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双晶構造を含む酸素欠損型 LaMnO_{3-x} の高分解能電子顕微鏡観察

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Oxygen-defective LaMnO_{3-x} with twin structure was studied using an HREM. On the basis of direct observation with a 200-kV HREM and with the aid of computer simulation, an optimum imaging condition was found, where metal La and Mn atoms and oxygen atoms were imaged as dark spots and bright spots, respectively. The through-focus observation and intensity profile observed from the image contrast support the view that the oxygen vacancies could be detected from the intensity distribution of bright spots in the observed image, which represents the positions of the oxygen atoms. A structure image under the optimum imaging condition reflected the twin structure with oxygen vacancies in LaMnO_{3-x} . Twin structures were found to consist of two kinds of twin planes, (110) and (112), including oxygen vacancies.

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1. Introduction

The LaMnO_3 system consists of stacked close-packed layers of LaO_3 with Mn metal atoms occupying the interlayer octahedral sites. LaMnO_3 is applicable as an electrode in high-temperature solid-state fuel cells or as a catalyst which oxidizes hydrocarbons.^{1),2)} Figure 1 shows the crystal structure of stoichiometric LaMnO_3 which has a perovskite-type structure with an orthorhombic cell.^{3),4)} Perovskite oxides and related oxides such as LaMnO_3 , BaMnO_3 ,⁵⁾⁻⁷⁾ SrMnO_3 ⁸⁾ and BaNiO_3 ⁹⁾ have a tendency to lose oxygen with increasing tempera-

ture and/or pressure and become nonstoichiometric.

One of the authors has reported the high resolution electron microscope (HREM) observation of BaMnO_{3-x} using a 200 kV electron microscope, and stated that under optimum imaging conditions, the oxygen defects in the oxide could be distinguished as bright white dots in the image contrast, where the dark spots represent the positions of the metal atoms such as Ba and Mn.¹⁰⁾ Furthermore, using a 300 kV electron microscope equipped with an imaging plate (IP), the optimum imaging conditions of an HREM for reflecting the oxygen-defect structure in LaMnO_{3-x} has been reported to reveal the oxygen-defective structure in the reduced oxide sample.¹¹⁾ In the high T_c superconductor $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$, the images observed with an HREM could provide information about the oxygen vacancies in the basal plane.¹²⁾ The influence of oxygen vacancies on image contrast cannot be neglected. Analyses of the oxygen-defective structure of perovskite and related oxides are of interest because its magnetic properties depend on the oxygen vacancy content. We report here the presence of twin structures accompanying oxygen vacancies in LaMnO_{3-x} on the basis of observation with a 200-kV HREM and the computer simulation of image contrast.

2. Experimental

A sample of LaMnO_3 used as the starting material was prepared by the sol-gel process at low temperature.¹³⁾ By reducing the stoichiometric

Fig. 1. Structure model of stoichiometric LaMnO_3 .

LaMnO_3 in vacuo around 10^{-4} Pa at 900°C , LaMnO_{3-x} samples with oxygen vacancies were prepared. To characterize the starting material samples and the reduced oxide samples with small amounts of oxygen vacancies, both X-ray powder diffraction and electron diffraction techniques were employed. Oxygen content in the sample was determined by the oxidation-reduction method.¹⁴ The HREM images have been interpreted through image simulation based on the multi-slice method. The X-ray powder diffraction patterns were obtained at room temperature with Ni-filtered Cu $K\alpha$ radiation and a monochromator. For electron microscope observation, the samples were gently ground, dispersed in absolute ethanol and mounted onto holey carbon microgrids. The HREM images were taken with a 200-kV electron microscope (JEM 200EX II) with a point resolution of better than 0.21 nm. The present samples were not subjected to changes in crystal structure by grinding or by electron beam irradiation during the observation. Image simulations were carried out using a personal computer with a 32 bit microprocessor. The digitized images for measuring the intensity profile were directly obtained from the photographs of the observed images using a CCD camera.

3. Results and discussion

The starting powder samples were identified as stoichiometric LaMnO_3 using an X-ray powder diffraction method. The X-ray diffraction pattern gave the lattice parameters of $a=0.5535$, $b=0.5758$ and $c=0.7708$ nm in an orthorhombic system, which agreed with those previously reported.^{3,4,15,16} The oxygen content in LaMnO_{3-x} ranged from 2.60 to 2.74.

3.1 Electron diffraction analyses

The typical electron diffraction patterns from a nonstoichiometric LaMnO_{3-x} sample with several incident beams of $[100]$, $[010]$ and $[1\bar{1}0]$ are shown in Figs. 2(a), (b) and (c). The reduced sample of LaMnO_{3-x} showed preservation of the unit cell of the stoichiometric LaMnO_3 structure. In Figs. 2(a), (b) and (c) several extra spots due to a change in

crystallographic symmetry were found as indicated by the arrows, which were not observed for stoichiometric LaMnO_3 because of the forbidden reflections. Extra spots in Figs. 2(a), (b) and (c) could be assumed to be due to orderly oxygen vacancies induced in the matrix of LaMnO_3 , as will be discussed later.

3.2 HREM observation

Figures 3(a) and (b) show the observed image and the selected-area electron diffraction pattern from the regions including P and Q of LaMnO_{3-x} , respectively. Figures 3(c) and (d) show the schemat-

Fig. 2. Electron diffraction patterns from the specimen of a non-stoichiometric LaMnO_{3-x} in (a) $[100]$, (b) $[010]$ and (c) $[1\bar{1}0]$ directions. Arrowheads indicate extra spots due to the phase transformation into the defective structure.

Fig. 3. (a) Typical observed images of LaMnO_{3-x} showing the twin structures with the (112) and (110) twin planes. A, B and C indicate the twin boundaries. (b) Electron diffraction pattern from regions P and Q. Arrowheads indicate the separation of the diffraction spots due to the presence of the twin structure. (c) and (d) Schematic diagrams showing the arrangements and indices of electron diffraction spots in (b).

ic diagrams of Fig. 3(b), and the arrangements of electron diffraction spots, respectively. The region marked as R in Fig. 3(a) shows the observed image in the $[\bar{1}\bar{1}0]$ direction. It could be ascertained from Fig. 3(b) that the letters P and Q in Fig. 3(a) mark the regions in the $[001]$ direction, where the twin plane as indicated by arrow C could be interpreted as consisting of the (110) plane. Boundaries A and B include the (112) twin plane tilted relative to the incident beam at the angle of about 41 degrees. In the present observation, the twin structures were widely and uniformly distributed in the specimens reduced in vacuo.

A structure model for the twin relation in Fig. 3(a) is shown in Figs. 4(a) and (b). The twin plane of (112) is indicated by the arrow in Figs. 4(a) and (b), and includes the oxygen vacancies, assuming the proposed defective structure model, as will be discussed later. Figure 3(b) obtained from both regions P and Q also indicated the presence of the twin structure, showing the separation in the electron diffraction spots of (110) , as indicated by the ar-

rows. It is suggested that the shift difference in lattice constants of a and b in an orthorhombic system resulted in the separated spots in the electron diffraction pattern shown in Fig. 3(b). It is also noted that periodic bright spots in the image contrast were observed in region R in Fig. 3(a) as indicated by the arrows labeled D.

Figure 5 shows a series of through-focus observed images in region R of Fig. 3(a). Such a characteristic image contrast was found for the observation of oxygen-defective structure using a 300-kV electron microscope with IP.¹¹⁾ In order to discuss the relationship between the oxygen-defective structure in LaMnO_{3-x} and such a characteristic image contrast, HREM images were interpreted by means of the image simulation on the basis of a dynamical electron diffraction theory. To give an adequate interpretation of the observed images of Fig. 5, the simulations for the stoichiometric structure of LaMnO_3 and the oxygen-defective structure of LaMnO_{3-x} previously reported¹¹⁾ were carried out.

The oxygen-defective structure model of

Fig. 4. Schematic diagram showing the twin relation found in Fig. 3. (a) $[\bar{1}\bar{1}0]$ direction. Twin plane of (112) is perpendicular to the plane of the paper. (b) $[001]$ and $[\bar{1}\bar{1}0]$ directions. Twin plane of (112) is tilted relative to the plane of the paper at an angle of about 41 degrees.

Fig. 5. Experimental through-focus series of HREM images of LaMnO_{3-x} . Simulation images for the two cases of 5.5 and 11.1 nm thickness are shown in insets.

LaMnO_{3-x} , where the oxygen vacancies are periodically located, as shown by the square symbols, is described in Fig. 6(a). Figure 6(b) shows the projection of the defective structure model of LaMnO_{3-x} in the $[\bar{1}\bar{1}0]$ direction, and indicates that the atomic arrangements along arrow x include the chain consisting of alternate La atoms and oxygen vacancies in LaMnO_{3-x} . Projection in the $[\bar{1}\bar{1}0]$ direction is advantageous for viewing the defective structure including oxygen vacancies. It is also possible to resolve with high accuracy the positions between metal and oxygen atoms using the present 200-kV HREM with a resolution of 0.21 nm.

Figures 7(a) and (b) show the results of the image simulations in the $[\bar{1}\bar{1}0]$ direction for LaMnO_3 without any defects and LaMnO_{3-x} with oxygen defects, respectively. The frameworks represent

Fig. 6. Schematic defective structure model used for calculation, where the oxygen vacancies are indicated by square symbols.

Fig. 7. Image simulation using multi-slice method: (a) perfect structure of LaMnO_3 , (b) oxygen-defective structure of LaMnO_{3-x} .

their unit cells. The calculation was carried out under the following imaging conditions: thickness, 4.0, 8.0, 12.0 and 16.0 nm; amount of defocus, 30, 40, 60, 90, 120 and 150 nm in underfocus; spherical aberration constant, 0.7 mm; focus spread, 15 nm; beam divergence semi-angle, 1.0 mR; and accelerating voltage 200 kV. The features in the image contrast under the optimum imaging condition near the Scherzer focus lead to the conclusion that dark spots represent the positions of the metal atoms such as La and Mn, and bright spots are those of the oxygen atoms in LaMnO_{3-x} . The images observed under such imaging conditions are called "dark-spot images".¹⁰⁾ However, the contrast due to Mn atoms was affected to some degree by nearby oxygen atoms.

The series of images in Fig. 7(b) shows that the characteristic image contrast due to oxygen defects could be observed, as indicated by the arrowheads, under the present imaging conditions of, for example, around 12 nm in thickness and 30–40 nm in underfocus. It was found by comparing the image contrast of Fig. 7(a) with that of 7(b) that the intensity of the bright spots corresponding to the positions of the oxygen atoms becomes stronger due to oxygen vacancies. It should be noted that the anomalous image contrast with the periodic bright spots in Fig. 7(b) could not be found in the series of Fig. 7(a), assuming a stoichiometric LaMnO_3 structure. There is a considerable difference in image contrast between Figs. 7(a) and (b), which could allow one to distinguish between the two structures of Figs. 1 and 6 from the observed image contrast.

Figures 8(a), (b) and (c) show the cross-sectional intensity profiles obtained from the simulation images of Fig. 7(b), which reflect the oxygen-defective structure. The line profiles show the relationship between the intensity distributions of the simulation images and the atomic positions for La, oxygen atoms and/or oxygen vacancies. The imaging condition was assumed to be about 11.1 nm in thickness, and 29 nm in underfocus, which could give dark spot images. The intensity profiles in Figs. 8(a), (b) and (c), obtained by plotting along lines x (dotted) and y (solid) as indicated in Fig. 6(b), show the results for the three atomic occupancies of 0.0, 0.7 and 1.0 in the oxygen sites. From the results shown in Figs. 8(b) and (c), the peaks corresponding to the oxygen vacancies (indicated by arrowheads) become higher than those of the sites occupied by oxygen atoms. The peak ratios of x to y in Figs. 8(b) and (c) are about 1.2 and 1.7, respectively. For the case without any defects, the two peaks along lines x and y show the same height as shown in Fig. 8(a).

Under the imaging conditions of Fig. 8, the positions of the oxygen atoms and their vacancies could be recognized as bright spots from the intensity distribution in the simulation image. It is also noted that the peak ratio becomes higher with decreasing oc-

Fig. 8. Intensity profile obtained from the results of image simulation. Letters x and y correspond to those in Fig. 6(b). (a)–(c) Variation due to the change of oxygen occupancy. (d)–(f) Variation due to the change of sample thickness.

cupancy of the oxygen atoms. On the other hand, the series in Figs. 8(d), (e) and (f) show the change in intensity profiles caused by variation in thickness of the sample with oxygen vacancies. The simulations of Figs. 8(d), (e) and (f) were also carried out with 29 nm in underfocus. The peak ratios in Figs. 8(d), (e) and (f) are 1.3, 1.5 and 1.5 for thicknesses of 5.5, 11.1 and 16.5 nm, respectively. It is suggested that in a region thinner than 10 nm, the bright spots due to oxygen vacancies become more intense with increasing thickness of the sample. These results shown in Fig. 8 are consistent with those obtained using a 300-kV electron microscope with IP.¹¹⁾

Figures 9(a) and (b) show the intensity profiles of the observed image shown in Fig. 5(a), taken directly from the photograph using a CCD camera. The profiles labelled x , X (dotted lines) and y , Y (solid lines) were plotted along the line indicated in Fig. 5(a). The region around the x and y lines in Fig. 5(a) lies near the edge of the sample, and is thinner than that between X and Y . Lines x and X correspond to the chains consisting of alternate La atom and oxygen vacancy. The difference on intensity profiles be-

Fig. 9. Intensity profiles obtained from the observed image. The profiles lettered x , X (dotted lines) and y , Y (solid lines) were plotted along the lines indicated in Fig. 5(a).

tween Figs. 9(a) and (b) is caused by variation in thickness. The average peak ratios from Figs. 9(a) and (b) are 1.2 and 1.4, respectively, which are semi-quantitatively in good agreement with those of the simulation results shown in Fig. 8. The intensity profiles of Fig. 9 and the results of image simulations with a defocus value of 29 nm and thicknesses of 5.5 and 11.1 nm were roughly compatible.

It is noted that the observed image in Fig. 5(a), a dark spot image, showed bright spots at the positions of the oxygen vacancies. The simulation images under the corresponding imaging conditions are shown in insets in the Figs. 5(a), (b) and (c). Simulation results of the two regions with 5.5 nm and 11.1 nm in thickness appear to be in good agreement with the observed images in the inset. In Fig. 5(a), the arrangement of not only the La and Mn atoms but also the defect structure including oxygen vacancies could be deduced from the observed image. Con-

sequently, Fig. 5(a), one of the observed through-focus images, was considered to be a structure image reflecting in particular, the oxygen-defective structure in LaMnO_{3-x} .

Although oxygen contents in LaMnO_{3-x} could be roughly estimated from the results shown in Figs. 8 and 9 on the basis of the proposed structure model of Fig. 6 (average oxygen atomic occupancy around 0.2 in Fig. 6), it should be considered that the characteristics of photographic film, namely low sensitivity and narrow dynamic range for the recording of electron intensity, prevent quantitative analysis.

Figure 5 shows a series of through-focus observed images in region R of Fig. 3(a). The reason why twin structures were frequently found in the present samples as shown in Fig. 3, may be because the twin plane consists of the (112) or (110) plane including the oxygen vacancies, as previously shown in Figs. 4 and 6. However, the distribution of oxygen vacancies along the column parallel to the incident beam has not been examined by the image analysis.

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