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# Infrared-to-ultraviolet up-conversion luminescence from $AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles prepared by pulsed laser ablation

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**Abstract**

$AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles were prepared by pulsed laser ablation (PLA). Under a 978 nm laser diode excitation, intense ultraviolet and weak blue up-conversion emissions were observed in the $AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles. Intensity dependence of the up-conversion 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 up-conversion process.


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## 1. Introduction

Recently, short-wavelength solid-state lasers in the ultraviolet (UV) to green spectral range have attracted much attention due to a wide range of applications including high-density optical data storage, color display, and infrared sensor. The phenomenon of frequency up-conversion by using the intrinsic energy level matching of certain rare-earth (RE) ions, as one of the available approaches exploring short-wavelength solid-state lasers, has been investigated widely during the past two decades [1–5]. Excited state absorption (ESA) and energy transfer (ET) can be efficient up-conversion mechanisms in RE doped materials. Shihua Huang et al. [6] reported up-conversion in $LaF_3$: $Tm^{3+}$ excited at 647.1 nm by ESA. Co-doping of $Yb^{3+}$ as sensitizer has yielded a substantial improvement on the up-conversion efficiency in $Tm^{3+}$, $Pr^{3+}$, $Ho^{3+}$ and $Er^{3+}$ doped systems due to the efficient ET between the sensitizer and the pair or triads of RE ions [7–9]. In $Yb^{3+}$-sensitzed RE doped materials, efficient infrared-to-UV up-conversion emissions at room temperature have been rarely investigated [9,10]. Studies on efficient UV luminescence materials are very necessary and valuable due to the need of developing short-wavelength solid-state lasers.

In this paper, we reported intense UV up-conversion properties of the $AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles prepared by pulsed laser ablation (PLA). With the excitation of a 978 nm-laser-diode (LD), intense UV and weak blue up-conversion emissions were observed. The mechanism responsible for the UV emission was discussed.

## 2. Results and discussion

1064 nm from a pulsed Nd:YAG laser was used as the light source for PLA. The laser beam was focused onto the target ($AlF_3$: 10%$Yb^{3+}$, 0.2%$Tm^{3+}$) prepared by solid state reaction (the raw materials are high purity (99.95%) $AlF_3$, $YbF_3$ and $TmF_3$) at 1000 °C for 1 h dipped in a beaker filled

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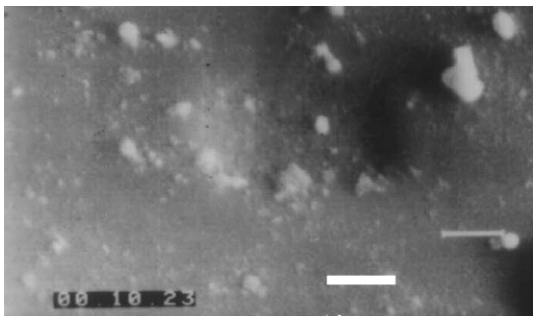

Fig. 1. The morphology of the particles measured with a transmission electron microscope.

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 and the shape is not regular measured with a transmission electron microscope (JEM-2010), as shown in Fig. 1. X-ray analysis data show that the particles are polycrystalline and mixed phase of α-$AlF_3$ and β-$AlF_3$. 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 up-conversion 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. 2 is the room temperature up-conversion emission spectrum of the particles excited at 978 nm. Emissions in the UV and visible comes from the following transitions: $^1I_6 \rightarrow {}^3H_6$ (~290 nm), $^1I_6 \rightarrow {}^3F_4$ (~347 nm), $^1D_2 \rightarrow {}^3H_6$ (~361 nm), $^1D_2 \rightarrow {}^3F_4$ (~451 nm), $^1G_4 \rightarrow {}^3H_6$ (~476 nm).

In $Yb^{3+}$–$Tm^{3+}$ co-doped systems, different process may result in up-conversion. Fig. 3 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 $^1G_4$ [1]. Though

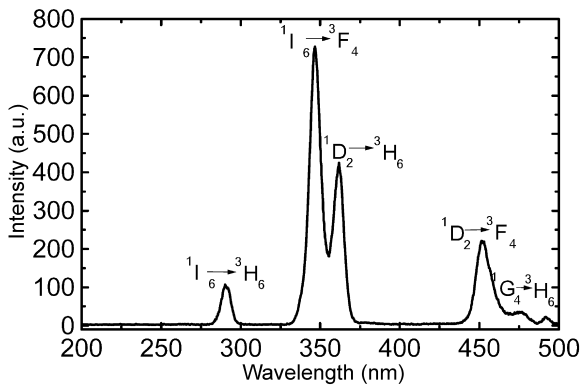


Fig. 2. Room temperature up-conversion emission spectra of $AlF_3$: 10%$Yb^{3+}$, 0.2%$Tm^{3+}$ particles (at the pump power = 600 mW).

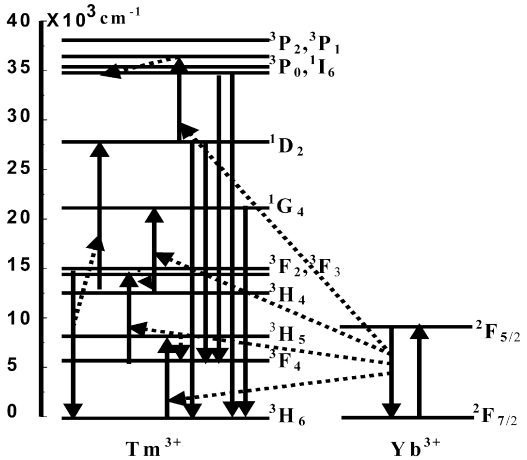


Fig. 3. Energy-level diagram of $Tm^{3+}$ and $Yb^{3+}$.

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 $^1D_2$ [10]. Thereafter, the state $^1I_6$ can be populated by $^2F_{5/2} \rightarrow {}^2F_{7/2}$ ($Yb^{3+}$): $^1D_2 \rightarrow {}^1I_6$ ($Tm^{3+}$).

For unsaturated up-conversion, 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 up-converted photon emitted [11]. In order to clarify the UV up-conversion mechanism, intensity dependence of the up-converted emissions are shown in Fig. 4 (the particles): at low pump power, $n = 4.91$ for the emission at 347 nm, $n = 4.02$ for the emission at 361 nm, $n = 4.18$ for the emission at 451 nm, and $n = 3.04$ for the emission at 476 nm. At high pump power, $n = 2.76$, 2,47, 2.65, 1.3 for the emissions at 347, 361, 451, 476 nm, respectively. 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 up-conversion process, which confirms that ET: $^3F_2 \rightarrow {}^3H_6$

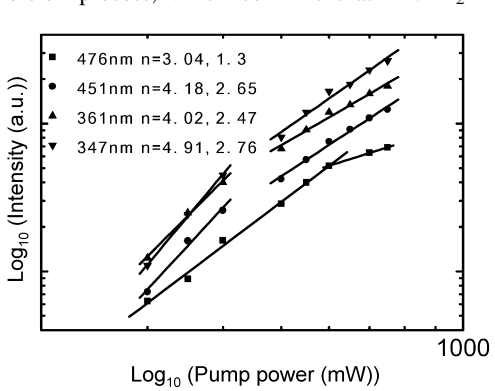


Fig. 4. Intensity dependence of the up-converted fluorescence on the pump power in $AlF_3$: 10%$Yb^{3+}$, 0.2%$Tm^{3+}$ particles.

Table 1
The intensity ratio $\sigma = I_{347\ nm}/I_{361\ nm}$ at different pump power

| The pump power (mW) | 300 | 350 | 400 | 500 | 550 | 600 | 650 | 700 | 750 |
|---|---|---|---|---|---|---|---|---|---|
| $\sigma$ | 0.89 | 0.97 | 1.12 | 1.19 | 1.31 | 1.38 | 1.37 | 1.44 | 1.48 |

($Tm^{3+}$): $^3H_4 \rightarrow {}^1D_2$ ($Tm^{3+}$) (four-photon up-conversion 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 up-conversion process).

The relative intensities of the UV up-conversion emissions versus excitation powers can be investigated simultaneously by recording the emission spectra at 300–400 nm at different excitation powers, as shown in Fig. 5. The results in Fig. 5 were listed in Table 1, which indicates that the intensity ratio $\sigma$ for 347 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 up-conversion mechanism as shown in Fig. 3, we would use the rate equation to explain it.

Let $\gamma$ 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 $^2F_{5/2} \rightarrow {}^2F_{7/2}$ ($Yb^{3+}$): $^1D_2 \rightarrow {}^1I_6$ ($Tm^{3+}$), $\beta$ the branching ratio of the $^1D_2 \rightarrow {}^3H_6$ transition, $F$ the pump power and $\Omega$ the absorption cross-section of $Yb^{3+}$. At steady state, from the rate equation [6], we have

$$\sigma = \frac{NN_0XF\Omega}{\gamma\beta} \tag{1}$$

From the formula (1), the intensity ratio $\sigma$ for 347 nm emission from $^1I_6 \rightarrow {}^3F_4$ transition to 361 nm from $^1D_2 \rightarrow {}^3H_6$ transition would be proportional to the pump power $F$. So increasing of $F$ would make $\sigma$ higher.

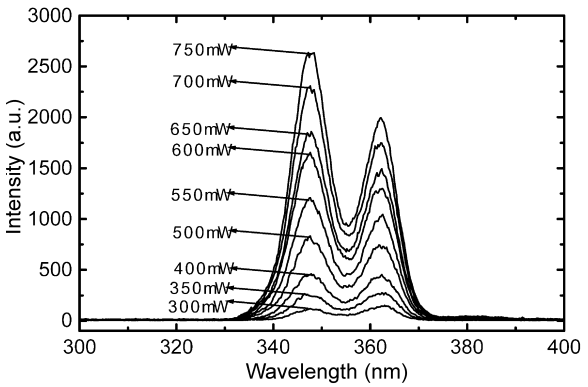


Fig. 5. Part of the emission spectra from $^1I_6 \rightarrow {}^3F_4$ and $^1D_2 \rightarrow {}^3H_6$ transitions measured at different excitation powers showing the emission intensity ratios between the two transitions with excitation at 978 nm.

## 3. Conclusion

In conclusion, $AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles were prepared by PLA. Under a 978 nm laser diode excitation, intense ultraviolet and weak blue up-conversion emissions were observed in the $AlF_3$: 0.2%$Tm^{3+}$, 10%$Yb^{3+}$ particles. Intensity dependence of the up-conversion emissions on the pump power 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 up-conversion process.

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