

# THE FORMATION AND STRUCTURE OF DELTA ALUMINA

By H. P. ROOKSBY

The General Electric Company Ltd., Hirst Research Centre,  
Wembley, England,

and C. J. M. ROOYMANS

Philips Research Laboratories, Eindhoven, Netherlands.

[Received 20th February, 1961]

## ABSTRACT

Delta alumina is a transition form obtained during the conversion of boehmite to corundum. Alternative methods have been found for preparing this alumina in a well crystallised condition, enabling detailed X-ray powder data to be compiled. The X-ray data are accounted for by a large tetragonal structure cell of which the axial ratio is 1.47, or  $3/2$  times the axial ratio of the spinel-like pseudo-cell of Saalfeld. The lattice parameters are  $a_0 = 7.96 \text{ \AA}$  and  $c_0 = 11.70 \text{ \AA}$ . This large cell provides an integral number of vacancies, contrasting with the  $2\frac{3}{8}$  vacancies of the pseudo-cell, and allows the atomic arrangement to be ordered.

## INTRODUCTION

Decomposition of bayerite,  $\text{Al}(\text{OH})_3$ , and/or boehmite,  $\text{AlOOH}$ , leads to metastable aluminas before transformation to corundum finally occurs. Three transition forms have been distinguished, namely  $\gamma$ ,  $\delta$  and  $\theta$ . The first of these,  $\gamma$ , is known to have an undistorted cubic spinel structure. The transition alumina obtained by dehydration of boehmite, however, has a modified crystal structure, as shown by X-ray powder diffraction analysis, and this modification has been denoted by the prefix  $\delta$  (Rooksby, 1958). This is the form described as *tetragonal  $\gamma$ -alumina* by Saalfeld (1958), during a study of the dehydration of gibbsite.  $\theta$ -Alumina is isomorphous with  $\beta$ - $\text{Ga}_2\text{O}_3$ .

$\delta$ -Alumina obtained from boehmite is difficult to crystallize to any considerable extent and X-ray powder photographs remain somewhat diffuse. Heat treatments to promote crystal growth generally result in formation of appreciable amounts of the  $\theta$  phase, the presence of which confuses interpretation. Other methods of preparation have been discovered, however, which have yielded  $\delta$ -alumina of good crystalline character, and such material has enabled detailed X-ray powder data to be compiled (Rooksby, 1958).

An analysis of these powder data has led to a first step in the solution of the crystal structure and this is different from that proposed by Saalfeld (1958). The results are reported below.

#### METHODS OF PREPARATION

The following methods of preparation have been used:

(a) Ignition at 950°C of ammonium alum impregnated with a small percentage of ammonium molybdate. The oxide of molybdenum appears to act as a mineralizer to promote rapid crystal growth but is not compounded with the alumina.

(b) Rapid quenching of alumina particles melted by passing through an oxy-hydrogen flame. This yields the so-called *spherulised alumina* described by Plummer (1958).

(c) Rapid condensation, after passing through an oxy-hydrogen flame, of material vaporised from a bath of aluminium chloride.

(d) Heat treatment at 1100-1150°C of the 'crystalline'  $\gamma$ -alumina deposited on a graphite base by flame-spraying.

It is not claimed that any of these methods has produced the  $\delta$  form absolutely free from  $\theta$ ; in several preparations some of the prominent reflections of  $\theta$  were just visible\*.

#### CRYSTAL STRUCTURE

Comparison of the X-ray patterns of several of the transition aluminas, e.g.,  $\gamma$ ,  $\delta$ , and  $\theta$ , shows that there are a few strong reflections which occur at nearly the same spacings in all these patterns. Particularly prominent are those in the neighbourhood of  $d=2.00 \text{ \AA}$  and  $d=1.40 \text{ \AA}$ , respectively: these correspond with the 400 and 440 reflections of a spinel structure.

Ervin (1952) has mentioned that such reflections denote the persistence through the transition sequence of a cubic close-packed oxygen-layer stacking, with  $\text{Al}^{3+}$  distributed in the octahedral and tetrahedral holes between the layers, but he pointed out that their presence gives no guidance as to possible ordering of the  $\text{Al}^{3+}$ . In the pattern of the  $\delta$  structure the reflections with planar spacings of about  $2.00 \text{ \AA}$  and  $1.40 \text{ \AA}$  are split, in contrast with the reflection at  $1.14 \text{ \AA}$ , which remains unsplit, and which corresponds to the 444 reflection of a spinel structure.

This, and the fact that the other lines are weak and not clearly distinguishable on the X-ray pattern of the  $\delta$  form obtained by de-

\*Detailed spacing lists for the different varieties of alumina will appear in the revised edition of X-ray Identification and Crystal Structures of Clay Minerals, Mineralogical Society, London, 1961, in a chapter by H. P. Rooksby.

hydration of boehmite, led Saalfeld (1958) to the conclusion that the  $\delta$  phase had a tetragonally deformed spinel lattice with cell dimensions of  $a=7.96 \text{ \AA}$  and  $c=7.80 \text{ \AA}$ . There are many other features of the X-ray pattern of well-crystallized preparations, however—in particular a multitude of extra lines—which cannot be accounted for on this simple interpretation of the  $\delta$  structure. The list of observed planar spacings is given in column 1 of Table 1. The complexity of this list compared with that for a spinel-type crystal structure suggests that  $\delta$ -alumina has a unit cell with at least one of the axes some multiple of the spinel dimension.

TABLE 1—Powder diffraction data for  $\delta$ -alumina  
Tetragonal structure with  $a_0=7.96 \text{ \AA}$   $c_0=11.70 \text{ \AA}$

| 1               | 2       | 3     | 1               | 2       | 3     |
|-----------------|---------|-------|-----------------|---------|-------|
| $d(\text{\AA})$ |         | $hkl$ | $d(\text{\AA})$ |         | $hkl$ |
| Obs.            | Calc.   |       | Obs.            | Calc.   |       |
| 7.97 (8)        | 7.96    | 100   | 1.796 (7)       | 1.799   | 225   |
| 6.58 (10)       | 6.581   | 101   | 1.759 (3)       | 1.759   | 421   |
| 5.85 (1)        | 5.850   | 002   | 1.730 (1)       | 1.730   | 413   |
| 5.07 (20)       | 5.072   | 111   | 1.701 (4)       | 1.703   | 422   |
| 4.71 (3)        | 4.714   | 102   | 1.616 (10)      | 1.619   | 423   |
| 4.05 (20)       | 4.056   | 112   | 1.602 (15)      | { 1.603 | 226   |
| 3.75 (2)        | 3.769   | 201   |                 | { 1.602 | 117   |
| 3.56 (7)        | 3.560   | 210   | 1.572 (1)       | 1.571   | 306   |
| 3.40 (10)       | 3.406   | 211   | 1.543 (10)      | 1.542   | 316   |
| 3.28 (15)       | 3.289   | 202   | 1.507 (20)      | 1.508   | 512   |
| 3.21 (10)       | 3.205   | 113   | 1.462 (8)       | { 1.464 | 335   |
| 3.03 (10)       | 3.041   | 212   |                 | { 1.461 | 326   |
| 2.783 (30)      | 2.785   | 203   | 1.435 (2)       | 1.433   | 522   |
|                 | { 2.745 | 104   | 1.407 (60)      | 1.407   | 440   |
| 2.737 (30)      | { 2.726 | 221   | 1.392 (100)     | 1.393   | 406   |
| 2.593 (70)      | 2.595   | 114   | 1.248 (10)      | 1.250   | 525   |
| 2.457 (70)      | 2.460   | 311   | 1.235 (10)      | 1.236   | 209   |
| 2.311 (40)      | 2.313   | 312   | 1.178 (5)       | { 1.180 | 229   |
| 2.277 (30)      | 2.282   | 223   |                 | { 1.178 | 526   |
| 2.156 (25)      | 2.160   | 115   | 1.140 (15)      | 1.141   | 446   |
| 1.989 (70)      | 1.990   | 400   | 1.105 (1)       | —       | —     |
| 1.950 (65)      | 1.950   | 005   | 1.050 (3)       | —       | —     |
| 1.833 (2)       | 1.833   | 412   | 1.049 (5)       | —       | —     |

The X-ray pattern has been satisfactorily indexed by referring the structure to a tetragonal cell of axial ratio 1.47 ( $3/2 \times 0.98$ ) and parameters  $a_0=7.96 \text{ \AA}$  and  $c_0=11.70 \text{ \AA}$ . Calculated spacings, based upon these parameters, and corresponding indices are shown in columns 2 and 3 of Table 1. The agreement between observed and calculated data is very good.

## DISCUSSION

In a cubic close-packed oxygen arrangement with cell dimensions of about 8 Å, there are a total of 32 O<sup>2-</sup> in the unit cell. For a spinel with the general formula A<sub>3</sub>O<sub>4</sub> this implies 24 cations, which are distributed in a completely ordered way on the available tetrahedral and octahedral sites between the oxygen anions.

By contrast, in the so-called cation-deficient spinel-like compounds, with the general formula A<sub>2</sub>O<sub>3</sub>, there can be only, on the average, 21 $\frac{1}{3}$  cations per spinel-type unit. There exist, therefore, two possible ways of accommodating these: either the cations are randomly arranged, so that in some unit cells there are, for example 21 cations and in others 22, or the cations are ordered, and one must look for a larger unit cell, in which there is an integral number of cations. Ordered arrangements exist in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -In<sub>2</sub>S<sub>3</sub> (Rooymans, 1959) and in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (with a very small percentage of Li<sup>+</sup>) of Kordes (1935).

Such considerations are also valid for the  $\delta$ -alumina described here. This appears to have an approximately cubic close-packed oxygen arrangement and at least two cell dimensions of about 8 Å. It is not necessary, however, to express the structure in terms of a simple spinel-like unit, for the larger unit cell established in the present analysis contains 48 oxygen ions, and therefore an integral number of aluminium ions, *i.e.*, 32, which can be distributed in an ordered way on the available sites. The fact that the *c* dimension is not an integral multiple of that of the spinel unit indicates that the structure is not simply a spinel arrangement with ordered vacancies but is essentially different. The distribution among the octahedral and tetrahedral sites has caused a relative contraction of the structure along the *c* axis.

It is also worth remarking here that three of the four methods of preparing  $\delta$ -alumina involve rapid crystallization of alumina which has been melted. This is consistent with the view that at high temperatures, or in the liquid just above the melting point, four-fold co-ordination of aluminium by oxygen is likely to be prevalent, as treated in some detail by Plummer (1958). The occurrence of a lower co-ordination number at high temperatures is a general phenomenon (Buerger, 1951). Thus on rapid solidification, structures in which tetrahedral co-ordination exists are formed more readily than corundum in which there is only octahedral co-ordination of aluminium by oxygen. It is relevant to note in

this connection that it has recently been proved that  $\text{Al}^{3+}$  is equally distributed between tetrahedral and octahedral sites in the structure of  $\theta\text{-Al}_2\text{O}_3$ . The  $\theta$  modification is isomorphous with  $\beta\text{-Ga}_2\text{O}_3$ , the structure of which has been solved independently by Geller (1960) and Saalfeld (1960).

#### REFERENCES

- BUERGER, M. J., 1951. *Phase Transformations in Solids*. John Wiley & Sons, New York, p. 202.
- ERVIN, G., 1952. *Acta cryst.*, **5**, 103.
- GELLER, S., 1960. *J. chem. Phys.*, **33**, 676.
- KORDES, E., 1935. *Z. Kristallogr.*, **91**, 193.
- PLUMMER, M., 1958. *J. appl. Chem.*, **8**, 35.
- ROOKSBY, H. P., 1958. *J. appl. Chem.*, **8**, 44.
- ROOYMANS, C. J. M., 1959. *J. inorg. nucl. Chem.*, **11**, 78.
- SAALFELD, H., 1958. *Clay Min. Bull.*, **3**, 249.
- SAALFELD, H., 1960. *Neues Jb. Miner., Abh.*, **95**, 1.