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Synthesis and Magnetic Properties of a New Layered Oxide La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}

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Abstract—A new oxide phase La_{1.5}Sr_{1.5}Mi_{0.75}O_{6.67 ± 0.05}, a member of the A_{n + 1}B_nO_{3n + 1} (n = 2) Raddlesden–Popper homologue series, was synthesized, and its structure and magnetic properties characterized. Magnetic anomalies associated with the competition between antiferromagnetic and ferromagnetic orders are observed in the range of the temperatures studied (2–400 K). The ESR spectra of the compound feature the constriction of a magnetic signal and a shift toward $g(Mn^{4+})$.

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Complex oxide homologues of the $A_{n+1}B_nO_{7-\delta}$ (n = 1, 2, 3) Raddlesden–Popper series have a perovskite-like structure and posses the entire set of properties intrinsic to the perovskite family. All members of the series are built of perovskite blocks of corner-sharing BO_6 octahedra, these blocks being infinite in plane xy and having n layers in direction z. Adjacent blocks are separated by rock-salt blocks, so that the formula unit may rightfully read $[(ABO_3)_n(AO)]$. Unlike classical perovskite compounds, the layered phases in guestion have anisotropic physicochemical properties. Of special interest are n = 2 oxides, which have diverse properties, such as superconductivity, giant magnetic resistance, and anionic conductivity. For example, magnetic resistance found in Sr_{1.8}La_{1.2}Mn₂O₇ exceeds 200% in low magnetic fields of 0.3 T. This value is far higher than in most manganese-based perovskites in the same magnetic fields [1]. The results obtained on manganites allow them to be recommended for use as magnetic storage elements, pickups, oxygen membranes, electrode materials, and catalysts.

Wide possibilities for substitutions in both position A and position B show a great potential for diverse applications. Raddlesden-Popper manganites substituted in position B are also of interest as model objects for studying the interactions of two magnetic sublattices. $A_{n+1}(Mn,B')_n O_{3n+1}$ (n = 2, 3) oxides where position A is occupied by either a rarer-earth element, or an alkaline-earth element, or their combination and position B' is occupied by another metal cation, have been studied extensively. A random partial substitution of a diamagnetic cation for manganese in octahedral positions of a perovskite layer is known to lead to the disappearance of magnetic order at low temperatures. In particular, $Sr_3ScMnO_{6.5}$ within the range 2–300 K has no magnetic anomalies and obeys the Curie-Weiss law until 150 K [2]. For Sr₃MnTiO₇, random cation distribution to positions B was also established; the oxidation state (+4) was determined for manganese, however, without specifying magnetic susceptibility as a function of temperature [3].

In turn, when magnetic and nonmagnetic cations are ordered by the NaCl type in a perovskite unit layer (La₂Sr₂LiRuO₈) but magnetic moments are randomly distributed between layers, there is Heisenberg antiferromagnetism between layers [4]. In La₃LiMnO₇, Mn cations inside each magnetic structural domain are antiferromagnetically ordered when T < 14 K because of the ordered lithium and manganese cation distribution over positions B. Unlike in La₂Sr₂LiRuO₈, however, there is no long-range magnetic order because of the random distribution of magnetic moments along axis c [5].

The more complex behavior in a magnetic field is characteristic of compounds having two magnetic cations in positions B. For example, undoped manganites may be antiferromagnets (as $Sr_2Mn_2O_7$) [6] or demonstrate ferromagnetic properties at low temperatures $(La_{2-2x}Sr_{1+2x}Mn_2O_7, where x = 0.3, 0.4)$ [7]. The magnetic properties of doped manganites are considerably affected by the doping level and the nature of a second magnetic cation. There are data on the behavior in a magnetic field for the following manganites: $Sr_3Mn_2 - {}_xFe_xO_7 - {}_{\delta}$ [8], $LaSr_2MnFeO_7$ [9], $La_{1,2}Sr_{1,8}Mn_2 - {}_xM_xO_7 - {}_{\delta}$ (M = Co, Fe, Cr) [10, 11], $La_{1,4}Sr_{1,6}Mn_{1-x}Cu_xO_{6+\delta}$ [12], Sr_3MnRuO_7 [13], and $LaSr_2MnCoO_7$ [14]. For low substitution levels of cobalt and iron for manganese, a ferromagnetic order is maintained; when the cobalt and iron percentages are higher than 20 at %, there occurs a transition to spin-glass and cluster-glass states [10]. In chromiumand ruthenium-containing oxides, ferromagnetic order appears even for high substitution levels (40 at %). The antiferromagnetic order of B-substituted strontium

manganites also tends to frustration induced by a random cation distribution over positions B.

Raddlesden–Popper complex oxides (n = 2) containing Mn and Ni in positions B have not been described. The literature only concerns the structure and magnetic properties of LnSrMn_{0.5}Ni_{0.5}O₄ (n = 1)and double perovskite La₂NiMnO_{6 - δ} [15–17]. The lack of data is possibly because Raddlesden–Popper phases with n = 2 are far from being always formed in the synthesis of A_{n + 1}(B,B')_nO_{3n + 1} (n = 2, 3) heterodoped oxides. In some cases, a sample forms a phase with n = 1 (the sample is not a single phase) or crystallizes in a quasi-one-dimensional structure [18, 19]. The crystallization direction depends on the mean oxidation number of A and B cations, as well as on the cation radius in the relevant coordination [20].

In this work, we report the synthesis, structural and magnetic characteristics of $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67\pm0.05}$, a new representative of the Raddlesden–Popper homologue series.

EXPERIMENTAL

Strontium and lanthanum nitrates (chemically pure samples), after being analyzed for the metal, were mixed in stoichiometric proportions and then dissolved in distilled water under gentle heating (~70-90°C). In parallel, calculated weighed portions of Mn_2O_3 and NiO were dissolved in dilute nitric acid under boiling. After cooling, the solutions were combined, and citric acid was added to the reaction mixture in a small excess relative to the equivalent amount required for converting nitrates to citrates. Following this, the solutions were concentrated to a jelly at 100-150°C. The resulting substance was stirred and exposed at 400-500°C until a dry residue was formed and the residue ignited in the self-propagating hightemperature mode. The residue was transferred to a crucible, heated to 700°C, exposed for 3-4 h at this temperature to remove organic components, then calcined at 900-950°C, after which compacted under 3000 kg/cm^2 and stepwise annealed with temperature elevated in 100-K steps. The final annealing was carried out at 1450C; the synthesis duration was 25 h.

X-ray diffraction was measured on DRON-UM-1 using CuK_{α} radiation. FULLPROF-2006 software was used in the full-profile Rietveld analysis of X-ray diffraction patterns.

Magnetic measurements were carried out on an MPMS-XL-5 Quantum Design SQUID magnetometer at 2–300 K in magnetic fields of 0.5 and 5.0 kOe after samples were cooled in a magnetic field (FC mode) or without field (ZFC mode).

ESR spectra were recorded on a CMS 8400 spectrometer in the X-band range at 118-473 K. The temperature maintenance accuracy was ± 3 K.

RESULTS AND DISCUSSION

Previous research [14, 20, 21] demonstrated that the quotient of the charges of BB' cations (B^{4+}/B^{3+}) or B^{4+}/B^{4+}) is significant for directing the crystallization of an A₃BB'O_{7 - δ} into Raddlesden–Popper (*n* = 2) structure (space group *I*4/*mmm*). When the mean oxidation number of BB' cations is lower than 3.5, the oxidation number of the A cation should be increased via substituting rare-earth for alkaline-earth cations in order for proper oxides to be prepared. Inasmuch as manganites are, as a rule, synthesized at rather high temperatures (1300–1400°C), the preferred oxidation state of B cations at this temperature should be taken into account in developing synthesis processes. The Mn⁴⁺/Ni²⁺ quotient characteristic of solid-phase synthesis processes does not favor the stabilization of tetragonal oxide structures; therefore, the mean cation oxidation number in position A should be increased by substituting lanthanum for strontium or temperature be lowered by using precursor technology. Compositions were calculated using the procedure proposed by Sarjeant et al. [22] who regarded a phase with an equivalent substitution in position B as a mean between the end-member compositions of unsubstituted oxides.

Samples of the $La_{15}Sr_{15}MnNiO_{7-\delta}$ and $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{7-\delta}$ as-batch compositions were synthesized using both routine ceramic technology and the aforementioned citrate procedure. The X-ray diffraction pattern of $La_{1.5}Sr_{1.5}MnNiO_{7-\delta}$ contains reflections from the target Raddlesden–Popper phase (n = 2), an impurity K₂NiF₄-type phase (Raddlesden-Popper structure, n = 1), and likely, a perovskite solid solution. Long-term exposure at 1450°C does not change the phase composition of the reaction mixture. Apparently, the solid-phase process stops with the formation of the K_2NiF_4 phase admixed with the targeted structure. The precursor synthesis, which involves the homogenization of the reaction mixture and the formation of microparticles as a result of the self-propagating high-temperature process, displaces equilibrium toward the major phase, which appears under the given conditions starting at about 1400°C. A singlephase sample of composition $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{7-\delta}$ was prepared by the precursor synthesis where final annealing was carried out at 1450°C for 25 h.

Oxygen was determined by the reduction of the sample in flowing hydrogen at 950°C for 5 h. Theoretically, the ultimate products of such a process are lanthanum oxide and strontium oxide, metallic nickel, and MnO. However, Millburn and Rosseinsky [15] reported that, during the reduction of an oxide having a similar elemental composition, LaSrMn_{0.5}Ni_{0.5}O_{4+δ}, under similar conditions (950°C, 3 h), the reaction does not go to an end. As an impurity, the ultimate products may contain manganese sesquioxide and an undecomposed K₂NiF₄-type oxide. Noteworthy, substituted manganites where positions B contain Co or



Fig. 1. Simulated, measured, and difference X-ray diffraction patterns for $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67 \pm 0.05}$.

Cu are reduced to the ultimate products in 30–45 min. In view of this, we increased the exposure time in flowing hydrogen to 5 h. Powder X-ray diffraction clearly shows SrO, La₂O₃, metallic nickel, and MnO in the reduction products. Apart from these products, there are low-intensity (~6–7%) reflections from a poorly crystallized phase, which we failed to identify. By the above data, we determined that the sample had oxygen nonstoichiometry ($\delta = 0.33$); in view of the occurrence of a foreign phase in the products, however, error in the oxygen index may be ±0.05. Because the sample was synthesized in a severe temperature schedule, the existence of nickel with an oxidation number exceeding +2 is hardly expectable; thus, the mean oxidation number of manganese in the compound is +3.47.

Figure 1 shows the X-ray diffraction pattern of $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$ after the Rietveld full-profile analysis using FULLPROF-2006 software.

Most of the $A_{n+1}B_nO_{3n+1}$ Raddlesden–Popper phases crystallize in tetragonal system (space group *I4/mmm*). When n = 2, La and Sr ions are in two positions (La1, Sr1) and (La2, Sr2) and oxygen resides in three positions (O1, O2, O3). For Ni and Mn cations, either random distribution over octahedral positions or NaCl-type ordering is possible. In cases where the order exists over the entire crystal lattice, the symmetry is lowered and space group changes; in cases of random distribution over B positions, space group *I4/mmm* is maintained. Analysis of diffraction data for La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67} showed that the least final values ($R_B = 11.6$, $R_f = 10.6$, $R_{wp} = 12.9$) are observed when there are equiprobable distributions of Mn and Ni cations over positions B and of oxygen vacancies over positions O3 and O1, with positions O2 being completely occupied.

The unit cell parameters of $La_{1.5}Sr_{1.5}Mn_{1.25}$ Ni_{0.75}O_{6.67} are as follows: a = 0.3847(2) nm, c = 2.0137(1) nm. Atomic coordinates and interatomic distances are listed in Tables 1 and 2.

Magnetic Properties

Figure 2 shows magnetic susceptibility curves for $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$ measured 0.5- and 5-kOe magnetic field. The curves do not allow a unique interpretation of the magnetic interactions in the sample, but we should mention that a magnetic order exists starting at rather high temperatures. The Curie–Weiss law does not hold even within 300–400 K; at 140 K in the 0.5-kOe field, the curve features a peak. The further trend of the curves provides evidence in favor of

Table 1. Atomic coordinates in $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$

Coordinate	Position	x	У	z
(La,Sr)2	2b	0	0	0.5
(La,Sr)2	2b	0.3164(2)	0	0
(Ni,Mn)	4e	0	0	0.0983(5)
01	8g	0	0	0.0935(11)
O2	4e	0	0	0.1982(14)
O3	2a	0	0	0

Bond	<i>d</i> , nm		
(La,Sr)1–Ni(Mn)	0.3364(5)		
(La,Sr)1–O1	0.2692(14)		
(La,Sr)1–O3	0.2720(1)		
(La,Sr)2–Ni(Mn)	0.3217(5)		
(La,Sr)2–O1	0.2644(4)		
(La,Sr)2–O2	0.2735(3)		
Ni(Mn)–O1	0.1926(1)		
Ni(Mn)–O2	0.2000(13)		
Ni(Mn)–O3	0.1979(8)		

Table 2. Interatomic distances in $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$ (space group *I4/mmm*)

the antiferromagnetic character of magnetic order, but the positive value of the Weiss constant (+185.16 K)signifies the occurrence of magnetic regions in the paramagnetic phase.

The ZFC and FC curves diverge at rather high temperatures (of about 100 K), and the ZFC curve at 20 K features a second maximum. On the whole, there is some similarity in the behavior of the nickel-substituted complex oxide and cobalt-substituted one [14]; however, their high-temperature transition points are different. The nonexistence of a rather extended linear segment in the paramagnetic region on magnetic susceptibility versus temperature curves until 400 K does not allow the determination of exact values of magnetic constants and, thus, the calculation of magnetic moments and oxidation numbers of B cations. Calculations on the basis of experimental magnetic susceptibility data within 350–400°C result in $\mu = 6.01 \ \mu B$. The theoretical magnetic moment calculated with account for oxygen nonstoichiometry for the $La_{1.5}Sr_{1.5}Mn^{IV}{}_{0.59}Mn^{III}{}_{0.61}Ni^{II}{}_{0.75}O_{6.67}$ formula unit is 5.54 μ B. However, the difference between the theoretical and experimentally determined values of the magnetic moments may arise not only from the small extent of the linear portion of the magnetic susceptibility versus temperature curve but also from an additional contribution of the orbital magnetic moment of the Ni²⁺ cation to the overall μ value. Hong et al. [16] report average theoretical and experimentally determined values of magnetic moments in LnSrMn_{0.5}Ni_{0.5}O₄. For any oxidation and spin ratios between manganese and nickel, the theoretical magnetic moment calculated from spin states solely is lower than the experimentally determined value.

The ESR spectra of $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$ recorded above 293 K are broad symmetrical Lorenzian singlets with a constant *g*-factor of 2.03. Above we demonstrated that this compound, including its oxygen nonstoichiometry, contains three magnetic ions:



Fig. 2. Magnetic susceptibility vs. temperature for La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67 \pm 0.05 in magnetic fields of 0.5 and 5 kOe during cooling in (*a*) FC and (*b*) ZFC modes. In the inset, $1/\chi = f(T)$ in a range of 70–400 K.}



Fig. 3. ESR line width vs. temperature. In the inset, g-factor vs. temperature.

Ni²⁺ (d^8 configuration), Mn⁴⁺ (d^3 configuration), and Mn³⁺ (d^4 configuration).

Ions having d^4 electronic configuration are rapidly relaxing ions; ESR spectra from them are observable only at temperatures near the liquid helium temperature. At higher temperatures, the spectral line broadens until becoming unobservable [23]. In the temperature range we studied, the relaxation times of Mn^{3+} ions are so small that these ions do not influence the surrounding magnetic ions and behave to them as a diamagnet. The Ni²⁺ and Mn⁴⁺ ions in the octahedral surrounding give rise to ESR spectra with g-factors of ~2.10-2.14 and ~1.98-1.99, respectively [24]. However, the spectral line observed is not characteristic of none of these ions. Line shape analysis showed that this signal is fitted by a single Lorenzian, which completely rules out a superposition of two lines having rather strongly differing g-factors.

The ESR signal observed in this magneto-concentrated compound may arise from the occurrence of strong exchange interactions between ions in planes containing Mn and Ni ions, leading to a signal contraction effect [25]. Given that exchange interactions are weak (exchange rates are low) and different types of ions occur in the unit cell, the resonance spectrum consists of separate resolved lines that have different g-factors. As the exchange rate becomes higher, the lines broaden and are drawn to each other. When $J \ge (g_1 + g_2)\beta H$, lines are contracted to one line with an average g-factor. As the exchange is progressively enhanced, this line will experience exchange narrowing. In the case where $S_1 = S_2 = 1/2$, the average $g = 1/2(g_1 + g_2)$, which was frequently observed for Cu²⁺ ions in various nonequivalent positions. In our case, we are dealing with different types of magnetic ions having different spins ($S(Mn^{4+}) = 3/2 > S(Ni^{2+}) = 1$), different energy level systems, and different relaxation times (Mn^{4+} ions relax more slowly than Ni²⁺ ions). Therefore, Mn^{4+} ions will make a greater contribution to the overall line [26], and the *g*-factor for the contracted signal will shift toward $g(Mn^{4+})$.

Figure 3 shows the g-factor and line width ΔH as functions of temperature. As temperature decreases from 473 to 278 K, the ESR line remains symmetric and has a fixed g = 2.03. The line width decreases smoothly from 538 to 374 Gs. As temperature decreases further, the line starts to broaden with a noticeable increase in the curvature of the $\Delta H(T)$ curve; at 118 K, ΔH reaches 3057 Gs and the g-factor increases to 2.12. The line shape becomes asymmetrical; namely, the half-width of the low-field wing decreases on the background of the general line broadening, and its amplitude rises over the half-width and amplitude of the high-field wing. These trends of the line width and g-factor as functions of temperature in $La_{1.5}Sr_{1.5}Ni_{0.75}Mn_{1.25}O_{6.67}$ are similar to the $\Delta H(T)$ and g(T) trends observed in ferromagnetic semiconductors [27, 28]. In these compounds, line narrowing occurs in the paramagnetic range of temperatures with a constant g value. In approach to the transition tempera-



Fig. 4. Evolution of ESR spectra vs. temperature: (1) T = 293 K, A = 1.00; (2) T = 158 K, A = 0.96; (3) T = 143 K, A = 0.72; (4) T = 123 K, A = 0.87; and (5) T = 118 K, A = 0.95.

ture T_c , g-factor increases because of the appearance of a local order; the line broadens to acquire a characteristic anisotropy. After reaching T_c , the g-factor and width of this line are so great that it becomes virtually unobservable.

Thus, presumably, strong exchange interactions existing inside Mn–Ni planes are of the ferromagnetic type. This fact is fully supported by the above results of magnetic susceptibility versus temperature measurements, which imply that the Weiss constant Θ (185.16 K) exceeds zero. Probably, there are exchange clusters in the system where ion spins at T > 278 K start to align to one another. As temperature approaches $T \approx 140$ K (a $\chi(T)$ maximum is observed at the same temperature), some anisotropy of the spectrum appear and are further enhanced; we ascertained this anisotropy as the ratio of the half-width of a low-field wing (lfw) to the half-width of a high-field wing (hfw) and as the wing amplitude ratio.

Figure 4 shows ESR spectra in the vicinity of $T \approx$ 140 K. At T = 173 K, the signal anisotropy $A = \Delta H_{\text{lfw}}/\Delta H_{\text{hfw}} \leq 1$; when T = 143 K, the signal anisotropy decreases to 0.72 and the amplitude ratio increases accordingly. In response to a further temperature depression, one might expect an even greater decrease in A and a dramatic downfield shift of the line, i.e., a considerable increase in g-factors. However, this effect

was actually unobserved, although the line continued broadening. Within 140–118 K, A again increases to approach unity on the background of a relatively small increase in g-factors (to 2.12) and a guite determinable ΔH , while the amplitude difference remains virtually unchanged. This may arise from the existence of a second type of exchange interactions in the system, namely, antiferromagnetic interactions. According to Huber [29], in the case of antiferromagnetic exchange in the region far from the antiferromagnetic order, the line width decreases with temperature elevation following a hyperbolic law and tends to an asymptote at high temperatures. The g-factor increases within narrow bounds with temperature elevation because of increasing total magnetization of the sample. From our $\Delta H(T)$ curve, if we move toward lower temperatures, it follows that the line width that arises from antiferromagnetic interactions remains virtually unchanged within 473-278 K. Within 140-118 K, the line broadens both on account of antiferromagnetic interactions and because of the appearance of a shortrange ferromagnetic order inside exchange clusters. At 140 K, in-cluster local ordering occurs. However, the overall moments of the clusters remain disordered, intercluster exchange interactions being antiferromagnetic.

In summary, our magnetic susceptibility study of complex oxide $La_{1.5}Sr_{1.5}Mn_{1.25}Ni_{0.75}O_{6.67}$ and the ESR spectra show the two types of magnetic interactions, which may be explained by a local order of B (Mn/Ni)cations. It is known [30] that Ni^{II}-O-Ni^{II} (d^8 -d⁸) and Mn^{IV}-O-Mn^{IV} interactions are antiferromagnetic, whereas Ni^{II}-O-Mn^{IV} interactions are ferromagnetic. According to Anderson's data, the M1–O–M2 atom order in positions B is characteristic of cations in different oxidation states; the greater the difference between the oxidation numbers, the more probable such an ordered distribution [31]. In this case, the B sublattice in Raddlesden–Popper phases with n = 2 is of the NaCl type, but given a local order, the X-ray diffraction pattern is indexed in terms of space group 14/mmm. In view of this, not only powder X-ray diffraction but also neutron diffraction fails to detect this order. For example, the difference between the oxidation numbers of lithium and manganese cations in La₃LiMnO₇ is sufficiently great (+3), but only ⁶Li NMR spectroscopy managed to discover the local order of these cations in positions B. The formation of antiferromagnetic Mn^{IV}-O-Mn^{IV} clusters enhances the appearance of a low-temperature antiferromagnetic transition in this oxide, which is in general paramagnetic [5]. In our case, apparently, both antiferromagnetic and ferromagnetic clusters are formed, the former enhancing the progressive deviation from the Curie–Weiss law in approach to the Néel temperature, while the latter being capable of interacting with one another by the antiferromagnetic scenario. Apart from the competitive interactions of magnetic clusters, the presence of Mn^{3+} ions in the high-spin state enhances an additional frustration of magnetic moments beyond ferromagnetic and antiferromagnetic clusters and is responsible for the considerable divergence of the FC and ZFC curves in the low temperature region.

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