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PHYSICAL METHODS OF INVESTIGATION

X-ray Diffraction Characteristics of New Chromitomanganites $LaM^{I}_{3}CrMnO_{6}$ and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{I} = Li, Na; M^{II} = Mg, Ca)

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Abstract— $LaM^{I}_{3}CrMnO_{6}$ (M^{I} = Li, Na) and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{II} = Mg, Ca) chromitomanganites were synthesized by ceramic technology from lanthanum oxide, chromium(III) oxide, manganese(III) oxide, lithium carbonate, sodium carbonate, magnesium carbonate, and calcium carbonate. X-ray powder diffraction shows that these compounds crystallize in cubic or tetragonal systems with the following unit cell parameters: for $LaLi_3CrMnO_6$ (cubic): $a = 10.98$ Å, $V^{\circ} = 1323.75$ Å^3, $Z = 8$, $V^{\circ}_{u.c} = 165.47$ Å^3, $\rho_X = 3.64$, $\rho_{pycn} = 3.60 \pm 0.04$ g/cm^3; for $LaNa_3CrMnO_6$ (tetragonal): $a = 10.96$ Å, $c = 15.73$ Å, $V^{\circ} = 1889.51$ Å^3, $Z = 16$, $V^{\circ}_{u.c} = 118.09$ Å^3, $\rho_X = 5.77$ g/cm^3, $\rho_{pycn} = 5.70 \pm 0.07$ g/cm^3; $LaMg_3CrMnO_{7.5}$ (cubic), $a = 10.98$ Å, $V^{\circ} = 1322.31$ Å^3, $Z = 8$, $V^{\circ}_{u.c} = 165.29$ Å^3, $\rho_X = 4.41$ g/cm^3, $\rho_{pycn} = 4.35 \pm 0.07$ g/cm^3; and for $LaCa_3CrMnO_{7.5}$ (cubic): $a = 10.97$ Å, $V^{\circ} = 1319.78$ Å^3, $Z = 8$, $V^{\circ}_{u.c} = 164.97$ Å^3, $\rho_X = 4.89$ g/cm^3, $\rho_{pycn} = 4.85 \pm 0.05$ g/cm^3.

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Rare-earth manganites have promising semiconductive, ferromagnetic, ferroelectric, and other properties [1, 2]. Rare-earth chromites with good electronic conductivity may also be qualified as promising compounds [3, 4]. We should note that the doping of rare-earth manganites and chromites with alkali and alkali-earth metal oxides gives rise to unique properties: the colossal magnetic resistance effect in manganites and a sharp decrease in electrical resistance at elevated temperatures in chromites [1, 3]. In the context of the abovesaid, the synthesis of compounds that contain oxides of rare-earth elements, manganese(III), chromium(III), alkali and alkali-earth metals simultaneously and the study of their properties are of interest from both theoretical and practical viewpoints.

The objective of our work is to synthesize $LaM^{I}_{3}CrMnO_{6}$ (M^{I} = Li, Na) and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{II} = Mg, Ca) chromitomanganites and to study them using X-ray diffraction analysis.

EXPERIMENTAL

Solid-phase synthesis of the compounds was performed by ceramic technology. The initial compounds used in synthesis were lanthanum oxide La_2O_3 (high purity); Cr_2O_3; Mn_2O_3; and lithium, sodium, magnesium, and calcium carbonates (pure for analysis). To remove adsorbate humidity, the initial compounds were calcinated at 300°C for 1 h. Their stoichiometric amounts were further carefully stirred and pounded in an agate mortar, transferred into alundum crucibles, and then annealed in a SNOL muffle furnace at 800°C for 10 h. The mixtures were then stirred again, pounded, and also subjected to thermal treatment at 1200°C for 10 h. To obtain stable equilibrium states, low-temperature anneals were then performed at 400°C with repeated stirring and pounding.

X-ray powder diffraction analysis of the synthesized compounds was performed on a DRON-2.0 diffractometer (CuK_{α} radiation; Ni filter; $U = 30$ kV; $I = 10$ mA; counter rotation velocity: 2 rpm; scale range: 1000 pulses/s; $\tau = 5$ s; $2\theta = 10°$–$90°$). The intensities of diffraction peaks were scored on a 100-point scale. We should emphasize that X-ray diffraction patterns did not contain diffraction peaks of initial phases.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the synthesized compounds were indexed by the homology method

Table 1. Indexing of X-ray powder diffraction patterns for $LaM^{I}_{3}CrMnO_6$ (M^{I} = Li, Na) and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{II} = Mg, Ca) chromitomanganites

I/I_0	d, Å	$10^4/d^2_{exp}$	hkl	$10^4/d^2$
		$LaLi_3CrMnO_6$		
22	3.8687	668.1	220	663.5
100	2.7404	1332	400	1327
9	2.4679	1642	420	1659
25	2.2394	1994	422	1991
11	2.0478	2385	333	2405
37	1.9379	2663	440	2654
5	1.8753	2843	540	2820
9	1.7345	3324	620	3318
32	1.5840	3985	444	3981
8	1.5737	4038	700	4054
11	1.3723	5310	800	5308
16	1.2277	6635	840	6635
		$LaNa_3CrMnO_6$		
25	3.8792	664.5	220	666.0
11	3.5708	784.0	301	789.9
7	3.1687	996	321	994
5	2.9798	1126	303	1123
20	2.8941	1194	313	1196
97	2.7467	1325	224	1312
100	2.7404	1332	400	1333
25	2.2459	1983	404	1978
10	2.2256	2019	423	2029
46	1.9385	2661	440	2665
7	1.7857	3136	611	3128
8	1.7435	3290	444	3311
34	1.5858	3976	624	3976
15	1.5737	4038	0.0.10	4038
15	1.3654	5364	4.0.10	5370
10	1.2251	6663	840	6663
		$LaMg_3CrMnO_{7.5}$		
9	4.8173	430.9	210	416.0
18	3.8687	668.1	220	664.2
100	2.7429	1329	400	1328
13	2.5101	1587	331	1586
19	2.2377	1997	422	1992
33	1.9402	2656	440	2650
9	1.7367	3316	620	3320
28	1.5847	3982	414	3980
4	1.5261	4294	640	4316
4	1.4764	4588	712	4565
13	1.3723	5310	800	5312
13	1.2277	6635	840	6640
		$LaCa_3CrMnO_{7.5}$		
21	3.8687	668.1	220	664.8
11	3.6247	761.1	300	747.9
8	3.0369	1084	320	1080
100	2.7410	1331	400	1330
17	2.2410	1991	422	1995
27	1.9402	2656	440	2660
11	1.9142	2729	441	2743
6	1.8486	2926	531	2910
6	1.7327	3331	620	3324
26	1.5840	3986	444	3989
11	1.5667	4074	700	4072
8	1.4519	4744	730	4737
11	1.3711	5319	800	5319
15	1.2267	6645	840	6649

Table 2. X-ray diffraction characteristics of $LaM^{I}_{3}CrMnO_6$ (M^{I} = Li, Na) and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{II} = Mg, Ca) chromitomanganites

Compound	Unit cell parameters, Å		Z	V°, Å^3	$V^{\circ}_{u.c.}$, Å^3	Density, g/cm^3	
	a	c				ρ_X	ρ_{pycn}
$LaLi_3CrMnO_6$	10.98	–	8	1323.75	165.47	3.64	3.60 ± 0.04
$LaNa_3CrMnO_6$	10.96	15.73	16	1889.51	118.09	5.77	5.70 ± 0.07
$LaMg_3CrMnO_{7.5}$	10.98	–	8	1322.31	165.29	4.41	4.35 ± 0.07
$LaCa_3CrMnO_{7.5}$	10.97	–	8	1319.78	164.97	4.89	4.85 ± 0.05

[4]. The homologue used was the perovskite structure type . The results of indexing are given below in Table 1. The pycnometric densities of the compounds was determined according to [5]. Toluene was used as an indifferent liquid.

Proceeding from the indexing of X-ray diffraction patterns, we have established that $LaLi_3CrMnO_6$, $LaMg_3CrMnO_{7.5}$, and $LaCa_3CrMnO_{7.5}$ crystallize in cubic system and $LaNa_3CrMnO_6$ crystallizes in hexagonal system with the corresponding unit cell parameters (Table 2).

A satisfactory agreement between the experimental and calculated values of $10^4/d^2$, X-ray and pycnometric densities, and theoretical and measured $V^{\circ}_{u.c}$ values validates the adequacy of the indexing.

Hence, the $LaM^{I}_{3}CrMnO_6$ (M^{I} = Li, Na) and $LaM^{II}_{3}CrMnO_{7.5}$ (M^{II} = Mg, Ca) compounds have been synthesized by ceramic technology for the first time, and their X-ray diffraction parameters have been determined.

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