Preparation of Non-Stoichiometric $Nd_{1-x}MnO_{3-y}$ by Coprecipitation Method

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The coprecipitate of carbonates was obtained by titrating an ammonium carbonate solution into an hydrochloric solution of MnO_2 and Nd_2O_3. The non-stoichiometric perovskite-type oxide, $Nd_{1-x}MnO_{3-y}$ was synthesized by firing the coprecipitate in air without flowing. For the products of $Nd_{1-x}MnO_{3-y}$ prepared at 1100 ℃, the single phase showing the stable y/x value 1.5 was obtained in the x=0.05 to 0.20 region, and a by-product Mn_3O_4 was appeared in x=0.25.

The ABO_3 perovskite-type oxide, $LnMnO_3$, is a material which attracts much attention in recent years, because it exhibits a large magnetoresistance and is regarded as a cathode material for solid fuel cells. An experiment for introducing vacancies into A sites in this system is interesting in terms of control of its physical properties. However, as for A site defect of this system, a $La_{1-x}MnO_{3-y}$ material (Ln=La in $LnMnO_3$) has been synthesized so far only for insomuch as $x \leqq 0.1$, and there is a report that Mn_3O_4 appeared as an impurity phase if the defects were intended to be introduced by the amount of 0.1 or more.[1] Lately a huge magnetoresistance has been discovered which accompanied with a charge ordering structure of Mn^{3+} and Mn^{4+} in a $NdMnO_3$ system.[2] Moreover, this system receives attentions in having a low reactivity with YSZ (yttria-stabilized zirconia) used as an electrolyte for a cathode material.[3] However, there are few investigations concerning the generation of the A site defect in this system.

We have successfully carried out an experiment to introduce vacancies into Nd sites of $NdMnO_3$ using a coprecipitation method reported by Uehara *et al.* (1998),[4] finding that a large amount of vacancies can be introduced thereby at a relatively low temperature.

Aqueous solutions of 0.5 M of Nd_2O_3 and Mn_3O_4 were prepared by dissolving Nd_2O_3 and Mn_3O_4 in 3 M and 5 M of hydrochloric acid, respectively. The amount of 5 ml of the Mn aqueous solution and a prescribed amount of the Nd aqueous solution were mixed and diluted with distilled water so as to make a solution of 1000 ml as a whole content. The excess amount of 3 M of ammonium carbonate was dropped into this solution while being stirred vigorously, so that coprecipitates were obtained. Then, $Nd_{1-x}MnO_{3-y}$ was synthesized by firing the centrifuged coprecipitates at temperatures from 600 ℃ to 1100 ℃ for 2 h in air.

Table 1. Chemical analysis of products

	x=0	x=0.05	x=0.1	x=0.15	x=0.20
Nd	57.0	56.7	55.4	55.0	54.0
Mn	21.9	22.8	23.5	24.4	25.3
O	20.4	19.8	20.3	20.2	20.4
total	99.3	99.3	99.2	99.6	99.7
	composition per Mn=1.00				
Nd	0.99 (0.93)[a]	0.95	0.90	0.86	0.81
Mn	1.00 (0.94)[a]	1.00	1.00	1.00	1.00
O	3.20 (3.00)[a]	2.98	2.97	2.84	2.77

[a] Composition on the basis of three oxygens.

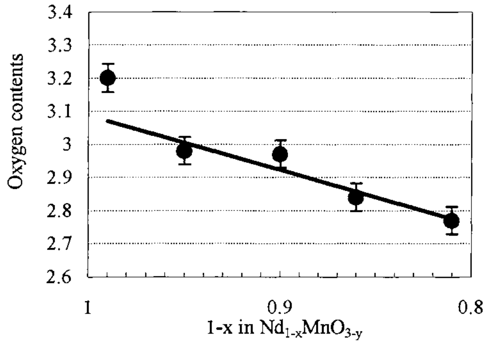

Figure 1. Oxygen contents with Nd deficiency for the $Nd_{1-x}MnO_{3-y}$. It is shown that the oxidation state of Mn for x =0.05 to 0.2 is $Mn^{3.1+}$

The compositions of major cations and oxygen in the products were determined by ICP and inert gas melt infrared spectroscopy, respectively. The result, as shown in Table 1, indicates that the composition of the products almost coincides with a starting composition. Since the content of chlorine in the samples is negligible by EPMA analysis, chlorine in the precipitates is considered to be almost completely evaporated away during the firing process. Figure 1 is a diagram obtained by plotting the amounts of oxygen versus (1-x) values in $Nd_{1-x}MnO_{3-y}$. This plotting confirms that oxidation number of Mn is almost equivalent $Mn^{3.1+}$, being constant, for the samples of x=0.05 to 0.2. From this fact, it is considered that defects were introduced into oxygen sites accompanied with the introduction of defects to the A sites, and the ratio of y/x = 1.5 was almost constant. A product with a stoichiometric, i.e. x=0, showed a composition with excess oxygen, however, it can be thought that metallic vacancies were generated, as Roosmalen *et al.*(1994) pointed out for a $LaMnO_{3+d}$ system.[5] Therefore it might be reasonable to designate that the product had a composition of $Nd_{0.93}Mn_{0.94}O_3$.

For each product, the X-ray powder diffraction (XRD) was carried out at room temperature using a monochromatized CuKα radiation. Figure 2 shows XRD patterns of $Nd_{1-x}MnO_{3-y}$ synthesized by firing at 1100 ℃. At x=0.25, a Mn_3O_4 phase appeared, however, single phases were obtained up to x=0.2.

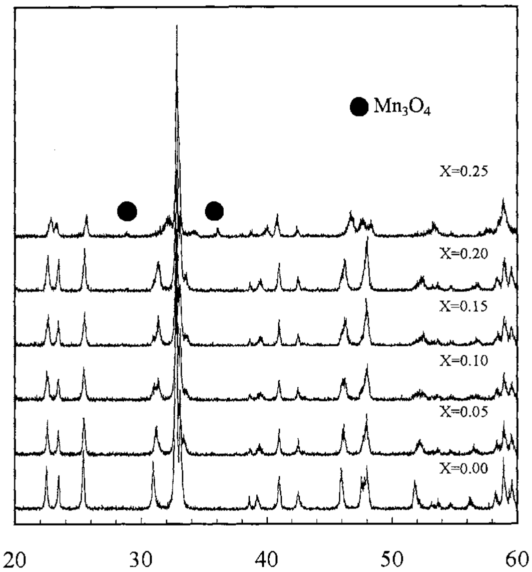

Figure 2. X-ray diffraction patterns of $Nd_{1-x}MnO_{3-y}$ prepared at 1100 ℃.

Moreover, since a peak profile of the perovskite phase for x=0.25, where a Mn_3O_4 was co-existed, was different from those for $x \leqq 0.20$, it is thought that there was a change in the crystal structure for x=0.25. Furthermore, in the synthesis at lower temperatures, a Mn_3O_4 phase was recognized at temperature below 800 ℃ for x=0.10, below 900 ℃ for x=0.15, and below 1000 ℃ for x=0.20, respectively. A single phase was obtained in the conditions at higher temperatures than each temperature mentioned above for each x value. Therefore, it is found that a single phase can be obtained at higher temperatures with increasing amount of defects. In addition, the sample of x=0.25 prepared at 1260 ℃, where Mn_3O_4 peaks were also observed, showed almost the same peak profile as that of the product obtained at 1100 ℃. On the other hand, in case that $Nd_{1-x}MnO_{3-y}$ was prepared using a solid state reaction with the same starting materials, a single phase perovskite was not obtained at this temperature region. A Mn_3O_4 phase was also recognized in the synthetic condition using solid state reaction at a higher temperature (1260 ℃). Hence, the coprecipitation method is considered to be one of effective synthetic processes for obtaining a single phase material since a large amount of defects can be easily introduced at a low temperature. Figure 3 shows lattice constants obtained by applying an orthorhombic system based on the report in JCPDF File No. 25-0565, and plotted versus x values. Figure 4 shows a peak which could not be designated by an index based on the symmetry described at JCPDS File No. 25-0565. This peak indicates that the defects of Nd and/or oxygen sites were introduced not by random but by a certain regularity for $x \geqq 0.1$, and the index was designated by postulating a twice cell in the direction of the *b* axis. As shown in Figure 3, a change for the *a* and *c* values was hardly recognized with respect to x values, however, the *b* value trended to decrease with increasing x values. The change in the lattice constant is dependent on both amounts of Nd and oxygen defects. It is known generally in a material having the crystal structure similar to $NdMnO_3$ that, the *a* and *c* values become smaller, while *b* value shows no change in case that Nd ions are substituted with the same trivalent cations having a smaller ionic radius (for example, Sm or Gd).[6] These facts expect that when the defects are introduced into both Nd and oxygen sites, the distortion of the MnO_6 octahedron is different from the case that ions having a smaller ionic radius are introduced only into Nd sites, and finally, a change in its physical properties should occur. The effects of defect introduction on physical properties will be published in details near feature.

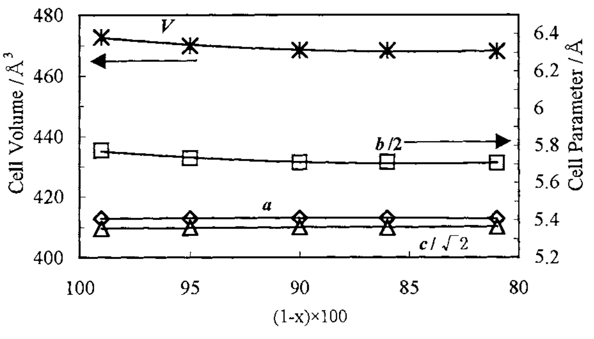

Figure 3. Variation of the lattice parameters for $Nd_{1-x}MnO_{3-y}$ prepared at 1100 ℃.

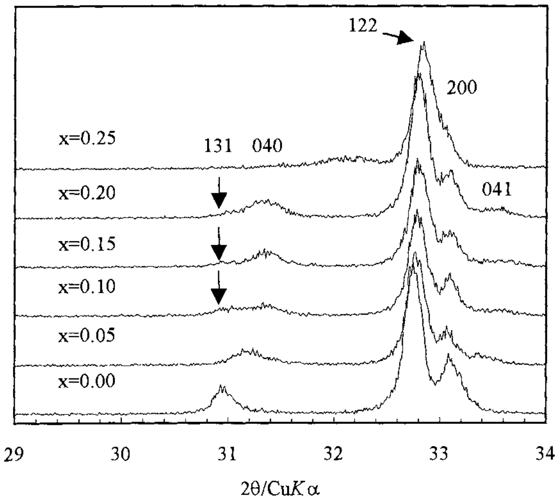

Figure 4. X-ray diffraction patterns of $Nd_{1-x}MnO_{3-y}$ prepared at 1100 ℃. (131 peaks could not be designated by an index based on the symetry described at JCPDS File No. 25-0565, and needed postulating a twice cell in the direction of the *b* axis.)

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References and Notes

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