Acta Cryst. (1962). **15**, 812

The unit cell and space group of $2Y_2O_3 . Al_2O_3$.

By John W. Reed* and A. B. Chase,† *Hughes Research Laboratories, Malibu, California, U.S.A.*

(*Received* 30 *January* 1962 *and in revised form* 27 *March* 1962)

The phase behavior of the system Y_2O_3–Al_2O_3 has not yet been completely determined, but it is agreed (Warshaw & Roy, 1959; Schneider, Roth & Waring, 1961) that compounds of the compositions $2\,Y_2O_3 . Al_2O_3$, $Y_2O_3 . Al_2O_3$, and $3\,Y_2O_3 . 5\,Al_2O_3$ exist. The 3:5 compound is well known and has the garnet structure. The 1:1 compound has a distorted perovskite structure (Geller & Wood, 1956), but there is some question as to its stability. The 2:1 compound, which has not up to now been studied in any detail, is the subject of the work reported here.

The only crystallographic information on the compound $2\,Y_2O_3 . Al_2O_3$ is given by Warshaw & Roy. They state, on the basis of the powder pattern, that it has a distorted cubic structure with a lattice constant of $10{\cdot}40 \pm 0{\cdot}05$ Å. They also state that the Al atoms must be in fourfold coordination, because Si and Ca can be substituted for Al and Y over a complete range of solid solution.

We have grown single crystals of a size suitable for X-ray diffraction work by the flame fusion method. A stoichiometric mixture, $2\,Y_2O_3$ to $1\,Al_2O_3$, was used. Except for a thin skin, the boule was composed of a single polycrystalline anisotropic phase. The skin contained two phases, one of them the same as the major phase, and the other Y_2O_3 (identified optically). The gravimetrically determined density of the anisotropic phase is $4{\cdot}53$ g.cm.$^{-3}$.

Irregular anhedral fragments of material from the inner part of the boule were used for the X-ray crystallographic work. Laue photographs were made of a large number of fragments in order to find suitable samples. Most of the fragments gave patterns with multiple spots and asterism, but it was possible to find some good single crystals.

The structure was found to be monoclinic from Weissenberg and precession photographs. Two systematic extinctions were observed, $(0k0)$ with k odd and $(h0l)$ with l odd, so that the space group is determined uniquely as $P2_1/c$. The lattice constants were determined from rotation photographs of the $(h0l)$ and $(0kl)$ zones. The crystal used was a ground sphere $\frac{1}{4}$ mm. in diameter. The photographs were taken on a $114{\cdot}6$ mm. camera, with the film cut in the Straumanis arrangement. The camera was a Philips powder camera modified so as to allow the use of a goniometer head for single crystal work. About twenty clearly resolved back reflections were indexed and measured on each photograph. The lattice constants of the two projected planar unit cells corresponding to the two zones of reflections were fitted to the data by least squares calculations. The dimensions of the monoclinic cell are

$$a=7{\cdot}373,\ b=10{\cdot}467,\ c=11{\cdot}121\ \text{Å};\ \beta=108{\cdot}53^\circ.$$

There are 4 formula units per unit cell; and the X-ray density is $4{\cdot}52$ g.cm.$^{-3}$. Since it is not known whether or not the sample was stoichiometric, no estimate of the accuracy of the lattice constant values is given (although the precision was very high, with all standard deviations less than $0{\cdot}01\%$).

Some of the reflections describe an approximately cubic lattice in reciprocal space, corresponding to a cell of about $5{\cdot}14$ Å edge in direct space. The two lattices are related by the transformation equations

$$\begin{aligned} h_c &= \tfrac{1}{3}(2h_m+l_m)\,, \\ k_c &= \tfrac{1}{2}k_m\,, \\ l_c &= \tfrac{1}{3}(-h_m+l_m)\,. \end{aligned}$$

The actual dimensions of this cell are

$$a=5{\cdot}130,\ b=5{\cdot}233,\ c=5{\cdot}057\ \text{Å};\ \beta=92{\cdot}75^\circ.$$

The relationship between the two cells is clarified by considering the ideal case in which the small cell is actually cubic. If a' represents this cell edge then the ideal monoclinic lattice constants are

$$a=\sqrt{(2)}a',\ b=2a',\ c=\sqrt{(5)}a',\ \beta=180^\circ-\tan^{-1}3\,.$$

A powder photograph of the material was found to agree with the patterns of Warshaw & Roy, and of Schneider, Roth & Waring, indicating that the material is the same as theirs. Because of the complexity of the calculated pattern for the monoclinic unit cell it is virtually impossible to index the observed powder pattern. Since the cubic cell edge reported by Warshaw & Roy is approximately twice the small pseudocubic cell edge, there must be a relationship between their indices and the true monoclinic indices. One might therefore wish to retain Warshaw & Roy's indices as representing those reflections (or groups of reflections), of the total possible number, which are observed in the powder pattern (in the manner that one might index a pattern with very weak superlattice lines on the basis of the smaller unit cell). This is not possible, as may be seen by the following reasoning. Consider the quantity $\varkappa=(6a'/d)^2$; it can be shown that $\varkappa_m=20h^2+8hl+8l^2+9k^2$ for the ideal monoclinic cell and $\varkappa_c=9(h^2+k^2+l^2)$ for the ideal large cubic cell. In order for this interpretation of Warshaw & Roy's indices to be valid, the value of $\varkappa_c$ for each reflection they list must appear in the sequence of $\varkappa_m$ values. This is not true for their (110) line, because $\varkappa_c$ has a value of 18 while the sequence of $\varkappa_m$ values is 0, 8, 9, 17, 20, 29, ... (neglecting the systematic extinctions); nor is it true for the seven other lines in Warshaw & Roy's pattern that have two odd indices.

The authors wish to express their thanks to R. A. Lefever for suggesting the problem, and for his helpful interest in it.

References

Geller, S. & Wood, E. A. (1956). *Acta Cryst.* **9**, 563.

Schneider, S. J., Roth, R. S. & Waring, J. L. (1961). *J. Research Natl. Bur. Standards*, A, **65**, 345.

Warshaw, I. & Roy, R. (1959). *J. Amer. Ceram. Soc.* **42**, 434.

---

* Present address: Department of Chemistry, Kent State University, Kent, Ohio, U.S.A.

† Present address: General Telephone and Electronics Laboratories, Palo Alto, California, U.S.A.