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

## 3. The Density of $(La,A)MnO_{3+\delta}$ ($A$ = Ca, Sr, Ba)

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The density of $La_{1-x}A_xMnO_{3+\delta}$ was determined for $x = 0, 0.15, 0.30$ ($A$ = Ca, Sr, Ba) and for $x = 0.50$ ($A$ = Sr) using a pycnometer, defect chemical considerations, lattice parameters, and chemical analyses. The oxygen excess in $LaMnO_{3+\delta}$ is compensated by both La and Mn vacancies in equal amounts. This is confirmed by density measurements. According to this defect model the density of $LaMnO_{3+\delta}$ is almost independent of $\delta$ for $0 \leq \delta \leq 0.18$ and is calculated to be $(6.57 \pm 0.02)$ g · cm$^{-3}$. The same defect model is applied to calculate the density of $La_{1-x}A_xMnO_{3+\delta}$.

### 1. INTRODUCTION

Sintering is an important step in the fabrication of solid oxide fuel cells (1). Porous components (cathode and anode) as well as dense components (electrolyte and interconnect) are needed for successful operation. The microstructure of the components has great influence on their properties, for instance, on the electrical conductivity (2, 3). To evaluate the sinter behavior of the powders that are used in the component fabrication it is necessary to know their theoretical densities. In the case of $(La,A)MnO_{3\pm\delta}$ ($A$ = Ca, Sr, Ba) the density depends on oxygen content ($\delta$) and $A$-content. To calculate the theoretical densities from the lattice parameters the nature of the lattice defects has to be known. In this article the nature of the defects in $LaMnO_{3+\delta}$ are determined. The densities of $(La,A)MnO_{3\pm\delta}$ ($A$ = Ca, Sr, Ba) with 0, 15, 30, and 50 at.% $A$ are calculated using that particular defect model and lattice parameters.

This article is part of a series discussing the defect chemistry of $LaMnO_{3\pm\delta}$. In part 1 defect models for $LaMnO_{3-\delta}$ are discussed (4). Part 2 and 4 describe the defect chemistry of $LaMnO_{3+\delta}$, structural aspects (5) and defect models (6), respectively. Part 5 deals with the thermodynamics of defect formation of both $LaMnO_{3-\delta}$ and $LaMnO_{3+\delta}$ (7).

### 2. EXPERIMENTAL

The $(La,A)MnO_3$ ($A$ = Ca, Sr, Ba) samples were prepared by a coprecipitation method similar to that described by Hashimoto (8). $La_2O_3$ (Highways International), $MnO_2$ (Baker), $SrCO_3$ (Baker), $CaCO_3$ (Baker), or $BaCO_3$ (Merck) was dissolved in the correct molar proportions in concentrated HCl forming a nearly saturated solution. This solution was added at a rate of 0.5 l · min$^{-1}$ to a threefold excess of a saturated $(NH_4)_2CO_3$ solution which was stirred at 20 Hz. The precipitate was filtered in a Buchner funnel and washed three times with water. The precipitates were dried at 380 K for 16 hr, and powdered and calcined at 1110 K for 16 hr. According to the X-ray diffraction patterns all powders were single phase perovskite-type oxides. The unit cell volumes of the samples were determined using standard X-ray powder diffraction techniques. The $Mn^{3+}/Mn^{4+}$ ratios were determined by redox titrations; chemical analyses indicated that the metal-to-metal ratios did not deviate from the intended values within experimental error.

The density of the $LaMnO_{3+\delta}$ samples was obtained by determining the volume of a known amount of powder in a pycnometer using water. The experiments were performed in a climate room (with a temperature of 20 to 21°C) because the pycnometer volume of about 25 ml was highly sensitive to temperature. The relatively high density of the powders with respect to the pycnometer volume made it necessary to use about 5 g of the powders for each determination. An error in the pycnometer volume of 0.002 ml then causes an error of 0.02 g · cm$^{-3}$, which is acceptable. To avoid trapped voids in the polycrystalline samples the pycnometer was filled in vacuum.

### 3. RESULTS AND DISCUSSION

The X-ray density is defined as

$$d = \frac{M \cdot Z}{V \cdot N}, \qquad [1]$$

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TABLE I

**Defect Models for the Uptake of Oxygen by $LaMnO_3$**

| Model | Description of the model | Formula unit of the model |
|---|---|---|
| 1 | Interstitial oxygen | $LaMnO_{3+\delta} = LaMnO_3O_{i_\delta}$ |
| 2 | Mn vacancies | $LaMn_{(3-2\delta)/3}O_3$ |
| 3 | La and Mn vacancies | $LaMnO_{3+\delta} = \frac{3+\delta}{3}\{La_{3/(3+\delta)}Mn_{3/(3+\delta)}O_3\}$ |
| 4 | La vacancies | $La_{(3-2\delta)/3}MnO_3$ |
| 5 | La and O vacancies | $La_{0.9}MnO_{2.85+\delta}$ |

in which $M$ is the molar mass of the formula unit, $Z$ the number of formula units per unit cell, $V$ the unit cell volume, $N$ the Avogadro constant. Van Roosmalen *et al.* (9) derived the unit cell volume for $LaMnO_3$ (four formula units) as a function of $\delta$:

$$V = (244.86 - 68.81 \cdot \delta) \cdot 10^{-24}\ \mathrm{cm}^3. \qquad [2]$$

The mass per formula unit follows from the defect model. There are a number of possibilities for the excess oxygen ions to be incorporated in the lattice. A possibility is the incorporation of oxygen in the lattice as interstitial oxygen ions (Table I, model 1). This model is hardly likely, since the $LaMnO_3$ structure consists of a close-packed $LaO_3$ lattice with Mn in the $O_6$ octahedral sites. Another possibility is the formation of metal ion vacancies, as in $FeO_{1+\delta}$ (10, 11). There might be Mn vacancies (model 2), La and Mn vacancies (model 3), La vacancies (model 4), or La and oxygen vacancies (model 5). Yet another possibility is crystallographic shear, as in $La_5Ti_5O_7$ (= $LaTiO_{3.4}$) (12). If a similar model would explain the defect chemistry of $LaMnO_{3+\delta}$ it would not be possible to determine the mass per unit cell, nor the unit cell volume.

The density calculated as a function of $\delta$ for the five models is represented in Fig. 1, together with the experimentally determined densities obtained on five different $LaMnO_{3+\delta}$ samples. From the agreement between the observed and calculated densities it is obvious that model 3 is the correct model.[1] This is in good agreement with the results obtained by neutron diffraction and High Resolution Transmission Electron Microscopy (HRTEM) (5). The results of Tofield and Scott (13), obtained by neutron diffraction, seem to indicate a situation intermediate between models 3 and 4, but there are strong indications that their La : Mn ratio was smaller than unity (9). Model 3 was suggested by Kuo *et al.* (14) to describe the defect chemistry of $LaMnO_{3+\delta}$. The actual defect chemistry is a little more complicated, as discussed by van Roosmalen *et al.* (6). Although the defect concentrations can become very large, the interactions between the point defects do not seem to result in defect clusters, like in $LaMnO_{3-\delta}$ (4). Model 5 was suggested by Shimoyama *et al.* (*15*). In model 5 it is assumed that only metal ion vacancies on the La site occur, with a fixed amount of about 10%. With 100% $Mn^{3+}$ there is also a large amount of oxygen vacancies that decreases if oxygen is picked up by the lattice.

According to model 3 the density of $LaMnO_{3+\delta}$ increases linearly from 6.56 g · cm$^{-3}$ for $\delta = 0$ to 6.59 g · cm$^{-3}$ for $\delta = 0.18$. For practical purposes, like in sinter experiments (2, 16), it is convenient to assume that the density is independent of $\delta$. From model 3 it follows that $d = (6.57 \pm 0.02)$ g · cm$^{-3}$ for $LaMnO_{3+\delta}$ for all values of $\delta$. The value of 6.57 g · cm$^{-3}$ is preferred above 6.58 g · cm$^{-3}$, because in practice $\delta$ seldomly exceeds 0.16 (6).

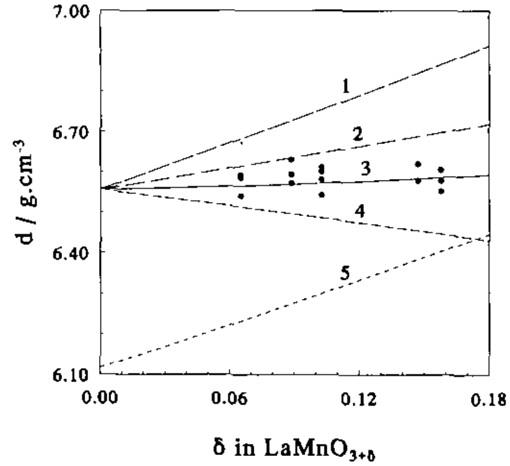

FIG. 1. The density of $LaMnO_{3+\delta}$ as a function of $\delta$ according to five general defect models: (1) Interstitial oxygen, $LaMnO_3O_{i_\delta}$; (2) Mn vacancies, $LaMn_{(3-2\delta)/3}O_3$; (3) La as well as Mn vacancies, $La_{3/(3+\delta)}Mn_{3/(3+\delta)}O_3$; (4) La vacancies, $La_{(3-2\delta)/3}MnO_3$; (5) La as well as O vacancies, $La_{0.9}MnO_{2.85+\delta}$. The measured densities of five $LaMnO_{3+\delta}$ samples are represented by closed circles.

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[1] If one of the models 2, 4, or 5 were the correct model, this would complicate the interpretation of the measured densities, since Mn (model 2) or La (model 4, 5) would be present in a different form from the form represented by the formulae (for instance, as $Mn_2O_3$ or $La_2O_3$). Neither phase separation nor any other form of Mn or La was observed by HRTEM and neutron diffraction.

TABLE II

$Mn^{3+}/Mn^{4+}$ Ratio, Formula Unit, $M$ (Molar Mass of the Formula Unit), $V$ (Volume of the Unit Cell), and $d$ (Calculated Density) for a Number of $La_{1-x}A_xMnO_{3+\delta}$ Samples (Estimated Errors in Parentheses)

| Composition | $Mn^{3+}/Mn^{4+}$ | Formula unit | $M$ (g) | $V$ ($10^{-30}$ m$^3$) | $d$ (g · cm$^{-3}$) |
|---|---|---|---|---|---|
| $La_{1-x}Ca_xMnO_{3+\delta}$ | | | | | |
| $x = 0.15$ | 2.13(1) | $La_{0.827}Ca_{0.146}Mn_{0.972}O_3$ | 222.1245 | 233.09(5) | 6.33(2) |
| $x = 0.30$ | 1.88(1) | $La_{0.694}Ca_{0.298}Mn_{0.992}O_3$ | 210.8410 | 231.52(8) | 6.05(2) |
| $La_{1-x}Sr_xMnO_{3+\delta}$ | | | | | |
| $x = 0.15$ | 1.79(1) | $La_{0.822}Sr_{0.145}Mn_{0.966}O_3$ | 227.9535 | 234.36(4) | 6.46(2) |
| $x = 0.30$ | 1.84(1) | $La_{0.694}Sr_{0.297}Mn_{0.991}O_3$ | 224.8653 | 234.12(3) | 6.38(2) |
| $x = 0.50$ | 1.06(1) | $La_{0.50}Sr_{0.50}MnO_{2.993}$ | 216.0870 | 233.28(8) | 6.15(2) |
| $La_{1-x}Ba_xMnO_{3+\delta}$ | | | | | |
| $x = 0.15$ | 2.63(1) | $La_{0.833}Ba_{0.147}Mn_{0.979}O_3$ | 237.6783 | 238.32(2) | 6.62(2) |
| $x = 0.30$ | 2.04(1) | $La_{0.697}Ba_{0.299}Mn_{0.995}O_3$ | 240.5403 | 239.36(2) | 6.67(2) |

To obtain the density for some $(La,A)MnO_{3+\delta}$ ($A$ = Ca, Sr, Ba) compositions a number of samples have been synthesized. Their composition ($Mn^{3+} : Mn^{4+}$) and unit cell volumes have been determined and are listed in Table II. The defect chemistry of $(La,A)MnO_{3+\delta}$ ($A$ = Sr) can also be described with model 3: $(La,A)_{3/(3+\delta)}Mn_{3/(3+\delta)}O_3$ (6), and probably also holds for Ca and Ba. From model 3 and the chemical compositions the formula units have been determined, and using the unit cell volumes the densities have been calculated (Table II).

As in $LaMnO_{3+\delta}$ the density in $(La,A)MnO_{3+\delta}$ ($A$ = Ca, Sr, Ba) is probably almost independent of $\delta$. This means that the calculated densities as listed in Table II can be used for all values of $\delta$ occurring in practice. This also holds for $La_{0.50}Sr_{0.50}MnO_{3+\delta}$, since the oxygen deficiency of the $La_{0.50}Sr_{0.50}MnO_3$ sample is so small that the effect on the density can be neglected. The density of (6.46 ± 0.02) g · cm$^{-3}$ for $La_{0.85}Sr_{0.15}MnO_{3+\delta}$ is in good agreement with the density of 6.48 g · cm$^{-3}$ that was determined by the Archimedes method for $La_{0.84}Sr_{0.16}MnO_3$ by Kertesz *et al.* (17). Using the densities in Table II, the sinter behavior of $(La,Sr)MnO_3$ can be described nicely (2, 16).

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