PHASE RELATIONS IN THE La(Sr)-Mn-Cu-O SYSTEM AND OXYGEN NONSTOICHIOMETRY OF COPPER-SUBSTITUTED LANTHANUM MANGANATES

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ABSTRACT

The phase relations in La-Mn-Cu-O system have been studied in air at 1373 K. The solid solution \( \text{La}_{1+z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} \) formed in the system with compositional range \(-0.04 < z < +0.12\) and \( 0.0 < x < 0.55\). Oxygen nonstoichiometry of \( \text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y} \) has been studied as a function of temperature (1150 - 1423 K) and oxygen pressure (10^{-3} \text{ atm} < P_{O_2} < 1). Metal nonstoichiometry (z) in copper substituted lanthanum manganates decreased with Cu-content increase. The solubility of manganese ions in \( \text{La}_2\text{CuO}_4 \) was not founded. The solubility regions of Cu - ions in strontium doped lanthanum manganates are \( x_{\text{Cu}} \approx 0.50 \) (for \( \text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3+y} \)) and \( x_{\text{Cu}} \approx 0.10 \) (for \( \text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3+y} \)). A defect model for copper-substituted lanthanum manganates \( \text{La}_{1+z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} \) is proposed. The important point defects in Cu-doped lanthanum manganates are concluded to comprise metal vacancies \( V'^{m}_{\text{La}} \), \( V'^{m}_{\text{Mn}} \), and electron defects which localized on 3d-metals (\( \text{Mn}^{3+} \) and \( \text{Cu}^{2+} \)).

1. INTRODUCTION

Great prospects for application of alkali earth doped lanthanum manganates in high temperature electrochemical devices have arisen a number of problems, concerning of the phase relations in La-M-Mn-Me-O system (M=Ca, Sr, Ba; Me=Co, Cu), their stability and compatibility at used conditions, heat treatment in orders to obtain materials with reproducible properties. However, an information about physico-chemical properties (ranges of phase stability, crystal structure of single phases, electrical and magnetic properties) and their relations to chemical composition, temperature and pressure are insufficient. These applies to four component La-Mn-Cu-O system. The phase equilibrium of only ternary system La-Mn-O (1-3), La-Cu-O (7-9), Mn-Cu-O (10,11) or doped by alkali earth metal La-M-Mn-O (4-6) and La-M-Cu-O (11) are studied in detail. There is little information on phase relations in the four component La-Mn-Cu-O system. It is known that partial replacement of manganese by...
copper in LaMnxCu_xO_{3+y} up to x=0.6 preserves the perovskite structure and leads to a high catalytic activity (14, 15).

In the present work, a systematic study of phase relation in four component La-Mn-Cu-O system and oxygen nonstoichiometry of mixed oxide LaMn_{0.9}Cu_{0.1}O_{3+y} has been carried out.

2. EXPERIMENTAL

Lanthanum oxide La_{2}O_{3} manganese oxide Mn_{2}O_{3}, and copper oxide CuO, with purities not less than 99.99% were used as starting materials. The specimens of appropriate composition with the fixed values of atom fraction of metals \( \xi_{La} \), \( \xi_{Mn} \), \( \xi_{Cu} \) (\( \xi_{La} = \frac{n_{La}}{n_{La} + n_{Mn} + n_{Cu}} \)) were prepared. Here \( n_{La} \), \( n_{Mn} \), and \( n_{Cu} \) are the numbers of moles of metals. The standard ceramic processing with three-stage firing in temperature range 1123-1373 K for 24 hrs at each stage was used for the sample preparation. At the last stage at the temperature 1373 K the samples were fired in air until the equilibrium state was reached and then were quenched to room temperature.

Phase identification and structural measurements were carried out by X-ray diffraction (XRD) method using Cu-K_{\alpha} radiation.

Oxygen nonstoichiometry was studied by means of thermogravimetry by equilibrating the specimens in flowing air - argon mixtures. Oxygen pressure was controlled by oxygen sensor (ZrO_{2}-Y_{2}O_{3}). Equilibrium were approached by both decreasing and increasing oxygen activities or temperature. The reversibility of mass changes proved that there were no other exchange between the solid and gas phases except those involving oxygen.

The absolute values of the oxygen nonstoichiometry were found by two procedures: by complete reduction of the samples in hydrogen and from the results of the iodometric titration (16).

3. RESULTS AND DISCUSSION

3.1. Phase relations at 1373 K in air.

\( (LaO_{1.5})-CuO \) system. Only one binary oxide La_{2}CuO_{4} with the K_{2}NiF_{4} - type structure is formed in air at 1373 K. According to our previous data (9) LaCuO_{2} with the CaFeO_{2} - type structure is stable below 1373 K at low oxygen pressure. The samples with 0.72<\( \xi_{Cu} >0.34 \) were consisted of CuO, La_{2}CuO_{4} and 1>\( \xi_{Cu} >0.72 \) of liquid phase.

\( (MnO_{1.5})-CuO \) system. In order to identify X-ray diffraction data of the samples with small lanthanum content MnO-CuO system were examined. The
formation of several solid solution (12, 13) was confirmed. The solid solutions marked as H, S, C and D has a hausmanite-type ($\alpha$-Mn$_3$O$_4$), a spinele-type (CuMn$_2$O$_4$), crederite-type (CuMnO$_2$) and delafossite-type structure, correspondingly.

($\text{LaO}_1.5$)-($\text{MnO}_1.5$) system. It is well known that the nonstoichiometric lanthanum manganate La$_{1\pm z}$Mn$_{3+y}$ with perovskite-like structure is formed for experimental conditions. According to the results of XRD patterns of the samples quenched in air from 1373 K the region of metal nonstoichiometry of the single phase is $0.48 \leq z \leq 0.56$. These data are in good agreement with literature (5).

($\text{LaO}_1.5$)-($\text{MnO}_1.5$)-CuO system. In lanthanum manganate manganese ions can be substituted by copper and LaMn$_{1-x}$Cu$_x$O$_{3+y}$ solid solution forms as a results. The structure behavior of LaMn$_{1+y}$ is very complicate (5) and lanthanum manganate can crystallized in either orthorhombic or rhombohedral symmetry, depending on the value of oxygen nonstoichiometry ($y=\frac{[\text{Mn}^{4+}]}{2}$). All investigated single phases in the copper-substituted lanthanum manganates La$_{1\pm z}$($\text{Mn}_{1-x}\text{Cu}_x$)O$_{3+y}$ system had orthorhombically distorted perovskite-like structure. The homogeneity range ($x$) in LaMn$_{1-x}$Cu$_x$O$_{3+y}$ have been refined as $0 \leq x \leq 0.55$ in relation to $x_{\text{Cu}}=0.6$ (14).

The initial refinements of X-ray diffraction data were carried out in the orthorhombic structure. The results are given in Table 1. While the Cu content increase the lattice constants slightly decrease. According to the approach proposed for LaMn$_{3+y}$ (5), the relationship between unit cell volume ($V$) and concentration of Mn$^{4+}$ ions ($[\text{Mn}^{4+}]=2y$) were described by the linear function ($V=(244.86-68.81\cdot y) \times 10^{-24}\text{cm}^3$). Following this conclusion partial replacement of manganese by copper leads to increase of Mn$^{4+}$ ions from $[\text{Mn}^{4+}]=0.15$ (in LaMn$_{0.9}$Cu$_{0.1}$O$_{3+y}$) to $[\text{Mn}^{4+}]=0.28$ (in LaMn$_{0.45}$Cu$_{0.55}$O$_{3+y}$)

| x    | a, 10$^{-8}$cm | b, 10$^{-8}$cm | c, 10$^{-8}$cm | V, 10$^{-24}\text{cm}^3$ |
|------|---------------|---------------|---------------|-----------------|
| 0.10 | 5.5127        | 5.6549        | 7.6796        | 239.4           |
| 0.30 | 5.5052        | 5.6463        | 7.7297        | 240.3           |
| 0.40 | 5.4849        | 5.6246        | 7.6230        | 235.2           |
| 0.45 | 5.4861        | 5.6280        | 7.7094        | 238.0           |
| 0.50 | 5.4785        | 5.6127        | 7.6429        | 235.4           |
| 0.55 | 5.4776        | 5.6104        | 7.6481        | 235.0           |

The solubility of manganese ions in La$_2$CuO$_4$ was not found. All samples with composition $x_{\text{Mn}}=n_{\text{Mn}}/(n_{\text{Cu}}+n_{\text{Mn}})<0.05$ were found to be mixtures of lanthanum oxide La$_2$O$_3$ and complex La$_{1.04}$($\text{Mn}_{0.58}\text{Cu}_{0.42}$)O$_{3+y}$ oxide.
The phase diagram of \((\text{LaO}_{1.5})-(\text{MnO}_{1.5})-\text{CuO}\) system was represented using the relative mole fraction of the metal content \(\xi = n_i / \sum n_i\). Oxygen content in solid phases have not been taken into account. The cross section of phase diagram as compositional triangle is shown in Fig. 1.

\((\text{LaO}_{1.5})-\text{SrO}-(\text{MnO}_{1.5})-\text{CuO}\) system. In addition the solubility of copper ions in \(\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3+y}\) and \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}\) were studied. According to the results of XRD patterns of the quenched samples in air the regions of solubility are \(x_{\text{Cu}} \leq 0.50\) for \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\) and \(x_{\text{Cu}} \leq 0.10\) for \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\). Inspection of the X-ray diffraction profiles shows that both series of samples are satisfactorily described by the rhombohedral system. The results are given in Table 2. While the Sr-content in lanthanum manganate increases the solubility of copper decreased considerably from \(x_{\text{Cu}} \leq 0.50\) in \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\) to \(x_{\text{Cu}} \leq 0.10\) in \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\).

Table 2. Lattice Parameters of \(\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\) and \(\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Cu}_{x}\text{O}_{3+y}\).

| \(x\) | \(a, 10^{-8}\text{cm}\) | \(\alpha^0\) | \(V, 10^{-24}\text{cm}^3\) |
|------|------------------|----------|------------------|
| 0.2  | 7.7716           | 90.058   | 469.3            |
| 0.3  | 7.7702           | 90.229   | 469.1            |
| 0.4  | 7.7386           | 90.564   | 463.4            |
| 0.5  | 7.7123           | 90.806   | 458.6            |

| \(x\) | \(a, 10^{-8}\text{cm}\) | \(\alpha^0\) | \(V, 10^{-24}\text{cm}^3\) |
|------|------------------|----------|------------------|
| 0.0  | 7.7597           | 90.37    | 467.1            |
| 0.1  | 7.7397           | 90.23    | 463.6            |

3.2. Oxygen nonstoichiometry of the mixed oxide \(\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}\).

The variation of oxygen nonstoichiometry in \(\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}\) was measured as a function of temperature at different oxygen pressure from \(6.17 \times 10^{-3}\) to 1 atm at different temperature. The oxygen content as a function of temperature at different oxygen pressures is shown at Fig. 2. Isothermal cross sections of temperature dependencies give us the plots of oxygen nonstoichiometry vs oxygen partial pressure (Fig. 3).

As follows from experimental data lanthanum manganate doped by copper \(\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}\) at near atmospheric pressure contains an oxygen excess. The transformation from oxygen excess to oxygen deficient oxide takes place at high temperature and low oxygen pressure.
The oxide systems studied exhibit a complex behavior as regards the
dependence of oxygen nonstoichiometry on the relative Cu content, temperature and
oxygen pressure. In this respect it is of interest to consider the defect structure of
these systems.

The important point defects in oxygen excess LaMn_{1-x}Cu_xO_3+\delta at near atmospheric
oxygen pressure are concluded to comprise metal vacancies \( V^{\prime \prime}_{La} \) and \( V^{\prime \prime \prime}_{Mn} \). The defect
equation for formation of metal vacancies and the corresponding defect equilibrium
may be written (17-20) as follows

\[
6Mn^{\prime \prime \prime}_{Mn} + \frac{3}{2}O_2 = V^{\prime \prime}_{La} + V^{\prime \prime \prime}_{Mn} + 6Mn^{\ast}_{Mn} + 3O^{\ast\ast}_0;
\]

\[
K_i = \frac{[V^{\prime \prime}_{La}][V^{\prime \prime \prime}_{Mn}][Mn^{\ast}_{Mn}]^6}{[Mn^{\prime \prime \prime}_{Mn}]^6P^{\delta}_{O_2}}
\]

The greater affinity of copper ions for free electrons in Cu-doped lanthanum
manganates LaMn_{1-x}Cu_xO_3+\delta leads to a changing oxidation state of copper from
Cu^{+3} \((Cu^{+3}_{Cu})\) to Cu^{+2} \((Cu^{+2}_{Cu}) = x\).

For this defect model the electroneutrality condition for LaMn_{1-x}Cu_xO_3+\delta is
given by

\[
[Mn^{\ast}_{Mn}] = 3[V^{\prime \prime}_{La}] + 3[V^{\prime \prime \prime}_{Mn}] + [Cu^{+2}_{Mn}]
\]

At sufficiently high oxygen activities the concentrations of point defects may
be expressed by oxygen excess \((y>0)\)

\[
[V^{\prime \prime}_{La}] = [V^{\prime \prime \prime}_{Mn}] = \frac{y}{3}
\]

\[
[Mn^{\ast}_{Mn}] = a0.1 + 2y
\]

\[
[Mn^{\prime \prime \prime}_{Mn}] = 0.8 - a0.1 - 2y
\]

\[
[O^{\ast\ast}_0] = 3 + y
\]

The equilibrium constant is written as

\[
K_i = \frac{(a0.1 + 2y)^6y^2(3 + y)^2}{3^2(0.8 - a0.1 - 2y)^6P^{\delta}_{O_2}} = F_i(y, a)P^{1.5}_{O_2}
\]

here “a” is the fraction of Cu^{+2} ions, i.e. \([Cu^{+2}_{Mn}] = ax; x = 0.1\).

The applicability of this model was tested using normalized axis for the oxygen
pressure. The data \(y\) vs. \(\log P_{O_2}\) were transformed to \(y\) vs. \(\log(P_{O_2}/P'_{O_2})\); where
\(\log(P_{O_2}/P'_{O_2})\) is a normalized axis, \(P_{O_2}\) and \(P'_{O_2}\) are the current oxygen pressure and

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oxygen pressure for some fixed oxygen nonstoichiometry \((y=y_1=\text{Const.})\), respectively. As an example, the normalized data for a chosen fixed value of \(y=0.02\) (oxygen content 3.02) for all temperatures are shown by means of points in Fig.4 (the dotted and solid lines will be discussed later). Oxygen pressure for this fixed nonstoichiometry are equal 6.16 \(10^{-3}\) atm (1173 K), 3.98 \(10^{-2}\) atm (1273 K), 0.178 atm (1373 K), and 0.426 atm (1473 K), respectively.

The curves obtained at different temperatures were transformed to a single master curve. Normalized axis is rather useful for compact presentation of experimental data and comparison with different theoretical curves. If the defect structure is the same under all experimental conditions the results at different temperatures are expected to be transformed to a single master curve where a fixed value of \(y_1\) has been chosen as a reference value.

In terms of normalized axis Eq.5 can be transformed as follow:

\[
\log \left( \frac{P_{O_2}}{P_{O_1}} \right) = \frac{2}{3} \left( \log F_1(y,a) - \log F_1(y_1 = 0.02, a) \right)
\]  

[6]

Theoretical curves at different values of “a” \((a=1.0; 0.75\) and 0.5) and experimental data are shown in Fig.4. As seen the experimental data of \(\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}\) and theoretical curve fit each other quite well in the region \(y>0.01\) at \(a=0.75\).

The mean values of logarithm of \(K_1\) (at a=0.75) have been plotted as a function of the reciprocal absolute temperature in Fig.5. This plot gives a value of 337±3 kJ/mol for the defect reactions 1 (Eq.5).

4. CONCLUSION

The phase relations in La-Mn-Cu-O system have been studied in air at 1373 K. The cross section of the phase diagram \((\text{LaO}_{1.5})-(\text{MnO}_{1.5})-\text{CuO}\) system was represented using relative mole fraction of the metal content \(\xi = n_i / \sum n_i\). Oxygen content in solid phases have not been taken into account. The solid solution \(\text{La}_{1+2x}\text{(Mn}_{1-x}\text{Cu}_{x})\text{O}_{3+y}\) formed in the system with compositional range \(-0.04 \leq x \leq +0.12\) and \(0.0 < x < 0.55\). Single phases in \(\text{La(Mn}_{1-x}\text{Cu}_{x})\text{O}_{3+y}\) system are shown orthorhombically distorted perovskite-like structure. The solubility of copper ions in \(\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3+y}\) and \(\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3+y}\) were studied. Oxygen nonstoichiometry of \(\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}\) has been studied. The oxygen excess (the value of \(y>0\)) decreases with increasing temperature and low oxygen pressure. It was proposed the defect model which satisfactorily describes experimental data. The equilibrium constants and enthalpies of defects formations were calculated.
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Fig. 1. The phase diagram of La-Mn-Cu-O system at 1100°C in air. The phase composition in the fields are:
1. \( \text{La}_2\text{O}_3 + \text{La}_2\text{CuO}_4 + \text{La}_{1.04}(\text{Mn}_{0.58}\text{Cu}_{0.42})\text{O}_{3+y} \);
2. \( \text{La}_2\text{O}_3 + \text{La}_{1+z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} \);
3. Single phase \( \text{La}_{1+z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} \);
4. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{H} \);
5. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{H} + \text{S} \);
6. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{S} \);
7. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{S} + \text{C} \);
8. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{C} \);
9. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{C} + \text{D} \);
10. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{D} \);
11. \( \text{La}_{1-z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} + \text{D} + \text{Liquid} \);
12. \( \text{La}_2\text{CuO}_4 + \text{LaMn}_{0.45}\text{Cu}_{0.55}\text{O}_{3+y} + \text{Liquid} \);
13. \( \text{La}_2\text{CuO}_4 + \text{La}_{1+z}(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3+y} (0 \leq z \leq 0.04) \);
14. \( \text{La}_2\text{CuO}_4 + \text{Liquid} \);
15. Liquid phase;
16. Liquid + D.
Fig. 2. Oxygen content in LaMn$_{0.9}$Cu$_{0.1}$O$_{3+y}$ as function of temperature at different oxygen pressures.

Fig. 3. Oxygen content in LaMn$_{0.9}$Cu$_{0.1}$O$_{3+y}$ as function of oxygen partial pressure at different temperatures.
Fig. 4. Oxygen nonstoichiometry of $\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_{3+y}$ at different temperature versus normalized ($y_i=0.02$) axis.

Fig. 5. The logarithm of $K_1$ (at $a=0.75$) as a function of the reciprocal absolute temperature.

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