

Mechanisms of Substituting Quadrivalent Ions Influence on the Properties of La–Sr Manganites

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Regularities of the influence of quadrivalent ions and oxygen concentrations on the structural characteristics, saturation magnetization, Curie point, temperature dependence of electrical conductance of ceramic manganites $\text{La}_{1-c-x}\text{Sr}_{c+x}\text{Mn}_{1-x}\text{Me}^{4+x}\text{O}_{3+\gamma}$ (Me = Ti, Ge; $0.17 \leq c \leq 0.35$; $0.025 \leq x \leq 0.125$) were established. The relation between experimental data on lattice parameters, electromagnetic properties and crystal chemistry characteristics (nonstoichiometry index, concentrations of ions residing at different charge states) was determined using the modified model of effective cation–anion distances. The data obtained provide some evidence that in Ti-containing manganites when Sr concentration is more than 0.375, single-charged oxygen ions can arise after reductive annealing.

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1. Introduction

Manganites with perovskite-type structure, as functional magnetic materials, are usually developed on the basis of La–Sr system with substitution for Mn of other metals. The mechanisms of phase formation in manganites of complex compositions and their properties are concerning with the concentration of different-valence ions, their localization and radii, and the oxygen content, which is associated with the occurrence of anion or cation vacancies [1–5]. The oxide solid solutions $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ are known to display oxygen-excess nonstoichiometry under the synthesis on air at the temperatures of about 900–1200 °C [1]. The electronic conductivity of these manganites is of *p*-type for $x < 0.5$ [1]. But concentration of the holes, their localization and mobility are the problems under consideration. Most often it is assumed that the charge compensation of divalent impurities is due to transition $\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$. However, there is the possibility of the compensation by the formation of single-charged ions of oxygen O^- [1, 6, 7]. In this case, the holes are of oxygen type, the excitation of the pair electron–hole means the transition of charge from *p*-level of oxygen at the *d*-level of manganese, and conductivity realizes in the anion sublattice [6, 8].

Previously reported results [9] showed that sintered at 1200 °C on air ceramic manganites of the system $\text{La}_{1-c-x}\text{Sr}_{c+x}\text{Mn}_{1-x}\text{Me}^{4+x}\text{O}_{3+\gamma}$ (Me = Ge^{4+} or Ti^{4+} , $c = 0.15, 0.17, 0.19$; $x \leq 0.125$) had an excess of oxygen content over stoichiometric one, that promoted the existence of rhombohedral and metallic phases. Concentration transition “semiconductor–metal” displaced in the region of higher “*c*”. Metal-similar state of manganites is more stable to substitution of Ge for Mn than of Ti.

In this paper, the regularities of the influence of Ge^{4+} , Ti^{4+} and oxygen concentrations on the parameters of defect structure of manganites were established by using the modified Poix method of unit cell volume calculation [10, 11], and the data on saturation magnetization, Curie point and electrical conductance of ceramic manganites $\text{La}_{1-c-x}\text{Sr}_{c+x}\text{Mn}_{1-c-x-2\gamma}\text{Mn}_{c+2\gamma}\text{Me}_x^{4+}\text{O}_{3+\gamma}$ ($0.17 \leq c \leq 0.35$; $0.025 \leq x \leq 0.125$). In this system the concentration of Mn^{4+} ions is independent of substituent quantity under the condition that oxygen content is stoichiometric ($\gamma = 0$).

2. Experimental

The experiments were performed on polycrystalline samples synthesized by traditional ceramic processing, included two grindings in a ball mill with addition of alcohol, preliminary burning at 1273 K for 4 h [9]. 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 $P_{\text{O}_2} = 10^{-1}$ Pa for 96 h. The choice of annealing conditions was based on the data of the work [1].

Phase composition and cell parameters were determined by powder X-ray diffraction at room temperature (diffractometer Shimadzu XRD-7000, Cu K_α radiation). The magnetization (per mass unit, σ , emu/g) was measured in magnetic field of 5.6 kOe. Measurements of dc electrical characteristics were made using copper electrodes sputter-deposited onto opposite planes of pellets. The Curie point (T_c) was determined as the temperature corresponding to the maximum of $|\text{d}\mu/\text{d}T|$, where $\mu(T)$ is magnetic permeability as a function of temperature.

3. Results and discussion

All synthesized manganites were single phase and crystallized in the rhombohedral structure. Table summarizes the unit cell volume (*v*), “metal–semiconductor”

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transition temperature (T_{ms}) for annealed samples. In addition, this table shows the increments of corresponding physical values (Δv , ΔT_{ms}) after annealing as regards initial (sintered) samples.

TABLE

Crystal chemistry parameters, and transition temperature T_{ms} of manganites after annealing.

Me	c	x	v [\AA^3]	Δv [\AA^3]	$\Delta\gamma$	T_{ms} [K]	ΔT_{ms} [K]
Ge	0.17	0.075	58.825	0.112	-0.010	185	-52
		0.025	58.785	0.000	0.000	175	-95
	0.19	0.050	58.727	0.000	0.000	173	-94
		0.075	58.640	0.001	-0.001	180	-80
		0.100	58.602	0.069	-0.005	217	-38
Ti	0.20	0.050	59.066	0.255	-0.024	181	11
		0.075	58.994	0.184	-0.017	130	>20
	0.30	0.050	58.566	0.042	-0.005	242	69
		0.025	58.329	0.029	-0.003	255	27
	0.35	0.050	58.352	0.013	-0.001	235	70
		0.075	58.282	0.017	-0.002	263	64
		0.100	58.267	0.011	-0.001	207	62
		0.125	58.251	0.015	-0.001	172	>72

Increment of nonstoichiometry index ($\Delta\gamma$) after annealing was calculated using Poix's model of characteristic cation-anion distances [10], modified by Kesler [11]. Poix's method assumes the dense packing of anions. Because perovskites ABO_3 are characterized by the absence of dense packing of oxygen ions, Kesler proposed the amendments to the characteristic distances, considering mixed cation-anion packing AO_3 as a topologically equivalent, and taking into account the difference of interionic distances in the octahedral sites of perovskites of different families — $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ and $\text{A}^{2+}\text{B}^{4+}\text{O}_3$.

Nonstoichiometric compounds can be considered as solid solutions, components of which are ions and point defects, so it is possible to calculate average values of characteristic distances for sublattices of manganites with the allowance for cation and anion vacancies.

In consideration of Kesler's corrections, effective characteristic cation-anion distances in octahedral sublattice will have following values: $\beta_{\text{Mn}^{3+}} = 1.99 \text{ \AA}$, $\beta_{\text{Mn}^{4+}} = 1.83 \text{ \AA}$; $\beta_{\text{Ti}^{4+}} = 1.94 \text{ \AA}$; $\beta_{\text{Ge}^{4+}} = 1.84 \text{ \AA}$; $\beta_{\square} = 2.248 \text{ \AA}$. For ions with coordination number 12 characteristic distances are equal to: $\theta_{\text{La}} = 2.72 \text{ \AA}$; $\theta_{\text{Sr}} = 2.80 \text{ \AA}$; $\theta_{\square} = 2.52 \text{ \AA}$. Here \square is cation vacancy.

In the crystal lattice of perovskites interionic distances (β_i , θ_j) and unit cell volume are connected by the equality $[(\sqrt{2} + 1)/2]v^{1/3} = \sum(C_{\text{VI}})_i\beta_i + \sum(C_{\text{XII}})_j\theta_j$, $\sum(C_{\text{VI}})_i = \sum(C_{\text{XII}})_j = 1$, where $(C_{\text{VI}})_i$, $(C_{\text{XII}})_j$ are the fractions (in formula units) of cations in corresponding sublattices.

Let us take into account cation vacancies existing in manganites with $\gamma > 0$. In the most likely case, vacancies are allocated among sublattices uniformly, and structural

formula at $\gamma \ll 1$ can be written as $\{\text{La}_{(1-c-x)(1-\gamma/3)}^{3+}\text{Sr}_{(c+x)(1-\gamma/3)}^{2+}\square_{\gamma/3}\}[\text{Mn}_{(1-x-c-2\gamma)(1-\gamma/3)}^{3+}\text{Mn}_{(c+2\gamma)(1-\gamma/3)}^{4+}\text{Me}_{x(1-\gamma/3)}^{4+}\text{O}_3^{2-}]$. The increment of unit cell volume as a function of c , x and γ is

$$\begin{aligned} \Delta v^{(3)} \approx & (\partial v/\partial c)\Delta c + (\partial v/\partial x)\Delta x + (\partial v/\partial \gamma)\Delta \gamma = \\ & 3v^{2/3}[(-0.066+0.038\gamma)\Delta c \\ & + (0.8285\beta_{\text{Me}^{4+}} - 1.5824 + 0.543\gamma - 0.276\gamma\beta_{\text{Me}^{4+}})\Delta x \\ & - (0.248 - 0.038c - 0.543x + 0.276x\beta_{\text{Me}^{4+}})\Delta \gamma]. \end{aligned}$$

Then, for Me = Ti,

$$\begin{aligned} \Delta v^{(3)} \approx & 3v^{2/3}[(-0.066+0.038\gamma)\Delta c \\ & + (0.0248+0.008\gamma)\Delta x - (0.248 - 0.038c - 0.008x)\Delta \gamma], \end{aligned}$$

and for Me = Ge

$$\begin{aligned} \Delta v^{(3)} \approx & 3v^{2/3}[(-0.066+0.038\gamma)\Delta c \\ & - (0.066 - 0.039\gamma)\Delta x - (0.248 - 0.038c - 0.039x)\Delta \gamma]. \end{aligned}$$

Last equations were used for the evaluation of $\Delta\gamma$ from experimental values of Δv (Table). One can see that concentrations of oxygen (and, correspondingly, of cation vacancies) in initial samples reduce with c and Ti concentration increasing, but rise with increase of Ge amount.

Experimental data indicate that unit cell volume of all annealed manganites decreases as a function of x at fixed c , and as a function of c at fixed x . These results are in agreement with the theory for Ge-substituted manganites, but the dependence of v on Ti concentration at $c = \text{const}$, $\gamma = 0$ contradicts to calculations, as $\partial v/\partial x \approx 0.074v^{2/3} > 0$.

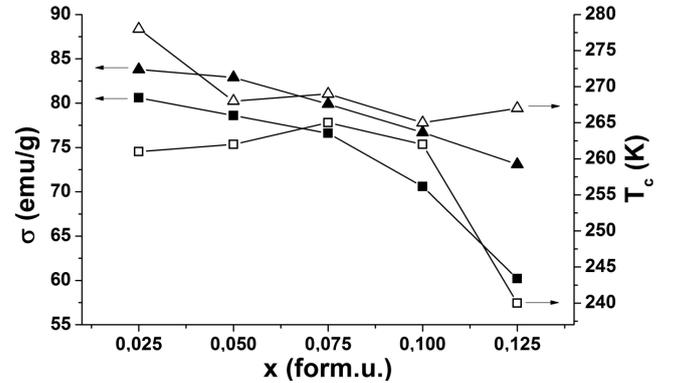


Fig. 1. Dependences of magnetization (\blacksquare , \blacktriangle) and of Curie point (\square , \triangle) upon concentration of substituents for annealed manganites: \blacksquare , \square — Me = Ti, $c = 0.35$; \blacktriangle , \triangle — Me = Ge, $c = 0.19$.

In Fig. 1 concentration dependences of magnetization and of Curie point for annealed Ti- and Ge-containing manganites are shown. Ge-substituted manganites have higher values of σ , T_c , and show less sharp decrease of these parameters as functions of x than Ti-containing compositions with higher concentration of Mn^{4+} . Taking

into account that after annealing of Ti-containing manganites T_c and σ increase at $c \leq 0.30$ and decrease at $c = 0.35$, while T_{ms} essentially rises (in contrast to Ge-substituted manganites, Table), we assume that charge compensation in manganites with $c = 0.35$ after reductive annealing realizes by means of formation of single-charged oxygen O^- ions, the content of which increases with increase of Ti concentration. In this case, structural formula of manganites at small value of O^- concentration ε can be written as $\{La_{(1-c-x)}^{3+}Sr_{(c+x)}^{2+}\} [Mn_{(1-x-c+\varepsilon)}^{3+}Mn_{(c-\varepsilon)}^{4+}Me_x^{4+}]O_{(3-\varepsilon)}^{2-}O_{\varepsilon}^-$. According to [7], the radius of single-charged oxygen ion may be accepted as 1.1 Å. Then the change of unit cell volume with O^- concentration may be expressed by the formula: $\Delta v^{(3)} \approx -0.036\varepsilon v^{2/3}$.

From the difference between experimental values of $v(x)$ and calculated ones without allowance for O^- presence (Fig. 2) the single-charged oxygen ions concentration $\varepsilon(x)$ was estimated for Ti-substituted manganite at $c = 0.35$. The results are given in Fig. 2.

The presence of anion vacancies here is hardly possible, because in this case ferromagnetic properties and characteristics of conductivity would sharply deteriorate [2, 12], which is not observed in our case.

In germanium-containing manganites after annealing T_c increases slightly, magnetization decreases, T_{ms} greatly reduces and varies nonmonotonically with x increasing because of various competitive actions.

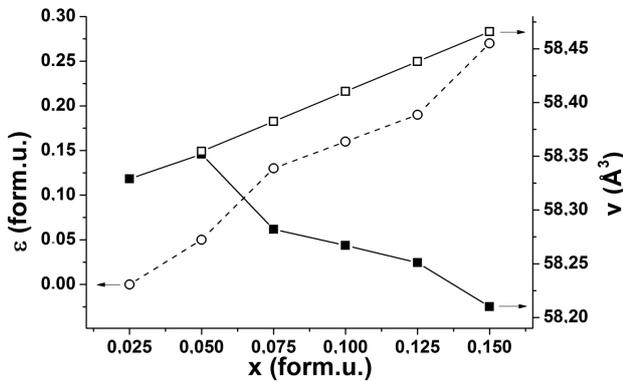


Fig. 2. Calculated concentration of single-charged oxygen ions (formula units, \circ), and unit cell volume of annealed Ti-substituted manganites: \blacksquare — experimental; \square — calculated without allowance for O^- presence.

4. Conclusions

>From the analysis of the data obtained it might be inferred that substituting $Ge^{4+}(3d^{10})$ and $Ti^{4+}(3p^6)$ ions in manganites of specifically designed systems $La_{1-c-x}Sr_{c+x}Mn_{1-x}Me_x^{4+}O_3$ have different effects on the structure, properties and mechanisms of charge compensation, especially at high concentration of strontium, that is associated with electronic configurations of these ions and thermodynamics of solid-atmospheric oxygen interaction. So, unlike titanium [13], germanium increases

the oxygen content in the manganites at the chosen conditions of synthesis. It is possible to conclude that when the concentration of Sr is greater than 0.375, in Ti-containing manganites single-charged oxygen ions occur after reductive annealing, the number of which increases with increase of titanium content. Simultaneously, a significant increase of the metal-semiconductor temperature T_{ms} takes place. Perhaps this is due to the hybridization of the d -levels of manganese and p -levels of titanium, just as it is in the interaction of manganese with oxygen [6, 14]. As a result, Ti then can take part in the processes of charge transfer.

Nonmonotonic variation of T_{ms} with x may be ascribed to a combination of various factors, such as diamagnetic dilution of octahedral sublattice, the change of lattice parameters c/a ratio, steric factor alteration and formation of clusters [9].

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