Excitation-emission properties of Er^{3+} ions doped in nonlinear optical $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glass by 800 nm femtosecond laser excitation

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By excitation with 800 nm femtosecond laser, we observed the green up-conversion fluorescence at 526 nm ($^2\text{H}_{11/2}\text{-}^4\text{I}_{15/2}$) and 548 nm ($^4\text{S}_{3/2}\text{-}^4\text{I}_{15/2}$) for Er^{3+} ions doped in 76 $\text{TeO}_2\text{-}20\text{Nb}_2\text{O}_5\text{-}4\text{ZnO}$ glass. From $I_{\text{H,S}} \sim P^n$ relationship ($I_{\text{H,S}}$; fluorescence intensity of $^2\text{H}_{11/2}\text{-}^4\text{I}_{15/2}$ and $^4\text{S}_{3/2}\text{-}^4\text{I}_{15/2}$, P : laser power density, n : the number of photons absorbed per visible photon emitted), the n values of 1.4 and 1.3 were obtained at room temperature for I_{H} and I_{S} , respectively, and approached “2” at lower temperatures and at lower excitation power densities. This indicates that two photons were involved in the excitation of the up-conversion fluorescence. Considering the up-conversion intensity at various repetition frequencies on fs laser excitation and the emission decay behaviors as well as the results of Judd–Ofelt analysis, we could explain this excitation mechanism in terms of energy transfer (ET: $^4\text{I}_{11/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2} + ^4\text{I}_{15/2}$, and $^4\text{I}_{9/2} + ^4\text{I}_{9/2} \rightarrow ^4\text{S}_{3/2} + ^4\text{I}_{13/2}$). We shall also discuss on a back transfer process of the latter ET for the reduction of the n value at room temperature.

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1. Introduction

A family of tellurite glasses is promising as a host material for rare-earth doping because of a low phonon energy of tellurite glasses (600–700 cm^{-1}). And it is known that Nb_2O_5 and ZnO can improve vitrification, chemical durability and optical nonlinearity of tellurite glasses.¹⁾ $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glass we selected for rare-earth doping is one of recently developed tellurite-based glass systems and is interesting for nonlinear optical material of third order $\chi^{(3)}$ as well.^{2–4)} We have investigated the optical properties of Er^{3+} -doped $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glasses excited by femtosecond (fs) laser irradiation at 800 nm.²⁾ When the near-infrared (NIR) fs laser was irradiated to Er^{3+} -doped TeO_2 -based glasses, green up-conversion fluorescence of Er^{3+} from $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels was observed. From the fluorescence analysis, it was found that the green up-conversion fluorescence could simultaneously monitor a fs laser heating of TeO_2 -based glass matrix, which had large nonlinear absorption properties, owing to an imaginary part of $\chi^{(3)}$ ($\text{Im}\chi^{(3)}$) and a lower thermal conductivity. This technique is very useful for the detection of laser spot temperature in 800 nm femtosecond laser manipulation.³⁾ However, we did not still address excitation-emission mechanism of the green up-conversion fluorescence under femtosecond laser excitation. In this paper, we discuss on it with fluorescence decay data and Judd–Ofelt analysis.

2. Experimentals

The TeO_2 -based glass sample was prepared using commercially-available chemicals TeO_2 (<99.99%, Kojundo Chemical Lab. Co., Ltd.), Nb_2O_5 , ZnO and Er_2O_3 (Shin-Etsu Chemical Co.,

Ltd.). The composition was 76 $\text{TeO}_2\text{-}20\text{Nb}_2\text{O}_5\text{-}4\text{ZnO}$ doped with 1.5 mass% Er_2O_3 . The powder was weighed precisely, mixed thoroughly, and melted in alumina crucible at 900°C for 30 min in air. The melt was poured onto a carbon mold, annealed at 400°C for 4 h, and then cooled down to the room temperature. Each of its planar surfaces was polished to optical-flat for the optical measurements. The femtosecond pulse laser from a regenerative Ti: Sapphire laser system (Spectra Physics, Hurricane) operating at a wavelength of 800 nm (spectral width: ~200 nm) with a 1 kHz repetition rate and approximately 170 fs pulse duration was focused on this sample through an objective lens of $\times 20$ magnification ($\text{NA} = 0.45$). The focal point was positioned just below the top surface (inside the glass investigated). The repetition frequency of fs laser was changed down by an optical chopper (New Focus, Model 3501). The gate width for the fluorescence detection was controlled in an image-intensified charge-coupled device (ICCD) system (Oriel Instruments, InstaSpec^{TM} V & DG535) equipped with a monochromator (Jobin Yvon, HR-320), and the fluorescence spectra were measured by different power densities of fs laser. The experimental condition for gating and delaying control is 200 ns and 300 μs , respectively.

For comparison, Er^{3+} -doped aluminosilicate glass (20 $\text{Al}_2\text{O}_3\text{-}80\text{SiO}_2$ doped with 10 mass% Er_2O_3) was also prepared. In this study, we have aimed to estimate optical properties of Er^{3+} doped into $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glass system recently developed, which has a high third-order nonlinear optical susceptibility with 76 $\text{TeO}_2\text{-}20\text{Nb}_2\text{O}_5\text{-}4\text{ZnO}$ composition as Lin et al. reported.⁴⁾ From the view of glass chemistry, Er^{3+} ions are expected to be clustered and to be neighbored each other via oxygen because of no network modifier oxide such as alkali- or alkaline-oxide. On the other hand, it is expected that Nb_2O_5 and ZnO act as intermediate oxide in tellurite glass network. To have good dispersivity of Er^{3+} ions in glass network, chemically stable

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aluminosilicate⁵⁾ is a typical choice as reference of host glass on the femto-second laser irradiation. However, in aluminosilicate system, it is suspected to have a large multi-phonon relaxation rate of the emitting levels and consequently a weak luminescence intensity of Er^{3+} ions. Thus, we prepared a reference of an aluminosilicate glass in which 10 mass% Er_2O_3 was doped with.

3. Results and discussion

We observed two green fluorescence lines of $^2\text{H}_{11/2}$ – $^4\text{I}_{15/2}$ at 526 nm and $^4\text{S}_{3/2}$ – $^4\text{I}_{15/2}$ at 548 nm for Er^{3+} ions excited by 800 nm femtosecond laser. The intensities of these green up-conversion fluorescence for increasing incident power density was obeyed by the relationship of $I_{\text{H,S}} = P^n$ (n : the number of photons excited for up-conversion fluorescence) and eventually the value of n was 1.4 and 1.3 at room temperature for $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ fluorescences, respectively. To use lower laser power densities in comparison with fs laser excitation (several hundred TW/cm^2), a continuous-wave (cw) 800 nm semiconductor laser was installed to excite Er^{3+} ions in TeO_2 – Nb_2O_5 – ZnO glass, which has several hundred mW power (several tens MW/cm^2). In the same way as the case in femtosecond laser excitation, two lines of up-conversion fluorescence from $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels (see Fig. 1) were observed. The log-log plot of I and P elucidated that the value of n was ~ 1.5 . Even in lower excitation power densities, the observed up-conversion fluorescence was the same $\log(I)$ – $\log(P)$ relationship as in the femtosecond laser excitation. At lower temperatures, the value approached “2”, indicating a two photon process accompanying with non-radiative relaxation.

As for up-conversion process of Er^{3+} fluorescence in TeO_2 – Nb_2O_5 – ZnO glass studied, the following three possibilities should be discussed (refer to Fig. 2). These processes are all involved with two photons.

(a) Direct two photon absorption (TPA) process: two photons were simultaneously absorbed and Er^{3+} ion was excited to higher energy levels, which is normally observed in a strong excitation condition. Owing to the large spectral width, ~ 200 nm, of the femto second pulse, some of Er^{3+} ions can be excited to $^4\text{I}_{11/2}$ level by one photon while most Er^{3+} ions are excited to $^4\text{I}_{9/2}$. Subsequently, direct TPA, if it were in case, would produce Er^{3+} ions in higher energy levels of $^2\text{H}_{9/2}$ and $^4\text{F}_{5/2, 3/2}$.

(b) Excited state absorption (ESA) process: one photon was used to excite Er^{3+} ion to an intermediate level and after non-

radiative relaxation to a lower excited level, then another sequential fs pulse excited it to a higher energy level.

(c) Energy transfer (ET) process: two photons excited two neighbouring Er^{3+} ions, which were interacted each other so that the absorbed energy in one Er^{3+} ions (A) was transferred to the other Er^{3+} ion (B), resulting in the excitation to a higher excited level of Er^{3+} ion (B).

On the other hand, it was found that Er^{3+} ions in aluminosilicate glass were excited via three photon process, resulting form a laser power dependence ($n = 3$) on green up-conversion intensity (not shown here). This could simply be explained by three photon absorption over a large band-gap energy of the aluminosilicate glass in a similar way as our previous report.⁶⁾ From these observations, it is concluded that direct TPA process by femtosecond 800nm laser pulses is forbidden for Er^{3+} -ions and a higher order phenomenon with three photons then occurs in well-dispersed system of Er^{3+} ions. Hence, the reduction of the n value from 2 in Er^{3+} -doped TeO_2 – Nb_2O_5 – ZnO glass will be attributable to absorption saturation of energy donor in ESA of Fig. 1(b) or induced relaxation, such as back transfer, of energy acceptor.

With different repetition ratios of sequential femtosecond laser pulses, the up-conversion fluorescence was estimated, as shown

Fig. 1. Up-conversion fluorescence spectra of 1.5 mass% Er_2O_3 doped 76TeO_2 : $20\text{Nb}_2\text{O}_5$: 4ZnO glass irradiated with semiconductor laser (800 nm).

Fig. 2. Schematic illustration of possible up-conversion mechanisms for Er^{3+} ions in TeO_2 – Nb_2O_5 ZnO glass.

Fig. 3. Up-conversion fluorescence spectra of 1.5 mass% Er₂O₃ doped 76TeO₂-20Nb₂O₅-4ZnO glass irradiated with femtosecond laser (800 nm).

in **Fig. 3**. The repetition ratio was changed from 1 kHz down to 35.7 Hz, resulting in no significant change in the green up-conversion fluorescence. This means that a train of femtosecond pulses could not be influenced with excited state absorption (ESA), though the lifetimes of intermediate excited states (⁴I_{9/2} and ⁴I_{13/2}) were originally in an order of millisecond (see also **Table 1**). Additionally, we have to remind ourselves that one femtosecond pulse is too short to excite Er³⁺ ions non-radiatively relaxed to an intermediate excited state in its time duration. Thus, it is very meaningful to consider the observed up-conversion fluorescence in terms of energy transfer (ET).

Next, we measured an optical absorption spectrum of Er³⁺-doped TeO₂-Nb₂O₅-ZnO glass studied and analyzed it in Judd–Ofelt theory,⁷⁾ which allowed us to obtain phenomenological parameters of Ω_2 , Ω_4 , Ω_6 , known as Judd–Ofelt parameters, for the prediction of a lifetime of each excited state of Er³⁺ ions in this glass. At 8 K, the fluorescence decay curves of ⁴I_{9/2}, ⁴F_{9/2} and ⁴S_{3/2} emissive level were detected to estimate the experimental values of lifetimes of the corresponding excited levels. The lifetimes of ⁴I_{11/2} and ⁴I_{13/2} were observed in the measurement of fluorescence decays at 77 K, where each of these lifetimes approached a constant value and so it was found that the temperature was low enough to estimate a radiative transition probability for each of them. Table 1 summarizes Judd–Ofelt parameters (Ω_2 , Ω_4 , Ω_6) with comparison of those of Er³⁺-doped TeO₂-Nb₂O₅-Na₂O glass found in literatures,⁸⁾ and the experimental and theoretical prediction for the lifetimes. In the obtained Judd–Ofelt parameters, Ω_2 and Ω_6 were lower than the values calculated for TeO₂-Nb₂O₅-Na₂O glass, while Ω_4 was larger. The predicted lifetimes of the excited state of Er³⁺ ions doped in these glasses are comparative to those for TeO₂-Nb₂O₅-Na₂O glass doped with Er³⁺ ions.⁸⁾ Curiously, the experimental values of the lifetimes for ⁴I_{9/2}, ⁴F_{9/2} and ⁴S_{3/2} levels were all shorter than the predicted values, strongly indicating that Er³⁺ ions in excited states could be interacted each other and excitation energy transfer processes were not negligible.

As a possible excitation-emission process, we can propose the following mechanism (see also **Fig. 4**): First, the transition from the ground state ⁴I_{15/2} to ⁴I_{9/2} occurs by the fs pulsed irradiation at 800 nm. High power density of fs laser, of the order of TW/

Table 1. Judd–Ofelt Parameters and Emission Lifetimes of 1.5 mass% Er₂O₃ Doped 76TeO₂-20Nb₂O₅-4ZnO Glass

		Judd–Ofelt theory		Experiment at 8 K
		Our work	Ref. ⁸⁾	
Ω_i ($\times 10^{-20} \text{ cm}^2$)	Ω_2	6.59	6.86	–
	Ω_4	1.70	1.53	–
	Ω_6	0.967	1.12	–
τ (μs)	⁴ S _{3/2}	304	230	48
	⁴ F _{9/2}	277	252	59
	⁴ I _{9/2}	2233	2430	64
	⁴ I _{11/2}	2,673	2,320	283*
	⁴ I _{13/2}	4,486	3,020	2,649*

Ref.⁸⁾: TeO₂-Nb₂O₅-Na₂O: Er³⁺ glass, * measured at 77 K.

Fig. 4. Energy level diagram of Er³⁺ and possible transition pathways in 1.5 mass% Er₂O₃ doped 76TeO₂-20Nb₂O₅-4ZnO glass.

cm², gives rise to high population of the excited ⁴I_{9/2} level. After multiphoton relaxation to ⁴I_{11/2}, or direct ⁴I_{11/2} pumping by broadband fs pulse, the excitation energy transfer between the excited Er³⁺ ions in nearest neighbor is possible to occur, eventually to populate one of Er³⁺ ions to ⁴F_{7/2} level higher than ⁴S_{3/2} and ²H_{11/2}, and the other to the ground state (energy transfer up-conversion (ETU)).⁹⁾ As a result of the subsequent multiphonon relaxation from ⁴F_{7/2} to these two levels investigated, the green up-conversion fluorescence was observed. Alternative energy transfer process is that via ⁴I_{9/2} level (⁴I_{9/2} + ⁴I_{9/2} → ⁴S_{3/2} + ⁴I_{13/2}). More or less, this ET process could be involved to the observed up-conversion fluorescence of Er³⁺ ions in TeO₂-Nb₂O₅-ZnO glass.

Several types of energy transfer process are reported for Er³⁺ ions.⁹⁾ In relation with the generation of Er³⁺ green up-conversion fluorescence, we have noted ⁴I_{11/2}, ⁴I_{11/2} → ⁴F_{7/2}, ⁴I_{15/2} (ETU1) and ⁴I_{9/2}, ⁴I_{9/2} → ⁴S_{3/2}, ⁴I_{13/2} (ETU2). As seen in Table 1, one can notice that ⁴S_{3/2} and ⁴F_{9/2} levels have much shorter lifetime than given theoretically from Judd–Ofelt analysis. It indicates that the fluorescence from these levels compete with energy transfer process as well. A plausible mechanism for lowering ⁴S_{3/2} and ⁴F_{9/2} lifetime is ⁴S_{3/2}, ⁴I_{13/2} → ⁴I_{9/2}, ⁴I_{9/2}, which is a back transfer process of ETU2, and ⁴F_{9/2}, ⁴F_{9/2} → ⁴F_{7/2}, ⁴I_{11/2}, respectively. The back transfer of ETU2 can also contribute to the reduction of the *n* value in the *I*–*P* correlation although two photons are used for exciting Er³⁺ ion to ⁴S_{3/2} level. As temperature is decreased, the forward ETU2 process has a faster rate because the population

of $^4I_{9/2}$ level is increased and the back transfer process becomes negligible. As a consequence, the value of n approaches “2” at lower temperatures.

4. Conclusion

In this paper, we discussed excitation-emission mechanisms of green up-conversion fluorescence for Er^{3+} ions in $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glass under excitation of 800 nm fs laser. We considered different types of two photon processes, direct two photon absorption (TPA), excited state absorption (ESA), and energy transfer (ET) process between neighbouring Er^{3+} ions. The plausible explanation was given in the following: First, the transition from the ground state $^4I_{15/2}$ to $^4I_{9/2}$ occurred by the fs pulsed irradiation at 800 nm. High power density of fs laser, of the order of TW/cm^2 , gave rise to high population of the excited $^4I_{9/2}$ level. After multiphonon relaxation to $^4I_{11/2}$, the excitation energy transfer between the excited Er^{3+} ions in nearest neighbor was possible to occur, eventually to populate one of Er^{3+} ions to $^4F_{7/2}$ level higher than $^4S_{3/2}$ and $^2H_{11/2}$, and the other to the ground state (energy transfer up-conversion (ETU)). As a result of the subsequent multiphonon relaxation from $^4F_{7/2}$ to these two levels investigated, the green up-conversion fluorescence was observed. Additionally, the ET process ($^4I_{9/2} + ^4I_{9/2} \rightarrow ^4S_{3/2} + ^4I_{13/2}$) could be involved to the observed up-conversion fluorescence of Er^{3+} ions in $\text{TeO}_2\text{-Nb}_2\text{O}_5\text{-ZnO}$ glass.

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