ELSEVIER

Ceramics International 31 (2005) 257–259

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

A structural consideration of the defect in $LaMnO_3$ phase around stoichiometric composition

Shunkichi Ueno[a,*], Akira Shimono[b], Hiromi Nakano[c], Naoki Kamegashira[a]

[a]*Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan*
[b]*Department of Chemistry and Biochemistry, Suzuka National College of Technology, Shiroko-cho, Suzuka 510-0294, Japan*
[c]*Electron Microscope Laboratory, Ryukoku University, Seta, Ohtsu 520-2194, Japan*

Received 19 April 2004; received in revised form 26 April 2004; accepted 24 May 2004
Available online 4 August 2004

Abstract

The defect structure of $LaMnO_3$ phase close to its stoichiometric composition was studied by transmission electron microscopy (TEM). The electron diffraction patterns of this phase showed two series of superlattice spots that are forbidden for *Pnma*(62), the reported symmetry for stoichiometric $LaMnO_3$. 0 0 *l* (*l* = odd) such as 0 0 1 and *h k* 0 (*h* = odd) such as 1 0 0 superlattice spots appeared in [1 1 0] and [0 1 1] zone patterns. The low magnification TEM images in [1 1 0] zone showed coherent twins. The twin plane was (1 1 2).

Keywords: B. Defects; B. Microstructure; D. Perovskites; Ceramics; Crystal structure

1. Introduction

The perovskite compound $LaMnO_3$ and its solid solutions are high potential for device applications in colossal magnetoresistance (CMR) and solid oxide fuel cells (SOFC) fields [1–3]. The interesting physical properties of these phases derived from the transition metal ion in the perovskite structure. The valence of manganese ion is 3+ in the stoichiometric composition, but stoichiometric $LaMnO_3$ is distorted into the orthorhombic system due to the Jhan-Teller effect [4]. Because manganese ion has 3+ and 4+ mixed valences, $LaMnO_3$ phase shows oxygen non-stoichiometry.

On the other hand, the ionic radii of Mn^{2+} ion is too large to fit in B-site of the perovskite structure [5], so oxygen deficient non-stoichiometry of $LaMnO_3$ dose not generally occur. However, Kamata et al. [6] suggested that $LaMnO_{3-\delta}$ phase appeared just before decomposition of this phase at low oxygen partial pressures at 1473 K.

Kamegashira and coworkers [7,8] presented the phase diagram for $LaMnO_3$ at 1273 K. In the equilibrium at 1273 K, $LaMnO_3$ decomposed directly into MnO and La_2O_3 phases without intermediate oxygen deficient non-stoichiometric phases.

Some structural models for oxygen deficient $LaMnO_{3-\delta}$ phase were proposed [9,10]. In these defect structural models, the oxygen defects lie on $\langle 1\ 1\ 0 \rangle_c$ direction, where the subscript c denotes a cubic perovskite structure that is the most simplified description of the perovskite structure.

In this study, the beginning of the formation defects in $LaMnO_3$ was examined just before decomposition at 1273 K by electron diffraction and electron microscopic observation.

2. Experimental

High purity La_2O_3 and Mn_2O_3 powders (all 99.99% purity) were used as the starting materials. A stoichiometric molar ratio of these powders were mixed in an agate mortar

* Corresponding author. Present address: National Institute of Advanced Industrial Science and Technology, 2268-1 Shimo-Shidami, Moriyama-ku, Nagoya 463-8687, Japan.
E-mail address: shunkichi.ueno@aist.go.jp (S. Ueno).

0272-8842/$30.00
doi:10.1016/j.ceramint.2004.05.010

and heated at 1573 K in air for 3 days. The phase identification was performed by powder X-ray diffraction method.

The sintered pellets kept at 1273 K in $P_{O_2} = 10^{-6}$ (Pa) environment for 3 days, where H_2/CO_2 mixed gas was used as the previous report [11]. The oxygen partial pressure was monitored by the electrical resistance of CoO oxide [11].

The annealed sample was crushed and mounted on the micro grid mesh. Transmission electron microscopic (TEM) observation was performed by JEOL-4000EX.

3. Results and discussion

The X-ray diffraction pattern of the sintered sample showed that this phase has an orthorhombic symmetry as reported previously [4]: the relations between cubic and the orthorhombic lattice are $a_o \approx \sqrt{2}a_c$, $b_o \approx \sqrt{2}a_c$ and $c_o \approx 2c_c$. Because $LaMnO_3$ phase has orthorhombic symmetry only around its stoichiometric composition, non-stoichiometry in the sintered sample can be considered small. The sintered sample was held in at 1273 K in log $P_{O_2} = 10^{-6}$ (Pa) environment for 3 days. The X-ray diffraction of the annealed sample also showed orthorhombic symmetry. From the phase diagram of this phase [7,8], the annealed sample must have stoichiometric composition.

Fig. 1 shows the electron diffraction patterns of this phase from [0 −1 1], [1 −1 0] and [−1 1 −1] zones. It is reported that the stoichiometric $LaMnO_3$ phase possesses *Pnma*(62) symmetry [6]. However, in the [0 −1 1] zone pattern, *h* 0 0 (*h* = odd), forbidden reflections such as 1 0 0 for *Pnma* symmetry can be clearly observed. Furthermore, in the [1 −1 0] zone pattern, 0 0 *l* (*l* = odd) reflections such as 0 0 1 that are forbidden can be clearly observed.

Shibahara et al. [12] suggested that the reflection conditions of oxygen deficient $LaMnO_3$ phase shows *h* 0 0 (*h* = odd) and 0 0 *l* (*l* = odd) superlattice, however, the electron diffraction patterns of the stoichiometric $LaMnO_3$ phase did not show the superlattice spots. From this point of view, it is considered that the sample prepared in this experiment possesses a small amount of non-stoichiometry, even if there is no evidence from the phase diagram at 1273 K [7,8].

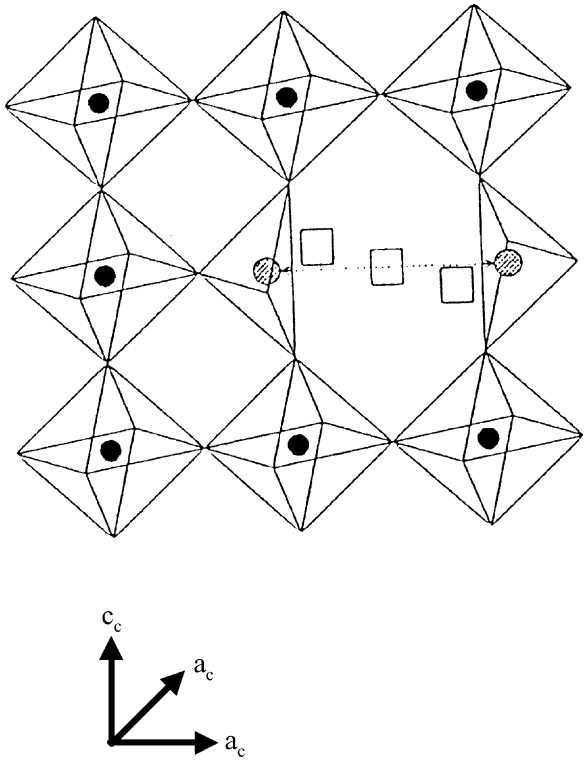

Fig. 2. The super structural model for $LaMnO_{3-\delta}$ phase.

Abbattista and Borlera [9] and Van Roosmalen and Cordfunke [10] proposed the defect superstructural model for $LaMnO_{3-\delta}$ phase shown in Fig. 2. In this model, oxygen vacancies lie on $[1\ 1\ 0]_c$ direction. They also reported that the powder X-ray diffraction pattern of the superstructure $La_4Mn_4O_{11}$ that possesses an orthorhombic cell with $a \approx \sqrt{2}a_c$, $b \approx 8a_c$ and $c \approx \sqrt{2}a_c$ shows 0 4 0 peak which cor-

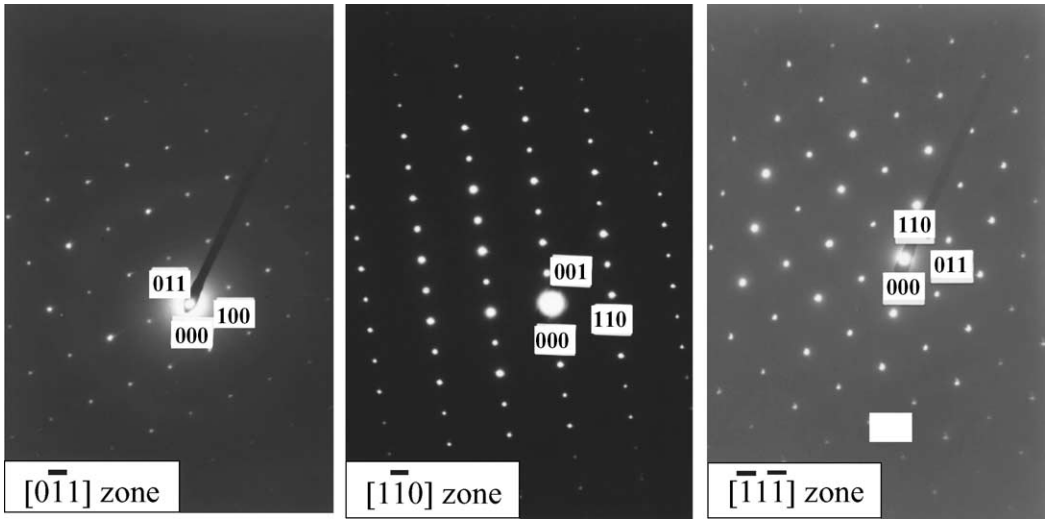

Fig. 1. The electron diffraction patterns from [0 −1 1], [1 −1 0] and [−1 1 −1] zones.

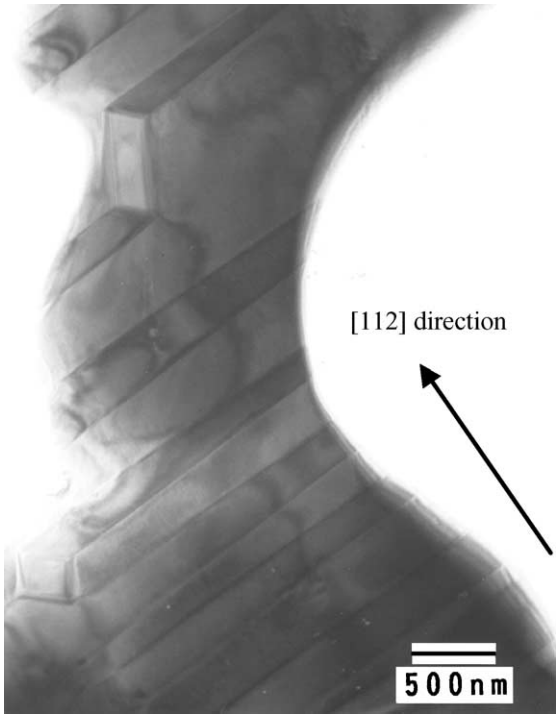

Fig. 3. Low magnification TEM image from [1 −1 0] zone.

respond to 0 0 1 in the $a_o \approx \sqrt{2}a_c$, $b_o \approx \sqrt{2}a_c$ and $c_o \approx 2c_c$ [9,10]. The reflection conditions of the $La_4Mn_4O_{11}$ phase is closed to that of the sample in this experiment, thus it can be considered that the defects in this sample have the same order as cited before.

Fig. 3 shows the low magnification TEM image from [1 −1 0] zone. A coherent twin with about 200 nm interspacing can be observed. From the electron diffraction pattern around the twin boundary, it can be confirmed that this twin consisted (1 1 2) basal plane. Such coherent twin can be also seen in Y-based high Tc superconductor oxide with oxygen deficient non-stoichiometry [13].

The sample that annealed at 1273 K in $P_{O_2} = 10^{-6}$ Pa environment can be confirmed as a phase just before decomposition, however, this phase possessed a small amount of oxygen vacancies and the vacancies ordered in the perovskite structure. Because the defect structure proposed earlier have large space in the structure, it can be considered that coherent twin formed to bury the spaces.

4. Conclusion

A defect structure can be confirmed in the $LaMnO_3$ phase, which is just before phase decomposition. The electron diffraction patterns of this phase showed a series of superlattice spots and its TEM images showed coherent twin in (1 1 2) basal plane.

Acknowledgement

This work was supported by the Grant-in-Aid for Scientific Research (B) (No. 13450259) by the Japan Society for the Promotion of Science.

References

[1] V. Caignaert, E. Suard, A. Maignan, C. Simon, B. Raveau, C.R. Acad. Sci. Ser. 321 (1995) 515–520.
[2] J.Y. Yi, G.M. Choi, J. Eur. Ceram. Soc. 24 (2004) 1359–1363.
[3] Y.J. Leng, S.H. Chan, K.A. Khor, S.P. Jiang, J. Appl. Electrochem. 34 (2004) 409–415.
[4] T. Arakawa, A. Yoshida, J. Shiokawa, Mater. Res. Bull. 15 (1980) 269–273.
[5] R.D. Shannon, A.W. Sleight, Inorg. Chem. 7 (1968) 1649–1653.
[6] K. Kamata, T. Nakajima, T. Hayashi, T. Nakamura, Mater. Res. Bull. 13 (1978) 49–54.
[7] N. Kamegashira, Y. Miyazaki, Y. Hiyoshi, J. Mater. Sci. Lett. 3 (1984) 899–900.
[8] N. Kamegashira, Y. Miyazaki, Mater. Res. Bull. 19 (1984) 1201–1206.
[9] F. Abbattista, L. Borlera, Ceram. Lett. 7 (1981) 137.
[10] J.A.M. Van Roosmalen, E.H.P. Cordfunke, J. Solid State Chem. 93 (1991) 212–219.
[11] T. Atsumi, T. Ohgushi, H. Namikata, N. Kamegashira, J. Alloys Compos. 252 (1997) 67–70.
[12] H. Shibahara, K. Numaguchi, N. Seo, M. Kawasaki, K. Ibe, H. Taguchi, J. Ceram. Soc. Jpn. 104 (1996) 11–16.
[13] M. Hervieu, B. Domenges, C. Michel, J. Provost, B. Raveau, J. Solid State Chem. 71 (1987) 263–273.