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Infrared-to-ultraviolet up-conversion luminescence of YF_3:Yb^{3+}, Tm^{3+} microsheets

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Abstract

YF_3:Yb^{3+},Tm^{3+} microsheets were synthesized by a simple hydrothermal method. The sheets structure was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Strong ultraviolet and blue up-conversion emissions were observed at 978 nm. The intensity dependence of up-conversion emission on pump power was measured, which shows that the populations of the states $^1I_6$, $^1D_2$ and $^1G_4$ may come from five-photon, four-photon and three-photon energy transfer up-conversion processes, respectively.

Keywords: Microstructures; Morphology; Luminescence

1. Introduction

Fluorides have been extensively studied due to their particular photoluminescence properties. It is well known that metal fluorides are efficient host lattices for luminescent centers because of their low phonon energy and optical transparency over a wide wavelength range. And rare-earth (RE) compounds have been extensively utilized as luminescent, magnetic, and other functional materials. Fluorides doped with RE ions have been demonstrated in many applications such as lasers [1], optical communications [2] and display devices [3]. 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, infrared sensor and so on. The phenomenon of frequency up-conversion by using the intrinsic energy level matching of certain RE ions, as one of the available approaches exploring short-wavelength solid-state lasers, has been investigated widely during the past two decades [4–8]. Excited state absorption (ESA) and energy transfer (ET) are efficient up-conversion mechanisms in RE-doped materials. Shihua Huang et al. [9] reported up-conversion in LaF_3: Tm^{3+} excited at 647.1 nm by ESA. Codoping 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 owing to the efficient ET between the sensitizer and the pairs or triads of RE ions [10–12]. However, in Yb^{3+}-sensitized RE-doped materials, efficient infrared-to-UV up-conversion emissions at room temperature have been rarely investigated [12,13]. Studies on efficient UV luminescence materials are very necessary and valuable in order to developing short-wavelength solid-state lasers.

2. Experimental

Orthorhombic YF_3 microsheets doped with Yb^{3+} and Tm^{3+} ions were synthesized by a facile hydrothermal method. A pale white product was prepared from a mixture with molar composition of 3.00 NaF/1.00 $Y(NO_3)_3$/

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12.00 NH_4F/0.10 EDTA/800 H_2O (EDTA = ethylenediaminetetraacetic acid) at 140 °C for 14 h.

Phase identification was performed via X-ray diffractometry (XRD) (modeRigaku RU-200b), using nickel-filtered CuKα radiation ($\lambda = 1.5406\,\mathring{A}$). The size and morphology were characterized by scanning transmission microscopy (SEM, KYKY 1000B) and transmission electron microscope (TEM, JEM 2010 with operating voltage of 200 kV). The specimen for TEM observations was placed on holey copper grids. The up-conversion emission spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer under the excitation of 978 nm diode lasers.

3. Results and discussion

Fig. 1 presents the XRD pattern of the as-prepared sample. All the diffraction peaks can be readily indexed to those of the orthorhombic YF_3 phase [space group Pnma 62] with lattice constants $a = 6.535$, $b = 6.850$, $c = 4.393$ nm, which are in good agreement with the standard values for the bulk orthorhombic YF_3 (JCPDS No. 74–0911). No other phases have been found in the synthesized products.

The morphology of the final products was characterized by the SEM and TEM observations. As can be seen in the typical SEM images (Fig. 2a), most of the particles dispersed on the copper grids have a sheet-morphology. TEM analysis confirms that the as-prepared products have a sheet-shape with a width of 1 μm and a length of 2 μm. The electron diffraction pattern in the inset, recorded perpendicularly to the sheet, indicates a single phase structure. It is worth to note that the structure is stable enough to withstand the irradiation of the convergent high-energy electron beam (see Fig. 2b).

The evolution of the room-temperature emission spectrum of the YF_3:Yb^{3+},Tm^{3+} microsheets with the pump power is presented in Fig. 3a, the excitation wavelength was 978 nm, in the Yb^{3+} ions $^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition spectral range. This fluorescence corresponds to the Tm^{3+} following transition: $^{1}I_{6}\rightarrow{}^{3}H_{6}$ (~291 nm), $^{1}I_{6}\rightarrow{}^{3}F_{4}$ (~345 nm), $^{1}D_{2}\rightarrow{}^{3}H_{6}$ (~361 nm), $^{1}D_{2}\rightarrow{}^{3}F_{4}$ (˜450 nm), and $^{1}G_{4}\rightarrow{}^{3}H_{6}$ (~475 nm), respectively. Fig. 3b shows that the up-conversion luminescence spectra of the YF_3:Yb^{3+},Tm^{3+} microsheets at different excitation powers. It is obvious that the relative intensity of the blue emissions increased slower than that of the ultraviolet emissions when the excitation power increased.

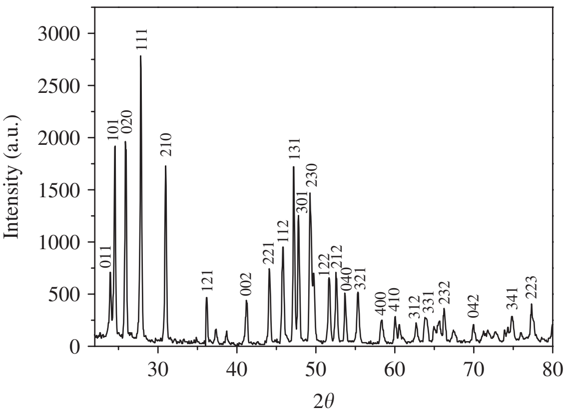

Fig. 1. XRD pattern of YF_3:Yb^{3+},Tm^{3+} microsheets.

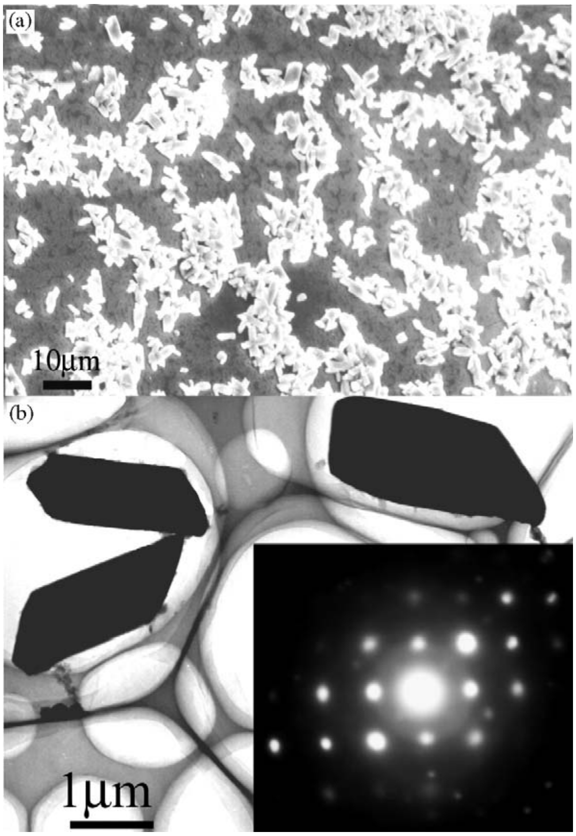

Fig. 2. Figure SEM (a) and TEM (b) maybe of the YF3:Yb^{3+},Tm^{3+} microsheets. The inset shows the electron pattern of a sheet.

Dependence of the up-converison luminescence intensity on pump power was actually performed to obtain a better understanding of the up-conversion processes. For unsaturated up-conversion luminescence, the emission intensity, I_{em}, is proportional to I_{ex}^{n}, where I_{ex} is the excitation intensity and the integer n is the order of up-conversion process. More specifically, n is the number of pump photons required to populate the emitting state, which can be determined from the slope of a Log–Log plot of the up-conversion intensity versus pump power [14]. As shown in Fig. 3b the intensity dependences on pump power are well fitted by log-log straight lines for the up-conversion emissions at 291 and 345 nm, 361 and 450 nm, and 475 nm, which mean five-, four- and three-photon processes, respectively.

Moreover, the emission intensity from the five-photon process increases more rapidly than those from the other processes when the pump power increases.

In Yb^{3+}–Tm^{3+} co-doped systems, different processes may result in up-conversion. Fig. 4 shows energy level

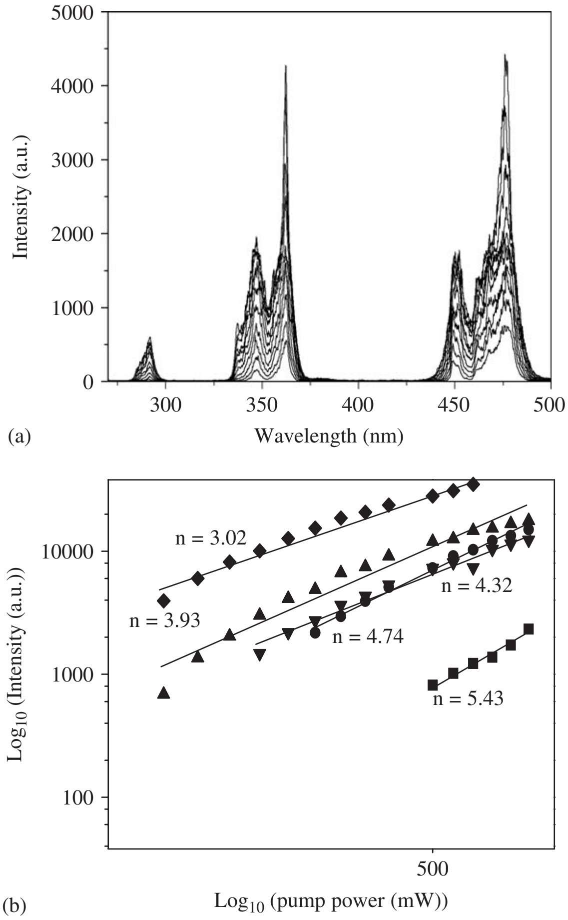

Fig. 3. up-conversion emission spectra of the YF$_3$:Yb^{3+},Tm^{3+} microsheets. (a) Emission spectra at various power (range: 300–700 mW) under 978 nm laser-diode excitation. (b) Log–Log plot of the up-convated fluorescence intensity versus the pump power at 291 nm (■) 345 nm (●) 361 nm (▲) 450 nm (▼) and 475 nm (◆). The slope values are indicated.

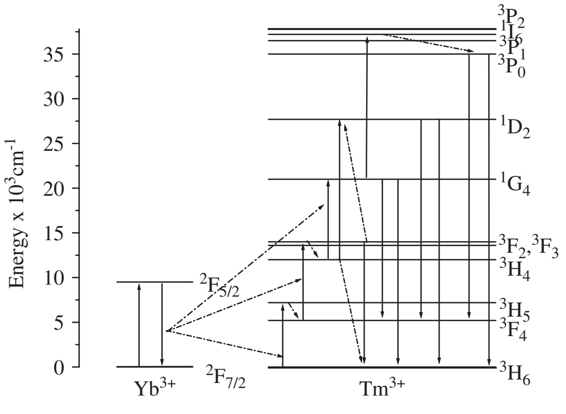

Fig. 4. Schematic diagram of Yb^{3+}-sensitized Tm^{3+} up-conversion in YF$_3$:Yb^{3+},Tm^{3+} 978 nm under excitation (Yb^{3+} absorption).

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 $^1G_4$. Although the Tm^{3+}–Tm^{3+} interaction is weak in the sample with low Tm^{3+} concentration due to the large energy mismatch (3516 cm^{-1}) in $^2F_{5/2}\rightarrow{}^2F_{7/2}$ (Yb^{3+}): $^1G_4\rightarrow{}^1D_2$ (Tm^{3+}), the process $^3F_3\rightarrow{}^3H_6$ (Tm^{3+}):$^3H_4\rightarrow{}^1D_2$ (Tm^{3+}) may alternatively play the most important role in populating $^1D_2$ [13]. 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 BaY$_2$F$_8$:Yb^{3+}, Tm^{3+} room-temperature UV up-conversion fluorescence was attributed to high Yb^{3+} and Tm^{3+} concentrations and low photon energy (300 cm^{-1}) [13]. Our microsheets have much lower Yb^{3+} and Tm^{3+} concentrations and larger photon energy (620 cm^{-1}) than those in Ref. [13]. To understand why intense ultraviolet up-conversion fluorescence can be observed in the microsheets, the sheet-morphology and micron-sizes should be considered.

4. Conclusion

In conclusion, Yb^{3+}/Tm^{3+} codoped YF$_3$ microsheets were synthesized by a simple hydrothermal method. Powder XRD analysis indicates an orthorhombic phase, while TEM image confirms the formation of the sheet morphology. The samples present strong UV and blue upconversion luminescence with under 978-nm diode laser excitation. The results show that the populations of the states $^1I_6$, $^1D_2$ and $^1G_4$ may come from five-, four- and three-photon energy transfer up-conversion processes, respectively.

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