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Citation: *J. Appl. Phys.* **93**, 4328 (2003); doi: 10.1063/1.1557775

View online: <http://dx.doi.org/10.1063/1.1557775>

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Enhancement of ultraviolet upconversion in Yb^{3+} and Tm^{3+} codoped amorphous fluoride film prepared by pulsed laser deposition

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(Received 21 October 2002; accepted 10 January 2003)

$\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$ amorphous fluoride film was prepared by pulsed laser deposition. Ultraviolet and blue up-conversion emissions were observed under infrared excitation at 978 nm. In comparison with the upconversion of the target, the ultraviolet emissions are enhanced greatly. The enhancement is attributed to a decrease of the Judd–Ofelt parameter Ω_2 induced by pulsed laser deposition, which precludes the transition rate from 3F_2 to 3F_4 and enhances the energy transfer process and populates the 1D_2 level: ${}^3F_2 \rightarrow {}^3H_6$ (Tm^{3+}): ${}^3H_4 \rightarrow {}^1D_2$ (Tm^{3+}). © 2003 American Institute of Physics. [DOI: 10.1063/1.1557775]

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, undersea communications, color displays, and infrared sensors. The phenomenon of frequency upconversion using intrinsic energy level matching of certain rare-earth (RE) ions, one of the approaches available to explore 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. Huang *et al.*⁶ reported upconversion in $\text{LaF}_3:\text{Tm}^{3+}$ excited at 647.1 nm by ESA. Codoping of Yb^{3+} as a sensitizer has yielded a substantial improvement in 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 triad of RE ions.^{7–9} In Yb^{3+} -sensitized RE doped materials, efficient infrared-to-UV up-conversion emissions at room temperature have rarely been investigated.^{10,11} Studies of new approaches to obtain efficient UV luminescence are very necessary and valuable due to the need for developing short-wavelength solid-state lasers.

By controlling the excited-state dynamics with a judiciously selected local environment, one can obtain efficient upconversion. Thus processing of materials to control the local environment of interion interactions and local phonon densities of state plays an important role in producing RE doped materials with highly efficient upconversion.¹² Pulsed laser deposition (PLD), as a high temperature and pressure laboratory for new metastable materials, has been investigated widely since the first ruby laser was invented. Compounds of deep earth, colossal magnetoresistant, supercon-

ductive, superhard, and nanometer materials (nanotubes, nanobelts, etc.) were studied by PLD.¹³ An example of the latter will be given here. Here, we reported infrared-to-UV up-conversion properties of $\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$ amorphous fluoride film excited at 978 nm. The film was prepared by PLD. In comparison with upconversion of the target, the UV emissions are enhanced greatly, which is attributed to a decrease of the Judd–Ofelt parameter Ω_2 induced by PLD.

Radiation of 1064 nm from a pulsed Nd:YAG laser (pulse width 10 ns, repetition rate 10 Hz) was used as the light source for PLD. The laser beam, with peak power of 10^6 W, was focused onto the target ($\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$ glass prepared by solid-state reaction) at an incidence angle of about 45° in air. The substrate (SiO_2 glass) was held 10–20 mm in front of the target at room temperature. The duration of exposure of the target

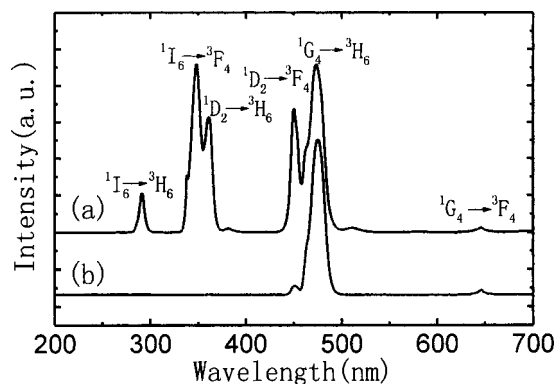


FIG. 1. Up-conversion emission spectra of $\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$: (a) the film; (b) the starting bulk material (at the same pump power of 600 mW).

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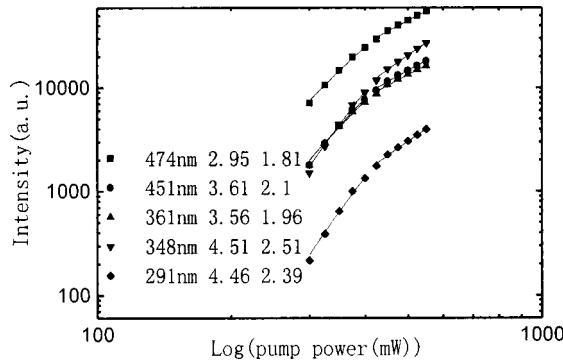


FIG. 2. Intensity dependence of the up-converted fluorescence on the pump power in $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ film.

for the formation of the film is about 15 min. Transmission electron microscope (JEM-2010) analysis shows that the film is amorphous. X-ray photoelectron spectroscopy (XPS) data show that the components of the film are the same as those of the target. The film was excited with a 978 nm laser diode and the up-conversion emission spectra were measured with a fluorescence spectrophotometer (Hitachi F-4500).

Figure 1(a) is a room temperature up-conversion emission spectrum of the film (the pump power 600 mW). Emissions in the UV and visible regions comes from the following transitions:

$$\begin{aligned}
 &^1I_6 \rightarrow ^3H_6 (\sim 291 \text{ nm}), \quad ^1I_6 \rightarrow ^3F_4 (\sim 348 \text{ nm}), \\
 &^1D_2 \rightarrow ^3H_6 (\sim 361 \text{ nm}), \quad ^1D_2 \rightarrow ^3F_4 (\sim 451 \text{ nm}), \\
 &^1G_4 \rightarrow ^3H_6 (\sim 474 \text{ nm}), \quad \text{and} \quad ^1G_4 \rightarrow ^3F_4 (645 \text{ nm}).
 \end{aligned}$$

Figure 1(b) shows the up-conversion emission spectrum of the target (the pump power 600 mW). The UV emission intensity of the film is greatly enhanced in comparison with that of the target.

For unsaturated up-conversion, emission intensity, I_s , is proportional to I^n , where I is the intensity of the excitation

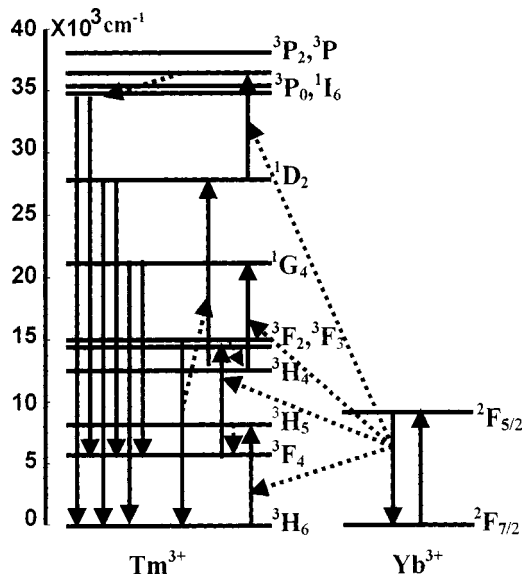


FIG. 3. Schematic diagram of Yb^{3+} -sensitized Tm^{3+} upconversion in $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.098}Yb_{0.1}Tm_{0.002}F_{2.354}$ film under 978 nm excitation.

TABLE I. Reduced matrix elements of the Tm^{3+} from the 1D_2 level to the 3F_4 and 3H_6 states.

Transition of Tm^{3+}	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
$^1D_2 \rightarrow ^3F_4$	0.5689	0.0961	0.0215
$^1D_2 \rightarrow ^3H_6$	0.0	0.3131	0.0958

light and the integer n is the number of photons absorbed per up-converted photon emitted.¹⁴ Intensity dependences of the up-converted emissions are shown in Fig. 2 (the film): at low pump power, $n=4.46$ for emission at 291 nm, $n=4.51$ for emission at 348 nm, $n=3.56$ for emission at 361 nm, $n=3.61$ for emission at 451 nm, and $n=2.95$ for emission at 474 nm. At high pump power, $n=2.39, 2.51, 1.96, 2.1,$ and $1.81,$ for the emissions at 291, 348, 361, 451, and 474 nm, respectively.

In $Yb^{3+}-Tm^{3+}$ codoped systems, different processes may result in upconversion. Figure 3 shows 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 Although the $Tm^{3+}-Tm^{3+}$ interaction is weak in the sample with low Tm^{3+} concentration, due to the large energy mismatch ($\sim 3516 \text{ cm}^{-1}$) in transfer, $^2F_{5/2} \rightarrow ^2F_{7/2}(Yb^{3+}): ^1G_4 \rightarrow ^1D_2(Tm^{3+}),$ process $^3F_2 \rightarrow ^3H_6 \times (Tm^{3+}): ^3H_4 \rightarrow ^1D_2(Tm^{3+})$ may alternatively play the most important role in populating 1D_2 .¹⁰ Thereafter, state 1I_6 can be populated by $^2F_{5/2} \rightarrow ^2F_{7/2}(Yb^{3+}): ^1D_2 \rightarrow ^1I_6(Tm^{3+}).$

In $BaYb_{0.99}Tm_{0.01}F_8$ and $CsYb_2Cl_9:Tm^{3+},$ room temperature UV up-conversion fluorescence was attributed to high Yb^{3+} and Tm^{3+} concentrations and low phonon energy ($\sim 300 \text{ cm}^{-1}$).^{10,11} Our film has much lower Yb^{3+} and Tm^{3+} concentrations and the phonon energy (620 cm^{-1}) is larger. To understand why intense UV up-conversion fluorescence can be observed in the film, but cannot in the target, we should consider the effects of PLD.

During PLD, a high fluence, pulsed laser beam strikes the material, evaporating some of the matter and forming a plasma plume. Then this plume interacts with the substrate, and condenses into a thin film. In this process, the initial temperatures within the still localized plasma can be in excess of 10 000 K and the initial plasma pressure is up to $10^9 \text{ Pa}.$ ¹⁵ With such high temperature and pressure, a new metastable structure will form. XPS data showed that the RE concentration was not changed during PLD. Therefore, the most possible mechanism responsible for the enhancement of the UV emission is the change of structure coupled with RE ions during PLD.

TABLE II. Reduced matrix elements of the Tm^{3+} from the 3F_2 level to the $^3H_5, ^3F_4,$ and 3H_6 states.

Transition of Tm^{3+}	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
$^3F_2 \rightarrow ^3H_5$	0.0	0.0012	0.0182
$^3F_2 \rightarrow ^3F_4$	0.3026	0.0562	0.0440
$^3F_2 \rightarrow ^3H_6$	0.0	0.0	0.2550

The transition rate between states J and J' can be written as^{16–18}

$$A_{J''J'} = \frac{64\pi^4\nu^3e^2}{3hc^2} \frac{1}{2J''+1} \frac{n(n^2+2)^2}{9} \sum_{\lambda} \Omega_{\lambda} U_{JJ'}^{(\lambda)}, \quad (1)$$

where Ω_{λ} ($\lambda=2, 4, 6$) are the Judd–Ofelt parameters, and $U_{JJ'}^{(\lambda)}$ are the reduced matrix elements of the rank λ unit tensor between J and J' . The data of $U_{JJ'}^{(\lambda)}$ of Tm^{3+} for $J = {}^1D_2$ and $J' = {}^3F_4$, and 3H_6 are listed in Table I. For the Tm^{3+} ion, since the $\langle ||U^{(2)}|| \rangle^2$ of the ${}^1D_2 \rightarrow {}^3F_4$ transition is large, the branching ratio of the blue 451 nm emission, β_{451} , would be largely enhanced by the increased value of Ω_2 , which reflects the asymmetry of the ligand field.¹⁹ In addition, $\beta_{451} + \beta_{361} \approx 1$, where β_{361} is the branching ratio of the ${}^1D_2 \rightarrow {}^3H_6$ transition.¹⁹ The fluorescence intensity ratio $R = I_{451\text{ nm}} / (I_{361\text{ nm}} + I_{451\text{ nm}}) \approx \beta_{451}$ will be influenced by the change of structure. From Fig. 1, we obtained $R=0.955$ for the target and $R=0.50$ for the film. The decrease of R shows that Ω_2 becomes smaller during PLD.

Considering the reduced matrix elements of the $\text{Tm}^{3+}: {}^3F_2$ level (shown in Table II)¹⁶ and formula (1), the transition rate from 3F_2 to 3F_4 will be precluded by a decrease of Judd–Ofelt parameter Ω_2 (the branching ratio of the ${}^3F_2 \rightarrow {}^3F_4$ transition is about 30%),²⁰ and this will enhance the ET process and populate the 1D_2 level: ${}^3F_2 \rightarrow {}^3H_6(\text{Tm}^{3+}): {}^3H_4 \rightarrow {}^1D_2(\text{Tm}^{3+})$. An increase of the population of the 1D_2 level will make ET ${}^2F_{5/2} \rightarrow {}^2F_{7/2}(\text{Yb}^{3+}): {}^1D_2 \rightarrow {}^1I_6(\text{Tm}^{3+})$ efficient and therefore the UV up-conversion emission (${}^1I_6 \rightarrow {}^3F_4, {}^3H_6, {}^1D_2 \rightarrow {}^3H_6$) enhanced.

In conclusion, a scheme for the conversion of IR radiation into UV emission in $\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$ amorphous fluoride film was reported. The results of Tm^{3+} as a probe of the structure indi-

cate that the Judd–Ofelt parameter Ω_2 becomes smaller during PLD, which precludes the transition rate from 3F_2 to 3F_4 and enhances the ET process and populates the 1D_2 level: ${}^3F_2 \rightarrow {}^3H_6(\text{Tm}^{3+}): {}^3H_4 \rightarrow {}^1D_2(\text{Tm}^{3+})$. Therefore intense UV up-conversion luminescence was obtained in $\text{Zn}_{0.3}\text{Al}_{0.25}\text{Pb}_{0.3}\text{Li}_{0.098}\text{Yb}_{0.1}\text{Tm}_{0.002}\text{F}_{2.354}$ amorphous film.

This research was supported by the State Key Project of Basic Research (973 G1998061309) and the Natural Science Foundation of China (10274082).

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