

Syntheses and Single-Crystal Data of Homologous Compounds, $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 3, 4,$ and 5), $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, 9,$ and 16) in the $\text{In}_2\text{O}_3\text{-ZnGa}_2\text{O}_4\text{-ZnO}$ System

Noboru Kimizuka,¹ Mitsumasa Isobe, and Masaki Nakamura

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba-shi, Ibaraki-ken 305, Japan

Received April 20, 1994; in revised form September 30, 1994; accepted October 3, 1994

Homologous compounds, $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 3$), $(\text{InGaO}_3)_2\text{ZnO}$, $\text{InGaO}_3(\text{ZnO})_m$ ($m \geq 1$), and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 7$) phases ($m =$ natural number) in the $\text{In}_2\text{O}_3\text{-ZnGa}_2\text{O}_4\text{-ZnO}$ system were synthesized at 1150–1550°C from In_2O_3 , Ga_2O_3 , and ZnO powders. The homologous compounds with smaller m are synthesized as temperature is elevated higher. Single crystals of $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 3, 4,$ and 5), $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 7, 8, 9,$ and 16) were grown by means of solid-state reactions in the mixtures of the starting compound powders with mixing ratio of $\text{In}_2\text{O}_3:\text{ZnO} = 1:m$ at 1550°C, $\text{In}_2\text{O}_3:\text{Ga}_2\text{O}_3:\text{ZnO} = 1:1:6$ at 1550°C, and $\text{Ga}_2\text{O}_3:\text{ZnO} = 1:m$ (in a mole ratio) at 1450–1550°C. The crystal data determined by means of a Weissenberg camera are as follows: $\text{In}_2\text{O}_3(\text{ZnO})_3$, $a = 3.34 \text{ \AA}$; and $c = 42.6 \text{ \AA}$; $\text{In}_2\text{O}_3(\text{ZnO})_4$, $a = 3.33 \text{ \AA}$ and $c = 33.5 \text{ \AA}$; $\text{In}_2\text{O}_3(\text{ZnO})_5$, $a = 3.32 \text{ \AA}$ and $c = 58.4 \text{ \AA}$; and $\text{InGaO}_3(\text{ZnO})_3$, $a = 3.29 \text{ \AA}$ and $c = 41.8 \text{ \AA}$. The crystal data determined by means of a single-crystal X-ray diffractometer are as follows: $\text{Ga}_2\text{O}_3(\text{ZnO})_7$, $a = 3.2512(1) \text{ \AA}$, $b = 19.654(3) \text{ \AA}$, and $c = 27.754(4) \text{ \AA}$; $\text{Ga}_2\text{O}_3(\text{ZnO})_8$, $a = 3.2497(1) \text{ \AA}$, $b = 19.682(3) \text{ \AA}$, and $c = 30.684(3) \text{ \AA}$; $\text{Ga}_2\text{O}_3(\text{ZnO})_9$, $a = 3.2520(1) \text{ \AA}$, $b = 19.707(4) \text{ \AA}$, and $c = 33.603(5) \text{ \AA}$; and $\text{Ga}_2\text{O}_3(\text{ZnO})_{16}$, $a = 3.2534(1) \text{ \AA}$, $b = 19.764(3) \text{ \AA}$, and $c = 54.208(5) \text{ \AA}$, orthorhombic crystal system in $Cmcm$ space group (No. 63). $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_m$ belong to $R\bar{3}m$ for $m =$ odd or $P6_3/mmc$ for $m =$ even, and their lattice constants are given in a hexagonal form. The crystal data for $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are discussed based upon the wurtzite-type crystal structure. © 1995 Academic Press, Inc.

INTRODUCTION

Indium sesquioxide (In_2O_3) is a useful compound for making transparent conductive electrodes and zinc oxide (ZnO) is used for varistors. Kasper (1) originally prepared $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 2\text{--}5$ and 7) and reported that they had layered structures related closely to the wurtzite structure. Kimizuka *et al.* (2) and Nakamura *et al.* (3–5) synthesized $(\text{InGaO}_3)_2(\text{ZnO})$ and $\text{InMO}_3(\text{ZnO})_m$ ($M = \text{Fe},$

$\text{Ga},$ or $\text{Al}; m = 1\text{--}13$) powders and estimated their crystal structures from those of LuMnO_3 (6), YbFe_2O_4 (7), and $(\text{YbFeO}_3)_2\text{FeO}$ (8) which were determined by single-crystal structural analyses. Cannard and Tilley (9) analyzed $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 4\text{--}7, 9,$ and 11) by high-resolution electron microscopy, and concluded that their structures are composed of the stacking of the metal–oxygen layers perpendicular to the c -axis in the hexagonal crystal system. Isobe *et al.* (10) determined crystal structures of $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4\text{--}6$) by single-crystal X-ray diffractometry, and concluded that they are composed of LuO_2^- and $(\text{FeZn}_m)\text{O}_{m+1}^+$ layers which were perpendicular to the c -axis in the hexagonal system. Crystal structures for $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4,$ and 5) are shown in Fig. 1. The Lu is in the octahedral site and both the Fe and Zn are in the trigonal bipyramidal sites in $\text{LuFeO}_3(\text{ZnO})_m$. $(\text{RMO}_3)_n(\text{M}'\text{O})_m$ in the $\text{R}_2\text{O}_3\text{-M}_2\text{O}_3\text{-M}'\text{O}$ systems ($R = \text{In}, \text{Sc}, \text{Y},$ or one of the rare earth elements; $M = \text{Fe}, \text{Ga},$ or $\text{Al}; M' =$ one of the divalent cation elements; n and m are integers) were reviewed from the viewpoints of thermochemistry, crystal chemistry, and solid-state physics (11). Nakamura *et al.* (4) determined the phase relations in the $\text{In}_2\text{O}_3\text{-ZnGa}_2\text{O}_4\text{-ZnO}$ system at 1350°C by a classical quenching method, and reported that there were homologous phases having solid solutions $(\text{InGaO}_3)_2\text{ZnO}$, $\text{In}_{1.33}\text{Ga}_{0.67}\text{O}_3(\text{ZnO})\text{-InGaO}_3(\text{ZnO})\text{-In}_{0.92}\text{Ga}_{1.08}\text{O}_3(\text{ZnO})$, $\text{In}_{1.68}\text{Ga}_{0.32}\text{O}_3(\text{ZnO})_2\text{-InGaO}_3(\text{ZnO})_2\text{-In}_{0.68}\text{Ga}_{1.32}\text{O}_3(\text{ZnO})_2$, and $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InGaO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Ga}_{1+x}\text{O}_3(\text{ZnO})_m$ ($m = 3\text{--}13$) ($0 < x < 1$). They measured the lattice constants of the solid solutions of the homologous phases by powder X-ray diffractometry and analyzed their data assuming $\text{InGaO}_3(\text{ZnO})_m$ to be isostructural with $\text{LuFeO}_3(\text{ZnO})_m$ without any single-crystal data. In the $\text{ZnO}\text{-ZnGa}_2\text{O}_4$ system, they concluded, there existed no binary compounds, but a solid solution of the ZnO phase, $(\text{Ga}_2\text{O}_3)_x(\text{ZnO})_{1-x}$ ($0 \leq x \leq 0.093$) was detected. The ZnO phase (at $x = 0$) has a wurtzite structure, and the crystal structure of the solid solution containing Ga_2O_3 was distorted from the wurtzite structure to a

¹ To whom correspondence should be addressed.

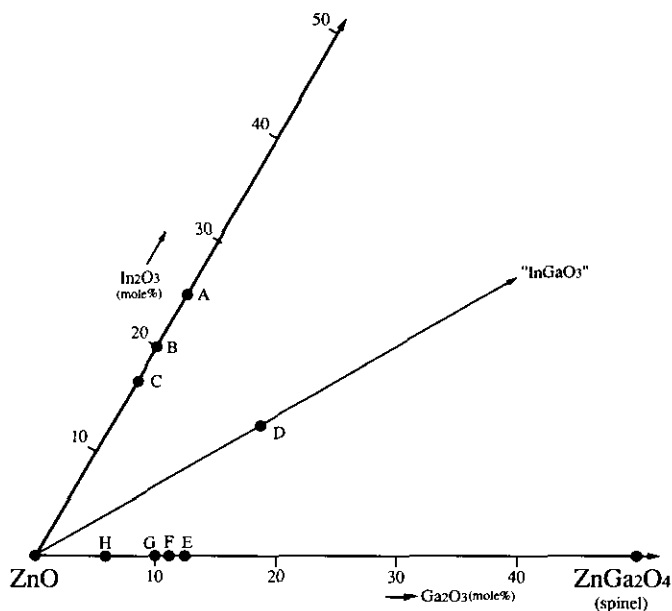


FIG. 2. Homologous compounds whose single-crystal X-ray data are obtained in the In_2O_3 - Ga_2O_3 - ZnO system at elevated temperatures: A, $\text{In}_2\text{O}_3(\text{ZnO})_3$; B, $\text{In}_2\text{O}_3(\text{ZnO})_4$; C, $\text{In}_2\text{O}_3(\text{ZnO})_5$; D, $\text{InGaO}_3(\text{ZnO})_3$; E, $\text{Ga}_2\text{O}_3(\text{ZnO})_7$; F, $\text{Ga}_2\text{O}_3(\text{ZnO})_8$; G, $\text{Ga}_2\text{O}_3(\text{ZnO})_9$; and H, $\text{Ga}_2\text{O}_3(\text{ZnO})_{16}$.

EXPERIMENTAL

1. Syntheses of the Homologous Compounds

$\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ at Elevated Temperatures

As starting compounds, we used In_2O_3 (99.9%), Ga_2O_3 (99.9%), and ZnO (99.9%) powders. Prior to mixing these starting compounds, we heated In_2O_3 at 800°C for 1 day, Ga_2O_3 at 900°C for 1 day, and ZnO at 1000°C for half a day in air. Stoichiometric proportions of these starting compounds were weighed and mixed in an agate mortar for half an hour. Each mixture of $\text{In}_2\text{O}_3 : \text{ZnO} = 1 : m$, $\text{In}_2\text{O}_3 : \text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : 1 : m$, or $\text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : m$ ($m = \text{natural number}$) (in a mole ratio) was sealed in a Pt tube (25 mm in length and 7 mm in diameter) for heating at temperatures above 1350°C . For preparation below 1250°C , each mixture was heated in an unsealed Pt tube. For the system Ga_2O_3 - ZnO , we heated mixtures above 1350°C , because the reaction rate in the Ga_2O_3 - ZnO mixtures were too slow at and below 1250°C . All the samples were rapidly cooled to room temperature after each heat treatment. Chemical reactions between the samples and Pt tubes were visually checked under a microscope. Evaporation of the samples during each heat treatment at this condition was negligible within experimental errors. Since the reaction rate in the formation of homologous compounds was relatively fast at and above 1350°C , we could obtain the desired single-phase compounds within 1 week, except $\text{In}_2\text{O}_3(\text{ZnO})_{2m}$ and $\text{InGaO}_3(\text{ZnO})_{2m}$ ($m \geq 3$)

4). However, at $T = 1150$ and 1250°C , the rates of the formation of $\text{In}_2\text{O}_3(\text{ZnO})_{2m}$ and $\text{InGaO}_3(\text{ZnO})_{2m}$ ($m \geq 3$) were so slow that the specimens in single phases were not obtained in our experimental conditions. $\text{InGaO}_3(\text{ZnO})_m$ ($m = 1-7$) prepared at $T = 1350$ or 1500°C did not decompose at 1150 or 1250°C for 1 week. Experimental facilities and methods we used were described elsewhere in detail (2).

2. Single-Crystal Growth of $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$

Single crystals of $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 3, 4, \text{ or } 5$), $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, 9, \text{ and } 16$) were grown by solid-state reactions in the mixtures of $\text{In}_2\text{O}_3 : \text{ZnO} = 1 : m$ ($m = 3, 4, \text{ and } 5$), $\text{In}_2\text{O}_3 : \text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : 1 : 6$, and $\text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : m$ ($m = 4, 7, 8, 9, \text{ and } 16$) at elevated temperatures. As the first step, all the mixtures sealed in Pt tubes were heated for a desired period and rapidly cooled to room temperature. Single crystals of $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ were reheated at 1350°C for 5 days. For growing single crystals of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, \text{ and } 9$) with suitable sizes, the mixture of $\text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : 4$ (in a mole ratio) was heated at 1450 - 1550°C for 5 days. $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, \text{ and } 9$) coexisting with ZnGa_2O_4 (spinel phase) was obtained. All the single crystals obtained were of two-dimensional thin plate. At and below 1550°C , we did not recognize a melt phase. We think crystal growth was occurred through vapor transport.

3. Determination of Crystal Data and Chemical Composition

Weissenberg photographs ($\text{CuK}\alpha$ radiation with a Ni filter) were taken of all the single crystals selected under a microscope, and their lattice constants and possible space groups were determined. The lattice constants for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were further refined using a single-crystal X-ray diffractometer ($\text{MoK}\alpha$ radiation with a graphite monochromator). $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ single crystals were supplied for EPMA analysis for determining their constituent chemical compositions, Ga_2O_3 and ZnO . We heated a mixture of $\text{Ga}_2\text{O}_3 : \text{ZnO} = 1 : 9$ (in a mole ratio) at 1350°C and obtained a powder specimen whose X-ray diffraction peaks were successfully indexed based upon the single-crystal data, $\text{Ga}_2\text{O}_3(\text{ZnO})_9$.

RESULTS AND DISCUSSION

1. Occurrence of the Homologous Compounds in the Systems In_2O_3 - ZnO , InGaO_3 - ZnO , and Ga_2O_3 - ZnO at Elevated Temperatures

In Fig. 3, we show the homologous compounds obtained in the present work and reported so far in the

TABLE 1A
Homologous Compounds $\text{In}_2\text{O}_3(\text{ZnO})_m$ Synthesized
at Various Temperatures

Mixing ratio of starting compounds, $\text{In}_2\text{O}_3 : \text{ZnO}$ (in a mole ratio)	T ($^{\circ}\text{C}$)	Period (day)	Phase(s) obtained
1:1	1150	9 + 5 + 7	IV + In_2O_3
1:4	1150	7 + 7	IV
1:5	1150	7	V
1:6	1150	8 + 8	V + VI(?) + VII
1:7	1150	9	VII
1:9	1150	7 + 9 + 5	IX
1:11	1150	7 + 9 + 5	XI
1:1	1250	7 + 8	IV + In_2O_3
1:4	1250	8 + 8	IV
1:5	1250	7	V
1:6	1250	8 + 8	V + VI(?) + VII
1:7	1250	7	VII
1:9	1250	7 + 9	IX
1:11	1250	7 + 9	XI
1:3	1550	5	III
1:4	1550	5	IV
1:5	1550	5	V

Note. ($s + t$) days means the following: After heating a specimen for s days, it was rapidly cooled to room temperature. Subsequently, the specimen was carefully crushed in an agate mortar under ethyl alcohol and heated for t days again, followed by a rapid cooling to room temperature.

In the $\text{Ga}_2\text{O}_3\text{-ZnO}$ system, it is already known that there is a spinel phase, ZnGa_2O_4 (space group $Fd\bar{3}m$, $a = 8.3349 \text{ \AA}$) (JCPDS, Card No. 38-1240) with cubic rather than hexagonal oxygen packing, it is therefore reasonable to assume that the $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ phases are limited to high m values only in the vicinity of ZnO phase (the wurtzite-type crystal structure with $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$, and space group $P6_3/mmc$) (14). Nakamura *et al.* (3) recently reported a phase with a distorted wurtzite structure, $(\text{Ga}_2\text{O}_3)_x(\text{ZnO})_{1-x}$ ($0 \leq x \leq 0.093$) in the $\text{ZnO-ZnGa}_2\text{O}_4$ system at 1350°C determined by powder X-ray

TABLE 1B
Homologous Compounds $\text{InGaO}_3(\text{ZnO})_m$ Synthesized at
Various Temperatures

Mixing ratio of starting compounds, $\text{In}_2\text{O}_3 : \text{Ga}_2\text{O}_3 : \text{ZnO}$ (in a mole ratio)	T ($^{\circ}\text{C}$)	Period (day)	Phase(s) obtained
$(\text{InGaO}_3)_2\text{ZnO}^a$	1150	5 + 7	$\text{In}_2\text{O}_3 + \text{ZnGa}_2\text{O}_4$
1:1:2	1150	7	I
1:1:3	1150	7 + 7	I + II
1:1:4	1150	7	II
1:1:5	1150	7 + 7	II + III
1:1:6	1150	7	III
1:1:7	1150	7 + 7	III + IV
1:1:8	1150	7	IV
1:1:9	1150	9 + 5	IV + V
1:1:10	1150	7 + 9	V
1:1:12	1150	7 + 9 + 5	V + VI(?) + VII
1:1:14	1150	9 + 5	VII
1:1:2	1250	7	I
1:1:3	1250	8	I + II
1:1:5	1250	8	II + III
1:1:7	1250	8	III + IV
1:1:8	1250	7	IV
1:1:10	1250	7	V
1:1:14	1250	8 + 8	VII
1:1:18	1250	8 + 8	IX
1:1:2	1550	3	I
1:1:4	1550	3	II
1:1:6	1550	3	III
1:1:8	1550	3	IV
1:1:10	1550	3	V
1:1:12	1550	3	VI
1:1:14	1550	3	VII
1:1:22	1550	3	XI
1:1:26	1550	3	XIII

^a The starting material $(\text{InGaO}_3)_2\text{ZnO}$ synthesized at 1350°C .

TABLE 1C
Homologous Compounds $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ Synthesized at Various Temperatures

Mixing ratio of starting compounds, $\text{Ga}_2\text{O}_3 : \text{ZnO}$ (in a mole ratio)	T ($^{\circ}\text{C}$)	Heating Period (day)	Phase(s) obtained
1:4	1350	4 + 3 + 4	$\text{Ga}_2\text{O}_3(\text{ZnO})_9$ + spinel
1:7	1350	7 + 6	$\text{Ga}_2\text{O}_3(\text{ZnO})_9$ + spinel
1:9	1350	4 + 3 + 4 + 4	$\text{Ga}_2\text{O}_3(\text{ZnO})_9$
1:11	1350	4 + 3 + 4 + 4	$\text{Ga}_2\text{O}_3(\text{ZnO})_{11}$
1:9	1450	4 + 5	$\text{Ga}_2\text{O}_3(\text{ZnO})_9$
1:4	1500	2 + 2	$\text{Ga}_2\text{O}_3(\text{ZnO})_8$ + spinel
1:7	1500	2 + 2	$\text{Ga}_2\text{O}_3(\text{ZnO})_8$ + spinel
1:4	1550	2 + 2	$\text{Ga}_2\text{O}_3(\text{ZnO})_7$ + spinel

TABLE 2
X-Ray Powder Data of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ Prepared at 1350°C

$h k l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)
0 0 2	16.69	16.78	3
4 0 9	2.9702	2.9726	1
6 0 5	2.9472	2.9486	5
3 1 0	2.9088	2.9127	1
3 1 2	2.8687	2.8698	14
6 0 6	2.8298	2.8309	8
3 1 3	2.8185	2.8187	12
4 0 10	2.7708	2.7731	<1
3 1 4	2.7509	2.7516	3
6 0 7	2.7072	2.7084	3
1 1 7	2.6649	2.6655	2
4 0 11	2.5923	2.5934	100
1 1 8	2.5474	2.5477	9
5 1 1	2.4993	2.4999	3
5 1 2	2.4786	2.4794	13
8 0 0	2.4615	2.4617	13
5 1 3	2.4453	2.4462	4
1 1 9	2.4313	2.4314	17
4 0 12	2.4313	2.4318	17
5 1 6	2.2866	2.2876	1
1 1 11	2.2108	2.2104	2
2 0 16	2.0517	2.0515	3
1 1 13	2.0111	2.0109	3
6 0 14	1.9356	1.9359	4
1 1 14	1.9205	1.9200	3
7 1 8	1.8967	1.8972	2
10 0 5	1.8893	1.8897	2
10 0 6	1.8581	1.8576	1
7 1 9	1.8479	1.8477	3
10 0 7	1.8222	1.8217	<1
9 1 8	1.6659	1.6659	5
9 1 9	1.6324	1.6321	10
12 0 2	1.6324	1.6334	10
0 2 0	1.6252	1.6251	11
8 0 16	1.5966	1.5966	3
12 0 2	1.6324	1.6334	10
0 2 0	1.6252	1.6251	11
8 0 16	1.5966	1.5966	3
2 2 2	1.5966	1.5961	3
9 1 10	1.5966	1.5966	3
11 1 2	1.5604	1.5614	1
0 2 6	1.5604	1.5606	1
0 0 22	1.5255	1.5255	14
11 1 6	1.5107	1.5100	4
1 2 9	1.4854	1.4855	3
3 1 20	1.4539	1.4540	3
12 0 11	1.4457	1.4453	5
6 2 4	1.4355	1.4349	1
14 0 3	1.3950	1.3957	6
4 2 11	1.3773	1.3771	10
13 1 0	1.3728	1.3731	7
13 1 2	1.3688	1.3685	3
14 0 6	1.3637	1.3642	2
6 2 9	1.3565	1.3566	3
8 2 0	1.3565	1.3562	3
8 0 22	1.2971	1.2967	5
16 0 0	1.2313	1.2309	1
18 0 4	1.0851	1.0849	1
1 3 1	1.0808	1.0812	2

TABLE 2—Continued

$h k l$	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)
1 3 8	1.0476	1.0475	1
5 3 2	1.0420	1.0426	1
5 3 3	1.0405	1.0401	1
1 3 9	1.0381	1.0389	1
5 3 8	1.0140	1.0136	2
14 2 10	1.0140	1.0139	2

Note. Orthorhombic: $a = 19.69(1)\text{Å}$, $b = 3.250(1)\text{Å}$, $c = 33.56(1)\text{Å}$, and $v = 2148(1)\text{Å}^3$.

diffraction. Although their solid solution range ($x = 0.093$) is reasonably close to $m = 9$ in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ within experimental error, we conclude that there is no solid solution which can be expressed as $(\text{Ga}_2\text{O}_3)_x(\text{ZnO})_{1-x}$, but instead there are a series of homologous phases $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (m is a natural number) in the $\text{ZnO-Ga}_2\text{O}_3$ system at elevated temperatures.

2. Crystal Structural Considerations for the Homologous Compounds $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$

In order to make the crystal structures of the homologous compounds clearer, we tried to grow their single crystals. Single-crystal growth conditions for $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 3, 4, \text{ and } 5$), $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, 9, \text{ and } 16$) are given in Table 3. All the crystal sizes we obtained were in the range $0.02 \times 0.1 \times 0.1 \text{ mm}^3$. Single-crystal data for $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are shown in Tables 4A and 4B. From the present single-crystal data, we can conclude the following:

(i) $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_3$ are isostructural with $\text{LuFeO}_3(\text{ZnO})_m$ (10) having space group $R\bar{3}m$ for $m = \text{odd}$ or $P6_3/mmc$ for $m = \text{even}$ and (ii) the crystal structural models for $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_m$ estimated from powder X-ray data (3) are consistent with those from the present single-crystal data.

In previous papers (3–5), we obtained the linear relations between c and m , where c is the lattice constant for $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InFeO}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, or $\text{AlO}_3(\text{ZnO})_m$ in the hexagonal crystal system (see Table 5). These relations can be understood if the crystal structures are composed of Z pieces of InO_2^- layers and Z pieces of $(M\text{Zn}_m)\text{O}_{m+1}^+$ layers ($M = \text{Fe, Ga, or Al}$) in which there are m pieces of ZnO layers. From the equations, we can see a common slope with 2.60–2.59 in the c - m diagram, which is in good agreement with $(\frac{1}{2}) \times (c = 5.200 \text{ Å})$ in which $c = 5.200 \text{ Å}$ is the lattice constant of ZnO (14) having wurtzite type. The lattice constants ($a = 3.3270(2) \text{ Å}$ and $c = 12.1750(1) \text{ Å}$) for InFeO_3 are re-

TABLE 3
Single-Crystal Growth Conditions for $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_3$, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ through Solid-State Reactions at Elevated Temperatures

Compound	Crystal growth conditions (Temp., period)		
	Starting mixture (In_2O_3 : Ga_2O_3 : ZnO)	First step	Second step
$\text{In}_2\text{O}_3(\text{ZnO})_3$	1 : 0 : 3	1550 °C, 5 days	1350 °C, 5 days
$\text{In}_2\text{O}_3(\text{ZnO})_4$	1 : 0 : 4	1550 °C, 5 days	1350 °C, 5 days
$\text{In}_2\text{O}_3(\text{ZnO})_5$	1 : 0 : 5	1550 °C, 5 days	1350 °C, 5 days
$\text{InGaO}_3(\text{ZnO})_3$	1 : 1 : 6	1550 °C, 5 days	1350 °C, 5 days
$\text{Ga}_2\text{O}_3(\text{ZnO})_7$	0 : 1 : 7	1550 °C, 5 days	
$\text{Ga}_2\text{O}_3(\text{ZnO})_8$	0 : 1 : 8	1550 °C, 5 days	
$\text{Ga}_2\text{O}_3(\text{ZnO})_9$	0 : 1 : 9	1450 °C, 5 days	
$\text{Ga}_2\text{O}_3(\text{ZnO})_9$	0 : 1 : 9	1550 °C, 7 days	1350 °C, 5 days
$\text{Ga}_2\text{O}_3(\text{ZnO})_{16}$	0 : 1 : 16	1550 °C, 5 days	

TABLE 4A
Single-Crystal Data for $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_3$

Compound	Single-crystal data					
	Lattice constants (Å)			Powder data ^a lattice constants (Å)		
	<i>a</i>	<i>c</i>	Space group	<i>a</i>	<i>c</i>	<i>c</i> _{calc}
$\text{In}_2\text{O}_3(\text{ZnO})_3$	3.34(1)	42.6(1)	$R\bar{3}m$	3.351(1)	42.48(1)	42.56
$\text{In}_2\text{O}_3(\text{ZnO})_4$	3.33(1)	33.5(1)	$P6_3/mmc$	3.337(1)	33.53(1)	33.56
$\text{In}_2\text{O}_3(\text{ZnO})_5$	3.32(1)	58.4(1)	$R\bar{3}m$	3.326(1)	58.103(1)	58.12
$\text{InGaO}_3(\text{ZnO})_3$	3.29(1)	41.8(1)	$R\bar{3}m$	3.288(1)	41.56(1)	41.56

^a From Nakamura *et al.* (4).

TABLE 4B
Single-Crystal Data for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, 9$, and 16)
[Space group: $Cmcm$ (No. 63), $Z = 8$]

Compound	Lattice constants (Å)		
	<i>a</i>	<i>b</i>	<i>c</i>
$\text{Ga}_2\text{O}_3(\text{ZnO})_7$	3.2512(1)	19.654(3)	27.745(4)
$\text{Ga}_2\text{O}_3(\text{ZnO})_8$	3.2497(1)	19.682(3)	30.684(3)
$\text{Ga}_2\text{O}_3(\text{ZnO})_9$	3.2520(1)	19.707(4)	33.603(5)
$\text{Ga}_2\text{O}_3(\text{ZnO})_{16}$	3.2534(1)	19.764(3)	54.208(5)
$\text{Ga}_2\text{O}_3(\text{ZnO})_9^a$	3.250(1)	19.69(1)	33.56(1)

^a The lattice constants were calculated by powder X-ray diffractometry.

TABLE 5
Relation between *c* (Å) and *m* in $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InFeO}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, and $\text{InAlO}_3(\text{ZnO})_m$

Compound	<i>c</i> (Å)	Ref.
$\text{In}_2\text{O}_3(\text{ZnO})_m$	$c = \{6.349 + 2.602 \times m\} \times Z$,	$m = 3-11, 13, 15, 20$ (3)
$\text{InFeO}_3(\text{ZnO})_m$	$c = \{6.105 + 2.596 \times m\} \times Z$,	$m = 1-11, 13, 15, 20$ (3)
$\text{InGaO}_3(\text{ZnO})_m$	$c = \{6.060 + 2.598 \times m\} \times Z$,	$m = 2-7, 9, 11, 13$ (4)
$\text{InAlO}_3(\text{ZnO})_m$	$c = \{5.932 + 2.598 \times m\} \times Z$,	$m = 9, 11, 13, 15, 17, 19$ (5)

Note. *c* was determined from X-ray powder data.

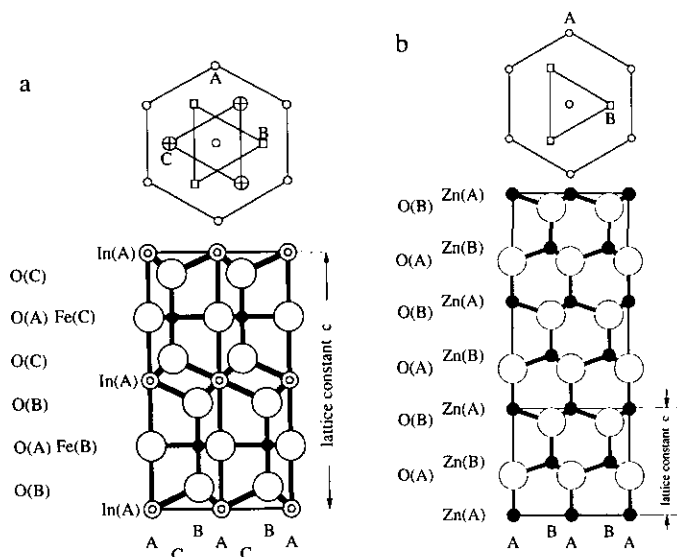


FIG. 4. Crystal structures for InFeO_3 and ZnO (wurtzite-type): (a) InFeO_3 and (b) ZnO .

ported by Giaquinta *et al.* (13). $(\frac{1}{2}) \times (c = 12.1750 \text{ \AA})$ is also in good agreement with the present value, 6.105 \AA . We listed c_{calc} for $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_3$ from the equations in Table 4A. We conclude that c_{obs} and c_{calc} are actually identical within experimental errors.

Crystal structures for InFeO_3 (13) and ZnO (wurtzite type) (14) are schematically shown in Fig. 4. If we compare the crystal structure of $\text{LuFeO}_3(\text{ZnO})$ with those in InFeO_3 and ZnO , we can easily understand the structural relations among them, namely, if we introduce a ZnO layer between the InO_2 layer and the FeO^+ layer perpen-

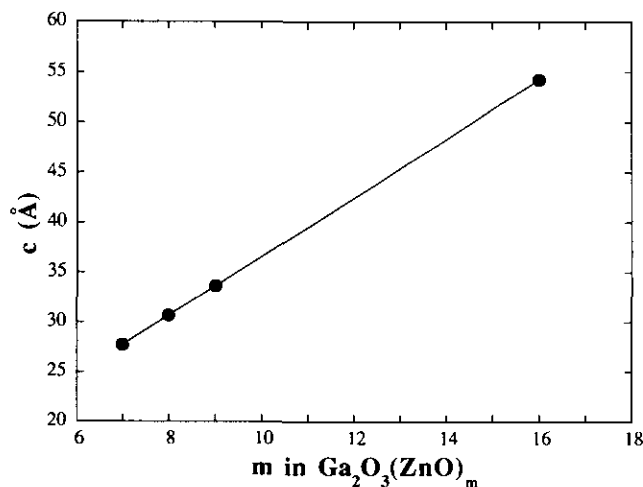


FIG. 5. The relation between the lattice constant, c , and m in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ with orthorhombic unit cell $c (\text{Å}) = 7.11(3) + 2.944(3) \times m$. c was determined from single-crystal data.

dicularly to the c -axis in the InFeO_3 structure, and randomly distribute zinc ions and iron ions in the tetrahedral/trigonal bipyramidal positions, we can obtain the crystal structure of $\text{InFeO}_3(\text{ZnO})$ which is isostructural with $\text{LuFeO}_3(\text{ZnO})$. If we introduce m pieces of ZnO layer, we can obtain $\text{InFeO}_3(\text{ZnO})_m$.

Lattice constants for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 7, 8, 9$, and 16) are listed in Table 4B together with a possible space group. From the Weissenberg photographs for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$, we observed extinction relations of $h + k \neq 2n$ for hkl and $l \neq 2n$ for $0kl$. The relations between c and m appears linear and given in Fig. 5. The analyses for the single-crystal structures are in progress by Isobe (15), however, from the tentative results obtained, we can conclude both the Zn and Ga are in tetrahedral sites and the crystal structures are constructed based upon the wurtzite-type structure.

Nakamura *et al.* (4) prepared powder samples with layered structures until $\text{In}_2\text{O}_3(\text{ZnO})_{13}$, $\text{InFeO}_3(\text{ZnO})_{13}$, and $\text{Fe}_2\text{O}_3(\text{ZnO})_{13}$ in the system $\text{In}_2\text{O}_3\text{-ZnFe}_2\text{O}_4\text{-ZnO}$ at 1350°C and concluded that there are solid solution ranges between $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 12$) having layered structures. In the system $\text{In}_2\text{O}_3\text{-ZnGa}_2\text{O}_4\text{-ZnO}$ at 1350°C , there is no full solid solution range between $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (3). Since $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ does not have $\text{LuFeO}_3(\text{ZnO})_m$ -type structure to which both $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InGaO}_3(\text{ZnO})_m$ belong, we think it is natural that there is no full solid solution range between $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. On the other hand, as already mentioned above, since $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ has the distorted $\text{LuFeO}_3(\text{ZnO})_m$ -type structure, it can become one of the end members of the solid solutions, $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m\text{-Fe}_2\text{O}_3(\text{ZnO})_m$.

In the systems $\text{ZnO-In}_2\text{O}_3$, ZnO-InFeO_3 , ZnO-InGaO_3 , ZnO-InAlO_3 , ZnO-RFeO_3 , ZnO-RGaO_3 , ZnO-RAlO_3 ($R = \text{Lu, Yb, or Tm}$), and $\text{ZnO-Fe}_2\text{O}_3$, there are $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{InFeO}_3(\text{ZnO})_m$, $\text{InGaO}_3(\text{ZnO})_m$, $\text{InAlO}_3(\text{ZnO})_m$, $\text{RFeO}_3(\text{ZnO})_m$, $\text{RGaO}_3(\text{ZnO})_m$, $\text{RAlO}_3(\text{ZnO})_m$, and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ which are isostructural with $\text{LuFeO}_3(\text{ZnO})_m$ or with slightly distorted $\text{LuFeO}_3(\text{ZnO})_m$; however, no layered compounds occurred in the systems $\text{ZnO-R}_2\text{O}_3$, $\text{ZnO-Sc}_2\text{O}_3$, $\text{ZnO-Cr}_2\text{O}_3$, or $\text{ZnO-Al}_2\text{O}_3$ at 1350°C (12), since $R(\text{III})$, $\text{Sc}(\text{III})$, and $\text{Cr}(\text{III})$ are unlikely to reside at a trigonal-bipyramidal site. Since $\text{Fe}(\text{III})$ can take octahedral sites and $\text{Ga}(\text{III})$ is not usually found octahedral sites in the oxide systems under a normal pressure, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ can take distorted $\text{LuFeO}_3(\text{ZnO})_m$ -type structure, and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ can have a structure in which both $\text{Ga}(\text{III})$ and $\text{Zn}(\text{II})$ take tetrahedral sites.

We obtained a series of new type of homologous phases, $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 9$) having an orthorhombic unit cell instead of a solid solution $(\text{ZnO})_{1-x}(\text{Ga}_2\text{O}_3)_x$ in the $\text{ZnO-Ga}_2\text{O}_3$ system at 1350°C . We are in process for

revising the phase relations in the $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_4\text{-ZnO}$ system at 1350°C reported by Nakamura *et al.* (4).

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