

Influence of Superstoichiometric Manganese on the Charge and Spin Polarization of Electron Subsystem of Magnetoresistance Ceramics

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Abstract—The structural, resistance, magnetoresistance and dielectric properties of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics with a concentration of $x = 0 - 0.3$ were investigated by X-ray diffraction, thermogravimetric, resistance, magnetoresistance and dielectric spectroscopy methods. It has been shown that a real perovskite structure contains variable valence of manganese ions as well as point defects of the vacancy type. It has been established that an increase in the dielectric permittivity ϵ' within the ultra high frequency range is observed with increase in concentration of superstoichiometric manganese in rare-earth manganites. The optimal composition of the rare-earth manganite with the high values of the magnetoresistance and ϵ' within the room temperature range is determined. Superstoichiometric manganese leads to an increase in the spin and charge polarization of the electronic subsystem.

Keywords—ceramics; defect structure; superstoichiometric manganese; dielectric permittivity; dielectric loss tangent; magnetoresistance effect

I. INTRODUCTION

The increased interest in rare-earth (RE) manganites, both from the point of view of fundamental and applied aspects of science, is caused by the unique interconnection of transport,

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magnetoresistance (MR) and dielectric properties in them [1–3]. RE manganites relate to strongly correlated systems with a large number of structural, magnetic and charge phase transformations [4]. These metal oxides can be used in systems of magnetic cooling, dielectric ultra high frequency (UHF) resonators and sensors [5–7].

Well-known RE manganites are $\text{La}_{1-x}\text{A}_x^{2+}\text{MnO}_3$ compositions with non-isovalent substitution of A-cation by divalent ions $\text{A} = \text{Ca}^{2+}$ or Sr^{2+} [8–10]. The most promising in terms of obtaining high values of MR effect and the magnetic ordering temperature are $(\text{Ln}_{0.7}\text{A}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ ($\text{Ln} = \text{La}, \text{Nd}$) compositions with a superstoichiometric manganese [11, 12].

Less studied manganites are $\text{La}_{1-x}\text{A}_x^+\text{MnO}_3$ compositions doped with monovalent ions $\text{A}^+ = \text{Na}^+, \text{K}^+, \text{Ag}^+$ [13–16]. Non-isovalent substitutions for both monovalent and divalent ions as well as availability of superstoichiometric manganese in RE $\text{La}_{1-x}\text{A}_{x1}^{2+}\text{A}_{x2}^+\text{Mn}_{1+x}\text{O}_3$ manganites are of a particular interest. It is supposed that these compositions have the high polarization properties in electron and spin subsystem.

Establishing the regularities in the influence of non-isovalent substitution of A-cation for monovalent potassium

and superstoichiometric manganese ions on defect structure and properties of magnetoresistance $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics ($x = 0 - 0.3$) with high values of MR effect and dielectric permittivity within a room temperature range causes the topicality of this work.

II. METHODS OF PREPARATION AND INVESTIGATION OF THE SAMPLES

Ceramic $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ samples were prepared by the solid-state reaction method from thoroughly mixed and ground stoichiometric La_2O_3 , Mn_3O_4 , CaO and KMnO_4 powders ($\geq 99.0\%$ purity). The investigated samples were enriched with oxygen at high synthesis temperatures due to the $\text{Mn}^{7+} \rightarrow \text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$ reduction process in the initial KMnO_4 powder. The $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics with concentration $x = 0, 0.1, 0.2$ and 0.3 were obtained after synthesizing at 900°C (20 h), subsequent grinding and pressing into a tablet (0.2 GPa) and annealing at 1350°C (3.5 h) in a slow heating and cooling regime in the air.

The following methods were used for studying the structure, its defectiveness as well as resistance, magnetoresistance and dielectric properties of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ manganites:

- X-ray diffraction method at room temperature using DRON-3 diffractometer with CuK_α -radiation to determine the type of crystalline structure, lattice parameters and phase composition;

- thermogravimetric $\Delta m/m$ method (Δm is a change in sample mass after synthesis) to study defect structure and determine the concentrations of point defects of the vacancy type;

- four-probe resistance method to determine resistivity ρ (measurement current 1 – 10 mA), study resistance properties, identify the temperature T_{ms} of the metal-semiconductor phase transition and the activation energy E_a ;

- magnetoresistance method to determine MR effect of $MR = \Delta\rho/\rho = (\rho - \rho_H) / \rho$, where ρ and ρ_H are resistivity in external magnetic fields $H = 0$ and 5 kOe, respectively;

- room temperature dielectric spectroscopy within the UHF range $F = 8.15 - 78.33$ GHz to investigate the dielectric properties, determine the relative dielectric permittivity ϵ' and dielectric loss tangent $\tan\delta$.

III. STRUCTURAL PROPERTIES

According to X-ray diffraction data, ceramic $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ samples with a concentration of $x = 0 - 0.2$ were single-phase and contained a perovskite structure of cubic symmetry. The samples with $x = 0.3$ had an insignificant amount of $\leq 3\%$ of the tetragonal phase of Mn_3O_4 .

With increase in the concentration x , the lattice parameter a increases from $a = 7.711 \text{ \AA}$ ($x = 0$) to 7.730 \AA ($x = 0.1$), 7.744 \AA ($x = 0.2$) and 7.758 \AA ($x = 0.3$) (see Fig. 1). The increase in the lattice constant a is due to substitution of A -cations of Ca^{2+} with an ionic radius $R_{\text{Ca}^{2+}} = 1.48 \text{ \AA}$ for a larger K^+ ions with $R_{\text{K}^+} = 1.78 \text{ \AA}$ [17, 18].

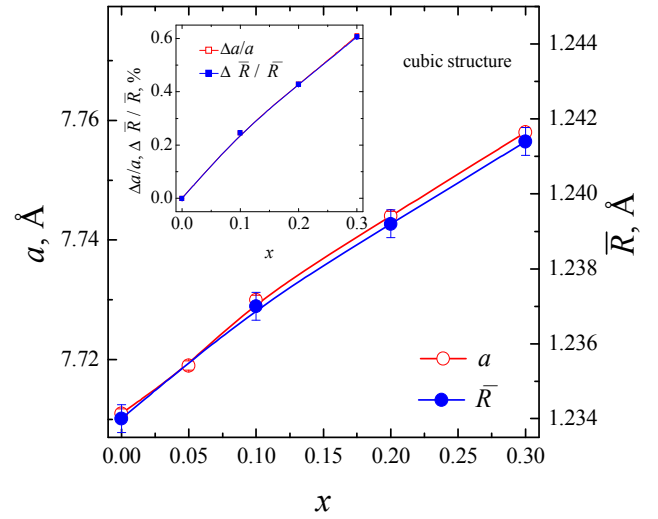


Fig. 1. Concentration dependences of the lattice parameter a , average ionic radius \bar{R} and their relative changes $\Delta a/a$, $\Delta \bar{R} / \bar{R}$ (insertion) of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

On the basis of the established defect formation mechanism [12], taking into account the cyclic changes in oxygen content δ and manganese valence during heating ($\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$) and cooling ($\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$) at elevated synthesis and annealing temperatures, the defect structure $V^{(a)}$ was determined, the molar formulas of which are given in Table.

An additional criterion for the correct determination of defect molar formulas (see Table) is the established correlation between the relative changes in the lattice parameter $\Delta a/a$ and average ionic radius $\Delta \bar{R} / \bar{R}$ (see the inset in Fig. 1).

As shown in Table, a real structure is defect and contains in A - and B -positions the different valence manganese ions (Mn_A^{2+} , Mn_B^{3+} and Mn_B^{4+}) as well as the point defects of the vacancy type (anionic $V^{(a)}$ and cationic $V^{(c)}$ vacancies). With increase in concentration of superstoichiometric manganese, the concentration of cationic $V^{(c)}$ vacancies in B -sublattice decreases and fills it up to completeness with subsequent appearing Mn^{2+} ions in A -positions and formation of nanostructural planar $(\text{Mn}_B^{4+})_{cl} - \text{O}^{2-} - (\text{Mn}_A^{2+})_{cl} - V^{(a)}$ clusters [19, 20].

Reduction of the defect structure from $V^{(a)} = 9.0$ to 6.3% (see Table) is confirmed by the results of thermogravimetric analysis from $|\Delta m/m| = 19.5\%$ ($x = 0$) to 16.6% ($x = 0.3$).

TABLE. THE MOLAR FORMULAS OF REAL DEFECT STRUCTURE, CONCENTRATION OF ANIONIC $V^{(a)}$ VACANCIES AND TOLERANCE FACTOR t OF $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ CERAMICS

x	Defect molar formulas	$V^{(a)}, \%$	t
0	$\{\text{La}_{0.67}^{3+}\text{Ca}_{0.30}^{2+}\text{V}^{(c)}\}_A[\text{Mn}_{0.63}^{3+}\text{Mn}_{0.24}^{4+}\text{V}^{(c)}]_B\text{O}_{2.73}^{2-}\text{V}^{(a)}_{0.27}$	9.0	0.94
0.1	$\{\text{La}_{0.64}^{3+}\text{Ca}_{0.20}^{2+}\text{K}_{0.09}^{+}\text{V}^{(c)}\}_A[\text{Mn}_{0.77}^{3+}\text{Mn}_{0.21}^{4+}\text{V}^{(c)}]_B\text{O}_{2.78}^{2-}\text{V}^{(a)}_{0.22}$	7.3	1.00
0.2	$\{\text{La}_{0.66}^{3+}\text{Ca}_{0.07}^{2+}\text{K}_{0.14}^{+}\text{Mn}_{0.04}^{2+}\text{V}^{(c)}\}_A[\text{Mn}_{0.74}^{3+}\text{Mn}_{0.26}^{4+}]_B\text{O}_{2.80}^{2-}\text{V}^{(a)}_{0.20}$	6.7	1.02
0.3	$\{\text{La}_{0.63}^{3+}\text{K}_{0.23}^{+}\text{Mn}_{0.05}^{2+}\text{V}^{(c)}\}_A[\text{Mn}_{0.60}^{3+}\text{Mn}_{0.40}^{4+}]_B\text{O}_{2.81}^{2-}\text{V}^{(a)}_{0.19}$	6.3	1.04

Calculation of the tolerance factor $t = (\bar{R}_A + \bar{R}_X) / (\sqrt{2}(\bar{R}_B + \bar{R}_X))$ was carried out for a real defect structure containing anionic $V^{(a)}$ and cationic $V^{(c)}$ vacancies (see Table). In the course of non-isovalent replacement of Ca^{2+} by K^+ ions, the fulfillment of the condition $t \rightarrow 1$, which is associated with an increase in the stability of the structure due to the denser packing of MnO_6 octahedral complexes around the $(\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x)\text{O}_{12}$ cube-octahedron, is caused both by the increase in the average ionic radius of A -cation (during substitution of Ca^{2+} for K^+ ions) and a decrease in the radius of A -position (decrease in the average radius of B -cation).

IV. RESISTANCE, MAGNETORESISTANCE AND DIELECTRIC PROPERTIES

Analysis of the temperature dependences of the resistivity $\rho(T)$ of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics (see Fig. 2) shows that for the compositions with $x = 0 - 0.3$ within the temperature range $T = 77 - 400$ K, phase transition "metal-semiconductor" is observed at temperature T_{ms} . With increase in x the temperature T_{ms} increases from $T_{\text{ms}} = 263$ K ($x = 0$) to 283 K ($x = 0.1$), 293 K ($x = 0.2$) and 293 K ($x = 0.3$) that is connected to a decrease in the defect structure $V^{(a)}$ (see Table). With increase in the concentration x , the resistivity ρ at T_{ms} nonmonotonically increases from $\rho(T_{\text{ms}}) = 132$ mOhm·cm ($x = 0$) to 77 mOhm·cm ($x = 0.1$), 81 mOhm·cm ($x = 0.2$) and 168 mOhm·cm ($x = 0.3$), which is caused by coexistence of two mechanisms of charge compensation. The first mechanism is due to a change in the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and its deviation from the optimal value of 2/1. The second mechanism is caused by decreasing the defect structure $V^{(a)}$. Both mechanisms influence the high-frequency electronic "double exchange" of $3d^4(\text{Mn}^{3+})-2p^6(\text{O}^{2-})-3d^3(\text{Mn}^{4+})-V^{(a)}-3d^4(\text{Mn}^{3+})$ and the formation transport properties.

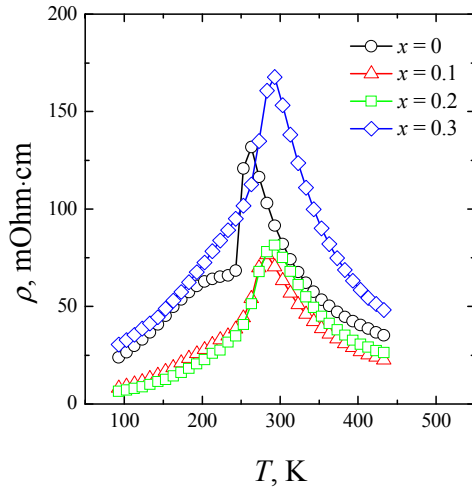


Fig. 2. Temperature dependences of the resistivity $\rho(T)$ of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

The concentration dependence of the activation energy $E_a(x)$ (see Fig. 3) is an important characteristic for the transport properties of RE manganites and characterizes the degree of inhomogeneity of the electronic state near the conduction band. The activation energy E_a was calculated for the paramagnetic semiconductor region ($T > T_C$, $T > T_{\text{ms}}$) from the diffusion type equations [21–25]:

$$\rho(T) = (k_B T / n e^2 D) \cdot \exp(E_a / k_B T),$$

where $D = a^2 \cdot \nu$ is the diffusion coefficient, e and n are the charge and its concentration, and ν is the frequency of hopping of the charge carriers over localized (polaron) states at a distance \sim the unit cell a . An increase in the activation energy E_a with increase in x (see Fig. 3) is associated to a change in the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and an increase in the concentration of AFM nanostructured planar $(\text{Mn}_B^{4+})_{cl} - \text{O}^{2-} - (\text{Mn}_A^{2+})_{cl} - V^{(a)}$ clusters (see Table).

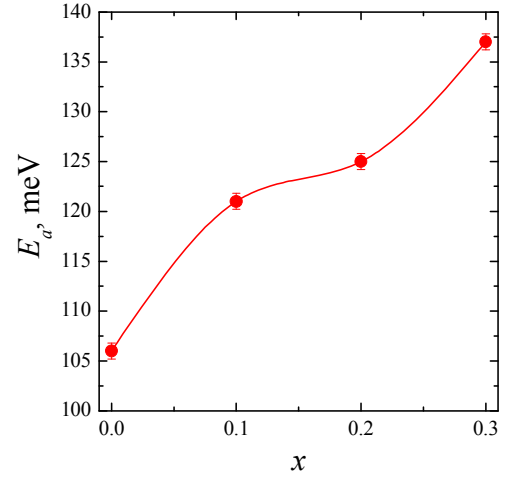


Fig. 3. The concentration dependences of the activation energy $E_a(x)$ of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

From the analysis of the temperature dependences of the magnetoresistance $MR(T)$ effect of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics (see Fig. 4), the temperature T_p of MR effect peak was determined. With increase in x , the temperature T_p increases from $T_p = 253$ K ($x = 0$) to 269 K ($x = 0.1$), 271 K ($x = 0.2$) and 273 K ($x = 0.3$), and the value of the MR effect at T_p decreases from $MR(T_p) = 32.3\%$ ($x = 0$) to 13.6% ($x = 0.1$), 12.5% ($x = 0.2$) and 10.7% ($x = 0.3$). Such increasing temperature T_p and a decreasing $MR(T_p)$ are caused by changing $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and decreasing concentration $V^{(a)}$ (see Table).

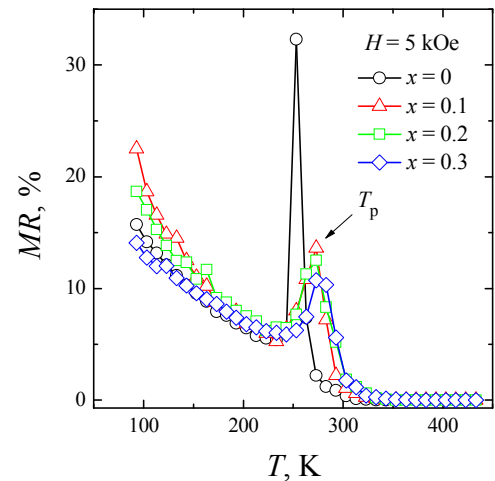


Fig. 4. The temperature dependences of the magnetoresistance effect $MR(T)$ of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

The nonstoichiometric $\text{La}_{0.7}\text{Ca}_{0.1}\text{K}_{0.2}\text{Mn}_{1.2}\text{O}_{3-\delta}$ manganite with a superstoichiometric manganese ~ 20 mol. % is an optimal composition with the highest value of magnetoresistance effect $MR(300\text{ K}) \approx 4.3\%$ within the room temperature range.

The dielectric properties of the ceramic $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ samples within UHF range are investigated. It was established that with an increase in the concentration of monovalent K^+ ions and superstoichiometric manganese it is observed an increase in the relative dielectric permittivity from $\epsilon' = 7.4$ ($x = 0$) to 7.6 ($x = 0.05$), 10.1 ($x = 0.1$), 11.1 ($x = 0.2$) and 13.9 ($x = 0.3$) (see Fig. 5). The dielectric loss tangent increases with increase in concentration x from $\tan\delta = 0.9 \cdot 10^{-4}$ ($x = 0$) to $3.3 \cdot 10^{-4}$ ($x = 0.1$), $4.5 \cdot 10^{-3}$ ($x = 0.2$) and $7.2 \cdot 10^{-3}$ ($x = 0.3$).

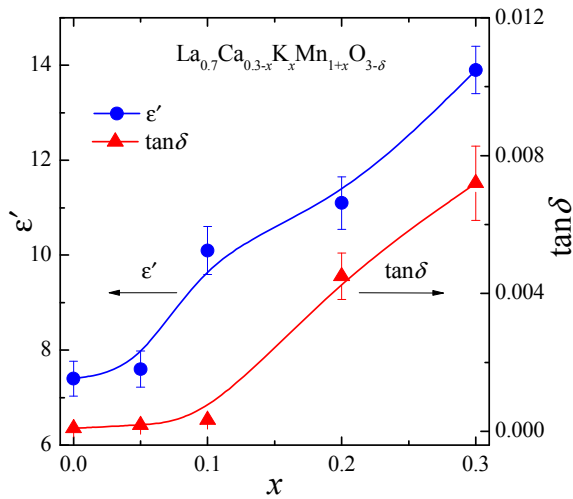


Fig. 5. Concentration dependences of the dielectric relative permittivity ϵ' and dielectric loss tangent $\tan\delta$ within UHF range (8...78 GHz) of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

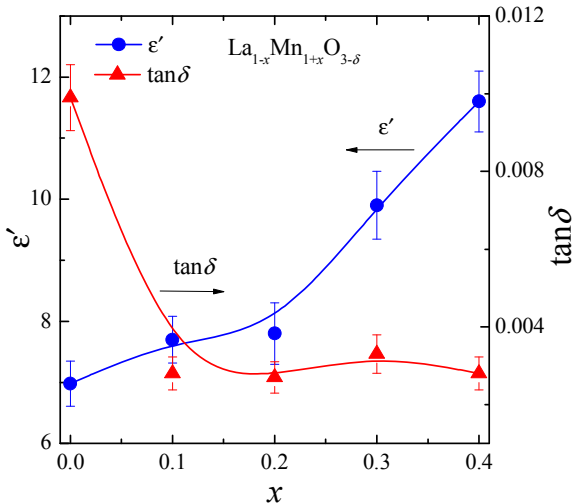


Fig. 6. Concentration dependences of the dielectric relative permittivity ϵ' and dielectric loss tangent $\tan\delta$ within UHF range (8...12 GHz) of $\text{La}_{1-x}\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics

The increase in ϵ' with increase in x (see Fig. 5) is due to an increase in the polarization of the electron subsystem by superstoichiometric manganese. The increase in $\tan\delta$ (see Fig. 5) is due to the influence of the relaxation scattering processes of conduction electrons on $(\text{Mn}_B^{4+})_{cl} - \text{O}^{2-} - (\text{Mn}_A^{2+})_{cl} - \text{V}^{(a)}$, the concentration of which increases with increasing x (see Table).

The conclusion of an increase in ϵ' of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ ceramics due to superstoichiometric manganese was additionally confirmed by studying the self-doped RE $\text{La}_{1-x}\text{Mn}_{1+x}\text{O}_{3-\delta}$ manganite (see Fig. 6).

V. CONCLUSIONS

On the basis of the analysis of X-ray diffraction, thermogravimetric, resistance, magnetoresistance and dielectric experimental studies of the nonstoichiometric ceramic $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ samples with concentration $x = 0 - 0.3$, the following conclusions can be made.

It has been established that the reasons for the change in the resistance, magnetoresistance and dielectric properties of the real structure of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ are connected to changing $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio and decreasing the concentration of anionic $\text{V}^{(a)}$ vacancies.

It has been shown that an increase in the content of K^+ ions and superstoichiometric manganese leads to a nonmonotonic increase in the resistivity ρ , an increase in the temperature of phase transition T_{ms} and the peak of the MR effect T_p as well as a decrease in the magnetoresistance MR . The nonmonotonic character of the change in functional properties is due to the redistribution of the contribution to the electroneutrality principle from the two mechanisms of charge compensation. In course of non-isovalent substitution of A -cation, the contribution to charge compensation occurs both due to a change in the valence of $\text{Mn}^{3+}/\text{Mn}^{4+}$ manganese and the defect structure.

The highest value of magnetoresistance effect has the nonstoichiometric composition of $\text{La}_{0.7}\text{Ca}_{0.1}\text{K}_{0.2}\text{Mn}_{1.2}\text{O}_{3-\delta}$ manganite with an optimal concentration of superstoichiometric manganese in which increase in polarization of spin subsystem is observed.

It has been established that superstoichiometric manganese leads to increasing the relative dielectric permittivity to $\epsilon' = 14$ within UHF range and as a consequence to increasing charge polarization of the electronic $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{Mn}_{1+x}\text{O}_{3-\delta}$ subsystem.

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