

SHORT COMMUNICATIONS

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Al₁₀N₈O₃ and Al₉N₇O₃, two new repeated-layer structures in the AlN–Al₂O₃ system. By S. F. BARTRAM and GLEN A. SLACK, *General Electric Research and Development Center, Schenectady, New York 12301, USA*

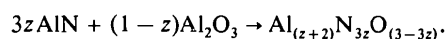
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Abstract

Crystals of Al₁₀N₈O₃ and Al₉N₇O₃ have been grown by sublimation. These oxynitrides are superstructures based on AlN with large repeat distances along the *c* axis. The hexagonal-cell *c*-axis lengths are 53·10 (5) and 72·24 (5) Å for Al₁₀N₈O₃ and Al₉N₇O₃ respectively.

Introduction

The AlN–Al₂O₃ system has been studied extensively in the last twenty years (Adams, AuCoin & Wolf, 1962; Collongues, Gilles, Lejus, Perez y Jorba & Michel, 1967; Gauckler, Lukas & Petzow, 1975; Gauckler & Petzow, 1977; Gilles, 1965; Jack, 1976; Lefebvre, 1975; Lejus, 1962, 1964; Long & Foster, 1961; Michel, 1972; Michel & Huber, 1970; Sakai, 1978; Slack, 1973; Yamaguchi & Yanagida, 1959). Phases in the system can be conveniently described by a parameter *z* defined by:



Here *z* = 1 is for pure AlN, and *z* = 0 is for pure Al₂O₃.

The intermediate phases have been identified as shown in Table 1 with approximate ranges for *z*. The AlN phase can accommodate a substantial amount of oxygen. The oxynitrides are superstructures based on the AlN structure, and have often been called polytypes. The spinel and δ phases

Table 1. *Composition ranges of the AlN–Al₂O₃ phases*

| Phase | High <i>z</i> value | Low <i>z</i> value | Reference |
|---|---------------------|--------------------|-----------|
| AlN | 1·000 | 0·889 | <i>a</i> |
| Oxynitrides | 0·727 | 0·625 | <i>b</i> |
| Spinel, γ | 0·250 | 0·018 | <i>c</i> |
| Delta, δ | 0·050 | 0·005 | <i>d</i> |
| Al ₂ O ₃ , α | <0·005 | 0·000 | <i>e</i> |

References: (*a*) Slack (1973). (*b*) This work; Gauckler *et al.* (1975); Jack (1976); Sakai (1978). (*c*) Adams *et al.* (1962); Collongues *et al.* (1967); Gilles (1965); Lejus (1962, 1964); Long & Foster (1961); Michel (1972); Yamaguchi & Yanagida (1959). (*d*) Adams *et al.* (1962); Collongues *et al.* (1967); Gilles (1965); Lejus (1962, 1964); Michel (1972); Michel & Huber (1970); Lefebvre (1975). (*e*) Collongues *et al.* (1967); Gilles (1965); Lejus (1962, 1964).

show some overlap in *z* values, particularly at high temperatures. The α -Al₂O₃ phase generally contains very little nitrogen. From Table 1 we see that oxynitride phases could possibly have *z* values of 0·889 > *z* > 0·250. This would correspond to chemical formulae of the form *m*AlN·1Al₂O₃ with 24 > *m* > 1. It is not clear how many of these phases exist. Gauckler, Lukas & Petzow (1975) and Gauckler & Petzow (1977) found phases with *m* = 5, 6. We report here on the two phases with *m* = 7 and 8. The phases 8*H*, 15*R*, 12*H* and 27*R* reported by Jack (1976) in the Si–Al–O–N phase diagram (his Fig. 11) might extend to the 0% Si boundary. If so, they would be the *m* = 2, 3, 4, and 7 phases. Sakai (1978) found the 27*R*, 16*H*, 21*R*, and 12*H* phases with *m* = 7, 6, 5, and 4. The nomenclature and structural considerations for these phases can be found in Verma & Krishna (1966).

Discussion

Single crystals of AlN have been grown by sublimation (Slack & McNelly, 1976, 1977). The oxygen content of these crystals was about 400 p.p.m. by weight or *z* = 0·9990. When the starting material for the sublimation contained 14 000 p.p.m. by weight of oxygen, then the material which condensed after the sublimation consisted predominantly of crystals of oxynitride [see section 5 of Slack & McNelly (1976)]. The sublimation was carried out for 5 to 8 h in sealed tungsten crucibles with the hot end at 2473 K and the cold end at 2313 K. The crucibles were of length 76 mm, diameter 13 mm and had a wall thickness of 0·75 mm. They were heated using a 0·5 MHz radio frequency generator, and were kept in 95% N₂ + 5% H₂ gas at 1 atm (10⁵ Pa). The oxynitride crystals have about seven times more oxygen in them than the starting material. This is a consequence of the preferential volatility of Al₂O.

The oxynitride products were examined by X-ray diffraction and extremely complex powder patterns were obtained. However, individual flakes from these materials produced single-crystal patterns; they have been studied with the Weissenberg camera. Layer-line and rotation photographs showed that two distinct crystallographic phases had been prepared with closely related structures. One of the compounds has a hexagonal cell with *a* = 3·09 (1), *c* = 53·10 (5) Å; the other has rhombohedral symmetry with hexagonal constants *a* = 3·08 (1), *c* = 72·24 (5) Å. This immediately

suggests a repeated-layer structure similar to that which has been observed for the aluminum carbonitrides by Von Stackelberg & Speiss (1935) and by Jeffrey & Wu (1963, 1966). A further verification of the presence of such structures is that the intensity sequences along the $h0l$ rows of reflections on layer-line photographs imply structures like the well known SiC polytypes. Prior to our findings, no such AlN–Al₂O₃ compounds had been reported. Since this work was done in 1974, papers on the Si–Al–O–N system have postulated the existence of such polytypes (Sakai, 1978; Gauckler & Petzow, 1977; Jack, 1976).

The actual composition of these Al–O–N crystals was determined by analogy with the Jeffrey & Wu (1963, 1966) analysis of Al₄C₃–AlN compounds. The strongest 00 l reflections were used as an indication of the number of Al layers present in each structure. The 00.20 spot is by far the strongest reflection for the hexagonal phase, hence 20 Al layers should be present in the unit cell. That is $(53 \cdot 10 \text{ \AA}/2 \cdot 66 \text{ \AA}) \approx 20$. The 2.66 \text{ \AA} average layer spacing comes from Table 2. Ten atoms in the half cell can be accounted for only by a mole ratio of 8AlN:1Al₂O₃ (assuming the lowest possible amount of oxide is present). Therefore, the hexagonal-cell composition is Al₁₀N₈O₃ and the cell contains 20 Al, 16 N and 6 O atoms. Its space-group symmetry is probably $P6_3mc$ as in the hexagonal aluminum carbonitrides.

For the rhombohedral cell, the hexagonal 00.27 reflection is strongest, *i.e.* $(72 \cdot 24 \text{ \AA}/2 \cdot 66 \text{ \AA}) \approx 27$. This indicates that there are three blocks of nine Al layers along the c axis. This can be accounted for by a mole ratio of 7AlN:1Al₂O₃ giving a composition of Al₉N₇O₃ for the rhombohedral phase.

As a means of checking the validity of these compositions the c -axis lengths can be estimated from the observed lengths

in AlN and α -Al₂O₃. In the 20H phase, progressing along the c axis, there are eight layers of AlN followed by a double layer of Al₂O₃, see Fig. 1. This structure is repeated a second time to give a total of 20 layers. The AlN layers are assumed to have the same molar volume as in pure AlN, which is $20 \cdot 91 \times 10^{-21} \text{ mm}^3$ per molecule. With an observed $a = 3 \cdot 085 \text{ \AA}$ the calculated thickness of a single AlN layer is $\Delta c = 2 \cdot 536 \text{ \AA}$. The atomic arrangement in the Al₂O₃ layer is unclear, although Thompson (1977) has found octahedrally coordinated metal atoms in some of the repeated-layer structures. We choose a hexagonal subunit containing one Al₂O₃ molecule from the α -Al₂O₃ structure ($a = 4 \cdot 7589$, $c = 12 \cdot 991 \text{ \AA}$, hexagonal) with $a' = a/\sqrt{3}$, $c' = c/2$. This subunit should contribute a Δc somewhere between 5.17 and 6.50 \text{ \AA}. The former value is based on maintaining the molar volume of α -Al₂O₃ in the new structure with $a = 3 \cdot 085 \text{ \AA}$. The latter value is equal to c' . The c axis lengths of the new phases are expected to be:

$$\begin{aligned} 20H: c &= 16(2 \cdot 536 \text{ \AA}) + 2(5 \cdot 17 \text{ to } 6 \cdot 50 \text{ \AA}) \\ &= 50 \cdot 92 \text{ to } 53 \cdot 58 \text{ \AA}, \end{aligned}$$

$$\begin{aligned} 27R: c &= 21(2 \cdot 536 \text{ \AA}) + 3(5 \cdot 17 \text{ to } 6 \cdot 50 \text{ \AA}) \\ &= 68 \cdot 77 \text{ to } 72 \cdot 76 \text{ \AA}. \end{aligned}$$

The measured values are close to the upper end of the calculated range. The measured value for the 27R phase of 72.24 \text{ \AA} is close to but larger than the value of 71.98 \text{ \AA} found for the 27R sialon by Jack (1976). The shrinkage in the hexagonal a axis of these repeated-layer structures compared to AlN is caused by the additional oxygen present. Pure AlN has $a = 3 \cdot 112$, $c = 4 \cdot 981 \text{ \AA}$. The calculated X-ray densities are all similar: AlN 3.26, Al₁₀N₈O₃ 3.33, Al₉N₇O₃ 3.26 Mg m⁻³. These are much less than the density of α -Al₂O₃, 3.975 Mg m⁻³.

Table 2. X-ray diffraction data on powders

| Rhombohedral Al ₉ N ₇ O ₃ | | | | Hexagonal Al ₁₀ N ₈ O ₃ | | | |
|--|-------------------|------------------|------------------|--|-------------------|------------------|------------------|
| hkl^* | d_{calc} | d_{obs} | I_{obs} | hkl | d_{calc} | d_{obs} | I_{obs} |
| 0 0 24 | 3.01 | 3.00 | w | 0 0 18 | 2.950 | 2.94 | w |
| 0 0 27 | 2.676 | 2.66 | vs | 1 0 1 | 2.674 | 2.66 | vs |
| 1 0 1 | 2.666 | | | 0 0 20 | 2.655 | | |
| 0 1 2 | 2.661 | | | 1 0 3 | 2.646 | | |
| 0 1 5 | 2.623 | 2.62 | s | 1 0 5 | 2.595 | 2.60 | vw |
| 0 1 8 | 2.558 | 2.55 | w | 1 0 7 | 2.524 | 2.51 | vw |
| 0 1 11 | 2.471 | 2.46 | mw | 1 0 9 | 2.437 | 2.44 | mw |
| 0 0 30 | 2.408 | 2.40 | s | 0 0 22 | 2.414 | 2.41 | vw |
| 1 0 13 | 2.405 | | | 1 0 10 | 2.390 | 2.39 | ms |
| 0 1 14 | 2.369 | 2.36 | w | 1 0 12 | 2.290 | 2.29 | w |
| 1 0 16 | 2.297 | 2.31 | vw | 0 0 24 | 2.213 | 2.22 | vw |
| 0 1 17 | 2.259 | 2.26 | w | 0 0 26 | 2.042 | 2.04 | vw |
| 0 0 33 | 2.189 | 2.18 | w | 1 0 20 | 1.885 | 1.89 | w |
| 0 1 26 | 1.924 | 1.91 | w | 1 0 21 | 1.838 | 1.84 | m |
| 1 0 28 | 1.854 | 1.86 | s | 1 0 23 | 1.748 | 1.742 | vw |
| 0 1 29 | 1.821 | 1.815 | mw | 1 1 0 | 1.536 | 1.53 | vs |
| 1 1 0 | 1.540 | 1.53 | vs | 1 0 30 | 1.476 | 1.472 | mw |
| 1 0 40 | 1.495 | 1.50 | vw | 1 0 32 | 1.410 | 1.415 | w |
| 1 0 43 | 1.422 | 1.415 | vw | 1 0 33 | 1.379 | 1.372 | vw |
| 0 1 44 | 1.398 | 1.39 | m | 1 1 18 | 1.369 | | |
| 1 0 46 | 1.353 | 1.345 | mw | 2 0 1 | 1.338 | 1.325 | s |
| 1 1 27 | 1.335 | | | 1 1 20 | 1.335 | | |
| 0 2 1 | 1.333 | 1.325 | s | 0 0 40 | 1.328 | | |
| 2 0 2 | 1.333 | | | 2 0 10 | 1.297 | 1.29 | m |
| 0 2 13 | 1.297 | 1.288 | mw | 1 1 24 | 1.267 | 1.265 | vw |
| 2 0 14 | 1.291 | | | 0 0 42 | 1.264 | | |
| 0 2 28 | 1.185 | 1.185 | vw | 2 0 21 | 1.183 | 1.18 | vw |

* For hexagonal cell.

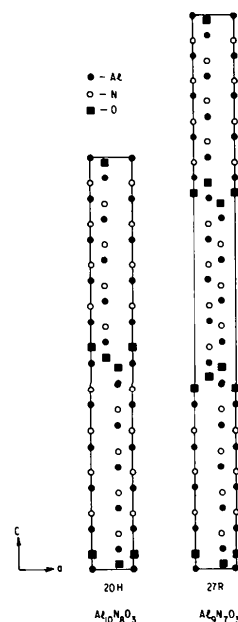


Fig. 1. Projections of the Al, N, and O atomic positions on the hexagonal (110) plane in the 20H and 27R aluminum oxynitrides.

These new AlN–Al₂O₃ compounds derived above completely confirm two of the 'sialon' phases postulated by Jack (1976) in the Si–Al–O–N system. In fact they can be considered as prototypes of his tetrahedral AlN 'polytypes' having *M/X* ratios of 10/11 and 9/10, respectively. In his phase diagram for Si₃N₄–AlN–Al₂O₃–SiO₂, the 27*R* line should now be extended to the join between Al₂O₃ and AlN. Furthermore, another line for the 20*H* structure should intersect this join to account for the existence of Al₁₀N₈O₃. It is of interest to note that although many crystals of this 20*H* compound were well ordered, others from the same preparation showed considerable streaking along the *h0l* rows on Weissenberg photographs. This indication of disorder is caused by mistakes in the stacking arrays along the *c* axis. The rhombohedral crystals of Al₉N₇O₃ exhibited a higher degree of order, probably because less faulting occurs for shorter 9Al-atom segments which characterize the structure of this compound. This type of disorder is common in SiC and other such polytypic compounds (Verma & Krishna, 1966).

Although the crystal structure has not been refined from single-crystal Weissenberg photographs, the idealized arrangement postulated by Jack (1976) gives reasonably good agreement with the observed intensities. Projections of the 20*H* and 27*R* structures on the hexagonal (110) plane are illustrated in Fig. 1. Their X-ray diffraction patterns are given in Table 2. Because of the large number of possible reflections only those observable are listed.

We expect further work will reveal other aluminum oxynitride repeated-layer structures. So far these exist for *m* = 4, 5, 6, 7, and 8.

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On the space groups of two thiospinels. By LEONARDO GASTALDI and LUCIO SCARAMUZZA, *Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del CNR, Via Montorio Romano 36, Roma, Italy*

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Abstract

Single crystals of CuIn₃S₈ and AgIn₃S₈ thiospinels have been examined by X-ray diffractometry, in order to assign the space groups. The ψ scan of some high-angle reflections, forbidden in the conventional space group *Fd3m*, showed that CuIn₃S₈ belongs to the alternative space group *F43m*.

In the last few years stimulating discussions have been reported in the literature on the correct assignment of space

group to the spinel-type compounds. The problem has been described by Thompson & Grimes (1977), who reviewed the results of previous work with electron and neutron diffraction techniques.

The alternative to space group *Fd3m*, usually assigned to spinels, is *F43m*, where the octahedral-site metal ions are displaced along the [111] directions and the tetrahedral ones split into two crystallographically independent sites, namely 4(*a*) and 4(*c*). The space-group assignment is usually based on the detection of *hk0* reflections with $h + k = 4n + 2$, forbidden in *Fd3m*, but allowed in *F43m*. The difficulty