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Vuk Uskoković

Chapman University, uskokovi@chapman.edu


Darko Makovec

Jožef Štefan Institute

Miha Drofenik

Jožef Štefan Institute

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Synthesis of Lanthanum-Strontium Manganites by a Hydroxide-Precursor Co-Precipitation Method in Solution and in Reverse Micellar Microemulsion

Vuk Uskoković^{1,a}, Darko Makovec^{1,b}, Miha Drofenik^{1,2,c}

¹»Jožef Stefan« Institute, Jamova 39, 1000 Ljubljana, Slovenia

²Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

vuk.uskokovic@ijs.si, darko.makovec@ijs.si, miha.drofenik@ijs.si

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Abstract Nanostructured lanthanum-strontium manganites have been synthesized using two different co-precipitation approaches, one in bulk solution, and the other in reverse micelles of CTAB/1-hexanol/1-butanol/water microemulsion. In both cases, precursor cations were precipitated by alkali precipitating agents. The properties of the material synthesized by using these two methods were compared in order to reveal potential advantages of microemulsion-assisted approach. The influence of the annealing conditions on the properties of synthesized manganites was investigated by using X-ray diffraction, transmission electron microscopy, differential thermal analysis, thermogravimetric analysis and magnetic measurements.

1. Introduction

A lot of attention is devoted today to the researches of lanthanum-strontium manganites [1-4], which are seen as attractive materials for the modern electronic applications, due to a range of diverse potential properties that these materials might possess. Unusual magnetotransport properties (as noticeable in the case of colossal magnetoresistance) and complex competition between a ferromagnetic metallic and antiferromagnetic insulating phases (as noticeable on the corresponding phase diagram [5]) might be seen as the cause for a large interest assigned to these materials. Depending on the exerted properties (that, on the other hand, depend a lot on the synthesis technique used [6]), LaSr-manganites might be used as cathode materials in solid oxide fuel cells, as colossal, giant or low-field magnetoresistant materials as well as magnetic drug carriers due to low Neel temperature.

This work comprises the results of a comparative investigation of two wet, co-precipitation approaches to the synthesis of LaSr-manganites. Both approaches, typical for the mixing of precursors on atomic scale, have been chosen with the basic idea of overcoming drawbacks of solid-state synthesis that require high temperatures with difficulties arising in achieving the desired stoichiometry. Reverse micelles have been in large extent exploited during the past two decades, since in certain cases monodisperse, size-controlled nanoparticles might be obtained [7, 8], which have suggested a general spatial correlations [9, 10] between nano-sized water pools of reverse micelles and the properties of synthesized particles.

2. Experimental

The bulk co-precipitation synthesis of LaSr-manganites was proceeding as follows. 3 ml, 2 ml and 1 ml of 0.5-M aqueous solutions of MnCl_2 , $\text{La}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$, respectively, were mixed. 20 ml of 1 M aqueous solution of NaOH was then added into the solution of precursor cations (pH = 13.54), which were thus precipitated in form of hydroxides, subsequently aged for 3 h at room temperature. The solid phase was then sedimented by using centrifugation, after which the powders were repeatedly washed with the pH = 14.5 aqueous solution of tetramethyl ammonium

hydroxide in order to eliminate residual surfactant and precipitated NaCl and NaNO₃. The as-dried powders were subsequently calcined at different temperatures in air in order to gain monophasic manganite samples.

The co-precipitation method for the synthesis of LaSr-manganite by using reverse micellar microemulsion was proceeding as follows. Two CTAB/1-hexanol/1-butanol/H₂O microemulsions of the same composition (CTAB:1-hexanol:1-butanol:H₂O = 32.3 : 15.2 : 22.2 : 30.3) were prepared, whereas in place of the aqueous phase, one microemulsion comprised 0.076-M overall precursor cation concentration (molar ratio of Mn²⁺ : La³⁺ : Sr²⁺ = 47.4 : 31.6 : 21) aqueous solution, formed by using MnCl₂, La(NO₃)₃ and Sr(NO₃)₂ as precursor salts, whereby the other microemulsion comprised 0.5-M aqueous solution of (CH₃)₄NOH, serving as the precipitating agent. The weight ratio of the precipitating microemulsion vs. the precursor microemulsion was set to 1.355 in order for pH of the resulting microemulsion to be 13.6, thus enabling all precursor cations to be precipitated in form of hydroxides. After the aging time of 1 h at room temperature, the powders were sedimented by using centrifugation and repeatedly washed with the pH = 14.5 aqueous solution of tetramethyl ammonium hydroxide in order to eliminate residual surfactant and oil phase molecules. The powders were subsequently calcined at different temperatures.

3. Results and discussion

XRD patterns of the samples synthesized using bulk co-precipitation procedure – as-dried and calcined at different temperatures in air for 2h, are shown in Fig.1. La(OH)₂ and SrCO₃ (the diffraction peaks denoted in Fig. 1 as L and S, respectively) are detected as crystalline phases in the as-dried sample. The only observed change in the XRD pattern after annealing at 450 °C is the appearance of the reflections from La₂O₂CO₃ (denoted with C). After the calcination at ≥ 600 °C, manganite perovskite phase (denoted with o) was obtained. Minor secondary phases were present in the annealed samples, including NaCl (denoted with n) formed due to using NaOH and MnCl₂ as reactants, MnO₂ (denoted with m) and either cubic La_{0.94}Mn_{0.98}O₃ or La(OH)₃ (denoted with l), that might in certain cases form spontaneously in air due to the presence of La₂O₃ on the particles surfaces.

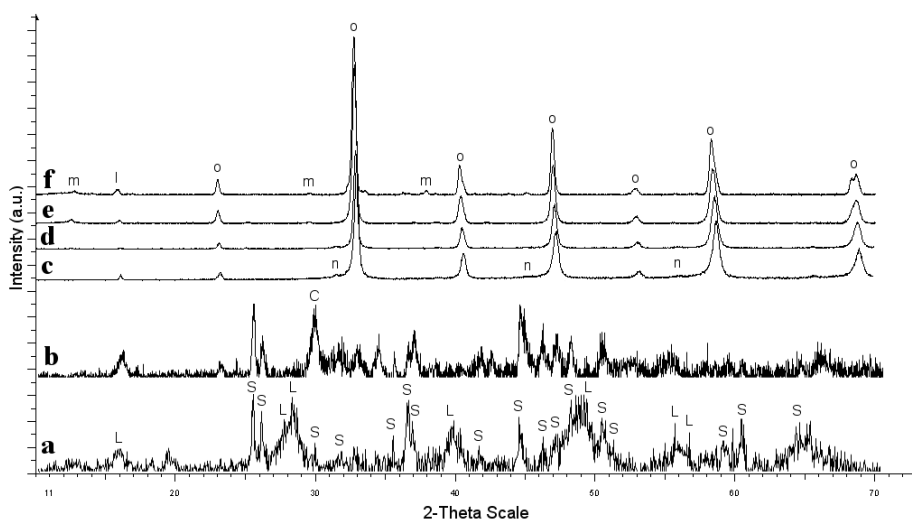


Fig. 1. Normalized XRD patterns of the bulk-synthesized samples, including as-dried powder (a) and the samples calcined at 450 °C (b), 600 °C (c), 800 °C (d), 1000 °C (e) and 1100 °C (f) in air for 2h.

For the case of bulk co-precipitation procedure, the average particle size is ~ 25 nm for all the calcined samples. No grain growth was observed with increasing the calcination temperature, as can be seen from Fig.2(l). On the other hand, the lattice parameter (a) of the perovskite manganite was noticed to linearly change with calcination temperature as is also shown in Fig. 2(l). From 0.5459 nm for the sample calcined at 600 °C, the lattice parameter value increased to 0.5470 nm for

the sample calcined at 1100 °C. The stoichiometric formula of the synthesized manganite compound was evaluated by using linearly fitted data (PCPDFI database) with regard to the dependence of lattice parameter (a) on parameter x in manganite stoichiometric formula – $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$. The proportion of lanthanum was found to increase with the increase in calcination temperature as is shown in Fig. 2(r), and that from 0.53 for the sample calcined at 600 °C to 0.58 for the sample heated at 1100 °C. This increase in proportion of lanthanum induces a decrease in manganese proportion due to the gradual distortion of orthorhombic crystal lattice (existing at $x = 0.5$) toward rhombohedral one (existing at $x > 0.5$), which is also evidenced by the gradual appearance of doublet peaks at $2\theta = 69^\circ$ with the increase in calcination temperature. The manganese proportion in LaSr-manganite stoichiometric formula is known to decrease with an increase in lanthanum stoichiometric proportion (x) over 0.5. Therefore, MnO_2 peaks gradually appear at the XRDs of the samples annealed at higher temperatures (1000 °C and 1100 °C). Oxidation of Mn ions to Mn^{4+} due to annealing in air as well might be the reason for the observed changes in manganite stoichiometry and the formation of the secondary MnO_2 phase. The latter fact is expected when the annealing temperature-dependent increase of the positive charges in manganite stoichiometric formula that follow the increase in lanthanum proportion is taken into account.

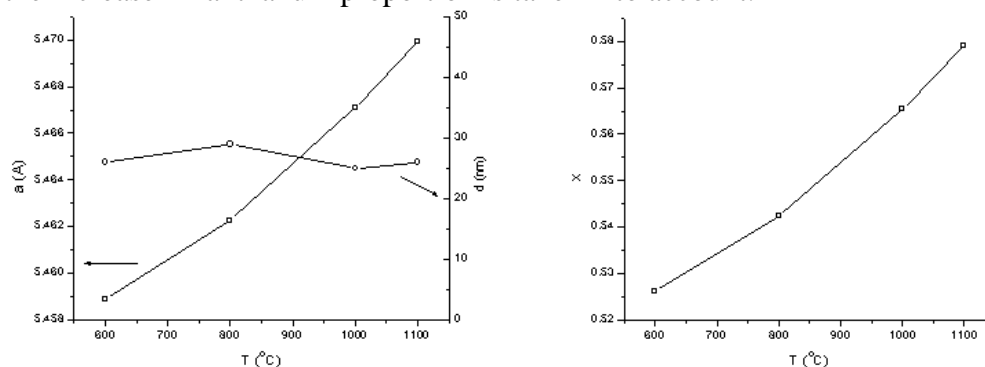


Fig. 2. Dependencies of the average particle size (d) and crystal lattice parameter (a) on the calcination temperature (left) and the dependency of lanthanum proportion in manganite stoichiometric formula vs. calcination temperature (right) for the annealed samples synthesized in bulk conditions.

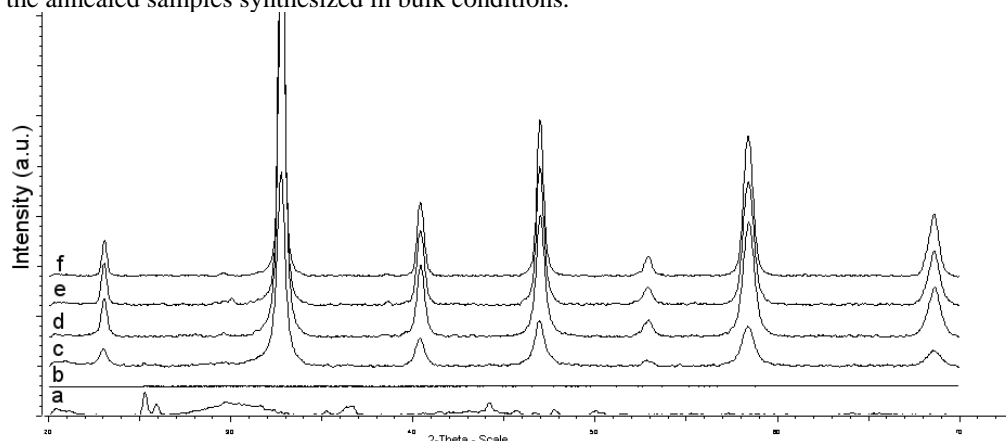


Fig. 3. XRD patterns of the sample synthesized in microemulsion. As-dried powder is denoted with a, whereby the samples calcined at 450 °C, 600 °C, 800 °C, 1000 °C and 1100 °C in air for 2 h are denoted with b, c, d, e and f, respectively.

XRD patterns of the samples synthesized using microemulsion-assisted co-precipitation procedure – as-dried and calcined at different temperatures in air for 2h, are shown in Fig.3. The only crystalline phase detected in the as-dried powder is SrCO_3 . There were no qualitative changes in the XRD pattern if the procedure of co-precipitation was performed at 85 °C. Perovskite manganite phase is formed after calcination at ≥ 600 °C. Changes in the average particle size, as evaluated by using Debye-Scherrer's equation, are presented in Fig. 4(l). With the increase in calcination temperature, a linear increase in average particle size - from 17 nm for the sample

calcined at 600 °C to 25 nm for the sample calcined at 1100 °C, was observed. On the other hand, no changes in lattice parameters were observed, and the mean value of crystal lattice parameter (a) was 0.5474 nm.

The difference between the XRD patterns of the samples synthesized in solution and in microemulsion, both calcined at 450 °C, offers a significant insight into the difference in the processes of formation of perovskite manganite by performing these two approaches. After heating at 450 °C, the formation of LaO_2CO_3 from the precursor $\text{La}(\text{OH})_2$ as well as the remaining of SrCO_3 within the sample might be noticed by comparing XRD patterns a) and b) in Fig. 1. The gradual incorporation of La ions from oxycarbonate compound into the manganite perovskite at ≥ 600 °C induces a gradual increase in La proportion within the manganite stoichiometric formula with the increase in the annealing temperature. On the other hand, the transformation of chemically similar as-dried composition into an amorphous structure for the microemulsion-assisted synthesized samples, is obvious when XRD patterns a) and b) in Fig. 3 are compared. More homogenous transition from the precursor compounds into manganite perovskite in the latter case is reflected on the more stable crystal structure formed at 600 °C with only subsequent grain growth noticed with the increase in the annealing temperature.

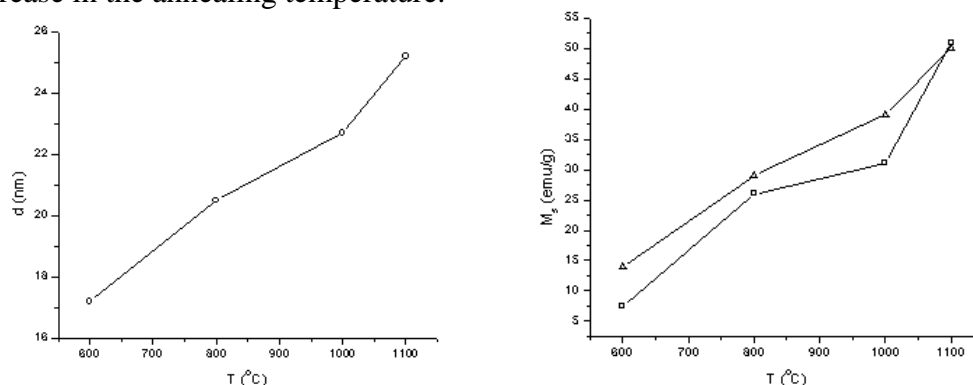


Fig. 4. Dependency of the average particle size vs. calcination temperature for the sample synthesized in microemulsion (left) and the dependence of saturation magnetization on the temperature of calcination for the samples synthesized in bulk conditions (-Δ-) and in microemulsion (-□-) (right).

Almost linear increase in saturation magnetization with the increase in annealing temperature is presented in Fig. 4(r). Improved effective superexchange interaction as the reason for increasing magnetization values with the increase in calcination temperature might be related to the high-temperature induced grain growth in case of the samples prepared in microemulsion, whereas the changes in the crystal structure, including the probable partial changes in Mn valence number implied by the compensation of charges, might be taken as the cause of such dependence in case of the bulk-synthesized sample.

TEM images of both bulk- and microemulsion-assisted- synthesized as-dried powders, and the powders annealed in air for 2h at 600 °C and 1100 °C in bulk-synthesized samples case, and 600 °C and 800 °C for the microemulsion-assisted synthesized samples, are shown in Fig. 5. Long acicular particles are visible in TEM images of the as-dried powders prepared in bulk conditions (Fig. 5a, b), whereby both amorphous regions and regions comprising spherical, polydispersed particles ranging to up to 50 nm in diameter, probably belonging to SrCO_3 phase, can be noticed in Fig. 5c, and 5d, respectively. However, it is more homogenous as-dried composition in case of the sample prepared in microemulsion comparing to the one prepared in bulk conditions that might naturally be ascribed to the observed difference in grain growth within these two synthesis approaches. Considering annealed manganite samples, much narrower distribution of particle sizes is evident for the samples co-precipitated by using microemulsion (calcined at 600 °C) comparing to very wide dispersion of particle sizes for the samples co-precipitated in ordinary aqueous solution, ranging from 20 – 120 nm in diameter as is visible on Fig. 5e, f. However, narrow size distribution of the grains of microemulsion-synthesized sample is destroyed after annealing at temperatures

higher than 600 °C due to the sintering of grains as is obvious by considering particles morphology transition on 600 °C – 800 °C increase in calcination temperature (Fig. 5g – Fig. 5h).

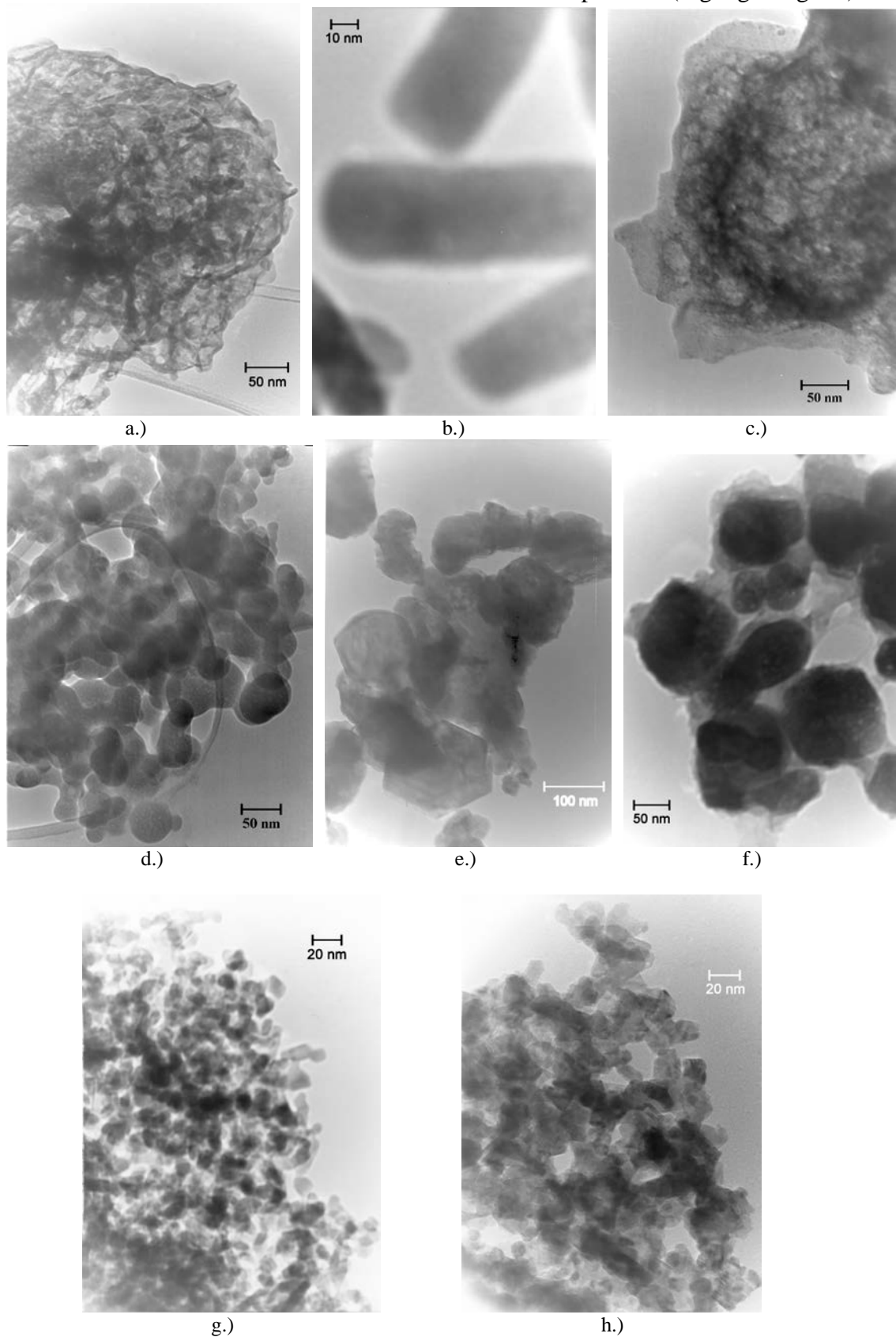


Fig 5. TEM images of the as-dried powders synthesized in bulk conditions (a, b) and in microemulsion (c, d) as well as of the calcined samples – co-precipitated in bulk conditions and annealed for 2 h in air at 600 °C (e) and 1100 °C (f), and co-precipitated in microemulsion and annealed for 2h in air at 600 °C (g) and 800 °C (h).

The results of DTA and TGA measurements over the as-dried powders are presented in Fig. 6. Crystallization of the secondary phases as well as larger distribution of the particle sizes for the bulk-synthesized sample, might be the reason for the difference in corresponding thermograms, taking into account both difference in the major exothermic peak structure and significantly lower weight loss noticed for the case of the bulk-synthesized sample.

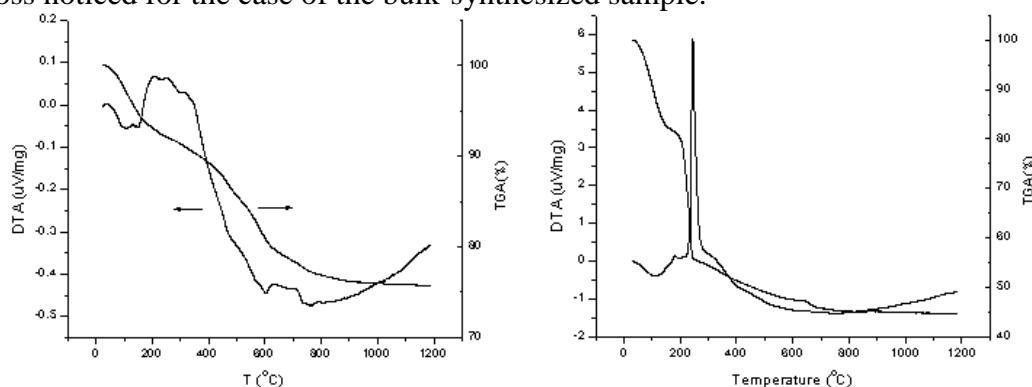


Fig. 6. DTA and TGA diagrams of the as-dried powders synthesized in solution (left) and in microemulsion (right).

4. Conclusions

LaSr-manganites were successfully prepared by performing two different wet co-precipitating approaches: one in an ordinary aqueous solution, using NaOH as the precipitating agent, and the other in CTAB/1-hexanol/1-butanol/H₂O microemulsion with the composition corresponding to reverse micellar domain, using tetramethyl ammonium hydroxide as the precipitating agent. Both as-dried powders were converted to the desired perovskite manganite phase after annealing in air at 600 °C for 2h. With the increase in calcination temperature, a constant average particle size and the linear increase in both lattice parameter (*a*) and lanthanum proportion in stoichiometric formula of manganite compound, were noticed in the case of the powder prepared in bulk conditions, whereas the lattice parameter was constant and the average particle size increased with the increase in calcination temperature in the case of the sample prepared by microemulsion-assisted procedure. The samples derived from microemulsion, calcined at 600 °C, are characterized with more uniform particle sizes as compared to widely distributed particle sizes corresponding to the samples derived from the ordinary solution, which suggests more dense and uniform crystallization nuclei formation and growth processes occurring in microemulsion than in bulk conditions. The latter fact is supported by the noticed existence of La₂O₂CO₃ and SrCO₃ as transient crystal structures in the process of formation of manganite perovskite when the as-dried powder derived from the synthesis in an ordinary aqueous solution is annealed, whereby the formation of amorphous transient composition, suggesting more homogenous crystallization processes, is noticed within the microemulsion-assisted synthesis.

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