

Modified self-propagating high-temperature synthesis of nanosized $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$

Ana Mraković^{a,*}, Jovan Blanuša^a, Darinka Primc^b, Marija Perović^a, Zvonko Jagličić^c,
Vladan Kusigerski^a, Vojislav Spasojević^a

^aThe Vinca Institute, University of Belgrade, P. O. BOX 522, 11001 Belgrade, Serbia

^bJožef Stefan Institute, Department for Materials Synthesis, Jamova cesta 39, 1000 Ljubljana, Slovenia

^cInstitute of Mathematics, Physics and Mechanics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia

Received 4 September 2012; received in revised form 16 October 2012; accepted 17 October 2012

Available online 30 October 2012

Abstract

A modified solid-state combustion route was developed for the preparation of nanocrystalline manganite $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ in a single-step process, using metal nitrates and glucose/ KNO_3 redox mixture. The obtained sample was found to crystallize within O' type of orthorhombic perovskite structure (space group $Pnma$), without the presence of other structural phases or impurities. Nanoparticles are found to have particle size in the range 12–35 nm, and to be highly crystalline without the presence of amorphous surface layer. Magnetic measurements show that nanoparticles display bulk-like magnetic properties, with ferromagnetic phase transition at 125 K and the absence of superparamagnetic or spin-glass behavior.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: B. X-ray methods; C. Magnetic properties; D. Perovskites; Combustion synthesis

1. Introduction

Doped rare earth manganites of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ composition are subject of significant research interest during the last two decades due to their rich phase diagram and intriguing physical properties like colossal magneto-resistance (CMR), charge ordering (CO) or orbital ordering (OO) effects [1–3]. With research focus shifted to nanoparticle form, a number of synthesis methods for doped nanoparticle manganites are proposed and tested, including variety of wet chemistry, mechanochemistry and combustion methods [4–10]. Combustion synthesis or SHS (self-propagating high-temperature synthesis), is one of the preparation methods capable of meeting conflicting demands required in synthesis of nanoparticle mixed manganites (and nanoparticle solid solutions in general): the detention of small particle size, and simultaneously, the high synthesis temperature.

One version of SHS process, known as solution combustion (SC), is frequently used for synthesis of nanoparticle solid solutions [11,12]. It is based on a brief, exothermic burning reaction between oxidizing agent (usually the mixture of metal nitrates or acetates) and organic fuel (glycine, citric acid, urea, sucrose, etc.). By mixing of nitrates and fuel in a form of liquid solution, this approach provides the highest possible degree of precursor homogenization. Compared to many of the wet chemistry routes, SC method is advantageous since it is very simple to implement, it is time- and cost-efficient and it can easily provide large amounts of material [13–15]. This, however, is achieved at a cost of inability to retain precise control over particle size and morphology. Stochastic character of self-ignition and/or burning process often leads to inhomogeneous heat and temperature distribution through the reacting media. Consequently, the resulting product may not be single phase and the size distribution of obtained nanoparticles is broad. In addition, it is rarely possible to obtain samples by SC in a single step process [15,16], and the usual need for additional annealing at $T \geq 800$ °C often

*Corresponding author. Tel.: +381 11 80 65 828;
fax: +381 11 80 65 829.

E-mail address: amrakovic@vinca.rs (A. Mraković).

hinders the possibility to obtain particles that are less than 30 nm in diameter.

SHS conducted in a solid state (SSC) represents another useful way to use combustion energy in synthesis of solid solutions [17,18]. In this approach, a mixture of reacting powders is pressed in cylindrical shape and ignited at one end, thus creating a heat wave that propagates (with well defined velocity) toward the other end of the cylinder. In SSC route, the burning reaction typically takes place between metal powder (as fuel) and the powders of metal oxides or nonmetallic elements (as oxidizers) [19]. However, with the combustion temperature commonly exceeding 2000 °C, this variation of SHS method was primarily developed for synthesis of polycrystalline ceramics that would be difficult to obtain by conventional sintering [17].

Application of standard SSC procedure in nanoparticle synthesis is limited both by its high temperature and by heterogeneity of powder mixture due to the micron-grade granular size. Nevertheless, better control over combustion process than in the case of SC synthesis represents an attractive motive for modification of SSC towards nanoparticle synthesis. Numerous attempts have been made in that direction, for example, through the reduction of temperature by adding rock salt to the mixture [20], or by subsequent high energy ball milling (HEBM) of polycrystalline products obtained under standard SSC procedure [21]. HEBM was also used to reduce the grain size of starting powders down to nanometric scale prior to combustion [21].

There were also attempts to replace the metal–metal oxide (thermite) type of reaction, in order to extend SSC applicability to a wider range of compounds, including manganites. For example, NaClO_4 was used as internal oxidizer of Mn metal during synthesis of polycrystalline mixed manganites [22], while the introduction of carbon as an internal fuel was reported in [23] for synthesis of submicron perovskite powders. Recently, Hwang et al. [24] have used aqueous solution of metal nitrates and organic fuel in the first phase of synthesis (as a part of typical SC procedure), but skipped self-ignition stage in liquid phase and conducted the combustion of the dried residue instead, to obtain nanoscale Ni–Zn ferrite powder.

In typical SC and SSC methods, metal salts or non-metallic elements are simultaneously involved in two parallel processes; they serve both as fuel oxidizers and cation source for solid state reaction to form the final compound. While such concept may simplify the procedure, the need to maintain critical fuel/oxidizer ratio necessary for ideally balanced reaction makes the temperature and rate of combustion intrinsic to the choice of used compounds, with limited possibilities for additional control. Changes in fuel/oxidizer ratio can influence combustion dynamics to some extent, but can also lead to either unburned fuel residue or to incompletely formed product. Thus, it is reasonable to assume that keeping burning reaction (with a sole purpose of providing thermal energy) and the solid state reaction of metallic compounds as two

simultaneous, albeit chemically independent processes, may offer more flexible control over the temperature and rate of solid state reaction.

In this work we propose the modification of SSC route, with the initial step in which both the internal oxidizer and organic fuel are added to the mixture of metal nitrates, all in the form of aqueous solution. The proposed modification has the main goal of setting up a simple, yet efficient and single step combustion process that will combine advantages of SC (good mixture homogenization) with those of SSC (better combustion control, higher degree of crystallinity). We demonstrate that this concept can be successfully applied to synthesis of nanoparticle $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) mixed manganite.

2. Materials and methods

In the modified SHS route, appropriate amounts of reactants (glucose, KNO_3 and nitrates of La, Ca and Mn) are dissolved and mixed as an aqueous solution providing the maximum degree of homogenization as in the case of classical SC approach. After drying, solid mixture was burned in typical SSC manner to produce $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ as the final product. The simple concept of this synthesis route is depicted in Fig. 1.

First, 1 M aqueous solutions of metal nitrates were mixed in the stoichiometric proportion according to manganite formula $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. To this solution, aqueous solution of redox mixture—potassium nitrate (KNO_3) and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) was added. The overall number of moles of metal nitrates was 0.02, and the molar ratio between metal nitrates/glucose/ KNO_3 was 1.01/0.28/1. The final solution was

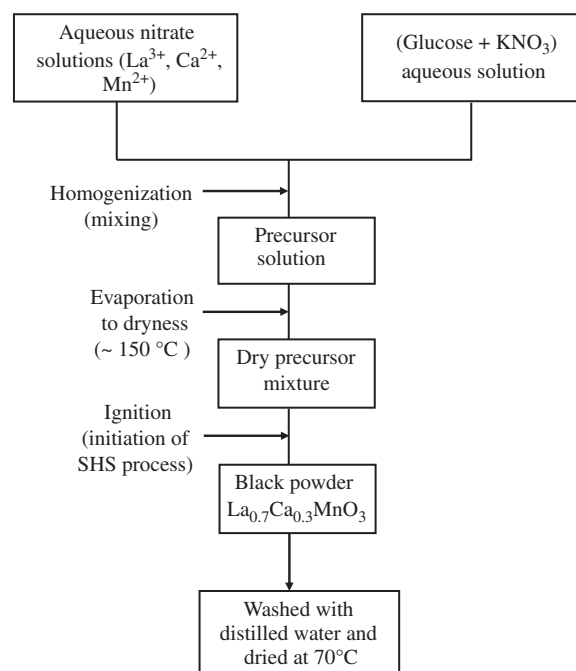


Fig. 1. Flow chart for combustion synthesis of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanopowder.

Download English Version:

<https://daneshyari.com/en/article/1461744>

Download Persian Version:

<https://daneshyari.com/article/1461744>

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