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Intense ultraviolet upconversion luminescence from Yb^{3+} and Tm^{3+} codoped amorphous fluoride particles synthesized by pulsed laser ablation

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Abstract

$Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ amorphous fluoride particles were prepared by pulsed laser ablation. Under a 978-nm laser diode excitation, intense ultraviolet and blue upconversion emissions were observed in the particles. Intensity dependence of the upconversion emissions on the pump power was measured. The results show that the population of the states $^1I_6$, $^1D_2$ and $^1G_4$ may come from a five-photon, four-photon and three-photon energy transfer upconversion process. In addition, ultraviolet ($^1I_6 \rightarrow {}^3F_4$ transition) and blue ($^1D_2 \rightarrow {}^3F_4$ transition) upconversion stimulated emissions were observed in the particles.

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1. Introduction

In recent years, short-wavelength solid-state lasers in the ultraviolet to green spectral range have attracted much attention due to a wide range of applications including high-density optical data storage, all color displays, undersea communications, biomedicine and infrared sensors. The phenomenon of frequency upconversion by using the intrinsic energy level matching of certain rare-earth ions, as one of the available approaches exploring short-wavelength solid-state lasers, has been investigated widely during the past two decades [1–10].

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Up to now, short-wavelength upconversion solid-state lasers in the visible region have been obtained [1]. Ultraviolet and violet upconversion solid-state lasers are the next objective of the researchers. For the realization of ultraviolet and violet upconversion solid-state lasers, the maximal obstacle is the search of ultraviolet and violet upconversion laser materials. Following S. Tanabe's pioneer work, in our previous work, we fabricated intense infrared-to-violet and ultraviolet (UV) upconversion luminescence materials by pulsed laser ablation (PLA) and investigated the relation of violet and UV upconversion luminescence to the Judd–Ofelt intensity parameters [10,11].

In this paper, we reported intense UV upconversion properties of $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ amorphous fluoride particles were prepared by PLA. With the excitation of a 978-nm LD, intense UV and blue upconversion emissions were observed, which were similar with that of the film [11]. In addition, ultraviolet ($^1I_6 \rightarrow {}^3F_4$ transition) and blue ($^1D_2 \rightarrow {}^3F_4$ transition) upconversion stimulated emissions were observed in the particles.

2. Results and discussion

Thousand and sixty four nanometer from a pulsed Nd:YAG laser was used as the light source for PLA. The laser beam was focused onto the target [11] ($Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ glass prepared by solid state reaction) dipped in a beaker filled with ethanol at an incidence angle of about 45°. The particles were collected in this beaker. The size of the particles is about 0.1–10 μm, most of them are larger than 1 μm and the shape is not regular measured with a scanned electron microscope. X-ray analysis data show that the particles are amorphous. X-ray photoelectron spectroscopy (XPS) data show that the components of the particles are identical to that of the target. A 978-nm laser diode was focused on a pile of particles by a object lens (20×), the upconversion emission spectra were measured with a fluorescence spectrophotometer (Hitachi F-4500) with the spectral resolution of 2 nm. The pump power of the 978-nm LD was numerate on the controller, which was used to modulate the electric current of the LD.

Fig. 1 is the room temperature upconversion emission spectrum of the particles excited at 978 nm, which is similar with that of the film [11]. Emissions in the UV and visible comes from the following transitions: $^1I_6 \rightarrow {}^3H_6$ (∼290 nm), $^1I_6 \rightarrow {}^3F_4$ (∼348 nm), $^1D_2 \rightarrow {}^3H_6$ (∼361 nm), $^1D_2 \rightarrow {}^3F_4$ (∼451 nm), $^1G_4 \rightarrow {}^3H_6$ (∼474 nm).

In Yb^{3+}–Tm^{3+} co-doped systems, different process may result in upconversion. Fig. 2 shows the energy level diagrams of Tm^{3+} and Yb^{3+}. The pump light excites only the Yb^{3+} ions, and three successive energy transfers from Yb^{3+} to Tm^{3+} populate $^3H_5$, ($^3F_3$, $^3F_2$), and $^1G_4$. Though the Tm^{3+}–Tm^{3+} interaction is weak in the sample with low Tm^{3+} concentration, owing to the large energy mismatch (∼3516 cm^{-1}) in the transfer $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^1G_4 \rightarrow {}^1D_2$ (Tm^{3+}), the process $^3F_2 \rightarrow {}^3H_6$ (Tm^{3+}): $^3H_4 \rightarrow {}^1D_2$ (Tm^{3+}) may alternatively play the most important role in populating $^1D_2$. Thereafter, the state $^1I_6$ can be populated by $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^1D_2 \rightarrow {}^1I_6$ (Tm^{3+}) [8].

For unsaturated upconversion, emission intensity, I_s, is proportional to I^n, where I is the intensity of the excitation light and the integer n is the number of photons absorbed per upconverted photon emitted [11]. In order to clarify the UV

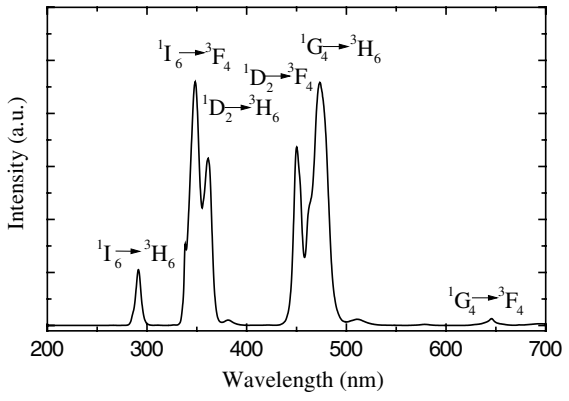

Fig. 1. Room temperature upconversion emission spectra of $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ particles (at the pump power = 600 mW).

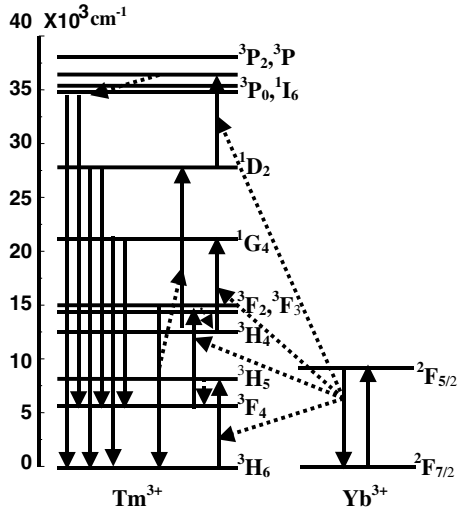

Fig. 2. Energy-level diagram of Tm^{3+} and Yb^{3+}.

upconversion mechanism, intensity dependence of the upconverted emissions are shown in Fig. 3 (the particles): at low pump power, $n = 4.43$ for the emission at 290 nm, $n = 4.48$ for the emission at 348 nm, $n = 3.52$ for the emission at 361 nm, $n = 3.59$ for the emission at 451 nm, and $n = 2.94$ for the emission at 474 nm. The results show that the population of the states $^1I_6$, $^1D_2$ and $^1G_4$ come from a five-photon, four-photon and three-photon upconversion process, which confirms that ET: $^3F_2 \rightarrow {}^3H_6$ (Tm^{3+}): $^3H_4 \rightarrow {}^1D_2$ (Tm^{3+}) (four-photon upconversion process) is the fundamental process to populate the state $^1D_2$. Thereafter, the state $^1I_6$ can be populated by $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^1D_2 \rightarrow {}^1I_6$ (Tm^{3+}) (five-photon upconversion process). Decreasing of n at high pump power is attributed to the saturation effect of the absorption of Yb^{3+} to the pump laser.

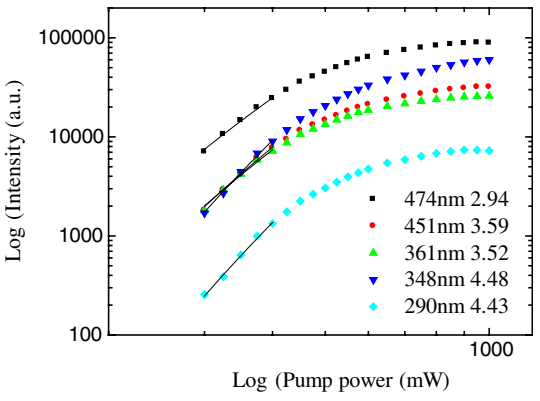

Fig. 3. Intensity dependence of the upconverted fluorescence on the pump power in $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ particles.

The relative intensities of the UV upconversion emissions versus excitation power can be investigated simultaneously by recording the emission spectra at 200–700 nm at different excitation powers, as shown in Fig. 4. The results in Fig. 4 were listed in Table 1, which indicates that the intensity ratio σ for 348 nm emission from $^1I_6 \rightarrow {}^3F_4$ transition to 361 nm from $^1D_2 \rightarrow {}^3H_6$ transition is augmented with increasing the 978-nm excitation power. Based on the UV upconversion mechanism as shown in Fig. 2, we would use the rate equation to explain it.

Let γ represents the radiative transition rate from the $^1D_2$ level, N_0 and N the population of the states $^2F_{5/2}$ (Yb^{3+}) and $^1D_2$ (Tm^{3+}), X the rate of ET $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^1D_2 \rightarrow {}^1I_6$ (Tm^{3+}), β the branching ratio of the $^1D_2 \rightarrow {}^3H_6$ transition, F the pump power and Ω the absorption cross-section of Yb^{3+}. At steady state, from the rate equation [12], we have

$$\sigma = \frac{NN_0XF\Omega}{\gamma\beta}. \quad (1)$$

From the formula (1), the intensity ratio σ for 348 nm emission from $^1I_6 \rightarrow {}^3F_4$ transition to 361 nm from $^1D_2 \rightarrow {}^3H_6$ transition would be proportional

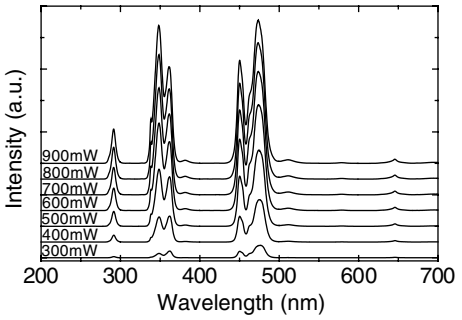

Fig. 4. The upconversion emission spectra measured at different excitation powers with excitation at 978 nm.

Table 1
The intensity ratio $\sigma = I_{348\ nm}/I_{361\ nm}$ at different pump power

The pump power (mW)	300	325	350	375	400	425	450	475	500	525	550
σ	0.84	0.92	1.05	1.16	1.25	1.35	1.43	1.48	1.54	1.61	1.68

to the pump power F. So increasing of F would make σ become bigger.

Fig. 5 shows the dependence of the upconversion emission intensity ratios $I_{451\ nm}/I_{361\ nm}$ and $I_{348\ nm}/I_{290\ nm}$ on the excitation power, which indicate that the intensity ratio $I_{451\ nm}/I_{361\ nm}$ (or $I_{348\ nm}/I_{290\ nm}$) grows above a well-defined threshold power. As we all know, the emissions at 451 and 361 nm (or 348 and 290 nm) come from the same upper state $^1D_2$ (or $^1I_6$), only stimulated emissions can alter the effect branching ratios from a single level to several others [13]. Specially, an important aspect of the power dependence of the intensity ratio $I_{451\ nm}/I_{361\ nm}$ on the excitation power is its linearity above threshold. At 350 mW, the intensity ratio $I_{451\ nm}/I_{361\ nm}$ begins to increase linearly until it saturates near 900 mW. Linearity is characteristic of oscillators, whereas exponential growth typifies amplifiers. This reveals that very effective feedback assists in the attainment of threshold in our samples. For the intensity ratio $I_{348\ nm}/I_{290\ nm}$, at 650 mW, it begins to increase linearly and the saturation is not observed in our measurement range (up to 1000 mW). So we conclude that ultraviolet (~348 nm) and blue (~451 nm) upconversion stimulated emissions were observed in the particles. It is evident that for the intensity ratio $I_{348\ nm}/I_{290\ nm}$, higher threshold power than that of $I_{451\ nm}/I_{361\ nm}$ is attributed to that the population of the state $^1I_6$ comes from the $^1D_2$ level with the excitation of a 978-nm LD. Since the diameter of the particles is larger than $\lambda/2$ (λ is the wavelengths of the upconversion emissions), the stimulated emissions are attributed to strong localization of light in the particles [13].

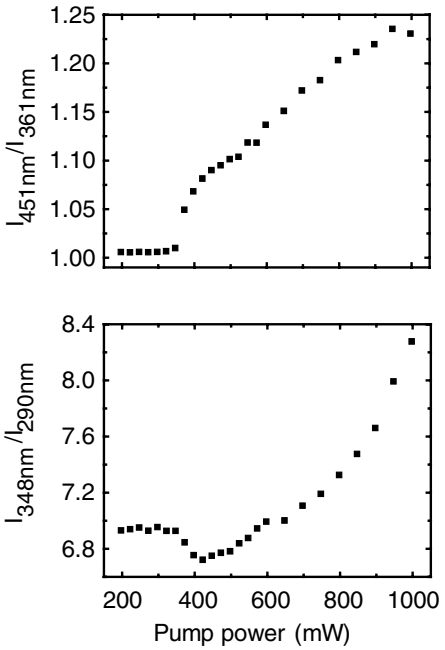

Fig. 5. The dependence of the upconversion emission intensity ratios $I_{451\ nm}/I_{361\ nm}$ and $I_{348\ nm}/I_{290\ nm}$ on the excitation power.

3. Conclusion

In conclusion, $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ amorphous fluoride particles were prepared by pulsed laser ablation. Under a 978-nm laser diode excitation, intense ultraviolet and blue upconversion emissions were observed in the particles. Intensity dependence of the upconversion emissions on the pump power was measured. The results show that the population of the states $^1I_6$, $^1D_2$ and $^1G_4$ may come from a five-photon, four-photon and three-photon energy transfer upconversion process. In addition, ultraviolet ($^1I_6 \rightarrow {}^3F_4$ transition) and blue ($^1D_2 \rightarrow {}^3F_4$ transition) upconversion stimulated emissions were observed in the particles.

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