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Molten salt route of La$_{1-x}$Ca$_x$MnO$_3$ nanoparticles: Microstructural characterization, magnetic and electrical transport properties

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ABSTRACT

Single-crystalline La$_{1-x}$Ca$_x$MnO$_3$ (LCMO, $x = 0.3$ and 0.5) nanoparticles synthesized by molten salt method, have been studied based on their microstructural characterization, magnetic and electrical transport property measurements. X-ray diffraction patterns and electron diffraction patterns reveal that all the LCMO nanoparticles crystallize in the orthorhombic perovskite structure (Pnma space group). TEM images show that the LCMO nanoparticles exhibit irregular shapes and their particle sizes are increased with increasing the annealed temperatures. The resolved (200) lattice fringes in high-resolution TEM images confirm the single crystalline nature of the LCMO nanoparticles. Magnetization measurements versus temperature show a paramagnetic – ferromagnetic transition for all the nanoparticles. Room temperature and low temperature M – H loops demonstrate that the LCMO nanoparticles exhibit ferromagnetic behavior at 5 K, whereas a paramagnetic behavior at 300 K. Resistivity behavior of the LCMO nanoparticles demonstrate that they exhibit a broad metal — insulator ($M - I$) transition, and the transition temperature shifts towards a high temperature under an external magnetic field. The magnetoresistance (MR) values of the LCMO nanoparticles were increased monotonically with decreasing the temperature below 300 K, and finally reached constant values at temperatures below 100 K. The MR value of the La$_{0.5}$Ca$_{0.5}$MnO$_3$ nanoparticles annealed at 650 °C for 3 h, was found to be 77% at 50 K in 5 T, and 57% for the La$_{0.7}$Ca$_{0.3}$MnO$_3$ nanoparticles annealed at 650 °C for 3 h. Such large MR values of the present LCMO nanoparticles make them ideal candidates for the spintronic devices.

1. Introduction

Recently, much attention has been given to perovskite manganite compounds, R$_{1-x}$A$_x$MnO$_3$ (R and A are rare-earth alkaline-earth/alkali elements, respectively) due to their colossal magnetoresistance (CMR), giant magnetic entropy effect, metal - insulator (M - I) transition, electronic phase separation, charge/orbital ordering, and rich structural phases in their phase diagrams [1–5]. Particularly, compounds, belonging to the prototypical system of La$_{1-x}$CaxMnO$_3$ manganites (LCMO), exhibit much rich structural phases such as canted antiferromagnetic (CAF), charge ordered, ferromagnetic (FM) metallic, paramagnetic (PM) insulating phases and others in the LCMO system, which are dependent upon the Ca-doping concentration [3–5]. Studies of the colossal magnetoresistance in LCMO manganites have led to many other new phenomena and properties such as charge-ordering and orbital ordering, which makes the physics of perovskite manganites interesting and challenging. It is known that as the particle sizes of perovskite manganites are reduced to the nanometer scale, they exhibit a number of outstanding physical properties (e.g., low-field mangnetoresistance, surface spin-glass (SG) behavior, super-paramagnetism (SPM), large coercivities, low-field saturation magnetization, and low Curie temperature, etc.) [6–8]. For example, charge ordering and antiferromagnetic states coexisting in half-doped La$_{0.5}$Ca$_{0.5}$MnO$_3$ manganite are suppressed as the particle size is reduced to the nanometer scale [9]. The reduced dimensionality of a perovskite manganite tends to broaden and shift the *FM-PM* transition towards lower temperatures, while the saturation magnetization is decreased [10]. These unusual magnetic behaviors can be ascribed to the finite-size and surface effects, where the magnetic disorder at surface and the broken bonds caused by the formation of grain boundaries can induce a decrease of the magnetization value [11]. Recently, the particle size effects on the structural and magnetic properties of the LCMO nanoparticles have been reported [12–15].

In the past decades various techniques such as sol-gel [16], Pechini route [17], polymeric precursor route [18], citrate auto-ignition method [19], mechanical (or mechanochemical) milling method [20–22] have been developed to synthesize the perovskite LCMO manganite nanoparticles. However, the products prepared by the above

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methods exhibited inferior particle morphology, and moreover the basic strategy for tailoring the particle size was based on the heat treatment at different temperatures. Therefore, the above methods usually have some disadvantages, e.g., complex synthetic routes, high synthetic cost, and high annealed temperatures needed to get crystallized nanoparticles. Meanwhile, the molten salt synthesis (MSS) is one of the simplest techniques to prepare pure, stoichiometric perovskite oxide powders. Due to the small diffusion distances of oxide mixtures in molten salts, the high reactivity of salts, and the high mobility of species, completed reactions can be achieved in a relatively short time [23]. Besides the relatively low processing temperature, the MSS method can also control the powder morphology as compared to other synthesis methods [24,25]. Up to date, MSS has been widely used to synthesize many perovskite oxide powders such as $BaTiO_3$ [26], $PbTiO_3$ [27], $BiFeO_3$ [28,29], and $La_{1-x}Sr_xMnO_3$ [30,31], however, there are few reports on the synthesis of LCMO nanoparticles by MSS method.

In this work, perovskite $La_{1-x}Ca_xMnO_3$ (x = 0.3 and 0.5) manganite nanoparticles were synthesized by a facile MSS technique using the molten salt in $NaNO_3$ - KNO_3 system at the temperatures from 550 to 700 °C. The effect of the annealed temperature on the microstructure, magnetic and electrical transport properties of the LCMO nanoparticles were systematically investigated.

2. Experimental

$La_{1-x}Ca_xMnO_3$ (x = 0.3 and 0.5) nanoparticles were synthesized by MSS method. The mixture of $NaNO_3$ and KNO_3 with a molar ratio of 2:1 was used as the molten salt. A homogeneous mixture of the nitrates $La(NO_3)_3 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, and $Mn(NO_3)_2 \cdot 4H_2O$ in a molar ratio of (1 − x): x: 1 (x = 0.3, 0.5) was well mixed with the molten salt using ethanol as the dispersion agent, in which the mass ratio of LCMO to molten salt was 1:5. The mixture was ground for 30 min in an agate mortar, and then placed in a crucible. The crucible containing the reagents was annealed at temperatures of 550–700 °C for 3 h in a furnace. Finally, the powder nanoparticles were collected after naturally cooling the furnace to room temperature, and then washed and centrifuged several times with distilled water to eliminate the excess alkali metal salts, and the filtrated insoluble oxides was finally dried at 70 °C for 6 h, thus obtaining the LCMO nanoparticles.

The crystal structure was examined by X-ray diffraction (XRD) (Rigaku D/Max-RA diffractometer, Cu Kα radiation, $\lambda = 1.5406$ Å). A typical scan rate of 0.02° per second was adopted and the data were collected at room temperature in the 2θ range of 20–80°. The average crystallite size (D) of the LCMO nanoparticles was evaluated through the line broadening of the (200) peaks using the Scherrer's equation [32]: $D = K\lambda / (\beta cos\theta)$, where K, λ, β and θ are the grain shape factor (K = 0.90), the wavelength of the X-ray used ($\lambda = 1.5406$ Å), the Bragg diffraction angle, and the full width at half maximum (FWHM) of the diffraction peak, respectively. The surface morphology of the LCMO nanoparticles was examined by transmission electron microscopy (TEM, Tecnai G2 S-Twin, FEI) operated at 200 kV and equipped with an Oxford Pentafet EDS system. The specimens for TEM and high-resolution TEM (HRTEM) observations were obtained by drying droplets of the LCMO powders from ethanol dispersion onto a holey carbon grid. All the TEM images and SAED patterns were recorded by a Gatan multiscan charge-coupled device (CCD) camera system. The magnetic properties of the LCMO nanoparticles were characterized using a SQUID magnetometer (Quantum design). Both zero-field-cooled (ZFC) and field-cooled (FC) data were recorded. The resistance was measured by the standard four-probe method from 2 to 300 K.

3. Results and Discussion

3.1. Microstructural Characterization of the LCMO Nanoparticles

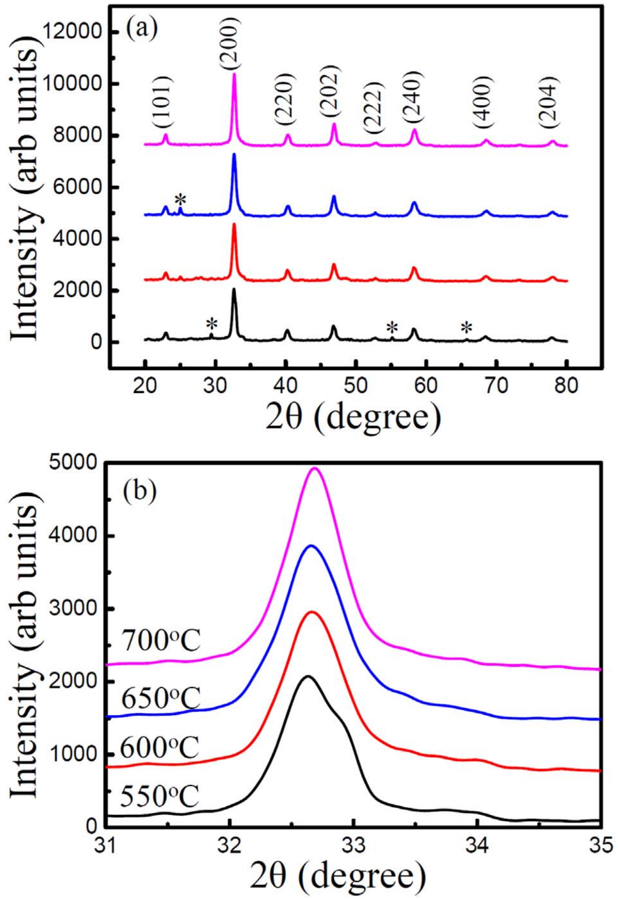

Fig. 1. (a) X-ray diffraction patterns of the $La_{0.7}Ca_{0.3}MnO_3$ nanoparticles annealed at different temperatures for 3 h. (b) Zoom of the strongest X-ray diffraction peak (200) in the diffraction patterns.

XRD patterns of the $La_{1-x}Ca_xMnO_3$ (x = 0.3) nanoparticles annealed at different temperatures (550 °C, 600 °C, 650 °C, and 700 °C) for 3 h, are shown in Fig. 1(a). By referring to the standard powder diffraction file ($La_{0.7}Ca_{0.3}MnO_3$, JCPDS card no.70-2664), the XRD patterns shown in Fig. 1(a) reveal that all the $La_{1-x}Ca_xMnO_3$ (x = 0.3) nanoparticles crystallize in the orthorhombic perovskite structure with a space group of Pnma. However, some weak diffraction peaks (marked with asterisks) are also observed in the LCMO nanoparticles annealed at 550 °C for 3 h (pattern A), which are assigned to the characteristic peaks of the hexagonal phase of La_2O_3 (JCPDS No. 05-0602, lattice constant $a = 3.397$ Å, $c = 6.129$ Å). The presence of the La_2O_3 phase with a low amount is attributed to the fact that small quantity of lanthanum from $La(NO_3)_3 \cdot 6H_2O$ is not incorporated into the LCMO perovskite framework. With increasing the annealed temperature from 600 °C to 700 °C, such weak impure diffraction peaks coming from the hexagonal La_2O_3 phase would nearly disappear, indicating that the lanthanum from $La(NO_3)_3 \cdot 6H_2O$ is almost incorporated into the lattice of perovskite LCMO nanoparticles. Actually, the LCMO nanoparticles annealed at 700 °C for 3 h became single pure phase and crystallized in the orthorhombic perovskite structure. The lattice parameters and unit cell volume of the LCMO nanoparticles deduced from XRD patterns are summarized in Table 1. For comparison, the structural data of the $La_{0.7}Ca_{0.3}MnO_3$ ceramics (PDF 70-2664) are also presented. Fig. 1(b) shows the zoom of the (200) diffraction peak of the diffraction patterns. Obviously, the central positions are shifted to high angles first, and then low angles with increasing the annealed temperatures, indicating the change of lattice parameter of a. Average crystallite size of the $La_{0.7}C_{0.3}MnO_3$ nanoparticles annealed at 550 °C, 600 °C, 650 °C and 700 °C, was calculated from Scherrer's equation, which was found to be 17, 18, 20 and 25 nm, respectively.