

Compounds Which Have $\text{InFeO}_3(\text{ZnO})_m$ -Type Structures ($m = \text{Integer}$)

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New $\text{RAO}_3(\text{MO})_m$ compounds [$R = \text{Sc, In, Y, or lanthanides}$; $A = \text{Fe, Ga, or Al}$; $M = \text{Mg, Mn, Co, Fe(II), or Zn}$; $m = \text{integer}$], having $\text{InFeO}_3(\text{ZnO})_m$ types of structures, were synthesized. The phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ system at 1300°C were determined by means of a classical quenching method, and a solid solution with spinel structure between In_2MgO_4 and Fe_2MgO_4 including $\text{InFeO}_3(\text{MgO})$ ($a = 8.632(1) \text{ \AA}$) was obtained. The crystal structures in the $(\text{InAO}_3)(\text{MO})_m$ types of compounds [$A = \text{In, Fe, Ga, Cr, or Al}$; $M = \text{divalent cation elements}$; $m = \text{integer}$] are summarized in $\text{In}_2\text{O}_3(\text{CuO})_2$, spinel, YbFe_2O_4 , and CaFe_2O_4 types of structures, and the relation between their crystal structures and the constituent cations is discussed. © 1989 Academic Press, Inc.

Introduction

It is valuable to classify the crystal structures of inorganic compounds systematically and to analyze the relation between the crystal structures and their constituent elements. In previous papers (1, 2) we reported homologous compounds, $\text{RAO}_3(\text{ZnO})_m$ [$R = \text{Sc, In, Y, Lu, Yb, Tm, or Er}$; $A = \text{Fe, Ga, or Al}$; $m = 1\text{-}11$], which have layered structures, and classified the crystal structures of $\text{RAO}_3(\text{MO})$ compounds [$R = \text{Sc, In, Y, or lanthanides}$; $A = \text{Fe, Ga, Cr, or Al}$; $M = \text{divalent cation elements}$] into four kinds of crystal structures: spinel, YbFe_2O_4 , CaFe_2O_4 , and K_2NiF_4 . The summary of the crystal structures of $\text{InFeO}_3(\text{ZnO})_m$ ($m = 1\text{-}10$) is shown in Table I and their positions in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{ZnO}_4\text{-}$

ZnO system are given in Fig. 1. The crystal structure of $\text{YbFeO}_3(\text{FeO})$ which corresponds to $m = 1$ in $\text{InFeO}_3(\text{ZnO})_m$ has already been analyzed by Kato *et al.* (3). $(\text{YbFeO}_3)_2\text{FeO}$, $(\text{YbFeO}_3)_3\text{FeO}$, and $(\text{YbFeO}_3)_4\text{FeO}$ were analyzed by both the single-crystal X-ray diffraction method and the electron diffraction method (4-7). The summary of the crystal structures of $(\text{YbFeO}_3)_n\text{FeO}$ ($n = \text{integer}$) is shown in Table II. In the present paper, we report $\text{InFeO}_3(\text{ZnO})_m$ types of compounds, containing MgO , MnO , FeO , CoO , or ZnO as one of the components, and the phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ system at 1300°C , which were determined by the classical quenching method, and discuss the relation between the crystal structures of $(\text{InAO}_3)(\text{MO})_m$ types of compounds [$A = \text{In, Fe, Ga, Cr, or Al}$; $M = \text{divalent cation elements}$; $m = \text{integer}$] and their constituent cation elements.

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TABLE I
THE SUMMARY OF THE CRYSTAL STRUCTURES OF InFeO₃(ZnO)_m (*m* = 1–10)

Compounds	Lattice constants (Å)		Space group	<i>z</i>	<i>u</i>	<i>w</i>	<i>x</i>	<i>p</i>	<i>c</i> (Å)/ <i>p</i>
	<i>a</i>	<i>c</i>							
InFeZnO ₄	3.321(1)	26.09(1)	$R\bar{3}m$	3	1 × 3	1 × 3	0	12	2.174
InFeZn ₂ O ₅	3.309(1)	22.57(1)	$P6_3/mmc$	2	1 × 2	1 × 2	1 × 2	10	2.257
InFeZn ₃ O ₆	3.300(1)	41.68(1)	$R\bar{3}m$	3	1 × 3	1 × 3	2 × 3	18	2.316
InFeZn ₄ O ₇	3.294(1)	32.99(1)	$P6_3/mmc$	2	1 × 2	1 × 2	3 × 2	14	2.356
InFeZn ₅ O ₈	3.288(1)	57.28(1)	$R\bar{3}m$	3	1 × 3	1 × 3	4 × 3	24	2.387
InFeZn ₆ O ₉	3.283(1)	43.36(1)	$P6_3/mmc$	2	1 × 2	1 × 2	5 × 2	18	2.409
InFeZn ₇ O ₁₀	3.279(1)	72.85(1)	$R\bar{3}m$	3	1 × 3	1 × 3	6 × 3	30	2.428
InFeZn ₈ O ₁₁	3.276(1)	53.75(1)	$P6_3/mmc$	2	1 × 2	1 × 2	7 × 2	22	2.443
InFeZn ₉ O ₁₂	3.274(1)	88.41(1)	$R\bar{3}m$	3	1 × 3	1 × 3	8 × 3	36	2.456
InFeZn ₁₀ O ₁₃	3.272(1)	64.02(1)	$P6_3/mmc$	2	1 × 2	1 × 2	9 × 2	26	2.462

Note. *z*, molecular numbers in a unit cell; *u*, number of InO_{1.5} layers; *w*, number of (FeZn)O_{2.5} layers; *x*, number of ZnO layers; *p*, number of oxygen layers.

Experimental

The experimental method, equipment, and starting compounds have already been described elsewhere (1, 2). In order to obtain $RGaO_3(MnO)_m$ compounds [*R* = In, Lu, Yb, Tm, Er, Ho, and Y; *m* = 2 and 3] and InFeO₃(ZnO)(FeO), mixtures of $R_2O_3:Ga_2O_3:MnO = 1:1:4$ (or 6) or $In_2O_3:Fe_2O_3:ZnO:Fe = 1:5/3:2:2/3$ (in

mole ratio) were heated at 1200°C for 3 days in an alumina crucible in an evacuated SiO₂ tube. In order to prepare Ca compounds we used CaCO₃ as the starting compound. Prior to mixing, powdered CaCO₃ (guaranteed reagent grade) was heated in air at 600°C for 1 day. A mixture of $Sc_2O_3:Fe_2O_3:CaCO_3 = 1:1:2$ (in mole ratio) was heated at 1300°C for 4 days in air. A mixture of $In_2O_3:Fe_2O_3:CaCO_3 = 1:1:2$ (in mole ratio) was heated at 900°C in air for 2 days and then sealed in a Pt tube which was reheated at 1200°C for 14 days. All the other mixtures in the systems, $R_2O_3-A_2O_3-MO$ or $R_2O_3-A_2O_3-MO-M'O$ [*R* = In, Y, and lanthanides; *A* = Fe, Ga, Cr, or Al; *M* and *M'* = divalent cation elements] were heated in sealed Pt tubes. After each heat treatment, all the samples were rapidly cooled in air. The identification and the measurement of the lattice constants for all of the samples obtained were made by means of a powder X-ray diffraction method (1).

Since each of the samples was obtained as a single phase, we estimated the stoichiometry for each compound from the mixing ratio of the starting compounds.

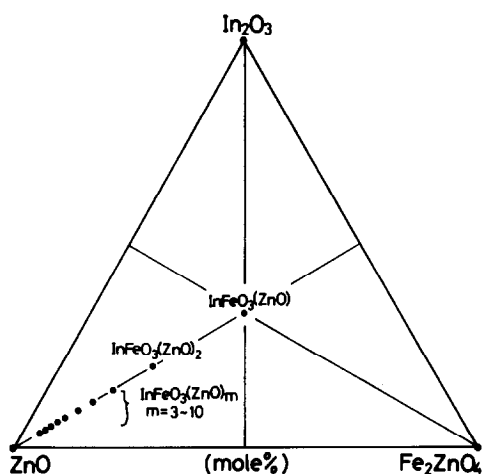


FIG. 1. InFeO₃(ZnO)_m (*m* = 1–10) in the In₂O₃–Fe₂ZnO₄–ZnO system.

TABLE II
THE SUMMARY OF THE CRYSTAL STRUCTURES OF $(\text{YbFeO}_3)_n\text{FeO}$ ($n = 1-4$)

n in $(\text{YbFeO}_3)_n\text{FeO}$	Compound	Lattice constants (\AA)			z	Space group	p	u	v	w
		a	c	z						
1	YbFe_2O_4	3.455(1)	25.05(1)	3	$R\bar{3}m$	12	3	0	3	
2	$\text{Yb}_2\text{Fe}_3\text{O}_7$	3.476(1)	28.43(1)	2	$P6_3/mmc$	14	4	2	2	
3	$\text{Yb}_3\text{Fe}_4\text{O}_{10}$	3.490(1)	60.79(2)	3	$R\bar{3}m$	30	9	6	3	
4	$\text{Yb}_4\text{Fe}_5\text{O}_{13}$	3.503(2)	53.03(2)	2	$P6_3/mmc$	26	8	6	2	

Note. p , number of oxygen layers; u , number of $\text{YbO}_{1.5}$ layers; v , number of $\text{FeO}_{1.5}$ layers; w , number of $\text{Fe}_2\text{O}_{2.5}$ layers.

In order to determine the phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ system at 1300°C , we used a classical quenching method which has already been described elsewhere (8).

Results and Discussion

The obtained compounds are presented in Table III (A and B), together with the conditions of synthesis and the hexagonal lattice constants.

[i] In the $R_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MnO}$ system [$R = \text{In, Lu, Yb, Tm, Er, Ho, or Y}$], we obtained $R\text{GaO}_3(\text{MnO})_2$ compounds at 1200°C , which are isostructural with $\text{InFeO}_3(\text{ZnO})_2$. $\text{InGaO}_3(\text{MnO})_3$ with the $\text{InFeO}_3(\text{ZnO})_3$ structure was obtained in the $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MnO}$ system. $R\text{GaO}_3(\text{MnO})$ [$R = \text{In, Lu, Yb, Tm, Ho, Er, or Y}$; YbFe_2O_4 structure] have already been reported in (9, 10).

[ii] In the $\text{In}_2\text{O}_3\text{-A}_2\text{O}_3\text{-MgO}$ system [$A = \text{Fe, Ga, or Al}$], we obtained $\text{InFeO}_3(\text{MgO})$ with the spinel structure (10) and $\text{InGaO}_3(\text{MgO})_2$ and $\text{InAlO}_3(\text{MgO})_2$ with the $\text{InFeO}_3(\text{ZnO})_2$ -type structure. $\text{InGaO}_3(\text{MgO})$ and $\text{InAlO}_3(\text{MgO})$ with the YbFe_2O_4 structure have already been reported in (2, 10). In order to make clear the formations of phases close to the composition, $\text{InFeO}_3(\text{MgO})$, we tried to establish the phase

relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ system at 1300°C . It is known that there is a spinel phase in both the $\text{MgO-In}_2\text{O}_3$ system (2, 11) and $\text{MgO-Fe}_2\text{O}_3$ systems (11), respectively. A complete solid solution range was found between In_2MgO_4 and Fe_2MgO_4 with spinel structure including $\text{InFeO}_3(\text{MgO})$ ($a = 8.632(1) \text{\AA}$) in the middle point of the whole range. Figure 2 shows the variation of the lattice constant of the $\text{In}_{2-x}\text{Fe}_x\text{MgO}_4$ solid solution as a function of x , which obeys Vegard's law on the whole range of composition. No $\text{InFeO}_3(\text{MgO})_2$ with an $\text{InFeO}_3(\text{ZnO})_2$ structure was obtained in the heat treatment for a mixture of $\text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 : \text{MgO} = 1 : 1 : 4$ (in mole ratio) in the temperature range from 1200 to 1450°C for 3 days in a Pt tube, but the coexistence of both MgO and spinel phases was observed. Each mixing ratio of the starting compounds, the heating periods, and the phases obtained shown in Table IV are necessary and sufficient for establishing the phase relations shown in Fig. 3. After each heat treatment for 3 days (2 days for the mixture $\text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 : \text{MgO} = 0.60 : 0.15 : 0.25$ (in mole ratio)), we reheated for 3 more days and could not see any difference in phase assemblages following the successive heat treatments.

[iii] As mentioned in the preceding section, both $\text{InGaMg}_2\text{O}_5$ and $\text{InAlMg}_2\text{O}_5$ compounds were identified in the $\text{In}_2\text{O}_3\text{-A}_2\text{O}_3\text{-}$

TABLE III
COMPOUNDS HAVING InFeO₃(ZnO)_m TYPE OF STRUCTURES, THE CONDITIONS OF SYNTHESIS AND THE LATTICE CONSTANTS AS HEXAGONAL SYSTEM

A					
Compound	Temperature (°C)	Heating period (day)	Lattice constants (Å)		
			<i>a</i>	<i>c</i>	
InGaO ₃ (MnO) ₂	1200	3	3.364(1)	22.88(1)	
LuGaO ₃ (MnO) ₂	1200	3	3.409(1)	22.47(1)	
YbGaO ₃ (MnO) ₂	1200	3	3.438(1)	22.41(1)	
TmGaO ₃ (MnO) ₂	1200	3	3.450(1)	22.36(1)	
ErGaO ₃ (MnO) ₂	1200	3	3.461(1)	22.32(1)	
HoGaO ₃ (MnO) ₂	1200	3	3.472(1)	22.26(1)	
YGaO ₃ (MnO) ₂	1200	3	3.474(1)	22.24(1)	
InGaO ₃ (MnO) ₃	1200	3	3.316(1)	42.12(1)	
InGaO ₃ (MgO) ₂	1300	5	3.309(1)	22.08(1)	
InAlO ₃ (MgO) ₂	1450	4	3.287(1)	21.81(1)	
InFeO ₃ (ZnO)(MgO)	1422	5	3.324(1)	22.32(1)	
LuFeO ₃ (ZnO)(MgO)	1422	5	3.389(1)	21.90(1)	
YbFeO ₃ (ZnO)(MgO)	1450	4	3.400(1)	21.82(1)	
TmFeO ₃ (ZnO)(MgO)	1450	4	3.411(1)	21.81(1)	
ScGaO ₃ (ZnO)(MgO)	1422	5	3.276(1)	22.24(1)	
InGaO ₃ (ZnO)(MgO)	1300	7	3.300(1)	22.30(1)	
LuGaO ₃ (ZnO)(MgO)	1422	5	3.367(1)	21.91(1)	
YbGaO ₃ (ZnO)(MgO)	1450	5	3.378(1)	21.83(1)	
TmGaO ₃ (ZnO)(MgO)	1450	5	3.391(1)	21.82(1)	
ScGaO ₃ (ZnO) ₂ (MgO)	1450	5	3.271(1)	41.14(1)	
InGaO ₃ (ZnO) ₂ (MgO)	1450	5	3.294(1)	41.21(1)	
ScAlO ₃ (ZnO)(MgO)	1450	3	3.249(1)	21.88(1)	
InAlO ₃ (ZnO)(MgO)	1450	4	3.287(1)	22.15(1)	
LuAlO ₃ (ZnO)(MgO)	1450	2	3.351(1)	21.58(1)	
YbAlO ₃ (ZnO)(MgO)	1450	4	3.361(1)	21.51(1)	
TmAlO ₃ (ZnO) _{1.5} (MgO) _{1.5}	1450	4	3.347(1)	39.78(1)	
InFeO ₃ (ZnO)(CoO)	1450	2	3.315(1)	22.46(1)	
InFeO ₃ (ZnO)(FeO)	1200	1	3.323(1)	22.58(1)	
ScGaO ₃ (ZnO)(CoO)	1450	3	3.270(1)	22.36(1)	
InGaO ₃ (ZnO)(CoO)	1450	2	3.300(1)	22.41(1)	
InGaO ₃ (MgO)(CoO)	1450	4	3.306(1)	22.18(1)	
ScAlO ₃ (ZnO)(CoO)	1450	4	3.251(1)	22.05(1)	
InAlO ₃ (ZnO)(CoO)	1450	4	3.297(1)	22.29(1)	

B					
Compound	Temperature (°C)	Heating period (day)	Lattice constants (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
InCrO ₃ (MgO)	1450	3	8.580(1)	(spinel)	
ScFeO ₃ (CaO) ^a	1300	4	9.339(1)	10.90(1)	3.084(1)
InFeO ₃ (CaO) ^a	1200	14	9.425(2)	11.03(1)	3.124(1)

^a CaFe₂O₄ type.

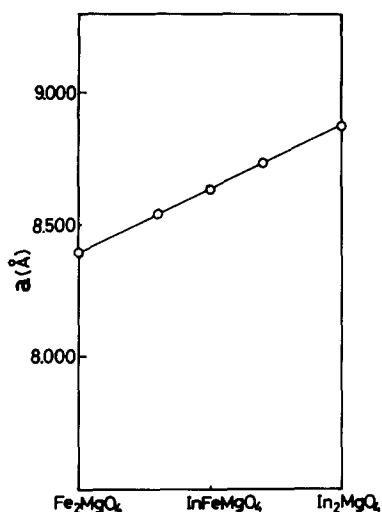


FIG. 2. The lattice constant of $\text{In}_{2-x}\text{Fe}_x\text{MgO}_4$ with spinel structure.

MgO system [$A = \text{Ga}$ or Al] and $R\text{FeO}_3(\text{ZnO})_2$ [$R = \text{Sc}, \text{In}, \text{Lu}, \text{Yb}, \text{Tm},$ or Er] have already been reported in the $R_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-ZnO}$ system (1, 2). We obtained $R\text{FeO}_3(\text{ZnO})(\text{MgO})$ [$R = \text{In}, \text{Lu}, \text{Yb},$ or Tm] in the $R_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-ZnO-MgO}$ system, which are isostructural with $\text{InFeO}_3(\text{ZnO})_2$.

[iv] In the $R_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO-MgO}$ system, we obtained $R\text{GaO}_3(\text{ZnO})(\text{MgO})$ [$R = \text{Sc}, \text{In}, \text{Lu}, \text{Yb},$ or Tm] which has the $\text{InFeO}_3(\text{ZnO})_2$ structure and $\text{ScGaO}_3(\text{ZnO})_2$

TABLE IV

MIXING RATIO OF STARTING COMPOUNDS, HEATING PERIOD, AND PHASES OBTAINED IN THE $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ SYSTEM AT 1300°C

Composition (in mole) $\text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 : \text{MgO}$	Heating period (day)	Phase(s)
0.40 : 0.25 : 0.35	3	In_2O_3 + Spinel
0.60 : 0.15 : 0.25	2	In_2O_3 + Spinel
0.25 : 0.10 : 0.65	3	MgO + Spinel
1 : 1 : 1	3	In_2O_3 + Spinel
0.35 : 0.15 : 0.50	3	Spinel
0.15 : 0.35 : 0.50	3	Spinel
1 : 1 : 2	3	Spinel
1 : 1 : 4	3	MgO + Spinel
0.70 : 0 : 0.30	3	In_2O_3 + Spinel
0.30 : 0 : 0.70	3	MgO + Spinel

Note. Each mixture was sealed in a Pt tube.

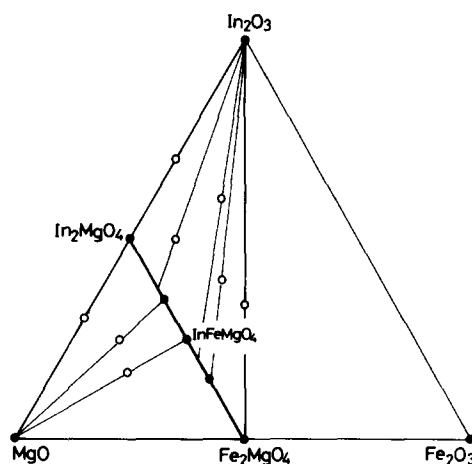


FIG. 3. The phase relations in the $\text{In}_2\text{O}_3\text{-Fe}_2\text{MgO}_4\text{-MgO}$ system at 1300°C .

(MgO) and $\text{InGaO}_3(\text{ZnO})_2(\text{MgO})$ which have the $\text{InFeO}_3(\text{ZnO})_3$ structure. $R\text{GaO}_3(\text{ZnO})_2$ [$R = \text{Sc}, \text{In}, \text{Lu}, \text{Yb}, \text{Tm},$ or Er] have already been reported in (1, 2).

[v] In the $R_2\text{O}_3\text{-Al}_2\text{O}_3\text{-ZnO-MgO}$ system, we obtained $R\text{AlO}_3(\text{ZnO})(\text{MgO})$ [$R = \text{Sc}, \text{In}, \text{Lu},$ or Yb] which has the $\text{InFeO}_3(\text{ZnO})_2$ structure and $\text{TmAlO}_3(\text{MgO})_{1.5}(\text{ZnO})_{1.5}$ which has the $\text{InFeO}_3(\text{ZnO})_3$ structure.

$R\text{AlO}_3(\text{ZnO})_m$ ($m = 2$ or 3) [$R = \text{Sc}, \text{In}, \text{Lu},$ or Yb] have already been reported in (1, 2)

[vi] In the $R_2\text{O}_3\text{-A}_2\text{O}_3\text{-ZnO-CoO}$ system [$R = \text{Sc}$ or $\text{In}; A = \text{Fe}, \text{Ga},$ or Al], we obtained $\text{InFeO}_3(\text{ZnO})(\text{CoO})$, $\text{InGaO}_3(\text{ZnO})(\text{CoO})$, $\text{InAlO}_3(\text{ZnO})(\text{CoO})$, $\text{ScGaO}_3(\text{ZnO})(\text{CoO})$, and $\text{ScAlO}_3(\text{ZnO})(\text{CoO})$ which have the $\text{InFeO}_3(\text{ZnO})_2$ structure.

[vii] In the $\text{In}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-ZnO-FeO}$ system and the $\text{In}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MgO-CoO}$ system, we obtained $\text{InFeO}_3(\text{ZnO})(\text{FeO})$ and $\text{InGaO}_3(\text{MgO})(\text{CoO})$ compounds, which have the $\text{InFeO}_3(\text{ZnO})_2$ structure. In the $\text{In}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MgO}$ system, we obtained In-CrMgO_4 with the spinel structure and in the $R_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CaO}$ system [$R = \text{Sc}$ or In],

we obtained InFeO₃(CaO) and ScFeO₃(CaO) which have the CaFe₂O₄ structure.

In the previous paper (2), we classified the crystal structures of $RAO_3(MO)$ compounds [$R = \text{Sc, In, Y, or lanthanides}$; $A = \text{Fe, Ga, Al, or Cr}$; $M = \text{divalent cation elements}$] into four types, K_2NiF_4 , $CaFe_2O_4$, $YbFe_2O_4$, and spinel. Kasper (12) and Cannard and Tilley (13) synthesized homologous compounds, $In_2O_3(ZnO)_m$, and reported their conditions of synthesis and lattice constant. On the other hand, In_2MO_4 [$M = \text{Mg, Ca, Mn, Fe, Co, Ni, Cd, and Hg}$] have the spinel structure and in these compounds, In_2MO_4 [$M = \text{Mg, Fe, Co, or Ni}$] are known as the inverse spinel (14). Including $In_2O_3(ZnO)_m$ and In_2MO_4 , we reclassified the crystal structures of $InAO_3(MO)_m$ compounds (2) into four types, $In_2O_3(CuO)_2$, $CaFe_2O_4$, $YbFe_2O_4$, and spinel types, and summarized the crystal structures of $(InAO_3)(MO)_m$ types of compounds [$A = \text{In, Fe, Ga, Al, or Cr}$; $M = \text{divalent cation elements}$] in Fig. 4. Both $InCrO_3(MO)$ [$M = \text{Ni, Mg, Cu, or Co}$] and $InAO_3(NiO)$ [$A = \text{In, Fe, Ga, Cr, or Al}$] have a spinel structure and $InAO_3(ZnO)$ [$A = \text{In, Fe, Ga, or Al}$] has a $YbFe_2O_4$ type. The crystal structures of the compounds, $InAO_3(MO)$, should be sensitive to temperature as in $InFeO_3(FeO)$, $InGaO_3(FeO)$, and $InFeO_3(MnO)$, which exhibit both spinel and $YbFe_2O_4$ types. Since Fig. 4 was constructed using previously published data, it may be the basis for constructing a more complete figure in the future as a result of the accumulation of the data of newer crystallographic transformations of $InAO_3(MO)$ compounds. We can conclude that about 70% of $(InAO_3)(MO)_m$ types of compounds which are known at present were classified into the above four types of structures.

The phase relations in the Eu_2O_3 - Fe_2O_3 - SrO system at 1300°C in air which were determined by a classical quenching method

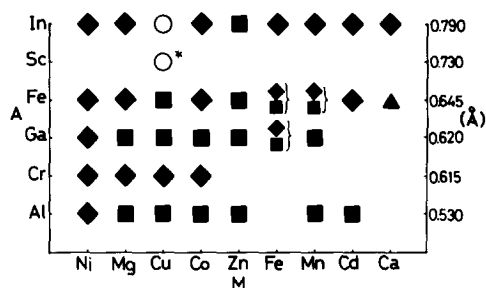


FIG. 4. The crystal structural classification of $(InAO_3)(MO)_m$ types of compounds ($m = \text{integer}$): \blacklozenge , spinel; \circ , $In_2Cu_2O_5$; \blacksquare , $InFeO_3(ZnO)_m$; \blacktriangle , $CaFe_2O_4$. * $InScO_3(CuO)_2$ was synthesized at $T = 1000^\circ\text{C}$ in air for 10 days in the present work. The lattice constants are $a = 26.48(1) \text{ \AA}$, $b = 6.487(1) \text{ \AA}$, $c = 26.46(1) \text{ \AA}$, and $\beta = 133.3(1)^\circ$ (20). Numbers along the vertical axis mean ionic radii of the trivalent cations ($= A$) with six coordination of oxygen ions (21).

reported by Drogenik *et al.* (15) are shown in Fig. 5. $(EuFeO_3)_n(SrO)$ are isostructural with $(KNiF_3)_nKF$ ($n = \frac{1}{2}, 1, \text{ or } 2$).

$InFeO_3(MgO)$, $InFeO_3(CoO)$ (8), and $InFeO_3(NiO)$ (2) have the spinel structure, and $InGaO_3(MgO)$ (8), $InGaO_3(CoO)$ (8), $InGaO_3(ZnO)_m$, and $InFeO_3(ZnO)_m$ have layered structures. To date, no

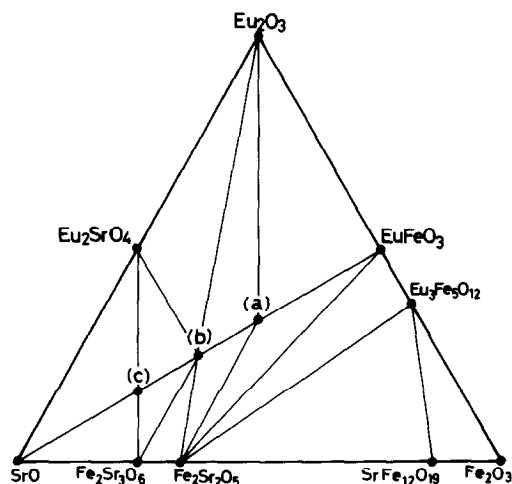
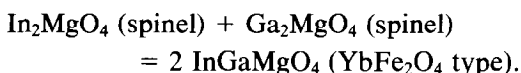
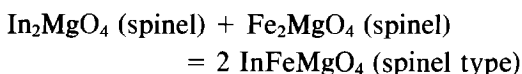


FIG. 5. The phase relations in the Eu_2O_3 - Fe_2O_3 - SrO system at 1300°C in air (9): (a) $(EuFeO_3)_2SrO$; (b) $(EuFeO_3)SrO$; (c) $(EuFeO_3)(SrO)_2$.

(KNiF₃)_nKF-type structure has been found in the In₂O₃-A₂O₃-MO system at elevated temperatures.

In the In₂O₃-Ga₂MgO₄-MgO system, we had InGaMgO₄ (8) with a layered structure between In₂MgO₄ (spinel type) and Ga₂MgO₄ (spinel type). We can see very clearly a different crystal chemical effect of Fe(III) and Ga(III) ions upon the formation of InAO₃(MO)-type compounds from In₂MgO₄ and A₂MgO₄ [A = Fe or Ga] at elevated temperatures.



It is well known that Ga(III) has a tendency to occupy tetrahedral sites in the oxides. It is understood that the difference in the crystal structures of InFeMO₄ and InGaMO₄ [M = Mg or Co] results from the difference in the site preference of Ga(III) and Fe(III). Kasper (12) and Cannard and Tilley (13) synthesized homologous compounds In₂O₃(ZnO)_m (m = 1-11) with layered structures which were analyzed by the powder X-ray diffraction method and high-resolution electron microscopy. They did not present each crystal structure of the homologous compounds; however, we can easily conclude that they are isostructural with InFeO₃(ZnO)_m. A study of the phase relations in the system In₂O₃-Fe₂O₃-ZnO at elevated temperatures is in progress by Nakamura *et al.* (16), and it will be shown that solid solutions exist between In₂O₃(ZnO)_m and InFeO₃(ZnO)_m at 1350°C (m = 3-9 and 11).

Now it is clear that K₂NiF₄, CaFe₂O₄, and YbFe₂O₄ each have homologous compounds, (KNiF₃)_nKF, (CaFe₂O₄)(FeO)_m (17), and (YbFeO₃)_n(FeO), respectively. However, no homologous compounds related to spinel-type structures have been reported so far. Instead of forming spinel-re-

lated homologous compounds, a wide solid solution between A₂O₃ and MO may be formed, the structure of which is spinel, because of the small difference in the ionic radii between trivalent cation and divalent cation which form the spinel structure. Wüstite (Fe_{1-x}O) is a well-known compound with a wide solid solution range (x = 0.0455-0.1421 at 1200°C) (18), which has an NaCl-type structure. We may be able to interpret that the wide solid solution in wüstite [we can formerly express it in the form (Fe₂O₃)(FeO)₄-(Fe₂O₃)(FeO)₁₉] corresponds to the homologous series in the other three structures. Another typical instance is a MgO(Al₂O₃) compound. According to Osborn (19), MgO(Al₂O₃) phase of a spinel structure has a wide solid solution range at 1700°C [in the chemical composition of MgO:Al₂O₃ = 1:1 to 1:2.33 (in mole ratio)].

All X-ray powder diffraction data which we obtained in the present work will be sent to the Joint Committee of the Powder Diffraction Standard (USA).

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