JOURNAL OF SOLID STATE CHEMISTRY 41, 166–173 (1982)

$Ln(GaM^{2+})O_4$ and $Ln(AlMn^{2+})O_4$ Compounds Having a Layer Structure [Ln = Lu, Yb, Tm, Er, Ho, and Y, and M = Mg, Mn, Co, Cu, and Zn]

NOBORU KIMIZUKA[1] AND EIJI TAKAYAMA

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

Received July 30, 1981; in revised form October 1, 1981

A series of new compounds $Ln(GaM^{2+})O_4$ and $Ln(AlMn^{2+})O_4$ having a layer structure were successfully prepared [Ln = Lu, Yb, Tm, Er, Ho, and Y, and M = Mg, Mn, Co, Cu, and Zn]. The synthesis conditions and the unit cell parameters for 23 compounds have been determined. These compounds are isostructural with $YbFe_2O_4$ (space group $R\bar{3}m$, a = 3.455(1) Å, and c = 25.109(2) Å).

Introduction

Recently Kimizuka and Katsura (*1–5*) prepared a series of new homologous compounds $(LnFeO_3)_nFeO$ [Ln = Lu, Yb, and Tm, and $n = 1, 2, 3, \ldots$] by the reaction of rare earth orthoferrites ($LnFeO_3$) with wustite (FeO) under controlled oxygen partial pressures at high temperatures. Kato *et al.* (*6, 7*) and Matsui *et al.* (*8*) reported the crystal structures of $YbFe_2O_4$ ($R\bar{3}m$, a = 3.455(1) Å, c = 25.109(2) Å), $Yb_2Fe_3O_7$ ($P6_3/mmc$, a = 3.473(1) Å, c = 28.351(1) Å), $Yb_3Fe_4O_{10}$ ($R\bar{3}m$, a = 3.490(1) Å, c = 60.79(2) Å), and $Yb_4Fe_5O_{13}$ ($P6_3/mmc$, a = 3.503(2) Å, c = 53.03(2) Å). They are compounds possessing a layer structure in which Fe^{2+} and Fe^{3+} are both in trigonal bipyramids formed by five oxygen ions. In previous work, Kimizuka and Takayama (*9*) prepared new $Ln(Fe^{3+}M^{2+})O_4$ compounds which are isostructural with $Yb(Fe^{3+}Fe^{2+})O_4$ and reported the synthesis conditions and the unit cell parameters based on a hexagonal cell [Ln = Lu, Yb, Tm, Er, Ho, and Y, and M = Mg, Mn, Co, Cu, and Zn]. The powder X-ray patterns of these compounds show no ordering phenomenon between Fe^{3+} and M^{2+}.

In the present work, we tried to replace Fe^{3+} in $Ln(Fe^{3+}M^{2+})O_4$ by other trivalent cations such as Ga^{3+} and Al^{3+} and obtained $Ln(GaM)O_4$ and $Ln(AlMn)O_4$ compounds [Ln = Lu, Yb, Tm, Er, Ho, and Y, and M = Mg, Mn, Co, Cu, and Zn] which are isostructural with $YbFe_2O_4$.

In the present paper, we present only the synthesis conditions of 23 compounds and their unit cell parameters measured by the powder X-ray method. Nakagawa *et al.* (*10*), Inazumi *et al.* (*11*), Tanaka *et al.* (*12*), and Akimitsu *et al.* (*13*) have reported electrical transport phenomena, magnetic properties, Mössbauer spectroscopy, and neutron diffraction data on $LnFe_2O_4$. They are currently studying the physical properties of the compounds reported in this paper.

---

[1] All correspondence should be addressed to Noboru Kimizuka.

0022-4596/82/020166-08$02.00/0

Experimental

Solid state reactions between Ln_2O_3, MO, and Ga_2O_3 or Al_2O_3 at high temperatures were carried out to prepare $Ln(GaM^{2+})O_4$ and $Ln(AlMn^{2+})O_4$ compounds. As starting reagents, Lu_2O_3, Yb_2O_3, Tm_2O_3, Er_2O_3, Ho_2O_3, Y_2O_3, MgO, MnO_2, Co_2O_3, CuO, ZnO, Al_2O_3 (99.99%) and Ga_2O_3 (99.9%) were used. Prior to use Ga_2O_3 and Al_2O_3 were calcined in air at 1200°C for 2 days and 1300°C for 3 days, respectively. Purities and the methods of pretreatment of the other materials were described previously (*9*). Ln_2O_3, MO, and Ga_2O_3 or Al_2O_3 were mixed in the mole ratio of 1 : 2 : 1, respectively. Temperature and heating period were determined by trial and error method for each sample. After the heat treatment, each sample was quenched to room temperature. For MnO-containing samples, the experiments were performed in a closed system to avoid oxidation of MnO. Evacuated silica tubes were used for the Ln_2O_3–MnO–Ga_2O_3 systems [Ln = Lu, Yb, and Tm] and Pt tubes were used for the system Ln_2O_3–MnO–Ga_2O_3 [Ln = Er, Ho, and Y] and Ln_2O_3–MnO–Al_2O_3 which need a higher temperature to react fully. All other samples were heated in air using a Pt crucible. No chemical reaction was observed visually between Pt or silica and the sample. Sample weights were measured before and after the heat treatment and no differences were detected. Powder X-ray patterns were recorded by using Cu$K\alpha$ radiation on a diffractometer (Philips Co. Type

TABLE Ia

POWDER X-RAY DATA FOR $Ln(GaMg)O_4$ (Ln = Er, Tm, Yb, AND Lu)

	$Er(GaMg)O_4$			$Tm(GaMg)O_4$			$Yb(GaMg)O_4$			$Lu(GaMg)O_4$		
$h\ k\ l$	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]
0 0 3	8.393	8.374	37	8.354	8.368	77	8.369	8.377	72	8.401	8.411	97
0 0 6	4.189	4.187	20	4.181	4.184	43	4.187	4.189	37	4.205	4.205	40
1 0 1	2.951	2.952	100	2.938	2.939	100	2.922	2.924	100	2.911	2.913	100
$1\ 0\ \bar{2}$	—	—	—	—	—	—	2.867	2.866	2	—	—	—
0 0 9	2.793	2.791	36	2.789	2.789	45	2.792	2.792	45	2.803	2.804	48
1 0 4	2.688	2.687	77	2.680	2.676	83	2.665	2.666	86	2.659	2.659	97
$1\ 0\ \bar{5}$	2.557	2.559	56	2.549	2.549	56	2.539	2.540	63	2.536	2.535	70
1 0 7	2.2897	2.2895	17	2.2824	2.2823	18	2.2752	2.2765	21	2.2747	2.2747	19
$1\ 0\ \bar{8}$	2.1590	2.1589	15	2.1521	2.1527	29	2.1477	2.1481	29	2.1477	2.1475	27
1 0 10	1.9194	1.9189	57	1.9141	1.9142	45	1.9111	1.9114	45	1.9126	1.9126	49
$1\ 0\ \overline{11}$	—	—	—	—	—	—	1.8052	1.8049	3	—	—	—
1 1 0	1.7184	1.7165	92	1.7083	1.7083	49	1.6998	1.6997	60	1.6934	1.6930	57
1 1 3	—	—	—	1.6740	1.6738	12	1.6656	1.6658	11	1.6603	1.6597	9
0 0 15	—	—	—	—	—	—	1.6757	1.6755	5	—	—	—
1 0 13	1.6198	1.6202	17	1.6174	1.6171	11	1.6161	1.6160	10	1.6195	1.6185	16
1 1 6	1.5884	1.5882	24	1.5813	1.5815	14	1.5743	1.5750	20	1.5705	1.5705	14
$1\ 0\ \overline{14}$	1.5367	1.5363	20	1.5336	1.5335	27	1.5330	1.5327	30	1.5352	1.5354	37
$2\ 0\ \bar{1}$	1.4841	1.4839	14	1.4769	1.4769	12	1.4696	1.4695	12	1.4636	1.4637	12
1 1 9	1.4621	1.4621	30	1.4568	1.4568	37	1.4527	1.4519	34	1.4491	1.4492	36
$2\ 0\ \bar{4}$	1.4467	1.4465	11	1.4401	1.4400	12	1.4332	1.4332	14	1.4281	1.4281	13
2 0 5	1.4250	1.4254	15	1.4190	1.4191	11	1.4130	1.4127	10	1.4080	1.4079	12
0 0 18	—	—	—	—	—	—	1.3960	1.3962	4	—	—	—
$2\ 0\ \overline{10}$	1.2793	1.2793	15	1.2747	1.2746	9	1.2702	1.2702	9	1.2676	1.2677	11

TABLE Ib

POWDER X-RAY DATA FOR $Ln(GaMn)O_4$ (Ln = Y, Ho, Er, Tm, Yb, AND Lu)

	$Y(GaMn)O_4$			$Ho(GaMn)O_4$			$Er(GaMn)O_4$		
h k l	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c[Å]	*I* [%]
0 0 3	8.409	8.431	7	8.377	8.379	19	8.425	8.433	43
0 0 6	4.216	4.215	26	4.189	4.189	20	4.216	4.216	32
1 0 1	2.986	2.982	81	3.001	3.001	100	2.987	2.987	100
0 0 9	2.811	2.810	100	2.793	2.793	41	2.810	2.811	54
1 0 4	2.714	2.712	51	2.724	2.724	99	2.716	2.717	98
$1\ 0\ \bar{5}$	2.583	2.582	68	2.591	2.591	84	2.585	2.586	77
1 0 7	—	—	—	2.3128	2.3125	6	2.3111	2.3121	7
$1\ 0\ \bar{8}$	2.1774	2.1772	20	2.1774	2.1784	23	2.1794	2.1796	20
1 0 10	1.9348	1.9344	54	1.9321	1.9327	42	1.9360	1.9362	39
1 1 0	1.7335	1.7336	43	1.7455	1.7452	69	1.7371	1.7369	53
1 1 3	—	—	—	—	—	—	1.7018	1.7012	35
1 0 13	—	—	—	—	—	—	—	—	—
1 1 6	—	—	—	1.6117	1.6110	9	1.6057	1.6059	12
$1\ 0\ \overline{14}$	1.5481	1.5480	22	—	—	—	1.5492	1.5490	23
$2\ 0\ \bar{1}$	—	—	—	1.5087	1.5087	12	1.5010	1.5015	11
1 1 9	—	—	—	1.4801	1.4800	37	1.4777	1.4775	34
$2\ 0\ \bar{4}$	—	—	—	1.4691	1.4695	15	1.4633	1.4633	13
2 0 5	—	—	—	1.4471	1.4474	12	1.4419	1.4418	12
$2\ 0\ \overline{10}$	—	—	—	1.2957	1.2953	8	1.2929	1.2929	8

	$Tm(GaMn)O_4$			$Yb(GaMn)O_4$			$Lu(GaMn)O_4$		
	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c[Å]	*I* [%]
0 0 3	8.580	8.564	31	8.622	8.567	44	8.613	8.608	56
0 0 6	4.285	4.282	19	4.283	4.284	26	4.303	4.304	31
1 0 1	2.975	2.973	90	2.963	2.962	100	2.950	2.949	100
0 0 9	2.855	2.855	45	2.856	2.856	45	2.868	2.869	70
1 0 4	2.714	2.713	100	2.706	2.705	89	2.697	2.697	51
$1\ 0\ \bar{5}$	2.587	2.586	65	2.581	2.579	72	2.573	2.573	95
1 0 7	2.3191	2.3196	6	2.3151	2.3148	9	2.3128	2.3126	10
$1\ 0\ \bar{8}$	2.1890	2.1896	20	2.1860	2.1857	26	2.1855	2.1849	27
1 0 10	1.9501	1.9495	37	1.9470	1.9469	43	1.9486	1.9482	46
1 1 0	1.7284	1.7282	51	—	—	—	1.7139	1.7136	55
1 1 3	1.6940	1.6940	6	1.6882	1.6880	9	1.6805	1.6807	7
1 0 13	1.6491	1.6492	11	1.6474	1.6478	16	1.6507	1.6509	16
1 1 6	1.6027	1.6026	8	1.5976	1.5975	12	1.5920	1.5921	12
$1\ 0\ \overline{14}$	1.5644	1.5644	27	1.5635	1.5633	26	1.5669	1.5667	36
$2\ 0\ \bar{1}$	1.4942	1.4941	12	1.4886	1.4886	14	1.4818	1.4816	12
1 1 9	1.4784	1.4784	39	1.4746	1.4745	44	1.4712	1.4712	43
$2\ 0\ \bar{4}$	1.4576	1.4576	17	1.4525	1.4525	16	1.4465	1.4463	17
2 0 5	1.4369	1.4369	13	1.4320	1.4321	16	1.4263	1.4263	12
$2\ 0\ \overline{10}$	1.2932	1.2932	8	1.2898	1.2897	9	1.2867	1.2867	10

TABLE Ic

POWDER X-RAY DATA FOR $Ln(GaCo)O_4$ (Ln = Tm, Yb, AND Lu)

	Tm(GaCo)O_4			Yb(GaCo)O_4			Lu(GaCo)O_4		
h k l	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]
0 0 3	8.354	8.364	29	8.354	8.360	53	8.393	8.397	51
0 0 6	4.179	4.182	24	4.179	4.180	45	4.201	4.199	31
1 0 1	2.956	2.956	100	2.938	2.938	100	2.922	2.924	94
0 0 9	2.786	2.788	53	2.787	2.787	70	2.799	2.799	46
1 0 4	2.689	2.689	77	2.677	2.676	83	2.666	2.667	100
1 0 $\bar{5}$	2.560	2.560	81	2.548	2.549	76	2.540	2.542	92
1 0 7	2.2897	2.2900	10	2.2813	2.2814	10	2.2791	2.2788	12
1 0 $\bar{8}$	2.1590	2.1591	18	2.1516	2.1518	20	2.1507	2.1506	26
1 0 10	1.9187	1.9185	54	1.9133	1.9132	42	1.9141	1.9142	50
1 1 0	1.7184	1.7185	60	1.7080	1.7083	59	1.6995	1.6999	78
1 1 3	—	—	—	1.6735	1.6737	16	1.6659	1.6661	8
1 0 13	1.6192	1.6196	12	1.6164	1.6161	11	1.6190	1.6187	14
1 1 6	1.5895	1.5895	13	1.5816	1.5813	11	1.5755	1.5756	15
1 0 $\overline{14}$	1.5359	1.5355	36	1.5328	1.5325	27	1.5355	1.5354	33
2 0 $\bar{1}$	1.4856	1.4856	13	1.4769	1.4768	11	1.4700	1.4696	9
1 1 9	1.4631	1.4629	34	1.4566	1.4564	33	1.4531	1.4529	40
2 0 $\bar{4}$	1.4481	1.4481	14	1.4399	1.4399	11	1.4342	1.4335	11
2 0 5	1.4271	1.4268	13	1.4188	1.4190	11	1.4130	1.4130	14
2 0 $\overline{10}$	—	—	—	1.2741	1.2742	8	1.2714	1.2710	12

TABLE Id

POWDER X-RAY DATA FOR $Ln(GaCu)O_4$ (Ln = Tm, Yb, AND Lu)

	Tm(GaCu)O_4			Yb(GaCu)O_4			Lu(GaCu)O_4		
h k l	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]	d_0 [Å]	d_c [Å]	*I* [%]
0 0 3	8.043	8.053	17	8.058	8.057	25	8.087	8.095	37
0 0 6	4.024	4.027	19	4.033	4.029	28	4.046	4.047	34
1 0 1	2.985	2.984	62	2.973	2.974	72	2.957	2.958	100
0 0 9	2.698	2.684	100	2.684	2.686	100	2.698	2.698	35
1 0 4		2.692			2.685		2.675	2.675	95
1 0 $\bar{5}$	2.554	2.553	51	2.546	2.547	59	2.540	2.540	88
1 0 7	2.2670	2.2672	3	2.2626	2.2632	5	2.2605	2.2605	7
1 0 $\bar{8}$	2.1308	2.1310	8	2.1270	2.1276	12	2.1265	2.1265	20
1 0 10	1.8835	1.8835	33	1.8810	1.8814	36	1.8828	1.8825	42
1 1 0	1.7374	1.7363	33	1.7298	1.7300	39	1.7208	1.7206	60
1 1 3	1.6978	1.6973	31	1.6923	1.6915	28	1.6837	1.6830	8
1 1 6	1.5949	1.5944	6	1.5896	1.5897	11	1.5831	1.5834	19
1 0 13	1.5809	1.5809	3	1.5809	1.5799	8		1.5827	
1 0 $\overline{14}$	1.4966	1.4968	7	1.4963	1.4960	23	1.4990	1.4991	23
2 0 $\bar{1}$	1.5012	1.5008	12		1.4954		1.4873	1.4873	11
1 1 9	1.4582	1.4579	20	1.4545	1.4544	28	1.4505	1.4507	24
2 0 $\bar{4}$		1.4591			1.4542		1.4471	1.4471	17
2 0 5	1.4361	1.4357	5	1.4310	1.4311	10	1.4248	1.4245	12
2 0 $\overline{10}$	1.2765	1.2766	4	1.2731	1.2735	9	1.2702	1.2700	10

TABLE Ie

POWDER X-RAY DATA FOR $Ln(GaZn)O_4$ (Ln = Tm, Yb, AND Lu)

	$Tm(GaZn)O_4$			$Yb(GaZn)O_4$			$Lu(GaZn)O_4$		
$h\,k\,l$	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]
0 0 3	8.314	8.355	31	8.362	8.364	39	8.417	8.418	39
0 0 6	4.171	4.178	45	4.183	4.182	30	4.208	4.209	32
1 0 1	2.949	2.950	21	2.935	2.937	87	2.923	2.925	100
0 0 9	2.784	2.785	100	2.790	2.778	55	2.806	2.806	52
1 0 4	2.683	2.684	21	2.674	2.675	100	2.668	2.669	97
1 0 $\bar{5}$	2.554	2.556	21	2.548	2.548	84	2.543	2.544	83
1 0 7	2.2858	2.2863	2	2.2813	2.2814	17	2.2808	2.2812	6
1 0 $\bar{8}$	2.1546	2.1557	4	2.1526	2.1519	18	2.1531	2.1532	26
1 0 10	1.9149	1.9157	11	1.9141	1.9134	48	1.9171	1.9169	48
1 1 0	1.7145	1.7150	13	1.7077	1.7077	44	1.7001	1.7001	66
1 1 3	—	—	—	—	—	—	1.6667	1.6665	7
1 0 13	1.6177	1.6173	3	—	—	—	1.6219	1.6215	13
1 1 6	1.5861	1.5865	2	1.5812	1.5810	10	1.5767	1.5764	10
1 0 $\overline{14}$	1.5335	1.5334	11	1.5321	1.5329	31	1.5383	1.5381	39
2 0 $\bar{1}$	1.4826	1.4826	3	1.4760	1.4763	14	1.4700	1.4699	13
1 1 9	1.4607	1.4604	8	1.4566	1.4562	44	1.4541	1.4540	37
2 0 $\bar{4}$	1.4455	1.4452	3	—	—	—	1.4340	1.4339	14
2 0 5	1.4239	1.4241	3	—	—	—	1.4137	1.4135	12
2 0 $\overline{10}$	1.2784	1.2778	2	1.2746	1.2741	6	1.2718	1.2719	8

TABLE If

POWDER X-RAY DATA FOR $Ln(AlMn)O_4$ (Ln = Tm, Yb, AND Lu) AND $Tm(FeZn)O_4$

	$Tm(AlMn)O_4$			$Yb(AlMn)O_4$			$Lu(AlMn)O_4$			$Tm(FeZn)O_4$		
$h\,k\,l$	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]	d_0 [Å]	d_c [Å]	I [%]
0 0 3	8.299	8.304	59	8.299	8.324	35	8.338	8.339	61	8.409	8.416	40
0 0 6	4.152	4.152	34	4.156	4.162	20	4.169	4.169	29	4.208	4.208	43
1 0 1	2.975	2.974	100	2.961	2.964	100	2.945	2.945	100	2.969	2.967	11
0 0 9	2.768	2.768	46	2.773	2.775	25	2.780	2.780	34	2.804	2.805	100
1 0 4	2.702	2.700	82	2.694	2.693	50	2.680	2.680	68	2.702	2.701	12
1 0 $\bar{5}$	2.567	2.567	85	2.562	2.563	41	2.550	2.551	47	2.572	2.572	7
1 0 7	2.2919	2.2918	13	2.2902	2.2895	7	2.2819	2.2822	9	2.3015	2.3010	1
1 0 $\bar{8}$	2.1590	2.1588	18	2.1570	2.1575	13	2.1516	2.1518	14	2.1698	2.1698	2
1 0 10	1.9152	1.9154	41	1.9160	1.9154	15	1.9126	1.9122	34	1.9286	1.9285	5
1 1 0	1.7289	1.7295	98	1.7235	1.7237	66	1.7127	1.7123	34	1.7251	1.7251	4
0 0 15	—	—	—	—	—	—	—	—	—	1.6831	1.6832	7
1 0 13	—	—	—	—	—	—	—	—	—	1.6283	1.6284	1
1 1 3	—	—	—	1.6888	1.6789	6	1.6766	1.6773	14	—	—	—
1 1 6	—	—	—	—	—	—	—	—	—	1.5957	1.5962	1
1 0 $\overline{14}$	1.5296	1.5298	13	1.5313	1.5312	15	1.5309	1.5305	18	1.5442	1.5440	4
2 0 $\bar{1}$	—	—	—	—	—	—	1.4805	1.4803	31	1.4913	1.4914	1
1 1 9	1.4667	1.4667	26	1.4646	1.4642	17	1.4578	1.4579	16	1.4697	1.4695	3
2 0 $\bar{4}$	—	—	—	1.4517	1.4518	8	1.4431	1.4429	15	1.4538	1.4538	1
2 0 5	—	—	—	1.4300	1.4303	8	1.4221	1.4217	14	1.4330	1.4326	1
0 0 18	—	—	—	—	—	—	—	—	—	1.4028	1.4027	7
2 0 $\overline{10}$	1.2837	1.2836	8	1.2814	1.2813	5	—	—	—	—	—	—

TABLE II

LATTICE CONSTANTS OF $Ln(AB)\mathrm{O_4}$ AS A HEXAGONAL CRYSTAL SYSTEM

	$\mathrm{Er(GaMg)O_4}$	$\mathrm{Tm(GaMg)O_4}$	$\mathrm{Yb(GaMg)O_4}$	$\mathrm{Lu(GaMg)O_4}$	$\mathrm{Y(GaMn)O_4}$	$\mathrm{Ho(GaMn)O_4}$
a(Å)	3.4330(4)	3.4166(2)	3.3994(3)	3.3859(2)	3.4673(7)	3.4905(4)
c(Å)	25.122(6)	25.103(4)	25.132(3)	25.232(4)	25.292(6)	25.136(8)
	$\mathrm{Er(GaMn)O_4}$	$\mathrm{Tm(GaMn)O_4}$	$\mathrm{Yb(GaMn)O_4}$	$\mathrm{Lu(GaMn)O_4}$	$\mathrm{Tm(GaCo)O_4}$	$\mathrm{Yb(GaCo)O_4}$
a(Å)	3.4737(3)	3.4564(1)	3.4435(2)	3.4273(1)	3.4370(3)	3.4165(1)
c(Å)	25.298(5)	25.690(2)	25.702(3)	25.824(2)	25.093(4)	25.081(2)
	$\mathrm{Lu(GaCo)O_4}$	$\mathrm{Tm(GaCu)O_4}$	$\mathrm{Yb(GaCu)O_4}$	$\mathrm{Lu(GaCu)O_4}$	$\mathrm{Tm(GaZn)O_4}$	$\mathrm{Yb(GaZn)O_4}$
a(Å)	3.3997(3)	3.4726(5)	3.4601(4)	3.4412(2)	3.4300(4)	3.4153(5)
c(Å)	25.192(5)	24.160(6)	24.172(6)	24.283(3)	25.066(6)	25.093(7)
	$\mathrm{Lu(GaZn)O_4}$	$\mathrm{Tm(AlMn)O_4}$	$\mathrm{Yb(AlMn)O_4}$	$\mathrm{Lu(AlMn)O_4}$	$\mathrm{Tm(FeZn)O_4}$	
a(Å)	3.4003(2)	3.4590(4)	3.4474(4)	3.4246(3)	3.4503(2)	
c(Å)	25.253(3)	24.912(4)	24.971(6)	25.016(6)	25.248(2)	

PW 1050/80). The unit cell parameters were calculated in the same way as described in the previous paper (9).

Results and Discussion

$Ln(\mathrm{Ga}M)\mathrm{O_4}$ and $Ln(\mathrm{AlMn})\mathrm{O_4}$ were prepared according to the following chemical equations,

$$Ln_2\mathrm{O_3} + 2M\mathrm{O} + \mathrm{Ga_2O_3} = 2Ln(\mathrm{Ga}M)\mathrm{O_4}$$

$$Ln_2\mathrm{O_3} + 2\mathrm{MnO} + \mathrm{Al_2O_3} = 2Ln(\mathrm{AlMn})\mathrm{O_4}.$$

Single phases of $Ln(\mathrm{GaMn})\mathrm{O_4}$ [Ln = Lu, Yb, and Tm] were obtained at or above 1000°C, during a heating cycle of 1 day. $Ln(\mathrm{GaMn})\mathrm{O_4}$ [Ln = Er, Ho, and Y] and

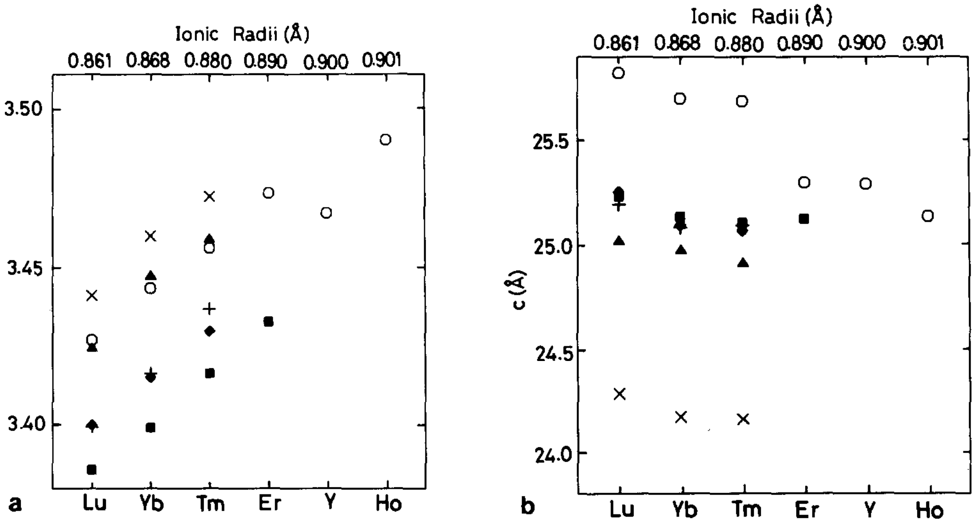

FIG. 1. The relationships between the unit cell parameters and the constituent rare earth ions in the $Ln(\mathrm{Ga}M)\mathrm{O_4}$ and $Ln(\mathrm{AlMn})\mathrm{O_4}$ compounds: (a) a axis and the rare earth element; (b) c axis and the rare earth element. ○, $Ln(\mathrm{GaMn})\mathrm{O_4}$; ■, $Ln(\mathrm{GaMg})\mathrm{O_4}$; ▲, $Ln(\mathrm{AlMn})\mathrm{O_4}$; +, $Ln(\mathrm{GaCo})\mathrm{O_4}$; ×, $Ln(\mathrm{GaCu})\mathrm{O_4}$; ◆, $Ln(\mathrm{GaZn})\mathrm{O_4}$.

Ln$(AlMn)O_4$ [*Ln* = Lu, Yb, and Tm] were obtained at and above 1300°C for 3 days and 1500°C for 3 days, respectively. All compounds described above are black. *Ln*$(GaMg)O_4$ [*Ln* = Lu, Yb, Tm, and Er] were synthesized at 1500°C for 3 days. These compounds are colorless except for $Er(GaMg)O_4$ which has a pink color. In the Ln_2O_3–CoO–Ga_2O_3 systems [*Ln* = Lu, Yb, and Tm], each mixture was heated at 1350°C for 3 days, to obtain black compounds. $Lu(GaCu)O_4$ and $Yb(GaCu)O_4$ could be prepared at 1010°C for 1 week. However, $Tm(GaCu)O_4$ could not be isolated as a single phase but could be obtained only as a mixture with starting reagents and $TmGaO_3$, in spite of continued heating at 1010°C for 2 weeks. The lines due to $Tm(GaCu)O_4$ were observed in the powder X-ray patterns and indexed. These three compounds were black.

$Lu(GaZn)O_4$ was formed at 1350°C for 3 days. $Yb(GaZn)O_4$ and $Tm(GaZn)O_4$ were also detected by means of the powder X-ray method, after heat treatment at 1350°C for 1 day. However, after a second heat treatment for 3 more days, both compounds decomposed totally. They were not obtained even at 1500°C for 2 more days. Finally, both mixtures were heated until melt phases appeared (1600°C) and after 5 min they were quenched to room temperature. The products thus obtained have characteristic powder X-ray patterns indicating that they are isostructural with $YbFe_2O_4$. $Yb(GaZn)O_4$ and $Tm(GaZn)O_4$ may be metastable. We are currently studying the phase diagram of the Yb_2O_3–ZnO–Ga_2O_3 system at 1300°C. Thermochemical stability of $Yb(GaZn)O_4$ will be determined in that study. The Zn-containing compounds formed in this study are colorless.

In the previous study, we did not report $Tm(FeZn)O_4$. Since we could prepare $Tm(GaZn)O_4$ in the present work, we tried to prepare $Tm(FeZn)O_4$ more carefully. After getting the melt phase, it was quenched to room temperature. Utilizing this method, single phase $Tm(FeZn)O_4$ was obtained. *d*-Spacings and unit cell parameters for this compound are listed in Tables I and II, together with the other compounds.

In the Ln_2O_3–NiO–Ga_2O_3 system [*Ln* = Lu and Yb], each mixture was heated until the melt phase appeared and then the product was quenched. However, no $YbFe_2O_4$ type of compounds were prepared.

In Tables I and II, the *d*-spacings and the unit cell parameters for the 23 compounds described above are listed. From the close correspondence of *d*-spacing in each compound to those of $YbFe_2O_4$, it can be concluded that they are isostructural with $YbFe_2O_4$. No extra peaks indicative of a super structure were detected. In Figs. 1a and b are shown the relationships between the lengths of the *a* axis and *c* axis and the constituent rare earth elements and their ionic radii adopted from Shannon and Prewitt (*14*).

From the above results and the previous conclusions (*9*), we can obtain the following qualitative conclusions concerning the synthesis conditions of *Ln*$(GaM)O_4$ and *Ln*$(AlMn)O_4$. (a) $Lu(GaM)O_4$ can be prepared at the lowest temperatures and for the shortest heating periods in the *Ln*$(GaM)O_4$ compounds. As the *Ln* becomes larger, the higher temperature and the longer heating period are necessary. (b) For Mn in the divalent state, we could obtain most kinds of compounds. The spherical shape and the ionic radius of Mn^{2+} may be favorable to occupy a trigonal bipyramidal site formed by oxygen ions. (c) *Ln*$(GaNi)O_4$ could not be prepared in the present trial as *Ln*$(FeNi)O_4$ could not be obtained (*9*). In order to construct a two-dimensional honeycomb structure with Ga^{3+} and O^{2-}, Ni^{2+} may be too small in size and too anisotropic. It is well known that Ni^{2+} in a tetrahedral or pentahedral site in oxide crystals is very rare. (d) As to trivalent cations, only the spherical one

[$Fe^{3+}(3d^5)$, $Ga^{3+}(3d^{10})$ and $Al^{3+}(2s^2)(2p^6)$] can form the $YbFe_2O_4$ type of compounds, at the present stage.

From the unit cell parameters, we can conclude the following: (a) The length of the *a* axis tends to increase with the ionic radius of the rare earth element for each kind of compound. (b) In contrast, the length of the *c* axis has the opposite tendency. These features are shown in Figs. 1a and b. Similar results have been obtained for $Ln(FeM)O_4$ (*9*).

Finally 23 new compounds of general formula $Ln(AB)O_4$ [A = trivalent element, B = divalent element] possessing a layer structure have been prepared at high temperature and their unit cell parameters have been determined. Preliminary physical measurements suggest that these compounds have interesting electrical and magnetic properties.

Acknowledgments

One of the authors (N.K.) expresses his sincere thanks to Dr. T. Kikuchi and Dr. A. Watanabe of the National Institute for Research in Inorganic Materials for their helpful discussion.

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. N. Kimizuka, A. Takenaka, Y. Sasada, and T. Katsura, *Solid State Commun.* **15,** 1192 (1974).
5. N. Kimizuka, K. Kato, I. Kawada, I. Shindo, and T. Katsura, *Acta Crystallogr. Sect. B* **32,** 1620 (1976).
6. K. Kato, I. Kawada, N. Kimizuka, and T. Katsura, *Z. Krist.* **141,** 314 (1975).
7. K. Kato, I. Kawada, N. Kimizuka, I. Shindo, and T. Katsura, *Z. Krist.* **143,** 278 (1976).
8. Y. Matsui, K. Kato, N. Kimizuka, and S. Horiuchi, *Acta Crystallogr. Sect. B* **35,** 561 (1979).
9. N. Kimizuka and E. Takayama, *J. Solid State Chem.* **40,** 109 (1981).
10. Y. Nakagawa, M. Inazumi, N. Kimizuka, and K. Shiratori, *J. Phys. Soc. Japan* **47,** 1369 (1979).
11. M. Inazumi, Y. Nakagawa, M. Tanaka, N. Kimizuka, and K. Shiratori, *J. Phys. Soc. Japan* **50,** 438 (1981).
12. M. Tanaka, M. Kato, N. Kimizuka, and K. Shiratori, *J. Phys. Soc. Japan* **47,** 1737 (1979).
13. J. Akimitsu, Y. Inada, K. Shiratori, I. Shindo, and N. Kimizuka, *Solid State Commun.* **32,** 1065 (1979).
14. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B* **25,** 925 (1969).