Laser Original

Ho³⁺ Doped 2.84 μ m Laser Glass for Laser Knives, Sensitized by Yb³⁺

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The fluorescence properties of the Ho³⁺ $^5I_6 \rightarrow ^5I_7$ transition in Yb³⁺—Ho³⁺ codoped aluminosilicate glasses were investigated. The emission wavelength of Ho³⁺ ($^5I_6 \rightarrow ^5I_7$) at 2.84 μ m is almost the same as the vibration oscillation absorption of hydroxyl (OH⁻¹) at 2.89 μ m. The emission intensity of Ho³⁺ ($^5I_6 \rightarrow ^5I_7$) transition in Yb³⁺—Ho³⁺ codoped aluminosilicate glass is 4.5 times higher than commercial 2.7 μ m Er³⁺ laser glass. As the lifetime of $^5I_7$ level is longer than $^5I_6$ level, the Nd³⁺, Eu³⁺, Pr³⁺, Sm³⁺ and Tb³⁺ were investigated as deactivator for decreasing the lifetime of $^5I_7$ level. Eu³⁺ and Tb³⁺ are good candidates for deactivator because they have energy levels which are close to the Ho³⁺ $^5I_7$ level to decrease the population of Ho³⁺ $^5I_7$ level by energy transfer and have not energy levels which are close to the Ho³⁺ $^5I_6$ level or Yb³⁺ $^2F_{5/2}$ level.

Key Words: 2.84 μ m laser glass, Laser knives, Yb³⁺—Ho³⁺ codoped aluminosilicate glass, Judd-Ofelt theory, Energy transfer analysis, deactivator

1. Introduction

Laser techniques are widely used for medical treatment. One such technique is a laser knife. When laser device emits fluorescence near 2.89 μ m which is the vibration absorption wavelength of hydroxyl, it can be used as laser knives. Presently, a 2.7 μ m Er³⁺ laser glass has successfully been used commercially for this purpose¹⁾. A 2.7 μ m Er³⁺: YAG laser was also reported, which has a higher efficiency and is better for medical use than commercial CO₂ laser^{2,3)}. Recently, a Yb³⁺ sensitized 2.7 μ m Er³⁺ laser glass was developed by Izumitani and Lin⁴⁾. In this paper, the Ho³⁺ doped 2.84 μ m laser glass sensitized by Yb³⁺ is reported and compared with commercial 2.7 μ m Er³⁺ laser glass; the energy transfer and energy

backtransfer between Yb³⁺ and Ho³⁺ ions have been analyzed based on fluorescence lifetime data. Since the fluorescence lifetime of the Ho³⁺ $^5I_7$ level is too long compared to the $^5I_6$ level, Nd³⁺, Eu³⁺, Pr³⁺, Sm³⁺ and Tb³⁺ were investigated as deactivator, for decreasing the lifetime of the $^5I_7$ level.

2. Experimental Procedure

The base composition of the glass in this study is 28.3% AlF₃, 14.4% ZrF₄, 51.0% (MgF₂ + CaF₂ + SrF₂ + BaF₂) and 6.3% (NaF + NaCl) in cat%. High purity materials were used to eliminate contamination by impurities. The glasses were prepared by melting the batch materials in glassy carbon crucible in a nonreactive gas atmosphere inside a silica tube. After melting, the glass was rapidly cooled to the glass transi-

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tion temperature and annealed. All of samples were fabricated to size of $25 \times 25 \times 5 \text{ mm}^3$ and optically polished.

The absorption spectra were measured by HITACHI330 spectrophotometer at room temperature. The emission spectra were obtained by exciting the samples with diode laser operating around 980 nm. The light from the diode laser was chopped at 80 Hz and focused to the $5 \times 25 \text{ mm}^2$ face of sample. The emission from the sample was focused to a monochromator and detected by InAs detector cooled at 77K. The signal was intensified with a lock-in amplifier and processed by a computer. The fluorescence lifetimes were measured by exciting the samples with Nd:YAG pulse laser, Xenon Lamp and detecting by InAs-detector, S - 1 photomultiplier tube. The fluorescence decay curves were recorded and averaged with a computer controlled transient digitizer.

The spontaneous-emission probability (A_{rad}), emission cross section and branch ratio of Ho^{3+} were calculated by Judd-Ofelt theory⁵⁾ based on absorption spectra. The energy transfer efficiencies were calculated by Reisfeld equation⁶⁾:

$$\eta = 1 - \tau / \tau_0 \quad (1)$$

where τ is donor and acceptor codoped donor's lifetime, τ_0 is the lifetime of donor only.

3. Results and discussion

The Ho^{3+} can emit fluorescence at 2.84 μm which is close to vibration absorption wavelength of hydroxyl (OH^{-1}) by a radiative transition from the $\text{Ho}^{3+} {}^5I_6$ level to $\text{Ho}^{3+} {}^5I_7$ level. The emission spectrum will be shown in Figure 6. Since the energy gap between $\text{Ho}^{3+} {}^5I_6$ level and ${}^5I_7$ level, corresponding to 2.84 μm emission, is small, the nonradiative decay easily occurs. Fluoride glass has the lowest phonon energy as compared to other glasses⁷⁾. There-

fore, the stable aluminozirco-fluoride glass which has good chemical properties⁸⁾ was selected as base glass.

The spontaneous-emission probability (A_{rad}) and branching ratio of Ho^{3+} in aluminozirco-fluoride glass are shown in Table I. The spontaneous-emission probability (A_{rad}) and branching ratio of $\text{Ho}^{3+} ({}^5I_6 \rightarrow {}^5I_7)$ transition are $18.8 (\text{s}^{-1})$ and 20%, respectively. It can be seen that the spontaneous-emission probability (A_{rad}) of the $\text{Ho}^{3+} ({}^5I_6 \rightarrow {}^5I_7)$ transition is the same as that of the $\text{Er}^{3+} ({}^4I_{11/2} \rightarrow {}^4I_{13/2})$ transition which is $18.7 (\text{s}^{-1})$ ¹⁾, and the branching ratio of $\text{Ho}^{3+} ({}^5I_6 \rightarrow {}^5I_7)$ transition is only 3% higher than that of $\text{Er}^{3+} ({}^4I_{11/2} \rightarrow {}^4I_{13/2})$ transition which is 17%. The intensity parameters (Ω_i) are $\Omega_2 = 5.70 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 3.10 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.37 \times 10^{-20} \text{ cm}^2$, respectively.

Because the spontaneous-emission probability (A_{rad}) of Yb^{3+} is higher than that of Ho^{3+} ⁵⁾, and is proportional absorption coefficient, and Yb^{3+} can be excited by diode laser directly. Yb^{3+} can be used as a sensitizer in order to obtain the efficient, compact and cheap source of laser radiation for the $\text{Ho}^{3+} {}^5I_6 \rightarrow {}^5I_7$ transition. Figure 1 shows the emission spectrum of the $\text{Yb}^{3+} {}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition and the absorption spectrum of $\text{Ho}^{3+} {}^5I_8 \rightarrow {}^5I_6$ transition. The Yb^{3+} ion has only one excited 4f state (${}^2F_{5/2}$ level) located at approximately 10000 cm^{-1} . When Yb^{3+} was pumped by diode laser operating at 980 nm, the $\text{Yb}^{3+} ({}^2F_{5/2} \rightarrow {}^2F_{7/2})$ emission band overlaps the Ho^{3+} absorption band of the ${}^5I_8 \rightarrow {}^5I_6$ transition. This means that the energy transfer from Yb^{3+} to Ho^{3+} is possible. The fluorescence mechanism of $\text{Ho}^{3+} {}^5I_6 \rightarrow {}^5I_7$ transition sensitized by Yb^{3+} can be described as follows. The absorbed energy of the $\text{Yb}^{3+} {}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition is transferred to $\text{Ho}^{3+} {}^5I_6$ manifold, then radiatively relax by emission at 2.84 μm to the ${}^5I_7$ state as shown in

Table I The calculated spontaneous-emission probability and branching ratio of Ho^{3+} in aluminozirco-fluoride glasses (AZF).

Transition	Average Frequency cm^{-1}	A_{ed} S^{-1}	A_{md} S^{-1}	$A_{\text{ed}}+A_{\text{md}}$ S^{-1}	$\Sigma A_{\text{ed}}+A_{\text{md}}$ S^{-1}	τ_{R} ms	Branching ratio
$^5I_7 \rightarrow ^5I_8$	5154	41.20	16.88	58.07	58.07	17.28	1
$^5I_6 \rightarrow ^5I_8$	8680	75.95	—	75.95	94.75	10.6	0.801
$^5I_7$	3539	9.58	9.22	18.80	—	—	0.199
$^5I_5 \rightarrow ^5I_8$	11230	31.43	—	31.43	88.18	11.3	0.356
$^5I_7$	6089	49.35	—	49.35	—	—	0.560
$^5I_6$	2550	3.45	3.95	7.47	—	—	0.084
$^5I_4 \rightarrow ^5I_8$	13333	0.23	—	0.23	51.2	19.53	0.004
$^5I_7$	8192	25.6	—	25.6	—	—	0.500
$^5I_6$	4653	20.58	—	20.58	—	—	0.402
$^5I_5$	2103	3.03	1.76	4.79	—	—	0.094
$^5F_5 \rightarrow ^5I_8$	15625	1064.2	—	1064.2	1377.35	0.73	0.772
$^5I_7$	10484	254.38	—	254.38	—	—	0.185
$^5I_6$	6945	54.46	—	54.45	—	—	0.040
$^5I_5$	4395	4.28	—	4.28	—	—	0.003
$^5I_4$	2292	0.03	—	0.03	—	—	0
$^5S_2 \rightarrow ^5I_8$	18315	723.25	—	723.25	1337.35	0.75	0.542
$^5I_7$	13174	487.2	—	487.2	—	—	0.364
$^5I_6$	9635	85.59	—	85.59	—	—	0.064
$^5I_5$	7085	20.63	—	20.63	—	—	0.015
$^5I_4$	4982	20.48	—	20.48	—	—	0.015
$^5F_5$	2690	0.20	—	0.20	—	—	0
$^5F_4 \rightarrow ^5I_6$	18587	1948.67	—	1948.67	2419.2	0.41	0.805
$^5I_7$	13446	224.23	—	224.23	—	—	0.093
$^5I_6$	9907	152.33	—	152.33	—	—	0.063
$^5I_5$	7357	76.13	—	76.13	—	—	0.032
$^5I_4$	5254	12.19	—	12.19	—	—	0.005
$^5F_5$	2962	3.10	2.58	5.68	—	—	0.002

A_{ed} :The spontaneous-emission probability for electric dipole radiation

A_{md} :The spontaneous-emission probability for magnetical dipole radiation

Figure 2. Figure 3 shows the dependence of the lifetimes at $^2F_{5/2}$ (Yb^{3+}) level on Ho^{3+} concentrations in aluminozirco-fluoride glass. When the concentration of Ho^{3+} increases, the lifetime of $^2F_{5/2}$ (Yb^{3+}) level decreases quickly. The relationship between the $^5I_6 \rightarrow ^5I_7$ (Ho^{3+}) fluorescence decay and the concentration of Yb^{3+} in aluminozirco-fluoride glass is illustrated in Figure 4. This figure shows that the fluorescence lifetime have not remarkably changed. We calculated the energy transfer effi-

ciency from Yb^{3+} to Ho^{3+} and the energy backtransfer efficiency from Ho^{3+} to Yb^{3+} by using equation (1) based on lifetime data. The results are also presented in Figure 3-4. It can be seen that the energy transfer from Yb^{3+} to Ho^{3+} is high and the energy backtransfer from Ho^{3+} to Yb^{3+} is low. Therefore, it is considered that the energy absorbed by Yb^{3+} due to the process $^2F_{7/2} \rightarrow ^2F_{5/2}$ is almost transferred to the $^5I_6$ energy level of Ho^{3+} .

Figure 5 shows the dependence of the Ho^{3+}

Fig. 1 The emission spectrum of Yb³⁺ ($^2F_{5/2} \rightarrow ^2F_{7/2}$) in Yb doped fluoride (AZF) glass and the absorption spectrum of Ho³⁺ ($^5I_6 \rightarrow ^5I_8$) in Ho doped fluoride (AZF) glass.

($^5I_6 \rightarrow ^5I_7$) emission intensity on the concentrations of Yb³⁺ and Ho³⁺. When Yb³⁺ is 16 cat% and Ho³⁺ is 2 cat%, the emission intensity is highest. The emission spectra of the Yb³⁺ 16 cat%, Ho³⁺ 2 cat% codoped aluminosilico-fluoride glass and commercial 2.7 μm Er³⁺ laser glass are illustrated and compared in Figure 6. It can be seen that although the spontaneous-emission probability (A_{rad}) and branching ratio of Ho³⁺ ($^5I_6 \rightarrow ^5I_7$) transition are almost same to that of the Er³⁺ ($^4I_{11/2} \rightarrow ^4I_{13/2}$) transition, the emission intensity of Ho³⁺ $^5I_6 \rightarrow ^5I_7$ transition in Yb³⁺ - Ho³⁺ codoped aluminosilico-fluoride glass is 4.5 times higher than commercialized 2.7 μm Er³⁺ laser glass (Er³⁺ doped aluminosilico-fluoride glass) and 4 times higher than Er³⁺ - Yb³⁺ codoped aluminosilico-fluoride glass. The high emission intensity come from that Yb³⁺ has a higher absorption coefficient than that of Er³⁺ as shown in Figure 7, allowing, Yb³⁺ to absorb energy more efficiently. Moreover, the energy transfer from Yb³⁺ to Ho³⁺ is high and energy backtransfer from Ho³⁺ is low. In case of Er³⁺ - Yb³⁺ codoped aluminosilico-fluoride glass, the concentration

Fig. 2 The energy levels of rare elements and fluorescence mechanism of Ho³⁺ $^5I_6 \rightarrow ^5I_7$ transition.

Fig. 3 The lifetimes of Yb³⁺ ($^2F_{5/2} \rightarrow ^2F_{7/2}$) versus concentration of Ho³⁺ in Yb³⁺ 16 cat% doped fluoride glasses and the energy transfer efficiency of Yb³⁺→Ho³⁺.

sensitizer Yb³⁺ is low since the energy back-transfer from Er³⁺ to Yb³⁺ is high when Yb³⁺ concentration over 2 cat%⁴⁾. Therefore, the absorption efficiency of energy in Er³⁺ - Yb³⁺ codoped aluminosilico-fluoride glass is lower than that in Yb³⁺ - Ho³⁺ codoped aluminosilico-fluoride glass. The calculated emission cross section and measured fluorescence lifetime of Ho³⁺ ($^5I_6 \rightarrow ^5I_7$) transition in Yb³⁺ - Ho³⁺ codoped aluminosilico-fluoride glass are also presented in Figure 6. The emission cross section (σ) is $1.17 \times 10^{-20} \text{ cm}^2$. The fluorescence

Fig. 4 The lifetimes of Ho^{3+} (${}^5I_6 \rightarrow {}^5I_7$) versus concentration of Yb^{3+} in Ho^{3+} 0.1 cat% doped fluoride glasses and the energy transfer efficiency of $\text{Ho} \rightarrow \text{Yb}$.

Fig. 5 The emission intensity of Ho^{3+} (${}^5I_6 \rightarrow {}^5I_7$) in Yb^{3+} - Ho^{3+} doped fluoride (AZF) glasses.

lifetime is 5.7 ms.

Because the fluorescence lifetime of Ho^{3+} ${}^5I_7$ level (26.7 ms) is too long as compared with the Ho^{3+} ${}^5I_6$ level (5.7 ms). It is necessary to decrease the fluorescence lifetime of Ho^{3+} at ${}^5I_7$ level for oscillation. For decreasing the lifetime of ${}^5I_7$ level, Nd^{3+} , Eu^{3+} , Pr^{3+} , Sm^{3+} and Tb^{3+} were investigated as deactivator ions. Figure

Fig. 6 The emission spectra of Ho^{3+} (${}^5I_6 \rightarrow {}^5I_7$) in Yb, Ho doped fluoride (AZF) glass, Er^{3+} (${}^4I_{11/2} \rightarrow {}^4I_{13/2}$) in Er doped fluoride (AZF) glass and Er^{3+} (${}^4I_{11/2} \rightarrow {}^4I_{13/2}$) in Er, Yb doped fluoride (AZF) glass. —: Yb16 cat%, Ho2 cat%; - - -: Yb2 cat%, Er10 cat%; - - - -: Er10 cat%.

Fig. 7 The absorption spectra of Yb^{3+} (9 cat%) and Er^{3+} (10 cat%) in aluminozirco-fluoride glass.

8 shows the the relationship between Ho^{3+} (${}^5I_6 \rightarrow {}^5I_7$) fluorescence lifetime and Nd^{3+} , Eu^{3+} , Pr^{3+} , Sm^{3+} and Tb^{3+} concentration in the Yb^{3+} 16 cat%, Ho^{3+} 2 cat% codoped aluminozirco-fluoride glass when Nd^{3+} , Eu^{3+} , Pr^{3+} , Sm^{3+} and Tb^{3+} are added as deactivators. It can be seen that when Nd^{3+} is added, the Ho^{3+}

Fig. 8 The fluorescence lifetime of Ho³⁺ (⁵I₇) level when put Eu³⁺, Nd³⁺, Tb³⁺, Pr³⁺ and Sm³⁺ in Yb16 cat%, Ho2 cat% doped fluoride glasses as a deactivator. □: Nd³⁺, ○: Eu³⁺, △: Tb³⁺, ■: Pr³⁺, ●: Sm³⁺.

Fig. 9 The emission intensity of Ho³⁺ (⁵I₆ → ⁵I₇) when put Eu³⁺, Nd³⁺, Tb³⁺, Pr³⁺ and Sm³⁺ in Yb16 cat%, Ho2 cat% doped fluoride glasses as a deactivator. □: Nd³⁺, ○: Eu³⁺, △: Tb³⁺, ■: Pr³⁺, ●: Sm³⁺.

(⁵I₇ → ⁵I₈) fluorescence lifetime decreases slowly compared with that when Eu³⁺, Pr³⁺, Sm³⁺ and Tb³⁺ are added. This is because that Nd³⁺ has no energy levels which are close to Ho³⁺ ⁵I₇

level as shown in Figure 2. Since Pr³⁺ ¹G₄ level and Sm³⁺ ⁶F_{9/2} level are close to the Yb³⁺ ²F_{5/2} level and Sm³⁺ ⁶F_{7/2} level is close to the Ho³⁺ ⁵I₆ level as shown in Figure 2, the energy transfers from Yb³⁺ ²F_{5/2} level and Ho³⁺ ⁵I₆ level to Pr³⁺ and Sm³⁺ occur easily. Therefore, when Pr³⁺ and Sm³⁺ are added, the Ho³⁺ (⁵I₆ → ⁵I₇) emission intensity decreases more rapidly than when Nd³⁺, Eu³⁺ and Tb³⁺ are added (Figure 9). Considering two factors, the Ho³⁺ (⁵I₆ → ⁵I₇) emission intensity and the Ho³⁺ (⁵I₇ → ⁵I₈) fluorescence lifetime, the Eu³⁺ and Tb³⁺ are selected as deactivators because they have energy levels which are close to Ho³⁺ ⁵I₇ level and do not have energy levels which are close to Ho³⁺ ⁵I₆ level or Yb³⁺ ²F_{5/2} level.

4. Conclusion

The transition wavelength of Ho³⁺ (⁵I₆ → ⁵I₇) at 2.84 μ m is very close to the hydroxyl vibration absorption at 2.89 μ m. Therefore, Ho³⁺ - doped glass can be used for laser knives. The spontaneous-emission probability (*A*_{rad}), emission cross section and branching ratio of Ho³⁺ in aluminosilico-fluoride glass were calculated by Judd-Ofelt theory. The spontaneous-emission probability (*A*_{rad}) and branching ratio of Ho³⁺ (⁵I₆ → ⁵I₇) transition are almost the same as that of the Er³⁺ (⁴I_{11/2} → ⁴I_{13/2}) transition. Since the Yb³⁺ absorbs energy more efficiently, moreover, the energy from Yb³⁺ (²F_{5/2}) level efficiently transfer to Ho³⁺ (⁵I₆) level and the energy backtransfer from Ho³⁺ to Yb³⁺ is low, the emission intensity of ⁵I₆ → ⁵I₇ (Ho³⁺) transition in Yb³⁺ - Ho³⁺ codoped aluminosilico-fluoride glass is 4.5 times higher than commercialized 2.7 μ m Er³⁺ laser glass. The lifetime of ⁵I₇ level is too long compared to ⁵I₆ level. For decreasing the lifetime of ⁵I₇ level, Nd³⁺, Eu³⁺, Pr³⁺, Sm³⁺ and Tb³⁺ were investigated as deactivator ions. Eu³⁺ and Tb³⁺ are good

deactivators because they have energy levels which are close to $\text{Ho}^{3+} {}^5I_7$ level and do not have energy levels which are close to the $\text{Ho}^{3+} {}^5I_6$ level and $\text{Yb}^{3+} {}^2F_{5/2}$ level.

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