Determination of Stoichiometry in Lanthanum Strontium Manganates(III)(IV) by Wet Chemical Methods

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Wet chemical analyses and powder diffractometry were used to characterize lanthanum strontium manganates(III)(IV) with a composition $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.00 \le x \le 0.50$). Two series prepared by different thermal treatments were investigated. In series I the materials were calcined in air. These materials were hexagonal. In series II the materials were prepared from series I materials by calcination in a nitrogen atmosphere. Series II materials with $0.00 \le x < 0.20$ were orthorhombic. For $x \ge 0.20$, series II materials were hexagonal. For series I δ decreases with increasing x until $x = 0.30$, where it becomes almost zero (and remains 0 for $x > 0.30$). For series I the molar ratio Mn(IV)/Mn(IV) + Mn(III) is a nearly constant 0.3 in the range $0.00 \le x \le 0.20$. For series II δ is near zero in the whole range. For these materials the ratio Mn(IV)/Mn(IV) + Mn(III) increases with x. The changes of unit cell volumes with x is shown to be consistent with the found composition of the materials. The observed and calculated densities of the materials are consistent with cation vacancies. Full descriptions of procedures for syntheses and analyses are reported. © 1994 Academic Press, Inc.

INTRODUCTION

Lanthanum manganese oxides and strontium-substituted lanthanum manganese oxides contain manganese in oxidation states (III) and (IV). They have distorted perovskite-type structures. The ratio Mn(IV)/Mn(IV) + Mn(III) varies with the partial pressure of oxygen during the calcination of the lanthanum strontium manganate (LSM) materials. The formulae of the materials may be written $La_{1-x}Sr_xMn(III)_zMn(IV)_yO_{3+\delta}$. As the chemical analyses showed that $y + z = 1$ for the investigated samples, we will use the simpler formula $La_{1-x}Sr_xMn$ $(III)_{1-y}Mn(IV)_yO_{3+\delta}$ ($\delta = (y - x)/2$) for the materials.

Ideal perovskite materials have the formula ABO_3. It is difficult to envisage interstitial oxygen ions in the perovskite structure. Tofield and Scott (1) searched potential positions for interstitial oxygen ions. They found them empty. Our results (unit cell dimensions, chemical analyses, and

densities) can be interpreted only in terms of vacancies on La(Sr) and Mn sites. Results from reported structure determinations (1, 2, 4) support this interpretation. The notation $La_{1-x}Sr_xMnO_{3+\delta}$ is somewhat misleading, as it indicates an excess of oxygen instead of cation vacancies. It is, however, commonly used and convenient. We will therefore use the formulation given above (with a δ).

Kamata *et al.* (3), Van Roosmalen *et al.* (4), Kuo *et al.* (5), Kamegashira *et al.* (6), and Nakamura *et al.* (7) used thermogravimetric methods to determine the dependence of δ upon the partial pressure of oxygen during calcination at various temperatures.

Tofield and Scott (1) determined the structure of $LaMnO_{3.12}$ prepared by solid-state reaction between La_2O_3 and Mn_3O_4. From refinement of neutron powder diffraction data they proposed the formula $La_{0.94}Mn_{0.98}O_3$. Van Roosmalen (4) prepared $LaMnO_{3.158}$ by a coprecipitation method. By refinement of population parameters the neutron diffraction powder data gave the best agreement for the composition $La_{0.95}Mn_{0.95}O_3$.

By wet chemical methods we have determined the content of La + Sr, Mn(III), Mn(IV), and total Mn in $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ (for $x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50$) prepared by the solid-state reaction method from acetates calcined in air at 1100°C (series I). Compounds reduced in a nitrogen atmosphere at 900°C were also prepared and analyzed (series II).

PREPARATION

Series I

Lanthanum acetate · 1.5H$_2$O (Heraeus), manganese acetate · 3.1H$_2$O (Riedel de Haen), and strontium carbonate (Merck) (dissolved in acetic acid and dried) were used. The water content in lanthanum acetate was determined by thermogravimetry. The formula weight of manganese acetate was determined by titration of manganese as described in Analysis Method 1 (below). Stoichiometric amounts of the acetates were mixed by ball milling in a polyethylene flask. Zirconium oxide balls were used with

TABLE 1
Unit Cell Dimensions for $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$

x	Series	a (Å)	b (Å)	c (Å)	V (Å^3)
0.00^a	I	5.5250(2)		13.3306(8)	352.40
0.05^a	I	5.5238(3)		13.3327(9)	352.31
0.10^a	I	5.5209(2)		13.3370(5)	352.05
0.15^a	I	5.5195(3)		13.3407(10)	351.97
0.20^a	I	5.5166(3)		13.3484(9)	351.81
0.25^a	I	5.5118(3)		13.3525(8)	351.31
0.30^a	I	5.5075(4)		13.3616(12)	350.99
0.40^a	I	5.4881(6)		13.3584(21)	348.44
0.50^a	I	5.4577(7)		13.3593(16)	344.62
0.00^b	II	5.5353(3)	7.7029(4)	5.7046(2)	243.23
0.05^b	II	5.5363(7)	7.7242(10)	5.6358(7)	241.00
0.10^b	II	5.5485(12)	7.7716(12)	5.5390(8)	238.85
0.15^b	II	5.4974(4)	7.7816(5)	5.5413(3)	237.05
0.20^a	II	5.5290(3)		13.3637(8)	353.79
0.25^a	II	5.5153(3)		13.3582(8)	351.89
0.30^a	II	5.5091(5)		13.3636(14)	351.25
0.40^a	II	5.4848(5)		13.3563(16)	347.97
0.50^a	II	5.4609(14)		13.3618(20)	345.08

Note. Series I materials calcined in air. Series II materials calcined in nitrogen.

^{a} Hexagonal phases.

^{b} Orthorhombic phases.

acetone as milling liquid. Acetone was evaporated, and the powder was heated at 350°C in a porcelain crucible for 6 hr. The black residue was crushed in an agate mortar and calcined in air at 800°C for 24 hr, and then at 1100°C for 16 hr in an aluminum oxide crucible. Between the two calcinations the compound was ball milled for 24 hr (as described above). After the final calcination the material was permitted to slowly cool in the oven.

Indexing of the powder diffractograms (Siemens D5000, $CuK\alpha_1$, $\lambda = 1.5405981$ Å) showed for all the preparations one crystalline phase without extra lines. Table 1 gives the unit cell dimensions.

Series II

When the materials from series I with x in the range $0.00 \leq x < 0.20$ were heated at 900°C in nitrogen for 40 hr and cooled to room temperature, they were orthorhombic. The materials with $x \geq 0.20$ remained hexagonal after such treatment. The unit cell parameters of the series II materials were determined by indexing and refined by least-squares procedures. The refined unit cell parameters are recorded in Table 1.

ANALYSIS METHODS

1. Determination of the Total Amount of Manganese (Mn_t)

Determination of the total amount of manganese (Mn_t) is based on the method described by Vogel (8) for determi-

nation of manganous ions with permanganate in a neutral pyrophosphate solution:

$$4Mn^{2+} + MnO_4^- + 8H^+ + 15H_2P_2O_7^{2-} \rightarrow$$
$$5Mn(H_2P_2O_7)_3^{3-} + 4H_2O.$$
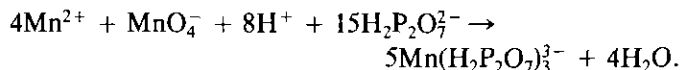
A weighed amount (0.1000–0.1400 g) of the LSM is dissolved in a mixture of 10 ml 0.5 M sulfuric acid and 10 drops of 30% hydrogen peroxide in a 100-ml small-necked bottle. All manganese is thereby reduced to oxidation state II. The solvent is removed on a boiling water bath. Surplus hydrogen peroxide is removed by heating on a hot plate until white fumes of sulfur trioxide appear. The residue is dissolved in 20 ml of water. Freshly prepared saturated sodium pyrophosphate solution (150 ml, 12 g $Na_4P_2O_7 \cdot 10H_2O$ per 100 milliliters H_2O) is adjusted to pH 7–7.5 with concentrated sulfuric acid (using a calibrated glass electrode). The manganese(II) solution is added dropwise to the well-stirred pyrophosphate solution. The resulting solution (slurry if strontium is present) is adjusted to pH 6.5 ± 0.1. The potentiometric titration with 0.02 M potassium permanganate should follow immediately. It is performed with platinum and mercury sulfate electrodes. The end point of the titration is 125 mV (Radiometer Titrator TTT60, prop. band 2).

The results for total manganese titration (Mn_t) are given in Table 2 and Table 3 as mole Mn_t per gram LSM.

2. Determination of Oxidation Equivalents of Manganese (Mn_{ox})

The iodometry method described by Vogel (9) is used, and the results are given in Tables 2 and 3. A weighed amount (0.1200–0.1500 g) of the LSM is placed in an all-glass distillation apparatus. A weak stream of carbon dioxide gas is passed through the whole system for half an hour before 15 ml of concentrated hydrochloric acid is added. The carbon dioxide stream is maintained during the final steps of the procedure. Chlorine is produced by the reactions

$$2Mn(III) + 2Cl^- \rightarrow Cl_2 + 2Mn(II)$$
$$Mn(IV) + 2Cl^- \rightarrow Cl_2 + Mn(II).$$
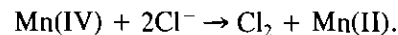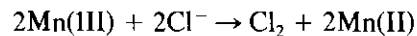
The produced chlorine (carried by the CO_2 stream) reacts with a surplus of potassium iodide solution present in a flask connected with the distillation apparatus, and iodine is formed. The only opening in the system through which chlorine could escape is "closed" by a tube containing glass beads moistened with potassium iodide solution. LSM materials dissolve completely in concentrated hydrochloric acid upon heating, and manganese is reduced to oxidation state II. When the reaction is complete the solution is clear and colorless. The flask with potassium

TABLE 2

Titration Results and Composition of $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ Prepared from Acetates, Calcined at 1100°C in Air (Series I)

x	Mn_t (mol/g × 10^6)	Mn_{ox} (eqv/g × 10^6)	F^- (mol/g × 10^6)	Coefficients for elements in formula				
				La	Sr	Mn(III)	Mn(IV)	O
0	4,112	5,310	12,107	1.00	0.00	0.72	0.28	3.14
	4,115	5,216	12,134	[0.99]		[0.73]	[0.28]	[3.14]
0.05	4,030	5,291	12,074	0.97	0.05	0.69	0.29	3.12
	4,033	5,194	12,126	[0.96]		[0.69]	[0.30]	[3.12]
0.10	4,150	5,295	11,931	0.91	0.10	0.70	0.29	3.09
	4,107	5,384	11,970	[0.90]		[0.71]	[0.29]	[3.10]
0.15	4,172	5,361	11,724	0.86	0.15	0.70	0.29	3.07
	4,170	5,403	11,877	[0.85]		[0.71]	[0.29]	[3.07]
0.20	4,257	5,447	11,562	0.81	0.20	0.71	0.28	3.04
	4,211	5,441	11,298	[0.78]		[0.73]	[0.29]	[3.05]
0.25	4,296	5,664		0.76	0.25	0.67	0.32	3.03
	4,276	5,643						
0.30	4,380	5,718		0.71	0.30	0.68	0.31	3.00
	4,351	5,755						
0.40	4,418	6,224		0.61	0.41	0.59	0.40	3.00
·	4,440	6,215						
0.50	4,585	6,793		0.50	0.50	0.51	0.48	2.99
	4,582	6,816						
Mn_2O_3	12,675	12,634				2.00		3.00
	12,709	12,693						

Note. For calculation of coefficients without brackets only Mn_t and Mn_{ox} results were used. For calculation of coefficients in square brackets Mn_t, Mn_{ox}, and fluoride titration results were used. In the bottom line titration results for pure Mn_2O_3.

iodide solution is disconnected, the tube with the glass beads is rinsed with water, and iodine in the combined potassium iodide solutions is titrated with sodium thiosulfate solution. The results are given in Table 2 and Table 3 as equivalent Mn_{ox} per gram LSM. The accuracy of the manganese determinations can be judged from the double determinations and from the analysis of pure Mn_2O_3 reported in Table 2.

3. Determination of Lanthanum + Strontium

A weighed amount (0.1200–0.1500 g) of the LSM is dissolved in approximately 15 ml concentrated hydrochloric acid. Alternatively the solution from the iodometry analysis can be transferred quantitatively from the distillation apparatus to a 100-ml beaker. The solution is evaporated to dryness to remove the surplus of hydrochloric acid. The residue is dissolved in 20 ml of water. A 20.00-ml solution of 0.1000 M sodium fluoride is added to precipitate lanthanum and strontium as fluorides. Thirty minutes

later the solution is adjusted to pH 5.5 with 0.1 M hydrochloric acid. The surplus of sodium fluoride ion is determined by titration with 0.02000 M lanthanum nitrate solution using a fluoride selectrode with a calomel reference electrode (Radiometer FK 1852 F-O).

The results are given in Tables 2 and 3 as mole fluoride ion used per gram LSM.

CALCULATION METHOD

1. By Use of Mn_t and Mn_{ox} Determinations Only

The composition of lanthanum manganates(III)(IV) may be written as a sum of oxides pLa_2O_3, qMn_2O_3, $rMnO_2$. Likewise the strontium-substituted materials may be written as $((1 - p)/2)La_2O_3$, $pSrO$, qMn_2O_3, $rMnO_2$. It is here assumed that the ratio between lanthanum and strontium is the same as that in the starting mixture.

Under the assumption that lanthanum has oxidation state (III), the formula for the lanthanum manga-

TABLE 3

Titration Results and Composition of $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ Calcined in Nitrogen Atmosphere 900°C (Series II)

x	Mn_t (mol/g × 10⁶)	Mn_{ox} (eqv/g × 10⁶)	F^- (mol/g × 10⁶)	Coefficients for elements in formula				
				La	Sr	Mn(III)	Mn(IV)	O
0	4,120	4,148	12,427	1.00	0	0.99	0.01	3.004
	4,151	4,188	12,247	[1.00]		[0.99]	[0.01]	[3.004]
0.05	4,144	4,398	12,175	0.96	0.05	0.93	0.06	3.007
	4,152	4,428	12,213	[0.95]		[0.94]	[0.06]	[3.007]
0.10	4,165	4,633	11,885	0.91	0.10	0.87	0.12	3.008
	4,167	4,687	12,066	[0.90]		[0.89]	[0.12]	[3.010]
0.15	4,196	4,889	11,786	0.86	0.15	0.83	0.15	3.002
	4,222	4,845	11,865	[0.84]		[0.85]	[0.16]	[3.004]
0.20	4,275	5,078	11,452	0.81	0.20	0.80	0.19	2.995
	4,267	5,122	11,238	[0.78]		[0.83]	[0.20]	[3.002]
0.25	4,275	5,627		0.76	0.25	0.68	0.30	3.025
	4,264	5,543						
0.30	4,382	5,784		0.70	0.30	0.67	0.32	3.010
	4,382	5,842						
0.40	4,442	6,163		0.61	0.40	0.60	0.39	2.991
	4,462	6,228					.	
0.50	4,606	6,746		0.50	0.50	0.55	0.45	2.973
	4,645	6,639						

Note. For calculation of coefficients without brackets only Mn_t and Mn_{ox} results were used. For calculation of coefficients in square brackets Mn_t, Mn_{ox}, and fluoride titration results were used.

nates(III)(IV) can be calculated from the results of the determination of total manganese content and the average oxidation state of manganese. As the analysis determines oxidation equivalents the possibility of disproportionation of Mn(III) to Mn(II) + Mn(IV) cannot be excluded.

From

$$Mn_t = n_1Mn(III) + n_2Mn(IV) \quad \text{and}$$

$$Mn_{ox} = n_1Mn(III) + 2 \times n_2Mn(IV),$$

it can be derived that

$$Mn(III) = 2 \times Mn_t - Mn_{ox} \quad \text{and}$$

$$Mn(IV) = Mn_{ox} - Mn_t.$$

The content of Mn(III) and Mn(IV) can then be calculated from the titration results.

An example for $LaMnO_{3+\delta}$ is given.

$$Mn(III) = 2 \times Mn_t - Mn_{ox} = 2 \times 0.4114 - 0.5263$$
$$= 0.2965 \text{ mole}/100 \text{ g sample.}$$

$$Mn(IV) = Mn_{ox} - Mn_t = 0.5263 - 0.4114$$
$$= 0.1149 \text{ mole}/100 \text{ g sample.}$$

The value of 0.2965 mole Mn(III)/100 g is equivalent to 23.405 g Mn_2O_3/100 g sample. The value of 0.1149 mole Mn(IV)/100 g is equivalent to 9.988 g MnO_2/100 g sample. The rest, 100 − (23.405 + 9.988) = 66.607 g, is La_2O_3; i.e., there is 0.4089 mole La/100 g sample. The coefficients for the elements in the formula are now normalized to give Σ cations = 2. The resulting formula is $La_{1.00}Mn(III)_{0.72}Mn(IV)_{0.28}O_{3.14}$. If we normalize to three oxygen as expected for the perovskite structure with vacancies the formula becomes

$$La_{0.95}Mn(III)_{0.69}Mn(IV)_{0.27}O_3.$$
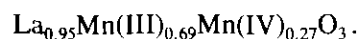
The formulae for the strontium-substituted LSM materials can be calculated in the same manner if we assume that lanthanum and strontium enter in the proportions they have when the acetates are mixed.

TABLE 4

Observed and Calculated Densities for Series I
$La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$

| | | Densities (g cm^{-1}) | |
| | | Calculated | |
x	Experimental	With interstitials, i.e., Σ cations $\equiv$ 12 per unit cell	With vacancies, i.e., Σ oxygen ions $\equiv$ 18 per unit cell
0.00	6.50(7)	6.90	6.59
0.10	6.54(8)	6.76	6.57

Note. The experimental densities were obtained as the mean value of five determinations (the figures in brackets are maximum deviations). Two sets of calculated values are reported. In the first interstitial oxygen atoms were assumed, and in the second vacancies.

2. By Use of Mn_t and Mn_{ox} and Lanthanum + Strontium Determinations

The calculations of coefficients including the titration results for lanthanum + strontium, Mn_t, and Mn_{ox} proceed as described above, employing in addition the following two expressions:

mole F$^-$ used/g = (3 × mole La^{3+}/g)
+ (2 × mole Sr^{2+}/g)

mole La^{3+}/mole Sr^{2+} = $(1 - x)/x$.

Coefficients from these types of calculations are in Tables 3 and 4 in square brackets. This second set of coefficients agree well with those calculated solely from manganese determinations.

DENSITY MEASUREMENTS

The densities of the series I materials with $x = 0.00$ and $x = 0.10$ were determined by helium pycnometry (Micromeritics Multivolume Pycnometer 1305). The experimental and calculated densities are reported in Table 4. The experimental densities were obtained as the mean value of five determinations (the figures in brackets are maximum deviations). In the calculations of densities assuming interstitial oxygen ions the unit cell contents were normalized to Σ cations $\equiv$ 12. In the calculations of densities with cation vacancies the unit cell contents were normalized to Σ oxygen ions $\equiv$ 18. The results are clearly in favor of structures with cation vacancies.

DISCUSSION

Series II

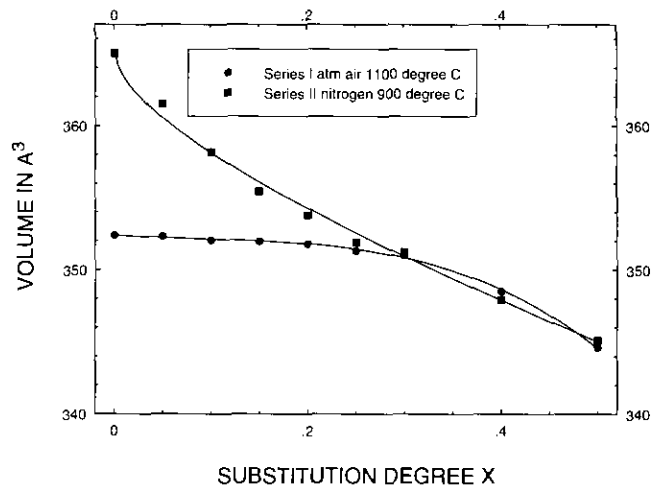LaMnO$_3$ prepared by calcination under inert atmosphere (N$_2$) at 900°C, and cooled to room temperature, is

FIG. 1. Unit cell volumes of $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ versus degree of strontium substitution x.

orthorhombic with 12 oxygen atoms per unit cell. According to our chemical analyses the composition is $La_{1.00}$ $Mn(III)_{0.99}Mn(IV)_{0.01}O_{3.005}$. The deviation from LaMnO$_3$ (with Mn solely in oxidation state (III)) is barely detectable.

$La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$, calcined under inert atmosphere (N$_2$) at 900°C, and cooled, are also orthorhombic for $x < 0.20$. For $x \geq 0.20$ the materials are hexagonal with 18 oxygen atoms per unit cell.

In Fig. 1 the dependence of the unit cell volume of the materials on the degree of substitution (x) is shown. In this figure the unit cell volumes for the orthorhombic materials have been multiplied by 18/12 to correct for the different unit cell contents of oxygen in the orthorhombic (12) and the hexagonal (18) cells.

The evident decrease in unit cell volumes with x is due to the substitution. There is a loss of charge by the replacement of La^{3+} with Sr^{2+}. As the oxygen content is almost constant, the loss of charge is compensated for by an equivalent replacement of Mn(III) with Mn(IV). It can be seen in Table 3 and Fig. 2 that the coefficients for Mn(IV) increase linearly as the coefficients for Sr increase. As the radii of La^{3+} and Sr^{2+} are almost equal and the radius of Mn(IV) is smaller than the radius of Mn(III), the unit cell volume decreases.

In Fig. 3 the variation of δ with substitution degree is shown. Except for $x = 0.25$, δ is close to zero. The nitrogen used in the experiments had an oxygen partial pressure $pO_2 \approx 10^{-6}$ atm. This means that LSM materials heat treated under a nitrogen atmosphere can be used as reference material with $\delta = 0$ in thermogravimetrical investigations. The exception at $x = 0.25$ is under investigation.

Series I

$LaMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$, prepared by calcination in air at 1100°C, is hexagonal with 18 oxygen atoms per unit
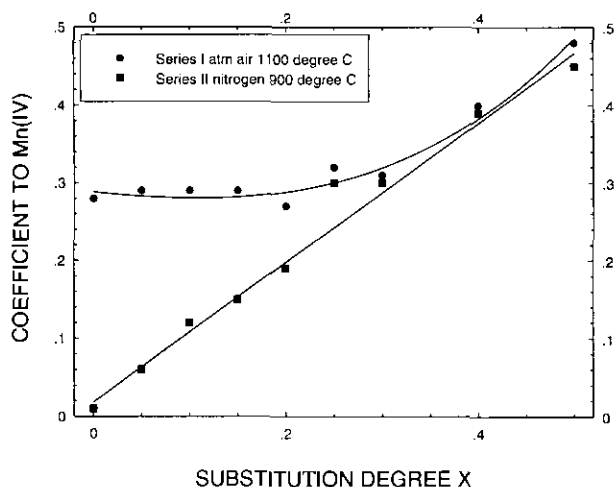
FIG. 2. Coefficients of Mn(IV) in $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ versus degree of strontium substitution x.

FIG. 4. Unit cell volumes versus coefficients of Mn(IV) in all the $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$. The least-squares fit to the observed unit cell volumes is given by

$$V = 48*[\sin(\alpha/2)*(2.00 - x*Mn(IV))]^3,$$

where α is the Mn–O–Mn angle and x is the difference between the Mn(III)–O and Mn(IV)–O distances. See the text for further details.

cell (1). According to our chemical analyses the composition is $La_{1.00}Mn(III)_{0.72}Mn(IV)_{0.28}O_{3.14}$. Under the calcination conditions in air 0.28 mole of Mn(III) per formula unit is oxidized to Mn(IV), and an equivalent amount of O^{2-} appears in the formula ($\delta = 0.14$). This formulation is practical (nonstoichiometry given by one parameter), but structurally misleading. There is no interstitial oxygen in the structures, but vacancies on cation sites corresponding to 0.28 positive charges per formula unit.

Strontium-substituted materials $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$, prepared by calcination in air at 1100°C, are hexagonal with 18 oxygen atoms per unit cell.

In Fig. 1 the dependence of the unit cell volume of the materials on the degree of substitution (x) is shown. In the range $0.00 \leq x \leq 0.20$ the decrease in unit cell volume
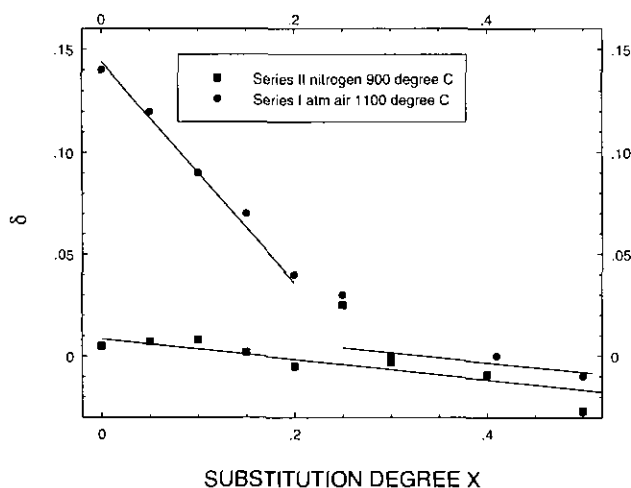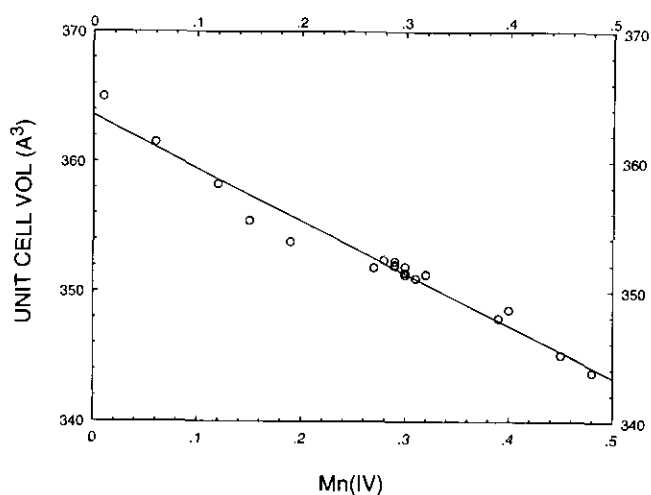

FIG. 3. δ values found by analysis of $La_{1-x}Sr_xMn(III)_{1-y}Mn(IV)_yO_{3+\delta}$ versus degree of strontium substitution x.

is small. The loss of charge by the replacement of La^{3+} with Sr^{2+} is compensated for by a decrease in oxygen content, while the Mn(IV) content is almost constant. In this range the vacancies are progressively filled. For $x >$ 0.25 the vacancies are completely filled and a decrease in unit cell volume is observed. This decrease in volumes with x is due to replacement of Mn(III) with Mn(IV). In Table 2 and Fig. 2 it can be seen that the coefficient for Mn(IV) increases as the coefficients for strontium increase when $x > 0.25$.

This interpretation is in accordance with the analytical results. In the range $0.00 \leq x \leq 0.30$ δ decreases from 0.14 to zero, while the proportions of Mn(IV) and Mn(III) are constant. For $x > 0.30$ δ remains zero, and Mn(IV) increases as the coefficients for Sr increase. The variation of δ with the substitution degree x is shown in Fig. 3.

In Fig. 4 the unit cell volumes for all the investigated materials are shown as a function of Mn(IV) content. It is seen that the unit cell volume is determined largely by the Mn(IV) content, and the variation with Sr content is small. As the ionic radii of La^{3+} and Sr^{2+} are almost equal, the unit cell volume is mainly determined by the difference in the Mn(III)–O and Mn(IV)–O distances. A simple model for simulating the dependence of the unit cell volume of the hexagonal and orthorhombic lanthanum strontium manganates(III)(IV) on the Mn(IV) content was derived. In the model unit cell, Mn is arranged in a cubic lattice as in the ideal perovskite structure. The Mn–O–Mn angle was allowed to deviate from 180°, so the model

unit cell is not cubic in crystallographic terms. A linear dependence of the Mn–O distance with the amount of Mn(IV) was introduced; i.e., Mn–O = 2.00 – $x * $ Mn(IV)–O, assuming a Mn(III)–O distance of 2.00 Å. The equation used in least-squares fit to the observed unit cell volumes is given by

$$V = 48 * [\sin(\alpha/2) * (2.00 - x * \text{Mn(IV)})]^3,$$

where α is the Mn–O–Mn angle and x is the difference between the Mn(III)–O and Mn(IV)–O distances. The result of the refinement is shown in Fig. 4. α refines to 158° and x to 0.075. There is reasonably good agreement between the observed and the calculated unit cell volumes, considering the simplicity of the model, where the symmetry is confined to cubic (except that the Mn–O–Mn angle is allowed to deviate from 180°) and the Mn–O–Mn angle is kept constant for all the samples. The difference between the Mn(IV)–O and Mn(III)–O distances is in good agreement with literature values. As the Mn–O–Mn angles vary from compound to compound, the angle α found using the simple model may be seen as an estimated mean value. It is close to the Mn–O–Mn angles found for hexagonal and orthorhombic lanthanum manganates(III)(IV) (2, 10).

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