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X-ray Diffraction Study of the $YbM_3^{II}Fe_5O_{12}$ (M^{II} = Mg, Ca, Sr) Ferrites

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Abstract—Three compounds with the general formula $YbM_3^{II}Fe_5O_{12}$ (M^{II} = Mg, Ca, Sr) have been prepared for the first time by high-temperature solid-state reactions between ytterbium(III) oxide, iron(III) oxide, and alkaline-earth carbonates. Their crystal class and unit-cell parameters have been determined by X-ray diffraction.

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Oxide materials with semiconducting, ferroelectric, piezoelectric, pyroelectric, and superconducting properties and high mixed (electronic–ionic or electronic–metallic) conductivity are currently the subject of intense research. Such materials include ferrites with the general formula $RM_3^{II}Fe_5O_{12}$ (R = rare-earth metal, M^{II} = alkaline-earth metal).

The discovery of high-transition temperature (high-T_c) superconductivity in rare-earth cuprates aroused interest in other oxide superconductors, free of copper [1].

In this paper, we report the synthesis and X-ray diffraction characterization of mixed ferrites with the general formula $YbM_3^{II}Fe_5O_{12}$, where M^{II} is an alkaline-earth metal (Mg, Ca, or Sr) possessing potentially attractive electrical (semiconducting, ferroelectric, magnetic, superconducting, and other) properties.

The compounds were prepared by standard solid-state reactions in three steps at different temperatures. The starting chemicals used were ytterbium oxide (extrapure grade), iron(III) oxide (reagent grade), and alkaline-earth carbonates (reagent grade). Appropriate amounts of the starting materials were weighed out to the fourth decimal place. The starting-mixture compositions were adjusted to give the final compositions of the mixed ferrites. The mixtures were thoroughly ground in an agate mortar and then reacted in Alundum crucibles placed in a Silit furnace. The synthesis process comprised firing at 800°C for 10 h, then at 1300°C for 10 h with several intermediate grindings in a mortar, and finally at 400°C for 20 h in order to obtain compounds stable under ordinary conditions.

The synthesized compounds were analyzed for iron by atomic absorption (Table 1). A comparative analysis of theoretical predictions and experimental data showed that the compounds had the intended compositions.

X-ray diffraction measurements were performed on a DRON-2.0 powder diffractometer (CuK_α radiation). The powder X-ray diffraction patterns of the new ferrites were indexed by the homology method [2] in the perovskite structure type. The density of the ferrites was determined by the Archimedes method, as described by Kivilis [3], using 1-mL glass pycnometers. Tetrabromoethane was used as a saturating and suspending medium, because it adequately wets the ferrites in question and is nonreactive with them, and its density varies little with temperature. The density of each compound was obtained as the average over five repeated measurements.

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

Thus, the $YbMg_3Fe_5O_{12}$, $YbCa_3Fe_5O_{12}$, and $YbSr_3Fe_5O_{12}$ ferrites have been prepared for the first time by a ceramic processing technique at temperatures from 800 to 1300°C.

Table 1. Iron content of the synthesized compounds

Compound	Weight percent Fe	
	nominal	atomic absorption data
$YbMg_3Fe_5O_{12}$	39.0	38.54
$YbCa_3Fe_5O_{12}$	36.6	35.58
$YbSr_3Fe_5O_{12}$	30.85	31.29

Table 2. Indexing schemes for the X-ray powder diffraction patterns of YbM$_3^{II}$Fe$_5$O$_{12}$ (Me^{II} = Mg, Ca, Sr)

I/I_0, %	d, Å	$10^4/d^2_{obs}$	hkl	$10^4/d^2_{calc}$
YbMg$_3$Fe$_5$O$_{12}$				
3	4.8379	427.3	210	434
8	4.2419	555.7	113	556
18	3.7920	695.4	220	694
13	3.6709	742.1	221	737
21	3.3946	867.8	310	868
89	3.0104	1103.4	214	1113
36	2.9632	1139	32	1128
12	2.7789	1295	322	1298
83	2.6883	1384	400	1388
53	2.6083	1470	410	1475
100	2.5287	1564	330	1562
6	2.4653	1645	412	1645
3	2.3269	1847	305	1842
5	2.2528	1970	216	1962
13	2.2000	2066	404	2068
6	2.1484	2167	500	2169
37	2.0992	2269	510	2256
8	2.0432	2395	316	2396
11	1.8967	2780	440	2777
10	1.8917	2794	425	2797
8	1.8677	2867	307	2861
51	1.8434	2943	442	2946
3	1.7889	3125	600	3124
10	1.7102	3419	228	3412
19	1.7015	3454	444	3456
30	1.6951	3480	407	3469
27	1.6137	3840	445	3838
26	1.5716	4049	526	4045
8	1.5342	4249	700	4252
13	1.5228	4312	319	4307
4	1.5021	4432	702	4422
47	1.4839	4541	641	4555
13	1.4533	4735	616	4739
6	1.4350	4856	447	4857
3	1.3677	5346	651	5335
7	1.3432	5543	800	5553
6	1.3253	5693	519	5695
6	1.3117	5812	3.3.10	5808
7	1.3057	5866	716	5867
8	1.2796	6107	735	6094
5	1.2608	6291	1.1.12	6288
4	1.2544	6355	655	6354
6	1.2161	6762	5.2.10	6762
8	1.2129	6798	753	6803
YbCa$_3$Fe$_5$O$_{12}$				
8	4.1828	572	212	569
19	3.7795	700	220	695
16	3.6709	742	213	736
8	3.3906	870	310	869
79	2.9739	1131	320	1130
24	2.7764	1297	106	1293
100	2.6786	1394	400	1390
56	2.6083	1470	410	1477
40	2.5101	1587	331	1598
6	2.4539	1661	324	1666
16	2.3975	1740	420	1738
6	2.2500	1975	325	1967
8	2.2337	2004	414	2013
15	2.2015	2063	316	2075
8	2.1484	2167	500	2173
8	2.1006	2266	424	2274
5	2.0399	2403	335	2402
4	1.9391	2659	522	2654
12	1.9029	2762	336	2771
11	1.8890	2802	109	2801
8	1.8645	2877	119	2888
47	1.8387	2958	530	2955
4	1.7367	3316	444	3317
26	1.7007	3457	516	3466
37	1.6930	3489	534	3491
3	1.6640	3612	622	3610
3	1.5970	3921	630	3911
21	1.5709	4052	615	4053
9	1.5622	4098	544	4099
7	1.5375	4230	1.1.11	4229
16	1.5228	4312	625	4314
7	1.5057	4411	518	4404
14	1.4863	4527	640	4519
16	1.4519	4744	4.0.10	4741
6	1.4349	4857	617	4857
3	1.4190	4966	519	4974
4	1.3894	5180	555	5183
4	1.3675	5347	733	5342
6	1.3421	5552	800	5562
8	1.3096	5831	654	5837
5	1.3037	5884	735	5878
4	1.2597	6302	4.1.12	6303
5	1.2129	6798	664	6793
YbSr$_3$Fe$_5$O$_{12}$				
3	4.621	468	202	462
6	4.2106	564	104	557
8	3.792	695	220	688
3	3.6592	747	005	736
2	3.5114	811	204	815
3	3.3709	880	311	889
82	2.9904	1118	320	1117
19	2.9191	1174	215	1166
43	2.7531	1319	314	1331
100	2.6964	1375	400	1375
34	2.6786	1394	323	1382
46	2.597	1483	216	1490
10	2.5048	1594	315	1596
5	2.443	1676	332	1665

Table 2. (Contd.)

I/I_0, %	d, Å	$10^4/d^2_{\mathrm{obs}}$	hkl	$10^4/d^2_{\mathrm{calc}}$	I/I_0, %	d, Å	$10^4/d^2_{\mathrm{obs}}$	hkl	$10^4/d^2_{\mathrm{calc}}$
10	2.4099	1722	420	1719	11	1.614	3839	419	3846
24	2.2247	2020	334	2018	11	1.5947	3932	527	3935
6	2.2054	2056	118	2056	38	1.5716	4049	3.2.10	4061
5	2.1484	2167	326	2177	7	1.5326	4257	545	4260
12	2.112	2242	510	2235	4	1.5212	4321	4.0.10	4319
8	2.0372	2410	503	2414	5	1.4838	4542	607	4537
6	2.0139	2466	109	2471	12	1.4691	4633	448	4635
4	1.9611	2600	336	2607	9	1.4519	4744	643	4735
7	1.9085	2745	440	2751	13	1.3661	5358	652	5361
32	1.8387	2958	524	2964	4	1.3466	5515	800	5501
15	1.6888	3506	329	3502	4	1.3245	5700	4.1.12	5701
9	1.6579	3638	542	3642	5	1.3076	5849	813	5852
6	1.6452	3695	623	3703	5	1.2994	5923	647	5912

Table 3. Crystal-chemical characteristics of the synthesized compounds

Compound	Lattice parameters, Å		V, Å^3	V_{subcell}, Å^3	Density, g/cm^3	
	a	c			X-ray	measured
$YbMg_3Fe_5O_{12}$	10.7	15.3	1768.74	221.09	5.38	5.37 ± 0.05
$YbCa_3Fe_5O_{12}$	10.72	17.27	1987.89	248.49	5.11	5.10 ± 0.03
$YbSr_3Fe_5O_{12}$	10.78	18.43	2144.05	268.01	5.62	5.66 ± 0.14

Tetragonal symmetry, $Z = 8$.

According to the above indexing results, the ferrites crystallize in tetragonal symmetry and have perovskite structure (sp. gr. $Pm3m$). The lattice parameters of the ferrites are listed in Table 3. The satisfactory agreement between the X-ray and measured densities of the ferrites suggests that the proposed indexing schemes are correct and that the lattice parameters were determined with adequate accuracy.

The increase in ionic radius in going from magnesium to strontium is accompanied by an increase in the unit-cell parameters and volume of the respective ferrites.

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