

Bright Green Luminescence from Zirconium Oxide Stabilized with Tb³⁺ Ions Synthesized by Solution Combustion Technique

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ABSTRACT

In this research, the structural phase composition and room temperature luminescence properties of terbium doped zirconium oxide powders obtained by solution combustion synthesis method are presented as a function of the terbium content. The doping with terbium ions was performed during the redox combustion process and after annealing at 900°C during 20 hours. With the incorporation of the terbium ions into the zirconium oxide host, the stabilization of the high temperature tetragonal crystalline phase, as determined by x-ray diffraction technique, was obtained. Under ultraviolet radiation a bright green luminescence was observed at room temperature corresponding to the (4f) electron configuration of the Tb³⁺ ion, namely the electronic transitions ⁵D₄ → ⁷F_n with n = 3 - 6. In addition, the undoped ZrO₂ material showed green photoluminescence with high intensity.

Keywords: Tetragonal and Monoclinic ZrO₂; Solution Combustion; Photoluminescence

1. Introduction

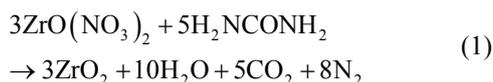
Since Harrison *et al.* [1] discovered a series of compounds with the general formula R₂²⁺R⁴⁺R₂⁵⁺O₉, where R²⁺ = Mg, Ca, Sr, Ba, Pb, Cd, Zn; R⁴⁺ = Ti, Zr, Sn; R⁵⁺ = P, As, Sb, V, which exhibited a blue broad band fluorescence, the research on host-luminescent materials is attracting considerable attention due to their excellent optical, luminescent efficiency, mechanical, electrical and thermal properties [2,3]. Among these materials, the ZrO₂ or zirconia has been considered as a host material with the before characteristics. The undoped ZrO₂ exists in three isomorphous forms depending of the annealing temperature T_a; if T_a < 1170°C the monoclinic (m) phase is present, if 1170°C < T_a < 2370°C ZrO₂ is tetragonal (t), while above of 2370°C ZrO₂ has a cubic (c) phase [4]. However, to obtain the tetragonal and cubic room, stabilized phase is no necessary an increase of temperature since actually there are some chemical methods to stabilize this phase at room temperature, these methods include producing material with grains below a critical size; Garvie [5], Stichert [6], and Valmalette [7] studied the influence of the crystallite size on the BET superficial area, the crystallization temperature, and the phase tran-

sition temperature; doping with foreign ions such as Eu³⁺, Tb⁴⁺, Ca²⁺, Mg²⁺, La³⁺, Y⁴⁺ [2,8-16] etc.; using specific solvents; Xiulin *et al.* [17] synthesized pure tetragonal and monoclinic phases using polyhydric alcohols and alkyl halides respectively. Stabilized ZrO₂ is useful in high temperature solid oxide fuel cells (SOFC), high temperature PH sensors, and as special refractory material [12-14] phase. Moreover, it is well known that the luminescence of the zirconia can be enhanced by an doping process with rare earth such as Tb³⁺, Pr³⁺, Er³⁺, Eu³⁺, and Sm³⁺ ions [2,8,11-21], these today are considered the better optical activators for luminescent devices and photonics. There are various routes for the ZrO₂ synthesis, among them the most used are: homogeneous precipitation [22-24], sol-gel method [13,25-27], spray pyrolysis [12], laser floating zone technique [28], solid reaction state [29], and solution combustion synthesis method [11,30-33], this last method is quite simple, fast and economical in which an oxidizer and a fuel in an highly exothermic redox chemical reaction stoichiometric produce ZrO₂, H₂O vapor, N₂, and CO₂. In this work, using Zirconil Nitrate ZrO(NO₃)₃ as oxidizer, urea (H₂NCONH₂) as fuel and terbium chloride as dopant, undoped and ter-

bium doped ZrO₂ is synthesized by solution combustion technique as a function of Tb³⁺ ion concentration in W%, later annealed at 900°C during 20 hours. Under ultraviolet (325 nm) radiation excitation their luminescent properties are investigated, as a function of the doping concentration.

2. Experimental Details

ZrO₂ doped with Tb³⁺ ions is obtained by a solution combustion redox chemical reaction stoichiometric using as raw materials ZrO(NO₃)₂ (oxidizer), H₂NCONH₂ (fuel) and TbCl₃ as doping source under the follow theoretical reaction chemical:



The Equation (1) was obtained by taken into account the oxidizer/fuel molar ratio (O/F = 1) required for a stoichiometric mixture which is determined by summing the total oxidizing and reducing valencies in the oxidizer compound and dividing it by the sum of the total oxidation and reducing valencies in the fuel compound [30]. Accordingly for the complete combustion of zirconyl nitrate-urea mixture, the molar ratio becomes 10/6 = 5/3, the molar balanced Equation (1) was obtained with this value. Using the atomic weight concept, the Equation (1) was translated to grams/mol and used to obtain 5 gr. of ZrO₂ for all the Tb³⁺ ion concentrations. The Tb³⁺ ion concentration was in the range from 0 to 10 (0, 1, 2, 3, 5 and 10) weight percent (W%) in relation to the ZrO₂ content. From the grams/mol equation stoichiometric (1), 9.78 gr of ZrO(NO₃)₂ was mixed with 4.057 gr of H₂NCONH₂ plus the grams number corresponding to each Tb³⁺ ion concentration and 20 ml of water on a flask glass and put on a hot plat at 450°C, after a few minutes the mixture boils, foams, ignites, and burns with an incandescent flame at a temperature of 1500°C [30] producing 5 gr of pure ZrO₂ plus water vapor, CO₂, and N₂. All produced powders were annealed at 900°C during 20 hours.

The material produced was characterized by X-ray diffraction (XRD) using a Philips PW 1800 diffractometer with Cu K α radiation (1.5406 Å), the morphology of the ZrO₂ powders obtained was studied using an scanning electron microscopy (SEM) JEOL JSM 840 A, and the photoluminescence (PL) spectra were recorded using a spectrofluorimeter Fluoro Max-P that uses a Xenon lamp as excitation source.

3. Results and Discussion

Figure 1 shows the XRD patterns for the ZrO₂ polycrystalline powder as a function of the Tb³⁺ doping concentration. It is observed that the XRD pattern for undoped

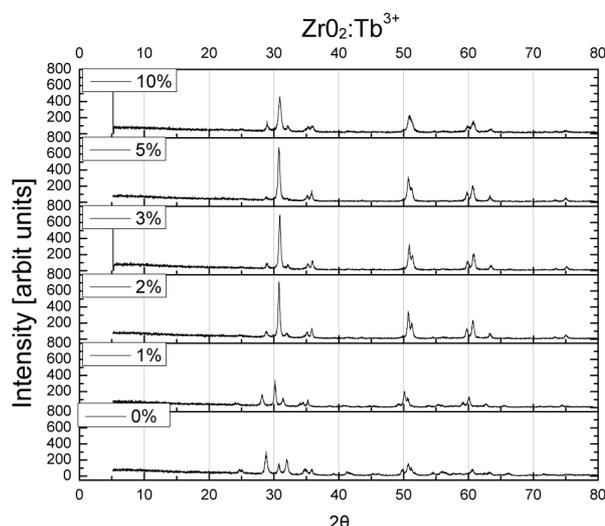


Figure 1. X-ray patterns of ZrO₂/Tb³⁺ annealed at 900°C by 20 hours showing the evolution of the crystalline phase as a function of the Tb³⁺ ions concentration.

zirconia sample shows various peaks that are associated to two crystalline phases: monoclinic (m), and tetragonal (t) phases. The peaks centered at 24.56° (1,1,0)_m, 28.40° (-1,1,1)_m and 31.41° (1,1,1)_m are characteristic peaks of the monoclinic phase, similarly, the peaks centered at 30.34° (1,0,1)_t, 35.40° (0,1,1)_t, 50.51° (2,1,1)_t and 60.40° (1,1,2)_t indicates the presence of the tetragonal phase. The aggregation of TbCl₃ for all concentrations in the redox reaction between fuel-oxidizer to doping ZrO₂ with the Tb³⁺ ion results in an phases composition and size crystallite change; the proportion of the phases monoclinic and tetragonal was obtained as an function of the Tb³⁺ ion concentration using the not entirely justified theoretically Garvie's equation [34]:

$$C_m = \frac{I_m(-1,1,1) + I_m(1,1,1)}{I_m(-1,1,1) + I_m(1,1,1) + I_t(1,0,1)} \quad (2)$$

$$C_t = 1 - C_m$$

where I is the integrated intensity in each peak and m and t indicate for monoclinic and tetragonal phases. The average crystallite sizes were calculated by means of the Scherrer formula

$$D = (0.9\lambda) / \beta \cos(\theta) \quad (3)$$

where λ is the X-ray wavelength, β is the half-width of the strongest diffraction peak and θ is the diffraction angle. The graphics of the Equations (2) and (3) are shows in **Figures 2(a)** and **(b)** respectively. From **Figure 2(a)** can be see that increasing the Tb³⁺ ion concentration the content of the metastable t phase was increased reaching the maximum for 5 W% of the ion dopant. For the content of the monoclinic phase this decrease with the increase of the ion concentration. The evolution of the av-

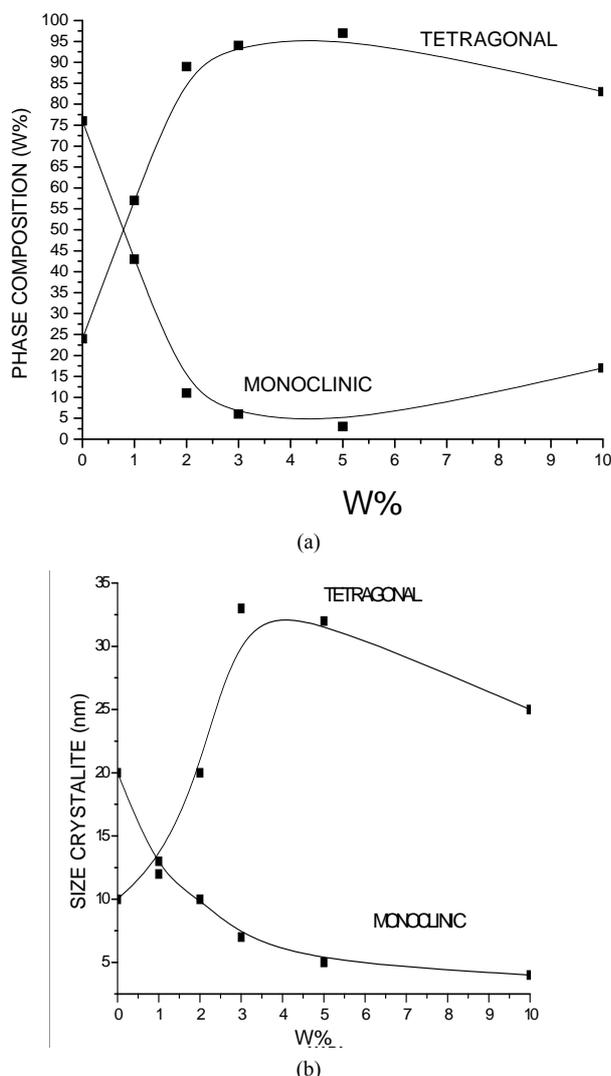


Figure 2. Evolution of phase composition (a), and size crystallite (b) as function of Tb³⁺ ion concentration for samples annealed at 900°C by 20 h. Lines are drawn as guides for the eyes.

verage crystallite size as an function of the ion concentration is shown in **Figure 2(b)**, it is observed that the size average for the t phase increase, while the m structure diminishes with the concentration. Also, the XRD pattern do not show a phase attributed to the presence of Tb₂O₃, suggesting that the Tb³⁺ ions are well inserted in the zirconia host. The tetragonal phase is consolidated as an effect of the increasing of the presence of the Tb³⁺ ions in the ZrO₂ crystalline structure indicating that it is possible to stabilizing the room temperature tetragonal phase of zirconia by doping it with rare earth ions. Also, a sliding of the peaks to lower 2θ values respect to the undoped zirconia showing small changes in the lattice parameters is observed due to the incorporation of the terbium ions without changes in the full-width at half maximum

(HWHM) of the peaks, indicating a grown uniform of the zirconia crystallites.

R. C. Garvie [35] was the first in to propose that the metastable tetragonal and cubic phases can be stabilized at room temperature when the crystallite size is below a critical size (which Garvie fixed in 300 Å) primarily due to very high surface energy associate with it, when the crystallite size exceeds this critical size by means of heat, the transformation of t and c metastable phases to monoclinic one occur due to decrease in surface energy; Filipovich and Kanilina [36] showed that the stable high temperature polymorph of a crystal can be stabilized at temperatures below its normal transformation temperature at some critical size if the high temperature polymorphic has a reduced surface free energy with respect to low temperature structure. Moreover, it has also been the cause of first-principles studies of phase transitions and doped-induced phase stabilization, for example the work by Hansen [37] on free-energy calculations, Kwok [38] and French [39] on optical properties and electronic-structure calculations, band an cluster-based electronic-structure calculations [36-38]. These results are compatibles with the results obtained by F. Ramos-Brito *et al.* for Pr³⁺ ion doped zirconia [11] who found that the monoclinic phase transforms to tetragonal phase when Pr³⁺ ion concentration exceeds 5% and with the results of W. Cordova-Martinez *et al.* [9] that experimentally showed that it is possible to obtain up to 73% of tetragonal phase by doping the ZrO₂ with 2 mol% of Sm₂O₃ or Tb₂O₃ and annealing at 1000°C. More recent theoretical and experimental studies carried out by French *et al.* [39] revealed that the high density of the doped-induced oxygen vacancies in the ZrO₂ electronic structure play a important role in the t-ZrO₂ stabilization; these oxygen vacancies are present in stabilized materials at high concentrations, for example 9.5 mol% Y₂O₃ stabilized c-ZrO₂ contains 4.75% oxygen vacancies. These oxygen vacancies are localized adjacent to Zr atoms reducing the symmetry and coordination of the Zr site.

Figures 3(a) and **(b)** show the photoluminescence spectrum for the sample of undoped ZrO₂ annealed at 900°C by 20 hours and for the sample of ZrO₂ unannealed respectively, the samples were UV radiated with a wavelength of 325 nm. The emission spectrum are alike for both samples and present a single and very broad band covering the range 400 - 600 nm peaking at 480 nm, but the intensity band of the annealed sample is higher than that for unannealed sample. From the XRD results (see **Figure 1**) it is concluded that the undoped ZrO₂ present two different phases: monoclinic and tetragonal, this result could indicate that both phases contribute to the PL emission bands. This result is in agreement with the reported by Numan Salah *et al.* [40]. From the results

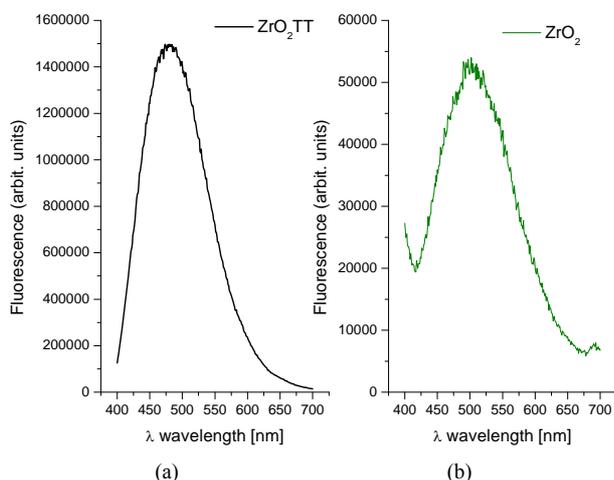


Figure 3. Photoluminescence spectra of undoped ZrO_2 annealed at $900^\circ C$ during 20 hours (a) and unannealed (b).

reported in the literature it is known that the PL emission band of ZrO_2 can be attributed to the formation of energy levels or electron/traps states created on the ZrO_2 surface in which electron transitions from the surface trap states in the conduction band to lower energy levels near to the valence band can occur [34]; Harrison *et al.* [1] in their luminescence study of ZrO_2 and ternary zirconate compounds showed that the zirconium ion plus its surrounding oxygen ion constitute the most conspicuous component of the luminescent center; their emission spectra for ZrO_2 also shows, as in our case, a broad band centered at 480 nm under similar excitation wavelength. Harrison attributed this broad band to the existence of the zirconium-oxygen ion complex. With respect to the monoclinic phase present in the ZrO_2 powders, McCullough *et al.* [41] studying the crystalline structure of monoclinic ZrO_2 found that the Zr^{4+} ion is surrounded by 7 oxygen ions at distances (Zr-O) ranging from 2.04 to 2.26 Å, thus the emission in ZrO_2 can be attributed to a distortion in the symmetry of the surrounding oxygen ions as showed by Harrison. Tahir *et al.* [42] found that exciting ZrO_2 with 270 nm radiation, a broad emission band ranging between 300 - 500 nm, peaking at 376 nm was observed; they have attributed this broad emission band to the narrow particle size distribution caused by the nanometric character of the ZrO_2 particles size, producing an inhomogeneous broad distribution of surface or defect states. Add to the before, the defects formed by the interfacing sites between the phases monoclinic and tetragonal, configure an wide band gap of the ZrO_2 that contain new energy levels and electron traps that can producing a lot of emissions.

Figure 4 shows the room temperature emission spectra of ZrO_2/Tb^{3+} powder annealed at $900^\circ C$ during 20 hours as a function of Tb^{3+} ions concentration; the powders

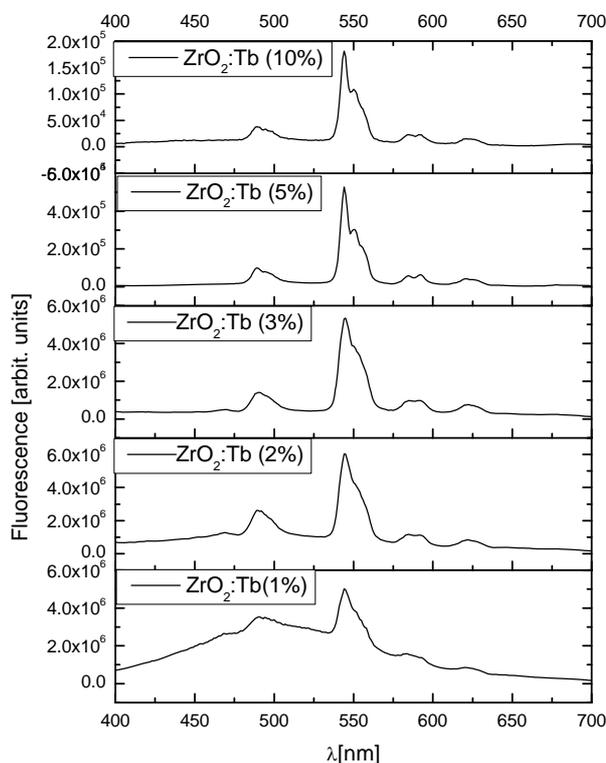


Figure 4. Photoluminescence emission spectra of ZrO_2/Tb^{3+} powders, as a function of Tb^{3+} ions concentration.

were excited by ultraviolet radiation (325 nm). All the spectra for doped samples show four principals emission bands peaking at about 490, 545, 588 and 620 nm; these peaks, correspond to the electronic transitions that occur in the Tb^{3+} ion, namely the $^5D_4 \rightarrow ^7F_6$, $^5d_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7D_4$, and $^5d_4 \rightarrow ^7F_3$ transitions. The strongest emission peak at 545 nm is responsible for the characteristic Tb^{3+} ion green light emission. These results are compatibles with those previously obtained by Garcia-Hipolito *et al.* [15] for ZrO_2/Tb^{3+} thin films by pneumatic spray pyrolysis and by B. Mari *et al.* [11] for the same product in powders synthesized by solution combustion. **Figure 5** shows the relative emission intensity, as a function of the Tb^{3+} ion concentration, for ZrO_2/Tb^{3+} powders considering only the emission intensity of the band centered at 545 nm; here it is observed a maximum intensity for 2 wt% doping concentration. After this value, a decrease of PL emission intensity is exhibited due to excess of activators ions, effect known as concentration quenching. In the literature, it is suggested that, at high doping concentration, the excitation energy can migrate from one luminescent center to another and eventually reach a sink (lattice defect), from which non-radiative processes can dissipate this excitation energy. This concentration quenching will not appear at low doping concentrations because the average distance between activators ions is so large

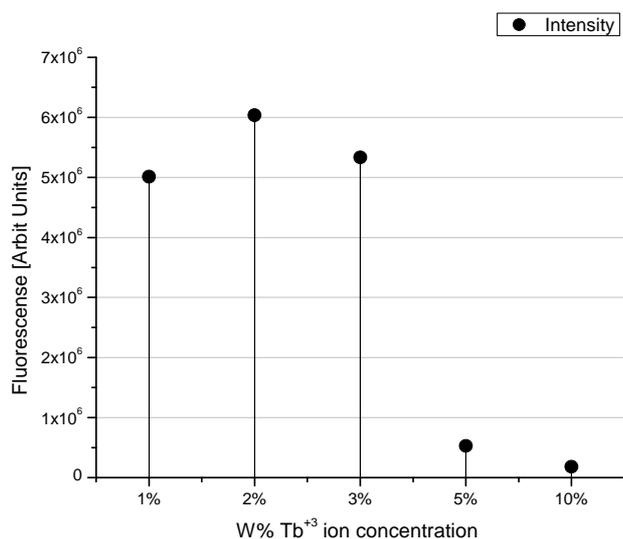


Figure 5. Relative intensity of the emission peak centered at 545 nm of ZrO₂/Tb³⁺ powders as a function of the Tb³⁺ ions concentration.

that the migration is prevented and the sinks are not reached [32].

Figure 6 shows the surface morphology and size of the ZrO₂/Tb³⁺ particles doped with 2 W% of Tb³⁺ ions, obtained by SEM. It is observed that the morphology and size of the particles is more or less uniform and similar to ovoid-like morphology. The ovoid-like particle size is less than 1.0 μm. The SEM images also exhibits pores and voids in the ZrO₂/Tb³⁺ sample, it is because in solution combustion synthesis the oxidizer-fuel redox reaction is performed in short times and evolve emitting a lot of gases like N₂, CO₂ and H₂O that can yields particles with pore and voids.

4. Conclusions

In this contribution, results about powders of ZrO₂ doped with 0, 1, 2, 3, 5, and 10 wt% of Tb³⁺ ions, are reported. These powders were synthesized by a simple and economical solution combustion technique, using zirconyl nitrate hydrate as oxidizer, urea as fuel and terbium chloride as doping impurity. The XRD studies revealed that the undoped powders (ZrO₂) show the room temperature monoclinic stabilized phase and the size-effect stabilized room temperature stabilized tetragonal phase.

Studies of the phases composition revealed that when the Tb³⁺ increase, the content of the monoclinic phase decreases while the content of the tetragonal phase increases.

Undoped tetragonal and monoclinic phases exhibited intense green photoluminescence by means of a broad band peaking at 480 nm. Presumably that PL emission is due to structural defects of the host lattice.

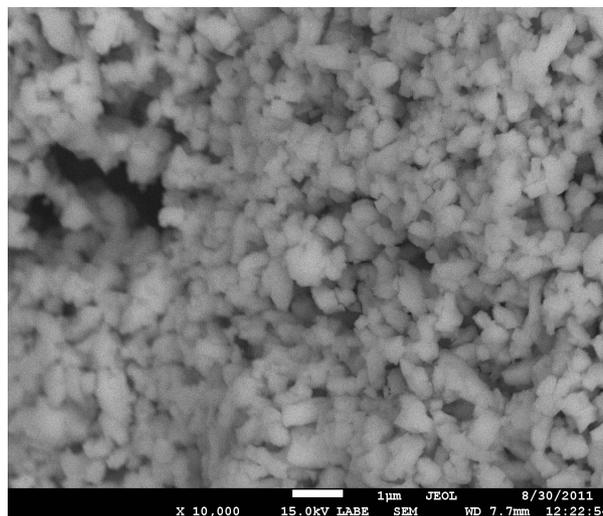


Figure 6. SEM micrograph of ZrO₂/Tb³⁺ powders annealed at 900°C during 20 hours, in this case the doping concentration was 2 wt%.

All ZrO₂/Tb³⁺ samples showed four emission bands peaking at 490, 545, 598, and 620 nm corresponding to the ⁵D₄→⁷F_n, n = 3 - 6, electronic transitions of the Tb³⁺ ion, when excited by ultraviolet radiation (325 nm). The sample doped with a 2 wt% of the Tb³⁺ ions showed the maximum green PL emission intensity. The observed green emission is very strong and it is possible to perceive it in normal room light with the naked eye.

SEM micrographs of the ZrO₂/Tb³⁺ powders showed a morphology constituted by particles with indefinite form similar to ovoids approximately of a micron in size. The estimated crystallite size, calculated by means of the Scherrer formula, was about 30 nm.

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