



Optical Properties of Yttria-Stabilized Zirconia Single-Crystals Doped with Terbium Oxide

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Abstract: A series of yttria-stabilized zirconia single-crystals doped with 0.000–0.250 mol% Tb₄O₇ was prepared by the optical floating-zone method. As shown by XRD and Raman spectroscopy, all of the crystals had a cubic-phase structure. These were initially orange–yellow in color, which is indicative of the presence of Tb⁴⁺ ions, but they then became colorless after being annealed in a H₂/Ar atmosphere as a result of the reduction of Tb⁴⁺ to Tb³⁺. The absorption spectra of the unannealed samples show both the 4*f* ⁸→4*f* ⁷5*d*¹ transition of Tb³⁺ ions and the Tb⁴⁺ charge-transfer band. In addition, the transmittance of the crystals was increased by annealing. Under irradiation with 300 nm of light, all of the single-crystal samples showed seven emission peaks in the visible region, corresponding to the decay from the ⁵D_{3,4} excited state of Tb³⁺ to the ⁷F_J (J = 6–0) states. The most intense emission was at 544 nm, which corresponds to the typical strong green emission from the ⁵D₄→⁷F₅ transition in Tb³⁺ ions.

Keywords: yttria-stabilized zirconia; Tb₄O₇-doped; annealed in H_2 /Ar atmosphere; optical properties; optical floating-zone method

1. Introduction

In recent years, the preparation and properties of optical materials containing rare earth ions have attracted wide-spread attention [1,2]. As a result of their partially filled 4f electronic configurations, rare earth ions have unique luminescence properties, including sharp emission peaks, long lifetimes, high quantum yields, and flexible tunability [3], and various optical materials, such as phosphors [4-6], glass ceramics [7-9], and optical crystals [10–13], are based on their excellent optical properties [2]. Among the rare earths, terbium (Tb) is an important element for green light-emitting devices, although its chemistry is complicated by its redox properties, which are manifested as Tb³⁺ ions in the reduced state and Tb^{4+} ions in the oxidized state. Tb^{3+} has a $4f^{8}$ electronic configuration, whereas Tb⁴⁺ is 4f⁷. Furthermore, an electron in Tb³⁺ can be excited to the 5*d*-energy level (4f $^8 \rightarrow 4f$ $^{7}5d^{1}$) and this can then undergo non-radiative relaxation from to the $^{5}D_{3,4}$ excited state and finally transition to the ${}^{7}F_{I}$ (J = 6–0) states with strong green emission near 545 nm [14]. The energy-level difference between the ${}^{5}D_{4}$ state and the Tb³⁺ ground state is about 15,000 cm $^{-1}$, which makes multi-phonon relaxation negligible. Therefore, emissions from the ${}^{5}D_{4}$ state usually have high quantum efficiency and good thermal stability [15], and the luminescence of Tb³⁺ ions in phosphors and lasers has been shown to have applications in medical imaging [8,16–18].

Terbium oxide in the form Tb_4O_7 contains both Tb^{3+} and Tb^{4+} ions. The standard redox potential (relative to the hydrogen electrode) of Tb^{3+}/Tb^{4+} is + 3.1 V [19,20], which is far greater than that of the most easily reduced rare earth ions, such as Eu^{2+}/Eu^{3+} (-0.35 V) [19]. Therefore, Tb^{4+} is relatively stable and optical materials doped with Tb^{4+}



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). appear yellow as a result of Tb⁴⁺ absorption [21]. Although Tb³⁺ and Tb⁴⁺ can coexist in the oxide, Tb⁴⁺ ions do not emit visible light after excitation; thus, its presence should not affect the green emission of Tb³⁺. However, investigating the optics and other physical and chemical properties of systems containing a combination of Tb³⁺ and Tb⁴⁺ should increase our understanding of their luminescence properties and help develop new applications of such rare earth-doped luminescence materials [21].

The absorption and emission intensity, light efficiency, luminescence lifetime, and quenching process of rare earth ion-based luminescent materials are strongly influenced by the host material [22]. Zirconia (ZrO₂) is a wide-bandgap semiconductor with a high melting point, high dielectric constant, good corrosion resistance, and low phonon energy [23], which is conducive to the observation of the luminescence of rare earth ions [24]. Besides its low phonon energy, a high refractive index and photochemical stability make ZrO_2 an ideal optical host material [25]. However, it is difficult to produce large highquality zirconia crystals because of large volume changes, which accompany transitions between its three-phase structures (monoclinic (m-ZrO₂) below 1443 K, tetragonal (t-ZrO₂) between 1443 K and 2643 K, and cubic (c-ZrO₂) above 2643 K). This commonly leads to the cracking of the crystals that are cooling from melts, which is not conducive to industrial production [26]. However, the high-temperature $c-ZrO_2$ form, which is most suitable for many types of technological applications, can be stabilized at room temperature by the addition of an appropriate amount of an oxide stabilizer, such as Y_2O_3 [27,28], and several studies have shown that the addition of 8.0 mol% Y_2O_3 to ZrO_2 (abbreviated to 8YSZ) effectively stabilizes the cubic-phase structure [29-31]. As a result, crystals with good optical transparency, a high refractive index, and stable photo-thermo-chemical properties can be produced [29,32,33]. Previous studies of Tb-doped zirconia have concentrated mainly on phosphors and nanomaterials [34], although Soares et al. successfully produced YSZ: Tb³⁺ fibers with a tetragonal crystal structure by the laser floating-zone method [35]. However, the luminescence properties of Tb-doped YSZ single-crystals in the cubic phase have not been reported previously.

In this paper, crystals were grown by the optical floating-zone method (OFZ) based on ZrO_2 stabilized with 8 mol% Y_2O_3 , which was partially replaced with various amounts of Tb_4O_7 . Its structure was characterized by X-ray diffractometry (XRD) and Raman spectroscopy, whilst the Tb oxidation states were determined by X-ray photoelectron spectroscopy (XPS). Optical properties were investigated using a combination of ultraviolet-visible (UV-Vis) absorption and transmission, photoluminescence excitation (PLE), photoluminescence emission (PL), and fluorescence-lifetime determination. These results could be explained by the physical mechanisms of luminescence and it lays the foundation for the wider application of green-laser and medical-imaging areas.

2. Experimental

2.1. Preparation of Crystals

 ZrO_2 , Y_2O_3 , and Tb_4O_7 powders (Aladdin, Shanghai, China) with 99.99% purity were weighed with a precision balance scale in the stoichiometric ratio of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.000, 0.050, 0.075, 0.100, 0.150, 0.200, and 0.250). The molar concentrations of the oxides used for the preparation of each sample are shown in Table 1. The weighed powders were suspended in ethanol and stirred on a magnetic stirrer for 24 h before drying in a constant-temperature oven at 85 °C for 24 h. The dried sample was added to cylindrical rubber molds, vacuum sealed, and set in a 50 MPa isostatic press for 20 min. The molds were then removed and the mixed powder bars were sintered at 1500 °C for 10 h to produce polycrystalline ceramic samples. These samples were used as the feed-and-seed rods for the crystal production in an optical suspension-zone furnace (FZ-T-12000-X-VII-VPO-GU-PC, Crystal Systems Co., Yamanashi, Japan). The optical floating zone could heat materials with high melting points and produce crystal samples with a high degree of purity. After production, some crystal samples were annealed at 1500 °C in a reducing atmosphere (7% H₂ + 93% Ar). After preparation, single-crystal rods were sliced and polished to produce disks with a thickness of 1 mm for optical measurements and fractions were ground into powders for structure determination. Figure 1 shows a photo of the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.200) crystals before and after annealing in 7% H₂ + 93% Ar. The original single-crystal sample was orange–yellow, with good uniformity and high transparency, but after annealing, it became colorless.

Composition (mol%) Samples ZrO₂ Y_2O_3 Tb_4O_7 92.00 $(ZrO_2)_{92}(Y_2O_3)_{8.00}$ 8.000 0.000 $(ZrO_2)_{92}(Y_2O_3)_{7.950}(Tb_4O_7)_{0.050}$ 92.00 7.950 0.050 $(ZrO_2)_{92}(Y_2O_3)_{7.925}(Tb_4O_7)_{0.075}$ 92.00 7.925 0.075 $(ZrO_2)_{92}(Y_2O_3)_{7.900}(Tb_4O_7)_{0.100}$ 92.00 7.900 0.100 92.00 7.850 0.150 $(ZrO_2)_{92}(Y_2O_3)_{7.850}(Tb_4O_7)_{0.150}$ $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ 92.00 7.800 0.200 (ZrO₂)₉₂(Y₂O₃)_{7.750}(Tb₄O₇)_{0.250} 92.00 7.750 0.250

Table 1. Composition of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$.





2.2. Phase and Structure Characterization

The phase and structure characterization of the samples was performed by X-ray diffractometry (XRD) using a DX-2700 X-ray powder diffractometer (Dandong Hao Yuan Company, Dandong City, Liaoning Province) with Cu K alpha ($\lambda = 0.15406$ nm) as the radiation source and Raman spectroscopy with a Finder One laser micro-Raman spectrometer, in which excitation was at 532 nm. X-ray photoelectron spectroscopy (ESCALAB 250XI+, Thermo Fisher Scientific Company, Shanghai, China) with a monochromatic Al-target X-ray source was used to characterize the elemental composition and oxidation states of the samples. The absorption and transmission spectra of the crystal samples were measured in the range of 200–800 nm using a UV-Vis spectrophotometer (UV-2700, Shimadzu, Kyoto, Japan) and both excitation and emission spectra were measured at room temperature with a ZLF-325 photoluminescence spectrometer (Zolix Instruments Co., Ltd., Beijing, China). The fluorescence-lifetime spectroscopy measurements were performed with an Edinburgh FLS1000 transient fluorescence spectrometer.

3. Results and Discussion

3.1. Crystal-Phase Structure Analysis

The XRD patterns from the powders of the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ crystal samples before annealing all consist of six diffraction peaks at ~30.12°, 34.94°, 50.18°, 59.64°, 60.56°, and 73.68° 2 θ , which correspond to the (111), (200), (220), (311), (222), and (400) planes, respectively, of the c-ZrO₂ structure (PDF 04-006-5589). There was no evidence of diffraction

peaks from the ZrO₂ monoclinic and tetragonal phases, and the phase structure was independent of the Tb₄O₇-doping concentration (in the range of x = 0.000-0.250). The annealed crystal samples show similar results (e.g., Figure 2b). As shown in Table 2, the unit cell parameters and volume were essentially constant in the unannealed crystals, but they increased in the annealed crystals. In 8YSZ, a considerable number of anion vacancies were introduced into the ZrO₂ structure to maintain the charge balance and computer simulations have shown that such vacancies tend to avoid direct association with Y^{3+} ions [36]. Consequently, there is a tendency for Zr^{4+} to adopt a seven-coordinate configuration, whilst Y³⁺ is coordinated to eight oxygen atoms. Considering that the radii of Tb⁴⁺ and Zr⁴⁺ are similar (0.76 and 0.78 Å, respectively, for the seven-coordination configuration), as are Tb³⁺ and Y³⁺ (1.04 and 1.019 Å, respectively, for the eight-coordination configuration) [37], we expect that Tb^{4+} will substitute for Zr^{4+} and Tb^{3+} for Y^{3+} in the unannealed crystals. Such substitutions would have little or no effect on the cell dimensions, as observed by XRD. A reduction of Tb⁴⁺ to Tb³⁺ because of the annealing results in an increase in the fraction of trivalent ions in the crystals and this must be accompanied by a decrease in the total anion charge. This could be achieved by a loss of oxygen from the structure or protonation of an appropriate number of structural oxygen atoms. However, the c-ZrO₂ structure accommodates a considerable range of Y^{3+} ions; thus, there should be no problem in accommodating the reduced Tb. Nevertheless, the larger size of Tb^{3+} compared to Tb⁴⁺ results in a lattice expansion, as shown in Table 2.



Figure 2. (a) XRD patterns of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.000-0.250) crystal powders before annealing. (b) XRD pattern of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystal powders before and after annealing at 1500 °C in a H₂/Ar atmosphere.

Table 2. The lattice parameter of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ crystals.

Samples	Lattice Parameter (nm)	Cell Volume (nm ³)	Before or after Annealing
(ZrO ₂) ₉₂ (Y ₂ O ₃) _{8.00}	0.5139	0.1357	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.950}(Tb_4O_7)_{0.050}$	0.5137	0.1355	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.925}(Tb_4O_7)_{0.075}$	0.5138	0.1357	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.900}(Tb_4O_7)_{0.100}$	0.5138	0.1356	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.850}(Tb_4O_7)_{0.150}$	0.5138	0.1357	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$	0.5138	0.1357	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.750}(Tb_4O_7)_{0.250}$	0.5137	0.1356	Before annealing
$(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$	0.5155	0.1370	After annealing

Raman spectroscopy is a sensitive method for distinguishing the phase structure of zirconia crystals because m-ZrO₂ has 18 Raman vibration modes $(9A_g + 9B_g)$ [29,38] and t-ZrO₂ has 6 strong Raman vibration modes $(A_{1g} + 2B_{1g} + 3E_g)$ [17], whereas c-ZrO₂ has only 1 (F_{2g}) [39]. The results in Figure S1 (see Supplementary Materials) show that the

Raman spectra of all the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.050-0.250) crystal disks before annealing have a single strong vibration at 620 cm⁻¹ under excitation with a laser light of 532 nm. Furthermore, the spectra recorded before and after annealing (Figure 3) were similar and, thus, all are consistent with the c-ZrO₂ structure.



Figure 3. Raman spectra of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystals before and after annealing at 1500 °C in a H₂/Ar atmosphere.

3.2. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation states of the elements in the (ZrO₂)₉₂(Y₂O₃)_{7.800}(Tb₄O₇)_{0.200} single-crystals before and after annealing. The survey spectrum (Figure 4) showed clear signals from the matrix elements Zr, Y, and O, and a weak signal from Tb. The expansion of the Tb 3d energy-level spectra of the crystalline samples before and after annealing are shown in Figure 5. The Tb 3d core-level spectrum contained peaks from the Tb $3d_{3/2}$ and Tb $3d_{5/2}$ spin-orbit states. In the unannealed sample, the peaks of Tb $3d_{3/2}$ and Tb $3d_{5/2}$ were at about 1277.1 and 1241.8.4 eV, respectively, and shifted to about 1276.8 and 1240.9 eV in the annealed sample. These are similar to the values of about 1277 and 1241 eV reported by Zhang et al. for the Tb^{3+} $3d_{3/2}$ and Tb³⁺ $3d_{5/2}$ peaks, respectively [40]. However, the low Tb content in the present work resulted in insufficient signal-to-noise values to allow for a conclusive assignment to the environments for Tb³⁺ and Tb⁴⁺. The XPS spectrum of the O 1s core-energy level (Figure 6) showed two peaks at 531.8 and 530.2 eV, corresponding to O^{2-} in the unannealed sample [41]. The positions of these peaks were similar to that in the annealed sample (531.6 and 529.9 eV) and there was also a small change in their relative intensities. We suggest that this is the result of a decrease in O^{2-} ions bound to two metal ions in the 4+ oxidation state (Zr^{4+} + some Tb^{4+}) and an increase in those bound to one 4+ and one 3+ ion as a result of the reduction of Tb^{4+} to Tb^{3+} . The XPS spectra of the matrix elements Zr and Y for the before-and-after annealing samples showed that Zr and Y were essentially unaffected by annealing [36,42] (see Supplementary Materials).



Figure 4. XPS survey spectrum of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ single-crystals before and after annealing in a H₂/Ar atmosphere.



Figure 5. XPS Tb 3d core-energy-level spectrum.



Figure 6. XPS O 1s core-energy-level spectrum.

3.3. Absorption and Transmission Spectrum

The absorption spectra of the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.000-0.250) crystal disks in the range of 220–800 nm are shown in Figure 7. In the absence of Tb, there was a single intense absorption at 243 nm, corresponding to the direct absorption in the wide-bandgap semiconductor ZrO_2 [32,43]. This transition was also present in the Tb₄O₇-doped samples, which show a total of three absorption peaks at 245, 300, and 370 nm. The peak at 300 nm corresponds to the 4f $^8 \rightarrow$ 4f $^75d^1$ transition in Tb³⁺ ions and the broad peak at

370 nm may originate from Tb⁴⁺ [20]. As the Tb doping concentration increased, the Tb³⁺ absorption peak underwent a red shift similar to that reported for Tb-doped Bi₂MoO₆ [44]; thus, this demonstrates that the presence of Tb affects the light absorption in the ZrO₂ host.



Figure 7. The absorption spectrum of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.000-0.250) crystal discs before annealing (the inset is the result of Gaussian peak fitting of the absorption spectrum of the $(ZrO_2)_{92}(Y_2O_3)_{7.950}(Tb_4O_7)_{0.050}$ crystal).

Transmission spectra of the $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystal disks were also measured before and after annealing, and were shown in Figure 8. The annealed crystals showed only two transmission peaks at 246 nm and 302 nm, and thus supports the assignment of the peak at 370 nm in the unannealed sample to Tb^{4+} ions. The large width of this peak (from 330 to 550 nm), which is much larger than that of the Tb^{3+} 4f $^8 \rightarrow 4f$ $^75d^1$ transition (280–335 nm), suggests that it may correspond to a charge-transfer transition in the Tb^{4+} ions [45]. The transmittance of the annealed crystals in the range of 550–800 nm was about 86%, whereas it was about 78% in the unannealed sample; thus, this shows that the transmittance of the crystals increased after annealing.



Figure 8. Transmission spectra of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystals before and after annealing at 1500 °C in a H₂/Ar atmosphere.

3.4. Photoluminescence Excitation (PLE) Spectra

The PLE spectra of the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.050-0.250) crystals monitored at 544 nm are shown in Figure 9. There were three excitation peaks in the range of 200–500 nm at 300, 377, and 484 nm. The excitation peak centered at 300 nm (230–360 nm) is broad and corresponds to the spin-allowed $4f^{-8} \rightarrow 4f^{-7}5d^1$ transition of Tb³⁺ ions [46]. In contrast, the

weak excitation peaks at 377 nm and 484 nm are sharp, which correspond to the forbidden electric-dipole transitions ${}^{7}F_{6} \rightarrow {}^{5}D_{3}$ and ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ in the Tb³⁺ 4*f* configuration [47,48].



Figure 9. Excitation spectra of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.050-0.250) crystals before annealing and monitored at 544 nm.

The PLE spectra of the $(ZrO_2)_{92}(Y_2O_3)_{7,800}$ (Tb₄O₇)_{0,200} crystals shown in Figure 10 remained unchanged during the annealing and demonstrated that there was no Tb⁴⁺excitation band. The excitation peak at 300 nm was red-shifted with the increasing Tb_4O_7 concentration, which probably reflects the changes in the energy of the lowest 5d-level of Tb^{3+} in the YSZ host. This has been shown to differ between different host materials and may be influenced by two independent factors: (1) the nephelauxetic effect, which corresponds to a shortening of the metal-ligand distance as a result of a decrease in the coordination number and results in a shift in the center of the mass of the 5d electrons from the free-ion energy level; and (2) a crystal field effect, which causes the 5d manifold to split into various sub-levels [49]. Considering that both the XRD and Raman results show that the phase structure of the crystals does not change, we presume that the red-shift phenomenon in these samples was caused by the nephelauxetic effect [50]. In Figure 9, the intensity of the excitation spectrum of the $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ crystal sample first increases with the concentration of Tb_4O_7 , reaches a maximum at x = 0.200, and then decreases, which may be the result of the cross-relaxation between two adjacent Tb^{3+} ions [51].



Figure 10. Excitation spectra of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystals before and after annealing at 1500 °C in a H₂/Ar atmosphere monitored at 544 nm.

3.5. Photoluminescence Emission (PL) Spectra

The PL spectra of the unannealed $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ crystal disks following irradiation at 300 nm at room temperature are shown in Figure 11. A bright green emission was observed and consisted of a total of seven peaks, all of which originate from $4f \rightarrow 4f$

transitions in Tb³⁺ ions. The weak peaks at 385, 422, and 441 nm, which are shown in the expanded form in Figure 12, are blue and correspond to the Tb³⁺⁵ $D_3 \rightarrow {}^7F_J$ (J = 6,5,4) transitions, whereas the peaks at 489, 544, 585, 621, and 677 nm are green and correspond to the Tb³⁺⁵ $D_4 \rightarrow {}^7F_J$ (J = 6,5,4,3,1) transitions. The strongest emission peak at 544 nm arose from the ${}^5D_4 \rightarrow {}^7F_5$ transition and is the typical strong-green emission from Tb³⁺ ions. No additional emission peaks that could originate from Tb⁴⁺ were observed in the unannealed samples (e.g., Figure 12), indicating that Tb⁴⁺ did not emit in the visible-light region, but the intensity of the spectrum of the annealed sample was appreciably higher because of the higher concentration of Tb³⁺. With the increasing Tb₄O₇ concentration, the intensity of the spectrum of the green emission (${}^5D_4 \rightarrow {}^7F_5$) first increased and then decreased, with the highest intensity at x = 0.100 (Figure 12), whereas the green emission (${}^5D_4 \rightarrow {}^7F_5$) first increased to reach a maximum intensity at x = 0.200 and then decreased with higher x (Figure 11). These different trends are the result of the cross-relaxation (CR) between neighboring Tb³⁺ ions. Considering that the excited states of two Tb³⁺ ions resonate with the ground state, the CR process can be expressed as:



$$\Gamma b^{3+} ({}^{5}D_{3}) + \Gamma b^{3+} ({}^{7}F_{0}) = \Gamma b^{3+} ({}^{5}D_{4}) + \Gamma b^{3+} ({}^{7}F_{6}).$$
(1)

Figure 11. Emission spectra of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.050-0.250) crystals before annealing.



Figure 12. Expansion of the emission spectra in the range 370–450 nm of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (*x* = 0.050–0.250) crystals before annealing.

The energy difference between the ${}^{5}D_{3}$ and ${}^{5}D_{4}$ states is about 5600 cm⁻¹, whilst that between the ${}^{7}F_{0}$ and ${}^{7}F_{6}$ states is about 5800 cm⁻¹, with the result that there is little difference in the total energy on each side of the above equation. Therefore, when the concentration of Tb³⁺ is high, energy can be transferred from the ${}^{5}D_{3}$ state of one Tb³⁺ ion to the ${}^{5}D_{4}$ state of a neighboring Tb³⁺ ion, and this results in a quenching of the emission from Tb³⁺ ions at the ${}^{5}D_{3}$ high-energy level and an increased emission from the lower ${}^{5}D_{4}$ -energy level.

The emission spectra of the $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystals before and after annealing in H₂ (Figure 13) confirm that all of the emissions in the visible region arise from Tb³⁺ $4f \rightarrow 4f$ transitions and indicate that their positions are unaffected by the presence

of Tb⁴⁺. Thus, the Tb³⁺ emission is independent of Tb⁴⁺ in Tb³⁺ and Tb⁴⁺ co-doped systems. However, the emission intensity of the annealed crystals was stronger than that of the unannealed crystals probably because of the higher Tb³⁺ concentration as a result of the Tb⁴⁺ reduction. The various excitation and emission transitions for Tb³⁺ ions are summarized in Figure 14.



Figure 13. Emission spectrum of $(ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ crystals before and after annealing at 1500 °C in a H₂/Ar atmosphere.



Figure 14. Energy-level-transition diagram of Tb³⁺ ions in the yttria-stabilized zirconia single-crystal.

3.6. Fluorescence Decay

The fluorescence-decay lifetime is an important parameter for understanding energy-transfer mechanisms and the curve for the fluorescence decay of the $(ZrO_2)_{92}(Y_2O_3)_{7,800}(Tb_4O_7)_{0,200}$ crystals before annealing is shown in Figure 15 for the 544 nm $({}^5D_4 \rightarrow {}^7F_5$, green) peak produced by the excitation at 300 nm.

The decay curve fits to a double exponential function, i.e.,

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right)$$
(2)

where I(t) is the PL intensity, τ_1 and τ_2 represent the fast and slow components of the luminescence lifetime, respectively, and A_1 and A_2 are fitting parameters. Additionally, the average decay time τ of the sample is defined as:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \tag{3}$$



Figure 15. Fluorescence-decay curve for the $\text{Tb}^{3+5}D_4 \rightarrow {}^7F_5$ transition in the $(\text{ZrO}_2)_{92}(Y_2O_3)_{7.800}(\text{Tb}_4O_7)_{0.200}$ single-crystals before annealing.

The values for these parameters obtained by computer fitting are A_1 = 0.49369, A_2 = 0.50033, τ_1 = 2.079 ms, and τ_2 =2.817 ms. From these results, τ is calculated to be 2.507 ms, which is longer than the values reported for that of BSGdCaTb glass (2.31 ms) [52] or Tb³⁺-doped germanium borosilicate (GBS) magneto-optical glass (2.317 ms) [53]. Furthermore, the double exponential function indicates that the Tb³⁺ ions may be located in two different environments in the yttria-stabilized zirconia crystal.

4. Conclusions

Yttria-stabilized zirconia crystals doped with terbium oxide (Tb₄O₇) were prepared by the optical floating-zone method and shown to be in the cubic form without cracks or inclusions. The crystals initially contained Tb in both the Tb^{3+} and Tb^{4+} forms but the Tb^{4+} was reduced to Tb³⁺ by annealing crystals at 1500 °C in an Ar/H₂ atmosphere, although the Tb⁴⁺ ions were reduced to Tb³⁺ through annealing. The XPS results showed that Zr, Y, and O were essentially unaffected because the change in the relative intensities of the peaks in the O spectra were small. The absorption spectra of the crystals showed three peaks at 240, 300, and 370 nm, corresponding to the Tb³⁺ 4f $^8 \rightarrow$ 4f $^75d^1$ transition and the Tb⁴⁺ charge-transfer band. This spectrum also showed a red shift with increasing Tb, indicating that Tb-doping affects the light absorption properties of the YSZ host. The transmission spectra showed that the crystals had higher transmittance after annealing, although both the excitation and emission spectra correspond to transitions within the 4f and 5d configurations of Tb^{3+} $(4f^{8} \rightarrow 4f^{7}5d^{1} \text{ and } 4f \rightarrow 4f \text{ configurations})$. No excitation or emission peaks were observed from Tb^{4+} and its presence did not influence the positions or shapes of the Tb^{3+} peaks. The PL spectra also showed emissions from the $Tb^{3+5}D_3$ and 5D_4 states, which exhibited different relationships with the level of Tb-doping as a result of the cross-relaxation between neighboring Tb³⁺ ions. The strongest emission peak from the crystals was located at 544 nm and corresponds to the Tb³⁺⁵ $D_4 \rightarrow {}^7F_5$ transition, which is the typical strong green-light emission of Tb^{3+} ions. The intensity of this emission increased initially with an increasing Tb_4O_7 concentration, reached a maximum at x = 0.200, and then decreased at a higher doping level. Overall, these results suggest that $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ single-crystals may have potential applications as green lasers and for use in medical imaging.

Supplementary Materials: The following supporting information can be downloaded at: https://www. mdpi.com/article/10.3390/cryst12081081/s1, Figure S1: Raman spectra of $(ZrO_2)_{92}(Y_2O_3)_{8-x}(Tb_4O_7)_x$ (x = 0.050-0.250) crystals before annealing; Figure S2: XPS Zr 3*d* core-energy-level spectrum of ($ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ single-crystals before and after annealing at 1500 °C in a H₂/Ar atmosphere; Figure S3: XPS Y 3*d* core-energy-level spectrum of ($ZrO_2)_{92}(Y_2O_3)_{7.800}(Tb_4O_7)_{0.200}$ single-crystals before and after annealing at 1500 °C in a H₂/Ar **Author Contributions:** Conceptualization, Y.W. and S.X.; methodology, Y.W. and Z.Z.; software, Y.W., S.T. and Z.C.; validation, Y.W., S.X., and W.D.; formal analysis, Y.W., Z.C. and P.Z.; investigation, Y.W., N.Z. and P.Z.; resources, W.D.; data curation, Y.W., Z.Z. and S.T.; writing—original draft preparation, Y.W.; writing—review and editing, Y.W., B.A.G. and W.D.; visualization, B.A.G., W.D. and S.X.; supervision, S.X. and W.D.; project administration, W.D.; funding acquisition, W.D. All authors have read and agreed to the published version of the manuscript.

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