ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 11, pp. 1761–1763. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © E.S. Mustafin, Kh.B. Omarov, R.Z. Kasenov, A.M. Pudov, D.A. Kaikenov, A.S. Satymbaeva, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 11, pp. 1769–1771.

New Ferrites of the Composition $TbM_3^{II}Fe_5O_{12}$ (M^{II} = Ca, Sr, or Ba) and Their XRD Properties

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

Buketov Karaganda State University, ul. Universitetskaya 28, Karaganda, 100024 Kazakhstan
e-mail: edigemus@mail.ru

Received August 15, 2011

Abstract—For the first time double ferrites from terbium oxide, iron carbonates, and alkaline earth metals were synthesized using a solid phase procedure. Symmetry and unit cell parameters of the synthesized compounds were determined by X-ray diffraction method.

DOI: 10.1134/S1070363212110023

The current stage of development in various fields of science and technology is characterized by an extensive use of complex oxides of rare-earth elements. Some of these materials are ferrites, the compounds of iron(III) oxides with other metal oxides. Ferrites possess a unique combination of magnetic and electric properties and are widely used in chemical technology. In this respect, the study of physical and chemical properties of new compounds based on the oxides of alkaline earths, rare earths, and iron(III) is of great importance for inorganic material science, is of theoretical and applied significance, it allows the identification of new materials for chemical engineering, methods of their preparation, and areas of application [1–3].

In this regard, the aim of this work was the synthesis and XRD study of terbium double ferrites.

The samples of $TbCa_3Fe_5O_{12}$, $TbSr_3Fe_5O_{12}$, and $TbBa_3Fe_5O_{12}$ were synthesized by solid-phase annealing at high temperature from terbium oxide, iron oxide,and calcium, barium and strontium carbonates in two steps.

In order to determine the equilibrium composition of phases, unit cell parameters, and the type of crystal system, the compounds were studied by the method of X-ray diffraction. Indexing of the phases obtained was performed by the homology method [4]. The perovskite of distorted type was taken as a homolog. The results are listed in Table 1.

From the results of indexing we found that all synthesized compounds crystallized in a tetragonal crystal system. The parameters of crystal lattices are listed in Table 2.

A satisfactory agreement between experimental and theoretical values of the reciprocals of the squares of the interplane distances (Table 1) confirms the reliability of indexing of the X-ray photographs.

The pycnometric density of the synthesized samples was determined in a 1 ml pycnometer using tetrabromoethane, as described in [5]. The values of pycnometric density obtained are in good agreement with the values of the X-ray density, which confirms the correctness of indexing of the X-ray photographs (Table 2).

The results of X-ray diffraction analysis showed that the synthesized double ferrites of $TbM_3^{II}Fe_5O_{12}$ (M^{II} = Ca, Sr and Ba) correspond to the space group of perovskite *Pm3m*. According to [6], it may be assumed that the Tb^{3+} and M^{2+} ions are located in the centers of the unit cells, and their coordination numbers with respect to the oxygen equal 12, while in the nodes of unit cells are located the Fe^{3+} ions, whose coordination number on oxygen is 6.

Thus, for the first time by the solid-phase annealing of oxides of terbium(III) and iron(III), and alkaline earth metal carbonates double ferrites $TbM_3^{II}Fe_5O_{12}$ were synthesized. By the method of X-ray phase analysis the types of crystal systems and unit cell

Table 1. Indexing of X-ray photographs of compounds $TbM_3^{II}Fe_5O_{12}$ (M^{II} = Ca, Sr, or Ba)

I/I_0, %	d, Å	$10^4/d^2_{exp}$	*hkl*	$10^4/d^2_{calc}$	I/I_0, %	d, Å	$10^4/d^2_{exp}$	*hkl*	$10^4/d^2_{calc}$
				$TbCa_3Fe_5O_{12}$					
8	3.8172	686	220	689	9	1.8512	2912	426	2907
5	3.4106	859	310	861	5	1.7435	3296	0.0.10	3290
3	3.2943	921	302	907	7	1.7058	3437	309	3440
18	2.7659	1307	304	1301	2	1.6600	3629	604	3628
100	2.6907	1381	400	1378	10	1.5822	3995	0.0.11	3980
24	2.6255	1451	410	1464	7	1.5392	4220	700	4222
3	2.4589	1654	324	1646	2	1.5277	4285	606	4286
3	2.1940	2077	334	2077	3	1.5133	4367	616	4372
3	2.1573	2149	500	2154	3	1.4393	4827	1.0.12	4823
4	2.1084	2250	424	2249	2	1.3845	5217	608	5207
5	2.0075	2481	317	2473	10	1.3466	5515	800	5514
21	1.9373	2664	009	2664	4	1.2211	6707	806	6699
4	1.9085	2745	109	2751	2	1.1869	7099	738	7103
4	1.8973	2778	514	2766					
				$TbSr_3Fe_5O_{12}$					
5	4.2898	543	004	545	5	1.9671	2584	218	2596
4	3.8661	669	220	669	24	1.9315	2680	440	2676
3	3.5357	800	222	805	3	1.9085	2745	327	2755
2	3.4616	835	310	836	21	1.8549	2906	426	2898
57	3.0338	1086	320	1087	2	1.8274	2995	407	3006
5	2.9484	1150	313	1143	2	1.8078	3060	601	3045
19	2.7920	1283	215	1269	4	1.6994	3463	541	3463
33	2.7659	1307	106	1309	1	1.6879	3510	309	3509
100	2.7378	1334	400	1338	3	1.6285	3771	630	3763
30	2.6221	1454	411	1456	8	1.6201	3810	2.1.10	3821
3	2.5153	1581	206	1560	5	1.6003	3905	632	3900
5	2.4791	1627	324	1632	35	1.5804	4004	444	4014
3	2.4195	1708	421	1706	4	1.5459	4184	419, 710	4178, 4181
20	2.2337	2004	207	2002	3	1.5148	4358	518	4352
2	2.1633	2137	501	2125	2	1.4839	4541	2111	4536
4	2.1264	2212	511	2208	7	1.4729	4609	528	4603
2	2.1048	2257	108	2262	2	1.4284	4901	0.0.12	4900
2	2.0908	2288	415	2273	2	1.4046	5069	1.1.12	5068
5	2.0565	2365	335	2356	2	1.3845	5217	2.0.12	5235
1	2.0139	2466	513	2480	10	1.3699	5329	706	5323
				$TbBa_3Fe_5O_{12}$					
15	4.7368	446	113, 211	431, 452	17	2.8947	1193	321	1183
12	4.6589	461	004	466	4	2.7278	1344	400	1352
6	4.3857	520	211	507	28	2.6907	1381	401	1381
5	4.2737	548	104	550	33	2.6198	1457	402	1468
9	4.0068	623	114	635	7	2.4689	1641	332	1638
9	3.7184	723	300	761	6	2.4244	1701	413	1699
6	3.6592	747	300	761	4	2.3769	1770	333	1784
9	3.3906	870	302	877	13	2.3251	1850	217	1849
96	3.1346	1018	303	1023	10	2.2920	1904	414	1903
100	3.0212	1096	320	1099	6	2.2658	1948	108	1948

Table 1. (Contd.)

I/I_0, %	d, Å	$10^4/d^2_{\mathrm{exp}}$	hkl	$10^4/d^2_{\mathrm{calc}}$	I/I_0, %	d, Å	$10^4/d^2_{\mathrm{exp}}$	hkl	$10^4/d^2_{\mathrm{calc}}$
				$TbBa_3Fe_5O_{12}$					
14	2.1120	2242	335	2249	17	1.6620	3620	1011	3607
29	2.0465	2387	503	2375	26	1.6421	3709	409	3710
12	2.0300	2427	520	2451	22	1.6285	3771	605	3771
16	2.0139	2466	513	2460	33	1.5804	4004	3.2.10	4009
12	1.9228	2705	440	2705	13	1.5612	4103	625	4109
7	1.8753	2844	505	2841	10	1.5459	4184	701, 616	4171, 4176
41	1.8534	2911	0.0.10	2911	9	1.5117	4376	3.1.11	4368
10	1.8003	3085	601	3072	10	1.4839	4541	552	4565
9	1.7920	3114	309, 427	3119, 3117	6	1.4519	4744	723	4742
12	1.6951	3480	443	3466	9	1.4284	4901	730	4903
23	1.6701	3585	614	3593	9	1.4203	4957	715	4954

Table 2. XRD characteristics of the synthesized compounds

Compound	Crystal system	Cell parameters, Å		V^0, Å^3	V^0_{cell}, Å^3	Z	Density, g cm^{-3}	
		a	c				ρ_{exp}	ρ_{calc}
$TbCa_3Fe_5O_{12}$	Tetragonal	10.77	17.43	2021.80	252.70	8	4.99	5.02±0.03
$TbSr_3Fe_5O_{12}$	Tetragonal	10.94	17.14	2051.38	256.42	8	5.85	5.79±0.06
$TbBa_3Fe_5O_{12}$	Tetragonal	10.88	18.53	2193.48	274.20	8	6.37	6.31±0.06

parameters of all synthesized phases were identified. The results obtained are the primary data for inclusion in databases and directories of XRD constants. They are of interest for the physicochemical modeling of reactions of the studied compounds and their analogs, as well as for the direct synthesis of substances with valuable physical and chemical properties.

EXPERIMENTAL

The studied compounds were synthesized by solid phase annealing at high temperature. For the synthesis terbium oxide of extra pure grade, iron(III) oxide of chemically pure grade, and alkaline earth carbonates of chemically pure grade were used. The samples of the starting materials were weighed to within four decimal places. Reagent mixture was thoroughly triturated in an agate mortar, then it was transferred quantitatively into an alundum crucible for annealing in air in a silicon carbide oven. Heat treatment was carried out as follows: annealing for 10 h at 800ºC, then for 20 h at 1300ºC. During the next 20 h the annealing at 400ºC was carried out in order to obtain stable compounds under normal conditions.

The duffractograms were obtained on a DRON-2.0 diffractometer with CuK α-radiation. As the internal reference sodium chloride of chemically pure grade was used, which provided a measurement of diffraction angles with a precision up to 0.05. The intensity of the diffraction maxima was assessed within a 100-point scale based on the most intense line.

REFERENCES

1. Mustafin, E.S., Tolokonnikov, E.G., Kasenov, B.K., Kasenova, Sh.B., Sagintaeva, Zh.I., Zhumadilov, E.K., and Akubaeva, M.A., *Zh. Neorg. Khim*., 2005, vol. 50, no. 2, p. 187.
2. Mustafin, E.S., Kasenov, B.K., Kasenova, Sh.B., Tolokonnikov, E.G., and Edil'baeva, S.T., *Zh. Neorg. Khim*., 2004, vol. 49, no. 1, p. 107.
3. Mustafin, E.S., Kasenov, B.K., Kasenova, Sh.B., Tolokonnikov, E.G., and Edil'baeva, S.T., *Vestnik PGU*, 2002, no. 4, p. 22.
4. Kovba, L.M. and Trunov, V.K., *Rentgenofazovyi analiz* (X-Ray Phase Analysis), 2nd ed., Moscow: MGU, 1976.
5. Kivilis, S.S., *Tekhnika izmerenii plotnosti zhidkostei i tverdykh tel* (Technique for Measuring Density of Liquids and Solids), Moscow: Standartgiz, 1959.
6. Portnoi, K.I. and Timofeev, N.I., *Kislorodnye soedineniya redkozemel'nykh elementov* (Oxygen Compounds of Rare Earth Elements), Moscow: Metallurgiya, 1986.