JOURNAL OF SOLID STATE CHEMISTRY 87, 449–455 (1990)

The Phase Relations in the System In_2O_3–A_2BO_4–BO at Elevated Temperatures (A: Fe, Ga, or Cr; B: Mg, Co, Ni, or Cu): Part II

NOBORU KIMIZUKA,[1] TAKAHIKO MOHRI, AND MASAKI NAKAMURA

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

Received December 11, 1989; in revised form April 30, 1990

The phase relations in the systems In_2O_3–Ga_2MgO_4–MgO at 1300°C, In_2O_3–Fe_2NiO_4–NiO at 1200°C, In_2O_3–Ga_2NiO_4–NiO at 1200°C, In_2O_3–Cr_2NiO_4–NiO at 1200°C, In_2O_3–Cr_2CoO_4–CoO at 1200°C, and In_2O_3–Cr_2CuO_4–CuO at 1000°C were determined by classical quenching methods. In the system In_2O_3–Ga_2MgO_4–MgO there exist two ternary phases, namely, $InGaO_3(MgO)$ with the $YbFe_2O_4$-type crystal structure and $InGaO_3(MgO)_2$ with the $InFeO_3(ZnO)_2$-type crystal structure. In the system In_2O_3–A_2NiO_4–NiO (A = Fe, Ga, or Cr), there is a spinel solid-solution between $InANiO_4$ and A_2NiO_4. There is no ternary compound in the systems In_2O_3–Cr_2CoO_4–CoO and In_2O_3–Cr_2CuO_4–CuO, respectively. The classification of the phase relations in the system In_2O_3–A_2BO_4–BO (A: Fe, Ga, or Cr; B: Mg, Co, Ni, Cu, or Zn) is made in terms of the crystal structure of the ternary $InABO_4$ compound.

Introduction

The rare earth elements (La–Lu, and including Y, In, and Sc) and transition elements can form many interesting condensed complex metal oxides with various types of crystal structures such as perovskite, garnet magnetoplumbite, K_2NiF_4-, $CaFe_2O_4$-, and $YbFe_2O_4$-type. In order systematically to understand the physical and chemical properties of these complex oxides, as a first step, we must delineate the stability regions (for instance, the temperature, pressure, oxygen fugacity, or oxygen nonstoichiometry ranges) for these compounds, so as to prepare them reproducibly. So far we have determined the phase relations in the systems R_2O_3–Fe_2O_3–FeO (R: La–Lu and Y) at elevated temperatures under controlled oxygen partial pressures, and reported the stability regions of $RFeO_3$ (perovskite), $R_3Fe_5O_{12}$ (garnet), and $(RFeO_3)_nFeO$ (n = 1, 2, . . .) with layered structures (*1*). We then began studying systems containing In_2O_3 as one of the components in the ternary systems. The phase relations in the systems In_2O_3–Fe_2O_3–CuO at 1000°C, In_2O_3–Ga_2O_3–CuO at 1000°C, In_2O_3–Fe_2O_3–CoO at 1300°C, and In_2O_3–Ga_2O_3–CoO at 1300°C were reported (*2*), and $InFeCuO_4$, $InGaCuO_4$, and $InGaCoO_4$ with $YbFe_2O_4$-type structure (*3*), $In_2Fe_2CuO_7$ and $In_2Ga_2CuO_7$ with $Yb_2Fe_3O_7$-type structure (*4*), and $In_3Fe_3CuO_{10}$ with $Yb_3Fe_4O_{10}$-type structure (*5*, *6*) were obtained. $InFeBO_4$ (B: Mg or Fe(II)), $InGaBO_4$ (B: Mg, Mn(II), Fe(II), Ni(II), or Zn), $InAlCuO_4$, $ScGaBO_4$ (B: Cu or Zn), $ScAlCuO_4$, $(InGaO_3)_2(ZnO)$,

[1] To whom all correspondence should be addressed.

0022-4596/90 $3.00

and $(ScGaO_3)_2(CuO)$ were prepared; a systematic scheme was provided for classifying $(InAO_3)_n(BO)_m$ (n and m: integer) compounds into four crystal structures: spinel, $YbFe_2O_4$, $In_2O_3(CuO)_2$, and $CaFe_2O_4$ (*7*, *8*). There is a solid-solution between $InFeCoO_4$ and Fe_2CoO_4 with spinel structure (*2*). Nakamura *et al.* (*9*) reported the phase relations in the system In_2O_3–Fe_2ZnO_4–ZnO at 1350°C, in which $In_2O_3(ZnO)_m$–$InFeO_3(ZnO)_m$–$In_{1-x}Fe_{1+x}O_3(ZnO)_m$ (m = 1–13, $0 \leq x \leq 1$) is stable with the $InFeO_3(ZnO)_m$-type layered structures (*10*). In the system Yb_2O_3–Cr_2O_3–BO (B: Co and Ni) at 1200 and 1300°C, and in the system Yb_2O_3–Ga_2O_3–NiO at 1200 and 1300°C, no ternary compounds occur with the $YbFe_2O_4$-type or spinel-type crystal structure, respectively (*11*). In the present paper, we report on the phase relations in the systems In_2O_3–Ga_2MgO_4–MgO at 1300°C, In_2O_3–Fe_2NiO_4–NiO at 1200°C, In_2O_3–Ga_2NiO_4–NiO at 1200°C, In_2O_3–Cr_2NiO_4–NiO at 1200°C, In_2O_3–Cr_2CoO_4–CoO at 1200°C, and In_2O_3–Cr_2CuO_4–CuO at 1000°C, all of which were determined by a classical quenching method. We also classify the phase relations in the system In_2O_3–A_2BO_4–BO (A: Fe, Ga, or Cr; B: Mg, Co, Ni, Cu, or Zn) at elevated temperatures, based upon both the A_2O_3 and BO components.

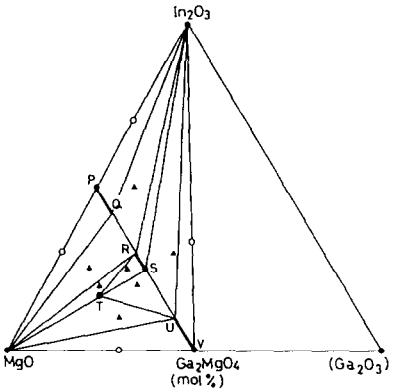

FIG. 1. Phase relations in the system In_2O_3–Ga_2MgO_4–MgO at 1300°C. The points in the diagram represent the following chemical compositions [In_2O_3 : Ga_2O_3 : MgO (in mole ratio)]: P, In_2MgO_4 (spinel type) (0.50 : 0.00 : 0.50); Q, (0.42 : 0.08 : 0.50); R, (0.30 : 0.20 : 0.50); S, $InGaO_3(MgO)$ ($YbFe_2O_4$ type) (0.25 : 0.25 : 0.50); T, $InGaO_3(MgO)_2$ ($InFeO_3(ZnO)_2$ type) (0.17 : 0.17 : 0.66); U, (0.10 : 0.40 : 0.50); and V, Ga_2MgO_4 (spinel type) (0.00 : 0.50 : 0.50). Symbols: ▲, three phases coexist; ○, two phases coexist; ●, a single phase exists.

Experimental

In_2O_3 (99.99%), Fe_2O_3 (99.9%), Ga_2O_3 (99.9%), Cr_2O_3 (99.9%), MgO (guaranteed reagent grade), CoO (99.9%), MnO (99.9%), NiO (99.9%), and CuO (guaranteed reagent grade) powders were used as starting compounds. Each of the mixtures in the system In_2O_3–Cr_2CuO_4–CuO was heated in a Pt crucible in air. In order to prepare $In_{2x}Fe_{2-2x}Mn(II)O_4$ with the spinel structure, mixtures of calculated weight of powders of In_2O_3, Fe_2O_3, and MnO were shaped into a cylindrical form in a piston pressure vessel and put in alumina crucibles which were sealed in silica glass tubes, and heated at 1250°C for 2 hr. All of the other mixtures were sealed in Pt tubes and heated at selected temperatures. The experimental method and equipment used in these experiments have been described elsewhere (*9*).

Results and Discussion

1. The phase relations in the system In_2O_3–Ga_2MgO_4–MgO at 1300°C. Figure 1 shows the phase relations in the system In_2O_3–Ga_2MgO_4–MgO at 1300°C. There are two ternary phases, $InGaO_3(MgO)$ and $InGaO_3(MgO)_2$. $InGaO_3(MgO)$ has the $YbFe_2O_4$ structure in the range from $InGaO_3(MgO)$ to $In_{1+x}Ga_{1-x}O_3(MgO)$ (x = 0.20). $InGaO_3(MgO)_2$ has the $InFeO_3(ZnO)_2$-type structure (a = 3.309(1) Å and c = 22.08(1) Å; space group: $P6_3/mmc$). Both $InGaO_3(MgO)$ and $InGaO_3(MgO)_2$ belong to a series of homologous compounds, with

$InFeO_3(ZnO)_m$-type structures. There are two spinel phase regions, In_2MgO_4–$In_{2-x}Ga_xMgO_4$ ($x = 0.32$) and Ga_2MgO_4–$Ga_{2-x}In_xMgO_4$ ($x = 0.40$), which approach each other. There is no full solid-solution range from In_2MgO_4 to Ga_2MgO_4 including $InGaMgO_4$ with a spinel structure, but the ranges are separated by $InGaO_3(MgO)$ with the $YbFe_2O_4$-type structure. Barbier (*12*) reported the refinement by neutron powder diffraction of the crystal structure of $In_{1.2}Ga_{0.8}MgO_4$ with lattice constants $a = 3.3243(4)$ Å and $c = 25.9543(3)$ Å, which was synthesized between 1100 and 1400°C. Barbier's chemical composition and lattice constants indicate that his sample is near one of the endpoints in the $InGaO_3(MgO)$ phase region. Kimizuka *et al.* (*13*) reported the phase relations in the system In_2O_3–Fe_2MgO_4–MgO at 1300°C in which there is a full solid-solution range between In_2MgO_4 and Fe_2MgO_4, including $InFeMgO_4$ with the spinel structure. As in the case of CoO in $InFeCoO_4$ (spinel type) and $InGaO_3(CoO)$ ($YbFe_2O_4$ type) (*2*), $InFeMgO_4$ has the spinel structure, and $InGaO_3(MgO)$ has the $YbFe_2O_4$ structure. However, we can safely assume that each region of the solid-spinel-type solutions in the system In_2O_3–Ga_2MgO_4–MgO become more widely extended with rising temperature, and that $InGaO_3(MgO)$ will be eventually transformed to a spinel structure, as is the case for $InFeO_3(MnO)$ (*14*) which will be described later. Barbier (*12*) heated $InGaO_3(MgO)$ with the $YbFe_2O_4$ structure at 1600°C for several days, but he could not obtain $InGaO_3(MgO)$ in the spinel form. We believe that 1600°C may be too low to form a spinel-type $InGaO_3(MgO)$ compound.

2. The system In_2O_3–A_2NiO_4–NiO (A: Fe, Ga, or Cr) at 1200°C. Figure 2 shows the phase relations in the system In_2O_3–Fe_2NiO_4–NiO at 1200°C, the system In_2O_3–Ga_2NiO_4–NiO at 1200°C, and the system In_2O_3–Cr_2NiO_4–NiO at 1200°C. There is a solid-solution between $InANiO_4$ and A_2NiO_4 with a spinel type of structure. The relations between each lattice constant and x in $In_xA_{2-x}NiO_4$ ($0 \le x \le 1$) are shown in Fig. 3. Both Fe_2NiO_4 and Ga_2NiO_4 form an inverse spinel and Cr_2NiO_4 forms a normal spinel (*15*).

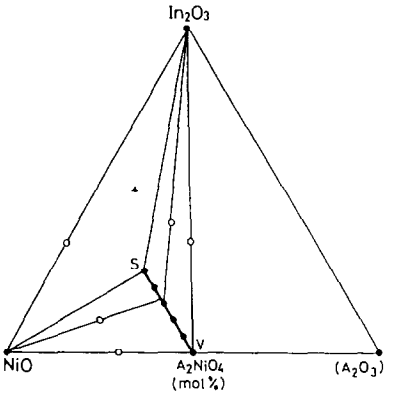

FIG. 2. Phase relations in the system In_2O_3–A_2NiO_4–NiO at 1200°C (*A*: Fe, Ga, or Cr). *S*, $InANiO_4$ (spinel type) [$In_2O_3 : A_2O_3 : NiO = 0.25, 0.25, 0.50$ (in mole ratio)]; V, A_2NiO_4 (spinel) [$In_2O_3 : A_2O_3 : NiO = 0.00 : 0.50 : 0.50$ (in mole ratio)]. Symbols in this figure as in the legend to Fig. 1.

These results are quite reasonable considering the characteristic properties of site preference effect of Cr(III), Ni(II), Fe(III), and Ga(III) in oxide crystals. The Fe(III) cation distribution in $InFeNiO_4$ has been already determined by ^{57}Fe Mössbauer spectroscopy (*14*), and the cation distribution of $(In(III)_{0.45}Ni(II)_{0.11}Fe(III)_{0.44})[In(III)_{0.55}Ni(II)_{0.89}Fe(III)_{0.56}]O_4$ was investigated. Here, ( ) and [ ] refer to the tetrahedral and the octahedral sites in the spinel structure, respectively. We did not experimentally measure the cation distribution in $InGaNiO_4$ or $InCrNiO_4$; however, we can reasonably advance the following distributions in first approximation: $(Ga)[InNi]O_4$ and $(Ni_xIn_{1-x})[Ni_{1-x}In_xCr]O_4$, ($0 \le x \le 1$), respectively. The various slopes of the relations between the lattice constants and x in Fig. 3 support the above hypothesis for the cation distribution.

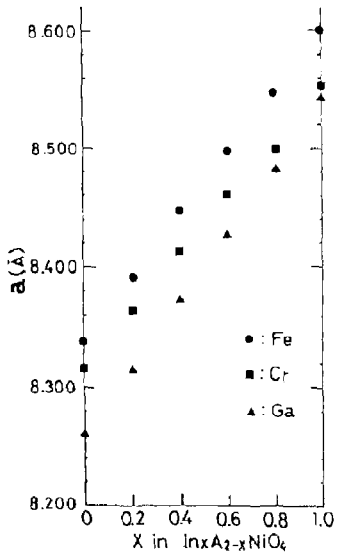

FIG. 3. Relations between the lattice constants of spinels and x in $In_xA_{2-x}NiO_4$ (A: Fe, Ga, or Cr) ($0 \leq x \leq 1$). Cr_2NiO_4 has a tetragonal unit cell at room temperature. (JCPDS Card 23-1273). $v^{1/3}$ ($v = a^2 * c$) at $x = 0$ in $In_xCr_{2-x}NiO_4$ has been plotted in this figure. $In_xCr_{2-x}NiO_4$ has a cubic unit cell ($0.20 \leq x \leq 1$).

3. The system In_2O_3–Cr_2CoO_4–CoO at 1200°C. Figure 4 shows the phase relations in the system In_2O_3–Cr_2CoO_4–CoO at 1200°C; there is no ternary phase but a solid–solution of the spinel phase was obtained which points toward the hypothetical phase "$InCrCoO_4$."

4. The system In_2O_3–Cr_2CuO_4–CuO at 1000°C. Figure 5 shows the phase relations in the system In_2O_3–Cr_2CuO_4–CuO at 1000°C, in which there is a binary phase, $In_2Cu_2O_5$ (*16*), but no ternary phase. We listed in Table I each of the chemical compositions of the starting mixtures, heating periods, and phases obtained necessary for establishing the phase relations in the system In_2O_3–A_2BO_4–BO [A: Ga, Fe, or Cr; B: Mg, Ni, Co, or Cu] at elevated temperatures. We did not quantitatively determine the various solid–solution ranges of In_2O_3 and BO (B: Mg, Co, Ni, or Cu) in the system In_2O_3–A_2BO_4–BO at elevated temperatures.

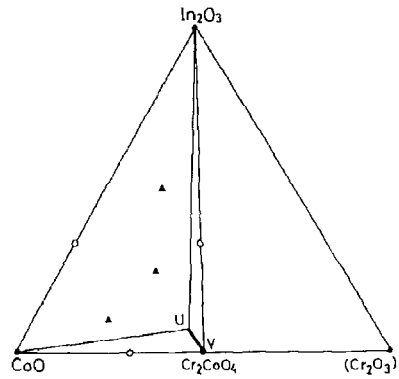

FIG. 4. Phase relations in the system In_2O_3–Cr_2CoO_4–CoO at 1200°C. U, (In_2O_3 : Cr_2O_3 : CoO = 0.08 : 0.42 : 0.50); V, Cr_2CoO_4 (spinel) [In_2O_3 : Cr_2O_3 : CoO = 0.00 : 0.50 : 0.50 (in mole ratio)]. Symbols as in the legend to Fig. 1.

5. The system In_2O_3–A_2MnO_4–MnO (A: Fe or Ga). In the system In_2O_3–A_2MnO_4–MnO (A: Fe or Ga) at elevated temperatures, $InGaO_3(MnO)$, $InFeO_3(MnO)$, $InGaO_3(MnO)_2$, and $InGaO_3(MnO)_3$ with $InFeO_3(ZnO)_m$-type structures and $(InGaO_3)_2(MnO)$ with $(YbFeO_3)_2(FeO)$-type structures have been already reported (*13*). We prepared $InFeO_3(MnO)_2$ (a = 3.368(1) Å, c = 22.85(1) Å) with the $InFeO_3(ZnO)_2$

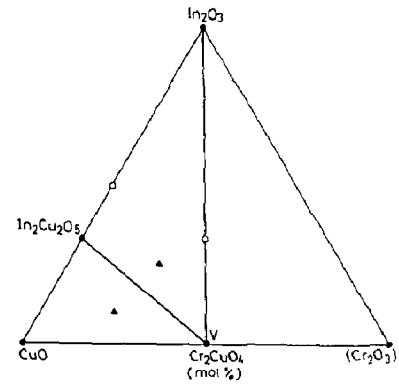

FIG. 5. Phase relations in the system In_2O_3–Cr_2CuO_4–CuO at 1000°C. V, Cr_2CuO_4 (spinel) [In_2O_3 : Cr_2O_3 : CuO = 0.00 : 0.50 : 0.50 (in mole ratio)]. Symbols as in the legend to Fig. 1.

TABLE I

THE MIXTURES, HEATING PERIODS, AND PHASES OBTAINED IN THE SYSTEM In_2O_3–A_2BO_4–BO (A: Ga, Fe, OR Cr; B: Mg, Ni, Co, OR Cu)

Starting mixture (in mole ratio) $In_2O_3 : A_2O_3 : BO$	Heating period (days)	Phases obtained
The system In_2O_3–Ga_2MgO_4–MgO at 1300°C (Fig. 1)		
1: 1: 1	2 + 2	In_2O_3, Ga_2MgO_4
3: 3: 4	2 + 3	$InGaMgO_4$, In_2O_3, Ga_2MgO_4
5: 1: 4	3 + 3	In_2O_3, In_2MgO_4, $InGaMgO_4$
25:10:65	2 + 2	$InGaMgO_4$, MgO, In_2MgO_4
10:25:65	2 + 2	$InGaO_3(MgO)_2$, MgO, Ga_2MgO_4
20:25:55	1 + 5	$InGaMgO_4$, $InGaO_3(MgO)_2$, Ga_2MgO_4
25:20:55	2 + 3	$InGaO_3(MgO)_2$, $InGaMgO_4$
20:15:65	3 + 2	$InGaMgO_4$, $InGaO_3(MgO)_2$, MgO
7: 0: 3	1 + 5	In_2O_3, In_2MgO_4
3: 0: 7	3 + 3	In_2MgO_4, MgO
0: 3: 7	2 + 2	Ga_2MgO_4, MgO
The system In_2O_3–A_2NiO_4–NiO at 1200°C (A: Fe, Cr, or Ga) (Fig. 2)		
1: 1: 1	7 + 7	In_2O_3, A_2NiO_4
1: 0: 2	7 + 7	In_2O_3, NiO
1: 1: 2	7 + 7	$InANiO_4$ (spinel type)
1: 2: 7	7 + 7	spinel type, NiO
40:25:35	7 + 7	In_2O_3, spinel type
50:15:35	7 + 7	In_2O_3, spinel type, NiO
0: 3: 7	7 + 7	A_2NiO_4, NiO
The system In_2O_3–Cr_2CoO_4–CoO at 1200°C (Fig. 4)		
1:1:1	7 + 7	In_2O_3, Cr_2CoO_4
1:1:2	7 + 7	In_2O_3, Cr_2CoO_4, CoO
1:2:7	7 + 7	Cr_2CoO_4, In_2O_3, CoO
0:3:7	7 + 7	Cr_2CoO_4, CoO
3:0:7	7 + 7	In_2O_3, CoO
The system In_2O_3–Cr_2CuO_4–CuO at 1000°C (Fig. 5)		
1:1:1	7 + 7	In_2O_3, Cr_2CuO_4
1:1:2	7 + 7	In_2O_3, Cr_2CuO_4, $In_2Cu_2O_5$
1:2:7	7 + 7	$In_2Cu_2O_5$, Cr_2CuO_4, CuO
1:1:0	7 + 7	In_2O_3, $In_2Cu_2O_5$

crystal structure by heating at 1000°C for 6 days. The d-spacings and relative intensities of X-ray powder diffraction of $InFeO_3(MnO)_2$ will be sent to the Joint Committee of Powder Diffraction Standard. We show in Fig. 6 the binary and ternary compounds that have been synthesized so far in the system In_2O_3–A_2MnO_4–MnO (A: Fe or Ga) and $InFeO_3(MnO)_2$. Since the reaction rate in forming the ternary phases from In_2O_3, Fe_2O_3 (or Ga_2O_3), and MnO powders was too slow, we could not present the phase relations In_2O_3–A_2MnO_4–MnO at elevated temperatures. Gerardin *et al.* (*14*) synthesized $InFeMnO_4$ with the spinel structure at 1175°C for 2 hr. Both In_2MnO_4 (*8*) and Fe_2MnO_4 have the spinel structure, so we can safely infer that a spinel solid–solution between In_2MnO_4 and Fe_2MnO_4 including $InFeMnO_4$ should exist at about 1200°C. We

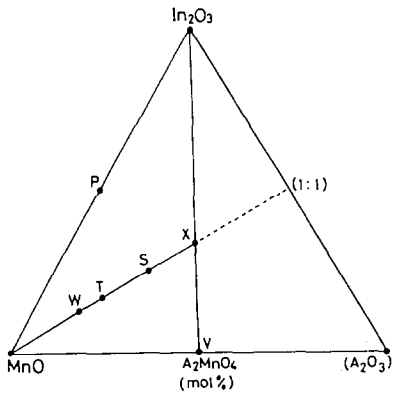

FIG. 6. Ternary compounds in the system In_2O_3–A_2MnO_4–MnO (A: Fe or Ga) at elevated temperatures. P, In_2MnO_4; S, $InAMnO_4$; V, A_2MnO_4; T, $InAO_3(MnO)_2$ (A: Fe or Ga); W, $InGaO_3(MnO)_3$; X, $(InGaO_3)_2MnO$.

show in Fig. 7 the lattice constants of the solid–solutions with a spinel structure. So far neither $(RAO_3)_nBO$ (n = integer) nor $RAO_3(BO)_m$ (m = integer) have been prepared coexistent in the same ternary system; however, $(InGaO_3)_2MnO$, $(InGaO_3)(MnO)$, $InGaO_3(MnO)_2$, and $InGaO_3(MnO)_3$ do occur in the system In_2O_3–Ga_2MnO_4–MnO. Thus, we could bridge the compounds having the $(YbFeO_3)_nFeO$-type crystal structures and the $InFeO_3(ZnO)_m$-type structures in the system In_2O_3–Ga_2MnO_4–MnO. We also encountered both $(InGaO_3)_2ZnO$ and $InGaO_3(ZnO)_m$ in the system In_2O_3–Ga_2ZnO_4–ZnO at 1350°C (*17*).

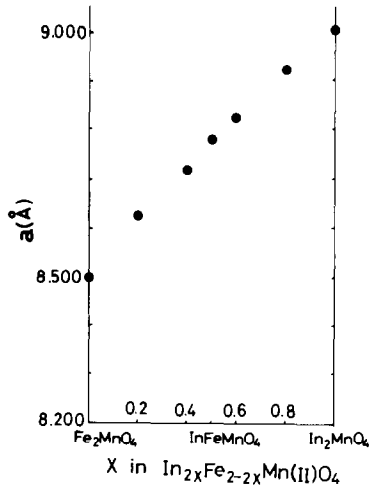

FIG. 7. The relation between the lattice constants of the spinel phase and x in $In_{2x}Fe_{2-2x}MnO_4$ ($0 \leq x \leq 1$).

In order systematically to understand the phase relations in the systems R_2O_3–A_2BO_4–BO (R: La–Lu, Y, In, and Sc; A: trivalent cation elements; B: divalent cation elements) at elevated temperatures which have been reported so far, we consider the following factors: (i) In(III) can occur in both the tetrahedral and octahedral sites of oxide crystals; however, the rare earth elements (La–Lu and Y) cannot reside on the tetrahedral sites. No (La–Lu)ABO_4 compounds with a spinel-type structure have been reported so far; however, InABO_4 compounds crystallize in two kinds of structures, namely the spinel- and $YbFe_2O_4$-types. $RABO_4$ (R: Lu, Yb, Tm, Er, Ho, or Y) has the $YbFe_2O_4$ structure. (ii) Both ZnO with the wurtzite structure and $InGaO_3(ZnO)$ with the $YbFe_2O_4$ structure can be considered to be layered compounds with two-dimensional triangular lattices of nearly similar size. $InGaO_3(ZnO)_m$ is formed by stacking of two of these layered types of structures. (iii) Both Ga(III) and Zn(II) with a tendency for tetrahedral site preference in oxide crystals, and both the spherical Mg(II) and Mn(II) ions can constitute phases having the $YbFe_2O_4$-layered structures together with In_2O_3. They cannot form the solid–solutions with A_2BO_4 having the spinel structure. (iv) $InAO_3(NiO)$ and $InFeO_3(BO)$ (A: Fe, Ga, or Cr; B: Mg or Co) have the spinel structure and can form solid–solutions with A_2BO_4. (v) The combination of Ga(III) and Zn(II), Mn(II), or Mg(II) is the most favorable for forming both $(InAO_3)_nBO$ and $InAO_3(BO)_m$ compounds with layered structures. (vi) In the binary system In_2O_3–BO (B: Mg, Mn, Cu, Co, or Zn) there are In_2MgO_4 and In_2MnO_4 having a spinel-

type, $In_2Cu_2O_5$, and $In_2O_3(ZnO)_m$ with layered structure (*9*, *18*). Evans (*19*) shows that both In_2NiO_4 and In_2CoO_4 adopt the spinel structure; however, we did not encounter any binary phases in the In_2O_3–BO (*B*: Ni or Co) under the present experimental condition. Recently, $MnGa_xCr_{2-x}S_4$ ($1.50 < x < 1.80$) with the layered $ZnIn_2S_4$-type structure was prepared (*20*), and the phase transformation between spinel type and $ZnIn_2S_4$ type was discussed. In $ZnIn_2S_4$ (space group: $R3m$) the sulfur atoms are in a mixed close packing, the sequence along the *c* axis being . . .*hhcchhcc*. . . The Zn atoms are on tetrahedral sites, and In occurs both on tetrahedral and octahedral sites (*21*). The higher order compounds, $InGaS_3(ZnS)_2$ and $InGaS_3(CdS)_2$, have also been investigated (*22*), because of their optical properties. Thus, AB_2X_4 (X = O, S, or Se) with the layered structure involving anions with the . . .*hhcchhcc*. . . sequence covers many inorganic compounds, as does the spinel structure.

Acknowledgment

The authors express their sincere thanks to Dr. M. Isobe (NIRIM) for helpful discussions.

References

1. N. KIMIZUKA, A. YAMAMOTO, H. OHASHI, T. SUGIHARA, AND T. SEKINE, *J. Solid State Chem.* **49,** 65 (1983).
2. N. KIMIZUKA AND E. TAKAYAMA, *J. Solid State Chem.* **53,** 217 (1984).
3. K. KATO, I. KAWADA, N. KIMIZUKA, AND T. KATSURA, *Z. Kristallogr.* **141,** 314 (1975).
4. K. KATO, I. KAWADA, N. KIMIZUKA, I. SHINDO, AND T. KATSURA, *Z. Kristallogr.* **143,** 278 (1976).
5. N. KIMIZUKA, K. KATO, I. SHINDO, I. KAWADA, AND T. KATSURA, *Acta Crystallogr., Sect. B* **32,** 1620 (1976).
6. Y. MATSUI, K. KATO, N. KIMIZUKA, AND S. HORIUCHI, *Acta Crystallogr., Sect. B* **35,** 561 (1979).
7. N. KIMIZUKA AND T. MOHRI, *J. Solid State Chem.* **60,** 382 (1985).
8. N.KIMIZUKA AND T. MOHRI, *J. Solid State Chem.* **78,** 98 (1989).
9. M. NAKAMURA, N. KIMIZUKA, AND T. MOHRI, *J. Solid State Chem.*, **86,** 16 (1990).
10. N. KIMIZUKA, T. MOHRI, Y. MATSUI, AND K. SIRATORI, *J. Solid State Chem.* **74,** 98 (1988).
11. N. KIMIZUKA AND E. TAKAYAMA, *J. Solid State Chem.* **43,** 278 (1982).
12. J. BARBIER, *J. Solid State Chem.* **82,** 115 (1989).
13. N. KIMIZUKA, T. MOHRI, AND M. NAKAMURA, *J. Solid State Chem.* **81,** 70 (1989).
14. R. GERARDIN, A. ALEBOUYEH, J. F. BRICE, O. EVRARD, AND J. P. SANCHEZ, *J. Solid State Chem.* **76,** 398 (1988).
15. R. J. HILLS, J. R. CRAIG, AND G. V. GIBBS, *Phys. Chem. Miner.* **4,** 317 (1979).
16. V. G. BERGERHOFF AND H. KASPER, *Acta Crystallogr., Sect. B* **24,** 388 (1968).
17. M. NAKAMURA, private communication (1990).
18. H. KASPER, *Z. Anorg. Allg. Chem.* **349,** 113 (1967).
19. R. C. EVANS, "Introduction to Crystal Chemistry," 2nd. ed., p. 173, Cambridge Univ. Press., London/New York (1966).
20. H. HAEUSELER AND W. KWARTENG-ACHEAMPONG, *Mater. Res. Bull.* **24,** 939 (1989).
21. R. W. G. WYCKOFF, "Crystal Structures," Vol. 3, 2nd. ed., Chap. VIIIB, p. 138, Interscience, New York (1965).
22. T. IRIE, S. ENDO, H. KUROGANE, H. NAKANISHI, AND T. TOYODA, *Japan. J. Appl. Phys.* **25,** 922 (1986).