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The Phase Relations in the In_2O_3–Ga_2ZnO_4–ZnO System at 1350°C

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The phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system at 1350°C are determined by a classical quenching method. In this system there exist an $(InGaO_3)_2ZnO$ phase with $Yb_2Fe_3O_7$-type structure and homologous phases with solid solution ranges $In_{1.33}Ga_{0.67}O_3(ZnO)$–$InGaO_3(ZnO)$–$In_{0.92}Ga_{1.08}O_3(ZnO)$, $In_{1.68}Ga_{0.32}O_3(ZnO)_2$–$InGaO_3(ZnO)_2$–$In_{0.68}Ga_{1.32}O_3(ZnO)_2$, $In_2O_3(ZnO)_3$–$InGaO_3(ZnO)_3$–$In_{0.54}Ga_{1.46}O_3(ZnO)_3$, $In_2O_3(ZnO)_4$–$InGaO_3(ZnO)_4$–$In_{0.46}Ga_{1.54}O_3(ZnO)_4$, $In_2O_3(ZnO)_5$–$InGaO_3(ZnO)_5$–$In_{1-x}Ga_{1+x}O_3(ZnO)_5$ $(0.68 \le x \le 0.72)$, $In_2O_3(ZnO)_6$–$InGaO_3(ZnO)_6$–$In_{1-x}Ga_{1+x}O_3(ZnO)_6$ $(0.68 \le x \le 0.79)$, $In_2O_3(ZnO)_7$–$InGaO_3(ZnO)_7$–$In_{1-x}Ga_{1+x}O_3(ZnO)_7$ $(0.70 \le x \le 0.74)$, $In_2O_3(ZnO)_8$–$InGaO_3(ZnO)_8$–$In_{1-x}Ga_{1+x}O_3(ZnO)_8$ $(0.60 \le x \le 0.68)$, $In_2O_3(ZnO)_9$–$InGaO_3(ZnO)_9$–$In_{1-x}Ga_{1+x}O_3(ZnO)_9$ $(0.56 \le x \le 0.72)$, $In_2O_3(ZnO)_{10}$–$InGaO_3(ZnO)_{10}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{10}$ $(0.47 \le x \le 0.67)$, $In_2O_3(ZnO)_{11}$–$InGaO_3(ZnO)_{11}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{11}$ $(0.57 \le x \le 0.64)$, $In_2O_3(ZnO)_{12}$–$InGaO_3(ZnO)_{12}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{12}$ $(x \le 0.64)$, and $In_2O_3(ZnO)_{13}$–$InGaO_3(ZnO)_{13}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{13}$ $(0.49 \le x \le 0.75)$ in which $InGaO_3(ZnO)_m$ $(m = 1–13)$ is isostructural with $InFeO_3(ZnO)_m$. ZnO has a solid solution range, $Zn_{1-x}Ga_{2x}O_{1+2x}$ $(x = 0–0.094)$ to the direction of Ga_2ZnO_4, and Ga_2ZnO_4 has a solid solution range, $Ga_{2-x}In_xZnO_4$ $(x = 0–0.128(4))$ to the direction of $InGaO_3(ZnO)$. A comparison between the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system and those in the In_2O_3–Fe_2ZnO_4–ZnO system is made, and the crystal chemical effects of Fe(III) and Ga(III) cations upon the phase relations in these systems are discussed.

Introduction

It is of importance for solid state scientists to know the relations between both the crystal stability and the structures of inorganic solid oxides and their constituent cation elements. So far, we have studied the phase relations in the In_2O_3–A_2BO_4–BO systems (A: Fe or Ga, B: Cu or Co) at elevated temperatures, and reported the relation between the crystal stability and structures of $InAO_3$ (BO) in these ternary systems and the components of both A_2O_3 and BO compounds (*1*). In a previous paper (*2*), we have reported the phase relations in the In_2O_3–Fe_2ZnO_4–ZnO system at 1350°C in which there were homologous phases with solid solution ranges, $In_{1+x}Fe_{1-x}O_3(ZnO)$–$InFeO_3(ZnO)$, $In_{1+x}Fe_{1-x}O_3(ZnO)_2$–$InFeO_3(ZnO)_2$–$In_{1-x}Fe_{1+x}O_3(ZnO)_2$, $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$In_{1-x}Fe_{1+x}O_3(ZnO)_m$ $(m = 3–11)$ and $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$Fe_2O_3(ZnO)_m$ $(m \ge 12)$ having layered structures. The crystal structural models of $In_2O_3(ZnO)_m$ and $InFeO_3(ZnO)_m$ were estimated by powder X-ray diffractometry and high resolution electron microscopy (*3–5*), and space groups of $InFeO_3(ZnO)_m$

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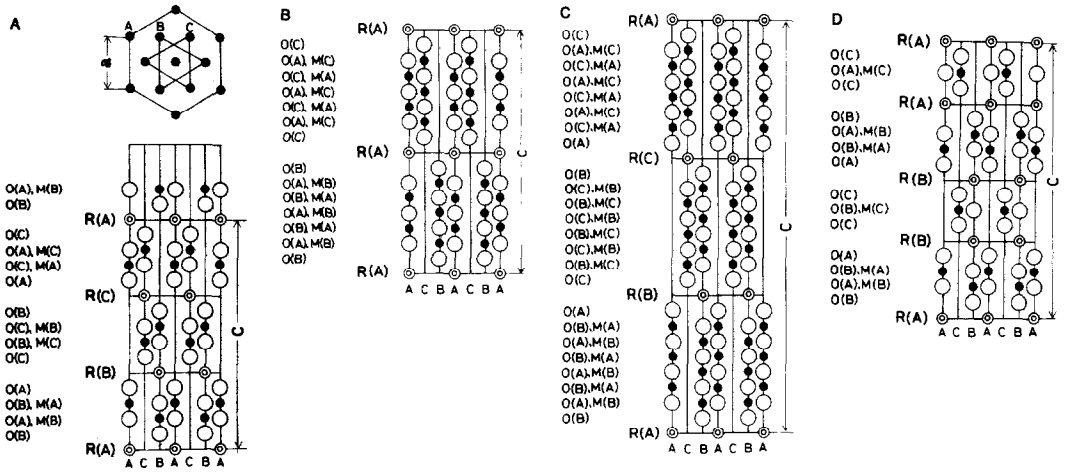

FIG. 1. The crystal structural models of $LuFeO_3(ZnO)$ in A, $LuFeO_3(ZnO)_4$ in B, $LuFeO_3(ZnO)_5$ in C, and $Yb_2Fe_3O_7$ in D: A, B, and C represent three kinds of triangular lattices. *M* sites are occupied by Fe and/or Zn ions for $LuFeO_3(ZnO)_m$, and Fe for $Yb_2Fe_3O_7$. ©, Lu or Yb ion; ●, *M* ion; ○, O ion.

(m = odd) and $InFeO_3(ZnO)_m$ (m = even) are $R\bar{3}m$ and $P6_3/mmc$, respectively. The structural analyses showing single crystal $YbFe_2O_4$ (*6*) and $LuFeO_3(ZnO)_m$ (m = 1, 4, 5, and 6) being isostructural with $InFeO_3(ZnO)_m$ were performed by Isobe *et al.* (*7, 8*), and their crystal structural models of $LuFeO_3(ZnO)_m$ (m = 1, 4, and 5) are shown in Figs. 1A, 1B, and 1C, respectively. In the present work, we report the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system at 1350°C which were determined by a classical quenching method, and compare the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system with those in the In_2O_3–Fe_2ZnO_4–ZnO system, and discuss the crystal chemical effects of Ga(III) and Fe(III) cations upon the phase relations in these systems.

Experimental

Experimental method and starting compounds except Ga_2O_3 powder have been described elsewhere (*2*). Ga_2O_3(99.99%) powder was heated at 900°C for 1 day in air prior to mixing the starting compounds. Analyses by X-ray powder and electron diffractometry and scanning electron microscopy (SEM) observations were applied for samples obtained. Although chemical reactions between the Pt tubes and the samples were checked visually, no detectable reactions were observed. Lattice constants were calculated by means of the least squares method.

Results and Discussion

1. *The Phase Relations in the In_2O_3–Ga_2ZnO_4–ZnO System at 1350°C*

Figure 2A shows the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system at 1350°C. The detailed phase relations in the vicinity of ZnO phase are shown in Fig. 2B. Mixing ratios of the starting compounds, heating periods, and phases obtained are given in Table I. In the In_2O_3–ZnO system there are $In_2O_3(ZnO)_m$ ($m \geq 3$) phases. Both the thermochemical stability and the crystal structures of these phases have been discussed in the literature (*2–4*). In the In_2O_3–Ga_2ZnO_4

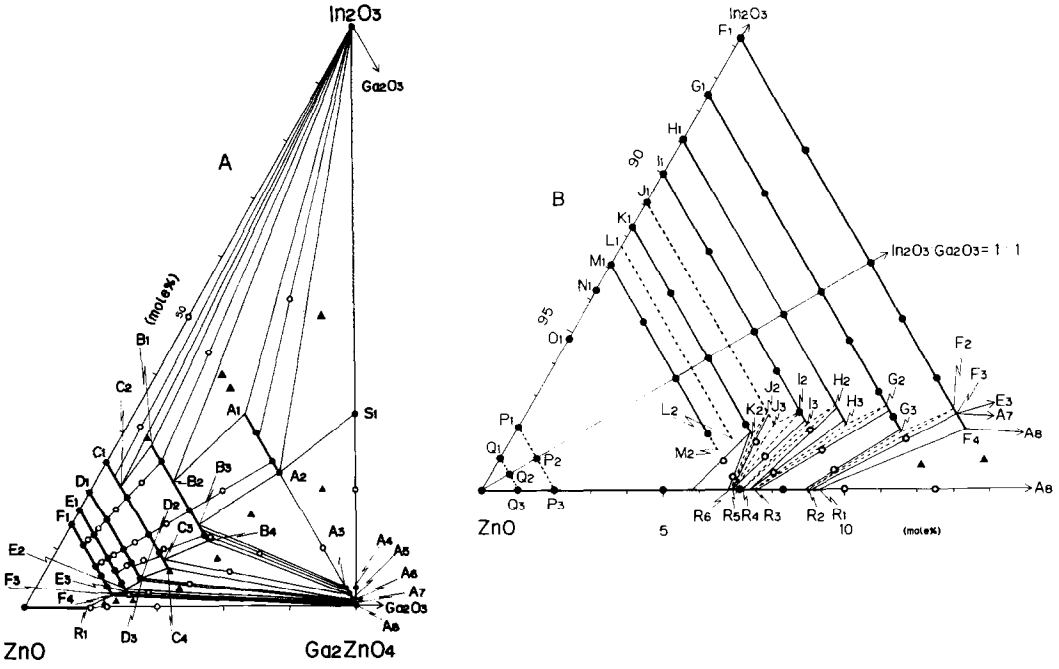

FIG. 2. The phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system at 1350°C. (p, q, r) indicates the composition (in mole fraction) of In_2O_3, Ga_2O_3, and ZnO. Symbols and numbers in the figures are as follows: A_1, (0.332, 0.168, 0.500); A_2, (0.230, 0.270, 0.500); A_3, (0.032, 0.468, 0.500); A_4, (0.018, 0.482, 0.500); A_5, (0.008, 0.492, 0.500); A_6, (0.006, 0.494, 0.500); A_7, (0.004, 0.496, 0.500); A_8, (0.000, 0.500, 0.500); B_1, (0.279, 0.054, 0.667); B_2, (0.215, 0.118, 0.667); B_3, (0.141, 0.192, 0.667); B_4, (0.113, 0.220, 0.667); C_1, (0.250, 0.000, 0.750); C_2, (0.207, 0.043, 0.750); C_3, (0.082, 0.168, 0.750); C_4, (0.067, 0.183, 0.750); D_1, (0.200, 0.000, 0.800); D_2, (0.050, 0.150, 0.800); D_3, (0.046, 0.154, 0.800); E_1, (0.167, 0.000, 0.833); E_2, (0.031, 0.136, 0.833); E_3, [(0.027, 0.140, 0.833)–(0.023, 0.144, 0.833)]; F_1, (0.143, 0.000, 0.857); F_2, [(0.029, 0.114, 0.857)–(0.024, 0.119, 0.857)]; F_3, [(0.029, 0.114, 0.857)–(0.024, 0.119, 0.857)]; F_4, [(0.023, 0.120, 0.857)–(0.015, 0.128, 0.857)]; G_1, (0.125, 0.000, 0.875); G_2, [(0.031, 0.094, 0.875)–(0.027, 0.098, 0.875)]; G_3, [(0.019, 0.106, 0.875)–(0.016, 0.109, 0.875)]; H_1, (0.111, 0.000, 0.889); H_2, [(0.031, 0.080, 0.889)–(0.026, 0.085, 0.889)]; H_3, [(0.022, 0.089, 0.889)–(0.018, 0.093, 0.889)]; I_1, (0.100, 0.000, 0.900); I_2, [(0.034, 0.066, 0.900)–(0.022, 0.078, 0.900)]; I_3, [(0.022, 0.078, 0.900)–(0.019, 0.081, 0.900)]; J_1, (0.091, 0.000, 0.909); J_2, [(0.028, 0.063, 0.909)–(0.024, 0.067, 0.909)]; J_3, [(0.024, 0.067, 0.909)–(0.015, 0.076, 0.909)]; K_1, (0.083, 0.000, 0.917); K_2, [(0.018, 0.065, 0.917)–(0.015, 0.068, 0.917)]; L_1, (0.077, 0.000, 0.923); L_2, [(0.038, 0.038, 0.924)–(0.014, 0.063, 0.923)]; M_1, (0.071, 0.000, 0.929); M_2, [(0.018, 0.053, 0.929)–(0.009, 0.062, 0.929)]; N_1, (0.063, 0.000, 0.937); O_1, (0.048, 0.000, 0.952); P_1, (0.020, 0.000, 0.980); P_2, (0.010, 0.010, 0.980); P_3, (0.000, 0.020, 0.980); Q_1, (0.010, 0.000, 0.990); Q_2, (0.005, 0.005, 0.990); Q_3, (0.000, 0.010, 0.990); R_1, (0.000, 0.093, 0.907); R_2, [(0.000, 0.091, 0.909)–(0.000, 0.089, 0.911)]; R_3, [(0.000, 0.076, 0.924)–(0.000, 0.074, 0.926)]; R_4, [(0.000, 0.074, 0.926)–(0.000, 0.069, 0.931)]; R_5, (0.000, 0.069, 0.931); R_6, [(0.000, 0.069, 0.931)–(0.000, 0.068, 0.932)]; S_1, (0.333, 0.333, 0.333).

system, there exists one binary phase, $(InGaO_3)_2ZnO$ (*9*), with $Yb_2Fe_3O_7$-type crystal structure (*10*) [See Fig. 1D.], and the ranges of solid solutions of In_2O_3 were observed for the volume changes of the unit cell. The lattice constants of the In_2O_3 phase, which is in equilibrium with various phases, are shown in Fig. 3. In the Ga_2ZnO_4–ZnO system, we concluded, there existed no binary compound, but a solid solution of the ZnO

phase, $Zn_{1-x}Ga_{2x}O_{1+2x}$ (x = 0–0.093) was detected. The ZnO phase (at x = 0) has a wurtzite structure (*11*), but the crystal structure of the solid solution containing Ga_2O_3 distorts from the wurtzite structure to a structure with a lower symmetry with increase in x. (Hereafter, this phase will be called the distorted wurtzite phase.) The relation between the Bragg's angle corresponding to $2\theta°$ of the 002 reflection of wurtzite structure (using Cu$K\alpha$ radiation) and Ga_2O_3 concentration in the distorted wurtzite phase is given in Fig. 4. Since the 002 diffraction peak of wurtzite structure does not split into two or more peaks in the distorted wurtzite phase, we could choose this diffraction angle as a "standard figure" for determining the solid solution range of the distorted wurtzite phase.

X-ray powder diffraction data for the phase $Zn_{1-x}Ga_{2x}O_{1+2x}$ (x = 0.093) which coexists with Ga_2ZnO_4 is shown in Fig. 5 and Table II. Comparing with ZnO (wurtzite structure) in Fig. 5, we could easily conclude that this phase has a distorted wurtzite structure. The structure of the distorted wurtzite is rather complicated and no crystal structure analysis for this phase was performed; however, we can reasonably consider that the cations of both Zn(II) and Ga(III) should occupy the tetrahedral site in this distorted wurtzite phase. On the other hand, near the ZnO phase in the Fe_2O_3–ZnO system at 1350°C there exists $Fe_2O_3(ZnO)_m$ ($m \geq 12$) having $InFeO_3(ZnO)_m$-type structures in which half of the Fe ions are considered to be in an octahedral site formed by oxygen ions (*2*). Isobe reports that the crystal system of $Fe_2O_3(ZnO)_9$ is slightly deformed from rhombohedral to monoclinic (*15*).

No solid solution of the spinel phase to the direction of the distorted wurtzite phase existed, since no volume difference of the unit cells was detected between stoichiometric Ga_2ZnO_4 in a single phase state and that in equilibrium with the distorted wurtzite phase. The lattice constant of Ga_2ZnO_4 is a = 0.8331(1) (nm) [JCPDS card No. 38-1240 shows a = 0.83349(1) (nm)]. Our main purpose is in the area of the layered compounds, so we did not investigate the details of the spinel phase region so intensively as in the layered compounds area.

In the ternary system In_2O_3–Ga_2ZnO_4–ZnO, there exist $In_{1.33}Ga_{0.67}O_3(ZnO)$–$InGaO_3(ZnO)$–$In_{0.92}Ga_{1.08}O_3(ZnO)$, $In_{1.68}Ga_{0.32}O_3(ZnO)_2$–$InGaO_3(ZnO)_2$–$In_{0.68}Ga_{1.32}O_3(ZnO)_2$, $In_2O_3(ZnO)_3$–$InGaO_3(ZnO)_3$–$In_{0.54}Ga_{1.46}O_3(ZnO)_3$, $In_2O_3(ZnO)_4$–$InGaO_3(ZnO)_4$–$In_{0.46}Ga_{1.54}O_3(ZnO)_4$, $In_2O_3(ZnO)_5$–$InGaO_3(ZnO)_5$–$In_{1-x}Ga_{1+x}O_3(ZnO)_5$ ($0.68 \leq x \leq 0.72$), $In_2O_3(ZnO)_6$–$InGaO_3(ZnO)_6$–$In_{1-x}Ga_{1+x}O_3(ZnO)_6$ ($0.68 \leq x \leq 0.79$), $In_2O_3(ZnO)_7$–$InGaO_3(ZnO)_7$–$In_{1-x}Ga_{1+x}O_3(ZnO)_7$ ($0.70 \leq x \leq 0.74$), $In_2O_3(ZnO)_8$–$InGaO_3(ZnO)_8$–$In_{1-x}Ga_{1+x}O_3(ZnO)_8$ ($0.60 \leq x \leq 0.68$), $In_2O_3(ZnO)_9$–$InGaO_3(ZnO)_9$–$In_{1-x}Ga_{1+x}O_3(ZnO)_9$ ($0.56 \leq x \leq 0.72$), $In_2O_3(ZnO)_{10}$–$InGaO_3(ZnO)_{10}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{10}$ ($0.47 \leq x \leq 0.67$), $In_2O_3(ZnO)_{11}$–$InGaO_3(ZnO)_{11}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{11}$ ($0.57 \leq x \leq 0.64$), $In_2O_3(ZnO)_{12}$–$InGaO_3(ZnO)_{12}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{12}$ ($x \leq 0.64$), $In_2O_3(ZnO)_{13}$–$InGaO_3(ZnO)_{13}$–$In_{1-x}Ga_{1+x}O_3(ZnO)_{13}$ ($0.49 \leq x \leq 0.75$), in which $InGaO_3(ZnO)_m$ (m = 1–13) is isostructural with $InFeO_3(ZnO)_m$. [Hereafter, the phases of $InGaO_3(ZnO)$, $InGaO_3(ZnO)_2$, . . . will be defined as Phase I, Phase II, . . .] The solid solution ranges and lattice constants of $(InGaO_3)_2ZnO$, Phase I, Phase II . . . Phase XIII are listed in Table III. The lattice constants of $(InGaO_3)_2ZnO$ or $InGaO_3(ZnO)_m$ indicate that they are actually identical to the previously published data within experimental errors (*5, 9*). In a process in which we established the present phase relations, we recognized the following items:

(1) the reaction rate in the formation of $InGaO_3(ZnO)_m$ with m = odd from In_2O_3, Ga_2O_3, and ZnO powders was faster than that in the phase with m = even;

TABLE I

MIXING RATIO OF THE STARTING COMPOUNDS (In_2O_3, Ga_2O_3, and ZnO), HEATING PERIOD, AND PHASES OBTAINED IN THE In_2O_3–Ga_2ZnO_4–ZnO SYSTEM AT 1350°C

In_2O_3	Ga_2O_3	ZnO	Days	Phases	a(nm)	c(nm)	In_2O_3	Ga_2O_3	ZnO	Days	Phases	a(nm)	c(nm)
1	1	1	3 + 3	$(InGaO_3)_2(ZnO)$	0.3306(1)	2.946(1)	1	0	1	3 + 3	In_2O_3	1.011(1)	
											III	0.3350(1)	4.246(1)
50	20	30	3 + 3	In_2O_3	1.006(1)								
				I	0.3289(1)	2.599(1)	3	2	5	3	I	0.3316(1)	2.626(1)
				$(InGaO_3)_2(ZnO)$	0.3306(1)	2.946(1)							
							1	1	2	3 + 3	I	0.3296(1)	2.602(1)
2	2	3	3 + 4	In_2O_3	*		23	27	50	3 + 4	I	0.3286(1)	2.601(1)
				I	0.3289(1)	2.602(1)							
				$(InGaO_3)_2(ZnO)$	0.3308(1)	2.948(1)	1	1	3	3 + 3	I	0.3296(1)	2.607(1)
											II	0.3286(1)	2.252(1)
19	5	12	3 + 4	In_2O_3	1.009(1)								
				I	0.3310(1)	2.620(1)	3	1	8	4 + 4	II	0.3331(1)	2.285(1)
3	1	4	4 + 3	In_2O_3	1.011(1)		1	1	4	3 + 4	II	0.3292(1)	2.251(1)
				I	0.3328(1)	2.644(1)							
				II	0.3315(1)	2.270(1)	3	5	16	3 + 4	II	0.3264(1)	2.260(1)
4	1	5	3 + 3	In_2O_3	1.010(1)		3	1	10	4 + 4	II	0.3329(1)	2.285(1)
				I	0.3325(1)	2.643(1)					III	0.3318(1)	4.199(1)
				II	0.3314(1)	2.269(1)	1	1	5	3 + 3	II	0.3290(1)	2.253(1)
											III	0.3284(1)	4.152(1)
7	1	8	3 + 4	In_2O_3	1.011(1)								
				II	0.3330(1)	2.285(1)	10	16	74	3 + 3	II	0.3264(1)	2.257(1)
											III	0.3263(1)	4.167(1)
7	1	16	3 + 3	In_2O_3	1.011(1)								
				II	0.3343(1)	2.297(1)	1	0	3	3 + 7	III	0.3351(1)	4.248(1)
				III	0.3330(1)	4.218(1)							
							3	1	12	3	III	0.3320(1)	4.203(1)
15	1	32	3 + 3	In_2O_3	1.011(1)								
				III	0.3338(1)	4.233(1)	1	1	6	4	III	0.3288(1)	4.156(1)
3	5	24	3	III	0.3263(1)	4.172(1)	1	1	10	3	V	0.3280(1)	5.713(1)

3	1	14	4 + 4	III	0.3318(1)	4.202(1)	3	5	40	3	V	0.3261(1)	5.726(1)
				IV	0.3310(1)	3.318(1)							
							1	3	20	3 + 3	V	0.3241(1)	5.748(1)
1	1*	7	4 + 3	III	0.3286(1)	4.157(1)							
				IV	0.3283(1)	3.289(1)	3	1	22	3 + 4	V	0.3300(1)	5.760(1)
											VI	0.3296(1)	4.358(1)
8	14	78	3 + 3	III	0.3259(1)	4.171(1)							
				IV	0.3260(1)	3.299(1)	1	1	11	4 + 3	V	0.3277(1)	5.709(1)
											VI	0.3275(2)	4.317(3)
1	0	4	4	IV	0.3337(1)	3.353(1)							
							1	0	6	3	VI	0.3316(1)	4.394(1)
3	1	16	4	IV	0.3311(1)	3.322(1)							
							3	1	24	4 + 3	VI	0.3296(1)	4.356(1)
1	1	8	3	IV	0.3284(1)	3.289(1)							
							1	1	12	4 + 3	VI	0.3277(2)	4.299(4)
3	5	32	4	IV	0.3263(1)	3.299(1)							
							3	5	48	3 + 4 + 5	VI	0.3259(1)	4.332(2)
1	3	16	3 + 3	IV	0.3241(1)	3.312(1)							
							1	3	24	4 + 3 + 3 + 5	VI	0.3241(1)	4.350(2)
3	1	18	3 + 4	IV	0.3309(1)	3.321(1)							
				V	0.3303(1)	5.758(1)	1	15	80	5 + 5 + 5	VI	0.3223(2)	4.345(3)
											D-ZnO	*	*
1	1	9	3 + 3	IV	0.3283(1)	3.289(1)					spinel	0.8329(1)	
				V	0.3280(1)	5.708(1)							
							1	15	96	5 + 7	VI	0.3229(1)	4.355(2)
7	12	81	3 + 3	IV	0.3260(1)	3.299(1)					D-ZnO	*	*
				V	0.3259(1)	5.720(2)					spinel	0.8333(1)	
1	0	5	3	V	0.3326(1)	5.810(1)	1	15	112	5 + 5 + 5	VI	0.3224(2)	4.347(4)
											D-ZnO	*	*
3	1	20	3	V	0.3303(1)	5.762(1)					spinel	0.8329(1)	
							3	1	36	3 + 4	IX	0.3285(1)	8.882(1)
1	0	7	3	VII	0.3310(1)	7.370(1)							
							1	1	18	3 + 3 + 3	IX	0.3270(1)	8.828(2)
3	1	28	3	VII	0.3292(1)	7.323(1)							
							3	5	72	3 + 4	IX	0.3256(1)	8.822(5)

Continued

TABLE I—*Continued*

In_2O_3	Ga_2O_3	ZnO	Days	Phases	*a*(nm)	*c*(nm)	In_2O_3	Ga_2O_3	ZnO	Days	Phases	*a*(nm)	*c*(nm)
1	1	14	4	VII	0.3276(1)	7.279(1)							
							1	3	36	4 + 4 + 6	IX	0.3244(2)	8.865(8)
3	5	56	4 + 4 + 4	VII	0.3257(1)	7.280(1)							
							0	1	9	4 + 3 + 4 + 4	D–ZnO	*	*
1	3	28	3 + 4	VII	0.3243(1)	7.309(3)					spinel	*	
3	13	112	5 + 5 + 5	VII	0.3230(1)	7.300(3)	1	0	10	3 + 3 + 7	X	*	6.545(57)
1	1	15	4 + 4	VII	0.3274(1)	7.273(1)	3	13	176	5 + 5 + 5	X	0.3235(2)	6.412(6)
				VIII	*	6.878					D-ZnO	*	*
1	7	72	4 + 3 + 4 + 7	VII	0.3235(1)	7.308(3)	1	0	11	3	XI	0.3292(1)	10.49(1)
				D-ZnO	*	*							
							3	1	44	3 + 4 + 6	XI	0.3276(1)	10.43(1)
1	15	144	5 + 5 + 5	VII	0.3227(3)	7.307(9)							
				D-ZnO	*	*	1	1	22	3 + 4 + 3	XI	0.3266(1)	10.38(1)
1	0	8	3 + 3 + 3	VIII	0.3304(1)	5.432(1)	1	3	44	4 + 3 + 7	XI	0.3245(1)	10.43(1)
3	1	32	4 + 3	VIII	*	*	1	7	88	4 + 7	IX	0.3240(2)	8.860(7)
											D-ZnO	*	*
1	1	16	4 + 3 + 4 + 3	VIII	*	*							
3	13	144	4 + 4 + 7 + 6	VIII	0.3238(1)	5.384(3)	1	15	208	5 + 5 + 5	XI	0.3240(3)	10.46(2)
				D-ZnO	*	*					D-ZnO	*	*
1	15	176	5 + 5 + 5	VIII	0.3238(3)	5.379(10)	1	7	104	5 + 5 + 5	XI	0.3240(2)	10.42(1)
				D-ZnO	*	*					D-ZnO	*	*
1	0	9	3	IX	0.3299(1)	8.926(1)	0	1	11	4 + 3 + 4 + 7 + 6	D-ZnO	*	*
1	0	13	3 + 7 + 3	XIII	0.3284(1)	12.04(1)							
							1	49	50	3 + 4	spinel	0.8340(1)	
3	1	52	4 + 4	XIII	0.3270(2)	12.00(1)							
							0	1	1	3 + 3	spinel	0.8331(1)	
1	1	26	4 + 4	XIII	0.3258(1)	11.92(1)							
							16	26	58	3 + 3	I	0.3284(1)	2.604(1)
1	3	52	3 + 4 + 7	XIII	0.3245(1)	11.99(1)					II	0.3276(1)	2.255(1)
											spinel	0.8370(1)	
0	1	13	3 + 4 + 7	D-ZnO	*	*							
							9	31	60	4 + 4	II	0.3270(1)	2.258(1)
1	0	15	7 + 7	XV	0.3284(1)	13.63(1)					spinel	0.8364(1)	

0	1	19	4 + 4 + 3	D-ZnO	*	*	12	22	66	3 + 3	II	0.3264(1)	2.261(1)
											spinel	0.8358(1)	
1	0	20[a]	1	XX	0.3271(1)	11.64(1)	1	3	8	3 + 3	II	0.3258(1)	2.262(1)
1	2	2	5 + 4	$(InGaO_3)_2(ZnO)$	0.3307(1)	2.947(1)					III	0.3257(1)	4.173(1)
				spinel	0.8363(1)						spinel	0.8350(1)	
							6	28	66	3 + 3	III	0.3257(1)	4.175(1)
20	35	45	3 + 3	I	0.3288(1)	2.600(1)					spinel	0.8352(1)	
				$(InGaO_3)_2(ZnO)$	0.3305(1)	2.946(1)							
				spinel	0.8361(1)		1	3	12	4 + 3 + 5	III	0.3242(1)	4.184(1)
											IV	0.3234(2)	3.308(2)
6	97	97	3 + 3 + 3	spinel	0.8348(1)						spinel	0.8339(1)	
							4	23	73	4 + 3	IV	0.3241(1)	3.311(1)
1	50	49	4	spinel	0.8337(1)						spinel	0.8340(1)	
1	4	5	3 + 3	I	0.3286(1)	2.601(1)							
				spinel	0.8366(1)		1	7	24	3 + 4 + 7	IV	0.3234(3)	3.316(4)
											V	0.3235(1)	5.753(2)
											spinel	0.8337(1)	
3	47	50	4	spinel	0.8365(1)								
							1	7	32	4 + 4 + 3 + 4	V	0.3229(1)	5.761(1)
2	48	50	3	spinel	0.8351(1)						spinel	0.8334(1)	
1	7	40	4 + 3	VI	0.3231(1)	4.360(1)							
				spinel	0.8335(1)								
1	7	56	3 + 4 + 3	VI	0.3231(2)	4.356(4)							
				D-ZnO	*	*							
0	1	4	4 + 3 + 3	D-ZnO	*	*							
				spinel	0.8332(1)								
0	1	7	7 + 6	D-ZnO	*	*							
				spinel	0.8332(1)								
0	0	1	3	ZnO	0.3248(1)	0.5204(1)							

Note. The lattice constants replaced with asterisks could not be determined.
[a] The mixture was heated at 1550°C.

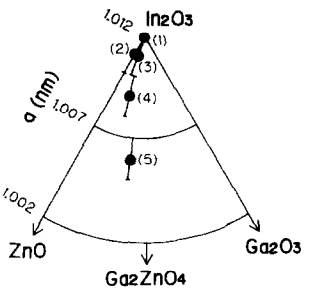

FIG. 3. The lattice constant of the In_2O_3 phase which is in equilibrium with various phases: (1) In_2O_3 in a single phase state (cf. JCPDS: Card No. 6-416) (2) Phase III, (3) Phase I and Phase II, (4) Phase I, (5) Phase I and $(InGaO_3)_2ZnO$.

(2) the reaction rate in the formation of the phase in the part between $In_2O_3(ZnO)_m$ and $InGaO_3(ZnO)_m$ is faster than that in the part between $InGaO_3(ZnO)_m$ and $In_{1-x}Ga_{1+x}O_3(ZnO)_m$;

(3) the reaction rate in forming $InGaO_3(ZnO)_m$ gets slower with increasing m in $InGaO_3(ZnO)_m$. We stopped our experiment at $m = 13$; however, it is certain that $InGaO_3(ZnO)_m$ ($m \geq 14$) will be formed if we heat the starting mixtures for a much longer period than in the present study. These three phenomena mentioned above could be observed in the In_2O_3–Fe_2ZnO_4–ZnO system also (2).

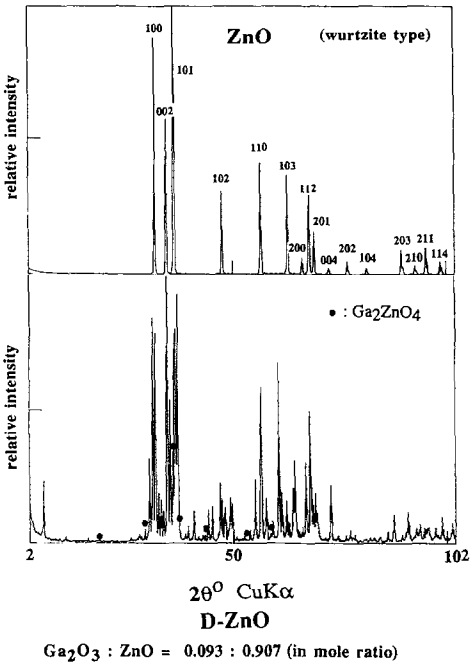

FIG. 5. X-ray powder diffraction data for a distorted wurtzite phase, $Zn_{1-x}Ga_{2x}O_{1+2x}$ ($x = 0.093$) which coexists with Ga_2ZnO_4 (spinel).

In the following we describe the characteristic features in the phase relations in Figs. 2A and 2B. In general, the features in

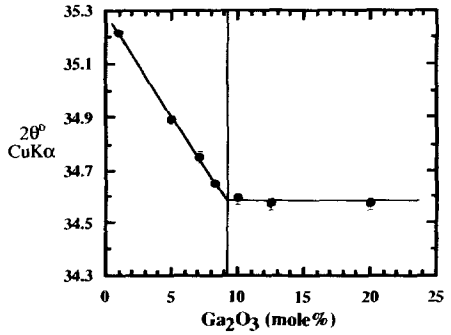

FIG. 4. The relation between the Bragg's angle, 2θ (°) of the 002 reflection of ZnO with wurtzite structure, and Ga_2O_3 concentration (mole%) in the distorted wurtzite phase (using Cu$K\alpha$ radiation).

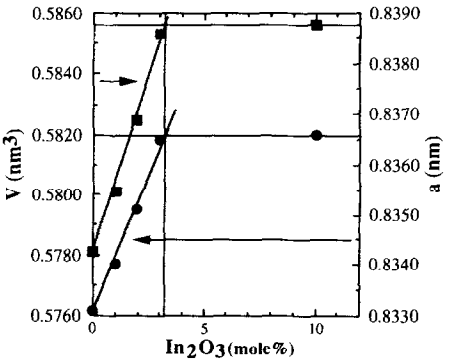

FIG. 6. The relation between the lattice constant and the concentration of In_2O_3 (mole%) in the spinel phase at 1350°C.

TABLE II

d-SPACINGS AND RELATIVE INTENSITIES OF "DISTORTED ZnO" PHASE AND WURTZITE(ZnO)

ZnO JCPDS No. 36-1451			D–ZnO (mol%) Ga_2O_3 : ZnO = 0.093 : 0.907		ZnO JCPDS No. 36-1451			D–ZnO (mol%) Ga_2O_3 : ZnO = 0.093 : 0.907	
hkl	*d*(nm)	Intensity (%)	*d*(nm)	Intensity (%)	*hkl*	*d*(nm)	Intensity (%)	*d*(nm)	Intensity (%)
			1.6692	3				0.1678	<1
			0.9829	<1				0.1666	5
			0.8371	<1				0.1632	10
			0.5583	<1	110	0.16247	32	0.1625	12
			0.3429	<1				0.1597	3
			0.3264	<1				0.1570	<1
			0.3219	<1				0.1561	2
			0.3193	<1				0.1526	15
			0.3148	<1				0.1511	4
			0.3056	1	103	0.14771	29	0.1485	3
			0.2994	<1				0.1454	4
			0.2993	<1				0.1446	6
			0.2970	1				0.1436	1
			0.2911	2				0.1423	<1
100	0.28140	57	0.2869	16	200	0.14072	4	0.1395	6
			0.2829	9	112	0.13782	23	0.1377	10
			0.2819	13				0.1373	2
			0.2772	1				0.1369	3
			0.2752	3	201	0.13583	11	0.1364	3
			0.2707	3				0.1356	4
			0.2666	2				0.1348	2
002	0.26030	44	0.2593	100	004	0.13017	2	0.1297	5
			0.2548	10	202	0.12380	4	0.1245	<1
			0.2499	6				0.1231	1
101	0.24759	100	0.2479	15				0.1223	<1
			0.2462	16				0.1217	<1
			0.2446	6	104	0.11816	1	0.1173	<1
			0.2431	18				0.1163	<1
			0.2318	<1				0.1150	<1
			0.2286	1				0.1146	<1
			0.2211	2				0.1127	1
			0.2155	<1				0.1112	2
			0.2108	<1	203	0.10931	7	0.1080	2
			0.2052	3				0.1067	<1
			0.2011	3	210	0.10638	3	0.1063	1
			0.1956	<1				0.1061	<1
			0.1936	5				0.1057	1
102	0.19111	23	0.1920	3				0.1048	1
			0.1897	3	211	0.10423	6	0.1045	1
			0.1890	2				0.1042	1
			0.1865	1				0.1041	1
			0.1858	1				0.1038	1
			0.1848	3				0.1026	1
			0.1833	3	114	0.10159	4	0.1014	2
			0.1822	1				0.1005	<1
			0.1797	<1				0.0997	1
			0.1739	<1					

TABLE III

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

	Kasper (3)		Cannard and Tilley (4)		Kimizuka *et al.* (5)	Present work			
Phase	Temperature (°C) Heating period (hr) Crystal system	Lattice constants (nm)	Temperature (°C) Heating period (day)	Lattice constant (nm)	Temperature (°C) Heating period (day) Space group	Lattice constants (nm)	$In_2O_3(ZnO)_m$ lattice constants (nm)	$InGaO_3(ZnO)_m$ lattice constants (nm)	$In_{1-x}Ga_{1+x}O_3(ZnO)_m$ lattice constants (nm)
$(InGaO_3)_2(ZnO)$					1450 6 $P6_3/mmc$	$(InGaO_3)_2(ZnO)$[a] a = 0.3308 c = 2.949		$(InGaO_3)_2(ZnO)$ a = 0.3306(1) c = 2.946(1)	
I					1450 1 $R\bar{3}m$	$InGaO_3(ZnO)$ a = 0.3295(1) c = 2.607(1)	$In_{1+x}Ga_{1-x}O_3(ZnO)$ (x = 0.33) a = 0.3328(1) c = 2.644(1)	$InGaO_3(ZnO)$ a = 0.3296(1) c = 2.602(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)$ (x = 0.08) a = 0.3286(1) c = 2.601(1)
II	1550 2 Hex.	$In_2O_3(ZnO)_2$ a = 0.3376(1) c = 2.3154(10)			1300 5 $P6_3/mmc$	$InGaO_3(ZnO)_2$ a = 0.3292(1) c = 2.252(1)	$In_{1+x}Ga_{1-x}O_3(ZnO)_2$ (x = 0.68) a = 0.3343(1) c = 2.297(1)	$InGaO_3(ZnO)_2$ a = 0.3292(1) c = 2.251(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_2$ (x = 0.32) a = 0.3258(1) c = 2.262(1)
III	1200 12 Rhom.	$In_2O_3(ZnO)_3$ a = 0.3355(1) c = 4.2515(20)			1450 4 $R\bar{3}m$	$InGaO_3(ZnO)_3$ a = 0.3288(1) c = 4.156(1)	$In_2O_3(ZnO)_3$[b] a = 0.3351(1) c = 4.248(1)	$InGaO_3(ZnO)_3$ a = 0.3288(1) c = 4.156(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_3$ (x = 0.46) a = 0.3242(1) c = 4.184(1)
IV	1200 50 Hex.	$In_2O_3(ZnO)_4$ a = 0.3339(2) c = 3.352(2)	1100 3	$In_2O_3(ZnO)_4$	1450 6 $P6_3/mmc$	$InGaO_3(ZnO)_4$ a = 0.3284(1) c = 3.289(1)	$In_2O_3(ZnO)_4$[b] a = 0.3337(1) c = 3.353(1)	$InGaO_3(ZnO)_4$ a = 0.3284(1) c = 3.289(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_4$ (x = 0.54) a = 0.3234(3) c = 3.316(4)
V	1050 100 Rhom.	$In_2O_3(ZnO)_5$ a = 0.3327(1) c = 5.8114(20)	1100 3	$In_2O_3(ZnO)_5$	1450 8 $R\bar{3}m$	$InGaO_3(ZnO)_5$ a = 0.3280(1) c = 5.714(1)	$In_2O_3(ZnO)_5$[b] a = 0.3326(1) c = 5.810(1)	$InGaO_3(ZnO)_5$ a = 0.3280(1) c = 5.713(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_5$ ($0.68 < x < 0.72$) a =[c] c =[c]

VI			1100 3	$In_2O_3(ZnO)_6$	1450 10 $P6_3/mmc$	$InGaO_3(ZnO)_6$ a = 0.3275(1) c = 4.326(1)	$In_2O_3(ZnO)_6$[b] a = 0.3316(1) c = 4.394(1)	$InGaO_3(ZnO)_6$ a = 0.3277(2) c = 4.299(4)	$In_{1-x}Ga_{1+x}O_3(ZnO)_6$ (0.68 < x < 0.79) a = 0.3229(1) c = 4.355(2)
VII	1310 2 Rhom.	$In_2O_3(ZnO)_7$ a = 0.3313(1) c = 7.362(4)	1100 3	$In_2O_3(ZnO)_7$	1450 2 $R\bar{3}m$	$InGaO_3(ZnO)_7$ a = 0.3274(1) c = 7.274(1)	$In_2O_3(ZnO)_7$[b] a = 0.3310(1) c = 7.370(1)	$InGaO_3(ZnO)_7$ a = 0.3276(1) c = 7.279(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_7$ (0.70 < x < 0.74) a =[c] c =[c]
VIII							$In_2O_3(ZnO)_8$[b] a = 0.3304(1) c = 5.432(1)	$InGaO_3(ZnO)_8$ a =[c] c =[c]	$In_{1-x}Ga_{1+x}O_3(ZnO)_8$ (0.60 < x < 0.68) a =[c] c =[c]
IX			1100 7	$In_2O_3(ZnO)_9$			$In_2O_3(ZnO)_9$[b] a = 0.3299(1) c = 8.926(1)	$InGaO_3(ZnO)_9$ a = 0.3270(1) c = 8.828(2)	$In_{1-x}Ga_{1+x}O_3(ZnO)_9$ (0.56 < x < 0.72) a =[c] c =[c]
X									$In_{1-x}Ga_{1+x}O_3(ZnO)_{10}$ (0.47 < x < 0.67) a =[c] c =[c]
XI			1100 3	$In_2O_3(ZnO)_{11}$			$In_2O_3(ZnO)_{11}$[b] a = 0.3292(1) c = 10.49(1)	$InGaO_3(ZnO)_{11}$ a = 0.3266(1) c = 10.38(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_{11}$ (0.57 < x < 0.64) a =[c] c =[c]
XII									$In_{1-x}Ga_{1+x}O_3(ZnO)_{12}$ (0 < x < 0.64) a =[c] c =[c]
XIII							$In_2O_3(ZnO)_{13}$[b] a = 0.3284(1) c = 12.04(1)	$InGaO_3(ZnO)_{13}$ a = 0.3258(1) c = 11.92(1)	$In_{1-x}Ga_{1+x}O_3(ZnO)_{13}$ (0.49 < x < 0.75) a =[c] c =[c]

Note. All of the lattice constants are given in the hexagonal crystal system. Hex., hexagonal; Rhom., rhombic.

[a] Ref. (*9*).

[b] The lattice constants of $In_2O_3(ZnO)_m$ ($m > 3$) are cited from Ref. (*2*).

[c] The lattice constants could not be determined.

the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system are very similar to those in the In_2O_3–Fe_2ZnO_4–ZnO system except the existences of the $(InGaO_3)_2ZnO$ phase and the region of a distorted wurtzite phase. (1) In_2O_3 is in equilibrium with $(InGaO_3)_2ZnO$, Phase I, Phase II, and Phase III. (2) $(InGaO_3)_2ZnO$ is in equilibrium with In_2O_3, spinel, and Phase I. (3) The spinel phase is in equilibrium with $(InGaO_3)_2ZnO$, Phase I, Phase II, Phase III, Phase IV, Phase V, and Phase VI and the distorted wurtzite phase. The solid solution range of the spinel phase from Ga_2ZnO_4 to the direction of Phase I and the lattice constants are shown in Fig. 6. The width of the solid solution range ($x = 0.128$) of the spinel in the direction of Phase I is narrower than that ($x = 0.40$) in the In_2O_3–Fe_2ZnO_4–ZnO system. No spinel phase with a cation excess ratio more than a cation : anion ratio = 3 : 4 was detected. (4) Phase I is in equilibrium with In_2O_3, $(InGaO_3)_2ZnO$, Phase II, and the spinel phase. (5) Phase II is in equilibrium with In_2O_3, Phase I, Phase III, and the spinel phase. (6) Phase III is in equilibrium with In_2O_3, Phase II, Phase IV, and the spinel phase. (7) Each of the higher order Phase W (W = IV or V) is in equilibrium with the spinel phase and both Phase ($W - 1$) and Phase ($W + 1$). (8) Phase VI is in equilibrium with Phase V, Phase VII, spinel, and distorted wurtzite, and Phase Y (VII < Y < XIII) is in equilibrium with Phase ($Y - 1$), Phase ($Y + 1$), and the distorted wurtzite phase. (9) The distorted wurtzite phase is in equilibrium with the spinel, Phase VI, Phase VII, Phase VIII, Phase IX, Phase X, Phase XI, Phase XII, and Phase XIII. In the case of the In_2O_3–Fe_2ZnO_4–ZnO system at 1350°C, there exist the solid solution ranges of $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$Fe_2O_3(ZnO)_m$ ($m > 11$); however, no full solid solution ranges of $In_2O_3(ZnO)_m$–$InGaO_3(ZnO)_m$–$Ga_2O_3(ZnO)_m$ ($m \leq 13$) exist in the In_2O_3–Ga_2ZnO_4–ZnO system. If we think that Ga(III) has a tendency to take the tetrahedral site more favorably than Fe(III) does in the oxide compounds, and Fe(III) can occupy positions both of octahedral and tetrahedral sites, it is reasonable that there are the distorted ZnO phase, $Zn_{1-x}Ga_{2x}O_{1+2x}$, in the In_2O_3–Ga_2ZnO_4–ZnO system and $Fe_2O_3(ZnO)_m$ in the In_2O_3–Fe_2ZnO_4–ZnO system.

We heated two series of mixtures: one is $In_2O_3 : Ga_2O_3 : ZnO = 2 : 0 : 98$, $1 : 1 : 98$, and $0 : 2 : 98$ at 1550°C for 2 days, respectively, and the other is $1 : 0 : 99$ at 1350°C for (4 + 7) days, $0.5 : 0.5 : 99$ at 1550°C for 2 days, and $0 : 1 : 99$ at 1350°C for (4 + 7) days, respectively. We then obtained two kinds of solid solutions, which could be considered to belong to distorted wurtzite structures or $InGaO_3(ZnO)_m$ types of homologous structures. When m is an extremely high value, a distorted wurtzite structure and a homologous structure may become identical; however, we think the details in this region are still open to question.

2. *Crystal Structural Consideration for the Homologous Solid Solutions of* $In_2O_3(ZnO)_m$–$InGaO_3(ZnO)_m$–$In_{1-x}Ga_{1+x}O_3(ZnO)_m$ (m = *Integer*)

Powder samples obtained were supplied for SEM observation. We could see clear plate-like crystals of the solid solutions, $In_2O_3(ZnO)_m$–$InGaO_3(ZnO)_m$–$In_{1-x}Ga_{1+x}O_3(ZnO)_m$. The hexagonal lattice constants of the homologous solid solutions of the $In_2O_3(ZnO)_m$–$InGaO_3(ZnO)_m$–$In_{1-x}Ga_{1+x}O_3(ZnO)_m$ are shown in Table III and Fig. 7. Since $InFeO_3(ZnO)_m$ can be considered to be composed of one $InO_{1.5}$ layer, one $(FeZn)O_{2.5}$ layer, and ($m - 1$) ZnO layers as indicated in our previous papers (*2*, *5*), we can apply this crystal structural model to the $InGaO_3(ZnO)_m$ compounds and their solid solutions, and calculate the thickness of the layers composed. From the dependence of (C_{obsd}/Z) upon ($m - 1$) (See Fig. 8.), we can determine the thickness of the ZnO layer. We show the thickness of the

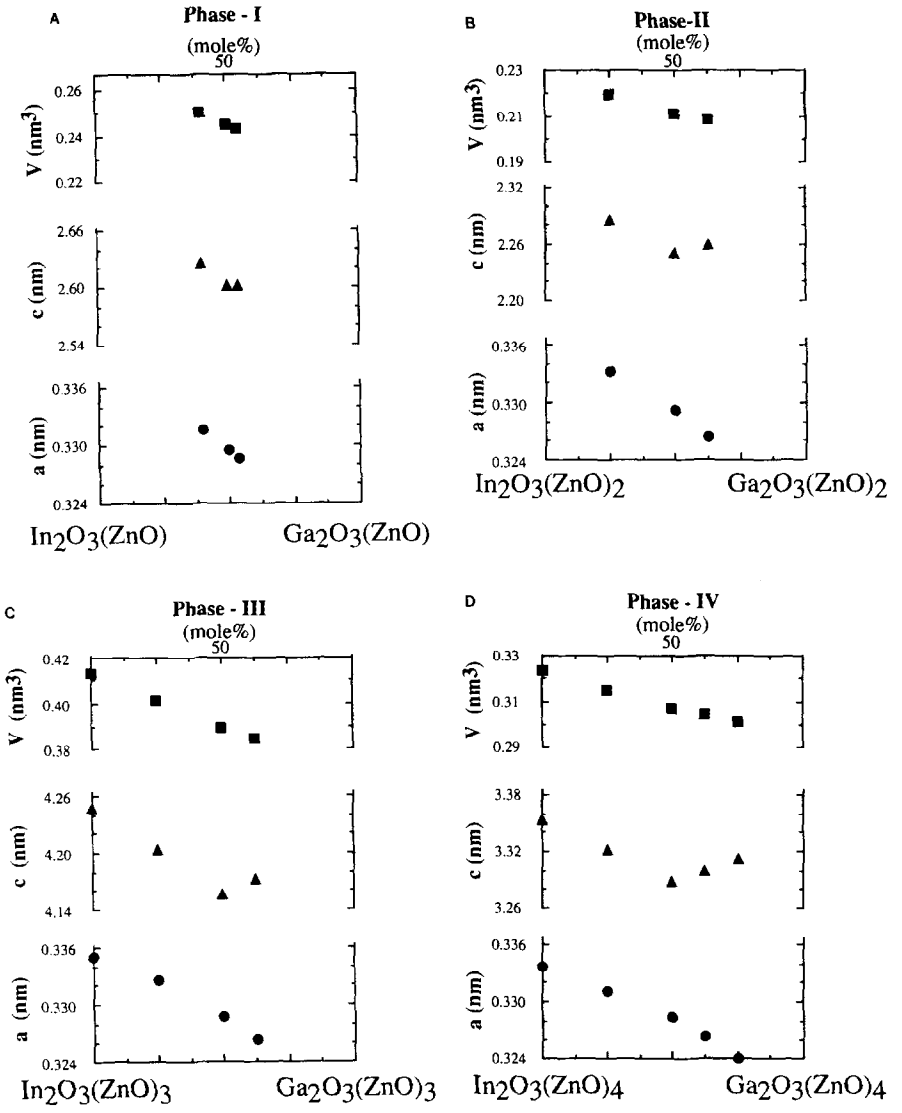

FIG. 7. The hexagonal lattice constants (a and c) and the unit cell volumes (V) of the layered phases in the system $In_2O_3(ZnO)_m$–$Ga_2O_3(ZnO)_m$ (A) Phase I, (B) Phase II, (C) Phase III, (D) Phase IV, (E) Phase V, (F) Phase VI, (G) Phase VII, (H) Phase VIII, (I) Phase IX, (J) Phase XI, and (K) Phase XIII.

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 $(In_{0.5}Ga_{0.5}Zn)O_{2.5}$ layer, the $InO_{1.5}$ layer and the $(GaZn)O_{2.5}$ layer, the $(In_{0.75}Ga_{0.25})O_{1.5}$ layer and the $(GaZn)O_{2.5}$ layer, and the $(In_{0.5}Ga_{0.5})O_{1.5}$ layer and the $(GaZn)O_{2.5}$ layer in Table IV. For calculating each thickness of the above layers, we considered that each compound actually consists of the following constituent parts:

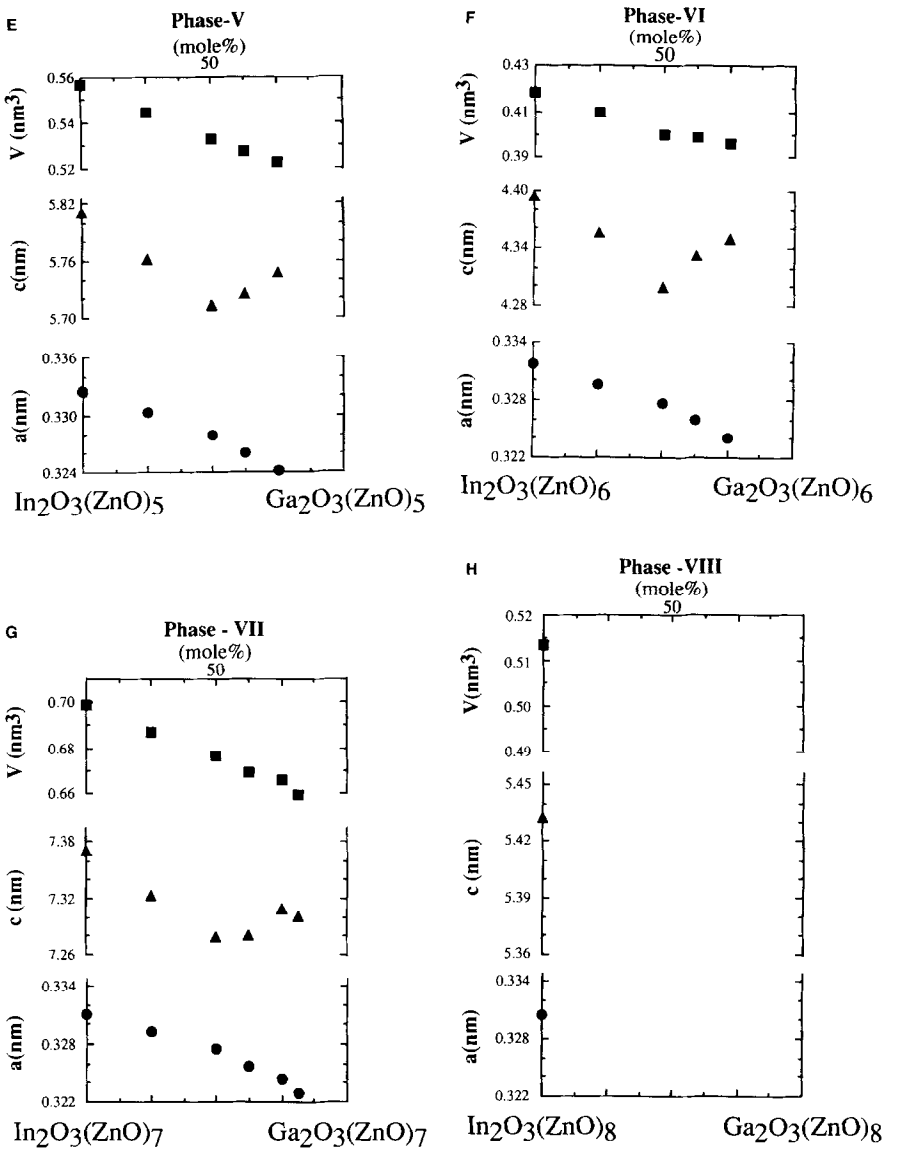

FIG. 7—*Continued*

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

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

$InGaO_3(ZnO)_m$
$InO_{1.5} + (GaZn)O_{2.5} + (m - 1)ZnO$

$In_{0.75}Ga_{1.25}O_3(ZnO)_m$
$(In_{0.75}Ga_{0.25})O_{1.5} + (GaZn)O_{2.5} + (m - 1)ZnO$

$In_{0.50}Ga_{1.50}O_3(ZnO)_m$
$(In_{0.50}Ga_{0.50})O_{1.5} + (GaZn)O_{2.5} + (m - 1)ZnO.$

Note that $\frac{1}{2}c$ (c = 0.5207 (nm)) is equal to 0.2604 (nm), in which c means the lattice constant of ZnO (wurtzite structure) (*11*). Kimizuka *et al.* (*12*) summarized the lattice

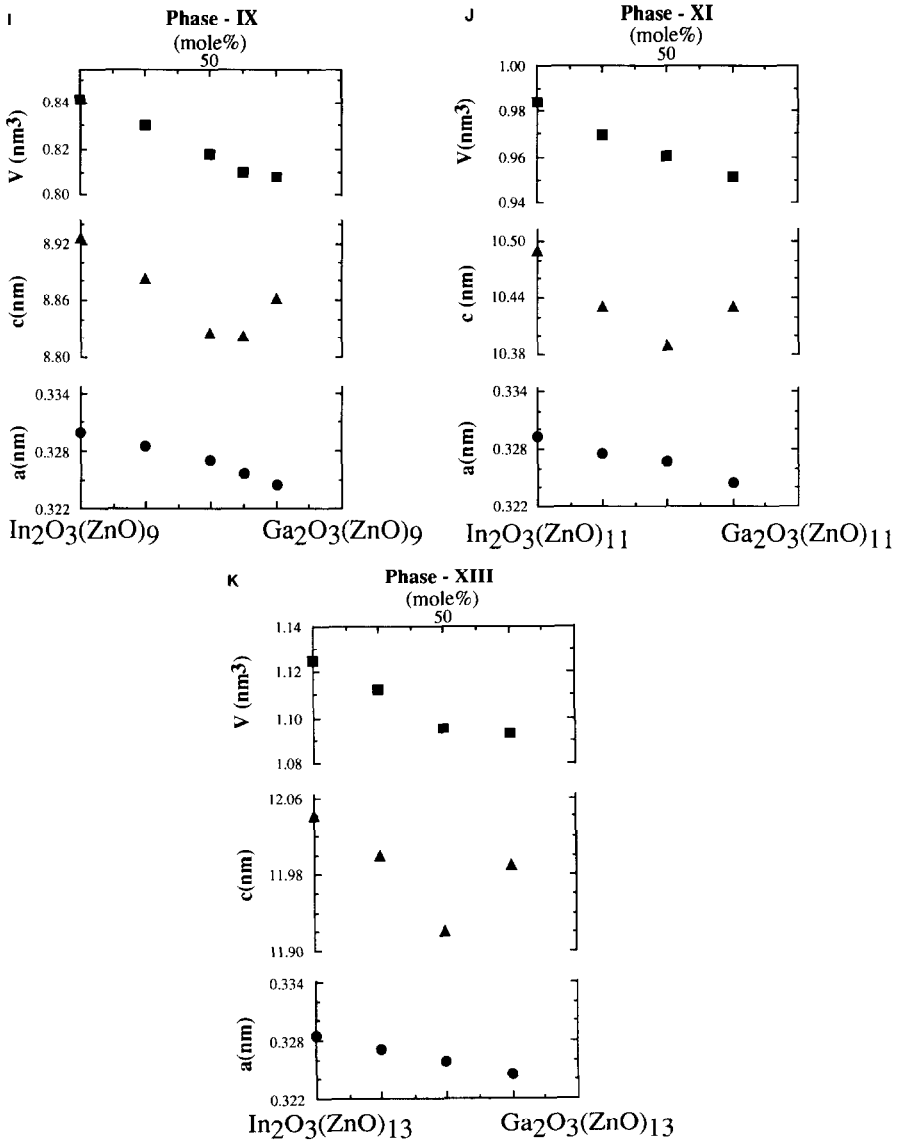

FIG. 7—*Continued*

constants of RFe_2O_4 (R: Y, Ho, Er, Tm, Yb, and Lu), which is isostructural with $InFeO_3(ZnO)$. The value of a increases but the value of c decreases with an increase in the ionic radius of the constituent R cation in RFe_2O_4. With an increase in the concentration of Ga(III) with a smaller ionic radius than In(III), the value of a decreases but the value of c increases in the region between $InGaO_3(ZnO)_m$ and $In_{1-x}Ga_{1+x}O_3(ZnO)_m$. We can infer that Ga(III) occupies the cation position in the $InO_{1.5}$ layer. In the region between $In_2O_3(ZnO)_m$ and $InGaO_3(ZnO)_m$, the Ga(III) occupies the In site in the (In Zn)$O_{2.5}$ layer, and values of both a and c decrease with an increase in the Ga(III) concentration. In Fig. 9, we summarized the thickness of the ZnO layer and $(U + W)$

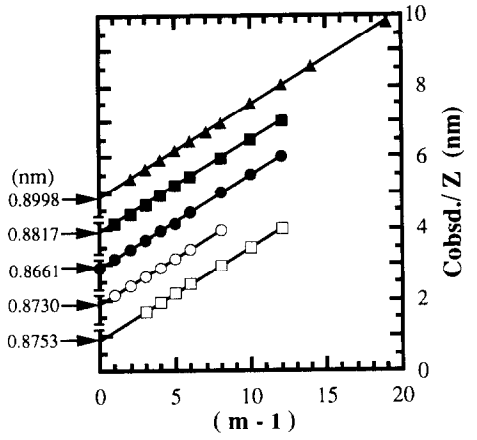

FIG. 8. The relation between C_{obsd}/Z and $(m - 1)$ in $In_2O_3(ZnO)_m$, $In_{1.5}Ga_{0.5}O_3(ZnO)_m$, $InGaO_3(ZnO)_m$, $In_{0.75}Ga_{1.25}O_3(ZnO)_m$, or $In_{0.5}Ga_{1.5}(ZnO)_m$. C_{obsd} (nm), the observed hexagonal lattice constant; Z, numbers of a molecular unit in a unit cell: $Z = 3$ for m = odd, $Z = 2$ for m = even. ▲, $In_2O_3(ZnO)_m$; ■, $In_{1.5}Ga_{0.5}O_3(ZnO)_m$; ●, $InGaO_3(ZnO)_m$; ○, $In_{0.75}Ga_{1.25}O_3(ZnO)_m$; □, $In_{0.5}Ga_{1.5}O_3(ZnO)_m$.

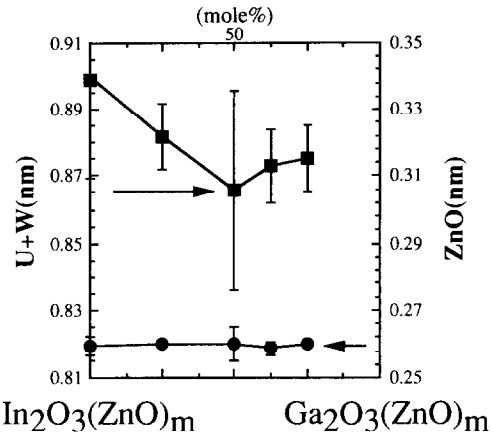

FIG. 9. The relation between the thickness of the ZnO layer or the $(U + W)$ layer, in the system $In_2O_3(ZnO)_m$–$Ga_2O_3(ZnO)_m$, in which U or W means as follows: U, $InO_{1.5}$, $(In_{0.75}Ga_{0.25})O_{1.5}$, or $(In_{0.5}Ga_{0.5})O_{1.5}$ layer; W, $(InZn)O_{2.5}$, $(In_{0.5}Ga_{0.5}Zn)O_{2.5}$ or $(GaZn)O_{2.5}$ layer.

layer estimated from Fig. 8. In the whole range between $In_2O_3(ZnO)_m$ and $In_{1-x}Ga_{1+x}O_3(ZnO)_m$, we can see a constant thickness of the ZnO layer and a reasonable change in the thickness of the $(U + W)$ layer. The crystal structures of $LuFeO_3(ZnO)_m$ (m = 1, 4, 5, and 6) determined by a single crystal, which are thought to be isostructural with $InFeO_3(ZnO)_m$, support our present hypothesis of the layered structural models for the solid solutions of homologous phases, $InFeO_3(ZnO)_m$. The lattice constant, a, versus m is shown in Fig. 10. All of the a values approach a =

TABLE IV

THE THICKNESS OF THE CONSTITUENT LAYERS IN THE SOLID SOLUTIONS OF $InGaO_3(ZnO)_m$

Compound	Constituent layer	Thickness of the constituent layer (nm)
$In_2O_3(ZnO)_m$	ZnO	0.2594(3)
	$InO_{1.5}$ + $(InZn)O_{2.5}$	0.8998(30)
$In_{1.5}Ga_{0.5}O_3(ZnO)_m$	ZnO	0.2597(1)
	$InO_{1.5}$ + $(In_{0.5}Ga_{0.5}Zn)O_{2.5}$	0.8817(10)
$InGaO_3(ZnO)_m$	ZnO	0.2598(5)
	$InO_{1.5}$ + $(GaZn)O_{2.5}$	0.8658(30)
$In_{0.75}Ga_{1.25}O_3(ZnO)_m$	ZnO	0.2587(2)
	$(In_{0.75}Ga_{0.25})O_{1.5}$ + $(GaZn)O_{2.5}$	0.8730(11)
$In_{0.5}Ga_{1.5}O_3(ZnO)_m$	ZnO	0.2601(1)
	$(In_{0.5}Ga_{0.5})O_{1.5}$ + $(GaZn)O_{2.5}$	0.8753(10)

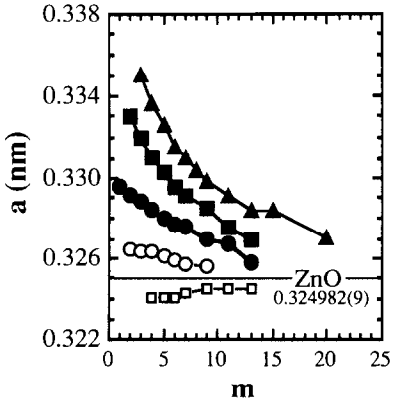

FIG. 10. The relation between a and m in $In_2O_3(ZnO)_m$, $In_{1.5}Ga_{0.5}O_3(ZnO)_m$, $InGaO_3(ZnO)_m$, $In_{0.75}Ga_{1.25}O_3(ZnO)_m$, or $In_{0.5}Ga_{1.5}O_3(ZnO)_m$.

0.3249(nm), the lattice constant of wurtzite, with increases in m (*11*).

The following conclusions are derived from the comparison between the phase relations in the In_2O_3–Ga_2ZnO_4–ZnO system and those in the In_2O_3–Fe_2ZnO_4–ZnO system at 1350°C. They are very similar to each other except for a few features: (1) $(InGaO_3)_2ZnO$ with $Yb_2Fe_3O_7$-type structure exists, but no $(InFeO_3)_2ZnO$ exists at 1350°C. (2) The solid solution range of the spinel phase of $Fe_{2-x}In_xZnO_4$ ($x = 0.40 \pm 0.02$) (*2*) is much wider than that of $Ga_{2-x}In_xZnO_4$ ($x = 0.128(4)$). Since both Ga_2ZnO_4 and Fe_2ZnO_4 belong to a normal spinel (*13*) and the lattice constant of Ga_2ZnO_4 ($a = 0.8331(1)$nm) is smaller than that of Fe_2ZnO_4 ($a = 0.8441(1)$nm) (*2*), we can conclude that it is more difficult for the In(III) ion to occupy the Ga position in Ga_2ZnO_4 than the Fe position in Fe_2ZnO_4 (*14*). (3) The solid solutions of both $InFeO_3(ZnO)_m$ and $InGaO_3(ZnO)_m$ are isostructural, and composed of one $InO_{1.5}$ layer, one (Fe or Ga,Zn)$O_{2.5}$ layer and $(m - 1)$ZnO layers. Each range of the solid solutions of $InGaO_3(ZnO)_m$ is comparable to that of $InFeO_3(ZnO)_m$ ($1 \leq m \leq 7$). (4) In the Ga_2O_3–ZnO system, there is a solid solution range of wurtzite, $Zn_{1-x}Ga_{2x}O_{1+2x}$ ($x = 0$–0.094); however, $Fe_2O_3(ZnO)_m$ ($m \geq 12$) exists in the Fe_2O_3–ZnO system. The ranges of the solid solutions of $InGaO_3(ZnO)_m$ ($7 \leq m \leq 13$) do not reach $x = 1$ in $In_{1-x}Ga_{1+x}O_3(ZnO)_m$. These features are derived from the well-known experimental data reported so far that Ga(III) occupies tetrahedral sites more favorably than Fe does in the oxides, and Fe(III) takes both tetrahedral and octahedral sites.

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