# Sm<sup>3+</sup>effects in the Tm<sup>3+</sup> doped tellurite glass for S-band amplification

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#### ABSTRACT

Thulium doped Samarium codoped tellurite-tungstate glasses were produced. Luminescence properties in the infrared region were investigated looking to observe improved properties for S-band amplification in the codoped samples. Thulium is well-known by the  ${}^{3}\text{H}_{4}$ - ${}^{3}\text{F}_{4}$  radiative transition emitting around ~1.47µm, which is a self-terminating transition in tellurite hosts due the longer lifetime of the lower level in relation to the upper level of this transition. Analysis of absorption and emission spectra showed that we could quench the 3F4 level significantly, what improved the intensity of the emission at 1.49µm. However, the state  ${}^{3}\text{H}_{4}$  were also quenched due the cross relaxation process due the absorption bands of Sm<sup>3+</sup> around 1.5µm.

Keywords: Samarium, Thulium, Luminescence, infrared, amplification.

### 1. INTRODUCTION

Nowadays the necessity of expand the information traffic capacity is evident and Internet is the leadership in traffic growth in the last decades. This growing process obey the Moore's law[1], and there is no sign that it is going to change in the next years. The number of devices connected to the internet is continuously increasing, at the same time that the content available consumes more and more bandwidth. It makes clear why so many researches aim to expand the optical windows in silica fibers[2], as well so many others aim to develop new amplifiers, exploring rare-earth ions[3,4,5], or even transition metals like bismuth[6,7]. Between the rare-earths,  $Tm^{3+}$  is well-known as an active ion for amplification at around 1470 nm, corresponding to the S-band of telecommunication. The terminal  ${}^{3}F_{4}$  level lifetime of this transition is too long, making necessary a double pumping scheme[8] or codoping with an ion able to quench the  ${}^{3}F_{4}$  level, such as  $Tb^{3+}$ , Ho<sup>3+</sup> or Eu<sup>3+</sup>[9,10]. This work summarizes some results obtained in the fiber glass[11] system TeO<sub>2</sub>-WO<sub>3</sub>-Na<sub>2</sub>O-Nb<sub>2</sub>O<sub>5</sub>, doped with Tm<sup>3+</sup> and codoped with Sm<sup>3+</sup>, investigating the energy transfer process between both and the possibility to enhance Tm<sup>3+</sup> emission in the S-band region by using Sm<sup>3+</sup> to quench the  ${}^{3}F_{4}$  level.

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# 2. EXPERIMENTAL PROCEDURES

The bulk samples were produced by the conventional melt-quenching process. Raw materials at least 99.99% pure were weight with 0.1mg of precision to produce 20g of each sample. An induction furnace in a glove box was used to heat the material in a controlled dry atmosphere, with about 1~2ppm of water. The raw material was preheated at 200°C for half an hour and melted at 700°C for an hour. The melt was shed in a stainless steel mold with approximately 1.5x1.0x0.5cm<sup>3</sup>. The obtained samples were optically polished. The absorption spectra were obtained in a Perkin-Elmer UV-VIS-NIR Lambda 9 spectrophotometer in the range 400-2500 nm. Near-infrared (NIR) luminescence and excitation spectra were measured in a Jobin-Yvon Fluorolog3 spectrofluorimeter which uses a 450W Xenon lamp as pump source and a photomultiplier tube (PMT) as detector in the range 900-1700 nm. Lifetime measurements were carried out pumping the sample with an electronically modulated diode laser (LD) and monitoring the luminescence with a InGaAs photodiode connected to an oscilloscope. Visible (VIS) luminescence spectra and some additional NIR spectra were obtained pumping the samples with an Argon laser at 488 nm and collecting the emission with a fiber coupled Ocean Optics HR4000 spectrophotometer to the range 400-1000nm or an Ocean Optics NIR256-2.1 to the range 1000-2100nm.

## 3. RESULTS AND DISCUSSION

Samples doped with up to 1.5% of  $Tm_2O_3$  and codoped with 1.5%  $Tm_2O_3 + up$  to 3.0% of  $Sm_2O_3$  were prepared. The figure 1 shows the VIS and NIR absorption spectra for single doped and codoped samples. As one can see, the band-gap of this glass is located in the blue region. The  ${}^4I_{11/2}$  level of  $Sm^{3+}$  at around 470 nm is hidden by this band-gap at low concentrations, and could be observed only for the sample doped at 3.0% of  $Sm_2O_3$ . In the NIR, all bands of both  $Sm^{3+}$  and  $Tm^{3+}$  can be easily identified for all samples.



Figure 1. Absorption spectra of Tm<sup>3+</sup> doped, Sm<sup>3+</sup> dopedand Tm<sup>3+</sup>/Sm<sup>3+</sup> codoped samples: a) In the VIS and b) NIR.

The figure 2 shows the NIR luminescence spectra of  $Tm^{3+}$  doped samples and lifetime decays for the  ${}^{3}F_{4}$  (inset in figure 2a) and  ${}^{3}H_{4}$  level (figure 2b). As we can see, the  ${}^{3}H_{4}$  level is strongly self-quenched. The lifetime falls from 346µs at 0.15% mol concentration to about a half (178µs) at a concentration of 0.5% mol. The lifetime for the ( ${}^{3}F_{4}$ ) end-level of this transition is much longer (1.8ms at 0.15% mol concentration), as we can see in the inset of figure 2a. Once that the

<sup>3</sup>F₄-<sup>3</sup>Ң 1,0-Excitation at 785 nm Emission at 1800 nm 0.050%Tm τ=1.8ms 0.150%Tm 0,8 0.500%Tm 1.500%Tm 0,6 Intensity  ${}^{3}H_{4} - {}^{3}F_{4}$ 0,4 0,2 a) 0,0 1800 1400 1600 2000 Wavelength (nm) Tm 0.150% Pumped at 785 nm Tm 0.500% Emission at 1500 nm Intensity 0,1 b) 600 200 400 800 1000 0 Time (µs)

 ${}^{3}\text{H}_{4}$  manifold remains populated for a time substantially longer than  ${}^{3}\text{F}_{4}$  manifold, the emission at 1.49 $\mu$ m is self-terminating.

Figure 2. a) NIR luminescence spectra and lifetime decay for the <sup>3</sup>F<sub>4</sub>level. b) Lifetime decays for the <sup>3</sup>H<sub>4</sub>level, corresponding to the emission at 1.49µm emission.

The VIS and NIR luminescence spectra for samples excited at 473 nm are shown in figure 3. The NIR luminescence spectra make clear that the relative intensity between 1.49 $\mu$ m and 1.8 $\mu$ m emission bands changed in favour of the emission of the short wavelength. It is an indication of the quenching process that we expected to see by adding Sm<sup>3+</sup>. On the other hand, the VIS luminescence spectrum shows the undesirable quenching of the <sup>3</sup>H<sub>4</sub> manifold, evidenced by the decrease of intensity around 800 nm with increasing Sm<sup>3+</sup> concentration. These results support the conclusion that Sm<sup>3+</sup> has quenched the <sup>3</sup>F<sub>4</sub> manifold strongly than the <sup>3</sup>H<sub>4</sub> manifold of Tm<sup>3+</sup> ions. The energy diagram shown in figure 4 helps to discuss this interpretation.



Figure 3.a) VIS and b) NIR luminescence for samples excited at 473 nm.

In the energy diagrams the more relevant absorption transitions are indicated in blue and the main emission transitions in red. As one can see, both  ${}^{1}G_{4}$  manifold in Tm<sup>3+</sup> ions and the  ${}^{4}I_{11/2}$  manifold in Sm<sup>3+</sup> ions are populated by ~470nm pumping. The  ${}^{3}H_{4}$  manifold is only ~2000cm<sup>-1</sup> above the  ${}^{6}F_{11/2}$  manifold, and once that this host has maximum phonon energy of ~790cm<sup>-1</sup> a multi-phonon relaxation process between these levels can be expected. On the other hand, the  ${}^{3}F_{4}$  manifold of Tm<sup>3+</sup> is only ~800cm<sup>-1</sup> above the  ${}^{6}H_{13/2}$  of Sm<sup>3+</sup>. The  ${}^{6}F_{5/2}$ ,  ${}^{6}F_{3/2}$ ,  ${}^{6}H_{15/2}$  and  ${}^{6}F_{1/2}$  of Sm<sup>3+</sup> are also very close the  ${}^{3}F_{4}$ . Additionally a cross-relaxation process also take place between the Tm<sup>3+</sup> emission at ~1.49µm and the ground state absorption bands of Sm<sup>3+</sup> around 1.5µm, which are indicated in the diagram by a dashed line. The final result is that both  ${}^{3}H_{4}$  and the  ${}^{3}F_{4}$  levels of Tm<sup>3+</sup> are quenched.



Figure 4. Energy diagram of Tm3+ and Sm3+ in TeO2-WO3-Na2O-Nb2O5 glass. More relevant absorption bands are indicated in blue and main emission bands in red. The cross relaxation process is indicated by the dashed line in the Sm3+ energy diagram.

# 4. CONCLUSIONS

In this work the  $Tm^{3+}$  emission at ~1.49µm were investigated in terms of the effect of  $Sm^{3+}$  addiction.  $Tm^{3+}$  doped  $Sm^{3+}$ codoped tellurite-tungstate glasses were investigated and the results confirm that  $Sm^{3+}$  can quench the terminating  ${}^{3}F_{4}$  level. Although the results showed an increase in the relative intensities between the transitions  ${}^{3}H_{4}$ - ${}^{3}F_{4}$  and the  ${}^{3}F_{4}$ - ${}^{3}H_{6}$ , the cross-relaxation process due the  $Sm^{3+}$  absorption around 1.5µm decreased the emission intensity in this region.

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