Luminescent properties of Tm$^{3+}$/Ho$^{3+}$ co-doped LiYF$_4$ crystals

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Ho$^{3+}$ with various concentrations and Tm$^{3+}$ with molar concentration of 1.28% are co-doped in LiYF$_4$ (YLF) single crystals. The luminescent properties of the crystals are investigated through emission spectra, emission cross section and decay curves under the excitation of 808 nm. The energy transfer from Tm$^{3+}$ to Ho$^{3+}$ and the optimum fluorescence emission of Ho$^{3+}$ around 2.05 µm are investigated. The emission intensity at 2.05 µm keeps increasing with the molar concentration of Ho$^{3+}$ improved from 0.50% to 1.51% when the molar concentration of Tm$^{3+}$ is kept at 1.28%. Moreover, for the co-doped crystals in which the molar concentrations of Tm$^{3+}$ and Ho$^{3+}$ are 1.28% and 1.51%, respectively, the maximum emission cross section reaches 0.760×10$^{-20}$ cm$^2$ and the maximum fluorescence lifetime is 21.98 ms. All the parameters suggest that these materials have more advantages in the future 2.0 µm laser applications.

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The 2 µm solid laser has attracted great interest due to its applications in optical communications, coherent laser radar, medical treatment, etc.$^{[1-3]}$. The luminescent ion Ho$^{3+}$ is important for the solid laser because of its emission at ~2 µm by $^5I_8\rightarrow^5I_2$ transition. There have been some researches on the lasers based on Tm$^{3+}$/Ho$^{3+}$ co-doped LiYF$_4$ (YLF) crystals because of the excellent optical and physical-chemical properties. Recently, the optical bistable performance, the longwave-infrared optical parametric oscillator and the tuning upconversion luminescence in Tm$^{3+}$/Ho$^{3+}$ co-doped YLF crystals have also been reported.$^{[4-6]}$. Although some parameters and properties of Tm$^{3+}$/Ho$^{3+}$ co-doped YLF crystals have been studied systematically, some aspects are not comprehensible enough. The energy transfer from Tm$^{3+}$:F$_4$ to Ho$^{3+}$:I$_1$ at room temperature in YLF crystals has been firstly reported by Brenier et al.$^{[7]}$. However, they just discussed the characteristics of singly-doped YLF crystals. Because of the main difficulty in growing YLF single crystals, including the oxidation and the volatilization of melting, it is difficult to obtain high-quality crystal.

In this paper, YLF single crystal is obtained by Bridgman method using a sealed platinum crucible in air atmosphere, in which the crucible is completely sealed to isolate the water and the oxygen from the atmosphere and to prevent the volatilization of the melting during crystal growth. This process is proven to improve the crystal quality of the rare earth ion doped YLF crystals. The efficient near infrared (NIR) emission spectra of YLF with optimum concentrations of Tm$^{3+}$ and Ho$^{3+}$ around 1.8 µm emission are obtained and investigated.

A series of Tm$^{3+}$/Ho$^{3+}$ co-doped YLF single crystals were grown in our laboratory using an improved Bridgman method. The molar concentration of TmF$_3$ in raw materials is held to be 1.3%, and that of HoF$_3$ is 0.5%, 1.0% and 1.5%, respectively. The detailed process of the growth and schematic diagram of the apparatus used for the experiment have been reported in our previous work.$^{[8]}$

The typical single crystal with the size of Φ10 mm×82 mm is shown in Fig.1(c). It is transparent with pale red, and the color changes gradually from light to dark along the growth direction due to the higher Ho$^{3+}$ dopant concentration. It can be seen that they are single crystals since they are highly transparent and no grain boundary is observed. The crystals were cut into pieces and well polished to 2.3 mm thickness for optical measurements. The concentrations of Tm$^{3+}$ and Ho$^{3+}$ in YLF single...
crystals were obtained by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). The measured molar concentrations of Tm$^{3+}$/Ho$^{3+}$ in YLF single crystals for three samples are 1.28%/0.5%, 1.28%/1.01% and 1.28%/1.51%, respectively. The structure of the crystal was analyzed by X-ray diffraction (XRD) using an XD-98X diffractometer (XD-3, Beijing). The absorption spectra were recorded with a Cary 500 UV/VIS/NIR spectrophotometer (Agilent Co., America). The emission spectra and fluorescence decay curves were detected by an FLSP 920 type spectrometer (Edinburgh Co., England) excited by 808 nm laser diode (LD). All the measurements were carried out at room temperature.

The XRD pattern for YLF sample with Tm$^{3+}$ (1.28%) /Ho$^{3+}$ (1.51%) is displayed in Fig.1(a). By comparison, the peak positions are consistent with those in JCPD 77-0816 ($a=b=0.517\pm0.001$ nm, $c=1.074\pm0.008$ nm) of YLF which is also listed in Fig.1(b). One can confirm that the current doping levels of Tm$^{3+}$ and Ho$^{3+}$ do not cause any obvious peak shift or second phase. The similar XRD patterns are obtained for YLF samples with 1.28% Tm$^{3+}$ /y% Ho$^{3+}$ ($y=0.50$, 1.01 and 1.51), which suggests that the samples have been crystallized into the pure orthorhombic phase.

Fig.2 shows the absorption spectra of Ho$^{3+}$/Tm$^{3+}$ co-doped YLF samples with different Ho$^{3+}$ doping concentrations. The characteristic absorption bands corresponding to the transitions of Tm$^{3+}$ and Ho$^{3+}$ from the ground state to the excited states are marked in the spectra. As can be seen from Fig.2, the corresponding absorption coefficient is proportional to the Ho$^{3+}$ doping level. However, the intensity ratio is increased rapidly when the molar concentration is further improved to 1.75% and 3.49%. We obtain the optimal doping concentration for Tm$^{3+}$ singly doped YLF crystal, which is 1.28%. On the basis of the optimum doping concentration of Tm$^{3+}$ singly doped YLF crystal, we further investigate the energy transfer of Tm$^{3+}$ and Ho$^{3+}$ in YLF crystals.