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SYNTHESIS AND STRUCTURE OF PHASES IN THE In_2O_3-Ga_2O_3 SYSTEM

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Abstract—Compositions $Ga_{2-x}In_xO_3$ ($x = 0{\cdot}0$–$1{\cdot}0$) having the β-Ga_2O_3 structure have been prepared in powder form and as single crystals by several techniques and characterized by X-ray and resistivity measurements. The composition $InGaO_3$ was found to transform at high pressures to a new phase, $InGaO_3$ II.

$InGaO_3$ II has a simple hexagonal oxide structure which is the first structure reported containing Ga^{+3} in five-fold co-ordination. The cell parameters are: $a = 3{\cdot}310 \pm 0{\cdot}002$ Å, $c = 12{\cdot}039 \pm 0{\cdot}002$ Å, $Z = 2$, $\rho_c = 6{\cdot}756$ g/cm³, space group $P6_3/mmc$.

Interatomic distances obtained from least-squares refinement results are In-O(1)[×2], 3·010 Å; In-O(2)[×6], 2·174 Å; Ga-O(1)[×3], 1·911 Å; Ga-O(2)[×2], 1·973 Å. $InGaO_3$ II is isotypic with hexagonal $YAlO_3$, and its structure is related to that of $YMnO_3$ which contains five-co-ordinated Mn^{+3}.

INTRODUCTION

THE Ga_2O_3-In_2O_3 system was originally investigated by Goldschmidt[1] who found three phases present having the α-alumina (corundum), β-gallia, and C rare-earth structures. From this work it is apparent that at low temperatures (<1000°C) Ga_2O_3 has the α-alumina structure and at higher temperatures the β-gallia structure, whereas In_2O_3 was found to have only the C rare-earth structure.

Goldschmidt[1] investigated the intermediate compositions in the In_2O_3-Ga_2O_3 system and found that these compositions occur in all three structures in the order C rare-earth (39–100 mole per cent In_2O_3), α-alumina (21–100 mole per cent Ga_2O_3), and β-gallia with increasing temperature. Beta $Ga_{2-x}In_xO_3$ structures were found to occur up to $x = 1{\cdot}0$ in the region 800°–1300°C. Schneider *et al.*[2] studied the composition In_2O_3:Ga_2O_3 and found a phase which they reported as having an unidentified structure similar to kappa alumina. MacDonald *et al.*[3] have recently confirmed the presence of Schneider's 1:1 phase. Our results on the In_2O_3-Ga_2O_3 system, obtained at lower temperatures than those of Schneider *et al.*, confirm those of Goldschmidt.

Remeika and Marezio[4] have shown that at pressures as high as 44 kbar for Ga_2O_3 the α-alumina structure is present, and Shannon[5] found that In_2O_3† also

*Contribution No. 1374.

†The usual convention for naming high-pressure forms of a material have been followed. The ambient-pressure form (C rare-earth type) of In_2O_3 is called In_2O_3 I and the high-pressure phase (corundum structure type) is called In_2O_3 II[5].

1. V. M. Goldschmidt, T. Barth and G. Lunde, *Skr. norske Vidensk.-Akad.* Mat.-Naturv. Kl. No. 7 (1925).
2. S. J. Schneider, R. S. Roth, and J. L. Waring, *J. Res. natn. Bur. Stan.* 65A, 345 (1961).
3. J. MacDonald, J. A. Gard and F. P. Glasser, *J. inorg. nucl. Chem.* **29**, 661 (1967).
4. J. P. Remeika and M. Marezio, *Appl. Phys. Lett.* **8**, 87 (1966).
5. R. D. Shannon, *Solid St. Commun.* **4**, 629 (1966).

has the α-alumina structure at 65 kbar. We were therefore surprised to find that high-pressure preparations of $Ga_2O_3 \cdot In_2O_3$ resulted in a different phase with a simple, unidentifiable X-ray powder pattern[6]. Only the β-gallia structure resulted from syntheses at ambient pressures with compositions $Ga_{2-x}In_xO_3$ ($x = 0{\cdot}0$–$1{\cdot}0$). Throughout this paper the latter form will be called β-$InGaO_3$ and the high-pressure phase $InGaO_3$ II. While this nomenclature is not very satisfactory, it seems to be the most reasonable choice until the complete system has been worked out.

Although the powder pattern of $InGaO_3$ II could not be identified, after the structure was solved and refined we found that a similar structure had been assigned to the low-temperature form of $YAlO_3$ by Bertaut and Mareschal[7]. In addition, the structure of $LuMnO_3$[8] is related but distorted, presumably because of a Jahn-Teller effect.

EXPERIMENTAL

Synthesis

Starting materials used in this investigation were Ga_2O_3 (6–9*s*) and In_2O_3 (5–9*s*) supplied by Spex Industries, Inc., Metuchen, N. J. Independent Spectrographic analysis of In_2O_3 showed in ppm: Fe, 50; Si, 50; Na, 50; and Mg, 10. The oxides were mixed in alcohol, dried, and remixed dry; this process was repeated twice. Several methods of synthesis were used.

(1) Ga_2O_3:In_2O_3 mixtures in ratios of 3 : 1, 2 : 1, and 1 : 1 were heated in Morganite Al_2O_3 crucibles in air at 1150°C for 24 hr. These samples were ground and reheated at 1250°C in air for 24 hr. X-ray diffraction patterns showed the presence of single phase β-$Ga_{2-x}In_xO_3$ solid solutions in the 3 : 1 and 2 : 1 mixtures. The 1 : 1 sample showed some unreacted In_2O_3. There was no evidence of the 1 : 1 phase reported by Schneider *et al.*[2] and MacDonald *et al.*[3]

(2) Similar mixtures were heated in sealed Pt tubes at 1200°C at a pressure of 3 kbar. A mixture with the composition $2In_2O_3$-Ga_2O_3 showed the presence of two phases: In_2O_3 and β-$Ga_{2-x}In_xO_3$. The other mixtures were single-phase β-$Ga_{2-x}In_xO_3$ solid solutions. The compositions were not determined analytically but were assumed to have the original composition since no second phases were detected.

(3) Millimeter-sized β-$Ga_{2-x}In_xO_3$ crystals were grown in several fluxes: PbF_2, PbF_2-Bi_2O_3, PbO-B_2O_3, and Bi_2O_3-B_2O_3. The mixtures were placed in 25 cc Pt crucibles, held at 1250°C for four days, cooled at 3°C/hr to 700°C, and quenched. The crystals varied from colorless to yellow and had rectangular or needle-like habit. Densities of three crystals were determined by the displacement method in bromoform. Although the melt compositions were Ga_2O_3:In_2O_3 the resulting crystals had widely varying compositions, as evidenced by the differing densities and cell dimensions. Table 1 summarizes the results of the flux growth experiments.

Resistivity data (Table 1) were obtained by the four-probe method on several crystals[9]. It appears that β-$Ga_{2-x}In_xO_3$ solid solutions are insulators, as is β-Ga_2O_3[10]. The anomalously low value obtained on one sample probably reflects the presence of an impurity. This is consistent with the density value of 6·48 and indicates the presence of either Pb or Bi.

(4) High-pressure synthesis was carried out using a tetrahedral anvil press. The procedure has been described elsewhere[9, 11]. Samples of the 1 : 1 composition were heated at 1200°C and a pressure of 65 kbar. Transparent, colorless crystals, which were later identified as a high-pressure variety of indium-gallium oxide ($InGaO_3$ II), were extracted from the Pt capsule. Unfortunately they were too small for an accurate density determination. The compositions $6In_2O_3$:$4Ga_2O_3$ and $4In_2O_3$:$6Ga_2O_3$ heated to 1300°C at 65 kbar resulted in mixtures of In_2O_3 II and $InGaO_3$ II and of α-Ga_2O_3

6. R. D. Shannon and C. T. Prewitt, *Am. Crystallogr. Assoc. Mtg.* Atlanta, Ga., Jan. 25–28, (1967).
7. F. Bertaut and J. Mareschal, *C.r. hebd. Séanc. Acad. Sci., Paris* **257**, 867 (1963).
8. H. L. Yakel, W. C. Koehler, E. F. Bertaut and E. F. Forrat, *Acta Crystallogr.* **16**, 957 (1963).
9. T. A. Bither, J. L. Gillson and H. S. Young, *Inorg. Chem.* **5**, 1559 (1966).
10. H. H. Tippens, *Phys. Rev.* **140A**, 316 (1965).
11. R. D. Shannon, *Inorg. Chem.* **6**, 1474 (1967).

Table 1. Summary of data on β-$Ga_{2-x}In_xO_3$ (flux-grown crystals)

Flux	Unit cell			Density	Approx. composition	ρ(25°C)Ω-cm	E*
	a	*b*	*c*				
PbF_2 4·5 g In_2O_3 } 0·5 Ga_2O_3 }	12·80 $\beta = 102{\cdot}4°$	3·198	5·966	6·20(obs.) 6·40(calc.)	$Ga_{1\cdot1}In_{0\cdot9}O_3$		
PbF_2 1·5 g Bi_2O_3 0·5 In_2O_3 } 0·5 Ga_2O_3 }	12·83 $\beta = 102{\cdot}4°$	3·192	5·973	6·48(obs.) 6·42(calc.)	$Ga_{1\cdot05}In_{0\cdot95}O_3$	10^3	0·28 eV
PbO 2·7 g B_2O_3 0·3 In_2O_3 } 0·5 Ga_2O_3 }	12·30 $\beta = 103{\cdot}7°$	3·049	5·820	5·92(obs.) 5·99(calc.)	$Ga_{1\cdot9}In_{0\cdot1}O_3$	10^{10}	1·1 eV
Bi_2O_3 0·9 g B_2O_3 0·1 In_2O_3 } 0·3 Ga_2O_3 }	12·836 $\beta = 102{\cdot}6°$	3·185	5·987	6·42(calc.)	$Ga_{1\cdot05}In_{0\cdot95}O_3$	10^{10}	

*Derived from the slope of $\log \rho$ vs. $1/T$.

and $InGaO_3$ II, respectively. Synthesis of $InGaO_3$ II at temperatures of 1100°C and pressures of 15, 20 and 30 kbar indicates a probable transition pressure for β-$GaInO_3 \rightarrow InGaO_3$ II to be in the vicinity of 3–15 kbar.

Crystals of $InGaO_3$ II when heated to 1020°C did not revert to the monoclinic structure; thus, this structure shows unusual stability for a high-pressure phase. These crystals, as observed under a hot-stage microscope, became brilliant yellow above 725°C. This thermochromic effect has also been noted for rutile. The resistivity of a single crystal of $InGaO_3$ II was found to be $1{\cdot}5 \times 10^{-2}$ Ω-cm and temperature independent from 4°K–298°K.

X-ray data

β-$Ga_{2-x}In_xO_3$. X-ray powder diffraction data were obtained with a Guinier-de Wolff camera on the samples prepared in the sealed Pt tubes using monochromatized CuKα radiation and a KCl internal standard. Films were read on a Mann film reader; d values were calculated using $\lambda(CuK\alpha_1) = 1{\cdot}54051$ Å and a (KCl) = 6·2931 Å. The samples were indexed on the basis of the monoclinic cell of β-Ga_2O_3; cell parameters were obtained by least-squares refinements. In Fig. 1 the cell dimensions are plotted for the β-$Ga_{2-x}In_xO_3$ solid-solution series. Table 3 gives refined cell dimensions for β-$Ga_{1\cdot0}In_{1\cdot0}O_3$ produced in a 3 kbar run.

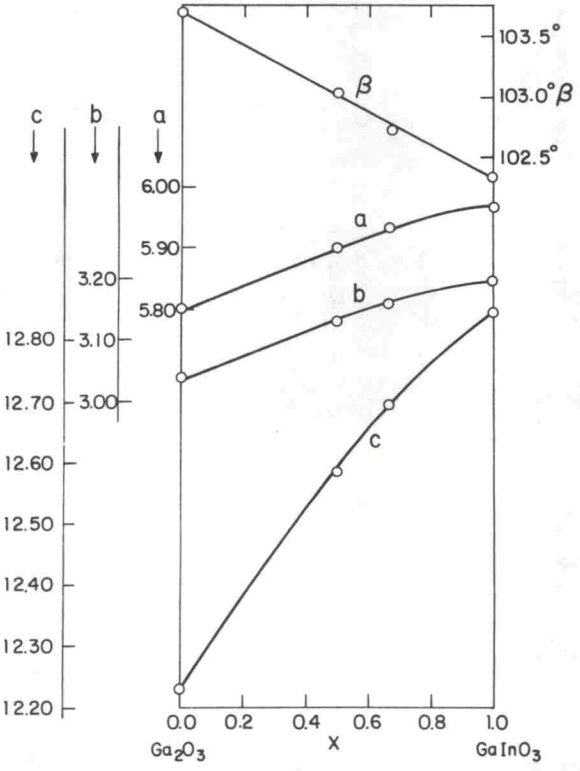


Fig. 1. Unit cell dimensions for β-$Ga_{2-x}In_xO_3$ solid solutions.

Unit-cell dimensions and space group data were obtained for three of the crystals. They were found to be of monoclinic symmetry with space group C2, Cm, or C2/m. The crystals were assumed to have the β-Ga_2O_3 structure with space group C2/m. The compositions of these crystals were approximated from the cell dimensions and the use of Fig. 1.

$InGaO_3$ II. Cell parameters for $InGaO_3$ II were obtained in the same manner as for β-$Ga_{2-x}In_xO_3$. Table 2 gives observed and calculated d values for $InGaO_3$ II and β-$GaInO_3$. The space group of $InGaO_3$ II was obtained from examination of precession photographs. Here the symmetry was hexa-

gonal with the only absences corresponding to $l \neq 2n$ for the *hhl* class of reflections. A test for piezoelectricity was negative, and the holosymmetric space group $P6_3/mmc$ was assigned and later confirmed in the structure analysis. Table 3 gives the pertinent cell data.

Table 2. Powder diffraction data for β-$GaInO_3$ and $InGaO_3$ II

	β-$GaInO_3$				$InGaO_3$ II		
Index	$d_{calc.}$	$d_{obs.}$	$I_{obs.}$	Index	$d_{calc.}$	$d_{obs.}$	$I_{obs.}$
200	6·274			002	6·019	6·010	35
001	5·827	5·833	2	004	3·010	3·007	80
20$\bar{1}$	4·817	4·815	15	100	2·867	2·867	55
201	3·874			101	2·789	2·789	80
400	3·137			102	2·588	2·588	100
110	3·104			103	2·333	2·333	10
40$\bar{1}$	3·049	3·047	15	104	2·076	2·076	40
002	2·913	2·919	15	006	2·006		
20$\bar{2}$	2·890	2·893	10	105	1·844	1·844	25
11$\bar{1}$	2·802	2·795	20	110	1·655	1·656	70
111	2·681	2·678	100	106	1·644	1·644	50
310	2·543	2·544	15	112	1·596	1·596	5
401	2·543			008	1·505	1·505	10
31$\bar{1}$	2·451	2·455	5	107	1·475	1·475	10
202	2·449	2·448	15	114	1·450	1·450	35
40$\bar{2}$	2·408	2·409	5	200	1·433	1·433	5
311	2·227	2·225	—0	201	1·423	1·424	10
11$\bar{2}$	2·183	2·182	15	202	1·394	1·395	20
60$\bar{1}$	2·118	2·118	5	203	1·350		
600	2·091	2·092	5	108	1·332		
112	2·070	2·070	2	204	1·294		
31$\bar{2}$	2·054	2·053	5	116	1·277		
20$\bar{3}$	1·979			205	1·232		
510	1·976	1·973	15	109	1·212		
51$\bar{1}$	1·975			0010	1·204		
003	1·942			206	1·166		
402	1·937			118	1·113		
60$\bar{2}$	1·904			1010	1·110		
601	1·846			207	1·101		
40$\bar{3}$	1·838			210	1·084		
312	1·803			211	1·079		
511	1·782			212	1·066		
51$\bar{2}$	1·781	1·781	20	213	1·046		
203	1·752			208	1·038		
11$\bar{3}$	1·687			1011	1·022		

A tabular crystal with irregular outline was selected for intensity collection. The dimensions of this crystal were approximately $0{\cdot}018 \times 0{\cdot}012 \times 0{\cdot}006$ cm with c parallel to the shortest dimension. Data were obtained with a Picker automatic diffractometer using a scintillation detector and MoKα ($\lambda = 0{\cdot}7107$) radiation. All reflections with positive $hk\ell$ out to a two theta of 90° were recorded and combined into a set of 181 non-equivalent reflections, all of which were above background and used in refinement. Reflections were scanned at 1°/min for a total angle of 2° plus the α_1-α_2 separation. Forty-second backgrounds were measured at the extremes of each scan. Along with the absorption correction[12], the Zachariasen[13] secondary extinction coefficient β was calculated for each reflection to

12. B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr.* **122**, 24 (1965).
13. W. H. Zachariasen, *Acta Crystallogr.* **16**, 1139 (1963).

Table 3. Cell data

	β-$InGaO_3$	$InGaO_3$ II
Structure	β-Ga_2O_3	$YAlO_3$
a	$12{\cdot}843 \pm 0{\cdot}002$	$3{\cdot}310 \pm 0{\cdot}002$ Å
b	$3{\cdot}195 \pm 0{\cdot}001$	—
c	$5{\cdot}974 \pm 0{\cdot}001$	$12{\cdot}035 \pm 0{\cdot}002$ Å
β	$102{\cdot}36 \pm 0{\cdot}01$	—
Z	4	2
Space group	C2/m	$P6_3/mmc$
Calculated density	6·447 g/cm³	6·756 g/cm³

be used later in least-squares refinement. Weights were applied to each observation using standard errors for each reflection computed from

$$\sigma_F = (LpT)^{-1/2}[(I+\sigma_I)^{1/2} - (I)^{1/2}]$$

where L, p, and T are the Lorentz, polarization, and transmission factors, respectively, and I is the integrated intensity. The standard deviation of the integrated intensity is

$$\sigma_I = \left[E + \left(\frac{T_c}{2T_B}\right) B + \epsilon^2 I^2\right]^{1/2},$$

where E is the total peak plus background, T_c the time for counting a peak, $2T_B$ the total background time, B the total background count, and ϵ an estimated deviation in the direct beam, set in this case to 0·03. Transmission factors varied from 0·07–0·24.

Structure and refinement

The structure was solved by assuming space group $P6_3/mmc$ and considering the equipoints available for locating each atom. Initially In was assigned to equipoint $2a$, Ga to $2c$, O(1) to $2d$, and O(2) to $4f$. Least-squares refinement reduced R to about 0·12, but no further. A Fourier synthesis showed that O(1) should have been placed on $2b$; when this change was made, the refinement proceeded normally to a final R of 0·028 for all reflections. The final weighted R was 0·044.

In the final stages of refinement, anisotropic temperature factors were varied along with the Zachariasen[13] secondary extinction parameter C where

$$F_{corr} = F_0[1 + C\beta I_0].$$

Atomic scattering factor curves used for structure factor calculations were taken from Cromer and Waber[14] for In^{+3}, International Tables for X-ray Crystallography (Vol. III) for Ga^{+3}, and Tokonami[15] for O^{-2}. Both real and imaginary anomalous dispersion terms were applied for In and Ga using values given by Cromer[16].

Table 4 lists the observed and calculated structure factors, each multiplied by 10. These represent averaged structure factors where equivalent reflections were recorded. Table 5 lists the final refined parameters.

DISCUSSION

β-$Ga_{2-x}In_xO_3$. Pure β-Ga_2O_3 is monoclinic with unit cell dimensions: $a = 12{\cdot}23$, $b = 3{\cdot}04$, $c = 5{\cdot}80$, and $\beta = 103{\cdot}7°$. The structure is composed of an array of cubic

14. D. T. Cromer and J. T. Waber, *Acta Crystallogr.* **18**, 104 (1965).
15. M. Tokonami, *Acta Crystallogr.* **19**, 486 (1965).
16. D. T. Cromer, *Acta Crystallogr.* **18**, 17 (1965).

Table 4. Observed and calculated structure factors for $InGaO_3$ II

K·L = 0, 0

H	FOB	FCA
1	2340	2180
2	1586	1609
3	3153	3257
4	884	921
5	673	727

K·L = 1, 0

H	FOB	FCA
1	5277	5225
2	1330	1311
3	1024	1010
4	2076	2000
5	659	628

K·L = 2, 0

H	FOB	FCA
2	2832	2789
3	856	847
4	731	675

K·L = 3, 0

H	FOB	FCA
3	1697	1687

K·L = 0, 1

H	FOB	FCA
1	2434	2218
2	1620	1568
4	749	753
5	559	549

K·L = 1, 1

H	FOB	FCA
2	1299	1228
3	887	862
5	474	469

K·L = 2, 1

H	FOB	FCA
3	696	669
4	511	506

K·L = 0, 2

H	FOB	FCA
0	1546	1256
1	3453	3373
2	2699	2726
3	613	601
4	1474	1512
5	1119	1152

K·L = 1, 2

H	FOB	FCA
1	771	856
2	2247	2255
3	1695	1692
4	451	455
5	990	987

K·L = 2, 2

	FOB	FCA
2	543	551
3	1399	1370
4	1076	1065

K·L = 3, 2

H	FOB	FCA
3	412	395

K·L = 0, 3

H	FOB	FCA
1	1012	900
2	939	886
4	497	493
5	364	364

K·L = 1, 3

H	FOB	FCA
2	758	763
3	565	562
5	312	315

K·L = 2, 3

H	FOB	FCA
3	443	439
4	335	337

K·L = 0, 4

H	FOB	FCA
0	5106	5177
1	2484	2556
2	1799	1822
3	2723	2660
4	1018	1028
5	802	807

K·L = 1, 4

H	FOB	FCA
1	3752	3911
2	1396	1473
3	1120	1130
4	1690	1691
5	684	694

K·L = 2, 4

H	FOB	FCA
2	2289	2313
3	951	944
4	770	748

K·L = 3, 4

H	FOB	FCA
3	1482	1437

K·L = 0, 5

H	FOB	FCA
1	1840	1796
2	1380	1355
4	714	696
5	507	517

K·L = 1, 5

H	FOB	FCA
2	1085	1093
3	778	790
5	415	444

K·L = 2, 5

H	FOB	FCA
3	622	623
4	479	477

K·L = 0, 6

H	FOB	FCA
0	360	210
1	3209	3363
2	2626	2659
3	136	179
4	1537	1528
5	1176	1176

K·L = 1, 6

H	FOB	FCA
1	192	63
2	2157	2218
3	1671	1698
4	193	199

K·L = 2, 6

H	FOB	FCA
2	138	196
3	1394	1391
4	1116	1088

K·L = 3, 6

H	FOB	FCA
3	182	180

K·L = 0, 7

H	FOB	FCA
1	1732	1644
2	1300	1274
4	706	686
5	522	517

K·L = 1, 7

H	FOB	FCA
2	1038	1045
3	768	773

K·L = 2, 7

H	FOB	FCA
3	625	618
4	488	479

K·L = 0, 8

H	FOB	FCA
0	3674	4009
1	1712	1751
2	1364	1407
3	2329	2330
4	902	899
5	704	713

K·L = 1, 8

H	FOB	FCA
1	3093	3205
2	1151	1209
3	945	978
4	1528	1557

K·L = 2, 8

H	FOB	FCA
2	2026	2066
3	826	831
4	670	661

K·L = 3, 8

H	FOB	FCA
3	1305	1334

K·L = 0, 9

H	FOB	FCA
1	868	838
2	709	715
4	422	421
5	317	326

K·L = 1, 9

H	FOB	FCA
2	595	613
3	465	469

K·L = 2, 9

H	FOB	FCA
3	374	382

K·L = 0, 10

H	FOB	FCA
0	632	675
1	2134	2182
2	1810	1859
3	487	489
4	1187	1194
5	935	941

K·L = 1, 10

H	FOB	FCA
1	576	577
2	1563	1625
3	1259	1309
4	398	376

K·L = 2, 10

H	FOB	FCA
3	1055	1098

K·L = 0, 11

H	FOB	FCA
1	1133	1097
2	917	915
4	561	558
5	435	437

K·L = 1, 11

H	FOB	FCA
2	782	786
3	614	616

K·L = 2, 11

H	FOB	FCA
3	496	510

K·L = 0, 12

H	FOB	FCA
0	3000	3223
1	1050	1016
2	936	902
3	2112	2132
4	655	649

K·L = 1, 12

H	FOB	FCA
1	2814	2732
2	812	820
3	686	698
4	1507	1500

Table 4. (*Contd.*)

K·L = 2, 12			K·L = 2, 13			K·L = 2, 14			K·L = 2, 15			K·L = 2, 16		
H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA
2	1862	1930	3	495	511	2	333	305	3	302	308	2	1303	1306
3	594	603				3	932	928						

K·L = 0, 13			K·L = 0, 14			K·L = 0, 15			K·L = 0, 16			K·L = 0, 17		
H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA
1	1060	1005	1	1629	1623	1	547	545	0	1851	1901	1	664	650
2	882	860	2	1444	1441	2	492	479	1	911	893	2	604	582
4	568	555	3	321	322	4	328	329	2	862	817	4	446	416
			4	1004	1001				3	1406	1417			
									4	607	600			

K·L = 1, 13			K·L = 1, 14			K·L = 1, 15			K·L = 1, 16			K·L = 1, 17		
H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA	H	FOB	FCA
2	766	754	1	336	352	2	436	428	1	1695	1704	2	526	528
3	608	607	2	1297	1299	3	366	355	2	778	754	3	471	447
			3	1081	1086				3	663	647			
			4	292	244									

close-packed oxygen atoms with two non-equivalent gallium sites[17]. Ga(1) occupies a distorted tetrahedral site and Ga(2) a distorted octahedral site. It is therefore not unreasonable to find that In substitutes in Ga(2) up to the composition $GaInO_3$. It is not clear why Schneider *et al.*[2] and MacDonald *et al.*[3] found no evidence of the β-Ga_2O_3 structure phase. It may be that the β-$Ga_{2-x}In_xO_3$ solid-solution series disproportionates in the temperature range 1250°C–1450°C. An approximate subsolidus phase diagram for Ga_2O_3-In_2O_3 was drawn by Schneider *et al.* on the assumption that there was a similarity to the Fe_2O_3-Ga_2O_3 diagram. It might be more appropriate to assume the phase diagram to be similar to that of the Yb_2O_3-Ga_2O_3 or Sc_2O_3-Ga_2O_3 systems. It is apparent that the diagram for Ga_2O_3-In_2O_3 is rather complex and needs detailed study.

Structure of $InGaO_3$ II

Figure 2 shows a portion of the structure and Table 6 gives the interatomic distances and interbond angles for $InGaO_3$ II. In is co-ordinated by six oxygens at 2·174 Å in a trigonal antiprism and by two more oxygens at 3·010 Å which lie

Table 5. Atom parameters in the $InGaO_3$ II structure

	In	Ga	O(1)	O(2)
x	0	$\frac{1}{3}$	0	$\frac{1}{3}$
y	0	$\frac{2}{3}$	0	$\frac{2}{3}$
z	0	$\frac{1}{4}$	$\frac{1}{4}$	0·0861(5)
$B_{eq.}$	0·54	0·34	0·58	0·67
$\beta 11$	0·0126(5)	0·0098(6)	0·0139(34)	0·0205(25)
$\beta 22$	0·0126	0·0098	0·0139	0·0205
$\beta 23$	0·00137(5)	0·00066(6)	0·0014(5)	0·0011(3)
$\beta 12$	0·00628	0·00493	0·0069	0·0102

17. S. Geller, *J. chem. Phys.* **33**, 676 (1960).

Table 6. Bond distances and angles in $InGaO_3$ II

2In—O(1)	3·010 Å
6In—	2·174(3)
3Ga—O(1)	1·911
2Ga—O(2)	1·973
Ga—O(ave.)	1·936
O(1)—O(1)	3·310
$O(2)^+$—$O(2)^+$	3·310
$O(2)^+$—$O(2)^-$	2·820(8)
O(1)—O(2)	2·747(4)
In—In	3·310
Ga—Ga	3·310
In—Ga	3·565
$O(2)^+$—In—$O(2)^+$	99·1(2)
$O(2)^+$—In—$O(2)^-$	80·9(2)
In—O(2)—Ga	118·5(2)
In—O(2)—In	99·1(2)

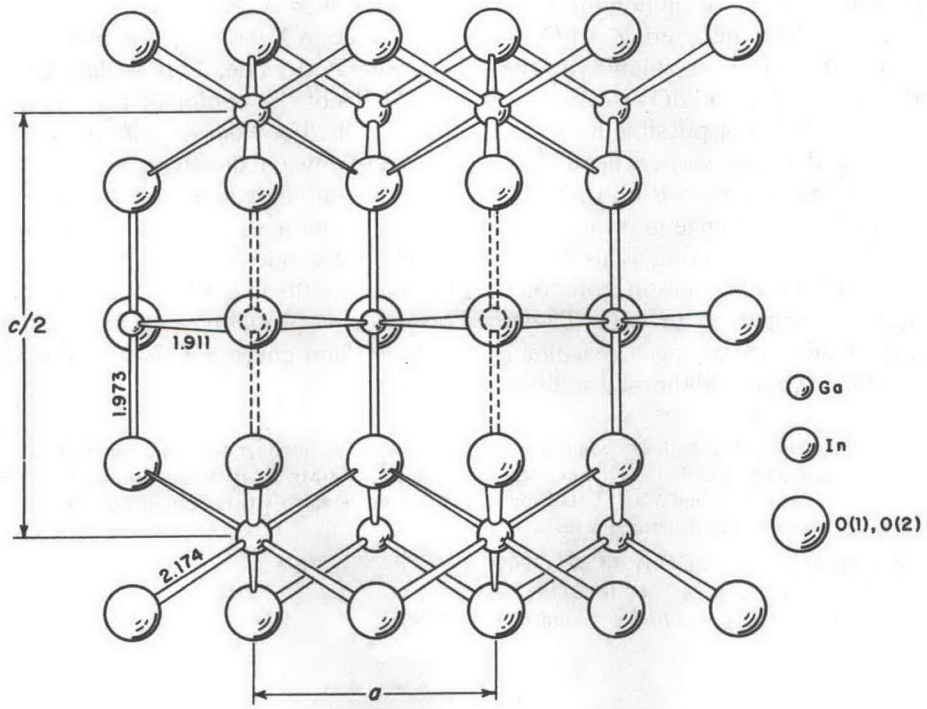


Fig. 2. Portion of the $InGaO_3$ II structure.

above and below the faces of the antiprisms perpendicular to the c axis. The indium polyhedra share edges and form a continuous layer normal to c. These layers alternate with layers of GaO_5^{-7} trigonal bipyramids, each of which shares its two apical vertices with three InO_6^{-9} polyhedra. The three equatorial Ga-O(1) distances are 1·911 Å and the other two are 1·973 Å, the average distance being 1·936 Å. This is about halfway between the tetrahedral Ga-O distance of 1·85 Å in $LiGaO_3$[18] and the octahedral distance of 2·00 Å in α-Ga_2O_3[19].

After the structure of $InGaO_3$ II was solved, we discovered that the structure reported by Bertaut and Mareschal[7] for hexagonal $YAlO_3$ is apparently the same as that of $InGaO_3$ II. Bertaut and Mareschal also found that Eu, Gd, Tb, Dy, Ho, and Er can substitute for Y in $YAlO_3$. Our attention was also drawn to $DyInO_3$[20], which has a powder pattern that can be indexed using a cell similar to that of $InGaO_3$ II except for one line with $d = 1·93$. Schneider also published patterns of $EuInO_3$ and $GdInO_3$ which have additional lines that cannot be indexed unless a is multiplied by $\sqrt{3}$. Such a cell would then correspond to the cell of $YMnO_3$ which contains Mn^{+3} in a distorted trigonal bipyramid. Since Mn^{+3} is a d^4 ion, this distortion is presumably due to the Jahn–Teller effect and it is not clear why $EuInO_3$ would be distorted. In any event, it is likely that $EuInO_3$ represents the first known compound with five-co-ordinated In.

If one uses a radius of 1·38 for four-co-ordinated oxygen in the various structures containing gallium, it is possible to assign average effective radii of 0·47, 0·56 and 0·62 Å, to four-, five-, and six-co-ordinated gallium ions, respectively. The radius for five co-ordination is just halfway between those for four and six. Analagous values for aluminum are 0·39, 0·48, and 0·54 Å. However, if 1·38 Å is subtracted from the average Al-O (2·00 Å) distance in $YAlO_3$[7], the aluminum radius is 0·62 Å, larger than even the six-co-ordinated value. This is difficult to understand unless $YAlO_3$ is disordered and Al is not the center of the trigonal bipyramid. It is not possible to tell from the published powder data if disorder is present, and further work is needed to explain these unusual distances.

The transformation β-$GaInO_3 \rightarrow InGaO_3$ II is another high-pressure transition involving a change in primary co-ordination. It involves a change from cubic closest packing of oxygens to a sequence ABACBC and is accompanied by a change in Ga co-ordination from four to five. This results in a 4·6 per cent change in density from 6·45 to 6·75. The transformation is probably a reconstructive transformation involving a reasonably high activation energy. This perhaps explains the exceptional thermal stability of $InGaO_3$ II.

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18. M. Marezio, *Acta Crystallogr.* **18**, 481 (1965).
19. M. Marezio, *J. chem. Phys.* **46**, 1862 (1967).
20. S. J. Schneider, *J. Res. natn. Bur.* Stand. **65A**, 429 (1961).