

Syntheses and Crystallographic Data of the Homologous Compounds $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 11, 13, 15,$ and 19) and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9) in the In_2O_3 - ZnFe_2O_4 - ZnO System

NOBORU KIMIZUKA,* MITSUMASA ISOBE, MASAKI NAKAMURA, AND TAKAHIKO MOHRI

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

Received June 24, 1992; in revised form September 10, 1992; accepted September 17, 1992

Syntheses of the homologous compounds $\text{InFeO}_3(\text{ZnO})_m$ ($m = \text{integer}$) in the In_2O_3 - ZnFe_2O_4 - ZnO system at 1150 - 1550°C are investigated. $\text{InFeO}_3(\text{ZnO})_m$ phases ($m = 1$ - 5 and 7) are stable above 1150°C . Single crystals of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 11, 13, 15,$ and 19) are grown by means of solid state reactions in mixtures of In_2O_3 , Fe_2O_3 , and ZnO powders, and crystals of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9) are grown from mixtures of Fe_2O_3 and ZnO powders at 1500 or 1550°C . The crystal data determined by means of a Weissenberg camera are as follows: $\text{InFeO}_3(\text{ZnO})$; $a = 3.32 \text{ \AA}$ and $c = 26.1 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_2$; $a = 3.31 \text{ \AA}$ and $c = 22.6 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_3$; $a = 3.30 \text{ \AA}$ and $c = 41.8 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_7$; $a = 3.27 \text{ \AA}$ and $c = 73 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_{11}$; $a = 3.27 \text{ \AA}$ and $c = 104 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_{13}$; $a = 3.27 \text{ \AA}$ and $c = 120 \text{ \AA}$; $\text{InFeO}_3(\text{ZnO})_{19}$; $a = 3.27 \text{ \AA}$ and $c = 167 \text{ \AA}$; and $\text{Fe}_2\text{O}_3(\text{ZnO})_8$; monoclinic crystal system with $a = 5.60 \text{ \AA}$, $b = 68.1 \text{ \AA}$, $c = 29.5 \text{ \AA}$, $\beta = 94.2^\circ$, and $C2/m$ space group. The crystal data determined by means of a single crystal X-ray diffractometer are as follows: $\text{InFeO}_3(\text{ZnO})_7$; $a = 3.267 \text{ \AA}$ and $c = 135 \text{ \AA}$; and $\text{Fe}_2\text{O}_3(\text{ZnO})_8$; orthorhombic crystal system with $a = 5.5987(4) \text{ \AA}$, $b = 68.358(7) \text{ \AA}$, $c = 53.67(4) \text{ \AA}$, and $Cmmm$ space group. $\text{InFeO}_3(\text{ZnO})_m$ belongs to $R\bar{3}m$ for $m = \text{odd}$ or $P6_3/mmc$ for $m = \text{even}$ and their lattice constants are given in a hexagonal form. The crystal data for $\text{InFeO}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are discussed based upon a wurtzite-type crystal structure. © 1993 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. They are also important constituents of many solid state multicomponent oxide compounds having interesting physical and/or chemical properties. Kasper (1) originally prepared the compounds $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 2$ - 5 and 7) and

reported that they had layered structures related closely to the structure of wurtzite. Kutoglu *et al.* (2) reported the crystal structure of InAlCuO_4 indexed as monoclinic (Cm) with $a = 5.728(3) \text{ \AA}$, $b = 3.309(2) \text{ \AA}$, $c = 8.352(3) \text{ \AA}$, and $\beta = 103.2(2)^\circ$, or indexed as pseudohexagonal with $a_h = 3.31 \text{ \AA}$ and $c_h = 24.39 \text{ \AA}$, using a single crystal grown from a flux. Kimizuka *et al.* (3) and Nakamura *et al.* (4, 5) synthesized $(\text{InGaO}_3)_2(\text{ZnO})$ and $\text{InMO}_3(\text{ZnO})_m$ ($M = \text{Fe, Ga, or Al, } m = 1$ - 13) powders and estimated their crystal structures from those of LuMnO_3

* To whom correspondence should be addressed.

(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 $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 4-7, 9$, and 11) by high resolution electron microscopy, and concluded that their structures are composed of the metal-oxygen layers stacked perpendicular to the c -axis in the hexagonal crystal system. Isobe *et al.* (10) determined crystal structures of $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4-6$) by single crystal X-ray diffractometry, and concluded that they are composed of $\text{LuO}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers which were perpendicular to the c -axis in the hexagonal system. Crystal structural models for $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4$, and 5) are shown in Fig. 1. The Lu is in the octahedral site, both the Fe and Zn are in the trigonal bipyramidal site, and the other Zn atoms are in the tetrahedral sites in $\text{LuFeO}_3(\text{ZnO})_m \cdot (\text{RMO}_3)_n(\text{M}'\text{O})_m$ in the R_2O_3 - M_2O_3 - $\text{M}'\text{O}$ systems (R : In, Sc, Y or one of the rare earth elements, M : Fe, Ga or Al, M' : one of the divalent cation elements, n and m : 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 In_2O_3 - ZnFe_2O_4 - ZnO system at 1350°C by a classical quenching method and reported that there were homologous phases having the solid solutions $\text{In}_{1.28}\text{Fe}_{0.72}\text{O}_3(\text{ZnO})$ - $\text{InFeO}_3(\text{ZnO})$, $\text{In}_{1.69}\text{Fe}_{0.31}\text{O}_3(\text{ZnO})_2$ - $\text{InFeO}_3(\text{ZnO})_2$ - $\text{In}_{0.85}\text{Fe}_{1.15}\text{O}_3(\text{ZnO})_2$, $\text{In}_2\text{O}_3(\text{ZnO})_m$ - $\text{InFeO}_3(\text{ZnO})_m$ - $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ ($m = 3-11$) ($0 < x < 1$), and $\text{In}_2\text{O}_3(\text{ZnO})_m$ - $\text{InFeO}_3(\text{ZnO})_m$ - $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 12$). They measured the lattice constants of the solid solutions of homologous phases by powder X-ray diffractometry and analyzed their data assuming $\text{InFeO}_3(\text{ZnO})_m$ to be isostructural with $\text{LuFeO}_3(\text{ZnO})_m$ without any single crystal data. From one of their conclusions, we can say that there are homologous phases $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 12, 13, \dots$) in the Fe_2O_3 - ZnO system at 1350°C analogous

to $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 3, 4, \dots$) in the In_2O_3 - ZnO system or $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, \dots$) in the InFeO_3 - ZnO system. In the present paper, we report (1) syntheses of homologous compounds $\text{InFeO}_3(\text{ZnO})_m$ in the InFeO_3 - ZnO system at the temperature range 1150-1550°C, and (2) single crystal data for $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 11, 13$, and 19) and $\text{Fe}_2\text{O}_3(\text{ZnO})_9$, which were determined by a Weissenberg camera and those for $\text{InFeO}_3(\text{ZnO})_{15}$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ determined by a single crystal X-ray diffractometer in the In_2O_3 - Fe_2O_3 - ZnO ternary system. (See Fig. 2.) The crystal structures of the $\text{InFeO}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are discussed based upon a wurtzite-type crystal structure.

Experimental

(1) Syntheses of the Homologous Compounds $\text{InFeO}_3(\text{ZnO})_m$ at Elevated Temperatures

As starting compounds, we used In_2O_3 (99.9%), Fe_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, Fe_2O_3 at 1000°C for 1 day, and ZnO at 1000°C for $\frac{1}{2}$ day in air. Stoichiometric proportions of these starting compounds were weighed and mixed in an agate mortar for half an hour. Each mixture of In_2O_3 : Fe_2O_3 : $\text{ZnO} = 1:1:m$ (m : integer) 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. All the samples were rapidly cooled at room temperature after each heat treatment. No chemical reactions between the samples and Pt tubes were seen under a microscope. Evaporation of the samples during each heat treatment under this condition is negligible within experimental errors. Since the reaction rate in the formations of homologous compounds was relatively fast at and above 1350°C, we could obtain the

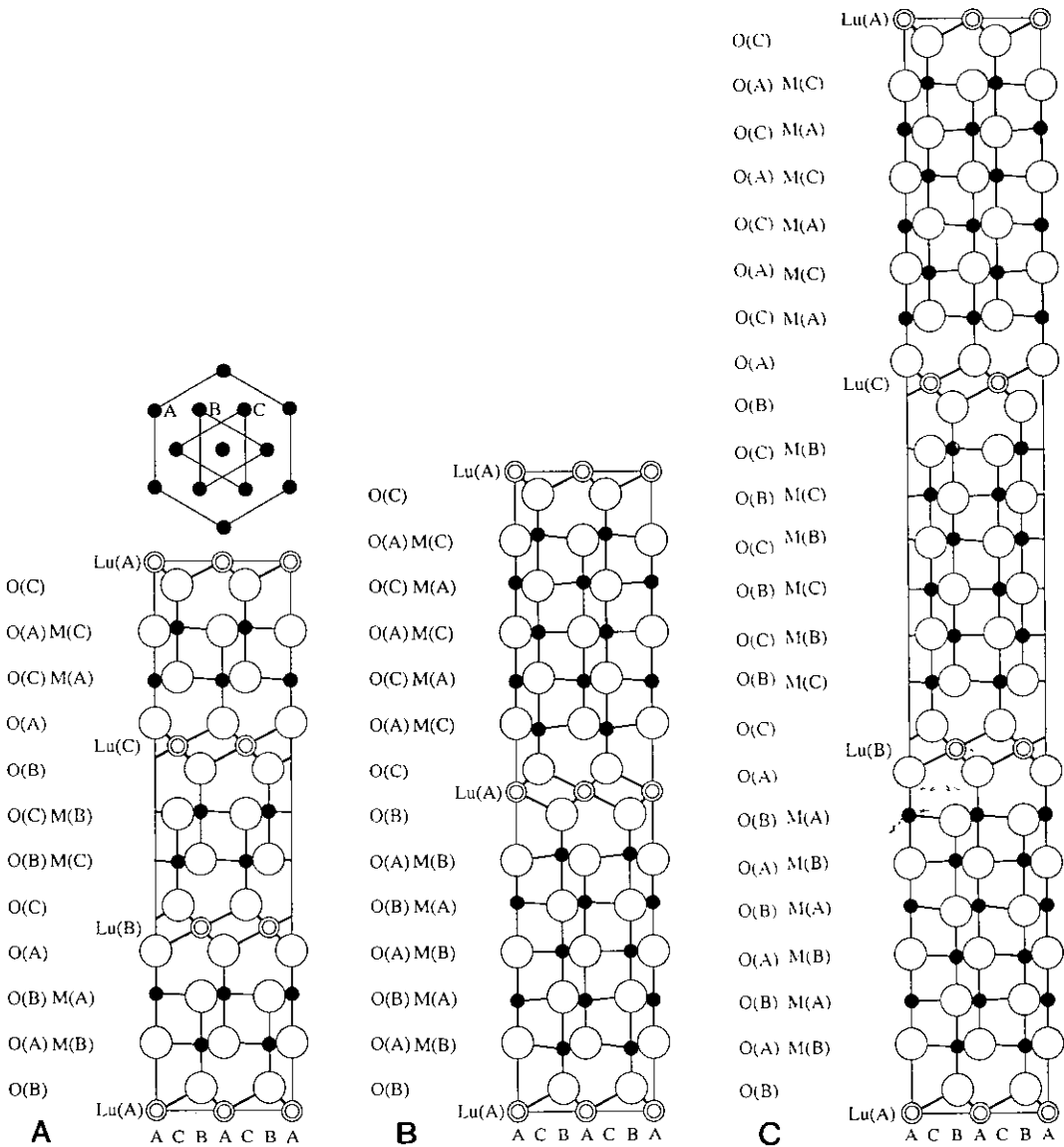


FIG. 1. Crystal structural models for LuFeO₃(ZnO) in A, LuFeO₃(ZnO)₄ in B and LuFeO₃(ZnO)₅ in C. A, B, and C represent three kinds of triangular lattices; *M* sites are occupied by Fe and/or Zn ions, Lu (○), Fe and/or Zn (●) and O (○).

desired single phase compounds within 1 week, except InFeO₃(ZnO)_{2m} ($m \geq 4$). However, at $T = 1150^\circ\text{C}$ and 1250°C , the rate of the formation of InFeO₃(ZnO)_{2m} ($m \geq 3$) was so slow that the specimens in single phases were not obtained in (7 + 9 + 5) or (7 + 9)

days. InFeO₃(ZnO)_m ($m = 1-7$) prepared at $T = 1350$ or 1500°C did not decompose at 1150 or 1250°C in the present experimental conditions. Experimental facilities and methods we used were described elsewhere in detail (4).

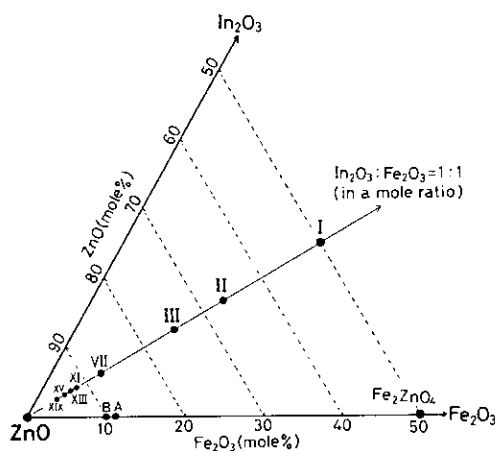


FIG. 2. Homologous compounds studied in the In_2O_3 - Fe_2O_3 - ZnO system at elevated temperatures: ●: $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 11, 13, 15$, or 19) or $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ or 9) whose single crystal data are obtained in the present work; (I) $\text{InFeO}_3(\text{ZnO})$, (II) $\text{InFeO}_3(\text{ZnO})_2$, (III) $\text{InFeO}_3(\text{ZnO})_3$, (VII) $\text{InFeO}_3(\text{ZnO})_7$, (XI) $\text{InFeO}_3(\text{ZnO})_{11}$, (XIII) $\text{InFeO}_3(\text{ZnO})_{13}$, (XV) $\text{InFeO}_3(\text{ZnO})_{15}$, and (XIX) $\text{InFeO}_3(\text{ZnO})_{19}$, (A) $\text{Fe}_2\text{O}_3(\text{ZnO})_8$, (B) $\text{Fe}_2\text{O}_3(\text{ZnO})_9$.

(2) Single Crystal Growth of $\text{InFeO}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$

Single crystals of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 9, 11, 13, 15$, and 19) were grown by solid state reactions in mixtures of In_2O_3 , Fe_2O_3 , and ZnO powders and those of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9) were grown from mixtures of Fe_2O_3 and ZnO powders at $T = 1500$ or 1550°C . As the first step, all the mixtures sealed in Pt tubes were heated for the desired period and rapidly cooled at room temperature (see Table II). Single crystals of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 7, 11, 13, 15$, and 19) could be picked up successfully after this process. For growing single crystals of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2$, and 3) with suitable sizes, the samples obtained in the first process were crushed in an agate mortar with ethyl alcohol for half an hour, and then reheated at 1500 or 1550°C for 5 days. For growing single crystals of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9), we heated three times. All

the single crystals obtained were thin two dimensional plates. At and below 1550°C , we did not recognize a melt phase. We think that crystal growth occurred through vapor transport.

(3) Determination of Crystal Data

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 both $\text{InFeO}_3(\text{ZnO})_{15}$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ were further refined using a single crystal X-ray diffractometer ($\text{MoK}\alpha$ radiation with a graphite monochromator).

Results and Discussion

(1) Occurrence of the Homologous Compounds in the InFeO_3 - ZnO System at Elevated Temperatures

(a) In Fig. 3A, we show the homologous compounds obtained in the present work and reported so far in the InFeO_3 - ZnO system at elevated temperatures. Starting mixtures, heating periods and phases obtained are summarized in Table I.

$\text{InFeO}_3(\text{ZnO})_m$ obtained as single phases at or above 1350°C were reheated at both 1150 and 1250°C for 7 days. No decompositions were observed in them and each X-ray powder diffraction peak of $\text{InFeO}_3(\text{ZnO})_m$ phases became sharper with increasing heating periods. We concluded that all the homologous phases, $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1$ -5 and 7), stable at or above 1350°C are stable at both 1150 and 1250°C also. At $T = 1150^\circ\text{C}$ and 1250°C , we could not obtain $\text{InFeO}_3(\text{ZnO})_{2m}$ ($m \geq 3$) in a single phase state. We could not conclude whether $\text{InFeO}_3(\text{ZnO})_{2m}$ ($m \geq 3$) was thermochemically unstable at this condition or the reaction rate in the formation from In_2O_3 , Fe_2O_3 , and ZnO powders was too slow. As we recognized in establishing the phase relations

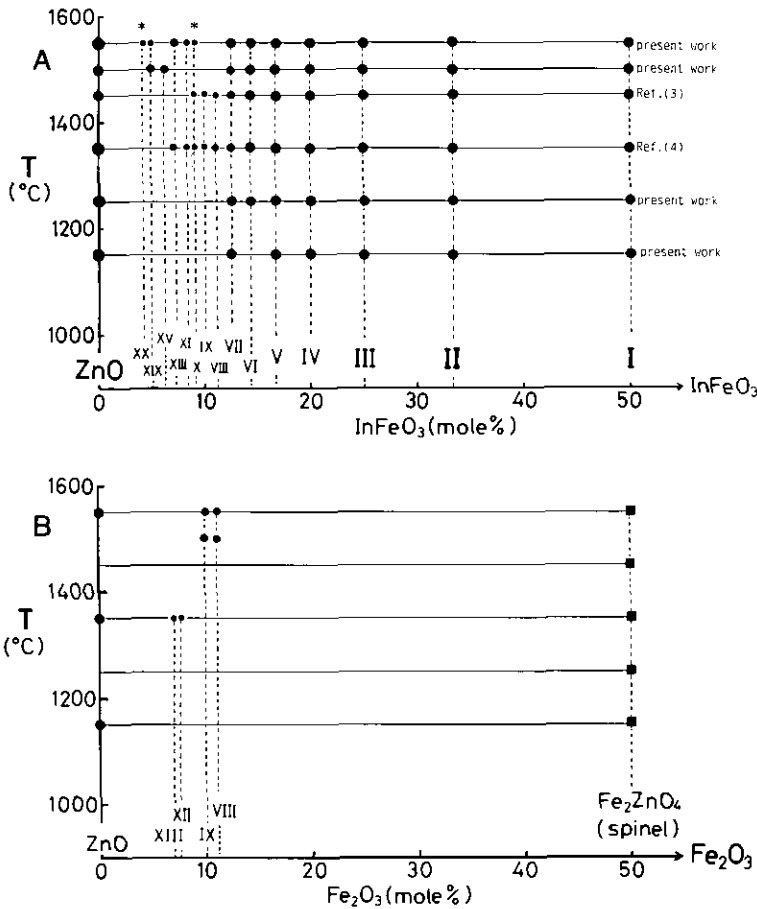


FIG. 3. (A) Homologous compounds, $\text{InFeO}_3(\text{ZnO})_m$ obtained at various temperatures. The results at 1350°C are cited from Ref. (4), and those at 1450°C are from Ref. (3). The data with * are cited from Ref. (4). (B) Homologous compounds, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ obtained at various temperatures. The results at 1350°C are cited from Ref. (4).

in the system $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ at 1350°C (4), the formation reaction rate in $\text{InFeO}_3(\text{ZnO})_{2m}$ is much slower than that in $\text{InFeO}_3(\text{ZnO})_{2m-1}$ at 1150°C .

Nakamura *et al.* (4) recently identified homologous compounds, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 12, 13, \dots$) in the $\text{Fe}_2\text{O}_3\text{-ZnO}$ system at 1350°C by powder X-ray. These are the end members in the solid solution ranges of $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m\text{-Fe}_2\text{O}_3(\text{ZnO})_m$. We obtained single crystals of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$

($m = 8$ and 9) at 1500°C and 1550°C (see Fig. 3B). In the $\text{Fe}_2\text{O}_3\text{-ZnO}$ system, there is a spinel phase, ZnFe_2O_4 (S.G.: $Fm\bar{3}d$, $a = 8.441 \text{ \AA}$) (JCPDS, Card No. 22-1012) with cubic rather than hexagonal oxygen packing; it is therefore reasonable to assume that the $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ phases are limited to high m values only in the vicinity of the ZnO phase (the wurtzite-type crystal structure with $a = 3.250 \text{ \AA}$, $c = 5.207 \text{ \AA}$, and space group $P6_3mc$) (12).

TABLE I
HOMOLOGOUS COMPOUNDS $\text{InFeO}_3(\text{ZnO})_m$
SYNTHESIZED AT VARIOUS TEMPERATURES

Mixing ratio of starting compounds: $\text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 : \text{ZnO}$ (in a mole ratio)	T(°C)	Period (day)	Phase(s) obtained
1:1:2	1150	7	I
1:1:4	1150	7	II
1:1:6	1150	7	III
1:1:8	1150	7	IV
1:1:10	1150	7 + 9	V
1:1:12	1150	7 + 9 + 5	V, VI(?), VII
1:1:14	1150	7 + 7	VII
1:1:3	1150	7 + 7	I, II
1:1:5	1150	7 + 7	II, III
1:1:7	1150	7 + 7	III, IV
1:1:2	1250	7	I
1:1:4	1250	7	II
1:1:6	1250	7	III
1:1:8	1250	7	IV
1:1:10	1250	7	V
1:1:12	1250	7 + 9	V, VI, VII
1:1:14	1250	7	VII
1:1:2	1500	5	I
1:1:4	1500	5	II
1:1:6	1500	5	III
1:1:8	1500	5	IV
1:1:10	1500	5	V
1:1:12	1500	5	VI
1:1:14	1500	5	VII
1:1:30	1500	3	XV
1:1:38	1500	3	XIX
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

(2) Crystal Structural Consideration for
the Homologous Compounds
 $\text{InFeO}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$

Single crystal growth conditions for $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, 7, 11, 13, 15,$ and 19) and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9) are given in Table II. All the crystal sizes we obtained were in the range $0.03 \times 0.1 \times 0.1$ mm. Single crystal data for $\text{InFeO}_3(\text{ZnO})_m$ are shown in Table IIIA. We can conclude from the present single crystal data that (1) $\text{InFeO}_3(\text{ZnO})$ is isostructural with $\text{LuFeO}_3(\text{ZnO})$ ($a = 3.4188(1) \text{ \AA}$ and $c =$

$25.46(2) \text{ \AA}$) (10), and the crystal structure of InAlCuO_4 is slightly distorted from that of $\text{InFeO}_3(\text{ZnO})$; (2) $\text{InFeO}_3(\text{ZnO})_m$ ($m = \text{odd}$) belongs to the $R\bar{3}m$ space group, and the single crystal data of $\text{InFeO}_3(\text{ZnO})_2$ and powder data of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 4, 6,$ and 8) (4) suggest that $\text{InFeO}_3(\text{ZnO})_{2m}$ belong to $P6_3/mmc$. The crystal structural models (4) for $\text{InFeO}_3(\text{ZnO})_m$ estimated from powder X-ray data are consistent with those from the present single crystal data.

In a previous paper (4), we obtained a relation between c , the lattice constants for $\text{InFeO}_3(\text{ZnO})_m$ in the hexagonal crystal system, and m : $c = \{p + q + (m - 1)r\}Z$, where Z is the number of molecular units in the unit cell ($Z = 3$ for $m = \text{odd}$ or $Z = 2$ for $m = \text{even}$), p is the thickness of the $\text{InO}_{1.5}$ layer (Å), q is the thickness of the $(\text{FeZn})\text{O}_{2.5}$ layer (Å), and r is the thickness of the ZnO layer. For this equation, ($p + q$) = 8.951 (Å) and $r = 2.602 \text{ (Å)}$ were calculated from the lattice constants of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1-7, 9, 11,$ and 13) in powder samples. This relation can be expected if the crystal structures are considered to be composed of Z pieces of $\text{InO}_{1.5}$ layers, Z pieces of $(\text{FeZn})\text{O}_{2.5}$ layers, and $(m - 1)Z$ pieces of ZnO layers perpendicular to the c -axis in a unit cell. We listed $c_{\text{calcd.}}$ for $m = 1-3, 7, 11, 13, 15,$ and 19 from

TABLE II
SINGLE CRYSTAL GROWTH CONDITIONS FOR
 $\text{InFeO}_3(\text{ZnO})_m$ THROUGH SOLID STATE REACTIONS
AT ELEVATED TEMPERATURES

Compound	Crystal growth condition (temp., period)		
	1st step	2nd step	3rd step
$\text{InFeO}_3(\text{ZnO})$	1500°C, 5 days	1550°C, 5 days	
$\text{InFeO}_4(\text{ZnO})_2$	1500°C, 5 days	1550°C, 5 days	
$\text{InFeO}_5(\text{ZnO})_3$	1500°C, 5 days	1550°C, 5 days	
$\text{InFeO}_6(\text{ZnO})_7$	1550°C, 3 days		
$\text{InFeO}_7(\text{ZnO})_{11}$	1550°C, 3 days		
$\text{InFeO}_8(\text{ZnO})_{13}$	1550°C, 3 days		
$\text{InFeO}_9(\text{ZnO})_{15}$	1500°C, 3 days		
$\text{InFeO}_{10}(\text{ZnO})_{19}$	1500°C, 3 days		
$\text{InFeO}_8(\text{ZnO})_8$	1500°C, 2 days	1500°C, 2 days	1550°C, 5 days
$\text{InFeO}_9(\text{ZnO})_9$	1500°C, 2 days	1500°C, 2 days	1550°C, 5 days

TABLE IIIA
SINGLE CRYSTAL AND POWDER DATA FOR $\text{InFeO}_3(\text{ZnO})_m$
($m = 1, 2, 3, 7, 11, 13, 15, \text{ and } 19$)

Compound	Single crystal data (Lattice constants and space group)			Powder data (Lattice constants)		
	a (Å)	c (Å)	S.G.	a (Å) ^a	c (Å) ^a	$C_{\text{calcd.}}$ (Å)
$\text{InFeO}_3(\text{ZnO})$	3.32	26.1	$R\bar{3}m$	3.320(1)	26.10(1)	26.10
$\text{InFeO}_3(\text{ZnO})_2$	3.31	22.6	$P6_3/mmc$	3.309(1)	22.58(1)	22.59
$\text{InFeO}_3(\text{ZnO})_3$	3.30	41.8	$R\bar{3}m$	3.299(1)	41.66(1)	41.68
$\text{InFeO}_3(\text{ZnO})_7$	3.27	73	$R\bar{3}m$	3.279(1)	72.86(1)	72.83
$\text{InFeO}_3(\text{ZnO})_{11}$	3.27	104	$R\bar{3}m$	3.268(1)	103.9(1)	104.0
$\text{InFeO}_3(\text{ZnO})_{13}$	3.27	120	$R\bar{3}m$	3.269(1)	119.6(1)	119.6
$\text{InFeO}_3(\text{ZnO})_{15}$	3.267	135	$R\bar{3}m$			135.1
$\text{InFeO}_3(\text{ZnO})_{19}$	3.27	167	$R\bar{3}m$			166.3

^a Ref. (4).

the above equation in Table IIIA. We think that $c_{\text{obsd.}}$ and $c_{\text{calcd.}}$ are actually identical within experimental errors.

Single crystal data for $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are given in Table IIIB. Extinction laws for $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ are $h + k \neq 2n$ for hkl and $l \neq$

$2n$ for $0kl$, and that for $\text{Fe}_2\text{O}_3(\text{ZnO})_9$ is $h + k \neq 2n$ for hkl .

The relation between the hexagonal unit cell for $\text{InFeO}_3(\text{ZnO})_8$ and the orthorhombic one for $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ is shown in Fig. 4A, and the relation between the hexagonal unit

TABLE IIIB
SINGLE CRYSTAL DATA FOR $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = 8$ and 9)

Compound	Single crystal data (Lattice constants and space group)		Relations to the hexagonal cell
	Weissenberg camera	Single crystal diffractometer	
	orthorhombic: $Ccmm$		
$\text{Fe}_2\text{O}_3(\text{ZnO})_8$	$a_0 = 5.60$ (Å) $b_0 = 68.4$ (Å) $c_0 = 53.7$ (Å)	$a_0 = 5.5987(4)$ (Å) $b_0 = 68.358(7)$ (Å) $c_0 = 53.67(4)$ (Å)	$\frac{1}{2} \times [a_0^2 + (b_0/21)^2]^{1/2} = a_h$ (= 3.238) $c_0 = c_h$ Note. $\text{InFeO}_3(\text{ZnO})_8$ S.G.: $P6_3/mmc$
	monoclinic: $C2/m$		
$\text{Fe}_2\text{O}_3(\text{ZnO})_9$	$a_m = 5.60$ (Å) $b_m = 68.1$ (Å) $c_m = 29.5$ (Å) $\beta = 94.2^\circ$		$\frac{1}{2} \times [a_m^2 + (b_m/21)^2]^{1/2} = a_h$ (= 3.24) $(9c_m^2 - a_m^2)^{1/2} = c_h$ (= 88.4) Note. $\text{InFeO}_3(\text{ZnO})_9$ S.G.: $R\bar{3}m$

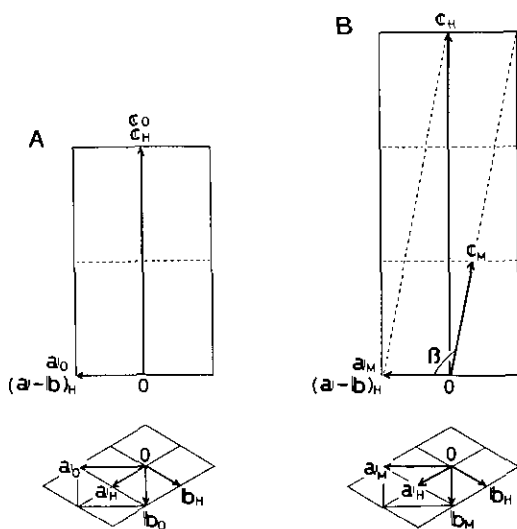


FIG. 4. (A) The relation between the unit cell of $\text{InFeO}_3(\text{ZnO})_8$ and that of $\text{Fe}_2\text{O}_3(\text{ZnO})_8$. (B) The relation between the unit cell of $\text{InFeO}_3(\text{ZnO})_9$ and that of $\text{Fe}_2\text{O}_3(\text{ZnO})_9$.

cell for $\text{InFeO}_3(\text{ZnO})_9$ and the monoclinic one for $\text{Fe}_2\text{O}_3(\text{ZnO})_9$ is shown in Fig. 4B. We think that, when the In(III) ions in the octahedral sites in $\text{InFeO}_3(\text{ZnO})_m$ ($m = 8$ or 9) are replaced by Fe(III) ions, (1) distortion of the crystal lattice occurs and the a - and b -axis in the hexagonal lattice do not remain equivalent, and (2) since some ordering in the arrangement of the Fe(III) and Zn(II) in the trigonal bipyramidal sites happens in the c -plane, a superlattice with 21 times the b -axis is found. Since the crystal structures for $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are considered to be distorted $\text{InFeO}_3(\text{ZnO})_m$ -types, there are at least two kinds of crystallographic sites for Fe ions in them. Single crystal structural analysis for $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ is in progress (15). Nakamura *et al.* (4) prepared powder samples with layered structures at 1350°C through $\text{InFeO}_3(\text{ZnO})_{13}$, $\text{Fe}_2\text{O}_3(\text{ZnO})_{13}$, and $\text{In}_2\text{O}_3(\text{ZnO})_{13}$, and they 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 the same crystal structures. How-

ever, from the present single crystal data for both $\text{Fe}_2\text{O}_3(\text{ZnO})_8$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_9$, we conclude that there are slight structural distortions in the range between $\text{InFeO}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$. In the Fe_2O_3 - ZnO system, single crystal data confirmed that there are homologous phases, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m = \text{integer}$). In contrast, in the Ga_2O_3 - ZnO system at 1350°C , there is a solid solution, $(\text{ZnO})_{1-x}(\text{Ga}_2\text{O}_3)_x$ ($0 \leq x \leq 0.093$), having a distorted wurtzite structure (5).

$\text{LuFeO}_3(\text{ZnO})_m$ and $\text{ScFeO}_3(\text{ZnO})_m$ are isostructural with $\text{InFeO}_3(\text{ZnO})_m$ (3). The ionic radius of In(III) ($= 0.80 \text{ \AA}$ in 6-coordination) is between that of Lu(III) ($= 0.86 \text{ \AA}$) and Sc(III) ($= 0.745 \text{ \AA}$) (13). The crystal structures of Lu_2O_3 ($a = 10.390 \text{ \AA}$) (JCPDS, Card No. 12-728), In_2O_3 ($a = 10.118 \text{ \AA}$) (JCPDS, Card No. 6-416), and Sc_2O_3 ($a = 9.845 \text{ \AA}$) (JCPDS, Card No. 5-629) under normal pressure belong to the so-called "C" type of rare earth sesquioxide structure. So we can say that Lu(III), In(III), and Sc(III) have similar crystal chemical properties in these respects. However, in other ways, In(III) behaves differently from Lu(III) and Sc(III). For instance, In(III) can take tetrahedral sites or trigonal bipyramidal sites in oxide compounds; however, both Lu(III) and Sc(III) merely assume octahedral coordination (13). Corundum-type In_2O_3 was obtained under high pressure (14) without forming the B-type rare earth structure which was observed in the transformations of both Lu_2O_3 and Sc_2O_3 .

As we mentioned above, $\text{InFeO}_3(\text{ZnO})_m$ and $\text{In}_2\text{O}_3(\text{ZnO})_m$ are isostructural with each other and there is a solid solution range between them (4). We heated mixtures of Lu_2O_3 : $\text{ZnO} = 1:1$ and mixtures of Sc_2O_3 : $\text{ZnO} = 1:1$ (in a mole ratio) at 1550°C for 3 days. No homologous phases $\text{Lu}_2\text{O}_3(\text{ZnO})_m$ or $\text{Sc}_2\text{O}_3(\text{ZnO})_m$ having $\text{InFeO}_3(\text{ZnO})_m$ types of crystal structures were obtained.

We think that one of the characteristic properties of In(III), namely, tetrahedral or

trigonal bipyramidal site preference in oxide compounds, is essential to the formation of $\text{In}_2\text{O}_3(\text{ZnO})_m$ at elevated temperatures, and the absence of this preference for Lu(III) or Sc(III) precludes the formation of analogous phases.

Acknowledgment

One of the authors (N.K.) expresses his sincere thanks to Dr. T. Ikegami (NIRIM) for his helpful discussion.

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