Magnetotransport and Dielectric Properties of Bi-Containing $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ Rare-Earth Manganites with B = Cr, Fe, Co, Ni

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***Abstract*— The effect of the replacement of manganese by 3*d*-ions of transition metals on the structural, microstructural, dielectric, and magnetotransport properties of nonstoichiometric $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ compositions with B = Cr, Fe, Co and Ni ($0 \le x \le 0.3$) was investigated. It is shown that in all compositions a weak change for the lattice parameter of the rhombohedral perovskite structure is observed. It is established that the real structure is defective and contains cationic $V^{(c)}$ and anionic $V^{(a)}$ vacancies. With increasing x, an increase in the resistivity and the absence of a metal-semiconductor phase transition for $x > 0.20$ are observed. The electron-phonon interaction constant γ_{ph} was determined. The most significant change in the structural and functional properties was observed for the compositions with B = Fe, for which constant $\gamma_{ph} \approx 7.7$ achieves a maximum value. At $x = 0.05$, an increase in magnetoresistance effect of the tunnel type is observed.**

Keywords*— *structural defectiveness; electronic transport; dielectric constant; electron-phonon interaction constant; magnetoresistance effect

I. INTRODUCTION

Increased interest both in terms of fundamental and applied aspects of science arises in the study and synthesis of multifunctional materials which simultaneously have high values of the colossal magnetoresistance (MR) effect, magnetization, Curie temperature T_C and at the same time exhibit dielectric properties [1-3]. Such materials include Bi-containing rare-earth (RE) manganites with the structure of perovskite, in which a large number of phase transitions coexistences with competing types of interactions [2, 4, 5]. We have established that $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1}O_{3-\delta}$ composition is optimal with the largest value of spontaneous magnetization and the magnitude of the MR effect near T_C.

The particular interest is the study of the effect of substitutions of B cations of manganese for the 3*d*-ions of the transition metals Cr, Fe, Co, and Ni on the formation of functional properties of Bi-containing RE manganites. The investigation of the structure and its defectiveness as well as microstructural, dielectric, transport and MR properties of the nonstoichiometric $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ compositions with B = Cr, Fe, Co and Ni ($0 \le x \le 0.3$) causes the relevance of this work.

II. OBJECTS AND RESEARCH METHODS

Synthesis of powders of all compositions was carried out by the conventional solid-state reaction method in two-stage from the corresponding carefully mixed stoichiometric mixtures of La_2O_3, SrO, Bi_2O_3, MnO_2, Cr_2O_3, Fe_2O_3, Co_3O_4 and NiO powders (purity > 99 %) at t_{synth} = 800 °C (18 h) and 850 °C (18 h). Ceramics $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ for B = Cr, Fe, Co, Ni with x = 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 were obtained from the synthesized powder with its repeated grinding, pressing into pellets under P = 0.2 GPa and annealing at t_{ann} = 1000 ºC (18 h) in the mode of slow heating and cooling in air. To study the structure and its defectiveness, as well as microstructural, dielectric, transport and MR properties of the ceramics the following experimental methods were used:

- X-ray diffraction (PANalitical X-Pert PRO MRD diffractometer) to determine the type of crystalline structure, phase composition and lattice parameters;

- thermogravimetric to determine the relative changes of mass loss of samples and the structure defects;

- iodometric titration to determine oxygen index and the average valence of manganese ions;

- scanning electron microscopy (SEM);

- four-probe resistance to determine resistivity and magnetoresistance effect;

- dielectric spectroscopy to determine relative dielectric permittivity.

III. RESULTS AND DISCUSSION

According to X-ray diffraction data, all ceramic samples $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1\text{-}x}B_xO_{3\text{-}\delta}$ with B = Cr, Fe, Co and Ni were single-phase with weakly changing lattice parameter of $R\bar{3}c$ rhombohedral distorted perovskite structure.

On the basis of the defect formation mechanism [6] it was established that the real structure $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1\text{-}x}B_xO_{3\text{-}\delta}$ with B = Cr, Fe, Co and Ni is defective and contains anionic $V^{(a)}$ and cationic $V^{(c)}$ vacancies as well as manganese ions Mn^{3+} and Mn^{4+} in the B-positions, whose concentration depends on the replacement 3d-ion $B = Cr^{3+}$, Fe^{3+}, $Co^{2+}(Co^{III})$, Ni^{2+}. For all compositions with increasing x, an increase in the concentration of anionic $V^{(a)}$ vacancies from $V^{(a)}$ = 6.3% (x = 0) to 7.3% (x = 0.3), 8.3% (x = 0.3), 8.7% (x = 0.3) and 10.3% (x = 0.3) is observed for B = Cr, Fe, Co and Ni, respectively.

The temperature dependences of the resistivity $\rho(T)$ of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1\text{-}x}B_xO_{3\text{-}\delta}$ samples with B = Cr, Fe, Co and Ni (Fig. 1) show that the temperature of the metal-semiconductor phase transition T_{ms} decreases with increasing x from T_{ms} = 205 K (x = 0) to 124 K (x = 0.15), 150 K (x = 0.05) and 122 K (x = 0.15) for B = Cr, Fe, and Co, respectively. The resistivity ρ at T_{ms} increases with increasing concentration of 3d-ions Cr, Fe, and Co from $\rho(T_{ms})$ = 1.7 Ohm·cm (x = 0) to 43.8 Ohm·cm (x = 0.15), 14.0 Ohm·cm (x = 0.05) and 15.5 Ohm·cm (x = 0.15), respectively. The composition with the replacement of Mn by Fe ions has higher values of the resistivity in comparison with B = Cr, Co and Ni (Fig. 2 a).

A decrease in T_{ms} and an increase in ρ with an increase in x as well as the absence of the metal-semiconductor phase transition for compositions with $x > 0.2$ are due to weakening of the double exchange $Mn^{3+}\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}$ by point defects of the vacancy type $Mn^{3+}\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}\leftrightarrow V^{(a)}\leftrightarrow Mn^{3+}$ and 3d-ions of the transition metals $Mn^{3+}\leftrightarrow O^{2-}\leftrightarrow B\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}$ with $B = Cr^{3+}$, Fe^{3+}, Co^{2+}, Co^{III} and Ni^{2+}.

Of particular interest are the transport properties of RE manganites in the paramagnetic semiconductor region at $T > T_{ms}$ and T_C. The most suitable conduction mechanism in the high-temperature region, as was shown in works [7], is the thermally activated process of the hopping conductivity of a small polaron for the Mott and Davis model [8]:

$$\rho/T^{n} = \rho_0\cdot\exp(E_\rho/k_BT), \tag{1}$$

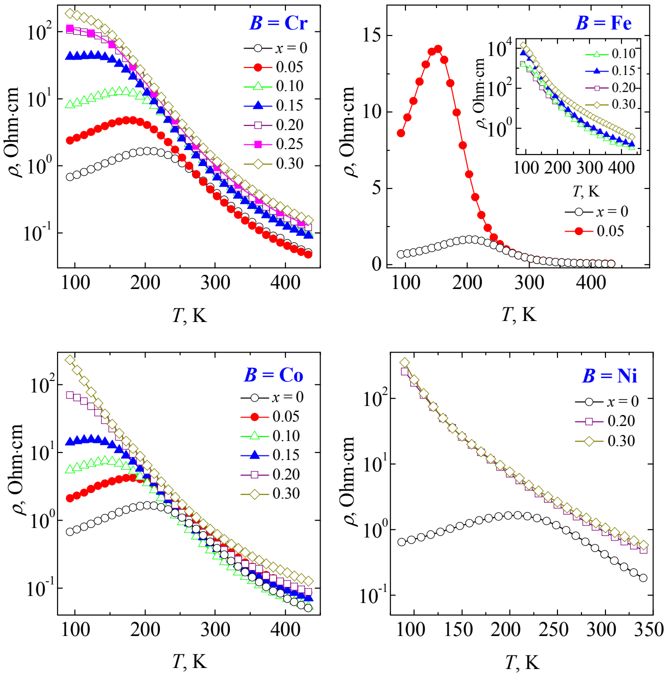


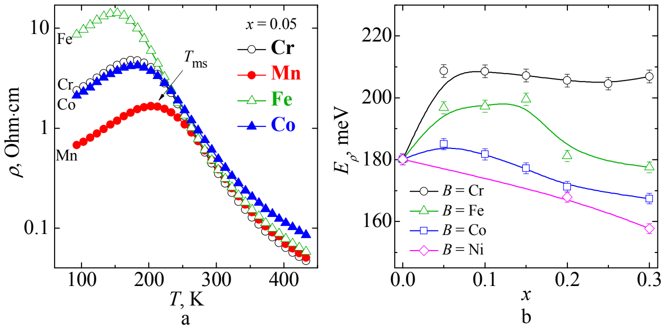
Fig. 1. Temperature dependences of resistivity of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1\text{-}x}B_xO_{3\text{-}\delta}$ ceramics with B = Cr, Fe, Co, Ni.

where $\rho_0 = [k_B/\nu_{ph}Ne^2R^2C(1\text{-}C)]\cdot\exp(2\alpha R)$; n is the exponent with a temperature factor for the adiabatic (n = 1) and non-adiabatic (n = 1.5) processes; k_B is the Boltzmann constant; T is the absolute temperature; N is the number of e_g-electrons Mn^{3+}, per unit volume, obtained from X-ray diffraction data taking into account structural defectiveness; $R = (1/N)^{1/3}$ is the average distance between the centers of the polarons; C is share of occupied positions by a polaron; α is the damping constant of the electron wave function; ν_{ph} is the optical phonon frequency, determined from the relation $h\nu_{ph} = k_B\theta_D$, where θ_D is the Debye temperature.

The activation energy is determined by [8]:

$$E_\rho = \begin{cases} W_H + W_D/2, \text{ for } T > \theta_D/2 \text{ and n} = 1 \\ W_D, \text{ for } T < \theta_D/4 \text{ and n} = 1.5 \end{cases}, \tag{2}$$

where W_D is the energy difference between the two polaron states (disorder energy) and W_H is the polaron hopping energy.



a b

Fig. 2. Comparative analysis of the temperature dependences of the resistivity for x = 0.05 (a) and concentration dependences of the activation energy for all x (b) of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1\text{-}x}B_xO_{3\text{-}\delta}$ ceramics B = Cr, Fe, Co, Ni.

To determine the activation energy E_ρ (see Table I), in the paramagnetic of the semiconductor region at $T > \theta_D/2$, considering the best linear approximation of the experimental values of the resistivity $\ln(\rho/T) = f(1/T)$, it was used adiabatic process with exponent n = 1 in equation (1). The deviation from the linear dependence $\ln(\rho/T) = f(1/T)$ corresponded to the temperature $T = \theta_D/2$. The concentration dependences of E_ρ for all compositions shown in Fig. 2b. The nonmonotonic increase of E_ρ with increasing x for compositions with B = Cr and Fe is observed. The decrease of E_ρ with increasing x for compositions with B = Co and Ni can be explained by the appearance of more conductive subsystems $Co^{2+}\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}$ and $Ni^{2+}\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}$, discussed in works [9, 10].

In the low-temperature region, at $T < \theta_D/4$, the activation energy $E_\rho = W_D$ was determined for a nonadiabatic process with n = 1.5 in expression (1). Based on the experimentally determined parameters (see Table I), the polaron hopping energy W_H from the system of equations (2), the electron-phonon interaction constant $\gamma_{ph} = 2W_H/h\nu_{ph}$ and the polaron radius r_p from the relation $W_H = e^2/4\varepsilon'(1/r_p - 1/R)$ were calculated. The ε' is a high-frequency relative permittivity which was measured in the microwave range f = 8.15-78.33 GHz.

As can be seen from Table I, for all compositions with B = Cr, Fe, Co, and Ni, as the x increases, the Debye temperature θ_D and the hopping frequency ν_{ph} decrease. A small change in the polaron radius r_p and the high-frequency relative permittivity ε' with increase in x is observed. The high values of the electron-phonon interaction constant $\gamma_{ph} > 4$ [8] indicate a partial localization of e_g-electrons of manganese ions as a result of the attenuation of the double exchange of $Mn^{3+}(3d^4)\leftrightarrow O^{2-}(2p^6)\leftrightarrow Mn^{4+}(3d^3)$ with manganese replacement by 3d-ions of transition metals Cr^{3+}, Fe^{3+}, Co^{2+}, Co^{III}, Ni^{2+} and the increase in point defects of the vacancy type.

An additional confirmation of the existence of a small polaron for all compositions with B = Cr, Fe, Co, and Ni is the Holstein condition [11], according to which $J < W_H/3$ (see Table I), where $J(T) \approx 0.67h\nu_{ph}(T/\theta_D)^{1/4}$ is the width of the polaron band at T = 300 K.

The temperature dependences of the MR effect of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ ceramics with B = Cr, Fe, Co and Ni shown in Fig. 3. In all compositions with B = Cr (x = 0.15-0.3), Fe (x = 0.05-0.3), Co (x = 0.1-0.3), and Ni (x = 0.2-0.3), the peak of the MR effect appears in the temperature range T_p = 192-203 K, T_p = 100-153 K, T_p = 160-203 K and $T_p \approx$ 150 K, respectively. The $MR(T_p)$ value decreases with increasing concentration x and is in the intervals $MR(T_p)$ = 5.9-7.5% for B = Cr, 1.9-13.3% for B = Fe, 5.4-8.9% for B = Co and 5% for B = Ni. This type of the MR effect at T_p is connected with the scattering process of spin-polarized charge transport on the intercrystalline magnetic inhomogeneities of the defect structure containing impurity ions Cr^{3+}, Fe^{3+}, Co^{2+} (Co^{III}) and Ni^{2+} as well as anionic $V^{(a)}$ and cationic $V^{(c)}$ vacancies. The absence of a peak in the $MR(T)$ dependencies at T_P for other compositions is connected with a small crystallite size ≤ 1 μm (see Fig. 4).

TABLE I. Comparative Analysis of the Transport (E_ρ, θ_D, ν_{ph}, W_H, γ_{ph}, J, r_p) and Dielectric (ε') Parametrs of the Studied $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ Ceramics with B = Cr, Fe, Co and Ni.

B	**x**	**E_ρ, meV**	**θ_D, K**	**ν_{ph}, THz**	**r_p, Å**	**ε'**	**J, meV**	**$W_H/3$, meV**	**γ**
Mn	0	180	594	12.7	1.8	6.4	28.9	60.1	7.1
Cr	0.2	205	606	12.6	1.7	6.8	29.3	65.7	7.5
	0.3	206	600	12.5	1.6	7.6	29.1	65.7	7.6
Fe	0.2	181	500	11.3	1.8	7.3	25.4	54.7	7.6
	0.3	177	458	10.0	2.0	6.8	23.8	50.7	7.7
Co	0.2	171	552	11.5	1.9	6.8	27.4	53.8	6.8
	0.3	167	540	11.2	2.1	6.7	26.9	49.6	6.4
Ni	0.2	167	612	12.7	2.1	6.3	29.6	48.5	5.5
	0.3	157	580	12.1	2.4	6.1	28.4	42.4	5.1

In the low-temperature region at $T \approx$ 77 K, a tunneling type of the MR effect is observed for all compounds, which is due to the tunneling processes through the intercrystalline boundaries [12]. The magnitude of this MR effect depends on the size of the crystallites D, the composition and the extent of the intercrystalline zones and is in the intervals MR(77 K) = 15.2-17.2% for B = Cr, 1.8-15.3% for B = Fe, 10.1-15.3% for B = Co and 9.4-15.3% for B = Ni. For all compositions with B = Cr, MR(77 K) and crystallite size $D \approx 1$ μm practically do not change (see Fig. 3 and 4). For other compositions with B = Fe, Co, and Ni, MR(77 K) decreases with increasing x, and the crystallite size increases to $D \approx$ 2-2.5 μm. An increase in the size of the crystallites D, which leads to a decrease in the extent of the intercrystalline zones, causes a decrease in the MR effect of the tunnel type [6].

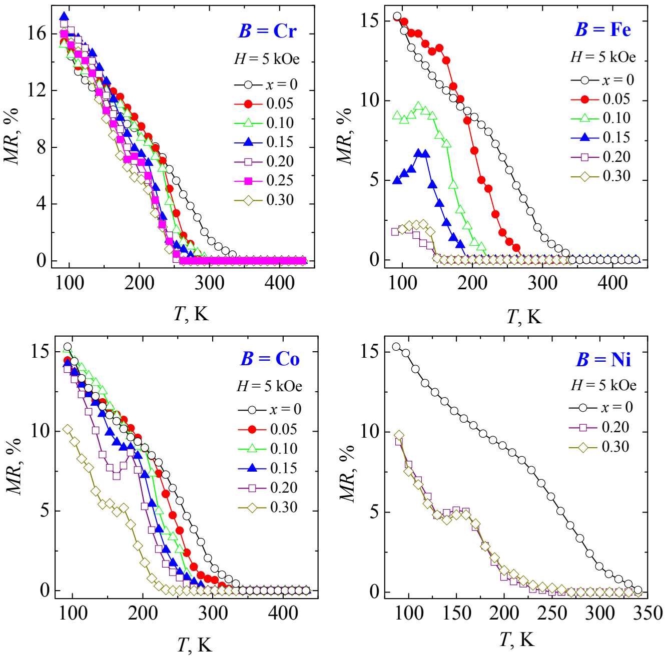


Fig. 3. Temperature dependences of the magnetoresistance effect in the field H = 5 kOe of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ ceramics with B = Cr, Fe, Co, Ni.

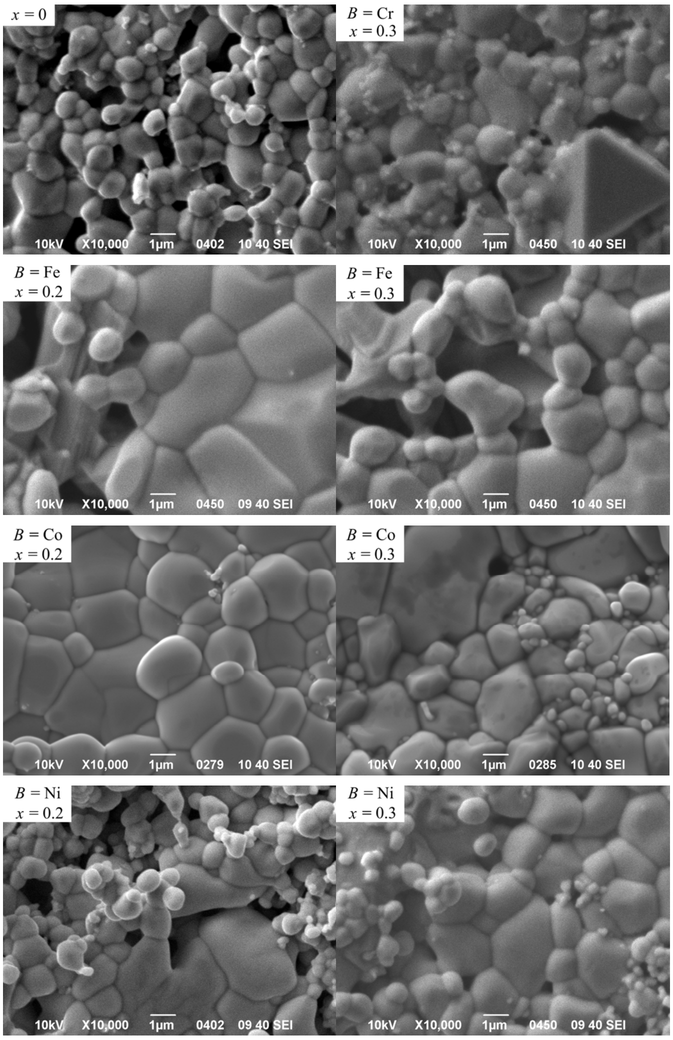


Fig. 4. Microstructure of $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ ceramics with B = Cr, Fe, Co and Ni (SEM method).

It should be noted that the compositions with Fe ($x = 0.05$) and Cr ($x = 0.15$) have the highest values of the MR effect $MR = 13.3\%$ at $T = T_p$ and $MR = 17.2\%$ at $T = 77$ K, respectively.

IV. CONCLUSIONS

All ceramic samples $La_{0.6}Sr_{0.15}Bi_{0.15}Mn_{1.1-x}B_xO_{3-\delta}$ with B = Cr, Fe, Co and Ni were single-phase and contain the $R\bar{3}c$ rhombohedral distorted perovskite structure for all concentration range x. It has been established that the real perovskite structure contains cationic $V^{(c)}$ and anionic $V^{(a)}$ vacancies, concentrations of which are increased with increase in x.

For all compositions with increasing x, an increase in the resistivity ρ and the absence of a metal-semiconductor phase transition for $x > 0.2$ are observed, which is caused by the weakening of the double exchange of $Mn^{3+}\leftrightarrow O^{2-}\leftrightarrow Mn^{4+}$ by point defects of the vacancy type and 3d-ions of the transition metals.

Using the small polaron hopping model, the electron-phonon interaction constant has been determined. It has been established that for all compounds a strong electron-phonon interaction ($\gamma_{ph} > 4$) is observed, which leads to a partial localization of e_g-electrons Mn^{3+} and is well correlated with data of the temperature dependences $\rho(T)$. The iron ions, for which the electron-phonon interaction constant achieves maximum values, have the strongest effect on the change in magnetotransport properties.

It has been established that the compositions with Fe ($x = 0.05$) and Cr ($x = 0.15$) have the highest values of MR effect $MR(T_p) = 13.3\%$ and $MR(77\text{ K}) = 17.2\%$, respectively.

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