Available online at www.sciencedirect.com

SciVerse ScienceDirect

www.elsevier.com/locate/matchar

$La_{0.7}Sr_{0.3}MnO_3$ nanopowders: Synthesis of different powders structures and real magnetic properties of nanomanganites

Igor Danilenko, Tetyana Konstantinova, Galina Volkova, Valentina Glazunova*

Donetsk Institute of Physics and Engineering NAS of Ukraine, R. Luxemburg Str. 72, Donetsk 83114, Ukraine

ARTICLE DATA

Article history:
Received 29 October 2012
Received in revised form 16 May 2013
Accepted 17 May 2013

Keywords:
Oxide nanoparticles
Synthesis
Structure
Lanthanum manganite
Precursors

ABSTRACT

The difference in the magnetic properties between two lanthanum manganite nanopowders with identical phase and chemical composition is discussed in terms of the influence of nanopowder synthesis conditions on their properties.

The aim of this investigation was to show the influence of precursor type and structure on the structure and properties of final $La_{0.7}Sr_{0.3}MnO_3$ nanopowders obtained by precipitation technique. The forming of a complex structure of precursor materials during drying and inheritance at firing stage led to the formation of bimodal particle size distribution and magnetic properties typical of coarse powders. The correct choice of precursor material and the technological conditions of the drying and firing stage were allowed for the creation of a uniform powder structure with special magnetic properties.

We showed that the magnetic properties of nanopowders were not always determined by chemical or phase composition and mean particle size of synthesized powders. The difference in precipitation process can lead to unpredictable and catastrophic results, and masked the effect of nanoparticles on the magnetic properties of the material.

1. Introduction

The magnetic properties of lanthanum manganites at the nanometer scale were actively investigated five to ten years ago. A number of investigations of the effects of grain size on magnetotransport, or of the magnetic properties of perovskites were published elsewhere [1–3]. It is known that the physical properties of materials depend on particle size, but the question is: if we have a wide spectrum of particle size distribution, what part has a large deposit in properties — small or large particles? Furthermore, what do we need to measure during the experiment? In all experiments, the average particle size was often used as a form of measurement, and wide particle size distribution was not taken into account. The presence of large or small particles in LSM powder distribution can lead to result distortion, as it is widely known that the particle size of manganites has a strong effect on their magnetic properties ("size effect") [4–9].

The ^{55}Mn nuclear magnetic resonance (NMR) investigations on a single-modal $La_{0.7}Sr_{0.3}MnO_3$ (LSM) nanopowder with an average particle size of 20 nm, as well as bimodal LSM nanopowders with two dominant peaks in particle size distribution of 30 nm and 200 nm showed significant differences in magnetic properties. In our work [1,10], it was shown that NMR signals from bimodal LSM powder (NP1) correspond to typical values for manganites with diphasic ferromagnetic states: F_gM and F_bM. This corresponds to the double exchange mechanism with fast holes switching between Mn^{3+}/Mn^{4+} states. In contrast, only one ferromagnetic state, which corresponds to the phase of F_b, was found in the single-modal LSM powder (NP2). The F_bM state was identified as a ferromagnetic phase with slower hole motion and a weaker double exchange. In addition, we found

* *Corresponding author*. Tel.: +380 62 3111121; fax: +380 62 3427513.
E-mail address: matscidep@aim.com (I. Danilenko).

1044-5803/$ – see front matter
http://dx.doi.org/10.1016/j.matchar.2013.05.012

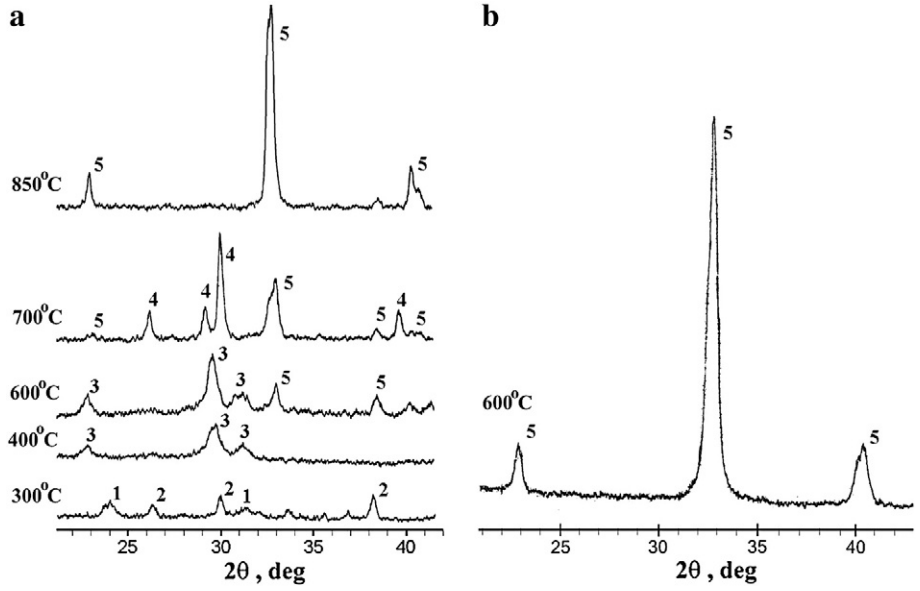

Fig. 1 – XRD patterns for NP1 (a) and NP2 (b) LSM nanopowders calcined at different temperatures. For NP1 powder the intermediate phases are shown as 1) — $Mn(CO)_3$, 2) — $La_2O(CO_3)_2 \times xH_2O$, 3) — La_2CO_5, 4) — La_2O_3, and 5) — $La_{0.7}Sr_{0.3}MnO_3$. For NP2 — only $La_{0.7}Sr_{0.3}MnO_3$ present from in temperature region 600–900 °C.

that the magnetization of NP1 bimodal powder was several times greater than that of NP2 powder, which consisted only of small particles. The NP1 and NP2 powders were obtained via identical technology, but showed different magnetic powders. Consequently, the process of powder synthesis led to a change in material structure and phase composition, which can ultimately change our knowledge about the material. The conditions of chemical synthesis such as drying, firing and other processes need to be developed for each type of material in order to provide adequate links between the structure and properties of the material.

There are many nanopowder synthesis methods that have been developed, such as synthesis through emulsions [11], molecular decomposition [12], mechanochemical synthesis [13], nonisothermal synthesis [14], and nanoexplosive synthesis [15]. The nanopowders obtained by these different methods have different structures and properties. The precipitation technique is one simple method that is used to obtain different types of complex oxide powders. In our earlier studies [16–19], we described a new method of oxide nanopowder synthesis, and we conducted an investigation of nanopowders and ceramic properties, such as magnetic, transport, and mechanical.

In our earlier work [1,10,20], the investigation of the magnetic properties of nanopowders was made without taking into account the features of powder structure formation. In this work, we examined how precursor structure can affect the structure of powders and the magnetic properties of LSM nanopowders. We also showed how the synthesis conditions can lead to the formation of material with identical chemical and phase composition, but with different structure and magnetic properties, placing a focus on lanthanum manganite nanopowders.

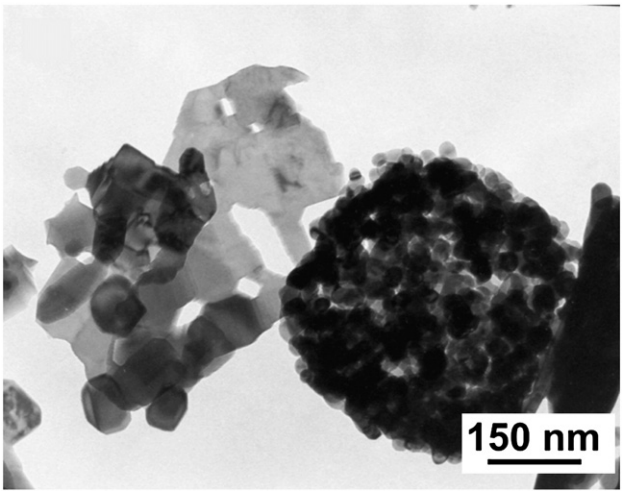

Fig. 2 – TEM image of the bimodal (NP1) nanopowder.

2. Experimental

We used the co-precipitation method for the synthesis of lanthanum manganite nanopowders. Stoichiometric amounts of La_2O_3, $SrCl_2 \cdot 2H_2O$, and $Mn(NO_3)_3 \cdot 6H_2O$ were used as starting materials, and NaOH and Na_2CO_3 were used as precipitants for the synthesis of $La_{0.7}Sr_{0.3}MnO_3$ powders. La_2O_3 was dissolved in nitric acid, and the LSM nanopowder obtained by precipitation in Na_2CO_3 was labeled as NP1, while the LSM nanopowder obtained by precipitation in NaOH was labeled as NP2. This labeling system was identical to that reported in [10], where we measured the magnetic properties of the powders. All of the chemicals used in the synthesis procedure were of a chemical grade. After precipitation, the solutions were mixed for 1 h at room temperature. After washing and filtration, the sediments