Structural and magnetic characteristics of manganites in La$_{1-c+x}$Sr$_{c-x}$Mn$_{1-x}$Ni$_x$O$_3$ system

A M Smirnov$^1$, S Kh Estemirova$^2$, V K Karpasyuk$^1$

$^1$Astrakhan State University, 414056, Astrakhan, Russia

$^2$Institute for Metallurgy UB RAS, 620016, Yekaterinburg, Russia

E-mail: vkarpasyuk@mail.ru

Abstract. Experimental data are shown for the influence of Ni and Sr concentration on phase composition, magnetic and electrical properties of La-Sr manganites with substitution of Mn by Ni. The system of chemical compositions La$_{1-c+x}$Sr$_{c-x}$Mn$_{1-x}$Ni$_x$O$_3$ is designed so that the sum of concentrations of divalent Sr and Ni remains constant ($c$). Under the condition that content of oxygen is stoichiometric, the values of $c$ are equal to concentrations of Mn$^{4+}$ (f.u.). These values are chosen near phase boundary “orthorhombic-rhombohedral structure” ($c=0.15$, 0.17, 0.19) on the classical phase diagram for La$_1$-Sr,MnO$_3$ system and at the region of rhombohedral metal phase ($0.20\leq c\leq 0.35$). It was found that substituting Ni$^{2+}$ ions shifted phase boundary to higher values of $c$. Of great interest is the phenomenon of phase conversion from rhombohedral to orthorhombic structure in the compositions with $c=0.19$ and 0.20 when $x$ varies from 0.100 up to 0.125. Fragments of $c$-$T$ and $x$-$T$ phase diagrams “ferromagnetic-paramagnetic” have been plotted.

1. Introduction

Phase formation processes and phase properties in complex multicomponent manganites essentially depend on the concentration of heterovalent ions, their localization and radii, and the occurrence of cation and anion vacancies [1-3]. Magnetic and electric properties of manganites are determined by the probability of the transfer of $e_g$ electrons between the positions of neighboring heterovalent ions Mn$^{3+}$ and Mn$^{4+}$, the carriers concentration, the size mismatch of substituting cations, the number of unpaired electrons in their shells [4-5].

Divalent cation substitution (such as Mg$^{2+}$, Ni$^{2+}$, …) for Mn in manganites results in increasing of Mn$^{3+}$ content and of Mn$^{4+}$/Mn$^{3+}$ ratio. In order to study the doping effect at fixed ratio, a series of “double-doped” manganites La$_{2/3+4x/3}$Sr$_{1/3-4x/3}$Mn$_{1-x}$Mg$_x$O$_3$ was synthesized in [6]. Reported results are much different from that of the “single doped” manganites.

In the present work experimental data are shown for the influence of Ni concentration ($0.025\leq x\leq 0.125$) on phase composition and magnetic properties of La-based manganites with substitution of Mn by Ni and, simultaneously, of La by Sr. In complex oxides, nickel (3d$^8$4s$^2$) most commonly has an oxidation degree of +2. The system of chemical compositions La$_{1-c+x}$Sr$_{c-x}$Mn$_{1-x}$Ni$_x$O$_3$ is designed so that the sum of concentrations of divalent Sr and Ni remains constant ($c$). Under the condition that content of oxygen is stoichiometric, the values of $c$ are equal to concentrations of Mn$^{4+}$ (f.u.). These values are chosen near phase boundary “orthorhombic-rhombohedral structure”
(c=0.15; 0.17; 0.19) on the phase diagram for La$_{1-c}$Sr$_c$MnO$_3$ system [7] and at the region of rhombohedral metal phase (0.20≤c≤0.35).

2. Experimental
The experiments were performed on polycrystalline samples synthesized by traditional ceramic processing. The starting components (dried La$_2$O$_3$, SrCO$_3$, MnO$_2$, NiO powders) were mixed in stoichiometric proportions and ground in a ball mill with addition of alcohol. Pellets compacted of the obtained charge mixture were then preliminarily burned at 1000$^o$C for 4 h. This operation was followed by grinding, introducing a binder (an aqueous solution of polyvinyl alcohol), pressing the samples, and burning out the binder. The final sintering step was performed at 1200$^o$C for 10 h, and the samples were cooled together with the furnace. Then, in order to provide stoichiometric oxygen content, the samples were annealed at 950$^o$C and partial pressure of oxygen P$_{O2}$=10$^{-1}$ Pa for 96 h. The choice of annealing conditions was based on the results of the works [8, 9].

Phase composition, and cell dimensions were determined by powder X-ray diffraction at room temperature (diffractometer Shimadzu XRD-7000, CuK$_\alpha$ radiation). The magnetization was determined by measuring the variation of magnetic flux that run through the measuring coil placed in the interpolar space of a constant magnet upon pulling a capsule with the powder sample out of it. The magnetic field strength in the interpolar space was 5600 Oe. Measurements of dc electrical characteristics and magnetoresistance were made using copper electrodes sputter-deposited onto opposite planes of pellets (thickness of about 4 mm). Magnetic field of 9200 Oe was parallel to the current direction. The temperature dependence of magnetic permeability ($\mu(T)$) was measured by the induction method at a frequency of 98.6 kHz. The Curie point ($T_c$) was determined as the temperature corresponding to the maximum of $\left|\frac{d\mu}{dT}\right|$.  

3. Results and discussion
Table 1 summarizes the structural parameters of initial (sintered) and annealed samples for the sets of composition. From the data obtained in [8, 9] it might be inferred that sintered manganites had an excess of oxygen content ($\gamma$>0). After annealing manganites became stoichiometric. Vacuum annealing results in decreasing of Mn$^{4+}$ content and of cation vacancies concentration, that determines the changes of structural, magnetic, and electrical parameters.

| Sample | Formula | c | x | State | Phase composition | Unit cell volume/ formula unit, Å$^3$ |
|--------|---------|---|---|-------|-------------------|--------------------------------------|
| Sintered/La$_{0.925}$Sr$_{0.075}$Mn$_{0.925}$Ni$_{0.075}$O$_{3+\gamma}$ | 0.15 | 0.075 | Orthorhombic | 59.16 |
| Annealed/La$_{0.925}$Sr$_{0.075}$Mn$_{0.925}$Ni$_{0.075}$O$_3$ | 0.15 | 0.075 | Orthorhombic | 59.03 |
| Sintered/La$_{0.905}$Sr$_{0.095}$Mn$_{0.925}$Ni$_{0.075}$O$_{3+\gamma}$ | 0.17 | 0.075 | Rhombohedral | - |
| + Orthorhombic | |
| Annealed/La$_{0.905}$Sr$_{0.095}$Mn$_{0.925}$Ni$_{0.075}$O$_3$ | 0.17 | 0.075 | Orthorhombic | 59.36 |
| Sintered/La$_{0.835}$Sr$_{0.165}$Mn$_{0.975}$Ni$_{0.025}$O$_{3+\gamma}$ | 0.19 | 0.025 | Rhombohedral | 58.92 |
| Annealed/La$_{0.835}$Sr$_{0.165}$Mn$_{0.975}$Ni$_{0.025}$O$_3$ | 0.19 | 0.025 | Rhombohedral | 58.79 |
| Sintered/La$_{0.860}$Sr$_{0.140}$Mn$_{0.950}$Ni$_{0.050}$O$_{3+\gamma}$ | 0.19 | 0.050 | Rhombohedral | 58.79 |
| Annealed/La$_{0.860}$Sr$_{0.140}$Mn$_{0.950}$Ni$_{0.050}$O$_3$ | 0.19 | 0.050 | Rhombohedral | 58.80 |
Of great interest is the phenomenon of phase conversion from rhombohedral to orthorhombic structure in the compositions with $c=0.19$ when $x$ varies from 0.100 up to 0.125, and in manganite $\text{La}_{0.900}\text{Sr}_{0.100}\text{MnO}_3$ ($c=0.20$) after annealing. These facts provide evidence for the shift of phase boundary “orthorhombic-rhombohedral structure” to higher values of $c$ as compared with that established for $\text{La}_{1-c}\text{Sr}_c\text{MnO}_3$ system ($c=0.175$) [7].

The magnetization of samples with $x=0.1$ slowly increases as a function of $c$ (Figure 1 (a)), however compositions with $c=0.35$ exhibit decrease of magnetization when concentration of Ni increases (Figure 1 (b)).

![Figure 1](image.png)

**Figure 1.** Dependences of magnetization on composition: a) $x = 0.1$; b) $c= 0.35$
Upon substitution, the Curie temperature of manganites increases as a function of $c$ at fixed Ni concentration (Figure 2), and show a sharp decrease as a function of $x$ (Figure 3).

The absolute value of magnetoresistance ($MR=(R(H)-R(0))/R(0)$) reaches 60% at 126 K in manganite $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_3$ (Figure 4), and oscillates in manganites with $c=0.35$ when Ni concentration rises (Figure 5). In latter case maximum value of 13 % takes place at 129 K in the sample $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.95}\text{Ni}_{0.05}\text{O}_3$.

The regularities of the influence of Sr$^{2+}$ and Ni$^{2+}$ concentrations on phase composition, saturation magnetization at different temperatures, Curie point, and magnetoresistance have been established for a series of “double-doped” manganites. It was found that substitution of Mn by Ni shifted the boundary of concentration phase transition “orthorhombic→rhombohedral structure” in the system $\text{La}_{1-c-x}\text{Sr}_{c-x}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ to higher values of $c$. Excess of oxygen content ($\gamma>0$) over stoichiometric one promotes the existence of rhombohedral phase at high values of $x$. Magnetization and $T_c$ rise with $c$.

4. Conclusion

The regularities of the influence of Sr$^{2+}$ and Ni$^{2+}$ concentrations on phase composition, saturation magnetization at different temperatures, Curie point, and magnetoresistance have been established for a series of “double-doped” manganites. It was found that substitution of Mn by Ni shifted the boundary of concentration phase transition “orthorhombic→rhombohedral structure” in the system $\text{La}_{1-c-x}\text{Sr}_{c-x}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ to higher values of $c$. Excess of oxygen content ($\gamma>0$) over stoichiometric one promotes the existence of rhombohedral phase at high values of $x$. Magnetization and $T_c$ rise with $c$. 
increasing at fixed value of $x$, and decrease as a functions of $x$ at fixed $c$. Absolute value of negative magnetoresistance in the system reaches 60% at low temperatures for magnetic field strength ~9 kOe.

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