

Survey of the Phase Formation in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MO}$ and $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MO}$ Systems in Air at High Temperatures (M : Co, Ni, Cu, and Zn)

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The phase relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CuO}$ system at 1000°C and the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$ system at 1350 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CoO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CuO}$ system at 1000°C, and the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-ZnO}$ system at 1300 and 1200°C were determined in air by means of a classical quenching method. YbGaCoO_4 ($a = 3.4165(1)$ and $c = 25.081(2)$ Å), YbGaCuO_4 ($a = 3.4601(4)$ and $c = 24.172(6)$ Å), and YbGaZnO_4 ($a = 3.4153(5)$ and $c = 25.093(7)$ Å), which are isostructural with YbFe_2O_4 (space group: $R\bar{3}m$, $a = 3.455(1)$ and $c = 25.109(2)$ Å), were obtained as stable phases. In the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system and the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MO}$ system (M : Co, Ni, Cu, and Zn), no ternary stable phases existed.

Introduction

Recently Kimizuka and Takayama reported a series of new compounds, LnABO_4 , with layered structure (Ln : Y, Ho, Er, Tm, Yb, and Lu; A : Fe, Ga, and Al; B : Mg, Fe, Mn, Co, Cu, and Zn) (1-2) which are isostructural with YbFe_2O_4 (space group: $R\bar{3}m$, $a = 3.455(1)$ and $c = 25.109(2)$ Å) and established the phase diagrams of the $\text{Yb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CoO}$ system at 1350 and 1300°C, the $\text{Yb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-CuO}$ system at 1000°C, and the $\text{Yb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-ZnO}$ system at 1300°C in air (3). YbFeCoO_4 , YbFeCuO_4 , and YbFeZnO_4 are stable in air at 1350, 1000, and 1300°C, respectively. In the $\text{Yb}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, no ternary

compounds existed. The phase diagrams of the $\text{Ln}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$ systems at 1200°C were reported by Kimizuka and Katsura (4-5) and Katsura *et al.* (6). As an example, the phase diagram of the $\text{Y}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$ system at 1200°C is illustrated with equilibrium oxygen partial pressures in Fig. 1 (4). The compounds with the YbFe_2O_4 type of structure are stable above certain temperatures (3-6). The crystal structure analyses of a series of new compounds, $(\text{YbFeO}_3)_n\text{FeO}$ ($n = 1, 2, 3, \dots$), were performed by Kato *et al.* (7-8) and Matsui *et al.* (9).

In the present paper, we report the phase relations of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CuO}$ system at 1000°C and the

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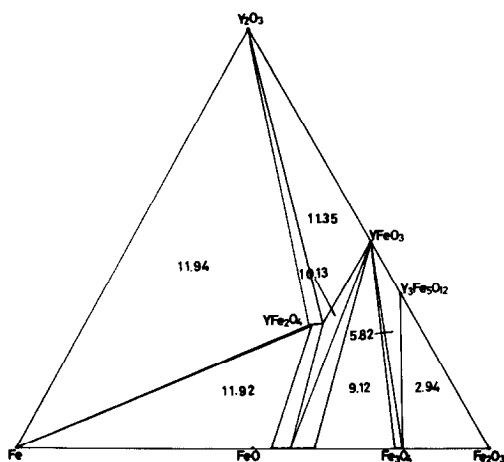


FIG. 1. The phase diagram of the $\text{Y}_2\text{O}_3\text{-Fe-Fe}_2\text{O}_3$ system at 1200°C . Numbers in three solid phases indicate equilibrium oxygen partial pressures ($-\log P_{\text{O}_2}$) measured by means of a stabilized zirconia cell.

$\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$ system at 1350 and 1200°C , the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CoO}$ system at 1300 and 1200°C , the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C , the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CuO}$ system at 1000°C , and the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-ZnO}$ system at 1300 and 1200°C , which were determined in air by means of a classical quenching method.

Experimental

Starting materials, procedure, and equipment. Ga_2O_3 (99.9%) and reagent-grade Cr_2O_3 were used as starting materials. The other starting materials have the same purity grades as reported in the previous paper (3). Pretreatment of the starting materials, procedure, and equipment employed in the present experiment were the same as previously reported (3). The heating period of each sample was between 7 days and $1\frac{1}{2}$ months. Each of the heat-treated samples was analyzed by means of conventional X-ray powder diffraction and identified from the ASTM cards. Sample weights were checked before and after heat treatment.

Results and Discussion

I. The Phase Relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MO}$ Systems in Air at High Temperatures (M: Co, Ni, Cu, and Zn)

(a-1) *The phase relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system in air at 1300°C .* In the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system, there was a stable $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ phase (garnet type of structure). No YbGaO_3 phase existed. Marezio *et al.* (10) reported that they synthesized YbGaO_3 compound (distorted perovskite structure) at 1000°C under 70 kbar and it was an unstable phase under 1 atmosphere. A stable Ga_2CoO_4 phase (spinel type of structure) existed in the $\text{Ga}_2\text{O}_3\text{-CoO}$ system. There was no binary stable phase in the $\text{CoO-Yb}_2\text{O}_3$ system. In the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system, there was a stable YbGaCoO_4 phase ($a = 3.4165(1)$ and $c = 25.081(2)$ Å) which was isostructural with YbFe_2O_4 compound (space group: $R\bar{3}m$, $a = 3.455(1)$ and $c = 25.109(2)$ Å) (7).

(a-2) *The phase relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system in air at 1200°C .* In the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system and the $\text{Ga}_2\text{O}_3\text{-CoO}$ system, there were the same phases as in those at 1350°C . No binary stable phase existed in the $\text{CoO-Yb}_2\text{O}_3$ system. The YbGaCoO_4 , which was prepared at 1350°C in air, decomposed into Yb_2O_3 , CoO , and $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ after 1 week at 1200°C . No ternary stable phase existed in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system at 1200°C in air.

(b) *The phase relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system in air at 1300 and 1200°C .* In the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3$ system, there was a stable $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ phase at 1200°C . In the $\text{Ga}_2\text{O}_3\text{-NiO}$ system, there was one stable Ga_2NiO_4 phase (spinel type of structure). No binary stable phase existed in the $\text{NiO-Yb}_2\text{O}_3$ system at 1300 and 1200°C as previously reported in (3). No ternary stable phases existed in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system in air at 1300 and 1200°C .

(c) *The phase relations in the Yb_2O_3 - Ga_2O_3 - CuO system in air at 1000°C .* In the Yb_2O_3 - Ga_2O_3 system, we concluded that a stable $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ existed. However, when we heated a mixture of Yb_2O_3 : Ga_2O_3 = 3:5 (in mole ratio) for $1\frac{1}{2}$ months at 1000°C , we could not obtain a single phase of $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ but a mixture of Yb_2O_3 , $\text{Yb}_3\text{Ga}_5\text{O}_{12}$, and Ga_2O_3 phases. The $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ which was prepared at 1350°C was heated at 1000°C for 1 month and no decomposition was observed. In the Ga_2O_3 - CuO and CuO - Yb_2O_3 systems, a stable Ga_2CuO_4 (spinel type of structure) and a stable $\text{Yb}_2\text{Cu}_2\text{O}_5$ ($\text{Cu}_2\text{In}_2\text{O}_5$ type of structure) (12) existed, respectively. In the Yb_2O_3 - Ga_2O_3 - CuO system, there was a stable YbGaCuO_4 ($a = 3.4601(4)$ and $c = 24.172(6)$ Å) which was isostructural with YbFe_2O_4 (7).

(d-1) *The phase relations in the Yb_2O_3 - Ga_2O_3 - ZnO system in air at 1350°C .* In the Ga_2O_3 - ZnO system, there was a stable Ga_2ZnO_4 phase (spinel type of structure) and no binary stable phase existed in the ZnO - Yb_2O_3 system. In the Yb_2O_3 - Ga_2O_3 - ZnO system, there was a stable YbGaZnO_4 phase ($a = 3.4153(5)$ and $c = 25.093(7)$ Å) which was isostructural with YbFe_2O_4 (7).

(d-2) *The phase relations in the Yb_2O_3 - Ga_2O_3 - ZnO system at 1200°C in air.* The phase relations in the Yb_2O_3 - Ga_2O_3 system, the Ga_2O_3 - ZnO system, and the ZnO - Yb_2O_3 system are the same as those at 1350°C in air. In the Yb_2O_3 - Ga_2O_3 - ZnO system, no ternary phase existed stably. The YbGaZnO_4 , which was prepared at 1350°C , decomposed into Yb_2O_3 , ZnO , and $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ phases after 1 week at 1200°C .

II. The Phase Relations in the Yb_2O_3 - Cr_2O_3 - MO Systems in Air at High Temperatures

(a) *The phase relations in the Yb_2O_3 - Cr_2O_3 - $M'\text{O}$ systems in air at 1300 and 1200°C (M' : Co, Ni, and Zn).* In the Yb_2O_3 - Cr_2O_3 system at 1300 and 1200°C , there was a stable YbCrO_3 phase (distorted

perovskite type of structure). No $\text{Yb}_3\text{Cr}_5\text{O}_{12}$ existed. Schneider *et al.* (11) reported that there was a stable YbCrO_3 phase in the Yb_2O_3 - Cr_2O_3 system in air above 1000°C under 1 atm. In the Cr_2O_3 - $M'\text{O}$ systems, there was one stable $\text{Cr}_2M'\text{O}_4$ phase (spinel type of structure). No binary stable phase existed in the $M'\text{O}$ - Yb_2O_3 systems. No ternary stable phases existed in the Yb_2O_3 - Cr_2O_3 - $M'\text{O}$ systems.

(b) *The phase relations in the Yb_2O_3 - Cr_2O_3 - CuO system in air at 1000°C .* In the Yb_2O_3 - Cr_2O_3 system at 1000°C , there was a stable YbCrO_3 phase. No $\text{Yb}_3\text{Cr}_5\text{O}_{12}$ existed. A stable Cr_2CuO_4 phase (spinel type of structure) in the Cr_2O_3 - CuO system existed. No ternary phase existed stably at 1000°C . The phase diagrams of the Yb_2O_3 - Ga_2O_3 - CoO system at 1300 and 1200°C , the Yb_2O_3 - Ga_2O_3 - NiO system at 1300 and 1200°C , the Yb_2O_3 - Ga_2O_3 - CuO system at 1000°C , and the Yb_2O_3 - Ga_2O_3 - ZnO system at 1350 and 1200°C are shown in Figs. 2a-d. The phase diagrams of the Yb_2O_3 - Cr_2O_3 - $M'\text{O}$ systems at 1300 and 1200°C are shown in Fig. 3a and the Yb_2O_3 - Cr_2O_3 - CuO system at 1000°C is shown in Fig. 3b. The experimental data points which are necessary and sufficient for establishing the above phase diagrams were summarized in Table I.

As previously reported (3), two stable phases exist YbFeO_3 (distorted perovskite type of structure) and $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ (garnet type of structure), in the Yb_2O_3 - Fe_2O_3 system above 1000°C under 1 atm. On the other hand, the YbCrO_3 phase is stable in the Yb_2O_3 - Cr_2O_3 system, and the $\text{Yb}_3\text{Ga}_5\text{O}_{12}$ phase is stable in the Yb_2O_3 - Ga_2O_3 system. This can be easily explained by site preferences of three cations, Fe^{3+} , Cr^{3+} , and Ga^{3+} . In order to elucidate cation distribution in the spinel-type compounds, McClure calculated the difference of crystal field stabilization energies between octahedral and tetrahedral sites for many cations (13). According to his calculation, Cr^{3+} has

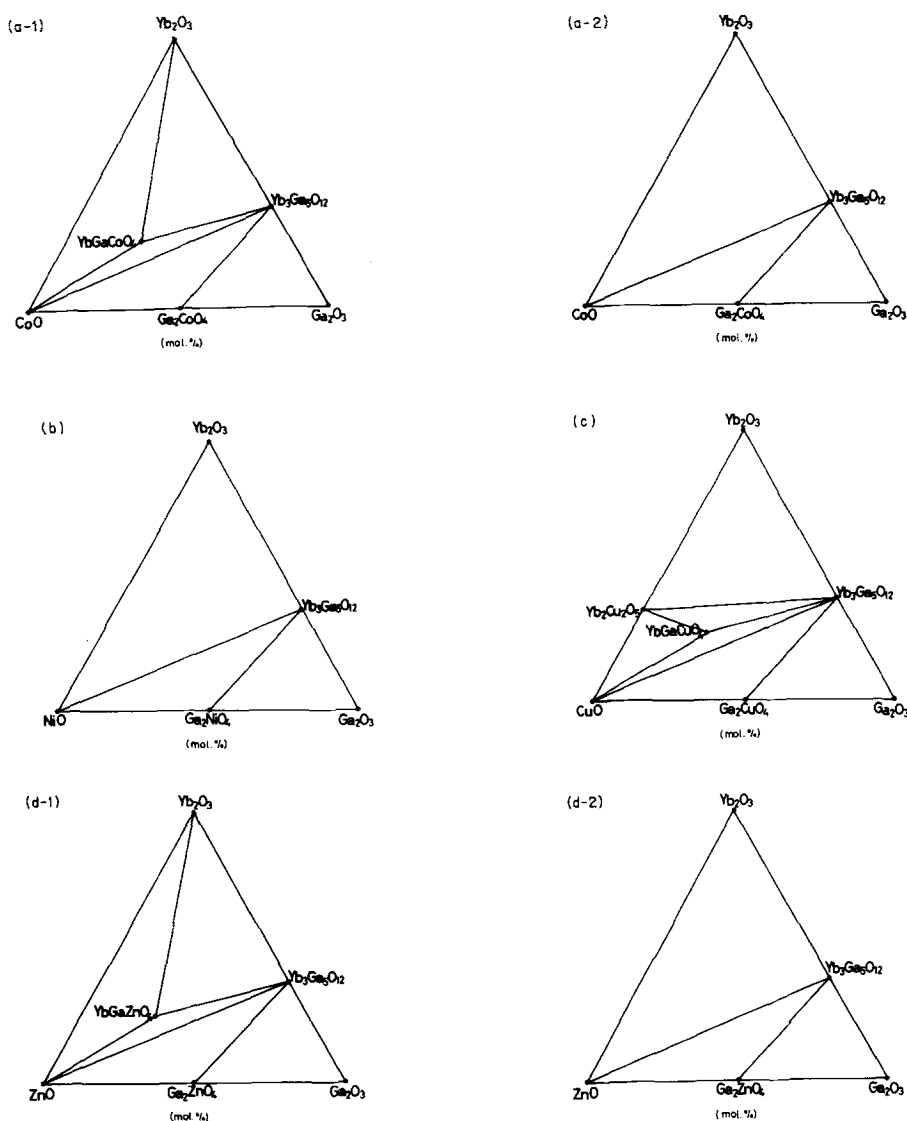


FIG. 2. (a-1) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system in air at 1300°C . (a-2) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system in air at 1200°C . (b) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system in air at 1300 and 1200°C . (c) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CuO}$ system in air at 1000°C . (d-1) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$ system in air at 1350°C . (d-2) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$ system in air at 1200°C .

very large octahedral site preference energy, while Fe^{3+} and Ga^{3+} have no preference energies. Therefore, Cr^{3+} prefers octahedral sites to tetrahedral sites compared with Fe^{3+} and Cr^{3+} . In addition, Ga^{3+} prefers tetrahedral sites to octahedral sites, in spite of the spherical electronic configuration

similar to that of Fe^{3+} (10). Fe^{3+} , Cr^{3+} , and Ga^{3+} occupy both the tetrahedral and the octahedral sites in the garnet-type compounds, while they occupy only an octahedral site in the perovskite-type compounds. The site preference is a possible reason why YbGaO_3 and $\text{Yb}_3\text{Cr}_5\text{O}_{12}$ are not stable at 1

TABLE I
THE PHASE RELATIONS IN THE $Yb_2O_3-A_2O_3-MO$ SYSTEMS IN AIR (A: Ga AND Cr; M: Co, Ni, Cu, AND Zn)

System	Composition (mole ratio)	Phases ^a	Period (days)	System	Composition (mole ratio)	Phases ^a	Period (days)
$Yb_2O_3-Ga_2O_3-CoO$ at 1300°C	50:25:25	Yb_2O_3 , 3-5-12, 1-1-1-4	12	$Yb_2O_3-Ga_2O_3-NiO$ at 1300 and 1200°C	40:20:40	Yb_2O_3 , NiO, 3-5-12	10
	30:10:60	1-1-1-4, Yb_2O_3 , CoO	12		10:30:60	NiO, 3-5-12, 2-1-4	10
	10:40:50	3-5-12, CoO, 2-1-4	12		10:65:25	2-1-4, Ga_2O_3 , 3-5-12	10
	20:25:55	1-1-1-4, CoO, 3-5-12	12	$Yb_2O_3-Ga_2O_3-ZnO$ at 1350°C	50:30:20	Yb_2O_3 , 1-1-1-4, 3-5-12	10
	10:65:25	2-1-4, 3-5-12, Ga_2O_3	12		30:10:60	ZnO, 1-1-1-4, Yb_2O_3	12
	25:25:50	1-1-1-4	12		20:25:55	ZnO, 1-1-1-4, 3-5-12	12
	50:25:25	Yb_2O_3 , 3-5-12, CoO	15		10:40:50	ZnO, 2-1-4, 3-5-12	12
	10:40:50	3-5-12, CoO, 2-1-4	15		10:65:25	2-1-4, 3-5-12, Ga_2O_3	10
	10:70:20	3-5-12, 2-1-4, Ga_2O_3	15	$Yb_2O_3-Ga_2O_3-ZnO$ at 1200°C	10:10:20	1-1-1-4	7
	60:20:20	Yb_2O_3 , 3-5-12, 2-2-5	14		40:20:40	Yb_2O_3 , ZnO, 3-5-12	15
$Yb_2O_3-Ga_2O_3-CuO$ at 1200°C	30:25:45	2-2-5, 1-1-1-4, 3-5-12	14		10:40:50	3-5-12, ZnO, 2-1-4	15
	20:10:70	2-2-5, CuO, 1-1-1-4	14	$Yb_2O_3-Cr_2O_3-M'O$ at 1300 and 1200°C	10:70:20	3-5-12, 2-1-4, Ga_2O_3	15
	10:25:65	CuO, 2-1-4, 3-5-12	14		40:20:40	Yb_2O_3 , 1-1-3, M'O	10
	25:35:40	1-1-1-4, CuO, 3-5-12	14		15:35:50	1-1-3, M'O, 2-1-4	10
	15:65:20	2-1-4, 3-5-12, Ga_2O_3	14	$Yb_2O_3-Cr_2O_3-CuO$ at 1000°C	20:65:15	1-1-3, 2-1-4, Cr_2O_3	10
	10:0:20	2-2-5	7		60:20:20	Yb_2O_3 , 2-2-5, 1-1-3	15
	10:10:20	1-1-1-4	10		25:15:60	2-2-5, CuO, 1-1-3	15
					10:30:60	CuO, 1-1-3, 2-1-4	15
					20:65:15	1-1-3, 2-1-4, Cr_2O_3	15

^a 3-5-12: $Yb_3Ga_5O_{12}$; 1-1-1-4: $YbGaMO_4$; 2-2-5: $Yb_2Cu_2O_5$; 2-1-4: A_2MO_4 ; 1-1-3: $YbCrO_3$.

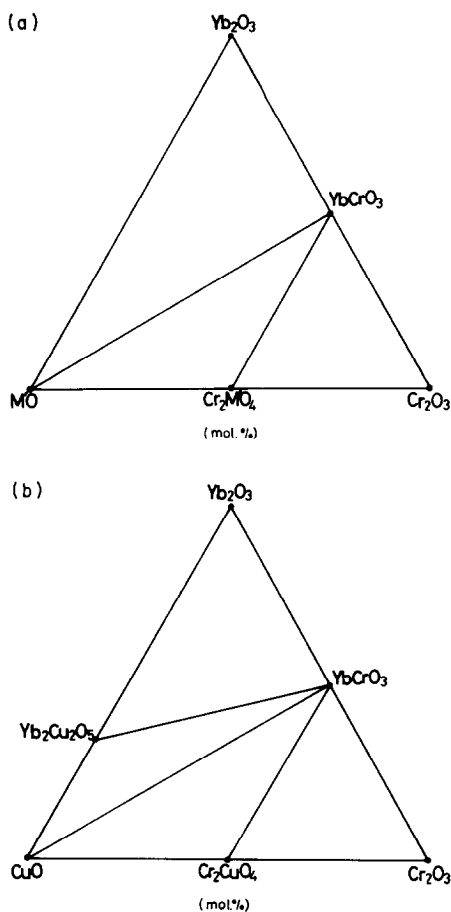


FIG. 3. (a) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-M}'\text{O}$ systems in air at 1300 and 1200°C (M' : Co, Ni, and Zn). (b) The phase diagram of the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CuO}$ system in air at 1000°C.

atm. These features of three cations may also affect the stability of the LnABO_4 type of compounds with layer structure. In the LnABO_4 compounds, A and B cations are both surrounded by five oxygen ions forming the trigonal bipyramid. Crystal field stabilization energies for trigonal bipyramidal geometry have already been reported by Wood (14). In $3d^3$ and $3d^8$ configurations, it was calculated to be $(25/4)\text{Dq}$ for a normal octahedral definition of Dq. This value is small compared with that of the octahedral site (12Dq). Cr^{3+} ($3d^3$) has, therefore, a large octahedral site preferential energy

compared to that of the trigonal bipyramidal site. This is one of the possible reasons why LnCrBO_4 compounds could not be prepared. The same explanation is possible for divalent cations. We could not obtain any LnANiO_4 compounds, while LnAMnO_4 could be synthesized very easily (1-2). Ni^{2+} ($3d^8$) like Cr^{3+} , has large octahedral site preferential energy compared to that of the trigonal bipyramidal site, whereas Mn^{2+} has no preferential energy.

In conclusion, the phase relations in the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CoO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-NiO}$ system at 1300 and 1200°C, the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-CuO}$ system at 1000°C, and the $\text{Yb}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-ZnO}$ system at 1350 and 1200°C were determined in air. The YbGaCoO_4 , YbGaCuO_4 , and YbGaZnO_4 phases which are isostructural with YbFe_2O_4 were stable at 1300, 1000, and 1350°C in air, respectively. The phase relations in the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CoO}$ system, the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-NiO}$ system, and the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-ZnO}$ system at 1300 and 1200°C in air and the $\text{Yb}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-CuO}$ system in air at 1000°C were established and no ternary stable phases existed.

Since we determined the stability conditions of YbABO_4 compounds at high temperatures in air, our research group will begin to study physical properties, such as magnetic property, Mössbauer spectroscopy, and neutron diffraction analysis, of LnABO_4 compounds with layered structure.

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