JOURNAL OF SOLID STATE CHEMISTRY 78, 98–107 (1989)

Structural Classification of $RAO_3(MO)_n$ Compounds (R = Sc, In, Y, or Lanthanides; A = Fe(III), Ga, Cr, or Al; M = Divalent Cation; n = 1–11)

NOBORU KIMIZUKA* AND TAKAHIKO MOHRI

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

Received March 7, 1988; in revised form August 18, 1988

A series of new compounds $RAO_3(MO)_n$ (n = 1–11) having spinel, $YbFe_2O_4$, or $InFeO_3(ZnO)_n$ types of structures were newly synthesized (R = Sc, In, Y, Lu, Yb, Tm, or Er; A = Fe(III), Ga, Cr, or Al; M = Mg, Mn, Fe(II), Co, Ni, Zn, or Cd) at elevated temperatures. The conditions of synthesis and the lattice constants for these compounds are reported. The stacking sequences of the $InO_{1.5}$, $(FeZn)O_{2.5}$, and ZnO layers for $InFeO_3(ZnO)_{10}$ and the $TmO_{1.5}$, $(AlZn)O_{2.5}$, and ZnO layers for $TmAlO_3(ZnO)_{11}$ are presented, respectively. The crystal structures of the $(RAO_3)_m(MO)_n$ phases (R = Sc, In, Y, or lanthanide elements; A = Fe(III), Ga, Cr, or Al; M = divalent cation elements; m and n = integer) are classified into four crystal structure types (K_2NiF_4, $CaFe_2O_4$, $YbFe_2O_4$, and spinel), based upon the constituent cations R, A, and M.

Introduction

It may be important to classify the crystal structures of inorganic compounds systematically and analyze the relations between the crystal structures and their constitutent cations. Wells (*1*) classified the XY_2O_4 type of compounds based upon the coordination numbers of oxygen of both X and Y cations.

The RFe_2O_4 compound in the R_2O_3–Fe_2O_3–FeO system (R = Y, Lu, Yb, Tm, Er, and Ho) is a thermochemically stable one which has a layered structure at elevated temperatures (*2, 3*). In this compound, the Fe ion is located in a trigonal bipyramid of oxygen and the R ion is located in an octahedral one. The constituent cations forming $RAO_3(MO)$ compounds with RFe_2O_4 type of structure which have been reported so far, are as follows: R = Sc, In, Y, Lu, Yb, Tm, Er, and Ho; A = Fe(III), Ga, or Al; M = Mg, Mn, Co, Fe(II), Cu, Zn, or Cd) (*4–7*). The new classification of XY_2O_4 type of compounds including $YbFe_2O_4$ type of compounds is shown in Table I which is a modification of the table originally presented by Wells (*1*). The phase transformation between Yb Fe_2O_4 type and spinel type was observed in $InGaMnO_4$ (*7*). The higher temperature phase has the spinel structure and the lower one has the $YbFe_2O_4$ structure. In the Yb_2O_3–Fe_2O_3–FeO system at 1550°C, $(YbFeO_3)_2FeO$, $(YbFeO_3)_3FeO$, $(YbFeO_3)_4FeO$ . . . in addition to $YbFe_2O_4$ compound were reported (*8–10*). $InFeO_3(ZnO)_n$ compounds (n = 1–9) in the In_2O_3–Fe_2O_3–ZnO system were synthesized at 1300–1450°C (*11*), and the stacking sequences of

---

* To whom all correspondence should be addressed.

0022-4596/89 $3.00

TABLE I

THE CLASSIFICATION OF THE CRYSTAL STRUCTURES OF XY_2O_4 TYPE OF COMPOUNDS

CN (*Y*): CN (*X*)	4	5	6	8	9 and/or 10
4	phenacite		olivine spinel	K_2WO_4	β-K_2SO_4
6		$\boxed{YbFe_2O_4}$	Sr_2PbO_4, Ca_2IrO_4, etc.		K_2NiF_4
8			$CaFe_2O_4$ $CaTi_2O_4$		

Note. CN (*X*), coordination number of *X*; CN (*Y*), coordination number of *Y*.

the $InO_{1.5}$, $(FeZn)O_{2.5}$, and ZnO layers in these compounds were presented, based upon the construction rules for the crystal structures of the $(YbFeO_3)_nFeO$ ($n = 1, 2, 3 \ldots$). The characteristic features of the crystal structures of the $InFeO_3(ZnO)_n$ are summarized in Table II.

In the present paper, we report the conditions of synthesis, the crystal structures, and the lattice constants of $RAO_3(ZnO)_n$ (R = Sc, In, Y, Lu, Yb, Tm, or Er; A = Fe(III), Ga, or Al; n = 1–11) and their related compounds having spinel, $YbFe_2O_4$, or $InFeO_3(ZnO)_n$ type of crystal structures and show the dependence of the crystal structures of K_2NiF_4, $CaFe_2O_4$, $YbFe_2O_4$, and spinel types upon the constituent cations.

Experimental

The experimental method, starting compounds, and equipment that we used in the present work are described elsewhere (*11*).

TABLE II

THE SUMMARY OF THE CRYSTAL DATA OF $InFeO_3(ZnO)_n$

Compounds	Lattice constant (Å)		Space group	*z*	*u*	*w*	*x*	*p*	*c* (Å)/*p*
	a	*c*							
$InFeZnO_4$	3.321(1)	26.09(1)	$R\bar{3}m$	3	1 × 3	1 × 3	0	12	2.174
$InFeZn_2O_5$	3.309(1)	22.57(1)	$P6_3/mmc$	2	1 × 2	1 × 2	1 × 2	10	2.257
$InFeZn_3O_6$	3.300(1)	41.68(1)	$R\bar{3}m$	3	1 × 3	1 × 3	2 × 3	18	2.316
$InFeZn_4O_7$	3.294(1)	32.99(1)	$P6_3/mmc$	2	1 × 2	1 × 2	3 × 2	14	2.356
$InFeZn_5O_8$	3.288(1)	57.28(1)	$R\bar{3}m$	3	1 × 3	1 × 3	4 × 3	24	2.387
$InFeZn_6O_9$	3.283(1)	43.36(1)	$P6_3/mmc$	2	1 × 2	1 × 2	5 × 2	18	2.409
$InFeZn_7O_{10}$	3.279(1)	72.85(1)	$R\bar{3}m$	3	1 × 3	1 × 3	6 × 3	30	2.428
$InFeZn_8O_{11}$	3.276(1)	53.75(1)	$P6_3/mmc$	2	1 × 2	1 × 2	7 × 2	22	2.443
$InFeZn_9O_{12}$	3.274(1)	88.41(1)	$R\bar{3}m$	3	1 × 3	1 × 3	8 × 3	36	2.456

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.

Er_2O_3 (99.9%), CdO(99.9%), and Fe metal powder (99.99%) were used. For preparing RGaO$_3$(FeO) compounds, we sealed a mixture of $R_2O_3 : Ga_2O_3 : Fe_2O_3 : Fe = 1 : 1 : 2/3 : 2/3$ (in mole ratio) in an evacuated silica tube (R = In, Lu, Yb, or Tm). After heating each sample for a prespecified period, it was rapidly cooled in water. The other samples, $RAO_3(MO)_n$ ($M \neq$ Fe) were prepared in sealed Pt tubes. The chemical reactions between the tubes and the powder samples were checked visually. We could not see any substantial reactions between them. The sample and tube was carefully weighed before and after each heat treatment. No volatilization effect during each heat treatment was observed. We determined each stoichiometry for the obtained compounds from the mixing ratio of starting compounds and affirmed it by each of their crystal structure models.

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 (*11*), and some of the samples were supplied for electron diffraction observation.

Results and Discussion

[I] In the Lu_2O_3–A_2O_3–ZnO system (A = Fe, Ga, or Al), we obtained $LuFeO_3(ZnO)_n$ (n = 1–7 and 9), $LuGaO_3(ZnO)_n$ (n = 1–8), and $LuAlO_3(ZnO)_n$ (n = 6–7 and 9) which are isostructural with $InFeO_3(ZnO)_n$ (*11*). The conditions of synthesis and the lattice constants for each compound are shown in Table IIIa. All $LuFeO_3(ZnO)_n$ are brown and all $LuGaO_3(ZnO)_n$ and $LuAlO_3(ZnO)_n$ are colorless. These results agree with the presence of d electrons in Fe ions, and their lack in Al and Ga ions.

TABLE IIIa

THE CONDITIONS OF SYNTHESIS AND THE LATTICE CONSTANTS FOR THE COMPOUNDS OBTAINED IN THE Lu_2O_3–A_2O_3–ZnO SYSTEM (A = Fe, Ga, OR Al)

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å)	
			a	*c*
$LuFeZnO_4$	1350	2	3.411(1)	25.39(1)
$LuFeZn_2O_5$	1300	11	3.377(1)	22.13(1)
$LuFeZn_3O_6$	1450	3	3.358(1)	40.99(1)
$LuFeZn_4O_7$	1450	2	3.327(1)	32.53(1)
$LuFeZn_5O_8$	1450	2	3.327(1)	56.35(1)
$LuFeZn_6O_9$	1450	1	3.317(1)	42.96(1)
$LuFeZn_7O_{10}$	1450	3	3.310(1)	72.22(1)
$LuFeZn_9O_{12}$	1450	3	3.297(1)	87.84(1)
$LuGaZnO_4$	1350	3	3.400(1)	25.25(1)
$LuGaZn_2O_5$	1300	5	3.365(1)	22.05(1)
$LuGaZn_3O_6$	1450	6	3.344(1)	40.88(1)
$LuGaZn_4O_7$	1450	6	3.328(1)	32.45(1)
$LuGaZn_5O_8$	1450	5	3.320(1)	56.44(1)
$LuGaZn_6O_9$	1450	1	3.313(1)	42.80(1)
$LuGaZn_7O_{10}$	1450	5	3.307(1)	72.01(1)
$LuGaZn_8O_{11}$	1450	6	3.301(1)	53.17(1)
$LuAlZn_6O_9$	1450	8	3.313(1)	42.82(1)
$LuAlZn_7O_{10}$	1450	3	3.288(1)	71.54(1)
$LuAlZn_9O_{12}$	1422	4	3.279(1)	87.36(4)

[II] In the Yb_2O_3–A_2O_3–ZnO system (A = Fe, Ga, or Al), we obtained $YbFeO_3(ZnO)_n$ (n = 1–7 and 9), $YbGaO_3(ZnO)_n$ (n = 1–7 and 9), and $YbAlO_3(ZnO)_n$ (n = 9 and 11) which are isostructural with $InFeO_3(ZnO)_n$. The conditions of synthesis and the lattice constants for each compound are shown in Table IIIb. All $YbFeO_3(ZnO)_n$ are brown and all $YbGaO_3(ZnO)_n$ and $YbAlO_3(ZnO)_n$ are colorless.

[III] In the Tm_2O_3–A_2O_3–ZnO system (A = Fe or Ga), we obtained $TmFeO_3(ZnO)_n$ (n = 1 and 5–10) and $TmGaO_3(ZnO)_n$ (n = 1–7 and 9) which are isostructural with $InFeO_3(ZnO)_n$. $TmFeO_3(ZnO)_{10}$ is isostructural with $InFeO_3(ZnO)_{10}$ which will be shown in [V]. The conditions of synthesis and the lattice constants for each compound are shown in Table IIIc. All $TmFeO_3(ZnO)_n$ are brown and all $TmGaO_3(ZnO)_n$ are colorless.

[IV] In the Er_2O_3–A_2O_3–ZnO system (A = Fe or Ga), we obtained $ErFeO_3(ZnO)_9$ and $ErGaO_3(ZnO)_n$ (n = 4 and 5) which are isostructural with $InFeO_3(ZnO)_n$. $ErFeO_3(ZnO)_9$ is brown and $ErGaO_3(ZnO)_n$ are colorless. The conditions of synthesis

TABLE IIIb

The Conditions of Synthesis and the Lattice Constants for the Compounds Obtained in the Yb_2O_3–A_2O_3–ZnO System (A = Fe, Ga, or Al)

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$YbFeZnO_4$	1350	2	3.425(1)	25.28(1)
$YbFeZn_2O_5$	1422	4	3.391(1)	22.05(1)
$YbFeZn_3O_6$	1450	3	3.368(1)	40.84(1)
$YbFeZn_4O_7$	1450	3	3.347(1)	32.45(1)
$YbFeZn_5O_8$	1450	3	3.328(1)	56.50(1)
$YbFeZn_6O_9$	1450	5	3.310(1)	42.92(1)
$YbFeZn_7O_{10}$	1450	1	3.307(1)	72.19(1)
$YbFeZn_9O_{12}$	1450	3	3.296(1)	87.79(1)
$YbGaZnO_4$	1350	1	3.415(1)	25.09(1)
$YbGaZn_2O_5$	1300	13	3.378(1)	21.98(1)
$YbGaZn_3O_6$	1450	2	3.352(1)	40.76(1)
$YbGaZn_4O_7$	1450	4	3.334(1)	32.38(1)
$YbGaZn_5O_8$	1450	4	3.322(1)	56.39(1)
$YbGaZn_6O_9$	1450	3	3.305(1)	42.80(1)
$YbGaZn_7O_{10}$	1450	3	3.300(1)	72.07(1)
$YbGaZn_9O_{12}$	1450	3	3.296(1)	87.66(1)
$YbAlZn_9O_{12}$	1450	4	3.280(1)	87.11(1)
$YbAlZn_{11}O_{14}$	1450	4	3.273(1)	102.60(2)

and the lattice constants for each compound are shown in Table IIId.

[V] In the In_2O_3–Fe_2O_3–ZnO system, we already reported $InFeO_3(ZnO)_n$ (n = 1–9).

TABLE IIIc

The Conditions of Synthesis and the Lattice Constants for the Compounds Obtained in the Tm_2O_3–A_2O_3–ZnO System (A = Fe or Ga)

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$TmFeZnO_4$	1450	1	3.449(1)	25.28(1)
$TmFeZn_5O_8$	1450	1	3.315(1)	56.61(1)
$TmFeZn_6O_9$	1450	1	3.316(1)	42.87(1)
$TmFeZn_7O_{10}$	1450	1	3.306(1)	72.57(3)
$TmFeZn_8O_{11}$	1450	3	3.301(1)	53.42(1)
$TmFeZn_9O_{12}$	1450	6	3.294(1)	87.77(1)
$TmFeZn_{10}O_{13}$	1450	6	3.285(1)	63.74(1)
$TmGaZnO_4$	1350	1	3.430(1)	25.07(1)
$TmGaZn_2O_5$	1300	11	3.392(1)	21.93(1)
$TmGaZn_3O_6$	1450	3	3.357(1)	40.70(1)
$TmGaZn_4O_7$	1450	3	3.331(1)	32.38(1)
$TmGaZn_5O_8$	1450	3	3.314(1)	56.50(1)
$TmGaZn_6O_9$	1450	4	3.309(1)	42.84(1)
$TmGaZn_7O_{10}$	1450	4	3.300(1)	72.11(1)
$TmGaZn_9O_{12}$	1450	3	3.292(1)	87.70(1)

TABLE IIId

The Conditions of Synthesis and the Lattice Constants for the Compounds Obtained in the Er_2O_3–A_2O_3–ZnO System (A = Fe or Ga)

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$ErFeZn_9O_{12}$	1450	4	3.288(1)	87.88(3)
$ErGaZn_4O_7$	1450	4	3.310(1)	32.51(1)
$ErGaZn_5O_8$	1450	4	3.298(1)	56.61(1)

TABLE IIIe

The Condition of Synthesis and the Lattice Constants for the Compound Obtained in the In_2O_3–Fe_2O_3–ZnO System

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$InFeZn_{10}O_{13}$	1450	7	3.272(1)	64.02(1)

TABLE IIIf

The Conditions of Synthesis and the Lattice Constants for the Compounds Obtained in the R_2O_3–A_2O_3–MO Systems (R = Sc, In, Lu, Yb, Tm, or Y; A = Fe(III), Ga, Cr, or Al; M = Mg, Mn, Co, Cd, or Ni)

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$ScGaMgO_4$	1400	7	3.272(1)	25.62(1)
$ScAlMgO_4$	1400	8	3.236(1)	25.15(1)
$InAlMgO_4$	1550	2	3.290(1)	25.66(1)
$ScAlMnO_4$	1400	5	3.260(1)	25.98(1)
$InFeMnO_4$	1100	5	3.356(1)	26.40(1)
$InAlMnO_4$	1500	5	3.319(1)	26.21(1)
$InAlCoO_4$	1400	7	3.301(1)	25.74(1)
$ScAlCoO_4$	1400	13	3.247(1)	25.19(1)
$InAlCdO_4$	1000	7	3.321(1)	27.50(1)
$InGaFeO_4$	1000	1	3.313(1)	26.17(1)
$LuGaFeO_4$	1100	4	3.430(1)	25.31(1)
$YbGaFeO_4$	1100	12	3.447(1)	25.18(1)
$TmGaFeO_4$	1100	12	3.466(1)	25.07(1)
$YFeZnO_4$	1450	3	3.489(1)	25.20(1)
$InFeNiO_4$	1200	10	8.601(1)	(spinel)
$InCrNiO_4$	1300	7	8.553(1)	(spinel)
In_2MnO_4	1000	7	9.000(1)	(spinel)
In_2MgO_4	1550	2	8.864(1)	(spinel)
			8.81(1) (*15*)	(spinel)

TABLE IVa

THE SUMMARY OF THE CRYSTAL STRUCTURES OF $InFeO_3(ZnO)_{10}$ AND $YbAlO_3(ZnO)_{11}$

Compounds	Lattice constants (Å)		Space group	z	u	w	x	p	c (Å)/p
	a	c							
$InFeO_3(ZnO)_{10}$	3.272(1)	64.02(1)	$P6_3/mmc$	2	1 × 2	1 × 2	9 × 2	26	2.462
$YbAlO_3(ZnO)_{11}$	3.273(1)	102.60(2)	$R\bar{3}m$	3	1 × 3	1 × 3	10 × 3	42	2.443

Note. z, Molecular numbers in a unit cell; u, number of $InO_{1.5}$ layers or $YbO_{1.5}$ layers; w, number of (Fe, Zn)$O_{2.5}$ layers or (Al, Zn)$O_{2.5}$ layers; x, number of ZnO layers; p, number of oxygen layers.

$InFeO_3(ZnO)_{10}$ was newly prepared in the present work, and the condition of synthesis and the lattice constants are shown in Table IIIe. $InFeO_3(ZnO)_{10}$ is brown.

Based upon the construction rules in the $(YbFeO_3)_nFeO$ (n = 1, 2, 3 . . .) structures and the $InFeO_3(ZnO)_n$ (n = 1–9) structures, we easily estimated the crystal structures of

TABLE IVb

THE STACKING SEQUENCES OF $InFeO_3(ZnO)_{10}$ AND $YbAlO_3(ZnO)_{11}$

$InFeO_3(ZnO)_{10}$			$InFeO_3(ZnO)_{10}$			$YbAlO_3(ZnO)_{11}$			$YbAlO_3(ZnO)_{11}$		
In	(Fe, Zn) or Zn	O	In	(Fe, Zn) or Zn	O	Yb	(Al, Zn) or Zn	O	Yb	(Al, Zn) or Zn	O
	e	g		g	e		e	g		f	g
	g	e		e	g		g	e		g	f
		g		g	e			g		f	g
e					g	e				g	f
		f	e					f		f	g
	f	e			f		f	e			f
	e	f		f	e		e	f	g		
	f	e		e	f		f	e			e
	e	f		f	e		e	f		e	g
	f	e		e	f		f	e		g	e
	e	f					e	f		e	g
	f	e					f	e		g	e
	e	f					e	f		e	g
	f	e					f	e		g	e
	e	f					e	f		e	g
	f	e					f	e		g	e
		f					e	f		e	g
e								e		g	e
		g				f				e	g
	g	e						g		g	e
	e	g					g	f			g
	g	e					f	g	e		
	e	g					g	f			f
	g	e					f	g		f	e
	e	g					g	f		e	f
	g	e					f	g		f	e
	e	g					g	f			

Note. e, f, and g have the same meanings as in Ref. (*11*).

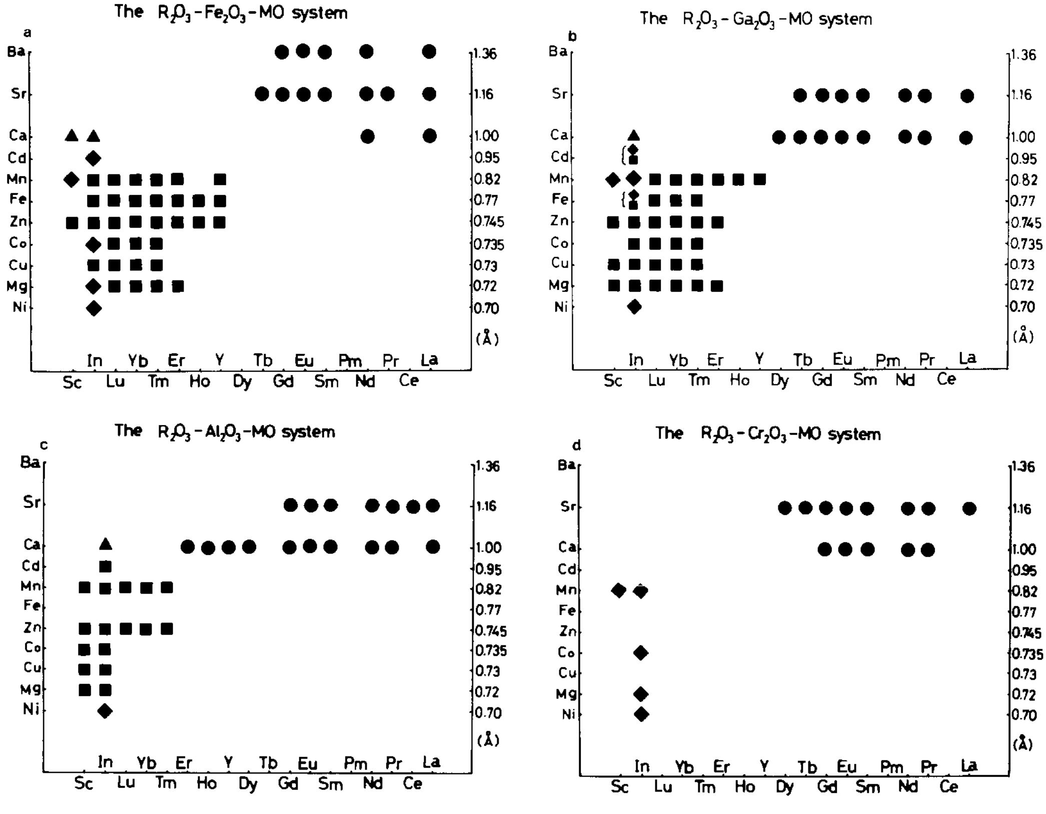

FIG. 1. (a–d) The classifications of the crystal structures for the compounds with $(RAO_3)_m(MO)_n$ type of stoichiometry in the R_2O_3–A_2O_3–MO system. The numbers along the right vertical axis indicate the six-coordinated ionic radii given by Shannon and Prewitt (O^{2-} = 1.40 Å) (*16*). ●, K_2NiF_4 type; ▲, $CaFe_2O_4$ type; ■, $YbFe_2O_4$ type; ◆, spinel type.

$InFeO_3(ZnO)_{10}$ and $YbAlO_3(ZnO)_{11}$ compounds. The summary of their crystal structures are shown in Table IVa. The stacking sequences of the $InO_{1.5}$, $(FeZn)O_{2.5}$ (or $(AlZn)O_{2.5}$), and ZnO layers for these compounds are given in Table IVb. The electron diffraction patterns and the high-resolution images were already observed in $LuFeO_3(ZnO)_2$ and $InGaO_3(ZnO)_5$ (*11*).

[VI] In the R_2O_3–A_2O_3–MO system (R = Sc, In, Lu, Yb, or Tm; A = Fe(III), Ga, or Al; M = Fe(II), Mg, Mn, Co, Cd, or Ni), we obtained $InGaFe^{2+}O_4$, $LuGaFe^{2+}O_4$, $YbGaFe^{2+}O_4$, and $TmGaFe^{2+}O_4$ compounds which are isostructural with $YbFe_2O_4$ compound (*3*). All of the compounds are black and do not attract a hand magnet at room temperature. In the previous paper (*7*), we reported on $InGaFe^{2+}O_4$ compound with spinel structure (a = 8.400(1) Å) which was obtained at 1000°C for 10 days. Under the present experimental condition, T = 1000°C for 1 day, we obtained $InGaFe^{2+}O_4$ with $YbFe_2O_4$ type of structure. We may consider that there exists a phase transformation between $YbFe_2O_4$ and spinel structures in this compound. All of the $ScGaMgO_4$, $ScAlMgO_4$, $InAlMgO_4$, $ScAlMnO_4$, $InFeMnO_4$, $InAlMnO_4$, $InAlCoO_4$,

TABLE Va

BIBLIOGRAPHIES FOR THE COMPOUNDS IN FIG. 1a

Compound	Reference	Compound	Reference	Compound	Reference
$(LaFeO_3)_2BaO$	Mat.Res.Bull.,6,341(1971)	$YFeO_3(MnO)$	J.Solid State Chem.,40,109(1981)	$LuFeO_3(MnO)$	ibid.,40,109(1981)
$LaFeO_3(SrO)$	J.Solid State Chem.,2,343(1970)	$YFeO_3(FeO)$	ibid.,13,176(1975)	$(LuFeO_3)_2FeO$	ibid.,17,49(1976)
$LaFeO_3(CaO)_2$	Mat.Res.Bull.,11,1219(1976)	$YFeO_3(ZnO)$	present work	$LuFeO_3(FeO)$	ibid.,17,49(1976)
$PrFeO_3(SrO)$	J.Solid State Chem.,2,343(1970)	$HoFeO_3(FeO)$	J.Solid State Chem.,23,43(1978)	$LuFeO_3(ZnO)_m$	present work
$(NdFeO_3)_2BaO$	J.Solid State Chem.,40,14(1981)	$HoFeO_3(ZnO)$	to be published	$LuFeO_3(CoO)$	J.Solid State Chem.,40,109(1981)
$NdFeO_3(BaO)$	Mat.Res.Bull.,6,341(1971)	$ErFeO_3(MnO)$	J.Solid State Chem.,40,109(1981)	$LuFeO_3(CuO)$	ibid.,40,109(1981)
$(NdFeO_3)_2SrO$	J.Solid State Chem.,40,14(1981)	$ErFeO_3(FeO)$	Bull.Chem.Soc.Japan,49,998(1976)	$LuFeO_3(MgO)$	ibid.,40,109(1981)
$NdFeO_3(SrO)$	ibid.,2,343(1970)	$ErFeO_3(ZnO)_9$	present work	$InFeO_3(CaO)$	to be published
$NdFeO_3(CaO)$	Mat.Res.Bull.,14,1601(1979)	$ErFeO_3(MgO)$	J.Solid State Chem.,40,109(1981)	$InFeO_3(CdO)$	to be published
$(SmFeO_3)_2BaO$	J.Solid State Chem.,40,14(1981)	$TmFeO_3(MnO)$	ibid.,40,109(1981)	$InFeO_3(MnO)$	present work
$SmFeO_3(BaO)$	ibid.,6,341(1971)	$(TmFeO_3)_2FeO$	ibid.,23,43(1978)	$InFeO_3(FeO)$	J.Solid state Chem.,60,382(1985)
$(SmFeO_3)_2SrO$	ibid.,40,14(1981)	$TmFeO_3(FeO)$	ibid.,23,43(1978)	$InFeO_3(ZnO)_m$	ibid.,in press(1988)
$SmFeO_3(SrO)$	ibid.,2,343(1970)	$TmFeO_3(ZnO)_m$	present work	$InFeO_3(CoO)$	ibid.,53,217(1984)
$(EuFeO_3)_2BaO$	ibid.,40,14(1981)	$TmFeO_3(CoO)$	J.Solid State Chem.,40,109(1981)	$(InFeO_3)_3CuO$	ibid.,53,217(1984)
$EuFeO_3(BaO)$	Mat.Res.Bull.,6,341(1971)	$TmFeO_3(CuO)$	ibid.,40,109(1981)	$(InFeO_3)_2CuO$	ibid.,53,217(1984)
$(EuFeO_3)_2SrO$	J.Less-Comm.Metals,37,281(1974)	$TmFeO_3(MgO)$	ibid.,40,109(1981)	$InFeO_3(CuO)$	ibid.,53,217(1984)
$EuFeO_3(SrO)$	ibid.,37,281(1974)	$YbFeO_3(MnO)$	ibid.,40,109(1981)	$InFeO_3(MgO)$	ibid.,60,382(1985)
$(GdFeO_3)_2BaO$	J.Solid State Chem.,40,14(1981)	$(YbFeO_3)_3FeO$	Acta Cryst.,B 35,561(1979)	$InFeO_3(NiO)$	present work
$(GdFeO_3)_2SrO$	ibid.,40,14(1981)	$(YbFeO_3)_2FeO$	J.Solid State Chem.,15,191(1975)	$ScFeO_3(CaO)$	to be published
$GdFeO_3(SrO)$	ibid.,2,343(1970)	$YbFeO_3(FeO)$	ibid.,15,191(1975)	$ScFeO_3(MnO)_2$	J.Solid State Chem.,submitted(1988)
$(TbFeO_3)_2SrO$	ibid.,7,337(1973)	$YbFeO_3(ZnO)_m$	present work	$ScFeO_3(ZnO)_m$	ibid.,in press(1988)
$TbFeO_3(SrO)$	ibid.,2,343(1970)	$YbFeO_3(CoO)$	J.Solid State Chem.,40,109(1981)		
		$YbFeO_3(CuO)$	ibid.,40,109(1981)		
		$YbFeO_3(MgO)$	ibid.,40,109(1981)		

TABLE Vb

BIBLIOGRAPHIES FOR THE COMPOUNDS IN FIG. 1b

Compound	Reference	Compound	Reference	Compound	Reference
LaGaO$_3$(SrO)	J.C.P.D.S.,No.24-1208	TmGaO$_3$(ZnO)$_m$	present work	InGaO$_3$(CoO)	ibid.,53,217(1984)
LaGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	TmGaO$_3$(CoO)	J.Solid State Chem.,41,166(1982)	(InGaO$_3$)$_m$CuO	ibid.,53,217(1984)
PrGaO$_3$(SrO)	Z.anorg.allg.Chem.,433,275(1977)	TmGaO$_3$(CuO)	ibid.,41,166(1982)	InGaO$_3$(MgO)	ibid.,60,382(1985)
PrGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	TmGaO$_3$(MgO)	ibid.,41,166(1982)	InGaO$_3$(NiO)	ibid.,60,382(1985)
NdGaO$_3$(SrO)	J.C.P.D.S.,No.24-1191	YbGaO$_3$(MnO)	ibid.,41,166(1982)	ScGaO$_3$(MnO)$_2$	ibid.,submitted(1988)
NdGaO$_3$(CaO)	J.C.P.D.S.,No.27-1050	YbGaO$_3$(FeO)	present work	ScGaO$_3$(ZnO)$_m$	ibid.,in press (1988)
SmGaO$_3$(SrO)	Z.anorg.allg.Chem.,433,275(1977)	YbGaO$_3$(ZnO)$_m$	present work	(ScGaO$_3$)$_2$CuO	ibid.,60,382(1985)
SmGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	YbGaO$_3$(CoO)	J.Solid State Chem.,41,166(1982)	ScGaO$_3$(CuO)	ibid.,60,382(1985)
EuGaO$_3$(SrO)	Z.anorg.allg.Chem.,433,275(1977)	YbGaO$_3$(CuO)	ibid.,41,166(1982)	ScGaO$_3$(MgO)	present work
EuGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	YbGaO$_3$(MgO)	ibid.,41,166(1982)		
GdGaO$_3$(SrO)$_2$	Z.anorg.allg.Chem.,433,275(1977)	LuGaO$_3$(MnO)	ibid.,41,166(1982)		
GdGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	LuGaO$_3$(FeO)	present work		
TbGaO$_3$(SrO)	Z.anorg.allg.Chem.,433,275(1977)	LuGaO$_3$(ZnO)$_m$	present work		
TbGaO$_3$(CaO)	Rev.Chim.Mineral,11,327(1974)	LuGaO$_3$(CoO)	J.Solid State Chem.,41,166(1982)		
DyGaO$_3$(CaO)	ibid.,11,327(1974)	LuGaO$_3$(CuO)	ibid.,41,166(1982)		
YGaO$_3$(MnO)	J.Solid State Chem.,41,166(1982)	LuGaO$_3$(MgO)	ibid.,41,166(1982)		
HoGaO$_3$(MnO)	ibid.,41,166(1982)	InGaO$_3$(CaO)	to be published		
ErGaO$_3$(MnO)	ibid.,41,166(1982)	InGaO$_3$(CdO)	Z.anorg.allg.Chem.,341,252(1965)		
ErGaO$_3$(ZnO)$_m$	present work	InGaO$_3$(CdO)	J.Solid State Chem.,(to be submitted)		
ErGaO$_3$(MgO)	J.Solid State Chem.,41,166(1982)	(InGaO$_3$)$_2$MnO	ibid.,60,382(1985)		
TmGaO$_3$(MnO)	ibid.,41,166(1982)	InGaO$_3$(MnO)	ibid.,60,382(1985)		
TmGaO$_3$(FeO)	present work	InGaO$_3$(FeO)	ibid.,60,382(1985)		
		InGaO$_3$(FeO)	present work		
		InGaO$_3$(ZnO)$_m$	ibid.,in press(1988)		

TABLE Vc

BIBLIOGRAPHIES FOR THE COMPOUNDS IN FIG. 1c

Compound	Reference	Compound	Reference
$LaAlO_3(SrO)$	C.R.Acad.Sci.Paris,Ser.C 274,1837(1972)	$YbAlO_3(ZnO)_m$	present work
$LaAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$LuAlO_3(MnO)$	J.Solid State Chem.,41,166(1982)
$CeAlO_3(SrO)$	Z.Naturforsch.,B 27,888(1972)	$LuAlO_3(ZnO)_m$	present work
$PrAlO_3(SrO)$	C.R.Acad.Sci.Paris,Ser.C 274,1837(1972)	$InAlO_3(CaO)$	to be published
$PrAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$InAlO_3(CdO)$	Z.anorg.allg.Chem.,341,252(1965)
$NdAlO_3(SrO)$	J.C.P.D.S.,No.24-1188	$InAlO_3(MnO)$	present work
$NdAlO_3(SrO)_2$	J.C.P.D.S.,No.31-1335	$InAlO_3(ZnO)_m$	J.Solid State Chem.,in press(1988)
$(NdAlO_3)_2SrO$	J.C.P.D.S.,No.31-1334	$InAlO_3(CoO)$	present work
$NdAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$(InAlO_3)_2CuO$	J.Solid State Chem.,60,382(1985)
$SmAlO_3(SrO)$	J.C.P.D.S.,No.24-1190	$InAlO_3(CuO)$	ibid.,60,382(1985)
$SmAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$InAlO_3(MgO)$	present work
$EuAlO_3(SrO)$	C.R.Acad.Sci.Paris,Ser.C 274,1837(1972)	$InAlO_3(NiO)$	Z.anorg.allg.Chem.,341,252(1965)
$EuAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$ScAlO_3(MnO)$	present work
$GdAlO_3(SrO)$	J.C.P.D.S.,No.24-1185	$ScAlO_3(ZnO)_m$	J.Solid State Chem.,in press(1988)
$GdAlO_3(CaO)$	Bull.Soc.Chim.France,10,3408(1970)	$ScAlO_3(CoO)$	present work
$DyAlO_3(CaO)$	ibid.,10,3408(1970)	$(ScAlO_3)_2CuO$	J.Solid State Chem.,60,382(1985)
$YAlO_3(CaO)$	ibid.,10,3408(1970)	$ScAlO_3(CuO)$	ibid.,60,382(1985)
$HoAlO_3(CaO)$	ibid.,10,3408(1970)	$ScAlO_3(MgO)$	present work
$ErAlO_3(CaO)$	ibid.,10,3408(1970)		
$TmAlO_3(MnO)$	J.Solid State Chem.,41,166(1982)		
$TmAlO_3(ZnO)_m$	present work		
$YbAlO_3(MnO)$	J.Solid State Chem.,41,166(1982)		

$ScAlCoO_4$, $InAlCdO_4$, and $YFeZnO_4$ are isostructural with $YbFe_2O_4$ compound. All of the $InFeNiO_4$, $InCrNiO_4$, In_2MnO_4, and In_2MgO_4 have a spinel structure. $ScGaMgO_4$, $ScAlMgO_4$, $InAlMgO_4$, and In_2MgO_4 are colorless, $YFeZnO_4$ is brown, and the other compounds are black. The conditions of synthesis and the lattice constants for each compound are shown in Table III(f).

$InCrMO_4$ and $InANiO_4$ compounds having $YbFe_2O_4$ structure have not yet been reported. Since both Cr(III) and Ni(II) have a tendency to take six coordination number of oxygen ions in oxide compounds, $InCrMO_4$ and $InANiO_4$ having $YbFe_2O_4$ structure may be considered to be unstable.

The *d*-spacings and relative intensities of the powder X-ray diffraction for each compound reported in Tables IIIa–IIIf will be sent to the Joint Committee of Powder Diffraction Standards.

In Figs. 1a–1d, we show the dependence of the crystal structure of $(RAO_3)_m(MO)_n$ type of compounds (R = Sc, In, Y, or lanthanide elements; A = Fe, Ga, Al, or Cr; M = divalent cation elements; m and n = integer). These data are taken from the present paper and bibliographies shown in Tables Va–Vd. We can easily recognize that K_2NiF_4 type of compounds are in the region of both the larger R and the larger M cations, and $YbFe_2O_4$ type of compounds are in the region of both the smaller R and the

TABLE Vd

BIBLIOGRAPHIES FOR THE COMPOUNDS IN FIG. 1d

Compound	Reference
$LaCrO_3(SrO)$	J.Solid State Chem.,22,121(1977)
$PrCrO_3(SrO)$	ibid.,2,343(1970)
$PrCrO_3(CaO)$	ibid.,5,57(1972)
$NdCrO_3(SrO)$	ibid.,22,121(1977)
$NdCrO_3(CaO)$	ibid.,5,57(1972)
$SmCrO_3(SrO)$	ibid.,22,121(1977)
$SmCrO_3(CaO)$	ibid.,5,57(1972)
$EuCrO_3(SrO)$	ibid.,22,121(1977)
$EuCrO_3(CaO)$	ibid.,5,57(1972)
$GdCrO_3(SrO)$	ibid.,22,121(1977)
$GdCrO_3(CaO)$	ibid.,5,57(1972)
$TbCrO_3(SrO)$	ibid.,22,121(1977)
$DyCrO_3(SrO)$	ibid.,22,121(1977)
$InCrO_3(MnO)_2$	J.Solid State Chem.,submitted(1988)
$InCrO_3(CoO)$	Z.anorg.allg.Chem.,341,252(1965)
$InCrO_3(MgO)$	J.Solid State Chem.,submitted(1988)
$InCrO_3(NiO)$	Z.anorg.allg.Chem.,341,252(1965)
$ScCrO_3(MnO)$	J.Solid State Chem.,submitted(1988)

smaller *M* cations. In the region of the smaller *R* and the larger *M* cations we can see the $CaFe_2O_4$ type of compounds. However, we cannot see any compounds in the field of the larger *R* cations and the smaller *M* cations. In the field of both the smallest *R* and the smallest *M* cations, we have the spinel type of compounds; however, InGa$Fe^{2+}O_4$, $InFeCdO_4$, and $InGaCdO_4$ may have both the spinel and $YbFe_2O_4$ type of structures. In addition to A = Fe, Ga, Cr, or Al, both Mn(III) and Cu(III) are candidate cations for constructing the K_2NiF_4 type of compounds (*12–14*). We will study whether or not there exist $RCu^{3+}MO_4$ and $RMn^{3+}MO_4$ compounds with $YbFe_2O_4$ type of structures in the near future. It is well known that the cite preference effect should be considered in addition to the size effect of the constituent cations in the oxide compounds when we show the relation between the crystal structure and the constituent cation. However, we can roughly classify the whole field of R_2O_3–A_2O_3–MO systems into at least four subterritories of K_2NiF_4, $CaFe_2O_4$, $YbFe_2O_4$, and spinel types, based upon the sizes of the constituent cations.

Acknowledgments

The authors express their sincere thanks to Dr. K. Siratori (Department of Physics, Faculty of Science, Osaka University, Japan) and Dr. E. Takayama-Muromachi (NIRIM) for their helpful discussions.

References

1. A. F. WELLS, "Structural Inorganic Chemistry," p. 490, Oxford Univ. Press (Clarendon), London/New York (1975).
2. N. KIMIZUKA, A. YAMAMOTO, H. OHASHI, T. SUGIHARA, AND T. SEKINE, *J. Solid State Chem.* **49,** 65 (1983).
3. K. KATO, I. KAWADA, N. KIMIZUKA, AND T. KATSURA, *Z. Kristallogr.* **141,** 314 (1975).
4. O. SCHMITZ-DUMONT AND H. KASPER, *Z. Anorg. Allgem. Chem.* **341,** 252 (1965).
5. N. KIMIZUKA AND E. TAKAYAMA, *J. Solid State Chem.* **40,** 109 (1981).
6. N. KIMIZUKA AND E. TAKAYAMA, *J. Solid State Chem.* **41,** 166 (1982).
7. N. KIMIZUKA AND T. MOHRI, *J. Solid State Chem.* **60,** 382 (1985).
8. N. KIMIZUKA, K. KATO, I. SHINDO, I. KAWADA, AND T. KATSURA, *Acta Crystallogr. Sect. B.* **32,** 1620 (1976).
9. Y. MATSUI, K. KATO, N. KIMIZUKA, AND S. HORIUCHI, *Acta Crystallogr. Sect. B* **35,** 561 (1979).
10. K. KATO, I. KAWADA, N. KIMIZUKA, I. SHINDO, AND T. KATSURA, *Z. Kristallogr.* **143,** 278 (1976).
11. N. KIMIZUKA, T. MOHRI, Y. MATSUI, AND K. SIRATORI, *J. Solid State Chem.* **74,** 98 (1988).
12. M. N. DESCHIZEAUX CHERUY, AND J. C. JOUBERT, *J. Solid State Chem.* **40,** 14 (1981).
13. A. BENABAD, A. DAUDI, R. SALMON, AND G. LEFLEM, *J. Solid State Chem.* **22,** 121 (1977).
14. J. B. GOODENOUGH, D. DEMAZEAUX, M. POUCHARD, AND P. HAGENMULLER, *J. Solid State Chem.* **8,** 325 (1973).
15. R. W. G. WYCKOFF, "Crystal Structures," 2nd. ed., Vol. III, p. 80, Interscience, New York (1960).
16. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. Sect. B* **25,** 925 (1969).