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Strong Enhancements of Infrared-to-Ultraviolet Upconversion Emissions in Yb^{3+} and Tm^{3+} Co-Doped Sub-Micron Fluoride Particles Prepared by Using Pulsed Laser Ablation

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Five Tm^{3+}-Yb^{3+} co-doped fluorides, ZnF_2, AlF_3, PbF_2, LiF, and ZAPL (30ZnF_2 - 25AlF_3 - 30PbF_2 - 9.8LiF - 5Yb_2O_3 - 0.2Tm_2O_3) glass, were prepared via solid state reactions. Taking them as targets, we prepared five fluoride particles by using pulsed laser ablation (PLA). Under 980 nm infrared excitation, the upconversion properties of these fluorides (targets and particles) were investigated. All of the PLA particles showed strong ultraviolet upconversion emission. Spectral analysis indicates that rare-earth ions might prefer to occupy the sites surrounded by Pb^{2+} ions in the ZAPL glass. The populations of the $^1I_6$ and the $^1G_4$ levels (Tm^{3+}) depended on the cation radii in the particles, and the population of the $^1D_2$ (Tm^{3+}) level remained in a relative narrow range both for the targets and the PLA particles. Prolonged fluorescence lifetimes of the $^1I_6$, the $^1D_2$, and the $^1G_4$ levels in the PLA particles were observed, which revealed that the energy transfer process from Yb^{3+} ions to Tm^{3+} ions was more efficient in the PLA particles than it was in the targets. Lattice defects and structural deformation induced by PLA were found in the ZnF_2 particles by using a transmission electron microscope, and the changed fluorescence branching ratios for the transitions from the $^1D_2$ level was proof of a variation in the crystal structure of the PLA particles.

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I. INTRODUCTION

The upconversion phenomenon of fluorescence was found by Auzel in 1966 [1]. Since then, much attention has been focused on the research topic for its potential applications and interesting mechanism. Fluorescent materials allowing generation of primary colors of light (red, green, and blue) are required for image devices that need high spatial resolution with a wide color image gamut. For the last decade, upconversion luminescence has been investigated in optical materials because of the basic research interest in the phenomenon, as well as the need for solid state lasers, in the red-ultraviolet (UV) range, which is a good candidate for building optoelectronic devices and high-density optical storage systems. 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 [2–6]. Excited state absorption (ESA) and energy transfer (ET)

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can be efficient upconversion mechanisms in RE doped materials. Shihua Huang *et al.* [7] reported upconversion in LaF_3: Tm^{3+} excited at 647.1 nm by ESA. Co-doping 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 [8–10]. The researchers of LESP (Laboratory of Excited State Processes, Chinese Academy of Sciences) reported an enhancement of the IR-to-UV upconversion induced by using the pulsed laser ablation method [11]. With those PLA materials, intense blue and ultraviolet upconversions were observed. A strong five-photon upconversion emission can be easily observed in the Yb-Tm co-doped fluoride particles; hereafter, we call them PLA particles. However, until now, no believable experimental proof has revealed the mechanism and origin of the novel phenomenon, though some explanations have been given in former publications [11,12].

In this paper, we explore the enhancement of high-order photon upconversion induced by pulsed laser ablation and report on an investigation of the PLA effect on the IR-to-UV upconversion properties of several Tm^{3+} and Yb^{3+} co-doped fluorides. The mechanism of high-order upconversions in the PLA particles is discussed. Comparing the upconversion spectra of the fluorides to one another, we find that the populations of the $^1I_6$ and the $^1G_4$ levels (Tm^{3+}) depend on the cation radii in the PLA fluoride particles and that the populations of the $^1D_2$ level remains in a relatively narrow range both for the targets and the PLA particles. The prolonged fluorescence lifetimes observed for the $^1I_6$, the $^1D_2$, and the $^1G_4$ levels in the PLA particles reveals that the energy transfer process from Yb^{3+} ions to Tm^{3+} ions is more efficient in the PLA particles than in the targets.

II. EXPERIMENTS

Tm^{3+} and Yb^{3+} co-doped ZAPL glass was prepared via a high-temperature solid-state reaction from spectral grade chemicals of $30ZnF_2$ - $25AlF_3$ - $30PbF_2$ - $9.8LiF$ - $5Yb_2O_3$ - $0.2Tm_2O_3$ (mol%). Tm^{3+} and Yb^{3+} co-doped ZnF_2, AlF_3, PbF_2, and LiF were also prepared in the same way. Taking these fluorides as targets, we prepared Tm^{3+} and Yb^{3+} co-doped fluoride particles by using pulsed laser ablation. The detailed process for preparation is described in Ref. 11. A YAG: Nd pulsed laser (duration of 10 ns and maximum energy of 0.6 J per pulse with second, third, and fourth harmonic generators and a Raman shifter) was used to produce the PLA particles. The Raman shifter was filled with high-purity hydrogen at 300 psi. Through an optical dispersing prism and a filter (gallium-arsenide slice), a second Stokes excited Raman laser at 953.6 nm was used as a pulsed excitation source. No obvious difference was found in the upconversion properties of the particles prepared with the different wavelengths (1064 nm, 953.6 nm, 532 nm, 366 nm and 255 nm).

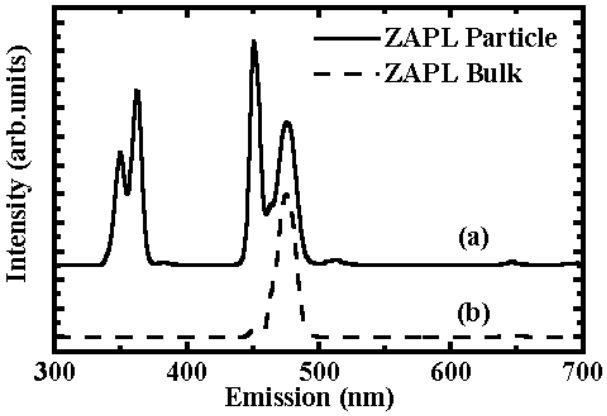

Fig. 1. Upconversion emission spectra of (a) ZAPL: 10 %Yb^{3+}, 0.2 %Tm^{3+} particles and (b) the target under 980 nm IR excitation (pump power = 800 mW). There is a significant difference between them and the intensities of the UV and the blue emissions from $^1I_6$ and $^1D_2$ (Tm^{3+}) are enhanced very much for the PLA particles.

In order to study the PLA particles, we collected them in a thin polyvinyl butyral (PVB) layer on a glass slice or in a beaker filled with ethanol. Spectral measurements indicated that the two kinds of particles collected in two ways were identical in their upconversion characteristics. The PLA particles were investigated morphologically by using a scanning electron microscope (SEM) and a transmission electron microscope (TEM, JEM-2010). Most of the particle sizes lay in a range of hundreds nanometers to microns (As shown in Fig. 1 of Ref. 11); some particles with diameters smaller than 50 nm were also observed under the TEM. The CW excitation source employed here was a diode laser operating at 980 nm. With a boxcar integrator, a Hamamatsu R955 photomultiplier mounted on a SPEX-1403 spectrophotometer, and the 953.6 nm pulsed laser, the populating processes of the Tm^{3+} excitation states in the fluorides were studied. The spectra of the collected particles were taken with an object lens (×20) and a spectrometer (Hitachi-4500). All the experiments were carried out at room temperature and under normal atmospheric pressure.

III. RESULTS AND DISCUSSION

When the 980 nm diode laser with a 1-W output was focused on a PLA particle in the PVB layer, the strong upconversion light from the particle was visible to the naked eye. At room temperature, we measured the upconversion spectra of the particle and the target of ZAPL: Tm^{3+}-Yb^{3+} glass. There was a significant difference between them, as shown in Fig. 1(a). The emissions in the UV and the visible ranges correspond to the

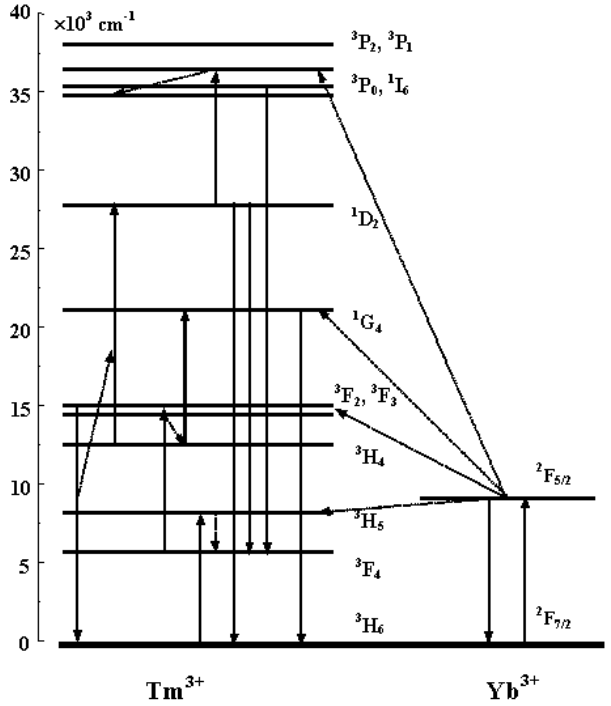

Fig. 2. Schematic diagram of Yb^{3+} -sensitized Tm^{3+} upconversion in fluoride samples under 980 nm excitation. The Yb^{3+} ion absorbs the energy of the 980 nm photon and is excited to its excitation state ($^2F_{5/2}$); then, energy transfer from Yb^{3+} to Tm^{3+} happens. More detailed descriptions about the populating processes of Tm^{3+} excitation states are in Ref. 11.

following transitions: $^1I_6 \rightarrow {}^3F_4$ (∼347 nm), $^1D_2 \rightarrow {}^3H_6$ (∼361 nm), $^1D_2 \rightarrow {}^3F_4$ (∼451 nm), $^1G_4 \rightarrow {}^3H_6$ (∼476 nm), $^1D_2 \rightarrow {}^3H_5$ (510 nm), and $^1G_4 \rightarrow {}^3F_4$ (645 nm), as shown in Fig. 2. The UV emission intensity of the particles is greatly enhanced in comparison with that of the target [Fig. 1(b)]. After we normalized the spectra with the emission at 476 nm ($^1G_4 \rightarrow {}^3H_6$), we could see a strong 362.4 nm emission ($^1D_2 \rightarrow {}^3H_6$), a much more intense 451 nm ($^1D_2 \rightarrow {}^3F_4$) emission and an intense 347 nm emission ($^1I_6 \rightarrow {}^3F_4$). Thus, under 980 nm IR excitation, the populations of the $^1I_6$ and the $^1D_2$ states of Tm^{3+} in the particles are much higher than those in the target. The variation of the fluorescence branching ratio for $^1D_2 \rightarrow {}^3F_4$ and $^1D_2 \rightarrow {}^3H_6$ reveals that a different structure exists in the PLA particles [13].

The blue fluorescence at 451.8 nm and the UV fluorescence at 362.4 nm correspond to four-photon upconversion emissions and the UV fluorescence at 347 nm to a five-photon upconversion process [11]. Two mechanisms might be causing the intense high-order upconversion in the particles. A) Excitation light is trapped inside the particles because of their small sizes, so the actual excitation power density in the particles is much higher than that excited the targets. A higher excitation power density induces higher populations in upper levels, which results in the intense high-order upconversion emissions. However, with this mechanism, the fluorescence branching ratio should not change. Furthermore, we performed the upconversion experiment with ground powder samples, which had been prepared by grinding the targets and which had similar grain sizes as the PLA particles. No evident difference was found in the upconversion spectra of the ground samples in comparison with these of the targets. Therefore, the strong UV upconversion emission in the PLA particles does not result from a trapping of the pump light. B) The concentrations or the local circumstances of RE ions in the PLA particles are changed by pulsed laser ablation. However, as fragments of the target, the PLA particles should have unaltered composition and RE concentrations as well as arbitrary grain shapes (As shown in Fig. 1 of Ref. 11). X-ray photoelectron spectroscopy (XPS) data also showed that the components of the particles were identical to those of the targets. Thus, the factors of composition, concentrations, and optical resonator can be ignored in considering the mechanism of enhanced UV upconversion in the PLA particles. To explore the real reason for the intense UV upconversion, we used a high-resolution TEM (JEM 2010) to investigate the atom images of the target (ground particles) and the PLA particles of ZnF_2: Tm^{3+}-Yb^{3+}, as shown in Fig. 3(a) and (b). For the ZnF_2:Tm^{3+}- Yb^{3+} sample, uniform rutile structure exists in the target, but many lattice defects and structural deformation are seen in the PLA particles. The rutile phase in ZnF_2 will change to a cubic phase when a pressure of more than 70 kbar is present [14]. In pulsed laser ablation, when micro-explosion occurs on the target surface under pulsed laser irradiation, the instantaneous high temperature (∼10,000 °C) and the high pressure (∼GPa) offer sufficient conditions for structural deformation. According to the TEM images and considering the variation of the fluorescence branching ratio of the $^1D_2$ level, we believe that structural deformation in the PLA particles is the key factor in enhancing the ultraviolet upconversion.

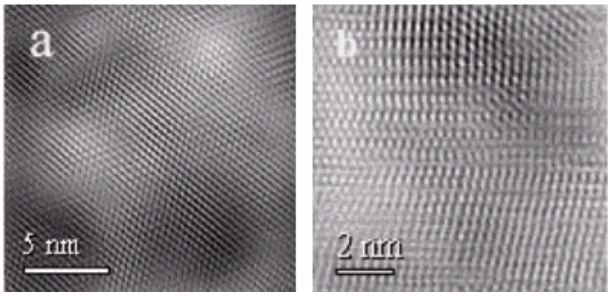

Fig. 3. Atom images of (a) the target (a ground particle) and (b) a PLA particle photographed with the CCD camera of the TEM. There is a uniform rutile phase in the target (the ground particle) and a structural deformation in the PLA particle.

All five fluorides showed greatly increased ultravio-

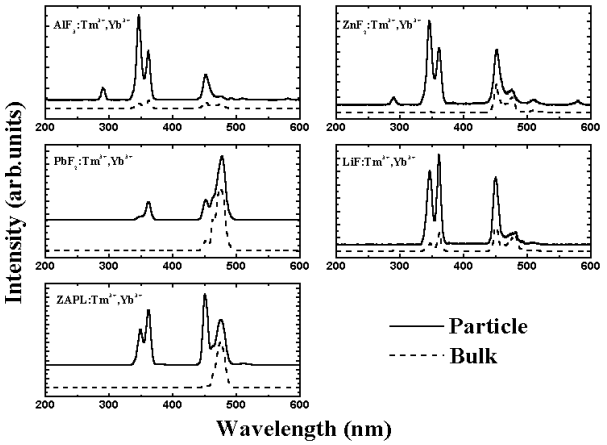

Fig. 4. Upconversion spectra of the PLA particles (solid lines) and the targets (dashed lines) under 980 nm IR excitation. All the fluorides co-doped with Tm^{3+} and Yb^{3+} showed greatly increased ultraviolet upconversion emissions after PLA.

Table 1. Population ratios of the $^1I_6$, the $^1D_2$, and the $^1G_4$ levels in the particles and the targets, which were obtained by fitting multi-peaks of the upconversion spectra.

Ratio (%)		LiF	AlF_3	ZnF_2	PbF_2	ZAPL
$^1I_6$	Targets	11.79	21.68	0.83	0	0
	Particles	32	53.89	38.35	1.38	14.21
$^1D_2$	Targets	49.45	50.39	53.84	1.4	2.71
	Particles	59.12	43.32	52.52	22.87	51.03
$^1G_4$	Targets	38.76	27.93	45.33	98.6	97.29
	Particles	8.88	2.78	9.13	75.75	34.76

let upconversion emissions after PLA, as shown in Fig. 4. The UV emission at 290 nm corresponds to the transition $^1I_6 \rightarrow {}^3H_6$ in AlF_3: Yb^{3+}-Tm^{3+} and ZnF_2: Yb^{3+}-Tm^{3+} PLA particles. By comparing the upconversion spectra with one another, we found the spectra of ZAPL:Yb^{3+}-Tm^{3+} and PbF_2:Yb^{3+}-Tm^{3+} to be similar. All the Yb^{3+}-Tm^{3+} co-doped fluoride targets, except ZAPL glass and PbF_2, give ultraviolet upconversion emissions. That might mean that the rare-earth ions prefer to take the sites nearby the Pb^{2+} ions in the ZAPL glass matrix. Based on the upconversion spectra, we calculated the areas of the fluorescent peaks through a deconvolution of the multi-peak, and the relative population ratios of the $^1I_6$, the $^1D_2$, and the $^1G_4$ levels in the particles and the targets were obtained, as listed in Table 1. Whereas all the fluorides emitted only very weak red upconversion under 980 nm IR excitation, we ignored the populations of other levels in the calculation. It was interesting to find that when the cation in the fluoride particles has a shorter radius, the population of the $^1I_6$ level is higher and the population of the $^1G_4$ level is lower; additionally, the population of the $^1D_2$ level changes in a relatively narrow range, as shown in Fig. 5. We listed all

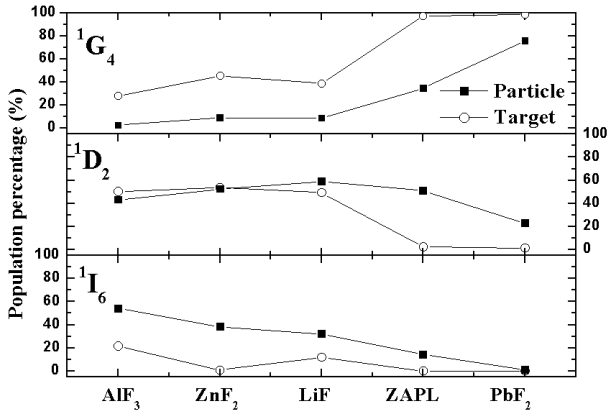

Fig. 5. Areas of the fluorescent peaks measured through deconvolution of the multi-peak in the upconversion spectra, and the relative population ratios of the $^1I_6$, the $^1D_2$, and the $^1G_4$ levels in the PLA particles (●) and the targets (■).

Table 2. Cations in the fluorides in terms of their ion radii from short to long. All values of radii are given in pm (picometers).

Ions	Al^{3+}	Zn^{2+}	Li^+	Pb^{2+}	Yb^{3+}	Tm^{3+}	F^-
Ion Radii (pm)	67.5	74	90	133	100.8	102	119

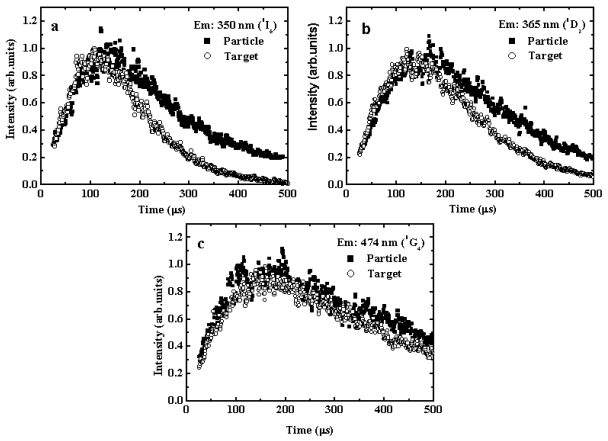

Fig. 6. Variations in the emissions from the $^1G_4$, the $^1D_2$, and the $^1I_6$ levels of the Tm^{3+} ion in ZnF_2 with time as measured by using a boxcar gated integrator and a Raman shifter laser of 953.6 nm (10 ns pulse width). All the levels ($^1G_4$, $^1D_2$ and $^1I_6$) have longer lifetimes in the PLA particles (■) than in the targets (◯).

the cations in terms of their ion radii from short to long in Table 2. As bulk samples, both LiF:Yb^{3+}-Tm^{3+} and AlF_3:Yb^{3+}-Tm^{3+} can emit upconversion light from $^1I_6$ under 980 nm IR excitation, but ZnF_2:Yb^{3+}-Tm^{3+} and PbF_2:Yb^{3+}-Tm^{3+} cannot. However, all the PLA particles showed a 5-photon upconversion transition from $^1I_6$.

The temporal properties of the $^1G_4$, the $^1D_2$, and the $^1I_6$ levels of Tm^{3+} ions in ZnF_2 were studied by using a

Table 3. Time parameters of the rise and the decay processes, as calculated by fitting the lifetime curves in Fig. 6.

Ex: 953.6 nm	$^1G_4$-$^3H_6$ (474 nm)		$^1D_2$-$^3H_6$ (362 nm)		$^1D_2$-$^3H_4$ (450 nm)		$^1I_6$-$^3H_4$ (350 nm)	
	Bulk	Particle	Bulk	Particle	Bulk	Particle	Bulk	Particle
Rise (μs)	37.5	44	35	42	32	46	33	39
Decay (μs)	320	347	81	150	79	142	87	133

953.6 nm Raman shifter laser and a boxcar gated integrator. As Fig. 6 shows, these levels have longer fluorescence lifetimes in the PLA particles than in the targets. The time parameters of the rise and the decay processes are listed in Table 3. They were calculated from fitting the lifetime curves in Fig. 6. A slower decay process is favorable in populating upper levels in an upconversion process with an excitation absorption mechanism. Two mechanisms can be considered in prolonging the fluorescence lifetimes. First, there might be fewer defects in the PLA particles than in the targets, so lower nonradiative transition rates would be expected in the PLA particles. However, the results of high-resolution TEM do not support such an explanation. From the atom images, we can see that there are more defects in the particles than in the targets. Second, the energy transfer from Yb^{3+} ions to Tm^{3+} ions is more efficient in the particles than that in the targets. The efficient ET process keeps the populations of $^3F_{2,3}$ at a high level, so the Tm^{3+}-Tm^{3+} interaction of $^3F_2$, $3\rightarrow{}^3H_6$ (Tm^{3+}): $^3H_4\rightarrow{}^1D_2$ (Tm^{3+}) becomes efficient in populating the $^1D_2$ level. The high population at the $^1D_2$ level is favorable for UV upconversion emissions from the $^1D_2$ and the $^1I_6$ levels.

IV. CONCLUSION

In pulsed laser ablation, micro-explosions occur on the target surface under a pulsed laser irradiation. In the micro-explosion zone, the instantaneous high temperature ($\sim$10,000 °C) and the high pressure ($\sim$GPa) induce a phase change in the PLA production. The novel upconversion properties in PLA particles come from their changed structure. For the Tm^{3+} and Yb^{3+} co-doped fluoride materials in our investigation, all the PLA particles emitted intense ultraviolet upconversion fluorescence under 980 nm infrared excitation. Through a comparison of the cation radii in these fluoride materials, the enhancement of the high-order IR-to-UV upconversion was found to be affected by the cation radii. The shorter the cation radius, the higher the population of the $^1I_6$ level and the lower the population of the $^1G_4$ level. On the other hand, a change in the fluorescence branching ratio of the $^1D_2$ level means changes in the structure phases in the PLA particles, which was confirmed with TEM images and which might be the reason for the strong IR-to-UV upconversion. Additionally, the efficient ET process ($Yb^{3+}\rightarrow Tm^{3+}$) produces a high populations at $^3F_{2,3}$, so the Tm^{3+}-Tm^{3+} interaction of $^3F_{2,3}\rightarrow{}^3H_6$ (Tm^{3+}): $^3H_4\rightarrow{}^1D_2$ (Tm^{3+}) is efficient in populating the $^1D_2$ level.

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