# SYNTHESIS OF FINE CERAMIC OXIDE PARTICLES BY THE SOL-GEL PROCESS IN SUPERCRITICAL $CO_2$

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## SUMMARY

An innovative method using supercritical $CO_2$ as synthesis medium is described for the formation of nanostructured oxygen ion-conducting ceramic materials. Three mixed oxide systems with a relatively high oxygen ion conductivity were selected to evaluate the potentialities of the method: doped $ZrO_2$, $CeO_2$ and $LaGaO_3$. The influence of operating parameters on the material characteristics is reported in this work. The particle size, morphology, homogeneity and crystalline structure revealed to be controlled by the $CO_2$ properties during the synthesis, but also by the type of co-solvent used to dissolve the precursors, their concentration and/or the synthesis duration in SC conditions.

*Keywords*: Supercritical $CO_2$; ion-conducting ceramics; Gd doped $CeO_2$; Y doped $ZrO_2$; $LaGaO_3$

## INTRODUCTION

The formation of nanophase ceramics by sintering of nanoparticulate powders is an attractive field of research and development dedicated to increasing control over material structures down to the nanometer scale. Anticipated applications range from conductive ceramics for fuel cells, gas probes, solar cells, electronic devices, and membrane reactors to structural ceramics [1-3]. The sol-gel process presents inherent advantages for the preparation of nanophase and/or nanoporous ceramic oxides, this because the nanostructure of the derived materials can be controlled together with their porous structure.

In other respects supercritical fluids (SCF) exhibit a large range of unusual properties that can be exploited for preparing new materials which are qualitatively different from those involving classical solid state chemistry or soft chemistry. Indeed, above its critical parameters, temperature and pressure, a SC fluid exists as a single phase, called SC phase. In those conditions, SC fluids offer a combination of gas-like (viscosity, diffusion coefficient) and liquid-like (density) properties and is suitable as an original solvent and/or drying media for ceramic forming. Moreover SC $CO_2$ ($T_c$=31°C, $P_c$=73.8 bar) has been suggested as a sustainable replacement for organic solvents, providing opportunities for "Green chemistry". These specific properties make SC $CO_2$ a suitable solvent for the sol-gel process provided the choice of well adapted precursors.

In this work, the sol-gel process has been investigated based on supercritical $CO_2$ (SC $CO_2$) to produce nanophase ceramic oxides. Processing ceramic precursors in SC-$CO_2$ media was already investigated in our group [4] as a suitable synthesis method yielding $SiO_2$ fibers, $TiO_2$ powders, as well as $TiO_2$ membranes [5]. In particular the size and morphology of $TiO_2$ nano-particles obtained by reacting an alkoxide precursor in SC-$CO_2$ media, was controlled by tuning the operating parameters such as pressure, temperature and residence time and the direct

formation of supported thin films revealed possible. Moreover, the anatase phase directly formed at 250°C in the autoclave during the synthesis experiment (alkoxide hydrolysis in SC CO$_2$), although it only forms at 350°C by classical heat-treatment of the hydroxide under atmospheric pressure. The driving idea of the present work was to transfer this promising method to the synthesis of oxygen ion-conducting ceramic materials with the following specific goals: i) obtain original and homogeneous nanophase microstructures, ii) reduce the crystallisation temperature, iii) eventually improve the conduction properties.

The influence of the operating parameters: pressure and temperature (both controlling the SC-CO$_2$ properties) but also the type of solvent used to dissolve the precursors, their concentration and/or the synthesis duration in SC conditions, on the characteristics of the synthesised materials (homogeneity, particle size, specific surface area, porous texture and crystalline structure) have been studied. On the basis of the results, different mechanisms involved in the formation of the studied oxides are proposed.

## I - MATERIALS AND METHODS

### I.1 Chemicals and experimental set-up

The metal-organic precursors used in this study are solids, except the cerium(III) 2-ethylhexanoate which is already dissolved in 2-ethylhexanoic acid (table 1). Contrary to the TiO$_2$ synthesis which started from a single liquid alkoxide precursor [5], we needed here to prepare an homogeneous solution of two metal-organic precursors in an adequate co-solvent (table 1). Typically 100 ml of co-solvent was used for preparing a solution yielding 1-2g of final oxide.

| Product | Supplier | Purity (%) | Function |
|---|---|---|---|
| La(CH$_3$OCHCH$_3$)$_3$ | GELEST | 95 | Precursor |
| La(CH$_3$COO)$_3$, x H$_2$O | STREM | 99.9 | Precursor |
| Ga(CH$_3$COCHCOCH$_3$)$_3$ | STREM | 99.99 | Precursor |
| Ce(CH$_3$COO)$_3$, x H$_2$O | ALDRICH | 99. 9 | Precursor |
| Ce(OOCCH(C$_2$H$_5$)C$_4$H$_9$)$_3$, 49% in 2-ethylhexanoic acid | STREM | 12% Ce | Precursor |
| Ce(OOCCH(C$_2$H$_5$)C$_4$H$_9$)$_3$ | ALDRICH | | Precursor |
| Gd(CH$_3$COO)$_3$, 4 H$_2$O | STREM | 99. 9 | Precursor |
| Zr(CH$_3$CO)$_x$(OH)$_y$, z H$_2$O (x+y = 4) | ALDRICH | | Precursor |
| Zr(CH$_3$CH$_2$CHO)$_4$, 70% in 2-propanol | ALDRICH | | Precursor |
| Y(CH$_3$COO)$_3$, x H$_2$O | ALDRICH | | Precursor |
| 2-propanol | PROLABO | 99 | Co-Solvent |
| 2-ethylhexanoic acid | ALDRICH | 99 | Co-Solvent |
| Water | Produced by a Milli-Q system | | Co-Solvent |
| Cyclohexane | ALDRICH | 99 | Co-Solvent |
| Pentane | ALDRICH | 99 | Co-Solvent |
| HNO$_3$ | FLUKA | 65 | Additive |

Table 1: List of chemicals used in this study

The experimental set-up used in this study is shown in Figure 1. The reaction was carried out in a high-pressure stirred vessel (reactor volume: 1L, max. temperature 600°C, max. pressure 400 bar, supplied by Autoclave-France). After introducing the solution of precursors in the reactor, liquid CO$_2$ (Carboxyque-France) was pumped into the vessel up to the operating pressure (30 MPa). The reaction temperature was regulated in the range 150-600°C using an external electric heater. When the operating conditions were reached, a significant residence

time of several minutes to few hours was achieved in the autoclave in order to allow the formation of powders.
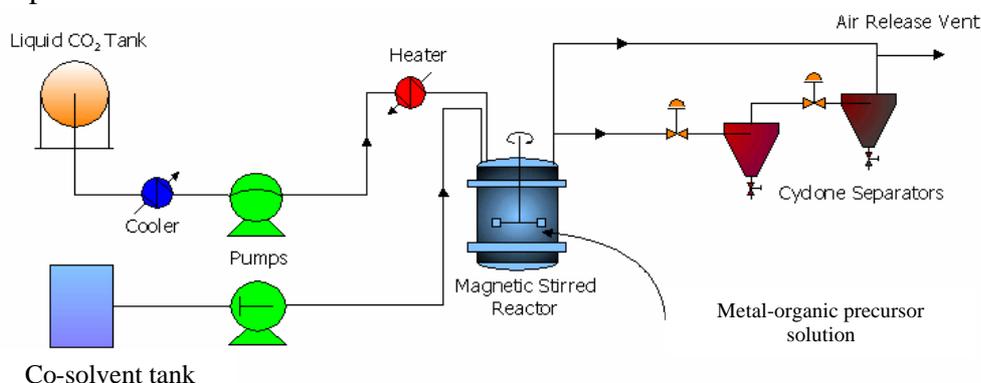


Figure 1: Scheme of the experimental device for inorganic synthesis in SC-CO$_2$

A different reactor was used in order to study the reaction mechanism. A sapphire window allowed to visualise the particle formation. The reaction temperature was regulated in the range 60-150°C using an external electrical heater. This system permits though an optical diagnostic to evaluate the time precipitation or reaction kinetics. When the particle formation occurred, a CO$_2$ washing was performed in order to remove the solvent initially used for preparing the solution of metal-organic precursors.

### I.2 Characterization methods

The morphology and homogeneity of the derived powders were studied using scanning electron microscopy (Hitachi S4500). Crystalline phases were determined by X-ray diffraction studies on powders (Brucker D800). Crystallite sizes of doped CeO$_2$ were evaluated by applying: i) the Scherrer method to the (202) XRD diffraction line width and ii) the method of Suzuki *et al.* [6] to the Raman absorption band at 463 cm$^{-1}$ (LRS Labram 1B spectrometer). Crystallite sizes of doped ZrO$_2$ were evaluated by applying the Scherrer method to the (101) XRD diffraction line width for the tetragonal phase and to the (-111) XRD diffraction line width for the monoclinic phase. The quantification of both m-ZrO$_2$ (X$_m$) and t-ZrO$_2$ modifications was calculated with the integrated intensities of the monoclinic peaks (-111$_m$ and 111$_m$) versus the tetragonal peak (101$_t$) using the relationship : $X_m = (I_{-111m} + I_{111m}) / (I_{-111m} + I_{111m} + I_{101t})$ [7]. The specific surface area of powders was determined by applying the BET equation to the N$_2$ adsorption isotherm (Micromeritics-Asap 2010).

## II – RESULTS AND DISCUSSION

### II.1 Synthesis and characterisation of LaGaO$_3$

The influence of synthesis parameters such as the nature of the precursor, the solvent and the operating temperature in the SC medium was investigated with relation to the material characteristics. Gallium acetylacetonate was the only gallium metal-organic precursor commercially available. Lanthanum isopropoxide was used first in order to mimic the sol-gel route previously used for preparing TiO$_2$ in SC-CO$_2$ and next lanthanum acetate due to its low cost compared to the isopropoxide. The results obtained for powder morphology and XRD patterns were very similar for both lanthanum isopropoxide and lanthanum acetate. Comparing two co-solvents, water and 2-propanol, only single oxides were detected in the XRD patterns for aqueous medium while the mixed oxide was detected in the alcoholic

medium. Finally the selected solution used for preparing the mixed oxide in SC-CO$_2$ was a stoichiometric mixture of lanthanum acetate and gallium acetylacetonate dissolved in 2-propanol with 5 wt % nitric acid. FESEM observations showed an agglomerated structure for the derived LaGaO$_3$ powders. Particle sizes were in the range 0.5-5 µm, although smaller sintered primary particles (10-20 nm) were evidenced at higher magnification.

The major crystalline phases (mixed or single oxides) detected from the XRD patterns were dependent on both the SC-CO$_2$ temperature and precursors concentration in the reactor. LaGaO$_3$-orthorhombic was detected as the major phase in powders prepared between 150°C and 600°C in SC-CO$_2$. For the deposited layers, the orthorhombic-LaGaO$_3$ phase was only detected beyond 200°C. The precursor concentration in the reactor has to be less than 60mM in order to obtain the LaGaO$_3$-orthorhombic phase. Above 60mM, the XRD pattern corresponds to a phase mixture which does not correspond to any oxide, single or mixed. In comparison with traditional solid-state synthesis from oxides, the crystallisation temperature of LaGaO$_3$ was decreased by more than 500°C in SC-CO$_2$, presumably due the solvo-thermal effect on the growing species during synthesis. The specific surface area of LaGaO$_3$ powders has been controlled by tuning the temperature: S$_{BET}$ increases from 2 to 40 m$^2$/g when the synthesis temperature decreases from 600°C to 150°C.

Further investigations are planed for preparing nanophase LaGaO$_3$ doped with Sr and Mg.

## II.2 Synthesis and characterisation of Gd doped CeO$_2$

The influence of the synthesis parameters previously studied for LaGaO$_3$ was also investigated in the case of Gd doped CeO$_2$. The selected metal-organic precursors were first cerium(III) 2-ethylhexanoate in 2-ethylhexanoic acid and gadolinium acetate. The derived solution (*solution I*) was a mixture of the two precursors dissolved in stoichiometric proportions (0.9Ce & 0.1Gd) in 2-ethylhexanoic acid. Starting from this solution, a paste was formed in the reactor at 250°C while a powder of Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ was directly collected at 450°C. In order to decrease both the synthesis temperature and the cost of precursors, other cerium precursor and co-solvents were used: cerium acetate and 2-propanol with 5 wt% of nitric acid (*solution II*).

Different morphologies were obtained under supercritical conditions depending on the precursors, temperature, pressure and solution concentration. When the solution takes up 10% of the reactor volume, spherical particles of Gd doped CeO$_2$ powders were obtained at 600°C from *solution I* and at 150°C from *solution II*. Particle diameters were in the range 0.5-3 µm, although smaller sintered primary particles were observed at higher magnifications, figure 2-a. When the solution takes up 80% of the total volume of the reactor, needles of Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ were obtained at 400°C from *solution II*.

The crystallisation temperature of the pure Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ cubic phase was found to depend on both the operating conditions (temperature, residence time) and the co-solvent used to dissolve the precursors. When using 2-ethylhexanoic acid as a co-solvent (*solution I*), the phase appears on the XRD patterns at 300°C for a residence time of 1 hour. Figure 2-b shows the XRD pattern of a powder prepared from *solution II* at 150°C in SC-CO$_2$ with a residence time of 10min. Comparing *solutions I* and *II*, the cubic Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ phase is immediately obtained and long residence time are needless in the case of *solution II*.

The Scherrer method applied to the (202) XRD line of Ce$_{1-x}$Gd$_x$O$_{2-x/2}$ derived from *solution II*, yields crystallite sizes in the range 35-50 nm. The crystallite sizes calculated by applying the relation of Suzuki *et al.* to the width of the Raman absorption lines are smaller and lie in the range 5-20 nm. The difference between the results of both methods has not been explained to date. A HRTEM analysis is under process.
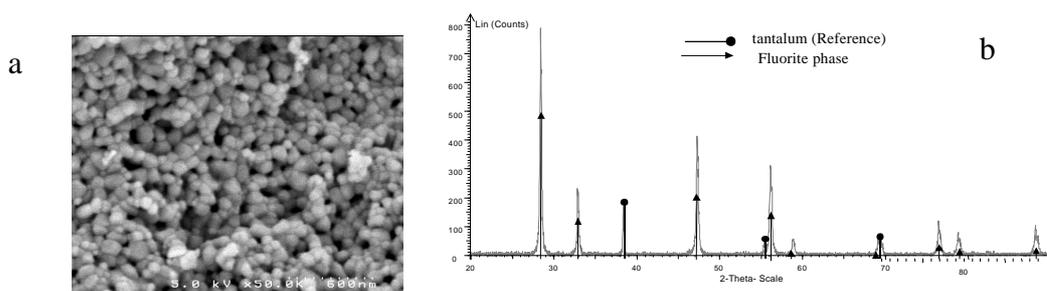
Figure 2: (a) FESEM micrographs and (b) XRD patterns of a $Ce_{1-x}Gd_xO_{2-x/2}$ powder obtained in SC-CO$_2$ (T= 150°C and P = 300 bar).

When the solution takes up 10% of the total reactor volume, the specific surface area measured for the $Ce_{1-x}Gd_xO_{2-x/2}$ powders derived from *solution II* can be varied from 10 to 60 m$^2$/g by decreasing the synthesis temperature from 600°C to 400°C. When the solution takes up more than 10% of the total reactor volume, the specific surface area and the crystallisation temperature of the $Ce_{1-x}Gd_xO_{2-x/2}$ powder increase.

## II.3 Synthesis and characterisation of Y doped ZrO$_2$

Yttrium partially stabilised zirconia was the third oxide investigated with reference to SC CO$_2$ oxide processing. Considering its phase diagram, the behaviour of zirconia is more complex than those of the other studied materials. Both doped (with low dopant concentration) and undoped materials undergo a martensitic-type phase transformation on heating and cooling: reversible transition from the high-temperature tetragonal phase (T) to the low-temperature monoclinic phase (M). The first investigated precursors were zirconium n-propoxide and yttrium acetate. In order to study the influence of the nature of the zirconium precursor, zirconium hydroxyacetate has been also considered.

The crystallisation temperature of the pure and stable $Zr_{1-x}Y_xO_{2-x/2}$ tetragonal phase was found to depend on both the operating conditions (temperature, residence time) and the solvent used to dissolve the precursors. Above 400°C, the stabilised tetragonal phase can be obtained from all the considered precursor and co-solvents (2-propanol, methanol, cyclohexane, pentane). In the temperature range 200°C-350°C, a mixture of tetragonal and monoclinic phases is obtained from zirconium hydroxyacetate in alkanes. In alcoholic medium, zirconium hydroxyacetate yields a crystalline powder above 300°C. With zirconium n-propoxide, the crystallisation temperature is above 350°C.

Whatever the precursors, the specific surface area of the zirconia powder is in the range 15-100 m$^2$/g when using alkane co-solvents and 100-300 m$^2$/g when using alcohols at 300-400°C. Further experiments are being processed in order to understand the mechanisms involved in the formation of either a pure tetragonal phase or phase mixture and also to determine the transition temperatures.

## II.4 Discussion

The above results demonstrate that the chemical composition, crystalline structure and specific surface area of powders are strongly related to the operating temperature in SC-CO$_2$, to the co-solvent used for the precursors and to the nature and concentration of the precursors.

Different types of reaction occur in SC-CO$_2$, which can explain the different crystalline structures (mixed or single oxides) obtained from the same precursor and different co-solvents. Starting with acetate precursors dissolved in aqueous medium, the mechanism is similar to precursor precipitation followed by a thermal decomposition: no reaction between the precursors occurs and only the single oxides are obtained. Starting from acetate

precursors, dissolved in 2-propanol and nitric acid, the mixed oxides are obtained. Lanthanum acetate and gallium acetylacetonate lead, in presence of nitric acid, to the rapid condensation of ionic species through olation (1) and oxolation (2) reactions.

$$M\text{-}OH + M\text{-}OH_2 \rightarrow M\text{-}OH\text{-}M + H_2O \qquad (1)$$
$$M\text{-}OH + M\text{-}OH \rightarrow M\text{-}O\text{-}M + H_2O \qquad (2)$$

On heating, the formation of an orange amorphous powder occurs above 85-90°C. Cerium acetate and gadolinium acetate lead, in presence of nitric acid, to the simultaneous condensation and coagulation of precursors which yields a yellow paste. The subsequent transformation of the amorphous powder or of the paste into crystalline oxide materials occurs during the thermal treatment.

Starting from zirconium alkoxide, the sol-to-gel transition in supercritical $CO_2$ is supposed to proceed as in organic solvents, through the following hydrolysis (3) and condensation (4,5) reactions:

$$M(OR)_n + H_2O \rightarrow M(OR)_{n-1}OH + ROH \qquad (3)$$
$$(OR)_{n-1}M\text{-}OR + HO\text{-}M(OR)_{n-1} \rightarrow (OR)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + ROH \qquad (4)$$
$$(OR)_{n-1}M\text{-}OH + HO\text{-}M(OR)_{n-1} \rightarrow (OR)_{n-1}M\text{-}O\text{-}M(OR)_{n-1} + H_2O \qquad (5)$$
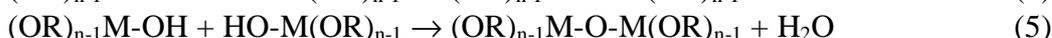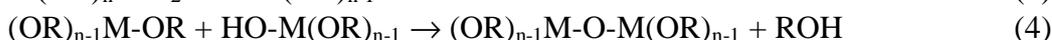
As for $TiO_2$ synthesis [5], the subsequent transformation of the $(OR)_{n-1}M\text{-}O\text{-}M(OR)_{n-1}$ clusters into crystalline oxide materials occurred during thermal treatment with incorporation of yttrium in the crystalline structure. Further experiments in SC $CO_2$ are in progress with the aim to explain the partially stabilised tetragonal phase formation obtained from yttrium acetate and zirconium n-propoxide precursors.

## CONCLUSION

Ceramic processing in SC-$CO_2$ is a very promising technique for creating nanocrystalline mixed oxide systems from metal alkoxides, acetates and acetylacetonate compounds at low temperature. The particle sizes, specific surface area, material homogeneity, porous texture and crystalline structure depend on the co-solvent and the nature of the precursors. All these characteristics can be controlled by tuning the operating parameters (temperature, residence time, precursor concentration). Different mechanisms related to soft chemistry processes can explain in situ reactions of the precursors (rapid condensation and co-precipitation, hydrolysis and condensation). Further work is now in progress related to the applications of these nanocrystalline oxygen ion conducting materials.

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