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Synthesis of Yttria Stabilized Zirconia by sol–gel route: Influence of experimental parameters and large scale production

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Abstract

This paper develops an advance in the field of new synthesis techniques for functional materials like Yttria Stabilized Zirconia (YSZ) used as sensors, thermal barriers or electrolytes for high-temperature fuel cells.

In recent years, sol–gel routes were developed to prepare, by suitable chemical modifications, submicronic based materials with a controlled morphology, which conventional solid state chemistry paths are unable to provide. Wet chemistry methods provide interesting alternative routes because mixing of species occurs on the atomic scale. In this paper, ultrafine powders were prepared by a novel wet chemistry method based on the sol–gel process. One of the advantages of this method is to decrease the crystallization temperature in comparison to the conventional ones, allowing the synthesis of reactive powders with nanometric particles size. In this study, several processing parameters have been investigated (the hydrolysis ratio, the concentration of metallic precursors in the sol and the role of organic compounds and additives). Pure phases of YSZ were obtained and the characteristics of these powders investigated (crystallographic study, morphology, phase composition, etc.). Also, our optimised synthesis was applied to large scale elaboration by increasing the quantity of precursors. This study underlines the interest of the sol–gel process both to control the morphology of oxides and to prepare large amounts of high purity powders for an eventual industrialization process.

Keywords: YSZ; Sol–Gel; Modifiers; Nanoparticles; Large scale synthesis

1. Introduction

Zirconia based ceramics are well known for their excellent mechanical, electronic, thermal and optical properties. This kind of ceramics is fully employed in several commercial fields. For example, zirconia doped with yttria is the most common material used for mechanical applications. Its fine-grained polycrystals (Y-TZP: Yttria stabilized Tetragonal Zirconia Polycrystal) exhibit excellent mechanical properties. The maximum strength is over 1.5 GPa for 2.5 mol% Y-TZP and the maximum toughness about 15 $\mathrm{MPa\,m^{1/2}}$ for 2 mol% Y-TZP [1]. Another kind of applications can be considered, due to good anionic conductivity and thermal stability of fully stabilized zirconia (F-YSZ: Fully Yttria Stabilized Zirconia). These properties make of this material an excellent candidate for catalytic applications like oxygen sensors or for applications as electrolyte in solid oxide fuel cells (SOFC) [2–5].

In this study, we propose a novel approach to prepare YSZ thick films with controlled thickness by the dispersion of nanometric particles of YSZ in various media. The first step will focus on the synthesis of ultrafine powders by sol–gel route. This method is versatile, relatively simple to transfer at an industrial scale and not very expensive. This soft chemical method is based on the hydrolysis and inorganic polymerization reactions of metal alkoxides. For these reactions, in the case of non-silicate tetravalent alkoxides ($Z = 4$), like zirconium, *inhibitors* or *complexants* (named “modifiers”) are required to decrease the condensation rate and, therefore to prevent the precipitation of hydroxides. Indeed, these alkoxides are very sensitive to moisture and they must be handled with care under a dry atmosphere to avoid precipitation. The modifiers able

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to control the reactivity can be inorganic acids, β-diketones, carboxylic acids or other complexing ligands which act as determinant groups for condensation. The nature and the molar ratio modifiers/Zr are important factors concerning the kinetics and consequently the homogeneity of the reactions in the sol. Other parameters are also essential in the synthesis like the molar ratios: H_2O/Zr and solvent/Zr. The crystallographic symmetry and the morphology of the resulting oxide powders strongly depend on the chemical procedure.

In this paper, we propose to compare the effect of three different modifiers on the YSZ particles: inorganic acids, β-diketones and carboxylic acids. The effect of the amount of water is then studied. For a potential extension of this process to an industrial scale, we have also studied the modifications needed for a larger scale production.

X-Ray analysis and Rietveld refinement have been performed to determine the crystallographic characteristics of the YSZ powders synthesized by the different routes according to the nature of modifiers used. The size of the crystallites was also estimated using the Sherrer formula.

2. Experimental

2.1. Synthesis of the gels

To study the influence of the three modifiers, i.e., inorganic acid, carboxylic acid and β-diketone, samples were prepared respectively with hydrochloric acid (HCl 37 wt%, Prolabo), acetic acid ($C_2H_4O_2$ 100 wt%, Normapur) and acetylacetone (AcAc, 2,4-Pentanodione 99 + wt%, Acros Organics).

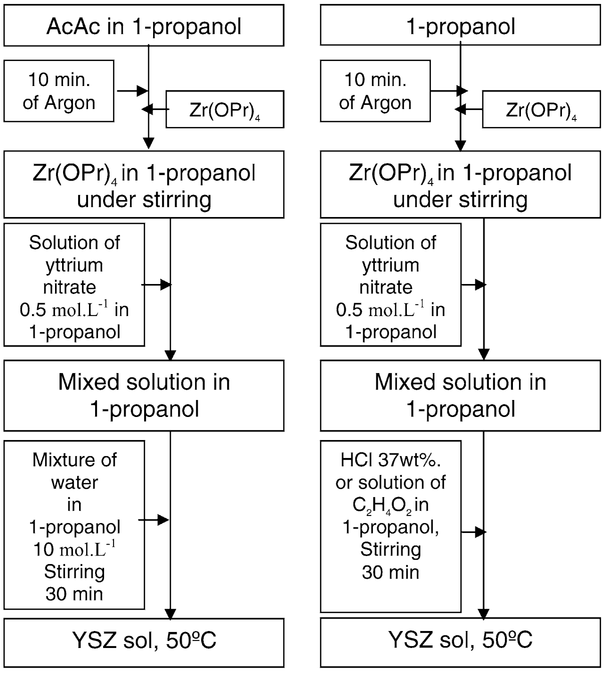
The zirconium alkoxide precursor was the zirconium (IV) propoxide ($Zr(OPr)_4$), 70 wt% solution in 1-propanol (Aldrich). The solvent of the synthesis was 1-propanol (99 + wt%, Acros Organics). The yttrium precursor was obtained by solubilization of yttrium (III) nitrate hexahydrate (99.9 wt%, Acros Organics) in 1-propanol (99 + wt%, Acros Organics) at a concentration of 0.5 $\mathrm{mol\,L^{-1}}$.

We have to notice the strong reactivity of $Zr(OPr)_4$ with water. So, in AcAc synthesis (see Fig. 1), demineralized water was not directly added. A mixture of 10 $\mathrm{mol\,L^{-1}}$ of water in 1-propanol (99 + wt%, Acros Organics) was prepared in order to avoid a local concentration of water in the solution with $Zr(OPr)_4$, that could induce a non-homogeneous gelation.

To avoid any problem of fast hydrolysis of alkoxide with water, always occurring in air, all the syntheses were performed under argon atmosphere.

Two syntheses procedures have been studied, one with AcAc (called (a) on Fig. 1) and the other corresponding to the acid synthesis (called (b)). For these two ways, the amount of yttrium introduced was kept constant to 9.7 mol% $YO_{1.5}$.

HCl is in solution (37 wt%, i.e., 12 $\mathrm{mol\,L^{-1}}$) so the addition of HCl implies the addition of water and the consequence is a fast start of gelation. Consequently, to have sufficient time to add the yttrium nitrate solution, the acid was the last added substance and 1-propanol was used without adding more water. In order to compare the influence of the acetic acid process, the same procedure was adopted for it.



(a) (b)

Fig. 1. (a) Procedure of synthesis with AcAc; (b) Procedure of synthesis in acid environment.

We can notice that in all syntheses, the molar ratios modifiers/Zr and 1-propanol/Zr were kept constant at respectively, 0.80 and 22.7.

2.2. Preparation of powders and crystallographic characterization

After the gelation step at 50°C, all samples were dried at 80 °C for a minimum of 24 hours in drying oven to obtain a xerogel. Then, they were calcined during 2 hours at 950 °C (heating rate: 100 °C/h). The resulting powders were then manually grinded.

The powders were then submitted to X-ray diffraction analysis coupled with Rietveld refinement. The patterns were measured at room temperature with a Seifert XRD 3003 TT diffractometer having Cu K_α radiation (1.5418 Å) and in configuration θ–θ. Samples were prepared by packing the powder into an acrylic holder.

3. Results and discussion

3.1. Influence of the modifiers nature

As explained above, different kinds of modifiers are able to limit the reactivity of the zirconium propoxide towards water. So HCl, $C_2H_4O_2$ and AcAc, respectively inorganic acid, carboxylic acid and β-diketone, were used as modifiers. We have to underline that the molar ratio modifiers/Zr was kept constant for each synthesis in order to compare their effect.

Table 1 summarizes the values of molar ratio H_2O/Zr and the time of gelation as a function of the modifiers nature. The

Table 1
Influence of the modifiers on the gelation time

Synthesis	H_2O/Zr molar ratio	Solution description	Gelation time
AcAc-a	2.9	Light yellow sol	1 month (at 50 °C)
HCl	2.7	White sol	Less than 1 minute
$C_2H_4O_2$-a	2.7	White sol/ nonhomogeneous	Instantaneous
$C_2H_4O_2$-b	1.1	White sol	1 hour (at 50 °C)

In all cases, the molar ratio modifiers/Zr is kept constant and equal to 0.8.

molar ratio H_2O/Zr was about the same for each experiment except for $C_2H_4O_2$-b. Indeed, the use of $C_2H_4O_2$ with the molar ratio H_2O/Zr equal to 2.7 induces the instantaneous gelation of the sample. Then, another sample—$C_2H_4O_2$-b—has been synthesized by using a fewer amount of water.

If we compare AcAc-a, HCl and $C_2H_4O_2$-a syntheses, which have approximately the same value of H_2O/Zr molar ratio, we note that the gelation time is much more important for AcAc-a, i.e., for β-diketone modifiers.

This can be explained by the formation of a very stable complex resulting from AcAc and $Zr(OPr)_4$ [6]. In fact, AcAc acts as a bidentate ligand on $Zr(OPr)_4$:

$$Zr(OPr)_4 + x\,AcAc \rightarrow Zr(OPr)_{4-x}(AcAc)_x + x\,PrOH.$$

These complexing ligands are much more difficult to hydrolize than zirconium alcoxide. This phenomenon tends to slow down the mechanisms of hydrolysis. Consequently, the condensation process is slower too. From a macroscopic point of view, gel formation occurs later.

In the acid synthesis, we used HCl 37 wt% in order to add a minimum water amount, since the water influence is very strong on sol–gel reaction. During the acid injection, white particles were observed. However, with vigorous stirring, the particles were solubilized before a fast gelation.

For comparison, the use of acetic acid with the same molar ratio H_2O/Zr than the synthesis with HCl—i.e., $C_2H_4O_2$-a—does not give rise to particles formation. Moreover the gelation is, in this case, instantaneous. This difference of behavior may be explained by the fact that the acid environment is directly correlated to the mechanism of hydrolysis.

In fact, the acetic acid is a catalyst towards the hydrolysis reaction as the hydrochloric acid. But $C_2H_4O_2$ is less strong than HCl, so the hydrolysis was not so favored. Consequently, the condensation, in this case, is more favorable because in less acid conditions, there are more free Zr–OH to do the nucleophilic attack. This may be explained the instantaneous reaction of the sample $C_2H_4O_2$-a. The $C_2H_4O_2$ can also form complexes with $Zr(OPr)_4$ [7] as β-diketones.

In the $C_2H_4O_2$-a synthesis, the acid concentration is larger due to the presence of less than a half water amount compared to synthesis $C_2H_4O_2$-b. In this case, the lower water concentration may allow the formation of [$C_2H_4O_2$–ZrO] more stable complexes and stabilize the hydrolysis-condensation process. This can explain the increase of gelation time to one hour.

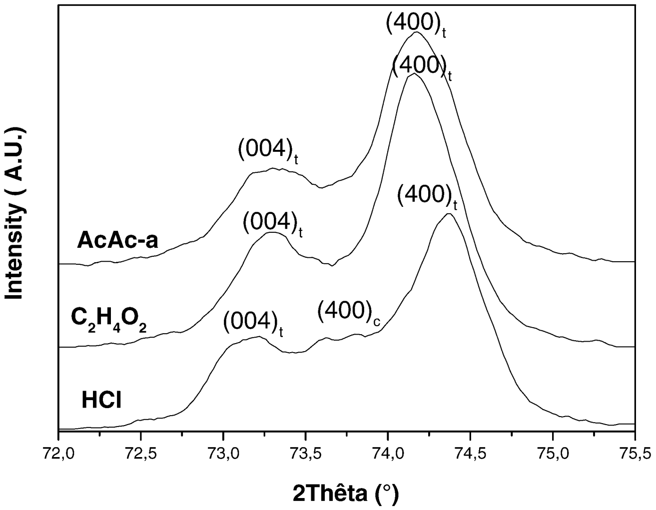


Fig. 2. Part of the diffractogrammes of powders obtained by varying the nature of the modifiers.

For comparison, in the acid synthesis, the obtained gel was white and the AcAc gel was yellow. This color change is probably due to the formation of [AcAc–ZrO] complexes.

3.1.1. Phases identification by X-ray diffraction

The powders obtained by each kind of synthesis were analyzed by X-ray diffraction (Fig. 2). The powders synthesized with AcAc and acetic acid exhibit a tetragonal symmetry (space group: $P4_2$/nmc). However, for HCl sample, we observe a mixture of cubic (space group: Fm3m) and tetragonal (space group: $P4_2$/nmc) phases.

This phenomenon can probably be explained by a nonhomogeneous reaction during this synthesis. Indeed, it was very fast and did not probably allow a good repartition of the precursors, in particular yttrium nitrate in the sol just before the gelation.

3.1.2. Tetragonal character of powders and size of the crystallites

In order to see if the synthesis pathway affects the tetragonal character of the samples, a Rietveld refinement was performed to find out the cell parameters in each case (Table 2). The tetragonal character was estimated via the $c/a\sqrt{2}$ ratio which characterizes the deviation from the cubic symmetry. From this, *tetragonalities* of the powders obtained with AcAc, and with $C_2H_4O_2$ are found identical.

The size of the crystallites was determined with the Sherrer formula $D = K\lambda/\beta\cos\theta$, where K is a constant equal to

Table 2
Crystallographic characterization of the samples

Sample	a (nm)	b (nm)	c (nm)	$c/a\sqrt{2}$	Crystallites size (nm)
AcAc-a	3.6143 $\pm 5 \times 10^{-4}$	3.6143 $\pm 5 \times 10^{-4}$	5.166 $\pm 1 \times 10^{-3}$	1.0107 $\pm 3 \times 10^{-4}$	31 ± 3
$C_2H_4O_2$-b	3.6153 $\pm 5 \times 10^{-4}$	3.6153 $\pm 5 \times 10^{-4}$	5.163 $\pm 1 \times 10^{-3}$	1.0100 $\pm 3 \times 10^{-4}$	37 ± 4

0.9 because of the pseudo-Voigt modelisation of the diffractograms; λ is the wavelength; β is the middle height width of the most intense peak and θ is the value of the diffraction angle. $\beta^2 = \beta_{\mathrm{m}}^2 - \beta_{\mathrm{s}}^2$, where β_{m} is the middle height width of the most important peak of the experimental diffractogram and β_{s} is the natural width resulting from the instrument contribution. β_{s} was determined with a standard silica sample, where β_{m} is negligible. From Table 2, it is clear that there is no difference between the samples and the crystallites sizes are quite identical. Therefore, from an experimental point of view, AcAc, i.e., β-diketones, seem to be the easier modifiers to handle. We have chosen these modifiers in the following of the study.

3.2. Influence of the water in the sol synthesis using β-diketones (AcAc)

To determine the influence of water on gelation time, four syntheses were carried out using AcAc. In all syntheses, the substitution rate in yttrium and the molar ratios AcAc/Zr were kept constant and respectively equal to 9.7 mol% $YO_{1.5}$ and 0.8. Table 3 shows the 1-propanol/Zr and the H_2O/Zr molar ratios and the gelation time observed at 50 °C.

In these mechanisms, propanol only is a solvent whereas water takes part to the reactions, that is the reason why we do not consider the 1-propanol/Zr molar ratio influence. Moreover, considering that the molar ratio AcAc/Zr is kept constant, the amount of water is the key parameter concerning the gelation time.

Table 3 shows that by increasing the H_2O/Zr molar ratio, a large decrease on the gelation time is involved. This phenomenon was expected because the sol–gel reaction is based on the hydrolysis and condensation of the zirconium alkoxide. In presence of water, it can quickly react with the $Zr(OPr)_4$ and form zirconium hydroxide, however, when AcAc is added to zirconium alkoxide, it forms very stable complexes [6]. The hydrolysis and consequently the condensation rates decrease [8] and the formation of a stable gel is observed. In this case, the amount of water added control the gelation speed. To the higher water amount studied (H_2O/Zr molar ratio equal to 13.3) the gelation process is instantaneous and the material is not homogeneous, so, the sample is rejected.

Changrong et al. [9] also studied the water influence towards YSZ synthesized by zirconium (IV) propoxide hydrolysis and condensation in presence of AcAc. However, the 1-propanol/Zr molar ratio and the AcAc/Zr molar ratio were different from this study, they were respectively equal to 50 and 0.24. Consequently, Changrong et al. used more than twice the amount of solvent that cause a decrease of the reaction rate, but they used less than half amount of AcAc, which exactly has the opposite effect. Despite these differences, the gelation times correlated to the H_2O/Zr ratio are similar in the two studies (Fig. 3).

Table 3
Water influence in the gelation time

Synthesis	1-propanol/Zr molar ratio	H_2O/Zr molar ratio	Gelation time (at 50 °C)
AcAc-a	22.7	2.9	1 month
AcAc-b	22.2	5.1	3 days
AcAc-c	21.1	9.5	1 day
AcAc-d	20.1	13.9	Instantaneous/ nonhomogeneous

In all cases, the molar ratio AcAc/Zr is kept constant and equal to 0.8.

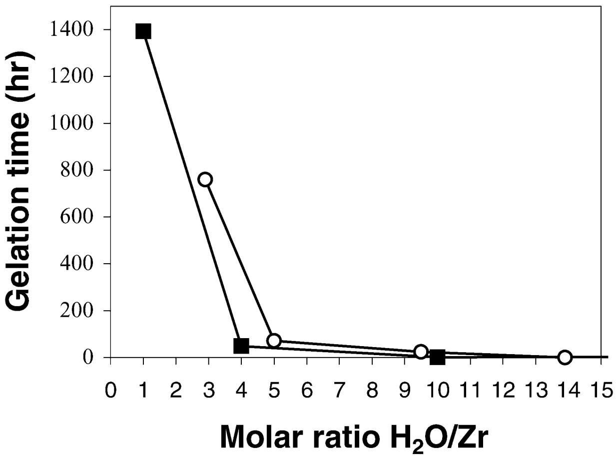


Fig. 3. Comparison of the gelation time concerning the Changrong et al. works (-■-) and the results corresponding to this study (-○-).

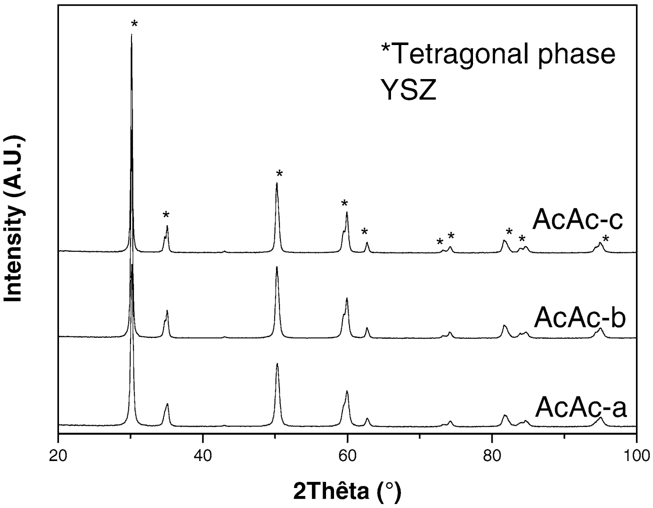


Fig. 4. Water influence study: diffraction patterns of powders (AcAc synthesis).

This comparison clearly evidences that the role of AcAc and water are quite opposite and the modification of these parameters allows a control of the gelation time. This underlines an advantage of the sol–gel process concerning the adaptability of the method and the easiness to control the gelation time.

Except for AcAc-d, each powder was obtained and characterized by X-ray diffraction (Fig. 4) followed by a Rietveld refinement. All the obtained powders have a tetragonal symmetry (space group: $P4_2/nmc$). The cell parameters have been determined to compare the *tetragonality* of the samples. Moreover the crystallites size has been estimated by the Scherrer formula. All these results are gathered in Table 4.

The increase of the water amount has no influence on the tetragonal character of the samples. Indeed the parameter $c/a\sqrt{2}$ is quite equal to 1.010. Moreover, no real difference concerning the size of the crystallites is noticed.

Table 4
Crystallographic characterization of the samples obtained using AcAc

Sample	H_2O/Zr molar ratio	a (nm)	b (nm)	c (nm)	$c/a\sqrt{2}$	Crystallites size (nm)
AcAc-a	2.9	3.6143 $\pm 5 \times 10^{-4}$	3.6143 $\pm 5 \times 10^{-4}$	5.166 $\pm 1 \times 10^{-3}$	1.0107 $\pm 3 \times 10^{-4}$	31 ± 3
AcAc-b	5.1	3.613 $\pm 1 \times 10^{-3}$	3.613 $\pm 1 \times 10^{-3}$	5.163 $\pm 2 \times 10^{-3}$	1.0104 $\pm 7 \times 10^{-4}$	49 ± 5
AcAc-c	9.5	3.6151 $\pm 5 \times 10^{-4}$	3.615 $\pm 5 \times 10^{-4}$	5.164 $\pm 1 \times 10^{-3}$	1.0100 $\pm 3 \times 10^{-4}$	49 ± 5

Table 5
Cell parameters and crystallites size of AcAc samples obtained by varying the amount of precursors

Sample	a (nm)	b (nm)	c (nm)	$c/a\sqrt{2}$	Crystallites size (nm)
Sx1	3.6151 $\pm 5 \times 10^{-4}$	3.6151 $\pm 5 \times 10^{-4}$	5.164 $\pm 1 \times 10^{-3}$	1.0100 $\pm 3 \times 10^{-4}$	49 ± 5
Sx5	3.6143 $\pm 4 \times 10^{-4}$	3.6143 $\pm 4 \times 10^{-4}$	5.1631 $\pm 8 \times 10^{-4}$	1.0101 $\pm 3 \times 10^{-4}$	41 ± 4
Sx10	3.6145 $\pm 4 \times 10^{-4}$	3.6145 $\pm 4 \times 10^{-4}$	5.1635 $\pm 8 \times 10^{-4}$	1.0101 $\pm 3 \times 10^{-4}$	50 ± 5

3.3. *Influence of a large scale synthesis*

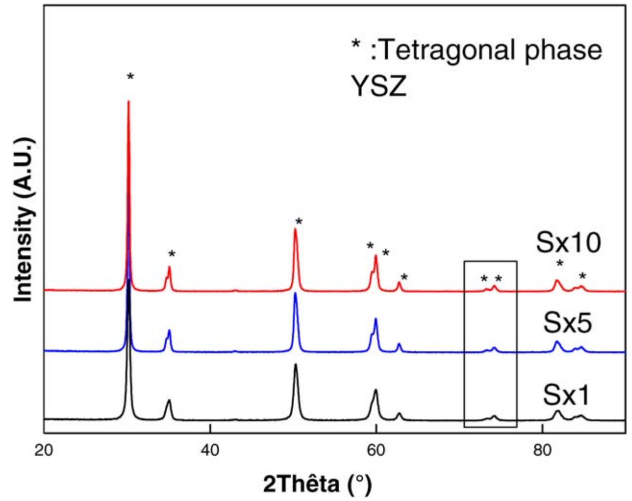
In the eventual industrialization of the process, a study of the synthesis in large amounts has been undertaken. The experimental procedure using AcAc, with the molar ratio H_2O/Zr equal to 9.5 (AcAc-c) has been selected referring to the different results previously obtained. Indeed this protocol allows to obtain the powder more quickly than other AcAc synthesis and is not as fast as acid syntheses.

Syntheses were performed following the mechanism (a) showed in the flowchart of Fig. 1 with molar ratio H_2O/Zr equal to 9.5. A scale factor of 5 and then 10 was applied for the quantity of precursors. With the standard synthesis, roughly 3 grams of powder were obtained. To compare with, 15 grams of powder were obtained by multiplying the precursor quantity by 5 and 30 grams by multiplying by 10. No mass losses due to this scale increase have been observed.

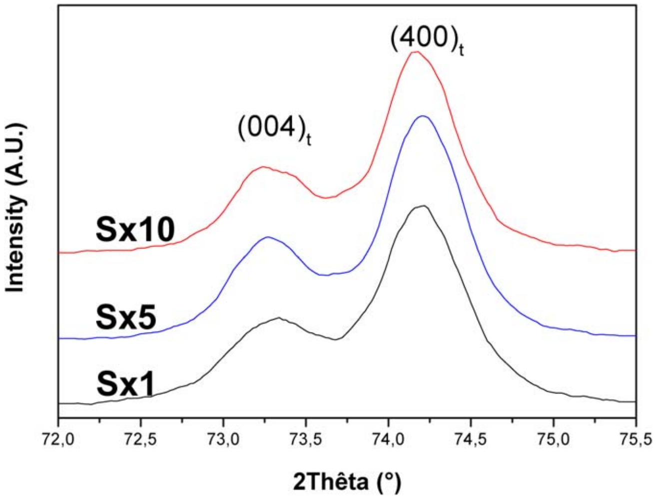
The X-ray diffraction patterns of these samples are shown in Fig. 5. The YSZ tetragonal structure is obtained in each case and there is no phase decomposition. The *tetragonality* (Table 5) is not affected. Indeed, the ($c/a\sqrt{2}$) ratio is always equal to 1.010.

No major variation is observed for the crystallites size and, for each powder, it is approximately equal to 45 nm.

From this study, we can conclude that the scale increase does not cause any modification concerning the purity of the obtained powders. Moreover, the crystallographic study has shown that the cell parameters and the crystallites size remain of the same order of magnitude.



(a)



(b)

Fig. 5. (a) X-ray diffraction patterns of powders obtained in big quantities (Sx5 and Sx10)-comparison with the initial synthesis Sx1. (b) Focus in the 74° region.

4. Conclusion

In this work, a new safe and straightforward sol–gel method for the preparation of Yttria Stabilized Zirconia (YSZ) was investigated. This method allowed the preparation of pure powders at relatively low temperature compared to conventional solid–solid methods, with uniform particle sizes. This process was chosen because it is an easy way and low cost technology which can be transferred at an industrial scale.

This work was made of two parts. The first one is the optimization of the experimental conditions of an YSZ "standard" synthesis and in particular the study of the influence of several additives and water on reactions progress. The second one is, on the basis of the results obtained for the "standard" synthesis, to prepare such oxides at a larger scale to test a possible integration of this method into an industrial process. In this case, the structural and microstructural characteristics of materials, in reference to the standard synthesis, were strictly preserved. This study underlines the interest of the sol–gel process both to control the morphology of oxides and to prepare large amounts of powders with the same characteristics (high purity, particle size and distribution . . .).

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