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Highly efficient blue up-conversion of Tm^{3+} in Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped ZrF_4-based fluoride glass

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Abstract

Up-conversion luminescence and energy-transfer processes in Nd^{3+}, Yb^{3+} and Tm^{3+} co-doped ZrF_4-based fluoride glasses have been studied under 800 nm light excitation. Blue up-converted emission around 478 nm which can be assigned to the Tm^{3+}:$^1G_4 \rightarrow {}^3H_6$ transition, was strongly observed. Up-conversion luminescence intensity exhibited an YbF_3-concentration dependence. Among the Nd^{3+}, Yb^{3+} and Tm^{3+}, Nd^{3+} and Tm^{3+} have ground state absorption bands due to the $(^2H_{9/2}, {}^4F_{5/2}) \leftarrow {}^4I_{9/2}$ and $^3F_4 \leftarrow {}^3H_6$ transitions, respectively, which can be directly pumped by 800 nm radiation. However, no emissions were observed in Tm^{3+} singly-doped and Tm^{3+}–Yb^{3+} doubly-doped glasses under 800 nm excitation. Therefore, a possible up-conversion mechanism may be proposed as follows: energy-transfer firstly occurs from Nd^{3+} to Yb^{3+} when Nd^{3+} is excited by 800 nm light, then the energy is transferred from Yb^{3+} to Tm^{3+} which is in the excited state and, finally, blue up-conversion emission of Tm^{3+} is observed through the Tm^{3+}:$^1G_4 \rightarrow {}^3H_6$ transition. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rare-earth; Fluoride glass; Up-conversion; Energy-transfer

1. Introduction

Fluoride glasses based on ZrF_4 have transparency in the wide wavelength range from the near UV to the middle IR. The phonon energies in the glasses are lower than those in oxide glasses. In addition, a large amount of transition metal and trivalent rare-earth ions can be incorporated into the glass matrixes. On the other hand, the glasses can be easily prepared and are relatively resistant to chemical attack. These properties make the ZrF_4-based glasses of interest for potential use for IR fibers and luminescent systems (see, e.g. [1–7]).

It has been widely known that some rare-earth ions can convert the wavelength of incident light to a shorter one via a multi-photon absorption mechanism. This phenomenon is of great interest because it can be utilized to build up a new laser system, in particular, a laser system in the visible to ultraviolet region.

On the other hand, it has been also recognized that luminescence intensities are enhanced or quenched by co-doping with other kinds of trivalent rare-earth ions. The phenomena take place as a result of the non-radiative energy-transfer from a rare-earth ion behaving as an energy-donor to an energy acceptor. Depending on the concentration and distribution of donors and acceptors, it is possible to obtain a more complex behavior; the excitation may migrate through the donor system when it comes into the vicinity of an acceptor and then transfer occurs. Such a phenomenon has a significant application to the research and development of luminescent materials.

The absorption band of Yb^{3+} due to the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition locates around 1 μm, which corresponds to the emission wavelength of a commercially available high-power InGaAs laser diode. Until now, therefore, the infrared to green and/or blue up-conversion luminescence based on the energy-transfer from Yb^{3+} ions to other rare-earth ions such as Er^{3+} [8–10], Ho^{3+} [11,12] and Tm^{3+} [13–17] have been extensively investigated in various crystalline and vitreous materials. In certain situations, however, Yb^{3+} ions can play a role of an energy-transfer bridging ion between a donor ion and an acceptor ion. That is, photon energies can be transferred from one activator ion to another one through Yb^{3+} ions. Thus, up-conversion luminescence can be obtained from the levels of rare-earth ions which cannot be excited without Yb^{3+} ions and, in addition, the intensities of up-conversion luminescence from the same levels of rare-earth ions may be greatly enhanced with the aid of Yb^{3+} ions.

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In our previous work, a specific up-conversion mechanism has been reported on the Ho^{3+} and Tb^{3+} up-conversion luminescence under 800 nm excitation in three kinds of rare-earth ions, Nd^{3+}–Yb^{3+}–Ho^{3+} [18] and Nd^{3+}–Yb^{3+}–Tb^{3+} [19], co-doped ZrF_4-based glasses. Consequently, these studies demonstrated a new use of Yb^{3+} ion as a sensitizer.

This paper reports the Tm^{3+} up-conversion emission properties and the energy-transfer processes in ZrF_4-based glasses doped with three kinds of rare-earth ions, i.e. Nd^{3+}, Yb^{3+} and Tm^{3+}. An 800 nm-light emitted from a high-power AlGaAs laser diode was used as an excitation source. It was found that the Yb^{3+}co-doping in Nd^{3+}–Tm^{3+} doubly-doped glasses gives rise to the Tm^{3+} up-conversion luminescence, though the Yb^{3+} ions are not excited by 800 nm light.

2. Results and discussion

The up-conversion luminescence spectrum in the range of 400–700 nm of a $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 4.4LaF_3 \cdot 0.5NdF_3 \cdot 5.0YbF_3 \cdot 0.1TmF_3$ glass under 800 nm diode laser light excitation is shown in Fig. 1. Two emission bands centered at 478 and 650 nm are observed. According to the energy-level diagram of Tm^{3+} ions, these emission bands correspond to the $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3H_4$ transitions, respectively.

The optical absorption spectra of Tm^{3+}, Nd^{3+} and Yb^{3+} in the $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0TmF_3 \cdot 5.0LaF_3$, $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0NdF_3 \cdot 5.0LaF_3$ and $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0YbF_3 \cdot 5.0LaF_3$ glasses are shown in Fig. 2. The Yb^{3+} has only one excited state of $^2F_{5/2}$, which locates at about 980 nm above the ground state $^2F_{7/2}$. Therefore, the 4f-electrons of Yb^{3+} cannot be directly excited to the $^2F_{5/2}$ state by an 800 nm radiation of a light source employed in this study. In the case of Nd^{3+} and Tm^{3+} ions, absorption bands centered around 800 nm, which correspond to the Nd^{3+}:($^4F_{5/2}$, $^2H_{9/2}$) $\leftarrow {}^4I_{9/2}$ and Tm^{3+}:$^3H_6 \leftarrow {}^3F_4$ transitions, are observed. In a Tm^{3+} singly-doped glass, however, no Tm^{3+} up-conversion luminescence was detected. According to the above results, two paths of energy-transfer between/among rare-earth ions can be assumed: (i) $nNd^{3+} \rightarrow Tm^{3+}$ and (ii) $nNd^{3+} \rightarrow n'Yb^{3+} \rightarrow Tm^{3+}$, where n and n' are the number of energy-donor ions consumed for one-Tm^{3+} excitation.

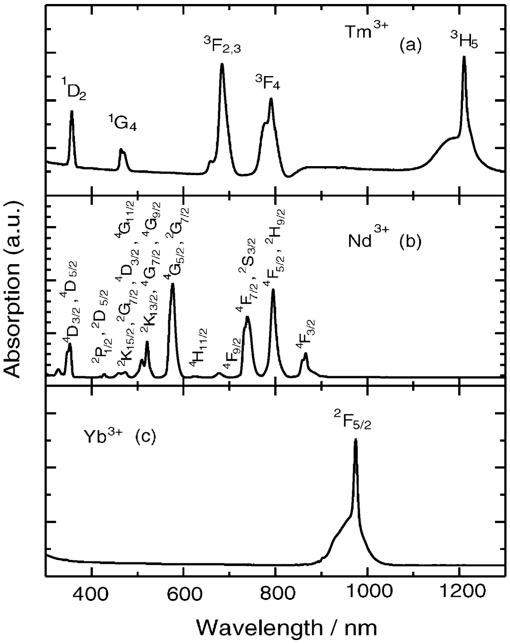

Fig. 2. Optical absorption spectra of (a) Tm^{3+} in $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0TmF_3 \cdot 5.0LaF_3$ glass, (b) Nd^{3+} in $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0NdF_3 \cdot 5.0LaF_3$ glass and (c) Yb^{3+} in $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 5.0YbF_3 \cdot 5.0\ LaF_3$ glass.

In the case of Nd^{3+}–Tm^{3+} co-doped glasses, the TmF_3-concentration dependence of the Nd^{3+}–Tm^{3+} fluorescence intensities around 1.064 μm in $60.0ZrF_4 \cdot 30.0BaF_2 \cdot (9.5 - x)LaF_3 \cdot 0.5NdF_3 \cdot xTmF_3$ glasses ($x = 0$, 0.1, 0.2, 0.3, 0.5 and 1.0) under 800 nm excitation are shown in Fig. 3. Since the

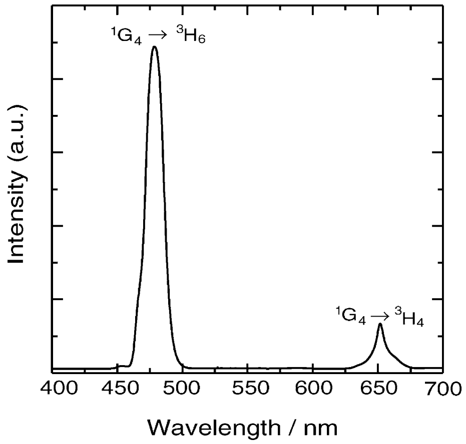

Fig. 1. Tm^{3+} up-conversion luminescence spectrum of $60.0ZrF_4 \cdot 30.0BaF_2 \cdot 4.4LaF_3 \cdot 0.5NdF_3 \cdot 5.0YbF_3 \cdot 0.1TmF_3$ glass under 800 nm excitation.

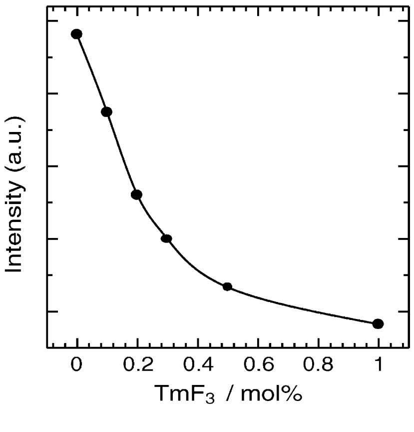

Fig. 3. TmF_3-concentration dependence of 1.064 μm fluorescence intensity in $60.0ZrF_4 \cdot 30.0BaF_2 \cdot (9.5 - x)LaF_3 \cdot 0.5NdF_3 \cdot xTmF_3 \cdot (x = 0$, 0.1, 0.2, 0.3, 0.5 and 1.0) glasses (the line is drawn as a guide to the eye).

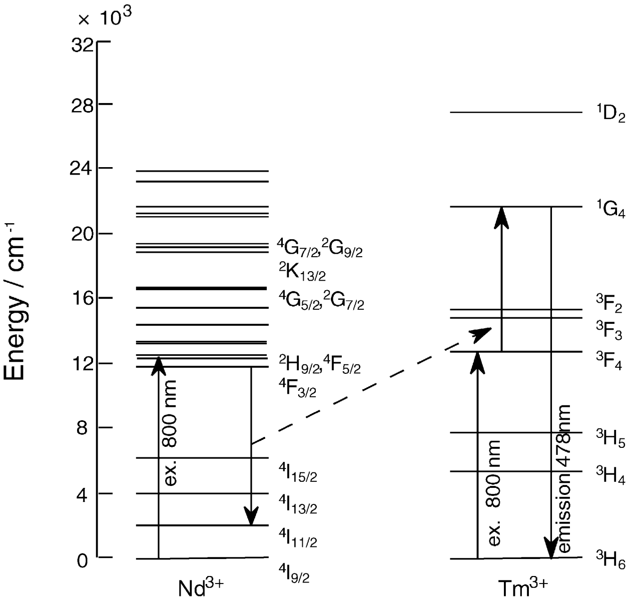

Fig. 4. Schematic diagram of energy-transfer from Nd^{3+} to Tm^{3+} in Nd^{3+}–Tm^{3+} co-doped glasses.

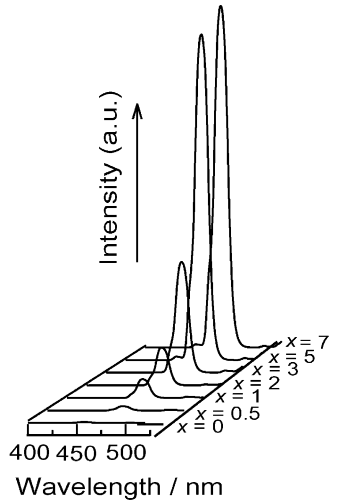

Fig. 5. YbF_3-concentration dependence of up-conversion luminescence intensity around 478 nm in $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.4-x)LaF_3{\cdot}0.5NdF_3{\cdot}xYbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0) glasses.

fluorescence intensity at 1.064 μm steeply decreases with increasing Tm^{3+}-concentration, the probability of energy-transfer from Nd^{3+} to Tm^{3+} ions is proved to be very high. A mechanism proposed for the energy-transfer between Nd^{3+} and Tm^{3+} is illustrated in Fig. 4. In the first process, 800 nm photons are absorbed by both Nd^{3+} and Tm^{3+} ions, provoking the Nd^{3+}:($^2H_{9/2}$, $^4F_{5/2}$) ← $^4I_{9/2}$ and Tm^{3+}:$^3F_4$ ← $^3H_6$ transitions and then the Nd^{3+}:$^4F_{3/2}$ level is populated through the ($^2H_{9/2}$, $^4F_{5/2}$) ← $^4F_{3/2}$ non-radiative relaxation processes. After these processes, the energy of Nd^{3+}:$^4F_{3/2}$ state is transferred to the 4f-electrons on the Tm^{3+}:$^3F_4$ state, then the 4f-electrons are excited to an upper $^1G_4$ level and finally, the Tm^{3+}:$^1G_4$ state relaxes to the $^3H_6$ ground state, emitting 478 nm luminescence.

If energy-transfer in rare-earth triply-doped glasses is caused mainly through the former path (i), the YbF_3 component is not concerned in Tm^{3+} up-conversion luminescence. In Nd^{3+}–Tm^{3+} co-doped glasses, however, blue up-conversion luminescence was hardly observed. On the contrary, the emission intensity of blue Tm^{3+} up-conversion luminescence exhibited a pronounced YbF_3-concentration dependence, as can be seen from Fig. 5 which shows the YbF_3-concentration dependence of up-conversion luminescence intensity in $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.4-x)LaF_3{\cdot}0.5NdF_3{\cdot}xYbF_3{\cdot}0.1TmF_3$ glasses ($x = 0$, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0). The fact that the Tm^{3+} blue up-conversion emission intensity increases with increasing YbF_3-concentration implies that Yb^{3+} ions undoubtedly contribute to the mechanism of Tm^{3+} blue up-conversion luminescence. In our previous work [20], it was proved that, under 800 nm excitation, the energies can be efficiently transferred from Nd^{3+} to Yb^{3+} through the Nd^{3+}:$^4F_{3/2}$ + Yb^{3+}:$^2F_{7/2}$ → Nd^{3+}:$^4I_{11/2}$ + Yb^{3+}:$^2F_{5/2}$ transition and/or the Nd^{3+}:$^4F_{3/2}$ + Yb^{3+}:$^2F_{7/2}$ → Nd^{3+}:$^4I_{9/2}$ + Yb^{3+}:$^2F_{5/2}$ transitions. Consequently, the latter path (ii) may be concluded to be essential for the excitation mechanism in the Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped glasses.

Blue up-conversion luminescence also has been observed in Tm^{3+}–Yb^{3+} doubly-doped materials upon 980 nm excitation [21,22]. Miyakawa and Dexter [23] have considered that a stepwise energy-transfer is dominant based on their calculation: the energy of an excited Yb^{3+} ion is first non-resonantly transferred to the $^3H_5$ level of Tm^{3+}. This transition requires the lattice phonon to absorb at about 1942 cm^{-1}. By multi-phonon emission this level relaxes non-radiatively to the $^3H_4$ level, from which a second transition to the $^3F_2$ level is caused by a second excited Yb^{3+} ion. This energy-transfer loses an energy of about 998 cm^{-1} as the lattice phonon. This $^3F_2$ level again relaxes to the $^3F_4$ level through the $^3F_3$ level by multi-phonon relaxation and a third non-resonant energy-transfer excites it to the $^1G_4$ level with an energy release of 1467 cm^{-1}. Then the luminescence can be observed at 478 nm by a transition from the $^1G_4$ level to the $^3H_6$ ground state. Since the stepwise energy-transfer occurs through three non-resonant energy-transfers, a lot of energy is lost in the energy-transfer processes, so that the efficiency of energy-transfer is quite low. Thus, the up-conversion luminescence in Yb^{3+}–Tm^{3+} doubly-doped glasses under 980 nm light are very weak compared with those in Nd^{3+}–Yb^{3+}–Tm^{3+} triply-doped glasses under 800 nm light with the same excitation laser power. Therefore, the excitation mechanism in the Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped glasses under 800 nm excitation is evidently different from that in Yb^{3+}–Tm^{3+} co-doped glasses under 980 nm excitation.

In the present Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped ZrF_4 glasses, the blue up-conversion emission at 478 nm under 800 nm excitation exhibited a quadratic dependence upon the

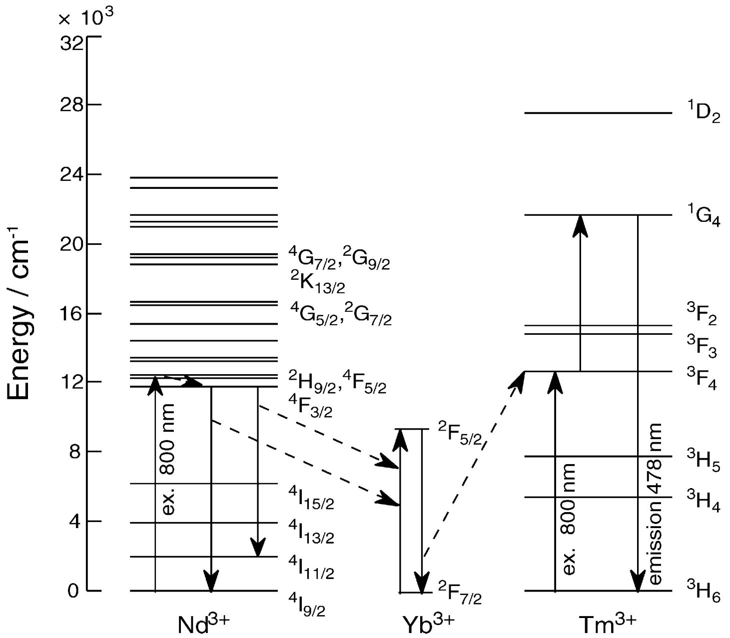

Fig. 6. Schematic diagram of up-conversion mechanism in Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped glasses under 800 nm excitation.

excitation power. This indicates that the up-conversion processes involve a two-photon absorption.

An up-conversion mechanism proposed for the Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped ZrF_4-based glasses is schematically depicted in Fig. 6. First, both Nd^{3+} and Tm^{3+} ions are excited by 800 nm radiation which corresponds to the Nd^{3+}:$(^2H_{9/2}, ^4F_{5/2}) \leftarrow {}^4I_{9/2}$ and Tm^{3+}:$^3F_4 \leftarrow {}^3H_6$ transitions. There is a degree of overlapping between the tail parts of Nd^{3+}:$^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence bands and the Yb^{3+}:$^2F_{7/2} \leftarrow {}^2F_{5/2}$ absorption band, and both the emissions intensity due to Nd:$^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transitions decrease with Yb addition under 800 nm excitation [19]. The Nd^{3+}:$(^2H_{9/2}, ^4F_{5/2})$ excited states relax quickly to the next-lower $^4F_{3/2}$ state by the multi-phonon relaxation and then an energy-transfer from Nd^{3+} to Yb^{3+} occurs through a pair of transitions: Nd^{3+}:$^4F_{3/2} \rightarrow {}^4I_{11/2}$ and/or $^4I_{9/2}$; Yb^{3+}:$^2F_{5/2} \leftarrow {}^2F_{7/2}$. Subsequently, the energies are transferred to the 4f-electron that is on the $^3F_4$ excited state of Tm^{3+}, resulting in the Tm^{3+}:$^1G_4 \leftarrow {}^3F_4$ transition. Finally, the Tm^{3+}:$^1G_4 \rightarrow {}^3H_6$ radiative transition takes place, giving very strong blue up-conversion luminescence around 478 nm. Under 800 nm excitation, therefore, Yb^{3+} ions are an essential dopant as a "bridging ion" between Nd^{3+} and Tm^{3+} ions.

On the other hand, the reason why the Tm^{3+} up-conversion luminescence becomes stronger when Yb^{3+} ions are added to Nd^{3+} and Tm^{3+} doubly-doped glasses is worth further consideration. The dipole–dipole energy-transfer rate, $P_{d\text{–}d}$, is given by Dexter [24] as follows:

$$P_{d\text{–}d} = \frac{3\hbar^4 c^4}{64\pi^5 n^4}\frac{1}{\tau_S}\left(\frac{1}{R_{SA}}\right)^6 Q_A \int_{SA} \frac{F_S(\nu)F_A(\nu)}{\nu^4}\,d\nu \qquad (1)$$

where R_{SA} is the separation of donor and acceptor, τ_S is the radiative lifetime of the donor, $F_S(\nu)$ and $F_A(\nu)$ the normalized lineshape functions for emission and acceptor absorption, respectively, ν is the photon energy, and Q_A is the integrated absorption cross-section of acceptor. Since the energy-transfer rate between two ions depends on their distances, the efficiency of up-conversion due to energy-transfer depends on the concentration of rare-earth ions. In other words, the distance between two ions is closer, the probability of the energy-transfer becomes higher and, consequently, up-conversion luminescence intensity becomes stronger. However, blue up-conversion emission was hardly observed in Nd^{3+}–Tm^{3+} co-doped glasses even in very high rare-earth concentrations. Since Nd^{3+} and Tm^{3+} are known to have several intermediate levels, the self-quenching takes place with high probability when their concentrations are increased. On the other hand, Yb^{3+} ions have only one excited state above the ground state. An Yb^{3+} donor ion in the excited state transfers all of its excitation energy to an Yb^{3+} acceptor ion that is in the ground state. This process can be repeated many times, resulting in the migration of energy through the material. The energy migration will continue until some other mechanism depletes the excited state. In Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped glass, Yb^{3+} plays a role as an energy-transfer bridging ion. In this case, the distance between Nd^{3+} and Tm^{3+} ions becomes contracted with the Yb^{3+} ion addition and consequently the efficiency of energy-transfer from Nd^{3+} to Tm^{3+} ions becomes high.

In order to select the proper NdF_3 and TmF_3-concentrations for up-conversion processes, the enhancement of blue up-conversion luminescence intensity was examined as a

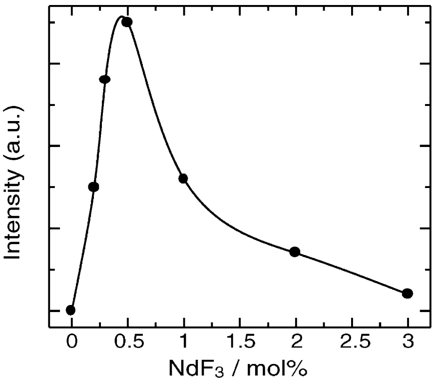

Fig. 7. NdF_3-concentration dependence of 478 nm up-conversion luminescence intensity of Tm^{3+} in $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.9-x)LaF_3{\cdot}xNdF_3{\cdot}3.0YbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.2, 0.3, 0.5, 1.0, 2.0 and 3.0) glasses under 800 nm excitation (the line is drawn as a guide to the eye).

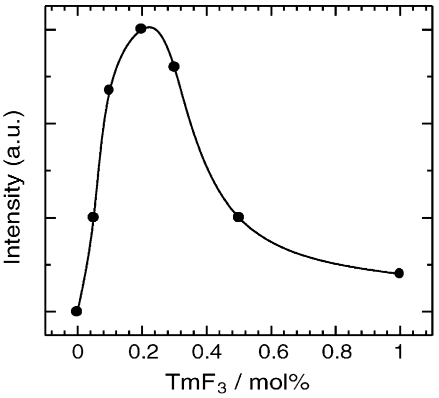

Fig. 8. TmF_3-concentration dependence of 478 nm up-conversion luminescence intensity of Tm^{3+} in $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.5-x)LaF_3{\cdot}0.5NdF_3{\cdot}3.0YbF_3{\cdot}xTmF_3$ ($x = 0$, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0) glasses under 800 nm excitation (the line is drawn as a guide to the eye).

function of the NdF_3 and TmF_3-concentrations under 800 nm excitation. Figs. 7 and 8 show that the NdF_3- and TmF_3-concentration dependence of the intensity of blue up-conversion luminescence centered around 478 nm in the $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.9-x)LaF_3{\cdot}xNdF_3{\cdot}3.0YbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.2, 0.3, 0.5, 1.0, 2.0 and 3.0) and $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.5-x)LaF_3{\cdot}0.5NdF_3{\cdot}3.0YbF_3{\cdot}xTmF_3$ ($x = 0$, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0) glasses, respectively. As can be seen from the figures, the strongest blue emission occurs when the concentrations of NdF_3 and TmF_3 are around 0.5 and 0.2 mol%, respectively.

3. Conclusion

The highly efficient blue up-conversion luminescence at around 478 nm, which corresponds to the Tm^{3+}:$^1G_4 \rightarrow {}^3H_6$ transition, was observed in Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped ZrF_4-based fluoride glasses of the $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.4-x)LaF_3{\cdot}0.5NdF_3{\cdot}xYbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0) compositions under 800 nm excitation. The Tm^{3+} blue up-conversion luminescence intensity remarkably depends on the YbF_3-concentration. This indicates that energies can be transferred from Nd^{3+} to Tm^{3+} ions through Yb^{3+} ions, because the Yb^{3+} ions shorten the energy-transfer distance between Nd^{3+} and Tm^{3+} ions and consequently the energy-transfer probability from Nd^{3+} to Tm^{3+} ions is increased. As a result, the Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped glass gives much stronger Tm^{3+} blue up-conversion luminescence than the Nd^{3+}–Tm^{3+} co-doped glass. Based on various spectral-analysis results, a most possible up-conversion mechanism was proposed for Nd^{3+}–Yb^{3+}–Tm^{3+} co-doped ZrF_4-based fluoride glasses.

4. Experimental

4.1. General experimental procedures

The following three series of ZrF_4-based glasses were prepared: (i) rare-earth (except for La) singly-doped glasses with the $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(10.0-x)LaF_3{\cdot}xLnF_3$ (Ln = Nd, Yb and Tm; $x = 5.0$) composition, (ii) rare-earth doubly-doped glasses with the $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.5-x)LaF_3{\cdot}0.5NdF_3{\cdot}xYbF_3$ ($x = 0$, 0.5, 1.0, 2.0, 3.0 and 5.0), $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.5-x)LaF_3{\cdot}0.5NdF_3{\cdot}xTmF_3$ ($x = 0$, 0.1, 0.2, 0.3, 0.5 and 1.0) and $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.9-x)LaF_3{\cdot}xNdF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.1, 0.2, 0.5, 1.0 and 3.0) compositions and (iii) rare-earth triply-doped glasses with the $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.9-x)LaF_3{\cdot}xNdF_3{\cdot}3.0YbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.2, 0.3, 0.5, 1.0, 2.0 and 3.0), $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(6.5-x)LaF_3{\cdot}0.5NdF_3{\cdot}3.0YbF_3{\cdot}xTmF_3$ ($x = 0$, 0.05, 0.1, 0.2, 0.3, 0.5 and 1.0) and $60.0ZrF_4{\cdot}30.0BaF_2{\cdot}(9.4-x)LaF_3{\cdot}0.5NdF_3{\cdot}xYbF_3{\cdot}0.1TmF_3$ ($x = 0$, 0.5, 1.0, 2.0, 3.0, 5.0 and 7.0) compositions.

Details of glass-preparation procedures have been described elsewhere [18].

4.2. Spectroscopic measurements

Up-conversion luminescence spectra under 800 nm excitation were measured in the wavelength range from 450 to 700 nm with a HITACHI F-3010 fluorescence spectrophotometer. A Sony SLD303-XT AlGaAs laser diode (maximum output power: 150 mW) was used as an excitation source.

Normal fluorescence spectra in the wavelength range from 360 to 700 nm were measured with a HITACHI F-3010 fluorescence spectrophotometer. Excitation was made with a Xe-lamp attached in the spectrophotometer. Near-infrared fluorescence spectra in the wavelength range from 800 to 1200 nm were measured with an ADVANTEST Q8383 spectrum analyzer, employing a Sony SLD303-XT AlGaAs laser diode as an excitation source.

Optical absorption spectra in the wavelength range from 200 to 3200 nm were measured with a HITACHI U-3500 spectrophotometer.

All the spectral measurements were performed at ambient temperature.

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