JOURNAL OF SOLID STATE CHEMISTRY 60, 382–384 (1985)

BRIEF COMMUNICATION

Spinel, $YbFe_2O_4$, and $Yb_2Fe_3O_7$ Types of Structures for Compounds in the In_2O_3 and Sc_2O_3–A_2O_3–BO Systems [*A*: Fe, Ga, or Al; *B*: Mg, Mn, Fe, Ni, Cu, or Zn] at Temperatures over 1000°C

NOBORU KIMIZUKA* AND TAKAHIKO MOHRI

National Institute for Research in Inorganic Materials, 1-1, Namiki, Sakuramura, Niiharigun, Ibaraki-ken, Japan 305

Received April 3, 1985

In the Sc_2O_3–Ga_2O_3–CuO, Sc_2O_3–Ga_2O_3–ZnO, and Sc_2O_3–Al_2O_3–CuO systems, $ScGaCuO_4$, $ScGaZnO_4$, and $ScAlCuO_4$ with the $YbFe_2O_4$-type structure and $Sc_2Ga_2CuO_7$ with the $Yb_2Fe_3O_7$-type structure were obtained. In the In_2O_3–A_2O_3–BO systems (*A*: Fe, Ga, or Al; *B*: Mg, Mn, Fe, Ni, or Zn), $InGaFeO_4$, $InGaNiO_4$, and $InFe^{3+}MgO_4$ with the spinel structure, $InGaZnO_4$, $InGaMgO_4$, and $InAlCuO_4$ with the $YbFe_2O_4$-type structure, and $In_2Ga_2MnO_7$ and $In_2Ga_2ZnO_7$ with the $Yb_2Fe_3O_7$-type structure were obtained. $InGaMnO_4$ and $InFe_2O_4$ had both the $YbFe_2O_4$-type and spinel-type structures. The revised classification for the crystal structures of AB_2O_4 compounds is presented, based upon the coordination numbers of constituent *A* and *B* cations.

In both the In_2O_3–Fe_2O_3–CuO system and the In_2O_3–Ga_2O_3–CuO system, there are $(InFeO_3)_nCuO$ (n = 1 and 2) and $(InGaO_3)_nCuO$ (n = 1, 2, and 3) which are isostructural with $(YbFeO_3)_nFeO$ (n = 1, 2, and 3), and in the In_2O_3–Fe_2O_3–CoO system there is a spinel type of $InFeCoO_4$ (*1–3*). In the present paper, we report both the conditions of synthesis and the lattice constants of $ScAlCuO_4$, $ScGaCuO_4$, $ScGaZnO_4$, $InGaMgO_4$, $InGaZnO_4$, and $InAlCuO_4$ having the $YbFe_2O_4$-type structure, $InGaFe^{2+}O_4$, $InGaNiO_4$, and $InFeMgO_4$ having the spinel structure, $Sc_2Ga_2CuO_7$, $In_2Ga_2MnO_7$, and $In_2Ga_2ZnO_7$ having the $Yb_2Fe_3O_7$ structure, and $InGaMnO_4$ and $InFe_2O_4$ which have both $YbFe_2O_4$- and spinel-type structures. Finally, the revised classification for crystal structures of AB_2O_4 compounds is presented, based upon the coordination numbers of the constituent *A* and *B* cations.

Experimental

Each of the starting compounds, Sc_2O_3 (99.9%), Al_2O_3 (99.99%), Ga_2O_3 (99.99%), CuO (guaranteed reagent grade), In_2O_3 (99.9%), Fe_2O_3 (99.9%), MgO (guaranteed reagent grade), ZnO (99.9%), and MnO_2 (99.9%) was heated at 1000°C for 1 day in air. NiO (99.9%) was heated at 1100°C for 15 hr and MnO was prepared at 1200°C in a mixture of CO_2/H_2 = 1 for 1 day.

Sc_2O_3 (or In_2O_3) : A_2O_3 : BO = 1 : 1 : 2 or 1 : 1 : 1 (mole ratio) were sealed in evacuated silica tubes, when mixtures were to be heated below 1200°C, and in Pt tubes above

* To whom all correspondence should be addressed.

0022-4596/85 $3.00

TABLE I

THE CONDITIONS OF SYNTHESIS AND THE LATTICE CONSTANTS (Å) OF $InABO_4$, $ScABO_4$, $In_2A_2BO_7$, AND $Sc_2A_2BO_7$ AT ROOM TEMPERATURE

Compound	Spinel ($Fm3d$)	$YbFe_2O_4$ ($R\bar{3}m$)[a]	$Yb_2Fe_3O_7$ ($P6_3/mmc$)
$InGaMgO_4$		a = 3.3036 (1) c = 25.805 (1) 1300°C, 6 days	
$InGaMnO_4$	a = 8.5760 (4) 1500°C, 3 days	a = 3.3291 (1) c = 26.521 (2) 1000°C, 14 days	
$InGaFeO_4$	a = 8.3998 (1) 1000°C, 10 days		
$InGaNiO_4$	a = 8.5467 (3) 1400°C, 7 days		
$InGaZnO_4$		a = 3.2948 (1) c = 26.071 (1) 1450°C, 1 day	
$InFeMgO_4$	a = 8.6320 (1) 1300°C, 6 days		
$InFe_2O_4$	a = 8.4483 (1) 1100°C, 7 days	a = 3.3391 (1) c = 26.076 (1) 1000°C, 1 day	
$InAlCuO_4$		a = 3.3148 (1) c = 24.359 (6) 1150°C, 7 days	
$ScGaCuO_4$		a = 3.3126 (1) c = 24.645 (1) 1150°C, 2 days	
$ScGaZnO_4$		a = 3.2593 (1) c = 25.912 (1) 1300°C, 8 days	
$ScAlCuO_4$		a = 3.2773 (1) c = 24.173 (1) 1150°C, 6 days	
$In_2Ga_2MnO_7$			a = 3.3327 (1) c = 29.691 (1) 1450°C, 2 days
$In_2Ga_2ZnO_7$			a = 3.3077 (1) c = 29.484 (1) 1450°C, 6 days
$Sc_2Ga_2CuO_7$			a = 3.3026 (1) c = 28.124 (1) 1150°C, 7 days

[a] The hexagonal lattice constants are given.

1200°C. For preparing $InGaFe^{2+}O_4$ and $InFe^{3+}Fe^{2+}O_4$, we used both Fe_2O_3 and Fe powder (99.99%). All of the mixtures containing MnO were heated in Pt tubes. Each sample was rapidly cooled in water or air after each heat treatment. The weight of each sample was carefully measured before and after the heat treatment. The absence of chemical reactions between samples and tubes were visually checked. X-Ray diffractometer powder-diffraction data for each sample thus obtained were taken at room tempera-

TABLE II

STRUCTURE TYPES FOR AB_2O_4 COMPOUNDS VERSUS COORDINATION NUMBERS (C.N.) OF *A* AND *B* CATIONS

C.N.:A	4	5	6	8	9 and/or 10
4	Phenacite		C.N.:B, Spinel	K_2WO_4	β-K_2SO_4
6		**$YbFe_2O_4$**	Sr_2PbO_4, Ca_2IrO_4, etc.		K_2NiF_4
8			$CaFe_2O_4$		
			$CaTi_2O_4$		

ture and the lattice constants were derived by means of least squares. (Si powder as a standard material, Mn-filtered Fe$K\alpha$ radiation, and a scintillation counter were employed.)

Results and Discussion

(1) In the Sc_2O_3–Ga_2O_3–CuO, Sc_2O_3–Ga_2O_3–ZnO, Sc_2O_3–Al_2O_3–CuO, and In_2O_3–Al_2O_3–CuO systems, $ScGaCuO_4$, $ScGaZnO_4$, $ScAlCuO_4$, and $InAlCuO_4$, having the $YbFe_2O_4$-type of structure, and $Sc_2Ga_2CuO_7$ having the $Yb_2Fe_3O_7$-type structure, were obtained. The $ScGaCuO_4$, $ScAlCuO_4$, and $InAlCuO_4$ powders are of a green-yellowish color.

(2) In the In_2O_3–Ga_2O_3–*B*O systems [*B*: Mg, Mn, Fe, Ni, Cu, and Zn], the In_2O_3–Fe_2O_3–FeO system, and the In_2O_3–Fe_2O_3–MgO system, $InGaMgO_4$ and $InGaZnO_4$ having the $YbFe_2O_4$-type structure were obtained, and $InGaFe^{2+}O_4$, $InGaNiO_4$, and $InFe^{3+}MgO_4$ having the spinel structure were also obtained. The crystal structures of $InGaCuO_4$ and $InGaCoO_4$ have been reported (*1*). Both $InGaMnO_4$ and $InFe_2O_4$ had spinel- and $YbFe_2O_4$-type structures. They may have a phase transformation above 800°C. $In_2Ga_2MnO_7$ and $In_2Ga_2ZnO_7$ having the $Yb_2Fe_3O_7$-type structure were obtained. The synthesis conditions and the lattice constants of these compounds are summarized in Table I. Investigations for the details of the phase transformation between $YbFe_2O_4$ and spinel structures are in progress.

A. F. Well (*4*) classified AB_2O_4-type compounds based upon the coordination numbers of the constituent *A* and *B* cations. More than about 60 compounds with $YbFe_2O_4$ structure (Yb: coordination number 6, Fe: coordination number 5) and the related structures have been reported (*1, 5*). Table II shows a newly revised classification of AB_2O_4-type compounds including the $YbFe_2O_4$-type structure.

References

1. N. KIMIZUKA AND E. TAKAYAMA, *J. Solid State Chem.* **53,** 217 (1984).
2. K. KATO, I. KAWADA, N. KIMIZUKA, AND T. KATSURA, *Z. Kristallogr.* **141,** 314 (1975).
3. K. KATO, I. KAWADA, N. KIMIZUKA, I. SHINDO, AND T. KATSURA, *Z. Kristallogr.* **143,** 278 (1976).
4. A. F. WELLS, "Structural Inorganic Chemistry," p. 490, *Oxford Univ. Press (Clarendon)* (1975).
5. N. KIMIZUKA AND T. KATSURA, *J. Solid State Chem.* **13,** 176 (1975); N. KIMIZUKA AND T. KATSURA, *ibid.*, **15,** 151 (1975); N. KIMIZUKA AND E. TAKAYAMA, *ibid.*, **41,** 166 (1982).