

# Synthesis and X-ray Diffraction Study of $\text{TmM}_3^{\text{II}}\text{Fe}_5\text{O}_{12}$ ( $\text{M}^{\text{II}} = \text{Ca}, \text{Sr}, \text{Ba}$ ) Compounds

E. S. Mustafin, Kh. B. Omarov, R. Z. Kasenov, A. M. Pudov,  
D. A. Kaikenov, and A. S. Satymbaeva

Karaganda State University, ul. Universitetskaya 28, Karaganda, 100028 Republic of Kazakhstan

Received August 15, 2011

**Abstract**—Double ferrites were synthesized by solid-phase annealing from thulium and iron oxides and alkaline-earth carbonates for the first time. Their symmetry systems and unit cell parameters were determined by X-ray diffraction analysis.

**DOI:** 10.1134/S0036023612090148

Ferrites—compounds of iron(III) oxide with other metal oxides—have a unique combination of magnetic and electric properties and find wide application in radio engineering and electronics. In this context, the synthesis and study of new compounds based on alkaline-earth, rare-earth, and iron(III) oxides is of great theoretical and practical interest [1–3].

The objective of our work is to synthesize and study the properties of thulium rare-earth double ferrites.

## EXPERIMENTAL

The compounds were synthesized by solid-phase annealing at high temperatures. Thulium oxide (high purity grade), iron(III) oxide (chemically pure grade), and alkaline-earth carbonates (chemically pure grade) were used as initial reagents. Appropriate portions of the initial compounds were weighed with an accuracy of four decimal places. Reagent mixtures were carefully ground in an agate mortar and then quantitatively transferred into alundum crucibles for annealing in air in a silicon carbide furnace. Heat treatment was performed as follows: annealing at 800°C for 10 h, at 1300°C for 20 h, and then at 400°C for 20 h to obtain compounds that stable under ordinary conditions.

The synthesized compounds were studied on a DRON-2.0 diffractometer ( $\text{CuK}_\alpha$  radiation) to determine their equilibrium phase composition, unit cell parameters, and symmetry system. Sodium chloride (chemically pure grade) was used as an internal standard to provide the measurement of diffraction angles with an accuracy of up to 0.05°. The intensity of diffraction peaks was evaluated on a 100-point scale.

A satisfactory agreement of the experimental and theoretical values of squared inverse interplanar distances (Table 1) confirms the reliability of the indexing results. The X-ray diffraction patterns of the obtained phases were indexed by the homology method [4].

The densities of the synthesized samples were determined in tetrabromoethane using a 1-mL pycnometer as described in [5]. The pycnometric densities are in good agreement with X-ray diffraction densities, thus confirming the correctness of the indexing of X-ray diffraction patterns (Table 2).

According to the results of X-ray diffraction analysis, the synthesized ferrites can be assigned to distorted perovskite space group  $Pm3m$ .

Hence, double ferrites  $\text{LnM}_3^{\text{II}}\text{Fe}_5\text{O}_{12}$  have been synthesized by solid-phase annealing from thulium(III) and iron(III) oxides and alkaline-earth carbonates for the first time. Using X-ray diffraction analysis, we determined the symmetry system and unit cell parameters of the synthesized phases were as follows: for  $\text{TmCa}_3\text{Fe}_5\text{O}_{12}$ :  $a = 10.79 \text{ \AA}$ ,  $c = 17.43 \text{ \AA}$ ,  $Z = 8$ ,  $V_{\text{cell}}^\circ = 2033.90 \text{ \AA}^3$ ,  $V^\circ = 254.20 \text{ \AA}^3$ ,  $\rho_X = 4.90 \text{ g/cm}^3$ ,  $\rho_{\text{pycn}} = 4.92 \pm 0.04 \text{ g/cm}^3$ ; for  $\text{TmSr}_3\text{Fe}_5\text{O}_{12}$ :  $a = 10.94 \text{ \AA}$ ,  $c = 17.03 \text{ \AA}$ ,  $Z = 8$ ,  $V_{\text{cell}}^\circ = 2038.20 \text{ \AA}^3$ ,  $V^\circ = 254.78 \text{ \AA}^3$ ,  $\rho_X = 5.82 \text{ g/cm}^3$ ,  $\rho_{\text{pycn}} = 5.76 \pm 0.06 \text{ g/cm}^3$ ; and for  $\text{TmBa}_3\text{Fe}_5\text{O}_{12}$ :  $a = 10.94 \text{ \AA}$ ,  $c = 18.59 \text{ \AA}$ ,  $Z = 8$ ,  $V_{\text{cell}}^\circ = 2224.91 \text{ \AA}^3$ ,  $V^\circ = 278.11 \text{ \AA}^3$ ,  $\rho_X = 6.22 \text{ g/cm}^3$ ,  $\rho_{\text{pycn}} = 6.18 \pm 0.04 \text{ g/cm}^3$ . The results may be included into the databases and handbooks of X-ray diffraction constants. They are of interest for the physicochemical modeling of reactions with participation of the com-

**Table 1.** Indexing of  $\text{TmM}^{\text{II}}\text{Fe}_5\text{O}_{12}$  ( $\text{M}^{\text{II}} = \text{Ca}, \text{Sr}, \text{Ba}$ ) X-ray diffraction patterns

$I/I_0, \%$	$d, \text{Å}$	$10^4/d_{\text{exp}}^2$	$hkl$	$10^4/d_{\text{calc}}^2$	$I/I_0, \%$	$d, \text{Å}$	$10^4/d_{\text{exp}}^2$	$hkl$	$10^4/d_{\text{calc}}^2$
$\text{TmCa}_3\text{Fe}_5\text{O}_{12}$					3	2.0908	2288	108	2291
7	5.0765	388	103	380	4	1.9671	2584	406	2579
12	3.8428	677	220	687	31	1.9326	2677	440	2675
7	3.6945	733	213	724	3	1.9085	2745	336	2747
9	3.4410	845	310	859	1	1.8279	2993	443	2986
5	3.3131	911	105	904	1	1.7313	3336	506	3332
56	2.7789	1295	304	1297	2	1.7189	3385	621	3379
99	2.7153	1356	116	1350	3	1.7102	3419	516	3416
100	2.6968	1375	400	1375	3	1.7015	3454	0.0.10	3449
14	2.6198	1457	410	1460	5	1.6640	3612	1.1.10	3616
3	2.4639	1647	324	1641	3	1.6304	3762	630	3763
8	2.2708	1939	325	1935	5	1.6208	3807	631	3797
9	2.2296	2012	423	2013	2	1.5261	4294	3.1.10, 058	4285, 4298
10	2.1862	2092	008	2096	2	1.4854	4532	537	4533
7	2.1191	2227	510	2234	5	1.4720	4615	635	4625
5	2.0107	2473	317	2464	1	1.4190	4966	0.0.12	4967
32	1.9432	2648	009	2652	2	1.3845	5217	608	5217
6	1.9085	2745	109	2738	16	1.3670	5351	800	5351
14	1.8710	2857	308	2869	$\text{TmBa}_3\text{Fe}_5\text{O}_{12}$				
9	1.8330	2976	407	2979	8	4.7171	449	202	450
9	1.7930	3111	601	3126	12	4.6589	461	004	463
5	1.7458	3281	0.0.10	3275	8	4.0040	624	114	630
9	1.7246	3362	1.0.10	3360	5	3.8687	668	220	668
9	1.7123	3411	516	3413	14	3.6968	732	005	723
6	1.6930	3489	613	3474	8	3.3611	885	214	880
15	1.6620	3620	2.0.10	3618	100	3.1346	1018	303	1012
12	1.5876	3968	0.0.11	3962	95	3.0369	1084	320	1085
11	1.5646	4085	527	4097	49	2.7278	1344	400	1336
15	1.5476	4175	633	4162	31	2.6907	1381	225	1392
9	1.5117	4376	429	4371	46	2.6336	1442	411	1448
4	1.4476	4772	617	4784	8	2.5847	1497	107	1501
4	1.3882	5189	608	5189	7	2.5153	1581	117	1585
14	1.3581	5422	5.0.10	5423	5	2.4195	1708	226	1709
9	1.3477	5506	5.1.10	5509	10	2.3358	1833	332	1837
4	1.3138	5794	803	5794	10	2.1709	2122	326	2127
6	1.2234	6681	806	6679	22	2.1105	2245	317	2253
$\text{TmSr}_3\text{Fe}_5\text{O}_{12}$					29	2.0478	2385	406	2377
1	4.2044	566	221	556	20	2.0139	2466	416	2461
6	3.8661	669	220	669	8	1.9344	2672	440	2672
2	3.5466	795	301	787	12	1.9257	2697	441	2700
3	3.4512	840	310	836	25	1.8753	2844	417	2837
1	3.3807	875	311	871	34	1.8592	2893	0.0.10	2893
1	3.2665	937	105	946	10	1.8382	2959	532	2955
27	3.0559	1071	303	1063	10	1.7906	3119	602	3122
9	2.9499	1149	313	1147	20	1.6681	3594	517	3589
1	2.8876	1199	205	1197	20	1.6519	3665	1.1.11	3668
100	2.7404	1332	400	1338	34	1.6401	3718	3.1.10	3728
16	2.6430	1432	410	1421	25	1.6331	3750	630	3758
14	2.6255	1451	411	1456	20	1.6285	3771	630	3758
2	2.5473	1541	331	1540	22	1.5966	3923	2.1.11	3918
2	2.5206	1574	206	1576	15	1.5629	4094	700	4092
5	2.4195	1708	241	1707	8	1.4854	4532	722	4541
4	2.1264	2212	008	2207	10	1.4203	4957	732	4959

**Table 2.** X-ray diffraction characteristics of the compounds synthesized

Compound	Symmetry system	Unit cell parameters, Å		$V^\circ, \text{Å}^3$	$V_{\text{cell}}^\circ, \text{Å}^3$	$Z$	Density, g/cm <sup>3</sup>	
		$a$	$c$				$\rho_x$	$\rho_{\text{pycn}}$
$\text{TmCa}_3\text{Fe}_5\text{O}_{12}$	tetragonal	10.79	17.43	2033.90	254.20	8	4.90	$4.92 \pm 0.02$
$\text{TmSr}_3\text{Fe}_5\text{O}_{12}$	tetragonal	10.94	17.03	2038.20	254.78	8	5.82	$5.76 \pm 0.06$
$\text{TmBa}_3\text{Fe}_5\text{O}_{12}$	tetragonal	10.94	18.59	2224.91	278.11	8	6.22	$6.18 \pm 0.04$

pounds studied and their analogues and for the targeted synthesis of compounds with important physicochemical properties.

#### REFERENCES

1. E. G. Tolokonnikov, E. S. Mustafin, B. K. Kasenov, et al., *Russ. J. Inorg. Chem.* **50**, 148 (2005).
2. B. K. Kasenov, E. S. Mustafin, Sh. B. Kasenova, et al., *Russ. J. Inorg. Chem.* **49**, 102 (2004).
3. E. S. Mustafin, B. K. Kasenov, Sh. B. Kasenova, et al., *Vestn. PGU*, No. 4, 22 (2002).
4. L. M. Kovba and V. K. Trunov, *X-ray Analysis* (Mosk. Gos. Univ., Moscow, 1976) [in Russian].
5. S. S. Kivilis, *Techniques for Measuring Densities of Liquids and Solids* (Standartgiz, Moscow, 1959) [in Russian].