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Structural Analysis of CoO-MgO System by XAFS

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Abstract. CoO-MgO samples ($\text{Co}_x\text{Mg}_{1-x}\text{O}$: $x = \text{mol of Co} / (\text{mol of Co} + \text{mol of Mg})$) were prepared by impregnation of MgO powder with an aqueous solution of $\text{Co}(\text{NO}_3)_2$, followed by calcination at 773 K. The atomic concentration range of Co for formation of a solid solution and the state of Co ions dissolving in the samples were investigated mainly by XAFS. XRD patterns showed that the dominant phase is MgO in the samples of $x < 0.3$ and the formation of small Co_3O_4 crystallite occurs in the samples of $x > 0.3$. For the samples of $x > 0.5$, the dominant phase was Co_3O_4 and the MgO phase was not detected by XRD. Co K-edge XANES spectra demonstrated that the octahedral symmetry around Co ions in the sample of $x = 0.02$ is distorted in the samples of $x \geq 0.04$, indicating the change in the state of dissolved Co ions. Co K-edge EXAFS spectra revealed that Co ions dissolve into MgO matrix substitutionally in the samples of $x < 0.04$ while the phase separation due to the formation of the Co_3O_4 structure occurs in the samples of $x \geq 0.04$.

1. INTRODUCTION

It is well known that Ni^{2+} , Co^{2+} , Mn^{2+} ions have a tendency to disperse into MgO lattice[1, 2]. Previously, we reported that Ni ions form a solid solution with MgO when the samples were prepared by impregnation of MgO powder with an aqueous solution of $\text{Ni}(\text{NO}_3)_2$, followed by calcination at 773 K[3]. In the present work, we prepared CoO-MgO samples ($\text{Co}_x\text{Mg}_{1-x}\text{O}$: $x = \text{mol of Co} / (\text{mol of Co} + \text{mol of Mg})$) with the same method, and investigated the atomic concentration range of Co for formation of a solid solution and the state of Co ions dissolving in the samples mainly by XAFS.

2. EXPERIMENTAL

The measurement of Co K-edge X-ray absorption spectra was carried out on the beam line 6B at Photon Factory in National Laboratory for High Energy Physics Tsukuba Japan with a ring energy 2.5 GeV and stored current 200-350 mA. (proposal No. 90144). X-ray absorption spectra were recorded in a transmission mode at room temperature with a Si(111) two-crystal monochromator. Mg K-edge X-ray absorption experiments were carried out on the beam line 7A at UVSOR, Institute for Molecular Science, Okazaki, Japan with a ring energy 750 MeV and stored current 80-200 mA (proposal No. 4-C542). X-ray absorption spectra were recorded at room temperature in a total electron yield mode, using a two-crystal beryl monochromator. Normalization of X-ray absorption spectra and the extraction of their EXAFS oscillations were performed as described elsewhere[4, 5].

3. RESULTS AND DISCUSSION

3.1 XRD

XRD patterns showed that the dominant phase is MgO in the samples with $x < 0.3$ although the diffraction peaks attributed to MgO phase were slightly broader for the samples with $x > 0.15$. The formation of small Co_3O_4 crystalline was detected for the samples of $x \geq 0.3$ and the diffraction peaks due to MgO phase was not observed for the samples with $x > 0.5$.

3.2 Co K-edge XAFS

To clarify the change in the symmetry around a Co ion with the cobalt concentration (x), Co K-edge XANES spectra of the samples were investigated. As for the sample with $x = 0.02$, the pre-edge peak of XANES spectrum was as small as that of CoO reference sample with CoO_6 octahedron. The pre-edge peak became more intense with an increase in x and became almost the same size of that of Co_3O_4 in the range with $x \geq 0.3$. As for the samples with $x \geq 0.3$, the feature of XANES was also similar to that of Co_3O_4 . These results indicate that the octahedral symmetry around a Co ion in the sample with $x = 0.02$ is distorted in the sample with $x \geq 0.04$ and the spinel structure of Co_3O_4 is formed at least in the samples with $x \geq 0.3$.

Fig. 1 shows k -weighted Mg K-edge EXAFS of MgO and Co K-edge EXAFS of the sample with $x = 0.02$. The patterns of these spectra are fundamentally the same, indicating that the surroundings around a Co ion in this sample is the same as that of the Mg ion. This result suggests that Co ions are substituted for Mg ions in MgO. The small pre-edge peak in the XANES spectrum of this sample should imply that Co ions are octahedrally coordinated by oxygen due to the Co-Mg substitution. In addition, the k^3 -weighted Co K-edge EXAFS of the sample of $x = 0.02$ (Fig. 2a) was almost identical to the k^3 -weighted Ni K-edge EXAFS of $\text{Ni}_{0.02}\text{Mg}_{0.98}\text{O}$ solid solution,[3] supporting the formation of $\text{Co}_{0.02}\text{Mg}_{0.98}\text{O}$ solid solution. As shown in Fig. 2b, by increasing x from 0.02 to 0.04, the pattern of the k^3 -weighted EXAFS spectrum changes; especially the amplitude in the range of $k = 3 - 7 \text{ \AA}^{-1}$ reduces remarkably. Taking into account that the area of the pre-edge peak in XANES increases for the sample of $x = 0.04$, the decrease in the amplitude of the spectrum would indicate the coexistence of the Co ions in different symmetries, that is the octahedral and a lower symmetry. The presence of Co ions in a lower symmetry may imply the formation of the distinct phase of cobalt oxide in the sample of $x = 0.04$. The phase would be Co_3O_4 since the EXAFS pattern demonstrates that the dominant local structure around a Co ion is Co_3O_4 spinel structure even in the low cobalt concentration $x = 0.11$ (Fig. 2c). On the basis of EXAFS patterns, it had been revealed that the local structure around a Co ion in the sample of $x \geq 0.35$ is identical to the structure of Co_3O_4 . Fig. 2d shows the EXAFS spectrum of $x = 0.35$ as an example. Since the EXAFS oscillation in the range of $k = 12 - 15 \text{ \AA}^{-1}$ is slightly weak compared to that of Co_3O_4 (Fig. 2e), it is expected that the particle size of the Co_3O_4 phase in the sample of $x = 0.35$ would be smaller than that of the Co_3O_4 reference sample. On the basis of the analyses of the Co K-edge XAFS mentioned above, we can conclude that the Co-MgO solid solution is formed only in the range of $x < 0.04$. The phase separation resulting from the formation of Co_3O_4 structure probably occurs in the samples of $x \geq 0.04$ in the short range order, although the phase separation can be detected only in the range of $0.3 < x < 0.5$ by XRD.

We also investigated Mg K-edge XANES of the samples and found that the feature of Mg K-edge XANES of the samples of $x \leq 0.8$ was almost the same as that of MgO regardless of the sample composition. This result supports that the separation of MgO phase from Co_3O_4 phase occurs in the wide range from $x = 0.04$ to at least $x = 0.8$.

As mentioned above, the tendency of a Co ion to dissolve into the MgO lattice is much different from that of a Ni ion. The formation of a Co-MgO solid solution by calcination at 773 K is difficult.

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Figure 1: k -weighted Mg K-edge EXAFS of a) MgO and k -weighted Co K-edge EXAFS of b) $\text{Co}_{0.02}\text{Mg}_{0.98}\text{O}$.

Figure 2: k^3 -weighted Co K-edge EXAFS of $\text{Co}_x\text{Mg}_{1-x}\text{O}$ and Co_3O_4 and CoO. a) $x = 0.02$, b) $x = 0.04$, c) $x = 0.11$ d) $x = 0.35$, e) Co_3O_4 and f) CoO.