Magnetic and electrical properties of La$_{1-c}$Sr$_c$Mn$_{1-x}$Ga$_x$O$_3$ manganites

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Abstract. The bulk manganites La$_{1-c}$Sr$_c$Mn$_{1-x}$Ga$_x$O$_3$ ($c$=0.15; 0.17; 0.19; 0.025≤$x$≤0.125) were prepared by solid state reactions. The regularities of the influence of Ga$^{3+}$ and Sr$^{2+}$ concentrations on saturation magnetization at different temperatures, Curie point ($T_c$), semiconducting-metallic transition and magnetoresistance have been established. It was found that magnetization at 80 K and $T_c$ rise with $c$ increasing at each fixed value of $x$, and decrease as a functions of $x$ at fixed $c$. Absolute value of negative magnetoresistance for some chemical compositions exceeds 80% at low temperatures for magnetic field strength ~9 kOe. Ga substitution for Mn shifts phase boundary “rhombohedral-orthorhombic structure” to lower value of $c$, moreover, excess of oxygen content over stoichiometric one promotes the existence of rhombohedral phase at $c$=0.15. Diamagnetic dilution of octahedral sublattice by Ga$^{3+}$ ions and cation vacancies induce semiconducting behaviour in rhombohedral phase, even at $c$=0.19. Metallic type of temperature dependence of resistivity observes in appropriate low temperature range in sintered manganites with $c$=0.17; 0.19 only at small $x$.

1. Introduction
Numerous papers have been devoted to the study of Mn site doping effects in manganites exhibiting colossal magnetoresistance (CMR) properties. CMR is generally agreed to be a result of the competition between certain phases with different electronic, magnetic and structural orders, and is mainly connected with double exchange and Jahn-Teller effect of Mn$^{3+}$ ions [1-4]. Phase formation and properties of manganites essentially depend on the concentration of heterovalent ions, their localization and radii, and the occurrence of vacancies in various sublattices [1,5-8]. Modifying the bonds between Mn$^{3+}$ and Mn$^{4+}$ ions, the doping by small amount of substituting cations and defects can lead to drastic changes in the main properties of manganites [1,7-10]. It is known that introduction of each Ga$^{3+}$ ion in LaMn$_{1-x}$Ga$_x$O$_3$ increases the magnetic moment per Mn by ~ 16 $\mu_B$ [10]. This is a significant effect to occur by a diamagnetic ion, and therefore the La$_{1-c}$Sr$_c$Mn$_{1-x}$Ga$_x$O$_3$ system generates considerable interest, but no systematic study of structural, magnetic and electrical properties of this system has been done. Ga substitution for Mn results in diamagnetic dilution, decreasing of Mn$^{3+}$ content, and, hence, decreasing of Jahn-Teller distortions.

In the present work experimental data are shown for the influence of Ga concentration (0.025≤$x$≤0.125) on phase composition, magnetic and electrical properties of La-Sr manganites. Under
the condition that content of oxygen is stoichiometric, the values of $c$ in La$_{1-c}$Sr$_c$Mn$_{1-x}$Ga$_x$O$_3$ are equal to concentrations of Mn$^{4+}$ ions (f.u.). These values are chosen near phase boundary “ferromagnetic insulator-ferromagnetic metal” ($c=0.15; 0.17; 0.19$) on the phase diagram for La$_{1-c}$Sr$_c$:MnO$_3$ system [11].

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$_2$, Ga$_2$O$_3$ 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 1273 K 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 1473 K 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 1223 K and partial pressure of oxygen $P_{O_2}=10^{-1} Pa$ for 96 h. The choice of annealing conditions was based on the results of the works [6, 12] which demonstrate the achievement of stoichiometry at above-mentioned temperature and $P_{O_2}$ almost independently of composition in the systems La$_{1-c}$Sr$_c$MnO$_3$ and La$_{1-c}$Ca$_c$MnO$_3$.

Phase composition was determined by powder X-ray diffraction at room temperature (diffractometer Shimadzu XRD-7000, Cu$K_\alpha$ radiation). The magnetization (per mass unit) was measured in magnetic field of 5.6 kOe. Measurements of dc electrical characteristics and magneto- resistance (MR=$(R(H)-R(0))/R(0)$) were made using copper electrodes sputter-deposited onto opposite planes of pellets (thickness of about 4 mm). Magnetic field of 9240 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 was determined as the temperature corresponding to the maximum of $|d\mu/dT|$.  

3. Results and discussion

It was found that all sintered samples in initial state were single phase and crystallized in the rhombohedral structure (Table 1). Dependence of unit cell volume on Ga concentration was nonmonotonic, because, on the one hand, ionic radius of Ga$^{3+}$ is smaller than Mn$^{3+}$, and the dilution of Mn sublattice by Ga reduces the oxygen content (like to the effect of Al substitution for Mn in La-Ca manganite [13]), that results in reduction of cation vacancies concentration; but on the other hand, the number of Mn$^{3+}$ ions increases simultaneously with the decrease of oxygen content. Rhombohedral structure of sintered manganites with $c=0.15$ may be due to the surplus of Mn$^{4+}$ associated with excess of oxygen content ($\gamma>0$) over stoichiometric one. According to [6], the oxygen-excess nonstoichiometry can be observed in La$_{1-c}$Sr$_c$MnO$_{3+\gamma}$ manganite for $c<0.4$, and oxygen excess is attributed to the formation of metal vacancies.

After annealing in vacuum, the structure of manganites with small amount of Sr and Ga ($c=0.15$, $x<0.125$) became orthorhombic (Table 1). Samples with $c=0.15$, $x=0.125$ contained the mixture of rhombohedral and orthorhombic phases.

All manganites with $c \geq 0.17$ in initial state and after annealing were rhombohedral.

It seems that substituting Ga ions shifted phase boundary “rhombohedral-orthorhombic structure” to lower value of $c$.

It was found that magnetization at 80 K and $T_c$ rise with $c$ increasing at each fixed value of $x$, and decrease as a functions of $x$ at fixed $c$ (Tables 1, 2). These regularities are related to the rising of Mn$^{4+}$ concentration when $c$ increases, and to dilution and destabilization of Mn sublattice by diamagnetic ions.

After annealing, magnetization increased in most cases (Table 1) as a result of reduction of cation vacancies concentration.
Table 1. Phase composition and magnetization (at 80 K) of synthesized manganites.

| Sample | Formula | c | x | State          | Phase composition | σ, emu/g |
|--------|---------|---|---|----------------|-------------------|---------|
|        |         | 0.15 | 0.025 | Initial | Rhombohedral | 68.4    |
|        |         | 0.15 | 0.050 | Initial | Rhombohedral | 61.9    |
|        |         | 0.15 | 0.075 | Initial | Rhombohedral | 56.6    |
|        |         | 0.15 | 0.100 | Initial | Rhombohedral | 53.2    |
|        |         | 0.15 | 0.125 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.150 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.175 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.200 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.225 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.250 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.275 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.300 | Initial | Rhombohedral | 48.9    |
|        |         | 0.15 | 0.325 | Initial | Rhombohedral | 48.9    |

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Table 2. Curie point, maximum value of magnetoresistance and corresponding temperature $T_{\text{max}}$ of sintered manganites

| Composition | $T_c$, K | $\left| \text{MR} \right|_{\text{max}}$, % | $T_{\text{max}}$, K |
|-------------|--------|----------------|--------------|
| 0.15        | 0.025  | 202            | 58           | 118          |
| 0.15        | 0.050  | 178            | 65           | 126          |
| 0.15        | 0.075  | 167            | 60           | 142          |
| 0.15        | 0.100  | 160            | 59           | 100          |
| 0.15        | 0.125  | 158            | 68           | 132          |
| 0.17        | 0.025  | 225            | 21           | 119          |
| 0.17        | 0.050  | 203            | 34           | 115          |
| 0.17        | 0.075  | 184            | 67           | 130          |
| 0.17        | 0.100  | 172            | 33           | 112          |
| 0.17        | 0.125  | 167            | 19           | 150          |
| 0.19        | 0.025  | 242            | 16           | 100          |
| 0.19        | 0.050  | 225            | 16           | 110          |
| 0.19        | 0.075  | 210            | 88           | 132          |
| 0.19        | 0.100  | 192            | 65           | 80           |

All samples of manganites with $c=0.15$ exhibit semiconducting properties in the investigated temperature range (Fig. 1). Metallic type of temperature dependence of resistivity we observed in appropriate low temperature regions in sintered manganites with $c=0.17$; 0.19 only at $x=0.025$ (Figures 2, 3). After annealing, manganite $\text{La}_{0.830}\text{Sr}_{0.170}\text{Mn}_{0.975}\text{Ga}_{0.025}\text{O}_3$ revealed no metallic behaviour (Fig. 2), but $\text{La}_{0.810}\text{Sr}_{0.190}\text{Mn}_{0.975}\text{Ga}_{0.025}\text{O}_3$ remained metallic near 125 K (Fig. 3). Manganites with $x \geq 0.05$ have semiconducting type of temperature dependence of resistivity for all $c$.

Figure 1. Temperature dependence of resistivity of manganites with $c = 0.150$

Figure 2. Temperature dependence of resistivity of manganites with $c = 0.170$
Figure 3. Temperature dependence of resistivity of manganites with $c = 0.190$

Characteristic temperature dependence of magnetoresistance is shown on Figure 4 for a certain sample. Maximum absolute value of negative magnetoresistance reached 88% at 132 K in manganite with $c = 0.19, x = 0.075$ (Table 2).

After annealing, the resistivity of all samples increased, and maximum absolute value of magnetoresistance decreased.

Figure 4. Temperature dependence of magnetoresistance of manganite with $c = 0.15, x = 0.125$

4. Conclusion
New data concerning the structure and properties of manganites La$_{1-c}$Sr$_c$Mn$_{1-x}$Ga$_x$O$_{3+\gamma}$ ($c=0.15; 0.17; 0.19; 0.025\leq x\leq 0.125; \gamma \geq 0$) were obtained. Substituting Ga$^{3+}$ ions shift phase boundary “rhombohedral-orthorhombic structure” in La$_{1-c}$Sr$_c$MnO$_3$ system to lower value of $c$, moreover, excess of oxygen content ($\gamma > 0$) over stoichiometric one promotes the existence of rhombohedral phase at $c=0.15$.

Diamagnetic dilution of octahedral sublattice by Ga$^{3+}$ ions and cation vacancies have significant influence on magnetic ordering and double-exchange interaction, inducing semiconducting behaviour in rhombohedral phase, even at $c=0.19$, when the charge carrier concentration is high enough. Metallic type of temperature dependence of resistivity observes in appropriate narrow low temperature regions in sintered manganites with $c=0.17; 0.19$ only at small Ga$^{3+}$ content ($x=0.025$). After annealing, manganite La$_{0.830}$Sr$_{0.170}$Mn$_{0.975}$Ga$_{0.025}$O$_3$ revealed no metallic behaviour as a result of the reduction of Mn$^{4+}$ ions concentration.
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References
[1] Dagotto E, Hotta T, Moreo A 2001 Colossal magnetoresistant materials: the key role of phase separation Physics reports 344 1
[2] Liu G.-L., Zhou J.-S., Goodenough J B 2001 Interplay between charge, orbital and magnetic ordering in La$_{1-x}$Sr$_x$MnO$_3$ Phys.Rev. B. 64 144414 1
[3] Zhou J.-S., Yin H Q and Goodenough J B. 2001 Vibronic superexchange in single-crystal LaMn$_{1-x}$Ga$_x$O$_3$ Phys. Rev. B. 63 184423
[4] Blundell S. 2003 Magnetism in condensed Matter Oxford: Oxford University Press 238
[5] Malavasi L, Ritter C, Mozzati M C, Tealdi C, Islam M S, Azzoni C B, Flor G. 2007 Effects of cation vacancy distribution in doped LaMnO$_{3+d}$ perovskites Front for the arXiv. – Cond-mat 0504334 27 http://front.math.ucdavis.edu/0504.0334
[6] Mizusaki J, Mori N, Takai H et al. 2000 Oxygen nonstoichiometry and defect equilibrium in the perovskite-type oxides La$_{1-x}$Sr$_x$MnO$_{3+d}$ Solid State Ionics 129 163
[7] De Leon-Guevara A M, Berthet P, Berthon J et al. 1997 Influence of controlled oxygen vacancies on the magnetotransport and magnetostructural phenomena in La$_{0.85}$Sr$_{0.15}$MnO$_3$ single crystals Phys.Rev. B. 56 6031
[8] Wilson M L, Byers J M, Dorsey P C et al. 1997 Effects of defects on magnetoresistivity in La$_{0.7}$Sr$_{0.3}$MnO$_3$ J.Appl. Phys 81 4971
[9] Orlova T S, Laval J Y, Monod Ph. et al. 2009 Influence of Mn-site doping on charge and orbital ordering in La$_{1/3}$Ca$_{2/3}$Mn$_{1-x}$M$_x$O$_3$ manganites (M=Ni, Ga) Phys.Rev. B. 79 134407
[10] Farrell J, Gehring G A 2004 Interplay between magnetism and lattice distortions in LaMn$_{1-x}$Ga$_x$O$_3$ New Journal of Physics 6 168
[11] Urushibara A, Moritomo Y, Arima T, Asamitsu A, Kido G, Tokura Y 1995 Insulator-metal transition and giant magnetoresistance in La$_{1-x}$Sr$_x$MnO$_3$ Phys.Rev.B. 51 14103
[12] Estemirova S Kh 2009 Thesis. Yekaterinburg: Institute for Metallurgy UB RAS 122
[13] Blasco J, Garcia J, de Teresa J M et al. 1997 Structural, magnetic, and transport properties of the giant magnetoresistive perovskites La$_{2/3}$Ca$_{1/3}$Mn$_{1-x}$Al$_x$O$_{3-\delta}$ Phys.Rev.B. 55 8905