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Study of $La_{1-x}MnO_{3-\delta}$ non-stoichiometry and defect structure using ESR and iodometry

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The oxidation states of manganese in the $La_{1-x}MnO_{3-\delta}$ ($x = 0.09$–0.11) were investigated by electron spin resonance (ESR) and iodometry. The ESR analysis carried out at room temperature for the samples prepared in air revealed the presence of broad peaks at $g = 2.0$, considered to be relevant to Mn^{2+}. It was also found that the intensity of the peak increased as lanthanum vacancy content increased. The average valence state of manganese, determined by iodometry, was approximately 3.2, and decreased by 1 as the lanthanum vacancy increased by 1. Similar trends were observed with the samples prepared at $P_{O_2} = 1 \times 10^{-7}$ atm. The results indicated that Mn^{2+} is stably present in the $La_{1-x}MnO_{3-\delta}$ having an average valence number exceeding 3.0. A series of experimental results with respect to the non-stoichiometry of $La_{1-x}MnO_{3-\delta}$ can be explained by assuming that Mn^{2+} is stabilized after forming a complex with a lanthanum vacancy and two oxygen vacancies.

1. Introduction

Shimoyama and co-workers [1, 2] investigated the relationship between oxygen non-stoichiometry in the $La_{1-x}MnO_{3-\delta}$ and oxygen partial pressure in the atmosphere and pointed out that a phase with lanthanum vacancies at the A-site is stable in air. Kuo *et al.* [3] investigated the relationship between oxygen partial pressure in the atmosphere and oxygen non-stoichiometry in the $LaMnO_x$ and proposed a model to explain the non-stoichiometry of $LaMnO_x$, in which the region where oxygen non-stoichiometry is independent of oxygen partial pressure in the atmosphere is a stoichiometric state. The model proposed by Kuo *et al.* is characterized by the formation of lanthanum vacancies in parallel with manganese vacancies in the oxygen-excess region, compared with the model proposed by Shimoyama and colleagues in which only lanthanum vacancies were considered.

The behaviour of lanthanum and oxygen vacancies in $La_{1-x}MnO_{3-\delta}$ and the accompanying change in the oxidation number of manganese are important phenomena for understanding the behaviour of $La_{1-x}MnO_{3-\delta}$: however, they are not yet clearly understood and the oxidation states of manganese have not been investigated.

In the present work, the oxidation states of manganese were directly observed by electron spin resonance (ESR) to clarify that Mn^{2+} is present in $La_{1-x}MnO_{3-\delta}$ even with $3 - \delta$ greater than 3. Based on these results and the results of the iodometry analysis, a new model to explain the non-stoichiometry of the $La_{1-x}MnO_{3-\delta}$ has been proposed.

2. Experimental procedure

The raw materials for the $La_{1-x}MnO_{3-\delta}$ were La_2O_3 and MnO_2 (99.99% purity, Rare Metallic Corporation). The powders were thoroughly mixed in a given ratio, pre-fired at 1273 K for 15 h in air, ground, fired at 1573 K for 24 h, and again ground to form $La_{1-x}MnO_{3-\delta}$ powders. These powders were further treated at 1073 K for 3 h at a given oxygen partial pressure and then quenched to establish a fixed oxygen vacancy. After dissolving in hydrochloric acid, the compositions of the samples were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). To analyse the crystal structure, the ordinary power X-ray diffraction (XRD) method was used. The ESR analysis was conducted at room temperature, using a Joel·X-band JES-FE3XG analyser.

The valence state of manganese was determined by iodometry, by dissolving approximately 50 mg oxide powder and 3 g KI in a mixture of 1 ml 10 N HCl and 40 ml distilled water in a nitrogen flow, and titrating the solution with 0.01 N $Na_2S_2O_3$, using a starch solution as the indicator.

3. Results and discussion

$La_{1-x}MnO_{3-\delta}$ ($x = 0.09$, 0.10 and 0.11) treated at 1073 K in air was analysed by ESR. The spectral patterns of them are shown in Fig. 1. Each sample had a signal which is almost 50 mT in width and showed no hyperfine structure at near 340 mT ($g = 2.0$). As the lanthanum content decreased, the intensity of this signal increased and the width of it slightly decreased.

TABLE I ESR spectral parameter of $La_{1-x}MnO_{3-\delta}$ produced in air

	$La_{0.89}MnO_{3-\delta}$	$La_{0.90}MnO_{3-\delta}$	$La_{0.91}MnO_{3-\delta}$
Normalized signal intensity	1.08	1.00	0.95
Signal width (mT)			
$\Delta H_{1/2}$	77	87	85
ΔH_{msl}	47	48	50
$\Delta H_{1/2}/\Delta H_{msl}$	1.6	1.7	1.7

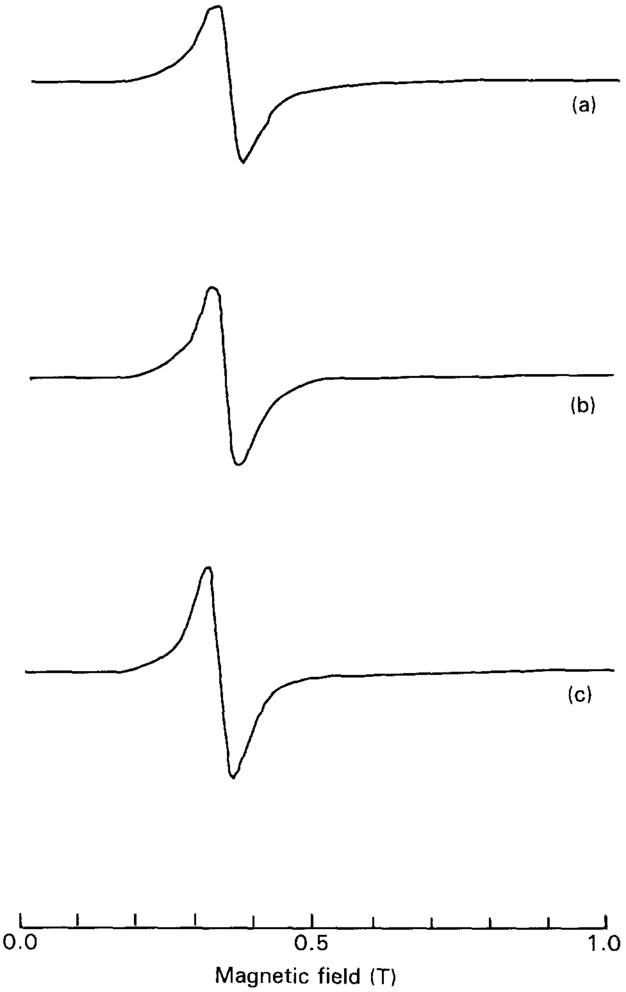

Figure 1 ESR spectra of $La_{1-x}MnO_{3-\delta}$ produced in air. (a) $La_{0.91}MnO_{3-\delta}$, (b) $La_{0.90}MnO_{3-\delta}$, (c) $La_{0.89}MnO_{3-\delta}$.

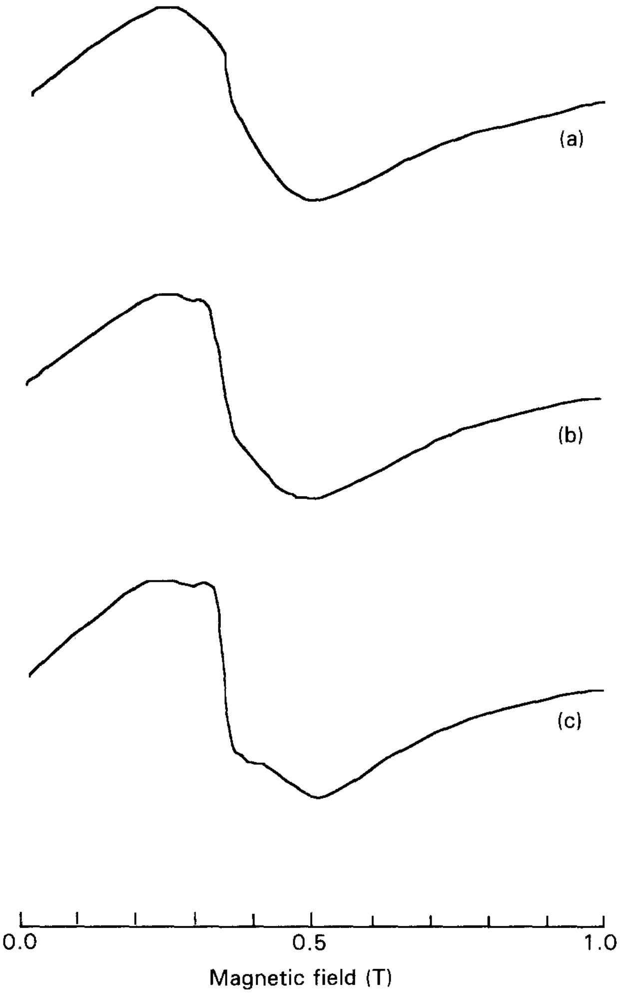

Figure 2 ESR spectra of $La_{1-x}MnO_{3-\delta}$ produced in low oxygen pressure ($P_{O_2} = 1 \times 10^{-7}$ atm). (a) $La_{0.91}MnO_{3-\delta}$, (b) $La_{0.90}MnO_{3-\delta}$, (c) $La_{0.89}MnO_{3-\delta}$.

The integrated intensities of these signals, normalized by the sample weight, are given in Table I. The widths, represented by width at half power, $\Delta H_{1/2}$, and width at the maximum slope, ΔH_{msl}, are also shown in Table I for comparison. The $\Delta H_{1/2}/\Delta H_{msl}$ ratio was about 1.7, indicating that the signals almost followed the Lorenz curve. The spin density, calculated from the ESR signal intensity, suggested that these signals were not derived from sample impurities but from the major elements, though obtained data were sufficient for quantitative discussion of the phenomena.

Fig. 2 shows the results of ESR analysis for $La_{1-x}MnO_{3-\delta}$ ($x = 0.09$, 0.10 and 0.11) treated at 1073 K at oxygen partial pressure of 1×10^{-7} atm. Each sample had a signal which is approximately 36 mT in width and showed no hyperfine structure in the region of 340 mT, and a very broad signal extending between 0 and 1 T. The intensity of the peak of the signal observed at near 340 mT tended to increase as the lanthanum content decreased.

The signal observed at near 340 mT, shown in Fig. 1, are apparently relevant to Mn^{2+} or Mn^{4+}, because Mn^{3+} has no unpaired electron. Comparing these signals with the results of ESR analysis for the manganese complexes by Richens and Sawyer [4], they are very similar to Mn^{2+} signals of the $Mn(H_2O)_6^{2+}$ ion in the solid phase, which was observed at 77 K in a methanol solution of sorbitol and Me_4NOH. Further, Ferrante *et al.* [5] and Richens and Sawyer [4] reported that the peaks of Mn^{4+} signal, coming from the zero-field splitting, observed at near $g = 4$ (approximately 160 mT); the signal is very different from that observed in this study. Comparing the spectral patterns of the samples prepared at

TABLE II Results of iodometry and calculated value of the manganese oxidation number

	Sample (produced oxygen partial pressure atm)					
	$La_{0.89}MnO_{3-\delta}$ (0.21)	$La_{0.90}MnO_{3-\delta}$ (0.21)	$La_{0.91}MnO_{3-\delta}$ (0.21)	$La_{0.89}MnO_{3-\delta}$ (10^{-7})	$La_{0.90}MnO_{3-\delta}$ (10^{-7})	$La_{0.91}MnO_{3-\delta}$ (10^{-7})
Oxygen non-stoichiometry, δ	0.06	0.04	0.02	0.18	0.16	0.14
Average Mn oxidation state	3.21	3.22	3.23	2.97	2.98	2.99
Calculated Mn oxidation state						
Mn^{2+}	0.11	0.10	0.09	0.11	0.10	0.09
Mn^{3+}	0.56	0.57	0.58	0.82	0.83	0.84
Mn^{4+}	0.33	0.33	0.33	0.07	0.07	0.07

varying oxygen partial pressures (Figs 1 and 2), no significant difference was observed in the intensity of the signals near 340 mT. It is inconceivable that these signals represent all of the Mn^{4+} ions in each sample, because the results of Shimoyama and co-workers [1, 2] and Kuo *et al.* [3] for the nonstoichiometry of $LaMnO_3$ systems and the results of iodometry discussed later, indicate that the Mn^{4+} content in the sample prepared at an oxygen partial pressure of 1×10^{-7} atm is one-third or less that of the sample prepared in air.

These results, therefore, strongly suggest that the signal near 340 mT is due to Mn^{2+}. Because electrons transfer between Mn^{4+} and Mn^{3+} very fast, the Mn^{4+} signal is considered unobservable. Manganese present in $La_{1-x}MnO_{3-\delta}$ has been considered, as discussed by Kuo *et al.* [3] and Shimoyama and co-workers [1, 2], to consist of Mn^{3+} and Mn^{4+} only; however, the results of ESR analysis have clarified that Mn^{2+} is present in compositions having an average valence state above 3.

Table II shows the results of iodometry, indicating that the average valance state of manganese decreases by 1 as the lanthanum vacancy content increases by 1, both with the samples synthesized in air and at an oxygen partial pressure of 1×10^{-7} atm, and in agreement with the results of ESR, showing that the intensity of the signal due to Mn^{2+} increases as the lanthanum vacancy content increases. The conventional models, proposed by Kuo *et al.* [3] and Shimoyama and co-workers [1, 2] suggest that the average valence state of manganese should increase as the lanthanum vacancy content increases, under electrically neutral conditions, which is incompatible with the results of iodometry. Some of the Mn^{4+} might be localized around lanthanum vacancies, for some reason, to give an ESR spectral pattern showing no hyperfine structure. This is one possibility which cannot be completely ruled out, in terms of the ESR results alone. Such a concept, however, is incompatible with the results of iodometry.

Kuo *et al.* [3] and Shimoyama and co-workers [1, 2] point out that the region where non-stoichiometry of the $La_{0.90}MnO_{3-\delta}$ is independent of oxygen partial pressure at 1073 K is $P_{O_2} = 10^{-9}$–10^{-13} atm. Therefore, it is difficult to consider, based on their discussion, that Mn^{2+} is formed by the reduction of $La_{0.90}MnO_{3-\delta}$ at an oxygen partial pressure of 1×10^{-7} atm, which is shifted to the oxygen-excess side from the above flat region. The iodometry results have shown that the average oxidation state of manganese is below 3.0, which supports the concept that Mn^{2+} is stable and independent of the redox reactions.

We have proposed a model based on the experimental results, where it is assumed that one lanthanum vacancy, one Mn^{2+} ion and two oxygen vacancies are combined to form a stable, electrically neutral complex. In accordance with this model, the intensity of the ESR signal of manganese is proportional to the lanthanum vacancy content, and hence the ratio of the ESR signal intensity to lanthanum vacancy content, x, will be almost constant. This concept is supported by the experimental results shown in Table I.

The proportions of Mn^{2+}, Mn^{3+} and Mn^{4+} in each sample are shown in Table II, where the proportion of Mn^{2+} is the same as the lanthanum vacancy content from the model, and those of Mn^{3+} and Mn^{4+} are calculated from the experimental results of iodometry. As shown, the model is compatible with the results of iodometry. Furthermore, the model will be supported, though qualitatively, by crystalline structure considerations, as discussed below.

1. The negative charge of the lanthanum vacancy will be the most stable in terms of enthalpy considerations, when neutralized by the positive charge of the nearest oxygen vacancy.

2. A sufficiently large space is provided for manganese atom around a lanthanum or oxygen vacancy, and Mn^{2+} having a large ionic radius will not expand the crystal as a whole. Therefore, Mn^{2+} is more stable than Mn^{3+} at the lattice point.

3. The complex, being electrically neutral as a whole, will not significantly affect the redox behaviour elsewhere.

This model also explains well the thermogravimetric analysis results, described in a previous paper [6], namely that the amount of oxygen desorption from $La_{1-x}MnO_{3-\delta}$ with different lanthanum vacancy contents are essentially unchanged.

4. Conclusion

ESR and iodometry analyses were carried out to investigate the oxidation states of manganese and the oxygen vacancy content for $La_{1-x}MnO_{3-\delta}$ ($x = 0.09$–0.11) prepared under different oxygen partial pressures. It was found that Mn^{2+} can exist stably in $La_{1-x}MnO_{3-\delta}$ having an average oxidation number above 3.0. The analytical results strongly suggest that the Mn^{2+} ion is stabilized after forming an electrically neutral complex with one lanthanum vacancy and two oxygen vacancies, independent of the redox reactions.

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