Chemical Analysis of Trace Elements by XAFS

Hiroshi Ohzono*(5227), Toshio Mori[1](7168), Shinji Ozaki[2](4142), Masao Takahashi[3](1285)

Matsushita Battery Industrial Co., Ltd., [1] Matsushita Electric Industrial Co., Ltd.[2] Matsushita Technoresearch Inc.,[3] The Institute of Scientific and Industrial Research, Osaka University

Manganese dioxide (MnO_2) and nickel oxyhydroxide [NiO(OH)] are used as cathode materials of alkaline manganese battery. The trace of iron in these materials plays an important role for performance of its batteries. In order to analyze chemical state of trace element, fluorescence yield X-ray absorption fine structure (XAFS) method is useful [1]. Generally, germanium type solid state detector (Ge-SSD) is heavily used for fluorescence yield XAFS measurement. However, in X-ray fluorescence (XRF) measurement for trace of iron in MnO_2, it is difficult to separate only Fe-Kα by Ge-SSD because of disturbance of Mn-Kβ. Then, we have attempted to apply the XAFS analysis in wavelength-dispersive (WD) XRF mode to characterization of chemical state of iron in MnO_2 and NiO(OH).

The Fe-K edge XAFS measurements were performed at BL16XU in WD-XRF mode using a LiF(200) crystal and at BL16B2 in the transmission mode.

The Fe-Kα XRF spectrum of MnO_2 is shown in Fig. 1. It is found that separation of Mn-Kβ and Fe-Kα is possible. The Fe-K edge XANES spectra of MnO_2 and NiO(OH) are shown in Fig. 2. The standard spectra of Fe and Fe_2O_3 are also shown in Fig. 2. As shown in Fig. 2, spectrum of MnO_2 shows approximately the same form as that of metal iron. On the other hand, spectrum of NiOOH shows the similar form as that of Fe_2O_3. The result indicates that the chemical state of Fe in MnO_2 differs from it of Fe in NiOOH.

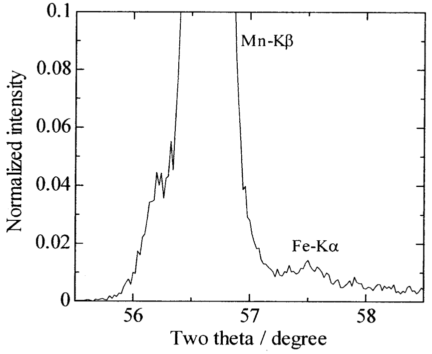

Fig. 1 Fe-Kα XRF spectrum of MnO_2

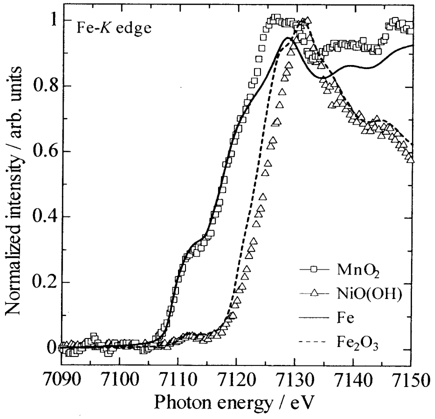

Fig. 2 Fe-K edge XANES spectra

References

[1] H. Ohzono et al., SPring-8 User Experimental Report No. 6(2000B) p. 200.

XAFS Analysis of Sr doped PZT Thin Films

K. Suenaga* (5088), K. Ogata (5029), A. Yoneyama (4140) [1)] and Y. Hirai (4083) [1)]

Production Engineering Research Laboratory, Hitachi Ltd.
[1)] Advanced Research Laboratory, Hitachi Ltd.

$Pb(Zr,Ti)O_3$ (PZT) is a well-known ferroelectric material having the perovskite structure. A major problem to utilize the material in ULSI, such as a non-volatile memory is process degradation. The PZT thin film is damaged in hydrogen condition during ULSI manufacturing process. The authors had reported relationships between the degradation and crystal morphology[1)] and hydrogen in interlayer dielectrics[2)].

It is reported that doping alkali earth metals such as Ca and Sr[3)] can decrease the degradation. The local structure of the dopant has been investigated in this work. Sr doped PZT thin films, $PbSr_x(Zr,Ti)O_3$ (x=0.02) were formed on $Pt/Ti/SiO_2/Si$ substrates by sputter evaporation method. The films were crystallized by rapid thermal annealing in different conditions; (a) and (b). Both films had similar remnant polarization, *Pr* after the crystallization process, however they showed different degradation behavior after metal layer and interlayer dielectrics fabrication process. As the *Pr* of (a) was strongly decreased to 50%, *Pr* of (b) maintained 80%. We measured the films of (a) and (b) after the crystallization process.

As the strontium concentration was only 0.4 atom %, fluorescent yield method was executed. The Sr-Kα(14.165keV) fluorescent yield of the films was measured by using pure germanium SSD. In order to weaken the obstacle fluorescence of major component, platinum and lead, an aluminum filter was installed in front of the SSD.

Figure 1 shows the Sr-K XAFS spectra of Sr doped PZT thin films with high (a) and low (b) degradation. Sr-K absorption edges of the both samples showed same energy. The measured spectra were analyzed by the one-electron scattering approximation method using Rehr's table. The mean free pass, λ, and Debye-waller factor, σ, were fixed to 0.8 nm and 0.001 nm. Analyzed inter-atomic distance and coordination number are listed in Table 1. The Sr-O coordination number of PZT (a) is smaller than PZT (b) by 1.4. We expected the difference of Sr-O coordination number was affected by existence of SrO or SrO_2 phases in the PZT.

References

1) K. Ogata et al., Ferroelectrics, 225 163 (1999).
2) K. Suenaga et al., Integrated Ferroelectrics, 31 323 (2000).
3) T. D. Hadnagy and T. Davenport, Integrated Ferroelectrics, 22 183 (1998).

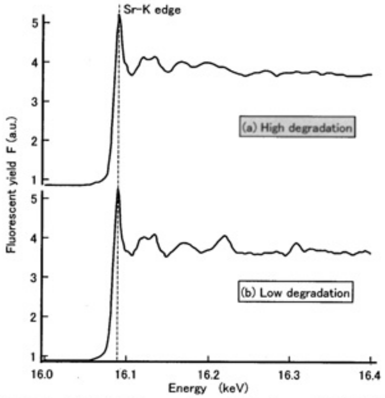

Fig.1. Sr-K XAFS spectra of Sr doped PZT thin films.

Table1. The Sr-O inter-atomic distance and coordination number of Sr doped PZT.

Sample	(a) High degradation	(b) Low degradation
Sr-O distance(nm)	0.1938	0.1959
Sr-O coordination number	2.7	4.1