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**Title:** Energy transfer study on Tb<sup>3+</sup>/Eu<sup>3+</sup> Co-activated sol-gel glass-ceramic materials containing MF<sub>3</sub> (M = Y, La) nanocrystals for NUV optoelectronic devices

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# Energy Transfer Study on Tb<sup>3+</sup>/Eu<sup>3+</sup> Co-Activated Sol-Gel Glass-Ceramic Materials Containing MF<sub>3</sub> (M = Y, La) Nanocrystals for NUV Optoelectronic Devices

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**Abstract:** In the present work, the Tb<sup>3+</sup>/Eu<sup>3+</sup> co-activated sol-gel glass-ceramic materials (GCs) containing MF<sub>3</sub> (M = Y, La) nanocrystals were fabricated during controlled heat-treatment of silicate xerogels at 350 °C. The studies of Tb<sup>3+</sup> → Eu<sup>3+</sup> energy transfer process (ET) were performed by excitation and emission spectra along with luminescence decay analysis. The co-activated xerogels and GCs exhibit multicolor emission originated from 4f<sup>n</sup>–4f<sup>n</sup> optical transitions of Tb<sup>3+</sup> (<sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub>, J = 6–3) as well as Eu<sup>3+</sup> ions (<sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub>, J = 0–4). Based on recorded decay curves, it was found that there is a significant prolongation in luminescence lifetimes of the <sup>5</sup>D<sub>4</sub> (Tb<sup>3+</sup>) and the <sup>5</sup>D<sub>0</sub> (Eu<sup>3+</sup>) levels after the controlled heat-treatment of xerogels. Moreover, for both types of prepared GCs, an increase in ET efficiency was also observed (from η<sub>ET</sub> ≈ 16% for xerogels up to η<sub>ET</sub> = 37.3% for SiO<sub>2</sub>-YF<sub>3</sub> GCs and η<sub>ET</sub> = 60.8% for SiO<sub>2</sub>-LaF<sub>3</sub> GCs). The changes in photoluminescence behavior of rare-earth (RE<sup>3+</sup>) dopants clearly evidenced their partial segregation inside low-phonon energy fluoride environment. The obtained results suggest that prepared SiO<sub>2</sub>-MF<sub>3</sub>:Tb<sup>3+</sup>, Eu<sup>3+</sup> GC materials could be considered for use as optical elements in RGB-lighting optoelectronic devices operating under near-ultraviolet (NUV) excitation.

**Keywords:** Tb<sup>3+</sup>/Eu<sup>3+</sup> energy transfer; sol-gel technique; glass-ceramics; NUV excitation

## 1. Introduction

The development of materials dedicated to photonic applications is a frontier area of current materials engineering research [1,2]. Thus, considerable efforts are still being made to improve the optical parameters of such materials, e.g., the tuning of emissions in the desired spectrum range. In this case, the willingly studied pathway for generation a white light is related to the mixing of three primary colors—red, green and blue (RGB)—in optical materials. Such red-green-blue multicolor visible light can be achieved via up-conversion of near-infrared radiation (NIR) [3–7] or via the conversion of near-ultraviolet (NUV) photons [8–10]. Since rare-earth ions (RE<sup>3+</sup>) exhibit a broad range of emission in the visible (VIS) spectral scope via interactions with NIR and NUV irradiation, they are considered as essential parts in the development of white-light-emitting RGB materials [11,12]. The first of abovementioned ways of generating RGB emission can be realized via NIR up-conversion excitation in doubly (e.g., Yb<sup>3+</sup>/Er<sup>3+</sup> [3,4], Yb<sup>3+</sup>/Tm<sup>3+</sup> [4]) and triply doped (e.g., Yb<sup>3+</sup>/Er<sup>3+</sup>/Tm<sup>3+</sup> [5,6], Tb<sup>3+</sup>/Tm<sup>3+</sup>/Yb<sup>3+</sup> [7]) optical systems. For example, for Yb<sup>3+</sup>/Er<sup>3+</sup>/Tm<sup>3+</sup> triply doped β-NaYF<sub>4</sub> microrods, Er<sup>3+</sup> ions are responsible for the generation of red (the <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition) as well as green (the <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> and the <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions) emissions through a two-photon absorption process involved in Yb<sup>3+</sup> → Er<sup>3+</sup> energy transfer. Simultaneously, due to the three-photon assisted process of Yb<sup>3+</sup> → Tm<sup>3+</sup> energy transfer, Tm<sup>3+</sup> ions are able to emit blue

light (the  $^1D_2 \rightarrow ^3F_4$  and the  $^1G_4 \rightarrow ^3H_6$  transitions) [5]. The second of the abovementioned routes can be realized via the successful conversion of NUV irradiation into VIS light. In this matter,  $Eu^{3+}$  ions are treated as a red or reddish-orange light source (the  $^5D_0 \rightarrow ^7F_J$  transitions,  $J = 0-4$ ) and  $Tb^{3+}$  ions are considered as one of the most important sources of green emission (the  $^5D_4 \rightarrow ^7F_5$  transition). Therefore, co-doping with  $Tb^{3+}/Eu^{3+}$  ions seems to be a promising strategy for the generation of multicolor luminescence, which plays a key role in RGB optical materials [13–16].

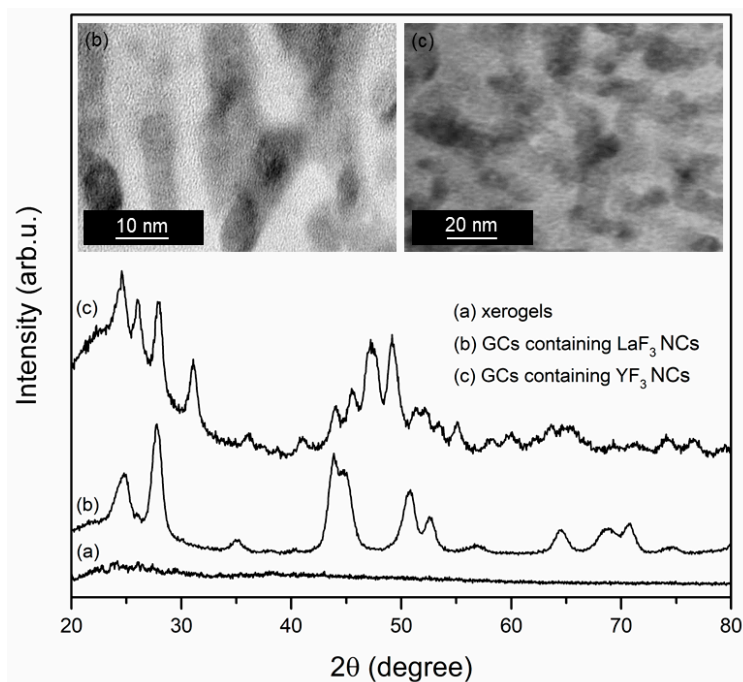
Another particularly important point in the field of substantial enhancement, the luminescence of  $RE^{3+}$  ions is related to the selection of a suitable host lattice with low phonon energy. Since the phonon energies of fluorides—usually in a range from 400 up to 500  $cm^{-1}$  [17]—are significantly lower compared to phosphates ( $\sim 1250\text{ cm}^{-1}$ ) [18] or borates ( $\sim 1350\text{ cm}^{-1}$ ) [19], they are considered as great candidates for generating an efficient and long-lived luminescence of  $RE^{3+}$ . Among fluorides, special attention should be paid to  $YF_3$  and  $LaF_3$  crystal phases characterized by wide band gap ( $>10\text{ eV}$ ) and exceptionally low-phonon energies equal to  $\sim 358$  as well as  $\sim 350\text{ cm}^{-1}$ , respectively, in which  $M^{3+}$  ( $M = Y, La$ ) cations from crystal lattices can be easily substituted by  $RE^{3+}$  ions without any charge compensation [20–23]. Due to the above reasons, the oxyfluoride glass-ceramic materials (GCs) containing fluoride nanocrystals are considered as an interesting class of advanced optical materials, which are frequently reported in the literature [24–28]. Indeed, they successfully combine the advantages of the individual fluoride crystal phase with good mechanical strength and thermal durability of oxide hosts [29,30]. It should also be noted that due to the compliance with the principles of green chemistry, the systematic elimination of  $PbF_2$  (characterized by exceptionally low-phonon energy equals to  $\sim 250\text{ cm}^{-1}$  [31]) during preparation is currently a very important aspect. Thus, taking the above considerations into account,  $Tb^{3+}/Eu^{3+}$  co-doped oxyfluoride GCs containing selected fluoride phases (e.g.,  $YF_3$  and  $LaF_3$ ) seems to be a good choice for the generation of efficient visible emissions.

The conventional melt-quenching method followed by controlled heat-treatment at specified time and temperature conditions is currently the most widely used technique for fabricating the class of oxyfluoride GCs [32–36]. On the other hand, the high melting temperatures of glass-forming components (e.g., 1450 °C, 1500 °C [37–39]) increase the risk of volatilization of the fluoride compounds, which may adversely affect the crystallization process of the fluoride fraction. Therefore, an alternative route to obtain oxyfluoride GCs is the sol-gel technique, characterized by low-temperature processing [40–42]. This method is based on hydrolysis, condensation and polycondensation reactions of organometallic precursors, usually alkoxysilanes  $Si(OR)_4$  ( $R = -CH_3, -C_2H_5$ , etc.) in a liquid phase at room temperature [43]. The in-situ crystallization of fluoride phases is possible due to introduction of a fluorinating reagent into reaction system at initial stages, whose role is commonly played by trifluoroacetic acid (TFA) [44]. Since the sintering of sol-gel materials is carried out at significantly lower temperatures (usually  $<500\text{ °C}$ ) than the conventional melt-quenching of glasses, a risk of volatilization of fluorides is adequately lower, meaning that sol-gel processing is preferred. Lower energy consumption also makes the sol-gel technique particularly advantageous and attractive from an environmental friendliness point of view. Simultaneously, to the best of our knowledge, the investigation of  $Tb^{3+}/Eu^{3+}$  energy transfer process in oxyfluoride GCs is extremely rarely described in the available literature. In the literature, there is only one excellent description concentrated on  $YF_3:Tb^{3+}, Eu^{3+}$  nanocrystalline-based GCs fabricated from  $44SiO_2-28Al_2O_3-17NaF-(10-x)YF_3-TbF_{3-x}EuF_3$  ( $x = 0, 0.1, 0.25, 1$ ) glasses during their heat-treatment at 670 °C per 2 h, as far as we know [45]. Due to the above reasons, it seems to be justified to study the  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer in sol-gel GCs containing  $MF_3$  ( $M = La$  or  $Y$ ) nanocrystals.

In the present work, the sol-gel oxyfluoride GCs materials containing  $MF_3:Tb^{3+}, Eu^{3+}$  ( $M = Y, La$ ) nanocrystals were successfully fabricated during controlled heat-treatment at low temperature (350 °C per 10 h) and characterized by detailed luminescence measurements. The studies were performed by means of excitation and emission spectra along with lifetime measurements. Based on photoluminescence results, the interactions between  $Tb^{3+}$  and  $Eu^{3+}$  dopant ions were systematically investigated and the incorporation of dopant ions into the fluoride environment was also analyzed.

## 2. Materials and Methods

The xerogels co-doped with  $Tb^{3+}$  and  $Eu^{3+}$  ions were synthesized using the low-temperature sol-gel method. All reagents used during the described procedure were taken from Aldrich Chemical Co. The sol-gel synthesis was started with the introduction of tetraethoxysilane (TEOS, 98%), ethyl alcohol (98%), deionized water (from Elix 3 system, Millipore, Molsheim, France) and acetic acid (99.5–99.9%) into round-bottom flasks. The molar ratio of components was equal to  $TEOS:C_2H_5OH:H_2O:CH_3COOH = 1:4:10:0.5$  (90 wt.%). To perform hydrolysis and to initialize a condensation reaction, the components were stirred for 30 min. During the next step, the appropriate amounts of acetates, i.e.,  $M(CH_3COO)_3$  ( $M = Y, La$ ; 99.9%) as well as  $Tb(CH_3COO)_3$  (99.999%) and  $Eu(CH_3COO)_3$  (99.999%) were weighed and dissolved in trifluoroacetic acid (TFA, 99%) and obtained mixtures were added into TEOS-based solutions. The molar ratio was equal to  $CF_3COOH:M(CH_3COO)_3:Tb(CH_3COO)_3:Eu(CH_3COO)_3 = 5:1:0.05:0.05$  (10 wt.%) ( $M = Y, La$ ). The resultant solutions were mixed for another 60 min. After sol-gel synthesis, the obtained liquid sols were dried at 35 °C for 7 weeks to form colorless and transparent solid xerogels (denoted in the text as XGs). Their further transformation into glass-ceramic materials containing  $YF_3$  and  $LaF_3$  nanocrystals was realized by controlled heat-treatment in a muffle furnace (FCF 5 5SHP produced by Czylok, Jastrzębie-Zdrój, Poland) at 350 °C per 10 h (the temperature was raised by 10 °C/min from room temperature). After this procedure, the samples were slowly cooled down to room temperature (denoted in the text as  $SiO_2-MF_3$ ,  $M = Y, La$ ). The successful formation of fluoride nanocrystals ( $LaF_3$  NCs:  $P6_3/mmc$ , ICDD PDF-2 No. 08-0461;  $YF_3$  NCs:  $Pnma$ , ICDD PDF-2 No. 32-1431) was verified using X-ray diffraction (XRD, X'Pert Pro diffractometer, Panalytical, Almelo, The Netherlands) and the nanocrystals imaging was done via high-resolution transmission electron microscope (HR-TEM, JEOL JEM 3010, Tokyo, Japan). The results are shown in Figure 1. The average diameters of fabricated nanocrystals were estimated to 8.1 nm for  $LaF_3$  and 15.4 nm for  $YF_3$ . The in-situ formation of  $LaF_3$  and  $YF_3$  nanocrystals during the thermal decomposition of  $La(CF_3COO)_3$  as well as  $Y(CF_3COO)_3$  in applied heat-treatment conditions (350 °C, 10 h) was confirmed and reported in details in our previous works [46,47].



**Figure 1.** Transmission electron microscope (TEM) images and X-ray diffraction (XRD) patterns of fabricated xerogels and glass-ceramic samples.

The excitation and emission spectra as well as decay curves were recorded on Horiba Jobin Yvon FluoroMax-4 spectrofluorimeter (Horiba Jobin Yvon, Longjumeau, France) supplied with 150 W Xe

lamp. The spectra were recorded with  $\pm 0.1$  nm resolution and the decay curves were recorded with  $\pm 2$   $\mu$ s accuracy. All structural and luminescence measurements were carried out at room temperature.

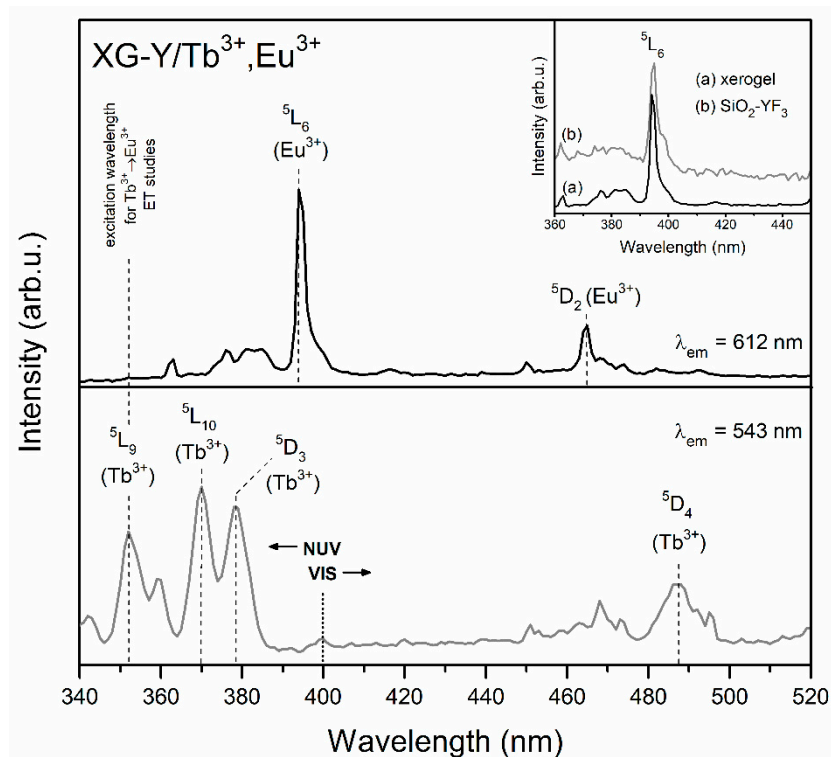
### 3. Results and Discussion

#### 3.1. Excitation Spectra of Fabricated $Tb^{3+}, Eu^{3+}$ Co-Doped Sol-Gel Materials

Figures 2 and 3 present the photoluminescence excitation (PLE) spectra of fabricated  $Tb^{3+}/Eu^{3+}$  co-doped xerogels. The PLE spectra were recorded in the spectral range from 340 to 520 nm and monitored at  $\lambda_{em} = 543$  nm and  $\lambda_{em} = 612$  nm emissions (the  $^5D_4 \rightarrow ^7F_5$  green line of  $Tb^{3+}$  ions and the  $^5D_0 \rightarrow ^7F_2$  red line of  $Eu^{3+}$ , respectively). The recorded bands were attributed to the  $4f^8-4f^8$  and  $4f^6-4f^6$  intra-configurational transitions from both of optically active ions. The bands originating from  $Eu^{3+}$  were assigned to the following transitions:  $^7F_0 \rightarrow ^5D_4$  (363 nm),  $^7F_0 \rightarrow ^5G_J, ^5L_7$  (from 372 nm to 389 nm),  $^7F_0 \rightarrow ^5L_6$  (394 nm) and  $^7F_0 \rightarrow ^5D_2$  (464 nm). Among the group of excitation bands originated from  $Tb^{3+}$  ions, the transitions were ascribed to the electronic transitions from the  $^7F_6$  ground level into the subsequent upper-lying states:  $^5L_9$  (352 nm),  $^5L_{10}$  (370 nm),  $^5D_3$  (378 nm) and  $^5D_4$  (488 nm).

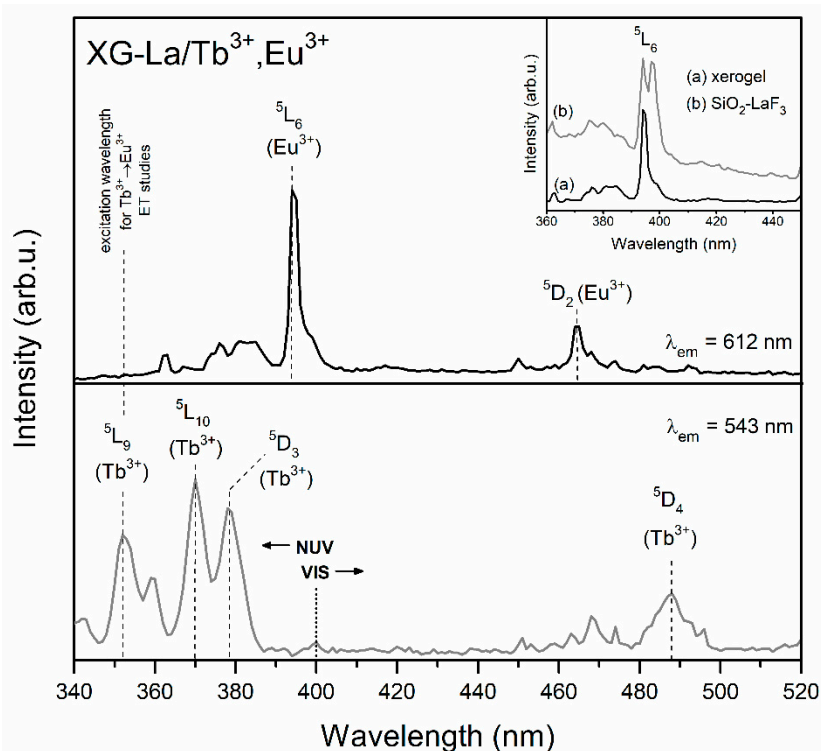
The selection of excitation parameters for further emission measurements and to study the  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer process was done from the near-UV (NUV) irradiation area ( $<400$  nm) due to the greater intensity of recorded excitation lines than in visible light (VIS) scope ( $>400$  nm). Indeed, the optical elements considered to be used in RGB-lighting devices should operate under NUV excitation. Since the  $^7F_0 \rightarrow ^5L_6$  excitation band of  $Eu^{3+}$  is the most intense, we decided to perform the luminescence measurements for  $Eu^{3+}$  ions using  $\lambda_{exc} = 394$  nm wavelength.

As the band associated to the  $^7F_6 \rightarrow ^5L_9$  transition of  $Tb^{3+}$  ions does not coincide with any excitation peak of  $Eu^{3+}$ , the choice of  $\lambda_{exc} = 352$  nm wavelength as the excitation source for the generation of the  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer seems to be reasonable. Additionally, in order to compare the luminescence behavior of sol-gel samples co-doped with  $Tb^{3+}/Eu^{3+}$  ions with samples singly doped with  $Tb^{3+}$  ions, all photoluminescence measurements for  $Tb^{3+}$  ions were performed using the  $\lambda_{exc} = 352$  nm excitation line.



**Figure 2.** Photoluminescence excitation (PLE) spectra of XG-Y/ $Tb^{3+}, Eu^{3+}$  co-doped sample, monitored at  $\lambda_{em} = 543$  nm and  $\lambda_{em} = 612$  nm.



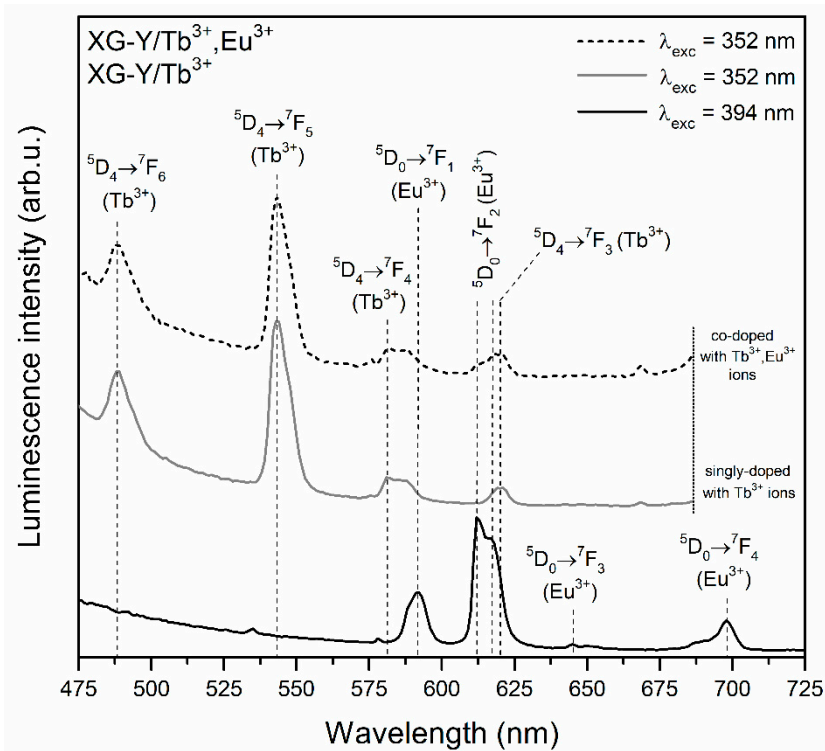


**Figure 3.** PLE spectra of XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup> co-doped sample, monitored at  $\lambda_{em} = 543$  nm and  $\lambda_{em} = 612$  nm.

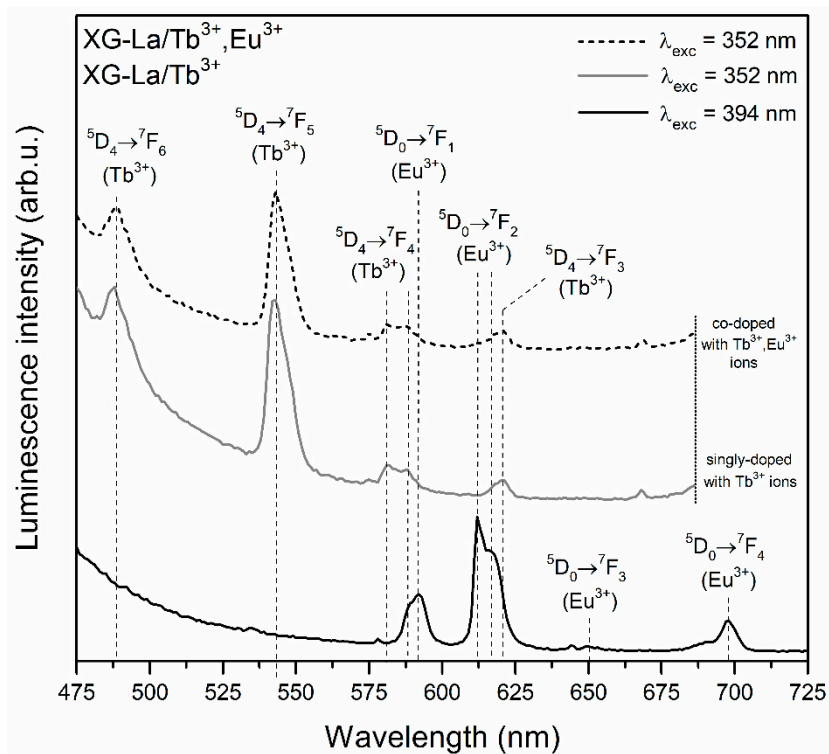
It should be also noted that for prepared GC samples, the  ${}^7F_0 \rightarrow {}^5L_6$  excitation line was split into two separated components, the maxima of which were located at 394 and 397 nm (shown in inset of Figures 2 and 3). Similar results were reported by A.C. Yanes et al. [48] for sol-gel glass-ceramics with 89.9SiO<sub>2</sub>-10LaF<sub>3</sub>:0.1EuF<sub>3</sub> (mol %) composition. Based on numerous photoluminescence measurements (excitation and emission spectra recorded at different temperatures: room temperature (RT), 100 and 13 K; analysis of emission spectra under excitation at 393 and 396 nm), it was clearly proven that the two PLE components are strictly related to the distribution of Eu<sup>3+</sup> between the SiO<sub>2</sub> sol-gel host (393 nm component) and LaF<sub>3</sub> nanocrystals (396 nm component). Thus, in the case of our studied sol-gel samples, we also assumed that the origin of such a split after the controlled heat-treatment of xerogels (XG-Y/Tb<sup>3+</sup>,Eu<sup>3+</sup> and XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup>) is related to the partial migration of rare-earths from silicate sol-gel host into MF<sub>3</sub> (M = Y, La) nanocrystals. It is quite interesting that deeper splitting of the  ${}^7F_0 \rightarrow {}^5L_6$  band was observed for SiO<sub>2</sub>-LaF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> GC and, in consequence, two strong components with maxima at 394 and 397 nm are visible. For the SiO<sub>2</sub>-YF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> GC sample, the 397 nm component is visible as a weak shoulder. This effect may suggest more efficient segregation of dopant ions in LaF<sub>3</sub> than YF<sub>3</sub> nanocrystals. Analogous results were reported earlier by us for singly doped SiO<sub>2</sub>-YF<sub>3</sub>:Eu<sup>3+</sup> [46] and SiO<sub>2</sub>-LaF<sub>3</sub>:Eu<sup>3+</sup> [47] GC sol-gel systems.

### 3.2. Influence of Controlled Heat-Treatment at 350 °C on Tb<sup>3+</sup> → Eu<sup>3+</sup> Energy Transfer

The photoluminescence (PL) spectra recorded for prepared silicate xerogels are illustrated in Figure 4 (XG-Y/Tb<sup>3+</sup> and XG-Y/Tb<sup>3+</sup>,Eu<sup>3+</sup>) as well as in Figure 5 (XG-La/Tb<sup>3+</sup> and XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup>). The excitation of Eu<sup>3+</sup> ions using the  $\lambda_{exc} = 394$  nm wavelength resulted in the appearance of luminescence bands located within the reddish-orange light area:  ${}^5D_0 \rightarrow {}^7F_0$  (578 nm),  ${}^5D_0 \rightarrow {}^7F_1$  (592 nm),  ${}^5D_0 \rightarrow {}^7F_2$  (611 nm),  ${}^5D_0 \rightarrow {}^7F_3$  (645 nm), and  ${}^5D_0 \rightarrow {}^7F_4$  (698 nm). Since the local framework around Eu<sup>3+</sup> ions in sol-gel host is non-symmetric, the most intense emission line corresponds to the  ${}^5D_0 \rightarrow {}^7F_2$  electric-dipole transition and red-to-orange ratio (R/O) values for fabricated xerogels are relatively high (R/O = 3.01 for XG-Y/Tb<sup>3+</sup>,Eu<sup>3+</sup>; R/O = 2.78 for XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup>).



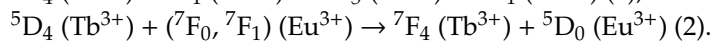
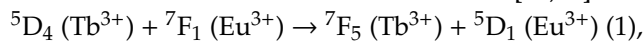
**Figure 4.** Photoluminescence (PL) spectra of XG-Y/Tb<sup>3+</sup> and XG-Y/Tb<sup>3+</sup>,Eu<sup>3+</sup> samples recorded upon near-ultraviolet (NUV) illumination at  $\lambda_{\text{exc}} = 352$  nm and  $\lambda_{\text{exc}} = 394$  nm.



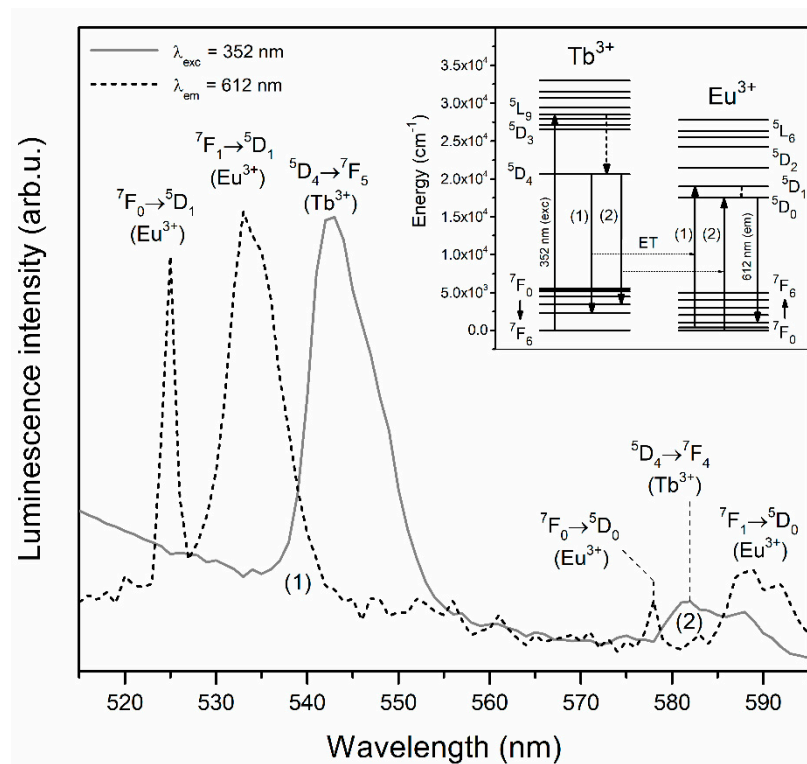
**Figure 5.** PL spectra of XG-La/Tb<sup>3+</sup> and XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup> samples recorded upon NUV illumination at  $\lambda_{\text{exc}} = 352$  nm and  $\lambda_{\text{exc}} = 394$  nm.

The PL spectra recorded upon excitation at  $\lambda_{\text{exc}} = 352$  nm for xerogels singly doped with Tb<sup>3+</sup> ions revealed two emission bands in the bluish-green spectral scope, i.e.,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$  (488 nm) and the most prominent  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  (543 nm) line. Two other emission bands of Tb<sup>3+</sup> ions were detected in

the yellowish-red range:  ${}^5D_4 \rightarrow {}^7F_4$  (584 nm) and  ${}^5D_4 \rightarrow {}^7F_3$  (619 nm). The excitation of  $Tb^{3+}/Eu^{3+}$  co-doped xerogels using  $\lambda_{exc} = 352$  nm wavelength led to generating the characteristic emission lines of  $Tb^{3+}$  ions; however, it should be noted that some spectral broadening of the  ${}^5D_4 \rightarrow {}^7F_4$  as well as the  ${}^5D_4 \rightarrow {}^7F_3$  bands was observed. Such broadening is a consequence of the energy transfer process from  $Tb^{3+}$  to  $Eu^{3+}$ , which resulted in the appearance of additional luminescence coming from  $Eu^{3+}$  dopant ( ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$  transitions) [49–52]. In general, the spectral matching of donor's emission ( $Tb^{3+}$ ) and acceptor's excitation ( $Eu^{3+}$ ) regions is a fundamental condition for energy transfer occurrence. In this way, upon irradiation using  $\lambda_{exc} = 352$  nm line from NUV spectral region,  $Tb^{3+}$  ions could be successfully pumped into the  ${}^5L_9$  level and then the non-radiative de-activation to the  ${}^5D_4$  state takes place. Since there is spectral overlapping between the  ${}^5D_4 \rightarrow {}^7F_5, {}^7F_4$  emissions of  $Tb^{3+}$  and the  ${}^7F_1 \rightarrow {}^5D_1$  and the  ${}^7F_0, {}^7F_1 \rightarrow {}^5D_0$  excitation bands of  $Eu^{3+}$ , the energy could be successfully transferred from  $Tb^{3+}$  into  $Eu^{3+}$  ions as follows [53,54]:



Hence, among the characteristic emission lines from  $Tb^{3+}$  ions, additional bands originated from  $Eu^{3+}$  can also be recorded. The matching of  $Tb^{3+}$  emission and  $Eu^{3+}$  excitation as well as illustration of energy levels involved in  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer process are depicted in Figure 6.

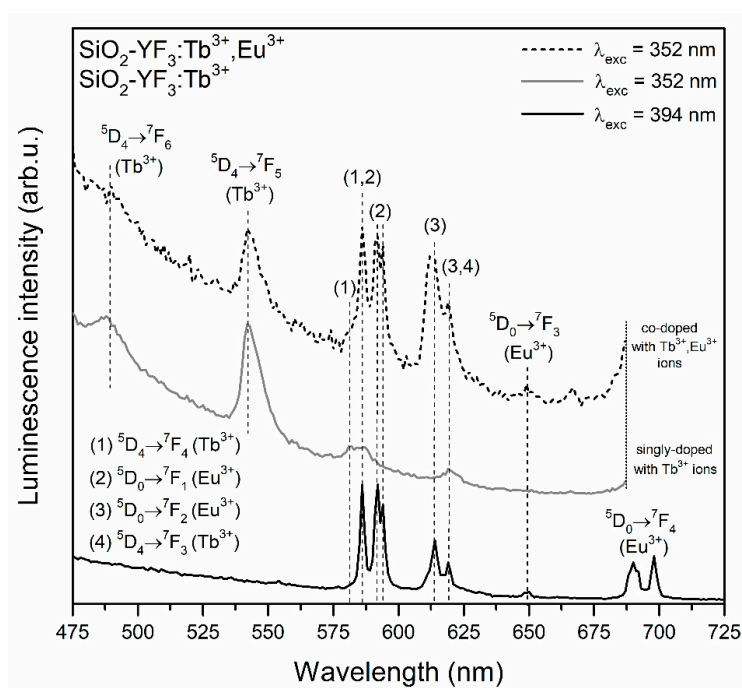


**Figure 6.** An overlap of  $Tb^{3+}$  emission ( $\lambda_{exc} = 352$  nm) and  $Eu^{3+}$  excitation ( $\lambda_{em} = 612$  nm) regions and illustration of energy levels involved in  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer process.

The PL spectra recorded for glass-ceramic materials are shown in Figure 7 ( $SiO_2-YF_3:Tb^{3+}$  and  $SiO_2-YF_3:Tb^{3+}, Eu^{3+}$ ) and Figure 8 ( $SiO_2-LaF_3:Tb^{3+}$  and  $SiO_2-LaF_3:Tb^{3+}, Eu^{3+}$ ). For both types of prepared co-doped GC, a well-resolved Stark structure of recorded luminescence bands of  $Eu^{3+}$  ions was observed, which points to crystalline-like environment around them. For  $SiO_2-YF_3:Tb^{3+}, Eu^{3+}$  GCs the following maxima are located at: 586/592/594 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ), 614 nm/619 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ), 650 nm ( ${}^5D_0 \rightarrow {}^7F_3$ ) and 690/692/698 nm ( ${}^5D_0 \rightarrow {}^7F_4$ ), while for  $SiO_2-YF_3:Tb^{3+}, Eu^{3+}$  GCs, the maxima of individual emission bands were detected at the following wavelengths: 590 nm ( ${}^5D_0 \rightarrow {}^7F_1$ ), 612 nm/618 nm ( ${}^5D_0 \rightarrow {}^7F_2$ ), 649 nm ( ${}^5D_0 \rightarrow {}^7F_3$ ) and 680/688/692 nm ( ${}^5D_0 \rightarrow {}^7F_4$ ). Such clear splitting is

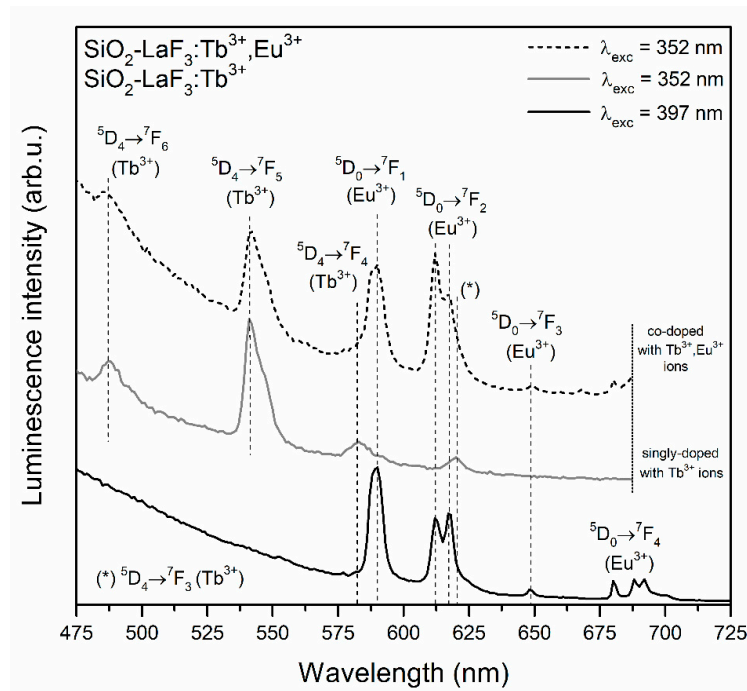


a consequence of the partial segregation of  $\text{Eu}^{3+}$  ions inside fluoride crystal lattices. Indeed, when  $\text{Eu}^{3+}$  ions are inserted into the crystal lattice, the subsequent energy levels get split by the crystal-field effect and the number of sub-levels depends on the local site symmetry. It is reported in the literature that in  $\text{YF}_3$  and  $\text{LaF}_3$  crystal lattices,  $\text{Eu}^{3+}$  ions occupy  $C_s$  and  $C_{2v}$  point symmetry sites, respectively [55,56]. If  $\text{Eu}^{3+}$  ions occupy  $C_s$  and  $C_{2v}$  site symmetry, the J term of the  ${}^7F_J$  levels should split into three ( $J = 1$ ), five ( $J = 2$ ), seven ( $J = 3$ ) and nine ( $J = 4$ ) sub-levels [57]. However, observation of such strong splitting for glass-ceramic systems is quite difficult due to the partial distribution of  $\text{Eu}^{3+}$  ions within the amorphous sol-gel host. Moreover, compared to xerogels, a significant increase in intensity of the  ${}^5D_0 \rightarrow {}^7F_1$  magnetic-dipole transition band was observed, while the intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  electric-dipole transition is strongly inhibited. Generally, the  ${}^5D_0 \rightarrow {}^7F_1$  magnetic-dipole transition is orbitally allowed and practically insensitive to symmetry in the local environment around  $\text{Eu}^{3+}$  ions. Conversely, the  ${}^5D_0 \rightarrow {}^7F_{0,2-4}$  electric-dipole transitions are forbidden in centrosymmetric sites due to the same parity of energy levels. However, if  $\text{Eu}^{3+}$  ions are located in non-centrosymmetric sites, the transitions became allowed as forced electric-dipole transitions due to the mixing of wavefunctions of  $4f^6$  sublevels with different J values. Therefore, the ratio of integrated luminescence intensity of the  ${}^5D_0 \rightarrow {}^7F_2$  electric-dipole transition to the  ${}^5D_0 \rightarrow {}^7F_1$  magnetic-dipole transition can inform us about local symmetry around  $\text{Eu}^{3+}$  ions and is called the R/O ratio. A decrease in R/O-ratio value clearly suggests that local symmetry around  $\text{Eu}^{3+}$  ions is closer to an inversion center. The calculated R/O ratio values after controlled heat-treatment are relatively low (R/O = 0.42 for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$ ; R/O = 0.89 for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$ ), which clearly points to the partial migration of  $\text{Eu}^{3+}$  ions from sol-gel host into more symmetric fluoride crystal phases.



**Figure 7.** PL spectra of  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}$  and  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  samples recorded under NUV excitation at  $\lambda_{\text{exc}} = 352$  nm and  $\lambda_{\text{exc}} = 394$  nm.

For the prepared  $\text{SiO}_2\text{-MF}_3\text{:Tb}^{3+}$  GC samples, the characteristic emission bands corresponding to the transitions from the  ${}^5D_4$  excited level into the  ${}^7F_6$ ,  ${}^7F_5$ ,  ${}^7F_4$  and  ${}^7F_3$  lower-lying states were detected. In the case of  $\text{SiO}_2\text{-MF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  co-doped GCs, the mutual coincidence of the luminescence lines originating from both of the rare-earths was clearly observed after excitation at the  $\lambda_{\text{exc}} = 352$  nm line. Therefore, an appearance of characteristic emission bands coming from  $\text{Eu}^{3+}$  ions upon excitation of  $\text{Tb}^{3+}$  confirms the occurrence of  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer.



**Figure 8.** PL spectra of  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}$  and  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  samples recorded under NUV excitation at  $\lambda_{\text{exc}} = 352 \text{ nm}$  and  $\lambda_{\text{exc}} = 397 \text{ nm}$ .

It should be particularly pointed out that the intensity of  $\text{Tb}^{3+}$  emission bands decreased, which was accompanied by the simultaneous enhancement of  $\text{Eu}^{3+}$  luminescence. Such an effect is much more observable for GC samples than for precursor xerogels. Hence, it could suggest that both of the optically active dopants were incorporated into the crystal lattices of the  $\text{YF}_3$  as well as  $\text{LaF}_3$  phases, causing there to be a shorter distance between neighboring  $\text{Tb}^{3+}\text{-Eu}^{3+}$  pairs in comparison with the sol-gel host. Thus, the  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  seems to be more efficient in glass-ceramic materials, which results in a much more intense emission of  $\text{Eu}^{3+}$  ions.

### 3.3. Luminescence Decay Analysis of the $^5\text{D}_4$ ( $\text{Tb}^{3+}$ ) and the $^5\text{D}_0$ ( $\text{Eu}^{3+}$ ) Levels in Sol-Gel Materials

To further optical examination of prepared xerogels and GC materials, the luminescence decay analysis of the  $^5\text{D}_4$  ( $\text{Tb}^{3+}$ ) and the  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) excited states was performed. The analysis of decay profiles allows for the deeper characterization of the  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer process and for establishing the relation between luminescence lifetimes and distribution of rare-earths within sol-gel materials.

Firstly, we compared the luminescence lifetimes of the  $^5\text{D}_4$  level of  $\text{Tb}^{3+}$  ions in singly doped sol-gel materials (Figure 9) and materials co-doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}$  ions (Figure 10). The decay curves were recorded upon NUV excitation ( $\lambda_{\text{exc}} = 352 \text{ nm}$ ) and monitoring a green emission related to the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition of  $\text{Tb}^{3+}$  ( $\lambda_{\text{em}} = 543 \text{ nm}$ ). For xerogels, the curves are well-fitted to mono-exponential functions given by:

$$I(t)/I_0 = A \times \exp(-t/\tau), \quad (1)$$

where  $\tau$  corresponds to the luminescence decay time. It was observed that the  $\tau$  ( $^5\text{D}_4$ ) estimated for  $\text{XG-Y/Tb}^{3+}$  and  $\text{XG-La/Tb}^{3+}$  is quite comparable and equals  $0.97 \pm 0.01$  and  $0.89 \pm 0.02 \text{ ms}$ , respectively. Such negligible differences in luminescence lifetime values are caused by considerable similarity of chemical environment around  $\text{Tb}^{3+}$  in fabricated silicate xerogels. Indeed, the non-radiative relaxation between subsequent J states might occur due to the interaction of electronic levels of  $\text{RE}^{3+}$  ions with suitable vibrational modes in their nearest surrounding. As was proven earlier by infrared measurements, some liquids (residual solvents used during sol-gel process and products of homo-

and heterocondensation reactions) are retained in xerogel pores [46]. In this way,  $Tb^{3+}$  and  $Eu^{3+}$  ions are coordinated by  $CF_3COO^-$  anions (C=O groups:  $\sim 1650\text{ cm}^{-1}$ , C–F bond:  $\sim 1200\text{ cm}^{-1}$ ) and OH groups ( $>3000\text{ cm}^{-1}$ ). According to energy gap law, an increase in the non-radiative decay rate is assisted by the decreasing number of phonons needed to cover the energy gap,  $\Delta E$ . Since OH groups are characterized by higher vibrational energy than  $CF_3COO^-$  anions, we assumed that OH groups with higher phonon energies play a major role in non-radiative relaxation from the  $^5D_4$  state. In this way, a maximum of five OH phonons are needed to cover the  $^5D_4 \rightarrow ^7F_0$  energy gap of  $Tb^{3+}$  ions ( $\Delta E = 15,000\text{ cm}^{-1}$ ); therefore, the probability of non-radiative depopulation from the  $^5D_4$  state in xerogels is relatively high.

A comparison of luminescence lifetimes of the  $^5D_4$  state for xerogels singly doped with  $Tb^{3+}$  ions and co-doped with  $Tb^{3+}/Eu^{3+}$  ions reveals a slight shortening when  $Tb^{3+}$  ions coexist with  $Eu^{3+}$  ions in the same host. Indeed, it was reported that there was a decrease from  $0.97 \pm 0.01$  to  $0.82 \pm 0.03$  ms for XG-Y/ $Tb^{3+}, Eu^{3+}$  and from  $0.89 \pm 0.02$  to  $0.75 \pm 0.03$  ms for XG-La/ $Tb^{3+}, Eu^{3+}$ . Therefore, such an effect is a clear evidence of  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer occurrence. The energy transfer efficiency ( $\eta_{ET}$ ) between  $Tb^{3+}$  and  $Eu^{3+}$  ions could be expressed by the following Equation [54,58]:

$$\eta_{ET} = \left(1 - \frac{\tau}{\tau_0}\right) \times 100\% \quad (2)$$

where  $\tau$  and  $\tau_0$  correspond to intrinsic the decay lifetime of the  $^5D_4$  excited level of  $Tb^{3+}$  in the presence and absence of acceptor ions ( $Eu^{3+}$ ) in the host lattice, respectively. Indeed, the shortening of the donor's lifetime when the acceptor coexists is a measure of its ability for energy transfer. The energy transfer efficiencies for prepared xerogels are depicted in Table 1. The calculated efficiencies of  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer for both of co-doped xerogels are comparable and they are close to  $\eta_{ET} \approx 16\%$ . The comparability in  $\eta_{ET}$  values is a consequence of the chemical similarity of the nearest framework around rare-earths ( $Tb^{3+}$ ,  $Eu^{3+}$ ) in xerogels. Such relatively low efficiencies are correlated with the long interionic distances between  $Tb^{3+}$  and  $Eu^{3+}$  ions dispersed within silicate sol-gel host.

**Table 1.** Luminescence lifetimes of the  $^5D_4$  state of  $Tb^{3+}$  ( $\tau$ ) and ET efficiencies ( $\eta_{ET}$ ) for fabricated silicate xerogels.

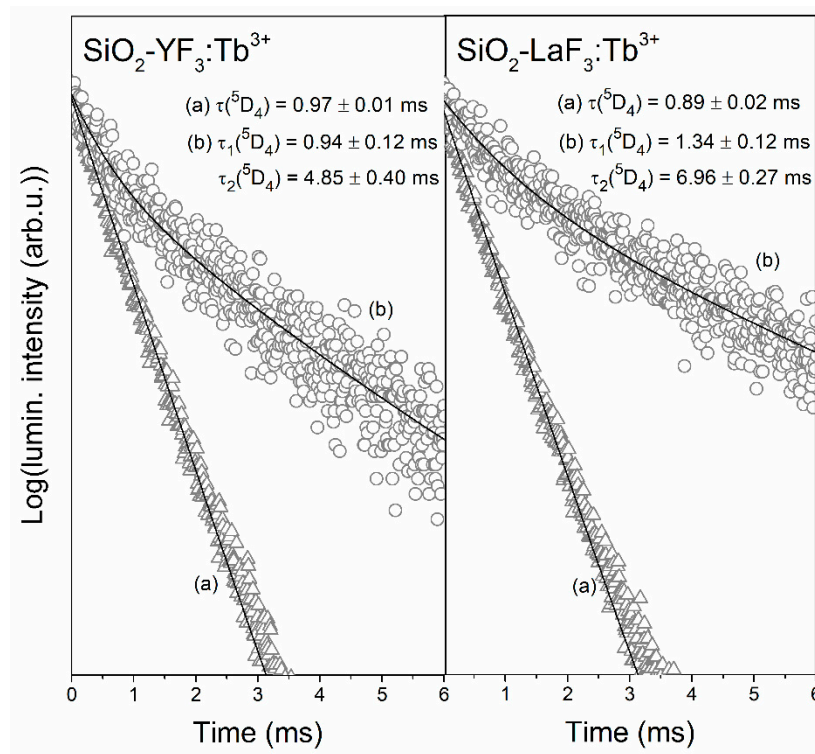
Sample	$\tau(^5D_4)$ (ms)	$\eta_{ET}$ (%)
XG-Y/ $Tb^{3+}, Eu^{3+}$	$0.82 \pm 0.03$	15.5
XG-Y/ $Tb^{3+}$	$0.97 \pm 0.01$	-
XG-La/ $Tb^{3+}, Eu^{3+}$	$0.75 \pm 0.03$	15.7
XG-La/ $Tb^{3+}$	$0.89 \pm 0.02$	-

For glass-ceramic samples the recorded decay curves are well-fitted to double-exponential functions, which can be expressed by following Equation:

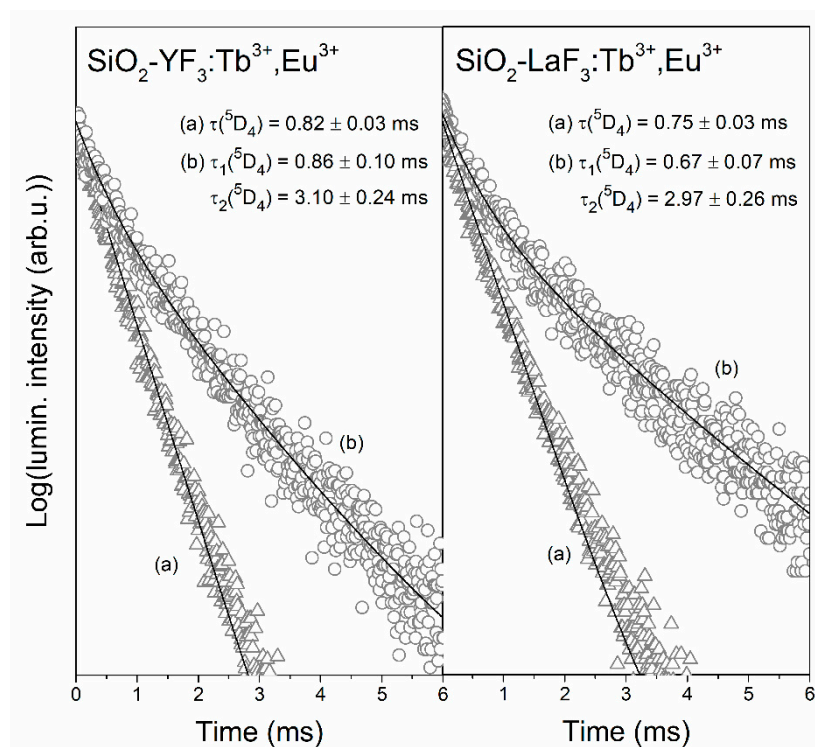
$$I(t)/I_0 = A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2), \quad (3)$$

where  $\tau_1$  is the decay time of a short lifetime component,  $\tau_2$  is the decay time of a long component, while the  $A_1$  and  $A_2$  parameters are amplitudes at  $t = 0$ . The double-exponential character of the decay curves clearly means that  $Tb^{3+}$  ions are distributed between two different surroundings in which decay processes take place with variable rates. The first of them is a silicate sol-gel network in which the luminescence lifetimes of the  $^5D_4$  state of  $Tb^{3+}$  ions are shorter ( $\tau_1$  decay component) due to presence of high-vibrational energy modes in their local framework (numerous  $Q^3$  units of  $SiO_4$  tetrahedrons ( $\sim 1050\text{ cm}^{-1}$ ) and residual Si–OH groups ( $>3000\text{ cm}^{-1}$ )). The second surrounding is according to fluorides, i.e.,  $YF_3$  and  $LaF_3$  nanocrystals. Due to their low-phonon energies close to  $\sim 358$  ( $YF_3$  phase) and  $\sim 350\text{ cm}^{-1}$  ( $LaF_3$  phase), the radiative relaxation from the  $^5D_4$  excited state is strongly promoted, and thus, the luminescence lifetimes are considerably prolonged ( $\tau_2$  decay component). In other words,

the change in decay profiles from mono-exponential functions (for xerogels) into double-exponential functions (for GCs) is evident proof, which allowed us to conclude that dopant ions are located either in a silicate sol-gel host or fluoride nanocrystals.



**Figure 9.** Luminescence decay curves of the  $^5D_4$  state of  $Tb^{3+}$  recorded for xerogels (a) and glass-ceramics (b) singly doped with  $Tb^{3+}$  ions.



**Figure 10.** Luminescence decay curves of the  $^5D_4$  state of  $Tb^{3+}$  recorded for xerogels (a) and glass-ceramics (b) co-doped with  $Tb^{3+}/Eu^{3+}$  ions.

It is quite interesting that the  $\tau_2(^5D_4)$  component for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}$  GC is longer ( $6.96 \pm 0.27$  ms) compared with the  $\tau_2(^5D_4)$  component for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}$  GC ( $4.85 \pm 0.40$  ms). Since the phonon energies of  $\text{YF}_3$  and  $\text{LaF}_3$  fluoride phases are almost the same, we assumed that such difference in  $\tau_2$  lifetime values may suggest that the migration of  $\text{Tb}^{3+}$  ions from silicate sol-gel host into  $\text{LaF}_3$  phase could be more efficient than into  $\text{YF}_3$  nanocrystals. It should be also pointed out that co-doping with  $\text{Eu}^{3+}$  ions lead to the considerable shortening of  $\tau_2(^5D_4)$  components due to occurrence of  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  ET process ( $3.10 \pm 0.24$  ms for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC and  $2.97 \pm 0.26$  ms for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC). To estimate the energy transfer efficiencies, we used the average luminescence lifetimes of the  $^5D_4$  state for glass-ceramic materials singly doped with  $\text{Tb}^{3+}$  and co-doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}$  ions calculated from the following Equation [59]:

$$\tau_{\text{avg}} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (4)$$

where  $A_1$  and  $A_2$  are fitting constants, and  $\tau_1$  and  $\tau_2$  are short and long decay components, respectively.

To determine the percentage contribution of short- ( $\tau_1$ ) and long-lived ( $\tau_2$ ) components involved in the total decay process, the following equations were used:

$$\%, \tau_1 = \frac{A_1}{A_1 + A_2} \times 100\%, \quad (5)$$

$$\%, \tau_2 = \frac{A_2}{A_1 + A_2} \times 100\%. \quad (6)$$

For both  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}$  as well as  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GCs, the percentage contributions of  $\tau_1$  and  $\tau_2$  are quite comparable and equal nearly 50%. A slightly different observation was attained for GCs containing  $\text{LaF}_3$  nanocrystals. The difference in contribution of  $\tau_1$  and  $\tau_2$  decay components is slightly more visible for GCs containing  $\text{LaF}_3$  nanocrystals. For the sample singly doped with  $\text{Tb}^{3+}$  ions, the contribution of the  $\tau_2$  component is slightly larger (56.42%) than that of the  $\tau_1$  component (43.58%); meanwhile, co-doping with  $\text{Eu}^{3+}$  ions results in an increase in the  $\tau_1$  component's contribution (57.16%) and slight decrease in  $\tau_2$  contribution (42.84%). The luminescence lifetimes of the  $^5D_4$  state of  $\text{Tb}^{3+}$  ions, their percentage contribution ( $\%, \tau_n(^5D_4)$ ), average lifetimes ( $\tau_{\text{avg}}$ ) and the  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  ET efficiencies ( $\eta_{\text{ET}}$ ) for fabricated GCs are depicted in Table 2.

**Table 2.** Luminescence lifetimes of the  $^5D_4$  state of  $\text{Tb}^{3+}$ , their contribution and energy transfer (ET) efficiencies ( $\eta_{\text{ET}}$ ) for fabricated glass-ceramics.

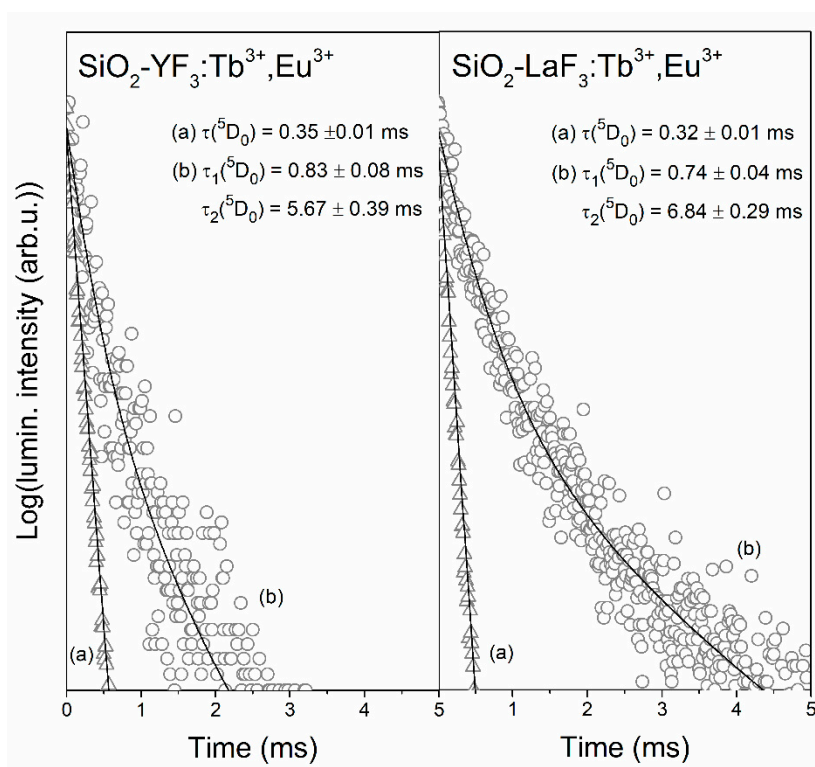
Sample	$\tau(^5D_4)$ (ms)	$\%, \tau_n(^5D_4)$	$\tau_{\text{avg}}(^5D_4)$ (ms)	$\eta_{\text{ET}}$ (%)
$\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$	$0.86 \pm 0.10$ ( $\tau_1$ )	49.79% ( $\tau_1$ )	2.62	37.3
	$3.10 \pm 0.24$ ( $\tau_2$ )	50.21% ( $\tau_2$ )		
$\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}$	$0.94 \pm 0.12$ ( $\tau_1$ )	51.50% ( $\tau_1$ )	4.18	-
	$4.85 \pm 0.40$ ( $\tau_2$ )	48.50% ( $\tau_2$ )		
$\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$	$0.67 \pm 0.07$ ( $\tau_1$ )	57.16% ( $\tau_1$ )	2.44	60.8
	$2.97 \pm 0.26$ ( $\tau_2$ )	42.84% ( $\tau_2$ )		
$\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}$	$1.34 \pm 0.12$ ( $\tau_1$ )	43.58% ( $\tau_1$ )	6.23	-
	$6.96 \pm 0.27$ ( $\tau_2$ )	56.42% ( $\tau_2$ )		

It was observed that the average luminescence lifetime for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC ( $\tau_{\text{avg}}(^5D_4) = 2.44$  ms) is 2.6-fold shorter than for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}$  GC ( $\tau_{\text{avg}}(^5D_4) = 6.23$  ms), while for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC ( $\tau_{\text{avg}}(^5D_4) = 2.62$  ms), it is 1.6-fold shorter than for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}$  GC ( $\tau_{\text{avg}}(^5D_4) = 4.18$  ms). The greater shortening of  $\tau_{\text{avg}}(^5D_4)$  luminescence lifetime for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC than for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  GC indicates a more efficient  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer. Indeed, the calculated ET efficiency value for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  ( $\eta_{\text{ET}} = 60.8\%$ ) is about 1.6-fold higher than for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+}, \text{Eu}^{3+}$  ( $\eta_{\text{ET}} = 37.3\%$ ). It should also be noted that the transformation from xerogels into glass-ceramic materials during controlled heat-treatment strongly determines the  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$



energy transfer efficiency,  $\eta_{ET}$ , which increased from ~16% (xerogels) up to 37.3% ( $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  GCs) and 60.8% ( $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  GCs).

The luminescence decay curves of the  $^5\text{D}_0$  state of  $\text{Eu}^{3+}$  ions in xerogels and  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  as well as  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  glass-ceramics were recorded for  $\lambda_{em} = 611$  nm (Figure 11). Similarly, as in the case of decay curves recorded for the  $^5\text{D}_4$  state of  $\text{Tb}^{3+}$  ions, the curves of the  $^5\text{D}_0$  level are well-fitted to mono-exponential functions for xerogels and to double-exponential functions for GCs. Relatively short luminescence lifetimes for xerogels are caused by the coordination of  $\text{Eu}^{3+}$  ions by high-vibrational OH groups, which are involved in the non-radiative depopulation of the  $^5\text{D}_0$  level (only four phonons are needed to cover energy gap,  $\Delta E = 12,500$   $\text{cm}^{-1}$ ). Since controlled heat-treatment of xerogels resulted in the partial migration of  $\text{Eu}^{3+}$  ions inside fluoride nanocrystals, we distinguished two significantly different luminescence lifetimes ( $\tau_1, \tau_2$ ). From the decays, it could be concluded that there is a clear correlation between the designated luminescence lifetimes and energy transfer efficiencies ( $\eta_{ET}$ ) related to the relative distribution of rare-earths between silicate sol-gel host and fluoride environment. The higher energy transfer efficiency for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  ( $\eta_{ET} = 60.8\%$ ) results in longer decay components ( $\tau_1(^5\text{D}_0) = 0.74 \pm 0.04$  ms,  $\tau_2(^5\text{D}_0) = 6.84 \pm 0.29$  ms) than for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  ( $\tau_1(^5\text{D}_0) = 0.83 \pm 0.08$  ms,  $\tau_2(^5\text{D}_0) = 5.67 \pm 0.39$  ms) with lower  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  energy transfer efficiency ( $\eta_{ET} = 37.3\%$ ). Indeed, it was observed that the average luminescence lifetime for  $\text{SiO}_2\text{-LaF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  ( $\tau_{avg}(^5\text{D}_0) = 5.87$  ms) is longer than the average lifetime for  $\text{SiO}_2\text{-YF}_3\text{:Tb}^{3+},\text{Eu}^{3+}$  ( $\tau_{avg}(^5\text{D}_0) = 4.59$  ms). Such an effect could also indicate that the interionic distance between neighboring  $\text{Tb}^{3+}$  and  $\text{Eu}^{3+}$  ions in  $\text{LaF}_3$  nanocrystals seems to be shorter than in the  $\text{YF}_3$  crystal lattice. In other words, this could suggest that the segregation of rare-earths inside the  $\text{LaF}_3$  crystal phase is greater, which promotes the  $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$  ET. The luminescence decay times, their percentage distribution as well as average lifetimes for both types of fabricated GC sample are depicted in Table 3.



**Figure 11.** Luminescence decay curves of the  $^5\text{D}_0$  state of  $\text{Eu}^{3+}$  recorded for xerogels (a) and glass-ceramics (b) co-doped with  $\text{Tb}^{3+}/\text{Eu}^{3+}$  ions.

**Table 3.** Luminescence lifetimes of the  $^5D_0$  state of  $Eu^{3+}$  and their contributions for fabricated glass-ceramics.

Sample	$\tau(^5D_0)$ (ms)	%, $\tau_n(^5D_0)$	$\tau_{avg}(^5D_0)$ (ms)
SiO <sub>2</sub> -YF <sub>3</sub> :Tb <sup>3+</sup> ,Eu <sup>3+</sup>	0.83 ± 0.08 ( $\tau_1$ )	66.30% ( $\tau_1$ )	4.59
	5.67 ± 0.39 ( $\tau_2$ )	33.70% ( $\tau_2$ )	
SiO <sub>2</sub> -LaF <sub>3</sub> :Tb <sup>3+</sup> ,Eu <sup>3+</sup>	0.74 ± 0.04 ( $\tau_1$ )	63.58% ( $\tau_1$ )	5.87
	6.84 ± 0.29 ( $\tau_2$ )	36.42% ( $\tau_2$ )	

The optical characterization of fabricated co-doped sol-gel samples was supplemented with calculations of quantum yields,  $\phi_{Eu}$ . The quantum efficiencies were calculated from  $\phi = k_R/k$  formula in which  $k$  is the total decay rate constant ( $k = 1/\tau$ ) and  $k_R$  is the radiative rate constant estimated from the following Equation [60]:

$$k_R = A_{MD,0}n^3 \left( \frac{I_{tot}}{I_{MD}} \right). \quad (7)$$

In above equation,  $A_{MD,0}$  is according to the Einstein spontaneous emission coefficient for the  $^5D_0 \rightarrow ^7F_1$  transition ( $14.65 \text{ s}^{-1}$  [61]);  $I_{tot}$  is the sum of integrated intensities of the  $^5D_0 \rightarrow ^7F_J$  ( $J = 0-4$ ) luminescence bands of  $Eu^{3+}$ ;  $I_{MD}$  is the integrated intensity of the  $^5D_0 \rightarrow ^7F_1$  magnetic-dipole transition and  $n$  is the refractive index. The refractive index of YF<sub>3</sub> and LaF<sub>3</sub> nanocrystals is almost the same and equals  $n = 1.55-1.56$ . Such values are comparable with previously published results [62,63]. It is quite interesting that the refractive index of LaF<sub>3</sub> nanocrystals is slightly lower than that of the corresponding LaF<sub>3</sub> single crystal, as was proven by Z. Wang et al. [64]. Finally, the calculated quantum yields are depicted in Table 4.

**Table 4.** Quantum yields ( $\phi_{Eu}$ ) calculated for fabricated xerogels and glass-ceramic materials.

Sample	$\phi_{Eu}$ (%)
XG-Y/Tb <sup>3+</sup> ,Eu <sup>3+</sup>	9.2
XG-La/Tb <sup>3+</sup> ,Eu <sup>3+</sup>	8.1
SiO <sub>2</sub> -YF <sub>3</sub> :Tb <sup>3+</sup> ,Eu <sup>3+</sup>	73.0
SiO <sub>2</sub> -LaF <sub>3</sub> :Tb <sup>3+</sup> ,Eu <sup>3+</sup>	49.5

The quantum efficiencies for xerogels are comparable and equal to 9.2% for XG-Y/Tb<sup>3+</sup>,Eu<sup>3+</sup> and 8.1% for XG-La/Tb<sup>3+</sup>,Eu<sup>3+</sup>. Much greater differences in quantum efficiencies were denoted for fabricated glass-ceramics. In fact, the  $\phi_{Eu}$  calculated for SiO<sub>2</sub>-YF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> GC equal to 49.5%, meanwhile for SiO<sub>2</sub>-LaF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> GC sample, the  $\phi_{Eu}$  value achieve even 73.0%. The observed significant difference is clearly related to Tb<sup>3+</sup> → Eu<sup>3+</sup> energy transfer, the efficiency of which is much greater for SiO<sub>2</sub>-LaF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> ( $\eta_{ET} = 60.8\%$ ) compared with SiO<sub>2</sub>-YF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> glass-ceramics ( $\eta_{ET} = 37.3\%$ ). Based on the current literature, the luminescence quantum yields for Tb<sup>3+</sup>,Eu<sup>3+</sup> co-doped nanocrystals are usually in a range from 32% to 61% [65]. It is very interesting that the  $\phi_{Eu}$  value for SiO<sub>2</sub>-YF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> is in good accordance with the presented data, but the SiO<sub>2</sub>-LaF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> GC sample is characterized by a greater quantum efficiency value. Furthermore, as was proven by N. Shrivastava et al. [66], the quantum yields for LaF<sub>3</sub>:Eu<sup>3+</sup> nanocrystals could vary from 67% up to 85% depending on the Eu<sup>3+</sup> concentration. Therefore, the obtained results suggest that fabricated sol-gel glass-ceramics could be considered as quite good candidates for visible light-emitting devices.

#### 4. Conclusions

In this work, SiO<sub>2</sub>-MF<sub>3</sub>:Tb<sup>3+</sup>,Eu<sup>3+</sup> (M = Y, La) glass-ceramic materials were prepared via sol-gel method during the controlled heat-treatment of silicate xerogels at 350 °C. The performed systematic photoluminescence measurements confirmed that fabricated sol-gel materials exhibit multicolor emission due to the coexistence of the characteristic emission bands originating from both dopant

ions, i.e.,  $Tb^{3+}$  ( $^5D_4 \rightarrow ^7F_J$ ,  $J = 6-3$ ) and  $Eu^{3+}$  ( $^5D_0 \rightarrow ^7F_J$ ,  $J = 0-4$ ) due to  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer occurrence. Based on performed luminescence decay analysis from the  $^5D_4$  ( $Tb^{3+}$ ) and the  $^5D_0$  ( $Eu^{3+}$ ) excited levels, the correlation between luminescence lifetimes and the distribution of rare-earth ions between the silicate sol-gel host and fluoride nanocrystals was clearly proven. Hence, it was suggested that more preferable segregation of rare-earth ions inside  $LaF_3$  nanocrystals occurred. Moreover, the transformation from xerogels into glass-ceramic materials during controlled heat-treatment determines the strong influence on  $Tb^{3+} \rightarrow Eu^{3+}$  energy transfer efficiency,  $\eta_{ET}$ , which increased from ~16% (xerogels) up to 37.3% and 60.8% ( $SiO_2$ - $YF_3:Tb^{3+},Eu^{3+}$  and  $SiO_2$ - $LaF_3:Tb^{3+},Eu^{3+}$  glass-ceramics, respectively). The obtained luminescent results clearly suggest that the prepared sol-gel glass-ceramic materials could be considered as promising candidates for use as optical elements in RGB-lighting optoelectronic devices operating under NUV excitation.

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