# Near Infrared Broadband Emission and Spectroscopic Properties of Tm<sup>3+</sup>/Nd<sup>3+</sup> Codoped Optical Fiber

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Abstract: The emission bands at 934, 1083, 1279, 1362, 1414 and 1720 nm were found to appear from the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fiber upon excitation at 633 nm. Near infrared emissions of Tm<sup>3+</sup> at 1279, 1414 and 1720 nm confirmed a very efficient energy transfer (ET) between Tm<sup>3+</sup> and Nd<sup>3+</sup> ions. Since the emission band of Nd<sup>3+</sup> at 1362 nm helped to bridge the wavelength gap between the emission peaks of Tm<sup>3+</sup> at 1279 and 1414 nm, the ET process made the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber applicable in broadband fiber laser operating around 1215–1515 nm. Further, cross-sections for the respective bands, spectroscopic properties and nonlinear characteristics of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber were investigated.

# **1 INTRODUCTION**

Because of the impact of wavelength division multiplexing (WDM) telecommunication systems, broadband light source and broadband amplifier have been received growing attention in world-wide optical communication (Tanabe, 2002). Nonetheless, rare-earth (RE) ions, so widely used as laser-active media in optical fiber, commonly have narrow absorption and emission bands arising from the parity-forbidden 4f-4f transitions (Zabicky, 2009). In order to broaden the emission bandwidth, the most attractive method is that RE ions are codoped into the core of the fiber where the energy transfer (ET) process takes place between different species of ions (Tanabe, 2002). Moreover, such ET process favours emission efficiency and enhances the gain of an amplifier (Brandão et al., 2006).

The present work, codoping Nd<sup>3+</sup> as a sensitizer for Tm<sup>3+</sup> in the core of the fiber, was concerned with the needs of broadband fiber laser and amplifier for future optical communication. The motivation for our investigation was that the emission of Nd<sup>3+</sup> around 1340 nm can fill the wavelength gap complementing the emission of  $\text{Tm}^{3+}$  in short wavelength band (S-band, 1460–1530 nm) (Shen et al., 2002). Moreover, since two excited levels, i.e., Nd<sup>3+</sup>: <sup>4</sup>F<sub>3/2</sub> and Tm<sup>3+</sup>: <sup>3</sup>H<sub>4</sub>, are well matched (Tanabe et al., 2000), the ET process is likely to occur and the lifetime of the Nd<sup>3+</sup> at <sup>4</sup>F<sub>3/2</sub> level is long enough to induce efficient ET. And, the large absorption cross-section of Nd<sup>3+</sup> around 600 nm provides powerful absorption for effective pumping with commercially available lasers (Zhang et al., 2010).

Although the enhancement of upconversion emission efficiency by using Nd<sup>3+</sup> as a sensitizer for Tm<sup>3+</sup> (Rakov et al., 2009); (Rakov et al., 2002) and the ET process between them (Brandão et al., 2006); (Chung and Heo, 200); (Lahoz et al., 2008); (Tanabe et al., 2000) were reported in different host materials, no broadband near infrared (NIR) emission of Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped silicate optical fiber was investigated. In this study, a wide range of NIR emission spectrum broadening from 1215 to 1515 nm with FWHM of 158 nm has been studied in Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber upon exciting at 633 nm.

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Further, the spectroscopic parameters of the  $Tm^{3+}/Nd^{3+}$  codoped fiber was determined by applying the Judd-Ofelt (JO) analysis. Furthermore, cross-sections for the respective bands were investigated and consequently its nonlinear optical properties were elucidated.

# 2 EXPERIMENTAL

Silicate glass-based optical fibers: Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber, Tm<sup>3+</sup> doped fiber and Nd<sup>3+</sup> doped fiber, were drawn from the preforms fabricated by a modified chemical vapour deposition (MCVD) process. The rare earth ions were incorporated into the core of the preforms using conventional solution doping method. The optical parameters of the fibers are listed in Table 1.

Table 1: The optical parameters, viz., refractive index on difference between the core and the cladding ( $\Delta$ n), core diameter (*d*) and cutoff wavelength ( $\lambda_c$ ), of the Tm<sup>3+</sup> doped, the Nd<sup>3+</sup> doped and the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fibers.

| Fiber name                         | Concentration (M%) | Δn     | d (um) | $\lambda_{c}$ (um) |
|------------------------------------|--------------------|--------|--------|--------------------|
| Tm <sup>3+</sup> doped             | 0.03 of Tm         | 0.0020 | 7.20   | 0.79               |
| Nd <sup>3+</sup> doped             | 0.03 of Nd         | 0.0051 | 8.44   | 1.34               |
| Tm <sup>3+</sup> /Nd <sup>3+</sup> | 0.10 of Tm         | 0.0039 | 7 52   | 1 25               |
| codoped                            | 0.05 of Nd         | 0.0039 | 1.52   | 1.23               |

The absorption spectra of the fibers were measured by the cutback method using optical spectrum analyzer (OSA) and white light source. To measure emission spectrum, the fibers were excited by a He-Ne laser (Melles Griot 9132EW-1) operating at 633 nm and the spectral output power was detected by an OSA. The fluorescent lifetime of the  $Tm^{3+}/Nd^{3+}$ codoped fiber was detected by an InGaAs photodetector, while  ${}^{4}F_{3/2}$  level of Nd<sup>3+</sup> was excited by a cw-Ti:sapphire laser (Mira-900, Coherent) operating at 800 nm.

To determine the nonlinear optical parameters, wavelength dependence of refractive indices of the  $Tm^{3+}/Nd^{3+}$  codoped fiber preform was measured by using a prism coupler (Sairon: SPA-4000). To avoid unnecessary measurement error due the relatively small core of the fiber preform (0.97 mm), the obtained refractive index results were compared with those of the GeO<sub>2</sub> doped SiO<sub>2</sub> glass, whereas both have GeO<sub>2</sub> concentration of nearly 3.1 M% (Kobayashi et al., 1977); (Kobayashi et al., 1978). Note that the refractive indices were taken by assuming that effect of  $Tm^{3+}$  and  $Nd^{3+}$  on them is

negligible due to their low concentrations.

# **3** THEORY

The measured line strength of the selected band can be determined by (Judd, 1962):

$$S_{med}(J \to J') = \frac{3ch(2J+1)n}{8\pi^3 \lambda_{peak} e^2 N} \left[ \frac{9}{(n^2+2)^2} \right] \Gamma \qquad (1)$$

where J and J' are the total angular momentum quantum numbers of initial and final states, respectively. c, h, n,  $\lambda_{peak}$ , e, N and  $\Gamma$  are the velocity of light, the Plank constant, the refractive index of glass, the peak absorption wavelength, the charge of the electron, the ion concentration and the integrated absorption coefficient, respectively.

Then, the calculated line strength, which depends on three parameters known as the JO parameters  $(\Omega_t, t = 2, 4, 6)$ , is defined as:

$$S_{cal}(J \to J') = \sum_{(t=2,4,6)} \Omega_t \left| \left\langle J \left\| U^{(t)} \right\| J' \right\rangle \right|^2.$$
(2)

In our calculations,  $|\langle J || U^{(r)} || J' \rangle|^2$ , the value of the double reduced matrix elements, was taken from Carnall et al. (Carnall et al., 1968). The radiative transition probability (*A*), the radiative lifetime ( $\tau_r$ ) and the fluorescence branching ratio ( $\beta$ ) are described as:

$$A(J \to J') = \frac{64\pi^4 e^2 n(n^2 + 2)^2}{3h\lambda_{peak}^3 (2J+1)9} S_{cal}(J \to J'), \quad (3)$$

$$\tau_r = \frac{1}{\sum A(J \to J')} \text{ and }$$
(4)

$$\beta(J \to J') = \frac{A(J \to J')}{\sum A(J \to J')} = A(J \to J')\tau_r.$$
 (5)

The emission cross-sections were determined by the Fuchtbauer-Ladenburg (FL) relation (Aull and Jenssen, 1982); (Fowler and Dexter, 1962); (Krupke, 1974) using the radiative parameters and the effective line width ( $\Delta \lambda_{eff}$ ) as follows:

$$\sigma_{e}\left(\lambda_{peak}\right) = \frac{\lambda_{peak}^{4} A(J \to J')}{8\pi c n^{2} \Delta \lambda_{eff}}.$$
(6)

The nonlinear optical parameters, viz., Abbe number  $(v_e)$ , nonlinear refractive index  $(n_2)$ , nonlinear

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refractive index coefficient ( $\gamma$ ) and susceptibility ( $\chi$ ), were evaluated by the following equations (Boling and Glass, 1978); Milam and Weber, 1976); (Weber et al., 1983):

$$V_{e} = \frac{n_{e} - 1}{n_{f} - n_{c}},$$
(7)

$$n_{2} = \frac{68(n_{e} - 1)(n_{e}^{2} + 2)^{2}}{v_{e}\sqrt{1.517 + \frac{(n_{e}^{2} + 2)(n_{e} + 1)v_{e}}{6n_{e}}}},$$
(8)
(in 10<sup>-13</sup> esu)

$$\gamma = 4\pi \times 10^3 n_2 / (cn_e) \text{ (in m}^2/\text{W) and } (9)$$

$$\chi = \left(\frac{4}{3}\right) \gamma c n_e^2 \varepsilon_0 \ (\text{in } \text{m}^2/\text{ V}^2) \tag{10}$$

where  $n_e$ ,  $n_f$  and  $n_c$  are the refractive indices at 546.1, 480, and 643.8 nm, respectively;  $\varepsilon_0$  is the permittivity of free space.

#### 4 **RESULTS AND DISCUSSION**

#### 4.1 **Absorption Spectrum**

SCIENCE

The absorption spectrum of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber measured over the wavelength range of 400-1700 nm with corresponding electronic energy levels is shown in Figure 1. As a comparison, the absorption spectra of the Tm<sup>3+</sup> doped and the Nd<sup>3+</sup> doped fibers are shown in Figure 2. In the absorption spectrum of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber, the absorption bands of Tm<sup>3+</sup> and Nd<sup>3+</sup> were overlapped as follows:

- 466 nm, Tm<sup>3+</sup>:  ${}^{3}H_{6} \rightarrow {}^{1}G_{4}$  and (i) Nd<sup>3+</sup>:  ${}^{4}I_{9/2} \rightarrow {}^{2}K_{15/2} + {}^{4}G_{11/2} + {}^{2}D_{3/2} + {}^{2}G_{9/2},$ (ii) 679 nm, Tm<sup>3+</sup>:  ${}^{3}H_{6} \rightarrow {}^{3}F_{2} + {}^{3}F_{3}$  and
- Nd<sup>3+</sup>:  ${}^{4}I_{9/2} \rightarrow {}^{4}F_{9/2}$ ,
- (iii) 784 nm,  $\text{Tm}^{3+}$ :  ${}^{3}\text{H}_{6} \rightarrow {}^{3}\text{H}_{4}$  and
- Nd<sup>3+</sup>:  ${}^{4}I_{9/2} \rightarrow {}^{2}H_{9/2} + {}^{4}F_{5/2}$ , (iv) 1575 nm, Tm<sup>3+</sup>:  ${}^{3}H_{6} \rightarrow {}^{3}F_{4}$  and Nd<sup>3+</sup>:  ${}^{4}I_{9/2} \rightarrow {}^{4}I_{15/2}$ .

Among them, the absorption intensity of the peak at 784 nm was higher than that of the others, since it was a combination of the strong absorption of Tm<sup>3+</sup>:  ${}^{3}\text{H}_{4}$  and Nd<sup>3+</sup>:  ${}^{2}\text{H}_{9/2}$ + ${}^{4}\text{F}_{5/2}$  levels (Rakov et al., 2009). In addition, the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber illustrated five well separated absorption bands. The bands were composed of a single separated absorption band of Tm<sup>3+</sup> at 1212 nm ( ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$  transition) and

four separated absorption bands of Nd<sup>3+</sup> located at 528, 582, 750 and 889 nm. They are corresponding to the transitions from  ${}^{4}I_{9/2}$  to  ${}^{2}K_{13/2} + {}^{4}G_{7/2}$ ,  ${}^{4}G_{5/2} +$  ${}^{2}G_{7/2}$ ,  ${}^{4}S_{3/2}$ + ${}^{4}F_{7/2}$  and  ${}^{4}F_{3/2}$ , respectively.

In the case of the Nd<sup>3+</sup> doped fiber, the absorption intensity of the peak at 582 nm was stronger than that of the others since it is dominant in silicate glasses (Stokowski et al., 1981); (Thomas et al., 1992), whereas for fluoride glasses it is comparable with that of 800 nm (Binnemans et al., 1998); (Digonnet, 1993); (Lucas et al., 1978). Since the absorption peak locations of Nd<sup>3+</sup> at 750 nm  $({}^{4}S_{3/2} + {}^{4}F_{7/2})$  and 810 nm  $({}^{2}H_{9/2} + {}^{4}F_{5/2})$  were close to the absorption peak of Tm<sup>3+</sup> at 791 nm (<sup>3</sup>H<sub>4</sub>, in Figure 2) (Chung et al., 1997), absorption bands located around 750 and 784 nm seemed to be overlapped each other in the codoped fiber as illustrated in Figure 1. Note that the peaks around 1383 nm indicated the presence of OH ions in the core of the fibers.

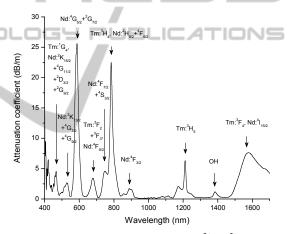


Figure 1: Absorption spectrum of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fiber.

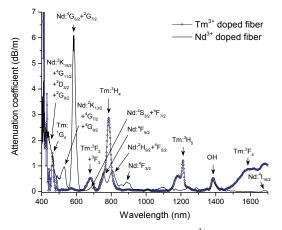


Figure 2: Absorption spectra of the Tm<sup>3+</sup> doped and the Nd<sup>3+</sup> doped optical fibers.

### 4.2 Emission Spectrum

In the absorption spectrum of the  $\text{Tm}^{3+}/\text{Nd}^{3+}$  codoped fiber, two obvious absorption bands existed at 582 and 784 nm. The former was the absorption of  $\text{Nd}^{3+}$  alone, but the latter was the absorption of both  $\text{Nd}^{3+}$  and  $\text{Tm}^{3+}$ . Therefore, the 582 nm absorption band was selected as a pump band to investigate an ET from  $\text{Nd}^{3+}$  to  $\text{Tm}^{3+}$ . The commercially available He-Ne laser was used to excite  $\text{Nd}^{3+}$  ions in the fiber core by coupling the laser light at 620 and 633 nm into the fiber core with the power of 0.01 and 4.4 mW, respectively.

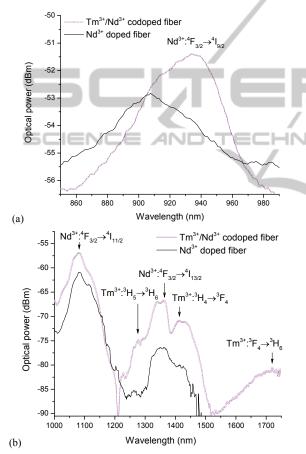


Figure 3: Emission spectra of the  $\text{Tm}^{3+}/\text{Nd}^{3+}$  codoped and the  $\text{Nd}^{3+}$  doped fibers upon pumping with He-Ne laser at 633 nm over the wavelength range of (a) 850–990 nm and (b) 1000–1750 nm. The fiber lengths used were 20 m.

The NIR emission spectrum of the  $\text{Tm}^{3+}/\text{Nd}^{3+}$  codoped fiber comparing with that of the Nd<sup>3+</sup> doped fiber upon pumping at 633 nm is shown in Figure 3. The emission bands appeared at 934, 1083 and 1362 nm from Nd<sup>3+</sup> ions in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber. Another emission bands from Tm<sup>3+</sup> also appeared at 1279, 1414 and 1720 nm. On account of the

emissions contributed from  $Nd^{3+}$ , the NIR emission spectrum of the  $Tm^{3+}/Nd^{3+}$  codoped fiber was broadened from 1215 to 1515 nm. On the other hand, the  $Nd^{3+}$  doped fiber showed the emission bands only at 934, 1083 and 1362 nm (Zhang et al., 2006) by exciting at 633 nm. No emission band was observed in the  $Tm^{3+}$  doped fiber upon pumping at 633 nm.

Figure 4 illustrates the electronic energy level diagram of Tm<sup>3+</sup> and Nd<sup>3+</sup> ions. The mechanism of the emission and ET process can be explained as follows. When the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber was pumped at 633 nm, Nd<sup>3+</sup> ions from the ground state  $({}^{4}I_{9/2})$  were excited to  ${}^{4}G_{5/2} + {}^{2}G_{7/2}$  and subsequently, decayed to the  ${}^{4}F_{3/2}$  metastable state. The emission bands of Nd<sup>3+</sup> appeared at 934, 1083 and 1362 nm correspond to the transitions from  ${}^{4}F_{3/2}$  to  ${}^{4}I_{9/2}$ ,  ${}^{4}I_{11/2}$ , and <sup>4</sup>I<sub>13/2</sub>, respectively. Because of the presence of competing emissions from the same level  $({}^{4}F_{3/2})$ , the emission intensity of the peak at 1362 nm was not as strong as that at 934 and 1083 nm (Choi et al., 2003); (Zhang et al., 2006). In addition, after the fast nonradiative decay processes, the ET process took place between two excited levels Nd3+: 4F3/2 and Tm<sup>3+</sup>: <sup>3</sup>H<sub>4</sub>. These two energy levels matched with the estimated energy gap of about  $1\Box 10^3$  cm<sup>-1</sup> (Tanabe et al., 2000).

As a result of the ET process, the  $\text{Tm}^{3+}/\text{Nd}^{3+}$ codoped fiber showed the emissions of  $\text{Tm}^{3+}$  around 1279, 1414 and 1720 nm. They are related to the radiative decay from  ${}^{3}\text{H}_{5} \rightarrow {}^{3}\text{H}_{6}$ ,  ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  and  ${}^{3}\text{F}_{4}$  $\rightarrow {}^{3}\text{H}_{6}$  transitions, respectively. The emission spectrum over the wavelength of 1750 nm was not possible to detect due to the limitation of the OSA.

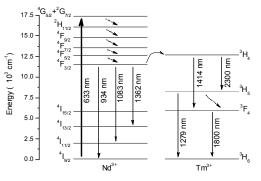


Figure 4: Schematic electronic energy levels and transitions of  $\text{Tm}^{3+}$  and  $\text{Nd}^{3+}$  ions upon exciting at 633 nm. Bold arrow, solid thin arrows, curved arrow and dashed arrows represent the pump wavelength, the emission wavelengths, the ET process and the nonradiative decays, respectively.

### 4.3 JO Parameters

The JO analysis was applied using the absorption bands of Nd<sup>3+</sup> in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fiber to characterize its spectroscopic properties. The concentration of Tm<sup>3+</sup> and Nd<sup>3+</sup> in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fiber was approximately taken as  $1.76 \times 10^{25}$  m<sup>-3</sup> and  $0.91 \times 10^{25}$  m<sup>-3</sup>, respectively. They were estimated from the  $Tm^{3+}$  doped and the  $Nd^{3-}$ doped optical fiber fabricated by modified solution doping method (Han and Kim, 2002). The values of the JO parameters were, respectively, 8.16×10<sup>-24</sup>,  $3.20 \times 10^{-24}$  and  $2.67 \times 10^{-24}$  m<sup>2</sup> for  $\Omega_2$ ,  $\Omega_4$  and  $\Omega_6$ . The JO intensity parameters of the present work compared with the results of the  $Tm^{3+}/Nd^{3+}$  codoped glasses (Brandão et al., 2006); (Chung and Heo, 2001), the Tm doped fibers (Peterka et al., 2004); (Walsh and Barnes, 2004), and the Nd doped fiber preform and glass (Martinez et al., 1998); (Thomas et al., 1992) are listed in Table 2.

The JO parameters obtained in the present work indicated the trend as  $\Omega_2 > \Omega_4 > \Omega_6$  as the same trend has been found in previous reports (Chung and Heo, 2001); (Martinez et al., 1998); (Thomas et al., 1992); (Walsh and Barnes, 2004). Nevertheless, the trend of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped glass (Brandão et al., 2006) showed higher  $\Omega_6$  than  $\Omega_4$  ( $\Omega_2 > \Omega_6 > \Omega_4$ ). Since the intensity parameter  $(\Omega_2)$  is related to the degree of covalence (Digonnet, 1993), the large value of  $\Omega_2$  in the present work indicates the presence of covalent bonding between Tm<sup>3+</sup> and Nd<sup>3+</sup>. It is known that ionic metals like fluoride and fluorophosphates glasses have very small values of  $\Omega_2$  (Binnemans et al., 1998), whereas covalent materials like silicate glasses have large values.  $\Omega_6$ is related to the rigidity of material and the higher ratio of  $\Omega_4/\Omega_6$  (= 1.2) implies that the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber possessed a good spectroscopic quality.

# 4.4 The Spectroscopic and Nonlinear Optical Parameters

The values of line strengths and absorption crosssections from the transitions of  ${}^{4}I_{9/2}$  to respective higher energy levels are listed in Table 3. The rms deviation (Yanbo et al., 2006) of the calculated and measured absorption line strengths was  $2.99 \times 10^{-25}$ m<sup>2</sup>. The spectroscopic parameters of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber are summarized in Table 4. In the transitions of Tm<sup>3+</sup>, the radiative transition probabilities were dominated by  ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transition. In addition,  ${}^{3}H_{5} \rightarrow {}^{3}H_{6}$  and  ${}^{3}F_{4} \rightarrow {}^{3}H_{6}$  transitions had strong line strengths and radiative transition probabilities which were the good evidence of the emissions of  $\text{Tm}^{3+}$  around 1279 nm (Yang, et al., 2006) and 1720 nm (Zou and Toratani, 1996). For the spectroscopic parameters of Nd<sup>3+</sup>,  ${}^{4}\text{F}_{3/2} \rightarrow {}^{4}\text{I}_{11/2}$  transition was more dominant than that of the others (Digonnet, 1993).

The branching ratios of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber hold the same significance as previous reports (Stokowski et al., 1981); (Thomas et al., 1992); (Walsh and Barnes, 2004); (Watekar et al., 2006). For the transitions originated from <sup>3</sup>H<sub>4</sub> level of Tm<sup>3+</sup>, the <sup>3</sup>H<sub>4</sub>  $\rightarrow$  <sup>3</sup>H<sub>5</sub> transition indicates the smallest branching ratios (1.57%). Therefore, the <sup>3</sup>H<sub>5</sub> level was not well populated and the emission efficiency of 1279 nm was generally smaller than that of 1414 nm (Heo et al., 1997). In general, Nd<sup>3+</sup> doped silica glass favours the <sup>4</sup>F<sub>3/2</sub>  $\rightarrow$  <sup>4</sup>I<sub>11/2</sub> transition and the branching ratio of it is closed to 50%.

When comparing the radiative lifetimes of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber with those of previous studies, the radiative lifetimes of Tm<sup>3+</sup> at <sup>3</sup>H<sub>5</sub> and <sup>3</sup>F<sub>4</sub> levels agreed well with those found by others (Peterka et al., 2004); (Walsh and Barnes, 2004), whereas the radiative lifetime of Tm<sup>3+</sup> at <sup>3</sup>H<sub>4</sub> level was slightly lower than that reported in previous studies (Peterka et al., 2004); (Walsh and Barnes, 2004); (Watekar et al., 2006). Moreover, the radiative lifetime of upper level ( ${}^{3}H_{4}$ , 0.54 ms) was too short to achieve the desired population inversion than that of the lower level ( ${}^{3}F_{4}$ , 3.70 ms). This is normally termed a self-terminating transition (Quimby and Miniscalco, 1989). As a result, in the glasses doped with Tm<sup>3+</sup> only, the population inversion is not possible under 800 nm excitation and the emission spectrum was hardly recorded (Lee et al., 2003). In the case of the radiative lifetime of  $Nd^{3+}$  in the  $Tm^{3+}/Nd^{3+}$  codoped fiber, that of  ${}^{4}F_{3/2}$ level was found to increase (Lu and Dutta, 2001); (Thomas et al., 1992); Yanbo et al., 2006). It is noted that the molar ratio of  $Tm^{3+}$  to  $Nd^{3+}$  (= 2) was a clear evidence of the optimum composition to deplete the clustering of the Nd<sup>3+</sup> ions (Chung et al., 1997). Since the clustering effect causes fast decay in the emission spectrum, it decreases the total radiative lifetime (Lu and Dutta, 2001).

The fluorescence lifetime of  ${}^{4}F_{3/2}$  level in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber upon exciting at 800 nm was 0.56 ms. It was more than or nearly equal to that reported by others (Krupke, 1974); (Stokowski et al., 1981); (Thomas et al., 1992). Nonradiative lifetime ( ${}^{4}F_{3/2}$  level) and radiative quantum efficiency (Krupke, 1974) of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber were 0.67 ms and 0.17, respectively. Because of the poor

| JO<br>parameter<br>(10 <sup>-24</sup> m <sup>2</sup> ) | Present<br>work | Tm <sup>3+</sup> /Nd <sup>3+</sup><br>codoped glass<br>(Brandão, et<br>al., 2006) | Tm <sup>3+</sup> /Nd <sup>3+</sup><br>codoped glass*<br>(Chung & Heo,<br>2001) | Tm doped<br>fiber<br>(Peterka, et<br>al., 2004) | Tm doped<br>fiber (Walsh<br>& Barnes,<br>2004) | Nd doped<br>fiber preform<br>(Martinez, et<br>al., 1998) | Nd doped<br>glass<br>(Thomas, et<br>al., 1992) |
|--|-----------------|---|--|---|--|--|--|
| $\Omega_2$   | $8.16\pm0.30$   | 7.28  | 3.74   | 3.26  | 6.23   | 5.81   | 9.31   |
| $\Omega_4$   | $3.20\pm0.13$   | 4.55  | 1.43   | 1.20  | 1.91   | 3.80   | 4.13   |
| $\Omega_6$   | $2.67 \pm 0.23$ | 6.18  | 1.09   | 0.46  | 1.36   | 2.42   | 3.91   |

Table 2: Comparison of the JO parameters in different types of materials.

\*The JO intensity parameters were taken from Tm<sup>3+</sup> doped glasses.

Table 3: The values of absorption cross-section ( $\sigma_a$ ), measured line strength ( $S_{med}$ ) and calculated line strength ( $S_{cal}$ ) estimated based on the absorption bands of Nd<sup>3+</sup> in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber.

| Transitions<br>(from <sup>4</sup> I <sub>9/2</sub> ) | λ <sub>peak</sub><br>(nm) | n (λ) | $(10^{-25} \text{ m}^2)$ | $\frac{S_{med}}{(10^{-24} \text{ m}^2)}$ | $\frac{S_{cal}}{(10^{-24} \text{ m}^2)}$ | $(\Delta S)^2$<br>(10 <sup>-50</sup> m <sup>4</sup> ) |
|--|---------------------------|-------|--------------------------|--|--|---|
| ${}^{2}K_{13/2} + {}^{4}G_{7/2} + {}^{4}G_{9/2}$     | 528                       | 1.481 | 4.38                     | 1.58                                     | 1.58                                     | 0.00  |
| ${}^{4}G_{5/2} + {}^{2}G_{7/2}$                      | 582                       | 1.473 | 23.12                    | 10.29                                    | 10.03                                    | 6.76  |
| ${}^{4}F_{7/2} + {}^{4}S_{3/2}$                      | 750                       | 1.460 | 4.32                     | 1.77                                     | 1.91                                     | 1.96  |
| ${}^{4}F_{3/2}$                                      | 889                       | 1.453 | 1.03                     | 0.83                                     | 0.88                                     | 0.25  |

Table 4: The spectroscopic parameters, viz., calculated line strength ( $S_{cal}$ ), radiative transition probabilities ( $A_{JJ'}$ ), fluorescence branching ratios ( $\beta_{JJ'}$ ), radiative lifetimes ( $\tau_r$ ), effective linewidths ( $\Delta \lambda_{eff}$ ) and emission cross-sections ( $\sigma_e$ ), of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber estimated along with peak emission wavelengths.

|   | Transitions  | λ <sub>peak</sub><br>(nm) | <i>n</i> (λ) | $\frac{S_{cal}}{(10^{-24} \text{ m}^2)}$ | $A_{JJ'}(s^{-1})$ | β <sub>JJ'</sub> (%) | $\begin{array}{c} \tau_r \\ (ms) \end{array}$ | $\Delta\lambda_{e\!f\!f}$ (nm) | $(10^{-25} \text{ m}^2)$ |
|---|--|---------------------------|--------------|--|-------------------|----------------------|---|--------------------------------|--------------------------|
|   | $^{3}\text{H}_{5} \rightarrow ^{3}\text{H}_{6}$              | 1279                      | 1.446        | 3.32                                     | 281.01            | 98.64                | 2.51  | 35.33                          | 13.50                    |
|   | ${}^{3}\text{H}_{5} \rightarrow {}^{3}\text{F}_{4}$          | 3870                      | 1.434        | 1.30                                     | 3.87              | 1.36                 | 3.51  | -                              | -                        |
| Tm <sup>3+</sup>  | $^{3}\text{H}_{4} \rightarrow ^{3}\text{H}_{6}$              | 800                       | 1.457        | 3.87                                     | 1674.71           | 90.14                | 0.54  | -                              | -                        |
|   | $^{3}\text{H}_{4} \rightarrow ^{3}\text{F}_{4}$              | 1414                      | 1.444        | 2.02                                     | 154.11            | 8.29                 |   | 61.08                          | 6.41                     |
|   | $^{3}\text{H}_{4} \rightarrow ^{3}\text{H}_{5}$              | 2300                      | 1.440        | 1.66                                     | 29.10             | 1.57                 |   | -                              | -                        |
|   | ${}^{3}F_{4} \rightarrow {}^{3}H_{6}$                        | 1800                      | 1.442        | 7.35                                     | 270.18            | 100.00               | 3.70  | -                              | -                        |
| Nd <sup>3+</sup> $\frac{{}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}}{{}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}}{{}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}}{{}^{4}F_{3/2} \rightarrow {}^{4}I_{15/2}}$ | 934  | 1.452                     | 0.88         | 532.40                                   | 42.92             |                      | 55.50   | 4.59                           |                          |
|   | ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$                   | 1083                      | 1.449        | 1.54                                     | 594.16            | 47.90                | 0.81  | 59.32                          | 8.71                     |
|   | ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$                   | 1362                      | 1.445        | 0.57                                     | 108.92            | 8.78                 |   | 49.61                          | 4.80                     |
|   | ${}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{15/2}$ | 1940                      | 1.441        | 0.07                                     | 4.94              | 0.40                 |   | -                              | -                        |

Table 5: Abbe number ( $v_e$ ), nonlinear refractive index ( $n_2$ ), nonlinear refractive index coefficient ( $\gamma$ ) and susceptibility ( $\chi$ ) of the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber comparing with the results reported previously.

|  | n <sub>e</sub> | Ve   | $\binom{n_2}{(10^{-13} \text{ esu})}$ | $(10^{-4} \text{ m}^2/\text{W})$ | $\chi^{(10^{-6} m^2/V^2)}$ |
|--|----------------|------|---------------------------------------|----------------------------------|----------------------------|
| Present work   | 1.478          | 20.0 | 5.69                                  | 1.61                             | 1.25                       |
| Yb <sup>3+</sup> /Tm <sup>3+</sup> codoped glass (Watekar, et al., 2005) | -              | 55.6 | 1.35                                  | 0.38                             | 0.30                       |
| Nd doped glass (Stokowski, et al., 1981)                                 | 1.720          | 45.0 | 3.44                                  | -                                | -                          |

emission intensity of the fiber upon exciting at 800 nm, the fluorescence lifetime of  $Tm^{3+}$  was not possible to observe.

The effective linewidths of Tm<sup>3+</sup> from  ${}^{3}H_{5} \rightarrow {}^{3}H_{6}$ and  ${}^{3}H_{4} \rightarrow {}^{3}H_{5}$  transition reported by other groups (Balda et al., 2008); (Yang et al., 2006); (Zhou et al., 2010) were broader by nearly 30 nm than the values estimated here. Nevertheless, the emission crosssections of Tm<sup>3+</sup> were found to increase significantly (Balda et al., 2008); (Yang, et al., 2006). On the other hand, in the case of  $Nd^{3+}$  the effective linewidths were larger but the peak emission cross-sections were smaller (Stokowski et al., 1981); (Thomas et al., 1992) since the decrease of the emission cross-section is mainly due to the increase of the effective linewidths (Choi et al., 2003).

The nonlinear optical parameters of the  $Tm^{3+}/Nd^{3+}$  codoped fiber comparing with that of the  $Yb^{3+}/Tm^{3+}$  codoped glass (Watekar et al., 2005) and the Nd doped glass (Stokowski et al., 1981) are

listed in Table 5. The calculated results showed low Abbe number and reasonably high nonlinear refractive index (Boling and Glass, 1978). Therefore, the  $Tm^{3+}/Nd^{3+}$  codoped fiber can also be applied to the development of future phase and amplitude modulators and fast all-optical switches for communication (Digonnet, 1993).

# 5 CONCLUSIONS

We fabricated the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped optical fiber by the MCVD process. The fiber was excited by the He-Ne laser operating at 633 nm and the emissions were found to appear at 934, 1083, 1279, 1363, 1414 and 1720 nm. The emission bands of  $Tm^{3+}$  at 1279, 1414 and 1720 nm assured the ET process between Tm<sup>3+</sup> and Nd<sup>3+</sup> ions. The process was so beneficial that the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber can be good candidate for the broadband fiber laser in NIR region. In addition, the trend of the JO parameters  $(\Omega_2 > \Omega_4 > \Omega_6)$  indicated that the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber occupied a good spectroscopic quality. Further, higher radiative lifetime and larger effective linewidths originated from  ${}^{4}F_{3/2}$  level as well as considerably large stimulated emission cross-sections at 1279 and 1414 nm were observed in the Tm<sup>3+</sup>/Nd<sup>3+</sup> codoped fiber. Furthermore, the nonlinear optical parameters of the fiber were calculated and the considerably highly nonlinear refractive index was found.

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# REFERENCES

Aull, B. & Jenssen, H., 1982. Vibronic interactions in

Nd:YAG resulting in nonreciprocity of absorption and stimulated emission cross sections. IEEE J. Quantum Electron., vol. 18, no. 5, pp. 925-930.

- Balda, R. et al., 2008. Spectroscopic properties of the 1.4  $\mu$ m emission of Tm<sup>3+</sup> ions in TeO<sub>2</sub>-WO<sub>3</sub>-PbO glasses. Opt. Express, vol. 16, no. 16, pp. 11836-11846.
- Binnemans, K., Deun, R. V., Gorller-Walrand, C. & Adam, J.L., 1998. Optical properties of Nd<sup>3+</sup>-doped fluorophosphate glasses. J. Alloy. Compd., vol. 275-277, pp. 455-460.
- Boling, N. L. & Glass, A. J., 1978. Empirical relationships for predicting nonlinear refractive index changes in optical solids. IEEE J. Quantum Electron., vol. 14, no. 8, pp. 601-608.
- Brandão, M. J. S. et al., 2006. Optical properties and energy transfer processes in (Tm<sup>3+</sup>, Nd<sup>3+</sup>) doped tungstate fluorophosphate glass. J. Appl. Phys., vol. 99, no. 11, p. 113525.
- Carnall, W. T., Fields, P. R. & Rajnak, K., 1968. Spectral intensities of the trivalent lanthanides and actinides in solution. II. Pm<sup>3+</sup>, Sm<sup>3+</sup>, EU<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup> and Ho<sup>3+</sup>. J. Chem. Phys., vol. 49, no. 10, pp. 4412-4423.
- Choi, J. H. et al., 2003. Optical absorption and emission properties of Nd<sup>3+</sup> doped fluorophosphates glass for
- broadband fiber amplifier applications. Proc. SPIE, vol. 4974, pp. 106-111.
- Chung, W. J. & Heo, J., 2001. Energy transfer process for the blue up-conversion in calcium aluminate glasses doped with Tm<sup>3+</sup> and Nd<sup>3+</sup>. J. Am. Ceram. Soc., vol. 84, no. 2, pp. 384-352.
- Chung, W. J., Yoo, J. R., Kim, Y. S. & Heo, J., 1997. Mechanism of the blue up-conversion in Tm<sup>3+</sup>/Nd<sup>3+</sup>doped calcium aluminate glasses. J. Am. Ceram. Soc., vol. 80, no. 6, pp. 1485-1490.
- Fowler, W. B. & Dexter, D. L., 1962. Relation between absorption and emission probabilities in luminescent centers in ionic solids. Phys. Rev., vol. 128, pp. 2154-2165.
- Digonnet, M. J. F. (ed.), 1993. Rare-earth-doped fiber lasers and amplifiers. Marcel Dekker, Inc.
- Han, W.-T. & Kim, Y. H., 2002. Linear and nonlinear optical properties of optical fibers containing PbTe quantum dots for all optical switching application. 2<sup>nd</sup> *Int. China-Korea Glass and Glass-Ceramics Symp.*, Shanghi.
- Heo, J., Cho, W. Y. & Chung, W. J., 1997. Sensitizing effect of  $Tm^{3+}$  on 2.9  $\mu m$  emission from  $Dy^{3+}$ -doped Ge<sub>25</sub> Ga<sub>5</sub> S<sub>70</sub> glass. J. Non-Cryst. Solids, vol. 212, pp. 151-156.
- Judd, B. R., 1962. Optical absorption intensities of rareearth ions. Phy. Rev., vol. 127, pp. 750-761.
- Kobayashi, S., Shibata, N., Shibata, S. & Izawa, T., 1978. Characteristics of optical fibers in infrared wavelength region. Review of ECL, vol. 26, no. 3, pp. 453-467.
- Kobayashi, S., Shibata, S., Shibata, N. & Izawa, T., 1977. Refractive-index dispersion of doped fused silica. I<sup>st</sup>International Conference on Integrated Optics and Optical Fiber Communication (IECE), Tokyo.
- Krupke, W. F., 1974. Induced-emission cross sections in neodymium laser glasses. *IEEE J. Quantum Electron.*,

vol. QE-10, no. 4, pp. 450-457.

- Lahoz, F., Shepherd, D. P., Wilkinson, J. S. & Hassan, M. A., 2008. Efficient blue upconversion emission due to confined radiative energy transfer in  $Tm^{3+}$ –Nd<sup>3+</sup> co-doped Ta<sub>2</sub>O<sub>5</sub> waveguides under infrared-laser excitation. Opt. Commun., vol. 281, pp. 3691-3694.
- Lee, D. J., Heo, J. & Park, S. H., 2003. Energy transfer and 1.48 μm emission properties in chalcohalide glasses doped with Tm<sup>3+</sup> and Tb<sup>3+</sup>. J. Non-Cryst. Solids, vol. 331, pp. 181-189.
- Lucas, J. et al., 1978. Preparation and optical properties of neodymium fluorozirconate glasses. J. Non-Cryst. Solids, vol. 27, pp. 273-283.
- Lu, K. & Dutta, N. K., 2001. Spectroscopic properties of Nd-doped glass for 944 nm laser emission. J. Appl. Phys., vol. 89, no. 6, pp. 3079-3083.
- Martinez, A., Zenteno, L. A. & Kuo, J. C. K., 1998. Optical and spectroscopic characterization of Nddoped aluminosilicate fiber preforms made by the MCVD method using chelate delivery. Appl. Phys. B, vol. 67, pp. 17-21.
- Milam, D. & Weber, M. J., 1976. Measurement of nonlinear refractive-index coefficients using timeresolved interferometry: application to optical materials for high-power neodymium lasers. J. Appl. Phys., vol. 47, pp. 2497-2501.
- Peterka, P. et al., 2004. Theoretical modelling of S-band thulium-doped silica fibre amplifiers. Opt. Quant. Electron., vol. 36, pp. 201-212.
- Quimby, R. S. & Miniscalco, W. J., 1989. Continuouswave lasing on a self-terminating transition. Appl. Opt., vol. 28, no. 1, pp. 14-16.
- Rakov, N., Gómez, L. A., Rátiva, D. J. & Maciel, G. S., 2002. Blue upconversion enhancement by a factor of 200 in Tm<sup>3+</sup>-doped tellurite glass by codoping with Nd<sup>3+</sup> ions. J. Appl. Phys., vol. 92, no. 10, pp. 6337-6339.
- Rakov, N., Gómez, L. A., Rátiva, D. J. & Maciel, G. S., 2009. Blue upconversion emission from Tm<sup>3+</sup> sensitized by Nd<sup>3+</sup> in aluminum oxide crystalline ceramic powders. Appl. Phys. B, vol. 94, pp. 199-202.
- Shen, S. et al., 2002. Tellurite glasses for broadband amplifiers and integrated optics. J. Am. Ceram. Soc., vol. 85, no. 6, pp. 1391-1395.
- Stokowski, S. E., Saroyan, R. A. & Weber, M. J., 1981. Nd-doped laser glass spectroscopic and physical properties. Lawrence Livermore National Laboratory, M-095, Rev. 2, 1.
- Tanabe, S., 2002. Rare-earth-doped glasses for fiber amplifiers in broadband telecommunication. C. R. Chim., vol. 5, no. 5, pp. 815-824.
- Tanabe, S., Feng, X. & Hanada, T., 2000. Improved emission of Tm<sup>3+</sup> doped glass for a 1.4-µm amplifier by radiative energy transfer between Tm<sup>3+</sup> and Nd<sup>3+</sup>. Opt. Lett., vol. 25, no. 11, pp. 817-819.
- Thomas, I. M., Payne, S. A. & Wilke, G. D., 1992. Optical properties and laser demonstrations of Nd-doped solgel silica glasses. J. Non-Cryst. Solids, vol. 151, no. 3, pp. 183-194.
- Walsh, B. M. & Barnes, N. P., 2004. Comparison of

Tm:ZBLAN and Tm:silica fiber lasers; spectroscopy and tunable pulsed laser operation around 1.9 μm. Appl. Phys. B, vol. 78, pp. 325-333.

- Watekar, P. R., Ju, S., Boo, S. & Han, W.-T., 2005. Linear and non-linear optical properties of Yb<sup>3+</sup>/Tm<sup>3+</sup> codoped alumino-silicate glass prepared by sol-gel method. J. Non-Cryst. Solids, vol. 351, pp. 2446-2452.
- Watekar, P. R., Ju, S. & Han, W.-T., 2006. A small-signal power model for Tm-doped silica-glass optical fiber amplifier. IEEE Photon. Technol. Lett., vol. 18, no. 19, pp. 2035-2037.
- Weber, M. J., Lynch, J. E., Blackburn, D. H. & Cronin, D. J., 1983. Dependence of the stimulated emission cross section of Yb<sup>3+</sup> on host glass composition. IEEE J. Quantum Electron., vol. 19, pp. 1600-1608.
- Yanbo, Q. et al., 2006. Spectroscopic properties of Nd<sup>3+</sup>doped high silica glass prepared by sintering porous glass. J. Rare Earth., vol. 24, pp. 765-770.
- Yang, Z., Luo, L. & Chen, W., 2006. The 1.23 and 1.47 μm emissions from Tm<sup>3+</sup> in chalcogenide glasses. J. Appl. Phys., vol. 99, no. 7, pp. 076107-3.
- Zabicky, J. (ed.), 2009. The chemistry of metal enolates, part 1. John Wiley & Sons Ltd.
- Zhang, J., Chung, W. J., Zhao, X. & Heo, J., 2010. Nd<sup>3+</sup> sensitized blue upconversion luminescence in Nd<sup>3+</sup>/Pr<sup>3+</sup> co-doped Ge–Ga–S–CsBr chalcohalide
- glasses. J. Non-Cryst. Solids, vol. 356, pp. 2406-2408. Zhang, J. W. et al., 2006. Optical amplification in  $Nd^{3+}$
- doped electro-optic lanthanum lead zirconate titanate ceramics. Appl. Phys. Lett., vol. 89, pp. 061113.
- Zhou, B., Lin, H. & Pun, E.Y.-B., 2010. Tm<sup>3+</sup>-doped tellurite glasses for fiber amplifiers in broadband optical communication at 1.20 μm wavelength region. Opt. Express, vol. 18, no.18, pp. 18805-18810.
- Zou, X. & Toratani, H., 1996. Spectroscopic properties and energy transfers in Tm<sup>3+</sup> singly- and Tm<sup>3+</sup>/Ho<sup>3+</sup> doubly-doped glasses. J. Non-Cryst. Solids, vol. 195, pp. 113-124.