CONTROLLED SYNTHESIS OF ALUMINA NANOPOWDERS USING SUPERCRITICAL FLUIDS FOR CERAMICS APPLICATIONS

C. Bousquet, F. Cansell, C. Elissalde, M. Maglione, C. Aymonier*

Institut de Chimie de la Matière Condensée de Bordeaux ICMCB-CNRS and ENSCPB, Université Bordeaux I, 87, Av. Dr A.Schweitzer, 33608 PESSAC Cedex (France).

Corresponding author: aymonier@icmcb-bordeaux.cnrs.fr, fax: 0033540002761

ABSTRACT

Alumina is the most widely used oxide ceramic material. It exists in many metastable forms which lead upon severe thermal treatment towards the thermodynamically stable phase alpha. Sintering of alumina generally takes part in a minimum of two stages: i) phase transition(s) towards the stable phase alpha and ii) densification of this phase alpha. The former step(s), linked to transition phase(s) is (are) strongly dependent on the crystallinity of the initial powders. Using this parameter, it is therefore possible to optimise the sintering properties, in particular to lower the transition temperature.
Such effect has been studied for aluminas elaborated in sub- and supercritical fluid media. This work highlights the possibilities to obtain, according to the nature of the fluid, different kind of transition aluminas: boehmite AlO(OH) or amorphous Al_2O_3. Sintering these powders led both to alpha-alumina but with different microstructures and densities. We could also observe a significant shift towards lower temperature for the gamma-Al_2O_3→alpha-Al_2O_3 transition in the case of amorphous alumina compare to the boehmite one.
The transfer to this know-how to the design of core-shell nanoparticles with alumina as a shell is investigated to develop nanostructured ceramics for telecommunications.

1 INTRODUCTION

Alumina is one of the most widely used oxide ceramic material. It exists in many metastable forms (γ, δ, θ, κ, ε, η, χ) which lead upon thermal treatment to the thermodynamically stable phase α-Al_2O_3.[1] This last phase is used in a wide range of ceramic and refractory applications.[2] A key interest for cost reduction is to soften sintering conditions necessary to obtain interesting alumina-based ceramics. It is interesting to underline that γ-Al_2O_3 has significant applications as catalyst support.[3] For all of these applications, the challenge remains a controlled synthesis of the alumina nanopowders as in most of the research works in Nanoscience and Nanotechnology.

Different chemical and physical methods have been studied to produce alumina nanopowders (solid state, sol-gel, co-precipitation, CVD …) with the associated powder characteristics.
As an alternative synthesis method, supercritical fluids offer a versatile route for controlling the nanopowder properties. The synthesis of alumina described in literature was mainly performed in supercritical water.[4] For instance, boehmite was obtained with different particle size and shape.[5] Other studies have concerned the direct synthesis of α-Al_2O_3.[6]
These different works were mainly focused on the study of the influence of the process operating parameters on alumina nanoparticle size and morphology. Very few works were dedicated to the sintering of these nanopowders to go towards the ceramics. In this way, the challenge for a better control of the ceramic

micro/nano-structure and cost reduction is to soften sintering conditions necessary to obtain interesting alumina-based ceramics.
In this context, we have worked on the control of the alumina powder characteristics playing with the chemistry in supercritical fluids to develop alumina-based ceramics.[7] Controlling this step, we have designed core-shell nanoparticles with an alumina shell for its dielectric properties to develop nanostructured ceramics for telecommunications.[8]

If we have a look at the literature, an improvement of α-Al_2O_3 densification is expected by lowering temperature transitions. Many strategies have thus been tested with a key result: the importance of starting powders crystallinity on the sintering process.[9,10,11] After the presentation of the synthesis of different kinds of alumina, the sintering of these nanopowders will be discussed. The transfer to the design of core-shell nanoparticles with alumina as a shell will be described.

2 EXPERIMENTAL SECTION

2.1 Thermodynamical properties of H_2O/EtOH and CO_2/EtOH mixtures

As discussed previously, most of the works were performed in sub- and supercritical water. Recently, we have attached a specific interest to the use of H_2O/EtOH as reaction media to lower the critical temperature (in respect with water) and to promote a new kind of reactivity for the synthesis of materials.[12-14] We are also interested for many years now to the study of the reactivity in CO_2/EtOH mixture. This know how has driven these research works towards the study of the influence of the reaction media, among H_2O/EtOH and CO_2/EtOH mixture, the precursor nature, among Al(acetylacetonate)$_3$ [Al(acac)$_3$] and $Al(NO_3)_3$,$9H_2O$ [$Al(NO_3)_3$], and the temperature.
Figure 1 represents the evolution of the critical coordinates of the mixtures H_2O/EtOH and CO_2/EtOH as a function of the mixture composition.

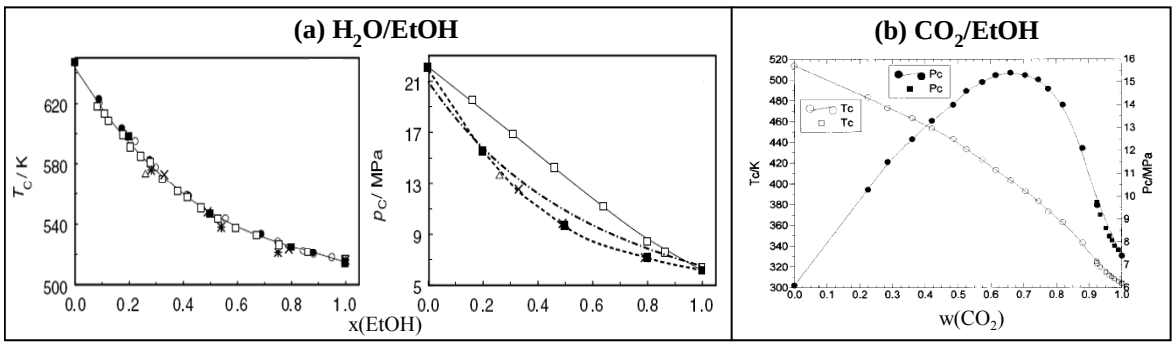

Figure 1. Critical temperature T_c and pressure p_c of the binary mixtures (a) H_2O/EtOH as a function of the ethanol molar fraction[15] (b) CO_2/EtOH as a function of the CO_2 weight fraction[16]

2.2 Alumina powder preparation

Two different reaction media were used to prepare alumina powder:

- carbon dioxide/ethanol-80/20 in mass: this ratio offers a good compromise between relatively low critical coordinates (14,5 MPa, 92°C) and good solvent properties,
- water/ethanol -50/50 in mass: this ratio was optimized in previous studies[12-14] for the synthesis of $Ba_xSr_{1-x}TiO_3$ ($0 \leq x \leq 1$). It had a significant influence on the cristallinity rate of the powder. The critical coordinates of this mixture is 11 MPa and 315°C.

In both case, the metal precursor used to produce the alumina (Al(acac)$_3$, $Al(NO_3)_3$) is solubilized in ethanol. This mixture is filled in the reactor with carbon dioxide for the first mixture and with water for the second one. The reactor is a high pressure and high temperature stirred vessel reactor (volume of 60 cm^3). For both mixtures, the operating conditions are presented in Table 1.

Reaction time in the reactor is one hour. At the end of the experiment, the organic residue resulted from aluminium precursor decomposition is removed. In water/ethanol, the reactor is opened after cooling. The powder as-synthesised is collected in the solvents mixture, filtered and washed. In carbon dioxide/ethanol, pure supercritical CO_2 flows though the reactor to remove ethanol and the organic residues. The powder is then collected in the vessel.

Table 1. Operating conditions for the synthesis of alumina in H_2O/EtOH and CO_2/EtOH mixture

Sample	Precursor		Complex Fluid		Conditions	
	Nature	n (mol)	Solvents-w_{EtOH}	Density ($kg.m^{-3}$)	p (MPa)	T (°C)
A1	$Al(acac)_3$	$4,6.10^{-3}$	CO_2/EtOH-0,2	<500	20	250
A2		$9,2.10^{-3}$	CO_2/EtOH-0,2		20	250
A3		$4,6.10^{-3}$	H_2O/EtOH-0,5	~650	10	250
A4		$9,2.10^{-3}$	Eau-0	~930-940	20-24	235
A5	$Al(NO_3)_3$, $9H_2O$	8.10^{-3}	H_2O/EtOH-0,5	~650-700	16-21	260
A6			CO_2/EtOH-0,2	<500	20-24	250

2.3 Characterization methods

Transmission electron microscopy (TEM) was investigated using a Philips Tecnai (100keV) equipped with a camera Megaview II. The specimen for the TEM imaging was prepared by depositing a few drops of a dilute nanoparticles suspension in ethanol onto a carbon-coated copper grid, followed by drying under ambient conditions.

Phase analysis was conducted using a diffractometer panalytical X'Pert MPD with geometry Bragg Brentano and CuK_α radiation (λ=1.5418Å).

Microstructure of ceramics was studied using a scanning electron microscope (SEM) JEOL JSM 6360A. A thin platinum coating was deposited on the fracture surface prior to observation.

3 RESULTS AND DISCUSSION

3.1 Synthesis of alumina nanopowder

Powder structures of obtained alumina have been compared for the different experiments. Figure 2 shows XRD patterns of these different powders.

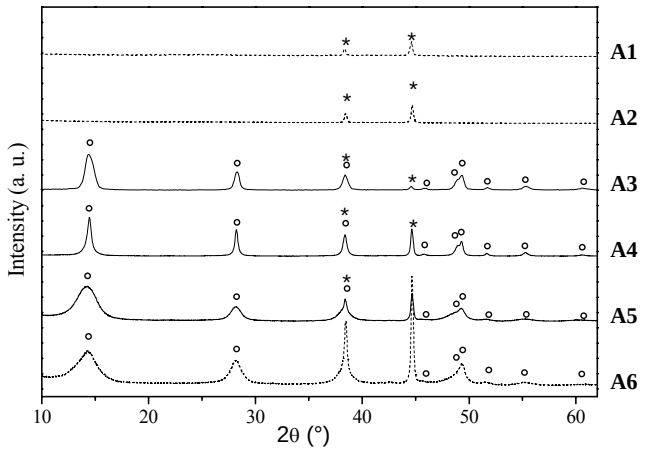

Figure 2. XRD patterns of the different alumina powder synthesized in CO_2/EtOH (dotted line) and in H_2O/EtOH (continuous line). *Al (Support), o Boehmite AlO(OH),

Regarding XRD patterns, three kinds of alumina powder are obtained:

- an amorphous powder for tests 1 and 2, resulting from the thermal decomposition of $Al(acac)_3$ in the supercritical CO_2/EtOH mixture,
- a crystalline powder of boehmite for tests 3 to 6, resulting from the transformation of $Al(acac)_3$, and $Al(NO_3)_3$ in the H_2O/EtOH mixture and from the transformation of $Al(NO_3)_3$ in the CO_2/EtOH mixture due to the presence of water molecules in the precursor,

The nature of the reaction media has thus a significant influence on the structure of alumina powders with the possibility to tune it from an amorphous powder to boehmite.

Figure 3 shows TEM micrographs of representative powders of an amorphous one (Figure 3a - A 1) and a boehmite one (Figure 3b - A 3).

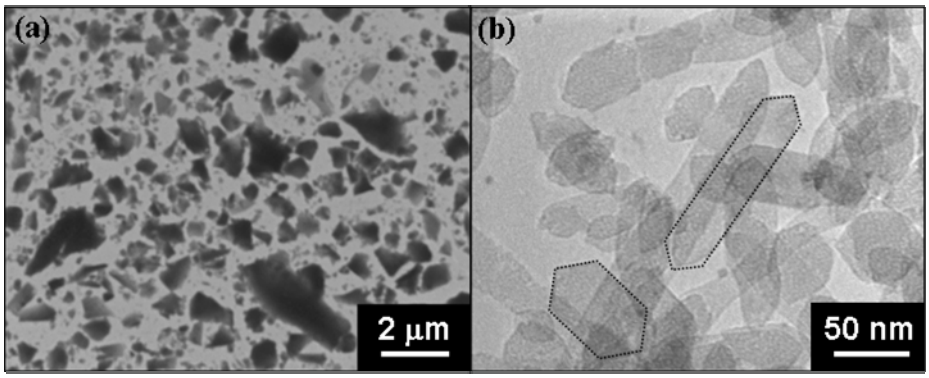

Figure 3. TEM micrographs of an amorphous alumina powder A1 (a) and of boehmite A3 (b)

The amorphous powder is constituted of micronic grains with a large size distribution. The size and morphology of boehmite nanoparticles is completely different. TEM picture of Figure 3b shows a mixture of two kinds of morphologies: plates and needles. The characteristics of the boehmite nanoparticles are intimely linked to the operating condtions, especially the ratio water/ precursor.

The synthesis of alumina powder in H_2O/EtOH or CO_2/EtOH mixture conducts to different powder properties in term of structure and cristallinity but also in term of size and morphology. This result has motivated a study on the influence of the starting alumina powder on sintering.

3.2 Effect of alumina cristallinity on sintering

Powders from tests 1 and 3 were retained to perform this study. The two powders were then sintered in order to obtain α-alumina ceramics. Figure 4 shows the final microstructures of the ceramics obtained after a thermal treatment at 1200°C during 4 hours. Boehmite, synthesized in water/ethanol, leads to a porous ceramic with a vermicular microstructure composed of submicrometers grains. In contrary, amorphous powders synthesized in carbon dioxide/ethanol medium gives dense ceramics made of large grains.

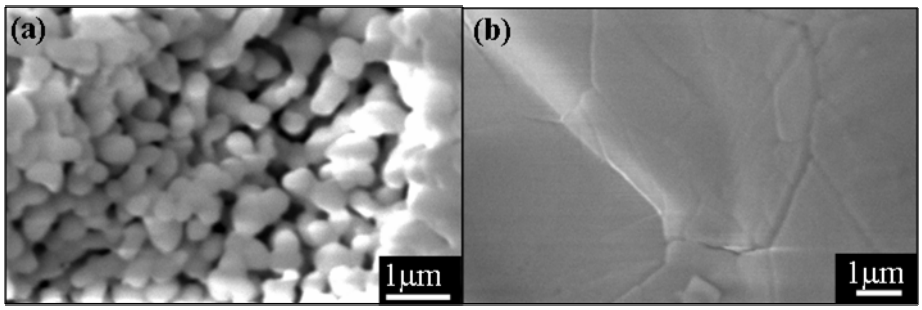

Figure 4. SEM micrographs of the final ceramics for both starting alumina powders (a) A1 et (b) A3 sintered at 1200°C during 4h.

The thermal behaviour of the two powders differed greatly depending on their crystalline state. The γ→α phase transition of the powder synthesized in water/ethanol actually started at 1150°C, whereas the transition of the powder obtained from CO_2/ethanol began at 1000°C. Therefore, a scheme illustrating the sintering path relative to each powder is proposed in Figure 5.[7]

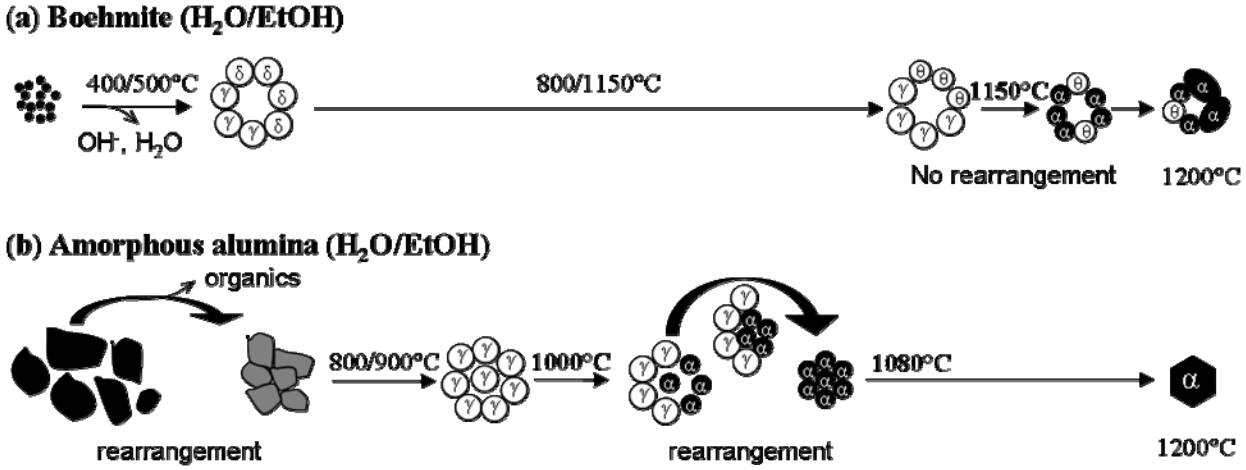

Figure 5. Proposed sintering paths for (a) boehmite obtained in water/ethanol and (b) amorphous alumina synthesised in CO_2/ethanol (from ref 7)

As explained in Figure 5, the mechanisms involved during sintering differ depending on the crystallinity of the starting powder. The amorphous character of the powder elaborated in CO_2/ethanol allows diminishing the temperature of the transition γ -Al_2O_3 → α-Al_2O_3 of 125°C (1125°C down to 1000°C). It leads to ceramic denser than ceramic resulting from boehmite powder crystallization.

3.3 Application to the design of alumina shell on nanoparticles for the development of nanostructured ceramics

Thanks to the above results, we have worked on the coating of barium strontium titanium ($Ba_xSr_{1-x}TiO_3$, $0 \leq x \leq 1$) nanoparticles with a shell of alumina (amorphous and boehmite) with the SuperCritical Fluid Deposition process (SCFD) to produce new ferroelectric composite ceramics with controlled physical properties.[8] The alumina shell is used to avoid the growth of the ferroelectric nanoparticles (physical size dependent properties) during sintering and to decrease the dielectric losses of ceramics.

In a typical experiment, the nanoparticles to be coated and the aluminium precursor are dispersed in ethanol with an ultrasonic horn and the solution is quickly added into the high pressure, high temperature stirred vessel reactor. Depending on the used reaction media, water is added to the reactor or the reactor is closed and filled with carbon dioxide and reaches the operating conditions: 20 MPa, 200°C.

Figure 6 shows a TEM micrograph of a core-shell nanoparticle obtained in CO_2/EtOH.

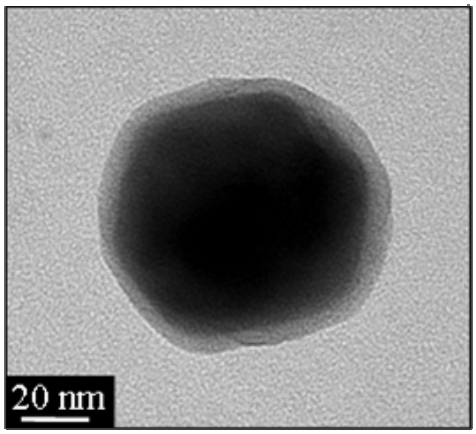

Figure 6. TEM micrographs of a $BaTiO_3$ nanoparticle coated with an amorphous shell of alumina

The chemistry developed on alumina can thus be applied to the design of more complex architectures as these core-shell structures. Effectively, working in a supercritical CO_2/EtOH mixture conducts to the formation of an amorphous shell of alumina and working in a H_2O/EtOH mixture allows to nanostructure the surface of $BaTiO_3$ nanoparticles with boehmite.
The sintering of these functional nanopowders conducts to the formation of nanostructured ferroelectric ceramics with interesting properties, a good permittivity with dielectric losses below 1%.

4 CONCLUSIONS

This work highlights the possibility to obtain, according to the nature of the fluid, CO_2/EtOH or H_2O/EtOH mixture, different kind of transition aluminas: boehmite AlO(OH) or amorphous Al_2O_3. The morphology of boehmite nanoparticles can also be controlled playing with the ratio H_2O/EtOH (linked to the ratio H_2O/precursor) from nanoparticles to needles via plates.
Sintering these powders led both to alpha-alumina but with different microstructures and densities. We could also observe a significant shift towards lower temperature for the gamma-Al_2O_3→alpha-Al_2O_3 transition in the case of amorphous alumina compare to the boehmite one.
This chemistry was applied for the design of more complex architectures, as in this study core-shell structures, with a possibility to tune the surface nanostructuration with amorphous alumina or boehmite. We have shown that this approach was very efficient to develop nanostructured ceramics with specific physical properties.

Acknowledgements

Financial support from the French National Center for Scientific Research (CNRS), the European Community in the frame of the “FAME” network of excellence, the French National Agency of Research (ANR) and the “Region Aquitaine” are gratefully acknowledged.

ICMCB is a member of the PILA network for high research and technological resources in multidisciplinary actions.

REFERENCES

[1] Levin, D. Brandon, “Metastable alumina polymorphs: crystal structures and transition sequences”, J. Am. Ceram. Soc., 81, pp. 1995-2012, 1998.
[2] Hidalgo H., “Dépôt chimique en phase vapeur de couches minces d'alumine dans une post-décharge micro-onde”, PhD manuscript, 2003.

[3] Guevara-Lara, A., Bacaud R., Vrinat, M., Highly active NiMo/TiO_2-Al_2O_3 catalysts: influence of the preparation and the activation conditions on the catalytic activity, Appl. Cat. A: General, 328, 99-108, 2007.
[4] Aymonier, C., Loppinet-Serani, A., Reverón, H., Garrabos, Y., Cansell, F., Review of Supercritical Fluids in Inorganic Materials Science, J. Supercrit. Fluids, 38, 242-251, 2006.
[5] Y. Hakuta, H. Ura, H. Hayashi, K. Arai, Effects of hydrothermal synthetic conditions on the particle size of γ-AlO(OH) in sub and supercritical water using a flow reaction system, Mater. Chem. Phys., 93, pp. 466-472, 2005,
T. Mousavand, S. Ohara, M. Umetsu, J. Zhang, S. Takami, T. Naka, T. Adshiri, Hydrothermal synthesis and in situ surface modification of boehmite nanoparticles in supercritical water, J. Supercrit. Fluids, 40, pp. 397-401 2007
[6] G.P. Panasyuk, M.N. Danchevskaya, V.N. Belan, I.L. Voroshilov, D.Y. Ivakin, "Phenomenology of corundum crystal formation in supercritical water fluid", J. Phys. Cond. Matter, 16, S1187-S1196, 2004.
[7] Bousquet, C., Elissalde, C., Aymonier, C., Maglione, M., Cansell, F., Heintz, J.M., Tunability of Al_2O_3 crystallinity using supercritical fluid media: effect on sintering, J. Eur. Ceram. Soc., 28, 223-228, 2008.
[8] Bousquet, C., Cansell, F., Elissalde, C., Maglione, M., Aymonier, C., manuscript in preparation.
[9] C. Legros, F. Herbst, S. Lartigue-Korinek, C. Carry, P. Bowen, "Sintering of nanostructured alumina: influence of various parameters", La revue de métallurgie, pp. 1073-1080, 2002.
[10] P.K. Sharma, V.V. Varadan, V.K. Varadan, "A critical role of pH in the colloidal synthesis and phase transformation of nano size α-Al_2O_3 with high surface area", J. Eur. Ceram. Soc., 23, pp. 659-666, 2003.
[11] T. Hernandez, M.C. Bautista, "The role of the synthesis route to obtain densified TiO_2-doped alumina ceramics", J. Eur. Ceram. Soc., 25, pp. 663-672, 2005.
[12] H. Reveron, C. Aymonier, A. Loppinet-Serani, C. Elissalde, M. Maglione, F. Cansell, Single-step synthesis of well-crystallized and pure barium titanate nanoparticles in supercriticals fluids, Nanotech., 16, 1137 – 1143, 2005.
[13] H. Reveron, C. Elissalde, C. Aymonier, M. Maglione, F. Cansell, Continous synthesis of well-crystallized BST nanoparticles under supercritical conditions and its ferroelectric properties, J Nanosci. Nanotech., 5(10), 1741 – 1744, 2005.
[14] H. Reverón, C. Elissalde, C. Aymonier, C. Bousquet, M. Maglione and F. Cansell, Continuous supercritical synthesis and dielectric behaviour of the whole BST solid Solution, Nanotech., 17, 3527-3532, 2006.
[15] BAZAEV A. R., ABDULAGATOV I. M., BAZAEV E. A., ABDURASHIDOVA A., (p, v, T, s) Measurements of [(1-x)H_2O+xC_2H_5OH] mixtures in the near-critical and supercritical regions, J. Chem. Thermodynamics, vol. 39, p. 385-411, 2007.
[16] POHLER H., KIRAN E., Volumetric properties of carbon dioxide + ethanol at high pressure, J. Chem. Eng. Data, vol. 42, p. 384-388, 1997.