

# Bi-directional energy transfer process in Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped fluorozirconate glasses

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Energy transfer direction in Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped fluorozirconate glasses has been studied. For Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped glasses, the dependence of the green emission intensity on the pump power ( $P_{ex}$ ) of 800 nm has ranged from  $(P_{ex})^2$  to  $(P_{ex})^3$ . From this multistep absorption, a 1.48  $\mu\text{m}$  emission from the  $^3F_4 \rightarrow ^3H_4$  transition on Tm<sup>3+</sup> ion has been found to transfer into  $^4I_{13/2}$ ,  $^4I_{9/2}$  and  $^4S_{3/2}$  on Er<sup>3+</sup> ion. In case of the 1.06  $\mu\text{m}$  pumping, the emission ratio of  $^3H_4$  level in Tm<sup>3+</sup> to  $^4I_{13/2}$  in Er<sup>3+</sup> showed that the amount of the energy transfer from Tm<sup>3+</sup> into Er<sup>3+</sup> increased with the increasing concentration of Tm<sup>3+</sup> ion. Our two kinds of pumping scheme suggest that the direction of dominant energy transfer between Er<sup>3+</sup> and Tm<sup>3+</sup> should be dependent on whether the  $^3F_4$  level resonates in Tm<sup>3+</sup> the level or not.

## I. INTRODUCTION

Recently, the infrared-to-visible upconversion has been extensively studied in rare-earth-ion doped materials by many investigators<sup>[1-9]</sup>. The advent of a powerful near-infrared AlGaAs diode laser has stimulated interest in the development of visible laser sources that are pumped by semiconductor diode lasers<sup>[2]</sup>. The up-conversion and the energy transfer of Er-doped materials have been widely studied since its green, 1.55  $\mu\text{m}$  and 2.7  $\mu\text{m}$  emission proved useful in optical data storage, optical communication and biological engineering respectively<sup>[4]</sup>. For maximum efficiency, the energy transfer between Er<sup>3+</sup> and other rare-earth ion has been reported by many researchers<sup>[4,5]</sup>. Most of them have reported that Tm<sup>3+</sup> ion effectively quenches the levels of Er<sup>3+</sup> ion by transferring  $^4I_{13/2}$  level emission in Er<sup>3+</sup> to  $^3H_4$  in Tm<sup>3+</sup>. For example, Yeh *et al.* have reported that Tm<sup>3+</sup> preferentially quenches the up-conversion efficiency of the green emission from the Er<sup>3+</sup> ion in a barium-thorium fluoride glass<sup>[4,5]</sup>. The measurement of the fluorescence output dependence on the excitation intensity is a key experiment in the study of both upconversion and energy transfer<sup>[6]</sup>. L.F. Johnson *et al.* observed the quadratic dependence of  $^4S_{3/2}$  energy level of Er<sup>3+</sup> ion in Er<sup>3+</sup>-Yb<sup>3+</sup> system, which confirmed that the  $^4S_{3/2}$  level was populated by two-photon absorption<sup>[7]</sup>. S. Arahira *et al.* have reported that the strong green fluorescence was emitted through the three-photon process in highly Er<sup>3+</sup>-doped fiber pumped by the 1.48  $\mu\text{m}$  laser diode<sup>[8]</sup>. As mentioned above, researchers reported one-way energy transfer processes for several rare-earth systems.

In this paper we report that for Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped

glasses, the  $^4I_{13/2}$  level on Er<sup>3+</sup> was populated or depopulated according to the direction of the dominant energy transfer between Er<sup>3+</sup> and Tm<sup>3+</sup>, which was dependent on the emission from the  $^3F_4 \rightarrow ^3H_4$  transition on Tm<sup>3+</sup> ion.

## II. EXPERIMENTAL

The compositions of the investigated glasses are shown in Table 1. The base composition was the well-known 53ZrF<sub>4</sub>-25BaF<sub>2</sub>-4LaF<sub>3</sub>-3AlF<sub>3</sub>-15NaF (mol%) of which 4LaF<sub>3</sub> was partially replaced by xTmF<sub>3</sub> and yErF<sub>3</sub>.

The doping concentration ratios of TmF<sub>3</sub> to ErF<sub>3</sub> (x/y) were 0, 1, 4, 10, and 19. The starting materials were all the metal fluorides with a purity of at least 99.9% (APL Engineered Materials, INC., U.S.A.). The experimental procedures of ZrF<sub>4</sub>-based glass fabrication were reported in our earlier paper<sup>[10]</sup>.

To determine the energy transfer from  $^3H_4$  level on Tm<sup>3+</sup> to  $^4I_{13/2}$  on Er<sup>3+</sup>, we measured the dependence of the green fluorescence from  $^4S_{3/2}$  on Er<sup>3+</sup> on the pump intensity scale. Emission spectra were obtained by exciting the samples

Table 1. Doping concentration and dependence of the green intensity on the pumping power for ZBLAETN glasses.

| Glasses      | Doping Concentration                      |  | Dependence of the green intensity on the pumping power | Standard Deviation |
|--------------|---|--|--|--------------------|
|              | ErF <sub>3</sub> :TmF <sub>3</sub> (mol%) | Tm <sup>3+</sup> /Er <sup>3+</sup> (x/y) |  |                    |
| ZBLAEN(I)    | 0.2:0                                     | 0  | 2.0  | 0.013              |
| ZBLAEN(II)   | 0.5:0                                     | 0  | 2.0  | 0.064              |
| ZBLAETN(I)   | 2:0                                       | 1  | 2.0  | 0.023              |
| ZBLAETN(II)  | 0.5:2                                     | 4  | 2.2  | 0.025              |
| ZBLAETN(III) | 0.2:2                                     | 10                                       | 2.3  | 0.027              |
| ZBLAETN(IV)  | 0.2:3.8                                   | 19                                       | 2.7  | 0.038              |

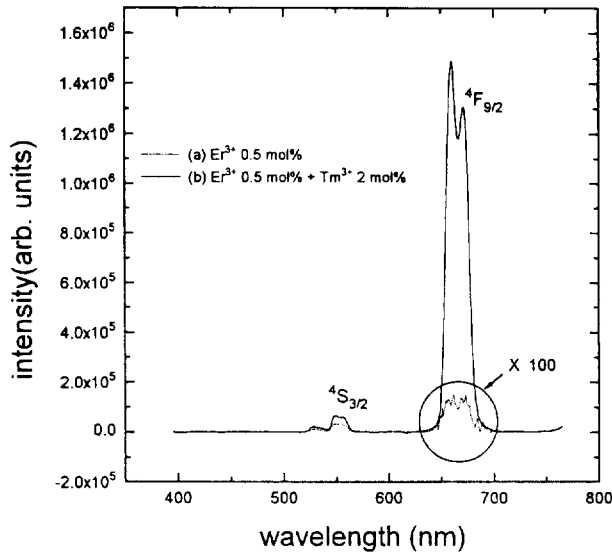


Fig 1. Visible upconversion emission for 0.5 %  $\text{Er}^{3+}$ -doped ZBLAEN(II) glass (a) and 0.5%  $\text{Er}^{3+}$ - 2%  $\text{Tm}^{3+}$ -codoped ZBLAETN(III) glass (b). The red emission for  $\text{Er}^{3+}$ -singly doped glass shown in the circle is magnified by a factor of 100. The green and red emissions from the  ${}^4\text{S}_{3/2}$  and  ${}^4\text{F}_{9/2}$  level of the  $\text{Er}^{3+}$  ion are enhanced by  $\text{Tm}^{3+}$  codoping.

with a focused beam from a 800 nm laser diode. The excited area of the sample was about  $0.001 \text{ cm}^2$  and the output power of the laser diode was controlled in the range between 20 mW and 70 mW. The fluorescence was guided into a 0.3 m Spex monochromator through a 1 m optical silica fiber and the appropriate detector was attached to the exit slit. A Newport RG. 850 colored glass filter was used inside the exit slit for the infrared detection. The detectors were a cooled RCA C31034 photomultiplier tube (PMT), for the visible emission, and a germanium photodiode for the infrared emission. The signal from the detector was preamplified and passed into a lock-in amplifier whose reference was a variable-speed light chopper in the excitation beam. The output of the lock-in amplifier was displayed on a computer with the help of a software called Auto-Scan that was supplied by Spex. The dependence of the green fluorescence on the pump intensity was obtained by the linear regression method for the log-log plot of the fluorescence intensity versus the pumping intensity<sup>[6,7]</sup>.

To determine the energy transfer from  ${}^4\text{I}_{13/2}$  in  $\text{Er}^{3+}$  to  ${}^3\text{H}_4$  level in  $\text{Tm}^{3+}$ , we excited  ${}^4\text{I}_{11/2}$  level in  $\text{Er}^{3+}$  using the  $1.06 \mu\text{m}$  YAG laser. In case of the  $1.06 \mu\text{m}$  pumping, the amount of the energy transfer from  $\text{Tm}^{3+}$  into  $\text{Er}^{3+}$  was estimated by the emission ratio of  ${}^3\text{H}_4$  level in  $\text{Tm}^{3+}$  to  ${}^4\text{I}_{13/2}$  in  $\text{Er}^{3+}$  with the increasing concentration of  $\text{Tm}^{3+}$  ions.

### III. RESULTS AND DISCUSSION

The emission spectra resulting from upconversion of

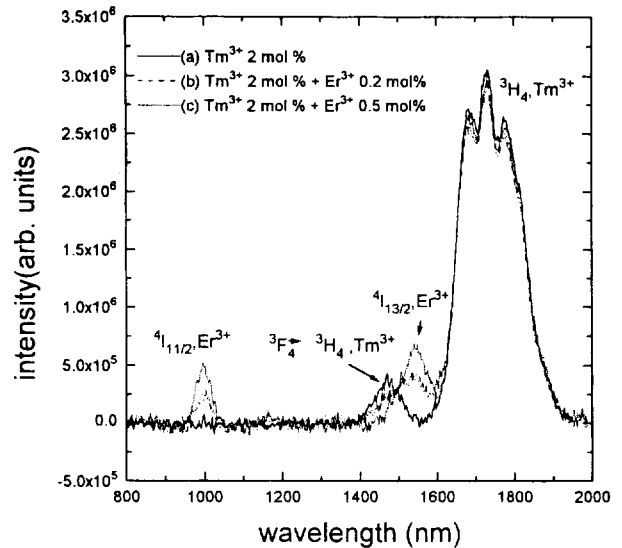


Fig 2. The infrared emission for  $\text{Tm}^{3+}$ -singly doped ZBLATN glass and  $\text{Er}^{3+}$ - $\text{Tm}^{3+}$ -codoped ZBLAETN(II), ZBLAETN(III) glasses. The  $1.48 \mu\text{m}$  emission from the transition of  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_4$  in the  $\text{Tm}^{3+}$  ion decreases with increasing  $\text{Er}^{3+}$  concentration.

800 nm excitation in the  $\text{Er}^{3+}$ -singly doped glasses are shown in Fig. 1(a). The spectra mainly consist of a green emission band around 550 nm with a sideband around 530 nm and a weaker red emission around 650 nm. These emissions have been reported before upon infrared excitation of  $\text{Er}^{3+}$ -doped fluoride glasses and correspond to the  ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  (550 nm), and  ${}^4\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$  (530 nm) and  ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$  (650 nm) transitions on the  $\text{Er}^{3+}$  ion<sup>[3,9]</sup>. The red emission is magnified by a factor of 100 in the line circle.

The emission spectra resulting from upconversion of 800 nm excitation in the  $\text{Er}^{3+}$ - $\text{Tm}^{3+}$ -codoped glasses are shown in Fig. 1(b). The spectrum consists of three bands that are found in the same wavelength ranges as the spectrum of  $\text{Er}^{3+}$ -singly doped glasses.  $\text{Tm}^{3+}$ -singly doped glasses reveal no significant visible upconversion spectrum when pumped with 800 nm laser diode. Therefore we believe that all the three visible emission bands shown in Fig. 1(b) can be ascribed to the same energy levels of the  $\text{Er}^{3+}$  ion in  $\text{Er}^{3+}$ -singly doped glasses. The green intensity was enhanced by a factor of about 2 or 3 compared with that of  $\text{Er}^{3+}$ -singly doped glass.

Fig. 2. shows the infrared emission spectra of both  $\text{Tm}^{3+}$ -singly doped and  $\text{Er}^{3+}$ - $\text{Tm}^{3+}$ -codoped glasses pumped with 800 nm laser diode. The infrared emission spectrum of  $\text{Tm}^{3+}$ -singly doped glass reveals two main emission bands of which the emissions around the  $1.48 \mu\text{m}$  wavelength and  $1.75 \mu\text{m}$  correspond to the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_4$  and  ${}^3\text{H}_4 \rightarrow {}^3\text{H}_6$  transitions on  $\text{Tm}^{3+}$  ion. The  $1.48 \mu\text{m}$  emission of  $\text{Tm}^{3+}$  ion decreases with increasing  $\text{Er}^{3+}$  ion

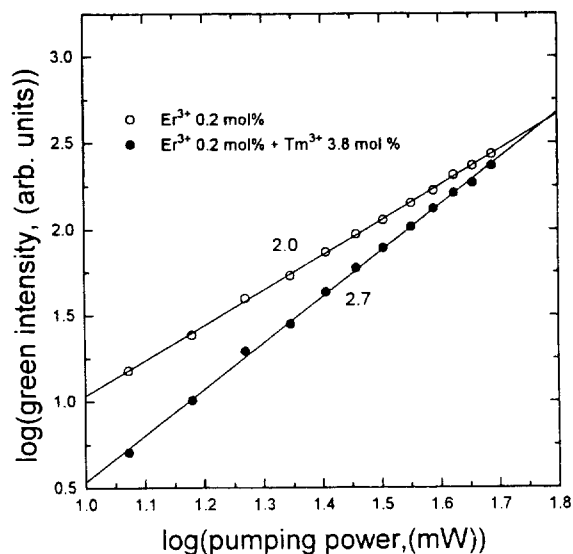


Fig. 3. The log-log plot for the green intensities vs. laser pumping powers. The units of the green intensity and the pumping power are an arbitrary unit and mW, respectively. The open circles represent the green intensities of the 0.2 % Er<sup>3+</sup>-doped ZBLAEN(I) glass and the closed circles represent those of the 0.2 % Er<sup>3+</sup>-3.8 % Tm<sup>3+</sup>-codoped ZBLAETN(IV) glass in which the doping ratio (Tm<sup>3+</sup>/Er<sup>3+</sup>) is about 20.

concentration, which enhances the green intensity as shown in Fig. 1 due to the energy transfer from Tm<sup>3+</sup> ion to Er<sup>3+</sup> ion.

Recently Zou *et al.* have also reported that the introduction of Tm<sup>3+</sup> into Er<sup>3+</sup> doped fluorozirconate glasses quenched the green upconversion fluorescence from Er<sup>3+</sup> ion due to the cross-relaxation of <sup>4</sup>I<sub>15/2</sub> → <sup>4</sup>I<sub>13/2</sub> (Er): <sup>3</sup>H<sub>6</sub> → <sup>3</sup>H<sub>4</sub>(Tm) at more than 3 mol % Er<sup>3+</sup> concentration<sup>[11]</sup>. Since the <sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>6</sub>(Tm) transition was neither enhanced nor quenched with the introduction of Er<sup>3+</sup> ion to 2 mol% Tm<sup>3+</sup>-doped glass as shown Fig. 2, we could conclude that the cross-relaxation of <sup>4</sup>I<sub>15/2</sub> → <sup>4</sup>I<sub>13/2</sub> (Er): <sup>3</sup>H<sub>6</sub> → <sup>3</sup>H<sub>4</sub>(Tm) was not dominant in our less than 2 mol % Er<sup>3+</sup>-doped fluorozirconate glasses.

Fig. 3. shows the intensities of the green emission of Er<sup>3+</sup>-singly doped and Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped glasses as functions of the 800 nm laser diode pumping power. For the Er<sup>3+</sup>-singly doped glass, the intensity of the green emission increases quadratically with pumping power, P<sub>ex</sub>. For Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped glass, the intensity of the green emission increases more rapidly than with (P<sub>ex</sub>)<sup>2</sup>. The intensity dependence of the <sup>4</sup>S<sub>3/2</sub> emission on the pumping power and its standard deviation are listed in Table 1. The <sup>4</sup>S<sub>3/2</sub> emission intensities increases more rapidly with increasing doping ratio (x/y) of Tm<sup>3+</sup> to Er<sup>3+</sup> ion.

Fig. 4. shows the energy diagram of the Er<sup>3+</sup> and the Tm<sup>3+</sup> ion for the green emission from both the Er<sup>3+</sup>-singly doped glasses (a) and the Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped glasses

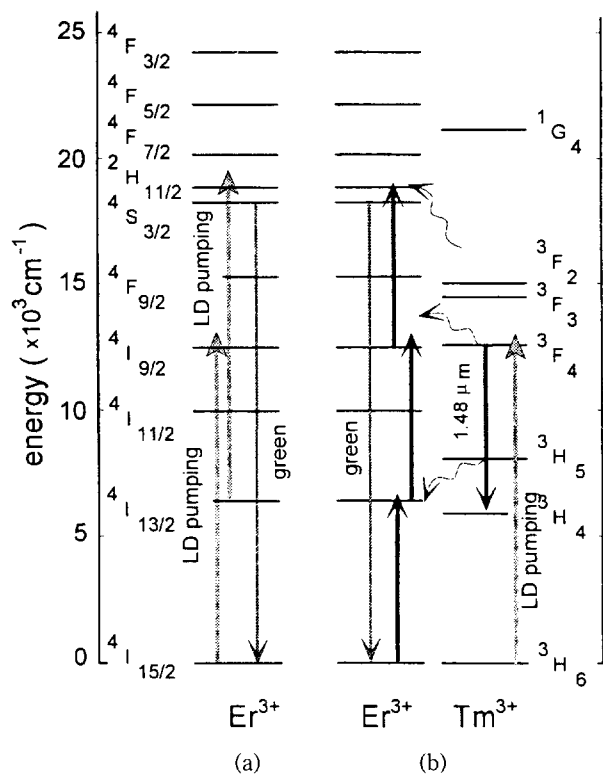


Fig. 4. The two kinds of possible upconversion mechanism for the green emission from the Er<sup>3+</sup> ions in Er<sup>3+</sup>-Tm<sup>3+</sup>-codoped glasses pumped with 800 nm. The two-photon absorption of the laser pumping light populates the <sup>4</sup>S<sub>3/2</sub> level of the Er<sup>3+</sup> ion (a). The three-photon absorption of the 1.48 μm emission populates the <sup>4</sup>S<sub>3/2</sub> level of the Er<sup>3+</sup> ion (b). The wavy arrows in (b) represent the possible energy transfer of the 1.48 μm emission from Tm<sup>3+</sup> to Er<sup>3+</sup> ion.

(b). The 800 nm laser line is absorbed on both <sup>4</sup>I<sub>15/2</sub> level of Er<sup>3+</sup> and <sup>3</sup>F<sub>4</sub> level of Tm<sup>3+</sup> ion.

When the <sup>4</sup>S<sub>3/2</sub> energy level of Er<sup>3+</sup> ion is populated via two photon absorption as shown in Fig. 4 (a), the intensity of the green emission from <sup>4</sup>S<sub>3/2</sub> to <sup>4</sup>I<sub>13/2</sub> transition on Er<sup>3+</sup> ion increased in proportion to (P<sub>ex</sub>)<sup>2</sup>. This quadratic dependence of the green intensity on the pumping intensity has been reported<sup>[9]</sup>.

In the case that the <sup>4</sup>S<sub>3/2</sub> energy level of Er<sup>3+</sup> ion is populated by three-photon absorption as shown in Fig. 4 (b), the green emission from <sup>4</sup>S<sub>3/2</sub> level has a cubic dependence on the pump intensity. This multistep excited state absorption (ESA) could be applied to our Tm<sup>3+</sup>-Er<sup>3+</sup>-codoped system where the 1.48 μm emission from the <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>4</sub> transition on Tm<sup>3+</sup> ions decreased through the energy transfer to Er<sup>3+</sup> ion as shown in Fig. 2. This energy transfer could be confirmed by the enhanced green intensity in Fig. 1. It has been also reported that the 1.48 μm emission from Tm<sup>3+</sup> transferred to Er<sup>3+</sup> and enhanced the green intensity in zirconiumfluoride glasses pumped by the 800 nm laser diode<sup>[9]</sup>.

Therefore the green fluorescence from <sup>4</sup>S<sub>3/2</sub> level of

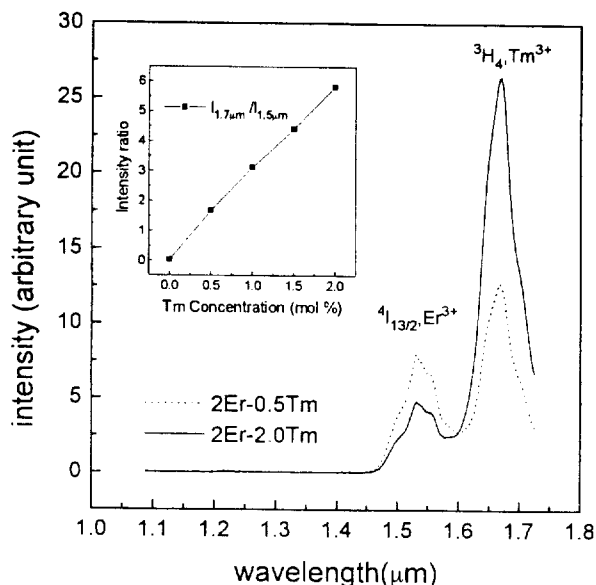


Fig. 5. The quenching effect of the  ${}^4I_{13/2}$  level in  $Er^{3+}$  due to the energy transfer to  ${}^3H_4$  in  $Tm^{3+}$  when pumped with  $1.06 \mu m$ . As  $Tm^{3+}$  ions were added to the constant 2 mol % Er-doped glasses, the emission intensity from  ${}^4I_{13/2}$  level in  $Er^{3+}$  decreased while the emission from the  ${}^3H_4$  level in  $Tm^{3+}$  increased. An inset shows that the normalized emission intensity of  ${}^3H_4$  in  $Tm^{3+}$ , based on the intensity of the  ${}^4I_{13/2}$  in  $Er^{3+}$ .

$Er^{3+}$  ion, excited via the two step absorption, has a quadratic dependence on the pump intensity, while it has a cubic dependence when excited via three-step absorption. When the  ${}^4S_{3/2}$  level was populated by both the two-step absorption and the three-step absorption as shown in Fig. 4 (a) and (b), the intensity dependence of the green emission on the pumping power would range between  $(P_{ex})^2$  and  $(P_{ex})^3$  and approach to  $(P_{ex})^3$  according to the contribution of the three step absorption.

Table 1. shows the  $Tm^{3+}/Er^{3+}$  doping ratio and the intensity dependence of the green emission. As the  $Tm^{3+}/Er^{3+}$  concentration ratio increases, the intensity dependence approaches from  $(P_{ex})^2$  to  $(P_{ex})^3$ . This means that the three step absorption of the  $1.48 \mu m$  emission from the  $Tm^{3+}$  ion to the  ${}^4S_{3/2}$  level of the  $Er^{3+}$  ion has become more dominant as the  $Tm^{3+}$ -doping concentration relatively increased. For the example, the intensity dependence of the green emission on the pumping power has been  $(P_{ex})^2$  for the 0.2 mol %  $Er^{3+}$ -singly doped glass ( $Tm^{3+}/Er^{3+}$  doping ratio = 0), and  $(P_{ex})^{2.7}$  for the 0.2 %  $Er^{3+}$ -3.8 %  $Tm^{3+}$ -codoped glass ( $Tm^{3+}/Er^{3+}$  doping ratio =  $\sim 20$ ). It was expected that the green intensity dependence on the pump power would approach the cubic dependence  $(P_{ex})^3$  with a higher doping ratio (x/y) than 20. In other words, the energy transfer of  ${}^3F_4(Tm) \rightarrow {}^4I_{13/2}, {}^4I_{9/2}, {}^4S_{3/2}(Er)$  would be dominant if  $Tm^{3+}$  ions were added to  $Er^{3+}$ -doped glasses und-

er the 800 nm pumping scheme.

Fig. 5 shows a well-known quenching effect of the  ${}^4I_{13/2}$  level in  $Er^{3+}$  due to the energy transfer to  ${}^3H_4$  in  $Tm^{3+}$  when pumped at the  $1.06 \mu m$ . Several investigators have also reported that  $Tm^{3+}$  ion effectively quenched the levels of  $Er^{3+}$  ion in other material matrixes. For example, Yeh et al. have reported that  $Tm^{3+}$  preferentially quenches the upconversion efficiency of the green emission from the  $Er^{3+}$  ion in a barium-thorium fluoride glass<sup>45</sup>. In their models for upconversion in  $Er^{3+}$ - $Tm^{3+}$  system, the  ${}^4I_{11/2}$  level of  $Er^{3+}$  was pumped as a first step absorption of which energy could not effectively pump the  ${}^3F_4$  level of  $Tm^{3+}$  ion. Since the  $1.06 \mu m$  YAG laser can not pump any level on  $Tm^{3+}$  except the  ${}^4I_{11/2}$  level in our  $Er^{3+}$ - $Tm^{3+}$ -codoped system, it was deemed appropriate to determine the energy transfer from  $Er^{3+}$  to  $Tm^{3+}$ . For the effective  $1.48 \mu m$  transfer from  $Tm^{3+}$  ion to be suppressed, the  ${}^3F_4$  level should not be resonantly pumped. As Tm ions were added to the constantly 2 mol % Er-doped glasses, the emission intensity from  ${}^4I_{13/2}$  level in  $Er^{3+}$  decreased while the emission from the  ${}^3H_4$  level in  $Tm^{3+}$  increased.

An inset in the Fig. 5 shows that the normalized emission intensity of  ${}^3H_4$  in  $Tm^{3+}$ , based on that of the  ${}^4I_{13/2}$  in  $Er^{3+}$ , almost linearly increased with the increasing Tm concentration up to 2 mol %. This linearity suggests that the directional cross-relaxation of  ${}^4I_{13/2} \rightarrow {}^4I_{13/2}(Er) : {}^3H_4 \rightarrow {}^3H_4(Tm)$  was maintained in our less than 2 mol %  $Er^{3+}$ -doped fluorozirconate glasses when pumped at  $1.06 \mu m$ .

#### IV. CONCLUSIONS

Energy transfer in  $Er^{3+}$ - $Tm^{3+}$ -codoped fluorozirconate glasses was studied for several  $Tm^{3+}/Er^{3+}$  doping ratios under the 800 nm and  $1.06 \mu m$  pumping scheme. For  $Er^{3+}$ - $Tm^{3+}$ -codoped glasses excited at the 800 nm, the green emission intensity increased between  $(P_{ex})^2$  and  $(P_{ex})^3$ . The variation of the intensity dependence on the pumping power showed that the emission of  ${}^3F_4(Tm) \rightarrow {}^3H_4(Tm)$  could increasingly transfer into  ${}^4I_{13/2}, {}^4I_{9/2}$ , and  ${}^4S_{3/2}(Er)$  as  $Tm^{3+}$  ions were added to  $Er^{3+}$ -doped glasses under the 800 nm pumping scheme. When the  ${}^3F_4$  level in  $Tm^{3+}$  was not resonantly pumped, the energy transfer of  ${}^4I_{13/2}(Er)$  to  ${}^3H_4(Tm)$  became dominant due to the cross-relaxation of  ${}^4I_{13/2} \rightarrow {}^4I_{13/2}(Er) : {}^3H_4 \rightarrow {}^3H_4(Tm)$ .

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