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# Particle size dependence of crystal structure for nanoparticles of perovskite manganite $TbMnO_3$

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## 1 Introduction

Perovskite manganites $RMnO_3$ (R: rare earth element) are well known as one of strongly correlated electronic materials. The materials exhibit quite interesting properties, such as colossal magnetoresistance effect and multiferroic behavior. The crystallographic structure of $RMnO_3$ is orthorhombic distorted perovskite structure. The nanoparticles of strongly correlated materials such as the $RMnO_3$ 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. The nanoparticles, because of their large fraction of surface atoms and finite size effects, possess interesting magnetic properties and crystal structures, which differ from those of the bulk crystals. In particular, distorted perovskite manganite $RMnO_3$ 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 for the $RMnO_3$ nanoparticles based on systematic experimental studies. The nanoparticles of $(La,Sr)MnO_3$ [1,2], $DyMnO_3$ [3], $BiMnO_3$ [4], and $GdMnO_3$ [5] 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. We focused on the size effect of crystal structure and magnetic property on $TbMnO_3$ nanoparticles. The bulk crystal of $TbMnO_3$ 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. We synthesized the $TbMnO_3$ nanoparticles with particle size of approximately 10–20 nm and investigated their magnetic properties and crystallographic structure. The magnetic measurement results indicated that the $TbMnO_3$ nanoparticles exhibited the superparamagnetic behaviors and their parameters, such as blocking temperature and coercive field, depended on the particle size. These values exhibited a pronounced changes at approximately particles size 16 nm. We report on the size dependence of the crystallographic structure for the nanoparticles obtained from X-ray diffraction experiments in the PFACR2019.

## 2 Experiments

The $TbMnO_3$ 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 with diameter approximately 5–30 nm are separated by silica walls. In this study, the $TbMnO_3$ nanoparticles were synthesized by soaking the SBA-15 with pore size of approximately 8 nm in a stoichiometric aqueous solution of $Tb(CH_3COO)_3 \cdot 4H_2O$ 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

We observed the powder XRD patterns of the $TbMnO_3$ nanoparticles synthesized in SBA-15 using incident X-ray energy of 18 keV at room temperature. The XRD patterns of the nanoparticles exhibited some broad Bragg peaks, which were corresponding to the space group *Pbam* of the $TbMnO_3$ bulk crystal. The average particle size of the $TbMnO_3$ 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 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 the $TbMnO_3$ nanoparticles. The lattice constants, $a$, $b$, and $c$, for the nanoparticles were slightly different from those for the bulk crystal and depended on the particle size. Above approximately 16 nm, the lattice constants $a$, $b$ and $c$ were almost constant. Below approximately 16 nm, the lattice constants $a$ and $b$ increased, whereas the lattice constant $c$ decreased with decreasing particle size. The results indicated that the crystallographic structure of the $TbMnO_3$ nanoparticles were distorted anisotropically from that of bulk crystal, and the magnitude of the strain increased with decreasing particle size below approximately 16 nm.

The $TbMnO_3$ nanoparticles have the Jahn–Teller distorted orthorhombic structure ($O$'-type structure: $b > a > c/\sqrt{2}$) similar to the $TbMnO_3$ bulk crystal. The orthorhombic distortion $b/a$ of the nanoparticles was slightly different from that of the bulk crystal, $b/a = 1.101$, as shown in Fig. 2. The value depended on the particle size: Above approximately 16 nm, the orthorhombic distortion was almost constant value ~1.099. Below approximately 16 nm, however, the value increased with decreasing particle size, such that it became larger than that of bulk crystal below approximately 14 nm. 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. Thus, it is considered that the magnitude of the Jahn–Teller effect for the nanoparticles changes with the particle size. The results of crystal structural analysis indicate that there is a strong correlation between the magnetic properties and the distortion of crystallographic structure of the nanoparticles, which is similar to the size effects on the $DyMnO_3$ and $GdMnO_3$ nanoparticles. The modulation of the crystallographic structure of the nanoparticles induces the changes in the magnetic interactions between the Mn spins, which result in the pronounced changes in the magnetic properties for the $TbMnO_3$ nanoparticles below approximately 16 nm.

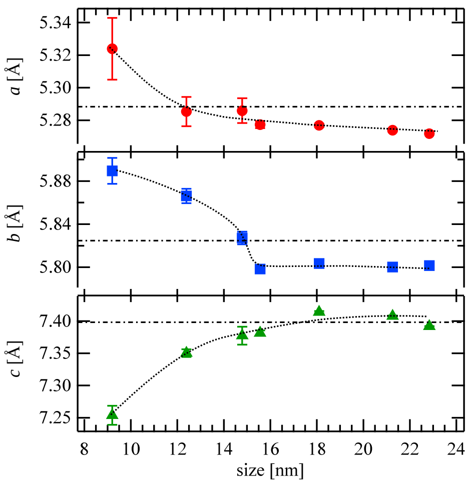


Fig. 1: Particle size dependence of lattice constants for $TbMnO_3$ nanoparticles. The horizontal dashed lines are the lattice constants of the bulk crystal.

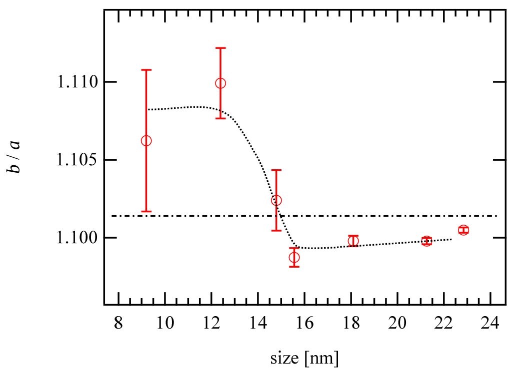


Fig. 2: Particle size dependence of orthorhombic distortion *b*/*a* for $TbMnO_3$ nanoparticles. The horizontal dashed lines is the value of *b*/*a* of the bulk crystal.

References

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