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EXAFS AND XANES STUDY ON SPINEL STRUCTURE MATERIALS AND THEIR APPLICATION TO HUMIDITY SENSOR

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The deterioration mechanism of the humidity sensors were investigated by Fe K-EXAFS and XANES. The humidity sensors were composed of spinel structure materials, $Zn_{0.98}Na_{0.02}Fe_2O_4$ and $Mg_{0.98}Na_{0.02}Fe_2O_4$. The former is excellent in durability, while the latter is poor. It was suggested that the deterioration of $Mg_{0.98}Na_{0.02}Fe_2O_4$ is attributable to the movement of Fe atoms. It was shown that a laboratory scale equipment is extremely useful tool to study not only the atomic radial distribution, but also the coordination geometry around excited atoms.

1. INTRODUCTION

The EXAFS system of laboratory scale has received special attention, because it is a manageable and useful equipment to study local structures around excited atoms¹⁻³⁾. Namely, the atomic radial distribution and the coordination geometry around excited atoms can be clarified⁴⁾ by using EXAFS and XANES techniques. In measuring XANES, an SR facility has been generally utilized. Here, the coordination geometry around excited atoms can also be obtained by derivative curve of XANES spectra, by using this laboratory scale equipment. The objects of this paper are to examine EXAFS and XANES spectra at the Fe K-edge for spinel compounds, and to describe the effectiveness of this equipment in laboratory.

2. SPECIMENS

Commercial ZnO, MgO, CuO, NaCO₃, and α -Fe₂O₃ in extra pure grades, were used in this study. By mixing these materials at optimum compositions, pressing and then sintering, iron spinel compounds of ZnFe₂O₄, MgFe₂O₄, CuFe₂O₄, $Zn_{0.98}Na_{0.02}Fe_2O_4$, and $Mg_{0.98}Na_{0.02}Fe_2O_4$ were prepared. Iron oxides, Fe₃O₄ and FeO, in extra pure grades, and pure Fe metal foil were also used for the references. The two compounds, $Zn_{0.98}Na_{0.02}Fe_2O_4$ and $Mg_{0.98}Na_{0.02}Fe_2O_4$, were used for humidity sensors which had been reported⁵⁾. It has been clarified from endurance tests that the durability of the former compound is excellent but the latter is not.

3. MEASUREMENT

The spectra of EXAFS and XANES at the Fe K-edge for spinel structure materials were measured at room temperature. A conventional X-ray generator of rota anode type (Rigaku, RU-200B) was operated on the conditions of 17 kV - 80 mA. The continuous X-ray from the Mo rota target was monochromatized by a Johansson cut Si(220) curved crystal. The energy resolution of this system was ca. 10 eV in the vicinity of the Cu K-edge²⁾. The absorption spectra were obtained by the transmission method.

4. RESULTS AND DISCUSSION

Fourier transforms, $|\phi_3(r)|$, and derivative curves of extracted XANES spectra are shown, respectively in Figs. 1~4. The Fourier windows in k-space of 3.5 to 12.9 \AA^{-1} were used for the Fourier transforms.

The Fe atoms have different local structures in ZnFe_2O_4 , Fe_3O_4 , MgFe_2O_4 and CuFe_2O_4 . All Fe atoms of ZnFe_2O_4 occupy octahedral sites and the nearest neighbour (Fe-O) distance is ca. 2.1 \AA . The half of Fe atoms in CuFe_2O_4 exists in tetrahedral sites with the nearest neighbour (Fe-O) distance of ca. 1.9 \AA and the remaining Fe and Cu exist in the octahedral sites. On the other hand, the Fe atoms in MgFe_2O_4 exists in both types of the sites at random, and Fe^{2+} and Fe^{3+} in Fe_3O_4 exist in tetrahedral and octahedral sites, respectively. Therefore, the first peaks of $|\phi_3(r)|$ lying at ~1.6 \AA of Fe_3O_4 and MgFe_2O_4 were found to be located between those of ZnFe_2O_4 and CuFe_2O_4 .

The $|\phi_3(r)|$ for the $\text{Zn}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test are found to be similar to those of ZnFe_2O_4 and the initial state of the $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$, respectively and the nearest neighbour distances of these specimens were greater than that of ZnFe_2O_4 . It can be deduced from these findings that the sodium atoms remain in the specimens. The lattice constants obtained by X-ray diffraction are also found to support the results for the sodium mentioned above. Besides, the $|\phi_3(r)|$ for the $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ after the endurance test was found to be similar to that of MgFe_2O_4 , and the nearest neighbour distance is shorter than in the initial state.

These facts indicate that whereas $\text{Zn}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ is a very stable material, $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ is unstable, and the local structure of Fe atoms in $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ is changed from ZnFe_2O_4 to MgFe_2O_4 type by the endurance test.

Extracted XANES spectra were found to be somewhat different from each others in the region of 7086 to 7156 eV. It is generally convenient to derive the raw spectra to enhance the relative differences between those specimens. From the first derivative curves for the references and the humidity sensor materials shown in Figs. 3 and 4, the following points are verified, (1) MgFe_2O_4 , Fe_3O_4 and CuFe_2O_4 , keeping Fe atoms in the tetrahedral sites, have a weak peak below the edge (ca. 7105 eV), while no peak was found in ZnFe_2O_4 . (2) The curves of the $\text{Zn}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test and of the $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ in the initial state are

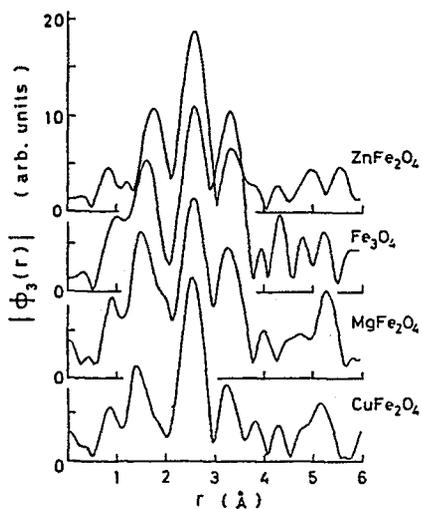


Fig. 1 Magnitude of the Fourier transforms of $k^3\chi(k)$ from the references.

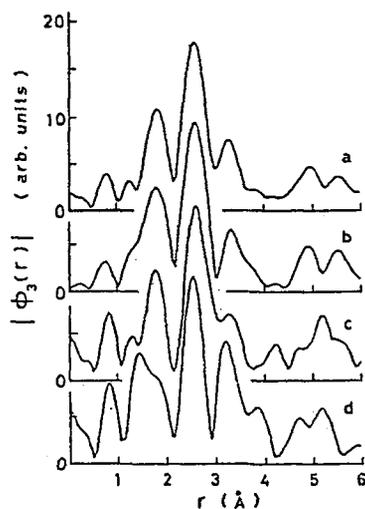


Fig. 2 Magnitude of the Fourier transforms of $k^3\chi(k)$ from the humidity sensors. (a and b: $\text{Zn}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test, c and d: $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test, respectively)

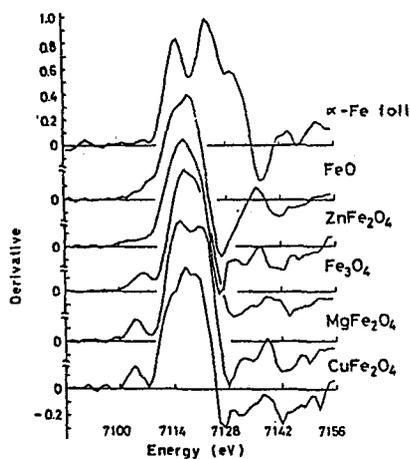


Fig. 3 Derivative curves for the references.

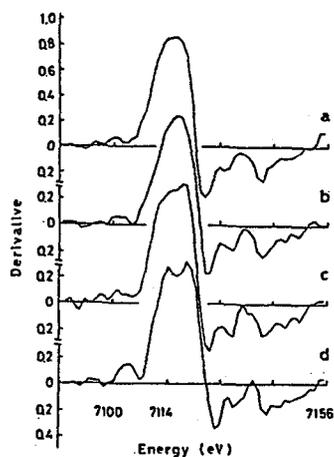


Fig. 4 Derivative curves for the humidity sensors. (a and b: $\text{Zn}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test, c and d: $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ before and after the endurance test, respectively)

similar to that of ZnFe_2O_4 , and the peak was not found in both sensor materials. The curve of the $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ after the endurance test is similar to that of MgFe_2O_4 , and the peak could be clearly distinguished. It is well known that the peak at the low energy side of the edge appears when absorbing elements take a Td symmetry^{6,7}). Therefore, it has been thoroughly recognized from the peak below the edge that Fe atoms are coordinated with the four oxygen atoms in the specimen. A large peak of the near edge of the $\text{Mg}_{0.98}\text{Na}_{0.02}\text{Fe}_2\text{O}_4$ after the endurance test is also similar to that of MgFe_2O_4 , which is split into twin peaks.

5. CONCLUSION

The spectra of EXAFS and XANES at the Fe K-edge for spinel structure materials were measured by the EXAFS system of laboratory scale. A pair of spectra of Fourier transformed EXAFS and derived XANES were examined for all specimens. The results were applied to analyse the deterioration mechanism of a humidity sensor of spinel type.

- (1) The cause of deterioration of the sensor was found to be closely related to the movement of Fe atoms from octahedral to tetrahedral sites in the spinel structure.
- (2) The EXAFS system of laboratory scale was found to be extremely useful for studying not only the atomic radial distributions but also the coordination geometries around excited atoms.

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