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The Defect Chemistry of $LaMnO_{3\pm\delta}$

4. Defect Model for $LaMnO_{3+\delta}$

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The defect model for $LaMnO_{3+\delta}$ has been studied. The defects that are formed in $LaMnO_{3+\delta}$ are La and Mn vacancies in equal amounts. Thermogravimetric analyses indicate that the relation between composition (δ) and oxygen partial pressure can be described by charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}. The same model holds for $(La,Sr)MnO_{3+\delta}$.

1. INTRODUCTION

In the previous parts of this series a defect model for $LaMnO_{3-\delta}$ (1), structural aspects of the defects in $LaMnO_{3+\delta}$ (2), and the density of $(La,A)MnO_{3+\delta}$, A = Ca, Sr, Ba (3), have been described. In this part a defect model is proposed that describes the relation between composition (δ) and oxygen partial pressure (p_{O_2}) for $LaMnO_{3+\delta}$. Finally, in part 5 the thermodynamics of the defect chemistry of $LaMnO_{3\pm\delta}$ will be discussed (4).

2. EXPERIMENTAL

The defect chemistry of $(La,Sr)MnO_{3+\delta}$ was studied by thermogravimetric analysis (TGA) between 1010 and 1290 K. $(La,Sr)MnO_{3+\delta}$ powders were obtained by a coprecipitation method described elsewhere (3). A Cahn D-101 digital recording balance was used to measure the weight changes of the samples of about 1 g with an accuracy of ±10 μg. The sample was placed in a Pt crucible and suspended from the balance by a Pt wire leading into a quartz tube positioned in a vertical furnace. Oxygen partial pressures between 1 and 1×10^{-4} atm were obtained by mixing oxygen with argon. For reduction of the samples 5% hydrogen in argon was used.

To obtain absolute values of δ the weight changes have to be related to a reference state. One reference state is the stoichiometric composition $(La,Sr)MnO_{3.000}$. Upon reducing $(La,Sr)MnO_{3+\delta}$ until it decomposes, a characteristic change in the weight loss is observed at the stoichiometric composition. The second reference state is reached upon further reduction, the formal state $(La,Sr)MnO_{2.5}$. The weights of both reference states are in good agreement and are combined to obtain the values of δ from the measurements. The reducing and oxidizing processes were also recorded with high-temperature X-ray diffraction. Upon reduction, at the stoichiometric composition a phase change occurs. Upon further reduction, $LaMnO_3$ decomposes into La_2O_3 and MnO, while $(La,Sr)MnO_3$ decomposes into $(La,Sr)_2MnO_4$ and MnO. The weight loss is fully reversible.

3. DEFECT MODELS

The defects in $LaMnO_{3+\delta}$ are La and Mn vacancies in equal amounts, as follows from neutron and electron diffraction (2) and density measurements (3). The overall defect chemical reaction is therefore:

$$LaMnO_3 + \frac{\delta}{2} O_2 = \frac{3+\delta}{3}\{(La_{3/(3+\delta)}\square_{\delta/(3+\delta)})(Mn_{3/(3+\delta)}\square_{\delta/(3+\delta)})O_3\}. \quad [1]$$

The final defect model that describes the relation between oxygen partial pressure and δ must be based on this overall defect model. Therefore, the defect model used by Shimoyama *et al.* (5) based on La and O vacancies will not be considered here.

Kuo *et al.* (6) used a model with La and Mn vacancies in equal amounts to describe the defect chemistry of $LaMnO_{3+\delta}$.

$$LaMnO_3 + \frac{\delta}{2} O_2 = (La\square'''_{\delta/3})(Mn^{\circ}_{1-2\delta}Mn^{\bullet}_{2\delta}\square'''_{\delta/3})O_{3+\delta}. \quad [2]$$

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This has to be corrected for $O_{3+\delta}$ to $((3+\delta)/3)O_3$, yielding

$$\begin{aligned}(\mathrm{La}\square'''_{\delta/3})(\mathrm{Mn}^{\circ}_{1-2\delta}\mathrm{Mn}^{\bullet}_{2\delta}\square'''_{\delta/3})\mathrm{O}_{3+\delta} &= \frac{3+\delta}{3}\{(\mathrm{La}_{3/(3+\delta)}\square'''_{\delta/(3+\delta)}) \\ &\quad (\mathrm{Mn}^{\circ}_{3\cdot(1-2\delta)/(3+\delta)}\mathrm{Mn}^{\bullet}_{3\cdot 2\delta/(3+\delta)}\square'''_{\delta/(3+\delta)})\mathrm{O}_3\},\end{aligned} \quad [3]$$

or in terms of species participating in the reaction;

$$6\mathrm{Mn}^{3+} + \tfrac{3}{2}\mathrm{O}_2 = 6\mathrm{Mn}^{4+} + 3\mathrm{O}^{2-} + \square_{\mathrm{La}} + \square_{\mathrm{Mn}}, \quad [4]$$

with the equilibrium constant

$$K_1 = \frac{(2\delta)^6 \cdot 3^3 \cdot \delta^2}{(1-2\delta)^6 \cdot (3+\delta)^2 \cdot p_{\mathrm{O}_2}^{3/2}}. \quad [5]$$

Another model in which the La:Mn ratio does not change is the uptake of oxygen at interstitial positions. Although from neutron and electron diffraction (2) and density measurements (3) it is evident that this is hardly likely, this model is included here for completeness:

$$\mathrm{LaMnO}_3 + \frac{\delta}{2}\mathrm{O}_2 = \mathrm{LaMn}^{\circ}_{1-2\delta}\mathrm{Mn}^{\bullet}_{2\delta}\mathrm{O}_3\mathrm{O}''_{i\delta}. \quad [6]$$

The reacting species are

$$2\mathrm{Mn}^{3+} + \tfrac{1}{2}\mathrm{O}_2 = 2\mathrm{Mn}^{4+} + \mathrm{O}_i^{2-}, \quad [7]$$

with the equilibrium constant

$$K_2 = \frac{(2\delta)^2 \cdot \delta}{(1-2\delta)^2 \cdot p_{\mathrm{O}_2}^{3/2}}. \quad [8]$$

There are a number of remarkable features concerning the defect chemistry of $(\mathrm{La,Sr})\mathrm{MnO}_{3+\delta}$ that cannot be explained easily by reaction [3] or by reaction [6]. The overall amount of Mn^{4+} in $(\mathrm{La,Sr})\mathrm{MnO}_{3+\delta}$ does not seem to exceed about 40% of the total amount of Mn. The overall amount of Mn^{4+} is found by

$$[\mathrm{Mn}^{4+}] = 2\delta + x. \quad [9]$$

The literature data on $\mathrm{LaMnO}_{3+\delta}$ does not exceed $\delta = 0.2$. This can be seen especially well in the low-temperature measurements, for instance those of Shimoyama *et al.* (5) In $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_{3+\delta}$ the maximum value of δ seems to decrease as a function of x, to about zero for $x = 0.40$ (7), keeping the maximum overall amount of Mn^{4+} more or less constant.

These features can be described by considering charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}, or in the Kröger–Vink notation

$$\mathrm{LaMnO}_3 = \mathrm{LaMn}'_{\xi}\mathrm{Mn}^{\circ}_{1-2\xi}\mathrm{Mn}^{\bullet}_{\xi}\mathrm{O}_3, \quad [10]$$

in which ξ is the amount of Mn^{2+} and Mn^{4+} that is formed by the charge disproportionation.

Charge disproportionation is not very common, although it has been observed in CaFeO_3 and related compounds ($\mathrm{Fe}^{4+} = \mathrm{Fe}^{3+} + \mathrm{Fe}^{5+}$) (8, 9). It is noteworthy that Fe^{4+} and Mn^{3+} have the same, relatively unstable, $3d^4$ configuration.

By the uptake of oxygen Mn^{2+} is oxidized to Mn^{3+}:

$$6\mathrm{Mn}^{2+} + \tfrac{3}{2}\mathrm{O}_2 = 6\mathrm{Mn}^{3+} + 3\mathrm{O}^{2-} + \square_{\mathrm{La}} + \square_{\mathrm{Mn}}. \quad [11]$$

The complete chemical reaction becomes

$$\begin{aligned}&\mathrm{LaMn}'_{\xi}\mathrm{Mn}^{\circ}_{1-2\xi}\mathrm{Mn}^{\bullet}_{\xi}\mathrm{O}_3 + \frac{\delta}{2}\mathrm{O}_2 \\ &= (\mathrm{La}\square'''_{\delta/3})(\mathrm{Mn}'_{\xi-2\delta}\mathrm{Mn}^{\circ}_{1-2\xi+2\delta}\mathrm{Mn}^{\bullet}_{\xi}\square'''_{\delta/3})\mathrm{O}_{3+\delta} \\ &= \frac{3+\delta}{3}\{(\mathrm{La}_{3/(3+\delta)}\square'''_{\delta/(3+\delta)})(\mathrm{Mn}'_{3\cdot(\xi-2\delta)/(3+\delta)} \\ &\quad \mathrm{Mn}^{\circ}_{3\cdot(1-2\xi+2\delta)/(3+\delta)}\mathrm{Mn}^{\bullet}_{3\xi/(3+\delta)}\square'''_{\delta/(3+\delta)})\,\mathrm{O}_3\}.\end{aligned} \quad [12]$$

The equilibrium constant for reaction (11) is represented by

$$K_3 = \frac{[\mathrm{Mn}^{3+}]^6 \cdot [\mathrm{O}^{2-}]^3 \cdot [\square_{\mathrm{La}}] \cdot [\square_{\mathrm{Mn}}]}{[\mathrm{Mn}^{2+}]^6 \cdot p_{\mathrm{O}_2}^{3/2}} \quad [13]$$

or $K_3 =$

$$\frac{\left(\frac{3\cdot(1-2\xi+2\delta)}{3+\delta}\right)^6 \cdot 3^3 \cdot \left(\frac{\delta}{3+\delta}\right)\cdot\left(\frac{\delta}{3+\delta}\right)}{\left(\frac{3\cdot(\xi-2\delta)}{3+\delta}\right)^6 \cdot p_{\mathrm{O}_2}^{3/2}} = \frac{(1-2\xi+2\delta)^6 \cdot 3^3 \cdot \delta^2}{(\xi-2\delta)^6 \cdot (3+\delta)^2 \cdot p_{\mathrm{O}_2}^{3/2}}. \quad [14]$$

4. TGA MEASUREMENTS

The results obtained by TGA between 1010 and 1290 K are shown in Fig. 1. To test the models only the 1010 and 1290 K results have been used. The values of K_1, K_2,

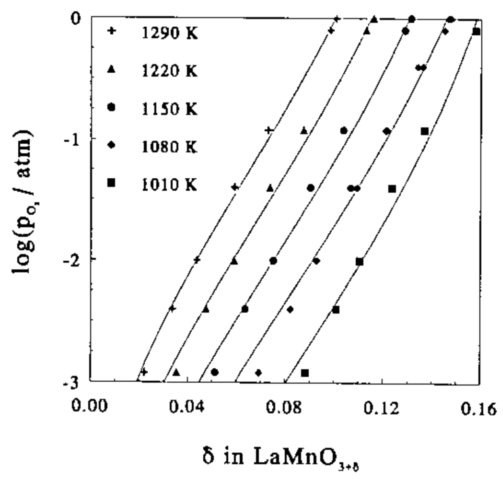

FIG. 1. Results of the thermogravimetrical analyses at 1010, 1080, 1150, 1220, and 1290 K. The data have been fitted according to model 3: charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} in combination with La and Mn vacancies in equal amounts.

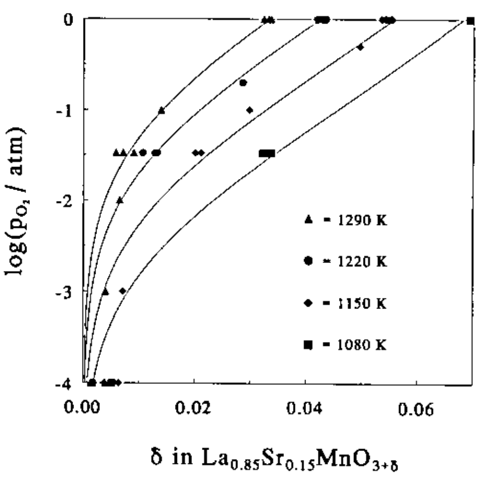

FIG. 3. Results of the thermogravimetrical analyses at 1080, 1150, 1220, and 1290 K for $La_{0.85}Mn_{0.15}O_{3+\delta}$, fitted according to the charge disproportionation model in combination with La and Mn vacancies.

and K_3 are obtained by a nonlinear least-squares analysis of the data. The total error that is made in the determination of δ from the measurements due to, for instance, fluctuations in temperature, weight, and oxygen partial pressure is estimated to be 0.002. In Fig. 2 the TGA results at 1010 and at 1290 K are plotted, together with the best fit of K_1, K_2, and K_3. From this figure it was clear that model 3 gives the best description of the data. This model was used to fit all data obtained by TGA, as can be seen in Fig. 1. The temperature dependence and other thermodynamic properties of defect formation will be discussed elsewhere (4).

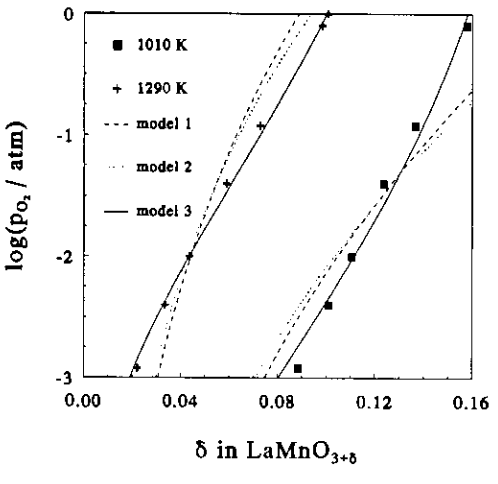

FIG. 2. Results of the thermogravimetrical analyses at 1010 and 1290 K for $LaMnO_{3+\delta}$, fitted according to various models. Model 1, La and Mn vacancies in equal amounts; model 2, interstitial oxygen ions; and model 3, La and Mn vacancies in equal amounts in combination with charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}.

5. THE EFFECT OF STRONTIUM

The radius of Sr^{2+} is about the same as that of La^{3+}. Therefore, Sr is incorporated in the $LaMnO_3$ lattice on the La site. The difference in charge between La^{3+} and Sr^{2+} can be compensated in two ways. The first is formation of Mn^{4+} ions in equal amounts to Sr, the second is the formation of oxygen vacancies, in half of the amount of Sr. In the oxygen excess region the charge is compensated by Mn^{4+} ions. Due to the oxygen excess there are even more Mn^{4+} ions than Sr^{2+} ions. The behavior of $La_{1-x}Sr_xMnO_{3+\delta}$ is very much the same as that of $LaMnO_{3+\delta}$. The same model can be applied to describe the defect chemistry. As mentioned before, the maximum amount of oxygen excess decreases with increasing Sr content, which means that the amount of Mn^{3+} that disproportionates decreases with increasing Sr content.

The same model as that for $LaMnO_{3+\delta}$ holds for $La_{1-x}Sr_xMnO_{3+\delta}$. This means that vacancies are formed on both (La,Sr) and Mn sites:

$$\begin{aligned}
&La_{1-x}Sr'_xMn^{\circ}_{1-x}Mn^{\bullet}_xO_3 + \frac{\delta}{2}O_2 \\
&\quad = \frac{3+\delta}{3}\{(La_{3\cdot(1-x)/(3+\delta)}Sr'_{3x/(3+\delta)}\square'''_{\delta/(3+\delta)}) \\
&\quad\quad (Mn'_{3\cdot(\xi-2\delta)/(3+\delta)}Mn^{\circ}_{3\cdot(1-x-2\xi+2\delta)/(3+\delta)} \\
&\quad\quad\quad Mn^{\bullet}_{3\cdot(x+\xi)/(3+\delta)}\square'''_{\delta/(3+\delta)})\,O_3\}
\end{aligned} \qquad [15]$$

The equilibrium constant becomes

$$K = \frac{(1 - x - 2\xi + 2\delta)^6 \cdot 3^3 \cdot \delta^2}{(\xi - 2\delta)^6 \cdot (3 + \delta)^2 \cdot p_{O_2}^{3/2}} \qquad [16]$$

The experimental results obtained by TGA are plotted in Fig. 3, together with the best fit according to the defect model. It is obvious that our defect model describes the measured data correctly.

6. CONCLUSIONS

Previous results (2, 3) have indicated that the defects formed in $LaMnO_{3+\delta}$ are La and Mn vacancies in equal amounts. A characteristic feature of the defect chemistry of $(La,Sr)MnO_{3\pm\delta}$ is the maximum overall amount of Mn^{4+} of about 40% of the total amount of Mn. This feature can be described by charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+}. The relation between composition (δ) and oxygen partial pressure (p_{O_2}) can be described satisfactory with this model. The amount of Mn^{3+} that is disproportionated seems to decrease with an increase of strontium content.

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