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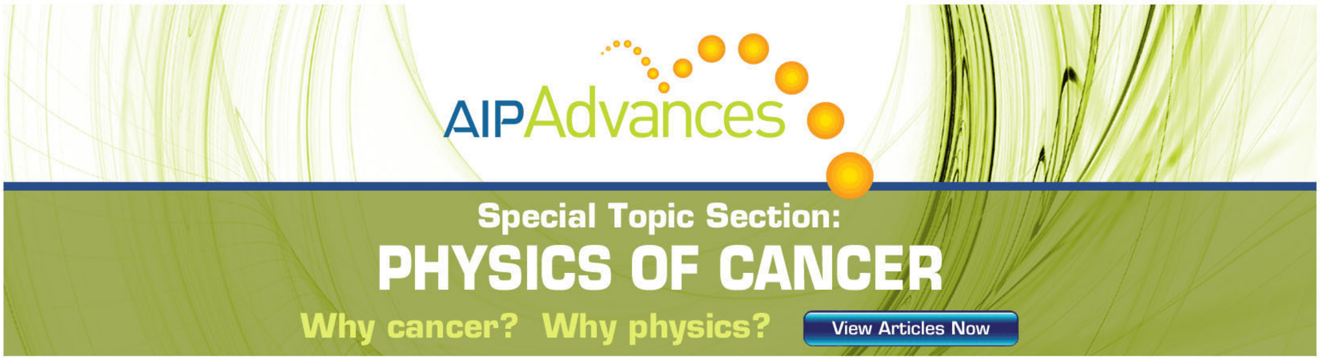

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Infrared-to-violet upconversion from Yb^{3+} and Er^{3+} codoped amorphous fluoride film prepared by pulsed laser deposition

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$Yb^{3+}-Er^{3+}$ codoped amorphous $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$ film has been prepared by pulsed-laser deposition. Violet, green, red, and ultraviolet upconversion emissions were observed under infrared excitation at 988 nm. In comparison with the upconversion of the target, the violet and ultraviolet emissions are enhanced greatly. The enhancement is attributed to the diminishing of the cross relaxation: ${}^4G_{11/2}\rightarrow{}^4F_{9/2}$ (Er^{3+}): ${}^2F_{7/2}\rightarrow{}^2F_{5/2}$ (Yb^{3+}) induced by the decrement of the structure parameter Ω_2. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1521801]

In recent years, 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 optical data storage, color displays, and infrared sensors. The phenomenon of frequency upconversion 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 a very efficient upconversion mechanism in RE doped materials. Huang *et al.*[6] reported upconversion in LaF_3: Tm^{3+} excited at 647.1 nm by ESA. Codoping of Yb^{3+} as a sensitizer has yielded a substantial improvement in the upconversion 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 or violet upconversion emissions at room temperature have been rarely investigated. Thrash *et al.*[10] reported upconverted UV luminescence in $BaYb_{0.99}Tm_{0.01}F_8$ crystal. Therefore, studies on new approaches to obtain efficient UV and violet luminescence are very necessary and valuable due to the need of developing short-wavelength solid-state lasers.

Among the upconversion materials, bulk crystals, glasses, and fibers are quite attractive but high costs associated with the material preparation and device packaging as well as not integrating with semiconductors may limit their applications. Films, on the other hand, combine the advantages of bulk materials and the compactness of fibers, offering good prospects for upconversion devices. Upconversion waveguides can be fabricated by pulsed-laser deposition (PLD), which would allow directly integrating on the same chip the upconversion device with the pump source and other optoelectronic components.

In this communication, we report the upconversion emission properties of the $Yb^{3+}-Er^{3+}$ codoped $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$ (ZAPL) film. With the excitation of a 988-nm-laser-diode (LD), violet, green, red, and UV emissions were observed. The mechanism responsible for the enhancement of the violet and UV emission was also discussed.

953.6 nm radiation, from a Raman shifter pumped by the second harmonic of a Nd: YAG pulsed laser (pulse width 10 ns, repetition rate 10 Hz) was used as the light source for PLD. The Stokes-shifted line with the peak power of 10^4 W was focused on to the target[11] (ZAPL glass) in air at an incidence angle of about 45°. The substrate (SiO_2 glass) was held 10–20 mm in front of the target at room temperature. The film is amorphous characterized by a transmission electron microscope (JEM-2010). X-ray photoelectron spectroscopy (XPS) data show that the components of the film are the same as those of the target. The upconverted emission spectra were measured under a power-adaptable 988-nm-LD excitation and were detected with a fluorescence spectrophotometer (Hitachi F-4500).

Figure 1(b) represents the upconversion emission spectrum of the film (pump power$=$800 mW). The emissions in the UV and visible ranges correspond to the following transitions: ${}^4G_{11/2}\rightarrow{}^4I_{15/2}$ (~380 nm); ${}^2H_{9/2}\rightarrow{}^4I_{15/2}$ (~408 nm); ${}^2H_{11/2}\rightarrow{}^4I_{15/2}$ (~520 nm); ${}^4S_{3/2}\rightarrow{}^4I_{15/2}$ (~548 nm); and ${}^4F_{9/2}\rightarrow{}^4I_{15/2}$ (~650 nm). Figure 1(a) shows the upconverted emission spectrum of the target (pump power$=$800 mW). It is obvious that the violet and UV emissions of the film are enhanced greatly, in comparison with that of the target.

For unsaturated upconversion, emission intensity, I_s, is proportional to I^n, where I is the intensity of the excitation light and n, the number of photons absorbed per upconverted photon emitted.[12] Intensity dependence of the upconversion emissions were obtained (data not shown): $n=3.02$ for the emission at 408 nm; $n=1.91$ for the 520 and 540 bands; and $n=2.01$ for the 652 nm emission.

In $Yb^{3+}-Er^{3+}$ codoped systems, upconverted emission may be resulted from different processes, including multistep excited state absorption (ESA), energy transfer (ET) between

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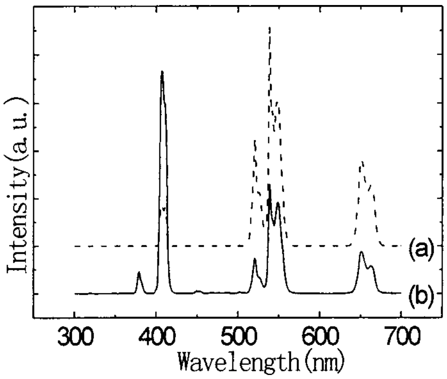

FIG. 1. Upconversion emission spectra of $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$: (a) starting bulk material; (b) the PLD film.

excited neighboring Er^{3+} ions, and addition de photons par transfer d'energie (APTE) between Yb^{3+} and Er^{3+}. Among these processes, APTE is the most efficient. Infrared to green ($^2H_{11/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions) and to red ($^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition) upconverted emissions in $Yb^{3+}-Er^{3+}$ codoped systems have been widely investigated.[13] Here, we focus our attention on the UV (~380 nm) and the violet (~408 nm) emissions.

As shown in Fig. 2, for the violet emission, there are two processes in populating the state $^2H_{9/2}$: (1) energy transfer $^2F_{5/2}\rightarrow{}^2F_{7/2}$ (Yb^{3+}): $^4F_{9/2}\rightarrow{}^2H_{9/2}$ (Er^{3+}) (ET1); and (2) energy transfer $^2F_{5/2}\rightarrow{}^2F_{7/2}$ (Yb^{3+}): $^4S_{3/2}\rightarrow{}^2G_{7/2}$ (Er^{3+}) (ET2), followed by fast cascading relaxation to the $^4G_{11/2}$ and $^2H_{9/2}$ states. On the other hand, the following cross relaxation (CR),[13] $^4G_{11/2}\rightarrow{}^4F_{9/2}$ (Er^{3+}): $^2F_{7/2}\rightarrow{}^2F_{5/2}$ (Yb^{3+}), would depopulate the state $^4G_{11/2}$. Figure 3 represents the excitation spectra of the target (a) $\lambda_{mon}=652$ nm, (b) $\lambda_{mon}=540$ nm. The results show that the excitation of the state $^4G_{11/2}$ would produce intense red emission which is attributed to the intense CR process: $^4G_{11/2}\rightarrow{}^4F_{9/2}$ (Er^{3+}): $^2F_{7/2}\rightarrow{}^2F_{5/2}$ (Yb^{3+}), and weak green emission from the relaxation of the high levels. In our film, XPS data showed that the RE concentration was not changed during PLD. Therefore, the most possible mechanism responsible for the enhancement of the violet emission is the change of structure coupled with RE ions during PLD.

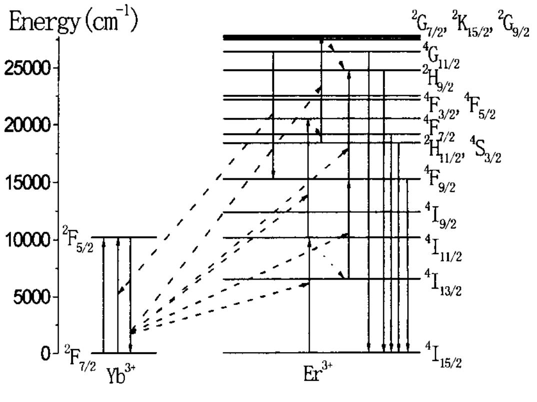

FIG. 2. Schematic diagram of Yb^{3+}-sensitized Er^{3+} upconversion in $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$ film under 988 nm excitation.

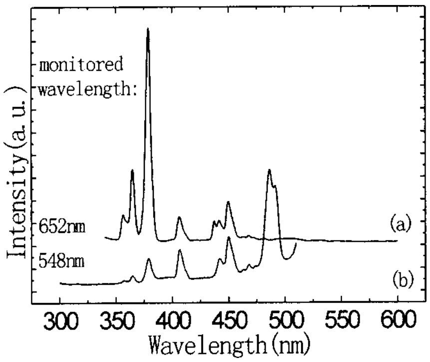

FIG. 3. Excitation spectra of the target (a) $\lambda_{mon}=652$ nm, (b) $\lambda_{mon}=540$ nm.

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.[14] In addition, $\beta_{451}+\beta_{361}\approx 1$, where β_{361} is the branching ratio of the $^1D_2\rightarrow{}^3H_6$ transition,[2] so the fluorescence intensity ration $\sigma=I_{451\,\mathrm{nm}}(^1D_2\rightarrow{}^3F_4$ transition)/ $[I_{361\,\mathrm{nm}}(^1D_2\rightarrow{}^3H_6$ transition) $+I_{451\,\mathrm{nm}}(^1D_2\rightarrow{}^3F_4$ transition)$]\approx\beta_{451}$ of Tm^{3+} will be influenced by the change of structure parameter Ω_2. In order to clarify the change of the structure during PLD, $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Tm_{0.01}F_{2.37}$ film was also prepared at the same PLD conditions. Figure 4 shows that the upconversion emission spectra of (a) the film and (b) the target excited at 988 nm (pump power $=800$ mW). From Fig. 4, we obtained $\sigma=0.95$ for the target, and $\sigma=0.55$ for the film. Decreasing of σ shows that the structure parameter Ω_2 becomes smaller during PLD.

Considering the reduced matrix elements of the Er^{3+}: $^4G_{11/2}$ level[15] (as shown in Table I) and the Einstein transition parameter formula

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

[where $\Omega_\lambda(\lambda=2,4,6)$ is the structure parameter, $U_{JJ'}^{(\lambda)}$ the matrix element], the transition rate from $^4G_{11/2}$ to $^4F_{9/2}$ will be precluded with decreasing the structure parameter Ω_2, which will enhance the $^4G_{11/2}\rightarrow{}^4I_{15/2}$ transition and also

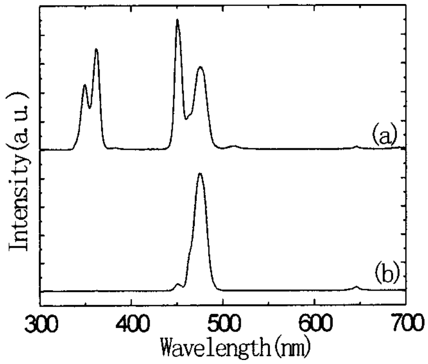

FIG. 4. Upconversion emission spectra of $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Tm_{0.01}F_{2.37}$: (a) the PLD film; (b) the starting bulk material.

TABLE I. Reduced matrix elements of the Er^{3+}: ${}^4G_{11/2}$ level.

Transitions of Er^{3+}	$(U^{(2)})^2$	$(U^{(4)})^2$	$(U^{(6)})^2$
${}^4G_{11/2} \rightarrow {}^4F_{9/2}$	0.4283	0.0372	0.0112

make the state ${}^2H_{9/2}$ populated efficiently by the nonradiation relaxation from the ${}^4G_{11/2}$ level. Therefore, we conclude that the decrement of the structure parameter Ω_2 during PLD lead to the enhancement of the violet upconversion luminescence in the film.

In conclusion, a scheme for the conversion of IR radiation into violet emission centered at 408 nm in a $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$ film was reported. The results of Tm^{3+} as a structure probe indicate that the structure parameter Ω_2 becomes smaller during PLD, which preclude the depopulation process of the state ${}^4G_{11/2}$: ${}^4G_{11/2} \rightarrow {}^4F_{9/2}$ (Er^{3+}): ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ (Yb^{3+}). Therefore, the intense violet upconversion luminescence was obtained in $Zn_{0.3}Al_{0.25}Pb_{0.3}Li_{0.09}Yb_{0.1}Er_{0.01}F_{2.37}$ film.

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