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Electrical and magnetic properties of $La_{1-x}Ag_yMnO_3$ recrystallized ceramics

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A method is presented to obtain silver-containing lanthanum manganites $La_{1-x}Ag_yMnO_{3+\delta}$ exhibiting GMR. Ceramic samples possessing high Curie temperature and showing a sharp maximum of metal-insulator transition near Curie temperature have been obtained. At the oxygen partial pressure of 1 bar, a sample of $La_{0.85}Ag_{0.15}MnO_{3+\delta}$ has been prepared showing the magnetoresistance of about 57 % in the magnetic field 1.1 T at 273 K. The oxygen partial pressure has been shown to influence the sintering mechanism of the ceramics. Magnetocaloric effect for the sample $La_{0.9}Ag_{0.1}MnO_{3+\delta}$ is ΔS = 2.9 J/(kg·K) at 291 K.

Представлен способ получения серебросодержащего манганита лантана, обладающего КМС. Получены керамические образцы, обладающие высокой температурой Кюри и проявляющие резкий максимум перехода металл-изолятор в области температуры Кюри. При парциальном давлении кислорода 1 атм получен состав $La_{0,85}Ag_{0,15}MnO_{3+\delta}$ с магнетоспротивлением ~57 % в поле 1.1 Тл при 273 К. Показано, что парциальное давление кислорода влияет на механизм спекания таких керамик. Магнетокалорический эффект для состава $La_{0,85}Ag_{0,15}MnO_{3+\delta}$ составляет ΔS = 2.9 Дж/(кг·К) при 291 К.

Rare-earth manganites of perovskite structure doped with monovalent cations of general formula $R_{1-x}A_xMnO_{3+\delta}$ (where R is a rare-earth element; A, the doping cation) are no doubt of interest as materials with the giant magnetoresistance (GMR). The main advantage of the rare-earth manganites doped with monovalent cations (Na^+, Ag^+) as compared to those doped with divalent cations is the high sensitivity of the electrical resistance to external magnetic field at room temperature [1–5].

Recently, it was shown that silver doped lanthanum manganites possess a high magnetoresistance near room temperature [6]. However, using such a high-mobility component as silver, it is necessary to control the chemical state and the content of silver in the sample. It was shown before that lanthanum vacancies in $La_{1-x}MnO_3$ can be filled with silver ions [7]. Also, it is known from literature that it is necessary to prevent possible silver loss during sintering of $La_{1-x}Ag_xMnO_3$ ceramics. That is why the compound was synthesized at about 800°C and using a charge enriched in silver [7], or at more elevated temperatures under excess oxygen pressure (>1 bar) [6]. These two methods produce samples of various microstructures. To improve the transport properties of the ceramic material, it is necessary to form coarse-grain ceramics with dense grain contacts. The microstructure features are reflected in the electrical resistance and mag-

netoresistance behavior of polycrystalline fine-grained manganites [8, 9]. Electrical resistance of such polycrystalline sample can be described as

$$\rho = \rho_0 + (L_1/L_0)\rho_1,$$

where ρ_0 is resistance of a crystallite of L_0 average size; ρ_1, grain boundary resistance of L_1 average width. The estimated ρ_0 value known from literature shows that ρ_0 is three decimal orders lower than ρ_1. For the ceramics samples with submicrometer grains and nano-width grain boundaries, it is just the latter that contribute mainly (~90 %) to the resistance. Accordingly, the electrical resistance maximum in such ceramics is appreciably lower than Curie temperature T_c, and the magnetoresistance does not exceed 13 % (H = 1 T). We demonstrate below, a very different behavior of the ceramic GMR manganites with few micrometer grain size and dense grain contacts.

In this work, we report a method to modify the ceramics of silver doped lanthanum manganite. We have found a drastic evolution of electrical and magnetic properties of the $La_{1-x}Ag_yMnO_{3+\delta}$. The magnetocaloric effect in modified ceramics was investigated as well.

All ceramic samples were prepared using chemical homogenization [11]. First, ash-free paper was soaked with aqueous solution of La, Ag and Mn nitrates, mixed in the proper ratio, and dried in air at 120°C. Then paper was burned, and the ash was annealed in air at 600°C for 30 min. The resulting powder was pressed in pellets. The silver containing oxide powder (La/Ag/Mn atomic ratio 0.7/0.4/1) was prepared by the same method. This powder was used as a "cover" to prevent the silver loss from the pellets. The silver-containing pellets were sintered at 800°C under a covering powder layer of the in alundum crucibles in air for 20 hours. The low sintering temperature provides the perovskite phase crystallization and prevents silver loss [7]. In this work, the following Ag-containing samples were obtained: $La_{0.9}Ag_{0.1}MnO_3$, $La_{0.8}Ag_{0.1}MnO_3$, $La_{0.8}Ag_{0.15}MnO_3$. These compositions were selected as the study objects because they possessed T_c near room temperature [7]. The magnetoresistance study near room temperature is of most interest from the standpoint of practical application.

To improve the transport properties of the ceramic material, a technique was proposed to modify the ceramic microstructure without the solid solution decomposition. The technique consists in the high temperature annealing at 1100°C, under $P(O_2)$ = 1–5 bar for 5–20 h in the presence of metal silver vapor.

Microstructure of the ceramics was studied by scanning electron microscopy (SEM) using JEOL JSM 840A (Japan) and LEO SUPRA 50VP (Carl Zeiss, Germany) microscopes. The cation stoichiometry and its homogeneity were controlled by EPMA (electron probe microanalysis). The SEM revealed the uniform ceramic microstructure with loosely connected submicrometer grains. Cation stoichiometry of the samples after recrystallization annealing was also uniform and corresponded to that of the precursor powder before the high temperature annealing, thus indicating that silver did not lost from the samples during annealing. The density of ceramic samples was determined by hydrostatic weighing. The shrinkage was calculated from geometric measurements.

Phase analysis of the prepared samples was accomplished with X-ray diffraction (Cu K_α radiation) using DRON 3M diffractometer. All samples prepared had the rhombohedral perovskite structure.

The magnetization was measured in the static magnetic field 230 Oe using a vibrating magnetometer. The resistance measurements were made by four-probe technique in the range 77–300 K using Keithley 2700 data acquisition system. The magnetocaloric effect was measured in the temperature range 77–300 K under quasiadiabatic conditions, in the field up to the 1.4 T (corrected for the demagnetization factor). The typical time of the magnetic field value establishment was approximately 3 seconds because of the large coil inductivity. To decrease the thermal exchange, a cylindrical sample (diameter 4 mm, height 8 mm) was inserted into a vacuum chamber (10^{-3} Torr) with long axis oriented along the magnetic field.

The metal-insulator transition in the samples obtained in the "soft" sintering conditions can be detected by magnetic measurements only. This is due to the features of the electrical resistance and magnetoresistance for the small-grained polycrystalline manganites as discussed above [8, 9]. The apparent electrical resistance maximum for such ceramics is distinctly lower than T_c, and magnetoresistance does not exceed 13 % (H = 1 T).

As a result of the ceramic microstructure modification, without solid solution decomposition (annealing conditions: T = 1100°C,

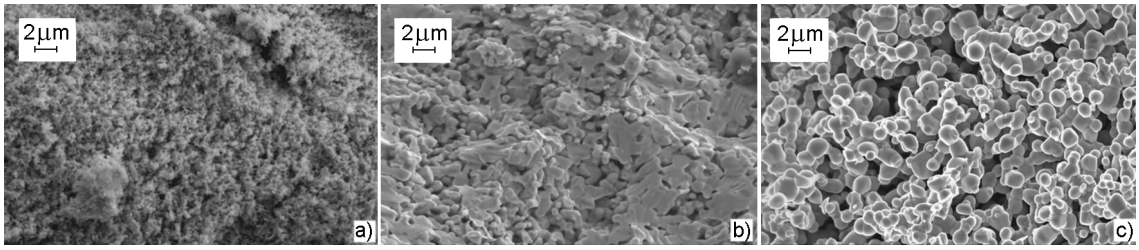

Fig. 1. Microstructure of the sample prepared under "soft" sintering conditions (a); morphology of the sample with modified microstructure after the high temperature annealing at $T = 1100$°C: $P(O_2) = 1$ bar, in the presence of silver metal vapor (b), $P(O_2) = 5$ bar in sealed ampoule with the metal silver (c).

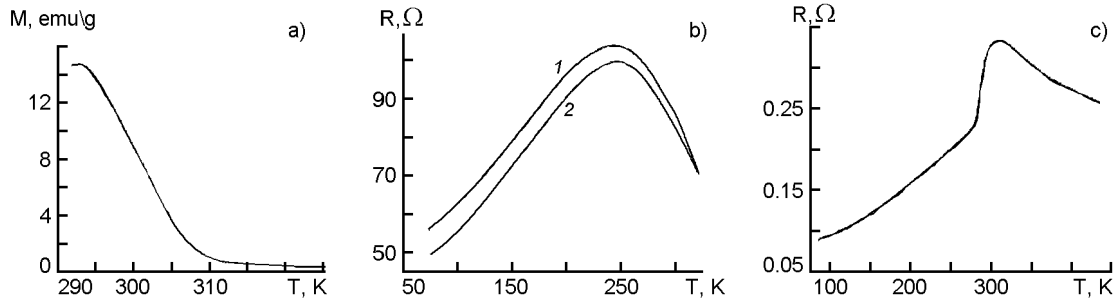

Fig. 2. Electrical and magnetic properties of a $La_{0.9}Ag_{0.1}MnO_3$ ceramic sample: magnetic susceptibility temperature dependence (a); temperature dependence of electrical resistance for the ceramic synthesized in the "soft" conditions (b); temperature dependence of electrical resistance for recrystallized ceramic (annealing conditions: 1100°C, $P(O_2) = 3$ bar, $t = 15$ h) (c).

P(O2) = 1–5 bar, $t = 5$–20 h, in the presence of the metallic silver vapor), the ceramics has been obtained having the density 70±1 % of the theoretical value for $P(O_2) = 1$ bar and 55±1 % for $P(O_2) = 5$ bar. The initial ceramic precursor density was 38±1 % of the theoretical value. The shrinkage is 65±3 % for $P(O_2) = 1$ bar and 52±3 % for $P(O_2) = 5$ bar, respectively. As Fig. 1 shows, the ceramic microstructure changes drastically during the high temperature annealing and the average grain size increases appreciably.

Electrical resistance of the recrystallized ceramics evidences a sharp metal-insulator transition near the Curie temperature in the $\rho(T)$ dependences (Fig. 2), in contrast to the fine-grained ceramics where there is a broad maximum at temperature lower than T_c ($T_p \approx 250$ K). However, comparison of the density data and microstructures of the obtained ceramics shows that the annealing at higher oxygen pressure results in ceramics consisting of larger grains but having a more porous structure and weaker grain contacts. Ceramics annealed at partial oxygen pressure 1 bar shows more developed grain boundaries. The magnetoresistance of such modified ceramics having composition

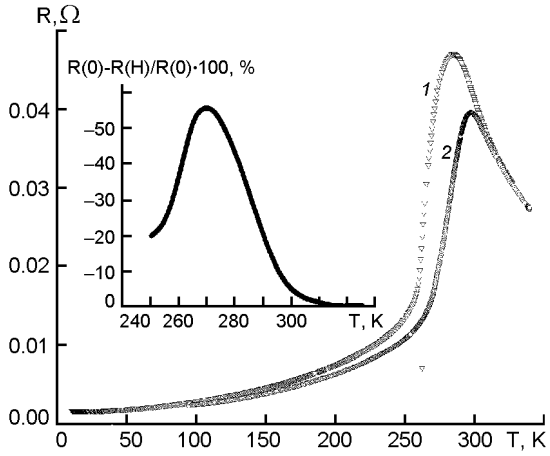

Fig. 3. Temperature dependence of electrical resistance for recrystallized $La_{0.8}Ag_{0.15}MnO_3$ ceramics (annealing at 1100°C, $P(O_2) = 1$ bar, $t = 20$ h). Inset: temperature dependence of magnetoresistance.

$La_{0.8}Ag_{0.15}MnO_3$ is 57 % in the field 1.1 T at 273 K (Fig. 3). This means a higher electrical resistance sensitivity to the magnetic field as compared to any $La_{1-x}Ag_yMnO_{3+\delta}$ ceramics sintered at high oxygen pressure (with the maximum magnetoresistance values of 65 % at 7 T field strength [6]).

Microstructure difference of the ceramic samples annealed at different $P(O_2)$ values

can be explained by the oxygen non-stoichiometry effect on the sintering process. Our earlier iodometric study [7] has shown that $La_{0.8}Ag_{0.2}MnO_{3+\delta}$ has $\delta \approx 0$ when being synthesized at 800°C in air. Respectively, at a lower silver content in $La_{0.8}Ag_{0.15}MnO_{3+\delta}$, the electroneutrality demands the decrease of δ down to negative values under the same preparation conditions. Also, the increase of the sintering temperature by 300°C should produce further loss of the oxygen content which hardly can be compensated by $P(O_2)$ increase from 0.21 atm to 1 atm. Thus, there are good reasons to conclude that the sintering of $La_{0.8}Ag_{0.15}MnO_{3+\delta}$ proceeds under the conditions of the oxygen deficit ($\delta<0$). The completeness of the oxygen sublattice increases with the $P(O_2)$. At the same time, the diffusion mobility of the ions decreases for the complete oxygen sublattice. Thus, it is possible to confirm, that optimal oxygen pressure for the increasing CMR effect value in the silver doped lanthanum manganite is about 1 bar.

Also the measurements of the magnetocalorical effect correlate with the chemical composition. All samples show rather sharp maximum of the magnetocaloric effect near T_c. But the sharpness of the peak and the maximum value of ΔT correlate with the sharpness of the magnetoresistance temperature dependence. For instance, $La_{0.8}Ag_{0.15}MnO_3$ had maximum value ΔT = 2.7 K at while $La_{0.9}Ag_{0.1}MnO_3$ has ΔT = 1.4 K in the 26 kOe field. $La_{0.8}Ag_{0.15}MnO_3$ has the value of ΔS = 2.9 J/(kg·K) at 291 K (Fig. 4). The magnetocaloric effect value for this composition is typical of the GMR manganites near room temperature [12], but for $La_{0.8}Ag_{0.15}MnO_3$, the peak magnetocaloric effect exceed even the value for metal gadolinium being the standard reference for the magnetocaloric effect. These results will be published in detail elsewhere.

Thus, a way to improve GMR of the silver containing lanthanum manganites $La_{1-x}Ag_yMnO_{3+\delta}$ is presented in this work. Starting from ceramics synthesized in the "soft" conditions, samples with high magnetoresistance values in low magnetic fields near room temperature have been obtained. The synthesis technique used in this work offers an advantage as compared to the techniques used in [6]. The silver-containing manganite ceramics with improved GMR can be synthesized without high oxygen pressure. Also, it is possible to obtain compositions with enhanced electrical resistivity sensitivity to magnetic field (up to 57 % in the field 1.1 T at 273 K for the composition $La_{0.8}Ag_{0.15}MnO_3$).

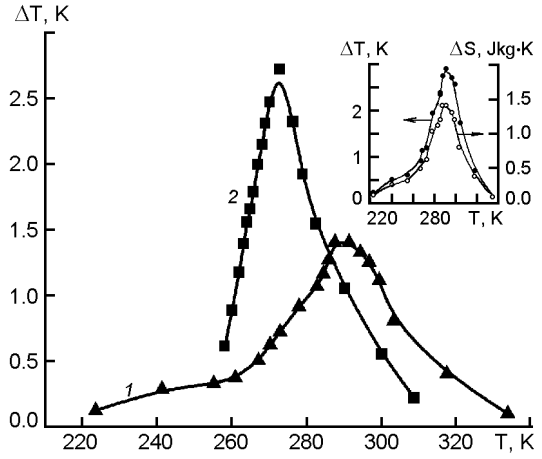

Fig. 4. Temperature dependence of magnetocaloric effect for $La_{0.9}Ag_{0.1}MnO_3$ (triangles) and $La_{0.8}Ag_{0.15}MnO_3$ (squares) in the field of 26 kOe. Inset: the entropy changes ΔS for $La_{0.9}Ag_{0.1}MnO_3$.

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Електричні та магнітні властивості перекристалізованої кераміки $La_{1-x}Ag_yMnO_3$

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Представлено спосіб одержання срібловмісного манганіту лантану, що має КМС. Отримано керамічні зразки, які мають високу температуру Кюрі та виявляють різкий максимум переходу метал-ізолятор поблизу температур Кюрі. При парціальному тиску кисню 1 атм отриманий склад $La_{0,85}Ag_{0,15}MnO_{3+\delta}$ з магнетоопором ~55 % у полі 1.1 Тл при 273 К. Показано, що парціальний тиск кисню впливає на механізм спікання таких керамік. Магнетокалоричний ефект для складу $La_{0,9}Ag_{0,1}MnO_{3+\delta}$ становить ΔS = 2.9 Дж/(кг·К) при 291 К.