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The Phase Relations in the In_2O_3–Al_2ZnO_4–ZnO System at 1350°C

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Phase relations in the In_2O_3–Al_2ZnO_4–ZnO system at 1350°C are determined by a classical quenching method. This system consists of In_2O_3, Al_2ZnO_4, ZnO, and homologous phases $InAlO_3(ZnO)_m$ (m = 2, 3, ...) having solid solutions with $LuFeO_3(ZnO)_m$-type crystal structures. These solid solution ranges are as follows: $In_{1+x_1}Al_{1-x_1}O_3(ZnO)_2$ ($x_1 = 0.70$)–$In_{1+x_2}Al_{1-x_2}O_3(ZnO)_2$ ($x_2 = 0.316$–0.320), $In_2O_3(ZnO)_3$–$In_{1+x}Al_{1-x}O_3(ZnO)_3$ ($x = 0.230$), $In_2O_3(ZnO)_4$–$In_{1+x}Al_{1-x}O_3(ZnO)_4$ ($x = 0.15$–0.16), $In_2O_3(ZnO)_5$–$In_{1+x}Al_{1-x}O_3(ZnO)_5$ ($x = 0.116$–0.130), $In_2O_3(ZnO)_6$–$In_{1+x}Al_{1-x}O_3(ZnO)_6$ ($x = 0.000$–0.111), $In_2O_3(ZnO)_7$–$In_{1+x}Al_{1-x}O_3(ZnO)_7$ ($x = 0.08$), $In_2O_3(ZnO)_8$–$In_{1+x}Al_{1-x}O_3(ZnO)_8$ (x: undetermined), and $In_2O_3(ZnO)_m$–$InAlO_3(ZnO)_m$ (m = 9, 10, 11, 13, 15, 17, and 19). The space groups of these homologous phases belong to $R\bar{3}m$ for m = odd or $P6_3/mmc$ for m = even. Their crystal structures, $In_{1+x}Al_{1-x}O_3(ZnO)_m$ ($0 < x < 1$), consist of three kinds of layers: an $InO_{1.5}$ layer, an $(In_xAl_{1-x}Zn)O_{2.5}$ layer, and ZnO layers. A comparison of the phase relations in the In_2O_3–M_2ZnO_4–ZnO systems (M = Fe, Ga, or Al) is made and their characteristic features are discussed in terms of the ionic radii and site preferences of the M cations.

Introduction

It is important for solid state chemists to know the relations between the thermochemical stabilities and the structures of solid complex inorganic oxides and their constituent cation elements. In previous papers (*1*, *2*), we established phase relations in the In_2O_3–Fe_2ZnO_4–ZnO and In_2O_3–Ga_2ZnO_4–ZnO systems at 1350°C by a classical quenching method. In the In_2O_3–Fe_2ZnO_4–ZnO system, there are $InFeO_3(ZnO)_m$-type homologous phases with solid solution ranges, $In_{1+x}Fe_{1-x}O_3(ZnO)$–$InFeO_3(ZnO)$, $In_{1+x}Fe_{1-x}O_3(ZnO)_2$–$InFeO_3(ZnO)_2$–$In_{1-x}Fe_{1+x}O_3(ZnO)_2$, $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$In_{1-x}Fe_{1+x}O_3(ZnO)_m$ for m = 3–11 ($0 < x < 1$), and full solid solution ranges of $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$Fe_2O_3(ZnO)_m$ for $m > 12$.

Homologous compounds, $Fe_2O_3(ZnO)_m$ ($m > 12$) having $InFeO_3(ZnO)_m$-type crystal structures were newly reported in the ZnO–Fe_2ZnO_4 system. A spinel solid solution range extends to $Fe_{2-x}In_xZnO_4$ ($x = 0.40 \pm 0.02$) from Fe_2ZnO_4. In the In_2O_3–Ga_2ZnO_4–ZnO system, there are $(InGaO_3)_2ZnO$ with $Yb_2Fe_3O_7$-type crystal structure (*3*) and $InGaO_3(ZnO)_m$-type homologous phases with solid solution ranges; $In_{1+x}Ga_{1-x}O_3(ZnO)$–$InGaO_3(ZnO)$–$In_{1-x}Ga_{1+x}O_3(ZnO)$, $In_{1+x}Ga_{1-x}O_3(ZnO)_2$–$InGaO_3(ZnO)_2$–$In_{1-x}Ga_{1+x}O_3(ZnO)_2$, $In_2O_3(ZnO)_m$-$InGaO_3(ZnO)_m$–$In_{1-x}Ga_{1+x}O_3(ZnO)_m$ for m = 3–9, 11, 13 ($0 < x < 1$). In the ZnO–Ga_2ZnO_4 system there is a solid solution, $(ZnO)_{1-x}(Ga_2O_3)_x$ ($0 < x < 0.093$) with a distorted wurtzite-type crystal structure. A spinel solid solution range extends to $Ga_{2-x}In_xZnO_4$ ($x = 0.128(4)$) from Ga_2ZnO_4. From the powder X-ray diffraction analysis we concluded that both $InFeO_3(ZnO)_m$ and $InGaO_3(ZnO)_m$ were isostructural with Lu

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FeO$_3$(ZnO)$_m$. The crystal structures of LuFeO$_3$(ZnO)$_m$ (m = 1, 4, 5, and 6) were clarified by Isobe *et al.* (*4*) using single crystal X-ray analyses. The space group for LuFeO$_3$(ZnO)$_m$ belongs to $R\bar{3}m$ for m = odd or $P6_3/mmc$ for m = even. Crystal structures for LuFeO$_3$(ZnO)$_m$ (m = 1 and 4) are shown in Figs. 1A and 1B. The crystal structure for InAlO$_3$(CuO) in a monoclinic crystal system has a_m = 0.5728(3) nm, b_m = 0.3309(2) nm, c_m = 0.8352(3) nm, and β = 103.2(2)° in space group Cm or in a pseudo hexagonal system has a_h = 0.331 nm and c_h = 2.439 nm, reported by Kutoglu *et al.* (*5*). The compounds $(RMO_3)_n(M'O)_m$ in the R_2O_3–M_2O_3–$M'O$ system (R = one of the rare earth elements; M = Fe, Ga, or Al; M' = divalent cation element; n and m = integer) were reviewed thermochemically, crystal-chemically, and from the viewpoint of solid state physics (*6*). In the present paper, we report phase relations in the In$_2$O$_3$–Al$_2$ZnO$_4$–ZnO system at 1350°C, which were determined by a classical quenching method; compare them to the phase relations in the In$_2$O$_3$–M_2ZnO$_4$–ZnO systems (M = Fe or Ga); and discuss the crystal-chemical effects of Fe(III), Ga(III), and Al(III) upon the characteristic features in these phase relations.

Experimental

Except for Al$_2$O$_3$, experimental methods and starting compounds have been described elsewhere (*1, 2, 7*). Al$_2$O$_3$ (99.99%) powder was heated at 1000°C for 1 day in air prior to mixing mixture with other mate-

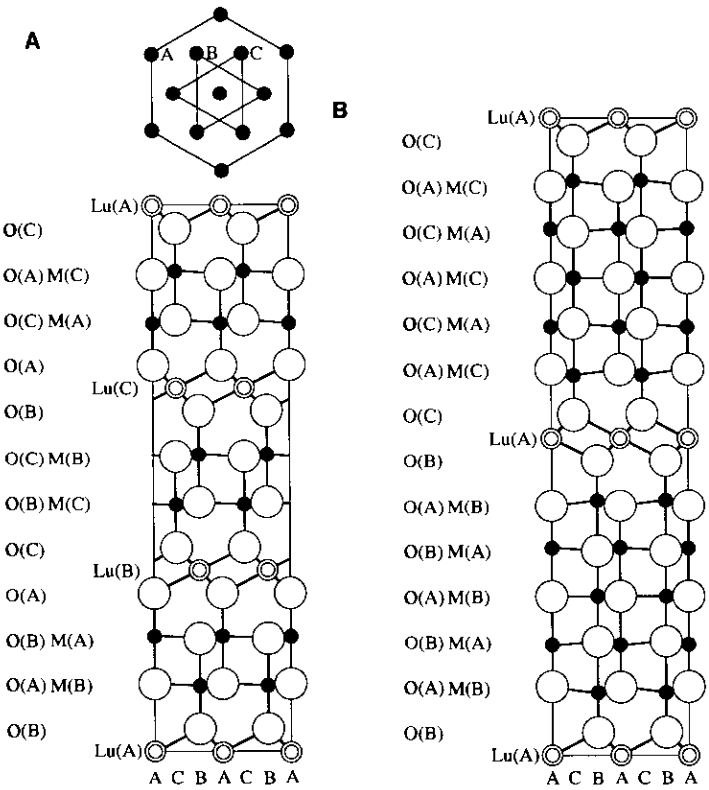

FIG. 1. Crystal structures for LuFeO$_3$(ZnO) in A and LuFeO$_3$(ZnO)$_4$ in B. A, B, and C represent three kinds of triangular lattices; M sites are occupied by Fe and/or Zn ions: ◎, Lu ion; ●, Fe and/or Zn ion; ○, O ion.

rials. Samples were analyzed by X-ray powder diffractometry and scanning electron microscopy (SEM). No detectable chemical reactions between the samples and the Pt tubes were found by careful visual checking. Lattice constants for the phases obtained were measured by X-ray powder diffractometry and calculated by the least squares method.

Results and Discussion

1. The Phase Relations in the In_2O_3–Al_2ZnO_4–ZnO System at 1350°C

Phase relations in the In_2O_3–Al_2ZnO_4–ZnO system at 1350°C are shown in Fig. 2A. Detailed phase relations near the ZnO phase are shown in Fig. 2B. Mixing ratios of the starting compounds, heating periods, phases obtained, and lattice constants for each phase are given in Table I.

There are homologous phases, $In_2O_3(ZnO)_m$ (m = 3, 4, 5, . . .), in the In_2O_3–ZnO binary system (*1, 2, 8, 9*). There are no compounds in the In_2O_3–Al_2ZnO_4 or the ZnO–Al_2ZnO_4 binary systems. No detectable solid solution of the ZnO phase exists to the direction of the spinel phase, since no volume difference of the unit cell of the ZnO phase was detected between the stoichiometric wurtzite in a single phase state and that in equilibrium with the spinel

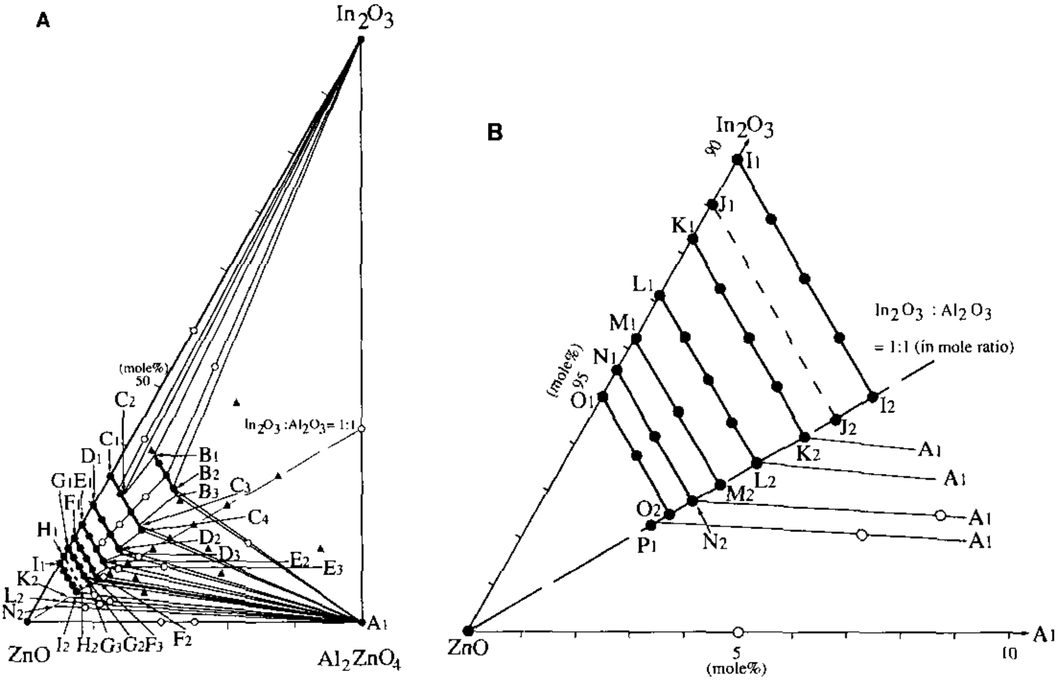

FIG. 2. The phase relations in the In_2O_3–Al_2ZnO_4–ZnO at 1350°C. (p, q, r) indicates the composition (in mole ratio) of In_2O_3, Al_2O_3, and ZnO. Symbols and numbers in the figures are as follows: A_1(0.000, 0.500, 0.500); (II) B_1(0.283, 0.050, 0.667), B_2(0.230, 0.103, 0.667), B_3(0.219, 0.114, 0.667); (III) C_1(0.250, 0.000, 0.750), C_2(0.214, 0.035, 0.750), C_3(0.164, 0.086, 0.750), C_4(0.156, 0.094, 0.750); (IV) D_1(0.200, 0.000, 0.800), D_2(0.125, 0.075, 0.800), D_3(0.115, 0.085, 0.800); (V) E_1(0.167, 0.000, 0.833), E_2(0.101, 0.066, 0.833), E_3(0.094, 0.073, 0.833); (VI) F_1(0.143, 0.000, 0.857), F_2(0.081, 0.062, 0.857), F_3[(0.080, 0.064, 0.857)–(0.072, 0.071, 0.857)]; (VII) G_1(0.125, 0.000, 0.875), G_2(0.069, 0.056, 0.875), G_3(0.068, 0.057, 0.875); (VIII) H_1(0.112, 0.000, 0.888), H_2(undetermined); (IX) I_1(0.100, 0.000, 0.900), I_2($\frac{1}{20}$, $\frac{1}{20}$, $\frac{18}{20}$); (X) J_1($\frac{1}{11}$, 0, $\frac{10}{11}$), J_2(undetermined); (XI) K_1($\frac{1}{12}$, 0, $\frac{11}{12}$), K_2($\frac{1}{24}$, $\frac{1}{24}$, $\frac{22}{24}$); (XIII) L_1($\frac{1}{14}$, 0, $\frac{13}{14}$), L_2($\frac{1}{28}$, $\frac{1}{20}$, $\frac{26}{28}$); (XV) M_1($\frac{1}{16}$, 0, $\frac{15}{16}$), M_2($\frac{1}{32}$, $\frac{1}{32}$, $\frac{30}{32}$); (XVII) N_1($\frac{1}{18}$, 0, $\frac{17}{18}$), N_2($\frac{1}{36}$, $\frac{1}{36}$, $\frac{34}{36}$); (XIX) O_1($\frac{1}{20}$, 0, $\frac{19}{20}$), O_2($\frac{1}{40}$, $\frac{1}{40}$, $\frac{38}{40}$); (XXI) P_1($\frac{1}{44}$, $\frac{1}{44}$, $\frac{42}{44}$).

TABLE I

MIXING RATIO OF THE STARTING COMPOUNDS (In_2O_3, Al_2O_3, AND ZnO), HEATING PERIOD, AND PHASES OBTAINED IN THE In_2O_3–Al_2ZnO_4–ZnO SYSTEM AT 1350°C

						Lattice constants	
No.	In_2O_3	Al_2O_3	ZnO	Period (day)	Phases	*a* (nm)	*c* (nm)
1	1	0	0	4	In_2O_3	1.012(1)	
2	0	1	0	4	Al_2O_3	0.4760(1)	1.299(1)
5	1	1	1	6 + 4	In_2O_3	1.011(1)	
					spinel	0.8087(1)	
10	1	0	1	3 + 3	In_2O_3	1.011(1)	
					III	0.3350(1)	4.246(1)
11	7	1	8	5 + 5	In_2O_3	1.012(1)	
					II	0.3312(1)	2.274(1)
12	3	1	4	5 + 6	In_2O_3	1.012(1)	
					II	0.3303(1)	2.266(1)
					spinel	0.8094(1)	
15	1	1	2	5 + 6	In_2O_3	1.012(1)	
					II	0.3302(1)	2.265(1)
					spinel	0.8096(1)	
17	1	3	4	5 + 7	In_2O_3	1.012(1)	
					II	0.3299(1)	2.268(1)
					spinel	0.8095(1)	
19	0	1	1	5	spinel	0.8085(1)	
315	1	1	3	5 + 4	In_2O_3	1.012(1)	
					II	0.3303(1)	2.265(1)
					spinel	0.8096(1)	
41p	15	24	61	5 + 5	II	0.3305(1)	2.266(1)
					spinel	0.8096(1)	
2e	15	1	32	5 + 5	In_2O_3	1.012(1)	
					III	0.3334(1)	4.230(1)
21	7	1	16	6 + 4	In_2O_3	1.012(1)	
					II	0.3336(1)	2.296(1)
					III	0.3324(1)	4.217(1)
2g	13	3	32	2	II	0.3328(1)	2.290(1)
22	3	1	8	2	II	0.3314(1)	2.277(1)
2j	11	5	32	2	II	0.3304(1)	2.263(1)
23	5	3	16	5 + 5	II	0.3300(1)	2.258(1)
					III	[a]	[a]
					spinel	0.8094(1)	
25	1	1	4	5 + 4	II	0.3298(1)	2.259(1)
					III	0.3292(1)	4.160(1)
					spinel	0.8094(1)	
26	3	5	16	9 + 6	II	0.3296(1)	2.258(1)
					III	0.3292(1)	4.155(1)
					spinel	0.8094(1)	
27	1	3	8	4 + 4	III	0.3286(1)	4.147(1)
					IV	0.3283(1)	3.282(1)
					spinel	0.8092(1)	
42p	12	19	69	5 + 5	III	0.3291(1)	4.154(1)
					spinel	0.8094(1)	
322	3	1	10	4 + 6	II	0.3315(1)	2.277(1)
					III	0.3306(1)	4.186(1)
325	1	1	5	5 + 4	II	0.3300(2)	2.262(1)
					III	0.3292(1)	4.155(1)
					spinel	0.8094(1)	

TABLE I—*Continued*

No.	In_2O_3	Al_2O_3	ZnO	Period (day)	Phases	Lattice constants	
						a (nm)	*c* (nm)
30	1	0	3	3 + 7	III	0.3351(1)	4.248(1)
31	7	1	24	4	III	0.3327(1)	4.221(1)
32	3	1	12	2	III	0.3307(1)	4.188(1)
33	5	3	24	5 + 8	III	0.3290(1)	4.148(1)
35	1	1	6	5 + 6	III	0.3287(1)	4.148(1)
					IV	0.3284(1)	3.280(1)
					spinel	0.8092(1)	
36	3	5	24	6 + 4	IV	0.3280(1)	3.277(1)
					spinel	0.8092(1)	
39	0	1	3	5	ZnO	0.3250(1)	0.5205(1)
					spinel	0.8089(1)	
332	3	1	14	4 + 5	III	0.3307(1)	4.188(1)
					IV	0.3301(1)	3.310(1)
335	1	1	7	4 + 4	IV	0.3282(1)	3.279(1)
					spinel	0.8093(1)	
40	1	0	4	4	IV	0.3337(1)	3.353(1)
41	7	1	32	4	IV	0.3318(1)	3.335(1)
42	3	1	16	4	IV	0.3299(1)	3.312(1)
43	5	3	32	4	IV	0.3284(1)	3.281(1)
45	1	1	8	4 + 5	IV	0.3277(1)	3.272(1)
					V	0.3275(1)	5.684(2)
					spinel	0.8086(1)	
46	3	5	32	6 + 5	V	0.3272(1)	5.687(1)
					VI	0.3270(2)	4.296(4)
					spinel	0.8091(1)	
47	1	3	16	5 + 5	VII	0.3265(1)	7.234(2)
					VIII	[a]	[a]
					spinel	0.8092(1)	
49	0	1	4	5 + 5	ZnO	0.3250(1)	0.5206(1)
					spinel	0.8090(1)	
342	3	1	18	4 + 9	IV	0.3298(1)	3.314(1)
					V	0.3295(1)	5.749(1)
345	1	1	9	4 + 5	V	0.3275(1)	5.688(1)
					spinel	0.8091(2)	
50	1	0	5	3	V	0.3326(1)	5.810(1)
51	7	1	40	5	V	0.3309(1)	5.785(1)
52	3	1	20	6	V	0.3294(1)	5.749(1)
53	5	3	40	4	V	0.3280(1)	5.701(1)
55	1	1	10	4 + 4	V	0.3270(1)	5.683(1)
					VI	0.3269(2)	4.310(3)
					spinel	0.8089(1)	
355	1	1	11	4 + 7	VI	0.3270(1)	4.313(3)
					spinel	0.8093(1)	
60	1	0	6	3	VI	0.3316(1)	4.394(1)
61	7	1	48	5 + 4	VI	0.3301(1)	4.375(1)
62	3	1	24	9 + 5	VI	0.3289(1)	4.352(1)
63	5	3	48	5 + 4	VI	0.3279(1)	4.317(1)
65	1	1	12	4 + 5	VI	[a]	[a]
					VII	0.3268(1)	7.237(1)
					spinel	0.8089(1)	
67	1	3	24	5 + 5	XI	0.3257(1)	10.35(1)
					spinel	0.8091(1)	

Continued

TABLE I—*Continued*

No.	In_2O_3	Al_2O_3	ZnO	Period (day)	Phases	Lattice constants	
						a (nm)	c (nm)
70	1	0	7	3	VII	0.3310(1)	7.370(1)
71	7	1	56	5	VII	0.3297(1)	7.345(1)
72	3	1	28	4	VII	0.3283(1)	7.310(1)
73	5	3	56	4	VII	0.3274(1)	7.266(1)
75	1	1	14	4 + 5	VII	0.3265(1)	7.236(1)
					VIII	[a]	[a]
					spinel	0.8089(2)	
76	3	5	56	5 + 5	IX	0.3262(1)	8.795(3)
					spinel	0.8090(1)	
77	1	3	28	5 + 5	XIII	0.3256(1)	11.92(1)
					spinel	0.8089(1)	
80	1	0	8	3 + 3 + 3	VIII	0.3304(1)	5.432(1)
82	3	1	32	9 + 5	VII[b]	[a]	[a]
					VIII[b]	[a]	[a]
					IX[b]	[a]	[a]
83	5	3	64	4 + 4	VII[b]	[a]	[a]
					VIII[b]	[a]	[a]
					IX[b]	[a]	[a]
85	1	1	16	4 + 5	VII[b]	[a]	[a]
					VIII[b]	[a]	[a]
					IX[b]	[a]	[a]
					spinel[b]	[a]	
90	1	0	9	3	IX	0.3299(1)	8.926(1)
91	7	1	72	4 + 4	IX	0.3288(1)	8.904(1)
92	3	1	36	4 + 5	IX	0.3279(1)	8.873(1)
93	5	3	72	4 + 4	IX	0.3269(1)	8.827(2)
95	1	1	18	4 + 5 + 8	IX	0.3262(1)	8.795(1)
97	1	3	36	4 + 9	XVII	0.3256(1)	15.02(1)
					spinel	0.8090(1)	
100	1	0	10	3 + 3 + 7	X	[a]	6.545(57)
105	1	1	20	9 + 4	IX[b]	[a]	[a]
					X[b]	[a]	[a]
					XI[b]	[a]	[a]
110	1	0	11	3	XI	0.3292(1)	10.49(1)
111	7	1	88	5 + 4	XI	0.3283(1)	10.46(1)
112	3	1	44	4 + 9	XI	0.3275(1)	10.44(1)
113	5	3	88	4 + 4	XI	0.3266(1)	10.38(1)
115	1	1	22	4 + 5	XI	0.3259(1)	10.35(1)
117	1	3	44	4 + 5 + 4	XXI	0.3253(1)	18.14(1)
					spinel	0.8089(1)	
130	1	0	13	3 + 7 + 3	XIII	0.3284(1)	12.04(1)
131	7	1	104	4 + 4	XIII	0.3280(1)	12.02(1)
132	3	1	52	4 + 7	XIII	0.3272(1)	11.99(1)
133	5	3	104	4 + 4	XIII	0.3264(1)	11.95(1)
135	1	1	26	4 + 5	XIII	0.3258(1)	11.92(1)
150	1	0	15	4 + 4	XV	0.3282(1)	13.60(1)
152	3	1	60	4 + 5	XV	0.3270(1)	13.54(1)
155	1	1	30	4 + 5	XV	0.3257(1)	13.47(1)
170	1	0	17	4 + 4	XVII	0.3279(1)	15.17(1)
172	3	1	68	4 + 5	XVII	0.3267(1)	15.11(1)
175	1	1	34	5 + 5	XVII	0.3257(1)	15.03(1)
190	1	0	19	4 + 4	XIX	0.3276(1)	16.73(1)

TABLE I—*Continued*

No.	In_2O_3	Al_2O_3	ZnO	Period (day)	Phases	Lattice constants a (nm)	Lattice constants c (nm)
192	3	1	76	4 + 5	XIX	0.3265(1)	16.67(1)
195	1	1	38	4 + 5	XIX	0.3256(1)	16.59(1)
199	0	1	19	4 + 4	ZnO	0.3249(1)	0.5204(1)
					spinel	0.8086(1)	
215	1	1	42	5 + 6	XXI	0.3254(1)	18.14(1)
401	0	55	45	6	Al_2O_3	0.4759(1)	1.299(1)
					spinel	0.8085(1)	
3	0	0	1	3	ZnO	0.3248(1)	0.5204(1)

Note. We heated a mixture of $In_2O_3 : Al_2O_3 : ZnO = 1 : 1 : 2$ (in mole ratio) at 1550°C for 1 day and obtained $In_{1+x}Al_{1-x}O_3(ZnO)$ (Phase I) and a spinel phase. We reheated this sample at 1350°C for 3 days and obtained In_2O_3, Phase II, and a spinel phase. This result is completely consistent with that from direct heating for a mixture having $In_2O_3 : Al_2O_3 : ZnO = 1 : 1 : 2$ at 1350°C.

[a] Lattice constants could not be determined.

[b] Data were considered to be in nonequilibrium states; however, since the reaction rate was too slow to arrive at the equilibrium states, we stopped heating in these states.

phase. We estimated that the range was within $(ZnO)_{1-x}(Al_2O_3)_x$ ($x = 0.000$).

There are homologous phases, $InAlO_3(ZnO)_m$ ($m = 2, 3, \ldots$), having $LuFeO_3(ZnO)_m$-type crystal structures in the In_2O_3–Al_2ZnO_4–ZnO ternary system. Hereafter, the phases for $InAlO_3(ZnO)$, $InAlO_3(ZnO)_2$, $InAlO_3(ZnO)_3, \ldots$, will be designated as Phase I, Phase II, Phase III, ... Phase I does not exist. Neither do $In_2O_3(ZnO)_2$ nor $InAlO_3(ZnO)_2$ exist. However, there is Phase II with nonstoichiometric composition. From Phase III to Phase VIII, there are solid solution ranges between $In_2O_3(ZnO)_m$ and $In_{1+x}Al_{1-x}O_3(ZnO)_m$ ($0 < x < 1$). Although we obtained Phase VIII from $In_2O_3(ZnO)_8$ to $In_{1+x}Al_{1-x}O_3(ZnO)_8$, we could not determine x, since the reaction rate in forming $In_{1+x}Al_{1-x}O_3(ZnO)_8$ was too slow. There exist stoichiometric solid solution ranges between $In_2O_3(ZnO)_m$ and $InAlO_3(ZnO)_m$ ($m = 9, 11, 13, \ldots$). The range for each homologous phase is shown in Table II.

We describe the characteristic features in the phase relations in Fig. 2A and Fig. 2B. In general, the features in the In_2O_3–Al_2ZnO_4–ZnO system are similar to those in the In_2O_3–Fe_2ZnO_4–ZnO system and in the In_2O_3–Ga_2ZnO_4–ZnO system, except that (1) there exists no Phase I and (2) there are no solid solution ranges which extend from $InAlO_3(ZnO)_m$ to $In_{1-x}Al_{1+x}O_3(ZnO)_m$ ($0 < x < 1$).

The In_2O_3 phase is in equilibrium with Phase III, Phase II, and the spinel phase. We could detect a decrease in the lattice constant for the stoichiometric In_2O_3 phase in the In_2O_3–M_2ZnO_4–ZnO system (M = Fe or Ga), from $a = 1.012(1)$ (nm) (*1*, *2*). No detectable change in the lattice constant of the In_2O_3 phase was seen in the In_2O_3–Al_2ZnO_4–ZnO system, however. (See Fig. 3.)

The spinel phase is in equilibrium with the In_2O_3 phase, Phase II, Phase III, Phase IV, ..., and the ZnO phase. The changes in the lattice constants for the spinel phase from those of stoichiometric Al_2ZnO_4 in the directions of the In_2O_3 phase, Phase W (W = II, III, ...), and the ZnO phase are shown in Fig. 4, where we can see the slight expansion of the lattice from that of stoichiometric Al_2ZnO_4 due to the occurrence of the excess Zn(II) cation and/or the existence of the In(III) cation in the stoichiometric Al_2ZnO_4.

TABLE II

THE SOLID SOLUTION RANGES OF THE LAYERED PHASES, THE LATTICE CONSTANTS, AND THE SPACE GROUP

	Kasper (*7*)		Cannard and Tilley (*8*)		Kimizuka *et al.* (*9*)	
Phase	Temperature (°C) heating period (hr) crystal system	Lattice constants (nm)	Temperature (°C) heating period (day)	Lattice constants (nm)	Space group Temperature (°C) heating period (day)	Lattice constants (nm)
I					$R\bar{3}m$ 1550 1	$InAlO_3(ZnO)$ $a = 0.3309(1)$ $c = 2.633(1)$
II	1550 2 Hex.	$In_2O_3(ZnO)_2$ $a = 0.3376(1)$ $c = 2.3154(10)$			$P6_3/mmc$ 1422 4	$InAlO_3(ZnO)_2$ $a = 0.3295(1)$ $c = 2.256(1)$
III	1200 12 Rhom.	$In_2O_3(ZnO)_3$ $a = 0.3355(1)$ $c = 4.2515(20)$			$R\bar{3}m$ 1450 6	$InAlO_3(ZnO)_3$ $a = 0.3281(1)$ $c = 4.135(1)$
IV	1200 50 Hex.	$In_2O_3(ZnO)_4$ $a = 0.3339(2)$ $c = 3.352(2)$	1100 3	$In_2O_3(ZnO)_4$	$P6_3/mmc$ 1450 8	$InAlO_3(ZnO)_4$ $a = 0.3277(1)$ $c = 3.272(1)$
V	1050 100 Rhom.	$In_2O_3(ZnO)_5$ $a = 0.3327(1)$ $c = 5.8114(20)$	1100 3	$In_2O_3(ZnO)_5$	$R\bar{3}m$ 1450 3	$InAlO_3(ZnO)_5$ $a = 0.3272(1)$ $c = 5.680(1)$
VI			1100 3	$In_2O_3(ZnO)_6$		
VII	1310 2 Rhom.	$In_2O_3(ZnO)_7$ $a = 0.3313(1)$ $c = 7.362(4)$	1100 3	$In_2O_3(ZnO)_7$	$R\bar{3}m$ 1450 4	$InAlO_3(ZnO)_7$ $a = 0.3263(1)$ $c = 7.224(1)$
VIII						
IX			1100 7	$In_2O_3(ZnO)_9$		
X						
XI			1100 3	$In_2O_3(ZnO)_{11}$		
XIII						
XV						
XVII						
XIX						
XXI						

Note. All the lattice constants are given in the hexagonal system: "Hex." = hexagonal, "Rhom." = rhombic. Lattice constants for $InAlO_3(ZnO)_m$ ($m = 1$–7) prepared at 1450°C or 1550°C by Kimizuka *et al.* (*7*) apparently indicate that each stoichiometry for their specimens, $InAlO_3(ZnO)_m$, should be $In_{1+x}Al_{1-x}O_3(ZnO)_m$ having the minimum x in the solid solution range ($0 < x < 1$) of the Phase W in the present work.

[a] The lattice constants could not be determined.

Phase II is in equilibrium with the In_2O_3 phase, Phase III, and the spinel phase. Phase III is in equilibrium with Phase II, Phase IV, and the spinel phase. Each of the higher order phases, Phase W (W = IV, V, VI, . . .), is in equilibrium with the spinel phase, Phase ($W - $ I), and Phase ($W + $ I).

In a process in which we established the

TABLE II—*Continued*

Nakamura *et al.* (*1*)	Present work		
Space group	$In_2O_3(ZnO)_m$ Lattice constants (nm)	$In_{1+x}Al_{1-x}O_3(ZnO)_m$ Lattice constants (nm)	$InAlO_3(ZnO)_m$ Lattice constants (nm)
$P6_3/mmc$	$In_{1+x_1}Al_{1-x_1}O_3(ZnO)_2$ ($x_1 = 0.70$) $a = 0.3336(1)$ $c = 2.296(1)$	$In_{1+x_2}Al_{1-x_2}O_3(ZnO)_2$ ($x_2 = 0.316$–0.320) $a = 0.3298(1)$ $c = 2.259(1)$	
$R\bar{3}m$	$In_2O_3(ZnO)_3$ $a = 0.3351(1)$ $c = 4.248(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_3$ ($x = 0.230$) $a = 0.3287(1)$ $c = 4.148(1)$	
$P6_3/mmc$	$In_2O_3(ZnO)_4$ $a = 0.3337(1)$ $c = 3.353(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_4$ ($x = 0.15$–0.16) $a = 0.3277(1)$ $c = 3.272(1)$	
$R\bar{3}m$	$In_2O_3(ZnO)_5$ $a = 0.3326(1)$ $c = 5.810(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_5$ ($x = 0.116$–0.130) $a = 0.3270(1)$ $c = 5.683(1)$	
$P6_3/mmc$	$In_2O_3(ZnO)_6$ $a = 0.3316(1)$ $c = 4.394(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_6$ ($x = 0.000$–0.111) $a =^a$ $c =^a$	
$R\bar{3}m$	$In_2O_3(ZnO)_7$ $a = 0.3310(1)$ $c = 7.370(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_7$ ($x = 0.08$) $a = 0.3265(1)$ $c = 7.236(1)$	
$P6_3/mmc$	$In_2O_3(ZnO)_8$ $a = 0.3304(1)$ $c = 5.432(1)$	$In_{1+x}Al_{1-x}O_3(ZnO)_8$ (undetermined, $0 < x < 1$) $a =^a$ $c =^a$	
$R\bar{3}m$	$In_2O_3(ZnO)_9$ $a = 0.3299(1)$ $c = 8.926(1)$		$InAlO_3(ZnO)_9$ $a = 0.3262(1)$ $c = 8.795(1)$
$P6_3/mmc$	$In_2O_3(ZnO)_{10}$ $a =^a$ $c = 6.545(57)$		$InAlO_3(ZnO)_{10}$ $a =^a$ $c =^a$
$R\bar{3}m$	$In_2O_3(ZnO)_{11}$ $a = 0.3292(1)$ $c = 10.49(1)$		$InAlO_3(ZnO)_{11}$ $a = 0.3259(1)$ $c = 10.35(1)$
$R\bar{3}m$	$In_2O_3(ZnO)_{13}$ $a = 0.3284(1)$ $c = 12.04(1)$		$InAlO_3(ZnO)_{13}$ $a = 0.3258(1)$ $c = 11.92(1)$
$R\bar{3}m$	$In_2O_3(ZnO)_{15}$ $a = 0.3282(1)$ $c = 13.60(1)$		$InAlO_3(ZnO)_{15}$ $a = 0.3257(1)$ $c = 13.47(1)$
$R\bar{3}m$	$In_2O_3(ZnO)_{17}$ a = 0.3279(1) $c = 15.17(1)$		$InAlO_3(ZnO)_{17}$ $a = 0.3257(1)$ $c = 15.03(1)$
$R\bar{3}m$	$In_2O_3(ZnO)_{19}$ $a = 0.3276(1)$ $c = 16.73(1)$		$InAlO_3(ZnO)_{19}$ $a = 0.3256(1)$ $c = 16.59(1)$
$R\bar{3}m$			$InAlO_3(ZnO)_{21}$ $a = 0.3254(1)$ $c = 18.14(1)$

present phase relations, we recognized the following phenomena;

(1) From In_2O_3, Al_2O_3 and ZnO powders, the rate of forming Phase *W* was faster with m = odd than with m = even.

(2) The rate of forming Phase *W* was faster with lower Al_2O_3 concentration than with higher Al_2O_3 concentration.

(3) The rate of forming Phase *W* becomes slower with increasing m in $InAlO_3(ZnO)_m$. We stopped our experimental work at m =

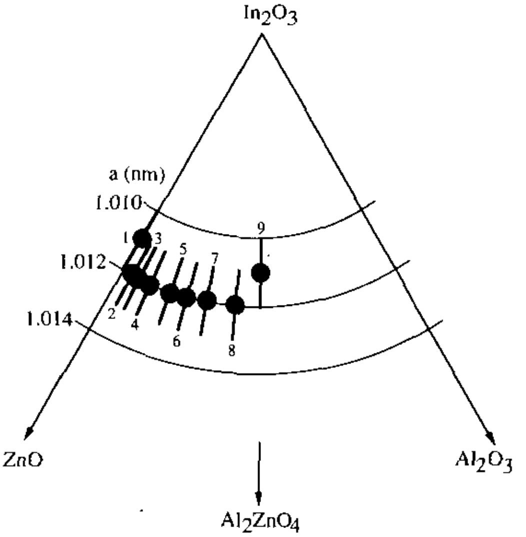

FIG. 3. The lattice constants for the In_2O_3 phase which is in equilibrium with various phases. Numbers are the experimental run numbers given in Table I: (1) 010, (2) 02e, (3) 021, (4) 011, (5) 012, (6) 315, (7) 015, (8) 017, (9) 005.

21; however, it is certain that $InAlO_3(ZnO)_m$ ($m > 21$) will be formed, if we heat the starting mixtures for a much longer period than in the present study.

The three phenomena mentioned above were observed in the In_2O_3–Fe_2ZnO_4–ZnO system and in the In_2O_3–Ga_2ZnO_4–ZnO system also.

2. *Crystal Structural Consideration for the Homologous Solid Solutions of* $In_{1+x_1}Al_{1-x_1}O_3(ZnO)_2$–$In_{1+x_2}Al_{1-x_2}O_3(ZnO)_2$, $In_2O_3(ZnO)_m$–$In_{1+x}Al_{1-x}O_3(ZnO)_m$ (*m* = *3–8*), *and* $In_2O_3(ZnO)_m$–$InAlO_3(ZnO)_m$ (*m* = *9, 10, . . .*)

Powder samples obtained were supplied for SEM observation. We observed clear plate-like crystals of the solid solutions $In_{1+x_1}Al_{1-x_1}O_3(ZnO)_2$–$In_{1+x_2}Al_{1-x_2}O_3(ZnO)_2$, $In_2O_3(ZnO)_m$–$In_{1+x}Al_{1-x}O_3(ZnO)_m$ (m = 3–8), and $In_2O_3(ZnO)_m$–$InAlO_3(ZnO)_m$ (m = 9, 10, . . .) as in $InMO_3(ZnO)_m$ (M = Fe or Ga). All X-ray powder diffraction peaks for these samples could be indexed on the hypothesis of a hexagonal unit cell as in $LuFeO_3(ZnO)_m$. So we eventually considered $InAlO_3(ZnO)_m$ to be isostructural with $LuFeO_3(ZnO)_m$ and not with $InAlO_3$ (CuO) in a monoclinic crystal system. The hexagonal lattice constants for the homologous solid solutions are shown in Table II

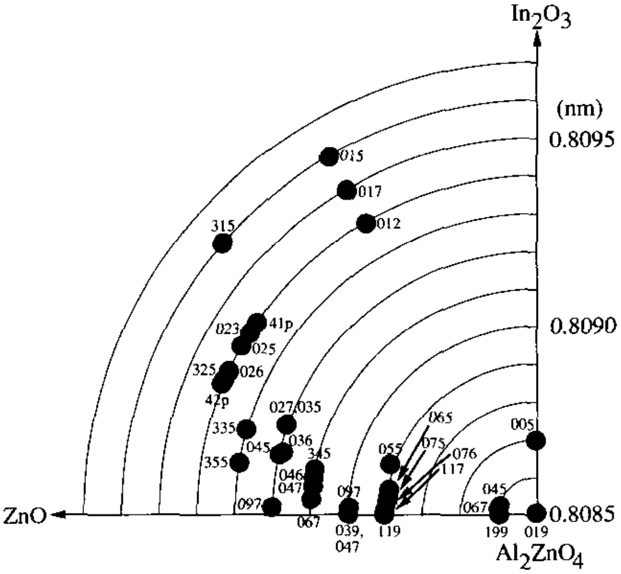

FIG. 4. The lattice constants for the spinel phase which is in equilibrium with various phases. Numbers are the experimental run numbers given in Table I.

and Fig. 5. All the lattice constants decrease with the concentration of Al_2O_3. As in $InFeO_3(ZnO)_m$ and $InGaO_3(ZnO)_m$, we can calculate the thickness of the constituent layers from the dependence of $c_{obsd.}/Z$ ($Z = 3$ for m = odd, $Z = 2$ for even) upon $(m - 1)$ (see Fig. 6). In Table III and Fig. 7, we show the thickness of the ZnO layer and each of the thicknesses of

the $InO_{1.5}$ layer and the $(InZn)O_{2.5}$ layer,
the $InO_{1.5}$ layer and the $(In_{0.75}Al_{0.25}Zn)O_{2.5}$ layer,
the $InO_{1.5}$ layer and the $(In_{0.50}Al_{0.50}Zn)O_{2.5}$ layer,
the $InO_{1.5}$ layer and the $(In_{0.25}Al_{0.75}Zn)O_{2.5}$ layer,
and the $InO_{1.5}$ layer and the $(AlZn)O_{2.5}$ layer.

To evaluate each thickness of the above layers, we considered that each compound actually consists of the following constituent parts:

$In_2O_3(ZnO)_m$:
$InO_{1.5} + (InZn)O_{2.5} + (m - 1)ZnO$

$In_{1.75}Al_{0.25}O_3(ZnO)_m$:
$InO_{1.5} + (In_{0.75}Al_{0.25}Zn)O_{2.5} + (m - 1)ZnO$

$In_{1.5}Al_{0.5}O_3(ZnO)_m$:
$InO_{1.5} + (In_{0.5}Al_{0.5}Zn)O_{2.5} + (m - 1)ZnO$

$In_{1.25}Al_{0.75}O_3(ZnO)_m$:
$InO_{1.5} + (In_{0.25}Al_{0.75}Zn)O_{2.5} + (m - 1)ZnO$

$InAlO_3(ZnO)_m$:
$InO_{1.5} + (AlZn)O_{2.5} + (m - 1)ZnO$.

Note that $\frac{1}{2} \times c$ ($c = 0.5207$ (nm)) is equal to 0.2604 (nm) in which c means the lattice constant of ZnO with wurtzite-type crystal structure (*10*).

The lattice constant a versus m is shown in Fig. 8. With increase in m, all the a values approach 0.3249 (nm), which is the lattice constant of ZnO with wurtzite-type crystal structure (*10*).

Both In(III) and Al(III) can coexist with Zn(II) in a trigonal bipyramidal site in the chemical composition range from $(InZn)O_{2.5}$ to $(AlZn)O_{2.5}$; however, since no solid solution range between $InAlO_3(ZnO)_m$ and $In_{1+x}Al_{1-x}O_3(ZnO)_m$ $(0 < x < 1)$ exists, we conclude that Al cannot occupy octahedral sites in the $InO_{1.5}$ layers.

The following conclusions are derived from comparison among phase relations in the In_2O_3–M_2O_3–ZnO systems (M = Fe, Ga, or Al) at 1350°C. They are similar to each other except for a few features:

(1) $InFeO_3(ZnO)$ and $(InGaO_3)_nZnO$ (n = 1 and 2) exist; however, no stoichiometric $(InAlO_3)_nZnO$ (n = 1 and 2) exist.

(2) Although there are solid solution ranges in $In_2O_3(ZnO)_m$–$InMO_3(ZnO)_m$–$In_{1-x}M_{1+x}O_3(ZnO)_m$ (M = Fe or Ga) $(0 < x < 1)$, there are no solid solution ranges in $InAlO_3(ZnO)_m$–$In_{1-x}Al_{1+x}O_3(ZnO)_m$ $(0 < x < 1)$. Al(III) is too small to occupy octahedral In(III) positions in the homologous phases.

(3) The solid solution ranges of the spinel phases $M_{2-x}In_xZnO_4$ from the stoichiometric M_2ZnO_4 (M = Fe, Ga, or Al) can be quantitatively compared. Note that both Fe_2ZnO_4 (*11*) and Ga_2ZnO_4 (*11*) are normal spinels, while Al_2ZnO_4 is referred to a normal spinel structure (the so-called "degree of inversion" is estimated to be 0.030 (*11*)). As M changes from Fe, Ga, to Al, the lattice constant of M_2ZnO_4 and x of $M_{2-x}In_xZnO_4$ reasonably decrease.

(4) There are homologous phases, $Fe_2O_3(ZnO)_m$ $(m \geq 12)$, having an $InFeO_3(ZnO)_m$-type crystal structure in the Fe_2O_3–ZnO system and a solid solution of $(Ga_2O_3)_x(ZnO)_{1-x}$ (x = 0–0.094) with a distorted wurtzite-type structure in the Ga_2O_3–ZnO system; however, neither a series of homologous phases nor a solid solution (in the range $x = 0.000$ in $(Al_2O_3)_x(ZnO)_{1-x}$) is observed in the Al_2O_3–ZnO system.

(5) The lattice constant of the In_2O_3 phase, which is in equilibrium with Phases I, II,and III or the $(InGaO_3)_2ZnO$ in the In_2O_3–M_2ZnO_4–ZnO system (M = Fe or Ga), decreases from $a = 1.0118$ (nm) for stoichiometric In_2O_3 (JCPDS, card No. 6-0416) having the so-called c-type of rare earth sesquioxide crystal structure. The lattice constant

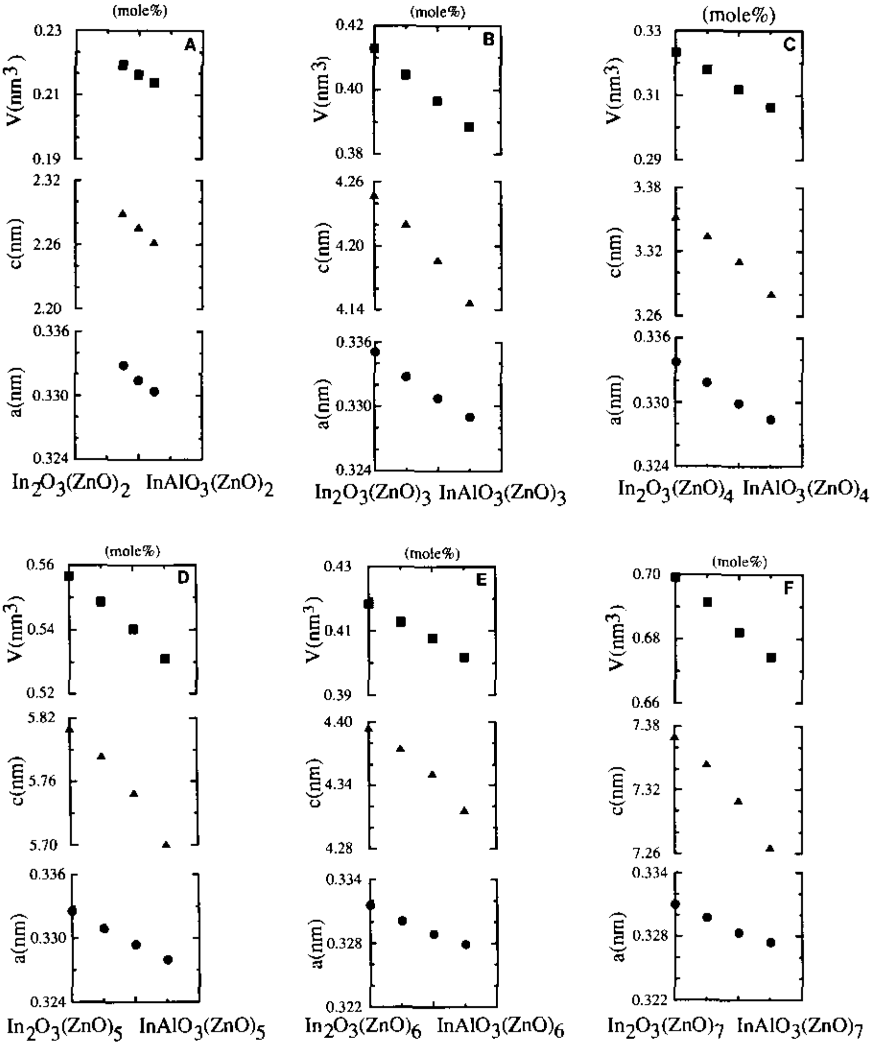

FIG. 5. The hexagonal lattice constants (a and c) and the unit cell volumes (V) of the layered phases in the system $In_2O_3(ZnO)_m$–$InAlO_3(ZnO)_m$: (A) Phase II, (B) Phase III, (C) Phase IV, (D) Phase V, (E) Phase VI, (F) Phase VII, (G) Phase VIII, (H) Phase IX, (I) Phase XI, (J) Phase XIII, (K) Phase XV, (L) Phase XVII, (M) Phase XIX, (N) Phase XXI.

TABLE III

THE THICKNESS OF THE CONSTITUENT LAYERS IN THE SOLID SOLUTIONS OF $InAlO_3(ZnO)_m$

	Constituent layers			Thickness	
Solid solutions	U layer	W layer	ZnO layer	(U + W) layers (nm)	ZnO layer (nm)
$In_2O_3(ZnO)_m$	$InO_{1.5}$	$(InZn)O_{2.5}$	ZnO	0.8965	0.2599
$In_{1.75}Al_{0.25}O_3(ZnO)_m$	$InO_{1.5}$	$(Al_{0.25}In_{0.75}Zn)O_{2.5}$	ZnO	0.8880	0.2599
$In_{1.5}Al_{0.5}O_3(ZnO)_m$	$InO_{1.5}$	$(Al_{0.5}In_{0.5}Zn)O_{2.5}$	ZnO	0.8771	0.2600
$In_{1.25}Al_{0.75}O_3(ZnO)_m$	$InO_{1.5}$	$(Al_{0.75}In_{0.25}Zn)O_{2.5}$	ZnO	0.8604	0.2601
$InAlO_3(ZnO)_m$	$InO_{1.5}$	$(AlZn)O_{2.5}$	ZnO	0.8530	0.2598

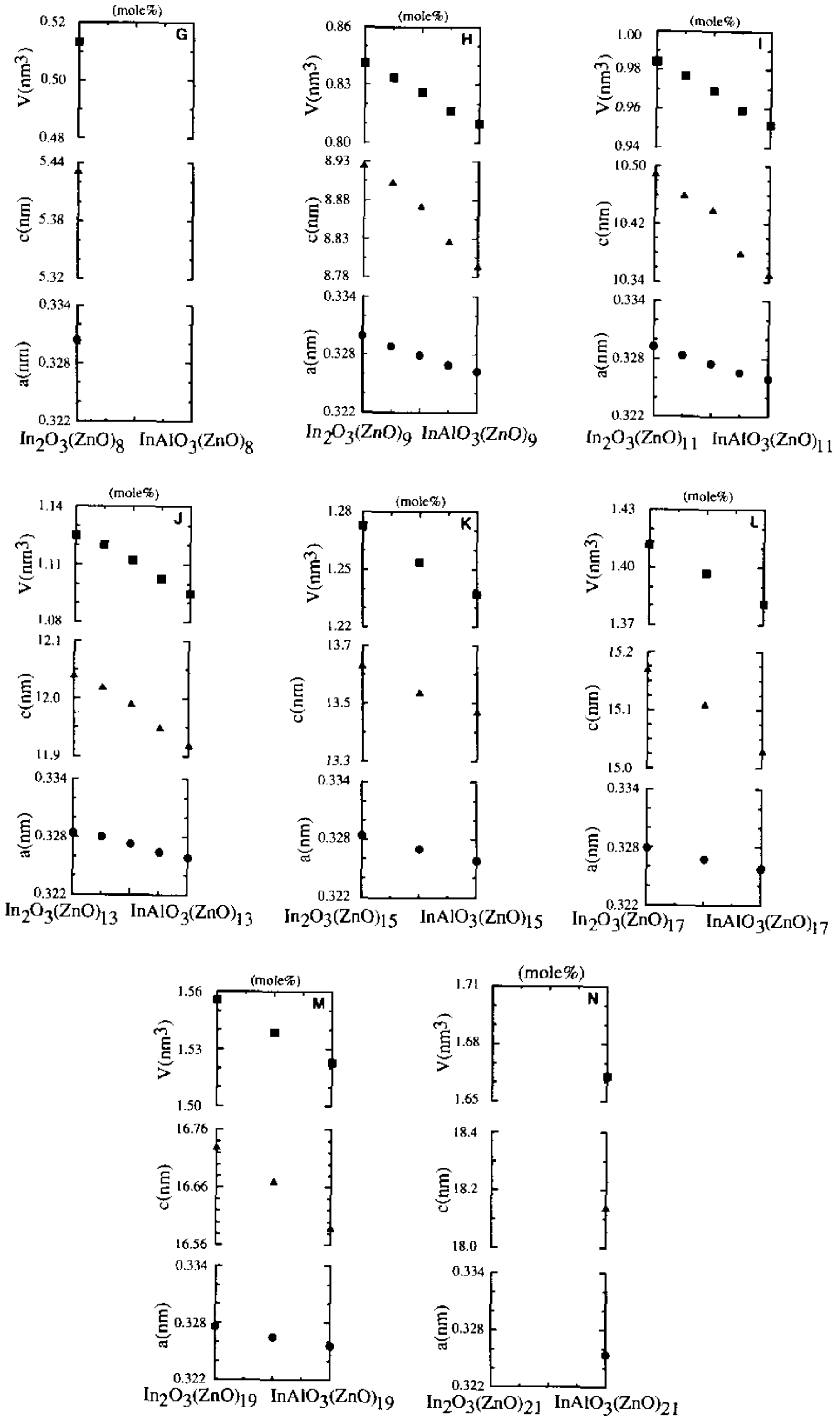

FIGURE 5—*Continued*

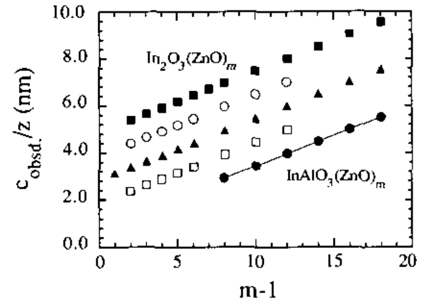

FIG. 6. The relation between $c_{obsd.}/Z$ and $(m-1)$ in $In_2O_3(ZnO)_m$, $In_{1.75}Al_{0.25}O_3(ZnO)_m$, $In_{1.5}Al_{0.5}O_3(ZnO)_m$, $In_{1.25}Al_{0.75}O_3(ZnO)_m$, or $InAlO_3(ZnO)_m$. $c_{obsd.}$ (nm): the observed hexagonal lattice constant; Z: numbers of a chemical formula unit per unit cell ($Z = 3$ for m = odd, $Z = 2$ for m = even). ■: $In_2O_3(ZnO)_m$, ○: $In_{1.75}Al_{0.25}O_3(ZnO)_m$, ▲: $In_{1.5}Al_{0.5}O_3(ZnO)_m$, □: $In_{1.25}Al_{0.75}O_3(ZnO)_m$, ●: $InAlO_3(ZnO)_m$.

of the In_2O_3 phase in equilibrium with Phase II, Phase III, or the spinel phase in the In_2O_3–Al_2ZnO_4–ZnO system, however, does not change. We conclude that the In_2O_3 phase has a solid solution range in the In_2O_3–Fe_2ZnO_4–ZnO and the In_2O_3–Ga_2ZnO_4–ZnO systems; however, no detectable solid solution of the In_2O_3 phase exists in the In_2O_3–Al_2ZnO_4–ZnO system. The Al(III) ion is too small to substitute for the In(III) ion with six coordination numbers in the In_2O_3phase.

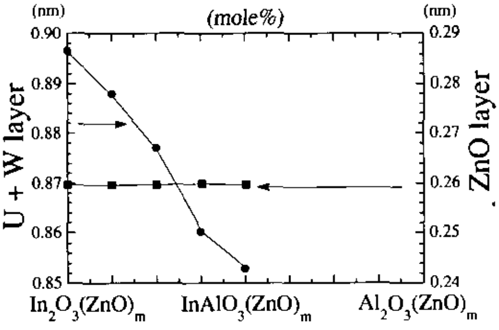

FIG. 7. The relation between the thickness of the ZnO layer or the $(U + W)$ layer in the $In_2O_3(ZnO)_m$–$InAlO_3(ZnO)_m$, in which U or W means as follows: U, $InO_{1.5}$; W, $(InZn)O_{2.5}$, $(In_{0.75}Al_{0.25}Zn)O_{2.5}$, $(In_{0.5}Al_{0.5}Zn)O_{2.5}$, $(In_{0.25}Al_{0.75}Zn)O_{2.5}$, or $(AlZn)O_{2.5}$ layer.

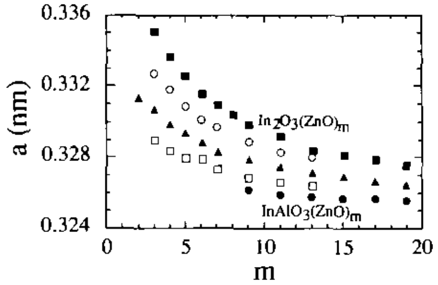

FIG. 8. The relation between a and m: ■: $In_2O_3(ZnO)_m$, ○: $In_{1.75}Al_{0.25}O_3(ZnO)_m$, ▲: $In_{1.5}Al_{0.5}O_3(ZnO)_m$, □: $In_{1.25}Al_{0.75}O_3(ZnO)_m$, ●: $InAlO_3(ZnO)_m$.

In the In_2O_3–Cr_2ZnO_4–ZnO system at 1350°C, there exist no $InCrO_3(ZnO)_m$ compounds; no solid solution phases in the ranges $In_2O_3(ZnO)_m$–"$InCrO_3(ZnO)_m$" are observed (*12*). We think that Cr(III), having a strong preference for the octahedral site in oxide compounds, cannot coexist with Zn(II) in a trigonal bipyramidal site. Trivalent cations such as In(III), Fe(III), Ga(III), and Al(III) can occupy a trigonal bipyramidal site in the $LuFeO_3(ZnO)_m$-type crystal structures. The ionic radii from In(III) to Al(III) with five coordination numbers changes widely (*13*); however, all of them are spherical.

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