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Luminescence Behavior of GdVO₄: Tb Nanocrystals in Silica Glass-Ceramics

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Abstract: Glass ceramics with GdVO₄: Tb nanocrystals impregnated in the highly transparent silica glass were prepared by the porous glass and sintering process and confirmed by XRD, Raman spectrum, and TEM. Spectral analysis shows that there are multifarious energy transfer processes in GdVO₄: Tb nanocrystals, such as VO₄^{3−} → Tb³⁺, Gd³⁺ → VO₄^{3−}, Gd³⁺ → VO₄^{3−} → Tb³⁺, and Gd³⁺ → Tb³⁺, and the main one is VO₄^{3−} → Tb³⁺. In this process, ³T_{1,2} → ¹A₁ transition of VO₄^{3−} transfers the energy to Tb³⁺ and generates ⁵D₃ → ⁷F_{6,5,4,3,2} and ⁵D₄ → ⁷F₅ transitions of Tb³⁺. The energy transfer efficiency is 29.5%, and the excitation wavelength range of Tb³⁺ ions can be shifted from 230–260 nm to 280–365 nm. This shows that GdVO₄ can effectively change the excitation wavelength of Tb³⁺, which is conducive to the application of Tb³⁺ ions excited by LED light sources.

Keywords: transparent glass-ceramics; GdVO₄: Tb; luminescence; energy transfer

1. Introduction

In recent years, rare-earth ion doped phosphors have been widely studied due to their excellent luminescent properties. Among many rare earth elements, the ⁵D₄ → ⁷F₅ transition of Tb³⁺ leads to a very strong green photoluminescence (PL) at around 545 nm. This kind of green fluorescence has strong potential applications in blue-green laser, undersea communication, and medical equipment [1,2]. However, due to the strictly forbidden 4f → 4f transitions, the optimal excitation wavelength of Tb³⁺ is near 240 nm, which is too short for a commercial Light-Emitting Diode (LED) light source, thus directly affecting the application of Tb³⁺ ions [3,4]. An effective way to change the excitation wavelength of Tb³⁺ is to introduce a suitable sensitizer, which can transfer the energy absorbed from LED light source to Tb³⁺. A large number of reports have been focused on this aspect, mainly through Ce³⁺ or Eu²⁺ to sensitize Tb³⁺ [1,5,6].

Rare earth doped gadolinium vanadate crystal (GdVO₄: RE) is considered as an excellent luminescent material because of its excellent chemical stability, high thermal conductivity, strong energy absorption, and high energy transfer efficiency [7,8]. GdVO₄: Tb can effectively improve the PL intensity and transfer excitation wavelength of Tb³⁺ due to its efficient absorption of ultraviolet light and energy transfer (ET) from Gd³⁺ and VO₄^{3−} to Tb³⁺, so as to expand the application of Tb³⁺ luminescent materials [9,10]. There are many papers about the GdVO₄: Tb, but most of them were nanocrystalline phosphors. If the nanocrystals can be synthesized into transparent glass, the application field of the luminescent nanocrystals will be further improved.

Due to their composition having more than 97% SiO₂ and distributed interconnected nanopores, nano-porous silica glass (NPSG) has been researched. Lots of works have reported that NPSG can

be used in many fields after doping and sintering due to its ability to effectively disperse rare-earth ions [11,12]. It is not difficult to imagine if luminescence nanocrystals can be grown in the connected nanopores, the size of the nanocrystals will be limited, and a transparent luminescence material could be obtained. In addition, luminescence nanocrystals can be effectively dispersed by interconnected nanopores in the glass, avoiding the clusters of luminescence ions and improving their luminescence properties. Simultaneously, as the protective shell of nanocrystals, silica glass can effectively improve the chemical, mechanical, and high temperature stability of luminescent materials.

The transparent glass ceramics doped with luminescent ions can effectively combine crystal and glass with many excellent properties, which makes it have many applications in the fields of luminescent, laser and nonlinear optics, and has been favored by many scholars in recent years [13–16]. Therefore, if we combine the excellent properties of $\text{GdVO}_4\text{: Tb}$ and silica glass together to synthesize a transparent glass ceramics, then this transparent luminescence glass-ceramics not only can be applicable to phosphor [17,18], but also to laser, such as laser medium materials [12,19], fiber core of microstructure fiber, and high-power fiber [20–22].

In general, the purpose of this research is to synthesize a transparent silica glass-ceramics (SGC) containing $\text{GdVO}_4\text{: Tb}$ nanocrystallites. The synthesized SGC contains the advantages of both silica glass and $\text{GdVO}_4\text{: Tb}$ crystal and is a green luminescent material. Moreover, we would comprehensively study the changes in the luminescent properties of Tb^{3+} and the ET process of Gd^{3+} and VO_4^{3-} to Tb^{3+} in this SGC.

2. Experiment

2.1. Synthesis of NPSG and SGC

The phase-separated alkali-borosilicate glass was made first. Then, the borate phase was removed by leaching with hot nitric acid solutions and NPSG was obtained. The obtained glass has a content of silica as high as 97% or more [23]. After that, NPSG were immersed in Gd^{3+} , V^{5+} , and Tb^{3+} mixed-ion solutions ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, VOSO_4 , and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) for 1–2 h and dried at room temperature for 20–40 h. Subsequently, the porous glass embedded with active ions was sintered at 1050 °C and 1150 °C in an oxygen atmosphere [11]. Finally, SGC and uncrystallized glass were obtained after being ground and polished. Basic information of various samples with different ion concentration and crystalline statuses are listed in Table 1.

Table 1. Name and ion concentration and crystallization status of various samples.

Sample	Tb^{3+} ($\times 10^{20}$ ion/cm ³)	Gd^{3+} ($\times 10^{20}$ ion/cm ³)	$\text{V}^{5+}(\text{VO}_4^{3-})$ ($\times 10^{20}$ ion/cm ³)	Crystallization or Not
T	0.3	0	0	Uncrystallized
G	0	1	0	Uncrystallized
GV	0	1	1	Crystallized
0.3TV	0.3	0	1	Crystallized
0.1TGV	0.1	1	1	Crystallized
0.2TGV	0.2	1	1	Crystallized
0.3TGV	0.3	1	1	Crystallized
0.4TGV	0.4	1	1	Crystallized

2.2. Instruments and Measurements

The X-ray diffraction (XRD) patterns of samples were carried out on a diffractometer with Cu K α radiation (Smartlab9, Rigaku, Japan). Measurements were performed in the angular range $10^\circ \leq 2\theta \leq 60^\circ$. The Micro-Raman spectra were collected using a laser Raman microscope (Renishaw InVia, Wotton-under-Edge, UK) equipped with a 488-nm laser. The micromorphology of samples was characterized by transmission electron microscopy (TEM) (FEI Tecnai G2 F20, Thermo Fisher Scientific, Waltham, MA, USA). Transmittance spectra were recorded with a

UV/visible/near-infrared spectrophotometer (Jasco V-570, Tokyo, Japan). The thickness of the samples is 1.5 mm. The photoluminescence excitation (PLE) spectra, photoluminescence (PL) spectra, and fluorescence lifetimes (FL) were measured at room temperature on a high-resolution spectrofluorometer (Photon Technology International (Canada) Inc. QM/TM/NIR, London, ON, Canada), utilizing a Xenon lamp as excitation source. Since the excitation and emission spectra are all arbitrary units, the experimental errors will not be discussed. The test errors of absorption spectra and lifetime are all within 5%. However, such errors do not affect the final research results.

3. Results and Discussion

3.1. Structure and Morphology

Figure 1a shows the XRD profiles of all samples. For the sample T, no diffraction peak was observed except for the typical amorphous broad scattering patterns, which can be ascribed to the silica glass substrate. In addition to the amorphous scattering patterns, the samples xTGV ($x = 0.1$ – 0.4) showed weak diffraction peaks at $2\theta = 24.67^\circ$, 33.23° , and 49.15° due to the (2 0 0), (1 1 2), and (3 1 2) reflections of tetragonal GdVO_4 . These peaks indicate that GdVO_4 nanocrystals were present in SGC.

Figure 1. (a) XRD patterns of samples (inset: the data of tetragonal GdVO_4); (b) micro-Raman spectra of samples (inset: the data of GdVO_4 crystal).

Micro-Raman spectroscopies of samples and GdVO_4 crystal were also tested and shown in Figure 1b. Several bands near 441 , 495 , 600 , 800 , and 1060 cm^{-1} can be seen in each sample, which can be assigned to the vibrational mode of SiO_2 glass [24–28]. In addition, some vibrations were detected in the Raman spectra of xTGV ($x = 0.1$ – 0.4), which were located at 263 , 380 , 485 , 820 , and 880 cm^{-1} . These peaks due to the modes of $(\text{VO}_4)^{3-}$ in GdVO_4 nanocrystals [29–32]. The observed peaks were detailed analysis in our early work [11]. Obviously, the existence of GdVO_4 : Tb was also confirmed by the micro-Raman spectra.

TEM and HR-TEM of sample 0.3TGV were investigated to exhibit the morphology of the grains GdVO_4 : Tb and its distribution in SGC. TEM micrograph in Figure 2a indicated that nanoparticles were uniformly distributed in SCG, and the diameters were less than 50 nm . Meanwhile, the HR-TEM micrograph in Figure 2b,c shows that a more obvious lattice fringe existed in the sample. The lattice fringes spaced by 0.36 nm and 0.29 nm coincide with the (2 0 0) and (2 1 1) planes of tetragonal GdVO_4 , respectively [11,33]. The results of the TEM and HR-TEM pictures prove the existence of GdVO_4 : Tb nanocrystals in SGC further.

Figure 2. (a) TEM morphology and (b), (c) HR-TEM morphology of sample 0.3TGV.

3.2. Spectral Properties

3.2.1. Absorption Properties

Figure 3 shows the transmittance spectra of xTGV ($x = 0.1–0.4$). It can be seen that the transmittance of the samples gradually decreased with the increase of the Tb^{3+} content, and the absorption edges shifted to long wavelengths, which implies that the increase of Tb^{3+} promotes the growth of microcrystalline in high silica glass. The results of some optical scattering and decreasing transmission is owing to the different refractive index between the particles and matrix glass. Another possibility of the red shifting is from nephelauxetic effect. Since the atomic number of Tb^{3+} is greater than Gd^{3+} , and the outer layer of Tb^{3+} has a higher electron density, it causes a decrease in the energy of upper level VO_4^{3-} through the electron cloud expansion. Therefore, the higher the concentration of Tb^{3+} , the higher the electron density in the whole glass, which increased the covalency around Tb^{3+} ions and led to the red shift of the absorption edge [34,35].

Figure 3. Transmittance spectra of sample xTGV ($x = 0.1–0.4$) and 0.3TV.

3.2.2. PLE/PL Properties

With a fixed concentration of Gd^{3+} and V^{5+} as $1 \times 10^{20} \text{ ion/cm}^3$, samples with different contents of Tb^{3+} were fabricated, the PLE spectra and PL spectra were measured and shown in Figure 4. It can be seen that the peak shapes of the PLE and PL spectra for these samples were similar. The main difference was changes in PL intensity. The PL intensity first increases, then starts to decrease with the increased contents of Tb^{3+} , and reaches the strongest when the doping concentration is $0.3 \times 10^{20} \text{ ion/cm}^3$, which is due to the fluorescence quenching due to the high concentration of Tb^{3+} . Therefore, the concentration of Tb^{3+} was fixed at $0.3 \times 10^{20} \text{ ion/cm}^3$ in the above and subsequent studies.

Figure 4. (a) PLE spectra and (b) PL spectra of xTGV ($x = 0.1\text{--}0.4$).

The PLE spectra of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} monitored at 542 nm are shown in Figure 4a. It can be seen that the main excitation peak of all samples was located near 330 nm, which reflects an energy transfer process between VO_4^{3-} and Tb^{3+} because the excitation peak is mainly caused by the absorption band of VO_4^{3-} [36–38] in contrast to the PLE spectrum of single Tb^{3+} doped sample T, which will be discussed in the following sections. In addition to the absorption band at 330 nm, a weak absorption peak near 375 nm also can be seen, which can be ascribed to the absorption of the Tb^{3+} ion $^7\text{F}_6 \rightarrow ^5\text{D}_3$ transition [39,40]. Another change is slight red-shifting of the excitation peak with the concentration increase of Tb^{3+} . The reason for this may be the electron cloud density increased with the increase content of Tb^{3+} , which led to a decrease in the energy of the upper level of VO_4^{3-} group [36]. The PL spectra of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} excited at 330 nm are shown in Figure 4b. The emission of $\text{Gd}^{3+} \ ^6\text{P}_{7/2} \rightarrow \ ^8\text{S}_{7/2}$ transitions occurred at 310 nm under 274 nm excited, and therefore does not appear in Figure 4b. Similar to the PLE spectra, the intensity of the emission peak also increased first and then decreased with the increase of Tb^{3+} concentration, which is also caused by the fluorescence quenching. The broadband emission at 400–650 nm was caused by the $^3\text{T}_{1,2} \rightarrow ^1\text{A}_1$ transition of VO_4^{3-} in each emission spectrum [11]. In addition to this emission band, the PL peaks at 425, 450, 467, and 542 nm were caused by the $^5\text{D}_3 \rightarrow ^7\text{F}_{4,3,2}$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions of Tb^{3+} ions [39,41]. This further illustrated that ET existed in these samples, so the ET process will be discussed in the subsequent chapter.

3.2.3. Energy Transfer Mechanism

As mentioned, ET between VO_4^{3-} and Tb^{3+} was observed in previous results. In order to clarify the ET processes between various active ions in GdVO_4 : Tb nanocrystals embedded in the synthesized SGC, the samples GV and T shown in Table 1 were fabricated, and PLE and PL spectra were measured, as displayed in Figure 5.

Figure 5. (a) PLE spectra and (b) PL spectra of GV, T, and 0.3TGV.

Firstly, the PLE spectra of samples T and 0.3TGV of the $^5D_4 \rightarrow ^7F_5$ transition of Tb^{3+} monitored at 542 nm were measured. For comparing, the PLE spectrum of sample GV monitored at 520 nm was also shown in Figure 5a. It can be seen that sample T also have some $f \rightarrow f$ transition absorptions in the range of 275–385 nm, including $^7F_6 \rightarrow ^5H_7$, $^7F_6 \rightarrow ^5D_2$, and $^7F_6 \rightarrow ^5D_3$ besides the main absorption band of $4f^8 \rightarrow 4f^75d^1$ transition of Tb^{3+} ion near 244 nm [42]. However, they are very weak. On the other hand, sample GV also shows strong absorption peaks of $^1A_1 \rightarrow ^1T_{1,2}$ transitions of VO_4^{3-} in the range of 225–375 nm [36–38]. Moreover, besides the absorption peaks of VO_4^{3-} , a weak peak of $^7F_6 \rightarrow ^5D_3$ transition of Tb^{3+} ion near 380 nm could also be seen in sample 0.3TGV. It is easy to see by comparing the samples T and 0.3TGV that the most obvious change was the FWHM range of excitation wavelength of Tb^{3+} shifting from about 230–260 nm to 280–365 nm, and the strongest excitation peak shifting from around 244 to 330 nm. At the same time, the PL intensity of Tb^{3+} ions also increased. These results proved the existed ET process of $VO_4^{3-} \rightarrow Tb^{3+}$ in SGC. Comparing the sample GV and 0.3TGV, it can be seen that there were two changes in the PLE spectra. One such change was a weak new absorption peak, which is resulting from $^7F_6 \rightarrow ^5D_2$ transition of Tb^{3+} ions, while the other was the position red-shifting of the optimal excitation wavelength, which may be due to the absorption red shifting of matrix after microcrystallization. In addition, it can be observed that the emission from $^3T_{1,2} \rightarrow ^1A_1$ transition of VO_4^{3-} was strong in Figures 4b and 5b, implying that there was low energy transfer efficiency from VO_4^{3-} to Tb^{3+} . Thus, the disappearance of $4f^8 \rightarrow 4f^75d^1$ transition of Tb^{3+} ion near 244 nm for 0.3TGV may be due to the $5d^1$ energy level causing a strong split after the Tb^{3+} entered the Gd^{3+} lattice, which resulted in a large red-shift of the $4f^8 \rightarrow 4f^75d^1$ transition and overlapped with the $^1A_1 \rightarrow ^1T_{1,2}$ transitions of VO_4^{3-} .

Figure 5b shows the PL spectra of samples GV, T, and 0.3TGV, and their respective characteristic excitation wavelengths were marked in the Figure 5b. The different between the PL spectra of GV and 0.3TGV were mainly two points. One was that the luminescence peak resulted from the $^3T_{1,2} \rightarrow ^1A_1$ transition of VO_4^{3-} at 400–650 nm was widened after adding Tb^{3+} ions, while the other was the emergence of some new emission peaks near 380, 425, 450, 467, and 542 nm, which can be ascribed to the $^5D_3 \rightarrow ^7F_{6,5,4,3,2}$ and $^5D_4 \rightarrow ^7F_5$ transitions of Tb^{3+} ions [39,41]. This shows again that partial energy of the $^3T_{1,2} \rightarrow ^1A_1$ transition transferred to the Tb^{3+} ion. In order to illustrate the above process, a schematic of the ET process in SGC is suggested in Figure 6, and the process of $VO_4^{3-} \rightarrow Tb^{3+}$ is ET_2 .

Figure 6. Schematic diagram of the energy transfer process in samples.

In addition to the emission of Tb^{3+} , there were also emission of Gd^{3+} and VO_4^{3-} in samples; and there were some overlap between the position of the emission peak of Tb^{3+} and the excitation wavelength of VO_4^{3-} as shown in Figure 5. Therefore, in order to verify whether there was a reverse ET from Tb^{3+} to VO_4^{3-} in the SGC, the sample 0.3TV was made and the PLE spectra of the samples GV, 0.3TV, and 0.3TGV monitored at 520 nm were measured and shown in Figure 7a. It can be seen that there were weak absorption peaks at 230–270 nm besides peaks of $^1\text{A}_1 \rightarrow ^1\text{T}_{1,2}$ transitions of VO_4^{3-} in both samples of 0.3TV and 0.3TGV. This may be evidence of the reverse ET process of $\text{Tb}^{3+} \rightarrow \text{VO}_4^{3-}$ in the SGC, but the transfer efficiency is low. This process is shown as ET₃ in Figure 6. In addition, it can be clearly seen in the Figure 7a that the excitation peaks of both samples of 0.3TV and 0.3TGV shifted to long wavelength compared to GV. As mentioned earlier, this may be due to the changes of energy levels of VO_4^{3-} group, which caused by the increased electron cloud density.

Figure 7. (a) PLE spectra of GV, 0.3TV, and 0.3TGV and (b) PL spectra of T, GV, 0.3TV, and 0.3TGV.

Further, the PL spectra of the samples T, GV, 0.3TV, and 0.3TGV were measured with the excitation wavelength of 244 nm, the results are shown in Figure 7b. The emission of Tb^{3+} in the sample T has been mentioned above, and thus is not repeated here. As can be seen, all samples behaved weak emission bands of $^3\text{T}_{1,2} \rightarrow ^1\text{A}_1$ transition of VO_4^{3-} except for sample T. There are two possibilities for the phenomenon. One may be that VO_4^{3-} has some absorptive capacity for the ultraviolet at about 244 nm, which results in the emission of VO_4^{3-} . The other may be resulting from the reverse ET process

of $\text{Tb}^{3+} \rightarrow \text{VO}_4^{3-}$. Namely, Tb^{3+} ions transferred the absorbing energy to VO_4^{3-} , and then VO_4^{3-} transferred back to Tb^{3+} . In these processes, a part of the energy generated $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions, and another part of the energy was lost in the form of heat, which in turn reduces the PL intensity of VO_4^{3-} in the sample 0.3TV and 0.3TGV. On the other hand, as mentioned above, the of $4f^8 \rightarrow 4f^75d^1$ transition would be a red shift in a strong crystal field, so it resulted in a weak emission of Tb^{3+} under the excitation wavelength of 244 nm as shown in Figure 7b.

In our previous report [11], it was found that there were various energy transfer processes in GdVO_4 : Eu nanocrystalline silica glass, including $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$, $\text{VO}_4^{3-} \rightarrow \text{Eu}^{3+}$, $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-}$, and $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Eu}^{3+}$. In this article, the Tb^{3+} is also in the GdVO_4 matrix. Therefore, based on the above discussion and previous report, it can be considered that there are also multiple ET processes of $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$, $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-}$, and $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ in the SGC, that is, the ET_2 and ET_1 processes in Figure 6.

Is there an energy transfer process of $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ in the SGC? In order to verify the speculation, the PLE spectra of samples T and 0.3TGV were measured with a monitored wavelength of 542 nm, as shown in Figure 8a. It can be seen that there is a weak shoulder near 260–280 nm of sample 0.3TGV, which may be due to the $^8\text{S}_{7/2} \rightarrow ^6\text{I}_J$ transition of Gd^{3+} [11] and it may make the intensity of this region enhanced [37,43]. However, the $4f^8 \rightarrow 4f^75d^1$ transition of Tb^{3+} is also absorbed nearby as shown in Figure 8a, and the shoulder may also be caused by this absorption.

Figure 8. (a) PLE spectra of T and 0.3TGV and (b) PL spectra of G, GV, and 0.3TGV.

In order to clarify the role of Gd^{3+} , sample G single doped with Gd^{3+} was prepared, and the PL spectra of G, GV, and 0.3TGV were tested with the excitation wavelength of 274 nm. The results are shown in Figure 8b. The peak at about 310 nm was reduced to 1/5 of the original intensity in sample G due to the strongly actual intensity (I_{actual}) of the $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$ transition of Gd^{3+} . Compared with sample G, the $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$ transition emission intensity of Gd^{3+} near 310 nm in GV and 0.3TGV decreased sharply, which was replaced by the $^3\text{T}_{1,2} \rightarrow ^1\text{A}_1$ transition emission peak of VO_4^{3-} . This indicates that Gd^{3+} mainly transfers energy to VO_4^{3-} . However, a weak luminescence peak of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb^{3+} ions can be seen near 542 nm in the sample 0.3 TGV, which also indicates that Gd^{3+} may transfer some energy to Tb^{3+} and includes the processes of $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$. In general, the both energy transfer processes of $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ and $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ can be seen in the SGC, which are shown as ET_1 , ET_2 , and ET_4 in Figure 6. However, there is no way to obtain each weight of both processes yet.

In the above analysis and discussion, the ET processes of $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$, $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-}$, $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ and $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ have been proven, and $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ was still the main process. The decay time (τ) of Gd^{3+} in samples GV and (0.1–0.4) TGV were measured, they are basically the same, about 600 μs . The decay time of Tb^{3+} in samples (0.1–0.4) TGV were also measured, they are

basically the same, about 290 μs . Therefore, only the decay time of VO_4^{3-} and transfer efficiency (η) of $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ were measured and discussed. Figure 9 depicts the decay curves of the ${}^3\text{T}_{1,2} \rightarrow {}^1\text{A}_1$ transition of VO_4^{3-} in GV and 0.3TGV.

Figure 9. Decay curves for 520 nm emission of VO_4^{3-} in samples GV and 0.3TGV.

Both of the decay curves followed a double-exponential decay. The equation $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, can be used to calculate the average decay times, where τ_1 is the short decay component and τ_2 is the long-decay component, respectively, while parameters A_1 and A_2 are the fitting constants [33]. The equation $\eta = 1 - \tau/\tau_0$ can be used to estimate the efficiency η of the ET, where τ_0 is the fluorescence lifetime before doping and τ is the fluorescence lifetime after doping. As can be seen, the average lifetime of the $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ transition decreases from 154.6 μs to 108.9 μs with the addition of Tb^{3+} , which indicates that energy of the ${}^3\text{T}_{1,2} \rightarrow {}^1\text{A}_1$ transitions transfers from VO_4^{3-} to Tb^{3+} ions, and the transfer efficiency was 29.6%. The transfer efficiency was not high, and it was consistent with the results in Figures 4b and 5b.

4. Conclusions

The glass-ceramics with GdVO_4 : Tb nanocrystals embedded in the highly transparent silica glass were prepared by the porous glass and sintering process. The existence of nanocrystals was confirmed by XRD, Raman spectrum, and TEM. The fluorescence performance of Tb^{3+} in the transparent SGCs with different concentrations Tb^{3+} were studied by PLE and PL spectra, and the best performance of 0.3TGV was obtained. In order to clarify the energy transfer mechanism, various samples with single, double, and triple active ions in SGCs were prepared and their spectra were analyzed. The results showed that there was an ET process of $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ in the SGC after the formation of nanocrystals by the comparison of the spectra of GV, T, and 0.3TGV. Namely, partial energy of the ${}^3\text{T}_{1,2} \rightarrow {}^1\text{A}_1$ transition of VO_4^{3-} transferred to the Tb^{3+} ion and generated the emission of ${}^5\text{D}_3 \rightarrow {}^7\text{F}_{6,5,4,3,2}$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$. Besides the $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$, processes of $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-}$, $\text{Gd}^{3+} \rightarrow \text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$, and $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ have been confirmed in the SGC through spectral comparison of samples, but the main process is $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$. Finally, the transfer efficiency of the ET of $\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$ was obtained by measuring and calculating the decay time of ${}^3\text{T}_{1,2} \rightarrow {}^1\text{A}_1$ transition of VO_4^{3-} ion before and after Tb^{3+} doping in the SGC, which was 29.6%.

To sum up, these ET processes in GdVO_4 : Tb nanocrystals enhanced the luminescence intensity of Tb^{3+} in the SGCs and shifted the FWHM range of excitation wavelength of Tb^{3+} from 230–260 nm to 280–365 nm, which is conducive to the application of Tb^{3+} ions excited by LED light sources.

Consequently, this new SGC can be used in the fields of LED excitation luminescence, displays, and lasers fiber that require high transparency, high power, and high chemical stability.

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