Structural and Magnetic Properties of La$_{0.9}$Sr$_{0.1}$MnO$_3$ Nanoparticles Prepared via Sol-gel Process

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In the present paper, nanosized La$_{0.9}$Sr$_{0.1}$MnO$_3$ particles were synthesized via a facile modified sol-gel route using two cheap and environmentally friendly organic chemicals, namely sucrose and pectin. The obtained powders were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetic measurements. The optimal temperature for obtaining nanosized particles was determined as 1000°C and 1h dwell time was enough to obtain crystalline nanoparticles. Magnetic properties of samples calcined with different calcination period were analyzed and both samples showed a transition temperature around 724 K.

Keywords: La$_{0.9}$Sr$_{0.1}$MnO$_3$; sol-gel preparation; thermal analysis; crystal structure; magnetic materials

Lanthanum strontium manganite (LSMO) compounds exhibit great interest due to their colossal magnetoresistance (CMR) and high phase transition temperature (370K), which determine their use in high sensitive magnetic sensors [1, 2]. Other potential applications are fuel cells [3], magnetic refrigeration [4], spintronics [5, 6], magnetic sensors [1, 2]. Other potential applications are electrolytes [12].

In this paper, La$_{1-x}$Sr$_x$MnO$_3$ (x=0.1) was synthesized via a facile modified sol-gel route using two cheap and environmentally friendly organic chemicals, namely sucrose and pectin. The obtained powders were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetic measurements. The optimal temperature for obtaining nanosized particles was determined as 1000°C and 1h dwell time was enough to obtain crystalline nanoparticles.

Magnetic properties of samples calcined with different calcination period were analyzed and both samples showed a transition temperature around 274 K.

Experimental part

The samples were prepared by the sol-gel method using following reagents: strontium chloride (SrCl$_2$·6H$_2$O, Fluka (99.99%)), manganese acetate (Mn(CH$_3$COO)·4H$_2$O, Sigma Aldrich (99.99%)) lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O, Alfa Aesar (99.99%)), nitric acid (1M HNO$_3$, Fluka), and commercially available sucrose and pectin. The reagents were used without any further purification. The sucrose: pectin ratio used for these syntheses was 5:1.

Stoichiometric amounts of La(NO$_3$)$_3$·6H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O, Mn, H$_2$O and SrCl$_2$, 6H$_2$O are individually dissolved in hot distilled water and three clear solutions are obtained. The sucrose is dissolved in lanthanum nitrate under vigorous stirring. A homogeneous solution is obtained by mixing together all three solutions under continuous stirring, using a hot plate magnetic stirrer. In order to obtain the gel chain-like network, the pH of the solution is maintained acidic by adding nitric acid. During this stage, the pectin is also added and the resulting solution was heated at 70°C and continuously stirred. The clear solution is slowly dried and the gel is slowly formed. The gel aging takes place by continuing the thermal treatment for 2 h. In order to eliminate all the water residues and to prevent gel shrinkage, the obtained gel is slowly dried for another 48 h. Finally, the obtained xerogel sample is calcined in air, at three different temperatures 900, 1000 and 1100°C, respectively, with a dwell time of 2h. The samples are marked as LSMO900, LSMO1000 and LSMO1100, respectively.

Beside this, two more samples from the dried xerogel are calcined at 1000°C, with a heating rate of 5°C/min, followed by two different calcination dwell periods: 1 (LSMO 1h) and 3 hours (LSMO 3h), respectively.

The calcinations processes were carried out using a Kaloria Denkal K8/1100 furnace. The TG-DSC curves were recorded using a TA Instruments DSC Q600 thermogravimetric analyser. Powder diffractograms were recorded, in the 2θ range 20°-90°, using a Bruker D8 Advance AXS X-ray diffractometer. The morphological studies were performed using a JEOL-JEM-1011 electron microscope. Magnetization measurements in the 4.2-300 K temperature range and external magnetic field up to 9T were realized using a 12 T VSM from Cryogenics.
Results and discussions

The xerogel TG-DTA curves (fig. 1) exhibit an endothermic process with a slight mass loss (about 5%), up to 153°C. This process is characteristic for the elimination of physical absorbed water. An important exothermic process occurs between 153 and 430°C, with a three-stage mass loss. The 400°C sharp peak is attributed to the decomposition of inorganic precursors and the oxidation of organic compounds, with the release of gases (especially CO₂). The sucrose acts as a fuel and accelerates the decomposition of the inorganic precursors. The TG curves have a flat profile after 430°C with no mass changes and no peaks are observed on the DTA curve, indicating that no phase transformation occurs.

The broadened XRD maxima indicates that the crystallite is in the nanometer range. The crystallite sizes for LSMO 1h (fig. 3a) and LSMO 3h (fig. 3b) were calculated using the Debye-Scherrer formula [23-25]:

\[ D_p = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \]

where \( \beta \) is the peak full width at half maximum (in radians) at the observed peak angle \( \theta \), \( k \) is the crystallite shape factor (was considered 0.94) and \( \lambda = 1.540562 \) Å is the X-ray wavelength.

The average crystallite size was calculated to be about 57 nm with a calcination time of 1h and about 63 nm for the LSMO sample with a 3h calcination period. Nanosized La₁₋ₓSrₓMnO₃ (x=0.1) was obtained using both calcination plateaus, but increasing the calcination plateau leads to crystallite growing (table 1).

![Fig. 1. The TG-DTA curves recorded for xerogel sample](image)

The diffractograms for LSMO900, LSMO1000, and LSMO1100 indicate that single-phase perovskite with rhombohedral structure (R₃c space group) was obtained at 1000 and 1100°C (fig. 2 ii and iii), while in the case of 900°C sample, the temperature was not high enough to lead to a well crystalized perovskite structure (fig. 2 i).

![Fig. 2. The XRD patterns for: i) LSMO900, ii) LSMO1000 and iii) LSMO1100](image)

The transmission electron microscopy (TEM) was used to determine the morphology and the particle size of the obtained nanoparticles (fig. 4, fig. 4a) shows small and round non crystalline La₀.₉Sr₀.₁MnO₃ particles. The particle sizes calculated from the TEM images are about 10-30nm.

For the La₀.₉Sr₀.₁MnO₃ sample calcined at 1000°C, the microscopy images revealed that the nanoparticles started to agglomerate in clusters (fig. 4b). The size of the nanoparticles is between 50-60 nm.

Despite the fact that the higher crystallinity of LSMO can be obtained at the temperature of 1100°C, the aim of the paper was to obtain nanosized La₀.₉Sr₀.₁MnO₃, and as it can be seen in fig.4c), very large sintered agglomerates were obtained (over 500nm) at 1100°C. Therefore, 1000°C is the recommended temperature for the synthesis of LSMO calcined at different calcination durations: a) LSMO1000 1h; b) LSMO1000 3h. Experimental data points are shown as dots, the calculated profile using Rietveld method and difference curve are shown as solid lines.

![Fig. 3. X-Ray diffraction patterns of LSMO calcined at different calcination durations: a) LSMO1000 1h; b) LSMO1000 3h](image)

| Table 1 | LATTICE PARAMETERS AND CRYSTALLITE SIZES ESTIMATED FROM XRD PATTERNS FOR LSMO CALCINED AT DIFFERENT CALCINATION PERIODS |
|---------|-------------------------------------------------------------------------------------------------------------|
|         | a (Å) | c (Å) | D (nm) |
| LSMO 1h | 5.519(3) | 13.356(3) | 57±1 |
| LSMO 3h | 5.519(3) | 13.356(3) | 63±1 |

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nanosized La$_{0.9}$Sr$_{0.1}$MnO$_3$ via the proposed modified sol-gel method.

The temperature dependence magnetization after cooling the sample, in external zero magnetic field (ZFC) and in a magnetic field of 0.2 T (FC), was measured under a 2 T magnetic field. Fig. 5a) shows the FC magnetization and its variation with the heat treatment duration of the sample. At low temperatures a difference of about 0.2 (µ/ f.u.) was noticed between the two samples.

The transition temperature from paramagnetic to magnetic state is obtained as the minimum derivative of the magnetization derivative versus temperature. For both samples, this transition temperature is around 274 K (fig. 5b).

At the temperature of 5K, the magnetization dependence on the applied magnetic field was studied. Magnetization saturation took place in a relative low magnetic field (1T), for both samples (fig. 5c), but the LSMO 3h presented a higher magnetization than LSMO 1h.

Conclusions

Nanosized La$_{0.9}$Sr$_{0.1}$MnO$_3$ perovskite was successfully synthesized via the proposed modified sol-gel method. The XRD spectra for the LSMO1000 and LSMO1100 samples showed the presence of a single-phase perovskite with rhombohedral structure (R-3c space group). However, the 900°C temperature was not high enough to lead to a well crystalized perovskite structure. Increasing the calcination plateau, at the 1000°C, from 1h to 3h, leads to an agglomeration of the particles, thus the 1h calcination plateau is enough to obtain LSMO nanoparticles. The TEM revealed that by increasing the calcination temperature of the xerogel to 1000°C, larger nanoparticles (about 65 nm) can be obtained. At 1100°C the nanoparticles sintered in very large clusters. Therefore, the 1000°C temperature is the recommended temperature for obtaining nanosized La$_{0.9}$Sr$_{0.1}$MnO$_3$. Magnetic properties of samples calcined with different calcination period were analyzed and both samples shown a transition temperature around 274 K. LSMO 3h had a higher magnetization with the applied magnetic field and both samples (LSMO 1h and LSMO 3h) magnetization saturated in a relative low magnetic field (1T).

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