Journal of the European Ceramic Society 35 (2015) 3545–3552

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Chemical vapour synthesis of lanthanum gallium oxide nanoparticles

Ivan Stijepovic[a,*], Ruzica Djenadic[b,c], Vladimir V. Srdic[a], Markus Winterer[b]

[a] Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Novi Sad, Serbia
[b] Nanoparticle Process Technology, Faculty of Engineering, and Center for NanoIntegration Duisburg-Essen, CENIDE, University of Duisburg-Essen, Duisburg, Germany
[c] Joint Research Laboratory Nanomaterials Technical University Darmstadt and Karlsruhe Institute of Technology, Darmstadt, Germany

ARTICLE INFO

Article history:
Received 16 December 2014
Received in revised form 13 May 2015
Accepted 15 May 2015
Available online 30 May 2015

Keywords:
CVS
Nanoparticles
Lathanum-gallate
Sinterability

ABSTRACT

Lanthanum-gallate nanoparticles have been prepared via chemical vapour synthesis (CVS) starting from metal acetylacetonates as solid precursors evaporated using a CO_2-laser. The temperature in the CVS reactor has significant influence on crystallinity and phase composition of the as-synthesized particles. Higher temperatures (1100 °C and 1300 °C) result in nanocrystalline particles with monoclinic $La_4Ga_2O_9$ and trigonal La_2O_3 as main phases due to gallium-oxide sublimation in the reactor. Lower temperatures (800 °C and 900 °C) limit evaporation, inhibit crystallization and yield amorphous particles. At 800 °C the volatility of Ga_2O_3 is low enough to generate nanoparticles containing an almost stoichiometric ratio of gallium to lanthanum of 1:1. Subsequent calcination is required to remove organic residues, however, the nanoscaled structure of the particles is preserved. Ceramics of lanthanum gallium oxide obtained by sintering CVS particles contain closed pores after sintering at 1300 °C and a microstructure with close to theoretical density after sintering for only 1 h at 1400 °C.

1. Introduction

Lanthanum-gallate ($LaGaO_3$, LGO) is a perovskite (ABO_3) type material with orthorhombic structure at room temperature. When doped with Sr and Mg at A and B sites respectively ($La_{1-x}Sr_xGa_{1-y}Mg_yO_3$, LSGM), it shows high ionic conductivity and excellent chemical stability both in oxidizing and reducing environments. This makes it a promising material to be used in gas sensors, membranes and electrochemical devices such as electrolytic cells and especially intermediate temperature solid oxide fuel cells (IT-SOFC). It is already used replacing conventional yttrium stabilized zirconia (YSZ) as an electrolyte material in SOFCs which work at temperatures as low as 600 °C [1–7]. Significant improvements have been achieved concerning the phase composition and density of the LSGM ceramics. Nevertheless, there is a quest for a decrease in sintering temperature and time [3,8–26]. One possible solution could be the use of nanoparticles which are better for sintering than agglomerated particles of micrometer size.

Chemical vapour synthesis (CVS) is a relatively new method for the synthesis of nanoparticles. It has been derived from chemical vapour deposition (CVD), a method, which is widely used for thin film preparation [27]. CVS is a modified CVD process where homogeneous nucleation and particle formation are favoured instead of film growth. This is typically accomplished using high temperatures and long residence times. Some advantages of CVS include short process time, small particle size with narrow size distribution, low agglomeration and high purity [28–33].

For the synthesis of complex oxides like perovskites great care has to be taken to obtain a stoichiometric ratio of the A and B cations (A:B = 1), which is a challenge especially due to the limited number of suitable precursors [34,35]. In case of the perovskite $LaGaO_3$, the only available chemically similar precursors for both lanthanum and gallium are solid chlorides and metallorganic complexes such as β-diketonates. Metallorganic precursors have already been used successfully in atomic layer epitaxy (ALE) of lanthanum-gallate thin films [36,37]. This technique also employs gas-to-solid conversion. However, the basic idea in ALE of $LaGaO_3$ is to build a solid film by depositing layer by layer of La, Ga and O species on a substrate finally forming the perovskite ABO_3 structure. Therefore, lanthanum and gallium precursor vapours are sequentially introduced into the reactor together with an oxidizing agent providing freedom to use separate delivery systems and if required reaction conditions for different precursors of different vapour pressures and decomposition kinetics, respectively. This is not possible in CVS where all gas species should enter the reactor and react simultaneously to generate homogeneous nanoparticles [27]. Full control over chemical composition and stoichiometry is difficult using precursors of different vapour pressures by simple thermal

* Corresponding author. Tel.: +381 21 485 3750; fax: +381 21 450 413.
E-mail addresses: ivan.stijepovic@gmail.com, ivan@tf.uns.ac.rs (I. Stijepovic).

http://dx.doi.org/10.1016/j.jeurceramsoc.2015.05.020
0955-2219/

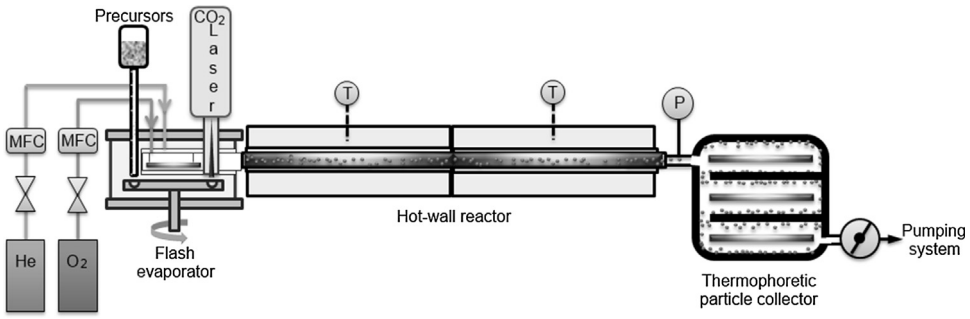

Fig. 1. CVS experimental set-up.

evaporation [34,35,38]. It has been reported previously that laser flash evaporation is able to solve this problem [35]. Most metallorganic components absorb IR light at 10.6 μm, the emission wavelength of the CO_2 laser. Solid precursor mixtures absorb these photons and all components evaporate simultaneously when irradiated with this laser. Vapours are then transported into the reactor by an inert carrier gas where they react with oxygen. It has been found that this method provides very good control over stoichiometry enabling synthesis of perovskite nanoparticles and other complex oxides [35,39,40].

In this work, CVS of lanthanum gallium oxide is reported for the first time and sinterability of the synthesised nanoparticles is studied.

2. Experimental

2.1. Sample preparation

Lanthanum-gallate nanoparticles were produced by CVS using the experimental setup illustrated in Fig. 1 [see 35, 39 for more details]. Solid precursors La-acetylacetonate, $La(acac)_3$ (Sigma Aldrich, 99.9% purity), and Ga-acetylacetonate, $Ga(acac)_3$ (Sigma Aldrich, 99.9% purity), were thoroughly mixed in a mortar inside a glove-box, corresponding to a stoichiometric ratio of La:Ga, and then transferred under inert conditions to the laser flash evaporator. Precursors were supplied slowly to the evaporation chamber from the glass vessel on to the rotating plate with the groove. The mixture was evaporated using a CO_2 laser (Coherent GEM 100 W) operating at 95 W, which was focused on the groove enabling sublimation of the precursor powder. The precursor vapours were transported into the hot wall reactor using helium as carrier gas (1020 sccm) where the precursors vapours react with oxygen (1000 sccm) and form oxide particles. The total pressure in the reactor was kept at 20 mbar using a pumping system, an absolute pressure gauge and a butterfly valve. The particles were thermophoretically separated from the gas flow in a particle collector. A series of four synthesis experiments were performed using different temperatures in the hot wall reactor, i.e. 800 °C, 900 °C, 1100 °C and 1300 °C. The as-synthesised samples were labelled according to their CVS synthesis temperature (Table 1). Additionally, two samples were prepared at 1100 °C with an excess of $Ga(acac)_3$ in the precursor mixture (Ga:La = 2:1, 5:1) in order to investigate the influence of the precursor stoichiometry on the phase composition. The black colour of the as-synthesised particles indicates incomplete precursor decomposition. Therefore, the particles were additionally calcined for 1 h at temperatures up to 1000 °C. The sample LG800 consisted of almost pure orthorhombic phase after calcination at 1000 °C, thus it has been chosen for further sinterability studies.

In order to prepare sintered samples, the as-synthesised particles (LG800) were calcined in two stages, first at 500 °C with 1 h dwell and after that at 700 °C for one additional hour. The calcined particles were then uniaxially pressed at 500 MPa for 5 min. The pressed samples were dried overnight at 105 °C and sintered at 1200 °C for 1 h. These samples were then additionally sintered at 1250 °C, 1300 °C, 1350 °C and 1400 °C for 1 h.

2.2. Sample characterisation

The crystal structure and phase composition of the samples were determined by X-ray diffraction (XRD) using a PANalytical X-ray diffractometer (X'Pert PRO) operating with Ni-filtered Cu $K\alpha$ radiation at 40 kV and 40 mA. The data were collected in a 2θ range from 20 to 120° with a step size of 0.03° and a sampling time of 200 s/step using an X'Celerator detector. Rietveld refinement of XRD data was performed using MAUD software (version 2.33) [41] in order to obtain information about phase composition of the samples. The result of Rietveld refinements could be found in Supporting information.

Fourier transform infrared spectroscopy (FT-IR) was used to examine the precursor powders which were mixed with KBr, ground and pressed into pellets to form samples. The FT-IR measurements were performed using a Nicolet Nexus 670 FT-IR spectrophotometer.

Transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM/EDS) was performed with Philips Tecnai F20 microscope operating at 200 kV. Particles were dispersed in ethanol using ultrasound agitation for 30 s. These suspensions were then transferred on to a nickel grids and left to dry.

DSC/TG analysis was performed using TA Instruments SDT Q600 instrument with 20 °C/min heating rate up to 1000 °C in nitrogen atmosphere.

A Micromeritics ASAP 2000 instrument was used for low-temperature nitrogen absorption. Specific surface area was calculated by the BET method [42] and pore size distribution was obtained from the desorption isotherm according to BJH method [43].

Table 1
Sample notation of as-synthetised samples.

Sample notation	Molar Ga:La ratio	Synthesis temperature [°C]
LG800	1:1	800
LG900	1:1	900
LG1100	1:1	1100
	2:1	
	5:1	
LG1300	1:1	1300