Effect of strontium doping level on electrical transport and magnetic properties of La$_{1-x}$Sr$_x$MnO$_3$ perovskite nanoparticles

Phan Van Cuong$^1$ and Do-Hyung Kim$^2$

$^1$ Department of Physics, Nha Trang University
$^2$ Nguyen Dinh Chieu, Nha Trang, Vietnam

Nano Applied Physics Laboratory (NAPL), Department of Physics
Kyungpook National University, Daegu 702-701, Republic of Korea

E-mail: cuongpv@cb.ntu.edu.vn

Abstract. La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.1, 0.2, and 0.3) nanoparticles (LSMO NPs) were successfully synthesized by a simple sonochemical-assisted method. The prepared samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The compositions of samples were determined by energy-dispersive spectroscopy (EDS) analysis. The temperature dependence of the resistivity of samples was measured using four-probe technique, and the magnetic measurement was performed in a Magnetic Property Measurement System (MPMS XL 7.0). SEM, TEM, and XRD show that LSMO NPs are 40~80 nm in diameter with a very clean surface, and exhibit single phase perovskite structure. The ferromagnetic transition temperature ($T_c$) and metal-insulator transition temperature ($T_p$) of the NPs increase with the doping level x. The maximum values of $T_c$ (377 K) and $T_p$ (264 K) occur at x = 0.3. In this work, the effect of strontium doping level on electrical transport and magnetic properties was systematically studied.

Keywords: Lanthanum compounds, nanoparticle, sonochemical, LSMO.

1. Introduction
The perovskite manganites La$_{1-x}$A$_x$MnO$_3$ (A = Sr, Ba, Ca, Pb) have attracted scientific investigations for many decades [1, 2]. These materials have novel physical properties and potential applications, such as magnetic-field sensors [3, 4], hard disk read heads [5], fuel cells [6, 7], infrared devices [8], spintronics, and micro-wave active components, etc. The doped perovskite manganites of La$_{1-x}$A$_x$MnO$_3$ have attracted much attention since the discovery of the colossal magnetoresistance effect and their intriguing physics [9]. Furthermore, the nanostructure material has been predicted to provide some new features in magnetic properties in comparison with bulk materials [10, 11]. The nano-sized particles may lead to some interesting magnetic and magnetoresistance properties than the bulk materials [12]. There have been several methods to prepare nano-sized manganites, such as the versatile chemical technique [13], anodized alumina oxide (AAO) template [14], hydrothermal [15-17], homogenous co-precipitation [18], etc. These methods have some disadvantages, for example, complex operating procedure [14], long reaction and treatment time [15-17], etc. The structure, electronic, and magnetic properties of La$_{1-x}$A$_x$MnO$_3$ perovskite usually depend on the doping level [19, 20] or the preparation routes [21-25].
In this work, using a sonochemical-assisted method, single crystalline phase La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.1, 0.2, and 0.3) nanoparticles were prepared. Compared to the above methods, the sonochemical-assisted method is a preferable alternative due to very short reaction time, simple synthetic apparatus and simple operating procedure. This method also allows to synthesis of LSMO NPs in large scale up to several tenth grams.

2. Experimental

The synthetic procedure was as follows. High-purity KMnO$_4$, MnCl$_2$.4H$_2$O, La(NO$_3$)$_3$.6H$_2$O, and Sr(NO$_3$)$_2$ were used as starting materials and KOH served as mineralizer. All chemicals were purchased from Sigma-Aldrich (USA) without further purification. All chemicals were dissolved in de-ionized water by stirring at room temperature. Finally, KOH was added and stirred vigorously to adjust the alkalinity. The sonication of the mixed solution was carried out for 5 minutes in air using an ultrasonic probe with a 1/2 inch titanium tip (Branson Digital Sonifier, Model 450). The probe tip was kept 1 cm from the top of the solution surface. After 5 minutes of sonicating, the solution was cooled down, centrifuged, and washed several times with de-ionized water. Then the samples were dried in a vacuum oven at 70°C for 12 h and a black powder was finally obtained. Subsequently this powder was pressed in the same pressure to make the pellets with the size of 10 mm × 4 mm × 1 mm. Then the pellets of La$_{1-x}$Sr$_x$MnO$_3$ x = 0.1, 0.2, and 0.3 (NPs) were finally annealed at 950°C for 10 h.

The prepared samples were investigated by X-ray diffraction (XRD, Rigaku, Japan), field emission scanning electron microscopy (FESEM, Hitachi S-4300, Japan), high-resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED, Philips CM 200 STEM). The chemical compositions of samples were determined by energy-dispersive spectroscopy (EDS) analysis. The temperature dependence of the resistivity of samples was measured by using four-probe technique, and the magnetic measurement was performed by using Magnetic Property Measurement System (Quantum Design, MPMS XL 7.0).

3. Results and discussion

LSMO NPs were synthesized by this method should be due to the generation of efficient droplet size induced by ultrasound. Ultrasound, itself, generates sufficient and strong mechanical forces which can easily and evenly disperse the aqueous solution containing all chemical reagents [26]. In sonochemistry, the three main involved events are the creation, growth, and collapse of bubbles that are formed in the liquid. The bubbles will be collapsed when their sizes reach the maximum value. According to the hot-spot mechanism, this implosive collapse can raise the local temperature up to 5000°C, the pressure up to 500 atm. and lifetimes of a few microseconds [27]. In alkaline environment, strong mechanical forces together with high temperature in a short time could be the mains reason for assisting the formation of LSMO NPs. It is worth to mention that micro-sized LSMO particles are usually obtained from the synthesis using solution-annealing process or solid sintering method. In addition, the nano-sized LSMO samples could not be obtained without sonochemical assistance in our previous experiments. Therefore, sonochemical-treatment plays an important role to assist the pre-formation of nano-sized particles. After sonicating and drying, nanoparticles could be obtained. The as-synthesized samples showed paramagnetic properties and the crystallinities were poor. Annealing step is very important one to enhance the crystallinity and to form desired properties of LSMO NPs. This method allows us to synthesize a large amount of LSMO NPs up to several tenth grams with the very simple equipment and process.

The chemical composition of all samples is examined by energy-dispersive spectroscopic. The results indicate that La: Sr: Mn molar ratios of the samples (x = 0.1, 0.2, and 0.3) are 0.89:0.11:1.00, 0.80:0.19:1.00, and 0.72:0.29:1.0, respectively. These values are consistent with nominal compositions within error of 5%.

XRD patterns of the annealed La$_{1-x}$Sr$_x$MnO$_3$ samples (x = 0.1, 0.2 and 0.3) and as-synthesis La$_{0.7}$Sr$_{0.3}$MnO$_3$ sample are shown in figure 1. Inset shows Rietveld refinement pattern for the annealed La$_{0.7}$Sr$_{0.3}$MnO$_3$ sample as a typical sample. The XRD patterns of annealed samples show that all
diffraction peaks are narrower in width and strongly higher in intensity than those of the as-synthesized samples. Whole pattern fitting refinements of the XRD patterns of all three samples were performed using the program FULLPROF, based on the Rietveld method. We obtained the best fit for the rhombohedral (space group of $R\overline{3}c$) structure of these three samples. These results are nearly consistent with those reported in reference [18].

Figure 1. XRD patterns of the sintered La$_{1-x}$Sr$_x$MnO$_3$ samples ($x = 0.1, 0.2$, and $0.3$) and as-synthesis La$_{0.7}$Sr$_{0.3}$MnO$_3$ sample. Inset: Rietveld refinement pattern of the sintered La$_{0.7}$Sr$_{0.3}$MnO$_3$.

Figure 2 presents the SEM images for typical La$_{1-x}$Sr$_x$MnO$_3$ NPs with $x = 0.3$. The LSMO NPs exhibit a sphere-like shape and their sizes are estimated to be within 40 and 80 nm.

Figure 3 shows TEM and HRTEM images of La$_{0.8}$Sr$_{0.2}$MnO$_3$ NPs. The images reveal that the surface of LSMO NPs is very clean without any sheathed amorphous phase. The inset shows the corresponding SAED pattern with [1 10] zone-axis and it indicates that LSMO NPs are single crystalline phase to be. The HRTEM image exhibits a lattice spacing of NPs of about 0.38 nm which corresponds to (100) plane. The ring patterns in the SAED were originated by the copper grid.

Figure 4 shows the dependence of the resistivity $\rho$ on temperature measured in the temperature range of 5 - 300 K at zero field for all three mentioned samples. The inset presents the dependence of $T_p$, $\rho_p$ on doping level ($\rho_p$ is resistivity at $T_p$). All samples show the metal-insulator transition. The transition temperature $T_p$ increases in conjunction with the increasing of the doping level, and the difference of $T_p$ (99 K) between sample $x = 0.1$ and sample $x = 0.3$ is clearly observed. The magnitude of $\rho$ decreases with increasing of the doping level. The insulator-metal transition temperatures $T_p$ of our samples are 165, 248, and 264 K for $x = 0.1, 0.2$, and $0.3$, respectively. These $T_p$ values are lower than that of other reports for nano-sized LSMO due to lower annealing temperatures [13, 19], but
higher than that of bulk LSMO [28].

Figure 3. Typical TEM (left) and HRTEM (right) images of La$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles. The inset shows the corresponding SAED pattern.

The measurement of magnetization $M$ as a function of temperature carried out with a magnetic field of 0.5 T in the temperature range of 25 - 400 K for La$_{1-x}$Sr$_x$MnO$_3$ NPs (figure 5). The inset presents the dependence of $T_c$ on the doping level. Our results clearly show that all samples undergo a ferromagnetic transition. This transition temperature $T_c$ increases with the doping level, thus, the $T_c$ values of samples ($x = 0.1$, 0.2, and 0.3) are found to be 321, 349, and 377 K, respectively. These values are higher than those of previous reports for single phase LSMO NPs [13, 18, 19]. It is very interesting that with the increasing of the doping level, the ferromagnetic transition temperature ($T_c$) is almost increased linearly. The values of magnetization $M$ at 25 K of samples ($x = 0.1$, 0.2, and 0.3) are 57, 69, and 70 emu/g, respectively.

Figure 4. Electrical resistivity vs temperature for samples ($x = 0.1$, 0.2, and 0.3).
The inset: The dependence of $T_p$ and $\rho_p$ depend on doping level ($\rho_p$ is resistivity at $T_p$).

The effect of the doping level on the LSMO magnetization was already studied in some literatures [18-20]. They found that the magnetization increases with the doping level. For our result, however, for samples $x = 0.2$ and 0.3, the magnetization values are almost the same. It can be explained that the chemical reaction may occur incompletely during synthesis process to provide a non-stoichiometric compound even the chemical analysis result for the La$_{0.7}$Sr$_{0.3}$MnO$_3$ shows the La: Sr: Mn of 0.72:0.29:1.0.
4. Conclusion
In summary, we have successfully synthesized single crystalline phase La$_{1-x}$Sr$_x$MnO$_3$ (x = 0.1, 0.2, and 0.3) nanoparticles by a simple sonochemical-assisted method with a significantly short reaction time. XRD pattern analysis shows that the samples have a perovskite structure of $R \bar{3}c$ symmetry. The results of SEM, TEM, HRTEM, and SAED measurements of studied compounds indicate that the particle size ranging from 40 to 80 nm, and the single crystalline phase was obtained for each with clean surface without any sheathed amorphous phase. The magnetic and transport properties of LSMO NPs are also investigated. The $T_p$ and $T_c$ increases systematically in proportion to the strontium doping level in La$_{1-x}$Sr$_x$MnO$_3$ nanoparticles and the maximum values of $T_p$ and $T_c$ occur at $x = 0.3$. In brief, it is important to adjust the doping level and synthesis route to get nano-sized particles and properties for application of these materials.

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