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

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## 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.

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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)<br>$Fe(NO_3)_3$ (0.05 mol/L)<br>NaOH (0.25 mol/L) | 300 | 440 |
| $BaZrO_3$ | $ZrO(NO_3)_2 \cdot 6H_2O$ 0.075 mol/L<br>$Ba(NO_3)_2$ 0.3 mol/L<br>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

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

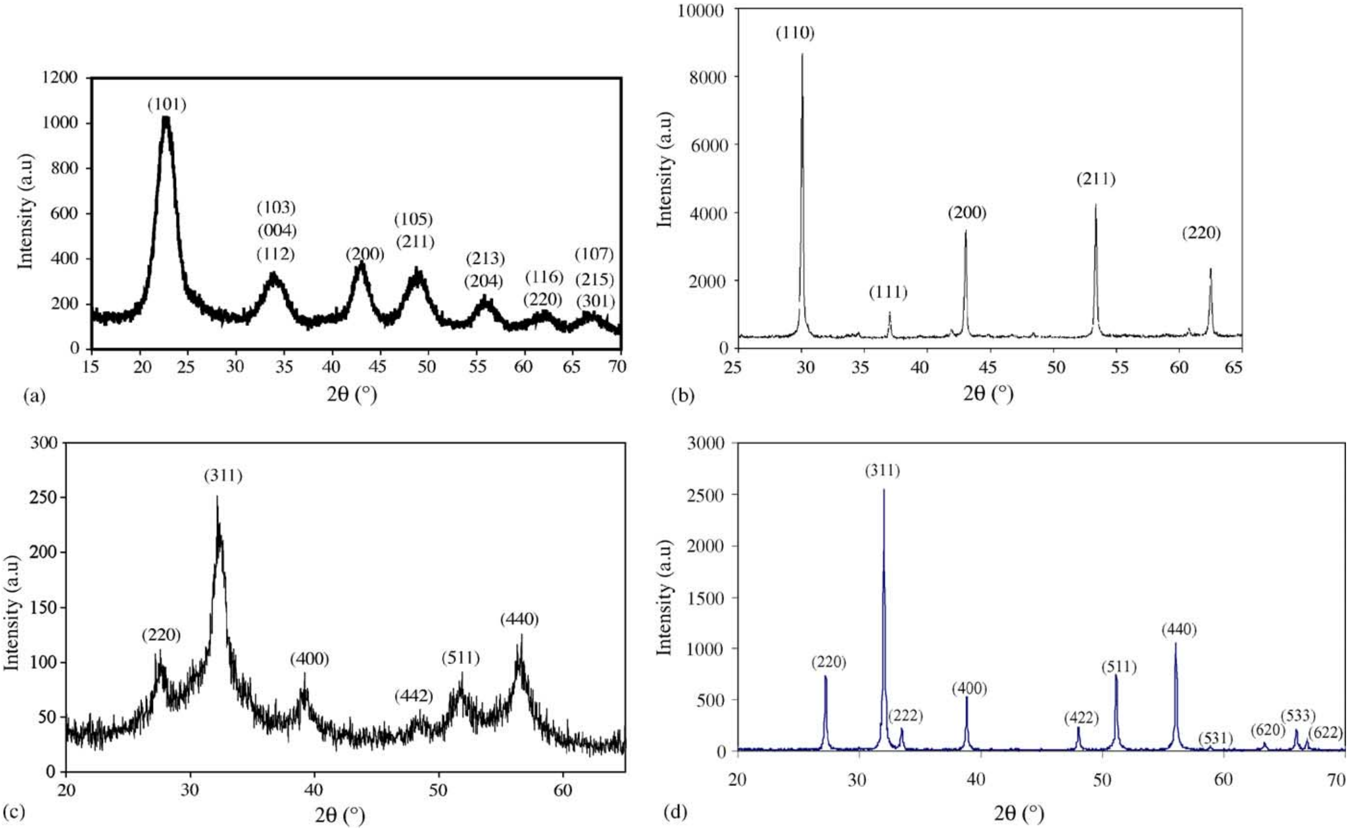

Fig. 1. X-ray diffractograms of (a) $TiO_2$; (b) $BaZrO_3$; (c) $Fe_2CoO_4$ powders obtained just after the freeze-dried process; (d) $Fe_2CoO_4$ obtained after a thermal annealing of 4 h at 600 °C under air atmosphere. (a), (c) and (d) XRD patterns are obtained with Cu Kβ radiation and (b) is obtained with Co $K\alpha_1$ radiation. The ICDD cards used to label the XRD patterns are the followings: (a) 21-1272; (b) 6-399; (c) and (d) 3-864. In the (b) XRD pattern, reflections not labeled are those of $BaCO_3$ (45-1471 ICDD card). This parasite phase appears when the suspension is in contact with air and can be eliminated after an appropriate washing with diluted acetic acid. In the (a) XRD pattern, the asymmetry of the (1 0 1) reflection of the anatase structure is due to the presence of the (1 1 0) reflection of the rutile structure (the more intense reflection of this phase).

by the Poix method is in relatively good agreement with the experimental one (the cation-oxygen distances used for the calculation of the lattice parameter are given in the reference).[14] The difference could be explained by a possible oxidation of the cobalt cation in $Co^{3+}$ (2.4% in order to obtain the experimental value). It cannot be explained by a redistribution of the cobalt cation in tetrahedral coordination, phenomenon which increases the lattice parameter (8.4099 Å if all the $Co^{2+}$ are in tetrahedral coordination). The coercive field of the freeze-dried powder is about 3730 Oe at 77 K (the powder has a superparamagnetic behavior at ambient temperature). The coercive field of the powder obtained after the thermal annealing is higher: 7350 Oe at 77 K (1180 Oe at ambient temperature). These higher values are due to the bigger particle size of the annealed powder. This powder could be a good candidate for magnetic recording.

For the first time a $BaZrO_3$ nanometric powder is obtained by a hydrothermal synthesis. Indeed, in a recent study, Kolenko et al. have obtained nanocrystalline $ZrO_2$ (8–12 nm), amorphous $ZrO(OH)_2$ or microcrystalline $BaZrO_3$ (2–5 μm) powders, depending of the synthesis conditions.[15] Powder

Table 2
Specific area measurements and X-ray diffraction analysis of $TiO_2$, $BaZrO_3$ and $Fe_2CoO_4$ powders

| | $S_{BET}$ ($m^2/g$) | Phase | EDXS | $a$ (Å) | $\phi_{XRD}$ (nm) | Hc (Oe) at 77 K |
|---|---|---|---|---|---|---|
| $TiO_2$ | 255 ± 2 | Anatase | – | – | 3 ± 1 | – |
| $Fe_2CoO_4$ | 236 ± 2 | Spinel | Fe/Co = 2.04 | – | 3 ± 1 | 3730 |
| $Fe_2CoO_4$ treated 4 h at 600 °C | 15.4 ± 0.1 | Spinel | Fe/Co = 2.03 | 8.3839 ± 0.0001 | 34 ± 1 | 7350 |
| $BaZrO_3$ | 9.75 ± 0.1 | Perovskite | Ba/Zr = 0.98 | 4.198 ± 0.001 | 74 ± 1 | – |

The XRD line profile analysis is performed according to Halder and Wagner method. Due to very large diffraction peaks, the lattice parameter cannot be determined for both $TiO_2$ and $Fe_2CoO_4$ powders obtained just after the thermohydrolysis. The EDXS ratio is determined by doing the average of about 10 measurements.

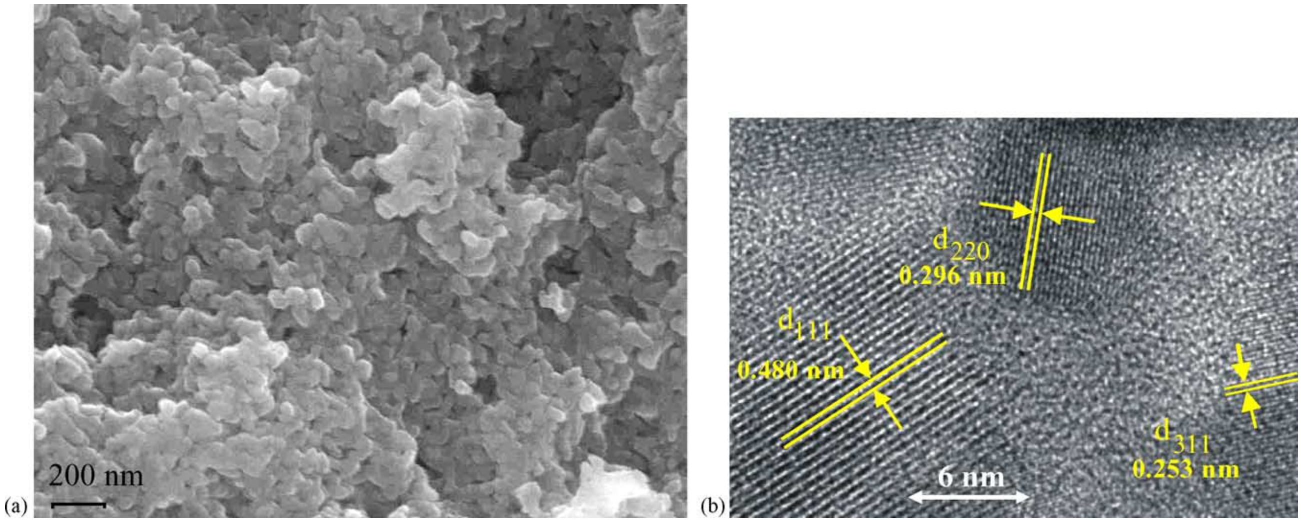

Fig. 2. (a) SEM micrograph of $Fe_2CoO_4$ obtained by thermohydrolysis in supercritical conditions and treated 4 h at 600 °C; (b) HRTEM micrograph of the same powder. Three nanocrystals with different orientations are visible in (b): $d_{311} = 0.253$ nm, $d_{220} = 0.296$ nm and $d_{111} = 0.480$ nm.

is very well dispersed with a grain size of about 74 nm deduced from XRD results. The lattice parameters of this perovskite phase is $a_{\text{exp}} = 4.198 \pm 0.001$ Å. This is to be compared with the value reported in the 6-399 ICDD card $a_{\text{ICDD}} = 4.193$ Å. In the XRD pattern of the Fig. 1(b), the reflections not labeled are those of $BaCO_3$. This parasite phase appears when the suspension is in contact with air and can be eliminated after an appropriate washing with diluted acetic acid. The $BaZrO_3$ nanometric powder obtained in this study may reveal a smaller sintering temperature than micrometric grains and could be interesting in aero-space and related industries or to made crucibles for growing high-quality high temperature superconductors single crystals (study in progress).[16]

## 4. Conclusion

Nanocrystalline $Fe_2CoO_4$ is synthesized in the spinel structure with very small grain size (about 3 nm). After an annealing at 600 °C, the grain size is always in a nanometric range (34 nm) and the cationic distribution is determined precisely thanks to the Poix method. The coercive field of this latest powder is very high (7350 Oe at 77 K). $TiO_2$ pure anatase is also obtained with a narrow size distribution of about 3 nm. Nanometric $BaZrO_3$ perovskite composition is prepared. Our technology has the main advantages to be easy to use compared to closed reactors and to have a high productivity. It opens news insights into the decrease of the sintering temperature of such interesting ceramic product.

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