Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 126 (2007) 181–186
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

High throughput screening of the propylene and ethanol sensing properties of rare-earth orthoferrites and orthochromites

Maike Siemons, Ulrich Simon *

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, 52056 Aachen, Germany

Available online 18 December 2006

Abstract

Perovskite-type $LnMO_3$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; M = Cr, Fe) oxides were prepared by the polyol mediated synthesis. Thick films of the prepared materials were electrically characterised using high throughput impedance spectroscopy (HT-IS). All samples showed p-type semiconductivity. Ethanol and propylene were used to test the gas sensing behaviour in a temperature range from 200 to 500 °C. A correlation between the (Ln–O) binding energy and the sensing properties is observed.

Keywords: $LnFeO_3$; $LnCrO_3$; Polyol method; High throughput impedance spectroscopy; Gas sensor

1. Introduction

Gas monitoring represents a growing demand resulting from strategies for intelligent process management, environmental protection and medical diagnostics as well as from the domestic and automobile sector. The four key parameters identifying a good sensor are sensitivity, selectivity, stability and response time [1]. However, the majority of the research activities on the development of fast responding, sensitive and especially highly selective gas sensor materials is often restricted to modification and improvement of known systems and only rarely being directed towards the search for alternative sensor materials. Therefore, nowadays commercial gas sensors are either based on few n-type conducting semiconductor materials, like, e.g. SnO_2, ZnO, WO_3, Fe_2O_3 or TiO_2, or, for more demanding applications, are based on sensor arrays of these materials enhancing selectivity with appropriate complex signal analysis.

The use of high throughput experimentation (HTE) techniques accelerates material synthesis and characterisation, enabling to investigate a multiplicity of materials compared to 'one at a time' strategy [2,3]. Besides, HTE allows the application of combinatorial strategies, which typically are based on evolutionary optimising of selected material properties. Most recently we have reported on the development of a high throughput impedance spectroscopy (HT-IS) setup for the analysis of the gas sensing properties of metal oxides together with a broad variety of different surface doping elements [4,5]. By means of selected examples we have demonstrated how materials with desired properties can be found in a huge variety of different combinations of metal oxides and surface doping.

In this work we report on the gas sensing properties of 25 nanoscaled p-type semiconducting $LnMO_3$ metal oxides with (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu; M = Cr, Fe) using an HTE methodology. The rare-earth perovskites ($LnMO_3$) containing transition metal ions (M) show a wide range of electrical properties. They show good thermal stability and have been tested, for example, as catalysts [6,7], photocatalysts [8], electrodes of fuel cells [9,10] and magneto-optics [11,12]. Some of them have been proposed as gas sensing materials for CO [13], NO_2 [14,15] and hydrocarbons [16–20].

We report about measurements on the sensitivity and response times in a temperature range from 200 to 500 °C towards ethanol and propylene. In continuation of our earlier studies [21] on $LnMO_3$ we took into account the sensitivity towards ethanol, which is a test gas of high interest in different field of application. In order to verify the model proposed for structure–property-relations we analysed the dependence between the (M–O) binding energy and the sensitivity of the materials towards ethanol.

* Corresponding author. Tel.: +49 241 80 94644; fax: +49 241 80 99003.
E-mail address: ulrich.simon@ac.rwth-aachen.de (U. Simon).

0925-4005/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2006.11.022

Table 1
Summary of materials prepared (DS stands for Debye–Scherrer)

Ln-precursor	Compound	DS (nm)	SEM (nm)[a]	Compound	DS (nm)	SEM (nm)[a]
$La(NO_3)_3{\cdot}6H_2O$; 99% Fluka	$LaFeO_3$	74	30–80	$LaCrO_3$	84	70–90
$Pr(NO_3)_3{\cdot}6H_2O$; 99.9% Aldrich	$PrFeO_3$	42	40–100	$PrCrO_3$	87	80–100
$Nd(CH_3COO)_3{\cdot}nH_2O$; 99% Alfa Aeser	$NdFeO_3$	55	50–70	–	–	–
$Sm(NO_3)_3{\cdot}6H_2O$; 99.9% Acros	$SmFeO_3$	55	30–60	$SmCrO_3$	131	Highly agglomerated
$Eu_2(CO_3)_3{\cdot}nH_2O$; 99.9% Alfa Aeser	$EuFeO_3$	62	50–80	$EuCrO_3$	108	60–100
$Gd(CH_3COO)_3{\cdot}nH_2O$; 99.9% Alfa Aeser	$GdFeO_3$	55	50–80	$GdCrO_3$	101	60–80
$Tb(NO_3)_3{\cdot}6H_2O$; 99.9% Acros	$TbFeO_3$	70	40–80	$TbCrO_3$	148	80–100
$Dy(NO_3)_3{\cdot}5H_2O$; 99.9% Alfa Aeser	$DyFeO_3$	71	30–70	$DyCrO_3$	94	50–100
$Ho(NO_3)_3{\cdot}5H_2O$; 99.9% Alfa Aeser	$HoFeO_3$	56	Highly agglomerated	$HoCrO_3$	132	Highly agglomerated
$Er_2(CO_3)_3{\cdot}nH_2O$; 99.9% Alfa Aeser	$ErFeO_3$	57	Highly agglomerated	$ErCrO_3$	82	70–90
$Tm(CH_3COO)_3{\cdot}nH_2O$; 99.9% Alfa Aeser	$TmFeO_3$	91	40–100	$TmCrO_3$	109	50–70
$Yb(NO_3)_3{\cdot}5H_2O$; 99.9% Strem	$YbFeO_3$	56	30–60	$YbCrO_3$	77	60–80
$Lu(CH_3COO)_3{\cdot}nH_2O$; 99.9% Alfa Aeser	$LuFeO_3$	120	Highly agglomerated	$LuCrO_3$	114	Highly agglomerated

[a] Size of visible spherical primary particles.

2. Experimental

2.1. Material preparation and characterisation

For the preparation of the perovskite compounds, which is described in detail elsewhere [21], stoichiometric amounts of $Fe(NO_3)_3{\cdot}9H_2O$ (Merck, p.a.) or $Cr(NO_3)_3{\cdot}9H_2O$ (Alfa Aeser, 96%) and a suitable lanthanoid precursor (see Table 1) were dispersed in diethylene glycol (DEG, Merck, 99.99%). The mixture was heated up to T_1 (80–140 °C) under vigorous stirring until a clear solution was obtained. If necessary, a sufficient surplus of hydrolysis agent was added. The emerging suspension was heated for 5 h up to T_2 (160–190 °C) and then cooled to room temperature. The preparation resulted in a stable suspension with a standard concentration in all experiments of typically 1 wt% (solid to DEG). For further characterisation the solid material was separated from the suspension via centrifugation and washing with acetone. These "as synthesised" samples were dried at 60 °C. To obtain crystalline materials the suspensions were dried at 400 °C (1 h) and then annealed at T_3 (700–900 °C) for 2–12 h. For each individual synthesis, reaction parameters needed to be optimised with respect to particle size, yield and purity.

The initial characterisation of the products was carried out by powder XRD measurements (Cu Kα, λ = 1.54059 Å) on thin films with a Huber Image Plate in transmission. Powder diffraction patterns were analysed using Stoe WinXPow 1.06 Software (Stoe & CIE GmbH). Powder morphology was examined by SEM analysis using a Zeiss DSM 982 Gemini and a LEO Supra 35 VP. For that purpose, all samples were sputtered with carbon. Table 1 summarises the composition as well as the mean particle size (diameter) obtained from SEM measurements and the mean crystallite size obtained from XRD measurements (Debye–Scherrer equation [22]).

2.2. Thick film preparation and high throughput setup

The prepared materials are well suited for thick layer preparation on interdigital electrode structures. These electrode substrates consist of an Al_2O_3-plate (side length of 105 mm) with 64 interdigital capacitors (IDC) made of platinum. The platinum IDC has a structure width of 110 μm and each well has a diame-

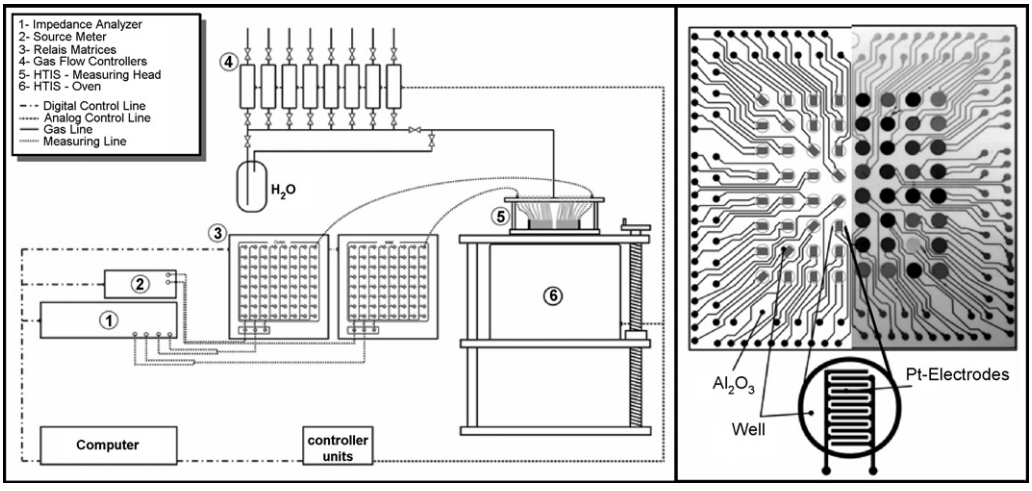

Fig. 1. *Left*: Scheme of the HT-IS setup. For reasons of clearness only two measuring lines are displayed. *Right*: Layout of the multielectrode array with photograph of an already deposited sample plate (adapted from Ref. [23]).