

Particle size and distortion effects on NiO nanoparticles embedded in one-dimensional pores of mesoporous silica

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1 Introduction

Crystal structure and physical properties for nanoparticles differ from those for the bulk crystal owing to the energy state and translation symmetry changes at the surface of a nanoparticle. In terms of the crystal structure, 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 of the crystallographic structure from that of the bulk crystal. For antiferromagnetic nanoparticles, the surface state of nanoparticles greatly affects the magnetic properties because uncompensated spins of sublattices appear on the surface of the particle and critically determine the magnetic properties of antiferromagnetic nanoparticles. We investigated the correlation between crystal structure and magnetic properties of nanoparticles of an antiferromagnetic compound NiO. The crystal structure and magnetic properties of NiO nanoparticles are sensitive to the particle size and have exhibited unique size dependences. To the best of our knowledge, there have been no reports of a correlation between crystal structure and magnetic properties based on detailed systematic experimental studies for NiO nanoparticles with particle size of 2–20 nm.

2 Experiment

The NiO nanoparticles were synthesized in one-dimensional pores with pore size of about 7 nm of mesoporous silica SBA-15. Powder X-ray diffraction (XRD) measurements for the NiO nanoparticles in SBA-15 were performed at room temperature. The energy of the incident X-rays was 18 keV, and their wavelength was calibrated using the CeO₂ powder XRD pattern. The magnetic properties of the NiO nanoparticles were investigated using a commercial SQUID magnetometer.

3 Results and Discussion

Figure 1 shows the powder XRD patterns for the NiO nanoparticles with particle size of 2.6, 4.3, 8.6, and 17.2 nm in SBA-15 at room temperature and simulated pattern for bulk crystal with rhombohedral symmetry. In previously reported results, the structure of different sized NiO nanoparticles at room temperature has been reported for the so-called rock-salt structure with cubic[1] and rhombohedral[2] symmetries. The obtained XRD patterns of all NiO nanoparticles in SBA-15 exhibited some broad Bragg peaks, which could be attributed to the rhombohedral distorted rock-salt structure. The average

particle size of the NiO nanoparticles was evaluated by using Scherrer's equation. The average particle size for the NiO nanoparticles in the SBA-15 pores ranged from 2.6 to 22 nm. The NiO nanoparticles with $d > 7$ nm should have spheroidal or rodlike shapes in the one-dimensional SBA-15 pores with diameters of approximately 7 nm, as observed by TEM.[3]

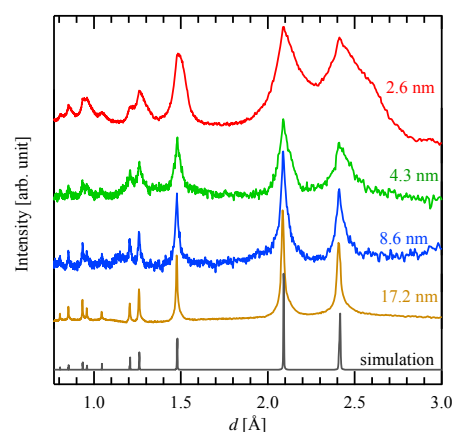


Fig. 1: Powder XRD patterns for NiO nanoparticles with particle size of 2.6, 4.3, 8.6, and 17.2 nm in SBA-15 and a simulated pattern with a rhombohedral distorted rock-salt structure.

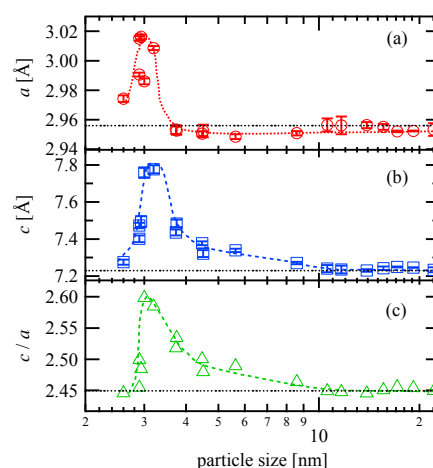


Fig. 2: (a, b) Particle size dependence of lattice constants, a and c , for the NiO nanoparticles in SBA-15. Horizontal dashed lines show the lattice constants for the bulk crystal. (c) Particle size dependence of lattice constant ratio c/a . Horizontal dashed line is equivalent to a value of c/a for a crystallographic structure with cubic symmetry.

The lattice constants for the NiO nanoparticle in SBA-15 estimated by Rietveld analysis. Figure 2 shows the size dependence of the lattice constants for the nanoparticles. The a and c values for the nanoparticles increased with increasing particle size and exhibited maxima around 3 nm. The lattice constant ratio c/a of $\sqrt{6}$ corresponds to the cubic symmetry. As the particle size increased, the value of c/a increased rapidly and exhibited a maximum at $d \approx 3$ nm. Above $d \approx 3$ nm, c/a decreased monotonically down to about $\sqrt{6}$ at $d = 10.6$ nm. These results indicate that the rhombohedral distortion of the rock-salt structure of the NiO nanoparticles becomes more pronounced, and its magnitude increases with decreasing particle size for particles sizes below approximately 10 nm.

The size dependences of the magnetic properties, such as coercive field, shell moment, blocking temperature, and magnetic anisotropy energy, exhibited qualitatively similar behaviors, which were characterized by the maxima for particle sizes between 3 and 11 nm and nearly constant values for particle sizes above ≈ 11 nm.[3] The results of crystal structural analysis showed that the lattice constants and the rhombohedral distortion of the rock-salt structure exhibited maxima at $d \approx 3$ nm and attained nearly constant values for particle sizes above ≈ 9 nm. The present results indicate that the magnetic properties were strongly correlated with rhombohedral distortion of the rock-salt structure. The variation in c/a led to the change in magnetic exchange interactions in NiO nanoparticles. The present results suggest that, for NiO nanoparticles, the rhombohedral distortion of the rock-salt structure strongly influences the local magnetic ordering in the NiO nanoparticles. Therefore, this suggests that the changes in the rhombohedral distortion produced the changes in the magnetic interaction and magnetic anisotropy constant of NiO nanoparticles. Thus, the distortion of crystal structure and change in sublattice spin order led to the observed unique size dependence of magnetic properties. The present experimental results suggest that the crystallographic structural distortion originating from the strong correlation between the spin and charge in NiO nanoparticles can be controlled by changing the particle size. In addition, the distortion of particle shape of the NiO nanoparticle affects magnetic properties.

References

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