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Selectively strong green up-conversion luminescence in Nd^{3+}–Ho^{3+} co-doped ZrF_4-based fluoride glasses under 800 nm excitation

J Qiu†, M Shojiya†, R Kanno†, Y Kawamoto† and M Takahashi‡

† Division of Molecular Science, Graduate School of Science and Technology, Kobe University, Nada, Kobe 657-8501, Japan
‡ Venture Business Laboratory, Kobe University, Nada, Kobe 657-8501, Japan

Abstract.   Blue, green and red up-conversion luminescences at around 490, 545 and 650 nm, which result from the $Ho^{3+}: {}^5F_3 \rightarrow {}^5I_8$, $({}^5F_4, {}^5S_2) \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$ transitions, respectively, were observed in Nd^{3+}–Ho^{3+} co-doped ZrF_4-based fluoride glasses under 800 nm excitation. Among these up-conversion luminescences, the green emission was extremely strong and the blue and red emission intensities were very weak. Selectively strong green up-conversion luminescences of these glasses indicate a high possibility for realizing a green up-conversion laser. Up-conversion processes for the blue, green and red emissions are two-photon processes assisted by $Nd^{3+} \rightarrow Ho^{3+}$ energy transfer. It is proposed that the up-conversion mechanism for the blue and green emissions is different from that for the red emission. The respective mechanisms are discussed.

1. Introduction

To date, optical properties of trivalent lanthanide ions such as Pr^{3+} [1], Er^{3+} [2, 3], Tm^{3+} [4], Ho^{3+} [5] and Nd^{3+} [6, 7] in crystals, glasses or glass–ceramics have been extensively studied to develop up-conversion visible or ultraviolet lasers which can be operated at room temperature.

An interaction between two lanthanide ions, one in its ground state and the other in some excited states, is possible so that energy transfer can occur from donor lanthanide ions in the excited states to acceptor lanthanide ions in the ground or excited states. Thus, lanthanide ion co-doped systems have been reported in order to enhance up-conversion efficiency, Yb^{3+}–Tm^{3+} [8, 9], Yb^{3+}–Er^{3+} [10, 11], Er^{3+}–Tm^{3+} [12] and Tm^{3+}–Yb^{3+}–Ho^{3+} [13, 14] co-doped glasses.

The holmium ion in its trivalent state has a large number of energy levels and radiative transitions from the energy levels, which can be used as lasers, are observed. On the other hand, the Ho^{3+} ion can be sensitized by a variety of lanthanide ions or transition-metal ions to achieve efficient laser emission [15–17]. In most of the previous reports, the 2 μm luminescence based on the $Ho^{3+}: {}^5I_7 \rightarrow {}^5I_8$ transition has been studied. It has been used for high resolution spectroscopy of low pressure gases and also for eye-safe laser radar.

More recently we found that selectively strong green up-conversion luminescence at about 545 nm can be obtained for Nd^{3+}–Ho^{3+} co-doped ZrF_4-based fluoride glasses by irradiating with 800 nm laser light. To the best of our knowledge, this finding is the first one. The result is reported in this article.

2. Experiment

Glass samples were prepared by using reagent grade ZrF_4, BaF_2, LaF_3, NdF_3 and HoF_3 as the starting materials. The compositions of glasses used in the present study are $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot 1.0 NdF_3 \cdot x\ HoF_3 \cdot (9.0 - x)\ LaF_3$ ($x = 0.3, 0.5, 1.0, 2.0$ and 3.0) and $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot y\ NdF_3 \cdot 1.0\ HoF_3 \cdot (9.0 - y)\ LaF_3$ ($y = 0.5, 1.0, 2.0$ and 3.0). About 5 g batches of the starting materials with an addition of a fluoridizing agent $NH_4F \cdot HF$ were melted at $450\,°C$ for 15 min and subsequently at $900\,°C$ for 15 min in Pt crucibles under an Ar gas atmosphere. The melts were cast into brass molds which were kept around 180–$200\,°C$. The glasses obtained were annealed at their glass transition temperatures determined by differential thermal analyses. These glasses were cut into $5.0 \times 5.0 \times 1.2\ mm^3$, and the two faces and the two opposite sides were polished to an optical finish.
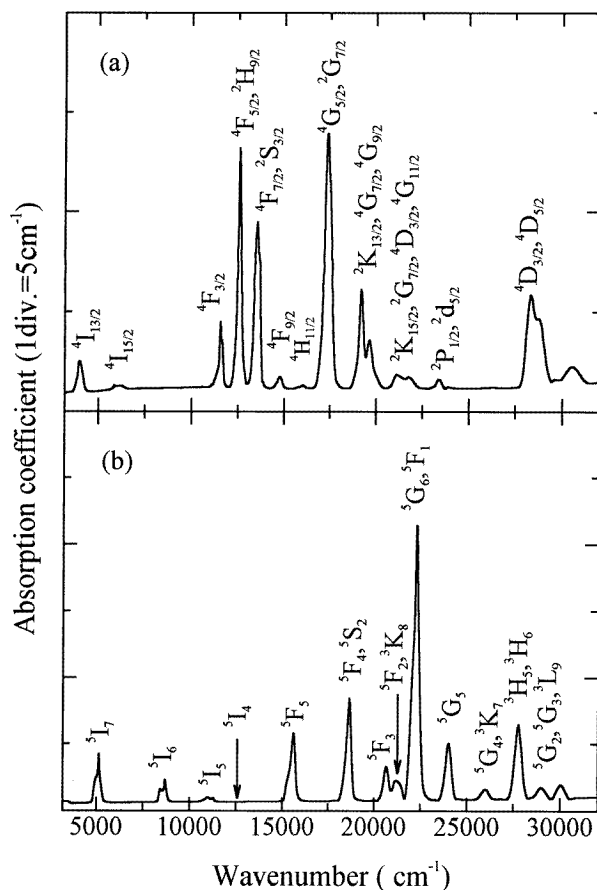

Figure 1. Optical absorption spectra of (a) $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot 1.0\ NdF_3 \cdot 9.0\ LaF_3$ and (b) $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot 5.0\ HoF_3 \cdot 5.0\ LaF_3$ glasses.

Optical absorption spectra in the wavelength range of 200–3200 nm were measured with a Shimadzu UV-2200 spectrophotometer. Up-conversion luminescence spectra under 800 nm excitation were measured in the wavelength range of 450–700 nm by using a Sony SLD303-XT AlGaAs laser diode ($\lambda_{emission} = 800$ nm) as an excitation source.
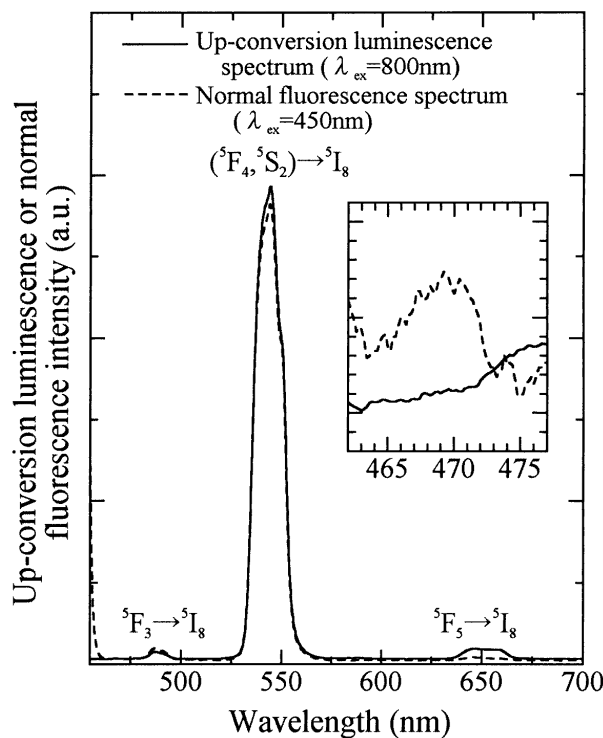
Figure 2. Ho^{3+} up-conversion luminescence spectrum under 800 nm excitation and Ho^{3+} normal fluorescence spectrum under 450 nm excitation in 60.0 ZrF$_4$ · 30.0 BaF$_2$ · 1.0 NdF$_3$ · 1.0 HoF$_3$ · 8.0 LaF$_3$ glass.

Normal fluorescence spectra in the wavelength range of 450–700 nm were measured with a Hitachi F-3010 fluorescence spectrophotometer by using an Xe lamp as an excitation source and those in the wavelength range of 900–1200 nm were measured with an Advantest Q8381A/8383 spectrum analyser by using a Sony SLD303-XT AlGaAs laser diode as an excitation source. All the spectroscopic measurements were made at ambient temperature.

3. Results and discussion

Figure 1 shows optical absorption spectra of the 60.0 ZrF$_4$ · 30.0 BaF$_2$ · 1.0 NdF$_3$ · 9.0 LaF$_3$ and 60.0 ZrF$_4$ · 30.0 BaF$_2$ · 5.0 HoF$_3$ · 5.0 LaF$_3$ glasses in the 3500–35 000 cm^{-1} range at room temperature. The first excitation levels by the 800 nm (i.e. 12 500 cm^{-1}) irradiation are the Nd^{3+}:(^{4}F$_{3/2}$, ^{2}H$_{9/2}$) levels and the Ho^{3+}:^{5}I$_4$ level. It is noted here that the energy gap between the (^{5}F$_2$, ^{3}K$_8$) and ^{5}I$_5$ levels in Ho^{3+} is equal to the energy gap between the ^{4}F$_{3/2}$ and ^{4}I$_{11/2}$ levels in Nd^{3+}. This good agreement in energy gap between Ho^{3+} and Nd^{3+} contributes to effectual energy transfer from Nd^{3+} ions to Ho^{3+} ions.

The up-conversion luminescence spectrum of the 60.0 ZrF$_4$ · 30.0 BaF$_2$ · 1.0 NdF$_3$ · 1.0 HoF$_3$ · 8.0 LaF$_3$ glass under 800 nm excitation is given in figure 2. In the up-conversion luminescence spectrum, very weak emission bands centred around 490 (blue) and 650 (red) nm correspond to the Ho^{3+}:^{5}F$_3$ → ^{5}I$_8$ and ^{5}F$_5$ → ^{5}I$_8$ transitions, respectively. An emission band at 550 nm (green), which corresponds to the (^{5}F$_4$, ^{5}S$_2$) → ^{5}I$_8$ transition,

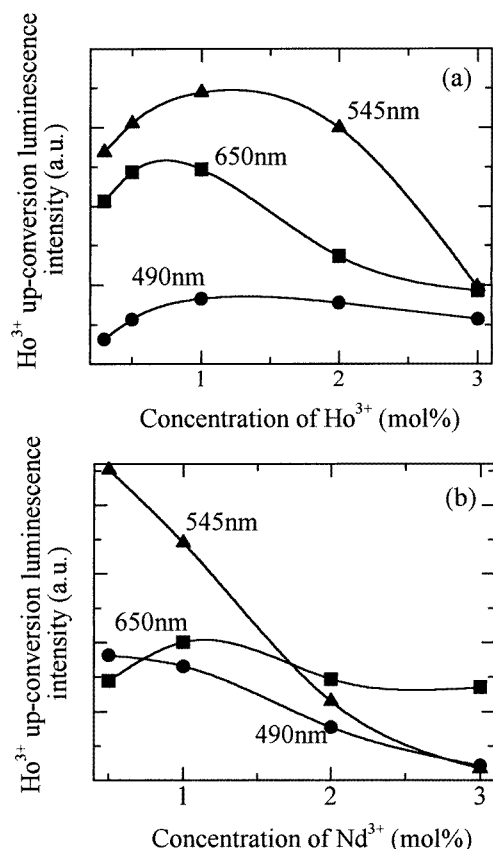**Figure 3.** Ho^{3+}- and Nd^{3+}-concentration dependences of Ho^{3+} up-conversion luminescence intensities in (a) $60.0 \ ZrF_4 \cdot 30.0 \ BaF_2 \cdot 1.0 \ NdF_3 \cdot x \ HoF_3 \cdot (9.0 - x) \ LaF_3$ and (b) $60.0 \ ZrF_4 \cdot 30.0 \ BaF_2 \cdot y \ NdF_3 \cdot 1.0 \ HoF_3 \cdot (9.0 - y) \ LaF_3$ glasses.

exhibits extremely strong intensity so that this emission light could be clearly observed by the naked eye even under a low excitation power of 100 mW.

As shown in figure 3(a) and 3(b), the emission intensities of the 490, 545 and 650 nm up-conversion luminescences in the $60.0 \ ZrF_4 \cdot 30.0 \ BaF_2 \cdot 1.0 \ NdF_3 \cdot x \ HoF_3 \cdot (9.0 - x) \ LaF_3$ and $60.0 \ ZrF_4 \cdot 30.0 \ BaF_2 \cdot y \ NdF_3 \cdot 1.0 \ HoF_3 \cdot (9.0 - y) \ LaF_3$ glasses significantly depend on the Ho^{3+} and Nd^{3+} concentrations, respectively. This fact implies that an interaction between Nd^{3+} and Ho^{3+} has a dominant effect on the 490, 545 and 650 nm emission bands. The Nd^{3+} concentration dependences of the 490 and 545 nm emission intensities are different from that of the 650 nm emission intensity. Thus it may be concluded that the excitation mechanism for the blue (490 nm) and green (545 nm) up-conversion and that for the red (650 nm) up-conversion are different.

Figure 4 shows a plot of the Nd^{3+} normal fluorescence intensity around 1064 nm (Nd^{3+}: $^4F_{3/2} \rightarrow \ ^4I_{11/2}$ transition) against the Ho^{3+} concentration in the $60.0 \ ZrF_4 \cdot 30.0 \ BaF_2 \cdot 1.0 \ NdF_3 \cdot x \ HoF_3 \cdot (9.0 - x) \ LaF_3$ glasses. The Nd^{3+} emission intensity steeply decreases with increasing Ho^{3+} concentration, proving that an interaction between Nd^{3+} and Ho^{3+} is strongly related to up-conversion processes. This steep decrease may be explained

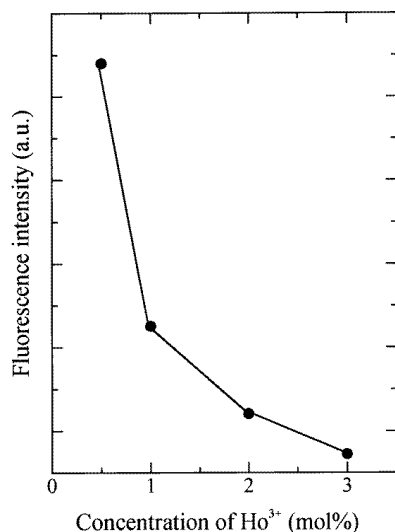**Figure 4.** Ho^{3+} concentration dependence of Nd^{3+} normal fluorescence intensity at 1064 nm corresponding to Nd^{3+} :$^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

based on self-quenching in higher Ho^{3+} concentration regions.

A comparison of the up-conversion luminescence spectrum and the normal fluorescence spectrum of Ho^{3+} in the $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot 1.0\ NdF_3 \cdot 1.0\ HoF_3 \cdot 8.0\ LaF_3$ glass is shown in figure 2. The intensity ratio of the $^5F_5 \rightarrow {}^5I_8$ transition (650 nm) to the $(^5F_4, {}^5S_2) \rightarrow {}^5I_8$ transition (545 nm) under 800 nm excitation is much larger than that under 450 nm excitation. Under the 450 nm excitation, the $^5F_5$ state is populated from the $(^5F_4, {}^5S_2)$ states through a multiphonon decay process across their energy gaps. This fact clearly indicates that mulitiphonon relaxation across the energy gaps between the $(^5F_4, {}^5S_2)$ states and the $^5F_5$ state is not concerned in the $^5F_5 \rightarrow {}^5I_8$ up-conversion emission process. In other words, the 4f electrons are directly excited to the $^5F_5$ state by the energy transfer process from Nd^{3+} under 800 nm excitation.

In order to examine the photon number involved in the 490, 545 and 650 nm up-conversion luminescences, the evolutions of peak intensities were plotted in a log–log scale as a function of incident excitation power. The example for the $60.0\ ZrF_4 \cdot 30.0\ BaF_2 \cdot 1.0\ NdF_3 \cdot 1.0\ HoF_3 \cdot 8.0\ LaF_3$ glass is shown in figure 5. It can be seen that all the intensities of 490, 545 and 650 nm up-conversion fluorescences have quadratic dependences. The slopes correspond to the number of photons needed for excitation. Therefore, a two-photon process is a main mechanism for the 490, 545 and 650 nm up-conversion processes.

Next, the up-conversion processes of the 490, 545 and 650 nm luminescences are discussed. As seen from figure 1, it can be understood that, in the Ho^{3+} singly doped glass, Ho^{3+}:4f electrons in the $^5I_8$ level are excited to the $^5I_4$ level under 800 nm excitation, but the 4f electrons in the $^5I_4$ level cannot be excited to the upper levels by absorbing 800 nm photons or through energy transfer. From figure 2 and the inset, it is noted that a peak around 470 nm is observed in the normal fluorescence spectrum with 450 nm excitation, but it cannot be observed in the up-conversion luminescence spectrum with 800 nm excitation. This suggests that, in the case of up-conversion with 800 nm excitation, the Ho^{3+}:4f electrons are not excited to the $^5G_6$ and $^5F_1$ levels and maybe they will be excited to the $(^5F_2, {}^3K_8)$ levels.

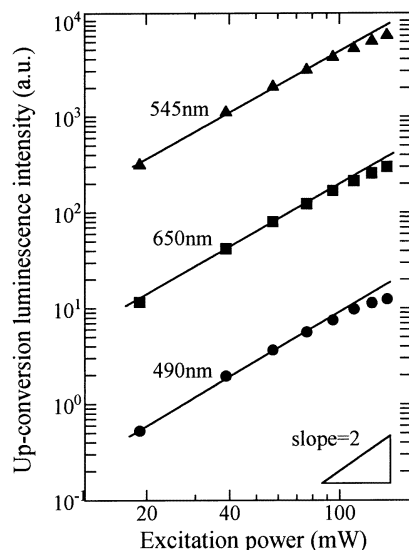**Figure 5.** Excitation power dependences of 490, 545 and 650 nm up-conversion luminescence intensities in 60.0 $ZrF_4 \cdot$ 30.0 $BaF_2 \cdot$ 1.0 $NdF_3 \cdot$ 1.0 $HoF_3 \cdot$ 8.0 LaF_3 glass.

Thus, the following three facts can be derived: (i) Interaction between Nd^{3+} and Ho^{3+} contributes to up-conversion process. (ii) Two photons participate in the up-conversion process. (iii) In spite of a similar excitation power dependence, the excitation mechanisms are different between the red up-conversion and the green and blue up-conversion.

The up-conversion mechanisms in the Nd^{3+}–Ho^{3+} co-doped ZrF_4-based glasses are proposed in figure 6. In the first process, 800 nm photons are absorbed by Nd^{3+} ions, provoking the $(^4F_{5/2}, {}^2H_{9/2}) \leftarrow {}^4I_{9/2}$ transition. Then the $^4F_{3/2}$ level is populated through a non-radiative relaxation process. At the same time, 800 nm photons are absorbed by Ho^{3+} ions, provoking the $^5I_4 \leftarrow {}^5I_8$ transition. Then, the $^5I_5$ level is populated through a non-radiative relaxation process. After these processes, the energy on the Nd^{3+}:$^4F_{3/2}$ state is efficiently transferred to the Ho^{3+}:$(^5F_2, {}^3K_8)$ states, then relaxes non-radiatively by multiphonon relaxation from the $(^5F_2, {}^3K_8)$ states to the $^5F_3$ or the $(^5F_4, {}^5S_2)$ states. Finally these states radiatively relax to the $^5I_8$ ground state, giving the blue (490 nm) and green (545 nm) up-conversion luminescences.

On the other hand, the up-conversion mechanism for red (650 nm) emission is explained as follows: The energy transfer from Nd^{3+} to Ho^{3+} is due to the cross relaxation of the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition instead of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. That is, the Ho^{3+}:4f electrons of the $^5I_5$ state absorb a photon due to Nd^{3+}:$^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition, and are excited to the $^5F_5$ state, then radiatively relax from the $^5F_5$ state to the $^5I_8$ ground state, giving red (650 nm) up-conversion luminescence.

4. Conclusion

Up-conversion luminescence in Nd^{3+}–Ho^{3+} co-doped ZrF_4-based fluoride glasses under 800 nm excitation was examined. It was found that the glasses exhibit a selectively strong green (545 nm) emission and very weak blue (490 nm) and red (650 nm) emissions. It was revealed that energy transfer between Nd^{3+} and Ho^{3+}, i.e. Nd^{3+}:$^4F_{3/2}$ + Ho^{3+}:$^5I_5 \rightarrow$
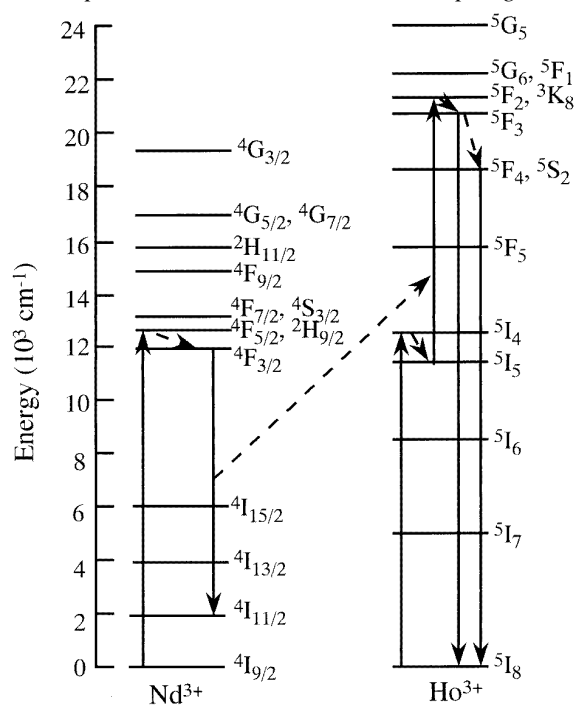
(a)
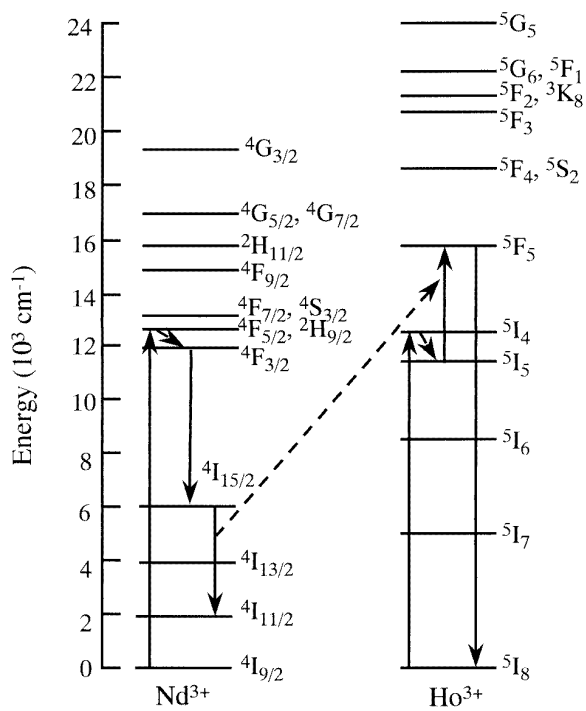
(b)

Figure 6. Up-conversion mechanisms of (a) 490 and 545 nm emissions, and (b) 650 nm emission in Nd^{3+}–Ho^{3+} co-doped ZrF_4-based fluoride glasses pumped by 800 nm light.

$Nd^{3+}:{}^4I_{11/2}+Ho^{3+}:({}^5F_2, {}^3K_8)$, is responsible for the population of the Ho^{3+} excited-state ${}^5I_5$ level, where Nd^{3+} and Ho^{3+} operate as an energy donor and an energy acceptor, respectively. Up-conversion luminescences around 490, 545 and 650 nm correspond to $Ho^{3+}:{}^5F_3 \rightarrow {}^5I_8$, $({}^5F_4, {}^5S_2) \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$ transitions, respectively. In conclusion the present glasses have a possibility for a green up-conversion laser which operates under 800 nm excitation because of the selectively strong green emission.

Acknowledgment

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