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Magnetic Size Effect of $LaMnO_{3+\delta}$ Nanocrystals in Mesoporous Silica

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Introduction

$LaMnO_3$ is the parent compound of a colossal family of magnetoresistance materials, $La_{1-x}A_xMnO_3$ (where A=Ca, Sr, Ba) which show a great variety of magnetic and transport properties. [1] The ground state of $LaMnO_{3+\delta}$(LMO) with an orthorhombic structure at δ=0 is an insulating A-type antiferromagnet below the Néel temperature, T_N≈140K, while that of LMO with a rhombohedral structure at $0 < \delta < 0.15$ is a ferroomagnet below the Curie temperature, T_C≈110-160K. Generally, magnetic nanocrystals show many interesting behaviors and size effects such as superparamagnetism and quantum tunneling. We prepared LMO nanocrystals in an SBA-15 mesoporous molecular sieve with a pore diameter of about 7.5 nm and investigated their nano-size effects using magnetic and ESR measurements. [2]

Experimental Results

The LMO nanocrystals were prepared by soaking the molecular sieve in an aqueous solution of $La(CHOO)_3 \cdot 1.5H_2O$ and $Mn(CHOO)_2 \cdot 4H_2O$. Then, the soaked samples were dried and calcinated in flowing oxygen at 750°C for 18h.

Powder X-ray diffraction (XRD) measurements at room temperature were carried out using a synchrotron – radiation X-ray diffractmeter at BL-1B of the Photon Factory of KEK. We performed XRD measurements using an incident X-ray wavelength of 0.068789 nm. Figure 1 shows the synchrotron-radiation (XRD) patterns for LMO nanocrystals in SBA-15 and for SBA-15 and simulated pattern for bulk LMO with a rhombohedral structure. The broad background of around 10 degrees and 25 degrees originated from the glass tube. The LMO

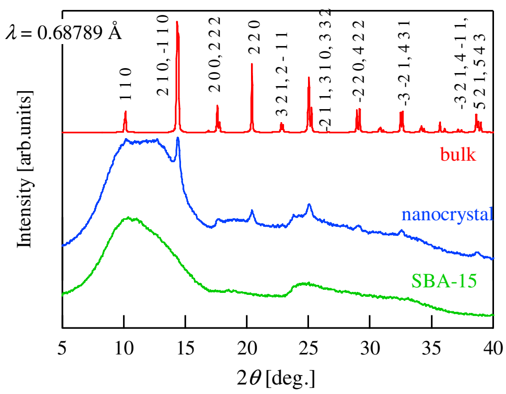

Fig. 1 XRD patterns for LMO nanocrystals in SBA-15 and for SBA-15 and simulated pattern for bulk LMO.

sample in SBA-15 shows some broad Bragg peaks corresponding to those of bulk LMO with a rhombohedral symmetry. Hence, LMO nanocrystals may include excess oxygen. The particle size of LMO was estimated from two Bragg peaks, (110) and (220), to about 7.5 nm in diameter using Scherrer's equation.

The magnetic properties of the LMO nanocrystals were measured using a SQUID magnetometer. The ac susceptibility experiment was carried out in zero dc field. The derivative of the out-of-phase susceptibility curve has two minima at 281 and 238 K, respectability. Figure 2 shows the magnetization curve at 77K for LMO nanocrystals. The observed magnetization curve can be reproduced by summating two components, ferromagnetic and antiferromagnetic superparamagnetic moments. The ESR measurement was performed using a standard X-band spectrometer down to liquid-nitrogen temperature. The absorption spectrum was found to deviate from the simple Lorentzian form, and was analyzed into two components. The change in the shapes of the absorption lines from the Gaussian to the Lorentzian line for the two components suggests that there are two transition temperatures, 278 K and 235K.

The results of the magnetic and ESR measurements for the LMO nanocrystals indicate the existence of the two transition temperatures above T_N for bulk LMO and antiferromagnetic and ferromagnetic LMO nanocrystals.

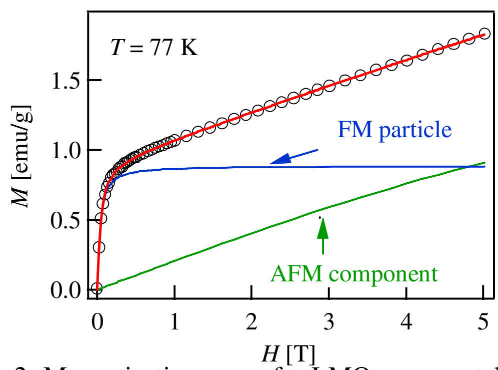

Fig. 2 Magnetization curve for LMO nanocrystals at T = 77 K. The red line shows the fitting line of the summation of the two Langevin functions for the antiferromagnetic and the ferromagnetic nanoparticles.

References

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