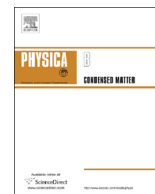




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Different dynamics of ultraviolet upconversion in Tm^{3+} :ZBLAN glass under blue laser excitation

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ABSTRACT

Ultraviolet upconversion luminescence around 292 nm, 350 nm and 363 nm in Tm^{3+} :ZBLAN glass was observed clearly by pulsed excitation at 464 nm. Upconversion dynamics was discussed in detail by an analysis of the measured intensity dependence, decay curves and excitation spectra of upconversion luminescence, from which it was clarified that upconversion luminescence around 292 nm and 350 nm from $^1\text{I}_6$ level was attributed to excited state absorption, while that around 363 nm from $^1\text{D}_2$ level was attributed to energy transfer process.

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1. Introduction

Recently, due to the wide applications of short-wavelength solid-state lasers from ultraviolet (UV) to green spectral range, more and more attentions have been paid to upconversion studies of rare earth (RE) ion-doped solid materials. As a promising host material, ZBLAN ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) glass has been attracting great interest for upconversion luminescence because it is relatively easy to prepare, can be doped with RE fluorides without the need of charge compensation, and more importantly has a very low multiphonon relaxation rate [1,2]. In Tm^{3+} doped materials, blue upconversion luminescence has been reported in numerous works and blue upconversion laser has been realized [3–5]. Recently, some groups have also demonstrated both blue and UV luminescence under red laser excitation [6–8]. However, in Tm^{3+} :ZBLAN glass only a few papers focused on the studies of UV upconversion luminescence [9,10].

In this study, under 464 nm pulsed laser excitation we demonstrated UV upconversion luminescence in Tm^{3+} :ZBLAN glass, which has a higher Tm^{3+} concentration than that in Ref. [10] ever reported by our group. UV luminescence with shorter wavelength

was observed under the same excitation as that in Ref. [10]. Compared with previous UV upconversion studies in Tm^{3+} :ZBLAN fiber pumped by continuous wave (CW) laser [9], the pulsed excitation source in this study can provide a better characterization of upconversion dynamics. By an analysis of the measured intensity dependence, decay curves and excitation spectra of upconversion luminescence, we discussed the UV upconversion dynamics in detail, and found it was obviously different from that reported in Ref. [10] because of the increase of Tm^{3+} concentration.

2. Experiments

The ZBLAN glass used in this study contains 2 mol% Tm, which has the size of $10 \times 10 \times 1 \text{ mm}^3$. The sample was excited from 455 to 475 nm by a dye laser (Sirah Cobra-Stretch) operating with coumarin 460 and 480, which was pumped by the frequency-tripled 355 nm Nd:YAG laser (Spectra-Physics Quanta-Ray Pro-Series) with a 10 Hz repetition and a 10 ns pulse duration. The laser spot size was about 1 mm^2 and the power density was about 2 mJ/mm^2 . The laser-induced fluorescence was collected by a lens ($f=15 \text{ cm}$) along a direction perpendicular to the laser beam direction, filtered by a 0.5 m monochromator with 0.1 nm resolution and finally detected by a photomultiplier tube with a response time of 2 ns (Hamamatsu R3896). The time-resolved fluorescence decay signals from the detector were recorded by a digital oscilloscope with a response time of 2 ns (Tektronix TDS 620B 500 MHz) and the fluorescence spectra were recorded with a

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boxcar integrator (Stanford Research Systems SR250). All experiments were performed at room temperature.

3. Results

Based on the energy level data reported by McDougall et al. [11,12], an energy level diagram of Tm^{3+} ions in ZBLAN glass is given in Fig. 1. When the $^1\text{G}_4$ level was resonantly excited by 464 nm pulsed laser, UV luminescence around 292 nm, 350 nm, and 363 nm was detected as shown in Fig. 2. The emission bands around 292 nm and 350 nm were assigned to the transitions $^1\text{I}_6 \rightarrow ^3\text{H}_6$ and $^1\text{I}_6 \rightarrow ^3\text{F}_4$ respectively. Their emission intensities have been corrected by the response of detection system, from which we obtained the area-intensity ratio (1:6.7) of these two emission bands, which is close to the calculated ratio of 1:6 [13]. For the emission band around 363 nm, it was assigned to the transition $^1\text{D}_2 \rightarrow ^3\text{H}_6$.

Fig. 3 shows the excitation spectra by monitoring the upconversion luminescence at 350 nm and 363 nm. As a comparison, the

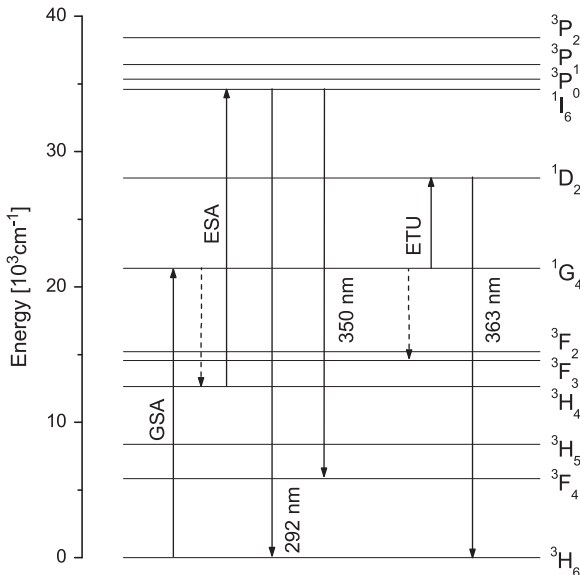


Fig. 1. Energy level diagram of Tm^{3+} ions in ZBLAN glass. Upconversion processes and emission transitions are also included.

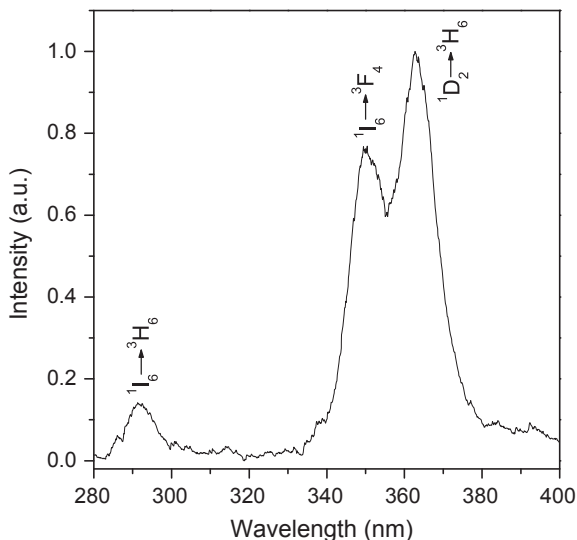


Fig. 2. Upconversion luminescence spectra under 464 nm excitation of $^1\text{G}_4$ level.

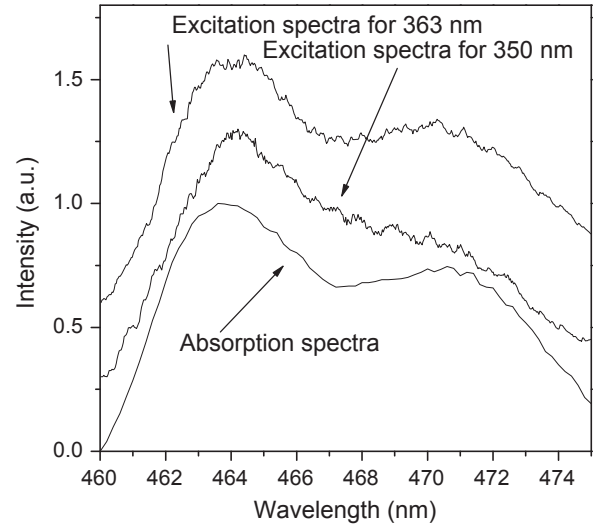


Fig. 3. Excitation spectra for 363 nm (top) and 350 nm (middle) upconversion luminescence, and absorption spectra (bottom) in the range from 460 to 475 nm.

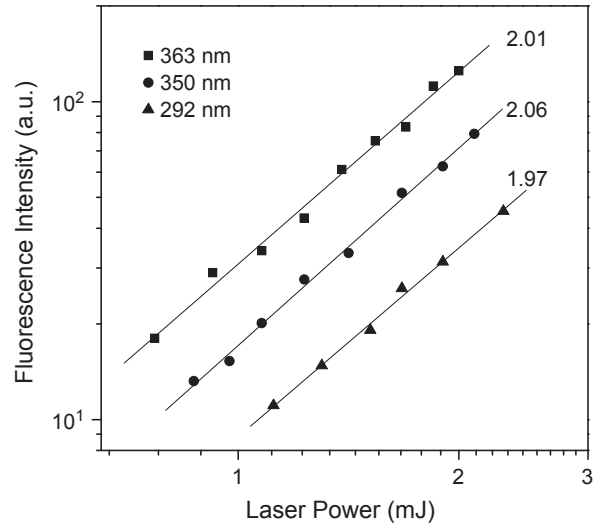


Fig. 4. The intensity dependence of 292 nm, 350 nm and 363 nm on the laser power. The slopes are given in the right hand.

absorption spectra of the $^1\text{G}_4$ level are also given. It can be seen clearly that the luminescence intensities of both 350 nm and 363 nm reach its maximum value when the laser wavelength is fixed on 464 nm, which is in good resonance with the transition $^3\text{H}_6 \rightarrow ^1\text{G}_4$ according to the absorption spectra. Fig. 4 shows the intensity dependence of UV luminescence on laser power. All of the slopes are close to 2 for 292 nm, 350 nm and 363 nm, which indicates that UV emissions from both $^1\text{I}_6$ and $^1\text{D}_2$ levels were induced by two-photon process.

4. Discussion

Generally, upconversion luminescence originates from two types of upconversion mechanisms, e.g. ESA and energy transfer upconversion (ETU), which are strongly dependent on doped concentration, excitation wavelength, host materials and so on. Tian et al. have reported UV upconversion luminescence from $^1\text{I}_6$ and $^1\text{D}_2$ levels in Tm^{3+} :ZBLAN fiber pumped with a 458 nm CW Ar^{3+} laser and a 585 nm dye laser [9], which has been also

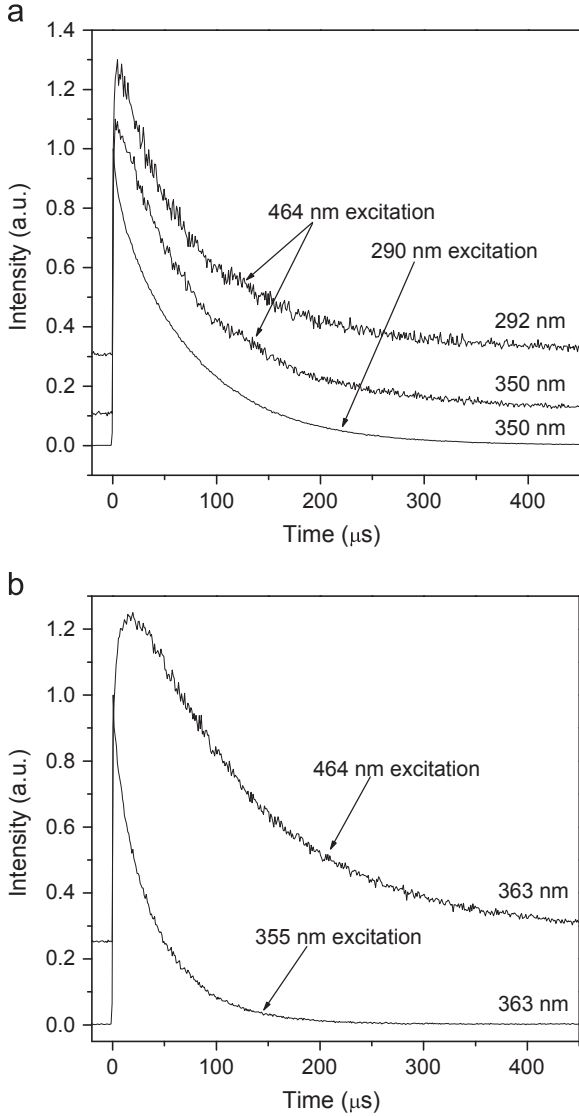


Fig. 5. (a): Decay curves at 292 nm (top) and 350 nm (middle) under 464 nm excitation, and 350 nm (bottom) under 290 nm excitation; (b): 363 nm under 464 nm (top) and 355 nm (bottom) excitation.

observed by Li et al. under blue laser excitation [10]. They all attributed UV luminescence to ESA processes. However, it is also possible that UV luminescence from 1I_6 and 1D_2 levels originates from ETU processes, which has been demonstrated in Tm^{3+} : $CsMgCl_3$ crystals when 1G_4 level was pumped by 465 nm pulsed laser [14].

A measured decay curve of upconversion luminescence can provide a distinct character in discerning ESA and ETU processes. The upconversion decay based on ESA generally exhibits a decay behavior similar to that under direct excitation, while the ETU decay exhibits a rise time followed by a decay, and its decay lifetime is much longer than that under direct excitation [15]. In this study in order to clarify UV upconversion dynamics, we measured the decay curves from 1I_6 and 1D_2 levels, respectively. Fig. 5a shows the upconversion decay curves of 292 nm and 350 nm from 1I_6 level under 464 nm excitation of 1G_4 level. As a comparison, the decay curve of 350 nm under 290 nm direct excitation of 1I_6 level is also given. Very clearly, the upconversion decay under 464 nm excitation exhibits the same behavior as that under 290 nm direct excitation. The measured lifetime (84.2 μs) of 1I_6 level under 464 nm excitation is very close to that (77.2 μs)

under direct excitation, from which we can conclude that ESA process produced the UV luminescence from 1I_6 level. As shown in Fig. 1, after ground state absorption (GSA) $^3H_6 \rightarrow ^1G_4$, the successive ESA process $^3H_4 \rightarrow ^1I_6$ happens by absorbing another photon according to the energy level data [11,12] and populates 1I_6 level resulting in UV luminescence around 292 nm and 350 nm by the transitions $^1I_6 \rightarrow ^3H_6$ and $^1I_6 \rightarrow ^3F_4$, respectively.

Fig. 5b shows the decay curves of 363 nm from 1D_2 level under 464 nm excitation and 355 nm direct excitation, respectively. For the upconversion decay curve under 464 nm excitation, an obvious rise time followed by a decay was observed, which is completely different from that under 355 nm direct excitation. Furthermore, the measured upconversion decay time of 126.7 μs is much longer than that of 44.5 μs under 355 nm direct excitation. These characters indicate that ETU process is responsible for producing the population of 1D_2 level. In Fig. 1, the energy gap between 1G_4 and 1D_2 levels well matches with that between 1G_4 and 3F_3 levels. When two Tm^{3+} ions are excited to the 1G_4 level, the ETU process $^1G_4 + ^1G_4 \rightarrow ^3F_3 + ^1D_2$ occurs, by which one ion loses energy and goes to the lower level of 3F_3 , while another gains energy and populates 1D_2 level. As a result, the emission around 363 nm was observed.

The decay of 1D_2 level in Fig. 5b from ETU is not a single-exponential decay. The decay behavior of 1D_2 population (N_D) can be described by the equation [16]

$$N_D = \frac{N_0 W_T}{W_D - 2W_G - W_T} (e^{-(2W_G + W_T)t} - e^{-W_D t}) \quad (1)$$

where N_0 is the initial number of doubly excited ion pairs of 1G_4 level, W_D and W_G are the relaxation rates of 1D_2 and 1G_4 , respectively, and W_T is the energy transfer rate of ETU process. From this equation, it can be seen that the decay of 1D_2 level is obviously composed of two exponential functions, and closely related to the lifetimes of both 1D_2 and 1G_4 levels. The decay curve of 1G_4 level under direct excitation (not shown) exhibits a non-exponential behavior because there exists energy transfer processes involving 1G_4 level [17]. 1G_4 lifetime of about 295 μs was obtained by an exponential fitting on the tail part of its decay curve, which is close to an exponential decay. Obviously, 1G_4 lifetime is much longer than that (44.5 μs) of 1D_2 level. Therefore, W_D is larger and related to the reciprocal of rise time in 1D_2 decay curve, whereas $2W_G + W_T$ is smaller and related to the reciprocal of decay time.

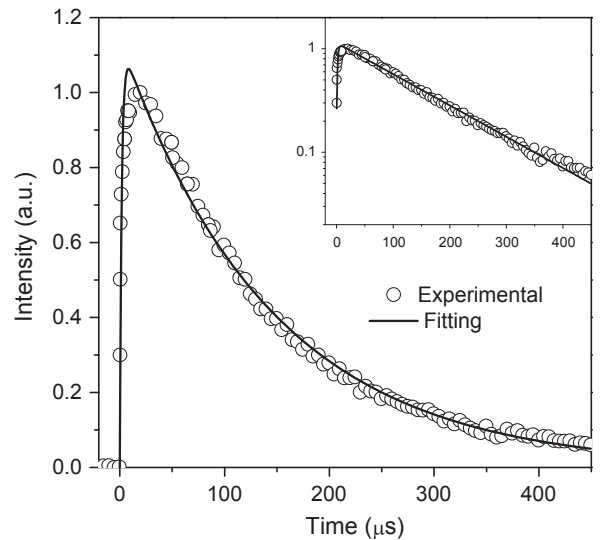


Fig. 6. Upconversion decay curve at 363 nm. The dots correspond to experimental data and the solid lines denote the fitted results. The inset is plotted by a logarithm scale.

By using Eq. (1), we fitted 1D_2 decay curve as shown in Fig. 6. A good agreement between experimental data and fitted results was obtained, from which the rise time of 2.1 μ s and decay time of 140 μ s were obtained. It is very reasonable that the decay time is close to the half of 1G_4 lifetime. However, the rise time is much shorter than 1D_2 lifetime, which has also been found in $Pr^{3+}:LaF_3$ [18] and $Pr^{3+}:ZBLAN$ [19], and should attribute to the limitations of the model assumed, i.e. in the concentrated Tm^{3+} systems 1G_4 decay is non-exponential and W_D values could be different for the specific ion pairs.

Due to different upconversion dynamics resulting in the population of 1I_6 and 1D_2 levels, the excitation spectra for 363 nm and 350 nm upconversion luminescence in Fig. 3 are also different. Because ETU process contributes 1D_2 population, its population is strongly dependent on 1G_4 population. Therefore, the excitation spectra at 363 nm have the same profile as the absorption spectra of 1G_4 level. However, for the 1I_6 population from ESA process, the excitation wavelength must be resonance with not only the transition: $^3H_6 \rightarrow ^1G_4$ but also the transition: $^3H_4 \rightarrow ^1I_6$. Thus, its population is dependent on not only GSA but also ESA, and consequently the excitation spectra at 350 nm exhibit a different behavior at the laser wavelength around 471 nm.

In Ref. [10], we have demonstrated UV upconversion luminescence from 1D_2 level by ESA process in $Tm^{3+}:ZBLAN$ glass with a Tm^{3+} concentration of 1 mol%. Under the same excitation, however, the upconversion mechanism of 1D_2 luminescence changed to ETU process when Tm^{3+} concentration increased to 2 mol%. This indicated that upconversion mechanisms were strongly dependent on Tm^{3+} concentration. When Tm^{3+} concentration is low, ESA process is the main upconversion mechanism due to the weak interaction between Tm^{3+} ions. With an increase in Tm^{3+} concentration, the interaction between Tm^{3+} ions becomes active, and consequently ETU process dominated UV upconversion luminescence from 1D_2 level.

5. Conclusion

We have demonstrated successfully UV upconversion luminescence around 292 nm, 350 nm and 363 nm in $Tm^{3+}:ZBLAN$ glass by pulsed excitation at 464 nm. The intensity dependence of upconversion luminescence indicated that UV luminescence originated from two-photon process. By the analysis of the measured decay curves and excitation spectra, we attributed the luminescence around 292 nm and 350 nm from 1I_6 level to ESA process, while that around 363 nm from 1D_2 level to ETU process.

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