

Preparation of $\text{ZrO}_2\text{:Tb}$ via microwave hydrothermal method

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Terbium doped zirconium dioxide was successfully synthesized using microwave hydrothermal method. The powder is strongly agglomerated and has mean crystallite size around 6 nm. The density of obtained powders is significantly lower than density of bulk zirconium dioxide indicating the existence of zirconium and dopant hydroxides remaining after the hydrothermal process. The effect of terbium on morphology, phase composition, specific surface area and density of the samples was determined.

Keywords: zirconia, terbium, microwave, hydrothermal.

1. Introduction

Zirconium dioxide is widely applied as ceramic material in gas sensors, solid oxide fuel cells and semiconductor devices. Luminescent properties make it usable in photonics. Zirconia has also attracted attention as a catalyst or catalyst support in many reactions.

At room temperature thermodynamically stable zirconium dioxide crystallizes in monoclinic system. With increasing temperature phase transitions occur [1]: monoclinic to tetragonal at 1170 °C and tetragonal to cubic, fluorite structure at 2370 °C. However, an increase of temperature is not necessary to carry out a phase transition. There are known many chemical routes to stabilize tetragonal or cubic ZrO_2 phase at room temperature, including doping with foreign ions, using specific solvent [2] or producing material with grains below critical size. Classic stabilizing ions are: Ca^{2+} , Mg^{2+} , La^{3+} and Y^{3+} . The influence of crystallite size on the properties of zirconium dioxide is reported in many papers [3–5]. There was also described stabilization influence of the surface of the nanostructures [6]. The size of crystallites

changes specific surface area as well as temperature of crystallization or temperature of phase transitions. Despite the fact that grains of zirconium dioxide below a certain size are tetragonal, there are a number of reports showing the possibility of producing monoclinic phase below the critical grain size [7]. Zirconium dioxide exhibits also high pressure orthorhombic structural polymorphs [8].

Zirconium dioxide can be synthesized in many ways, including sol–gel, precipitation–calcination, combustion, hydrothermal, and others [9]. Solvothermally produced ZrO_2 was described before many times [10]. The solvent is usually near-critical or supercritical water [11–13]. Microwave heating ensures fast increment and low gradient of temperature in the reaction mixture.

Rare earth ions doped zirconia exhibits luminous properties [14]. More complicated are systems with two or more kinds of rare earths in the zirconia matrix. Non-radiative energy transfer between dopant ions is the phenomenon allowing us to obtain material with increased emission efficiency. This occurrence was also discussed in other matrixes [15].

This work focuses on terbium doped zirconium dioxide – material of potential use as a light source. The aim of the work is to determine terbium influence on morphology, phase composition, specific surface area and density of the samples.

2. Experimental

2.1. Sample preparation

Three kinds of samples were prepared: zirconium dioxide doped with Tb^{3+} ions only, zirconium dioxide doped with Tb^{3+} and Tb^{4+} ions, zirconium dioxide doped with Tb^{3+} and Y^{3+} ions. The first step was preparation of particular ion solutions. In only Tb^{3+} containing samples, Tb^{3+} ions were introduced to solution by dissolving $\text{Tb}(\text{NO}_3)_3$ salt in water. Yttrium ions were introduced to solution by dissolving Y_2O_3 in concentrated nitric acid. In the case of both Tb^{3+} and Tb^{4+} ions Tb_4O_7 was dissolved in concentrated nitric acid. The source of zirconium was $\text{ZrO}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ – a salt well soluble in water. All the solutions prepared were transparent. The second step was a precipitation of hydroxides. The residue was obtained by rapid adding to the metals solution a 25% ammonia solution in water. Adding of NH_3 was finished when a final pH of 10 was reached. The pH value was controlled by pH-meter. The precipitation was conducted under continuous stirring at room temperature. All the residues were washed in water three times, then centrifuged to wash away nitrate and ammonium ions. The third step was the microwave hydrothermal process. Wet precipitates were mixed with 96% ethanol to the total volume of 80 cm^3 , then placed in the PTFE vessel of microwave hydrothermal reactor Ertec. All the processes were performed at a temperature of 533 K and pressure of 5.5 MPa. The time of the process under such T - p conditions was 20 minutes for all the samples. The power of microwaves was adjusted to 4 W/cm^3 . After the microwave process wet powders were washed three times in water and once in 2-propanol. All the powders were dried overnight at the room temperature. Concentration of terbium was 0.1, 0.5, 1, and 5 wt.% for all the series. Content of

yttrium was constant and maintained at the level of 6.6 wt.%. A pure zirconium dioxide sample was also prepared as a reference sample.

2.2. Characterization

Samples were characterized by a number of methods listed below.

X-ray diffraction measurements were conducted by X'Pert X-ray powder diffractometer with $Cu\ K\alpha$ radiation (1.54056 Å). Mean crystallite size (MCS) was calculated using Scherrer's formula. The raw data was processed using X'Pert Highscore software. SEM observations were performed with LEO 1530 scanning electron microscope. Multipoint BET measurements were performed using Micromeritics Gemini instrument. Density was measured using Micromeritics AccuPyc 1330 helium pycnometer.

3. Results and discussion

Diffraction patterns are shown in Fig. 1. The main phase component in all the samples is tetragonal ZrO_2 . Terbium doped samples (without yttrium) contain also a quantity of monoclinic ZrO_2 phase. It is clear that samples containing 0, 0.1, 0.5 and 1 wt.% of terbium contain monoclinic phase. In the 5 wt.% samples the reflections responsible for monoclinic phase are not seen, which suggests a full stabilisation of tetragonal phase. However, low grain size broadening of the peaks and high level of the background, makes this conclusion less accurate. Diffraction patterns of yttrium stabilized samples do not differ much from one another. These samples contain mainly tetragonal and/or cubic phase of zirconium dioxide and no other reflections can be seen.

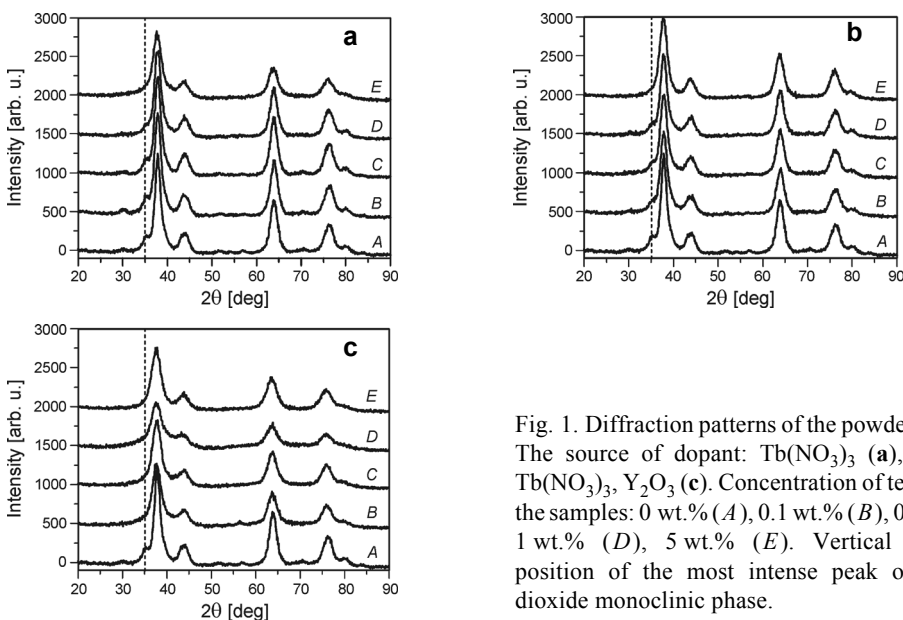


Fig. 1. Diffraction patterns of the powders obtained. The source of dopant: $Tb(NO_3)_3$ (a), Tb_4O_7 (b), $Tb(NO_3)_3, Y_2O_3$ (c). Concentration of terbium for all the samples: 0 wt.% (A), 0.1 wt.% (B), 0.5 wt.% (C), 1 wt.% (D), 5 wt.% (E). Vertical line shows position of the most intense peak of zirconium dioxide monoclinic phase.

Table. Mean crystallite sizes of obtained samples calculated using Scherrer's formula (MCS), compared to Φ values.

Source of dopant	Concentration of terbium [wt.%]	MCS [nm]	Φ [nm]
—	0	7	7
Tb(NO ₃) ₃	0.1	7	7
	0.5	6	7
	1	6	6
	5	5	5
	0.1	7	6
Tb ₄ O ₇	0.5	6	6
	1	6	6
	5	5	6
	0.1	5	5
Tb(NO ₃) ₃ , Y ₂ O ₃	0.5	5	5
	1	4	5
	5	4	5

Mean crystallite sizes are shown in the Table. Samples without yttrium contain grains with MCS of 5–7 nm and yttrium doped ones contain grains with MCS of 4–5 nm, then the difference is not significant. Another method of determining crystallite size, assuming that particles are spherical and of the same diameter, was the use of the formula:

$$\Phi = \frac{6}{SSA \cdot \rho}$$

where: Φ [m] – average size of spherical particle, SSA [m²/g] – specific surface area, ρ [g/m³] – density of material.

Both values MCS and Φ are in good agreement, as shown in the Table.

SEM images are shown in Fig. 2 and reveal complicated structure of the powders obtained. We can observe round or oval structures with average size of 20–60 nm, and since MCS of all the samples is below 10 nm, it can be concluded that these structures are agglomerates of individual grains of zirconium dioxide. The agglomerates are bound to each other creating large aggregated structures. The binding between agglomerates in large aggregate is rather weaker than between individual grains of zirconium dioxide. Grain boundaries between agglomerates are well seen in the images. We cannot observe other structures, concluding that the powder obtained is homogenous.

Density of the samples obtained is shown in Fig. 3. The density of bulk zirconia is 5.89 g/cm³. Samples without addition of yttrium have density around 4.9 g/cm³. Lower value indicates that some unreacted zirconium hydroxide is present in

the samples and that the contribution of surface, in the case of structure of the grain with average size as low as 6 nm, to density is very high. However, additional investigations have to be performed to get more detailed information related to grain surface and boundaries. Diffraction patterns show no reflections originated from

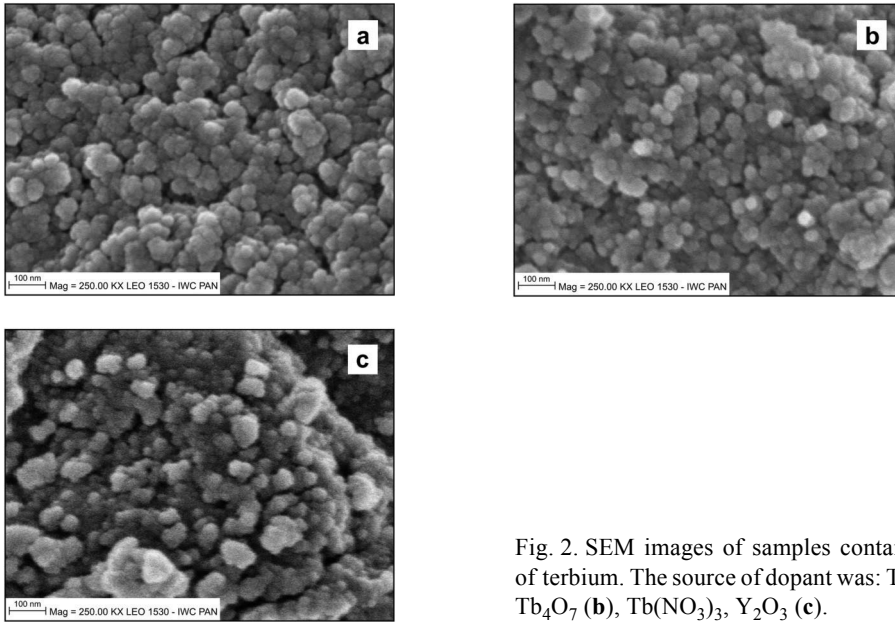


Fig. 2. SEM images of samples containing 5 wt.% of terbium. The source of dopant was: $Tb(NO_3)_3$ (a), Tb_4O_7 (b), $Tb(NO_3)_3, Y_2O_3$ (c).

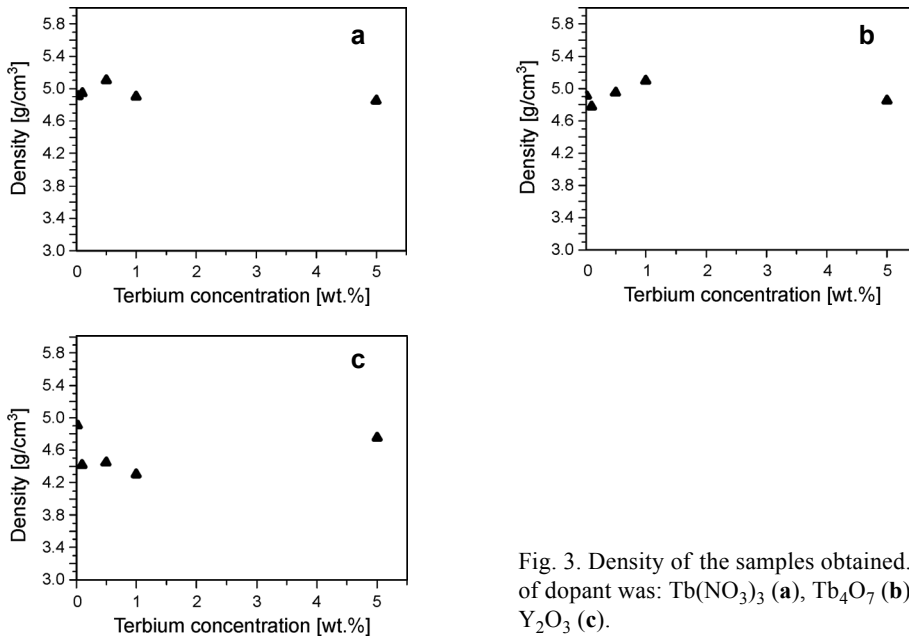


Fig. 3. Density of the samples obtained. The source of dopant was: $Tb(NO_3)_3$ (a), Tb_4O_7 (b), $Tb(NO_3)_3, Y_2O_3$ (c).

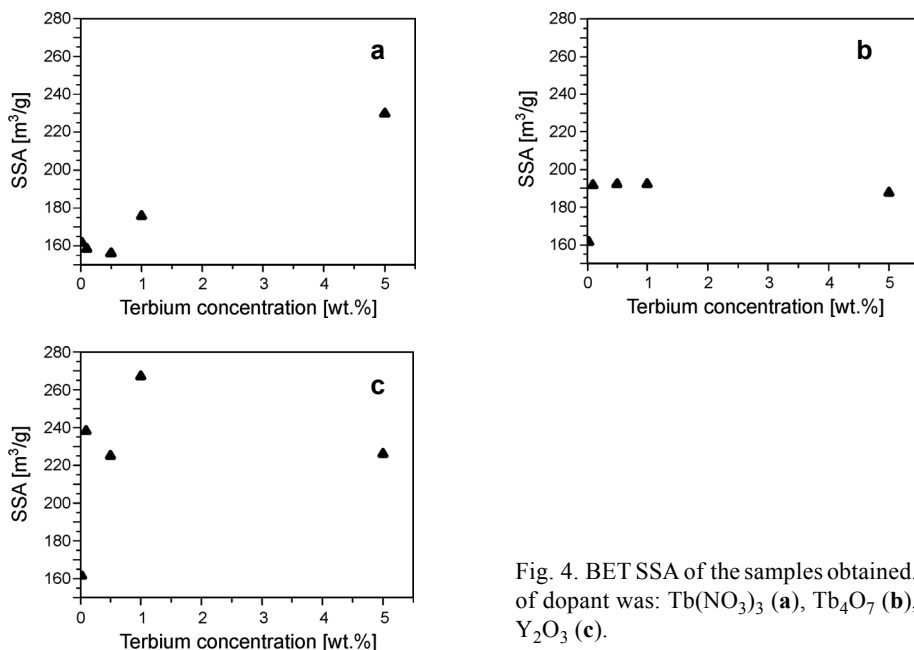


Fig. 4. BET SSA of the samples obtained. The source of dopant was: $\text{Tb}(\text{NO}_3)_3$ (a), Tb_4O_7 (b), $\text{Tb}(\text{NO}_3)_3, \text{Y}_2\text{O}_3$ (c).

zirconium hydroxide. The density yttrium doped samples is also constant and has a value of approximately 4.5 g/cm^3 . The density value as low as 4.5 g/cm^3 is due to 6.6 wt.% contribution of yttrium oxide, the bulk density of which is 5.01 g/cm^3 . Here, also yttrium hydroxide has its influence on total density.

Specific surface area for all the samples is shown in Fig. 4. Only for samples with different concentration of terbium, prepared using Tb_4O_7 SSA is constant with the value of $190 \text{ m}^2/\text{g}$. Both series with $\text{Tb}(\text{NO}_3)_3$ as a source of terbium have SSA fluctuating in the range from 150 to $230 \text{ m}^2/\text{g}$. In samples Tb^{3+} doped only, SSA increases with an increase of terbium concentration. In yttria stabilized samples there is no evident tendency in changing SSA with an increase of terbium content. It is not clear why this phenomenon occurs. It is known that many factors influence the microwave hydrothermal process and it is not easy to control all of them. The energy absorbed by reaction mixture was not measured, and one or many of these factors can have an effect on absorption. It becomes even much more interesting when we compare SSA with the size of the grains. MCS is almost constant for all the samples, which suggests that factor influencing SSA is not related with the microwave hydrothermal process.

4. Summary

Terbium doped zirconium dioxide was successfully synthesized by microwave hydrothermal method. Grain sizes in the powders obtained varied from 4 to 7 nm and were assumed constant. The main component in all powders was tetragonal ZrO_2 , but

in all the samples, except yttrium stabilized, some amount of monoclinic phase is present. Densities of the materials obtained are lower than that of bulk zirconium dioxide, indicating the presence of unreacted hydroxides and influence of grain surface and boundaries. The $ZrO_2:Tb$ powders obtained are potential candidate for application in photonics.

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Received June 23, 2009