

## Structure of nano-crystalline $\text{MnCo}_2\text{O}_4$ prepared by low-temperature decomposition of nitrates and chlorides

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### Introduction

Developing synthesis methods for preparing nano-crystalline manganese cobaltite spinel  $\text{MnCo}_2\text{O}_4$  is very important, because it is a promising electrochemical catalyst. Although low-temperature synthesis is generally desirable in order to make the size of the crystals as small as possible, it is known that the lattice constant obtained is always smaller than that when synthesized at the normal higher temperature [1]. In this report, Mn K near-edge spectra were studied for nano-crystalline  $\text{MnCo}_2\text{O}_4$  by decomposition of nitrates and chlorides.

### Experimental

A small amount of aqueous solution containing  $\text{CoCl}_2$  and  $\text{MnCl}_2$  with a mole ratio of 2:1 was heated in a Pyrex® glass beaker on a hot plate kept at 350 °C, and evaporated to dryness. Excess nitric acid was added to the above chloride solution and heated in the same way (therefore regarded as decomposition of nitrate). The XRD patterns, TEM images and electron diffraction patterns of both oxides obtained were observed [2]. Mn K near-edge spectra were collected in transmission mode to compare the manganese states.

### Results and Discussion

XRD patterns of the oxides were identified as cubic spinel-type  $\text{MnCo}_2\text{O}_4$ . TEM and electron diffraction observation showed a micro-crystalline (20-80nm) formation. However, the *nitrate* sample has smaller cell parameter values (about 1.5 %) than that of the *chloride* sample. When the samples were annealed at 800 °C for 10 hours, the lattice parameter shortened violently for the *nitrate* sample, though that of chloride hardly did.

The Mn-K XANES obtained are shown in Figure 1 with some manganese oxides of different valences as references. The spectra of the *chloride* and *annealed* samples roughly coincide, though the spectrum of the *nitrate* sample shows a different aspect. The shift of the absorption edge for *nitrate* sample was larger than that of the *chloride* and *annealed* samples, proving that *nitrate* sample has a higher valence state (around IV). It has been often explained that the charge is compensated for by the excess of oxygen, and that the lattice contracted due to the vacancy of metal atom site. This excess of oxygen is removed with the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  when the sample is heated [3]. In the spectra, there are other different features. The *chloride* and *annealed* spectra have a shoulder in the low-energy side of the absorption peak, though the *nitrate* spectra do not. Therefore, in the *nitrate* sample, the electronic structure of manganese is somehow different from the others. Some researchers have reported on the origin of the

shoulder that emerges in the low-energy side of the absorption peak. A distorted  $\text{MnO}_6$  octahedron can cause splitting of the 4p levels and produce the shoulder. Or, the way in which the octahedra are linked in the crystal structure can change the local structure of the edge crest [4]. But, in this case, both the *chloride* and *nitrate* samples have basically the same cubic spinel-type structure, therefore they have a highly symmetric octahedral Mn site (B site), and of course the same linkage of octahedra. Therefore, we do not subscribe to the above assumptions in this case. In spinel-type structures, metal atoms can also occupy the tetrahedral site (A site). Another kind of manganese spinel  $\text{MnCr}_2\text{O}_4$  has Mn occupying only A site, the spectra from which show a prominent shoulder. The shoulders in the  $\text{MnCo}_2\text{O}_4$  may be of the same origin, because lower-valent Mn in the *chloride* and *annealed* samples can select the A site, though tetravalent Mn prefers to occupy the B site. EXAFS analysis will give more information about the local structure. In summary, it has been found that different starting salts introduce different states and distributions of metal atoms in the spinel lattice. Chloride produce more normal product, because the manganese state is similar to annealed sample.

### References

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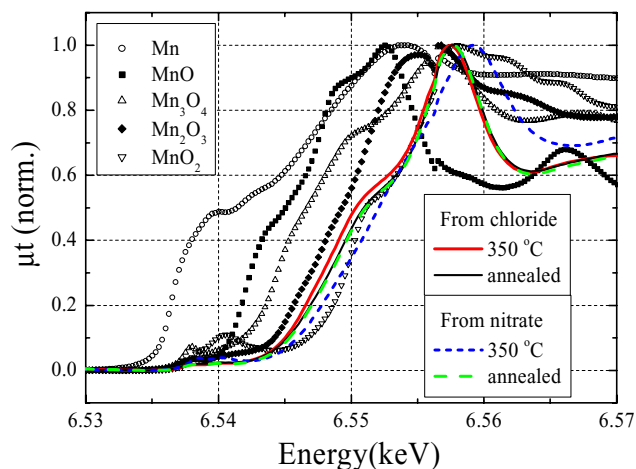


Figure 1 XANES spectra of  $\text{MnCo}_2\text{O}_4$  prepared from different salts and annealed. Spectra of standard manganese oxides are also shown.