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ScienceDirect
Materials and Design 28 (2007) 667–672
Materials & Design
www.elsevier.com/locate/matdes

# Four novel co-precipitation procedures for the synthesis of lanthanum-strontium manganites

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Received 15 March 2005; accepted 4 July 2005
Available online 24 August 2005

## Abstract

Lanthanum-strontium manganites were synthesized using co-precipitation method with a reverse micellar microemulsion. Either oxalic acid, sodium hydroxide or tetramethylammonium hydroxide was used for the precipitation of precursor cations in a form that was subsequently calcined under various conditions in order to obtain perovskite manganite phase. Correlations between the properties of the synthesized powder and the calcination conditions have been put forth. The properties of the microemulsion-assisted synthesized material were compared with the samples prepared by following the supposedly similar chemical recombinations in bulk solutions, with an aim to challenge the fact that microemulsions in general have only templating effects on the morphology of co-precipitated powder. TEM measurements, X-ray diffraction analyses and magnetic measurements were used in order to gain an insight into the mentioned difference, which is an important one for the future understanding of the role that reverse micelles play in the processes of materials synthesis.

*Keywords:* A. Nano materials; B. Particulates and powders; E. Magnetic

## 1. Introduction

Lanthanum-strontium manganites belong to the family of attractive magnetic ceramics for the contemporary electronic industry, due to the wide range of potential applications that these materials might possess [1], depending largely on the method of synthesis performed [2]. High electrical conductivity [3] – as exploited in solid oxide fuel cells; catalytic activity [4,5] – suited for waste gas purification and catalytic combustion processes; colossal, giant, or low-field magnetoresistance [6]; and relatively low Curie temperature [2] – interesting for biomedical applications, are some of the typical properties that caught scientific attention to these materials.

Reverse micellar synthesis of materials is since 1982 [7] known as a viable method for producing relatively uniform and monodispersed particles. Direct correlations between size of the reverse micelles – as nano-sized multimolecular structures existing at particular compositional range of microemulsions, and size of the particles prepared within, were proposed [8,9]. However, a number of recent studies [10,11] have indicated that such oversimplified correlations (especially when aimed at reaching a generalized character) could not be justified [12], and that dynamic, non-linear, and rich in molecular species-interactional character introduces much more complexities (than proposed within the routinely used correlations) and in most cases, as of today's knowledge on the field, necessitates a trial-and-error approach in the processes of materials design by using reverse micelles.

Four different wet, co-precipitation approaches to the synthesis of lanthanum-strontium manganites were

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doi:10.1016/j.matdes.2005.07.002

performed within this work. With an aim of a clearer and more concise presentation of the part of the obtained results, comparison of the methods that included the presence of a reverse micellar microemulsion with the ones excluding it, has been used.

## 2. Experimental procedure

Two pairs of correspondent co-precipitation approaches – being different in the precipitation agent used – were followed in the process of the synthesis of lanthanum-strontium manganites with the desired stoichiometric formula of $La_{0.67}Sr_{0.33}MnO_{3+\delta}$. In each case of the synthesis, two solutions were mixed at room temperature and aged for 1 h in case of the microemulsion-assisted hydroxide-co-precipitation synthesis, and for 3 h in all of the three other synthesis approaches. Centrifugation was used for the sedimentation of the dispersed, solid phase, which is then repeatedly washed, dried and calcined in air at various temperatures. The produced powders were characterized by performing TEM measurements (JEOL JEM-2000FX), X-ray diffraction analyses (D4 Endeavor), and magnetic measurements (Manics DSM10). The solutions used to initiate the precipitation reactions were:

(i) In case of the bulk hydroxide-co-precipitation synthesis [13], the first solution comprised 3, 2 and 1 ml of 0.5 M aqueous solutions of $MnCl_2$, $La(NO_3)_3$ and $Sr(NO_3)_2$, respectively, whereby the second solution comprised 20 ml of 1 M aqueous solution of NaOH.

(ii) In case of the microemulsion-assisted hydroxide-co-precipitation synthesis [13], the first solution comprised 0.076-M overall precursor cation concentration (molar ratio of $Mn^{2+}$:$La^{3+}$:$Sr^{2+}$ = 47.4:31.6:21) aqueous solution (formed by using $MnCl_2$, $La(NO_3)_3$ and $Sr(NO_3)_2$ as precursor salts) within CTAB:1-hexanol:1-butanol: $H_2O$ = 32.3: 15.2:22.2 : 30.3 (wt%) microemulsion, whereby the second solution comprised microemulsion of the same composition carrying 0.5 M aqueous solution of $(CH_3)_4$ NOH, the weight ratio of the precipitating microemulsion vs. the precursor microemulsion being 1.355.

(iii) In case of the bulk oxalate-co-precipitation synthesis, the first solution comprised 6 ml of hydroalcoholic solution ($C_2H_5OH$:$H_2O$ = 1:2, volume ratio) of precursor cations (Mn:La:Sr = 4.6:2.2:1, molar ratio), whereby the second solution comprised 0.84 M oxalic acid, with 1.1 being the volume ratio of the second solution to the first one.

(iv) In case of the microemulsion-assisted oxalate-co-precipitation synthesis, the first solution comprised aqueous solution of $MnCl_2$, $La(NO_3)_3$, and $Sr(NO_3)_2$ –with the resulting cation concentration of 0.5 M and the molar ratio of $Mn^{2+}$:$La^{3+}$:$Sr^{2+}$ = 5:2:1 – within CTAB:1-hexanol:$H_2O$ microemulsion (CTAB:1-hexanol:$H_2O$ = 29.7:55.1:15.2 weight ratio), whereby the second solution comprised the microemulsion of the same composition carrying 0.84 M aqueous solution of oxalic acid. The weight ratio between precursor and precipitating microemulsion was set to 1.5.

The reason for the use of NaOH as the precipitating agent within the bulk hydroxide-co-precipitation synthesis was that, somehow, monophase desired products could not have been obtained with using tetramethylammonium hydroxide as the precipitating agent in bulk conditions. The reason for the use of hydroalcoholic solution in case of the bulk oxalate-co-precipitation synthesis lies in the fact that in the presence of $NO_3^-$, $Mn^{2+}$ in pure aqueous solution forms complexes together with $C_2O_4^{2-}$ and thus resists the precipitation in form of hydroxides. These differences are significant since they include important obstacles in bringing about correlations between the corresponding procedures, from which the role of the reverse micelles, as proposed within this work, might more clearly emanate.

## 3. Results and discussion

The difference in the mechanism of the formation of LaSr-manganite between bulk- and microemulsion-assisted- prepared powders when using hydroxides co-precipitation approach, during the annealing can be observed by comparing XRD patterns presented in Fig. 1. Whereas in case of the bulk synthesis, growth of $SrCO_3$ crystallites comprising the as-dried powder as well as the transformation of $La(OH)_2$ into $La_2O_2CO_3$ is evident from comparing the XRD patterns (a)

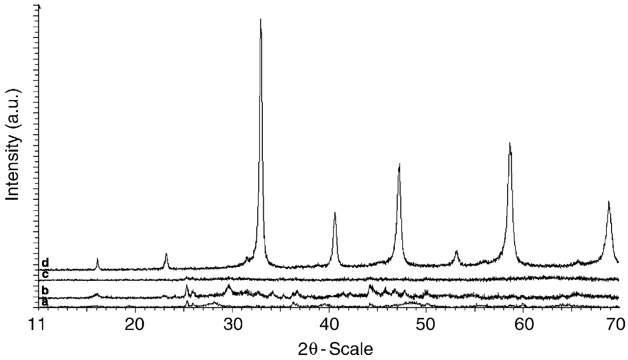

Fig. 1. XRD patterns of the as-dried powder synthesized by hydroxide co-precipitation procedure in solution (a), the same powder calcined at 450 °C (b) and 600 °C (d) for 2 h in air and of the sample co-precipitated within hydroxide approach in reverse micelles and calcined at 450 °C in air for 2 h (c).