DOI: 10.15826/chimtech.2015.2.4.031

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Oxygen non-stoichiometry and defect structure of $LaMn_{1-z}Cu_zO_{3+\delta}$

The quantitative model analysis of the defect structure of copper doped lanthanum manganites $LaMn_{1-z}CuzO_{3+\delta}$ (z = 0.05 and 0.1) was performed. In the framework of the model, the independent course of the three reactions of defect formation, including the electronic exchange between manganese and copper, completion of a lattice by the absorption of oxygen and the disproportionation of manganese was considered. It is shown that the increase in the dopant content leads to a change in the dominant electronic process. This is reflected in the lock and disproportionation and leads to the increase in the concentration of holes and decrease the concentration of electrons localized on the manganese atoms.

Keywords: lanthanum manganites; oxygen non-stoichiometry; thermodynamic characteristics of reactions; disproportionation

Introduction

The study of lanthanum manganite $LaMnO_{3\pm\delta}$ started with published in 1950, the work of Jonker and van Santena Santena [1] and has continued at present. The reason is that lanthanum manganites, partially doped alkaline earth metals, mainly calcium or strontium, are today indispensable cathode materials for high-temperature fuel cells [1, 2, 3]. Lanthanum manganites with partial substitution of manganese for other 3d-metals have been studied less.

However, the isomorphic substitution of manganese for copper leads to a substantial change of the magnetic and catalytic performance of lanthanum manganite [4], most likely due to the increased lability of the oxygen sublattice [5] and presence of 3d-metal in mixed oxidation states [4]. In his early work [6] we have analyzed the oxygen non-stoichiometry $LaMn_{1-z}Cu_zO_{3+\delta}$ and proposed a model of its defect structure. However, quantitative analysis of this model was not performed. In this paper, we present the results of this analysis.

Theory

As oxygen non-stoichiometry of copper substituted lanthanum manganites are studied exclusively in the area of excess oxygen, the modeling of the defect structure in these manganites is only for this area. According to Jonker [7], if in $LaMnO_{3+\delta}$ Mn is substituted for copper, which is more electronegative 3d-metal, we should expect the reaction.

$$Mn_{Mn}^{\times} + Cu_{Mn}^{\times} = Mn_{Mn}^{\circ} + Cu_{Mn}^{/} \quad (1)$$

with the equilibrium constant

$$K_1 = \frac{[Mn_{Mn}^{\circ}][Cu_{Mn}^{/}]}{[Mn_{Mn}^{\times}][Cu_{Mn}^{\times}]},$$

where $Cu_{Mn}^{\times}$ и $Cu_{Mn}^{/}$ – Cu^{+3} и Cu^{+2}, accordingly recorded in the system of Kroger-Vinca. Taking into account the reaction of completing the grid

$$6Mn_{Mn}^{\times} + \frac{3}{2}O_2 \Leftrightarrow V_{La}^{///} + V_{Mn}^{///} + 3O_O^{\times} + 6Mn_{Mn}^{\circ} \quad (2)$$

with the equilibrium constant

$$K_2 = \frac{\left[O_O^{\times}\right]^3 \cdot \left[V_{La}^{///}\right] \cdot \left[V_{Mn}^{///}\right] \cdot \left[Mn_{Mn}^{\circ}\right]^6}{\left[Mn_{Mn}^{\times}\right]^6 \cdot p_{O_2}^{3/2}},$$

where $Mn_{Mn}^{\times}$ и Mn_{Mn}° – Mn^{+3} и Mn^{+4}, respectively, as well as the disproportionation of manganese

$$2Mn_{Mn}^{\times} \Leftrightarrow Mn_{Mn}^{\circ} + Mn_{Mn}^{/} \quad (3)$$

with the equilibrium constant

$$K_3 = \frac{\left[Mn_{Mn}^{\circ}\right] \cdot \left[Mn_{Mn}^{/}\right]}{\left[Mn_{Mn}^{\times}\right]^2},$$

where $2Mn_{Mn}^{\times} \Leftrightarrow Mn_{Mn}^{\circ} + Mn_{Mn}^{/}$, together with the relevant conditions of mass balance and electroneutrality, we obtain the system of equations that defines the model of the defect structure of $LaMn_{1-z}Cu_zO_{3+\delta}$

$$\begin{aligned}
&K_1 = \frac{\left[Mn_{Mn}^{\circ}\right] \cdot \left[Cu_{Mn}^{/}\right]}{\left[Mn_{Mn}^{\times}\right] \cdot \left[Cu_{Mn}^{\times}\right]} = K_1^0 \exp\left(-\frac{\Delta H_1}{RT}\right) \\
&K_2 = \frac{\left[O_O^{\times}\right]^3 \cdot \left[V_{La}^{///}\right] \cdot \left[V_{Mn}^{///}\right] \cdot \left[Mn_{Mn}^{\circ}\right]^6}{\left[Mn_{Mn}^{\times}\right]^6 \cdot p_{O_2}^{3/2}} = K_2^0 \exp\left(-\frac{\Delta H_2}{RT}\right) \\
&K_3 = \frac{\left[Mn_{Mn}^{\circ}\right] \cdot \left[Mn_{Mn}^{/}\right]}{\left[Mn_{Mn}^{\times}\right]^2} = K_3^0 \cdot \exp\left(-\frac{\Delta H_3}{RT}\right) \\
&3\left[V_{Mn}^{///}\right] \quad 3\left[V_{La}^{///}\right] \quad \left[Mn_{Mn}^{/}\right] = \left[Mn_{Mn}^{\circ}\right] \\
&\left[Mn_{Mn}^{\circ}\right] \quad \left[Mn_{Mn}^{/}\right] \quad \left[Mn_{Mn}^{\times}\right] = \frac{(1-z)\cdot 3}{3 \quad \delta} \\
&\left[Cu_{Mn}^{/}\right] \quad \left[Cu_{Mn}^{\times}\right] = \frac{z \cdot 3}{3 \quad \delta} \\
&\left[V_{La}^{///}\right] = \left[V_{Mn}^{///}\right] = \frac{\delta}{3 \quad \delta} \\
&\left[O_O^{\times}\right] = 3
\end{aligned} \quad (4)$$

The solution of system (5) is rather complicated dependence of the general form,

$$\begin{aligned}
&\log(pO_2 / \text{atm}) = f(\delta), \\
&K_3 = f(T), K_1 = f(T), K_2 = f(T)
\end{aligned} \quad (5)$$

the explicit form which because of its bulkiness was omitted in the text.

Results and discussion

In Fig. 1, 2 there are the dependences of the absolute oxygen non stoichiometry of substituted manganites $LaMn_{1z}Cu_zO_{3+\delta}$, where $z = 0.05$ and 0.10, respectively, from the partial pressure of oxygen and temperature.

It follows from these figures that in the whole studied range of temperatures and pressures of oxygen manganite $LaMn_{0.95}Cu_{0.05}O_{3+\delta}$ and $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ remain beyond stoichiometric on oxygen.

For $LaMn_{0.80}Cu_{0.20}O_{3\pm\delta}$ was set to [6], that the value of the oxygen content varies slightly, decreasing from 3.024 at 1173 K in a pure oxygen atmosphere to a value almost equal to three for $\log(p_{O2}/\text{атм}) = -2.76$ and $T = 1373$ K. The sample $LaMn_{0.70}Cu_{0.30}O_{3+\delta}$ has been investigated [6] only in the environment of air in the

temperature interval 1173 – 1473 K. The obtained data showed that in all investigated temperature interval, the sample remained stoichiometric relative to the oxygen.

In Fig. 1 and 2 the results of the verification of the model, according to equation (5), $LaMn_{1-z}Cu_zO_{3+\delta}$ are shown using temperature dependences of the equilibrium constants (see system (4)). The parameters of the corresponding temperature dependences obtained by minimizing the deviation of model surfaces from experimental data, together with correlation coefficients are summarized in table 1. As can be seen from this table and Fig. 1, between the values of pO_2 calculated by the proposed model and defined experimentally, good agreement is observed.

It follows from table 1 that the addition of copper (z=0.05 and 0.10) in $LaMnO_{3+\delta}$ practically does not change the thermodynamic characteristics of reactions of completion of construction of the lattice of perovskite (2) compared with neoperabelny manganite of lanthanum [8]. A small addition of copper (z = 0.05) in $LaMnO_{3+\delta}$ has little impact on the course of the disproportionation of manganese (3), as this enthalpy of this reaction increases slightly. However, the increase in copper (z = 0.10) is expressed in a dramatic change in the process of disproportionation (3), which acquires a pronounced thermally activated character, as evidenced by the anomalously large value of enthalpy, *k J* 6000, compared to almost zero enthalpy of disproportionation to unsubstituted $LaMnO_{3+\delta}$ [8]. It should be noted that the equilibrium constant of reaction (4) for $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ in the temperature interval investigated takes extremely low values, varying from 10 to 60 at 1173 K up to 1373 K. Therefore, the equilibrium in the disproportionation of (3) is almost completely shifted to manganese ions Mn+3. Therefore, is reasonable to simplify the model of the defect structure of $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ by removing from consideration the disproportionation of manganese. The corresponding simplification of the system (4) leads to a relatively simple model equation.

$$\log(p_{O_2}/\text{atm}) = -\frac{\left(\frac{\delta}{3+\delta}\right)^{\frac{1}{3}}\cdot\sqrt{3}\cdot\left(\frac{6\cdot\delta}{3+\delta}-\frac{A}{2}\right)\cdot(3+\delta)}{(-2.7+6.9\delta-\frac{3}{2}A-\frac{1}{2}A\delta)\cdot K_2^{\frac{1}{6}}}, \qquad (6)$$

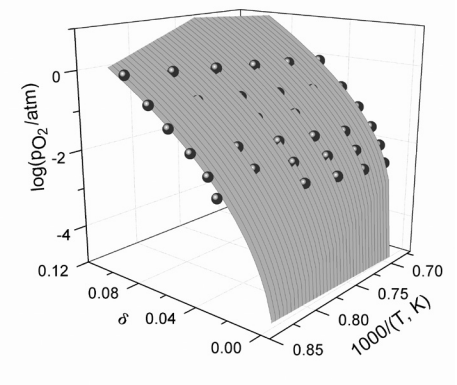

Fig. 1. The result of the model analysis of the defect structure of LaMn0.95Cu0.05O3+δ. Filled symbols – experiment [6]; surface corresponds to the equation (5)

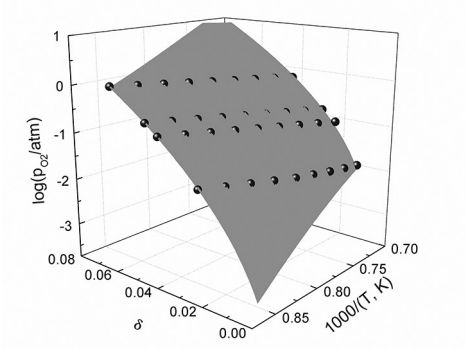

Fig. 2. The result of the model analysis of the defect structure of $LaMn_{0.9}Cu_{0.1}O_{3+\delta}$. Filled symbols – experiment [6]; surface corresponds to the equation (5)

where $A = \frac{7K_{2\,Mn\,Cu}\delta - 6\delta - 3K_{2\,Mn\,Cu} + \sqrt{B}}{(K_{2\,Mn\,Cu} - 1)\cdot(3+\delta)}$ и

$B = (46.24\delta^2 + 5.76 - 32.64\delta)K_{2\,Mn\,Cu}^2 +$

$+(26.64\delta^2 + 3.24 - 81.24\delta)K_{2\,Mn\,Cu} + 36\delta^2$

The results of the verification of a simplified model of the defect structure of $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ according to equation (6) are also presented in table 1. As can be seen, for this model the correlation coefficient R^2 was significantly closer to 1 compared with a model taking into account reaction (3). It should be added that the sum of squared deviations for the model which corresponds to equation (6) is 0.068, while for the sought model considering reaction (3) is 0.224. Therefore further calculations of concentrations of defects for $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ was carried

Table 1

The values of thermodynamic parameters temperature dependences of the equilibrium constants of the processes of disordering $LaMn_{1-z}Cu_zO_{3+\delta}$

z	Equation	Reaction	ΔH, $\frac{kj}{mol}$	$ln(K_0)_i$	R^2
0.05	5	3	85.1	1.53	0.996
		1	52.8	14.2	
		2	–293.4	–38.0	
0.1	5	3	6000	477	0.976
		1	118.0	29.3	
		2	–242.6	–34.2	
0.1	6	1	178±33	14.9±3	0.994
		2	–163±30	–29.5±3	

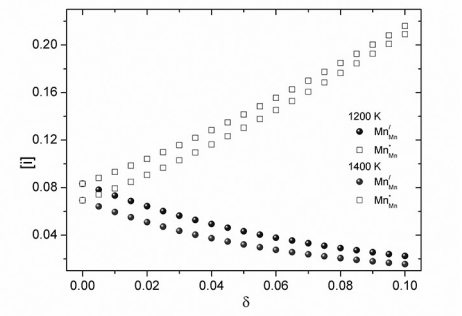

Fig. 3. The dependence of the concentration of electronic defects in $LaMnO_{3+\delta}$ from oxygen non stoichiometry [8] at different temperatures

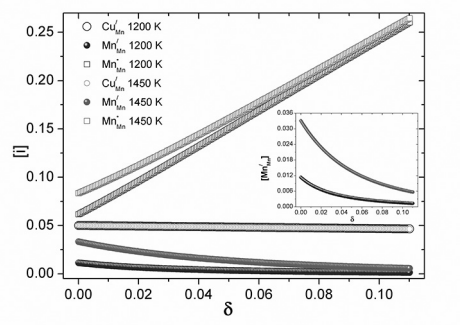

Fig. 4. The dependence of the concentration of electronic defects $LaMn_{0.95}Cu_{0.05}O_{3+\delta}$ from oxygen non stoichiometry at different temperatures

out on the basis of results of model analysis of equation (6).

As an example in Fig. 3–6 the dependencies of the concentration of localized electronic defects from oxygen nonstoichiometry $LaMn_{1z}Cu_zO_{3+\delta}$ are z = 0, 0.05 and 0.1, respectively. For comparative purposes, based on the concentration of holes localized on the manganese atoms, the magnitude of δ for various compositions $LaMn_{1z}Cu_zO_{3+\delta}$ is shown in Fig. 6.

As can be seen from these drawings, the addition of copper in $LaMnO_{3+\delta}$ leads to a noticeable change in the electronic disordering manganese sublattice, which is reflected in the increase in the concentration of holes and decrease of the concentration of electrons localized on the manganese atoms.

The concentration of electrons localized at the copper atoms is almost constant in the whole area of excess oxygen for manganite $LaMn_{0.95}Cu_{0.05}O_{3+\delta}$ and does not depend on temperature, being equal to the total copper content, whereas this value for $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ varies in a wide interval when changing the oxygen content and temperature.

The observed increase in the content of Mn^{+4} in the lanthanum manganite when it is doped with copper is consistent with the findings of [9], made on the basis of the redox titration of samples of copper substituted lanthanum manganites. Found in the present work, the change in the concentration of Cu^{+2} for $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ depending on the oxygen index and temperature beyond stoichiometric indirectly supported by the results of [10], which is obtained for this composition range x-ray photoelectron spectroscopy was unable to decipher in the assumption that all copper is located only in the state +2. At the same time the authors [10] found the absence of Mn^{+2} in $LaMn_{0.90}Cu_{0.10}O_{3+\delta}$ is consistent with the results of the model analysis of the defect structure of the manganite which is made in the present work.

Conclusions

Doping of the lanthanum manganite of copper has a significant impact primarily on the oxygen content and its electronic subsystem. This is observed in the consecutive change of the dominant electronic process from the dispropor-

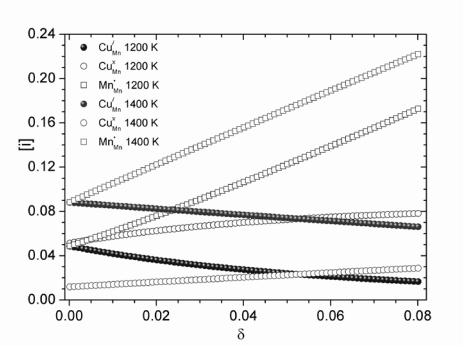

Fig. 5. The dependence of the concentration of electronic defects $LaMn_{0.9}Cu_{0.1}O_{3+\delta}$ from oxygen non stoichiometry at different temperatures

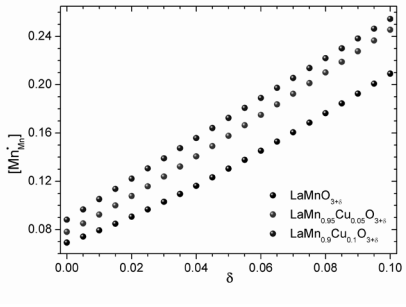

Fig. 6. The dependence of the concentration of electronic defects $LaMn_{1-z}Cu_zO_{3+\delta}$ from oxygen non stoichiometry at different temperatures

tionation of manganese to the reaction of the electronic exchange between the manganese and copper increases the content in $LaMn_{1-z}Cu_zO_{3+\delta}$, and decrease in oxygen content. When the concentration of the dopant is $z = 0.3$, the response of the electronic exchange between manganese and copper, apparently, is the only process of disordering $LaMn_{1-z}Cu_zO_3$, that is expressed in its stoichiometric composition of oxygen in the whole studied range of temperature.

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