indices of $R_{\text{wp}}=6.97\%$, $S=1.68$, $R_{\text{p}}=5.45\%$, $R_{\text{B}}=5.13\%$ and $R_F=4.56\%$, indicating that the disordered arrangements of Al4, Al5 and Al6 sites can be represented adequately with the modified structural model in Fig. 3. We examined the possibility of noncentrosymmetric models, including those with space group $P6_3mc$. However, this attempt was entirely unsuccessful, because the structural models still required the split sites. We summarized the crystal data in Table 1, and the final atomic positional and *U* parameters in Table 2. The separation distances of atoms are 0.076(2) nm for Al4A–Al4B, 0.0873(8) nm for Al5A–Al5B and 0.0979(11) nm for the split Al6 sites. Selected interatomic distances and their standard deviations are given in Table 3. It should be noted that the *g*-values of split Al sites are necessarily expressed by the relatively simple fractions such as $g(\text{Al4A}) \approx 5/6$ ($=0.8333$), $g(\text{Al4B}) \approx 1/6$ ($=0.1667$), $g(\text{Al5A}) \approx 2/3$ ($=0.6667$) and $g(\text{Al5B}) \approx 1/3$ ($=0.3333$).

As for the coexisting phases (i.e., AlN, 27*R*-AlON, 21*R*-AlON and 12*H*-AlON), we independently refined their scale factors and unit-cell dimensions, while we used the same profile parameters as those of 20*H*-AlON throughout the Rietveld refinement process. In addition, we always fixed their atom coordinates and atomic displacement parameters. As a result, the deviations of unit-cell dimensions of the coexisting phases were necessarily within 0.06% from their initial values. The R_{B} and R_F values of 27*R*-AlON were, respectively, 5.74% and 4.55%.

We quantitatively determined the phase composition of the sample using the phase-analysis method based on Brindley's procedure [23], the subroutine of which was implemented in the