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Size control of Mn-Zn ferrite nanoparticles and their XANES spectra

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Introduction

Magnetic nanoparticles are expected to be many, not only in high-density magnetic recording but also as biological applications[1] such as an agent for MRI or hyperthermia. It is very important to clarify the local structure and how to control size of nanoparticles because the study is guide the development for various applications.

In this study, Mn-Zn ferrite nanoparticles were produced, and controlled their particle sizes by the amount of an Ar gas, and valences of Mn ion were qualitatively analyzed using XANES spectra. Mn-Zn ferrite bulk crystal has large magnetization value at room temperature and is composed of biocompatible element.

Experimental

Mn-Zn ferrite nanoparticles surrounded by amorphous SiO_2 were produced by mixing aqueous solutions of $MnCl_2 \cdot 4H_2O$, $ZnCl_2$, $FeCl_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$. The mole ratio of the prepared reagent was Mn:Zn:Fe:Si = 0.5:0.5:2:3. The obtained precipitates were washed several times and dried at about 350 K in a thermostat. The as-prepared samples were annealed in air or Ar gas (40, 80 ml/min) at temperature 1143 K.

Bulk crystal of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ was produced by mixing aqueous solutions of each metal chloride and NaOH, and was annealed in Ar gas (40 ml/min) at temperature 1273 K.

The X-ray powder diffraction (XRD) patterns of all samples were identified spinel structure, and no other phase is present. The particle sizes of $Mn_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles were estimated from XRD patterns as 17, 24, 41 nm and depend on the amount of Ar gas flow.

The measurements of XANES spectra at Mn, Fe, and Zn K-edge in the room temperature were carried out in transmission mode at the beam line BL-9C and BL-12C.

Results and discussion

Figure 1 shows Mn K-edge XANES spectra for each Mn oxide bulk crystal and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ bulk crystal (a), annealed in air (b), annealed in Ar gas (40 ml/min) (c), annealed in Ar gas (80 ml/min) (d), respectively. From this figure, spectra of Mn-Zn ferrite nanoparticles are obviously different from that of in an Ar gas. The overall shape of the spectrum from nanoparticles annealed in Ar is similar to that from the bulk, and in air is similar to Mn_3O_4. In the result, nanoparticles annealed in air may include Mn_3O_4 which has spinel structure. Comparing spectra of Mn-Zn ferrite nanoparticles with Mn oxide, valences of Mn ions of nanoparticles annealed in air include almost Mn^{3+} ions, annealed in Ar reflect almost Mn^{2+} ions, though a few Mn^{3+} ions exist.

Fe K-edge XANES spectra shows that there was no difference between air and Ar. Spectra of all Mn-Zn ferrite nanoparticles were similar to spectrum of γ-Fe_2O_3, Fe_3O_4, $MnFe_2O_4$, $ZnFe_2O_4$, respectively. Valences of Fe ions of all samples are mostly considered to be Fe^{3+} ions. Likewise Zn K-edge XANES spectra shows no difference depending on atmosphere. Spectra of all samples were similar to spectrum of $ZnFe_2O_4$ reagent. Zn^{2+} ions valences are clearly confirmed.

Analysis of EXAFS spectra are now in progress and will be reported in near future.

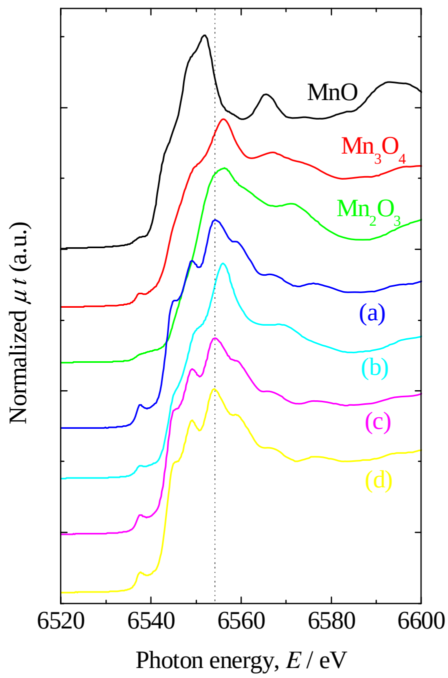

Figure 1. Mn K-edge XANES spectra of Mn oxide and $Mn_{0.5}Zn_{0.5}Fe_2O_4$ bulk crystal (a), nanoparticles annealed in air (b), annealed in Ar (40 ml/min) (c), annealed in Ar (80 ml/min) (d).

References

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