TECHNICAL ARTICLE

Crystal structure of $Al_5O_3N_3$ (15R)

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Having synthesised an AlON-bonded ceramic corundum material, $Al_5O_3N_3$ (15R) polytype coexisting with α-Al_2O_3 was identified. The sample was prepared from an alumina-rich mixture of Al_2O_3 and AlN substrates and fired at 1650 °C in a nitrogen atmosphere. Using the X-ray external standard quantitative method, one of the reaction products, α-Al_2O_3, was quantified. From the remaining substrates the stoichiometric composition of the second phase was calculated. The applied method of crystal structure determination consisted of three stages. In the first stage, the Le Bail method of X-ray pattern decomposition was used for the extraction of $Al_5O_3N_3$ (15R) diffraction lines from a two-phase diffractogram. The space group and unit-cell dimensions from the isostructural $SiAl_4O_2N_4$ SiAlON phase, producing the same X-ray pattern, were used as input data. Next, the direct structure determination in real space was applied for initial structural model derivation, which was followed by Rietveld refinement. The solved crystal structure of $Al_5O_3N_3$ (15R), except the stacking sequence, proved to be closely related to the structure of $Al_7O_3N_5$ (21R) polytype. The $Al_5O_3N_3$ (15R) is trigonal with space group *R*-3*m*, unit-cell dimensions $a_0 = 3.0128$ Å, $c_0 = 41.8544$ Å, and volume $V = 329.00$ Å^3. The model of $Al_5O_3N_3$ (15R) polytype structure has positional disordering in one of three (6c) Al sites, which leads to stacking faults in six tetrahedral layers. Every third tetrahedron from L_{R3} and L_{R4}, L_{R8} and L_{R9}, L_{R13} and L_{R14} layers is rotated by 180°. © *2017 International Centre for Diffraction Data*. [doi:10.1017/S088571561700001X]

Key words: aluminium oxynitride, AlON, $Al_5O_3N_3$

I. INTRODUCTION

Determination of the crystal structure of aluminium oxynitride allows better understanding of its physical properties and currently plays an important role because of the increasing use of this group of materials in a few branches of industry, such as refractory and optic materials.

In the AlN–Al_2O_3 pseudo-binary phase diagram described in the literature, there are three polytypes of aluminium oxynitrides, which differ in the sequence of stacking: $Al_9O_3N_7$ (27R), $Al_7O_3N_5$ (21R), and $Al_6O_3N_4$ (12H) (McCauley, 2002). The possibility for 15R politype to appear in the Al–O–N system by analogy to similar Si–Al–O–N system is postulated (Jack, 1976). In literature, only the crystal structure of the three of them is described: Al_3O_3N (cubic), $Al_7O_3N_5$ (21R), and $Al_9O_3N_7$ (27R) (Lejus, 1962; Asaka *et al*., 2013a, b).

The aim of the work was to solve the crystal structure of the transition phase of $Al_5O_3N_3$ (15R), co-existing in the composite material with α-Al_2O_3 (corundum).

II. EXPERIMENTAL

A. Preparation of aluminium oxynitride-bonded composite

The sample was prepared in the process of two-step synthesis, in a graphite furnace in a nitrogen atmosphere. In the first step, the aluminium powder was fired at 1450 °C in a nitrogen atmosphere. The obtained product contained mainly AlN and small amounts of unreacted Al, α-Al_2O_3, γ-Al_2O_3 solid solution and several forms of aluminium oxynitrides: $Al_8O_3N_6$, $Al_7O_3N_5$, $Al_6O_3N_4$. In the second step, pure α-Al_2O_3 (99.9 wt%), homogenised in ethanol, and the AlN powder, obtained in the first step, were mixed in the ratio of 21:79% by weight, palletised and fired at 1650 °C in a nitrogen atmosphere. The goal was to obtain an AlON-bonded alumina ceramic composite. In the sample, the following were identified: α-Al_2O_3 (corundum) and solid solution isostructural with $SiAl_4O_2N_4$. Figure 1 presents the result of identification of the phase composition of the corundum material with an oxynitride bonding. Owing to the lack of silicon in the material produced, it was assumed that the identified compound was the 15R polytype, $Al_5O_3N_3$, which is isostructural with $SiAl_4O_2N_4$ [PDF 00-042-0160 (ICDD, 2015)].

B. Experimental methods

One of the reaction products, α-Al_2O_3 in a synthesised AlON-bonded alumina composite was quantified using the external standard X-ray method. It was found that the corundum content was 73 wt%. From the remaining substrates the stoichiometric composition of the second phase was calculated. The results of calculations revealed that the second phase could be $Al_5O_3N_3$, whose structure should be solved.

The applied method of crystal structure determination consisted of three stages. In the first stage, the Le Bail method of X-ray pattern decomposition for the extraction of $Al_5O_3N_3$

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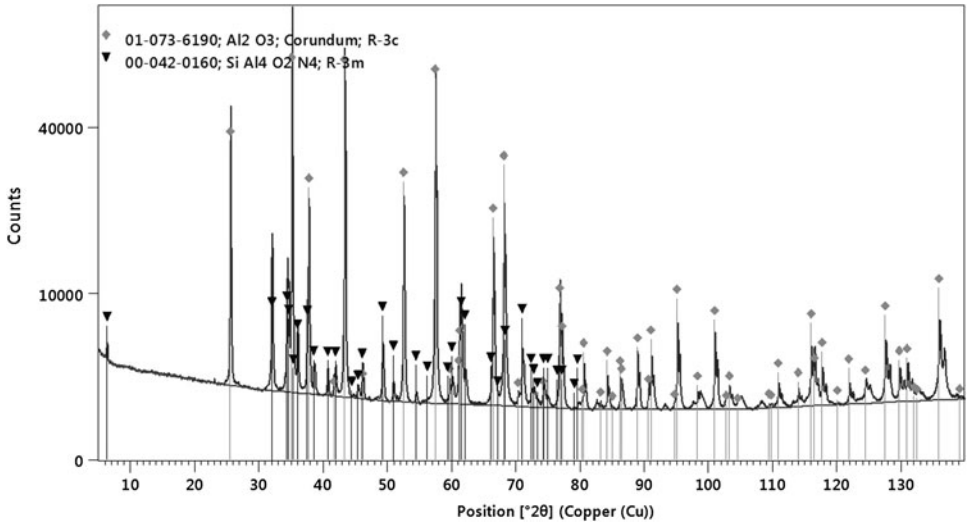

Figure 1. X-ray pattern of Al_2O_3–AlON composite material with identified $SiAl_4O_2N_4$ isostructural with an $Al_5O_3N_3$ aluminium oxynitride compound [PDF 00-042-0160 (ICDD, 2015)].

(15R) diffraction lines from a two-phase diffractogram was used (Le Bail *et al.*, 1988). For this purpose, the HighScorePlus software (PANalytical, 2015) was applied. The space group and unit-cell dimensions from the isostructural $SiAl_4O_2N_4$ phase producing the same X-ray pattern were used as input data [PDF 00-042-0160 (ICDD, 2015)]. After X-ray pattern decomposition only diffraction lines of $Al_5O_3N_3$ (15R) for structure solving were used and input file for next step was prepared. Diffraction lines of corundum were rejected. Only the strongest (40) reflections below 77.3° 2θ and relatively well separated from α-Al_2O_3 ones were taken for structure solving. The high-angle part of a diffraction pattern of $Al_5O_3N_3$ (15R) could be subject to errors both in 2θ and intensity values because of low intensity and several overlaps with α-Al_2O_3 reflections. Next, the direct structure determination in real space was applied for the initial structural model derivation using the Endeavour software (Putz *et al.*, 1999; Crystal Impact, 2009). Endeavour is used for solving structures by means of real-space method based on energy minimisation (Lennard–Jones potential). The advantage of the programme is the fact that it allows using a diffraction pattern in the form of discrete values of intensity and position of reflections, which enables testing samples that are not single phase. The last step of solving the crystal structure of $Al_5O_3N_3$ was Rietveld refinement. In this stage of investigations, HighScorePlus was used.

A PANanalytical X'PERT PRO MPD diffractometer was used for powder X-ray diffraction pattern collection. Data collection within the angular range of 5 to 140°2Θ with Cu$K\alpha$ radiation (40 kV, 30 mA), Ni filter, fixed slits, 0.04 rad. Soller slits and X'Celerator detector was carried out.

III. RESULTS

The $Al_5O_3N_3$ (15R) is trigonal with space group R-3m and refined unit-cell parameters $a_0 = 3.0128$ Å, $c_0 = 41.8544$ Å, and volume $V = 329.00$ Å^3. The calculated density is 3.405 g cm^{-3} and the unit cell contains 33 atoms. The solved crystal structure is presented in Table I and in Figure 2. The model of the structure of $Al_5O_3N_3$ (15R) polytype has positional disordering in Al2 (6c) site; as a result, one-third of the tetrahedrons from layers L_{3R} and L_{4R}, L_{8R} and L_{9R}, L_{13R} and L_{14R} are rotated by 180°. Those stacking faults between layers L_{3R}–L_{4R}, L_{8R}–L_{9R} and L_{13R}–L_{14R} allow joining oxygen/nitrogen layers in the crystal structure. In consequence, the structure consists of 18 layers and in nine of them the tetrahedral

TABLE I. Crystal structure of $Al_5O_3N_3$ (15R).

Atom	Atomic coordinates (x, y, z)	Displacement parameter, U_{iso}	Site occupancy factor, SOF	Multiplicyty, Wyckoff letter
Al1	0, 0, 0	0.0110(6)	1	3a
O1/N1	0, 0, 0.07888(7)	0.024(1)	1	6c
Al2a	0, 0, 0.12661(7)	0.0040(6)	2/3	6c
Al2b	0, 0, 0.1479(2)		1/3	
O2/N2	0, 0, 0.19497(9)	0.040(1)	1	6c
Al3	0, 0, 0.26687(3)	0.0055(5)	1	6c
O3/N3	0, 0, 0.30985(8)	0.011(1)	1	6c
Space group R-3m				
$a_0 = 3{,}01276(5)$ Å				
$b_0 = 3{,}01276(5)$ Å				
$c_0 = 41{,}8544(8)$ Å				
$\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$				
$Z = 3$				
$D_x = 3.405$ g cm^{-3}				

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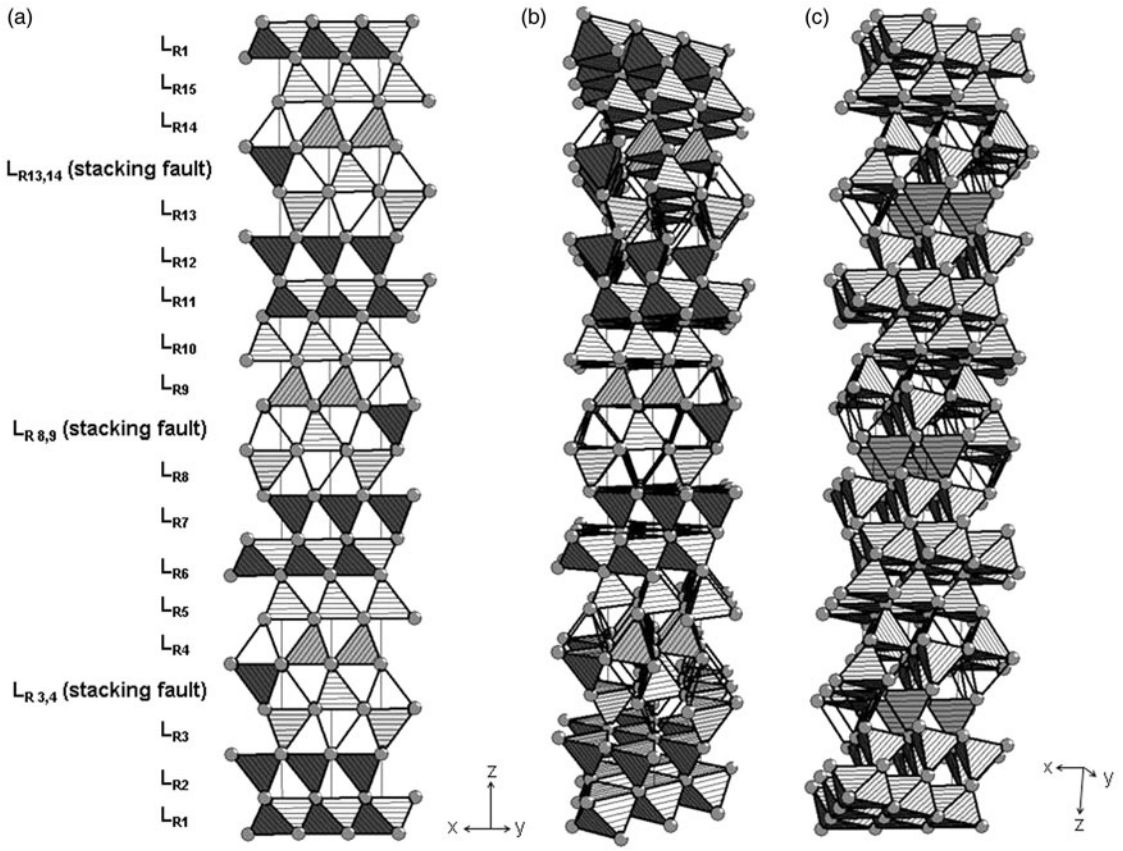

Figure 2. Crystal structure of AlON polytype $Al_5O_3N_3$ (15R): (a) 110 projection, (b) 110 perspective projection, and (c) random projection. The empty tetrahedrons represent unoccupied sites Al2a and Al2b from Table I.

voids are not fully occupied by cations. The empty tetrahedrons in Figure 2 present unoccupied Al2a and Al2b sites. If these both sites Al2a and Al2b were fully occupied, then the unit cell would contain 39 instead of 33 ions. As a result, the stoichiometry corresponding to $Al_5O_3N_3$ would not be retained, leading to densification in the unit cell. The authors of the work (Asaka *et al.*, 2013a), who have solved the structure of a similar solid solution of $Al_7O_3N_5$ (21R), found two separate sites in the structure. They interpreted the obtained result as the existence of five domains differing in their local symmetry: one with *R*-3*m* symmetry and four with *R*-3*m* symmetry.

Table II presents the average cation–anion distances in the tetrahedrons and octahedrons. In the tetrahedrons, they range from 1.784 to 1.998 Å, whereas in the octahedrons they reach 1.998 Å. According to Shannon, the theoretical values of the cation–anion distance in oxides for Al–O in the tetrahedron are 1.770 Å, and in the octahedron – 1.915 Å (Shannon, 1976). On the other hand, in case of the tetrahedral coordination, the Al–N distances calculated from the data published in ICDD database [PDF 01-080-6097 (ICDD, 2015)] reach 1.883 (×3) and 1.927 (×1) Å, whereas in case of the octahedral coordination the distances calculated from ICDD data are 2.023 Å [PDF 00-046-1200 (ICDD, 2015)]. An analysis of the data contained in Table II allows concluding that in O2/N2 site the oxygen ions may be prevailing, while in the remaining anion sites their prevalence is invisible. In the tetrahedrons composed of Al cations from Al2A and Al2b sites, one of the cation–anion distances is extended to the value of 1.998 and 1.971 Å for Al2a–O1/N1 and Al2b–O2/N2, respectively (Table II). The Al2a and Al2b sites are not fully occupied, giving rise to stacking faults.

TABLE II. Average cation–anion distances in octa- and tetrahedral coordinations in the $Al_5O_3N_3$ structure.

Coordination	Ions	Distance (Å)
Octahedral	Al1–O3/N3	1.9978(2) × 6
Tetrahedral	Al2a–O2/N2	1.808(1) × 3
	Al2a–O1/N1	1.998(4) × 1
Tetrahedral	Al2b–O2/N2	1.784(2) × 3
	Al2b–O2/N2	1.971(8) × 1
Tetrahedral	Al3–O1/N1	1.815(1) × 3
	Al3–O3/N3	1.799(3) × 1

The obtained result – the solved structure of alumina oxynitride $Al_5O_3N_3$ (15R) was used to conduct a quantitative analysis of the two-phase mixture consisting of the title compound and corundum by the Rietveld method. The result has been given in Figure 3. The obtained result agrees with the result of a quantitative analysis of corundum in the examined material obtained after its synthesis (73%) within the uncertainty limit.

IV. SUMMARY

The crystal structure of $Al_5O_3N_3$ was solved by X-ray powder diffraction data using the direct space method. The investigations were conducted on a sample of a two-phase mixture consisting of the title compound and corundum. Reflections of $Al_5O_3N_3$ were extracted by the Le Bail method.

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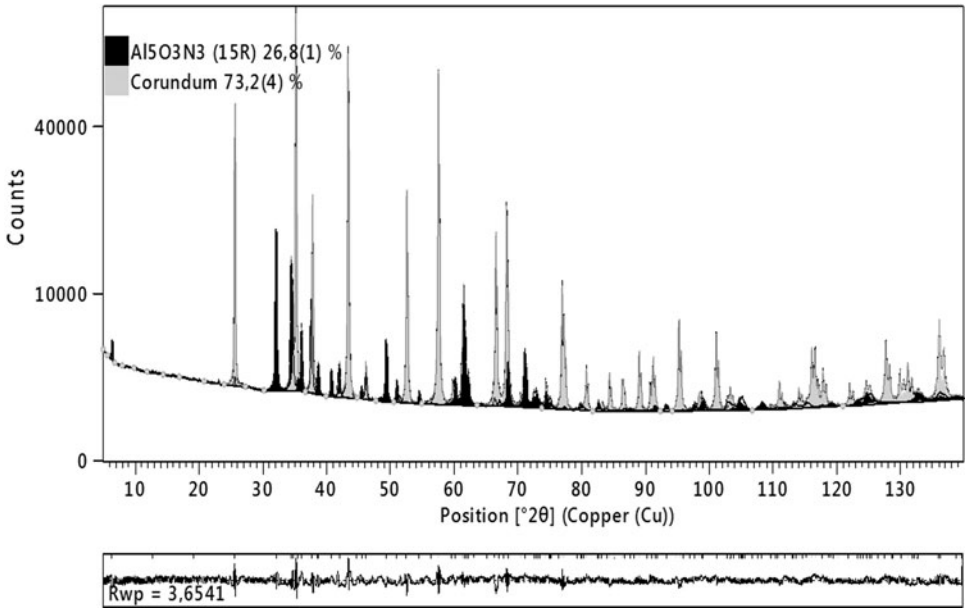

Figure 3. Results of the Rietveld refinement of Al_2O_3–AlON composite material ($GoF = 1.78$; $R_{wp} = 3.65$; $R_{exp} = 2.05$).

The $Al_5O_3N_3$ (15R) is trigonal with space group R-3m, unit-cell dimensions $a_0 = 3.0128$ Å, $c_0 = 41.8544$ Å, and volume $V = 329.00$ Å^3. It was expected that the crystal structure of $Al_5O_3N_3$ (15R) was formed from 15R layers, three octahedral and 12 tetrahedral ones. Stacking faults were found between six tetrahedral layers L_{3R} and L_{4R}, L_{8R} and L_{9R}, L_{13R} and L_{14R}. The stacking fault layers are made up of one-third of the tetrahedrons from these layers, rotated by 180°. These stacking faults between layers L_{3R}–L_{4R}, L_{8R}–L_{9R} and L_{13R}–L_{14R} allow joining oxygen/nitrogen layers in the crystal structure. As a result, the structure consists of 18 layers, three octahedral and 15 tetrahedral ones. In nine of these layers 2/3 of the tetrahedral voids are occupied by cations.

SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/S088571561700001X.

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