THE MODELING OF THE DEFECT STRUCTURE OF LnMnO$_{3+x}$ (Ln=Pr, Nd)

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ABSTRACT

The modeling of the defect structure of LnMeO$_{3+x}$ (Me=Pr, Nd) has been made based on the results obtained by high temperature TGA. It was shown that results are very sensitive to the Ln:Mn ratio which can change during the preparation procedure. The homogeneity range in the praseodymium manganite was found to exist in the metal sublattices. The Pr:Mn ratio can vary from 0.85:1 to 1:0.9 at 1100°C in air.

INTRODUCTION

The phase equilibria in the Ln-Mn-O system and oxygen nonstoichiometry of LnMnO$_{3+x}$ (Ln=Pr, Nd) have been studied recently (1,2). TGA together with neutron diffraction measurements have shown that the oxygen excess is realized by the vacancies in the metal sublattices. Similar results were obtained earlier for LaMnO$_{3+x}$ (3-7).

The results of structural refinement of LnMnO$_{3+x}$ (Ln=Pr, Nd) gave the probabilities of metal atom occupation, which have led to the following formulas: Pr$_{0.95}$Mn$_{0.94}$O$_3$ and Nd$_{0.97}$Mn$_{0.95}$O$_3$ (2). Based on these results the modeling of defect structure of praseodymium and neodymium manganites has been carried out in the present work. We also checked the ability of praseodymium manganite to form a homogeneity range in metal components, found for LaMnO$_3$ (5,8,9).

EXPERIMENTAL

The details of TGA experiments, results and dependencies of oxygen nonstoichiometry versus temperature and oxygen partial pressure were presented in (2).

The samples for determination of the homogeneity range in metal components were prepared from Pr$_2$O$_3$ and Mn$_2$O$_3$ as starting materials. They were mixed in appropriate ratios. All mixtures were fired at 850°C for 24 hrs., 950°C for 24 hrs. and at 1100°C for...
100 hrs. with intermediate grinding. The crystal structure of the samples was obtained from X-ray diffraction measurements using UM-1 diffractometer with copper radiation.

**RESULTS AND DISCUSSION**

If we assume that the defects in LnMnO$_3$+$\delta$ are lanthanum and manganese vacancies in equal amount, as was done by Kuo et al. [4], the process of oxygen intercalation to the ideal crystal can be written as follows (model I):

$$LnMnO_3 + \frac{\delta}{2} O_2 = \{Ln(V'_{La})_{\delta/3}\} \{Mn^{3+}_{l-2\delta}\} Mn^{4+}_{2\delta} (V''_{Mn})_{\delta/3} O_{\delta + \delta} =$$

$$= \frac{2\delta}{3} \left[Ln_{3(3+3\delta)} (V''_{La})_{\delta/(3+3\delta)} \{Mn^{3+}_{3(1-2\delta)/(3+3\delta)} Mn^{4+}_{6\delta/(3+3\delta)} (V''_{Mn})_{\delta/(3+3\delta)} O_{3}\right]$$  \[1\]

In terms of Kroger and Vink notation this process can be written as follows:

$$6Mn^{3+}_{Mn} + \frac{3}{2} O_2 = 3O^{2-}_{O} + V''_{La} + V''_{Mn} + 6Mn^{4+}_{Mn}$$  \[2\]

The equilibrium constant of this process is:

$$K_1 = \frac{[O^{2-}_{O}][V''_{La}][V''_{Mn}][Mn^{4+}_{Mn}]}{[Mn^{3+}_{Mn}]}$$  \[3\]

Using the equilibrium concentrations of the defects in accordance with equation (1) the equilibrium constant can be transformed to the form:

$$K_1 = \frac{3^3\delta^2 (2\delta)^6}{(1-2\delta)^6 (3+\delta)^2} P^{\frac{2}{3}}_{O_2}$$  \[4\]

A comparison of model I with experimental results in coordinates log(P$_{O_2}$)-f(\delta) using the procedure of nonlinear curve fitting in program Microcalc “Origin 5.0” shows poor correlation. Same results were obtained by Roosmalen et al. for LaMnO$_3$+$\delta$ (6). In order to improve correlation with the experimental results, Roosmalen et al. (6,7) suggested to take into account the process of charge disproportionation by following formula:

$$LaMnO_3 = LaMn^{2+}_{x}Mn^{3+}_{1-2\delta} Mn^{4+}_{\xi}O_3$$  \[5\]

here $\xi$ is the amount of Mn$^{2+}$ or Mn$^{4+}$, that is formed by the charge disproportionation. Combining equation [5] with atomic disorder process:

$$6Mn^{3+}_{Mn} + \frac{3}{2} O_2 = 3O^{2-}_{O} + V''_{La} + V''_{Mn} + 6Mn^{4+}_{Mn}$$  \[6\]

They assumed that the concentration of Mn$^{4+}$ ions remained constant, i.e. the value of $\xi$=const. This assumption seems to be questionable. The process of charge disproportionation can be written as follows:

$$2Mn^{2+}_{Mn} = Mn^{4+}_{Mn} + Mn^{3+}_{Mn}$$  \[7\]

The equilibrium constant for reaction [7] is represented by

$$K_2 = \frac{[Mn^{4+}][Mn^{3+}]}{[Mn^{2+}]}$$  \[8\]

It is easy to see that at constant temperature simultaneous decrease of Mn$^{2+}$ concentration together with the increase of Mn$^{3+}$ concentration (according to reaction [6]) has to change...
the concentration of Mn$^{4+}$ ions (eq. [8]). Moreover, reactions [2], [6] and [7] are not independent. Any of them can be obtained as the combination of other two. We decided to make calculations taking into account both reactions [2] and [7] (or reactions [7] and [8] which is the same) as model II. An appearance of three variables (the concentration of Mn$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$ ions) significantly complicated the presentation of the dependence of $P_{O_2}=f(\delta)$ or $\log(P_{O_2})=f(\delta)$ in the form of one equation. However, the system of equations can be solved using the program “Scientist”. Using the equations [4] and [8] together with the mass balance in the form:

$$[Mn^+] + [Mn^{2+}] + [Mn^{3+}] + [V_{Mn}^{\text{m}}] = 1$$  \[9\]

and the equation of electroneutrality:

$$[Mn^+] + 3[V_{La}^{\text{m}}] + 3[V_{Mn}^{\text{m}}] = [Mn^{2+}]$$ \[10\]
a fitting of the model (II) with the experimental data has been done. Obtained results showed that model (II) was not suited well to the experimental results. It is interesting to note that $K_1$ varied during fitting to some magnitude, while the value of $K_2$ did not influence the results. This confirms that the process of charge disproportionation did not much affect the defect structure as a whole in the range of defect concentration under consideration.

It was shown earlier that LaMnO$_{3+x}$ has relatively wide homogeneity range in metal components (5,8,9). The La:Mn ratio can deviate significantly from 1:1 in both directions. Praseodymium deficient manganite of the general formula Pr$_{1-x}$Mn$_{1+x}$O$_3$ with $x=0.08$ was obtained in (10). Neutron diffraction measurements of PrMnO$_{3+x}$ and NdMnO$_{3+y}$ showed nonequivalent occupation of La and Mn positions in the lattice (2). The formulas of manganites derived from the neutron diffraction measurements were Pr$_{0.95}$Mn$_{0.94}$O$_3$ or Nd$_{0.97}$Mn$_{0.95}$O$_3$.

In order to check the existence of the homogeneity range in praseodymium manganite a series of samples with the Pr:Mn ratio equal to 1:0.80; 1:0.85; 1:0.90; 1:0.95; 1:1; 0.95:1; and 0.85:1 was prepared according to the scheme mentioned above. According to XRD all samples were single phase. Thus the homogeneity range at 1100°C in air can be expressed as Pr$_{1-x}$Mn$_{1+x}$O$_3$ with $-0.8 \leq x \leq 0.17$. The unit cell parameters versus composition are shown in Fig.1. One can see that the sample mixed as 1:1, probably has a composition which differs from expected one.

Unexpected deviation from the stoichiometry in the metal sublattices can be caused by a number of reasons such as: errors in the weighing of starting materials or errors in the mixing, coprecipitation, losses during washing during wet techniques; high hygroscopicity of the lanthanum oxide; possible reactions of oxides with the material of crucibles, etc.

Let's assume that the initial deficit of manganese with respect to Ln:Mn=1:1 ratio in the complex oxide is equal to $\alpha$. Then reaction (1) will transform to following:

$$\text{LnMn}^{3+}_{(3a)} + \text{Mn}^{4+}_{(3b)} (V_{Mn}^{\text{m}})_{(3\delta)} O_3 + \frac{\delta}{3} O_2 = \text{Ln}(V_{La}^{\text{m}})_{(3\delta)} \{\text{Mn}^{3+}_{(3a-2\delta)} \text{Mn}^{4+}_{(3a+2\delta)} (V_{Mn}^{\text{m}})_{(3\delta)} O_3\}$$

$$= \frac{2\delta}{3} \left[ (\text{Ln})_{(3+\delta)} (V_{La}^{\text{m}})_{(3+\delta)} \{\text{Mn}^{3+}_{(3\delta-2\delta)} \text{Mn}^{4+}_{(3\delta+2\delta)} (V_{Mn}^{\text{m}})_{(3\delta)} O_3\} \right]$$ \[11\]

Electrochemical Society Proceedings Volume 99-19 391
Fig. 1  The unit cell parameters for the samples with general composition PrMn$_{1-x}$O$_{3-\delta}$. Short dash – expected stoichiometry in the metal sublattices, long dash – nominal stoichiometry point.

In this case the quasichemical reaction of disordering process which leads to formula [11] can be represented by equation [2] and equilibrium constant by formula [3]. However the substitution of the equilibrium defect concentrations from [11] to equation [3] gives (model III):

$$K_3 = \frac{3^3 \delta (3a + \delta)(3a + 2\delta)^6}{(1-4a-2\delta)^6(3+\delta)^2} \frac{P_{ox}^{3+}}{P_{ox}^{4+}}$$ \hspace{1cm} [12]

here $a$ is the initial deficit of manganese with respect to Ln:Mn=1:1 ratio in the complex oxide.

It should be noted that the deficit of lanthanide with respect to Ln:Mn=1:1 ratio in the complex oxide practically does not change the equation of equilibrium constant after the substitution of correspondent defect concentrations in comparison with [12]:

$$Ln_{1-a}(V_{La}^{3+})_a Mn^{4+}_{3a-3\delta}O_{3\delta} + \frac{3}{2} O_2 = \{Ln(V_{La}^{3+})_{a+2/3}\} \{Mn^{4+}_{3a+2\delta} (V_{Mn}^{3+})_{3/3}\} O_{3+5} =$$

$$= \frac{3\delta}{3} \left[ \{Ln_{3(1-a)/(3+\delta)}(V_{La}^{3+})_{3a+2\delta/(3+\delta)}\} \{Mn^{4+}_{3(3a+2\delta)/(3+\delta)} (V_{Mn}^{3+})_{3(3+\delta)}\} O_{3+5} \right]$$ \hspace{1cm} [13]
A comparison of model III with experimental results in coordinates log(Po2)-f(δ) using the procedure of nonlinear curve fitting in program Microcalc "Origin 5.0" shows their good correlation (Fig.2). Because in model III two parameters have been statistically fitted at the same time, it is not strange that the value of parameter a, which should be constant for one sample and independent of different temperatures, was slightly different for different isotherms. Using the values of parameter a obtained in the first round, the mean value $\bar{a}$ was calculated. Then second round of calculations with fixed mean parameter $\bar{a}$, where only equilibrium constant was fitted, has been made.

Obtained values of the equilibrium constants for different temperatures were in good linear fashion in log ($K$)=f(1/T) coordinates (Fig.3). The calculations by least square method according to equation log $K$ = $-\Delta H^o$ 1 $R$ $T$ + Const allowed to evaluate the enthalpy of disordering processes. Obtained values of equilibrium constants $K_3$ and parameter $a$ are listed in Table I. Despite the fact that different samples were used for TGA and neutron diffraction measurements, the values of parameter $a$ were close to each other and did not contradict the homogeneity range found for praseodymium manganite.

Table I
The values of parameter $a$ and equilibrium constants $K_3$ for the disordering process (11) in PrMn$_{1-a}$O$_3$ according to the model III.

| T,K | First round | Second round |
|-----|-------------|--------------|
|     | $a$ | $K_3$ | $\chi^2$ | $\bar{a}$ | $\chi^2$ | $K_3$ | $\chi^2$ | $\Delta H^o$ kJ/mole |
| 1170 | 0.0269 | 0.00027 | 0.0013 | 0.00006 | 0.0160 | -257.3 |
| 1220 | 0.0231 | 0.00005 | 0.0015 | 0.00002 | 0.0076 | || |
| 1300 | 0.0190 | 4.382*10^-6 | 0.0019 | 0.018 | 3.507*10^-6 | 0.0174 | 75.0 |
| 1370 | 0.0159 | 5.677*10^-7 | 0.051 | 9.682*10^-7 | 0.0403 | 75.0 |
| 1470 | 0.0092 | 1.836*10^-8 | 0.053 | 3.049*10^-7 | 0.0825 | 75.0 |

Here $\chi^2$ is the correlation factor in the Levenberg-Marquardt algorithm in nonlinear least squares fitting.

SUMMARY

The dynamics of defect concentration changes in rare earth manganites is strongly dependent on the Ln/Mn ratio in these oxides, which can vary over wide ranges. Unexpected deviations from the required ratio can lead to un reproducibility of the results from different samples.
Fig. 2 Experimental results and nonlinear curve fitting for PrMnO$_{3+x}$
Fig. 3 Temperature dependence of the equilibrium constant for the reaction according model III.

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