Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 2013–2016
www.elsevier.com/locate/jeurceramsoc

Hydrothermal synthesis of nanostructured inorganic powders by a continuous process under supercritical conditions

N. Millot *, B. Xin, C. Pighini, D. Aymes

LRRS, UMR 5613 CNRS/Université de Bourgogne, BP 47870, 21078 Dijon Cedex, France

Available online 12 April 2005

Abstract

In this study, using a prototype of hydrothermal synthesis in subcritical and supercritical water working in a continuous way, nanometric ceramic precursors with perfectly defined composition are produced: spinel ferrites such as Fe_2CoO_4, TiO_2 with anatase structure and also perovskite structures such as $BaZrO_3$. The as-prepared powders are fully characterized by complementary experiments: X-ray diffraction, electron microscopies, EDX spectrometry, surface area measurement, etc. Thus, particles size, morphology, aggregation state, crystal structure, composition are investigated. Moreover, magnetic properties of the ferrites products are studied. The powders obtained are pure phases very well crystallized in a nanometric range.

Keywords: Powders-chemical preparation; Grain size; Ferrites; Perovskites; TiO_2

1. Introduction

Nanostructured ceramic materials for electronic applications draw industry and scientist attention because of their physical properties depending on grain size.[1] Since surface energy allows stabilizing highly symmetrical phases apart from the usual limits, new materials can be obtained.[2] Then, synthesis methods of nanometric powders are very interesting. In preliminary works about ferrites obtained by both soft chemistry and mechanosynthesis, our research group present three original approaches: (i) control of grain size and morphologies of these nanograined powders is possible by adaptation of the synthesis route;[3] (ii) getting simultaneously homogeneity in both morphological and chemical properties is a challenge in nano-chemistry;[4] (iii) surface energy, which allows to stabilize highly symmetrical phases apart from the usual limits, leads to new materials.[2,5,6] Nevertheless, soft chemistry technologies do not allow having a huge production and cannot be developed at industrial level. Continuous synthesis technologies, allowing several tens grams per hour production, are then very interesting. In this perspective, a continuous production prototype of hydrothermal synthesis in subcritical and supercritical water has been developed.[7] Recent papers[8,9] summarize the specific features of supercritical fluid processes for material synthesis and processing. The mechanism of nanoparticle formation has been discussed with emphasis on the solubility of the metal oxide and kinetics of the hydrothermal synthesis, both of which significantly vary around the critical point due to the change of properties of water. Synthesized oxide powders in supercritical water have revealed three interesting qualities: they can have nanometric grain size with control particle morphology, they are very well crystallized and they have clean surface grains. Then, the two aims of this new study are both to illustrate these particularities and to show the versatility of supercritical media by producing three different oxides very interesting for their potential applications: Fe_2CoO_4 (spinel), $BaZrO_3$ (perovskite) and TiO_2 (anatase). These syntheses are original because of both the purity of the crystalline phase obtained and the very low size of the grains. Furthermore, the originality of the prototype device developed in this study is to allow huge production, thanks to a continuous process.

* Corresponding author. Tel.: +33 3 80 39 59 37; fax: +33 3 80 39 61 67.
E-mail address: nmillot@u-bourgogne.fr (N. Millot).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.202

Table 1
Synthesis conditions of TiO_2, $BaZrO_3$ and Fe_2CoO_4

	Precursors	P (bar)	T (°C)
TiO_2	Bis(ammonium lactato)titanium dihydroxide (ALT: Aldrich): 50% in mass in water	300	300
Fe_2CoO_4	$Co(NO_3)_2$ (0.025 mol/L) $Fe(NO_3)_3$ (0.05 mol/L) NaOH (0.25 mol/L)	300	440
$BaZrO_3$	$ZrO(NO_3)_2{\cdot}6H_2O$ 0.075 mol/L $Ba(NO_3)_2$ 0.3 mol/L NaOH 2 mol/L	350	500

2. Experimental procedure

The synthesis conditions are described in Table 1 and the experimental apparatus used for these hydrothermal synthesis (in sub or supercritical conditions) is described in others publications.[7,9,10] The metal salt aqueous solution is prepared and fed into the apparatus in one stream. In another stream, distilled water is pressurized and then heated to a temperature that is above the temperature desired. The pressurized metal salt solution stream and the pure supercritical water stream (eventually a basic solution is fed in a third way) are combined in a mixing point just before the reactor, which leads to rapid heating and subsequent reaction in the reactor. The pump flows are given here only for the $BaZrO_3$ synthesis: cationic solutions 8.1 mL/min; water 29.5 mL/min; basic solution 12.4 mL/min. The residence time of the solution in the reactor is of 10 s in most of the experiments (the reactor is an Inconel serpentine with a length of 2 m and a diameter of 2.3 mm). After the reactor, the solution is rapidly quenched and filters remove agglomerated particles. Then, the suspension obtained is centrifuged and washed with deionized water under ultrasonication for 5 min. After about 10 washings, the centrifugation is not possible, a sol is formed which is freeze-dried.

Surface area measurements are performed using AUTOSORB apparatus with N_2 adsorbing gas. Samples (150–200 mg of powder) are outgassed at 493 K. The BET method is used in calculation of surface area values from the isotherm of nitrogen adsorption.

Powders are all characterized by X-ray diffraction (XRD) using a Siemens D5000 automatic powder diffractometer, operating at 35 mA and 50 kV. The radiation used is precised Fig. 1. Correction for instrumental broadening is determined from a standard reference material, annealed BaF_2. Pseudo-Voigt peak profile analysis, using the Langford method,[11] is performed to determine both the average crystallite size (size of a region over which the diffraction is coherent) and crystallographic imperfections (microdistorsions, stacking faults, etc.). The lattice parameters of the powders are deduced from XRD line positions using a least-squares refinement method. [1]

Powders are all characterized by scanning electron micrographs (SEM)(JEOL JSM-6400F) coupled with a LINK OXFORD Energy Dispersive X-ray analyzer, which allows the determination of the chemical composition of the samples. They were also analyzed with a 2010 FEG-TEM operating at 200 kV for high-resolution imaging with a practical resolution of 0.19 nm. Powders are dispersed on copper grid with a carbon membrane.

The hysteresis loops of samples are measured with a M2100 50 Hz magnetometer.

3. Results and discussion

Bis(ammonium lactato)titanium dihydroxide (ALT) is hydrolysed at a temperature of 300 °C under 300 bar (Table 1). As seen in Fig. 1(a), pure anatase form is obtained. All the reflections of the TiO_2 pattern are difficult to label because some of them are mixed due to their very large widths. This width is significant of a very small crystallites size, which is also proved by high specific surface (255 m^2/g, Table 2). The Langford method leads to a crystallite size of about 3 nm. The narrow size distribution of the grains is attested by TEM micrographs and low frequency Raman scattering measurements of the nanoparticles vibration eigenmodes (study in progress). The advantages of this new synthesis is to allow huge production (several tens grams per hour) contrary to a precedent study where the hydrolysis of the ALT precursor has been realized in sealed glass ampoules.[12] Moreover, the powders obtained in our study have smaller size: 3 nm at 300 °C contrary to the 16 nm obtained by Möckel et al. at the same temperature.[12]

Fe_2CoO_4 powder is very well dispersed and homogeneous with a grain size of about 3 nm deduced from XRD results. This value matches quite well the average particle diameter deduced from specific area measurements ($S_{BET} = 236\ m^2\ g^{-1}$ which yields a diameter of 4.8 nm). The grain size distribution is quite narrow, even after a thermal annealing of 4 h at 600 °C (Fig. 2(a)). This treatment leads to a grain size increase: $\Phi_{XRD} = 34$ nm. Powders are very well crystallized as shown by the TEM micrograph of the Fig. 2(b). The lattice parameters of the Fe_2CoO_4 spinel phase treated 4 h at 600 °C is $a_{exp} = 8.3839 \pm 0.0001$ Å. This is to be compared with the value reported in literature $a_{lit} = 8.35 \pm 0.01$ Å for a powder obtained by soft chemistry and heated at 500 °C.[13] The calculated value $a_{cal} = 8.3878$ Å

[1] In-house software taking into account the effect of sample gap.