

The Phase Relations in the $\text{In}_2\text{O}_3\text{--Fe}_2\text{ZnO}_4\text{--ZnO}$ System at 1350°C

MASAKI NAKAMURA, NOBORU KIMIZUKA,¹
AND TAKAHIKO MOHRI

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

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The phase relations in the $\text{In}_2\text{O}_3\text{--Fe}_2\text{ZnO}_4\text{--ZnO}$ system at 1350°C are determined by means of a classical quenching method. There are a series of homologous solid solutions, $\text{In}_{1.28}\text{Fe}_{0.72}\text{O}_3(\text{ZnO})\text{--InFeO}_3(\text{ZnO})$, $\text{In}_{1.69}\text{Fe}_{0.31}\text{O}_3(\text{ZnO})_2\text{--InFeO}_3(\text{ZnO})_2\text{--In}_{0.85}\text{Fe}_{1.15}\text{O}_3(\text{ZnO})_2$, $\text{In}_2\text{O}_3(\text{ZnO})_3\text{--InFeO}_3(\text{ZnO})_3\text{--In}_{0.78}\text{Fe}_{1.22}\text{O}_3(\text{ZnO})_3$, $\text{In}_2\text{O}_3(\text{ZnO})_4\text{--InFeO}_3(\text{ZnO})_4\text{--In}_{0.62}\text{Fe}_{1.38}\text{O}_3(\text{ZnO})_4$, $\text{In}_2\text{O}_3(\text{ZnO})_5\text{--InFeO}_3(\text{ZnO})_5\text{--In}_{0.67}\text{Fe}_{1.33}\text{O}_3(\text{ZnO})_5$, $\text{In}_2\text{O}_3(\text{ZnO})_6\text{--InFeO}_3(\text{ZnO})_6\text{--In}_{0.60}\text{Fe}_{1.40}\text{O}_3(\text{ZnO})_6$, $\text{In}_2\text{O}_3(\text{ZnO})_7\text{--InFeO}_3(\text{ZnO})_7\text{--In}_{0.51}\text{Fe}_{1.49}\text{O}_3(\text{ZnO})_7$, $\text{In}_2\text{O}_3(\text{ZnO})_8\text{--InFeO}_3(\text{ZnO})_8\text{--In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_8$ ($0.44 \leq x \leq 0.64$), $\text{In}_2\text{O}_3(\text{ZnO})_9\text{--InFeO}_3(\text{ZnO})_9\text{--In}_{0.20}\text{Fe}_{1.80}\text{O}_3(\text{ZnO})_9$, $\text{In}_2\text{O}_3(\text{ZnO})_{10}\text{--InFeO}_3(\text{ZnO})_{10}\text{--In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_{10}$ ($0.74 \leq x \leq 0.89$), $\text{In}_2\text{O}_3(\text{ZnO})_{11}\text{--InFeO}_3(\text{ZnO})_{11}\text{--In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_{11}$ ($0.60 \leq x < 1.00$), and $\text{In}_2\text{O}_3(\text{ZnO})_{13}\text{--InFeO}_3(\text{ZnO})_{13}\text{--Fe}_2\text{O}_3(\text{ZnO})_{13}$ having the layered structures with space group $R\bar{3}m$ ($m = \text{odd}$) or $P6_3/mmc$ ($m = \text{even}$) for m in the $\text{InFeO}_3(\text{ZnO})_m$. We conclude that there are a series of homologous phases, $(\text{Fe}_2\text{O}_3)(\text{ZnO})_m$ ($m \geq 12$), in the binary $\text{ZnO--Fe}_2\text{O}_3$ system. The lattice constants for these solid solutions are presented as a hexagonal crystal system. It is also concluded that the crystal structures for each solid solution consist of three kinds of layers which are stacked perpendicular to the c -axis in the hexagonal crystal system. $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})_m$ ($0 \leq x \leq 1$) is composed of the $\text{InO}_{1.5}$, $(\text{In}_x\text{Fe}_{1-x}\text{Zn})\text{O}_{2.5}$, and ZnO layers, and $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ ($0 \leq x \leq 1$) is composed of $(\text{In}_{1-x}\text{Fe}_x)\text{O}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers, respectively. The solid solution range between Fe_2ZnO_4 and $\text{In}_x\text{Fe}_{2-x}\text{ZnO}_4$ ($x = 0.40 \pm 0.02$) with a spinel structure is observed. © 1990 Academic Press, Inc.

Introduction

It may be interesting to analyze the relation between crystal structures of complex inorganic compounds and their constituent cations. In previous papers (1, 2), we presented the phase relations in the $\text{In}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--CuO}$ system at 1000°C, $\text{In}_2\text{O}_3\text{--Ga}_2\text{O}_3\text{--CuO}$ system at 1000°C, $\text{In}_2\text{O}_3\text{--Fe}_2\text{O}_3\text{--CoO}$ system at 1300°C, $\text{In}_2\text{O}_3\text{--Ga}_2\text{O}_3\text{--CoO}$ system at 1300°C, and $\text{In}_2\text{O}_3\text{--Fe}_2\text{MgO}_4\text{--MgO}$ system at 1300°C, which were determined by means of a classical quenching method, and showed (In

$\text{FeO}_3)_n\text{CuO}$ ($n = 1, 2, \text{ and } 3$) and (In $\text{GaO}_3)_n\text{CuO}$ ($n = 1 \text{ and } 2$) having $(\text{Yb FeO}_3)_n\text{FeO}$ structures (3–5), and both In $\text{FeO}_3(\text{CoO})$ and $\text{InFeO}_3(\text{MgO})$ having spinel structure (1, 2). Kasper prepared $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 2\text{--}5, \text{ and } 7$) in the $\text{In}_2\text{O}_3\text{--ZnO}$ system at 1050–1550°C, and reported their conditions of synthesis and the lattice constants as those in a hexagonal system (6). Cannard and Tilley (7) observed $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 4\text{--}7, 9, \text{ and } 11$) by high resolution electron microscopy and concluded from their lattice images for each phase that the structures of $\text{In}_2\text{O}_3(\text{ZnO})_m$ are composed of both the $\text{InO}_{1.5}$ and ZnO layers. In the $\text{R}_2\text{O}_3\text{--M}_2\text{O}_3\text{--ZnO}$ system at elevated

¹ To whom correspondence should be addressed.

temperatures, $R\text{MO}_3(\text{ZnO})_m$ ($R = \text{Sc}$ and In ; $M = \text{Fe}$, Ga , and Al) having layered structures with space groups $R3m$ ($m = \text{odd}$) or $P6_3/mmc$ ($m = \text{even}$) were synthesized and the crystal structural models for each compound composed of $\text{RO}_{1.5}$, $(M\text{Zn})\text{O}_{2.5}$, and ZnO layers were presented by Kimizuka *et al.* (8). $R\text{MO}_3(\text{ZnO})$ is isostructural with YbFe_2O_4 (3). $R'\text{MO}_3(\text{ZnO})_m$ ($R' = \text{Lu}$, Yb , Tm , Er , Ho , and Y) and $R'\text{MO}_3(M'\text{O})_m$ ($R' = \text{Sc}$, In , Lu , Yb , Tm , Ho , Er , and Y ; $M = \text{Fe}$, Ga and Al ; $M' = \text{Mg}$, Mn , Co , and Fe(II)) which were isostructural with $\text{InFeO}_3(\text{ZnO})_m$ were reported by Kimizuka and Mohri (9) and Kimizuka *et al.* (2), respectively. In the present paper, we report the phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ system at 1350°C which were determined by means of a classical quenching method, and show a series of homologous solid solutions which are isostructural with $\text{InFeO}_3(\text{ZnO})_m$. The $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})_m$ structure (the value of x for each m is given in the fifth column of Table II) is interpreted as the stacking of $Z * 1 \text{ InO}_{1.5}$, $Z * 1 (\text{In}_x\text{Fe}_{1-x}\text{Zn})\text{O}_{2.5}$, and $Z * (m - 1) \text{ ZnO}$ layers perpendicular to the c -axis in the unit cell (Z is the molecular number in the unit cell; $Z = 3$ for $m = \text{odd}$, $Z = 2$ for $m = \text{even}$). $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ (the value of x for each m is given in the last column of Table II) is consisted of $Z * 1 (\text{In}_{1-x}\text{Fe}_x)\text{O}_{1.5}$, $Z * 1 (\text{FeZn})\text{O}_{2.5}$, and $Z * (m - 1) \text{ ZnO}$ layers.

Experimental

In_2O_3 (99.9%), Fe_2O_3 (99.99%), and ZnO (99.99%) were used as starting compounds. Prior to mixing, In_2O_3 was heated at 800°C for one day, ZnO at 1000°C for half a day, and Fe_2O_3 at 1000°C for one day. Calculated amounts of the starting compounds were weighed and thoroughly mixed in an agate mortar under ethyl alcohol. Each of the mixtures was sealed in a Pt tube and heated in a vertical quench furnace with a

SiC heating element. The temperature was maintained at $1350 \pm 3^\circ\text{C}$ by a PID electronic controller. After heat treatment, the samples were rapidly cooled to room temperature, and supplied to X-ray powder diffractometry for phase identification and measurement of the lattice constants. The samples were heated successively until equilibrium was obtained. It was considered that equilibrium was attained when the X-ray powder diffraction pattern of a specimen showed no change with successive heat treatment of the specimen. In order to ascertain whether the equilibrium states in the ternary system were reached or not, we heated some of mixtures containing binary compounds and/or ternary compounds which were prepared from the starting compounds, besides heating the mixture composed of In_2O_3 , Fe_2O_3 , and ZnO . We obtained the same phase assemblages from different starting mixtures with the same chemical compositions. Lattice constants were calculated by means of the least-squares method. When the samples were obtained in single phase states, we estimated the stoichiometry from the mixing ratio of the starting compounds. Before and after each heat treatment, the weights of the tubes including the samples were measured. No evaporation of the samples could be detected in the process of heat treatment. Although chemical reaction between the Pt tube and the samples were checked visually, no detectable reaction was observed. Some of the samples obtained were supplied for SEM and high resolution electron microscopy in order to observe the morphology and the lattice images for the layered compounds.

Results and Discussion

(I) The Phase Relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ System at 1350°C

The phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ system at 1350°C are shown

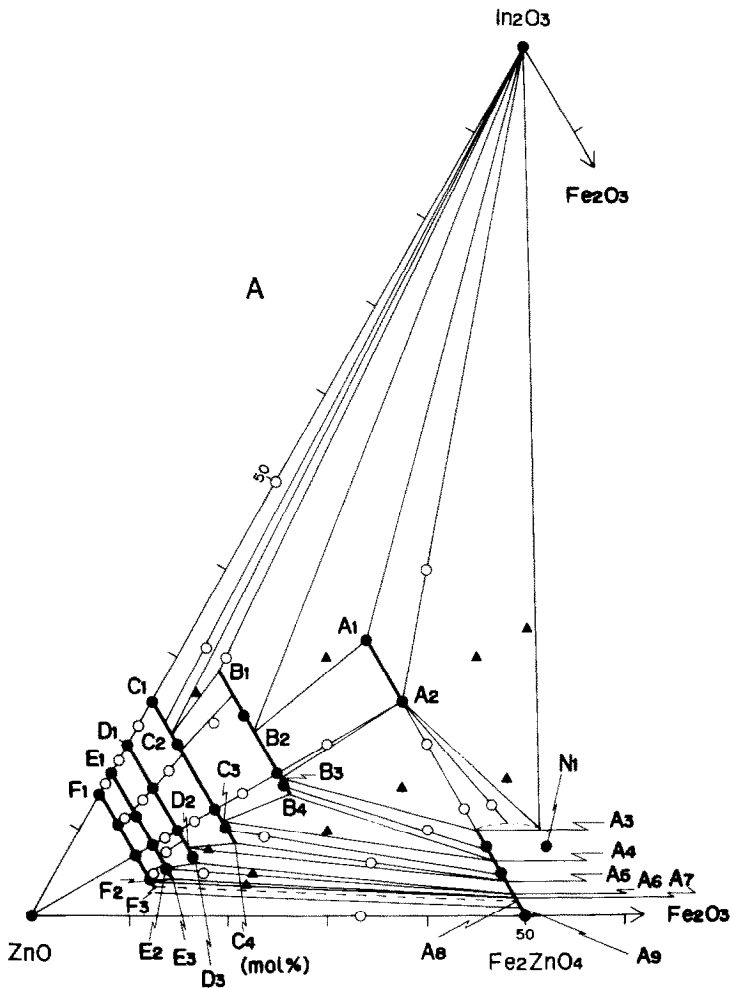


FIG. 1. The phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ system at 1350°C . Symbols and numbers in the figure are as follows; A_1 : (0.320, 0.180, 0.500), A_2 : (0.250, 0.250, 0.500), A_3 : (0.100, 0.400, 0.500), A_4 : (0.064, 0.436, 0.500), A_5 : (0.041, 0.459, 0.500), A_6 : (0.026, 0.474, 0.500), A_7 : (0.021, 0.479, 0.500), A_8 : (undetermined), A_9 : (0.011, 0.489, 0.500). B_1 : (0.282, 0.051, 0.667), B_2 : (0.214, 0.119, 0.667), B_3 : (0.160, 0.173, 0.667), B_4 : (0.141, 0.192, 0.667). C_1 : (0.250, 0.000, 0.750), C_2 : (0.212, 0.038, 0.750), C_3 : (0.111, 0.139, 0.750), C_4 : (0.084, 0.166, 0.750). D_1 : (0.200, 0.000, 0.800), D_2 : (0.080, 0.120, 0.800), D_3 : (0.062, 0.138, 0.800). E_1 : (0.167, 0.000, 0.833), E_2 : (0.056, 0.111, 0.833), E_3 : (0.041, 0.126, 0.833). F_1 : (0.143, 0.000, 0.857), F_2 : (0.043-0.030, 0.100-0.113, 0.857), F_3 : (between F_2 and 0.030, 0.113, 0.857). G_1 : (0.125, 0.000, 0.875), G_2 : (0.031, 0.094, 0.875). H_1 : (0.111, 0.000, 0.889), H_2 : (0.031-0.020, 0.080-0.091, 0.889). I_1 : (0.100, 0.000, 0.900), I_2 : (0.010, 0.090, 0.900). J_1 : (0.091, 0.000, 0.909), J_2 : (0.011-0.005, 0.079-0.086, 0.909). K_1 : (0.083, 0.000, 0.917), K_2 : (0.017-0.000, 0.066-0.083, 0.917). L_1 : (0.077, 0.000, 0.923), L_2 : (0.000, 0.077, 0.923). M_1 : (0.071, 0.000, 0.929), M_2 : (0.000, 0.071, 0.929). N_1 : (0.080, 0.480, 0.440).

in Fig. 1. Mixing ratio of the starting compounds, heating periods, and phases obtained for establishing the phase relations in

the present system are shown in Tables I(A) and I(B). In the $\text{In}_2\text{O}_3\text{-ZnO}$ system, there exist homologous binary phases, In_2

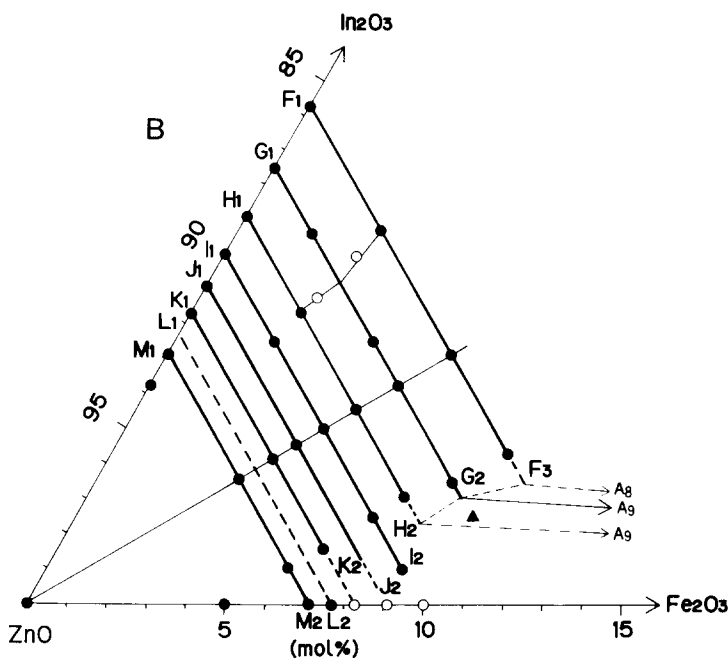


FIG. 1—Continued

$\text{O}_3(\text{ZnO})_m$ ($m = 3\text{--}13$), which are isostructural with $\text{InFeO}_3(\text{ZnO})_m$. Kasper (6) originally prepared $\text{In}_2\text{O}_3(\text{ZnO})_m$ in air at elevated temperatures and reported the lattice constants of the samples obtained under the conditions of synthesis. Cannard and Tilley (7) concluded from the lattice images for $\text{In}_2\text{O}_3(\text{ZnO})_m$ by a high resolution electron microscopy that the structures having the layered structures are composed of $\text{InO}_{1.5}$ and ZnO layers. We could not observe $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 1$ and 2) at 1350°C . The reaction rate of formation for $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = \text{even}$) from both In_2O_3 and ZnO powders were much slower than that of $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = \text{odd}$). Although $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($3 \leq m \leq 13$) is clearly identified by means of powder X-ray diffractometry, $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 14$) heated at 1350°C could not be identified, because X-ray powder diffraction peaks were too broad. The phases obtained between $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 13$) and ZnO are different from both ZnO and

$\text{In}_2\text{O}_3(\text{ZnO})_{13}$, therefore it is clear that there should exist $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 14$) between ZnO and $\text{In}_2\text{O}_3(\text{ZnO})_{13}$. A couple of mixtures in the $\text{In}_2\text{O}_3\text{-ZnO}$ system were heated at 1550°C and the results are shown in Table I(C). We did not explicitly describe the phases with $m \geq 14$ in Fig. 1. However, we can guess from the viewpoint of the structural aspect that there should exist infinite numbers of phases to be described as $\text{In}_2\text{O}_3(\text{ZnO})_m$ between ZnO and $\text{In}_2\text{O}_3(\text{ZnO})_m$ ($m = 13$). The crystallographic considerations to the phases of $\text{In}_2\text{O}_3(\text{ZnO})_m$ will be described in Section II. The lattice constant of In_2O_3 phase in equilibrium with $\text{In}_2\text{O}_3(\text{ZnO})_3$ and that of the In_2O_3 in a single phase state are $a = 1.011(1)$ (nm) and $a = 1.012(1)$ (nm) (JCPDS Card No. 6-416 shows $a = 1.0118$ (nm)), respectively. We concluded that the In_2O_3 phase does not have a solid solution range in the direction to ZnO. The lattice constants of the In_2O_3 phase which is in equilibrium with various

TABLE I(A)
MIXING RATIO OF THE STARTING COMPOUNDS (In_2O_3 , Fe_2O_3 , ZnO), HEATING PERIOD, AND
PHASES OBTAINED IN THE In_2O_3 - Fe_2ZnO_4 - ZnO SYSTEM AT 1350°C

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In_2O_3	Fe_2O_3	ZnO			
2	0	1	3+3	In_2O_3	a=1.011(1)
				III	a=0.3342(1) c=4.243 (1)
1	0	1	3+3	In_2O_3	a=1.011(1)
				III	a=0.3350(1) c=4.246 (1)
16	9	25	3+8	I	a=0.3341(1) c=2.635 (1)
27	23	50	7+3+4	I	a=0.3325(1) c=2.615 (1)
1	1	2	3+3+4+3+8	I	a=0.3320(1) c=2.610 (1)
37	3	80	3+8	In_2O_3	a=1.011(1)
				III	a=0.3341(1) c=4.229 (1)
7	3	20	4+3	II	a=0.3334(1) c=2.278 (1)
1	1	4	3+3	II	a=0.3309(1) c=2.258 (1)
23	27	100	4+4	II	a=0.3301(1) c=2.257 (1)
1	1	5	3+3	II	a=0.3306(1) c=2.258 (1)
				III	a=0.3298(1) c=4.164 (1)
1	0	3	3+7	III	a=0.3351(1) c=4.248 (1)
4	1	15	3	III	a=0.3322(1) c=4.210 (1)
1	1	6	3+3	III	a=0.3299(1) c=4.166 (1)
52	73	375	4+4	III	a=0.3286(1) c=4.168 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
1	1	7	3+3	III	a=0.3295(1) c=4.165 (1)
				IV	a=0.3290(1) c=3.296 (1)
2	0	7	3+3	III	a=0.3350(1) c=4.247 (1)
				IV	a=0.3335(1) c=3.351 (1)
1	0	4	4	IV	a=0.3337(1) c=3.353 (1)
3	1	16	3+4	IV	a=0.3315(1) c=3.320 (1)
1	1	8	3+3	IV	a=0.3292(1) c=3.298 (1)
7	13	80	7+3	IV	a=0.3271(1) c=3.301 (1)
1	1	9	3+3	IV	a=0.3289(1) c=3.296 (1)
				V	a=0.3285(1) c=5.722 (1)
2	0	9	3+3	IV	a=0.3334(1) c=3.352 (1)
				V	a=0.3324(1) c=5.806 (1)
1	0	5	3	V	a=0.3326(1) c=5.810 (1)
7	3	50	3	V	a=0.3304(1) c=5.750 (1)
1	1	10	3+3	V	a=0.3287(1) c=5.727 (1)
1	2	15	7	V	a=0.3265(1) c=5.734 (1)
2	0	11	3+3	V	a=0.3320(1) c=5.808 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
				VI	a=0.3315(1) c=4.389 (1)
1	0	6	3	VI	a=0.3316(1) c=4.394 (1)
3	1	24	4+3	VI	a=0.3301(1) c=4.361 (1)
1	1	12	3+3	VI	a=0.3283(1) c=4.339 (1)
3	7	60	7+3	VI	a=0.3258(1) c=4.335 (1)
1	0	7	3	VII	a=0.3310(1) c=7.370 (1)
17	3	140	3	VII	a=0.3302(1) c=7.346 (1)
3	2	35	3+3	VII	a=0.3286(1) c=7.293 (1)
1	1	14	3+3	VII	a=0.3279(1) c=7.286 (1)
7	18	175	3+4	VII	a=0.3256(1) c=7.289 (1)
1	0	8	3+3+3	VIII	a=0.3304(1) c=5.432 (1)
3	1	32	3+4	VIII	a=* c=5.386(68)
1	1	16	3+3+3+4+7	VIII	a=* c=5.374(17)
7	18	200	4+4	VIII	a=0.3257(3) c=5.376 (5)
1	0	9	3	IX	a=0.3299(1) c=8.926 (1)
3	1	36	3	IX	a=0.3288(1) c=8.879 (1)
1	1	18	3+3+3+4	IX	a=0.3274(1) c=8.843 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
3	7	90	3+4	IX	a=0.3256(1) c=8.845 (3)
1	9	90	3+4	XI	a=0.3243(2) c=10.41 (1)
				spinel	a=0.8445
0	1	9	3+3+7	XII	a=0.3243(1) c=7.442(2)
				spinel	a=0.8440(1)
1	0	10	3+3+7	X	a=* c=6.545(57)
3	1	40	3+3	X	a=* c=6.470(57)
1	1	20	3+2+3	X	a=* c=6.427(69)
1	3	40	3+3	X	a=* c=6.462(79)
0	1	10	3+4	XII	a=0.3246(3) c=7.421(9)
				spinel	a=0.8436(1)
1	0	11	3	XI	a=0.3292(1) c=10.49 (1)
3	1	44	3+3	XI	a=0.3276(1) c=10.44 (1)
1	1	22	3+4+4	XI	a=0.3268(1) c=10.39 (1)
1	4	55	3+4	XI	a=0.3251(2) c=10.42 (1)
0	1	11	3+4+4	XII	a=0.3242(3) c=7.425(8)
				spinel	a=0.8433(3)
0	1	12	3+3+4	XII	a=0.3243(2) c=7.422(7)
1	0	13	3+7+3	XIII	a=0.3284(1) c=12.04 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
1	1	26	3+3	XIII	a=0.3269(2) c=11.96 (1)
1	6	91	3+4	XIII	a=0.3250(3) c=11.93 (1)
0	1	13	3+4	XIII	a=0.3241(3) c=11.91 (1)
1	0	15	7+7	XV	a=0.3284(1) c=13.63 (1)
0	1	19	7+3	IXX	a=0.3240(2) c=16.55 (1)
0	1	39	3+8+7	IXXXX	a=0.3248(1) c=32.19 (1)
6	1	13	4+2+3	In ₂ O ₃	a=1.011(1)
				II	a=0.3351(1) c=2.295 (1)
6	3	11	3+3	In ₂ O ₃	a=1.009(1)
				I	a=0.3341(1) c=2.635 (1)
				II	a=0.3326(1) c=2.273 (1)
1	1	3	7+4	I	a=0.3319(1) c=2.609 (1)
				II	a=0.3308(1) c=2.257 (1)
13	2	35	3+3	In ₂ O ₃	a=1.010(1)
				II	a=0.3351(1) c=2.294 (1)
				III	a=0.3336(1) c=4.217 (1)
9	3	28	3+3	II	a=0.3343(1) c=2.284 (1)
				III	a=0.3331(1) c=4.203 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
27	9	124	3+3	III	a=0.3326(1) c=4.201 (1)
				IV	a=0.3316(1) c=3.320 (1)
3	1	18	3+3	IV	a=0.3318(1) c=3.320 (1)
				V	a=0.3309(1) c=5.760 (1)
3	4	33	4+3	IV	a=0.3285(1) c=3.300 (1)
				V	a=0.3279(1) c=5.726 (1)
3	1	22	3+3	V	a=0.3307(1) c=5.765 (1)
				VI	a=0.3301(1) c=4.362 (1)
1	2	17	3+3	V	a=0.3270(2) c=5.735 (3)
				VI	a=0.3268(7) c=4.344 (7)
3	1	26	3+3	VI	a=0.3300(1) c=4.362 (1)
				VII	a=0.3298(1) c=7.313 (1)
3	1	30	3+3+3+7	VII	a=0.3295(1) c=7.319 (2)
				VIII	a=0.3293(1) c=5.398 (1)
2	1	2	4+3	In ₂ O ₃	a=1.006(1)
				I	a=0.3328(1) c=2.618 (1)
1	1	1	4+7	In ₂ O ₃	a=1.004(1)
				I	a=0.3320(1) c=2.611 (1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In ₂ O ₃	Fe ₂ O ₃	ZnO			
				spinel	a=0.8538(1)
3	3	4	4+7	In ₂ O ₃	a=1.004(1)
				I	a=0.3321(1) c=2.609 (1)
				spinel	a=0.8535(1)
16	40	44	3+3	In ₂ O ₃	a=1.003(1)
				I	a=0.3320(1) c=2.609 (1)
				spinel	a=0.8537(1)
13	40	47	3+3	I	a=0.3318(1) c=2.609 (1)
				spinel	a=0.8535(1)
2	3	5	3+3+3	I	a=0.3316(1) c=2.608 (1)
				spinel	a=0.8525(1)
1	3	4	3+3+3+8	I	a=0.3313(1) c=2.611 (1)
				spinel	a=0.8528(1)
0	1	1	3	spinel	a=0.8441(1)
1	9	10	3+3+3	spinel	a=0.8485(1)
4	21	25	3+3+3+3	spinel	a=0.8510(1)
8	48	44	3	spinel	a=0.8509(1)
3	6	11	3+3	I	a=0.3316(1) c=2.610 (1)
				II	a=0.3305(1) c=2.258 (1)
				spinel	a=0.8530(1)
2	7	11	3+3	II	a=0.3298(1) c=2.259 (1)
				spinel	a=0.8506(1)

TABLE I(A)—Continued

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Day)	Phases and their lattice constants (nm)	
In_2O_3	Fe_2O_3	ZnO			
2	5	13	3+3	II	a=0.3293(1) c=2.259 (1)
				III	a=0.3291(1) c=4.166 (1)
				spinel	a=0.8496(1)
1	5	10	3+3+7	III	a=0.3280(1) c=4.172 (1)
				spinel	a=0.8476(1)
1	4	15	3+3	IV	a=0.3260(1) c=3.304 (1)
				V	a=0.3269(1) c=5.732 (1)
				spinel	a=0.8463(1)
1	3	16	3+3	V	a=0.3264(1) c=5.739 (1)
				spinel	a=0.8463(1)
37	200	763	4+4+4	V	a=0.3260(1) c=5.746(1)
				VI	a=0.3257(2) c=4.352(2)
				spinel	a=0.8459(1)
1	4	35	4+3	VII	a=0.3252(1) c=7.297 (3)
				VIII	a=* c=*
				spinel	a=0.8450(2)
0	1	2	3+3	XII	a=0.3238(1) c=7.455 (4)
				spinel	a=0.8440(1)

Note. The homologous phase with $m = 1, 2, \dots$, or 13 in the $\text{InFeO}_3(\text{ZnO})_m$ is defined as Phase-I, Phase-II, . . . , or Phase-XIII. The lattice constants with * could not be determined.

TABLE I(B)
MIXING RATIO OF THE VARIOUS STARTING PHASES, HEATING PERIOD, AND PHASES OBTAINED
IN THE $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ SYSTEM AT 1350°C

Mixing ratio of starting phases (in mole ratio)	Heating Period (Day)	Phases and their lattice constants (nm)
$\text{InFeO}_3(\text{ZnO})_3 : \text{InFeO}_3(\text{ZnO})_4 : \text{Fe}_2\text{ZnO}_4$ = 8 : 5 : 7	4+3	III $a=0.3283(1)$ $c=4.171(1)$ spinel $a=0.8483(1)$
$\text{InFeO}_3(\text{ZnO})_4 : \text{InFeO}_3(\text{ZnO})_5 : \text{Fe}_2\text{ZnO}_4$ = 5 : 9 : 6	4+3	III $a=0.3279(1)$ $c=4.174(1)$ IV $a=0.3277(1)$ $c=3.301(1)$ spinel $a=0.8477(1)$
$\text{In}_2\text{O}_3 : \text{Fe}_2\text{ZnO}_4$ = 1 : 1	7	In_2O_3 $a=1.003(1)$ I $a=0.3317(1)$ $c=2.607(1)$ spinel $a=0.8529(1)$
$\text{InFeO}_3(\text{ZnO})_{11} : \text{ZnO}$ = 1 : 1	3	IX $a=*$ $c=8.933$ XI $a=0.3289(1)$ $c=10.48(1)$ XII $a=*$ $c=*$ XIII $a=*$ $c=12.01(3)$

Note. The homologous phase with $m = 1, 2, \dots$, or 13 in the $\text{InFeO}_3(\text{ZnO})_m$ is defined as Phase-I, Phase-II, . . . , or Phase-XIII. The lattice constants with * could not be determined.

phases are shown in Fig. 2. In the $\text{ZnO-Fe}_2\text{ZnO}_4$ system there exist new binary phases. The reaction rate of formation for $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ from both Fe_2O_3 and ZnO powders is not so slow that we could obtain each of the single phases in the system. They seem to belong to a distorted wurtzite phase; however, they are eventually homologous phases with composition, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 12$). The details of both

the chemical compositions and the structures for these phases will be given later. It was concluded that no solid solution of the spinel phase to the direction to ZnO phase exists, since no volume change of the unit cell was detected between stoichiometric Fe_2ZnO_4 in a single phase state and that in equilibrium with the $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ phase ($m = 12$). The lattice constant of Fe_2ZnO_4 is $a = 0.8439(1)$ (nm) (JCPDS Card No. 22-1012

TABLE I(C)
MIXING RATIO OF THE STARTING COMPOUNDS (In_2O_3 , Fe_2O_3 , ZnO), HEATING PERIOD, AND
PHASES OBTAINED IN THE $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ SYSTEM AT 1550°C

Mixing ratio of starting compounds (in mole ratio)			Heating Period (Hour)	Phases and their lattice constants (nm)	
In_2O_3	Fe_2O_3	ZnO			
1	0	2	3+24	In_2O_3	$a=1.012(1)$
				III	$a=0.3354(1)$ $c=4.251(1)$
1	0	10	24	IX	$a=*$ $c=8.930(28)$
				X	$a=*$ $c=6.471(38)$
				XI	$a=*$ $c=10.49(1)$
3	1	40	4+22	X	$a=*$ $c=6.471(71)$
1	1	20	18	IX	$a=*$ $c=*$
				X	$a=*$ $c=*$
				XI	$a=0.3272(1)$ $c=10.40(1)$
1	0	20	24	XX	$a=0.3271(1)$ $c=11.64(1)$
1	1	40	24	XX	$a=0.3259(2)$ $c=11.61(2)$

Note. The homologous phase with $m = 1, 2, \dots$, or 13 in the $\text{InFeO}_3(\text{ZnO})_m$ is defined as Phase-I, Phase-II, . . . , or Phase-XIII. The lattice constants with * could not be determined.

shows $a = 0.84411$ (nm)). In the $\text{Fe}_2\text{ZnO}_4\text{-In}_2\text{O}_3$ system, there exists no binary phase, but the ranges of solid solutions of both the spinel and In_2O_3 were observed from the volume changes of each unit cell. The solid solution of spinel phase was observed in the range between Fe_2ZnO_4 and $\text{In}_x\text{Fe}_{2-x}\text{ZnO}_4$ ($x = 0.40 \pm 0.02$). The relation between the lattice constant and the concentration of In_2O_3 is shown in Fig. 3. Our main purpose

is in the area of the layered compounds, so we did not investigate the details of this spinel phase region so intensively as in the layered compounds area.

In the ternary $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-ZnO}$ system, there exist $\text{InFeO}_3(\text{ZnO})_m$ ($m = \text{integer}$) types of homologous solid solutions. In the case of $m = 1$, the solid solution of $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})\text{-InFeO}_3(\text{ZnO})$ exists. In the case of $m = 2$, the solid solution range

VII	1310	$\text{In}_2\text{O}_3(\text{ZnO})_7$ a=0.3313(1) c=7.362(4)	1100 3	$\text{In}_2\text{O}_3(\text{ZnO})_7$ a=0.3279(1) c=7.285(1)	1450 2 R3m	$\text{In}_2\text{O}_3(\text{ZnO})_7$ a=0.3310(1) c=7.370(1)	$\text{InFeO}_3(\text{ZnO})_7$ a=0.3279(1) c=7.286(1)	$\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_7$ (x=0.50) a=0.3252(1) c=7.297(3)
VIII				$\text{InFeO}_3(\text{ZnO})_8$ a=0.3276(1) c=5.375(1)	1450 7 P6 ₃ /mmc	$\text{In}_2\text{O}_3(\text{ZnO})_8$ a=0.3304(1) c=5.432(1)	$\text{InFeO}_3(\text{ZnO})_8$ a=** c=5.374(17)	$\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_8$ (0.44 ≤ x ≤ 0.64) a=** c=**
IX			1100 7	$\text{InFeO}_3(\text{ZnO})_9$ a=0.3274(1) c=8.841(1)	1450 3 R3m	$\text{In}_2\text{O}_3(\text{ZnO})_9$ a=0.3299(1) c=8.926(1)	$\text{InFeO}_3(\text{ZnO})_9$ a=0.3274(1) c=8.843(1)	$\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_9$ (x=0.80) a=3.246(2) c=8.840(7)
X			1450 7 P6 ₃ /mmc	$\text{InFeO}_3(\text{ZnO})_{10}$ a=0.3272(1) c=6.402(1)	1450 7 P6 ₃ /mmc	$\text{In}_2\text{O}_3(\text{ZnO})_{10}$ a=** c=6.545(57)	$\text{InFeO}_3(\text{ZnO})_{10}$ a=** c=6.427(69)	$\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_{10}$ (0.74 ≤ x ≤ 0.89) a=** c=**
XI			1100 3	$\text{In}_2\text{O}_3(\text{ZnO})_{11}$		$\text{In}_2\text{O}_3(\text{ZnO})_{11}$ a=0.3292(1) c=10.49(1)	$\text{InFeO}_3(\text{ZnO})_{11}$ a=0.3268(1) c=10.39(1)	$\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_{11}$ (0.60 < x < 1.00) a=** c=**
XII				$\text{InFeO}_3(\text{ZnO})_{12}$		$\text{In}_2\text{O}_3(\text{ZnO})_{12}$ a=** c=**	$\text{InFeO}_3(\text{ZnO})_{12}$ a=** c=7.422(7)	$\text{Fe}_2\text{O}_3(\text{ZnO})_{12}$ a=0.3243(2) c=7.422(7)
XIII				$\text{In}_2\text{O}_3(\text{ZnO})_{13}$ a=0.3284(1) c=12.04(1)		$\text{In}_2\text{O}_3(\text{ZnO})_{13}$ a=0.3284(1) c=12.04(1)	$\text{InFeO}_3(\text{ZnO})_{13}$ a=0.3269(2) c=11.96(1)	$\text{Fe}_2\text{O}_3(\text{ZnO})_{13}$ a=0.3241(3) c=11.91(1)

Note. All of the lattice constants are given in the hexagonal crystal system. Hex., hexagonal; Rhom., rhombic. The lattice constants with * could not be determined.

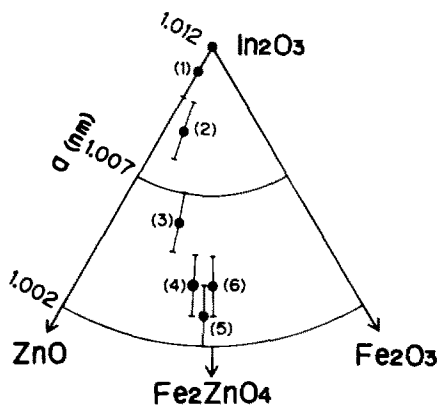


FIG. 2. The lattice constants of In_2O_3 phase which is in equilibrium with various phases: (1) Phase-III, (2) Phase-I and Phase-II, (3) Phase-I, (4) Phase-I and spinel, (5) Phase-I and spinel, and (6) Phase-I and spinel.

of $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})_2$ – $\text{InFeO}_3(\text{ZnO})_2$ – $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_2$ exists. In the case of $m = 3$ to 7, each of the solid solution ranges of $\text{In}_2\text{O}_3(\text{ZnO})_m$ – $\text{InFeO}_3(\text{ZnO})_m$ – $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ exists. The formation reaction of $\text{InFeO}_3(\text{ZnO})_m$ ($m = \text{even}$) is much slower than that of $\text{InFeO}_3(\text{ZnO})_m$ ($m = \text{odd}$) as in the binary system In_2O_3 – ZnO . The phases with $m = 8, 10,$ and 12 (except $\text{Fe}_2\text{O}_3(\text{ZnO})_{12}$) could not be obtained as the single

phase state within our present experimental conditions; however, the quantity of these phases increased with increasing heating period. Therefore, we concluded that these phases should be stable. We could not present both the solid solution ranges and the lattice constants for these phases so correctly as in the experimental data for the case of $m = \text{odd}$. In the case of phases with $m = 12$ and 13 , the solid solutions range from $\text{In}_2\text{O}_3(\text{ZnO})_m$ to $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ including $\text{InFeO}_3(\text{ZnO})_m$. The solid solution ranges in each phase, the lattice constants and space group are listed in Table II together with the data reported by Kasper (6), Cannard and Tilley (7), and Kimizuka *et al.* (8). The characteristic features of the phase relations in the present ternary systems are summarized as follows. Phase-I is in equilibrium with In_2O_3 , Phase-II, and spinel. Phase-II is in equilibrium with In_2O_3 , Phase-I, Phase-III, and spinel. Phase-III is in equilibrium with In_2O_3 , Phase-II, Phase-IV, and spinel. Phase-IV is in equilibrium with Phase-III, Phase-V, and spinel. Phase-V to Phase-XII have similar phase relations to Phase-IV. Phase-XIII or its higher order should be in equilibrium with two other homologous phases on both

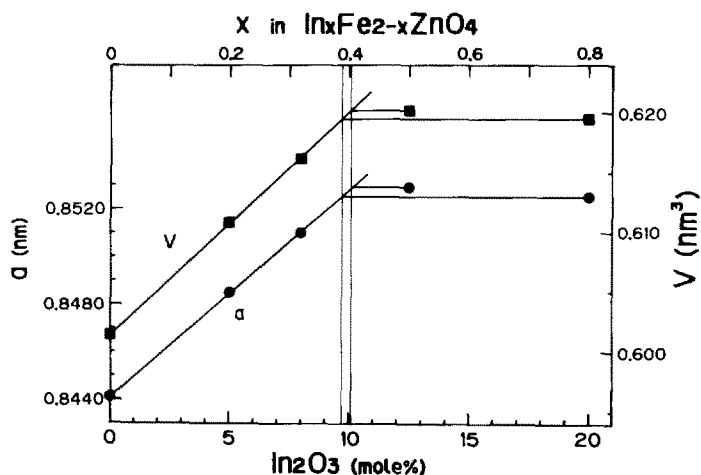


FIG. 3. The lattice constants of $\text{In}_x\text{Fe}_{2-x}\text{ZnO}_4$ with spinel structure $x = 0$ – 0.40 .

sides. $\text{Fe}_2\text{O}_3(\text{ZnO})_{12}$ was obtained in Phase-XII; however, neither $\text{In}_2\text{O}_3(\text{ZnO})_{12}$ nor $\text{InFeO}_3(\text{ZnO})_{12}$ was observed in a single phase state. $\text{In}_2\text{O}_3(\text{ZnO})_{15}$ in Phase-XV was obtained at 1550°C. ZnO is in equilibrium with a very high order homologous phase which we could not describe exactly here. Solid solutions of the layered phases with nonintegral m could not be detected within our experimental conditions.

(II) *Crystal Structural Consideration for the Homologous Solid Solution of $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ ($m = \text{integer}$)*

$\text{InFeO}_3(\text{ZnO})_m$ ($m = 1$ and 2) obtained by solid state reactions from In_2O_3 , Fe_2O_3 , and ZnO powders at 1350°C were observed by SEM. We could see well-developed plate-like single crystals. The lattice constants for the homologous solid solutions of the $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ are shown as a hexagonal system in Fig. 4.

Kimizuka *et al.* (8) reported that $\text{InFeO}_3(\text{ZnO})$ is isostructural with YbFe_2O_4 (3) composed of both $\text{YbO}_{1.5}$ and $\text{Fe}_2\text{O}_{2.5}$ layers, and $\text{InFeO}_3(\text{ZnO})_m$, of $\text{InO}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers. The crystal structural models for the compounds $\text{InFeO}_3(\text{ZnO})$, $\text{InFeO}_3(\text{ZnO})_2$, $\text{InFeO}_3(\text{ZnO})_3$, and $\text{InFeO}_3(\text{ZnO})_4$ as the representatives in $\text{InFeO}_3(\text{ZnO})_m$ compounds are shown in Figs. 5A, 5B, 5C, and 5D, respectively. In $\text{InFeO}_3(\text{ZnO})$, In^{3+} ion is in the octahedral site, and both Fe^{3+} and Zn^{2+} ions are in the trigonal bipyramidal site. In $\text{InFeO}_3(\text{ZnO})_m$ ($m \geq 2$), the In ion and both the Fe and Zn ions are located as in $\text{InFeO}_3(\text{ZnO})$, but additional Zn ions are in the tetrahedral site. These crystal structural models were concluded from the crystallographic consideration to $(\text{YbFeO}_3)_n\text{FeO}$ ($n = 1, 2,$ and 3) structures and the powder X-ray data of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3,$ and 4) compounds (3–5, 10, and 11). From these crystal models, it is easy to understand the

relation between a (or c) and the Fe_2O_3 concentration in the region between $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{InFeO}_3(\text{ZnO})_m$. As shown in Fig. 4, the lattice constants a and c decrease with increasing Fe_2O_3 concentration. From the above consideration, therefore, in the $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})_m$ compounds, the Fe in $(\text{FeZn})\text{O}_{2.5}$ layers is replaced by In^{3+} forming $(\text{In}_x\text{Fe}_{1-x}\text{Zn})\text{O}_{2.5}$ layers. So the $\text{In}_{1+x}\text{Fe}_{1-x}\text{O}_3(\text{ZnO})_m$ compound should exist in $Z * 1$ pieces of $\text{InO}_{1.5}$, $Z * 1 (\text{In}_x\text{Fe}_{1-x}\text{Zn})\text{O}_{2.5}$, and $Z * (m - 1)$ ZnO layers. So we can calculate the c values from the following equation as already discussed in the literature (8),

$$C_{\text{calcd}} = \{p + q + (m - 1) * r\} * Z, \quad (1)$$

where C_{calcd} (nm) is the thickness of the unit cell of the compounds, $\text{InFeO}_3(\text{ZnO})_m$ or $\text{In}_2\text{O}_3(\text{ZnO})_m$. p , thickness of $\text{InO}_{1.5}$ layer (nm); q , thickness of $(\text{FeZn})\text{O}_{2.5}$ or $(\text{InZn})\text{O}_{2.5}$ layer (nm); r , thickness of ZnO layer (nm); Z , molecular number in a unit cell. We listed experimental values together with calculated values from the above equation in Tables III(A) and III(B), in which $(p + q) = 0.8951$ (nm) and $r = 0.2602$ (nm) were hypothetically used for $\text{In}_2\text{O}_3(\text{ZnO})_m$. In the case of $\text{InFeO}_3(\text{ZnO})_m$, we could calculate C_{calcd} (nm) in the same model using $(p + q) = 0.8701$ (nm) and $r = 0.2596$ (nm). Note that $(\frac{1}{2}) * (c = 0.5207)$ (nm) is equal to 0.2604 (nm), where c means the lattice constant of ZnO (11). Also we show the relation between c_{obsd}/Z and m in Figs. 6A and 6B. We can see a good linearity in them. In the region of the $\text{InFeO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$, the a -axis decreases with increasing concentration of Fe^{3+} , but slight change in the c -axis was actually observed (Fig. 4). In this region, the In^{3+} in the $\text{InO}_{1.5}$ layer is replaced by Fe^{3+} , forming the $(\text{In}_{1-x}\text{Fe}_x)\text{O}_{1.5}$ layer. So there should exist $(\text{In}_{1-x}\text{Fe}_x)\text{O}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers. When In^{3+} is partly substituted by Fe^{3+} , the octahedron in which In^{3+}

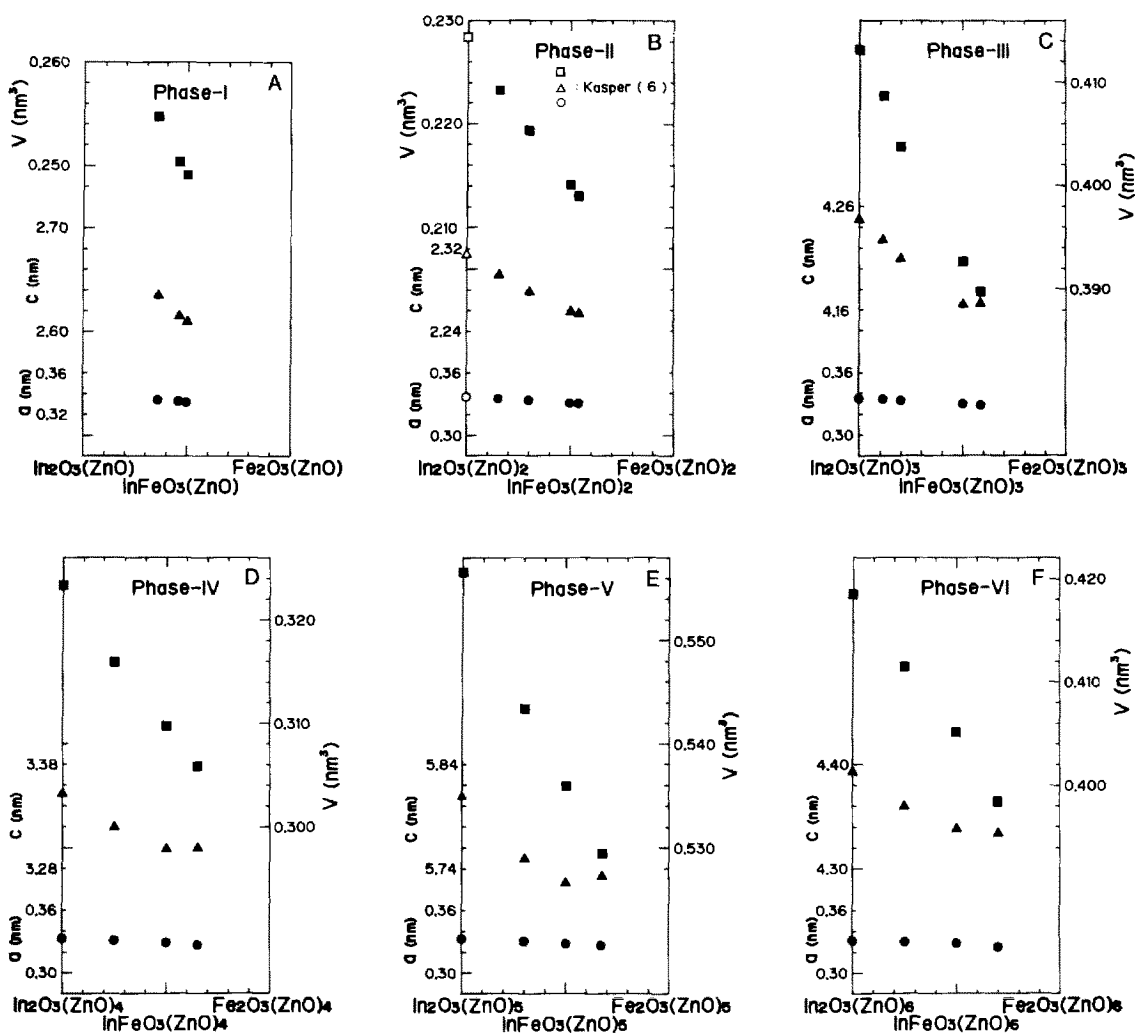


FIG. 4. The dependence of the hexagonal lattice constants (a and c) of the layered phases upon the Fe_2O_3 concentration. (A) Phase-I. (B) Phase-II. (C) Phase-III. (D) Phase-IV. (E) Phase-V. (F) Phase-VI. (G) Phase-VII. (H) Phase-VIII. (I) Phase-IX. (J) Phase-X. (K) Phase-XI. (L) Phase-XII. (M) Phase-XIII.

centrally exists will be shrunk. This shrinkage effect upon the a -axis is clearly greater than that on the c -axis. The a values for the compounds $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ were calculated based upon $\text{InFeO}_3(\text{ZnO})_m$ type of crystal structures. We show the dependency of the a upon the m in Fig. 6C. We can see that all of the a values approach the a of wurtzite with increasing m in $\text{In}_2\text{O}_3(\text{ZnO})_m$, InFeO_3

$(\text{ZnO})_m$, and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$. From the dependence of both the a and c values upon the Fe^{3+} concentration in both $\text{In}_2\text{O}_3(\text{ZnO})_m$ - $\text{InFeO}_3(\text{ZnO})_m$ and $\text{InFeO}_3(\text{ZnO})_m$ - $\text{In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ regions, we can safely conclude that the crystal structural model for $\text{InFeO}_3(\text{ZnO})_m$ composed of the stacking of $\text{InO}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers is quite satisfactory. The

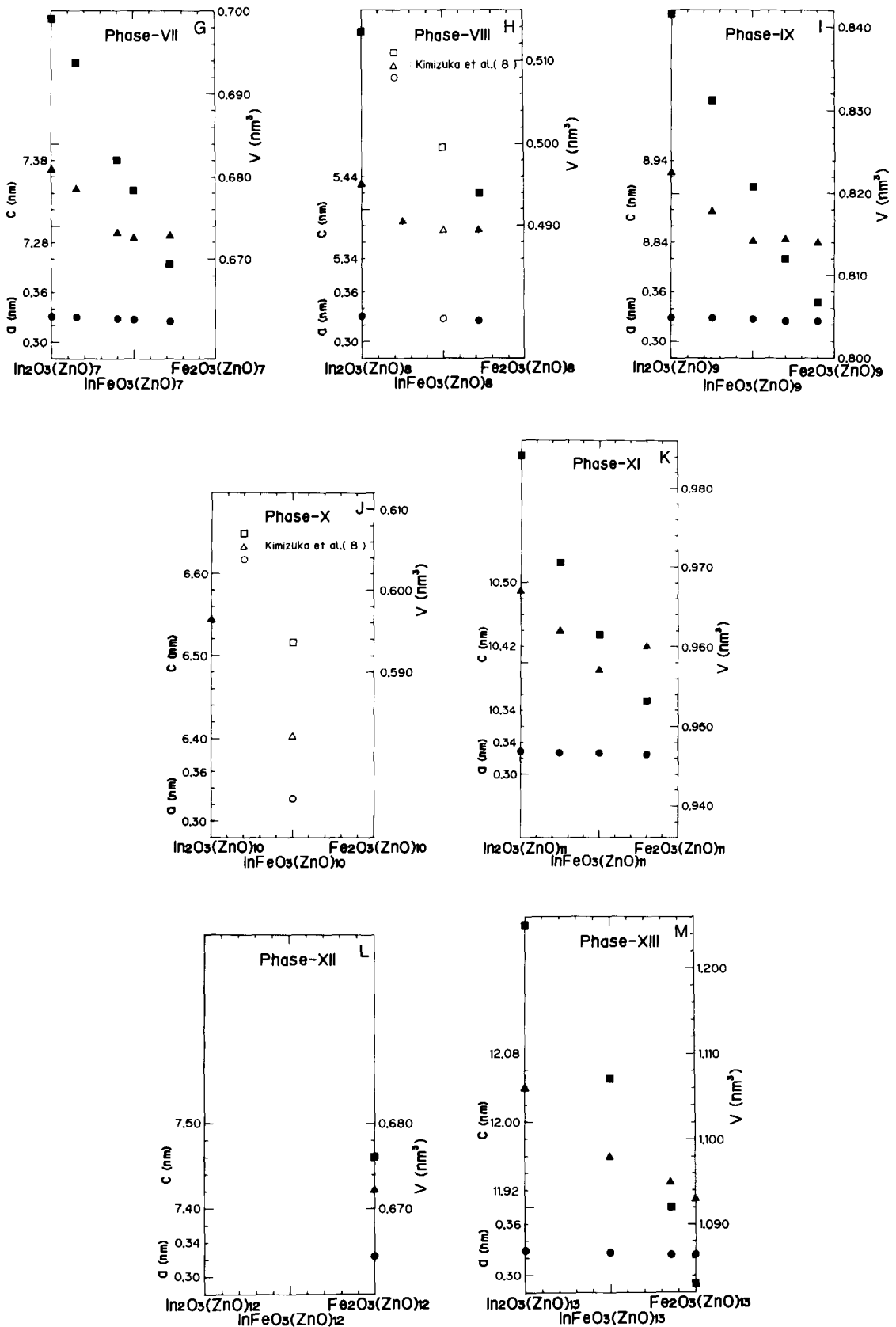


FIG. 4—Continued

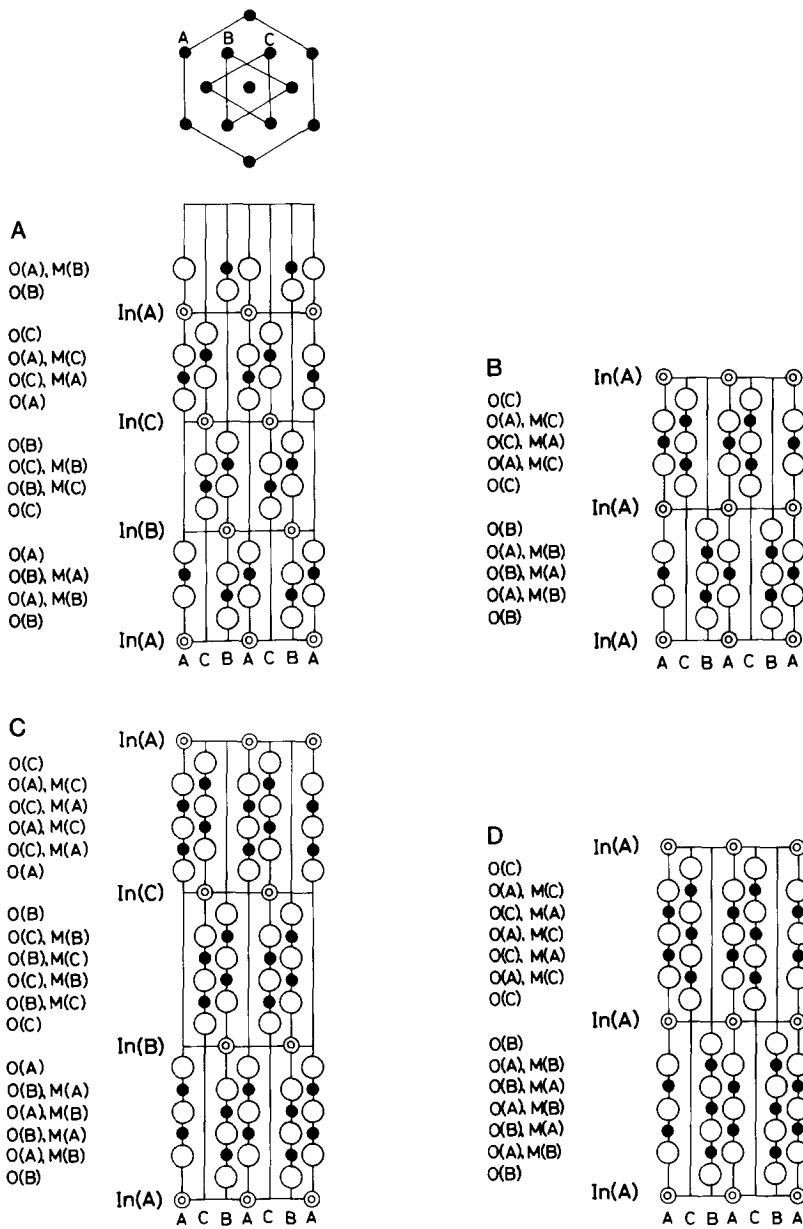


FIG. 5. The crystal structural models of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1, 2, 3, \text{ and } 4$). A, B, and C represent three kinds of triangular lattices. *M* sites are occupied by Fe and/or Zn ions. \odot , In ion; \bullet , Fe and/or Zn ion; \circ , O ion.

structural analyses for single crystal of $\text{LuFeO}_3(\text{ZnO})_m$ ($m = 1, 4, 5, \text{ and } 6$) which are isostructural with $\text{InFeO}_3(\text{ZnO})_m$ are in progress by Isobe (12).

In conclusion, (i) there are a series of homologous solid solutions, $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Fe}_{1+x}\text{O}_3(\text{ZnO})_m$ ($m = 1\text{-}13$) at 1350°C , (ii) in the binary $\text{ZnO-Fe}_2\text{O}_3$

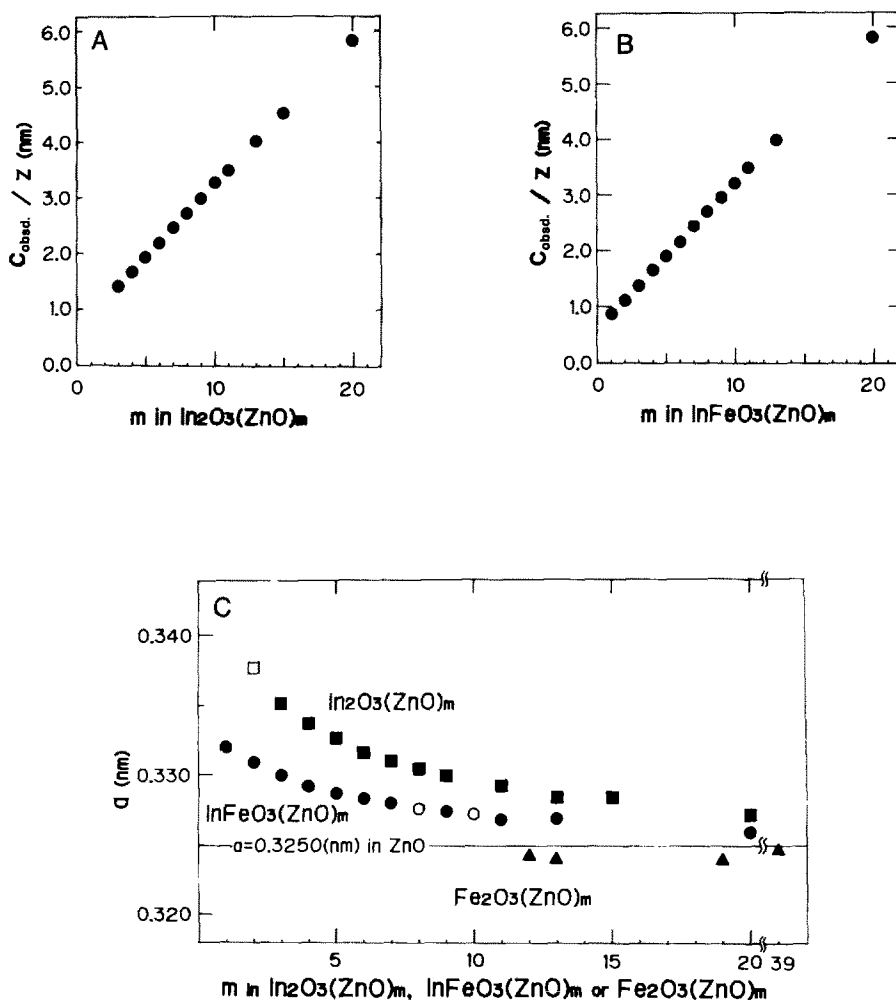


FIG. 6. (A) The relation between $c_{\text{obsd.}}/z$ and m in $\text{In}_2\text{O}_3(\text{ZnO})_m$. (B) The relation between $c_{\text{obsd.}}/z$ and m in $\text{InFeO}_3(\text{ZnO})_m$. (C) The relation between a and m in $\text{In}_2\text{O}_3(\text{ZnO})_m$ (\square , \blacksquare), $\text{InFeO}_3(\text{ZnO})_m$ (\circ , \bullet), and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ (\blacktriangle). \square , Kasper (6); \circ , Kimizuka *et al.* (8); \blacksquare , \bullet , \blacktriangle , this work.

system, there should exist $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ ($m \geq 12$) which are isostructural with $\text{InFeO}_3(\text{ZnO})_m$ at 1350°C , and (iii) the crystal structures for the homologous solid solutions are composed of the $\text{InO}_{1.5}$, $(\text{In}_{1-x}\text{Fe}_x\text{Zn})\text{O}_{2.5}$ and ZnO layers in the region of $\text{In}_2\text{O}_3(\text{ZnO})_m\text{-InFeO}_3(\text{ZnO})_m$, and $(\text{In}_{1-x}\text{Fe}_x)\text{O}_{1.5}$, $(\text{FeZn})\text{O}_{2.5}$, and ZnO layers in the region of the $\text{InFeO}_3(\text{ZnO})_m\text{-In}_{1-x}\text{Fe}_{1+x}$

$\text{O}_3(\text{ZnO})_m$. We will report the detailed crystal structures of the phases in the vicinity of ZnO in the system $\text{ZnO-Fe}_2\text{O}_3$ at 1350°C in the near future, and clarify whether the phases will be able to be identified by means of a distorted wurtzite structure or a series of homologous phases, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ with $\text{InFeO}_3(\text{ZnO})_m$ -type structure ($m = \text{integer}$).

TABLE III(A)
 $C_{\text{obsd.}} \text{ (nm)}$ AND $C_{\text{calcd.}} \text{ (nm)}$ FOR $\text{In}_2\text{O}_3(\text{ZnO})_m$ COMPOUNDS

Compound	$C_{\text{obsd.}} \text{ (nm)}$	$C_{\text{calcd.}} \text{ (nm)}$	$C_{\text{obsd.}} \text{ (nm)} - C_{\text{calcd.}} \text{ (nm)}$
$\text{In}_2\text{O}_3(\text{ZnO})$		2.685	
$\text{In}_2\text{O}_3(\text{ZnO})_2^{(6)}$	2.3154(10)*	2.311	0.0044
$\text{In}_2\text{O}_3(\text{ZnO})_3$	4.248(1)	4.247	0.001
$\text{In}_2\text{O}_3(\text{ZnO})_4$	3.353(1)	3.352	0.001
$\text{In}_2\text{O}_3(\text{ZnO})_5$	5.810(1)	5.808	0.002
$\text{In}_2\text{O}_3(\text{ZnO})_6$	4.394(1)	4.393	0.001
$\text{In}_2\text{O}_3(\text{ZnO})_7$	7.370(1)	7.370	0.000
$\text{In}_2\text{O}_3(\text{ZnO})_8$	5.432(1)	5.433	-0.001
$\text{In}_2\text{O}_3(\text{ZnO})_9$	8.926(1)	8.931	-0.005
$\text{In}_2\text{O}_3(\text{ZnO})_{10}$	6.545(57)*	6.474	0.071
$\text{In}_2\text{O}_3(\text{ZnO})_{11}$	10.49(1)	10.49	0.00
$\text{In}_2\text{O}_3(\text{ZnO})_{12}$		7.515	
$\text{In}_2\text{O}_3(\text{ZnO})_{13}$	12.04(1)	12.05	-0.01
$\text{In}_2\text{O}_3(\text{ZnO})_{14}$		8.556	
$\text{In}_2\text{O}_3(\text{ZnO})_{15}$	13.63(1)	13.61	0.02
$\text{In}_2\text{O}_3(\text{ZnO})_{16}$		9.597	
$\text{In}_2\text{O}_3(\text{ZnO})_{17}$		15.18	
$\text{In}_2\text{O}_3(\text{ZnO})_{18}$		10.64	
$\text{In}_2\text{O}_3(\text{ZnO})_{19}$		16.74	
$\text{In}_2\text{O}_3(\text{ZnO})_{20}$	11.64(1)*	11.68	-0.04

Note. These data with * were not used for $C_{\text{calcd.}}$.

TABLE III(B)
 $C_{\text{obsd. (nm)}}$ AND $C_{\text{calcd. (nm)}}$ FOR $\text{InFeO}_3(\text{ZnO})_m$ COMPOUNDS

Compound	$C_{\text{obsd. (nm)}}$	$C_{\text{calcd. (nm)}}$	$C_{\text{obsd. (nm)}} - C_{\text{calcd. (nm)}}$
$\text{InFeO}_3(\text{ZnO})$	2.610(1)	2.610	0.000
$\text{InFeO}_3(\text{ZnO})_2$	2.258(1)	2.259	-0.001
$\text{InFeO}_3(\text{ZnO})_3$	4.166(1)	4.168	-0.002
$\text{InFeO}_3(\text{ZnO})_4$	3.298(1)	3.298	0.000
$\text{InFeO}_3(\text{ZnO})_5$	5.727(1)	5.726	0.001
$\text{InFeO}_3(\text{ZnO})_6$	4.339(1)	4.336	0.003
$\text{InFeO}_3(\text{ZnO})_7$	7.286(1)	7.283	0.003
$\text{InFeO}_3(\text{ZnO})_8$ ⁽⁸⁾	5.375(1)*	5.375	0.000
$\text{InFeO}_3(\text{ZnO})_9$	8.843(1)	8.841	0.002
$\text{InFeO}_3(\text{ZnO})_{10}$ ⁽⁸⁾	6.402(1)*	6.413	-0.011
$\text{InFeO}_3(\text{ZnO})_{11}$	10.39(1)	10.40	-0.01
$\text{InFeO}_3(\text{ZnO})_{12}$		7.452	
$\text{InFeO}_3(\text{ZnO})_{13}$	11.96(1)	11.96	0.00
$\text{InFeO}_3(\text{ZnO})_{14}$		8.490	
$\text{InFeO}_3(\text{ZnO})_{15}$		13.51	
$\text{InFeO}_3(\text{ZnO})_{16}$		9.529	
$\text{InFeO}_3(\text{ZnO})_{17}$		15.07	
$\text{InFeO}_3(\text{ZnO})_{18}$		10.57	
$\text{InFeO}_3(\text{ZnO})_{19}$		16.63	
$\text{InFeO}_3(\text{ZnO})_{20}$	11.61(2)*	11.61	0.00

Note. These data with * were not used for $C_{\text{calcd.}}$.

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