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Homologous Compounds, $InFeO_3(ZnO)_m$ (m = 1–9)

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New homologous compounds, $InFeO_3(ZnO)_m$ (m = 1–9), were synthesized through solid-state reactions between In_2O_3, Fe_2O_3, and ZnO in Pt tubes at 1300–1550°C. The crystal structures of each compound were estimated through both X-ray powder diffraction analysis and electron diffraction analysis, based upon the construction rules which control the crystal structures of $(YbFeO_3)_nFeO$ (n = 1, 2, 3, 4 . . .). Each of the crystal structures of $InFeO_3(ZnO)_m$ is considered to be composed of the $InO_{1.5}$, $(FeZn)O_{2.5}$, and ZnO layers which are stacked perpendicularly to the c-axis in the hexagonal system (e.g., $R\bar{3}m$ for m = even, $P6_3/mmc$ for m = odd), and all of the cations and anions are located on the three kinds of trigonal net planes. Isostructural compounds were prepared in the systems In_2O_3–Ga_2O_3–ZnO, Sc_2O_3–Fe_2O_3–ZnO, Sc_2O_3–Ga_2O_3–ZnO, In_2O_3–Al_2O_3–ZnO, and Sc_2O_3–Al_2O_3–ZnO and the conditions of their syntheses and the lattice constants in the hexagonal crystal system are given.

Introduction

In the Yb_2O_3–Fe_2O_3–FeO system, there exist a number of $(YbFeO_3)_nFeO$ (n = 1, 2, 3, 4 . . .) phases having layered structures. The crystal structural analyses for $YbFe_2O_4$ and $Yb_2Fe_3O_7$ were performed by single crystal X-ray diffraction methods (*1–3*) and those for $Yb_3Fe_4O_{10}$ and $Yb_4Fe_5O_{13}$ were made using both X-ray powder diffraction and electron diffraction methods (*4, 5*). The crystal structural models for $YbFe_2O_4$ and $Yb_2Fe_3O_7$ are shown in Figs. 1a and 1b and the characteristic features of these homologous compounds are summarized in Table I. The crystal structures of these compounds are considered to be composed of the packing of three kinds of triangular net planes (e, f, and g in Fig. 1). In the $YbFe_2O_4$ compound, there are $YbO_{1.5}$ and $Fe_2O_{2.5}$ layers, and in $Yb_2Fe_3O_7$ and its higher order compounds, there are $FeO_{1.5}$ layers in addition to the layers which exist in the $YbFe_2O_4$ compound. (There is only one crystallographic site for the iron ions in the $YbFe_2O_4$ compound, so we could tentatively assume that there was a $Fe^{2.5+}$ ion state in the structure. Thereafter, Mössbauer study on this compound at room temperature by Tanaka *et al.* (*6*) confirmed the above assumption.)

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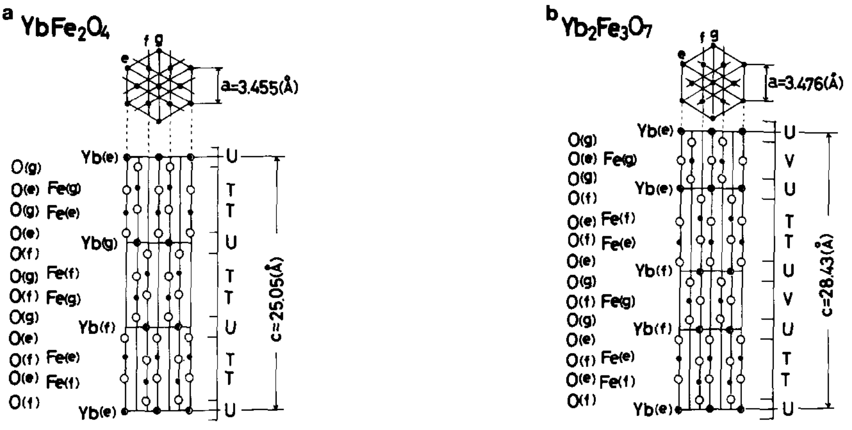

FIG. 1. e, f, and g indicate three sets of triangular lattices as shown in the upper parts of the figures.

Another prominent characteristic in these structures is that there are layers which contain both cation and anion nets at almost the same level (denoted as *T* and *V* in Fig. 1). To construct the crystal structure by stackings of the *T* layers and the *U* block layers, coulomb energy will be minimized when a cation net plane is aligned on an anion triangle. Based upon this construction rule, whole stackings of the crystal structures are built and the characteristic coordination polyhedra of trigonal bipyramids are formed.

$LnABO_4$ (*Ln* = Sc, In, Lu, Yb, Tm, Ho, Er, or Y; *B* = Fe, Ga, or Al; *A* = Mn, Co, Fe, Zn, Cu, Mg, or Cd) which is isostructural with $YbFe_2O_4$ was prepared, and the conditions of synthesis and the lattice constants were reported (*7–9*).

In the present paper, we will report the conditions of the syntheses and some crystal data of $InFeO_3(ZnO)_m$ (m = 1–9), and their isostructural compounds, $LnAO_3(ZnO)_m$ (*Ln* = In or Sc; *A* = Fe, Ga, or Al).

Experimental

(*1*) *Sample Preparation*

Each compound was synthesized through a solid-state reaction between Ln_2O_3 (*Ln* = Sc or In), A_2O_3 (*A* = Fe, Ga, or Al), and ZnO in a sealed Pt tube which was heated at elevated temperatures, followed by rapid cooling in air or water. Differences due to the cooling method were not detected in the crystal structures of the samples. A vertical furnace with a SiC heating element was used. The temperature fluctua-

TABLE I

THE SUMMARY OF THE CRYSTAL DATA OF $(YbFeO_3)_nFeO$

n	Compound	*a* (Å)	*c* (Å)	*Z*	Space group	*u*	*v*	*w*	*p*
1	$YbFe_2O_4$	3.455(1)	25.05(1)	3	$R\bar{3}m$	3	0	3	12
2	$Yb_2Fe_3O_7$	3.476(1)	28.43(1)	2	$P6_3/mmc$	4	2	2	14
3	$Yb_3Fe_4O_{10}$	3.490(1)	60.79(2)	3	$R\bar{3}m$	9	6	3	30
4	$Yb_4Fe_5O_{13}$	3.503(2)	53.03(2)	2	$P6_3/mmc$	8	6	2	26

Note. *u*, number of $YbO_{1.5}$ layers; *v*, number of $FeO_{1.5}$ layers; *w*, number of $Fe_2O_{2.5}$ layers; *p*, number of oxygen layers.

TABLE II

THE CONDITIONS OF THE SYNTHESES AND THE CRYSTAL DATA OF $InFeO_3(ZnO)_m$

Compounds	Mixing ratio (in mole) of starting compounds In_2O_3	Fe_2O_3	ZnO	Temperature (°C)	Heating period (day)	Lattice constant (Å) a	c	Space group	z	u	w	x	p	c (Å)/p
$InFeZnO_4$	1	1	2	1300	6	3.321(1)	26.09(1)	$R\bar{3}m$	3	1 × 3	1 × 3	0	12	2.174
$InFeZn_2O_5$	1	1	4	1300	13	3.309(1)	22.57(1)	$P6_3/mmc$	2	1 × 2	1 × 2	1 × 2	10	2.257
$InFeZn_3O_6$	1	1	6	1450	2	3.300(1)	41.68(1)	$R\bar{3}m$	3	1 × 3	1 × 3	2 × 3	18	2.316
$InFeZn_4O_7$	1	1	8	1450	2	3.294(1)	32.99(1)	$P6_3/mmc$	2	1 × 2	1 × 2	3 × 2	14	2.356
$InFeZn_5O_8$	1	1	10	1450	2	3.288(1)	57.28(1)	$R\bar{3}m$	3	1 × 3	1 × 3	4 × 3	24	2.387
$InFeZn_6O_9$	1	1	12	1450	1	3.283(1)	43.36(1)	$P6_3/mmc$	2	1 × 2	1 × 2	5 × 2	18	2.409
$InFeZn_7O_{10}$	1	1	14	1450	2	3.279(1)	72.85(1)	$R\bar{3}m$	3	1 × 3	1 × 3	6 × 3	30	2.428
$InFeZn_8O_{11}$	1	1	16	1450	7	3.276(1)	53.75(1)	$P6_3/mmc$	2	1 × 2	1 × 2	7 × 2	22	2.443
$InFeZn_9O_{12}$	1	1	18	1450	3	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.

tion was limited within ±1°C by means of a PID electronic controller. Prior to mixing the starting compounds, we heated Sc_2O_3 (99.9%), Fe_2O_3 (99.99%), and Al_2O_3 (guaranteed reagent grade) at 1000°C for 1 day. ZnO (guaranteed reagent grade), Ga_2O_3 (99.99%), and In_2O_3 (99.99%) were heated at 900°C for 1 day.

Calculated weights of Ln_2O_3, A_2O_3, and ZnO were thoroughly mixed under ethyl alcohol in an agate mortar and each mixture was sealed in a Pt tube. The change in the total weight of the sample and the tube during heat treatment at elevated temperatures was carefully measured.

(2) *X-Ray Diffraction and Electron Diffraction Methods*

X-ray powder diffraction patterns taken with a diffractometer fitted with a graphite monochromator and employing Cu*Kα* radiation were used to identify the phases and to measure the *d*-spacings of each compound. The hexagonal lattice constants of each compound were obtained by least-squares refinement of the measured *d*-spacings.

The samples of $YbFe_2O_4$ (*10*), $LuFeZn_2O_5$ (*11*), and $InGaZn_5O_8$ were examined by high-resolution electron microscopy. They were ground gently in an agate mortar and dispersed on holy carbon microgrids. High-resolution electron microscope observations were made using a JEM-4000 FX-type 400-kV microscope. All electron micrographs shown in the present paper were taken from the thin edges of crystal fragments at the objective lens defocus near Scherzer condition (around 67 Å).

Results and Discussion

In the In_2O_3–Fe_2O_3–ZnO system, we obtained $InFeO_3(ZnO)_m$ (m = 1–9) (*9*). The conditions of the syntheses and the lattice constants in the hexagonal system for these compounds are shown in Table II. $InFeO_3(ZnO)_m$ (m = 1, 3, 5, 7, and 9) has the space group $R\bar{3}m$ (extinction law: $-h + k + l \neq 3n$) and $InFeO_3(ZnO)_m$ (m = 2, 4, 6, and 8) has $P6_3/mmc$ (extinction law: $1 \neq 2n$ for hhl). Based upon the construction rules mentioned above and the c-values which we measured in the present work, we could easily determine the stacking sequences of $InFeO_3(ZnO)_m$ compounds. They are shown in Table III. We present the number of $InO_{1.5}$ layers (= u), $(FeZn)O_{2.5}$ layers (= w), ZnO layers (= x), and oxygen layers (= p) in Table II.

TABLE III

The Stacking Sequences of $\mathrm{InFeO_3(ZnO)}_m$

In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O
	$\mathrm{InFeZn_2O_5}$			$\mathrm{InFeZn_4O_7}$			$\mathrm{InFeZn_6O_9}$			$\mathrm{InFeZn_8O_{11}}$	
	e	g									
	g	e									
		g			g			g			g
e			e			e			e		
		f			f			f			f
	f	e		f	e		f	e		f	e
	e	f		e	f		e	f		e	f
	f	e		f	e		f	e		f	e
		f		e	f		e	f		e	f
e				f	e		f	e		f	e
		g			f		e	f		e	f
	g	e	e				f	e		f	e
	e	g			g			f		e	f
	g	e		g	e	e				f	e
		g		e	g			g			f
e				g	e		g	e	e		
		f		e	g		e	g			g
	f	e		g	e		g	e		g	e
	e	f			g		e	g		e	g
	f	e	e				g	e		g	e
		f			f		e	g		e	g
				f	e		g	e		g	e
				e	f			g		e	g
				f	e	e				g	e
								f		e	g
							f	e		g	e
							e	f			g
							f	e	e		
								f			f
										f	e
										e	f
										f	e
											f
	$\mathrm{InFeZn_3O_6}$			$\mathrm{InFeZn_5O_8}$			$\mathrm{InFeZn_7O_{10}}$			$\mathrm{InFeZn_9O_{12}}$	
										g	e
											g
							g	e	e		
								g			f
		e			e	e				f	e
		g			g			f		e	f
e			e				f	e		f	e
		f			f		e	f		e	f
	f	e		f	e		f	e		f	e
	e	f		e	f		e	f		e	f
	f	e		f	e		f	e		f	e
	e	f		e	f		e	f		e	f
		e		f	e		f	e		f	e
f				e	f		e	f		e	f

TABLE III—*Continued*

In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O	In	(Fe, Zn), Zn	O
		g			e			e			e
	g	f	f			f			f		
	f	g			g			g			g
	g	f		g	f		g	f		g	f
	f	g		f	g		f	g		f	g
		f		g	f		g	f		g	f
g				f	g		f	g		f	g
		e		g	f		g	f		g	f
	e	g		f	g		f	g		f	g
	g	e			f		g	f		g	f
	e	g	g				f	g		f	g
	g	e			e			f		g	f
		g		e	g	g				f	g
e				g	e			e			f
		f		e	g		e	g	g		
	f	e		g	e		g	e			e
	e	f		e	g		e	g		e	g
				g	e		g	e		g	e
					g		e	g		e	g
			e				g	e		g	e
					f		e	g		e	g
				f	e		g	e		g	e
				e	f		e	g		e	g
					e		g	e		g	e
								g		e	g
						e				g	e
								f			g
							f	e	e		
											f
										f	e
										e	f

Each c length of the $InFeO_3(ZnO)_m$ compounds could be estimated from the following hypotheses: the thickness of the ZnO layer equals 2.597 Å, and the summation of the thickness of the $InO_{1.5}$ layer and that of the $(FeZn)O_{2.5}$ layer equals 8.698 Å. In Table IV, we show the c lengths which were calculated from these hypotheses. We can see good consistency. Under normal pressure, ZnO has a wurtzite structure (a = 3.249 Å and c = 5.205 Å). The estimation for the thickness of the ZnO layer as 2.598 Å is consistent with the value of 5.205 Å × $\frac{1}{2}$ of crystalline ZnO.

TABLE IV

THE OBSERVED AND ESTIMATED C LENGTHS OF $InFeO_3(ZnO)_m$

Compound	C_{obs} (Å)	C_{calc} (Å)	C_{obs} (Å)–C_{calc} (Å)
$InFeZnO_4$	26.09	26.09	0.00
$InFeZn_2O_5$	22.57	22.59	−0.02
$InFeZn_3O_6$	41.68	41.68	0.00
$InFeZn_4O_7$	32.99	32.98	+0.01
$InFeZn_5O_8$	57.28	57.27	+0.01
$InFeZn_6O_9$	43.36	43.37	−0.01
$InFeZn_7O_{10}$	72.85	72.86	−0.01
$InFeZn_8O_{11}$	53.75	53.77	−0.02
$InFeZn_9O_{12}$	88.41	88.42	−0.01

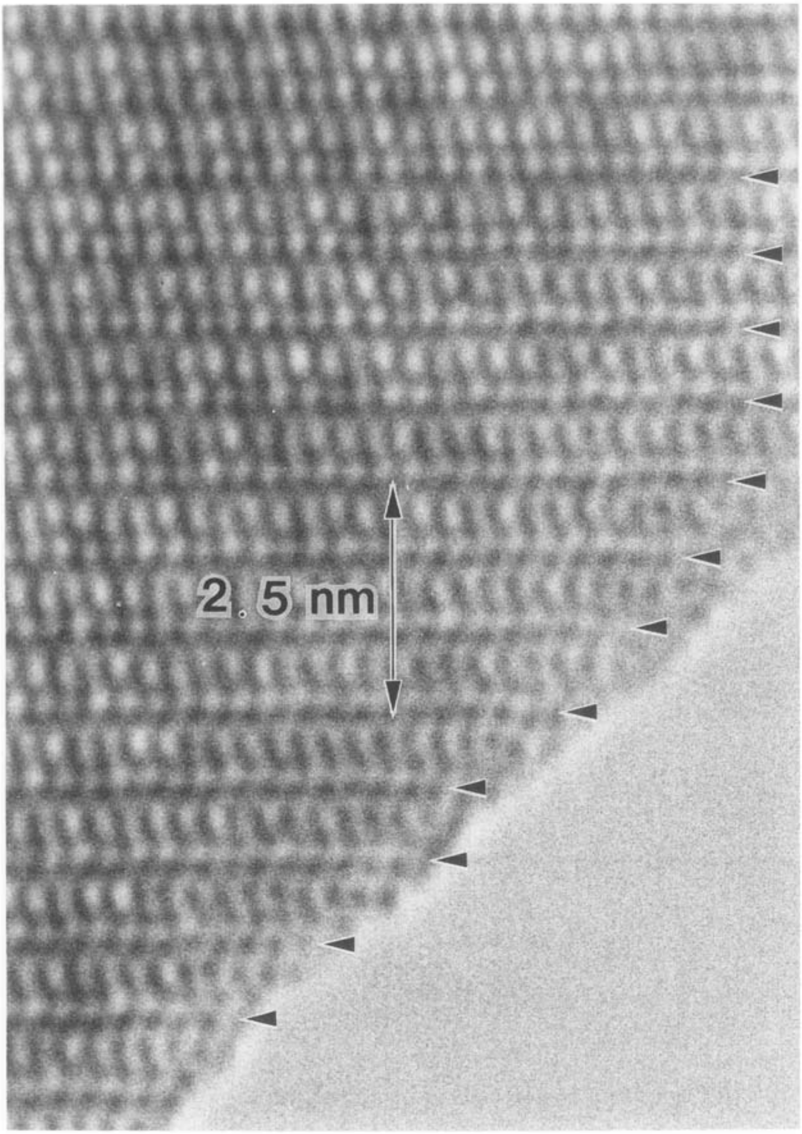

FIG. 2. The lattice image of $YbFe_2O_4$ projected along the [110] direction.

In order to verify the above conclusion, we made observations using electron diffraction. Figure 2 shows the image of $YbFe_2O_4$ (*10*) projected along the [110] direction. As we already showed for $Yb_3Fe_4O_{10}$ (*4, 5*) the layers of Yb ion are imaged as black dots and the double layers of Fe ion as dark dots. In this way, it was confirmed that the octahedral layers of the heavier atoms give darker dots in high-resolution electron micrographs. Figures 3a and 3b are the electron diffraction patterns of $LuFeZn_2O_5$ (*11*) taken with incident electron beam along the [110] and the [100] directions of the hexagonal lattice. These spots along 001 with l = odd in Fig. 3a are the result of double dif-

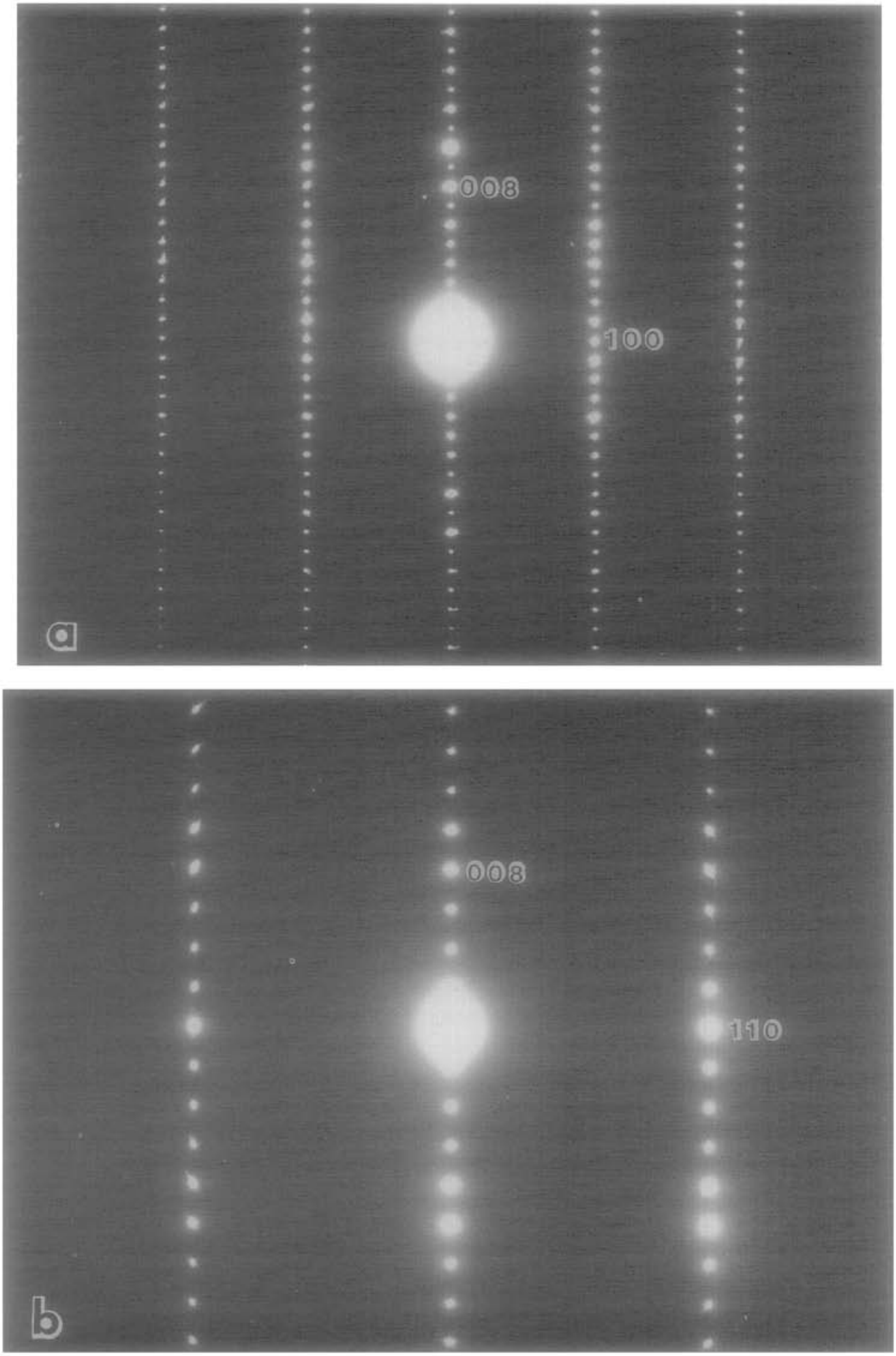

Fig. 3. The electron diffraction patterns of LuFeZn$_2$O$_5$ taken with incident beam along the [110] and the [100] directions of the hexagonal lattice.

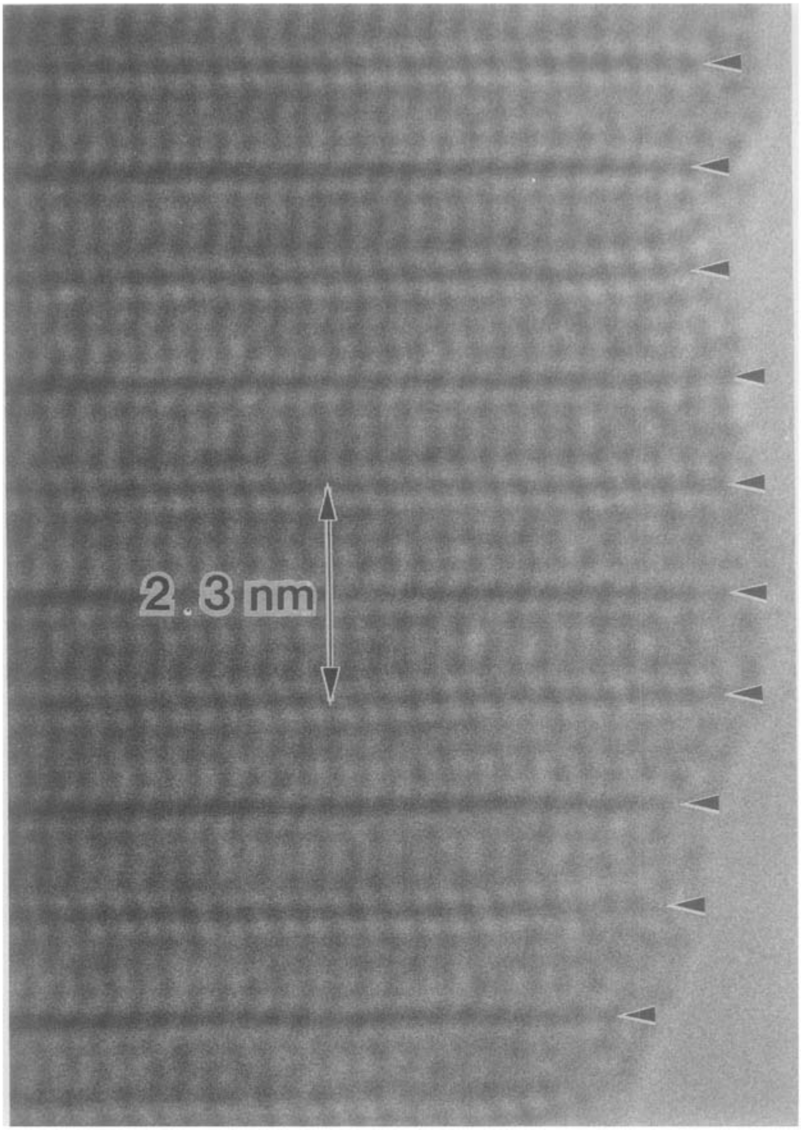

FIG. 4. The high-resolution image of $LuFeZn_2O_5$ projected along the [110] direction.

fraction. Figure 4 is the high-resolution image of $LuFeZn_2O_5$ projected along [110] direction. The line of darker dots indicated by the arrows are considered to be the layers of Lu ions. Three layers of gray spots are inserted between the two darker layers. These are considered to be Fe ion and Zn ion layers. The crystal structure derived from this image is consistent with that in Table II. Figures 5a and 5b are the electron diffraction patterns from $InGaZn_5O_8$ projected along [110] and [100] directions, respectively. A high-resolution electron micrograph corresponding to Fig. 5a is shown in Fig. 6. Again the hexagonal layers of the heavier In atoms are imaged as lines of dark

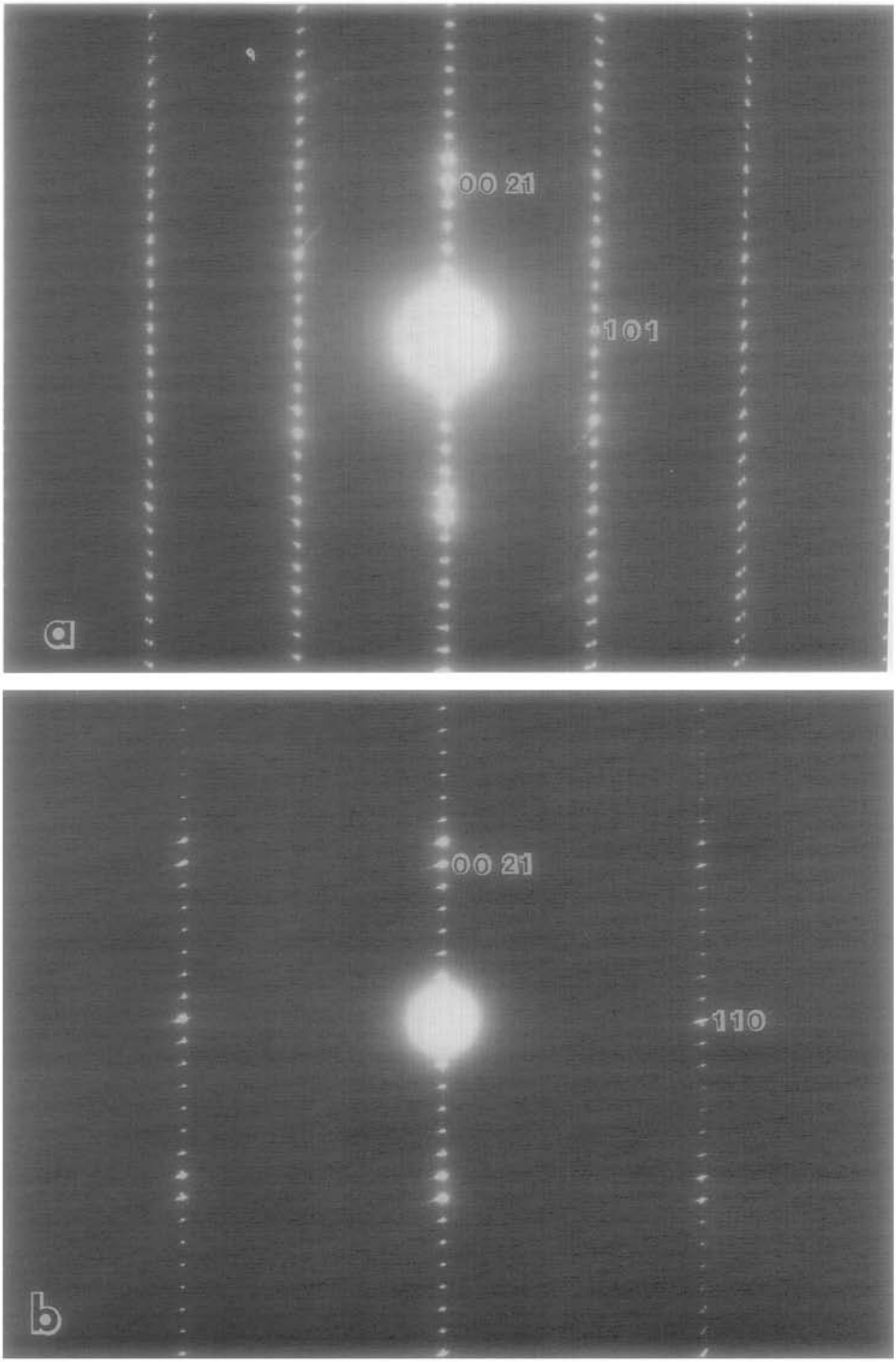

FIG. 5. The electron diffraction patterns from $InGaZn_5O_8$ projected along the [110] and the [100] directions.

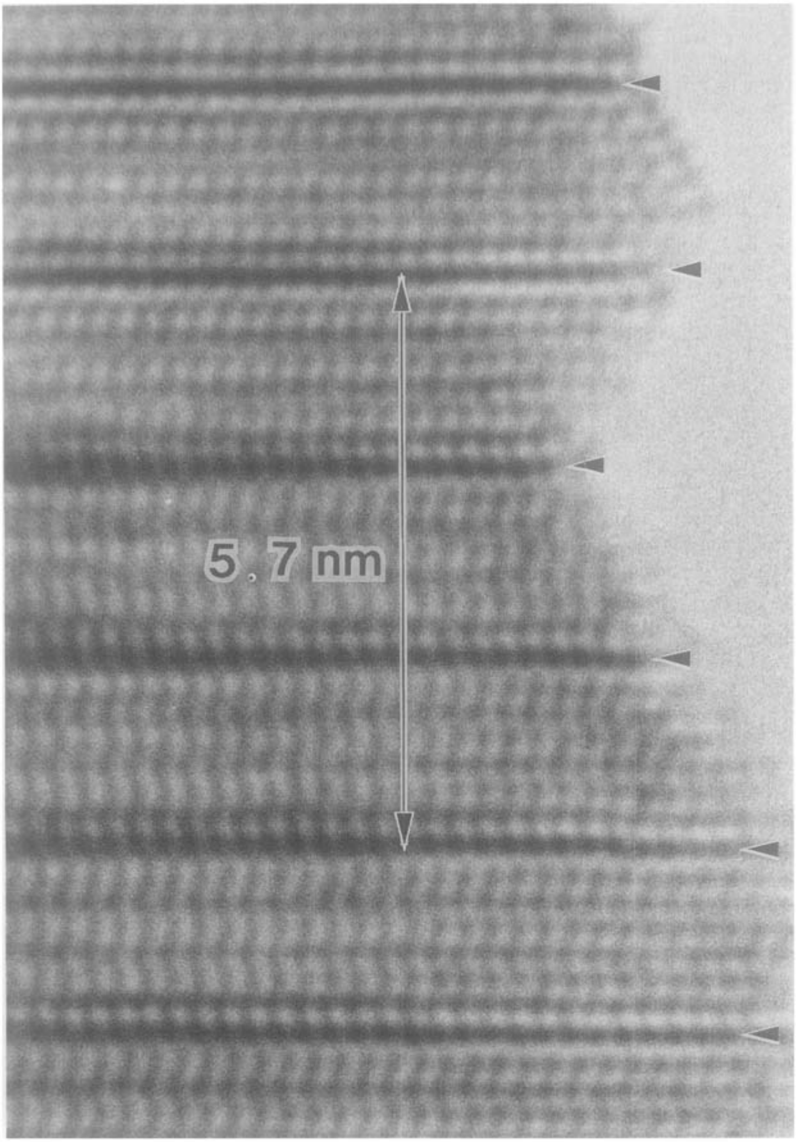

FIG. 6. The high-resolution electron micrograph corresponding to Fig. 5a.

dots and six layers of Ga and Zn are imaged as lighter dark dots.

Along with the above homologous compounds, we tried to prepare the isostructural compounds with $InFeO_3(ZnO)_m$ compounds in the systems In_2O_3–Ga_2O_3–ZnO, Sc_2O_3–Fe_2O_3–ZnO, Sc_2O_3–Ga_2O_3–ZnO, In_2O_3–Al_2O_3–ZnO, Sc_2O_3–Al_2O_3–ZnO. The obtained compounds, their conditions of syntheses, and the lattice constants are summarized in Tables VA, VB, and VC.

Now there are a series of $InFeO_3(ZnO)_m$ compounds in the ZnO–$InFeO_3$ system and $(YbFeO_3)_n$FeO in the $YbFe_2O_4$–$YbFeO_3$ system. From the stand point of the crystal structures of these two homologous com-

TABLE VA

THE CONDITIONS OF SYNTHESES AND THE LATTICE CONSTANTS OF $ScFeO_3(ZnO)_m$

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$ScFeZn_2O_5$	1450	4	3.278(1)	22.51(1)
$ScFeZn_3O_6$	1450	5	3.274(1)	41.59(1)
$ScFeZn_4O_7$	1450	6	3.271(1)	32.92(1)
$ScFeZn_5O_8$	1450	6	3.267(1)	57.21(1)
$ScFeZn_6O_9$	1450	3	3.264(1)	43.62(1)
$ScFeZn_7O_{10}$	1450	2	3.263(1)	72.81(1)
$ScFeZn_9O_{12}$	1450	3	3.263(1)	88.51(2)

pounds, we can conclude that ZnO (wurtzite structure) is one of the end members and $YbMnO_3$ structure is the other (*12*). In the $YbMnO_3$ structure (probable space group *P*6_3/*cm*), Mn^{3+} has five oxygen ion neighbors in trigonal bipyramidal coordination. It is well known that $YbFeO_3$ has the $GdFeO_3$ structure (*13*) at room temperature; however, we may guess from the present results that $YbFeO_3$ has a rhombohedral form at elevated temperature as in $LaFeO_3$ (*14*).

TABLE VB

THE CONDITIONS OF SYNTHESES AND THE LATTICE CONSTANTS OF $InGaO_3(ZnO)_m$ AND $ScGaO_3(ZnO)_m$

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$InGaZnO_4$	1450	1	3.295(1)	26.07(1)
$InGaZn_2O_5$	1300	5	3.292(1)	22.52(1)
$InGaZn_3O_6$	1450	4	3.288(1)	41.56(1)
$InGaZn_4O_7$	1450	6	3.284(1)	32.89(1)
$InGaZn_5O_8$	1450	8	3.280(1)	57.14(1)
$InGaZn_6O_9$	1450	10	3.275(1)	43.26(1)
$InGaZn_7O_{10}$	1450	2	3.274(1)	72.74(1)
$ScGaZnO_4$	1300	8	3.259(1)	25.91(1)
$ScGaZn_2O_5$	1300	8	3.262(1)	22.50(1)
$ScGaZn_3O_6$	1450	4	3.263(1)	41.54(1)
$ScGaZn_4O_7$	1450	6	3.262(1)	32.89(1)
$ScGaZn_5O_8$	1450	10	3.261(1)	57.10(1)
$ScGaZn_6O_9$	1450	6	3.258(1)	43.24(1)
$ScGaZn_7O_{10}$	1450	2	3.258(1)	72.74(1)

TABLE VC

THE CONDITIONS OF SYNTHESES AND THE LATTICE CONSTANTS OF $InAlO_3(ZnO)_m$ AND $ScAlO_3(ZnO)_m$

Compound	Temperature (°C)	Heating period (day)	Lattice constant (Å) *a*	*c*
$InAlZnO_4$	1550	1	3.309(1)	26.33(1)
$InAlZn_2O_5$	1422	4	3.295(1)	22.56(1)
$InAlZn_3O_6$	1450	6	3.281(1)	41.35(1)
$InAlZn_4O_7$	1450	8	3.277(1)	32.72(1)
$InAlZn_5O_8$	1450	3	3.272(1)	56.80(1)
$InAlZn_7O_{10}$	1450	4	3.263(1)	72.24(1)
$ScAlZnO_4$	1550	1	3.242(1)	25.54(1)
$ScAlZn_2O_5$	1450	4	3.245(1)	22.24(1)
$ScAlZn_3O_6$	1450	6	3.242(1)	41.12(1)
$ScAlZn_4O_7$	1450	8	3.243(1)	32.55(1)
$ScAlZn_5O_8$	1450	3	3.245(1)	56.46(1)
$ScAlZn_6O_9$	1450	3	3.246(1)	42.93(1)
$ScAlZn_7O_{10}$	1450	2	3.247(1)	72.19(1)

It is known that rare-earth elements with large ionic radii such as La, Nd, or Eu, divalent cations such as Sr, Ba, or Ca, and trivalent cations such as Fe, Ga, or Al form the $(KNiF_3)_nKF$ type of compound (n = 1, 2, 3 . . .). Drofenik *et al.* (*15*) established the phase diagram of the Eu_2O_3–Fe_2O_3–SrO system at 1300°C in air and reported $(EuFeO_3)_nSrO$ (n = 1 and 2) as having $(KNiF_3)_n$KF structure. From the previous and the present work, we can safely conclude that the *Ln* ions with smaller size (Lu, Yb, Tm, In, or Sc), the trivalent cations (Fe, Ga, or Al), and the divalent cations (Mn, Co, Fe, Cu, Mg, or Cd) form the $(YbFeO_3)_nFeO$ type of layered structures (*11*).

The *d*-spacings and the relative intensities of the powder X-ray diffraction for all of the compounds which were newly prepared in the present work will be sent to the Joint Committee of the Powder Diffraction Standards (USA).

It is well known that $R$$FeO_3$ and $R_3Fe_5O_{12}$

in the R_2O_3–Fe_2O_3 system (R = rare-earth elements) are magnetically interesting compounds. We are currently studying magnetic properties of these $InFeO_3(ZnO)_m$ compounds.

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