

$Ln(Fe^{3+}M^{2+})O_4$ Compounds with Layer Structure [Ln : Y, Er, Tm, Yb, and Lu, M : Mg, Mn, Co, Cu, and Zn]

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A series of new compounds $Ln(Fe^{3+}M^{2+})O_4$ [Ln : Y, Er, Tm, Yb, and Lu, M : Mg, Mn, Co, Cu, and Zn] were successfully synthesized and their lattice constants were determined. These compounds have the same crystal structure as $YbFe_2O_4$ and Fe^{3+} and M^{2+} are both surrounded by five oxygen ions forming a trigonal bipyramid. The synthetic conditions are presented. They are strongly dependent upon the constituent cations of the compound.

Introduction

In the process of establishing the phase diagrams of the $FeO-Fe_2O_3-Y_2O_3$ system and the $FeO-Fe_2O_3-Yb_2O_3$ system at $1200^\circ C$ under controlled oxygen partial pressures, Kimizuka and Katsura found YFe_2O_4 (1), $YbFe_2O_4$ (2), and isostructural compounds of $HoFe_2O_4$, $ErFe_2O_4$, $TmFe_2O_4$, and $LuFe_2O_4$ (3). These compounds have a homogeneity range of composition, for instance, the composition of $YbFe_2O_4$ ranges from $YbFe_2O_{4.052}$ to $YbFe_2O_{3.929}$ at $1200^\circ C$ (2).

$LnFe_2O_4$ compounds [Ln : Y, Ho, Er, Tm, Yb, and Lu] have a layer structure in which Fe^{3+} and Fe^{2+} occupy equivalent crystallographic sites surrounded by five oxygen ions forming a trigonal bipyramid. In Fig. 1 the crystal structure of $YbFe_2O_4$ is schematically shown. One of the $Fe-O$ distances in the trigonal bipyramid of the $YbFe_2O_4$ compound is nearly equal to the

summation of the ionic radii of ferrous ion and oxygen ion and another $Fe-O$ distance is nearly equal to the summation of the ionic radii of ferric ion and oxygen ion. The other three bond distances are intermediate between the two values of $Fe^{3+}-O^{2-}$ and $Fe^{2+}-O^{2-}$ distances. The oxygen ions form a kind of closest packing of spheres (4).

The magnetic properties and Mössbauer spectroscopy of YFe_2O_4 , $YbFe_2O_4$, and $LuFe_2O_4$ were studied, and it was discovered that the deviation from stoichiometry of the compounds (x in $LnFe_2O_{4-x}$) played an important role in the physical properties such as electrical transport phenomenon, magnetic behavior, and structural transformation at lower temperature (5-9). Electron exchange was observed between Fe^{3+} and Fe^{2+} in the same crystallographic site in the compound and the exchange rate was found to depend on the ratio of Fe^{3+} and Fe^{2+} , namely, on the deviation from stoichiometry. This electron exchange complicates the understanding of the physical properties observed. If Fe^{2+} can be substi-

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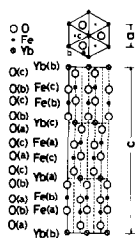


FIG. 1. The crystal structure of YbFe_2O_4 . Space group: $R\bar{3}m$, a, b, and c indicate the position in a unit cell.

tuted by other divalent cations, these complicating features of the compounds may become clearer. For this purpose, we tried to replace Fe^{2+} by other ions such as Mg^{2+} , Co^{2+} , Mn^{2+} , Cu^{2+} , and Zn^{2+} and successfully synthesized a series of new compounds $\text{Ln}(\text{Fe}^{3+}\text{M}^{2+})\text{O}_4$ [Ln : Y, Er, Tm, Yb, and Lu, M : Mg, Mn, Co, Cu, and Zn] by solid-state reactions at high temperatures. In this paper, we present the synthetic conditions of these new compounds, which have the same crystal structure as YbFe_2O_4 , and their lattice constants, and we discuss the synthetic conditions relating to the constituent cations.

Experimental

Reagent grade of MnO_2 , Co_2O_3 , ZnO and MgO (Wako Junyaku Co. Japan) and 99.9% purity grade of Fe_2O_3 , Y_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 and Lu_2O_3 were used as the starting materials. Prior to use, Y_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 , and ZnO were heated at 1200°C in air for 1 day. MgO was heated at 1300°C in air for 1 day. Fe_2O_3 and CuO were heated at 900°C in air for 1 day. MnO was obtained from MnO_2 under a reduced atmosphere ($\text{CO}_2/\text{H}_2 = 1$) at 1200°C (10). CoO was obtained from Co_2O_3 by heating in air at 1300°C for 1 week (11). The stoichiometries of CoO and MnO were checked by means of a thermogravimetric method (1). Each sample thus obtained was

identified by means of X-ray powder diffraction.

The preheated starting materials were mixed to desired ratios under ethyl alcohol in an agate mortar. In the $\text{Ln}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MnO}$ systems (Ln : Y, Er, Tm, Yb, and Lu), the mixture of Ln_2O_3 : Fe_2O_3 : $\text{MnO} = 1:1:2$ (in mole ratio) was put in a transparent silica tube and was evacuated through a mechanical oil pump for 3 hr and sealed. Each sealed tube was heated in a tubular-type vertical furnace at 1100°C . The temperature was controlled within an accuracy of $\pm 1^\circ\text{C}$. After heating, we rapidly cooled the sample to room temperature. Although we could obtain a single phase of LnFeMnO_4 within 1 hr, we heated each sample for 1 day in order to ensure obtaining the equilibrium state. No chemical reaction between the sample and the silica tube could be observed visually.

In the $\text{Ln}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MO}$ systems (M : Mg, Co, Cu, and Zn), the mixture of Ln_2O_3 : Fe_2O_3 : $\text{MO} = 1:1:2$ was placed in a platinum or alumina crucible and was heated in a furnace with a SiC heating element. The temperature was regulated to an accuracy of $\pm 2^\circ\text{C}$. The heating temperature was selected by trial and error. After heating the sample for a fixed time, we rapidly cooled the sample to room temperature. Each sample except the system containing MgO was heated in air. The $\text{Ln}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$ system was heated in oxygen atmosphere. The reaction period was between 1 hr and 5 days. Sample weights were measured before and after heat treatment. No difference in the weight was detected except in the $\text{Ln}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MgO}$ system, where weight loss of the sample was observed due to the partial reduction of Fe_2O_3 . The details of this process will be described in the results and discussion section of LnFeMgO_4 .

For each sample the X-ray powder diffraction pattern, (Mn-filtered $\text{FeK}\alpha$ radiation and a scintillation counter were em-

TABLE IA
POWDER X-RAY DATA FOR YbFe_2O_4 AND $\text{Ln}(\text{FeMn})\text{O}_4$ ($\text{Ln} = \text{Y}, \text{Er}, \text{Tm}, \text{Yb}, \text{AND Lu}$)

$h k l$	YbFe_2O_4			$\text{Y}(\text{FeMn})\text{O}_4$			$\text{Er}(\text{FeMn})\text{O}_4$		
	$d_o[\text{\AA}]^a$	$d_c[\text{\AA}]^b$	$[\%]^c$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.377	8.370	94	8.518	8.485	19	8.537	8.515	63
0 0 6	4.183	4.185	65	4.248	4.243	24	4.261	4.257	41
1 0 1	2.972	2.972	100	3.008	3.007	100	2.994	2.993	100
1 0 $\bar{2}$	2.910	2.911	6	2.946	2.946	10	—	—	—
0 0 9	2.790	2.790	59	2.830	2.829	43	2.840	2.838	48
1 0 4	2.702	2.701	82	2.735	2.734	92	2.727	2.726	92
1 0 5	2.571	2.571	67	2.603	2.603	60	2.596	2.596	76
1 0 7	2.2982	2.2979	15	2.3278	2.3270	8	2.3238	2.3238	22
1 0 $\bar{8}$	2.1660	2.1659	18	2.1940	2.1935	19	2.1920	2.1917	29
1 0 10	1.9232	1.9235	35	1.9485	1.9485	52	1.9485	1.9487	49
1 1 0	1.7275	1.7278	33	1.7481	1.7482	74	1.7399	1.7400	54
1 1 3	1.6916	1.6921	9	—	—	—	1.7045	1.7048	23
0 0 15	1.6737	1.6739	4	—	—	—	—	—	—
1 0 13	1.6228	1.6228	9	1.6442	1.6443	10	1.6460	1.6460	13
1 1 6	1.5970	1.5970	12	1.6161	1.6164	12	1.6110	1.6107	22
1 0 $\bar{14}$	1.5387	1.5384	18	1.5588	1.5588	31	1.5610	1.5609	26
2 0 $\bar{1}$	1.4935	1.4937	9	1.5114	1.5113	17	1.5043	1.5043	10
1 1 9	1.4690	1.4689	28	1.4872	1.4871	39	1.4836	1.4834	36
2 0 $\bar{4}$	1.4558	1.4555	12	1.4729	1.4729	14	1.4668	1.4666	15
2 0 5	1.4340	1.4340	8	1.4514	1.4512	15	1.4454	1.4453	13
2 0 8	1.3509	1.3507	4	—	—	—	—	—	—
2 0 $\bar{10}$	1.2853	1.2854	6	—	—	—	1.2979	1.2979	15
$h k l$	$\text{Tm}(\text{FeMn})\text{O}_4$			$\text{Yb}(\text{FeMn})\text{O}_4$			$\text{Lu}(\text{FeMn})\text{O}_4$		
	$d_o[\text{\AA}]^a$	$d_c[\text{\AA}]^b$	$[\%]^c$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.550	8.521	68	8.570	8.540	63	8.557	8.544	83
0 0 6	4.264	4.260	34	4.274	4.270	38	4.274	4.272	38
1 0 1	2.985	2.984	100	2.975	2.973	100	2.966	2.963	100
1 0 $\bar{2}$	2.927	2.925	3	2.916	2.915	4	2.909	2.906	7
0 0 9	2.840	2.840	47	2.848	2.847	38	2.848	2.848	46
1 0 4	2.720	2.719	95	2.713	2.712	63	2.706	2.705	92
1 0 5	2.591	2.590	67	2.585	2.585	54	2.579	2.579	69
1 0 7	2.3203	2.3202	18	2.3176	2.3171	17	2.3124	2.3129	17
1 0 $\bar{8}$	2.1889	2.1888	28	2.1866	2.1868	26	2.1824	2.1834	28
1 0 10	1.9473	1.9469	32	1.9464	1.9464	38	1.9435	1.9442	35
1 1 0	1.7345	1.7347	46	1.7284	1.7283	44	1.7231	1.7225	49
1 1 3	1.7003	1.6998	13	1.6941	1.6940	8	1.6890	1.6885	10
0 0 15	—	—	—	—	—	—	—	—	—
1 0 13	1.6456	1.6453	11	1.6460	1.6460	11	1.6462	1.6449	12
1 1 6	1.6069	1.6066	15	1.6023	1.6021	13	1.5975	1.5975	17
1 0 $\bar{14}$	1.5601	1.5603	28	1.5612	1.5613	20	1.5605	1.5604	15
2 0 $\bar{1}$	1.4996	1.4997	13	1.4941	1.4942	10	1.4891	1.4892	10
1 1 9	1.4805	1.4804	31	1.4775	1.4773	28	1.4732	1.4739	37
2 0 $\bar{4}$	1.4627	1.4624	12	1.4577	1.4575	13	1.4536	1.4529	11
2 0 5	1.4412	1.4413	11	1.4369	1.4367	9	1.4320	1.4323	8
2 0 8	—	—	—	—	—	—	—	—	—
2 0 $\bar{10}$	1.2950	1.2952	15	1.2925	1.2924	8	—	—	—

^a Observed d value. ^b Calculated d value. ^c Relative intensity.

TABLE IB
POWDER X-RAY DATA FOR $Ln(FeMg)O_4$ ($Ln = Er, Tm, Yb, \text{ AND } Lu$)

$h k l$	Er(FeMg) O_4			Tm(FeMg) O_4			Yb(FeMg) O_4			Lu(FeMg) O_4		
	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.557	8.562	65	8.492	8.516	100	8.415	8.387	85	8.466	8.436	68
0 0 6	4.288	4.281	51	4.261	4.258	69	4.200	4.194	48	4.225	4.218	76
1 0 1	3.029	3.028	100	3.012	3.012	69	2.953	2.949	100	2.951	2.948	79
1 0 $\bar{2}$	—	—	—	—	—	—	2.892	2.890	7	—	—	—
0 0 9	2.855	2.854	74	2.841	2.839	78	2.796	2.796	40	2.813	2.812	100
1 0 4	2.757	2.755	86	2.740	2.740	49	2.687	2.686	85	2.689	2.688	74
1 0 $\bar{5}$	2.620	2.622	26	2.608	2.608	40	2.558	2.558	68	2.563	2.561	66
1 0 7	—	—	—	—	—	—	2.2895	2.2895	29	2.2946	2.2943	17
1 0 $\bar{8}$	2.2112	2.2111	11	2.1986	2.1993	5	2.1599	2.1593	30	2.1652	2.1647	23
1 0 10	1.9641	1.9646	45	1.9542	1.9541	21	1.9196	1.9198	38	1.9268	1.9259	47
1 1 0	1.7606	1.7605	59	1.7513	1.7514	21	1.7152	1.7146	40	1.7145	1.7139	54
1 1 3	—	—	—	—	—	—	1.6794	1.6799	16	—	—	—
1 0 13	—	—	—	—	—	—	1.6216	1.6215	13	1.6283	1.6279	13
1 1 6	—	—	—	—	—	—	1.5870	1.5871	21	1.5878	1.5878	11
1 0 $\bar{14}$	—	—	—	—	—	—	1.5375	1.5376	34	1.5435	1.5439	13
1 1 9	—	—	—	—	—	—	1.4618	1.4616	32	1.4630	1.4635	22
2 0 $\bar{4}$	—	—	—	1.4759	1.4757	14	—	—	—	—	—	—

TABLE IC
POWDER X-RAY DATA FOR $Ln(FeCo)O_4$ ($Ln = Tm, Yb, \text{ AND } Lu$)

$h k l$	Tm(FeCo) O_4			Yb(FeCo) O_4			Lu(FeCo) O_4		
	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.415	8.390	100	8.402	8.400	58	8.460	8.437	100
0 0 6	4.198	4.195	68	4.200	4.200	79	4.220	4.218	50
1 0 1	2.974	2.972	61	2.949	2.950	17	2.943	2.942	42
0 0 9	2.797	2.797	81	2.800	2.800	100	2.812	2.812	73
1 0 4	2.705	2.703	70	2.687	2.687	17	2.685	2.683	43
1 0 $\bar{5}$	2.574	2.572	53	2.559	2.559	7	2.557	2.557	28
1 0 7	2.3002	2.3002	9	2.2920	2.2911	2	2.2920	2.2916	9
1 0 $\bar{8}$	2.1682	2.1684	13	2.1603	2.1610	3	2.1626	2.1625	12
1 0 10	1.9260	1.9263	48	1.9219	1.9215	10	1.9239	1.9243	26
1 1 0	1.7282	1.7278	46	—	—	—	1.7108	1.7104	29
1 1 3	1.6926	1.6923	6	—	1.6803	—	—	—	—
0 0 15	—	—	—	1.6800	1.6799	12	1.6882	1.6873	6
1 0 13	1.6260	1.6256	8	1.6224	1.6233	2	1.6269	1.6270	5
1 1 6	1.5981	1.5976	9	—	—	—	1.5856	1.5851	8
1 0 $\bar{14}$	1.5412	1.5411	41	1.5395	1.5393	4	1.5430	1.5432	18
2 0 $\bar{1}$	1.4936	1.4937	10	—	—	—	—	—	—
1 1 9	1.4698	1.4699	23	1.4627	1.4624	4	1.4611	1.4614	18
2 0 $\bar{4}$	1.4558	1.4558	7	—	—	—	—	—	—
2 0 5	1.4341	1.4343	9	—	—	—	—	—	—
0 0 18	—	—	—	1.4001	1.3999	8	—	—	—
2 0 8	1.3513	1.3513	5	—	—	—	—	—	—

TABLE ID
POWDER X-RAY DATA FOR $Ln(FeCu)O_4$ ($Ln = Tm, Yb, \text{ AND } Lu$)

$h k l$	$Tm(FeCu)O_4$			$Yb(FeCu)O_4$			$Lu(FeCu)O_4$		
	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.092	8.027	52	8.034	8.033	54	8.069	8.060	59
0 0 6	4.024	4.014	45	4.015	4.017	54	4.034	4.030	40
1 0 1	3.010	3.005	100	2.991	2.991	86	2.978	2.978	80
1 0 4	2.710	2.706	30	2.696	2.696	78	} 2.687	2.688	} 100
0 0 9	2.679	2.676	61	2.677	2.678	100		2.686	
1 0 $\bar{5}$	2.567	2.564	77	2.556	2.556	71	2.549	2.550	51
1 0 7	2.2746	2.2733	13	2.2679	2.268	9	2.2649	2.2654	11
1 0 $\bar{8}$	2.1366	2.1351	18	2.1311	2.1308	20	2.1293	2.1295	19
1 0 10	1.8857	1.8850	42	1.8821	1.8824	37	1.8829	1.8828	39
1 1 0	1.7492	1.7486	57	1.7406	1.7404	42	1.7327	1.7326	35
1 1 3	1.7078	1.7086	24	1.7011	1.7009	13	1.6943	1.6939	10
0 0 15	—	—	—	1.6068	1.6067	5	—	—	—
1 1 6	1.6034	1.6031	19	1.5972	1.5969	13	1.5921	1.5917	14
1 0 13	1.5801	1.5803	7	1.5794	1.5791	9	1.5808	1.5809	5
2 0 $\bar{1}$	1.5113	1.5114	17	1.5041	1.5043	11	1.4972	1.4976	31
1 0 $\bar{14}$	1.4952	1.4957	19	1.4949	1.4949	28	—	—	—
2 0 4	1.4685	1.4686	17	—	—	—	} 1.4563	1.4563	} 47
1 1 9	1.4634	1.4638	38	1.4595	1.4593	33		1.4560	
2 0 5	1.4445	1.4446	29	1.4386	1.4385	12	1.4336	1.4331	14

ployed) was obtained using silicon powder as an internal standard. Furthermore, every sample was magnetically investigated.

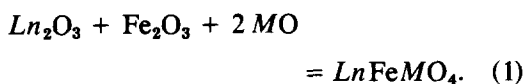
TABLE IE
POWDER X-RAY DATA FOR $Ln(FeZn)O_4$ ($Ln = Yb$
AND Lu)

$h k l$	$Yb(FeZn)O_4$			$Lu(FeZn)O_4$		
	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$	$d_o[\text{\AA}]$	$d_c[\text{\AA}]$	$I[\%]$
0 0 3	8.447	8.427	54	8.492	8.462	72
0 0 6	4.215	4.214	39	4.234	4.231	37
1 0 1	2.947	2.946	95	2.935	2.935	82
0 0 9	2.809	2.809	55	2.821	2.821	48
1 0 4	2.687	2.685	100	2.680	2.678	100
1 0 5	2.559	2.559	66	2.553	2.554	84
1 0 7	2.2920	2.2922	13	2.2912	2.2905	10
1 0 $\bar{8}$	2.1630	2.1628	25	2.1622	2.1623	19
1 0 10	1.9239	1.9241	45	1.9257	1.9254	32
1 1 0	1.7123	1.7125	47	1.7054	1.7057	40
1 1 3	—	—	—	1.6717	1.6720	6
1 0 13	1.6267	1.6264	14	1.6289	1.6290	10
1 1 6	1.5867	1.5865	13	1.5826	1.5819	13
1 0 $\bar{14}$	1.5427	1.5425	23	1.5455	1.5454	20
2 0 $\bar{1}$	1.4808	1.4805	6	1.4748	1.4747	10
1 1 9	1.4618	1.4622	38	1.4594	1.4596	32
2 0 4	1.4440	1.4439	8	—	—	—
2 0 5	1.4234	1.4231	8	—	—	—

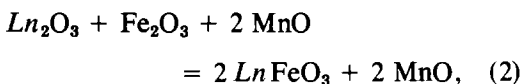
Whereas $LnFeO_3$ (perovskite-type compound), $Ln_3Fe_5O_{12}$ (garnet-type compound), and Fe_3O_4 (magnetite), which exist near the $LnFeMO_4$ compounds in each phase diagram, are strongly magnetic at room temperature, the $LnFeMO_4$ phases are nonmagnetic. The magnetic investigation method was more sensitive in detecting small amounts of magnetic impurities than X-ray powder diffraction. The lattice constants were calculated by least-squares methods.

Results and Discussion

By solid-state reaction of the starting materials, Ln_2O_3 , Fe_2O_3 , and MO , we synthesized $LnFeMO_4$ compounds according to the following chemical equation:



In the Ln_2O_3 - Fe_2O_3 - MnO systems (Ln : Y, Er, Tm, Yb, and Lu), at 1050°C and above, single-phase $LnFeMnO_4$ black compounds were obtained. The X-ray powder diffraction patterns showed that $YFeMnO_4$, $ErFeMnO_4$, $TmFeMnO_4$, $YbFeMnO_4$, and $LuFeMnO_4$ are isomorphous with the structure of $YbFe_2O_4$ shown in Fig. 1. When mixtures of Fe_2O_3 , MnO and the rare earth sesquioxides lighter than Er_2O_3 were heated until the melt phase appeared, $LnFeMnO_4$ compounds could not be obtained but $LnFeO_3$ and MnO formed according to:



where $Ln = Ho, Dy, Gd, \text{ and } La$.

In the Ln_2O_3 - Fe_2O_3 - MgO systems (Ln : Er, Tm, Yb, and Lu) $LnFeMgO_4$ dark brown compounds were obtained at 1440°C and above in an oxygen atmosphere. The reaction period was 2 days. Sample weight loss was detected after reaction. According to Darken and Gurry (12) and Muan and Somiya (13), coexistence of Fe_2O_3 and Fe_3O_4 has an equilibrium oxygen partial pressure of 1 atm at about 1450°C. So we may conclude that the compounds obtained should contain Fe^{2+} ion. Shindo and Takekawa are currently studying the phase diagram of the Yb_2O_3 - Fe_2O_3 - MgO system at higher temperatures. The homogeneity range of the $YbFeMgO_4$ compound will be reported by them (14). The powder diffraction patterns obtained were rather broad. As the constituent rare earth element becomes lighter, the rate of solid-state reaction becomes slower. The $LnFeMgO_4$ in which Ln is lighter than Er could not be obtained.

In the Ln_2O_3 - Fe_2O_3 - CoO systems (Ln : Tm, Yb, and Lu), $LnFeCoO_4$ black compounds were obtained at 1380°C in air. The heating period was 1.5 days. The Ln

$FeCoO_4$ phase in which Ln is lighter than Tm could not be obtained in spite of heating the mixture until the melt phase appeared.

In the Ln_2O_3 - Fe_2O_3 - CuO systems (Ln : Tm, Yb, and Lu), black $LnFeCuO_4$ compounds were obtained at 1010°C in air. The heating period was 5 days. Above 1050°C, CuO decomposed to Cu_2O and oxygen gas (15) and the $LnFeCuO_4$ could not be obtained. The $LnFeCuO_4$ compounds in which Ln is lighter than Tm could not be prepared under the experimental condition used. In the Ln_2O_3 - Fe_2O_3 - ZnO systems (Ln : Yb and Lu), dark brown $LnFeZnO_4$ compounds were obtained at 1350°C in air. The heating period was 2 days. The $LnFeZnO_4$ compound in which Ln is lighter than Tm could not be prepared.

Each $LnFeMO_4$ compound obtained is nonmagnetic and electrically semiconducting or insulating at room temperature. When the reaction temperature was too low to form $LnFeMO_4$ phases, the corresponding perovskite type compounds were synthesized according to a chemical equation similar to (2).

We heated mixtures of Ln_2O_3 , Fe_2O_3 , and NiO (Ln : Yb and Lu) in order to synthesize $LnFeNiO_4$ compounds until the melt phase appeared, but we were not successful in these attempts. According to Shannon and Prewitt (16), the ionic radius of Ni^{2+} is smaller than the ionic radii of Mg^{2+} , Co^{2+} , Cu^{2+} , Zn^{2+} , and Fe^{2+} . The ionic radius of Ni^{2+} may be too small to form the $LnFeNiO_4$ compound.

In a previous work, Katsura *et al.* (17), Kimizuka and Katsura (18), and Sugihara *et al.* (19) reported the standard free energy of formation of $LnFe_2O_4$ type of compound (Ln : Ho, Er, Tm, Yb, Lu, and Y) at higher temperatures and concluded that $LnFe_2O_4$ compounds become more stable with decreasing ionic radius of the constituent rare earth ion. In the Ln_2O_3 - Fe_2O_3 - MO systems, the compounds which contain Lu

TABLE II
LATTICE CONSTANTS OF $Ln(FeM)O_4$ AS A HEXAGONAL CRYSTAL SYSTEM

	Er(FeMg)O ₄	Tm(FeMg)O ₄	Yb(FeMg)O ₄	Lu(FeMg)O ₄	Y(FeMn)O ₄	Er(FeMn)O ₄
$a(\text{\AA})$	3.5210(8)	3.5028(3)	3.4292(4)	3.4279(6)	3.4964(2)	3.4800(1)
$c(\text{\AA})$	25.687(9)	25.547(6)	25.162(4)	25.307(6)	25.456(3)	25.545(2)
	Tm(FeMn)O ₄	Yb(FeMn)O ₄	Lu(FeMn)O ₄	YFe ₂ O ₄	HoFe ₂ O ₄	ErFe ₂ O ₄
$a(\text{\AA})$	3.4694(2)	3.4567(1)	3.4450(4)	3.516(2)	3.519(1)	3.497(1)
$c(\text{\AA})$	25.562(3)	25.619(2)	25.632(7)	24.788(4)	24.813(2)	24.938(2)
	TmFe ₂ O ₄	YbFe ₂ O ₄	LuFe ₂ O ₄	Tm(FeCo)O ₄	Yb(FeCo)O ₄	Lu(FeCo)O ₄
$a(\text{\AA})$	3.473(1)	3.455(1)	3.437(1)	3.4557(2)	3.4298(5)	3.4208(4)
$c(\text{\AA})$	25.014(2)	25.109(2)	25.253(2)	25.169(4)	25.198(3)	25.310(3)
	Tm(FeCu)O ₄	Yb(FeCu)O ₄	Lu(FeCu)O ₄	Yb(FeZn)O ₄	Lu(FeZn)O ₄	
$a(\text{\AA})$	3.4972(5)	3.4808(2)	3.4652(3)	3.4251(2)	3.4113(3)	
$c(\text{\AA})$	24.082(6)	24.100(2)	24.178(5)	25.282(2)	25.386(4)	

Note. Standard errors in parentheses apply to the last digits.

were obtained at the lowest temperatures and as the constituent rare earth element becomes lighter, the formation temperature becomes higher. This seems to be related to the free energy of formation as mentioned above.

The powder X-ray data for the compounds obtained were indexed on the assumption of a hexagonal lattice. The results are shown in Tables IA–E, in which the data for $YbFe_2O_4$ are listed as a reference. The powder X-ray patterns of $ErFeMgO_4$ and $TmFeMgO_4$, in spite of long heating at higher temperatures showed fewer and rather broad diffraction peaks. The relative intensities of X-ray powder diffraction lines were sensitive to the manner of loading the samples into the sample holder because of the effect of the layer structure of the compounds. As shown in Table I, only diffraction peaks of each compound corresponding to those of $YbFe_2O_4$ were seen, indicating that these compounds have essentially the same crystal structure as that of $YbFe_2O_4$. The lattice constants are listed

in Table II, together with those of $LnFe_2O_4$ (Ln : Ho, Er, Tm, Yb, Lu, and Y). In Fig. 2a and b, the relationships between the lengths of a and c axis and the constituent rare earth element and their ionic radii (l_6) are shown. As shown in Fig. 2a, the length of a axis tends to increase with the ionic radius of rare earth element for each com-

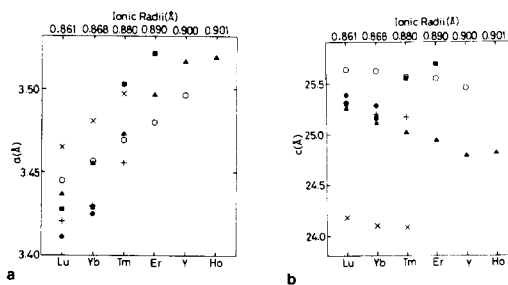


FIG. 2. The relationships between the lattice constants and the constituent rare earth element ions in the $LnFeMO_4$ compounds: (a) a axis in a hexagonal system and the rare earth element; (b) c axis in a hexagonal system and the rare earth element. (○: $LnFeMnO_4$; ■: $LnFeMgO_4$; ▲: $LnFe_2O_4$; +: $LnFeCoO_4$; ×: $LnFeCuO_4$; ◆: $LnFeZnO_4$.)

pound. In contrast, the length of c axis has the opposite tendency, as shown in Fig. 2b. Since the detailed structural analyses are not yet finished, except for YbFe_2O_4 , we cannot present a reasonable interpretation for these results at the present stage. The crystal growth and the structural analyses are in progress.

References

1. N. KIMIZUKA AND T. KATSURA, *J. Solid State Chem.* **13**, 176 (1975).
2. N. KIMIZUKA AND T. KATSURA, *J. Solid State Chem.* **15**, 246 (1975).
3. N. KIMIZUKA, A. TAKENAKA, Y. SASADA, AND T. KATSURA, *Solid State Commun.* **15**, 1321 (1974).
4. K. KATO, I. KAWADA, N. KIMIZUKA, AND T. KATSURA, *Z. Kristallogr.* **141**, 314 (1975).
5. T. SUGIHARA, M. ABE, AND T. KATSURA, *J. Phys. Soc. Japan* **40**, 1211 (1976).
6. T. SUGIHARA, K. SHIRATORI, I. SHINDO, AND T. KATSURA, *J. Phys. Soc. Japan* **45**, 1191 (1978).
7. Y. NAKAGAWA, M. INAZUMI, N. KIMIZUKA, AND K. SHIRATORI, *J. Phys. Soc. Japan* **47**, 1369 (1979).
8. M. TANAKA, M. KATO, N. KIMIZUKA, AND K. SHIRATORI, *J. Phys. Soc. Japan* **47**, 1737 (1979).
9. J. AKIMITSU, Y. INADA, K. SHIRATORI, I. SHINDO, AND N. KIMIZUKA, *Solid State Commun.* **32**, 1065 (1979).
10. W. C. HAHN, JR., AND A. MUAN, *Amer. J. Sci.* **258**, 66 (1960).
11. B. FISHER AND D. S. TANNHAUSER, *J. Electrochem. Soc.* **111**, 1194 (1964).
12. L. S. DARKEN AND R. W. GURRY, *J. Amer. Chem. Soc.* **68**, 798 (1946).
13. A. MUAN AND S. SOMIYA, *J. Amer. Ceram. Soc.* **43**, 205 (1960).
14. S. TAKEKAWA AND I. SHINDO, private communication.
15. A. M. M. GADALLA, W. F. FORD, AND J. WHITE, *Trans. Brit. Ceram. Soc.* **62**, 57 (1963).
16. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. Sect. B* **25**, 925 (1969).
17. T. KATSURA, K. KITAYAMA, T. SUGIHARA, AND N. KIMIZUKA, *Bull. Chem. Soc. Japan* **48**, 1809 (1975).
18. N. KIMIZUKA AND T. KATSURA, *Bull. Chem. Soc. Japan* **47**, 1801 (1974).
19. T. SUGIHARA, N. KIMIZUKA, AND T. KATSURA, *Bull. Chem. Soc. Japan*, **48**, 1806 (1975).