



# Influence of surface and finite size effects on the structural and magnetic properties of nanocrystalline lanthanum strontium perovskite manganites



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## ABSTRACT

Syntheses of nanocrystalline perovskite phases of the general formula  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  were carried out employing sol–gel technique followed by thermal treatment at 700–900 °C under oxygen flow. The prepared samples exhibit a rhombohedral structure with space group  $R\bar{3}c$  in the whole investigated range of composition  $0.20 \leq x \leq 0.45$ . The studies were aimed at the chemical composition including oxygen stoichiometry and extrinsic properties, i.e. size of the particles, both influencing the resulting structural and magnetic properties. The oxygen stoichiometry was determined by chemical analysis revealing oxygen excess in most of the studied phases. The excess was particularly high for the samples with the smallest crystallites (12–28 nm) while comparative bulk materials showed moderate non-stoichiometry. These differences are tentatively attributed to the surface effects in view of the volume fraction occupied by the upper layer whose atomic composition does not comply with the ideal bulk stoichiometry.

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## 1. Introduction

The mixed oxides of the general formula  $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$ , where RE and AE denote trivalent rare-earth and bivalent alkaline-earth elements, respectively, constitute a large family of the manganese perovskites interesting from the fundamental as well as application aspects, e.g. in the field of the colossal magnetoresistance [1]. Their properties can be controlled by the doping level which determines the manganese oxidation state and influences the structural distortions from the idealized cubic lattice.

The undoped stoichiometric  $\text{LaMnO}_3$  oxide is an antiferromagnetic insulator possessing orthorhombic structure ( $Pbnm$ ) distorted by simultaneous acting of the electronic and steric phenomena [2]. In the former case it is the Jahn–Teller effect, that causes deformation of the octahedra occupied by  $\text{Mn}^{3+}$  cations characterized by doubly degenerate  $e_g$  level in the octahedral crystal field. On the other hand, the steric distortion

is provoked by mutually inadequate sizes of the cations placed in the dodecahedral *A* sites and octahedral *B* sites of the  $\text{ABO}_3$  structure. For  $\text{LaMnO}_3$  and lightly-doped compositions, large collective and coherent distortions occur. However, further replacement of lanthanum by strontium ions is leading both to the dilution of the Jahn–Teller active  $\text{Mn}^{3+}$  ions and to the decrease of steric distortion (up to  $x \approx 0.5$ ). As a consequence, the coherent distortions are suppressed. Simultaneously a structural transition from the orthorhombic to rhombohedral ( $R\bar{3}c$ ) symmetry takes place.

The properties of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  manganites were preferentially investigated on bulk materials, often the single crystals grown by the floating-zone method usually in a flow of air, alternatively under gases of different oxygen partial pressures in order to diminish the deviations from the ideal oxygen stoichiometry. For such samples, the dependences of the structural, magnetic and electronic domains on the temperature and composition were determined [3–8]. The as-obtained structural, magnetic and electronic phase diagrams exhibit a great complexity that mainly results from the interplay of two dominant indirect interactions between manganese ions—the double exchange and superexchange interactions.

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However, less is known about the effects of non-stoichiometry. A dependence of the ferromagnetic behaviour on the oxygen stoichiometry was evidenced by annealing of  $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_{3-\delta}$  polycrystalline samples at 1000 °C under  $p(\text{O}_2)$  of 0.195 atm and  $p(\text{O}_2)$  of 0.001 atm, respectively. A lower oxygen partial pressure led to a decrease of the relative content of  $\text{Mn}^{4+}$  ( $\text{Mn}^{4+}/(\text{Mn}^{3+}+\text{Mn}^{4+})$ ) and consequently to a significant decrease of Curie temperature  $T_C$  from 248 to 200 K [9]. Analogous effect was reported for the series of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_{3-\delta}$  samples where the decrease of the oxygen content in the range of  $0 \leq \delta \leq 0.1$  obtained by application of a titanium getter caused a gradual decrease of  $T_C$  from 363 K down to 273 K [10].

More recently, the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  manganites with mean size of crystallites lower than  $\approx 100$  nm were found attractive for medical applications [11–14]. Their magnetic properties differ from the bulk counterparts due to the surface and finite size effects. The lower magnetization of ferromagnetic nanoparticles in comparison to bulk samples is usually explained on the basis of the surface “magnetically dead” layer whose contribution to the magnetic moment of a nanoparticle is negligible relatively to the magnetic contribution of its core. Similar decline is observed also for the Curie temperature, but its decrease is related to the finite size of the nanoparticles limiting the maximum correlation length of a ferromagnetic arrangement.

The present paper aims at detailed investigation of the interplay between the composition, structural properties and size of the nanoparticles, simultaneously influencing the resulting magnetic properties. The accurately determined oxygen stoichiometry is compared with bulk samples and analyzed with respect to possible presence of cation vacancies and surface effects. The study is intentionally limited to the composition of  $0.2 \leq x \leq 0.45$  being interesting for preparation of self-regulated heating agents suitable for magnetic fluid hyperthermia (MFH) and efficient  $T_2$  contrast agents for magnetic resonance imaging (MRI).

## 2. Experimental part

### 2.1. Synthesis

Nanocrystalline  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  samples with composition in the range of  $0.2 \leq x \leq 0.45$  were prepared from the starting compounds  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{MnCO}_3$  whose actual content of metal cations was determined by chemical analysis (complexometric titration of La and Mn and gravimetric analysis of Sr). The syntheses were carried out via sol–gel technique using citric acid and ethylene glycol according to the procedure published in details elsewhere [12]. Further steps included drying of the precursor, its calcination at 400 °C and final annealing at selected temperature of 700, 800 or 900 °C for 3 h under a flow of oxygen. In addition, the series of comparative  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  bulk samples was prepared by heating the pressed pellets at 1050 °C under a flow of oxygen for 24 h.

### 2.2. Characterization

The oxygen stoichiometry was determined by the reverse cerimetric titration employing  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  as the reducing agent. Its standard solution was prepared in the diluted HCl (1:1) under an inert atmosphere. Subsequently the solution was used in an excess to dissolve a manganite sample by heating the mixture under strictly inert conditions. Thus the manganese was reduced from  $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$  to soluble  $\text{Mn}^{2+}$  while the inert atmosphere enabled the precise determination of excessive  $\text{Fe}^{2+}$  as follows. The solution was left to cool down and the ferrous ions were titrated by 0.02 M  $\text{Ce}(\text{SO}_4)_2$  with ferroin as an indicator.

The phase purity, lattice parameters and mean size of crystallites  $d_{\text{XRD}}$  were evaluated from X-ray powder diffraction using Bruker D8 diffractometer ( $\text{CuK}\alpha$ , Sol-X energy dispersive detector). The diffraction patterns were analyzed with the Rietveld method using the FULLPROF program (Version 2.20-Sep2002-LLB JRC). The Thompson–Cox–Hastings pseudo-Voigt profile was used to resolve instrumental, strain and size contributions to the peak broadening. The parameter  $X$  describing the  $1/\cos\theta$  dependence of the Lorentzian line width was refined to determine the  $d_{\text{XRD}}$  values [15]. The strain contribution to line width was found to be negligible in the studied samples and was fixed to zero in the final refinements. Instrumental resolution was determined by measuring a strain-free tungsten powder with a grain size of 9.4  $\mu\text{m}$ .

The morphology of the products was observed by transmission electron microscopy (TEM) using Philips CM 120 apparatus (120 kV,  $\text{LaB}_6$ ) on samples prepared by slow evaporation of a drop of highly diluted ethanol suspension on a carbon-coated copper grid.

The DC magnetic measurements were carried out by means of the SQUID magnetometer MPMS-5S (Quantum Design) in the temperature range of 5–350 K and fields up to 1600 kA/m. The Curie temperatures  $T_C$  were evaluated using Arrott plots according to the relation  $H/M = s(T - T_C) + rM^2$  where  $H$ ,  $M$  and  $T$  denote the intensity of magnetic field, the magnetization and temperature, respectively, while  $s$  and  $r$  are constants obtained by a regression analysis.

## 3. Results and discussion

### 3.1. Phase composition

The powder XRD analysis showed that all the nanocrystalline and comparative bulk  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  samples were prepared as single phase products. An example of a diffraction pattern including the Rietveld refinement is given in Fig. 1. The XRD phase purity of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$  nanocrystalline products prepared by the sol–gel technique is related particularly to the annealing temperature. The temperature has to be sufficiently high to fully achieve the reaction as it was shown previously for the composition of  $x = 0.25$

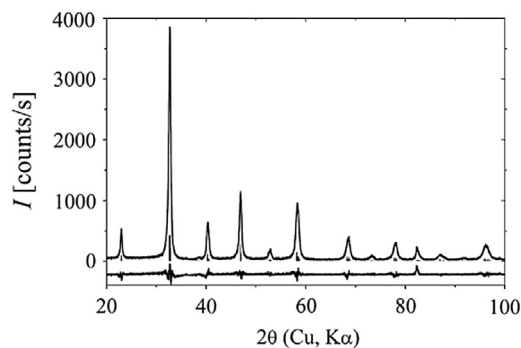


Fig. 1. XRD pattern and Rietveld refinement of the  $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3+\delta}$  sample annealed at 700 °C for 3 h, the difference between observed and calculated data is indicated by the lower line.

where single-phase samples were produced at temperatures higher than 650 °C [16].

### 3.2. Morphology and crystallite sizes

The morphology of as-obtained products, show a distinctive feature, i.e. the presence of nascent connecting bridges between nanoparticles, see Fig. 2. Their origin is related to sintering

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