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X-ray Diffraction Study of the $Tm_2M^I_3Fe_5O_{12}$ (M^I = Li, Na, K) Ferrites

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Abstract—The $Tm_2M^I_3Fe_5O_{12}$ (M^I = Li, Na, K) compounds have been prepared for the first time by solid-state reactions between thulium(III) oxide, iron(III) oxide, and alkali metal carbonates, and their symmetry class and unit-cell parameters have been determined by X-ray diffraction.

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Variable-valence metal oxides with a perovskite-like structure exhibit a number of interesting effects of practical importance: metal–dielectric transitions, various types of magnetic ordering, and superconductivity [1]. For this reason, such materials are of interest not only for basic research aimed at understanding the nature of these physical phenomena but also for producing various devices that take advantage of the electronic properties of oxides.

Rare-earth oxide compounds possess a unique combination of electrical, magnetic, thermal, optical, and other properties owing to the specific features of the electronic structure of lanthanides and may find wide application in modern microelectronics for producing multifunctional systems [2, 3]. The diversity of their properties depends on the composition, structure, and preparation procedure of a particular oxide.

The objectives of this work were to synthesize alkali-metal rare-earth ferrites with the general formula $Tm_2M^I_3Fe_5O_{12}$ (M^I = Li, Na, K) and characterize them by X-ray diffraction (XRD).

The ferrites were prepared by standard solid-state techniques in three steps at different temperatures. The starting chemicals used were thulium oxide (extrapure grade), iron(III) oxide (reagent grade), and alkali metal carbonates (reagent grade). Appropriate amounts of the starting materials (for particular mixed ferrite compositions) were weighed out to the fourth decimal place and mixed. The mixtures were thoroughly ground in an agate mortar and then fired in Alundum crucibles placed in a Silit furnace, first at 800°C for 10 h (step I), then at 1300°C for 10 h with several intermediate grindings in a mortar (step II), and finally at 400°C for 20 h (step III) in order to obtain compounds stable under ordinary conditions.

XRD measurements were performed on a DRON-2.0 powder diffractometer (CuK_α radiation). Powder XRD patterns were indexed by the homology method [4] in the perovskite structure type. The density of the ferrites was determined by the Archimedes method, as described by Kivilis [5], using 1-mL glass pycnometers. Tetrabromoethane was used as a saturating and suspending medium because it adequately wets the ferrites in question, is nonreactive with them, and has an almost temperature-independent density. Each density value was obtained as the average over five repeated measurements.

The validity of the indexing schemes derived from our XRD data was confirmed by satisfactory agreement between the observed and calculated $10^4/d^2$ values (table).

The indexing results indicate that the ferrites crystallize in tetragonal symmetry. The measured and X-ray densities of the ferrites are in satisfactory agreement, confirming the indexing schemes and indicating that the lattice parameters of the ferrites were determined with high accuracy.

Thus, the $Tm_2Li_3Fe_5O_{12}$, $Tm_2Na_3Fe_5O_{12}$, and $Tm_2K_3Fe_5O_{12}$, ferrites have been prepared for the first time by a ceramic processing technique at temperatures from 800 to 1300°C. According to XRD data, the ferrites crystallize in tetragonal symmetry.

Indexing schemes for $Tm_2M^I_3Fe_5O_{12}$ (M^I = Li, Na, K) powders

I, %	d, Å	$10^4/d^2_{obs}$	hkl	$10^4/d^2_{calc}$	I, %	d, Å	$10^4/d^2_{obs}$	hkl	$10^4/d^2_{calc}$
$Tm_2Li_3Fe_5O_{12}$					26	1.6440	3700	524	3691
8	4.2578	552	113	545	4	1.5629	4094	2.1.10	4081
6	3.8046	691	220	692	5	1.5392	4221	633	4219
3	3.7208	722	203	718	2	1.5070	4403	0.0.11	4415
7	3.4005	865	301	865	2	1.4747	4598	1.1.11	4588
2	3.3321	901	311	906	6	1.4533	4735	722	4728
100	3.0181	1098	214	1094	2	1.3944	5143	705	5149
12	2.9381	1158	303	1150	10	1.3769	5275	538	5275
5	2.7920	1283	322	1289	18	1.3443	5534	800	5534
23	2.6883	1384	400	1383	4	1.3288	5663	811	5657
50	2.6198	1457	215	1466	4	1.3128	5802	5.0.10	5810
26	2.5101	1587	331	1597	3	1.2701	6199	744	6204
8	2.4689	1641	412	1635	2	1.2084	6848	6.1.10	6848
5	2.3956	1742	430	1755	2	1.1754	7238	835	7224
2	2.3448	1819	305	1812	$Tm_2K_3Fe_5O_{12}$				
4	2.1558	2152	325	2161	9	5.9940	278	003	284
4	2.1048	2257	306	2267	10	4.3060	539	221	558
40	2.0769	2318	502	2327	10	3.8223	685	220	689
13	2.0552	2368	207	2372	8	3.4206	855	310	857
7	1.9097	2742	108	2733	100	3.0102	1104	320	1113
4	1.8928	2761	440	2766	15	2.8321	1247	322	1248
50	1.8528	2913	514	2909	12	2.7920	1283	304	1276
4	1.8486	2926	442	2932	8	2.7595	1313	116	1308
2	1.7481	3272	602	3278	35	2.6907	1381	400	1386
13	1.7015	3454	620	3458	17	2.6690	1404	323	1406
5	1.6170	3825	623	3830	48	2.6255	1451	401	1471
4	1.6021	3896	630	3890	10	2.5724	1511	402	1512
36	1.5804	4004	526	3996	9	2.4770	1630	107	1633
7	1.5459	4184	507	4187	5	2.4490	1667	403	1670
4	1.5392	4221	1.0.10	4221	7	2.3815	1763	421	1760
5	1.5277	4285	701	4277	3	2.3358	1833	333	1833
7	1.5133	4367	711	4364	6	2.2418	1989	316	1993
3	1.4824	4551	634	4552	8	2.1618	2140	500	2141
26	1.4706	4624	721	4623	4	2.1120	2242	227	2235
2	1.4547	4726	409	4733	11	2.0565	2365	208	2362
2	1.4393	4827	2.2.10	4827	7	1.9114	2737	119	2729
4	1.4284	4901	339	4905	6	1.8973	2778	440	2740
2	1.4020	5087	1.0.11	5090	44	1.8549	2906	209	2903
3	1.3711	5319	651	5315	3	1.8023	3079	600	3083
$Tm_2Na_3Fe_5O_{12}$					12	1.7050	3440	534	3441
20	5.0314	395	201	382	6	1.6909	3498	418	3492
20	3.2794	930	204	929	4	1.6323	3753	623	3745
100	2.7505	1321	006	1310	5	1.6208	3807	622	3768
9	2.6907	1381	400	1383	30	1.5822	3995	1.1.11	3991
13	2.6175	1460	323	1452	7	1.5476	4175	2.0.11	4165
36	2.5101	1587	331	1592	6	1.5293	4276	701	4276
2	2.4147	1715	403	1711	7	1.5155	4354	711	4362
3	2.1709	2122	207	2133	10	1.4885	4513	2.2.11	4508
19	1.9949	2513	118	2508	2	1.4561	4716	1.1.12	4717
3	1.8163	3031	228	3027	4	1.4407	4818	519	4808
14	1.7761	3170	407	3171	3	1.4284	4901	2.0.12	4891
38	1.7058	3437	603	3441	4	1.3466	5515	734	5520
8	1.6555	3641	229	3647					

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