BL-8B/2021G038

Size and temperature dependence of crystal structure on Mn_3O_4 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

Spinel oxides with a general formula AB_2O_4 have tetrahedral A site with four oxygen and octahedral B site with six oxygen arranged in a pyrochlore lattice. When magnetic ions occupy the B site, geometric magnetic frustration often occurs owing to the strong antiferromagnetic interactions between the B sites. For Mn_3O_4, the tetrahedral A site and octahedral B site are selectively occupied by Mn^{2+} and Mn^{3+} ions, respectively. Since Mn^{3+} ions at the MnO_6 octahedral site have one electron in the doubly degenerate e_g states, 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]. Below $T_N = 42$ K, the Mn_3O_4 bulk crystal undergoes structural transition to orthorhombic phase, which coexists with the tetragonal phase [1]. The Mn_3O_4 bulk crystal exhibits a ferrimagnetic ordering, called Yafet-Kittel phase, at $T_N = 42$ K, where the magnetic moments are oriented along the [110] direction. In addition, as temperature decreases, the magnetic phase changes successively to an incommensurate (IC) phase at $T_1 = 40$ K, and finally to a commensurate phase, called cell-doubled (CD) phase at $T_2 = 34$ K, where the magnetic unit cell is doubled along the [110] direction from that of the original cubic spinel structure. The magnetic properties for the Mn_3O_4 nanoparticles are expected to be different from those for bulk crystal owing to the modulation of magnetic frustration and lattice distortion due to the surface effect. We investigated correlation between crystal structure and magnetic properties as a function of particle size and temperature.

2 Experiment

The Mn_3O_4 nanoparticles were synthesized in one-dimensional pores of mesoporous silica SBA-15 with pore size of approximately 8 nm [3]. The SBA-15 was used as a template to equalize the particle size in the fabrication of the nanoparticles. The Mn_3O_4 nanoparticles were synthesized by soaking the SBA-15 in a aqueous solution of $MnCl_2 \cdot 4H_2O$. Then, the soaked samples were dried and calcinated in oxygen atmosphere. Powder X-ray diffraction (XRD) measurements for the nanoparticles were carried out ranging from 30 to 300 K using the a Debye-Scherrer camera at the beamline BL-8B. The particle size and lattice constants of the synthesized nanoparticles were evaluated from powder XRD patterns.

3 Results and Discussion

The observed powder XRD patterns of the Mn_3O_4 nanoparticles exhibited some broad Bragg peaks, which were corresponding to the space group $I4_1/amd$ of the Mn_3O_4 bulk crystal at room temperature. The lattice constants of the nanoparticles were estimated from the peak position of the Bragg peaks. The lattice constants a and c depended on the particle size at room temperature as shown in Fig. 1. As particle size decreased, the lattice constant a increased and exhibited rapid increase below 10 nm (Fig. 1(a)), while the value of c represented a minimum at 10 nm and a rapid increase below 10 nm (Fig. 1(b)). The size dependence of tetragonal distortion, $c/\sqrt{2}a$, was similar to that of c as shown in Fig. 1(c). On the other hand, the magnetic properties exhibited characteristic size dependences; The transition temperature and coercive field decreased rapidly below 10 nm. In addition, the T_1 was seem to disappear below 9 nm. These results suggested that the modulation of crystallographic structure of the nanoparticles induced changes in the magnetic exchange interactions, resulting in the characteristic magnetic phase diagram which was different from that of bulk crystal.

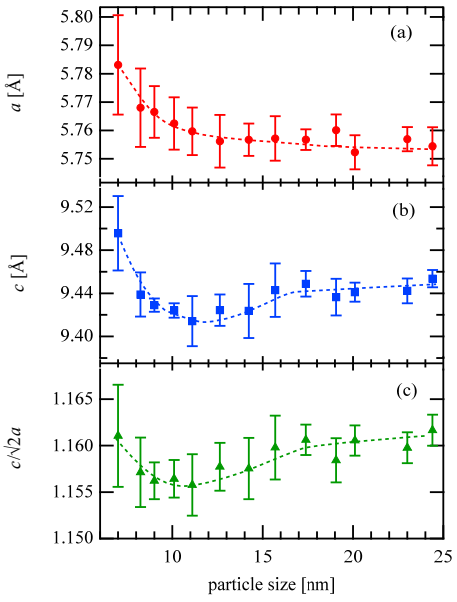

Fig.1: Particle size dependences of lattice constants (a) a, (b) c, and (c) tetragonal distortion of Mn_3O_4 nanoparticles at room temperature.

Figure 2 shows temperature dependence of lattice constants of Mn_3O_4 nanoparticles with particle size of 9.1 nm. As temperature decreased from 300 K, the lattice constant *a* decreased with three pronounced drops at approximately 190, 110, and 40K (Fig. 2(a)). The *c* reached maximum at approximately 220 K, decreased monotonically with decreasing temperature, and then exhibited rapid decrease at 40 K (Fig. 2(b)). As temperature decreased, the tetragonal distortion had a tendency to increase and maintained nearly constant between 200 and 40K, and then increased below 40K. The significant changes in lattice constants were due to the structural phase transition at approximately 40 K [1]. On the other hand, the Mn_3O_4 bulk crystal did not exhibit the anomaly of lattice constants at approximately 200 K.

ESR spectra of Mn_3O_4 nanoparticles were different from that of bulk crystal at room temperature; The spectra of nanoparticles contained a broad component and six narrow spectra, whereas bulk crystal exhibited a broad absorption line. The six absorption lines correspond to the hyperfine splitting of the spectrum owing to the interaction between the electron spin S=5/2 and the nuclear spin I=5/2 for Mn^{2+} ions at surface of the nanoparticles [4]. The Mn_3O_4 nanoparticles exhibited noticeable changes in the absorption profile, resonance field, linewidth, and hyperfine coupling constant at approximately 200 K in the considered temperature region, 100–320K. The temperature dependence of the ESR absorption parameters exhibited pronounce inflection points at approximately 120, 200, and 230 K, which was suggested that the changes in ESR spectra were attributed to the modulation of crystal structure.

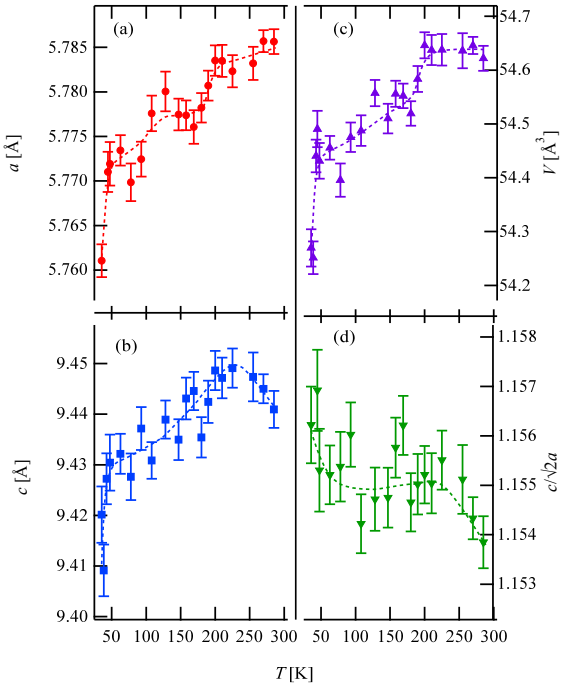

Fig.2: Temperature dependences of lattice constants (a) *a*, (b) *c*, (c) *V*, and (d) tetragonal distortion of Mn_3O_4 nanoparticles with particle size of 9.1 nm.

It is concluded that the Mn_3O_4 nanoparticles has strong correlation between the crystal structure and magnetic properties; The distortion of unit cell, i.e., MnO_4 tetrahedra and MnO_6 octahedra, induces the characteristic magnetic properties.

Acknowledgement

We would like to thank Prof. H. Deguchi of Kyushu Institute of Technology in the present study.

References

[1] M. C. Kemei, *et al*., *Phys. Rev. B* **90**, 064418 (2014).
[2] H. Lv, *et al*., *J. Phys. Chem. C*, **116**, 2165 (2011).
[3] T. Tajiri *et al*., *IEEE Trans. Magn*. **55**, 2300204 (2019).
[4] E. Winkler *et al*., *Phys. Rev. B* **70**, 174406 (2004).

* tajiri@fukuoka-u.ac.jp