

CHARACTERIZATION OF β -Ga₂O₃ AND ITS ALUMINA ISOMORPH, θ -Al₂O₃*

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ABSTRACT

Considerable disagreement exists in the literature on the question of whether or not the many varieties of alumina represent discrete phases. It has previously been shown that the high-temperature form of gallia (β) is isostructural, and forms a complete solid solution series, with θ -alumina. Lath-shaped crystals of β -Ga₂O₃, of sufficient size for single-crystal x-ray diffraction studies, have been grown from the vapor phase and were studied by optical and x-ray techniques. A twinned morphology was established, the true unit cell being monoclinic:

$$\begin{array}{ll} a_0 = 5.80 \pm 0.01 \text{ \AA} & \beta = 103^\circ 42' \\ b_0 = 3.04 \pm 0.01 \text{ \AA} & Z = 4 \\ c_0 = 12.23 \pm 0.02 \text{ \AA} & \text{Space Group} = A2/m \end{array}$$

All crystals examined were multiply twinned on (001), resulting in an apparent orthorhombic diffraction symmetry.

The cell dimensions of the isostructural alumina phase (θ) are contracted by approximately 3%. The characterization of β -Ga₂O₃ as a discrete crystallographic phase establishes θ -Al₂O₃ as a distinct polymorph of alumina. This lends support to the belief that other forms of alumina may well be represented by discrete crystalline phases.

INTRODUCTION

Many varieties of alumina are reported in the literature. The nature of these phases and their interrelationships are still unsettled issues (1). One group of investigators favors a type of order-disorder sequence (2) or a relationship involving crystallite size (3). A second school (4,5,6) interprets the various x-ray diffraction patterns as arising from a number of discrete crystalline phases. The major reported varieties of alumina include α -(corundum; hexagonal) (7), β -(containing Na (8), K (8), Mg (9), Ca (10), or Ba (11); hexagonal), γ -(cubic (12), tetragonal or orthorhombic (5)), δ -(orthorhombic (5)), κ -(orthorhombic (5)), η -(cubic, spinel type) (5), θ -(hexagonal) (13), χ -(approximately cubic) (5), and ζ -Al₂O₃ (Li₂O-containing; cubic) (14,15). A complete compilation of the known forms of alumina and hydrated alumina is given by Russell *et al.* (16).

Striking analogies have been observed between the oxides of aluminum and gallium. These are to be expected owing to the similarity between the two elements, both chemically and with respect to atomic radii. As a result, an extensive series of solid solutions (4,17) can exist between

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the stable, isomorphous alumina and gallia end members. The reported varieties of gallia include α -(hexagonal) (18), β -(non-cubic) (18), γ -(cubic) (19), δ -(body-centered cubic) (20), ϵ -(non-cubic) (20), Na₂O- or K₂O-containing-(hexagonal) (6), and Li₂O-containing-Ga₂O₃ (cubic) (6).

Unfortunately, the lack of systematic nomenclature among the alumina and gallia phases has in some cases confused the obvious parallelism between the two series. The following isomorphous pairs have been reported in the literature: α -Al₂O₃ and α -Ga₂O₃ (18), β -Al₂O₃ and the corresponding alkali-containing-Ga₂O₃ phases (6), γ -Al₂O₃ and γ -Ga₂O₃ (19), κ -Al₂O₃ and ϵ -Ga₂O₃ (4), θ -Al₂O₃ and β -Ga₂O₃ (6), and ζ -Al₂O₃ and Li₂O-containing-Ga₂O₃ (6).

The present study is concerned with a characterization of the unit cell and space group of β -Ga₂O₃ (the so-called high-temperature gallia) and consequently, its alumina isomorph, θ -Al₂O₃. The isomorphism of these two phases has been based upon their analogous *x*-ray powder patterns (6) and a complete solid solution between the two end members (4). However, no conclusive crystallographic characterization of this isostructural pair has yet been reported.

PREPARATION OF β -Ga₂O₃

The crystals of β -Ga₂O₃ used in the present study were prepared during the growth of gallium phosphide from excess gallium. Elemental phosphorus and gallium were sealed in an evacuated silica tube (25 μ Hg), held at 1100° C. for three hours, and slow-cooled at approximately 40° C./hr. The reaction product consisted of GaP crystals (major phase) and a minor amount of lath-shaped, light-blue crystals, the latter having formed on the tube wall in a cool region above the melt level. The minor-phase crystals, later shown to be β -Ga₂O₃, were formed from the vapor phase, probably by a reaction of gallium with residual oxygen. Spectrochemical analysis of the β -Ga₂O₃ crystals revealed minor amounts of Fe, Ca, Cu, Mg, Si and In; the latter element possibly imparted the light-blue color.

The high affinity of gallium for oxygen was clearly shown in another experiment: Elemental gallium was heated to 1100° C. in a stream of nitrogen. The light-grey, finely-fibrous reaction product consisted entirely of β -Ga₂O₃, as shown by *x*-ray powder patterns. The oxygen impurity in the nitrogen was apparently sufficient to oxidize the gallium.

β -Ga₂O₃ was also formed by heating elemental gallium in a quartz crucible at 700–800° C. in air. A surface layer of oxide, which readily formed over the molten gallium, inhibited oxidation, necessitating frequent agitation to insure a complete reaction. *X*-ray powder patterns showed the light-grey, finely-crystalline reaction product to be β -Ga₂O₃.

Stoichiometry

The light-blue crystals obtained from the first preparation method described above and the reaction products from the last two techniques were shown to be the same phase by *x*-ray powder diffraction. Furthermore, the pattern of this phase was found to be in good agreement with the powder data for β -Ga₂O₃ published by Roy *et al.* (20) The stoichiometry was confirmed by gain-in-weight measurements made in conjunction with the aforementioned direct heating of elemental gallium in air. A further confirmation of the stoichiometry was obtained from direct chemical analysis (21). Two determinations for Ga gave 74.48% and 74.73%. The average 74.61% compares favorably with the theoretical amount for Ga₂O₃, namely 74.41%.

UNIT CELL AND SPACE GROUP

The lath-shaped crystals of β -Ga₂O₃ were first examined with a polarizing microscope. They were found to be anisotropic, with parallel extinction when viewed normal to the lath axis, i.e., normal to either the face or edge of the lath. This implies either tetragonal, hexagonal, orthorhombic, or monoclinic symmetry. In the first two instances, it is further required that the *c* axis be coincident with the lath direction. The latter, in case of monoclinic symmetry, is coincident with the *b* axis for all practical purposes.

Interfacial angles around the lath direction were measured with a two-circle optical goniometer. The values obtained ($\sim 53^\circ$ and 76°) were inconsistent with uniaxial symmetry. Thus either orthorhombic or monoclinic symmetry is indicated for β -Ga₂O₃.

The optical findings were in apparent agreement with the results obtained using the precession and Weissenberg techniques. Preliminary interpretation of these diffraction patterns indicated an orthorhombic unit cell of the following dimensions:

$$\begin{aligned} a_0 &= 5.80 \pm 0.01 \text{ \AA} \\ b_0 &= 3.04 \pm 0.01 \text{ \AA} \\ c_0 &= 23.76 \pm 0.02 \text{ \AA} \end{aligned}$$

On the basis of this unit cell, the following absences were noted on the single-crystal patterns:

$$\begin{aligned} hkl &\text{ with } h+l \neq 2n \text{ (B-face centering)} \\ h_{2n}k_{2m}l &\text{ with } h+l \neq 4n \\ h_{2n}k_{2m+l} &\text{ with } h+l = 4n \end{aligned}$$

These absences were not consistent with any orthorhombic space group. Accordingly, the remaining symmetry possibility, monoclinic, was considered.

It is known that orthorhombic symmetry can be derived from monoclinic symmetry by twinning. Accordingly, a closer examination was made of the lath-shaped crystals under high magnification, and the presence of reentrant angles typical of twinning was noted. The photomicrograph reproduced in Fig. 1 offers a view of the serrated or saw-

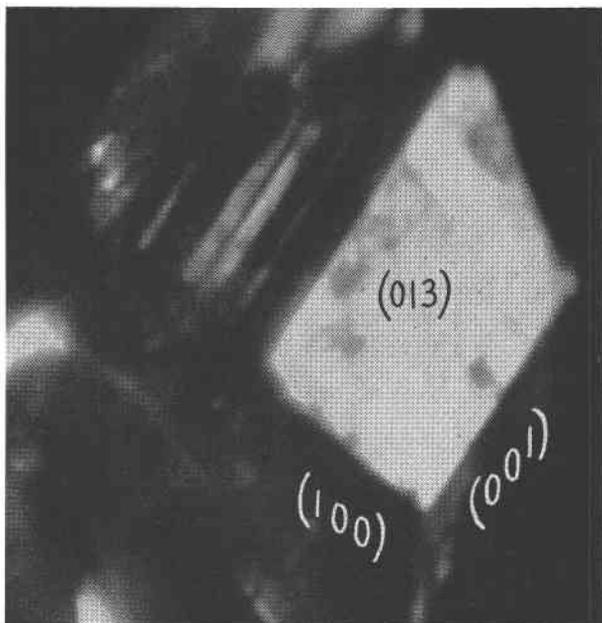


FIG. 1. Photomicrograph of a typical $\beta\text{-Ga}_2\text{O}_3$ crystal. The faces are indexed after the monoclinic unit cell. The zone of reentrant angles lies in $\{0kl\}$. (570 \times).

toothed zone. It will be recalled from the optical findings (see above) that, in case of monoclinic symmetry, the b -axis is coincident with the lath direction. The latter is essentially vertical in the photomicrograph. The composition plane of the proposed twin contains the lath direction, and therefore the b -axis, and consequently is of the type $(h0l)$.

Assuming the twin plane to be (001) , the $(h0l)$ reciprocal lattice shown in Fig. 2 was constructed. The relationship between orthorhombic and monoclinic symmetry is apparent. The observed reflections have been indexed using the orthorhombic and both (normal and twinned) monoclinic unit cells. Considering only the normal (lower) monoclinic cell, it was found that the observed absences ((hkl) with $k+l \neq 2n$) were consistent with the space group $A2/m$. All observed reflections were accounted for by the composite lattice constructed from both monoclinic

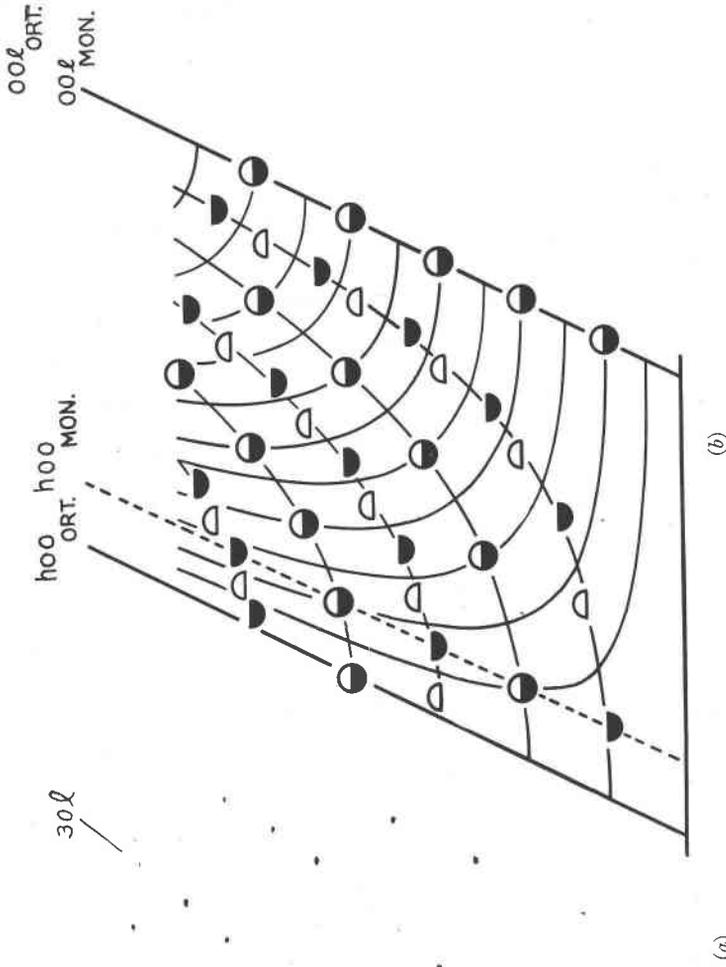


FIG. 3. (a) Portion of the $\beta\text{-Ga}_2\text{O}_3$ b -axis zero-level Weissenberg pattern. (b) Schematic interpretation of (a) (cf. Fig. 2 for explanation of symbols).

TABLE 1. X-RAY POWDER DATA FOR β -Ga₂O₃ AND ITS ALUMINA ISOMORPH, θ -Al₂O₃

Radiation: Cu/Ni filter. Camera diam.: 114.59 mm.

β -Ga ₂ O ₃				θ -Al ₂ O ₃				
Ortho- rhombic <i>hkl</i>	Monoclinic		<i>d</i> _{obs.} Å	<i>I</i>	<i>d</i> _{obs.} Å (5)	<i>I</i>	Tertian's Hexagonal Cell (2)	
	<i>hkl</i>	<i>d</i> _{calc.} Å					<i>d</i> _{calc.} Å	<i>hkl</i>
1 0 1	1 0 0	5.63	5.60	W+	5.25	W		
1 0 3	1 0 2	4.68	4.65	M	4.55	M	4.55	0 0·3
1 0 5	1 0 2	3.68	3.66	W	3.56	VW	3.64	2 0·0
0 0 8	0 0 4	2.970	2.967	VS	2.87	MS	2.84	2 0·3
1 0 7	1 0 4	2.930	2.924	VS				
2 0 2	2 0 0	2.817	2.816	VS	2.74	MS		
1 1 I	1 1 I	2.675	2.673	M	2.58	W		
1 1 3	1 1 1	2.549	2.547	VS	2.45	MS		
1 0 9	1 0 4	2.403	2.396	S	2.325	M		
1 1 5	1 1 3	2.343	2.344	S	2.26	M	2.27	0 0·6
1 1 7	1 1 3	2.110						
2 1 0	2 1 I	2.098	2.103	M	2.03	MS	2.02	3 1·0
1 0 II	1 0 6	2.024	2.020	M-				
0 0 12	0 0 6	1.980						
2 1 4	2 1 1	1.979	1.978	M+	1.92	MW	1.927	2 0·6
0 1 10	0 1 5	1.872	1.869	M	1.81	W	1.818	4 0·0
2 0 10	2 0 4	1.838	1.835	W+				
3 0 5	3 0 4	1.791	1.791	W	1.745	VVW		
1 0 13	1 0 6	1.743	1.737	W				
1 1 11	1 1 5	1.685						
3 0 7	3 0 2	1.680	1.678	W+	1.625	VW		
3 1 1	3 1 I	1.628	1.626	VW				
3 1 3	3 1 3	1.598	1.598	M	1.55	M	1.543	2 2·6
3 0 9	3 0 6	1.560	1.561	W+				
3 1 5	3 1 1	1.543	1.542	M	1.495	MW	1.508	3 1·6
1 0 I5	1 0 8	1.528	1.527	M				
0 2 0	0 2 0	1.520	1.521	W	1.461	MW		
0 0 16	0 0 8	1.485						
0 1 14	0 1 7	1.482	1.479	M	1.435	VVW	1.424	1 1·9
0 2 4	0 2 2	1.473						
4 0 0	4 0 2	1.450	1.450	W+	1.41	M	1.420	4 0·6
1 2 3	1 2 2	1.446						
2 1 12	2 1 5	1.440	1.439	VS	1.395	S	1.400	3 3·0
1 0 17	1 0 8	1.359						
0 2 8	0 2 4	1.353	1.353	M, Br.				
1 2 7	1 2 4	1.349						
2 2 2	2 2 0	1.338	1.337	M-	1.293	W		
3 1 II	3 1 7	1.302						
4 1 2	4 1 I	1.301	1.301	M-	1.265	VW		

TABLE 1. (continued)

$\beta\text{-Ga}_2\text{O}_3$			$\theta\text{-Al}_2\text{O}_3$					
Ortho- rhombic <i>hkl</i>	Monoclinic		$d_{\text{obs.}} \text{ \AA}$	<i>I</i>	$d_{\text{obs.}} \text{ \AA}$ (5)	<i>I</i>	Tertian's Hexagonal Cell (2)	
	<i>hkl</i>	$d_{\text{calc.}} \text{ \AA}$					$d_{\text{calc.}} \text{ \AA}$	<i>hkl</i>
1 2 9	1 2 4	1.285	1.283	M-	1.235	VW		
3 0 15	3 0 6	1.225	1.222	W	1.188	?		
1 0 $\bar{1}9$	1 0 $\bar{1}0$	1.222						
3 1 13	3 1 5	1.217						
			1.210	VW	1.161	VVW		
			1.169	VW	1.113	VW		
			1.159	VW-				
			1.146	M				
			1.133	W+				
			1.098	W	1.069	VVW		
			1.089	VW				
			1.076	W+	1.041	VW		
			1.060	VW, Br.				
			1.050	W+				
			1.043	VW	1.015	W		
			1.033	M, Br.	1.001	W		
			1.017	W				
			1.013	W+, Br.	0.977	VW		
			0.988	M	0.957	VW		
			0.976	VW				
			0.964	VW	0.938	VW		
			0.953	VW				
			0.945	VVW	0.919	VVW		
			0.937	W	0.910	VVW		
			0.930	W, Br.	0.893	VW		
			0.909	W, Br.				
			0.895	W, Br.				
			0.891	W+				
			0.881	W+	0.857	VVW		
			0.871	W+, Br.				
			0.861	M-	0.84	VVW		
			0.845	W	0.825	MW		
			0.843	W				
			0.836	M-				
			0.829	M				
			0.818	W+				
			0.815	W				
			0.798	M-				
			0.796	W				
			0.789	M-				
			0.784	M-				
			0.775	M				

A portion of the b -axis zero-level Weissenberg pattern is reproduced in Fig. 3*a*. The schematic interpretation is presented in Fig. 3*b*, in which it can be seen that certain sets of reflections derive from the normal (lower) monoclinic cell, whereas others derive from the cell in twinned position. In particular, along the $(30l)$ lattice row of Fig. 3*a*, the reflections alternate in character, every other one being visibly multiple. This demonstrates that the crystals consist of sections in twinned orientation sandwiched between portions in normal position. Depending on the relative masses of the two portions in a given crystal, the relative intensity of the set of reflections from one orientation should differ with respect to that from the other orientation. This effect has been noted, further substantiating the postulated twinned monoclinic morphology.

CHARACTERIZATION OF θ - Al_2O_3

Table 1 presents the powder diffraction data for both β - Ga_2O_3 and θ - Al_2O_3 . The observed Ga_2O_3 reflections are indexed with respect to both orthorhombic and monoclinic unit cells. The d -spacings have been calculated and compared with observed values. Isomorphism of the two compounds permitted direct indexing of the Al_2O_3 pattern. The cell dimensions of θ - Al_2O_3 are contracted with respect to those of its Ga_2O_3 isomorph by approximately 3%. The only other cell listed for θ - Al_2O_3 is one of hexagonal symmetry ($a_0 = 8.40 \text{ \AA}$, $c_0 = 13.65 \text{ \AA}$) given by Tertian (13), who reported obtaining crystals of this phase by calcining monocrystals of hydrated alumina. Using Tertian's cell, Ervin (2) calculated the d -spacings listed in Table 1. It will be noted that these spacings do not account for all the lines of the observed single-phase powder pattern, especially four rather prominent reflections between 2.325 and 2.74 \AA .

It has been demonstrated by the foregoing evidence that β - Ga_2O_3 is a distinct crystalline phase, characterized by a specific unit cell. Its alumina isomorph, θ - Al_2O_3 , with which it forms a complete solid solution series, has thus been identified as an equally discrete phase of alumina. This characterization of θ - Al_2O_3 lends credence to the belief that other varieties of alumina, as well as gallia, might similarly be described as equally discrete crystalline phases.

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