Excitation-emission properties of Er\(^{3+}\) ions doped in nonlinear optical TeO\(_2\)–Nb\(_2\)O\(_5\)–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 (\(^{4} \text{H}_{11/2} \rightarrow ^{4} \text{I}_{15/2}\)) and 548 nm (\(^{4} \text{S}_{3/2} \rightarrow ^{4} \text{I}_{15/2}\)) for Er\(^{3+}\) ions doped in 76TeO\(_2\)·20Nb\(_2\)O\(_5\)·4ZnO glass. From \(I_{\text{flu}} \sim P^n\) relationship \(I_{\text{flu}}\) fluorescence intensity of \(^{4} \text{H}_{11/2} \rightarrow ^{4} \text{I}_{15/2}\) and \(^{4} \text{S}_{3/2} \rightarrow ^{4} \text{I}_{15/2}\), \(P\): 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 \(I_{\text{flu}}\) and \(I_{\text{flu}}\), 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: \(^{4} \text{I}_{11/2} + ^{4} \text{I}_{11/2} \rightarrow ^{2} \text{F}_{7/2} + ^{4} \text{I}_{15/2}\) and \(^{4} \text{I}_{11/2} + ^{4} \text{I}_{11/2} \rightarrow ^{2} \text{S}_{9/2} + ^{4} \text{I}_{13/2}\)). 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\(_2\)O\(_5\) and ZnO can improve vitrification, chemical durability and optical nonlinearity of tellurite glasses.\(^5\)–\(^8\) TeO\(_2\)-Nb\(_2\)O\(_5\)-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.\(^9\)–\(^12\) We have investigated the optical properties of Er\(^{3+}\)-doped TeO\(_2\)-Nb\(_2\)O\(_5\)-ZnO glasses excited by femtosecond (fs) laser irradiation at 800 nm.\(^12\) 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 \(^{4} \text{H}_{11/2}\) 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 \(\chi^{(3)}\) (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.\(^15\) 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. Experiments

The TeO\(_2\)-based glass sample was prepared using commercially-available chemicals TeO\(_2\) (> 99.99%, Kojundo Chemical Lab. Co., Ltd.), Nb\(_2\)O\(_5\), ZnO and Er\(_2\)O\(_3\) (Shin-Etsu Chemical Co., Ltd.). The composition was 76TeO\(_2\)-20Nb\(_2\)O\(_5\)-4ZnO doped with 1.5 mass% Er\(_2\)O\(_3\). 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 20 magnification (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\(^{\text{TM}}\) 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 30 μs, respectively.

For comparison, Er\(^{3+}\)-doped aluminosilicate glass (20Al\(_2\)O\(_3\)-80SiO\(_2\); doped with 10 mass% Er\(_2\)O\(_3\)) was also prepared. In this study, we have aimed to estimate optical properties of Er\(^{3+}\) doped into TeO\(_2\)-Nb\(_2\)O\(_5\)-ZnO glass system recently developed, which has a high third-order nonlinear optical susceptibility with 76TeO\(_2\)-20Nb\(_2\)O\(_5\)-4ZnO 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\(_2\)O\(_5\) and ZnO act as intermediate oxide in tellurite glass network. To have good dispersivity of Er\(^{3+}\) ions in glass network, chemically stable
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 \(^2H_{11/2} \rightarrow \ ^4I_{15/2}\) at 526 nm and \(^4S_{3/2} \rightarrow \ ^4I_{15/2}\) 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 \(I_{H,S} = P^n\) (\(n\): 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 \(^2H_{11/2}\) and \(^4S_{3/2}\) fluorescence, 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 \(^2H_{11/2}\) and \(^4S_{3/2}\) 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 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 femtosecond pulse, some of Er\(^{3+}\) ions can be excited to \(^4I_{11/2}\) level by one photon while most Er\(^{3+}\) ions are excited to \(^4I_{9/2}\). Subsequently, direct TPA, if it were in case, would produce Er\(^{3+}\) ions in higher energy levels of \(^2H_{9/2}\) and \(^4F_{5/2, 3/2}\).

(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 from 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
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_{13/2} and 4I_{15/2}) were originally in an order of millisecond (see also Table 1). Additionally, we have to remind oneself that one femtosecond pulse is too short to excite Er^{3+} 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 Er^{3+}-doped TeO_{2}–Nb_{2}O_{5}–ZnO glass studied and analyzed it in Judd–Ofelt theory,\(^6\) which allowed us to obtain phenomenological parameters of \(\Omega_{2}\), \(\Omega_{4}\), \(\Omega_{6}\), known as Judd–Ofelt parameters, for the prediction of a lifetime of each excited state of Er^{3+} ions in this glass. At 8 K, the fluorescence decay curves of \(4I_{13/2}\), \(4F_{9/2}\), and \(4S_{3/2}\) emittive level were detected to estimate the experimental 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 summaries Judd–Ofelt parameters (\(\Omega_{2}\), \(\Omega_{4}\), \(\Omega_{6}\)) with comparison of those of Er^{3+}-doped TeO_{2}–Nb_{2}O_{5}–Na_{2}O glass found in literatures,\(^8\) and the experimental and theoretical prediction for the lifetimes. In the obtained Judd–Ofelt parameters, \(\Omega_{2}\) and \(\Omega_{6}\) were lower than the values calculated for TeO_{2}–Nb_{2}O_{5}–Na_{2}O glass, while \(\Omega_{4}\) was larger. The predicted lifetimes of the excited state of Er^{3+} ions doped in these glasses are comparative to those for TeO_{2}–Nb_{2}O_{5}–Na_{2}O glass doped with Er^{3+} ions.\(^9\) Curiously, the experimental values of the lifetimes for \(4I_{13/2}\), \(4F_{9/2}\), and \(4S_{3/2}\) levels were all shorter than the predicted values, strongly indicating that Er^{3+} 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 \(4I_{13/2}\) occurs by the fs pulsed irradiation at 800 nm. High power density of fs laser, of the order of TW/cm², gives rise to high population of the excited \(4I_{13/2}\) 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 Er^{3+} ions in nearest neighbor is possible to occur, eventually to populate one of Er^{3+} ions to \(4F_{9/2}\) level higher than \(4S_{3/2}\) and \(4I_{11/2}\), and the other to the ground state (energy transfer up-conversion (ETU)).\(^9\) As a result of the subsequent multiphoton relaxation from \(4F_{9/2}\) to these two levels investigated, the green up-conversion fluorescence was observed. Alternative energy transfer process is that via \(4I_{13/2}\) level (\(4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4S_{3/2} \rightarrow 4I_{13/2}\)). More or less, this ET process could be involved to the observed up-conversion fluorescence of Er^{3+} ions in TeO_{2}–Nb_{2}O_{5}–ZnO glass.

Several types of energy transfer process are reported for Er^{3+} ions.\(^9\) In relation with the generation of Er^{3+} green up-conversion fluorescence, we have noted \(4I_{11/2} \rightarrow 4I_{11/2} \rightarrow 4F_{9/2} \rightarrow 4I_{13/2} \rightarrow 4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4I_{11/2} \rightarrow 4F_{9/2} \rightarrow 4I_{13/2}\) (ETU1) and \(4I_{13/2} \rightarrow 4F_{9/2} \rightarrow 4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4S_{3/2} \rightarrow 4I_{13/2}\) (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 \(4S_{3/2} \rightarrow 4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4I_{11/2} \rightarrow 4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4I_{13/2} \rightarrow 4I_{11/2} \rightarrow 4I_{11/2} \rightarrow 4F_{9/2}\), which is a back transfer process of ETU2, and \(4F_{9/2} \rightarrow 4I_{11/2} \rightarrow 4F_{9/2}\), 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 Er^{3+} ion to \(4S_{3/2}\) level. As temperature is decreased, the forward ETU2 process has a faster rate because the population

<table>
<thead>
<tr>
<th>(\Omega)</th>
<th>(\Omega_{2})</th>
<th>(\Omega_{4})</th>
<th>(\Omega_{6})</th>
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<tbody>
<tr>
<td>(\times 10^{-20}) cm²</td>
<td>6.59</td>
<td>1.70</td>
<td>0.967</td>
</tr>
<tr>
<td>(\mu s)</td>
<td>68.6</td>
<td>1.53</td>
<td>1.12</td>
</tr>
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Table 1. Judd–Ofelt Parameters and Emission Lifetimes of 1.5 mass% Er_{2}O_{3} Doped 76TeO_{2}·20Nb_{2}O_{5}·4ZnO Glass

<table>
<thead>
<tr>
<th>(\Omega)</th>
<th>(\Omega_{2})</th>
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<tbody>
<tr>
<td>(\times 10^{-20}) cm²</td>
<td>0.967</td>
<td>1.70</td>
<td>6.59</td>
</tr>
<tr>
<td>(\mu s)</td>
<td>1.12</td>
<td>1.53</td>
<td>6.86</td>
</tr>
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Ref.\(^8\): TeO_{2}–Nb_{2}O_{5}–Na_{2}O: Er^{3+} glass, \(^8\) measured at 77 K.

Fig. 3. Up-conversion fluorescence spectra of 1.5 mass% Er_{2}O_{3} doped 76TeO_{2}·20Nb_{2}O_{5}·4ZnO glass irradiated with femtosecond laser (800 nm).

Fig. 4. Energy level diagram of Er^{3+} and possible transition pathways in 1.5 mass% Er_{2}O_{3} doped 76TeO_{2}·20Nb_{2}O_{5}·4ZnO glass.
of \textit{4I}_{9/2} \text{ level is increased and the back transfer process becomes negligible. As a consequence, the value of } n \text{ approaches "2" at lower temperatures.}

4. Conclusion

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

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