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The crystal structure of an oxygen-deficient manganite perovskite $La_xSr_{1-x}MnO_{(5+x)/2}$ $(0 \leq x \leq 0.5)$

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Abstract

The crystal structure of $La_xSr_{1-x}MnO_{(5+x)/2}$ was analyzed from the powder diffraction data and Rietveld method. The specimen was prepared by the solid-state reaction method under low oxygen partial pressure. The results of the structural analysis showed several different structures which were modified from perovskite type with ordered arrangement of oxygen vacancies, depending on the composition. $La_{0.1}Sr_{0.9}MnO_{2.55}$ had orthorhombic structure (*Pbam*) with the lattice dimension of $\sqrt{2}a_p \times 2\sqrt{2}a_p \times 1a_p$. $La_{0.2}Sr_{0.8}MnO_{2.60}$ and $La_{0.3}Sr_{0.7}MnO_{2.65}$ had a monoclinic structure (*P*2/*m*) with the lattice dimension of $\sqrt{5}a_p \times 1a_p \times \sqrt{5}a_p$. $La_{0.4}Sr_{0.6}MnO_{2.70}$ had a cubic cell (*Pm*3*m*) with the lattice dimension of $1a_p \times 1a_p \times 1a_p$. $La_{0.5}Sr_{0.5}MnO_{2.75}$ had a tetragonal structure (*I*4/*mmm*) with the lattice dimension of $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$.

Keywords: Chemical synthesis; Crystal structure and symmetry; X-ray diffraction

1. Introduction

There are numerous studies of oxide with perovskite-type structure ABO_3 [1,2]. Especially, the perovskite structures with transition metal in B site easily make the oxygen vacancies, because B ions can take several valence states. In little oxygen deficiency, the oxygen vacancies arrange randomly, while these make the ordered arrangement in a crystal structure as the oxygen vacancies increase. The structures with ordered oxygen defects have been reported as new crystal structures in several papers [3–5].

When the materials with perovskite structure have oxygen vacancies, BO_6 octahedra transform to BO_5 pyramids, BO_4 square planes or BO_4 tetrahedra. $Sr_2Fe_2O_5$ is well known as being brownmillerite-type structure, which have alternate sheets of FeO_6 octahedra and FeO_4 tetrahedra along the *b*-axis [3]. $Ca_2Mn_2O_5$ also have the structure with oxygen vacancies with which ordered arrangement in this structure, which has the sheets of MnO_5 square pyramids along the *c*-axis [4]. $La_2Ni_2O_5$ structure has NiO_6 octahedra and NiO_4 square planes alternating in the *ab* plane [5].

We already reported the crystal structures of $La_xSr_{1-x}MnO_{(5+x)/2}$ $(0.8 \leq x \leq 1.0)$ which is reductively compounds of $La_xSr_{1-x}MnO_3$ with perovskite structure [6]. These exhibited random arrangements of oxygen vacancies for little oxygen defects. In relation to this, we attempted to research the crystal structures of $La_xSr_{1-x}MnO_{(5+x)/2}$ $(x \leq 0.5)$ with large oxygen defects. This paper describes the synthesis and crystal structures of these materials.

2. Experimental

Adequate amounts of La_2O_3, $SrCO_3$ and Mn_2O_3 with an appropriate molar ratio were first mixed and heated at 1523 K in Ar for 2 days, and then heated at 573 K in air in order to obtain non-stoichiometric perovskite structure (first stage). The valence state of manganese ion at this first stage was determined by gravimetric analysis by H_2-reduction.

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Then, in order to obtain the composition $La_xSr_{1-x}MnO_{(5+x)/2}$ with trivalent Mn state, the resulting products obtained at the first stage were heated in flow of mixing gas [0.1% H_2 + Ar] at 1373 K for long time (more than 3 days) and quenched to ice point. The valence state of manganese ion at this second stage was determined by calculating the weight change from the first stage. We repeated this heating and quenching operations until the valence state of manganese ion became trivalent (second stage).

Single phase was ascertained by X-ray power diffractometry at room temperature, where no other impurity phase was seen. The powder X-ray diffraction data were collected with Cu Kα radiation using MAC MXP^{18} powder X-ray diffractometer equipped with a single-crystal graphite monochromator at room temperature. The conditions for data collection were as follows: 2θ range, $5^\circ \le 2\theta \le 120^\circ$; step width ($2\theta$), 0.04°; counting time, 4 s. The powder X-ray diffraction patterns obtained were analyzed by Rietveld method using the program RIETAN [7,8].

3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) patterns of $La_xSr_{1-x}MnO_3$ at the first stage. XRD patterns below $x = 0.3$ showed the ideal cubic perovskite structure, which is similar to that of β-$SrMnO_3$ [9]. The structures of these have a cubic cell of dimensions with $1a_p \times 1a_p \times 1a_p$ in the space group $Pm\bar{3}m$, where a_p is ideal cubic perovskite cell parameter. In $x = 0.4$ and 0.5, these XRD patterns showed a tetragonal cell of dimensions with $1a_p \times 1a_p \times 1a_p$ in the space group $P4/mmm$. These cell sizes were similar as normal perovskite structure.

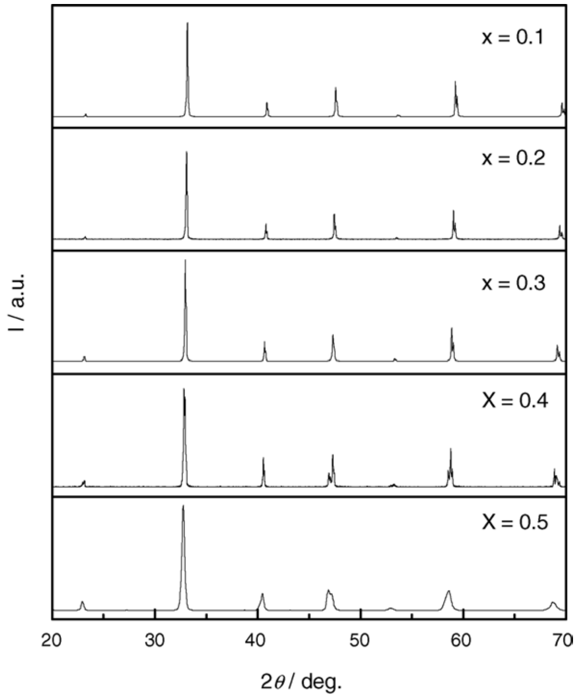

Fig. 1. XRD patterns of $La_xSr_{1-x}MnO_3$, before reduction.

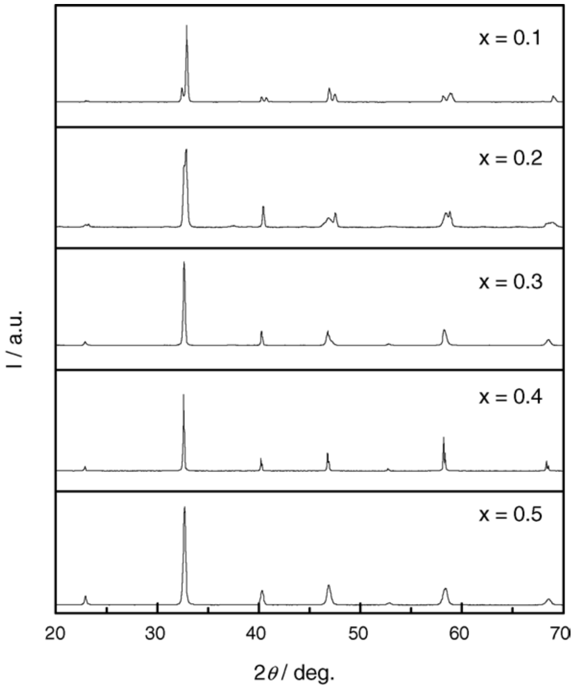

Fig. 2. XRD patterns of $La_xSr_{1-x}MnO_{(5+x)/2}$, after reduction.

The cell parameters were increasing with increasing the value of x in $La_xSr_{1-x}MnO_3$. Because the mean ionic radii of the cation at B site become larger with increasing x (Mn^{3+} ion is larger than that of Mn^{4+}). From gravimetric analysis by H_2-reduction, these samples were almost stoichiometry. These values were 2.99, 3.00, 3.00, 3.00 and 3.01 for $x = 0.1$, 0.2, 0.3, 0.4 and 0.5, respectively. The oxygen components of each sample were almost three.

Fig. 2 shows XRD patterns of reduced perovskite structures at the second stage. These XRD patterns had many peaks rather than previous XRD pattern (Fig. 1) and the cell parameters of these compounds exhibited the super-lattice of ideal perovskite structure. $La_{0.1}Sr_{0.9}MnO_{2.55}$ have orthorhombic structure with the lattice dimension of $\sqrt{2}a_p \times 2\sqrt{2}a_p \times 1a_p$. $La_{0.2}Sr_{0.8}MnO_{2.60}$ and $La_{0.3}Sr_{0.7}MnO_{2.65}$ has a monoclinic structure with the lattice dimension of $\sqrt{5}a_p \times 1a_p \times \sqrt{5}a_p$. $La_{0.4}Sr_{0.6}MnO_{2.70}$ has a cubic cell with the lattice dimension of $1a_p \times 1a_p \times 1a_p$. $La_{0.5}Sr_{0.5}MnO_{2.75}$ has a tetragonal structure with the lattice dimension of $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$.

Fig. 3(a) shows the crystal structure of $La_{0.1}Sr_{0.9}MnO_{2.55}$. The Rietveld analysis of this XRD diffraction pattern at room temperature was carried out using the space group *Pbam*. The structure of $La_{0.1}Sr_{0.9}MnO_{2.55}$ is built up like $SrMnO_{2.5}$ structure [10], where the corner-sharing MnO_5 pyramids forms pseudo-hexagonal tunnel running along [0 0 1]. It appears that the formation of ordered oxygen defects results in a building of the MnO_5 pyramids around the c axis.

The crystal structure of $La_{0.2}Sr_{0.8}MnO_{2.60}$ and $La_{0.3}Sr_{0.7}MnO_{2.65}$, were obtained by Rietveld method with using

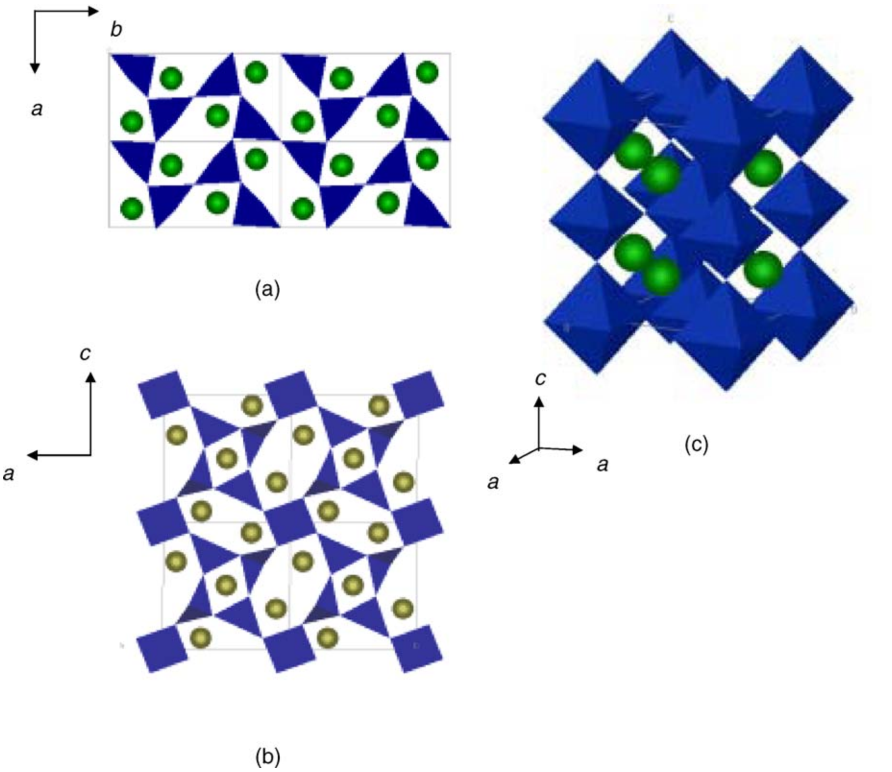

Fig. 3. The crystal structures of $La_{0.1}Sr_{0.9}MnO_{2.55}$ (a), $La_{0.2}Sr_{0.8}MnO_{2.60}$ (b) and $La_{0.5}Sr_{0.5}MnO_{2.75}$ (c).

the space group $P2/m$, were shown in Fig. 3(b). These compounds also have ordered oxygen defects and the corner-sharing MnO_5 pyramids forms pseude-hexagonal tunnel running along [0 1 0]. Some of the MnO_6 octahedrons remained in these structures.

In the case of $La_{0.4}Sr_{0.6}MnO_{2.70}$, this crystal structure is perovskite structure ($Pm3m$) with random arrangement of oxygen vacancies.

The crystal structure of $La_{0.5}Sr_{0.5}MnO_{2.75}$ is shown in Fig. 3(c). This crystal structure was refined with using a tetragonal structure ($I4/mmm$). The large size MnO_6 and small size MnO_6 were arranged alternately in this crystal structure. The oxygen vacancies were included in small size MnO_6. Thus this structure also had ordered oxygen defects.

$La_xSr_{1-x}MnO_3$ ($0.5 \leq x \leq 1$) was well-known to transform the charge ordering of Mn^{3+} and Mn^{4+} at low temperature [11]. The selective arrangement of oxygen

Table 1
Refined parameters of $La_{0.1}Sr_{0.9}MnO_{2.55}$

Atom	Site	g	x	y	z	B (10^{-2} nm^2)
La, Sr	4h	1.0	0.270(2)	0.376(1)	0.500	2.9(1)
Mn	4g	1.0	0.262(3)	0.126(2)	0.500	1.5(1)
O	4h	1.0	0.733(8)	−0.144(5)	0.500	1.0
O	4g	1.0	0.518(8)	0.238(5)	0.500	1.0
O	2a	1.0	0.000	0.000	0.000	1.0
O	2c	0.1	0.500	0.000	0.000	1.0

Space group: $Pbam$, $R_{wp} = 14.34$, $R_P = 10.71$, $R_E = 7.43$, $R_I = 5.37$, $R_F = 5.71$, $S(R_{wp}/R_E) = 1.93$, $a = 0.55097(3)$ nm, $b = 1.08479(6)$ nm, $c = 0.38233(2)$ nm.

Table 2
Refined parameters for $La_{0.2}Sr_{0.8}MnO_{2.60}$

Atom	Site	g	x	y	z	B (10^{-2} nm^2)
La, Sr	1h	1.0	0.500	0.376(1)	0.500	3.1(9)
La, Sr	2n	1.0	0.107(2)	0.500	0.341(2)	1.0(3)
La, Sr	2n	1.0	−0.302(2)	0.500	0.09(1)	1.3(3)
Mn	1a	1.0	0.000	0.000	0.000	0.1(9)
Mn	2m	1.0	0.423(3)	0.000	0.188(2)	1.8(4)
Mn	2m	1.0	−0.188(2)	0.000	0.188(2)	1.9(4)
O	1d	1.0	0.000	0.500	0.000	1
O	2m	1.0	0.322(1)	0.000	0.421(1)	1
O	2m	1.0	−0.39(1)	0.000	0.421(1)	1
O	2m	1.0	0.210(2)	0.000	0.263(1)	1
O	2m	1.0	−0.102(1)	0.000	0.191(1)	1
O	2n	1.0	0.422(1)	0.500	0.180(1)	1
O	2n	1.0	−0.213(1)	0.500	0.341(1)	1

Space group: $P2/m$, $R_{wp} = 9.84$, $R_P = 7.13$, $R_E = 4.71$, $R_I = 5.73$, $R_F = 4.57$, $S = 2.09$, $a = 0.86776(6)$ nm, $b = 0.38586(3)$ nm, $c = 0.86567(6)$ nm, $\beta = 90.281(9)$ nm.

Table 3
Refined parameters of $La_{0.5}Sr_{0.5}MnO_{2.75}$

Atom	Site	g	x	y	z	B (10^{-2} nm^2)
La, Sr	4d	1.0	0.000	0.500	0.250	1.4(1)
Mn	2a	1.0	0.000	0.000	0.000	1.4(1)
Mn	2b	1.0	0.000	0.000	0.500	1.6(1)
O	4e	0.75	0.000	0.000	0.255(1)	2.1(5)
O	8h	1.0	0.246(6)	0.246(6)	0.000	2.5(2)

Space group: $I4/mmm$, $R_{wp} = 8.91$, $R_P = 6.98$, $R_E = 4.72$, $R_I = 4.08$, $R_F = 2.83$, $S = 1.89$, $a = 0.54806(3)$ nm, $c = 0.77206(6)$ nm.

vacancies such as $x = 0.2$ and 0.5 in $La_xSr_{1-x}MnO_{(5+x)/2}$ might be related to this property.

The refined parameters of $La_{0.1}Sr_{0.9}MnO_{2.55}$, $La_{0.2}Sr_{0.8}MnO_{2.60}$ and $La_{0.5}Sr_{0.5}MnO_{2.75}$ were shown in Tables 1–3.

4. Conclusion

$La_xSr_{1-x}MnO_{(5+x)/2}$ were synthesized by the solid-state reaction method under low oxygen partial pressure and the crystal structures of these materials were revealed by using Rietveld method. The arrangement of oxygen vacancies was dependent on these compositions.

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