

Thermal decomposition of cerium propionate in oxidant atmosphere to obtain ceria nanocrystalline films at low temperature

P. Roura^{}, J. Farjas^{*}, J. Camps^{*}, S. Ricart[&], N. Mestres[&], T. Puig[&] and X. Obradors[&]*

^{}University of Girona, Campus Montilivi, Edif. PII, E17071 Girona, Catalonia, Spain*

[&]Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193

Bellaterra, Catalonia, Spain

pere.roura@udg.es

Ceria-based oxides deserve great attention because of their broad range applications covering fields as diverse as catalysis [1], electrolyte materials for fuel cells [2], oxygen sensors [3] and buffer layers for coated superconductor architectures [4]. This last application requires the epitaxial crystallization of a multilayered structure of several oxides on metallic Ni-W tapes. Nanometric buffer layers of (Y)ZrO₂ and CeO₂ are usually grown between the upper YBa₂Cu₃O₇ superconductor layer and the substrate to promote epitaxy while avoiding interdiffusion [4].

Chemical solution deposition offers a low cost route for obtaining such multilayers with good chemical purity and thickness control [5, 6]. The precursors are decomposed by thermal treatment in inert atmosphere to avoid substrate oxidation [7]. However, this practice is detrimental for the CeO₂ quality because elimination of carbonaceous residues is achieved at the expense of partial reduction of Ce⁴⁺ to Ce³⁺ [8].

In this communication, we will present our recent results on the thermal decomposition of cerium(III) propionate in atmospheres with varying oxygen partial pressure. It is shown that the decomposition temperature is as low as 300°C in air and that crystallization and oxidation of Ce³⁺ to Ce⁴⁺ occurs before complete decomposition has been achieved so that nanocrystalline CeO₂ layers can be obtained at a temperature range where oxidation of the metallic substrate is negligible.

A range of thermoanalytical techniques has been applied to characterize the decomposition processes. In particular, mass spectroscopy of the volatile species has proven essential in elucidating the microscopic processes leading from propionate to ceria nanoparticles. The degree of crystallization of the intermediate and final products has been analyzed by x-ray diffraction (XRD) and transmission electron microscopy (TEM), whereas the cerium oxidation state has been quantified by x-ray photoelectron spectroscopy (XPS) and by magnetic susceptibility measurements (SQUID).

This work has been funded by the Spanish Plan Nacional de Materiales through projects MAT2009-08385 and MAT2008-01022.

References:

- [1] A. Trovarelli, Catal. Rev. Sci. Eng., **38** (1996) 439.
- [2] E. P. Murray, T. Tsai and S.A. Barnett, Nature, **400** (1999) 649.
- [3] N. Izu, W. Shin, N Murayama, Sens. Actuators B, **93** (2003) 449.
- [4] A. Goyal, M. Parans Paranthaman and U. Schoop, MRS Bull. **29** (2004) 552.
- [5] R. Schwartz, T. Scheneller and R. Waser, C.R.Chimie, **7** (2004) 433.
- [6] M. W. Rupich, D. T Verebelyi, W. Zhang, T. Kodenkandath and X. Li, MRS Bull. **29** (2004) 572.
- [7] M. Coll, J. Gazquez, F. Sandiumenge, T. Puig, X. Obradors, J. P Espinos and R. Hühne, Nanotechnology, **19** (2008) 395601.
- [8] S. Masson, P Holliman, M. Kalaji and P. Kluson, J. Mat. Chem. **19** (2009) 3517.

Figures:

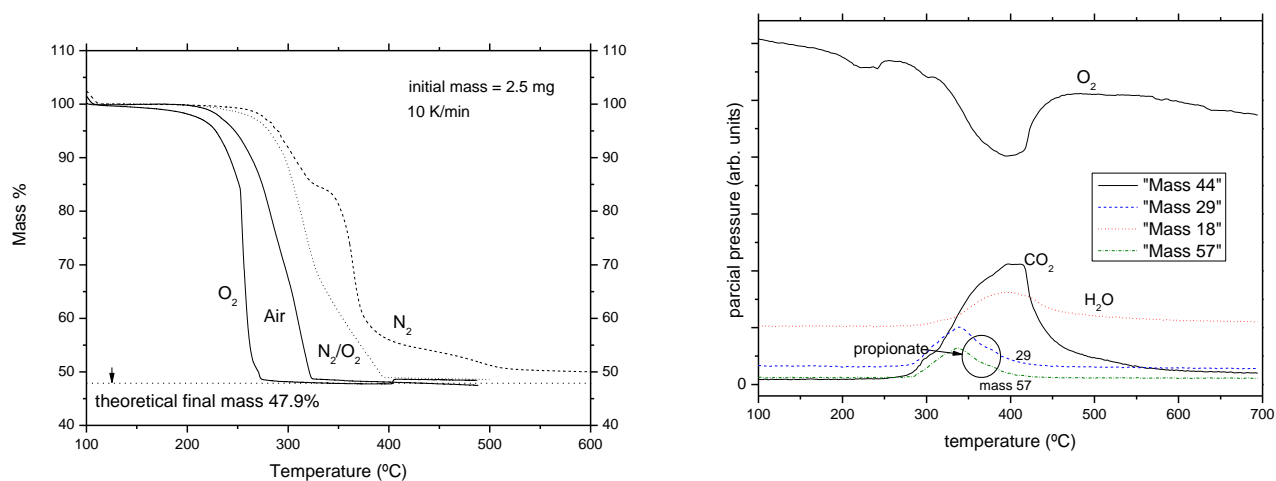


Figure 1.- a) Thermogravimetric curves showing the mass loss when cerium propionate is heated at constant rate in atmospheres with varying oxygen partial pressure; b) the mass spectroscopy curves of the main volatile species detected in air.

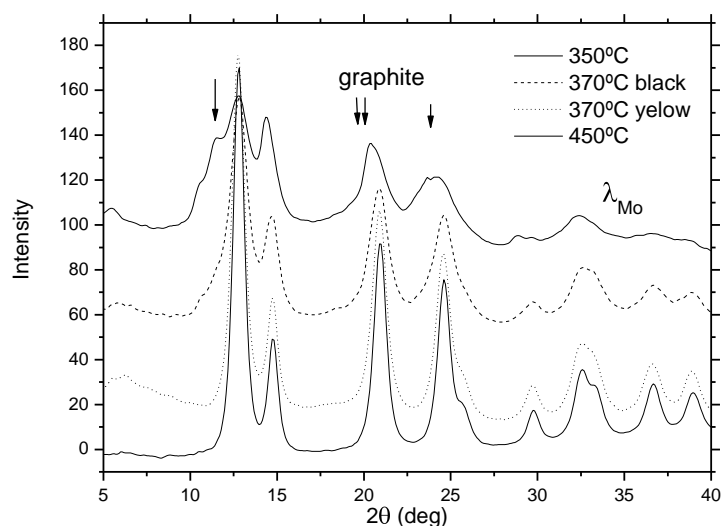


Figure 2.- X-ray diffraction curves obtained at different steps of the decomposition process. The peaks corresponding to CeO₂ are already present before decomposition has finished.