

# Effect of Pressure on Synthesis of Pr-Doped Zirconia Powders Produced by Microwave-Driven Hydrothermal Reaction

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A high-pressure microwave reactor was used to study the hydrothermal synthesis of zirconia powders doped with 1 mol % Pr. The synthesis was performed in the pressure range from 2 to 8 MPa corresponding to a temperature range from 215°C to 305°C. This technology permits a synthesis of nanopowders in short time not limited by thermal inertia of the vessel. Microwave heating permits to avoid contact of the reactants with heating elements, and is thus particularly well suited for synthesis of doped nanopowders in high purity conditions. A mixture of ZrO<sub>2</sub> particles with tetragonal and monoclinic crystalline phases, about 15 nm in size, was obtained. The p/T threshold of about 5–6 MPa/265–280°C was necessary to obtain good quality of zirconia powder. A new method for quantitative description of grain-size distribution was applied, which is based on analysis of the fine structure of the X-ray diffraction line profiles. It permitted to follow separately the effect of synthesis conditions on the grain-size distribution of the monoclinic and tetragonal phases.

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## 1. INTRODUCTION

Several papers report microwave- (MW-) driven hydrothermal synthesis of nano-sized powders at elevated pressure [1–5] stimulated by some reports on acceleration of chemical reaction rates when microwaves are used to heat the reactants [4], which however can be rationalized in terms of local superheating of the fluids during microwave heating [6–8]. Most commercial microwave hydrothermal apparatuses used for the production of nanocrystalline powders work at maximum pressure/temperature in range of 2–3 MPa/200°C [9–11]. Very few commercial apparatuses have been built in order to reach extreme reaction conditions: 260°C and 10 MPa [12], in practice pressure exceeding 5 MPa has been applied rarely.

In the present paper, we report the results of the effect of pressure on the synthesis of nanosized ZrO<sub>2</sub> powders doped with 1 mol% of Pr, in a microwave-driven hydrothermal reaction in a range of pressures 2–8 MPa. The investigation of the evolution of grain phase distribution and phase composition of zirconia nanopowders aroused from its widespread applications [13–16]. In particular, Pr-doped zirconia is used

as pigment [17, 18], and as luminescent material [19, 20]. Both the tetragonal and monoclinic phases or their mixtures are usually present in the powders synthesized hydrothermally [21–24] and it is also well known that a decrease in grain size leads to an increase in the content of tetragonal phase, which for larger than 10 nm grained material is metastable at room temperature [25, 26]. Since for a range of applications, like ceramics with superior mechanical properties or luminescent material, the phase composition of the powders plays an important role, the stability of the tetragonal phase in nano-sized powders and methods to control it were extensively discussed.

Garvie et al. [26] explained the stability of tetragonal 1–9 nm diameter nanopowders assuming a lower surface energy of the tetragonal phase compared to the monoclinic one, so that at low grain sizes, where the surface energy is a considerable fraction of the total energy of the system, it is favorable to form the tetragonal phase. The threshold value for the stability of the tetragonal phase was also explained in terms of internal strain energy [27] or internal pressures resulting from surface stress terms [27, 28]. The above threshold value is close to that calculated by Simeone et al. [23] who

obtained a value of 13.7 nm. However, some authors report observations of 6 nm diameter monoclinic zirconia nanoparticles [29].

The mechanisms of crystallization of the tetragonal and monoclinic phases and their mutual transformation under hydrothermal conditions were extensively investigated by Yoshimura et al. [30–32]. Their experimental results can be explained in terms of dissolution/precipitation, structural rearrangement of the tetragonal phase, or simultaneous nucleation of the two phases of  $\text{ZrO}_2$ . Mineralogical, morphological, and physical characterizations were combined to get additional insight in the nucleation and growth mechanism which are then discussed in the context of the above presented concepts on the synthesis and grain-growth process. The kinetics and conditions for zirconia precipitation were recently reviewed by Piticescu et al. [33].

It should be noted that the presence of 1% of Pr in the zirconia ceramics does not influence significantly phase equilibrium, as it is seen from phase diagrams of zirconia doped with rare earth ions [34, 35]. The effect on the synthesis conditions on luminescence properties of Pr in nanosized  $\text{ZrO}_2$  is the subject of separate papers [19]. The high-pressure microwave reactor used for this investigation provided shorter reaction times than those reported in literature, so that the properties of the product depended solely on the process parameters, and the kind of powder produced can be rapidly changed by changing the teflon vessel [1, 19, 20, 36–38]. Particularly interesting is the possibility of doping nanopowders with rare earth ions in very high purity conditions ensured in the reactor heated by means of microwaves, in a pure teflon vessel, without any contamination sources. The present study is one of the first in a series of planned works on application of microwave-driven hydrothermal reactors for the synthesis of doped nanopowders.

## 2. EXPERIMENTAL METHODS

### 2.1. Sample preparation

$\text{ZrO}_2$  powders containing 1 mol% praseodymium were obtained through the addition of praseodymium (III) nitrate  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  to 0.5 M  $\text{ZrOCl}_2$  aqueous solutions. The solutions were neutralized with 1 M NaOH to  $\text{pH} = 10$  and were poured in a PTFE reaction vessel of the MW reactor. The MW reactor (produced by “ERTEC,” Wroclaw, Poland) working at 2.45 GHz delivers a maximum unpulsed power of 270 W to a fluid volume of 70 mL, hence the delivered power density reaches 4 W/mL. The system can be operated at a maximum autogenous pressure of 12 MPa closed vessel. The design of the reactor is schematically shown in Figure 1. The time, pressure, and power, are computer-controlled and a typical run is given in Figure 2. In the present experiments, the feedback signal was delivered to the control system by the pressure gauge. A thermocouple is situated outside the reaction vessel and displays the temperature change with a delay of about 100 seconds, and for this reason is of limited use as a feedback signal for short processes. The reaction temperature was calculated from p/T diagram of water so only pressure was controlled during the process and kept constant at

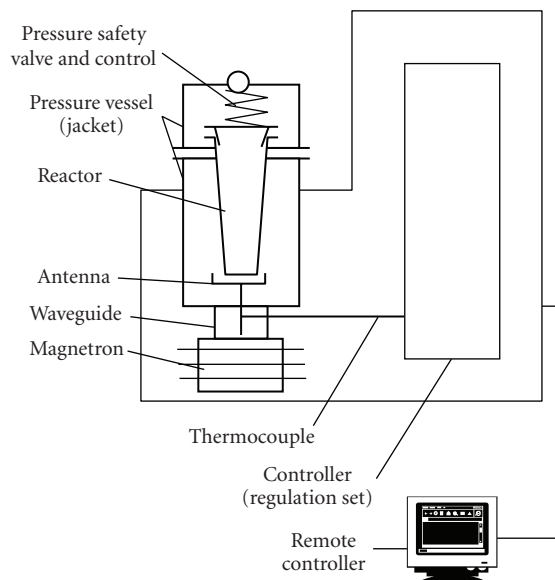


FIGURE 1: Scheme of the MW reactor.

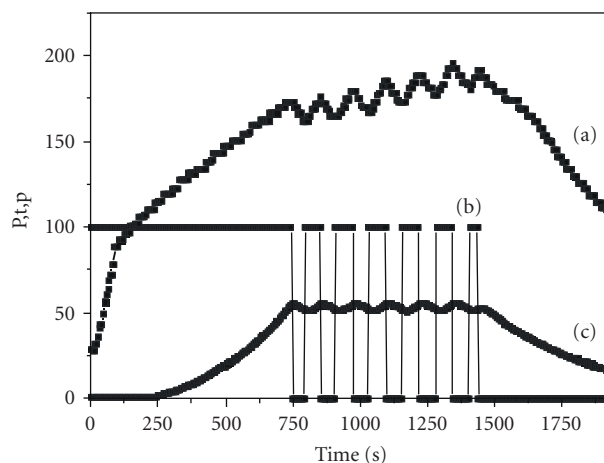


FIGURE 2: The chart of typical reaction with pressure kept as the control parameter. Curves are for (a) temperature, (b) power, (c) pressure.

seven different pressures from 2 to 8 MPa with an accuracy of 0.5 MPa, which corresponds to temperature range 215–305 °C. The overall reaction time was 40 minutes, heating for 30 minutes and cooling time was 10 minutes. The reproducibility of the process was tested by repeating the synthesis at 5 MPa six times and simultaneous measurements of grain size and phase composition of the powders by XRD method.

After syntheses, the powders were centrifuged, washed, and dried prior to their characterization.

### 2.2. Characterization of samples

For all the powders, thermogravimetric analysis (TGA) was performed (using a Netzsch STA 402, Selbs, Germany). The

sample weight was approximately 100 mg and the sample was dried in the air at room temperature before analyses. The density of the powders was measured using helium picnometry (Model AccuPyc 1330, Micromeritics Instruments, Norcross, Ga, USA). The density measurement procedure was as follows: the powders were flushed in a helium atmosphere for 120 minutes at a temperature of 200°C, weighted, and transferred to the helium picnometer. The results of density measurements could be influenced by air absorbed at the surface of the nanopowders. Therefore, the measurements were repeated up to 100 times, and the density as a function of number of cycles was determined. The process was interrupted when the results reached an asymptotic value which was considered as the result of the measurement.

The X-ray diffraction (XRD) patterns were collected in  $2\Theta$  range of  $20^\circ$ – $90^\circ$  at room temperature, with a step of  $0.05^\circ$  using an X-ray ( $\text{CuK}\alpha$ ) diffractometer (Model D5000, Siemens, Germany). The grain-size distributions (GSDs) were determined using a newly developed method of XRD peak fine structure analysis of polydispersed powders (XRD-GSD) [39, 40]. This method permits to fit the peaks using an analytical function with fitting parameters: average particle diameter  $\langle R \rangle$  and dispersion of particle sizes  $\sigma$  as fitting parameters. The ratio of the volume fraction of the monoclinic and tetragonal phases was determined by measuring the peaks area belonging to the respective phases. In order to compare phase-specific (T/M) GSD measurements to the grain-size readings from other methods (e.g., BET), joint T and M grain size was calculated as weighted average of T and M phases. For comparison, the well-known Scherrer method for average crystallite diameter evaluation was applied [41].

The specific surface area analysis was conducted by means of the multipoint BET method (Gemini 2360, Micromeritics Instruments, Norcross, Ga, USA), using nitrogen as an adsorbate. Based on BET data, the particle size was calculated, assuming that the particles are spherical, using the equation

$$\phi = \frac{6}{S\rho}, \quad (1)$$

where  $\phi$  (m) is the average diameter of a spherical particle,  $S$  ( $\text{m}^2/\text{g}$ ) is specific surface area of powder, and  $\rho$  ( $\text{g}/\text{m}^3$ ) the density value of crystalline zirconia ( $5.6 \times 10^6 \text{ g}/\text{m}^3$ ).

In addition to the grain size calculated assuming spherical particles, (2) permits to calculate the average chord crossing the particles without any assumption on their shape [42]:

$$\langle l \rangle = \frac{2}{S_v}, \quad (2)$$

where  $\langle l \rangle$  is the average chord and  $S_v$  is the relative surface [1]. Finally, for comparison, the well-known Scherrer method for average crystallite diameter evaluation was applied [41].

### 3. RESULTS

The weight-loss curve can be divided into two stages. (1) From room temperature up to 200°C, the weight loss is at-

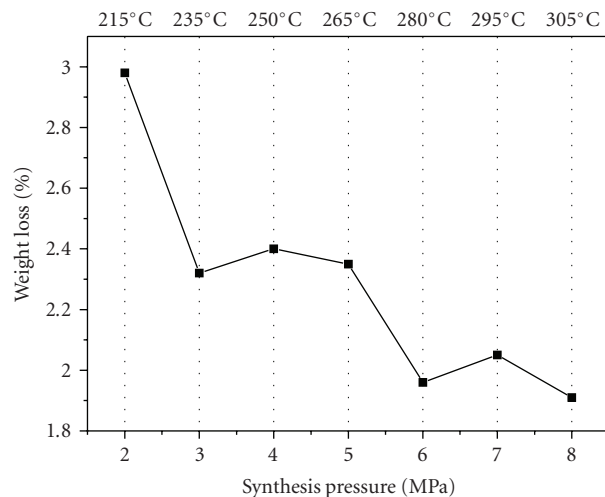


FIGURE 3: Weight loss of the powders in the temperature range 200–700°C as a function of synthesis pressure.

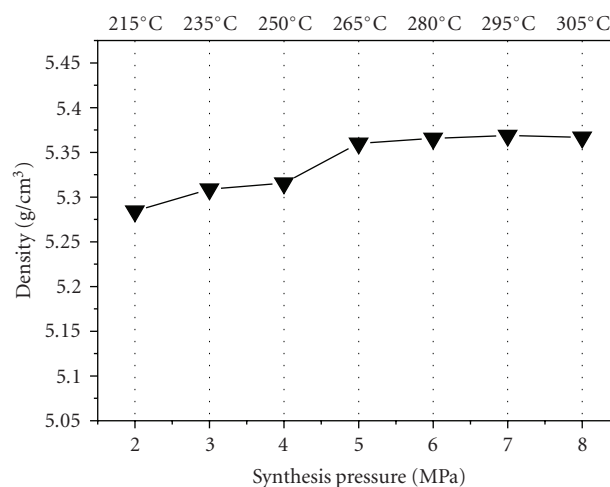


FIGURE 4: Density of nanopowders as a function of synthesis pressure.

tributed to evaporation of water absorbed on the powders surface. (2) In the range 200–700°C, the loss is attributed to transformation of hydroxide that remained after synthesis into oxide [43]. It is important to notice how the overall weight loss in the range 200–700°C decreases when the synthesis pressure increases (Figure 3). The weight loss in the range 2.3–3.0% above 200°C for powders synthesized under pressure up to 5 MPa indicated a high content of hydroxides. The decrease in weight loss correlates well with the increase of density of the nanopowders as the synthesis pressure is increased (Figure 4), and again a threshold pressure of 5 MPa is observed above which the density reaches 95% of the density of a single crystal.

Figure 5(a) shows X-ray diffraction patterns of  $\text{ZrO}_2$  doped with 1% of Pr synthesized at seven different pressures. No peaks belonging to phases other than  $\text{ZrO}_2$  phases have

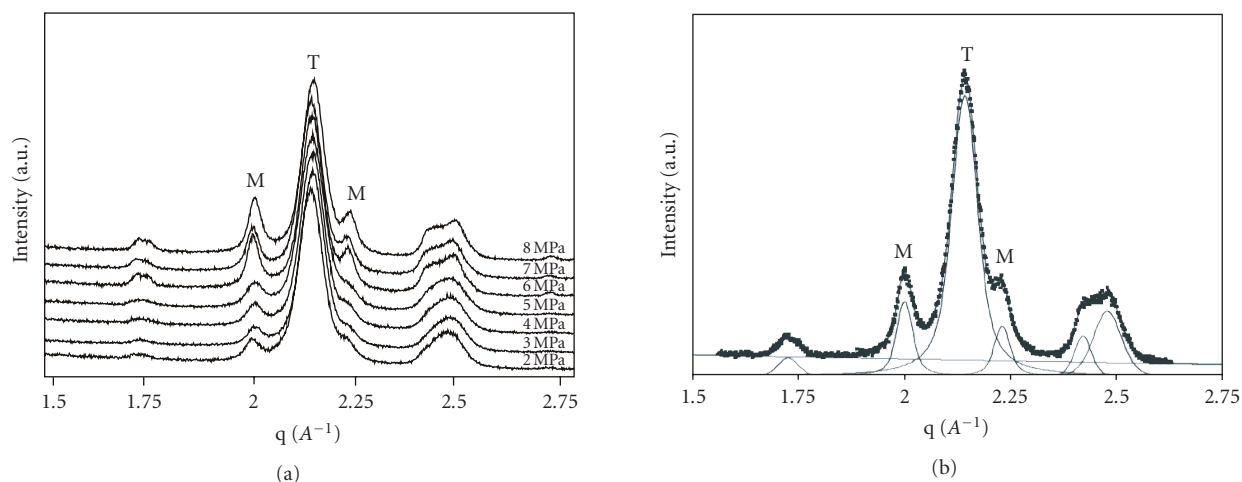


FIGURE 5: (a) X-ray diffraction patterns of Pr-doped  $\text{ZrO}_2$  powders synthesized at pressures in the range 2–8 MPa. The diffraction peak from the tetragonal phase is indicated by “T” and from the monoclinic phase by “M,” respectively. (b) Example of simultaneous evaluation of phase composition and grain-size distribution (GSD) by analysis of the peak profiles.

been recognized. Figure 5(b) shows an example of evaluation of the GSD by analysis of the fine structure of the X-ray peak profile.

The average grain size  $\langle R \rangle$ , dispersions of sizes  $\sigma$ , and contents of monoclinic/tetragonal phases derived by analysis of the peak profile are given in Tables 1 and 2. In particular, Figure 6(a) shows the average grain size as a function of synthesis pressure obtained by means of Scherrer’s method, specific surface measurements, and XRD-GSD data. Figure 6(b) shows the average size estimated from XRD line profile analysis, for monoclinic and tetragonal crystalline phases separately.

The error in grain size measured based on XRD investigations has been estimated as a result of 6 subsequent synthesis at 5 MPa. The standard deviations were 1.0 nm for monoclinic and 0.3 nm, respectively, for tetragonal phase. The volume fraction of the tetragonal phase decreases from 89% for 2 MPa to 77% for 8 MPa (Figure 6(d) and Table 2).

Table 3 shows specific surface areas and derived particle-size parameters as well as the density of the powders.

#### 4. DISCUSSION

The present results confirmed the advantages of microwave heating during hydrothermal synthesis of nanocrystalline powders. Microwaves transmit the energy directly to the reaction media, thus shortening both the heating and cooling times, which saves energy on heating the thick walls used usually for a pressurized reaction vessel. For such reactors, thermal inertia forces to carry out the reaction for much longer time than it is needed for the reaction to be completed. In addition, the temperature control is more difficult than in low thermal inertia systems. Application of microwaves to heat the reagents during hydrothermal reac-

TABLE 1: Grain-size distribution parameters for  $\text{ZrO}_2$  1 mol% Pr nanopowders synthesized at pressures ranging from 2 to 8 MPa as measured by means of XRD. The values provided are the average ones from the given fraction of tetragonal and monoclinic phases, where the XRD-GSD parameters were obtained for each phase separately.

Synthesis pressure/ temperature (MPa/°C)	XRD (both phases)	
	$\langle R \rangle$ (nm)	$\sigma$ (nm)
2/215	$13.7 \pm 1.2$	$2.5 \pm 0.6$
3/235	$14.2 \pm 1.0$	$1.9 \pm 0.3$
4/250	$14.2 \pm 1.0$	$1.4 \pm 0.3$
5/265	$13.6 \pm 1.0$	$1.1 \pm 0.3$
6/280	$16.6 \pm 1.3$	$3.0 \pm 0.6$
7/295	$16.2 \pm 1.2$	$2.2 \pm 0.4$
8/305	$16.7 \pm 1.2$	$3.2 \pm 0.6$

tion permitted to precisely control the process parameters: time and pressure, and ensure high purity of reaction conditions, since the substrates of the reaction were enclosed in a teflon vessel and had no contact with heating elements. The precise control of the synthesis pressure and time enabled to study the effects of the synthesis pressure on the phase composition and grains-size distribution of the nanopowders. In particular, it can be shown that there is a threshold pressure above which the quality of the powders (measured indirectly, by assessing their density and weight loss during thermogravimetric tests) may be significantly improved.

The TGA results indicate a low content of volatile phases for samples obtained at pressure above 5 MPa (Figure 3). The first stage of heating, from room temperature up to 200°C, is connected most likely with evaporation of water absorbed at the surface of the powders. Further weight loss in the temperature range 200–700°C (Figure 3) is most

TABLE 2: Grain-size distribution parameters for ZrO<sub>2</sub> 1 mol% Pr nanopowders synthesized at pressures ranging from 2 to 8 MPa as measured by means of XRD-GSD method applied separately to the monoclinic phase and tetragonal phase. Column “%” shows the volume fraction of the tetragonal or monoclinic phases.

Synthesis pressure/temperature (MPa/°C)	Monoclinic				Tetragonal			
	$\langle R \rangle$ (nm)	$\sigma$ (nm)	$\sigma/\langle R \rangle$	%	$\langle R \rangle$ (nm)	$\sigma$ (nm)	$\sigma/\langle R \rangle$	%
2/215	19 ± 5	9 ± 4	0.49	11	13.1 ± 0.6	1.8 ± 0.2	0.14	89
3/235	22 ± 5	4 ± 1	0.16	8	13.5 ± 0.6	1.8 ± 0.2	0.13	92
4/250	21 ± 5	4 ± 1	0.17	10	13.4 ± 0.6	1.2 ± 0.1	0.09	90
5/265	16 ± 3	6 ± 2	0.40	15	13.2 ± 0.6	0.2 ± 0.02	0.01	85
6/280	25 ± 3	7 ± 2	0.29	21	14.3 ± 0.7	1.8 ± 0.2	0.13	79
7/295	24 ± 3	6 ± 1	0.24	19	14.4 ± 0.7	1.4 ± 0.2	0.10	81
8/305	24 ± 3	7 ± 1	0.27	23	14.5 ± 0.7	2.3 ± 0.3	0.16	77

likely connected with decomposition of hydroxides that remained bound to the particles after the synthesis process [43]. The pressure of 5 MPa is a threshold, above which there are no much changes in weight loss of the powders. Therefore above this pressure of synthesis, a minimum of hydroxides content in the reaction product was achieved.

Also the powder density increases with synthesis pressure from 5.28 g/cm<sup>3</sup> for powder produced at pressure of 2 MPa to 5.37 g/cm<sup>3</sup> for powder produced at a pressure of 8 MPa (Figure 4), that is, 95.3% of that of microcrystalline ZrO<sub>2</sub>, which is 5.6 g/cm<sup>3</sup>. An additional result of the present study is that measurements of density of nanopowders using helium pycnometry are a simple tool for characterizing their quality, provided that proper measurement procedures are applied.

The average grain size increases when synthesis pressure is increased (Figure 6(a)). For sake of comparison, the results of particle-size evaluation using three different methods (BET, Scherrer’s, and XRD-GSD) are reported in a single plot (Figure 6(a)). Using Scherrer’s formula or specific surface measurements give values on the average 5 and 3 nm smaller for the average grain size than the XRD-GSD method. This result indicates that application of Scherrer’s formula or BET method to powders with a wide or bimodal gain size distribution may lead to considerable errors.

The XRD-GSD analysis permitted us to get insight in the grain growth of the tetragonal and monoclinic phases separately (Figure 6(b)). The average grain size of the monoclinic phase drops from about 20 nm to 16 nm at 5 MPa, and then increases to 24–26 nm for synthesis pressures above 6 MPa. The average grain size of the tetragonal phase remains below 14 nm for all the pressures of synthesis applied.

The volume fraction of the monoclinic phase increases with synthesis pressure from 11% for 2 MPa to 23% for 8 MPa (Figure 6(d)).

The GSD of the tetragonal phase is relatively independent of the time and pressure of synthesis. On the other hand, the GSD for the monoclinic phase and its coefficient of variation  $C_v$  ( $\sigma/\langle R \rangle$ ) are very sensitive for the conditions of synthesis. In our previous work [40, 44], we have found that the coefficient of variation is a fingerprint of the synthesis mechanism. Therefore the synthesis or growth mechanism of the two phases must be different, and for the monoclinic phase it depends on synthesis pressure. Figure 6 shows an apparent drop of grain size of zirconia grain with the monoclinic phase, but this drop is within the experimental error (see error bars).

The average grain size and grain-size dispersion of the tetragonal phase are relatively independent of synthesis pressure (the variations are in the range of 2 nm), while that of the monoclinic phase is affected by the synthesis pressure (variations in the range 10 nm). The observed behavior of the GSD functions of the two phases can be interpreted as follows (Figure 7). The two phases nucleate in parallel at pressures about 2 MPa (temperature about 215°C). With further increase of pressure of synthesis, the average grain size of the monoclinic phase as well as its dispersion increase more rapidly, while there is an upper limit for the grain size of the tetragonal phase at about 20 nm. This evolution of GSD leads to a bimodal grain-size distribution.

The synthesis pressure range 5-6 MPa is crucial for the quality of the powders. Above 6 GPa, the density of the powders reaches 95% of the density of ZrO<sub>2</sub> and stabilizes. At the same time, the results of the thermogravimetric studies show a low weight loss of powders produced above 5 MPa pressure, that is, above 265°C. These results indicate that for hydrothermal synthesis of zirconia nanopowders below these pressures or temperatures, a high fraction of hydroxide phase is expected to be present. Such a third phase may influence phase equilibria, stabilizes the monoclinic phase below grain sizes of 10 nm, and leads to deviations between experimental



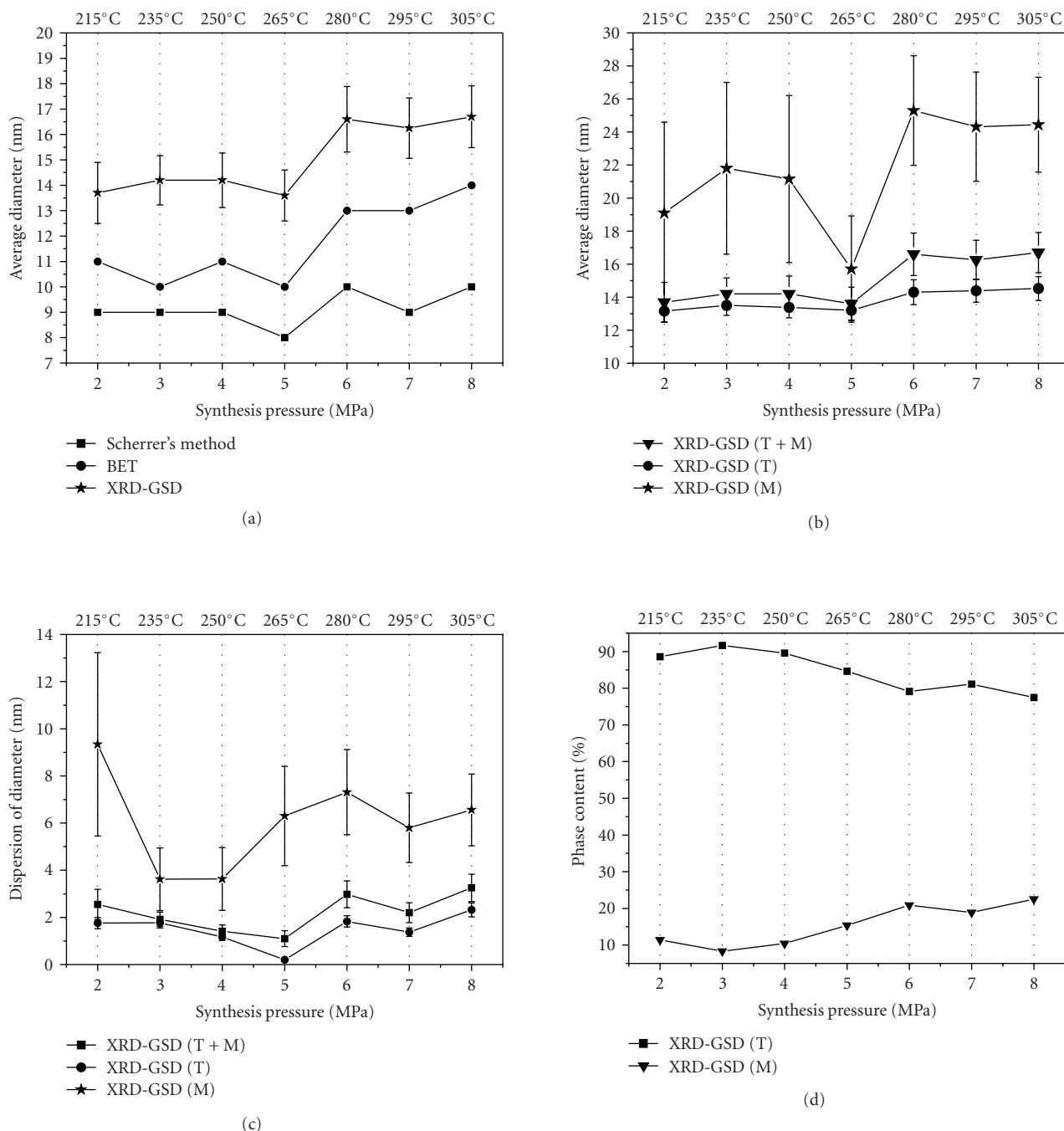


FIGURE 6: (a) Average size of nanopowders (both phases) as a function of pressure as measured using three methods indicated in the figure. (b) Average size of monoclinic (M) and tetragonal (T) phases evaluated from XRD line profile analysis. (c) Dispersion of the GSD as a function of synthesis pressure for M and T phases. (d) Phase content of the powders synthesized.

results and theoretical predictions on the stability of the two phases.

## 5. CONCLUSIONS

Microwave-driven hydrothermal synthesis permits to precisely control the time, pressure, and temperature during the

synthesis of zirconia nanopowders and to perform the reactions in high purity conditions. The high power density achieved during synthesis, which reaches 4 W/mL, permits to shorten synthesis time to 15 minutes.

The pressure/temperature of 5 MPa/265°C is a threshold where the zirconia powders reached a high density indicating a fairly perfect crystalline structure.

TABLE 3: Density and specific surface area measured by BET method and evaluation of the average particle diameter  $\langle\phi\rangle$  and chord  $\langle l\rangle$ .

Synthesis pressure/ temperature (MPa/°C)	Density (g/cm <sup>3</sup> )	Specific surface area by BET method (m <sup>2</sup> /g)	Grain size calculated from specific surface area	
			Average diameter $\langle\phi\rangle$ (nm)	Average chord $\langle l\rangle$ (nm)
2/215	5.284	101	11	1.9
3/235	5.309	102	10	1.9
4/250	5.315	101	11	2.0
5/265	5.360	103	10	1.9
6/280	5.366	83	13	2.4
7/295	5.369	85	13	2.3
8/305	5.367	78	14	2.5

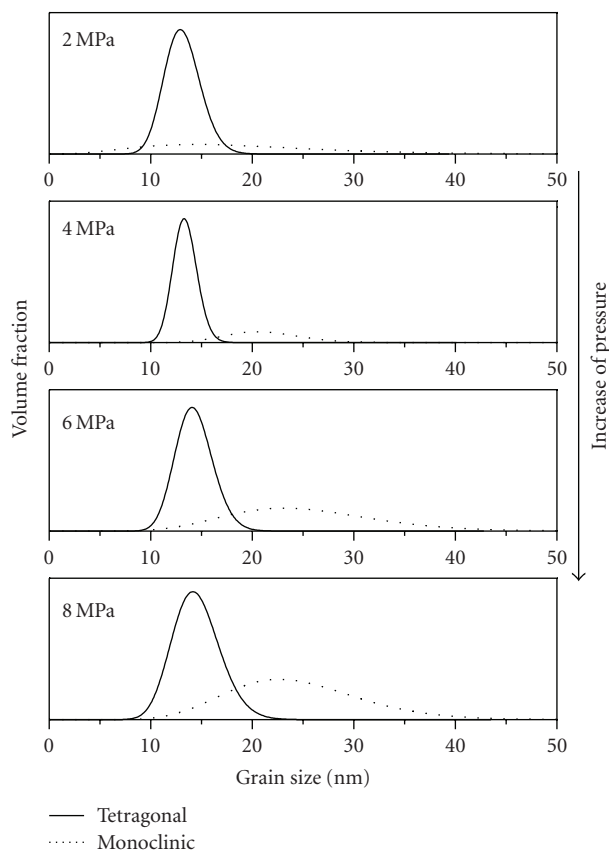


FIGURE 7: Model of the grain-size distribution changes for the monoclinic and tetragonal phases with increasing pressure.

Measurements of density of nanopowders using helium pycnometry is a convenient method for determination of the quality of the powders.

The XRD-GSD analysis permitted us to get insight into the grain growth of the tetragonal and monoclinic phases separately. The two phases are nucleated in parallel at less than 2 MPa synthesis pressure. Presence of hydroxides should be taken into account when discussing phase equilibria, grain-growth mechanisms, and properties of zirconia produced hydrothermally at pressures below 5 MPa.

## ACKNOWLEDGMENTS

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