

Synthesis and X-ray Diffraction Study of New Nanostructured Manganite Ferrites $\text{NdM}_{1.5}^{\text{II}}\text{MnFeO}_6$ ($\text{M}^{\text{II}} = \text{Mg, Ca, Sr, Ba}$)

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Abstract—Manganite ferrites $\text{NdM}_{1.5}^{\text{II}}\text{MnFeO}_6$ ($\text{M}^{\text{II}} = \text{Mg, Ca, Sr, Ba}$) were synthesized from neodymium(III), manganese(III), and iron(III) oxides and alkaline-earth metal carbonates by a ceramic technology. By grinding the obtained compounds in a ball mill, their nanostructured particles were produced, the sizes of which were determined with an electron microscope. X-ray diffraction study established that the nanostructured compounds crystallize in the cubic and tetragonal systems with the following lattice parameters: $\text{NdMg}_{1.5}\text{MnFeO}_6$ (tetragonal): $a = 10.955 \text{ \AA}$, $c = 17.848 \text{ \AA}$, $V^0 = 2141.975 \text{ \AA}^3$, $Z = 16$, $V_{\text{el.cell}}^0 = 133.873 \text{ \AA}^3$, $\rho_{\text{X-ray}} = 4.80 \text{ g/cm}^3$, and $\rho_{\text{pycn}} = 4.76 \pm 0.05 \text{ g/cm}^3$; $\text{NdCa}_{1.5}\text{MnFeO}_6$ (cubic): $a = 10.809 \text{ \AA}$, $V^0 = 1262.864 \text{ \AA}^3$, $Z = 8$, $V_{\text{el.cell}}^0 = 157.858 \text{ \AA}^3$, $\rho_{\text{X-ray}} = 4.32 \text{ g/cm}^3$, and $\rho_{\text{pycn}} = 4.27 \pm 0.03 \text{ g/cm}^3$; $\text{NdSr}_{1.5}\text{MnFeO}_6$ (cubic): $a = 10.911 \text{ \AA}$, $V^0 = 1298.953 \text{ \AA}^3$, $Z = 8$, $V_{\text{el.cell}}^0 = 162.369 \text{ \AA}^3$, $\rho_{\text{X-ray}} = 4.93 \text{ g/cm}^3$, and $\rho_{\text{pycn}} = 4.88 \pm 0.05 \text{ g/cm}^3$; and $\text{NdBa}_{1.5}\text{MnFeO}_6$ (tetragonal): $a = 11.011 \text{ \AA}$, $c = 18.001 \text{ \AA}$, $V^0 = 2182.479 \text{ \AA}^3$, $Z = 16$, $V_{\text{el.cell}}^0 = 136.405 \text{ \AA}^3$, $\rho_{\text{X-ray}} = 6.78 \text{ g/cm}^3$, and $\rho_{\text{pycn}} = 6.75 \pm 0.07 \text{ g/cm}^3$.

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Currently, there is a growing interest in oxide materials with semiconducting, magnetic, ferroelectric, piezoelectric, pyroelectric, and superconducting properties and also with high mixed (electronic and ionic or metallic) conductivities. Among such materials are rare-earth metal manganites and ferrites. The discovery of giant magnetoresistance (1993–1994) in manganites of the type $\text{La}(\text{Ca, Ba})\text{MnO}_3$ with the perovskite structure inspired the synthesis and investigation of new, previously unknown, compounds forming in systems comprising rare-earth element oxides, alkaline-earth metals, and manganese(III).

To date, mainly individual rare-earth element manganites and ferrites, alloyed with light metal oxides, have been investigated. In our opinion, it was of a certain theoretical and practical interest to combine manganites and ferrites within the same compound.

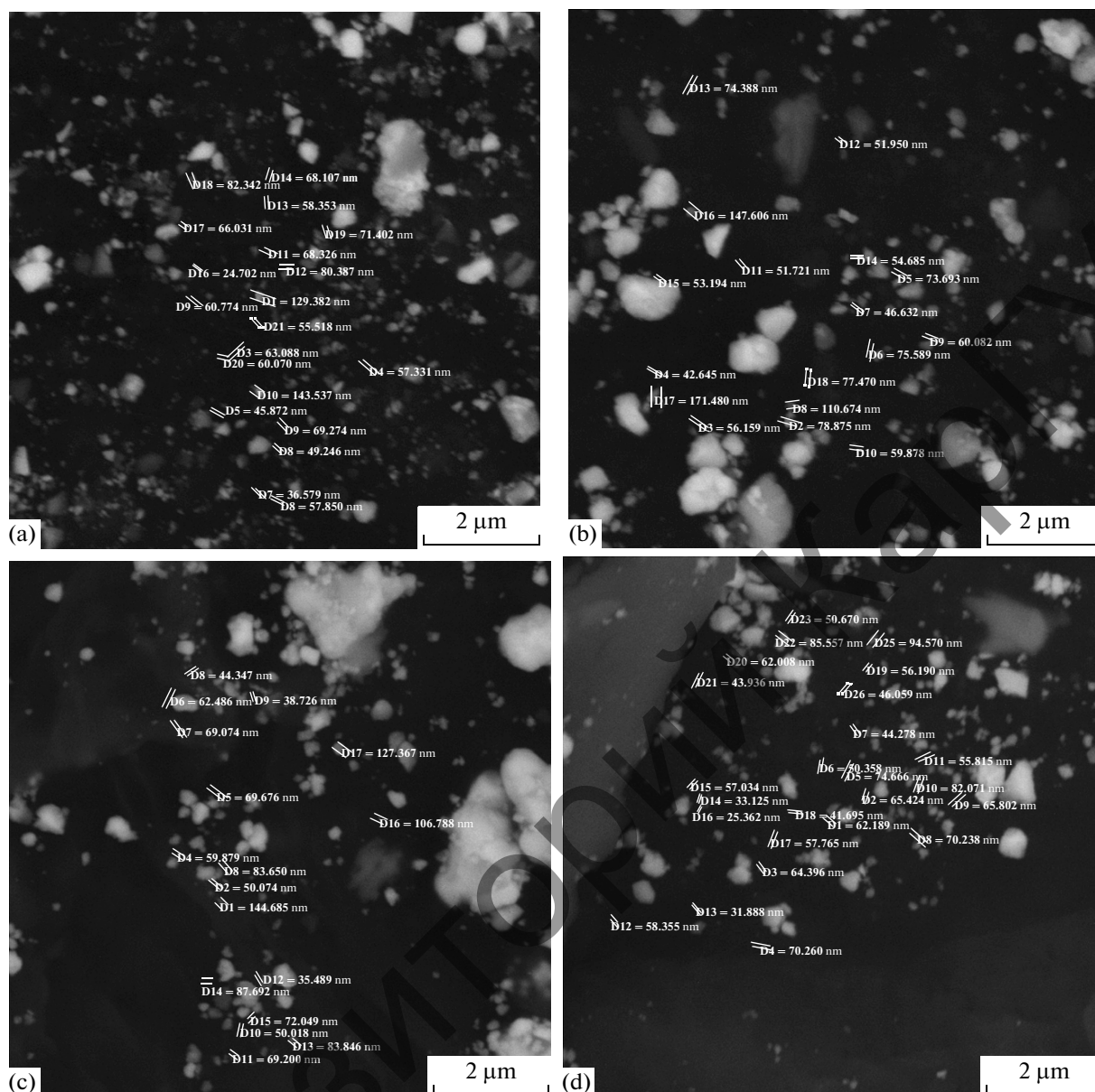
In this context, the purposes of this work were the synthesis and X-ray diffraction study of nanostructured manganite ferrites $\text{NdM}_{1.5}^{\text{II}}\text{MnFeO}_6$, where $\text{M}^{\text{II}} = \text{Mg, Ca, Sr, or Ba}$.

EXPERIMENTAL

The solid-phase synthesis of the compounds was performed by a ceramic technology from stoichiometric amounts of special-purity grade neodymium(III) oxide and analytically pure iron(III) oxide, manganese(III) oxide, and alkaline-earth metal carbonates. The initial substances dehydrated preliminarily at 400°C were thorough mixed in a stoichiometric ratio in an agate mortar, ground, and transferred to aluminum crucibles, which were heated at 800–1200°C in a SNOL furnace for 20 h. After 6–7 h of annealing, the mixtures were cooled, mixed again, and ground. To obtain equilibrium and stable states, annealing at 400°C for 20 h was performed again.

To produce nanostructured particles of the compounds being studied, the compounds were ground in a Retsch MM301 ball mill (Germany). This mill is designed for grinding and homogenization of soft, fibrous, and brittle materials in the dry and wet states. The mill motor speed is 180–1800 rpm (3–30 Hz), and the grinding duration was 40 min.

The sizes of the obtained particles were determined with a TESCAN electron microscope, which allows



Electron micrographs of nanoparticles of (a) $\text{NdMg}_{1.5}\text{MnFeO}_6$, (b) $\text{NdCa}_{1.5}\text{MnFeO}_6$, (c) $\text{NdSr}_{1.5}\text{MnFeO}_6$, and (d) $\text{NdBa}_{1.5}\text{MnFeO}_6$.

one to evaluate particle sizes down to 3 nm. The figure presents the electron micrographs of nanoparticles of the studied compounds.

The X-ray diffraction study of nanostructured particles of the compounds was made with a DRON-2.0 diffractometer ($\text{CuK}\alpha$ radiation, Ni filter, $U = 30\ \text{kV}$, $I = 10\ \text{mA}$, counter speed 2 rpm, scale 1000 pps, $\tau = 5\ \text{s}$, $2\theta = 10^\circ - 90^\circ$). The intensities of diffraction maxima were evaluated on a 100-point scale. The X-ray diffraction patterns of the compounds contained no lines of diffraction maxima of the initial phases.

RESULTS AND DISCUSSION

The electron microscopy data in the figure suggest the presence of nanostructured particles of $\text{NdMg}_{1.5}\text{MnFeO}_6$, $\text{NdCa}_{1.5}\text{MnFeO}_6$, $\text{NdSr}_{1.5}\text{MnFeO}_6$, and $\text{NdBa}_{1.5}\text{MnFeO}_6$ of sizes down to 24.702, 46.632, 35.489, and 25.362 nm, respectively.

The X-ray diffraction patterns of nanoparticles of the studied compounds were indexed by the homology method (the homologue is the structural type of perovskite) [2]. The results of the indexing are presented

Table 1. Results of the indexing of the X-ray diffraction patterns of nanostructured particles of $\text{NdM}_{1.5}\text{MnFeO}_6$ ($\text{M}^{\text{II}} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$)

I/I_0	$d, \text{\AA}$	$10^4/d_{\text{exp}}^2$	hkl	$10^4/d_{\text{clcd}}^2$	I/I_0	$d, \text{\AA}$	$10^4/d_{\text{exp}}^2$	hkl	$10^4/d_{\text{clcd}}^2$
NdMg_{1.5}MnFeO₆					14	1.3511	5478	800	5478
11	4.8586	423.6	210	416.7	6	1.2089	6483	840	6848
21	3.8818	663.6	220	666.6	NdSr_{1.5}MnFeO₆				
11	3.4762	828	310	833	8	3.8739	666.4	2200	670.8
14	2.9753	1130	006	1130	3	3.6592	746.8	300	754.6
27	2.7920	1283	116	1297	2	3.4720	830.0	310	838.4
100	2.7404	1332	400	1333	100	2.7378	1334	400	1342
10	2.6140	1463	206; 402	1464; 1459	17	2.2337	2004	420	2012
45	2.5365	1554	216	1547	4	2.0950	2278	333	2264
6	2.3358	1833	404	1836	29	1.9297	2686	440	2683
13	2.2641	1951	217	1955	7	1.7255	3359	620	3354
15	2.2272	2016	008	2009	4	1.6480	3682	622	3689
11	2.1484	2167	510	2167	28	1.5776	4018	444	4025
27	1.9449	2644	440	2667	4	1.5560	4130	700	4110
6	1.7906	3119	0.0.10	3139	11	1.3651	5366	800	5366
8	1.7417	3297	309; 516	3293; 3297	11	1.2251	6708	840	6708
14	1.7123	3411	540	3417	NdBa_{1.5}MnFeO₆				
19	1.6208	3807	2.2.10	3806	15	4.0408	612.4	203	607.6
13	1.6007	3903	544	3919	24	3.8960	658.8	220	659.8
26	1.5772	4020	633	4032	10	3.4887	822.0	310	824.8
24	1.4869	4523	0.0.12	4520	12	3.3131	911.0	214	906.2
12	1.3694	5333	800	5333	27	3.1179	1029	303	1020
10	1.2833	6072	830	6083	12	3.0057	1107	006	1110
14	1.2226	6690	5.1.12	6687	71	2.8596	1223	304	1236
NdCa_{1.5}MnFeO₆					100	2.7544	1318	400	1320
8	3.4206	854.7	310	855.9	27	2.2500	1975	008	1975
100	2.7029	1369	400	1370	12	2.1596	2144	510	2144
8	2.3076	1878	332	1883	49	1.9473	2637	440	2639
16	2.2097	2048	422	2054	15	1.7417	3297	620	3299
25	1.9125	2734	440	2739	12	1.7015	3454	604	3463
8	1.8534	2911	530	2910	20	1.6021	3896	1.1.11	3899
26	1.5560	4130	444	4109	22	1.3770	5273	800	5278
13	1.5459	4184	700	4194	15	1.2310	6598	840	6598

in Table 1; the synthesized phases crystallize in the cubic and tetragonal systems.

The data in Tables 1 and 2 show satisfactory agreement between the experimental and calculated values

of $10^4/d^2$ and also the X-ray diffraction and pycnometric densities, which is indicative of the accuracy of the results of the indexing. Note that the reliability of the results of the indexing is also confirmed by good agree-

Table 2. X-ray diffraction characteristics of nanostructured manganite ferrites $\text{NdM}_{1.5}^{\text{II}}\text{MnFeO}_6$ ($\text{M}^{\text{II}} = \text{Mg, Ca, Sr, Ba}$)

Compounds and their symmetry systems	Lattice parameters, Å		Z	$V^0, \text{Å}^3$	$V_{\text{el.cell}}^0, \text{Å}^3$	Density, g/cm ³	
	a	c				$\rho_{\text{X-ray}}$	ρ_{pycn}
$\text{NdMg}_{1.5}\text{MnFeO}_6$ (tetragonal)	10.955	17.848	16	2141.975	133.873	4.80	4.76 ± 0.05
$\text{NdCa}_{1.5}\text{MnFeO}_6$ (cubic)	10.809	—	8	1262.864	157.858	4.32	4.27 ± 0.03
$\text{NdSr}_{1.5}\text{MnFeO}_6$ (cubic)	10.911	—	8	1298.953	162.369	4.93	4.88 ± 0.05
$\text{NdBa}_{1.5}\text{MnFeO}_6$ (tetragonal)	11.011	18.001	16	2182.479	136.405	6.78	6.75 ± 0.07

ment between the experimental and calculated values of $V_{\text{el.cell}}^0$ of the studied compounds. In the series $\text{Mg} \rightarrow \text{Ca} \rightarrow \text{Sr} \rightarrow \text{Ba}$, $V_{\text{el.cell}}^0$ increases from Mg to Sr and decreases from Sr to Ba, which indicates a secondary periodicity, probably, because of the lanthanide contraction.

Thus, for the first time, nanostructured particles of $\text{NdM}_{1.5}^{\text{II}}\text{MnFeO}_6$ ($\text{M}^{\text{II}} = \text{Mg, Ca, Sr, Ba}$) were synthesized by a ceramic technology, their sizes were determined, and their crystal systems and lattice parameters were found by X-ray diffraction analysis.

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