2.0-μm emission and energy transfer of Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ single crystal excited by 980 nm*

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Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ single crystals with various Yb^{3+} concentrations and ~0.98 mol% Ho^{3+} concentration are grown by the Bridgman method under the conditions of taking LiF and YF_3 as raw materials and a temperature gradient (40 °C/cm–50 °C/cm) for the solid–liquid interface. The luminescent performances of the crystals are investigated through emission spectra, infrared transmittance spectrum, emission cross section, and decay curves under excitation by 980 nm. Compared with the Ho^{3+} single-doped $LiYF_4$ crystal, the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ single crystal has an obviously enhanced emission band from 1850 nm to 2150 nm observed when excited by a 980-nm diode laser. The energy transfer from Yb^{3+} to Ho^{3+} and the optimum fluorescence emission around 2.0 μm of Ho^{3+} ions are investigated. The maximum emission cross section of the above sample at 2.0 μm is calculated to be 1.08×10^{-20} cm^2 for the $LiYF_4$ single crystal of 1-mol% Ho^{3+} and 6-mol% Yb^{3+} according to the measured absorption spectrum. The high energy transfer efficiency of 88.9% from Yb^{3+} to Ho^{3+} ion in the sample co-doped by Ho^{3+} (1 mol%) and Yb^{3+} (8 mol%) demonstrates that the Yb^{3+} ions can efficiently sensitize the Ho^{3+} ions.

Keywords: Ho^{3+}/Yb^{3+}, energy transfer, 2.0-μm emission, $LiYF_4$ crystal

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1. Introduction

In recent years, infrared solid state lasers working around 2.0 μm have received much attention due to its extensive applications, such as eye-safe laser radars, remote sensing, atmosphere pollution monitoring, etc.[1–3] The 2.0-μm lasers based on the $^5I_7 \rightarrow {}^5I_8$ transition of Ho^{3+} ions have been investigated in some crystalline materials,[4,5] and the fiber laser performances have been studied in tellurite, oxyfluoride, and silica fibers.[6–8]

Because the absorption band of the Ho^{3+} ion are mainly located in a range from 400 nm to 700 nm with a small absorption cross section, it is difficult to choose a favorable laser diode (LD) to pump the Ho^{3+} singly doped material. As is well known, the Yb^{3+} ions can be used as an effective sensitizer for the Er^{3+} ion because of the strong absorption of 980-nm transition from $^2F_{7/2}$ to $^2F_{5/2}$ and well matching between Yb^{3+}:$^2F_{5/2}$ and Er^{3+}:$^4I_{11/2}$ energy levels. Actually, the Ho^{3+}:$^5I_6$ is very close to the Yb^{3+}:$^2F_{5/2}$ from the energy level diagram, it is proposed that the Yb^{3+} should transfer energy to Ho^{3+} through the transition of $^2F_{5/2} \rightarrow {}^5I_6$. The performance between Ho^{3+} and Yb^{3+} has been demonstrated in previous studies.[9,10]

As the rapid multiphonon effect,[11] the luminescence of Ho^{3+} is easily quenched when it is doped in traditional oxide glass due to its high phonon energy. It is necessary to explore new host material with low phonon energy. Compared with the traditional oxides, the fluoride host crystals have a long lifetime with the excited electronic states. There have been some studies conducted about the properties of Ho^{3+}/Yb^{3+} co-doped glasses and crystals.[12] Due to the low phonon energy of the matrix, good chemical–physical performance, and high doping concentration for trivalent rare-earth ions which take the place of the Y^{3+} ions, the $LiYF_4$ single crystal is preferred to be used as solid material for the mid-infrared laser. However, there are rare studies on 2.0-μm emission in Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal.

In this work, Yb^{3+} and Ho^{3+} singly-doped, and Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystals are grown by the Bridgman method, and Yb^{3+} as the sensitizer is introduced into $LiYF_4$ crystal to improve the pump efficiency of 980-nm diode laser. By analyzing the fluorescence characteristics, the mechanisms for 2.0-μm emission in Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal and the energy transfer processes between Yb^{3+} and Ho^{3+} are understood.

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2. Experiment

The Ho^{3+}/Yb^{3+} co-doped and Yb^{3+} singly doped $LiYF_4$ crystals were grown by the Bridgman method. The molar compositions of the raw materials were $51.5LiF–(47.5-x)YF_3–1.0HoF_3–xYbF_3$ ($x = 0$, 2.0, 4.0, 6.0, 8.0) and $51.5LiF–46.5YF_3–2YbF_3$. The obtained samples were designated respectively as LFHY0, LFHY2, LFHY4, LFHY6, LFHY8, and LFY2. Each sample was mixed and ground adequately for 50 min in a mortar. In order to obtain anhydrous Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ polycrystalline materials, each mixed powder was put into apparatus for the anhydrous process for about 5 h–6 h at 760°C–780 °C in a dried HF condition. The polycrystalline materials were put into some Pt sealed crucibles, and then placed in a Bridgman furnace for crystal growth. The temperature gradient of the solid–liquid interface was measured to be 40 °C/cm–50 °C/cm. The detailed processes for crystal growth are described elsewhere.[13,14]

The grown crystal with about $\phi 10$ mm×78 mm was shown in Fig. 1(a). The crystal was sliced into pieces and polished to about 2.2-mm-thickness for the optical performance measurements. The polished slice of crystal was also shown in the right of the inset. The structures of crystals were measured by the use of an XD-98X diffractometer (XD-3, Beijing) for x-ray diffraction. The concentrations of Ho^{3+} and Yb^{3+} in these samples are listed in Table 1, and detected severally with inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Inc., Optima 3000). The absorption spectrum was investigated with a Cary 5000 UV/VIS/NIR spectrophotometer in a wavelength range from 200 nm to 2500 nm. The emission spectrum was recorded under the excitation of 980-nm LD by a Triax 320 type spectrometer with a range of 1000 nm–3000 nm. The fluorescence lifetime was obtained with the FLSP920 fluorescence spectrophotometer. All these measured data were obtained at room temperature atmosphere in the same conditions.

Table 1. Concentrations of Ho^{3+} ions and Yb^{3+} ions in these samples (mol%).

Samples	LFHY0	LFHY2	LFHY4	LFHY6	LFHY8	LFY2
Ho^{3+}	0.98	0.99	0.98	0.97	0.97	0
Yb^{3+}	0	1.96	3.92	5.90	7.88	1.97

3. Results and discussion

3.1. The x-ray diffraction

From Fig. 1(b), x-ray diffraction (XRD) measurement at room temperature of Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal (LFHY8) is presented. The other samples also show a similar XRD pattern. Compared with those of the JCPDS card (77-0816) of $LiYF_4$, the relative intensity and diffraction locations of the crystal sample are almost the same in the XRD spectrum. The similar XRD patterns demonstrate that all the crystals have been almost crystallized into a pure tetragonal phase, and neither an obvious peak shift nor a second phase is caused at this doping level. The cell parameters are calculated to be $a = b = 0.5162$ nm and $c = 1.0735$ nm for sample LFHY8.

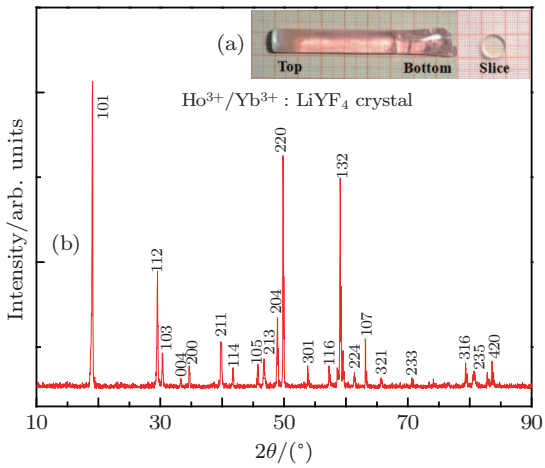


Fig. 1. (color online) (a) Photograph of Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal. (b) Powder XRD pattern of Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal.

3.2. Absorption and emission spectrum

The absorption spectra of Ho^{3+} singly doped (LFHY0) and Ho^{3+}/Yb^{3+} co-doped (LFHY8) $LiYF_4$ crystals from 300 nm to 2200 nm are shown in Fig. 2. It could be seen for both LFHY0 and LFHY8 samples, seven absorption peaks at 412, 446, 481, 539, 639, 1144, and 1936 nm, which correspond to Ho^{3+} transitions from the $^5I_8$ ground state to $^5G_5$, $^5G_6$, $^5F_3$, $^5F_4–^5S_2$, $^5F_5$, $^5I_6$, and $^5I_7$ excited states. It is also observed that a very intense absorption peak at 980 nm of Yb^{3+} ion, which relates to the Yb^{3+} transition that the ground state $^2F_{7/2}$ transits into an excited state $^2F_{5/2}$, appears in the LFHY8 sample. The intense absorption peak corresponding to nearly 980 nm demonstrates that Yb^{3+} acts as an excellent sensitizer to absorb the pump light. Apparently, the co-doped sample LFHY8 does not change the level positions and the shapes of the absorption peaks compared with the singly doped LFHY0 sample.

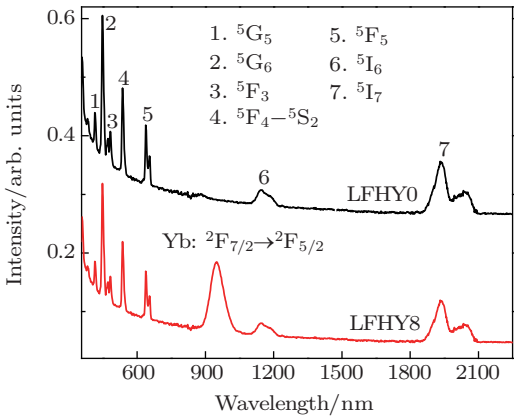


Fig. 2. (color online) Absorption spectra of Ho^{3+} single-doped and Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal.

The infrared transmittance spectrum in a wavelength range of 2500 nm–6000 nm for sample LFHY8 with 2.3 mm in thickness is shown in Fig. 3. It can be observed from the spectrum that the maximum transmittance reaches up to 91.8%, which indicates that oxide and oxyfluoride compounds are almost inexistent in the sample. A very weak absorption band of the OH^- ions at 2751 nm is observed. The absorption coefficient of the OH^- vibration peak at 2751 nm describes the quantity of OH^- groups, and can be calculated to be 0.128 cm^{-1}. It is noted that the transmittance at ~2 μm is about 91%, indicating that the $LiYF_4$ crystal has high transparency and scarce absorption for the light.

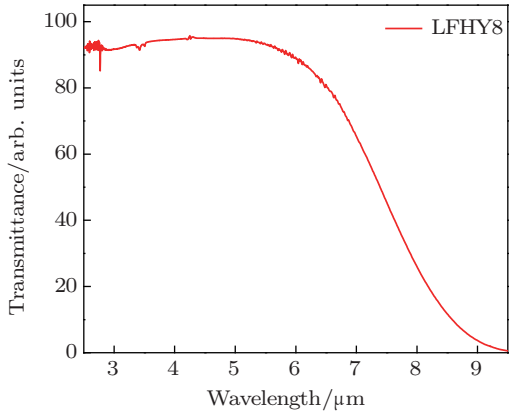


Fig. 3. (color online) Infrared transmittance spectrum of LFHY8.

Figure 4 shows the emission spectra of Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystals with different concentrations under excitation at 980-nm LD in the same condition. A strong emission band from 1850 nm to 2150 nm, centered at 2000 nm, which is attributed to the transition $^5I_7 \rightarrow {}^5I_8$ of Ho^{3+}, is obtained. However, the 1.66-μm emission band associated with the transition $^5I_5 \rightarrow {}^5I_7$ of Ho^{3+} almost disappears due to the lack of efficient energy transfer channels to populate Ho^{3+}:$^5I_5$ in the 980-nm LD. From the emission spectra it follows that the 2.0-μm emission intensity is strengthened with the concentration of Yb^{3+} ions increasing from 2 mol% to 8 mol%. In this study, the maximum emission intensity at ~ 2.0 μm is produced by the sample with a concentration of ~ 8-mol% Yb^{3+} and 0.98-mol% Ho^{3+} ions (LFHY8). There appears to be no quenching effect at that doping concentration of Yb^{3+} ions. It indicated that the $LiYF_4$ crystal is very favorable for Yb^{3+}/Ho^{3+} incorporation to obtain high emission intensity.

The inset of Fig. 4 shows the energy level scheme and the relevant energy transfer channels between the Yb^{3+} ions and Ho^{3+} ions. The possible mechanism of the energy transfer processes between Yb^{3+} and Ho^{3+} has also been reported elsewhere.[15] Compared with those of Ho^{3+}/Yb^{3+}-doped fluorophosphate glass, [9,15] the emission spectra have many peaks at ~ 2.0 μm which are corresponding to Ho^{3+} transitions that the $^5I_7$ energy levels split into the energy levels of the $^5I_8$ ground state, and they appear to be sharper.

The Yb^{3+} ions are pumped from the $^2F_{7/2}$ ground state to an excited state $^2F_{5/2}$ under the excitation of 980-nm LD, and then the energy is transferred to the level $^5I_6$ of Ho^{3+} ions. The processes are as follows:

$$Yb^{3+}\ (^2F_{5/2}) + Ho^{3+}\ (^5I_8) \rightarrow Yb^{3+}\ (^2F_{7/2}) + Ho^{3+}\ (^5I_6),$$
$$Ho^{3+}\ (^5I_6) \rightarrow Ho^{3+}\ (^5I_7) \rightarrow Ho^{3+}\ (^5I_8).$$

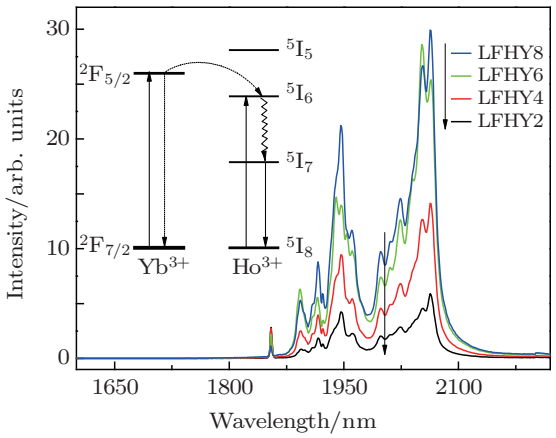


Fig. 4. (color online) Emission spectra of LFHY2, LFHY4, LFHY6, and LFHY8 samples. Inset shows the energy level scheme and energy transfer processes.

The above energy transfer is a phonon-assisted energy transfer process due to the energy mismatch between the Yb^{3+}:$^2F_{5/2}$ and Ho^{3+}:$^5I_6$ levels. Some phonons are needed in such an energy transfer process. Most ions on the $^5I_6$ state of the Ho^{3+} level mainly non-radiatively decay to the $^5I_7$ state of the Ho^{3+} level, and then to the $^5I_8$ state with 2.0-μm emission. Figure 5 shows the changes of emissions at 1945 nm, 2023 nm, and 2063 nm with concentration ratio between Yb^{3+} and Ho^{3+} ions, in which the Ho^{3+} concentration is kept at ~ 0.98 mol%. It is clearly shown that the fluorescence intensities of these samples in the region of near 2.0 μm are the maximum values when the concentration ratio between Yb^{3+} and Ho^{3+} ions reaches 8. It is indicated that the Ho^{3+} ions can be successfully sensitized by the co-doped Yb^{3+} ions, achieving the 2.0-μm emission in $LiFY_4$ crystal.

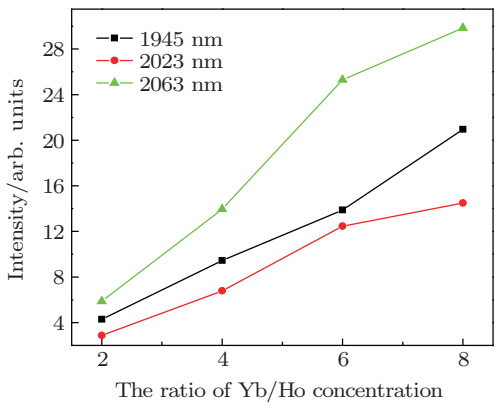


Fig. 5. (color online) Fluorescence intensity variations with the ratio of Yb/Ho concentration.

3.3. Fluorescence decay and energy transfer efficiency

The stimulated emission cross section of laser crystal is one of the important parameters in evaluating the quality properties of a laser. The 2.0-μm emission cross section (σ_{em}) of $^5I_7 \rightarrow {}^5I_8$ transition can be calculated by the McCumber theory.[16] The free energy (ε) of the $^5I_7 \rightarrow {}^5I_8$ transition is 5153 cm^{-1}. The maximum emission cross section in the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal (LFHY6) at 2.0 μm reaches 1.08×10^{-20} cm^2, which is higher than Ho^{3+} single-doped $LiYF_4$ crystal (0.51×10^{-20} cm^2).

The fluorescence decay curves for $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+} at 1019 nm in the Yb^{3+} single-doped sample and Ho^{3+}/ Yb^{3+} co-doped samples under the excitation of 940-nm LD are measured to detect the dynamics of energy transfer processes between the Yb^{3+} ions and Ho^{3+} ions. Figure 6 shows the fluorescence decay curves of LFY2 and LFHY2 samples. From the decay curves, the average fluorescent lifetime can be calculated by the following formula:[17]

$$\bar{\tau} = \frac{\int I(t)t\,\mathrm{d}t}{\int I(t)\,\mathrm{d}t}, \tag{1}$$

where $I(t)$ represents the luminescence intensity as a function of time t. The measured lifetime of Yb^{3+}:$^2F_{5/2}$ decreases from 3.196 ms for the Yb^{3+} singly doped $LiYF_4$ crystal (LFY2) to 0.756 ms for the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal (LFHY2), indicating that the energy transfers from the Yb^{3+} ions to Ho^{3+} ions.

The energy migration process strongly dominates the energy transfer from the Yb^{3+} ions to Ho^{3+} ions. The energy transfer rate W_{ET} is related to the effective lifetime by[18]

$$W_{ET} = \frac{1}{\tau} - \frac{1}{\tau_s}, \tag{2}$$

where τ is the lifetime of the Yb^{3+}:$^2F_{5/2}$ level in the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystals, and τ_s is the lifetime of the Yb^{3+}:$^2F_{5/2}$ level in single-doped $LiYF_4$ crystal. The energy transfer efficiency of η of Yb^{3+} can be calculated by the lifetime values from

$$\eta = 1 - \frac{\tau}{\tau_s}. \tag{3}$$

The fluorescence decay curves at 1019 nm are monitored, the obtained energy transfer rate (W_{ET}) and energy transfer efficiency (η) of Yb^{3+}:$^2F_{5/2}$ are 1008 s^{-1} and 76.3%, respectively.

Figure 7 shows the fluorescence decay curves of samples doped with different concentrations. The Yb^{3+}:$^2F_{5/2}$ level decay curves in the four samples present nearly singular exponential behaviors. The fluorescence decay lifetime increases with the decrease of Yb^{3+} ion concentration. It is most likely to be due to the fact that the higher concentration induces self-quenching in the excited energy migration-assisted energy transfer process.

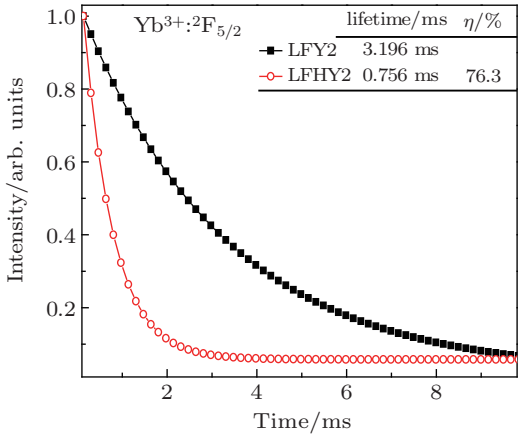


Fig. 6. (color online) Fluorescence decay curves of LFY2 and LFHY2 by 940-nm excitation.

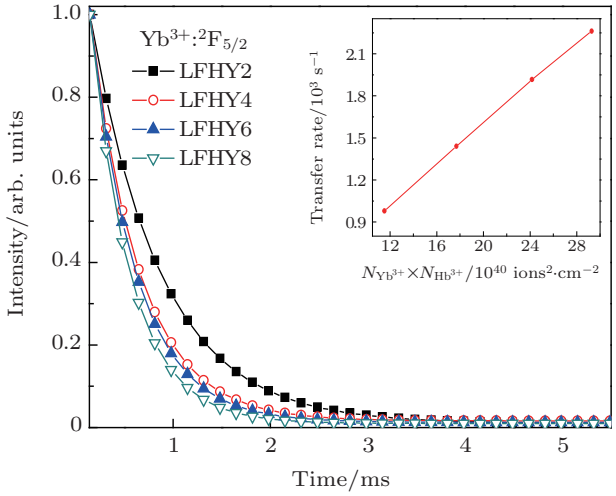


Fig. 7. (color online) Fluorescence decay curves of LFHY2, LFHY4, LFHY6, LFHY8 at 1019 nm by 940-nm excitation. Inset shows the relationship between energy transfer rate and ion concentration.

The inset of Fig. 7 exactly describes the relationship of energy transfer rate W_{ET} with the concentration of Yb^{3+} ions and Ho^{3+} ions. The energy transfer rate W_{ET} in the co-doped crystal can be described as

$$W_{ET} = a \times N_{Yb^{3+}} \times N_{Ho^{3+}}, \tag{4}$$

where a is a constant equal to $a = 0.85\times10^{-38}$ cm^6·s^{-1} in the present crystal.[18] The energy transfer rate shows the linear dependence on the product of Yb^{3+} and Ho^{3+} ions concentration.

The lifetimes of samples LFHY2, LFHY4, LFHY6, and LFHY8 are listed in Table 2, the values of W_{ET} are calculated by Eq. (4), and the values of τ_s are computed by Eq. (2). The energy transfer efficiencies in samples LFHY2, LFHY4, LFHY6, and LFHY8 are calculated to be 74.0%, 81.7%, 86.8%, and 88.9% respectively. The high energy transfer efficiency from Yb^{3+} to Ho^{3+} enhances the population of $^5I_7$ of the Ho^{3+} level. It is beneficial for achieving an enhanced 2.0-μm emission in $LiYF_4$ crystal.

Table 2. Values of lifetime at 1019 nm, energy transfer rate, and calculated values (τ_s) of samples LFHY2, LFHY4, LFHY6, and LFHY8.

Samples	LFHY2	LFHY4	LFHY6	LFHY8
τ/ms	0.756	0.567	0.453	0.393
W_{ET}/s^{-1}	978.7	1440.1	1915.6	2261.9
τ_s/ms	2.906	3.091	3.426	3.538

4. Conclusions

Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ with good spectral performances is grown by the Bridgman method. The concentration of Yb^{3+} significantly affects the optical properties. The Yb^{3+} ion is an excellent sensitizer for Ho^{3+} in $LiYF_4$ single crystal that produces an intense 2.0-μm emission under excitation of 980 nm. When the concentration of Ho^{3+} is kept at 0.98 mol%, the optimal concentration for 2.0 μm is 8 mol% of the Yb^{3+} ion and the maximum emission cross section in the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal at 2.0 μm is calculated to be 1.08×10^{-20} cm^2 in the present research. The high 88.9% energy efficiency from Yb^{3+} to Ho^{3+} ions demonstrates that the Ho^{3+}/Yb^{3+} co-doped $LiYF_4$ crystal is a potential promising material for a 2.0-μm laser.

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