BL-8B/2015G528

# Size effects on crystal structure of $GdMnO_3$ nanoparticles

Takayuki Tajiri[1,*] and Masaki Mito[2]
[1] Faculty of Science, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan
[2] Graduate School of Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu 804-8550, Japan

## 1 Introduction

Crystal structure of nanoparticles differs from that of the bulk crystal owing to the changes in energy state and translation symmetry at the surface of a nanoparticle because the fraction of atoms at or near the surface increases with decreasing particle size. The surface states of nanoparticles are likely changed by the development of the lattice strain owing to the existence of edges and defects at the surface of a particle as well as the difference in the crystallographic structure from that of the bulk crystal. In particular, strongly correlated materials $RMnO_3$ (R = rare earth) are expected to show anomalous size effects due to strong couplings among the lattice, spin, charge, and orbital degrees of freedom. We focused our attention on the size effects on $GdMnO_3$ nanoparticles. $GdMnO_3$ has been known as multiferroic material with magneto-electric effect and shows a complex magneto-electric phase diagram such as commensurate–incommensurate transition with a spiral magnetic structure.

## 2 Experiment

The $GdMnO_3$ nanoparticles were synthesized in one-dimensional pores with diameter of approximately 8 nm of mesoporous silica SBA-15. The SBA-15 was used as a template to equalize the particle size in the fabrication of the nanoparticles. SBA-15 has a well-ordered two-dimensional mesoporous structure with hexagonal symmetry, and the one-dimensional pores are separated by silica walls [1]. The $GdMnO_3$ nanoparticles were synthesized by soaking the SBA-15 in a stoichiometric aqueous solution of $Gd(CH_3COO)_3{\cdot}4H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$. Then, the soaked samples were dried and calcinated in oxygen atmosphere.

Powder X-ray diffraction (XRD) measurements for the nanoparticles were carried out at room temperature using the a Debye-Scherrer camera at the beamline BL-8B. The incident X-ray wavelength was calibrated using the XRD pattern of the $CeO_2$ powder.

## 3 Results and Discussion

The powder XRD patterns for $GdMnO_3$ nanoparticles synthesized in the SBA-15 were obtained at room temperature. The powder diffraction patterns of the nanoparticles exhibited some broad Bragg peaks, which were attributed to the orthorhombic symmetry with space group *Pbam* of $GdMnO_3$ bulk crystal. The average particle size for the $GdMnO_3$ nanoparticles was estimated based on the peak positions and the full width at half maximum of the some Bragg peaks using Scherrer's equation. The results indicated that successful synthesis of the $GdMnO_3$ nanoparticles with average particle sizes ranging from approximately 10 to 18 nm. The lattice constants for the nanoparticles are slightly different from those for bulk crystal and depend on particle size: As particle size decreases, the lattice constants, $a$ and $b$, for the nanoparticles hardly depend on the particle size, whereas the lattice constant $c$ exhibited an abrupt decrease below 12 nm. The results indicated that the crystallographic structure of the nanoparticles is distorted anisotropically from that for bulk crystal. Here, the crystal structure for the nanoparticles of $LaMnO_3$ with A-type antiferromagnetic ordered phase is rhombohedral symmetry in spite of orthorhombic one for bulk crystal [2], whereas the nanoparticles of multiferroic compound $DyMnO_3$ with a spiral magnetic structure has the same symmetry as bulk crystal and their crystallographic structure is distorted anisotropically from that for bulk crystal below specific particle size [3]. The $GdMnO_3$ nanoparticles exhibit similar tendency to $DyMnO_3$ nanoparticle rather than $LaMnO_3$ nanoparticles. Therefore, it is suggested that the size effect on crystal structure of $RMnO_3$ are correlated with the magnetic phase at low temperature.

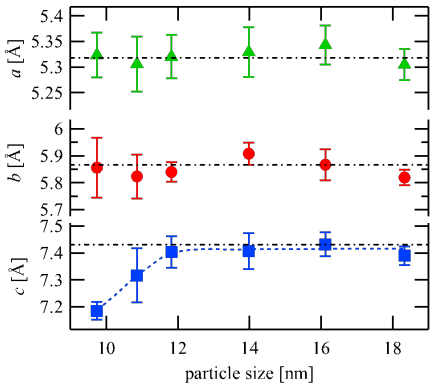


Fig. 1: Particle size dependence of lattice constants for $GdMnO_3$ nanoparticles. Horizontal dashed lines show lattice constants for bulk $GdMnO_3$ crystal.

## References

[1] D. Zhao *et al.*, SCIENCE **279**, 548 (1998).
[2] T. Tajiri *et al.*, J. Phys. Soc. Jpn. **75**, 113704 (2006).
[3] T. Tajiri *et al.*, J. Magn. Magn. Mater. **345**, 288 (2013).

* tajiri@fukuoka-u.ac.jp