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Particle Size Dependence of Crystal Structure of Mn_3O_4 Nanoparticles

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1 Introduction

The nanoparticle of strongly correlated materials such as manganese oxide are expected to exhibit characteristic size effects on crystal structure and magnetic property owing to the strongly electron correlation and strong coupling among spin, orbital, and lattice. Spinel oxides with a general formula AB_2O_4 has tetrahedral A site with four oxygen and octahedral B site with six oxygen arranged in a pyrochlore latteice. Mn_3O_4 has geometrical frustration derived from the antiferromagnetic interactions between the B sites of spinel oxide. The Mn_3O_4 exhibits interesting phenomena such as magnetodielectric, magnetoelastic and magnetocaloric behaviors, and successive phase transformations owing to the strong coupling among spin, orbital, and lattice degrees of freedom [1-3]. For Mn_3O_4, the tetrahedral A sites and octahedral B sites are selectively occupied by Mn^{2+} and Mn^{3+} ions, respectively. Since Mn^{3+} ions at the MnO_6 octahedral site with one electron in the doubly degenerate e_g states, the Mn_3O_4 exhibits a structural phase transition from cubic to tetragonal at 1443 K due to the strong instability of the Jahn-Teller distortion, whose magnitude is estimated to be $c/\sqrt{2}\ a \sim 1.16$ based on the ratio of lattice constants ($a \sim 5.76$ Å and $c \sim 9.47$ Å) [1,2].We synthesized the Mn_3O_4 nanoparticles in the pores of mesoporous silica, and their crystallographic structure and magnetic properties were investigated. In this report, we show the results of crystal structural analysis for the Mn_3O_4 nanoparticles.

2 Experiment

The Mn_3O_4 nanoparticles were synthesized in the pores, with a diameter of approximately 7 nm, of mesoporous silica SBA-15. SBA-15 was used as a template to equalize the particle size in the fabrication of the Mn_3O_4 nanoparticles and to deflocculate synthesized nanoparticles since it has a two-dimensional hexagonal mesoporous structure and its pores are separated by silica wall [4]. The Mn_3O_4 nanoparticles were synthesized by soaking the SBA-15 in a aqueous solution of $MnCl_2 \cdot 4H_2O$. The soaked SBA-15 was then dried and calcinated in an air atmosphere. The powder X-ray diffraction (XRD) measurements for the synthesized nanoparticles were carried out at room temperature by using a Debye-Scherrer camera at the beamline BL-8B. The X-ray wavelength was calibrated using the XRD pattern of CeO_2 powder.

3 Results and Discussion

We observed powder XRD patterns for the synthesized Mn_3O_4 nanoparticles in the pores of SBA-15 at room temperature. The diffraction patterns of the Mn_3O_4 nanoparticles exhibited broad Bragg peaks, which were attributed to the tetragonal symmetry with space group $I4_1/amd$ the same as that of bulk crystal. Note that the particle sizes of the Mn_3O_4 nanoparticles were estimated based on the peak positions and the full widths at half maximum of the Bragg peaks using Scherrer's equation. These results indicated successful synthesis the Mn_3O_4 nanoparticles with mean particle size raging from approximately 7 to 30 nm.

The lattice constants of the nanoparticles were estimated from XRD patterns. The lattice constants were calculated from the relation between lattice constants and plane indices determined from the Bragg peak angles for the all observed diffraction peaks. Figure 1 shows the size dependences of the lattice constants for the nanoparticles. The lattice constants for the nanoparticles were slightly different from those for bulk crystal [1] and depended on the particle size. The lattice constant a exhibits pronounced increase with decreasing particle size below ~12 nm, while it is almost constant value above ~12 nm. As particle size decreases, lattice constant c gradually decreases above ~12 nm, then the value increases drastically below ~12 nm. These results indicate that, compared with bulk crystal, the crystallographic structure for the nanoparticles distorts from that for bulk crystal, and the distortion of unit cell depends on the particle size. We estimated the tetragonal distortion, $c/\sqrt{2}\ a$, which has been used to describe the Jahn-Teller distortion in Mn_3O_4. The Mn_3O_4 bulk crystal has huge tetragonal distortion, $c/(\sqrt{2}\ a) = 1.162$ [1]. The estimated tetragonal distortion for the nanoparticles depends on the particle size as shown in Fig. 2. The Jahn-Teller distortion for Mn_3O_4 nanoparticles is suppressed as compared with the bulk crystal, and its magnitude changes with decreasing particle size. As particle size decreases, the Jahn-Teller distortion gradually decreases above ~12 nm, and then the value increases below ~12 nm. On the other hand, we investigated the magnetic properties for the synthesized Mn_3O_4 nanoparticles, which exhibit the drastic changes in the magnetic properties, the transition temperatures and coercive field, below ~12 nm. The crystal structural analysis and the magnetic measurement results suggest that the Mn_3O_4 nanoparticles have strong correlation between crystal structure and magnetic property. The modulation of the lattice constants and the Jahn-Teller distortion varies the magnetic interactions between the Mn spins, which result in the pronounced changes in the transition temperatures and coercive field for the Mn_3O_4 nanoparticles.

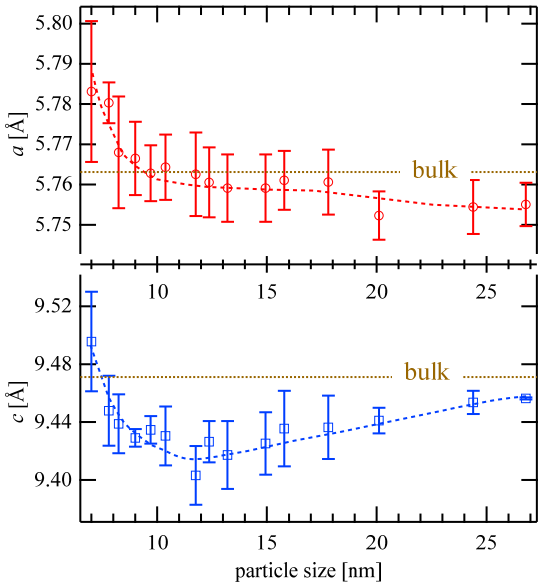

Fig. 1. Particle size dependences of lattice constants for the Mn_3O_4 nanoparticles.

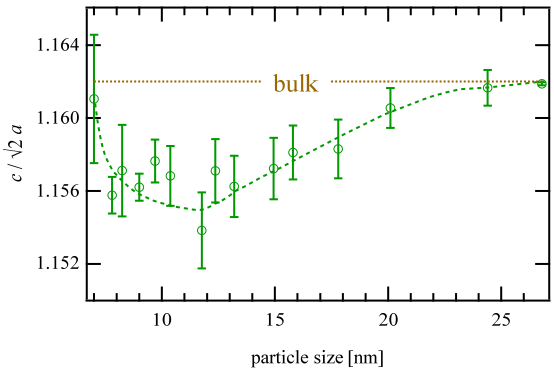

Fig. 2. Particle size dependences of tetragonal distortion for the Mn_3O_4 nanoparticles.

References
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