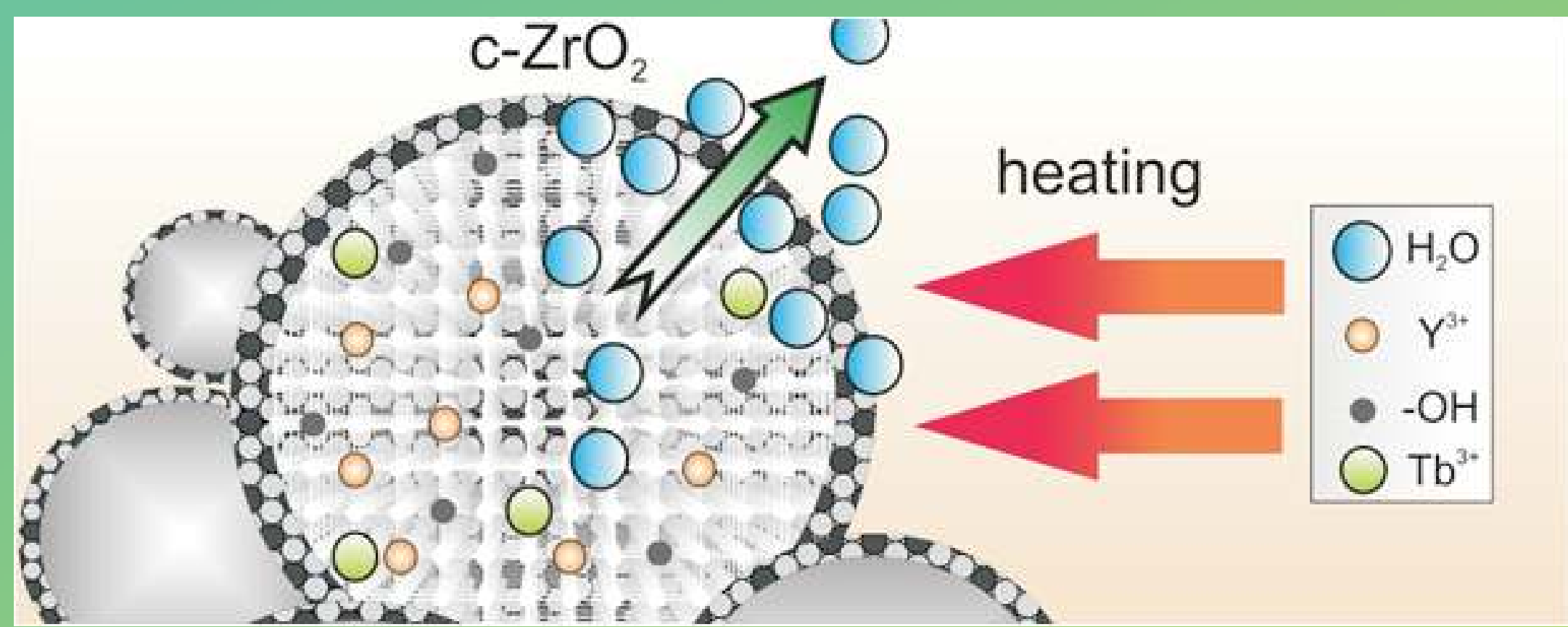


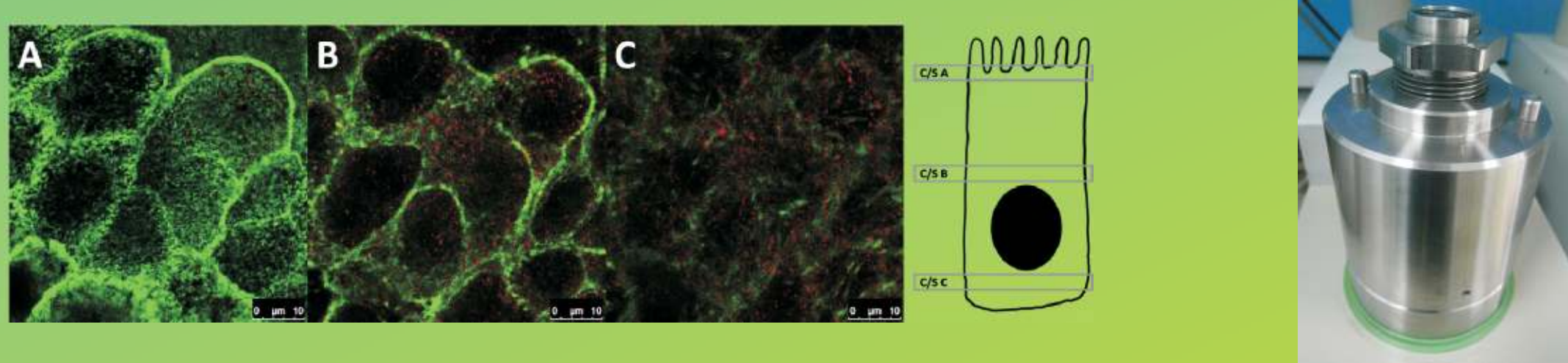
# Y<sup>3+</sup> ions prevent Tb<sup>3+</sup> ions from oxidation in luminescent biocompatible ZrO<sub>2</sub>:Tb nanoparticles

Jarosław Kaszewski, Bartłomiej S. Witkowski, Anna Stońska-Zielonka, Izabela Serafińska, Łukasz Wachnicki, Anna Wolska, Marcin Klepka, Hanka Przybylińska, Bolesław Kozankiewicz, Ewa Mijowska, Zdzisław Gajewski, Michał M. Godlewski, Marek Godlewski

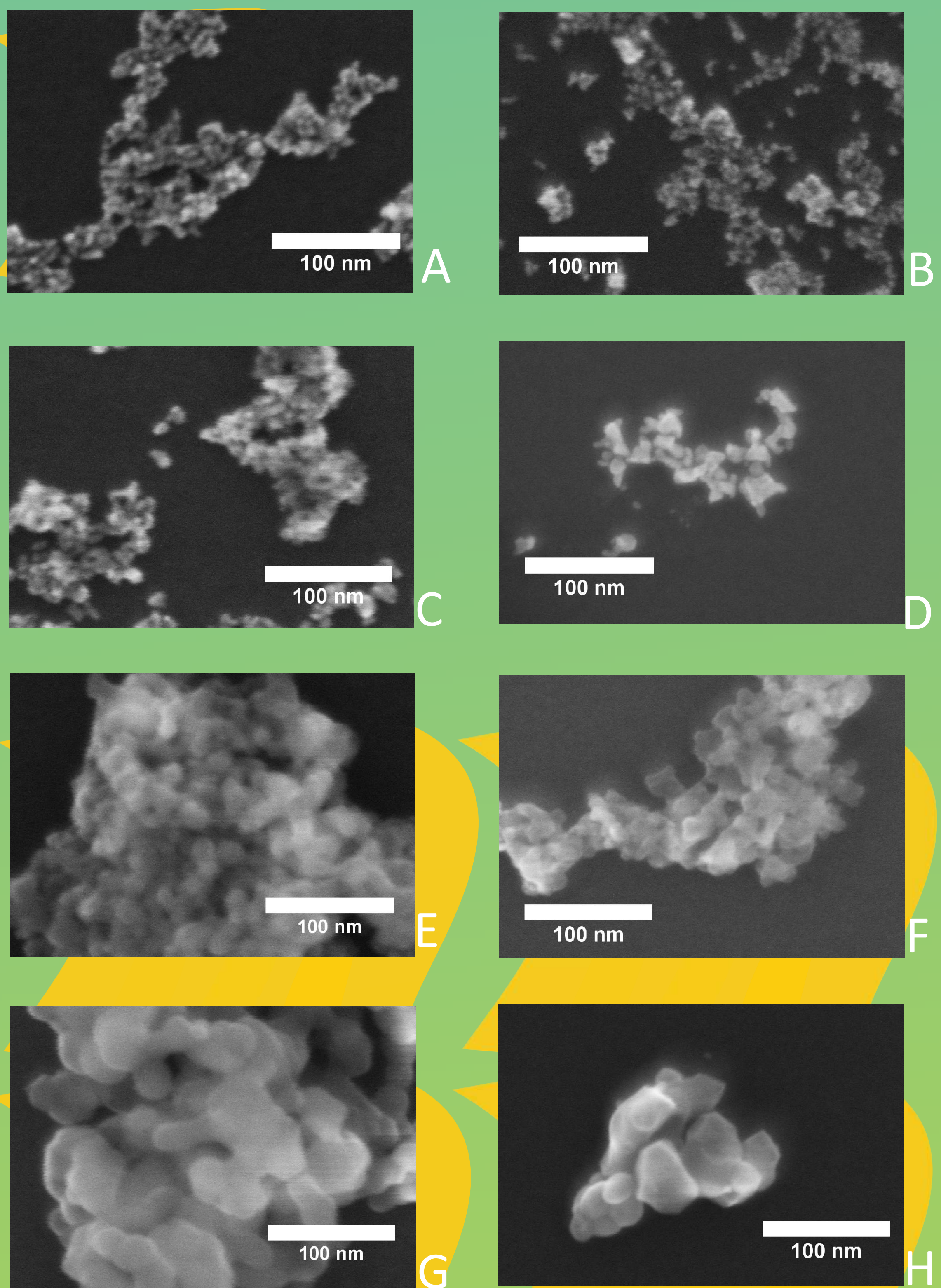
Instytut Fizyki PAN, al. Lotników 32/46, 02-668 Warszawa  
kaszewski@ifpan.edu.pl



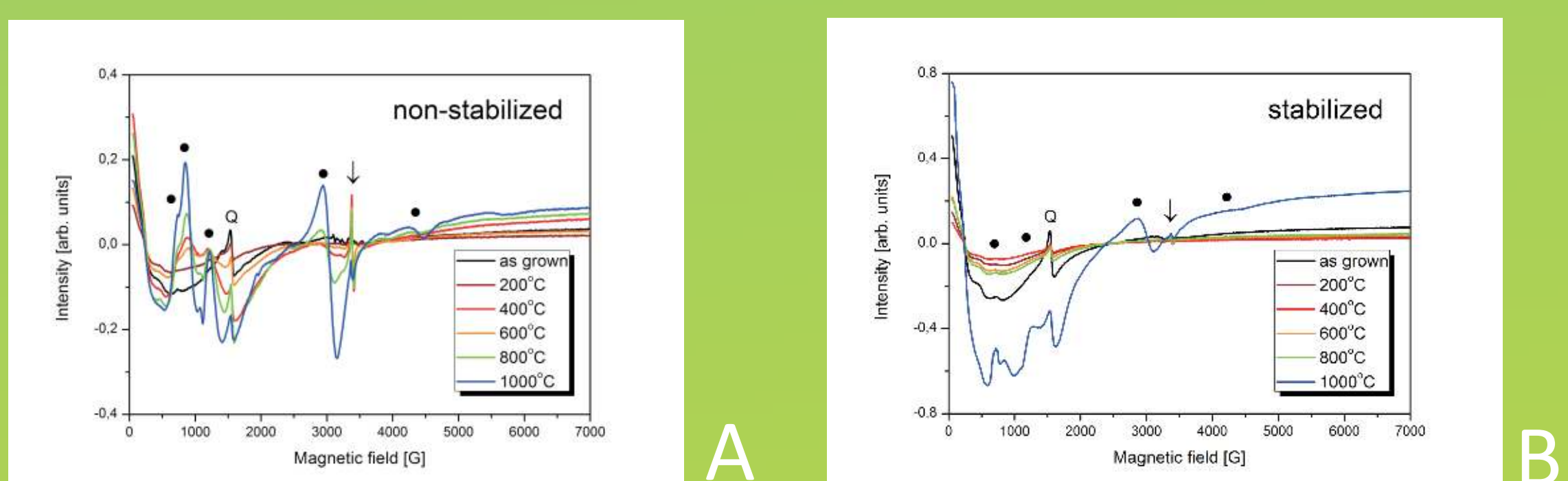
Nanoparticles of ZrO<sub>2</sub>:Tb were synthesized using microwave driven hydrothermal method. Terbium content was set to 0.5% mol. in all the samples. Yttrium concentration was changing in the range of 0-10% mol., where stabilization of tetragonal and cubic ZrO<sub>2</sub> forms has a place.



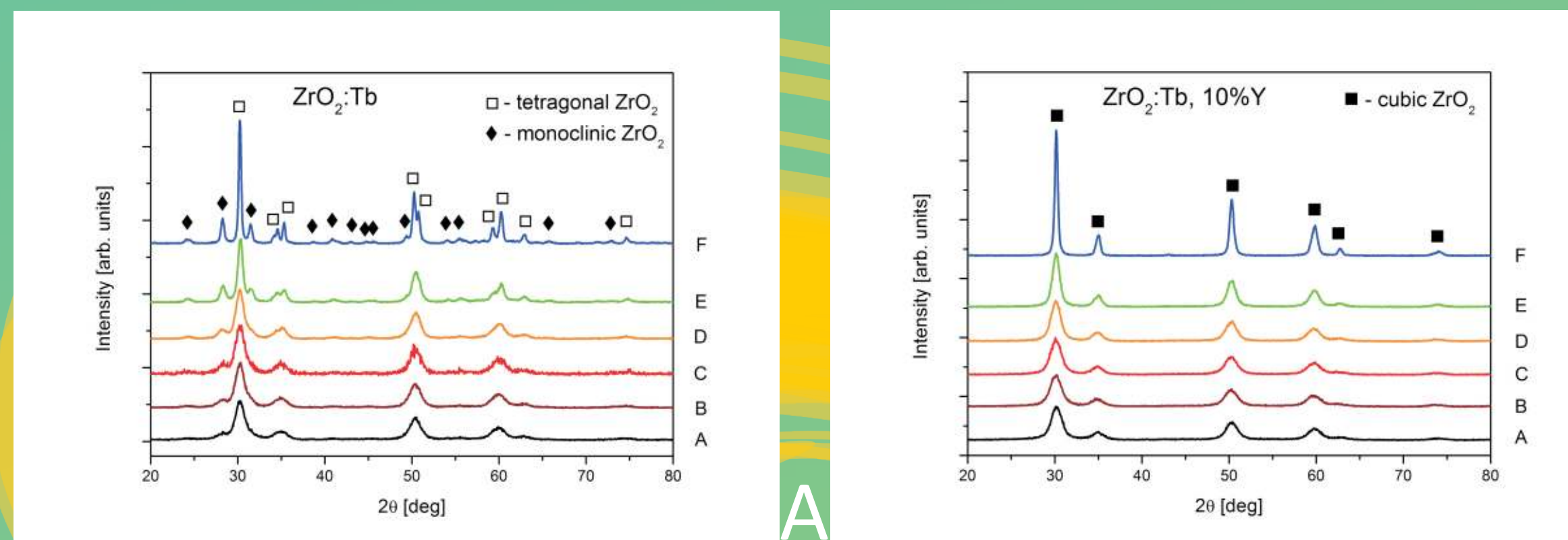
ZrO<sub>2</sub>:Tb nanoparticles (0.001 mg/ml) absorption into the confluent, polarised cell culture of Caco-2 cells, as a model of small intestine absorption. Fluorescence of nanoparticles (red) following 1 h incubation can be observed primarily in the middle and bottom cross-sections of the cells (C/S B and C). In the top cross-section (C/S A) the intensive green fluorescence of the actin filaments can be observed (structural element of the microvilli).



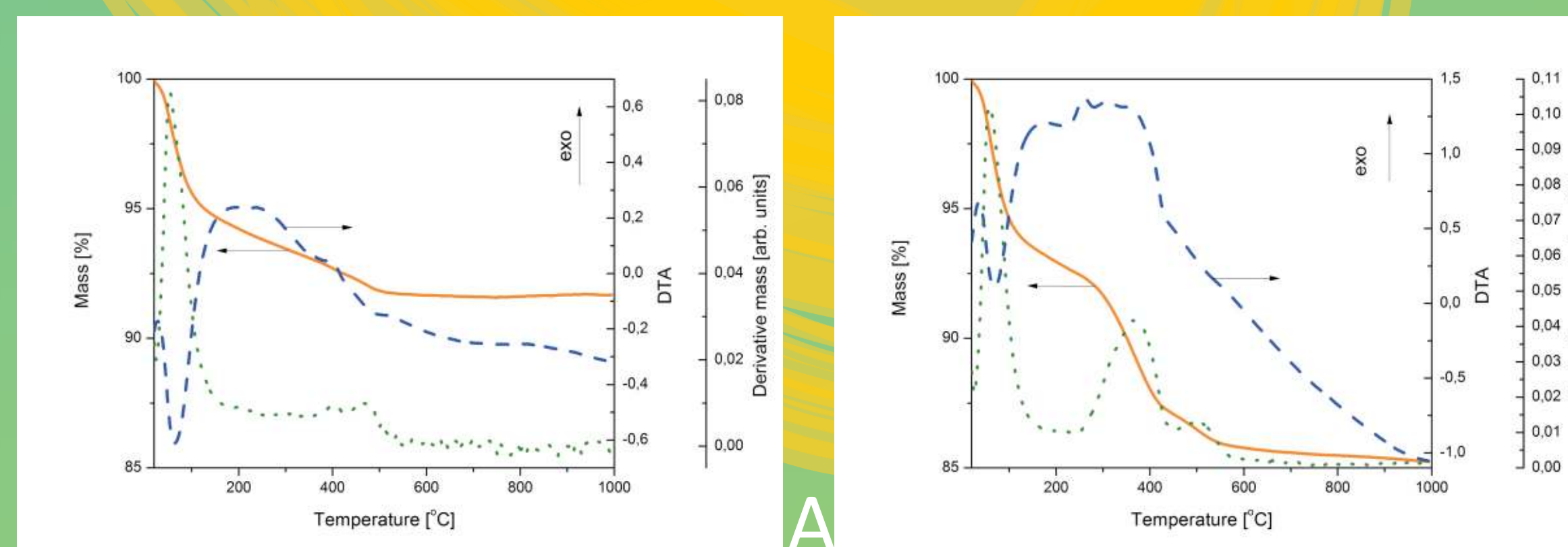
SEM images of ZrO<sub>2</sub>:Tb samples without yttrium stabilization (A, B, C, D) and stabilized with 10%mol. yttrium (E, F, G, H). Samples as grown in microwave hydrothermal process (A, E) and additionally calcined at: 400°C (B, F), 600°C (C, G) and 1000°C (D, H).



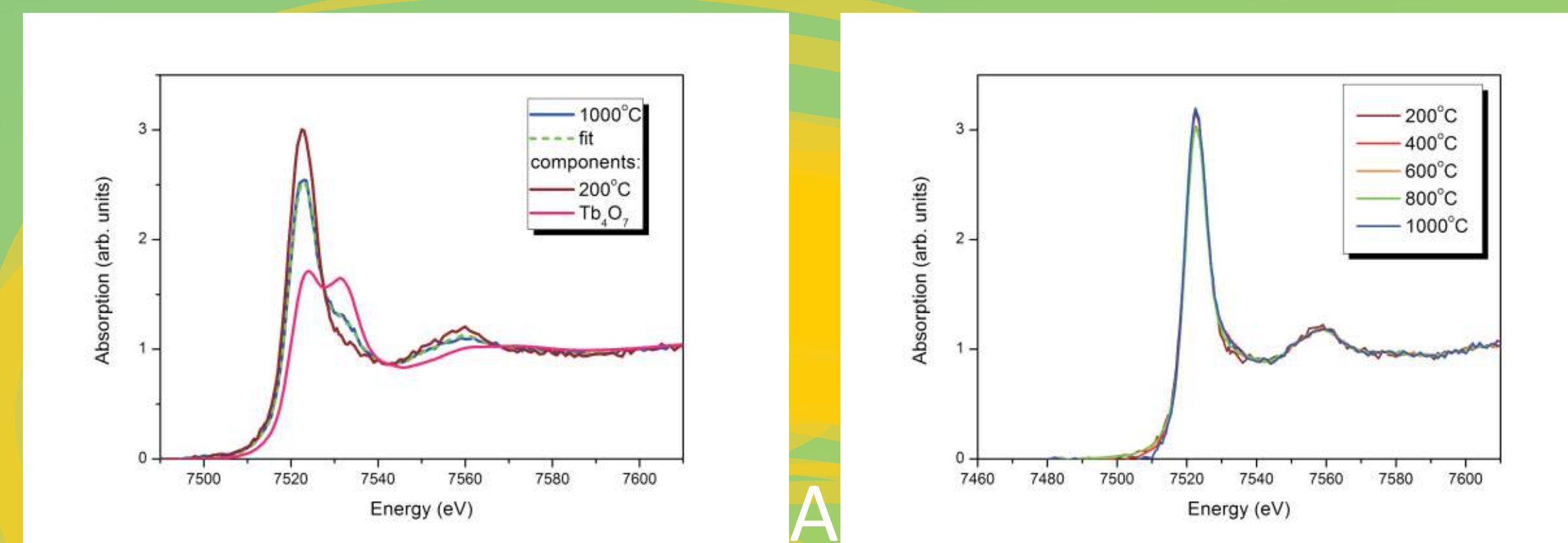
EPR spectra of ZrO<sub>2</sub>:Tb samples calcined at the different temperatures, recorded at 3K. A - non stabilized samples, B - samples stabilized with 10%mol. Y. Symbols: ● - Tb<sup>3+</sup> ions signal, Q - quartz tube signal, \* - lattice defect or Tb<sup>3+</sup> related signal.



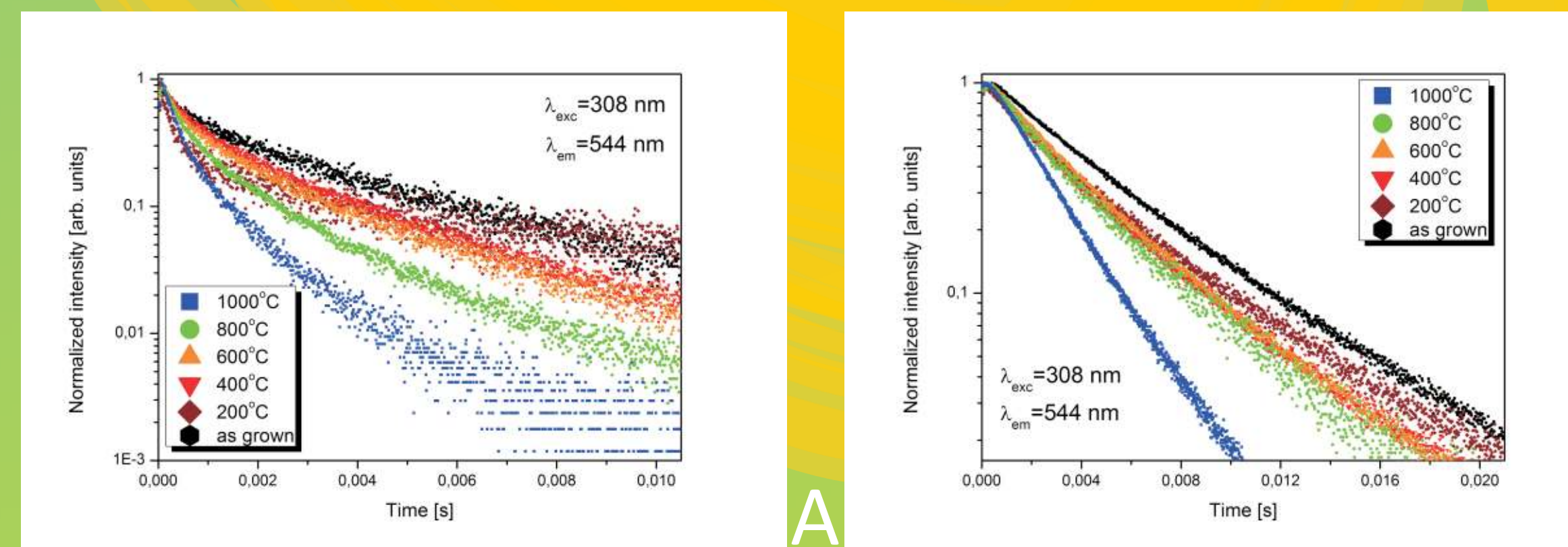
XRD patterns of ZrO<sub>2</sub>:Tb nanoparticles stabilized with 0 (A) or 10% mol. of yttrium (B) and calcined at the temperatures: A - as crystallized in microwave hydrothermal process, B - 200°C, C - 400°C, D - 600°C, E - 800°C, F - 1000°C.



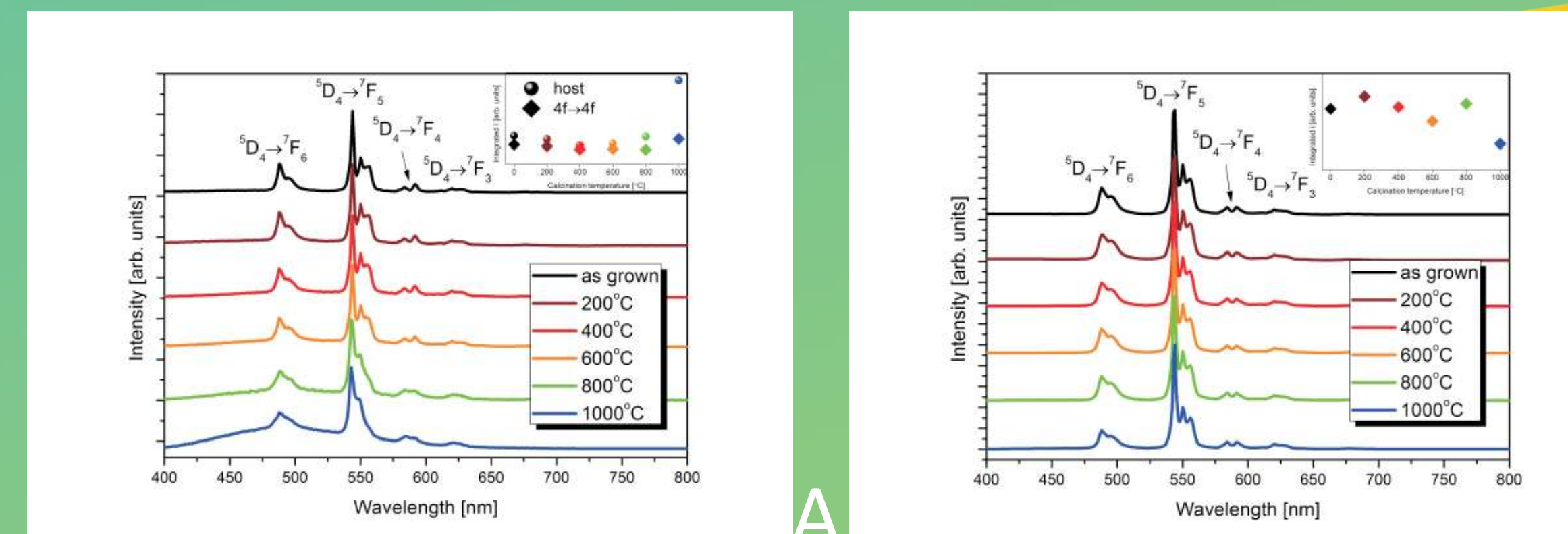
TG/DTG curves of ZrO<sub>2</sub> nanopowders. A - pure ZrO<sub>2</sub>, B - 10%Y stabilized ZrO<sub>2</sub>.



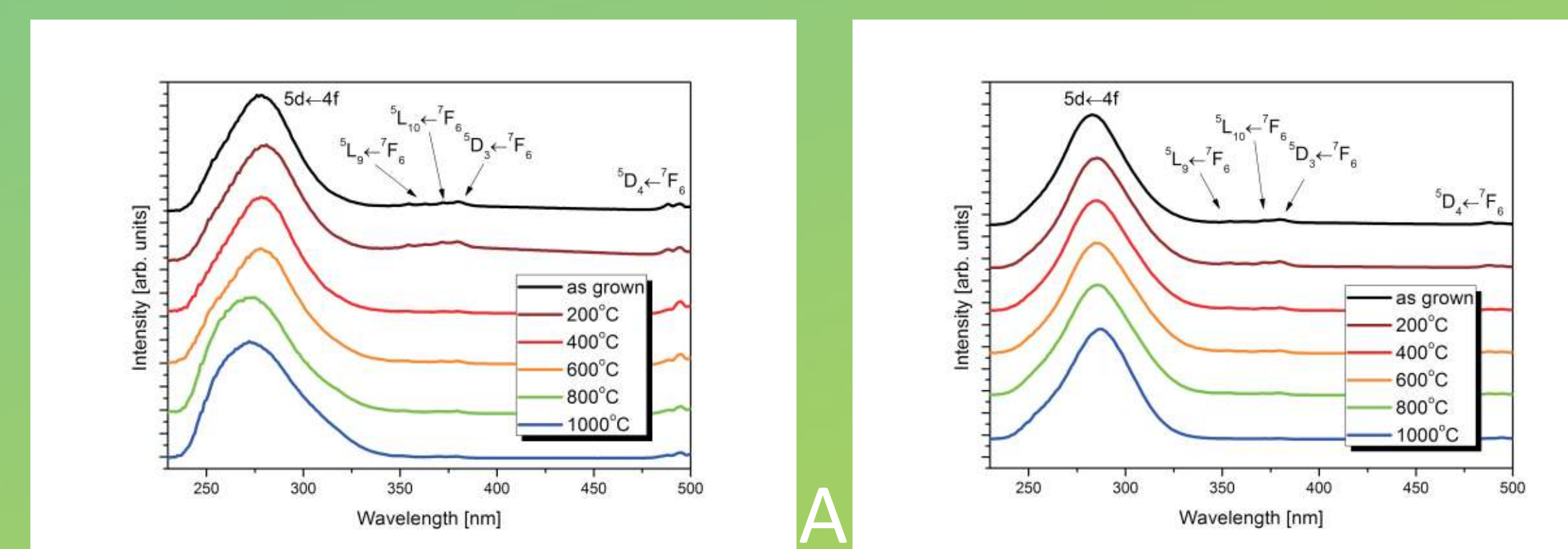
XANES spectra of ZrO<sub>2</sub>:Tb samples calcined at the different temperatures. A - non stabilized sample calcined at 1000°C fitted with two component spectra; sample calcined at 200°C and terbium oxide reference. B - samples stabilized with 10%mol. Y.



Decay curves of ZrO<sub>2</sub>:Tb (λ<sub>exc</sub>=544 nm, <sup>5</sup>D<sub>0</sub> - <sup>7</sup>F<sub>5</sub> of Tb<sup>3+</sup>) samples calcined at the different temperatures A - non stabilized and B - stabilized with 10%mol. Y.



PL spectra of ZrO<sub>2</sub>:Tb nanopowders calcined at the different temperatures. A - samples without yttrium stabilization, B - samples with 10%mol. yttrium stabilization. Excitation wavelength λ<sub>exc</sub>=280 nm. Inset: intensities of 4f-4f luminescence (diamonds) and host lattice luminescence (balls).



PLE spectra of ZrO<sub>2</sub>:Tb nanopowders calcined at the different temperatures. A - samples without yttrium stabilization, B - samples with 10%mol. yttrium stabilization. Emission wavelength λ<sub>em</sub>=543 nm.

ZrO<sub>2</sub>:Tb nanoparticles were prepared as follows. Water solution of metals' nitrates(V) was prepared by addition to 200 ml of the distilled water adequate mass of ingredients (J: zirconyl nitrate(V) (Zr(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O; x76; 99.8%; Sigma-Aldrich), yttrium nitrate(V) (Y(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O; 99.9%; Sigma-Aldrich) and terbium(III) nitrate(V) (Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O; 99.99%; Sigma-Aldrich). Clear solution was then alkalinized by addition of aqueous ammonia solution (25%; J.T. Baker) to form precipitate. Residue was then triply washed to dispose of nitrate(V) groups and excess of precipitation agent. The precipitate was then closed in 100 ml teflon reaction vessel. Microwave power was set to ca. 4 W/ml and process was performed at 6 MPa by 20 minutes. After the reaction was conducted, resulting residue was dried and calcined in the air atmosphere at 200, 400, 600, 800 and 1000°C, one sample for each concentration was left uncalcined. Reference Tb<sub>2</sub>O<sub>3</sub> sample was prepared by calcination of terbium(III) nitrate(V) at 200, 400, 600, 800 and 1000°C in the air atmosphere.

Electron paramagnetic resonance (EPR) spectra recorded at 3K are shown. Discussed system contains zirconium, yttrium and terbium elements in ionized form. Both Zr<sup>3+</sup> and Y<sup>3+</sup> are closed outer shell ions with complex electronic structure (3d<sup>1</sup> 4f<sup>14</sup>), Tb<sup>3+</sup> with 4f<sup>9</sup> configuration are non Kramers ions, therefore all present ions are EPR blind. However, due to redox phenomena in solid state, paramagnetic Zr<sup>3+</sup> (4d<sup>1</sup>, S=1/2) and Tb<sup>3+</sup> (4f<sup>9</sup>, S=7/2) ions may occur. Hyperfine structures may appear due to nuclear spin I=3/2 of <sup>159</sup>Tb (100% abundance) and I=5/2 of <sup>89</sup>Zr (1.1%). Despite Tb<sup>3+</sup> does not show EPR features, very broad signal was reported in hydrated zeolites. Tb<sup>3+</sup> ions spectra vary from those of Eu<sup>3+</sup> and Gd<sup>3+</sup>, despite similar electronic structure. First, non-S-state rare earth ions show very broad features and present in disordered solids were observed before at temperature of 4K. For Tb<sup>3+</sup> ions dominating signal is located at g=8.3.

XANES spectra gathered for the yttrium stabilized samples annealed at the different temperatures shows the same spectral features. It suggests that structure around the Tb atoms stays unchanged over whole series. Position of white line is close to 7522 eV which implies that terbium is in the 3+ valence state. In case of the non stabilized samples, spectrum of the sample annealed at 200°C exhibits the same spectral features as the stabilized ones. However, in the non stabilized 1000°C sample shape of the spectrum changes, existing peaks are getting smaller and additional peak close to 7530 eV becomes visible. This peak is an indication of the presence of Tb<sup>4+</sup> ions in the sample.

**Influence of yttrium stabilization and heating**  
ZrO<sub>2</sub>:Tb nanoparticles obtained in microwave hydrothermal process exhibit phase composition depending on both yttrium content and crystallite size, in agreement with stabilization theory. Mixing of the concentration and size stabilization effects resulted in the cubic zirconia samples (10% yttrium) and tetragonal/monoclinic in 0% Y samples. As the yttrium content increase, crystallite sizes are prevented from growing further by oxygen vacancies introduced into the host lattice as a result of charge compensation mechanism, as shown in the samples series with various yttrium content. Additionally, 3+ charged ions tend to enrich surface of nanoparticles causing magnification of the effect. Yttrium stabilization growth suppression is depicted mainly in calcined nanoparticles, as the crystals are sized for narrow X-ray diffraction reflexes allowing demonstration of the effect. Stabilization with yttrium also induce higher overall mass loss during calcination step, despite the crystal phase of Y<sub>2</sub>O<sub>3</sub> nor Y<sub>2</sub>O(OH)<sub>2</sub>(NO<sub>3</sub>) does not appear. Additional mass loss is caused likely by sintering of smaller ZrO<sub>2</sub> nanocrystals with more surface amorphous hydroxide or by substitution mechanism discussed later on. It is accompanied by larger exothermic effect occurring ca. 400°C. After reaction of remaining hydroxides, only growth of crystals has a place in the range 600-1000°C.

**Photoluminescence behavior**  
Tb<sup>3+</sup> ions characteristic luminescence occurs in cases of high symmetry and low symmetry host lattices. In the first case, only activator's luminescence is seen, in the second, however, there is also seen additional host lattice emission. It seems that the intensity of this broad range emission with the zirconia crystallites sizes, yet this is not the case, as fully cubic calcined samples do not exhibit host luminescence. The origin of broad emission in this spectral range was attributed to monoclinic ZrO<sub>2</sub> intrinsic defects. As <sup>5</sup>D<sub>0</sub> - <sup>7</sup>F<sub>5</sub> transitions within Tb<sup>3+</sup> ions are considered hypersensitive, one can find emission spectra indicative for the local symmetry of the activator's environment. Changes in the activator's site symmetry are found in the non-stabilized samples as a function of calcination temperature. Stark component of the <sup>5</sup>D<sub>0</sub> - <sup>7</sup>F<sub>5</sub> transition located at 556 nm disappears in samples calcined at 800 and 1000°C suggesting that most of the Tb<sup>3+</sup> ions have changed its positions in the crystal lattice. Likely, coordination has changed from octahedral or distorted octahedral (cubic or tetragonal ZrO<sub>2</sub> phase) to pentagonal bipyramidal adequate for monoclinic ZrO<sub>2</sub>. This phenomenon occurs in the thermal region of crystal growth and is not related to the chemical reaction but to the t-ZrO<sub>2</sub> - m-ZrO<sub>2</sub> phase shift. Relationship between components in fully stabilized sample remain similar for all the temperatures. Additionally, broadening related with Tb<sup>3+</sup> luminescence from many different nonequivalent sites is not occurring. Luminescence spectra as well as 5d-4f bands in excitation spectra do not change, when samples are calcined. The excitation are 5d-4f bands, where with increase of calcination temperature band peaking ca. 260 nm and seen as a shoulder of the one present in all the samples. The appearance of this UV band is associated with m-ZrO<sub>2</sub> content in the sample. As intensity of emission is considered there are not significant changes in the function of calcination temperature, which is indicator, that water and hydroxyls presence have no essential impact on the luminescence quenching in the material.

Thank you and have a nice day!