

Zirconia Based Nanomaterials for Oxygen Sensors – Generation, Characterisation and Optical Properties

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Abstract: Microwave driven hydrothermal synthesis and hydrothermal synthesis were used to obtain ZrO₂ nanopowders. Their production with varying phase composition, the characterisation and selected optical properties concerning their potential use as luminescence oxygen sensors are reported. It was found that the powders obtained by the microwave driven hydrothermal method and annealed at 750 °C in air show experiment repeatability within an accuracy of 6 %.

Introduction

Oxygen, which first appeared in significant quantities on Earth during the Paleoproterozoic era (between 2.5 and 1.6 billion years ago) as a product of the metabolic action of early anaerobes (archaea and bacteria) [1], is the most important gas in the environment. It is a component or product of many reactions occurring in nature and industry. For people's health and life protection it is important to measure the oxygen saturation in other gasses. It has been shown that the luminescence intensity of ZrO₂ nanocrystals depends on the temperature during heating and cooling in vacuum [2]. It was assumed that the oxygen content in ZrO₂ nanocrystals changes the luminescence intensity. Since the oxygen exchange between a nanocrystal and the surrounding media occurs from surfaces, which is nanocrystal size dependent. It is known [3] that the luminescence of nanocrystalline ZrO₂ annealed in oxygen and nitrogen mixtures depends on the oxygen partial pressure. It is hoped that the effect can be used in optical oxygen pressure sensors.

The main purpose of the work is to select the technology to produce appropriate ZrO₂ luminescent powder for intended use as an oxygen detector. It is known that the hydrothermal and microwave driven hydrothermal synthesis enables precise control of the time, pressure and temperature during the synthesis of zirconia nanopowders and the reactions to be performed in high purity conditions [4, 5]. In this work the density, specific surface area, phase composition and grain size distribution, morphology and luminescence properties of the synthesized ZrO₂ nanopowders were analyzed. Important parameters such as the accuracy of luminescence repeatability were determined.

Experimental

Microwave driven hydrothermal synthesis of ZrO₂ nanopowder The precursor solution was prepared by dissolution of pure zirconium (IV) oxide chloride octahydrate (ZrOCl₂·8H₂O) min. 99.5% produced by Riedel-de Haen (Germany) into distilled water and adjusted to pH=10 by 1M sodium hydroxide (NaOH) min. 98.8% purchased from CHEMPUR (Poland). The solution was poured into a 110 ml polytetrafluoroethylene (PTFE) vessel and ZrO₂ was synthesized in the microwave (MW) ERTEC reactor at Wroclaw, Poland, under a pressure of 6 MPa (accuracy – 0.5

MPa) at 270 °C (calculated from p/T diagram for water). The overall reaction time was 30 min, heating for 20 min and cooling for 10min. The precipitates obtained after microwave-hydrothermal treatment were filtered, washed with distiller water to remove the soluble chlorides followed by izopropanol to reduce agglomeration and then dried at 90°C in air for 24 hours and ground. Some parameters were determined for this powder prior to heating it to 750 °C in air, holding at 750 °C for 30 minutes and subsequent cooling. One run produced approximately 2g of ZrO₂ nanopowder.

Hydrothermal synthesis of ZrO₂ nanopowder. The precursor solution was prepared by diluting analytically tested zirconium chloride (ZrOCl₂) (Zr= 106,60 g/l, H⁺= 2,34 g/l) in distilled water and adjusting the pH to 9 with an aqueous solution of 25% NH₄OH (S.C. MICROMCHIM SRL, Bucharest). This solution was poured into a Teflon Parr autoclave (Bucharest, Romania), with a volume of 1300 ml, and synthesized in the furnace for 2 hours at 230°C (before proper synthesis one hour was needed to stabilise the temperature). The precipitates obtained after hydrothermal treatment were filtered, washed with distiller water to remove the soluble chlorides and with ethanol to reduce agglomeration and then air dried at 100°C for 24 hours and then ground. A similar procedure to that for microwave driven hydrothermal synthesised powder was prepared, except for heating at 600 °C. One run produced approximately 8g of ZrO₂ nanopowder.

Annealing of ZrO₂ nanopowder under different oxygen partial pressures. Both ZrO₂ nanopowders obtained were placed in quartz tubes from which the air was evacuated. The tubes was filled with mixtures of oxygen and nitrogen and heated to 340°C, for 15 minutes, cooled to room temperature and opened. The individual stages of powder treatment are presented in Figure 1.

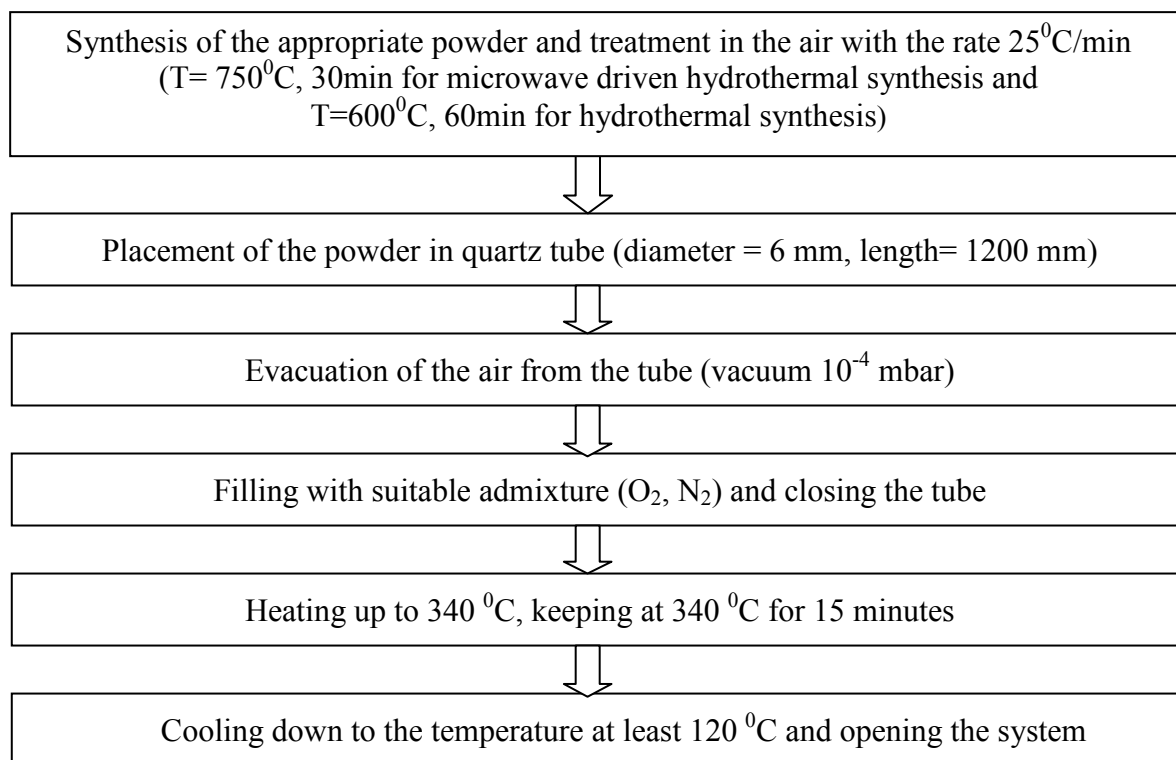


Figure 1 . Scheme of the ZrO₂ nanopowders annealed at different gases admixture (O₂, N₂)

Characterisation

The density of the nanopowders was measured by helium picnometry using a AccuPyc 1330, produced by Micrometrics Instruments, Norcross, GA, U.S.A. X-ray diffraction (XRD) patterns were collected in the 2 theta range of 10 – 100° at room temperature, with a step of 0.05° using a Siemens, Germany, D5000 X-ray diffractometer employing CuK_{α1} radiation. The Grain Size Distributions (GSD) were determined using a newly developed method of XRD peak fine structure analysis of polydispersed powders (XRD-GSD) [6]. This method permits fitting the peaks using an analytical function using: average particle diameter <R> and dispersion of particle sizes σ as the fitting parameters. The ratio of the volume fraction of the dispersion of monoclinic and tetragonal phases was determined by measuring the peak area of the respective phases. The specific surface area analysis was determined by the multipoint B.E.T. method (Gemini 2360, Micromeritics Instruments, Norcross, GA, USA), using nitrogen as an adsorbate. Based on the B.E.T., data the particle size was calculated, assuming spherical particles, using the equation:

$$\phi = (6/S\rho), \quad (1)$$

where ϕ (in m) is the average diameter of a spherical particle, S [m²/g] is the specific BET surface area of powder and ρ [g/m³] the density value of crystalline zirconia (5.6*10⁶ g/m³). For comparison the Scherrer's method for average crystalline diameter evaluation was applied [7]. The powder morphology was determined from high resolution SEM images, using a LEO 1530 field emission scanning microscope. The study of spectra and the decay of luminescence were performed using pulsed laser excitation (4,66 eV, < 8, ns) at room temperature. Registration carried out by PMT (HAMAMATSU H8259) and a photon counting board (Fast ComTec Communication Technology module P 7888-1E). The time resolution was down to 2 ns.

Results and discussions

Density. The nanopowders produced by hydrothermal method (Hy) showed low density, about 82% of theoretical value, since the Zr content in the oxides was too low with respect to the content in hydroxides. In the case of ZrO₂ nanopowders produced by microwave driven hydrothermal method (MWHy) the density was about 90% of the theoretical value. However, for luminescence experiments, a grain size of above 20nm for the monoclinic and tetragonal phases was necessary. This shows the importance of carrying out nanopowder annealing at sufficiently high temperatures. It is well known that in the range 200-700°C the transformation of the remaining hydroxide into oxide take place causing a loss of powder mass [8]. The powder obtained by hydrothermal method was annealed at 600 °C, since this temperature enabled fine crystalline powder to be obtained and at below the temperature at which a tetragonal structure is metastable. In order to obtain monoclinic ZrO₂ nanopowder the thermal treatment of ZrO₂ obtained by MWHy was conducted at 750°C. The results of density determination for both powders are given in Table 1.

Synthesis and sample name	Density, [g/cm ³]	Percentage of theoretical density [%]	Specific surface area by B.E.T. method [m ² /g]	Grain size calculated from specific surface area
				Average diameter ϕ [nm]
MW Hy ZrO ₂	5.59 ± 0.05	99,75 ± 0.89	21.3	50.4
Hy ZrO ₂	5.53 ± 0.04	98.68 ± 0.71	55.9	19.4

Table 1. Density and specific surface area measured by B.E.T. and average particle diameter ϕ.

XRD. Figure 1 shows the X-ray diffraction patterns of ZrO₂ powders synthesised by the two different methods. No peaks belonging to phases other than ZrO₂ have been identified. The X-ray

diffraction pattern for the powder obtained by the MWHy method displayed only peaks generated by the monoclinic phase while Hy produced powder showed peaks belonging to the monoclinic and tetragonal phases.

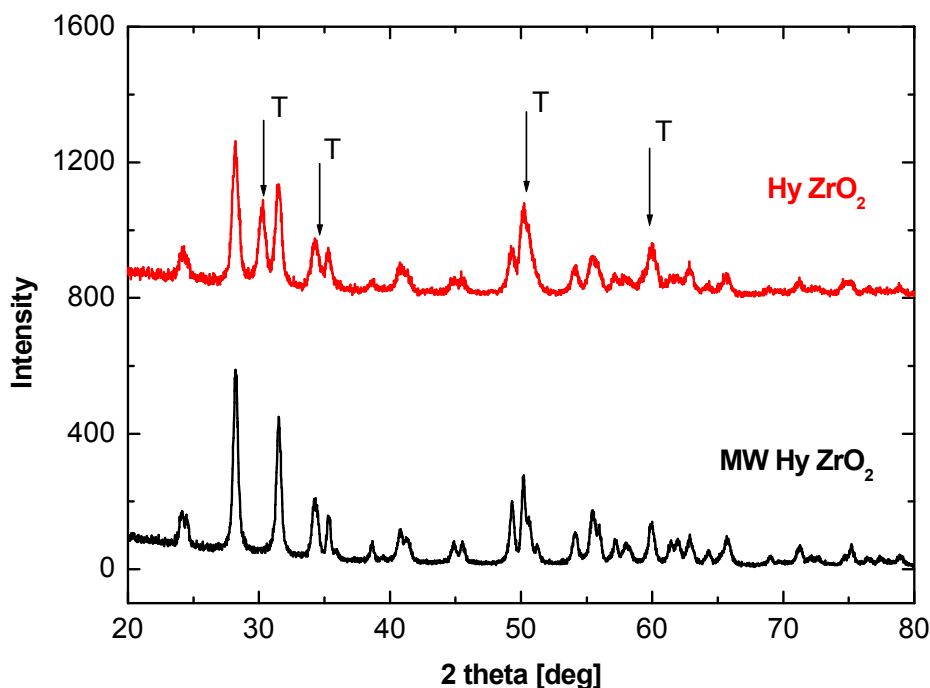


Figure 1: X-ray diffraction patterns of ZrO_2 nanopowders obtained by microwave driven hydrothermal synthesis and annealed at $750^\circ C$ for 30min (MWHy ZrO_2) and hydrothermal synthesis and annealed at 600° for 60 min. (Hy ZrO_2). Tetragonal structure peaks are indicated with arrows.

The average grain size $\langle R \rangle$ dispersion of sizes, σ , and the content of monoclinic and tetragonal phases derived by analysis of the peak profile (GSD by analysis of the fine structure of the X-ray peak) is given in Table 2.

Synthesis Name/ Temperature [$^\circ C$]	Monoclinic				Tetragonal			
	$\langle R \rangle$ [nm]	σ [nm]	$\sigma/\langle R \rangle$	%	$\langle R \rangle$ [nm]	σ [nm]	$\sigma/\langle R \rangle$	%
MW Hy ZrO_2 / 750	31	3.8	0.12	100	-	-	-	-
Hy ZrO_2 / 600	23.5	0.6	0.02	75	21.4	1.2	0.06	25

Table 2. Grain Size Distribution parameters for ZrO_2 nanopowders synthesized by the microwave driven hydrothermal method and the hydrothermal method as measured by means of the XRD-GSD method applied separately to the monoclinic and tetragonal phases. Column “%” shows the volume fraction of the tetragonal or monoclinic phases.

The average grain size $\langle R \rangle$ for Hy ZrO_2 powder was 23.5 nm for the monoclinic and 21.4 nm for the tetragonal phase, while the standard deviations were 0.6 nm and 1.2 nm, respectively. The MW Hy ZrO_2 monoclinic powder had an average grain size of 31 nm with a standard deviation 3.8 nm.

Figure 2 compares the volume fraction of tetragonal/monoclinic phases given by the GSD evaluation from the XRD data. In both cases a narrow grain size distribution range is observed.

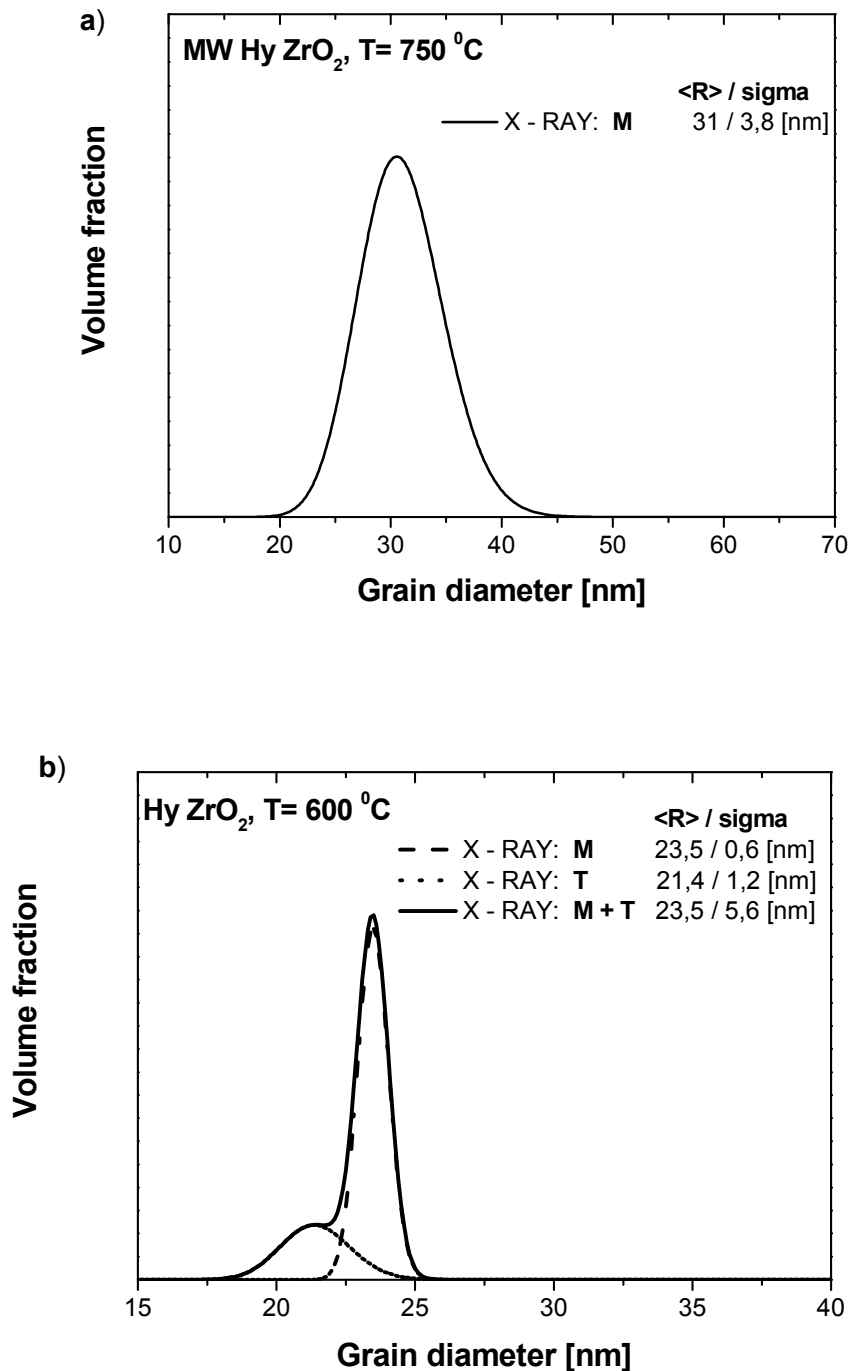


Figure 2. GSD of the ZrO₂ nanopowders obtained from analysis of the XRD data. M-Monoclinic, T-Tetragonal phases. $\langle R \rangle$ stands for average grain size, σ – for distribution of sizes, a) microwave driven hydrothermal synthesis; b) hydrothermal synthesis.

BET. The BET results shown that the largest specific surface area was possessed by the powders obtained by hydrothermal synthesis (55.8762 m²/g). The grain size for the Hy ZrO₂ powder calculated from specific surface areas is in good agreement with the average grain size obtained from XRD (Table 1).

SEM The high resolution SEM) was used to characterize the nanoparticles morphology. Fig 3. shows the morphology of ZrO_2 powders obtained by hydrothermal and microwave driven hydrothermal synthesis and heated at different temperatures. Very small particles are visible in both cases. Fig. 3a shows that the powder obtained by MWHy was less aggregated than that obtained by the Hy method.

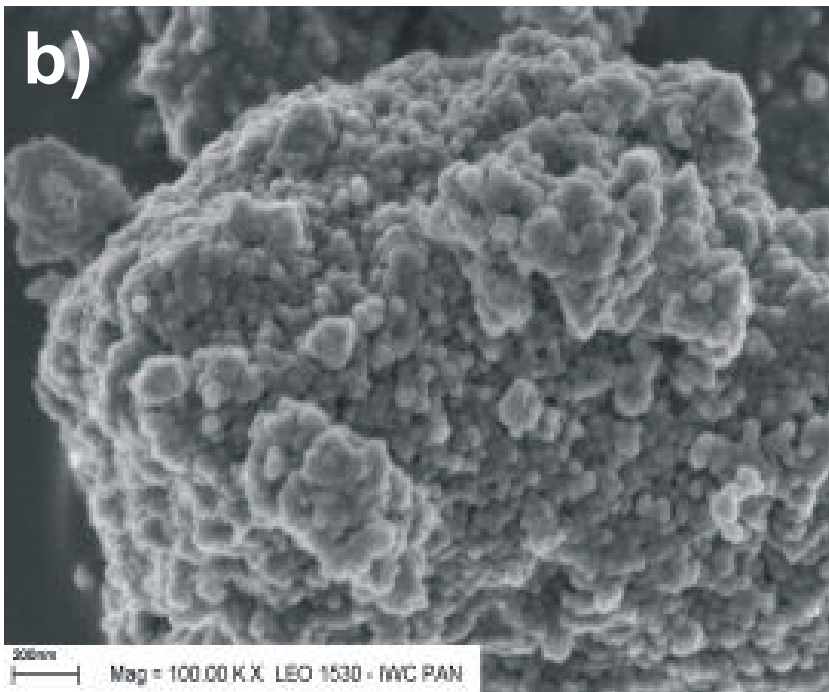
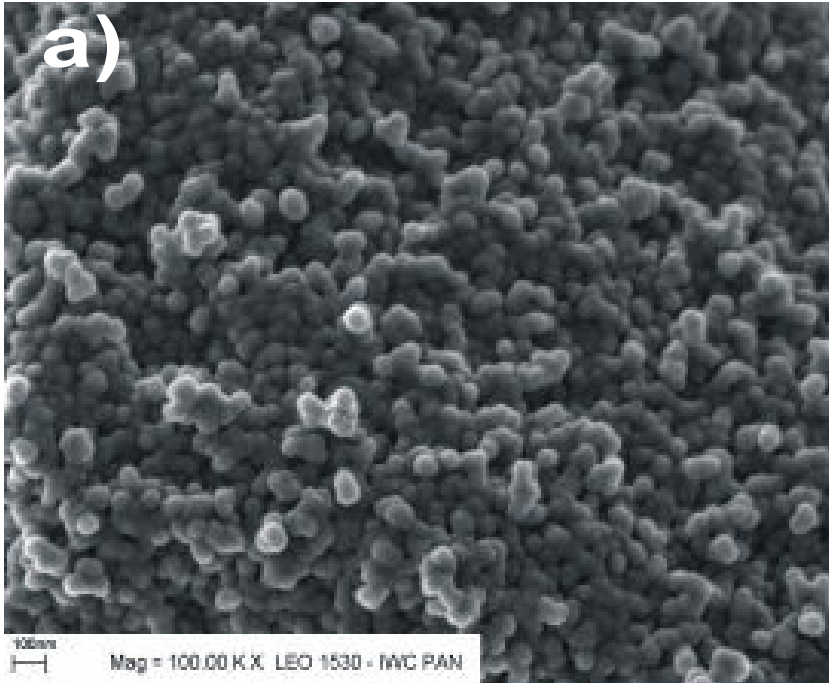


Figure 3: SEM pictures of nanoscaled ZrO_2 obtained by a) microwave driven hydrothermal synthesis (annealed at $750^{\circ}C$, 30min) and b) hydrothermal synthesis (annealed at $600^{\circ}C$, 60min).

Results of ZrO_2 luminescence intensity repeatability after cycling in different gas mixtures.

These experiments were carried out to determine the luminescence dependence on the oxygen content in the samples after multifold heating and cooling in different concentrations oxygen – nitrogen gas mixtures.

Two sets of the samples were analysed. The first being for powders obtained by MWHy while second was for those obtained by Hy. Individual sample descriptions of both sets are presented in Table 3.

Sample from microwave driven hydrothermal synthesis (MW Hy)	
Name	Description
MW Hy ZrO ₂ (1)	ZrO ₂ nanopowder annealed at 310 ⁰ C in the air and than in the admixture of 8%O ₂ and 92%N ₂
MW Hy ZrO ₂ (2)	The powder MW Hy ZrO ₂ (1) in sequence heated at 310 ⁰ C in the following admixtures of the gases: a) 23.4%O ₂ and 76.6%N ₂ ; b) 3.62%O ₂ and 96,38N ₂ ; c) 8%O ₂ and 92%N ₂
Samples from hydrothermal synthesis (Hy)	
Name	Description
Hy ZrO ₂ (1)	The powder annealed at 310 ⁰ C in the air
Hy ZrO ₂ (2)	The powder Hy ZrO ₂ (1) annealed at 310 ⁰ C in the admixture of 8%O ₂ and 92%N ₂
Hy ZrO ₂ (3)	The powder Hy ZrO ₂ (2) annealed at 310 ⁰ C in the admixture of 23.4%O ₂ and 76.6%N ₂
Hy ZrO ₂ (4)	The powder Hy ZrO ₂ (3) annealed at 310 ⁰ C in the admixture of 3.62%O ₂ and 96,38N ₂
Hy ZrO ₂ (5)	The powder Hy ZrO ₂ (4) annealed at 310 ⁰ C in the admixture of 8%O ₂ and 92%N ₂

Table 3: Overview of the samples used in the luminescence experiment

The samples MW Hy ZrO₂ (1) and MW Hy ZrO₂ (2) from the first set under laser excitation (cw, 266nm, RT) show the same spectra and close intensities of luminescence (see Fig.4).

However, the intensity of luminescence from sample MW Hy ZrO₂ (2) was somewhat lower than that from sample MW Hy ZrO₂ (1). Therefore two additional experiments were undertaken. In the first, sample MW Hy ZrO₂ (1) was placed once more in the camera and the luminescence spectrum was recorded. This experiment verifies the accuracy of the measured result if the samples in the chamber were changed, or if the same sample is placed in the chamber again. In other words - how accurately is it possible to restore the position of sample in the chamber. The result is presented in Fig. 4. From these data it can be deduced that the experiment repeatability is within an accuracy 6 % and the results from both samples are within this range. It was also established that after multifold heating in oxygen–nitrogen gas mixtures it was possible to return to the same luminescence intensity as after a single cycle.

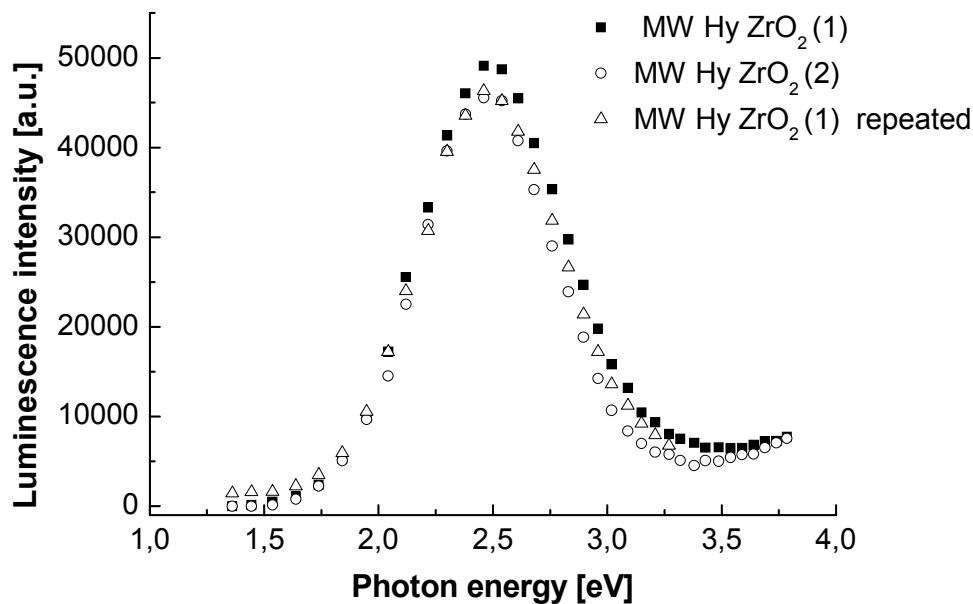


Fig.4. Luminescence spectra for samples annealed in gases mixtures.

The symbols are for different samples, the matching of the spectra is good, the squares and triangles are the same sample, if sample is removed and then replaced for a second run.

The second experiment showed how the intensity of luminescence changes during measurement. This experiment was undertaken for both samples. The 10 measurements were completed in 27 minutes, the measurement of intensity was made every 3 minutes. The results show the change of luminescence intensity was negligible during the measurement period, as shown in Figure 5.

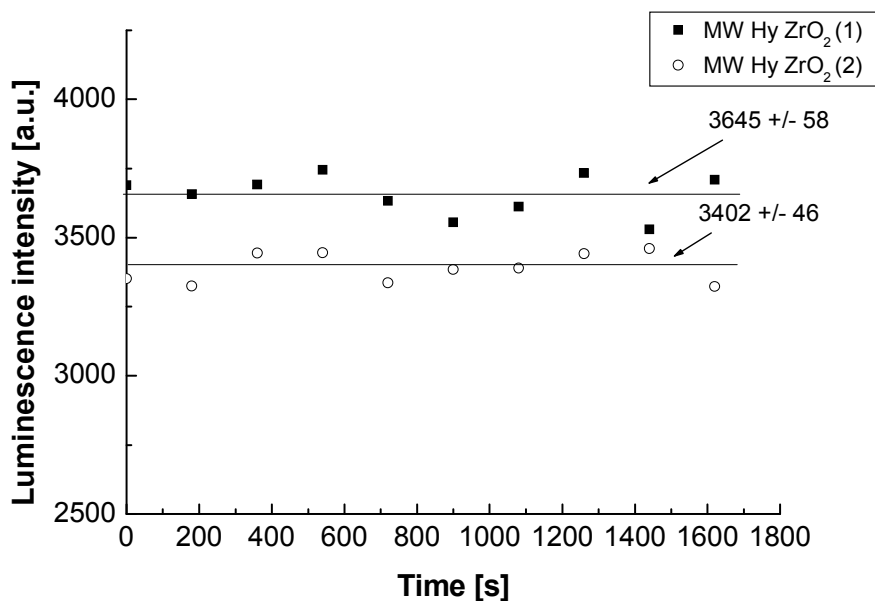


Fig. 5. Luminescence intensity dependence on time at 2.5 eV, the intensity units were not the same as in Fig.4., the intensity in Fig.5. is reduced by a factor 12.5 during the data treatment.

The lines in Fig. 5 represent the average values of luminescence intensity. The origin of small difference of luminescence intensities between samples MW Hy ZrO₂ (1) and MW Hy ZrO₂ (2) is

not clear, however the average difference (6.9%) is close to the repeatability accuracy in the case of samples changing (6%).

The samples from the second set (5 samples) shown rather different feature what is presented on the Figure 6.

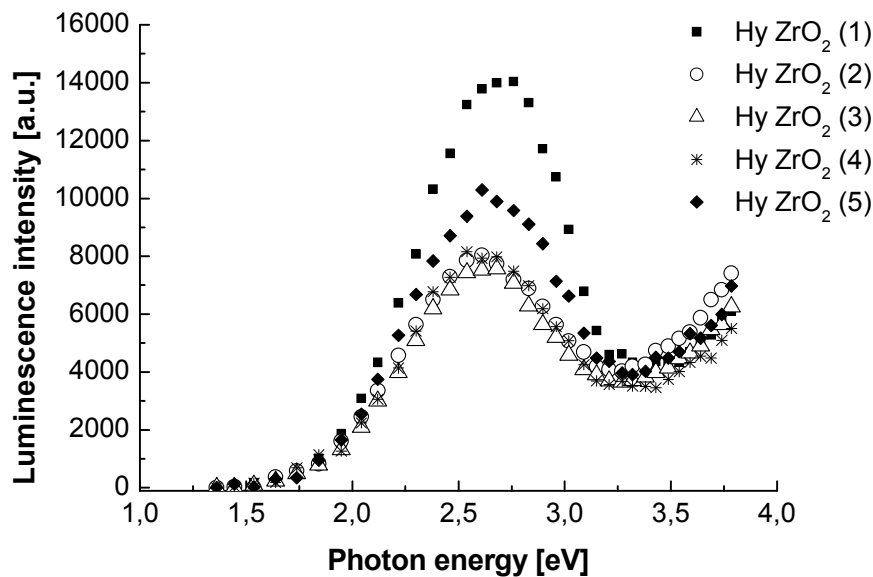


Fig.6. Luminescence spectra for the samples from Hy ZrO₂ (1) to Hy ZrO₂ (5).

It can be seen that the difference between luminescence intensities for sample Hy ZrO₂ (2) and Hy ZrO₂ (5) is at least 25%. The greatest intensity is for the sample treated in air.

The samples from the second set showed a luminescence spectra different from those of samples from the first set (Fig.6 and Fig.4). However all the spectra for samples within the second set have the similar shape. The main features are

:

1. The intensities of luminescence of all samples from set Hy ZrO₂ (1) - Hy ZrO₂ (5) were significantly lower than those from samples MW Hy ZrO₂ (1) and MW Hy ZrO₂ (2).
2. The maxima of luminescence spectra is at ~ 2,75 eV. The reason of the luminescence band shift is the complex nature of band – time-resolved luminescence study gave a strong witness that at least two overlapping bands contribute. One of these bands peaks within 2.1-2.4 eV, another within 2.6 – 2.9 eV. Therefore the resulting peak position depends on relative intensities of overlapping bands. It is observed that after heating in vacuum disappear band at 2,75 - 2,80 eV and another band peaking at 1,9-2,2 eV survive.
3. The sample Hy ZrO₂ (2) (annealed in 8% oxygen, 92% nitrogen) and sample Hy ZrO₂ (5) (after cyclic annealing in 8% oxygen, 92% nitrogen) show different intensities of luminescence (Fig.6) These differences were in the range 25% - 30% which is significantly greater than the scatter of results due to the repeatability of the samples position (Fig.4).

It should be noted the powders of these samples are a mixture of the monoclinic and tetragonal phases of ZrO₂.

Summary

Two important methods of ZrO₂ nanopowders synthesis have been demonstrated. The density, specific surface area, phase composition and grain size distribution, morphology and luminescence properties of the materials produced have been analysed. It can be assumed that the measurements of the density of the nanopowders using helium pycnometry provide a convenient assessment of the quality of the powders. Selected optical properties, important for the material's application in an oxygen sensor, are reported. The luminescent properties of the samples obtained by MW HY synthesis and by HY synthesis were not the same. Probably the differences follow from the different structures, phase compositions, degree of crystallinity etc. It was found that the powders obtained by microwave driven hydrothermal method and annealed in 750 °C in air shows an accuracy of experiment repeatability within a range of 6 %. Further investigation will attempt to determine which structure of the ZrO₂ powder is the most appropriate for application in a luminescence oxygen sensor.

Acknowledgements

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