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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Received 26 October 2002; received in revised form 29 November 2002; accepted 06 December 2002 by B. Jusserand

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 $^1$I$_6$, $^1$D$_2$ and $^1$G$_4$ may come from a five-photon, four-photon and three-photon energy transfer up-conversion process.

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PACS: 78.55.Hx; 78.20. – e; 78.47. + p
Keywords: E. Luminescence; D. Optical properties

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$^{3+}$-sensitized 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...
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-AlF₃ and β-AlF₃. 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 an objective 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 come from the following transitions: ¹I₆ → ³H₆ (~290 nm), ¹I₆ → ³F₄ (~347 nm), ¹D₂ → ³H₆ (~361 nm), ²F₄ → ²F₃ (~451 nm), ³G₄ → ³H₆ (~476 nm).

In Yb³⁺–Tm³⁺ co-doped systems, different processes may result in up-conversion. Fig. 3 shows the energy level diagrams of Tm³⁺ and Yb³⁺. The pump light excites only the Yb³⁺ ions, and three successive energy transfers from Yb³⁺ to Tm³⁺ populate ³H₆, (²F₃, ²F₂), and ³G₄ [1].

Though the Tm³⁺–Tm³⁺ interaction is weak in the sample with low Tm³⁺ concentration, owing to the large energy mismatch (~3516 cm⁻¹) in the transfer ²F₅/₂ → ²F₇/₂ (Yb³⁺): ³G₄ → ¹D₂ (Tm³⁺), the process ²F₂ → ³H₆ (Tm³⁺): ³H₄ → ¹D₂ (Tm³⁺) may alternatively play the most important role in populating ¹D₂ [10]. Thereafter, the state ¹I₆ can be populated by ²F₅/₂ → ²F₇/₂ (Yb³⁺): ¹D₂ → ¹I₆ (Tm³⁺).

For unsaturated up-conversion, emission intensity, Iₑ, is proportional to Iⁿ, 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 ¹I₆, ¹D₂ and ³G₄ come from a five-photon, four-photon and three-photon up-conversion process, which confirms that ET: ²F₂ → ³H₆.
The intensity ratio \( \sigma = \frac{I_{347\text{nm}}}{I_{361\text{nm}}} \) at different pump power

<table>
<thead>
<tr>
<th>Pump power (mW)</th>
<th>( \sigma )</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>0.89</td>
</tr>
<tr>
<td>350</td>
<td>0.97</td>
</tr>
<tr>
<td>400</td>
<td>1.12</td>
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<tr>
<td>500</td>
<td>1.19</td>
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<td>550</td>
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<td>600</td>
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<td>650</td>
<td>1.37</td>
</tr>
<tr>
<td>700</td>
<td>1.44</td>
</tr>
<tr>
<td>750</td>
<td>1.48</td>
</tr>
</tbody>
</table>

\( \text{(Tm}^{3+}: 3\text{H}_4 \rightarrow 1\text{D}_2 (\text{Tm}^{3+}) \text{ (four-photon up-conversion process)}) \) is the fundamental process to populate the state \( 1\text{D}_2 \). Thereafter, the state \( 1\text{I}_6 \) can be populated by \( 2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2} (\text{Yb}^{3+}) \); \( 1\text{D}_2 \rightarrow 1\text{I}_6 (\text{Tm}^{3+}) \) (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 \( 1\text{I}_6 \rightarrow 3\text{F}_4 \) transition to 361 nm from \( 1\text{D}_2 \rightarrow 1\text{H}_6 \) 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 \( 1\text{D}_2 \) level, \( N_0 \) and \( N \) the population of the states \( 2\text{F}_{5/2} (\text{Yb}^{3+}) \) and \( 1\text{D}_2 (\text{Tm}^{3+}) \), \( X \) the rate of ET \( 2\text{F}_{5/2} \rightarrow 2\text{F}_{7/2} (\text{Yb}^{3+}) \); \( 1\text{D}_2 \rightarrow 1\text{I}_6 (\text{Tm}^{3+}) \), \( \beta \) the branching ratio of the \( 1\text{I}_6 \) transition to \( 1\text{H}_6 \) transition, \( F \) the pump power and \( \Omega \) the absorption cross-section of \( \text{Yb}^{3+} \). At steady state, from the rate equation [6], we have

\[
\sigma = \frac{N_0 \omega \times F \Omega}{\gamma \beta}
\]  

(1)

From the formula (1), the intensity ratio \( \sigma \) for 347 nm emission from \( 1\text{I}_6 \rightarrow 3\text{F}_4 \) transition to 361 nm from \( 1\text{D}_2 \rightarrow 1\text{H}_6 \) 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 \( 347\text{nm} \) and \( 361\text{nm} \) transitions measured at different excitation powers showing the emission intensity ratios between the two transitions with excitation at 978 nm.](image-url)

3. Conclusion

In conclusion, AlF\(_3\): 0.2%\( \text{Tm}^{3+}, 10\%\text{Yb}^{3+} \) 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%\( \text{Tm}^{3+}, 10\%\text{Yb}^{3+} \) particles. Intensity dependence of the up-conversion emissions on the pump power that the population of the states \( 1\text{I}_6 \), \( 1\text{D}_2 \) and \( 1\text{G}_4 \) may come from a five-photon, four-photon and three-photon energy transfer up-conversion process.

This work was supported by the State Key Project of Basic Research of China and Natural Science Foundation of China (10274082).

References