



ELSEVIER

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

The magnetic and neutron diffraction studies of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ nanoparticles prepared via molten salt synthesis

M. Kačenka^{a,b}, O. Kaman^{a,b,*}, Z. Jiráček^b, M. Maryško^b, P. Veverka^b,
M. Veverka^b, S. Vratilav^c

^a Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic

^b Institute of Physics, AS CR, Cukrovarnická 10, 162 00 Praha 6, Czech Republic

^c Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University, Břehová 7, 115 19 Praha 1, Czech Republic

ARTICLE INFO

Article history:

Received 20 June 2014

Received in revised form

11 October 2014

Accepted 20 October 2014

Available online 29 October 2014

Keywords:

Magnetic nanoparticles

Manganite

Molten salt synthesis

Neutron diffraction

ABSTRACT

Series of single-phase $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ nanoparticles ($x=0.25-0.47$) with the size of about 50 nm was prepared in molten NaNO_2 . TEM evidenced well dispersed particles that are not interconnected by sintering bridges in contrast to traditional products. Interestingly, some reduction of the perovskite cell volume, particularly at higher Sr-contents, was detected by XRD. Moreover, reduced magnetization and decreased Curie temperature in comparison to sol-gel samples were observed. Neutron diffraction analysis of the as-prepared nanoparticles and several comparative samples with $x=0.37$ indicated that the anomalous behavior of studied particles probably originate in the overdoped outer shell. The overdoping might result from both the surface oxygen chemisorption and from an increased Sr concentration in the shell. By all means, the overdoping would lead to compressive surface stress, driving the $x=0.37$ ground state toward a mixture of FM and A-type AFM ordering as observed by neutron diffraction.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The magnetic and transport properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) perovskite phases have been extensively studied thanks to their fascinating complexity and in particular due to prospects for colossal magnetoresistance. Although bulk samples have been crucial for such studies, nanocrystalline hole-doped manganites including LSMO phases have recently attracted a lot of attention [1–3]. Furthermore, the LSMO nanoparticles whose ferromagnetic behavior can be varied by their composition and size are promising materials for applications in biological research and biomedicine. This concerns especially their use in the magnetic resonance imaging (MRI) [4] or magnetic hyperthermia where Curie temperature, suitably adjusted above the physiological temperature 37 °C, is an advantage over the metallic iron or iron oxide nanoparticles not providing the self-regulated heating mechanism [5].

Most of the methods employed for the preparation of LSMO nanoparticles are based on the sol-gel process [6], coprecipitation [7], or similar techniques leading to a chemically complex precursor

* Corresponding author at: Institute of Physics AS CR, Cukrovarnická 10, 162 00 Praha 6, Czech Republic. Tel.: +420 220 318 418; fax: +420 233 343 184.

E-mail address: kamano@seznam.cz (O. Kaman).

that requires following annealing at higher temperature, typically above 650 °C. Such thermal treatment is inevitably leading to the onset of sintering between the resulting particles. Even if the mean size of crystallites remains low, a harsh mechanical processing and subsequent size fractionation pose the only way how to separate individual LSMO nanoparticles. However, the mechanical treatment like rolling or milling is accompanied by undesirable broadening of the size distribution [8] and moreover, the product might be contaminated by the material of milling chambers. In contrast, the low-temperature synthesis of LSMO nanoparticles in a melt of an inert salt, via so called molten salt synthesis (MSS), could resolve the described problems since no sintering process would take place in an agitated flux.

The MSS method was successfully used for the preparation of nanoparticles of various perovskite phases including e. g. doped LaAlO_3 aluminates [9], different LaMO_3 ($M=\text{Fe}, \text{Co}$ or Ni) phases [10], perovskite manganite LaMnO_3 [11] or double-perovskite structures like La_2BMnO_6 ($B=\text{Ni}$ or Co) [12]. For these syntheses alkali metal nitrates or nitrites were predominantly employed as the melts. Similarly, the preparation of LSMO nanoparticles via MSS, specifically in molten KNO_3 , was already attempted with promising results [13]. However, detailed structural and magnetic characterizations of LSMO nanoparticles prepared in a molten salt have not been performed so far. The current contribution addresses these

issues and suggests an explanation for the peculiar properties of the as-prepared MSS nanoparticles in relation to the distinctive conditions of their synthesis.

2. Nanoparticle preparation and characterization

The nanoparticles of general composition $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (see Table 1 for the list of samples) were prepared in molten NaNO_2 according to the following procedure. A homogeneous mixture of the nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and NaNO_3 in a molar ratio $1-y:y:1:20$ was prepared by the dissolution of the starting metal nitrates in water, subsequent evaporation of the solution and grinding of the dry material with additional NaNO_3 in an agate mortar. The mixture (28 g) was poured into the mechanically agitated flux of NaNO_2 (200 g) preheated at 490°C (measured by a thermocouple). The synthesis was performed in a stainless steel crucible inside an open shaft furnace. After 4 h the melt was poured into a large stainless steel dish and the solidified material was dissolved in water. The particles were separated via centrifugation and washed several times with water. Final purification of the particles involved washing one time with ice-cold 1 M HNO_3 , one time with ice-cold 0.1 M citric acid and again several times with water. The product was dried in vacuo at 40°C , yielding 1.8 g of the as-prepared LSMO nanoparticles (sample A).

Further, several comparative samples with the composition $x=0.37$ were prepared either by post-synthesis treatments of the as-prepared nanoparticles A or by the synthesis of LSMO particles de novo by the sol-gel route (see Table 2 for all the comparative samples and respective preparation conditions). Specifically, the samples C and D were prepared by annealing the as-prepared sample A at a given temperature in an oxygen or air atmosphere. The sample E was prepared by further sintering the pellet of D to achieve a bulk sample from the original MSS product. Alternatively, the sample A was coated with a protective silica shell at first according to the published procedure [14] with several modifications (no mechanical treatment of the as-prepared particles, only an ultrasonic agitation employed to disperse the particles, 260 mg of LSMO as the starting mass for the encapsulation, 1 ml of tetraethoxysilane, 400 ml of the encapsulation mixture). All the silica coated particles were separated by centrifugation without any size fractionation, dried and then subjected to annealing at 700°C . Finally, their manganite cores were isolated by the dissolution of the silica shells by means of heating the material in 4 M NaOH , multiple washing and drying leading to the sample B. The sol-gel synthesis of the sample S was carried out exactly as it was previously described [8] for the composition of $x=0.25$ and the specific conditions of the thermal treatment are given in Table 2.

The mechanically treated sample M was obtained from S by three cycles of rolling followed by mixer milling at frequency of 21 Hz for 1 h (for further details see also [8]). Finally, a series of LSMO bulk samples with $x=0.20-0.45$ was prepared by the same sol-gel procedure and final annealing of the pressed pellets at 1050°C under an oxygen flow for 24 h [15].

The actual content of La, Sr and Mn as well as a possible presence of Na in the samples prepared via MSS were analyzed by means of XRF spectroscopy (AXIOS). For all the samples the phase composition, crystal structure and the mean size of crystallites d_{XRD} were determined by X-ray diffraction (Bruker D8 diffractometer) at room temperature using $\text{CuK}\alpha$ radiation. The XRD patterns were evaluated by the Rietveld method using FULLPROF program [16]. The Thompson-Cox-Hastings pseudo-Voigt profile was employed to resolve instrumental, strain and size contributions to the peak broadening and the instrumental resolution was determined on a strain-free tungsten powder with the grain size of $9.4\ \mu\text{m}$. The d_{XRD} values were calculated on the basis of the refinement of parameter X describing the $1/\cos\theta$ dependence of the Lorentzian linewidth [17]. The transmission electron microscopy (Philips CM 120 with a LaB_6 cathode) with an accelerating voltage 120 kV was used to inspect the morphology and size of particles as well as to allow the supplemental phase analyses. Magnetic properties were probed by SQUID magnetometry (Quantum Design MPMS-5S) on well-compacted powder samples. The Curie temperature was calculated from the Arrott plot. The neutron diffraction (ND) studies were performed for the as-prepared sample A, the same sample after annealing (D), the corresponding bulk sample prepared by sintering (E) and also for a comparative sol-gel material (S). The measurements at room temperature and 7 K were done on the KSN-2 instrument in Řež near Prague using the neutron wavelength $1.362\ \text{\AA}$. Additional determination of oxygen stoichiometry in A and E was carried out by the reverse cerimetric titration. The sample intended for this analysis was purified only by washing with the ice-cold 1 M HNO_3 and water while the washing cycle with citric acid was omitted since its residual presence could distort the results of the redox titration. The Mohr's salt $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used for reduction of the sample and ferroin was employed as the indicator [15].

3. Structure and magnetic properties of the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series

The structural parameters, derived by the Rietveld analysis of XRD patterns presented in Fig. 1, are summarized in Table 1. The data show that all the samples prepared via MSS are of single

Table 1

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ nanoparticles prepared by MSS: composition of product determined by XRF, composition of the melt described by y , the mean size of crystallites d_{XRD} and structural parameters including cell parameters a and b respective to the hexagonal setting of the $R\bar{3}c$ structure together with cell volume V divided by number of formula units ($Z=6$). The lattice parameters for $x=0.37$ and 0.47 closely approach the cubic metrics and were fixed to ideal ratio $c/a=\sqrt{6}$. The simple perovskite subcell and its rhombohedral distortion are further described by lattice parameter a_p and angle α_p and selected bond length and angles are added.

Sample	$\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3$	$\text{La}_{0.72}\text{Sr}_{0.28}\text{MnO}_3$	$\text{La}_{0.63}\text{Sr}_{0.37}\text{MnO}_3$ (A)	$\text{La}_{0.53}\text{Sr}_{0.47}\text{MnO}_3$
La:Sr:Mn (XRF)	0.76:0.25:0.98	0.73:0.28:0.99	0.63:0.37:0.99	0.53:0.47:1.00
y	0.25	0.30	0.40	0.50
d_{XRD} [nm]	47	54	45	40
a [Å]	5.5052(3)	5.4977(3)	5.4674(1)	5.4546(1)
c [Å]	13.3776(13)	13.3757(14)	13.3916(2)	13.3615(2)
V/Z [Å ³]	58.519(7)	58.352(8)	57.780(5)	57.380(5)
a_p [Å]	3.8824	3.8787	3.8659	3.8571
α_p [deg]	90.304	90.258	90	90
Mn–O [Å]	1.953(7)	1.951(6)	1.942(6)	1.933(11)
O–Mn–O [deg]	90.7(5)	90.2(4)	90.2(9)	90.1(9)
Mn–O–Mn [deg]	167.2(8)	167.3(6)	170.2(14)	172.6(12)

Download English Version:

<https://daneshyari.com/en/article/1329646>

Download Persian Version:

<https://daneshyari.com/article/1329646>

[Daneshyari.com](https://daneshyari.com)