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# Particle size dependence of crystal structure for nanoparticles of perovskite manganese oxide

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## 1 Introduction

The nanoparticles 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. 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. In particular, distorted perovskite manganite $RMnO_3$ (R = rare earth) is expected to show anomalous size effects, resulting in a complex phase diagram. In our previous works, we have studied the correlation between crystal structure and magnetic properties based on systematic experimental studies. Nanoparticles of $(La,Sr)MnO_3$ [1,2], $DyMnO_3$ [3], and $BiMnO_3$ [4], with particle sizes of approximately 10 nm, exhibited characteristic size effects on the magnetic properties and crystallographic structure, which are different from the usual size effects in other magnetic materials. Now, 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 and A-type antiferromagnetic order. We synthesized the $GdMnO_3$ nanoparticles and have investigated their magnetic properties [5]. The magnetic measurement results for the $GdMnO_3$ nanoparticles indicated that the magnetic properties, such as transition temperature and coercive field, exhibited the characteristic size dependences: these values exhibited a pronounced changes approximately particles size 14 nm. We report on the size dependence of the crystallographic structure for the nanoparticles obtained from X-ray diffraction experiments.

## 2 Experiments

The $GdMnO_3$ nanoparticles were synthesized in one-dimensional pores 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. The pore size and silica walls are able to control by changing synthesis conditions [6]. The $GdMnO_3$ nanoparticles were synthesized by soaking the SBA-15 with pore size of approximately 8 nm 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 [5].

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 the $GdMnO_3$ nanoparticles synthesized in SBA-15 were collected using incident X-ray energy of 18 keV at room temperature. The powder diffraction patterns of the nanoparticles exhibited some broad Bragg peaks, which were attributed to the orthorhombic symmetry, with the space group *Pbam* of the $GdMnO_3$ 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 8 to 23 nm. The lattice constants for the nanoparticles were estimated from the peak position of the observed Bragg peaks. Figure 1 shows the particle size dependence of the lattice constants for $GdMnO_3$ nanoparticles. The lattice constants for the nanoparticles are slightly different from those for the bulk crystal. The lattice constant $a$ was almost constant value, whereas the lattice constants $b$ and $c$ exhibited a relatively large dependence below approximately 13 nm. As particle size decreases, the $b$ increased whereas the $c$ decreased monotonically below approximately 13 nm. The size dependence indicated that crystallographic structure of the nanoparticles distorted anisotropically from that for bulk crystal.

The $GdMnO_3$ nanoparticles have the Jahn–Teller distorted orthorhombic structure ($O$'-type structure: $b > a > c/\sqrt{2}$) same as the $GdMnO_3$ bulk crystal. The orthorhombic distortion $b/a$ for the nanoparticles is slightly smaller than that for the bulk crystal, 1.103. The change in the orthorhombic distortion suggested modulation of the symmetry of the $MnO_6$ octahedra and the Jahn–Teller distortion from those for the bulk crystal.

The value of $b/a$ for the nanoparticles increased rapidly with decreasing particle size below approximately 14 nm whereas it kept almost constant for above approximately 14 nm. Thus, it can be concluded that the magnitude of the

Jahn–Teller effect for nanoparticles changes with the particle size.

The results of crystal structure analyses indicated a correlation between the magnetic properties and the distortion of the crystallographic structures. It is considered that 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 magnetic properties for the $GdMnO_3$ nanoparticles below approximately 14 nm.

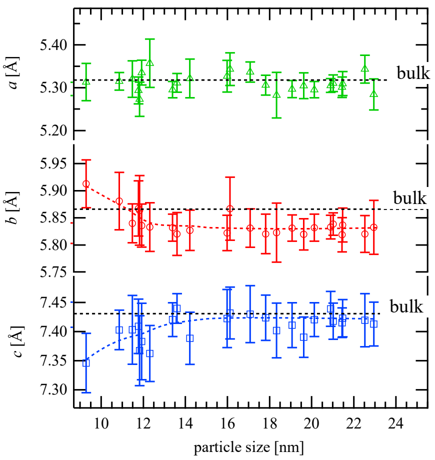


Fig. 1: Particle size dependence of lattice constants for $GdMnO_3$ nanoparticles.

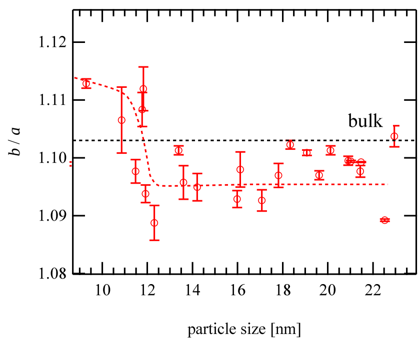


Fig. 2: Particle size dependence of orthorhombic distortion *b*/*a* for $GdMnO_3$ nanoparticles.


References

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