The Defect Chemistry of LaMnO$_{3\pm\delta}$

5. Thermodynamics

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The temperature dependence of the relationship between composition and oxygen partial pressure has been described for LaMnO$_{3+\delta}$ and LaMnO$_{3-\delta}$ on the basis of an assessment of literature data obtained by TGA by several authors. The thermodynamics of defect formation is calculated on the basis of these results. For the formation of lanthanum and manganese vacancies in LaMnO$_{3+\delta}$, it has been determined that ΔH°_V = (−380 ± 6) kJ · mole^{-1}, and ΔS°_V = (−266 ± 5) J · mole^{-1} · K^{-1}. For the formation of oxygen vacancy clusters in LaMnO$_{3-\delta}$, ΔH°_V = (349 ± 6) kJ · mole^{-1}, and ΔS°_V = (96.4 ± 4.9) J · mole^{-1} · K^{-1}. © 1994 Academic Press, Inc.

1. INTRODUCTION

This article is the last of a series concerning the defect chemistry of LaMnO$_{3\pm\delta}$. Part 1 was concerned with defect models to describe the relationship between oxygen partial pressure (p_{O_2}) and composition (δ) for LaMnO$_{3-\delta}$ (1). The structural aspects of the defect chemistry of La MnO$_{3+\delta}$ (2) were discussed in Part 2. The results were used to obtain the density of (La,A)MnO$_3$ (A = Ca, Sr, Ba) (3) in Part 3. Part 4 dealt with defect models to describe the relationship between oxygen partial pressure and composition for LaMnO$_{3+\delta}$ (4).

The temperature dependence of the relationship between composition (δ) and oxygen partial pressure (p_{O_2}) is discussed in this article. The results on LaMnO$_{3+\delta}$ obtained by thermogravimetric analysis (TGA) by several authors are discussed. Literature results on LaMnO$_{3-\delta}$ are assessed and compared with literature results obtained on LaCoO$_{3-\delta}$. The thermodynamic properties of the defect reactions and defect formation are derived from this temperature dependence.

2. THERMODYNAMICS OF DEFECT CHEMISTRY

The thermodynamic properties of most interest in this study, $\Delta \overline{H}_{O_2}$, $\Delta \overline{S}_{O_2}$, ΔH°_V, and ΔS°_V, are derived from the

temperature dependence of the relationship between composition (δ) and oxygen partial pressure. ΔH°_V and $\Delta \overline{H}_{O_2}$ stand for the enthalpy of defect formation and the partial oxygen enthalpy, respectively, and likewise for ΔS°_V and $\Delta \overline{S}_{O_2}$. For every defect reaction, ΔH°_V and ΔS°_V are different. Relationships between composition and oxygen partial pressure can be generalized by

$$K_V = p_{O_2}^x \cdot f(\delta) \qquad [1]$$

or

$$\ln K_V = x \ln p_{O_2} + \ln f(\delta) \qquad [2]$$

$$-RT \ln K_V = -xRT \ln p_{O_2} - RT \ln f(\delta) \qquad [3]$$

$$\Delta H_V - T \cdot \Delta S_V = -x\{\Delta \overline{H}_{O_2} - T \cdot \Delta \overline{S}_{O_2}\} - RT \ln f(\delta), \qquad [4]$$

thus,

$$\Delta H^\circ_V = -x\Delta \overline{H}_{O_2} \qquad [5]$$

$$\Delta S^\circ_V = -x\Delta \overline{S}_{O_2} + R \ln f(\delta). \qquad [6]$$

It should be noted that Eqs. [1–6] hold only in situations with one defect model. In the defect regions discussed for LaMnO$_{3-\delta}$ and LaCoO$_{3-\delta}$ (1) and LaMnO$_{3+\delta}$ and La$_{1-x}$Sr$_x$MnO$_{3+\delta}$ (4), there is only one defect model. By plotting ln K versus the reciprocal of temperature for a temperature region with only one defect model, ΔH°_V and ΔS°_V can be found.

3. LaMnO$_{3+\delta}$

The defect chemistry of LaMnO$_{3+\delta}$ is characterized by the formation of lanthanum and manganese vacancies in

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TABLE 1

Equilibrium Constants for LaMnO$_{3+\delta}$, La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$, LaMnO$_{3-\delta}$, and LaCoO$_{3-\delta}$

T	ln K_V	Ref.	T	ln K_V	Ref.	T	ln K_V	Ref.
LaMnO$_{3+\delta}$			1473	0.519	(5)	1473	−17.2	(5)
			1473	2.12	(7)	1473	−18.4	(7)
873	21.7	(9)	1473	−1.06	(9)	1473	−17.0	(9)
923	18.2	(9)	1573	−3.04	(9)	1573	−14.8	(9)
973	14.9	(9)						
1010	12.4	(4)	*La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$*			*LaCoO$_{3-\delta}$*		
1073	10.7	(9)				1123	−12.1	(11)
1080	9.89	(4)	1080	4.85	(4)	1173	−11.2	(11)
1150	7.62	(4)	1150	2.92	(4)	1178	−11.1	(10)
1173	7.27	(9)	1220	0.953	(4)	1200	−10.8	(10)
1188	5.92	(6)	1290	−0.411	(4)	1205	−10.6	(10)
1220	5.59	(4)				1223	−10.3	(11)
1273	2.69	(8)	*LaMnO$_{3-\delta}$*			1226	−10.1	(10)
1273	2.73	(7)				1236	−9.91	(10)
1273	4.09	(9)	1073	−27.5	(9)	1258	−9.54	(10)
1277	3.61	(6)	1173	−24.6	(9)	1268	−9.48	(10)
1290	3.79	(4)	1273	−21.2	(8)	1273	−9.30	(11)
1330	2.63	(6)	1273	−22.8	(7)	1285	−9.18	(10)
1370	1.33	(6)	1273	−21.6	(9)	1300	−8.72	(10)
1373	0.877	(7)	1373	−21.4	(7)	1311	−8.77	(10)
1373	1.55	(9)	1373	−19.1	(9)			

a Obtained by fitting their respective defect models to the experimental data on the relationship between oxygen partial pressure and composition reported by various authors.

equal amounts together with the partial charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} (2–4). For the relationship between composition (δ) and oxygen partial pressure (p_{O_2}) this means

$$K_V = \frac{(1 - 2\xi + 2\delta)^6 \cdot 3^3 \cdot \delta^2}{(\xi - 2\delta)^6 \cdot (3 + \delta)^2} \cdot p_{O_2}^{-3/2}, \qquad [7]$$

in which ξ is a measure for the disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} (4). Experimental data on this relation have been obtained using TGA by Kamata et al. (5), Kamegashira et al. (6), Kuo et al. (7), Nakamura et al. (8), van Roosmalen et al. (4), and Shimoyama et al. (9). At first the results for each individual temperature were analyzed to investigate the behaviour of ξ as a function of temperature. Although the values of ξ vary between 0.33 and 0.38, there are no indications that ξ is temperature dependent, and the average value of 0.352 is used in further calculations. The equilibrium constant then becomes

$$K_V = \frac{(0.296 + 2\delta)^6 \cdot 27 \cdot \delta^2}{(0.352 - 2\delta)^6 \cdot (3 + \delta)^2} \cdot p_{O_2}^{-3/2}. \qquad [8]$$

The values of K are calculated using Eq. [8]. The results are listed in Table 1 and shown in Fig. 1.

The results of Kamata et al. (5), Kuo et al. (7), and Nakamura et al. (8) cannot be described properly with the proposed defect model (Fig. 2). These results will not
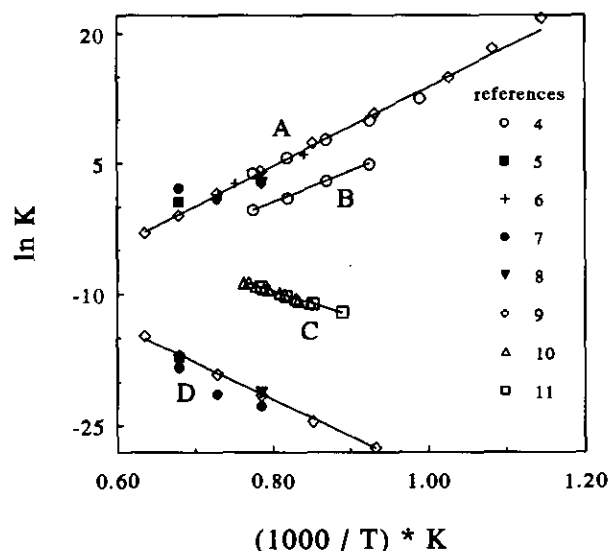
FIG. 1. Equilibrium constants obtained by fitting the experimental data of various authors on the relationship between oxygen partial pressure and composition, for (A) LaMnO$_{3+\delta}$, (B) La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$, (C) LaCoO$_{3-\delta}$, and (D) LaMnO$_{3-\delta}$. By plotting the equilibrium constants as a function of $1/T$, the enthalpies and entropies of defect formation can be obtained.

be used here. The results of Kamegashira et al. (6), van Roosmalen et al. (4), and Shimoyama et al. (9) are in good agreement (see Fig. 2). These results will be used in the calculations, except the 873 K results of Shimoyama et al. (9), because there are only four points in a relatively small experimental region, and they show little connection.

The temperature dependence of K is obtained by plotting $\ln K$ versus $1/T$, a straight line according to theory (Eqs. [3, 4]). The result is shown in Fig. 1, line (A):

$$\ln K_V = \frac{4.57 \times 10^4}{T} - 32.0. \qquad [9]$$

Thus, the thermodynamic properties of defect formation can be obtained for LaMnO$_{3+\delta}$. Using Eqs. [3], [4], and [9], $\Delta H_V^\circ = (-380 \pm 6)$ kJ $\cdot$ mole^{-1} and $\Delta S_V^\circ = (-266 \pm 5)$ J $\cdot$ mole$^{-1} \cdot$ K^{-1} are obtained. Using x (Eq. [1]) $= -3/2$ (Eq. [8]), it follows from Eqs. [5] and [6] that $\Delta \overline{H}_{O_2} = (-253 \pm 4)$ kJ $\cdot$ mole^{-1} and $\Delta \overline{S}_{O_2} = ((-177 \pm 3) - 5.54 \ln f(\delta))$ J $\cdot$ mole$^{-1} \cdot$ K^{-1} ($f(\delta)$ is obtained from Eq. [8]). The thermodynamic properties for the defect chemis-
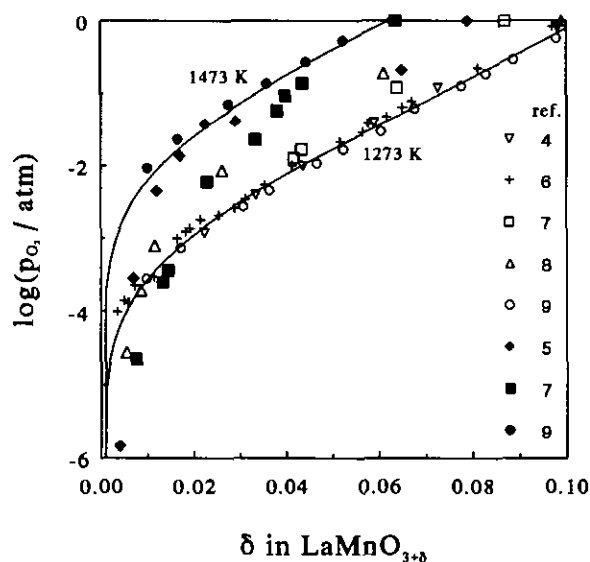

FIG. 2. Experimental data on the relationship between oxygen partial pressure and composition for LaMnO$_{3+\delta}$, measured by Kamata et al. (5) (1473 K), Kamegashira et al. (6) (1277 K), Kuo et al. (7) (1273 and 1473 K), Nakamura et al. (8) (1273 K), van Roosmalen et al. (4) (1290 K), and Shimoyama et al. (9) (1273 and 1473 K). All data, except those by Kamata et al. (5) and van Roosmalen et al. (4), are obtained from the graph. The calculated relationships according to the proposed defect model at 1273 and 1473 K are plotted, as is indicated in the graph. It can be seen that the results of Kamata et al. (5), Kuo et al. (7), and Nakamura et al. (8) cannot be described properly with the proposed defect model, while the results of Kamegashira et al. (6), van Roosmalen et al. (4), and Shimoyama et al. (9) are in good agreement both with each other and with the line calculated according to the defect model.

try of LaMnO$_{3+\delta}$ are valid in the temperature region 873 K $\leq T \leq$ 1573 K.

4. THE EFFECT OF Sr ON THE DEFECT CHEMISTRY OF LaMnO$_{3+\delta}$

As was concluded earlier (4), the defect chemistry of (La,Sr)MnO$_{3+\delta}$ is based on the same defect formation as in LaMnO$_{3+\delta}$. The defect chemistry can be described by

$$K_V = \frac{(1 - x - 2\xi + 2\delta)^6 \cdot 3^3 \cdot \delta^2}{(\xi - 2\delta)^6 \cdot (3 + \delta)^2} \cdot p_{O_2}^{-3/2}. \qquad [10]$$

The results obtained by van Roosmalen et al. (4) on La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$ are fitted to this equation. The average value of $\xi = 0.244$. With this value of ξ, the data have been fitted again; the results are listed in Table 1. No other data are available for La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$. It follows that

$$\ln K_V = \frac{3.56 \times 10^4}{T} - 28.0. \qquad [11]$$

The result is shown in Fig. 1, line (B). From Eqs. [1, 3–6, 10], it is calculated that $\Delta H_V^\circ = (-296 \pm 9)$ kJ $\cdot$ mole^{-1}, $\Delta S_V^\circ = (-233 \pm 7)$ J $\cdot$ mole$^{-1} \cdot$ K^{-1}, $\Delta \overline{H}_{O_2} = (-197 \pm 6)$ kJ $\cdot$ mole^{-1}, and $\Delta \overline{S}_{O_2} = ((-155 \pm 5) - 5.54 \ln f(\delta))$ J $\cdot$ mole$^{-1} \cdot$ K^{-1} ($f(\delta)$ is obtained from Eq. [10]). The thermodynamic properties of defect formation obtained for La$_{0.85}$Sr$_{0.15}$MnO$_{3+\delta}$ are valid in the temperature region 1080 K $\leq T \leq$ 1290 K.

5. LaMnO$_{3-\delta}$

In contrast to LaMnO$_{3+\delta}$, there are no indications that charge disproportionation occurs in LaMnO$_{3-\delta}$, and it is suggested that the defect chemistry of LaMnO$_{3-\delta}$ can be described as previously published (1). On reduction together with an oxygen vacancy, two Mn^{2+} ions are formed, leading to the neutral cluster $\langle$Mn^{2+}–V$_O$–Mn$^{2+}\rangle$, or in Kröger–Vink notation $\langle$Mn$'_{Mn}$–V$_O^{\cdot\cdot}$–Mn$'_{Mn}\rangle$. The relationship between δ and p_{O_2} is then described by

$$K_V = \frac{\delta}{(1 - 2\delta)^2 \cdot (3 - \delta)} \cdot p_{O_2}^{1/2}. \qquad [12]$$

The results of Kamata et al. (5), Nakamura et al. (8), and Shimoyama et al. (9) are in good agreement. The results of Kuo et al. (7) seem not to be correct. The fitted values of K are shown in Table 1 and Fig. 1, line (D). From the plot of $\ln K$ versus $1/T$, it follows that

$$\ln K_V = \frac{-4.20 \times 10^4}{T} + 11.6. \qquad [13]$$

and the thermodynamic properties of defect formation can be obtained for $LaMnO_{3-\delta}$. For the oxygen deficiency cluster model, $x = \frac{1}{2}$. From Eqs. [1, 3–6, 13], it is calculated that $\Delta H_V^\circ = (349 \pm 6)$ kJ · mole^{-1}, $\Delta S_V^\circ = (96.4 \pm 4.9)$ J · mole^{-1} · K^{-1}, $\Delta \overline{H}_{O_2} = (-698 \pm 12)$ kJ · mole^{-1}, and $\Delta \overline{S}_{O_2} = ((-193 \pm 10) + 16.6 \ln\{\delta/(1 - 2\delta)^2 \cdot (3 - \delta)\})$ J · mole^{-1} · K^{-1}. They are valid in the temperature region $1073 \text{ K} \leq T \leq 1573$ K.

These results can be compared with results obtained by Seppänen et al. (10) and by Mizusaki et al. (11) for $LaCoO_{3-\delta}$. The fit of the equilibrium constants is shown in Fig. 1, line (C), and in Table 1. The results are

$$\ln K_V = \frac{-2.76 \times 10^4}{T} + 12.4, \quad [14]$$

and the thermodynamic properties of defect formation can be obtained for $LaCoO_{3-\delta}$. From Eqs. [1, 3–6, 13] it is calculated that $\Delta H_V^\circ = (229 \pm 5)$ kJ · mole^{-1}, $\Delta S_V^\circ = (103.0 \pm 4.3)$ J · mole^{-1} · K^{-1}, $\Delta \overline{H}_{O_2} = (-458 \pm 10)$ kJ · mole^{-1}, and $\Delta \overline{S}_{O_2} = ((-206 \pm 9) + 16.6 \ln\{\delta/(1 - 2\delta)^2 \cdot (3 - \delta)\}$ J · mole^{-1} · K^{-1}. They are valid in the temperature region $1123 \text{ K} \leq T \leq 1311$ K.

6. DISCUSSION

In the compound series $LaMO_3$ (M = Ti, Cr, Fe, Mn, Co, Ni), $LaMnO_3$ is the only compound that exhibits excessive oxygen excess. It is likely that the relatively rare partial charge disproportionation of Mn^{3+} into Mn^{2+} and Mn^{4+} is unique in this series. The formation of La and Mn vacancies is coupled with the charge disproportionation and, therefore, is only found in $LaMnO_3$.

The charge disproportionation in $LaMnO_{3+\delta}$ is not a function of δ, but is influenced by the strontium content. The introduction of Sr^{2+} on La^{3+} sites increases the overall valence of manganese and reduces the charge disproportionation. In $LaMnO_3$, ξ (Eq. [7]) = 0.352; in $La_{0.85}Sr_{0.15}MnO_3$, $\xi = 0.244$; and in $La_{0.60}Sr_{0.40}MnO_3$, ξ is close to zero. This can be concluded from the measurements of Mizusaki et al. (12), since almost no oxygen excess was found. Apparently, it is less favorable to form defects with increasing strontium content, and, as a consequence, ΔH_V° is less negative for $La_{0.85}Sr_{0.15}MnO_3$ ($-296 \pm$ kJ · mole^{-1}) than for $LaMnO_3$ ($-380 \pm$ kJ · mole^{-1}).

In $LaMnO_{3-\delta}$ and $LaCoO_{3-\delta}$, the defect chemistry can be described with a cluster model. There are no indications for charge disproportionation as in $LaMnO_{3+\delta}$, at relatively high oxygen partial pressures, whereas the oxygen deficiency of $LaMnO_{3-\delta}$ is found only at low oxygen partial pressures. For charge disproportionation of Fe^{4+} into Fe^{3+} and Fe^{5+} (13, 14) it was also noted that environmental conditions, such as temperature and oxygen partial

pressure, are of great influence on the charge disproportionation.

The defect chemistry of $LaMnO_{3-\delta}$ and $LaCoO_{3-\delta}$ can be described by the same defect model, so the entropies of defect formation should be the same for both compounds. The values found, (96.4 ± 4.9) and (103 ± 4.3) J · mole^{-1} · K^{-1}, respectively, are in good agreement. This is also an indication that the cluster model is the appropriate model to describe the oxygen deficiency of La $MnO_{3-\delta}$; in other words, there is no charge disproportionation in $LaMnO_{3-\delta}$. The large difference between the enthalpies of defect formation for $LaMnO_{3-\delta}$ and La $CoO_{3-\delta}$ is mostly a consequence of the difference in reducibility between Co^{3+} and Mn^{3+}. The same defect model is probably valid in $LaFeO_3$ as well, as was mentioned in Part 1 (1). Unfortunately, no experimental data are available to determine ΔH_V°, but it is known that $LaFeO_3$ is even harder to reduce than $LaMnO_3$, so it is expected that ΔH_V° is even more negative.

With the present results, the defect chemistry of La $MnO_{3+\delta}$ can be described between 873 and 1573 K, and the defect chemistry of $LaMnO_{3-\delta}$ between 1073 and 1573 K. To visualize their relative contributions to the overall defect chemistry of $LaMnO_3$, the defect chemistry of $LaMnO_{3+\delta}$ and $LaMnO_{3-\delta}$ are combined at 1073 K, 1273 K, and 1473 K in Fig. 3. It should be noted that the lines in Fig. 3 probably cross the decomposition limits for $LaMnO_{3-\delta}$ upon reduction. For $LaMnO_{3+\delta}$, the maximum value for δ ($\xi/2$) is not reached at 1073 K. It can be seen that the two nonstoichiometric regions are clearly
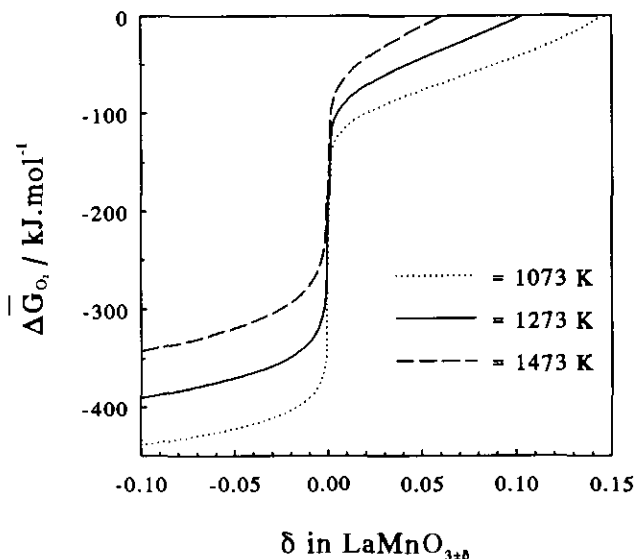

FIG. 3. The relationship between the Gibbs free energy for oxygen and the composition of $LaMnO_{3\pm\delta}$, at 1073, 1273, and 1473 K, obtained by evaluating the experimental data measured by various authors according to the proposed defect models for $LaMnO_{3-\delta}$ and $LaMnO_{3+\delta}$.

separated, although the stoichiometric region, in which the two defect mechanisms are combined, narrows with increasing temperature. At higher temperatures the oxygen excess region will disappear (in the f_{O_2}-region under investigation).

REFERENCES

1. J. A. M. van Roosmalen and E. H. P. Cordfunke, *J. Solid State Chem.* **93**, 212 (1991).
2. J. A. M. van Roosmalen, E. H. P. Cordfunke, R. B. Helmholdt, and H. W. Zandbergen, *J. Solid State Chem.* **110**, 100 (1994).
3. J. A. M. van Roosmalen and E. H. P. Cordfunke, *J. Solid State Chem.* **110**, 106 (1994).
4. J. A. M. van Roosmalen and E. H. P. Cordfunke, *J. Solid State Chem.* **110**, 109 (1994).
5. K. Kamata, T. Nakajima, T. Hayashi, and T. Nakamura, *Mater. Res. Bull.* **13**, 49 (1978).
6. N. Kamegashira, Y. Miyazaki, and H. Yamamoto, *Mater. Chem. Phys.* **11**, 187 (1984).
7. J. H. Kuo, H. U. Anderson, and D. M. Sparlin, *J. Solid State Chem.* **83**, 52 (1989).
8. T. Nakamura, G. Petzow, and L. J. Gauckler, *Mater. Res. Bull.* **14**, 649 (1979).
9. J. Shimoyama, J. Mizusaki, and K. Fueki, Fall Meeting Chem. Soc. Japan, 3Q06 (1986), quoted by J. Mizusaki and H. Tagawa, Intern. Symp. Solid Oxide Fuel Cell 65–70, Nagoya, 1989.
10. M. Seppänen, M. Kytö, and P. Taskinen, *Scand. J. Metall.* **9**, 3 (1980).
11. J. Mizusaki, Y. Mima, S. Yamauchi, K. Fueki, and H. Tagawa, *J. Solid State Chem.* **80**, 102 (1989).
12. J. Mizusaki, H. Tagawa, K. Naraya, and T. Sasamoto, *Solid State Ionics* **49**, 111 (1991).
13. M. Takano, N. Nakanishi, Y. Takeda, S. Naka, and T. Takada, *Mater. Res. Bull.* **12**, 923 (1977).
14. S. Komornicki, L. Fournès, J.-C. Grenier, F. Ménil, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **16**, 967 (1981).
15. J. Mizusaki, M. Yoshihiro, S. Yamauchi, and K. Fueki, *J. Solid State Chem.* **58**, 257 (1985).