Size Effect in Nanocrystalline Manganites

La$_{1-x}$A$_x$MnO$_3$ ($A =$ Ag, Sr)

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Abstract—Nanocrystalline samples of the manganites La$_{0.9}$Ag$_{0.1}$MnO$_3$, La$_{0.7}$Ag$_{0.3}$MnO$_3$, and La$_{0.7}$Sr$_{0.3}$MnO$_3$ were synthesized through pyrolysis and isothermally annealed. The atomic, subatomic, and magnetic structures of these manganites were studied using magnetic, x-ray, and neutron diffraction measurements. Increasing the annealing temperature from 600 to 1200°C coarsens the grains from 30–40 to 600–700 nm in size. All the samples studied have rhombohedral structure and are ferromagnets. The Curie temperature decreases for the samples doped by silver and increases for the samples doped by strontium as the anneal temperature is increased. The magnetization of the Mn ions increases with nanoparticle size in all the three systems, which indicates the presence of a size effect. © 2003 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The manganites La$_{1-x}$A$_x$MnO$_3$, which exhibit colossal magnetoresistance, have recently been attracting heightened interest (see, e.g., [1, 2]). Studies performed on ceramic and single-crystal samples revealed a number of remarkable properties of these manganites, such as the charge, orbital, and spin ordering; a metal–insulator transition; etc. A correlation has been found to exist between the parameters describing the crystal structure of the manganites and the parameters characterizing their magnetic properties. It was shown, in particular, that the Curie temperature $T_C$ depends on the Mn–O–Mn bond angle $\Theta_{Mn–O–Mn}$

The origin of the manganite magnetoresistance is assigned [3] to three carrier-scattering processes. One of them, the critical scattering from magnetization fluctuations, provides the major contribution to magnetoresistance at temperatures close to $T_C$. The other two processes, the inter- and intragrain scattering, are significant for $T < T_C$. Intergrain scattering involves domain walls, which coincide, as a rule, with grain boundaries. This scattering is absent in perfect single crystals [4] and is observed in microcrystalline samples already in a weak external magnetic field; this mechanism is most probably associated with interdomain carrier tunneling [5]. Intragrain scattering is observed at higher fields and is due to the ordering of magnetic moments, which form a spin-glass-type state in the absence of a field. This effect originates apparently from the grain crystalline (and magnetic) structure being heavily defected.

Therefore, in order to elucidate the mechanism responsible for the colossal magnetoresistance in the manganites, it appears reasonable to study nanocrystalline samples in which the particle size is comparable to the domain dimensions. Nanocrystalline manganites are also of interest from the application viewpoint, because they feature higher values of the low-field magnetoresistance compared to those for ceramic samples [6] and, hence, can be used in magnetic sensors.

The available scarce publications on nanocrystalline manganites show that the properties of these compounds can change substantially with decreasing particle size. For instance, samples of La$_{2/3}$Sr$_{1/3}$MnO$_3$ with particles $L = 30$ nm in size and smaller do not exhibit metallic conduction [6], unlike the corresponding ceramic samples. According to [7], spontaneous magnetization $\sigma$ of La$_{0.85}$Sr$_{0.15}$MnO$_3$ increases approximately twofold as $L$ decreases from 1000 to 20 nm. By contrast, a decrease in $\sigma$ by about two times was observed to occur in the manganites La$_{1-x}$A$_x$MnO$_3$ ($A$ = Ca, Sr; $x \approx 0.3$) [7, 8]. The conclusion was drawn in [7] that the growth of $\sigma$ and $T_C$ in nanocrystalline La$_{0.85}$Sr$_{0.15}$MnO$_3$ and the decrease in these quantities in La$_{0.65}$Sr$_{0.35}$MnO$_3$ are related to the change in the bond angle $\Theta_{Mn–O–Mn}$. The values of this angle were calculated for samples annealed at various temperatures with inclusion of only the variation in the lattice parameters with the anneal temperature. Possible variation of the coordinates of the oxygen atoms was neglected, because no neutron diffraction measurements were conducted in [7]. Another opinion on the reasons for the variation in $\sigma$ was put forward in [8], where it was suggested that the decrease in $\sigma$ in La$_{0.67}$Ca$_{0.33}$MnO$_3$ could be associated with the increase in the fractional volume...
of the amorphous phase existing in nanocrystalline samples at low anneal temperatures.

This study was aimed at establishing the relation connecting the magnetic moment and the Mn–O–Mn bond angle with the size of nanoparticles in the manganites La$_{1-x}$Ag$_x$MnO$_3$ ($x = 0.1, 0.3$) and La$_{0.7}$Sr$_{0.3}$MnO$_3$ with the use of neutron diffraction data. Note that we are not aware of any neutron diffraction studies on the magnetic state of nanocrystalline manganites.

2. SAMPLES AND EXPERIMENTAL TECHNIQUES

The starting nanocrystalline manganites La$_{1-x}$Ag$_x$MnO$_3$ with $x = 0.1$ and $0.3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ were prepared through pyrolysis. The weighted lanthanum and silver nitrates (and of strontium in the case of La$_{0.7}$Sr$_{0.3}$MnO$_3$) were dissolved under heating in a $10\%$ solution of polyvinyl alcohol, and the required amount of a manganese nitrate solution was added. The solution thus obtained was vaporized, and the solid residue left was calcined to complete the synthesis and subsequent sintering. All samples were prepared from the same solution. To vary the particle size, annealing was carried out for 4 h at temperatures $T_a$ ranging from 600 to 1200°C for samples doped by silver and from 700 to 1300°C for samples doped by strontium. To reach a constant value of the oxygen off-stoichiometry in different samples, the samples were subjected to a normalizing anneal at $700^\circ$C.

Structural characterization was performed on a DRON-UM-1 diffractometer with CuK$_a$ radiation (filtered by a pyrographite crystal) in the diffracted beam at 293 K. The magnetization of the La$_{0.9}$Ag$_{0.1}$MnO$_3$ samples was measured with an MPMSR5-XL SQUID magnetometer (Quantum Design). The Curie temperatures of La$_{0.7}$Ag$_{0.3}$MnO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ were derived from data on the $ac$ susceptibility in a field of 10 Oe and at a frequency of 1 kHz.

The neutron diffraction measurements were conducted on D-2 and D-3 diffractometers operating at neutron wavelengths $\lambda = 0.180$ and 0.243 nm, respectively. X-ray and neutron diffraction patterns were calculated with the Fullprof code [9].

The particle size was derived from neutron small-angle scattering scans ($\lambda = 0.45$ nm) obtained with a D-6 diffractometer. Plexiglas was used to reduce the measured intensities on cross sections. The D-2, D-3, and D-6 diffractometers were installed in horizontal channels of an IVV-2M reactor.

3. EXPERIMENTAL RESULTS

3.1. Crystal Structure at 293 K

The x-ray diffraction patterns of nanocrystalline samples of La$_{0.9}$Ag$_{0.1}$MnO$_3$, La$_{0.7}$Ag$_{0.3}$MnO$_3$, and La$_{0.7}$Sr$_{0.3}$MnO$_3$ obtained at 293 K were found to be similar. An analysis of the patterns revealed all the manganites studied by us to have rhombohedral structure (space group $R\bar{3}c$). The diffractograms of the silver-doped samples showed, in addition to the reflections of the main phase, weak reflections due to metallic silver. Unfortunately, we did not succeed in determining the silver content in the manganites. Qualitative estimates suggest that the main phase in La$_{0.7}$Ag$_{0.3}$MnO$_3$ contains more silver than that in La$_{0.9}$Ag$_{0.1}$MnO$_3$.

Figure 1 displays the dependence of the unit cell parameters $a$ and $c$ (based on the hexagonal notation for the $R\bar{3}c$ group) on annealing temperature for three groups of samples. An increase in the temperature $T_a$ is seen to cause an expansion of the lattice in the basal plane and its contraction along the hexagonal axis in all samples. These lattice changes are approximately of the same relative magnitude, $\Delta a/a = \Delta c/c = 0.2\%$. On the whole, this brings about a certain increase in the unit cell volume ($\Delta V/V = 0.5\%$) with increasing $T_a$. Figure 1