INFLUENȚA CONDIȚIILOR DE PREPARARE ASUPRA CARACTERISTICILOR NANOMETRICE ALE PULBERILOR DE ZIRCONĂ ŞI ALUMINĂ

INFLUENCE OF PREPARATION CONDITIONS ON NANOMETRIC CHARACTERISTICS OF ZIRCONIA AND ALUMINA POWDERS

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Scopul lucrării îl reprezintă sinteza şi caracterizarea unor pulberi ceramice de zirconă total stabilizată cu Y_2O_3 (8%) şi de alumină, obținute prin metoda (co)-precipitării, din cloruri metalice corespunzătoare. Ca solvenți s-au folosit apa şi etanolul, iar pentru precipitare, pH-ul soluției a fost variat, prin folosirea de amoniac. Valorile de pH considerate au fost 7,5, 10,5 şi 12,5. Precipitatele obținute au fost uscate la 80°C, timp de 24 de ore şi ulterior calcinate la 350°C, timp de 2 ore.

Pulberile au fost evaluate prin analize termice diferențiale, prin difracție de raze X, prin microscopie electronică de baleaj şi transmisie.

În cazul pulberilor de 8YSZ, difractogramele de raze X atestă prezența ZrO_2 tetragonal, iar pentru pulberea de alumină, pe lângă γ-Al_2O_3 alumină se decelează şi δ-Al_2O_3. Din imaginile TEM se observă că granulele de ZrO_2 tetragonal prezintă o morfologie aproape sferică, particulele având dimensiuni cuprinse între 5 nm şi 12 nm. De asemenea s-a observat că cea mai bună condiție de obținere a nanopulberilor a fost, utilizarea apei ca solvent şi asigurarea unui pH bazic de 12,5.

The paper's aim was to prepare and characterize ceramic powders of fully stabilized zirconia (with 8 mol% yttria), and alumina, obtained through co-precipitation starting from the corresponding chlorides. Co-precipitation was taken using water or ethanol as a solvent and considering the pH influence (7.5, 10.5 and 12.5 obtained by using ammonia solution) upon precipitation was analyzed. The obtained powders were dried at 80 °C for 24 h and afterwards calcinated at 350°C for 2 hours.

The powders were evaluated through thermal analysis, X-ray diffraction, scanning electron microscopy and transmission electron microscopy.

The XRD results show that 8YSZ calcinated powders is a tetragonal ZrO_2 and, concerning alumina powder, besides γ-Al_2O_3, δ-Al_2O_3 was identified. The TEM examination shows that the tetragonal ZrO_2 has a spherical like morphology with a size ranging from 5 nm to 12 nm. Also, it was observed that the best condition for nanopowders obtaining was using as solvent water and a pH value of 12.5.

Keywords: *zirconia, alumina, nanopowders, (co-)precipitation*

1. Introduction

In recent years, more and more attention has been attracted by nanotechnology, which produces materials with sizes in the range of 1-100 nm. The new trend is developing nanotechnologies towards achieving cheap experimental procedures, which allow obtaining reproducible results. [1].

Both zirconia and alumina are important for a wide range of applications, starting with ceramic and ending with the catalysts [2,3].

A convenient method for obtaining nanomaterials is the hydrocompounds calcination, which are obtained by hydrolysis of salts in different liquid media. It has been shown that the final properties of zirconia and alumina powders depend on certain chemical parameters like: the precursor salts, precipitation environment, etc. [2]. These parameters act on the tendency of agglomeration of primary particles during the formation of new structural networks [2].

There are many methods for obtaining nanopowders, like: sol-gel, hydrothermal, combustion, precipitation, etc [4]. Among these methods, the cheapest one proves to be the precipitation. This method allows obtaining pure fine particles, for both, unary as well as multicomponent oxide systems. [5]. Moreover, if during the precipitation, pH environment, the temperature or reaction time is controlled, the ceramic particles might have some predefined size [6].

The present study aims to obtain fully stabilized zirconia and alumina nanopowders by means of (co)-precipitation method, varying the pH and the precipitation environment, analyzing in this way the influence of these two parameters on nanopowders characteristics.

2. Experimental procedure

Fully stabilized zirconia (with 8 mol% yttria), and alumina powder was obtained through (co-) precipitation method starting from the correspon-

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ding chlorides ($ZrCl_4$, YCl_3, $AlCl_3$). As solvents distillated water and ethanol were used. For precipitation, the pH was varied using different proportions of ammonia, added drop by drop. The pH values considered were: 7.5, 10.5 and 12.5. There were prepared two types of powders: alumina and zirconia.

After (co-)precipitation, the precipitates were filtered and washed, until neutral pH, and further dried at 80°C for 24 hours.

Later on, the powders were calcinated and characterized in the terms of diffraction analysis, particle size distribution, scanning and transmission electron microscopy (SEM and TEM).

3. Results and discussion

3.1. Characterization of precipitation aggregates

After precursors (co-)precipitation, the precipitates were dried at 80°C, for 24 hours.

The microstructure of the obtained aggregates was observed by means of scanning electron microscopy (Figures 1 - 2).

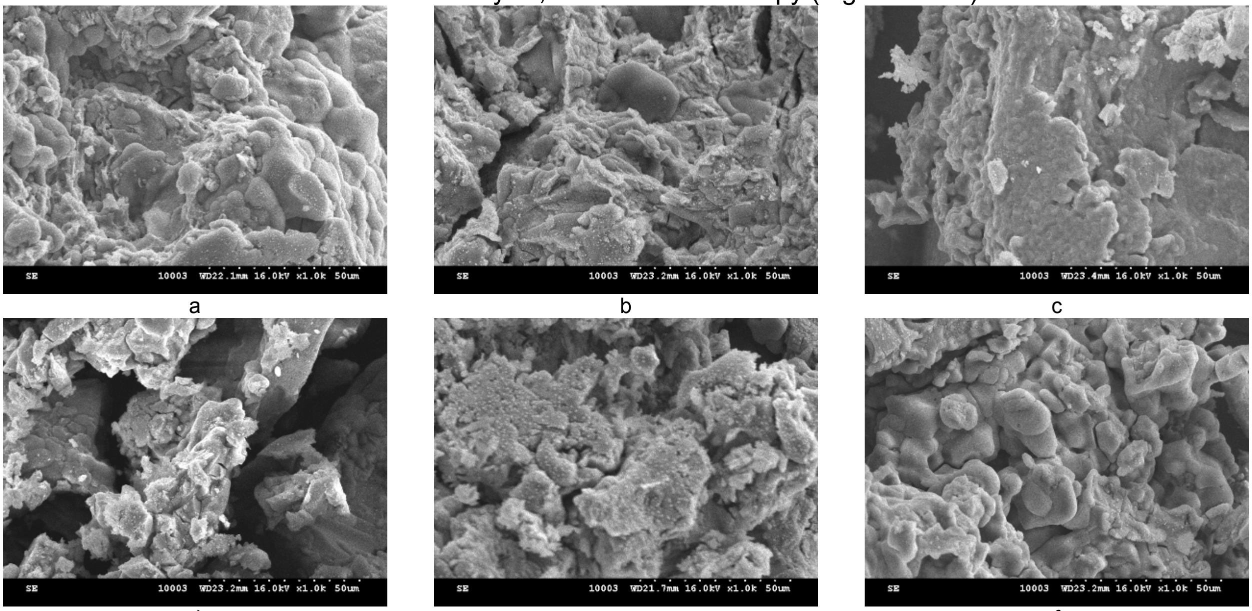


Fig. 1 - SEM images of aggregates obtained through (co-)precipitation of zirconia powder precursors in water (a,b,c) and ethanol (d,e,f) at pH = 7.5 (a and d); pH = 10.5 (b and e); pH = 12.5 (c and f).

Imagini MEB ale agregatelor obţinute prin (co-)precipitarea precursorilor de zirconă în apă (a,b,c) şi în etanol (d,e,f) la pH = 7,5 (a şi d); la pH = 10,5 (b şi e); la pH = 12,5 (c şi f).

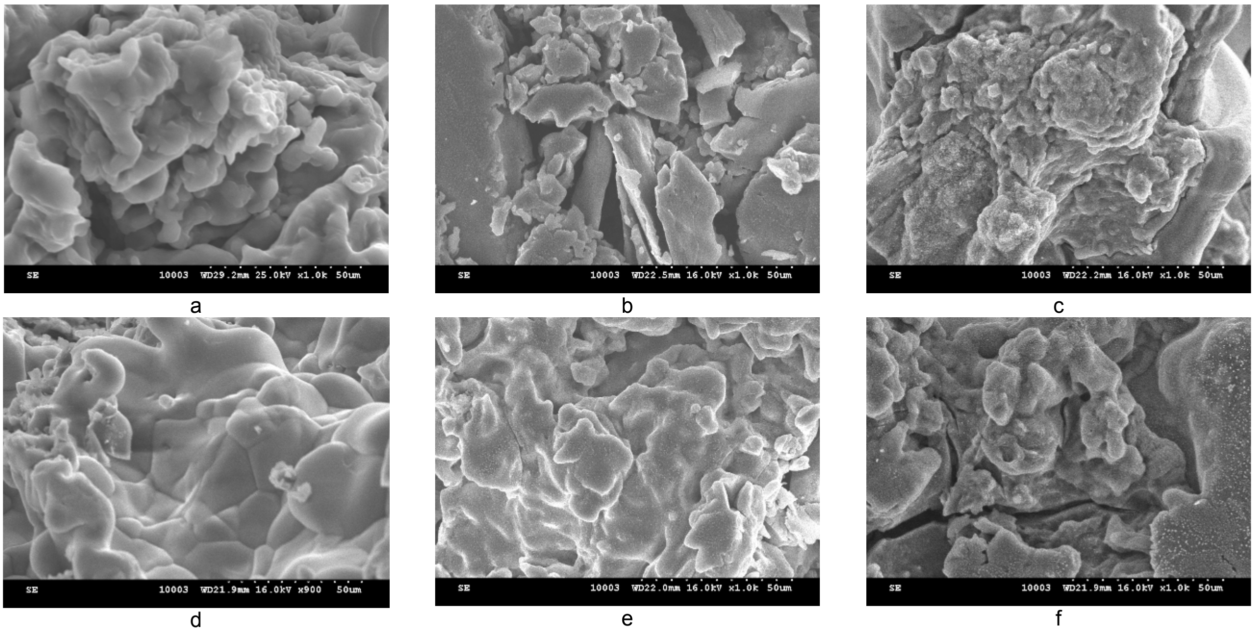


Fig. 2 - SEM images of aggregates obtained through precipitation of alumina powder precursor in water (a,b,c) and ethanol (d,e,f) at pH = 7.5 (a and d); pH = 10.5 (b and e); pH = 12.5 (c and f).

Imagini MEB ale agregatelor obţinute prin precipitarea precursorului de alumină în apă (a,b,c) şi în etanol (d,e,f) la pH = 7,5 (a şi d); la pH = 10,5 (b şi e); la pH = 12,5 (c şi f).

It can be said that the precipitation aggregates are irregular, with different sizes, depending on the (co)-precipitation environment and pH. By increasing the pH value, the aggregates tend to a smaller size. It is noted that in case of using ethanol as a (co-)precipitation media, both powder tend to consolidate.

To highlight the behavior of co-precipitates, the powders were characterized in terms of differential thermal analysis. The results are shown in Figure 3.

transformation phenomenon of $Al(OH)_3$ and γ-AlOOH into γ-alumina [7].

Following this results, it can be conclude that 350°C is the most appropriate calcination temperature (calcination time = 2h).

3.2. Powder characterization after calcinations process

Using X ray diffraction analysis, the phase composition of calcinated nanopowders, was determined. The X ray patterns are presented in Figure 4. Thus, the X ray patterns (Figures 4a and b)

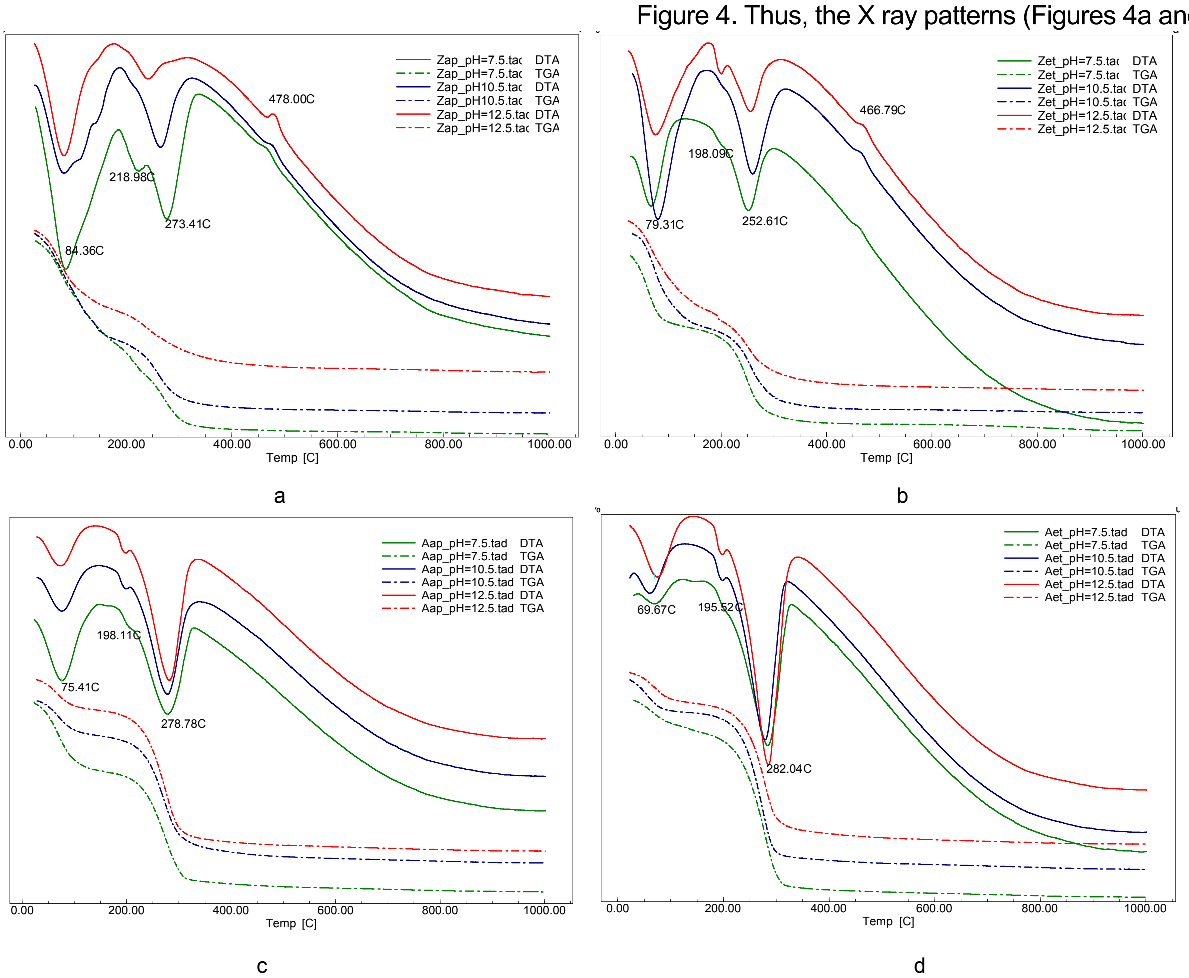


Fig. 3 - *Thermal analysis of dried precipitates: zirconia co-precipitated in the presence of water (a) and ethanol (b) and alumina precipitated in water (c) and ethanol (d).*
Analizele termice pentru precipitatele uscate: zircona co-precipitată în apă (a) şi etanol (b) şi alumina precipitată în apă (c) şi etanol (d).

It can be easily seen that all prepared mixtures present the following temperature ranges:

• In case of any type of solvent or precursor, it is noticed that between 30 and 200°C endothermic picks occur due to physical water evaporation.

• The endothermic effect at 280°C belongs to dehydration reaction of zirconium hydroxide. Also, for zirconium oxide powder is observed a weak exothermic effect at 480°C which shows the crystallization phenomenon of polymorphic form of tetragonal ZrO_2 [7].

•For alumina powder, at 300°C an endothermic effect occurs, corresponding to the

show the presence of tetragonal phase of ZrO_2 in calcinated precipitate at 350°C, for 2 hours. In case of calcinated alumina powder, the X ray patterns attest, beside γ-alumina, the presence of δ-alumina (Figures 4.c and d).

It can be noticed the effects of specific diffraction of ZrO_2 tetragonal phase in all zirconia samples (precipitated at different pH values). For alumina powders, beside γ-Al_2O_3, diffraction patterns characteristic to δ-alumina were observed.

Because all zirconia samples have a single phase and are very well crystallized it was possible to calculate, based on full width at half maximum

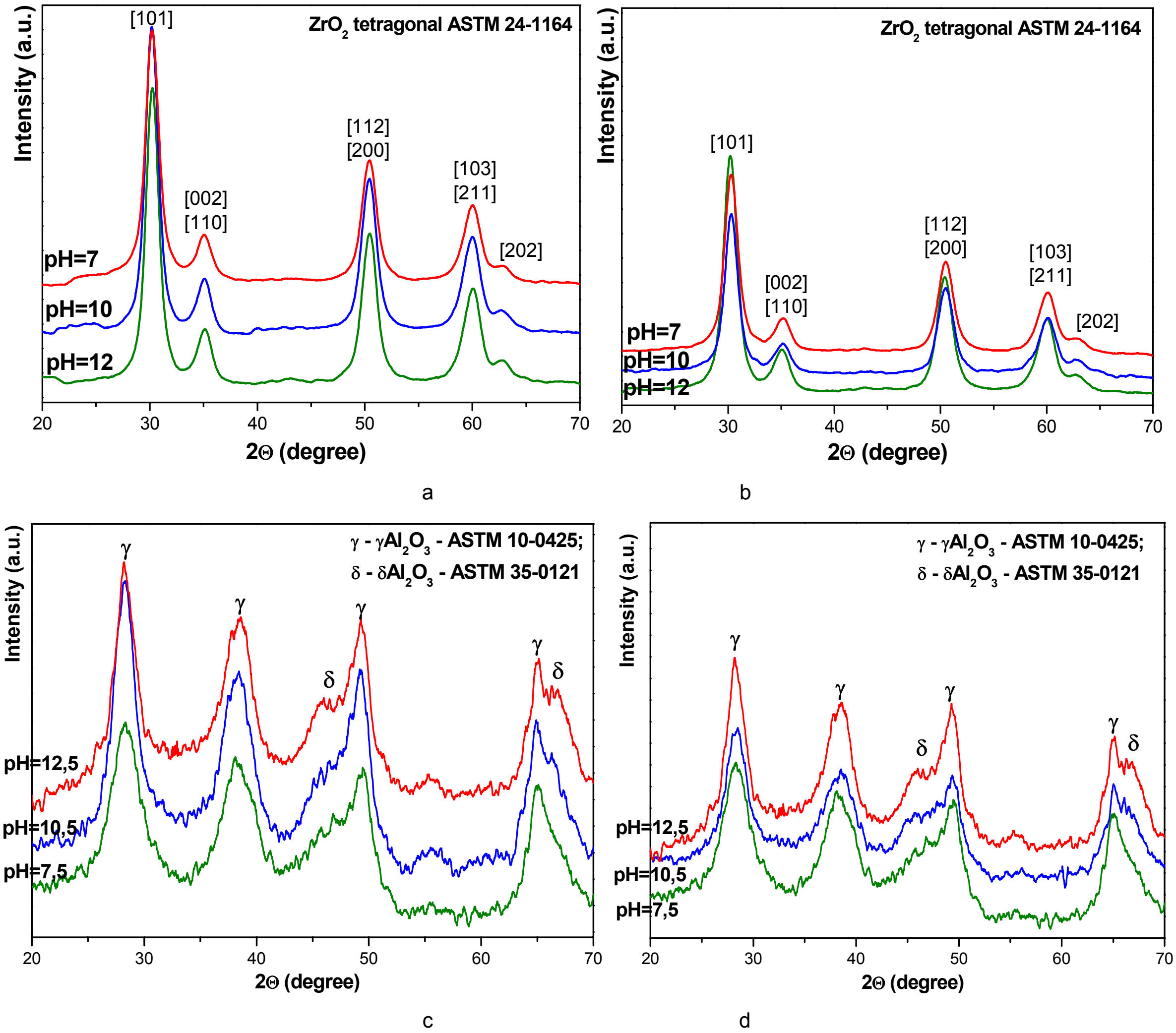


Fig. 4 - X-ray diffraction spectra of zirconia obtained in the presence of water (a) and ethanol (b), and X-ray diffraction spectra of alumina obtain in water(c) and ethanol (d).
Fig. 4 – *Spectrele de difracţie a razelor X pentru pulberile de zirconă obţinută în apă (a) şi etanol (b), şi pentru pulberile de alumină obţinută în apă (c) şi etanol (d).*

(FWHM), the crystallite sizes, by means of Scherrer equation. The results are presented in Table 2.

Scherrer equation allows the determination of crystallite size, using the following formula:

$$D = \frac{k\lambda}{\beta\cos\theta}$$

were: D – crystallite (size; λ - wave length of X – ray (Å); β - is the line broadening at the half of maximum intensity (FWHM - deg); θ - the angle between the beam axis and the ring (scattering angle - deg); k – constant, usually equal with 0,89.

The above formula applies to the first three lines, the most intense ones of the characteristic diffraction spectra of each sample. Subsequently, all the obtained values are averaged.

It can be noted that a high pH value of precipitation media allows obtaining a smaller crystallite dimension. Also, using ethanol as a precipitation media doesn't help obtaining a smaller crystallite.

Table 2

Crystallite size for zirconia powder
Dimensiunea de cristalit pentru pulberea de zirconă

Sample		Crystallite dimension (nm)		
		pH=7,5	pH=10,5	pH=12,5
Zirconia	Water	6.66	5.62	5.34
	Ethanol	6.89	6.22	6.90

The prove that the synthesized powders have nanometric sizes is TEM images of the compositional series presented in the Figures 5-10.

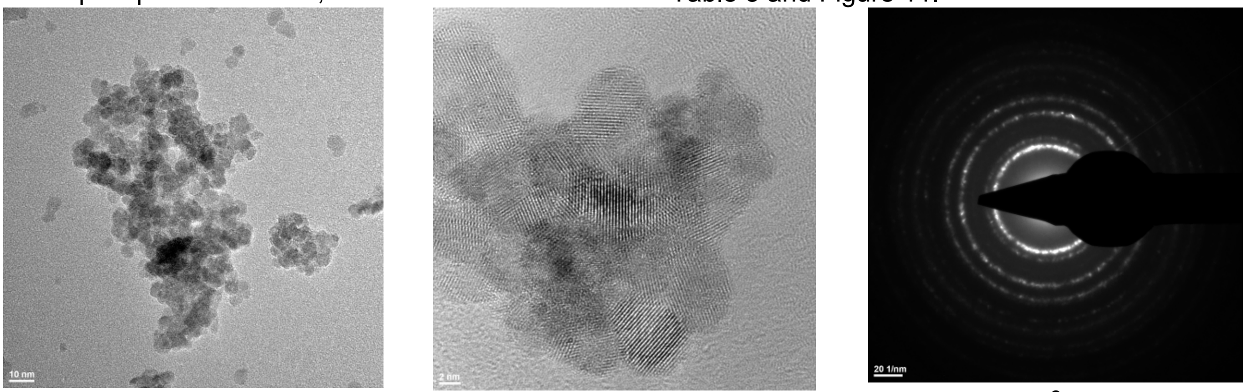
It can be noted that the zirconia powder precipitated in water, at different pH values, exhibit small particle size (less than 7.5 nm) with a high crystallinity, with nearly spherical shape and with a tendency of agglomeration. The observed planes belong to a tetragonal zirconia and the electron diffraction on selected surface areas have wide bands, characteristic to a very small crystals.

Also, it should be noted that, the precipitation at higher pH leads to a smaller particles (for example, at pH = 12.5, the particle size average is about 5 nm, in case of fully stabilized zirconia).

Regarding the precipitation environment impact, it can be said that the change from water to ethanol does not bring positive effects in terms of nanometric size of the obtained particles. Also, the TEM images for zirconia precipitated in ethanol, shows the presence of amorphous phases.

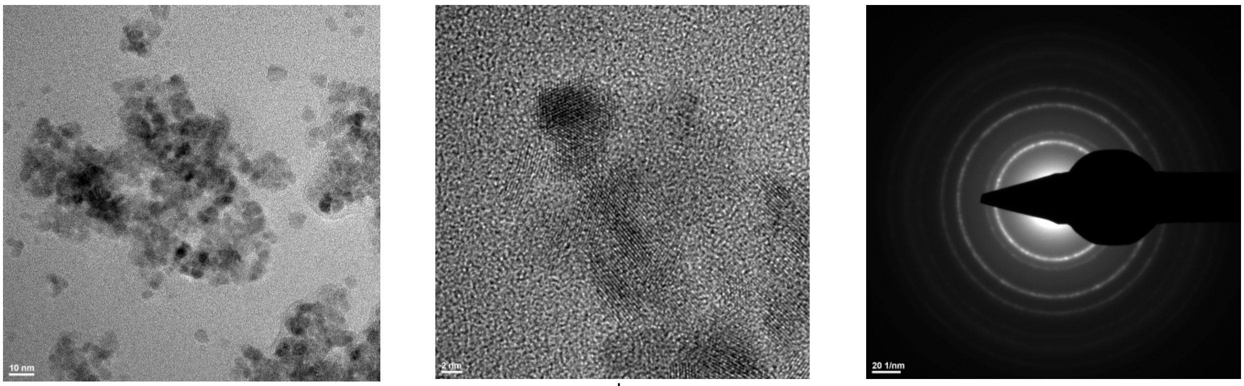
For alumina powders precipitated at pH = 12.5, in water or in ethanol, the TEM images (figure 9 and 10) reveal totally different features. In case of alumina precipitated in water, it can be identified particles with different size and shapes, characteristic to γ-alumina and δ-alumina phases, and alumina precipitated in ethanol shows a very high proportion of crowded amorphous phases.

For calcinated zirconia and alumina nanopowder, precipitated in water at pH 12.5, specific surface (BET and Langmuir, through absorption - desorption isotherms with nitrogen) were estimated. The obtained values are shown in Table 3 and Figure 11.



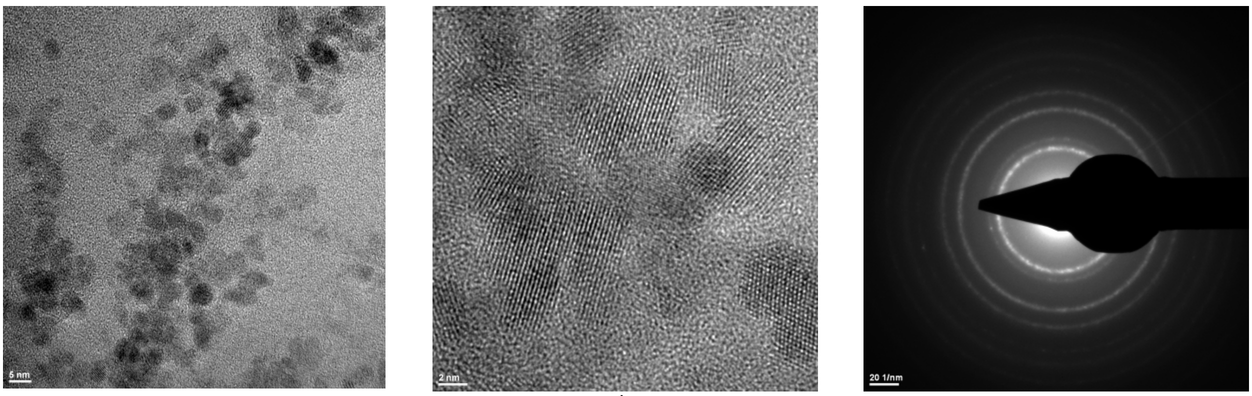
a b c

Fig. 5 - TEM images for zirconia calcined powder, precipitated in water pH = 7.5:
a,b – transmission electron microscopy in a bright field, c. electron diffraction on selected surface area.
Imagini TEM pentru pulberea calcinată de zirconă, precipitată în apă la pH = 7,5:
a,b – microscopie electronică de transmisie în camp luminat, c. difracţie de electroni pe arie selectată.



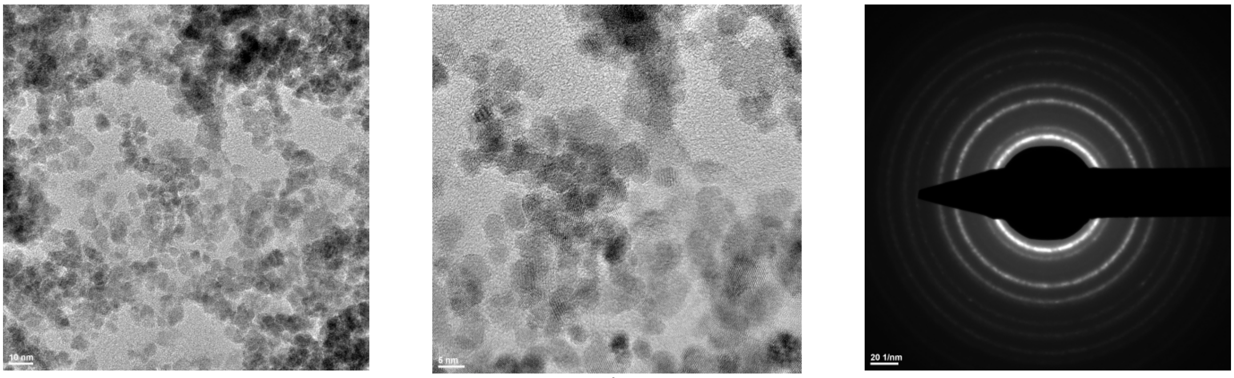
a b c

Fig. 6 - TEM images for zirconia calcined powder, precipitated in water pH = 10.5:
a,b – transmission electron microscopy in a bright field, c. electron diffraction on selected surface area.
Imagini TEM pentru pulberea calcinată de zirconă, precipitată în apă la pH = 10,5:
a,b – microscopie electronică de transmisie în camp luminat, c. difracţie de electroni pe arie selectată.



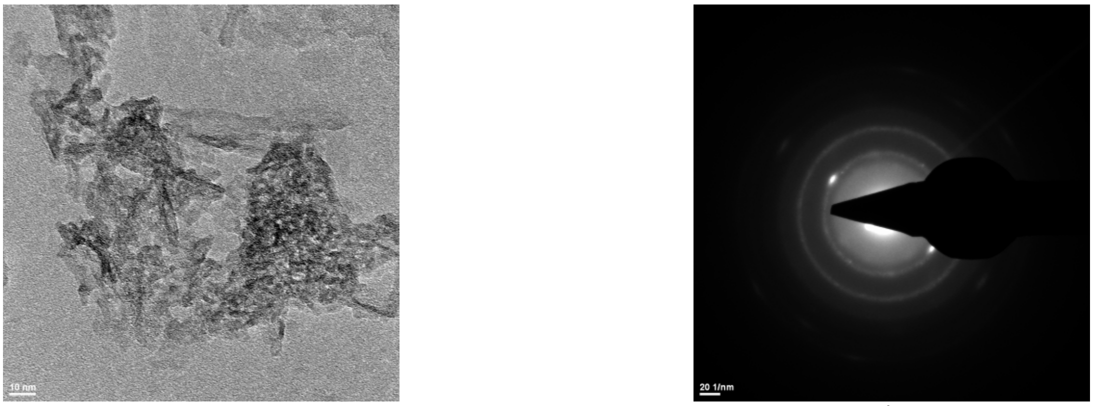
a b c

Fig. 7 - TEM images for zirconia calcined powder, precipitated in water pH = 12.5:
a,b – transmission electron microscopy in a bright field, c. electron diffraction on selected surface area
Imagini TEM pentru pulberea calcinată de zirconă, precipitată în apă la pH = 12,5:
a,b – microscopie electronică de transmisie în camp luminat, c. difracţie de electroni pe arie selectată.



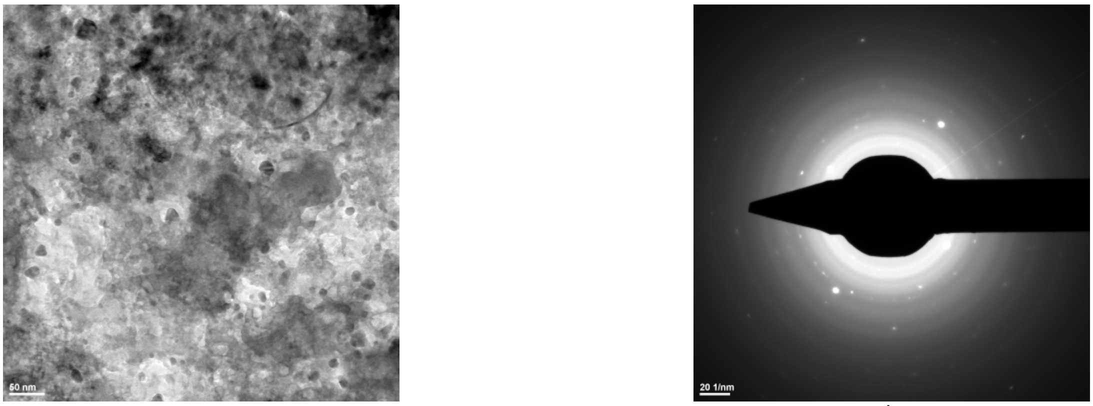
a b c

Fig. 8 - TEM images for zirconia calcined powder, precipitated in ethanol pH = 12.5:
a,b – transmission electron microscopy in a bright field, c. electron diffraction on selected surface area.
Imagini TEM pentru pulberea calcinată de zirconă, precipitată în etanol la pH = 12,5:
a,b – microscopie electronică de transmisie în camp luminat, c. difracţie de electroni pe arie selectată.



a b

Fig. 9 - TEM images of calcinated alumina powder, precipitated in water pH = 12.5:
a – transmission electron microscopy in light field, b. electron diffraction on selected surface area
Imagini TEM pentru pulberea calcinată de alumină, precipitată în apă la pH = 12,5:
a – microscopie electronică de transmisie în camp luminat, b. difracţie de electroni pe arie selectată.



a b

Fig. 10 - TEM images of calcinated alumina powder, precipitated in ethanol pH = 12.5:
a – transmission electron microscopy in bright field, b. electron diffraction on selected surface area
Imagini TEM pentru pulberea calcinată de alumină, precipitată în etanol la pH = 12,5:
a – microscopie electronică de transmisie în camp luminat, b. difracţie de electroni pe arie selectată.

Table 3

Specific surface area obtained by BET analysis
Suprafaţa specifică obţinută prin analize BET

Sample	**Specific surface area**		**Pores medium size diameter**
	BET	**Langmuir**	
Zirconia (water. pH = 12,5)	106 m²/g	168 m²/g	4.85 nm
Alumina (water. pH = 12,5)	196 m²/g	313 m²/g	4.68 nm

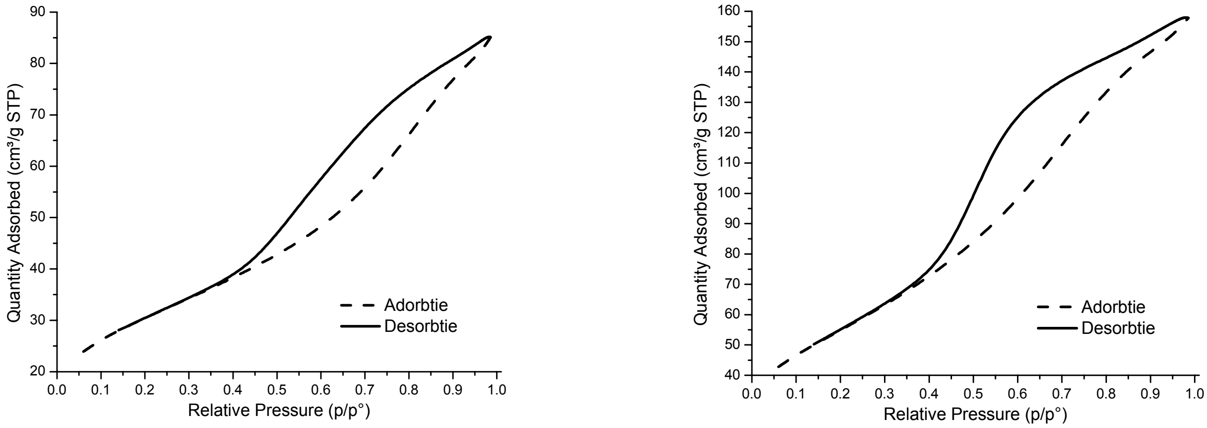


Fig. 11 - Absorption – desorption isotherms of zirconia (a) and alumina (b) powder
Izotermele de absorbţie – desorbţie pentru pulberile de zirconă (a) şi alumină (b)

Both isotherms are type IV, being characterized by hysteresis, which are specific to the mesoporous structure materials, aerogels and porous oxide materials.

4. Conclusion

The present work reports the synthesis of zirconia and alumina nanopowders through precipitation route, using different solvents for raw materials (water and ethanol) and different pH conditions.

All powders were evaluated through thermal analysis, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The XRD results show that zirconia based calcinated powders contains tetragonal ZrO_2 and, for alumina powder, besides γ-Al_2O_3, δ-Al_2O_3 was identified. The TEM examination shows that the tetragonal ZrO_2 has a spherical like morphology with a size ranging from 5 nm to 12 nm.

Also, it was observed that the best condition for nanopowders preparation was using water as solvent and a pH value of 12.5.

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