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Citation for published version (APA):

Willems, H. X., With, de, G., Metselaar, R., Helmholtz, R. B., & Petersen, K. K. (1993). Neutron diffraction of γ -aluminium oxynitride. *Journal of Materials Science Letters*, 12(18), 1470-1472.
<https://doi.org/10.1007/BF00591611>

DOI:

[10.1007/BF00591611](https://doi.org/10.1007/BF00591611)

Document status and date:

Published: 01/01/1993

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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Neutron diffraction of γ -aluminium oxynitride

H. X. WILLEMS, G. DE WITH*, R. METSELAAR

Centre for Technical Ceramics, Eindhoven University of Technology, POB 595, 5600 AN Eindhoven, The Netherlands

R. B. HELMHOLDT, K. K. PETERSEN†

Netherlands Energy Research Foundation, POB 1, 1755 ZG Petten, The Netherlands

γ -Aluminium oxynitride (Alon) is a ceramic material which can be sintered to transparency [1]. It has a spinel-type crystal structure (space group $Fd\bar{3}m$) and its defect structure can be described with the constant anion model proposed by McCauley [2]. In this model all anion sites are completely occupied whereas the cation sites are only partly occupied. In the spinel-type crystal structure the position of the cation sites can vary according to a certain "spinel parameter" (or " u -parameter"; see, for instance, Galasso [3]). Neutron diffraction was used to establish the exact positions and occupation of sites in the Alon lattice for three compositionally different Alons. Reports of neutron diffraction studies on Alon of a single composition have appeared previously in the literature [4, 5], but the results are inconsistent with respect to the occupation of the cation sites.

Neutron diffraction experiments were performed on Alon powders with compositions corresponding to 67.5, 73 and 77.5 mol % Al_2O_3 . The 73 mol % powder was produced by reacting Al_2O_3 and AlN powders for 3 h at 1750 °C. After reaction the resultant powder was ground with a mortar and pestle to eliminate large particles. X-ray diffraction (XRD) of the powder revealed that residual AlN was present.

Because the other two powders are not stable at 1750 °C [6], these powders were made at the higher temperature of 1850 °C. When reacting the powders at this temperature a large amount of sintering occurs and side reactions contaminate the powder (mostly with AlN). For these reasons the 67.5 and 77.5 mol % Al_2O_3 powders were made in a different way. Tablets of about 10 g were reaction sintered; after sintering, the outer layer was removed and the tablets were crushed in an iron mortar and milled for 8–24 h in isopropanol with iron balls in an iron container. The iron contamination was then removed with HNO_3 and H_2SO_4 , the powder was washed with ethanol and water, and was subsequently dried in an oven. After milling, the primary particles are rather small: from measurements using the method for determining specific surface area devised by Brunauer, Emmet and Teller a mean

particle size of 0.1 μm was obtained. This resulted in broadening of peaks in the X-ray diffraction pattern. The lattice parameters established with XRD were 0.7951, 0.7941 and 0.7935 nm (sample standard deviation 0.0001 nm) for Alon powder with 67.5, 73 and 77.5 mol % Al_2O_3 , respectively.

The neutron diffraction measurements were performed on the powder diffractometer at the High Flux Reactor (HFR) at Petten. Neutrons of $\lambda = 0.25717(3)$ nm were obtained by using the beam reflected from the (111) planes of a single crystal of copper and reducing the λ/n contamination to <0.1% by means of a filter of pyrolytic graphite. Soller slits with a horizontal divergence of 30' were placed between the reactor and the monochromator and in front of the four 3He -counters. Scattering angles between 5 and 155° of 2θ were scanned with a step size of 0.1° and 1' step⁻¹. The Rietveld refinement technique [7] was used to analyse the diffraction patterns obtained. Calculations were performed with the assumptions that Al occupies the 8a and 16d sites, and that nitrogen and oxygen randomly occupy the 32e sites. To a first approximation, vacancies were situated at the 16d sites.

The three powders all showed AlN contamination, but the AlN content in 67.5 and 77.5 mol % Al_2O_3 powders is very low. However, introducing AlN as a second phase in the refinement programme does not increase the quality of the fit. The diagrams also show copper peaks (111 and 200) and an unidentified peak at $d = 0.214$ nm. The copper peaks are due to insufficient shielding of the copper end-caps of the sample holder.

The neutron diffraction patterns of the powders with 67.5 and 77.5 mol % Al_2O_3 showed peak broadening due to the small crystals in the sample, whereas the pattern of the powder with 73 mol % Al_2O_3 was much sharper. To a first approximation peaks were considered to be Gaussian. Fig. 1 shows the experimental and the calculated pattern of Alon with a composition of 73 mol % Al_2O_3 .

An overview of the results obtained with the Gaussian peak shape is given in Table I: the standard deviations of the spinel parameter (u) and the lattice parameter (a) are given in parentheses, and R_{wp} and χ^2 are fitting criteria. The definitions of these criteria are identical with the definitions given by Young and Wiles [8]. As can be seen from Table I, the peaks of the Alon with 67.5 and

*Also affiliated with: Philips Research Laboratories, POB 80000, 5600 JA Eindhoven, The Netherlands.

†Present address: University of Twente, POB 217, 7500 AE Enschede, The Netherlands.

Figure 1 (a) Neutron diffraction pattern of Alon with a composition of 73 mol % Al_2O_3 and calculated pattern, assuming Gaussian peak shape. (○) Observed diffraction pattern and (—) the calculated pattern. (b) The difference between the observed and the calculated pattern.

77.5 mol % Al_2O_3 are not very well approximated by the Gaussian peak shape.

The peak shape in the patterns of 67.5 and 77.5 mol % Al_2O_3 is approximated better by a Pearson-VII function, given by

$$f(\theta_i) = \frac{C_4}{H_k} \left(1 + 4(2^{1/m} - 1) \frac{(2\theta_i - 2\theta_k)^2}{H_k^2} \right)^{-m}$$

in which

$$C_4 = \frac{2}{m} (2^{1/m} - 1)^{1/2} / (m - 0.5) \pi^{1/2}$$

where H_k is the full width at half-maximum, θ_k is the Bragg reflection angle and $m = N_a + (N_b/2\theta) + [N_c/(2\theta)^2]$. N_a , N_b and N_c parameters are free (see Table II for the results).

If the Al vacancies were allowed to occupy both 8a and 16d sites while the total amount of Al atoms were held constant, the occupation of the tetrahedral sites remained almost unity. The number of atoms at the tetrahedral site was $8.00 (\pm 0.09)$, $7.92 (\pm 0.04)$ and $7.80 (\pm 0.10)$ for Alon with 67.5, 73 and 77.5 mol % Al_2O_3 , respectively. The numbers given in parentheses are the standard deviations. The R_{wp} and χ^2 values decreased only very slightly, by about 0.02. This is consistent with the view that the vacancies are located on the octahedral sites of the lattice.

However, when the constant-cation model of McCauley [2] was used instead of the constant-anion model (complete occupation of the 8a, 16d and 32e sites plus random anion interstitials) the results were

TABLE I Results from the neutron diffraction experiments assuming Gaussian peak shape

Composition (mol % Al_2O_3)	u	a (nm)	Overall temperature factor (nm^2)	R_{wp} (%)	χ^2
67.5	0.3812(2)	0.795 26(5)	43(7)	9.9	66.1
73	0.3813(1)	0.794 35(2)	39(4)	4.9	21.0
77.5	0.3802(2)	0.793 76(6)	54(7)	9.2	45.0

TABLE II Results from the neutron diffraction experiments on Alon with 67.5 and 77.5 mol % Al_2O_3 assuming Pearson-VII peak shape

Composition (mol % Al_2O_3)	u	a (nm)	Overall temperature factor (nm^2)	R_{wp} (%)	χ^2
67.5	0.3812(1)	0.795 278(9)	52(6)	4.8	16.7
77.5	0.3802(2)	0.793 78(1)	61(6)	5.3	14.3

only slightly inferior. The R_{wp} value for Alon with 73 mol % Al_2O_3 increased from 4.9 to 5.3%, whereas χ^2 increased from 21.0 to 24.3. The values of the spinel and the lattice parameters remained the same within the uncertainty of the measurement.

Table III gives the interatomic distances. The anion–cation distances (AX and BX) were derived from

$$AX = a(u - \frac{1}{4})3^{1/2}$$

and

$$BX = a(\frac{5}{8} - u)$$

and the cation–cation distances (AB) were calculated from

$$AB = \frac{1}{8} a 11^{1/2}$$

The lattice and spinel parameters obtained in this work are not very sensitive to changes in the description of the lattice or to peak broadening, and are hence considered to be quite accurate. The lattice parameters obtained with neutron diffraction are slightly larger than those obtained with XRD. The difference is approximately 0.0002 nm, which is twice the standard deviation of the XRD measurements.

The constant-anion model is considered to be more appropriate than the constant-cation model. This is based not only on the small difference in the quality of the fit, but also on the electrical properties of Alon [9] and the consideration that large anions cannot easily be accommodated interstitially in the spinel lattice. Vacancies in Alon are then situated almost completely at octahedral sites of the lattice. This is the same result as obtained by Goursat *et al.* [4] with neutron diffraction and by Westwood [10] with computer simulations. On the basis of these findings, the results of Labbe *et al.* [5], which indicate complete occupation of both the octahedral and the tetrahedral sites, are considered to be incorrect.

TABLE III Interatomic distances in Alon

Composition (mol % Al_2O_3)	AX (nm)	BX (nm)	AB (nm)
67.5	0.1807	0.1939	0.3297
73	0.1806	0.1936	0.3293
77.5	0.1790	0.1943	0.3291

The spinel parameters observed for Alon in this work are almost the same as those reported in the literature for Alon. Goursat *et al.* [4] reported a spinel parameter of 0.3816 for Alon with a lattice parameter of 0.79447 nm and Labbe *et al.* [5] reported a spinel parameter of 0.3814 for Alon with a lattice parameter of 0.79417 nm.

One of the differences between the Gaussian and the Pearson VII shape is that the latter has more degrees of freedom. For this reason the Pearson VII shape can accommodate the deviant shape of the peaks in the diagram better. However, fitting the neutron diffraction patterns of Alon with 67.5 and 77.5 mol % Al_2O_3 with either the Gaussian or the Pearson VII peak shape leads to the same spinel and lattice parameters.

In conclusion, the Alon structure can be described with the constant-anion model. In this case the vacancies in the cation lattice are located almost completely at octahedral sites in the lattice. Neutron diffraction yields approximately the same lattice parameter for the Alons as XRD: 0.7953, 0.7944 and 0.7938 for Alon with a composition of 67.5, 73 and 77.5 mol % Al_2O_3 , respectively. The spinel parameter of Alon is not or is only very weakly dependent on the composition of the Alon and is approximately equal to 0.3812.

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Received 15 January
and accepted 20 May 1993