

# Generation of Short Wavelength in Up-Conversion of $Tm^{+3}$ Doped Fluoride Glass and Its Application in Fiber Lasers

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## ABSTRACT

We report on the experimental study of the visible and ultraviolet (UV) fluorescence emission in a (1% molar) Thulium ( $Tm^{+3}$ )-doped Zirconium fluoride glass sample. From red at 650 nm, blue (453 & 480 nm) and UV at 365 & 284 nm, have been observed under excitation of a Nd:YAG laser at 1.064  $\mu m$ . The responsible up-conversion mechanisms are investigated based on experimental data. The related problem of photo-degradation associated with formation of color centers is also addressed.

## KEYWORDS

Fluoride Glass; Up-Conversion Pumping; Spectroscopy

## 1. Introduction

Heavy-metal fluorozirconate glasses and fibers are finding increased interest for the compact devices that generate short wavelengths in the visible and UV region. The importance for such emissions is needed for many applications, such as data storage, medical applications like photodynamic therapy, for pumping of solid state lasers (e.g. Cr:LiSAF) and all color display [1-4].

Among rare earth (RE) ions,  $Tm^{+3}$  showed a versatile candidate that converts low-energy infrared photons to high-energy photons in the visible and ultraviolet spectral under up-conversion processes [5-8]. The first upconversion-pumped visible laser was demonstrated in a  $Tm^{+3}$ -doped  $ZrF_4$ - $BaF_2$ - $LaF_3$ - $AlF_3$ - $NaF$  (ZBLAN) fiber at 455 nm ( $^1D_2 \rightarrow ^3F_4$ ) and 480 nm ( $^1G_4 \rightarrow ^3H_6$ ) with additionally some UV fluorescence at 288 nm ( $^1I_6 \rightarrow ^3H_6$ ) [9]. Spontaneous emission has also been observed from the  $Tm^{+3}$   $^1I_6$  at 290 nm in ZBLAN, which requires the energy of five 1140 nm pump photons [10]. Unstable laser operation at 284 nm ( $^1I_6 \rightarrow ^3H_6$ ) is demonstrated in  $Tm^{+3}$ -doped ZBLAN under up-conversion pumping [11]. As presented in Ref.

[11], the obtained UV laser at 284 nm was shut down after a few minutes of operation due to photo-degradation problem. Photo-degradation is the absorption of visible and short wavelengths or so called color centre problem. Stability and power scaling can be reached with the improvement of the ZBLAN material through the modulation of the component of the fiber, introducing other ions into the core of the fiber to preclude the photo-degradation effect [7]. Additionally, fibers with small numerical aperture (NA) by adjusting the refractive indices of the fiber core and cladding may also reduce the photo-darkening effect [2]. Usually, this effect can be removed almost entirely by circulating blue light or wavelength of 514 nm through the fiber core [2,7]. This problem of photo-degradation associated with formation of color centers is solved temporally by circulating 514 nm through the fiber core as reported in ref. [7].

In this paper we reported on the experimental study of the excitation and emission mechanisms of fluorescence in a (1% molar) Thulium ( $Tm^{+3}$ )-doped Zirconium fluoride glass sample. Ultra-violet (at 365 nm & 284 nm), visible (at 453, 480 and 650 nm) radiation was observed under excitation at 1.064  $\mu m$ . The responsible up-con-

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version mechanisms are investigated based on experimental data. The photo-curing of the photo-darkening effect is also addressed.

## 2. Experiment

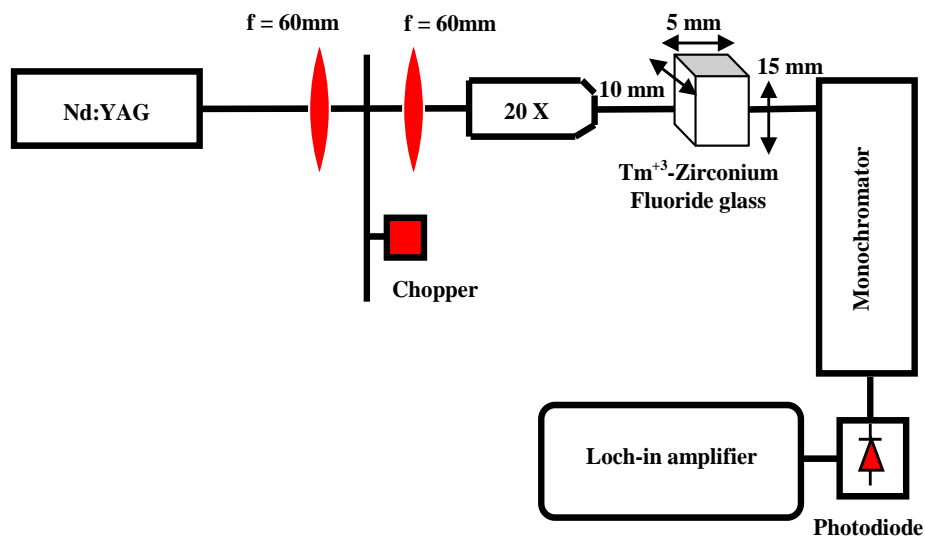
The ( $\text{Tm}^{+3}$ )-doped Zirconium fluoride glass sample used in the experiment is (1% molar)  $5 \times 10 \times 15$  mm and was excited by a Nd:YAG laser (Laserlabcomponets IR CWL 1064-3). The experimental arrangement is shown in **Figure 1**. The pump laser is a Nd:YAG laser operated at  $1.064 \mu\text{m}$ . The beam of the Nd:YAG laser is chopped mechanically and focused onto the glass sample by a  $20\times$ -microscope objective. A lens with a focal length of 25 mm collects the fluorescence of the glass sample and directs it onto the entrance slit of a monochromator 1200 groves/mm grating monochromator (Newport oriel 74125) blazed for 500 nm with a resolution set to 0.8 nm.

Photodiodes (SicB-type, 200 - 1100 & InGaAs 1200 - 2600 nm Thorlabs), a lock-in amplifier (Stanford SR830 DSP), digital oscilloscope (Tektronix TDS3084B) and power meter were employed to record the temporal behavior of the emitted spectrum and its intensity profile.

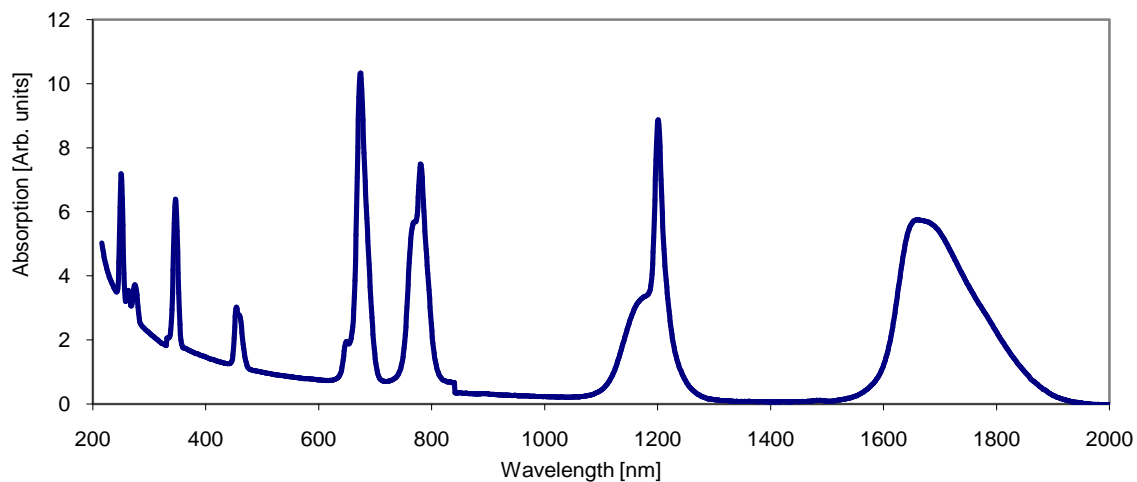
## 3. Results and Discussion

The absorption spectrum of the glass sample at room temperature is presented in **Figure 2**. A spectrophotometer (Jasco 670) was used for measurements, the spectrum covering the spectral region 200 - 2000 nm and identified all the J levels of  $\text{Tm}^{+3}$ .

**Table 1** lists peak position bands of the absorption spectrum of the sample at room temperature covering the spectral region 200 - 2000 nm. The spectrum consists of several groups corresponding to transitions from the ground state  $^3\text{H}_6$  to the excited state of  $\text{Tm}^{+3}$ .



**Figure 1.** Experimental setup.



**Figure 2.** Absorption spectrum of 1% molar  $\text{Tm}^{+3}$ -doped zirconium fluoride glass.

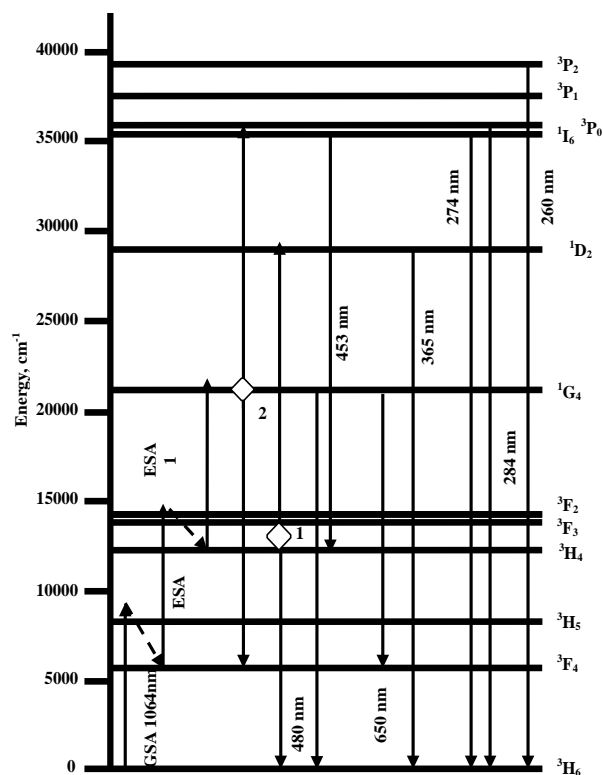
**Table 1.** Peak positions of absorption bands in  $\text{Tm}^{+3}$ : zirconium fluoride glass.

Level	Wavelength [nm]	Energy [ $\text{cm}^{-1}$ ]
$^3\text{F}_4$	1671	5984
$^3\text{H}_5$	1210	8264
$^3\text{H}_4$	790	12,652
$^3\text{F}_3$	684	14,649
$^3\text{F}_2$	658	15,187
$^1\text{G}_4$	470	21,277
$^1\text{D}_2$	355	28,018
$^1\text{I}_6$	287	34,810
$^3\text{P}_0$	284	35,185
$^3\text{P}_1$	273	36,602
$^3\text{P}_2$	260.8	38333.5

The excitation scheme is shown in **Figure 3**. In up-conversion processes, usually three processes are considered. One is the excited state absorption (ESA) process, which consists of two consecutive excitation steps on a single ion. The other one is the energy transfer up-conversion (ETU) process, in which two ions in an intermediate state interact resulting in that the energy of an ion is transferred non-radiatively onto another ion thereby exciting it into a higher excited state. The third one is the photon avalanche up-conversion, which can be excluded in our case as ignored in most cases in 1% molar  $\text{Tm}^{+3}$ -doped ZBLAN glass [12-14].

Based on our measured emission spectrum and time resolved spectroscopy we proposed the excitation mechanism as following: the first three excitation steps are assumed to occur as described in [6,7,11]. Excitation occurs in a first step by ground state absorption (GSA) to  $^3\text{H}_5$  with subsequent relaxation to the metastable level  $^3\text{F}_4$ . The energy difference from  $^3\text{H}_6$  to  $^3\text{H}_5$  is  $8230 \text{ cm}^{-1}$  [6] which is quite far away from the pump energy of  $9398 \text{ cm}^{-1}$  at a wavelength of 1064 nm. It is, however sufficient to accumulate population in  $^3\text{F}_4$ , which leads to strong excited state absorption (ESA) processes as presented in [11]. The second step of excitation is assigned to ESA from  $^3\text{F}_4$  to  $^3\text{F}_2$  with subsequent population of  $^3\text{H}_4$ . This ESA is detuned from the optimum energy difference of the levels of  $9138 \text{ cm}^{-1}$  [8] by only 260 wave-numbers. This step is also weakened by the (ETU) process  $^3\text{H}_4, ^3\text{F}_2 \rightarrow ^1\text{D}_2, ^3\text{H}_6$  shown by arrow 1 in **Figure 3**.

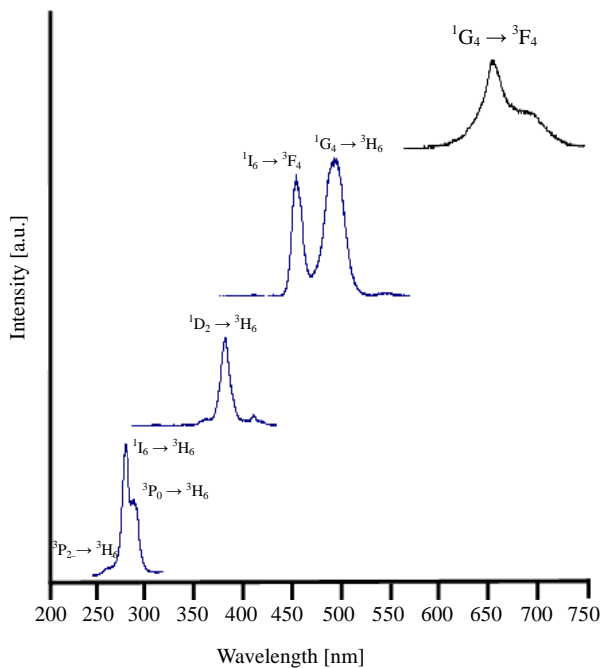
Moreover, the third step is assigned to ESA from  $^3\text{H}_4$  to  $^1\text{G}_4$ . With an energy level difference of  $8599 \text{ cm}^{-1}$  [6,7], the detuning in this case is 800 wave-numbers. The fourth step from the  $^1\text{G}_4$  level to  $^1\text{I}_6$  is assigned to the (ETU)  $^1\text{G}_4, ^1\text{G}_4 \rightarrow ^1\text{I}_6, ^3\text{F}_4$  shown by arrow 2 in **Figure 3**.

**Figure 3.** Shows energy level diagram for the 1% molar  $\text{Tm}^{+3}$ -doped Zirconium fluoride glass [2] showing the excitation and up-conversion processes.

**Figure 4** shows the measured emission up-conversion spectrum in 1% molar  $\text{Tm}^{+3}$ -doped Zirconium fluoride glass under excitation wavelength of 1064 nm. The results show that broad up-conversion fluorescence band (from 260 to 650 nm). The peaks are at 260 nm ( $^3\text{P}_2 \rightarrow ^3\text{H}_6$ ), 274 nm ( $^3\text{P}_0 \rightarrow ^3\text{H}_6$ ), 284 nm ( $^1\text{I}_6 \rightarrow ^3\text{H}_6$ ), 365 ( $^1\text{D}_2 \rightarrow ^3\text{H}_6$ ), 453 nm ( $^1\text{I}_6 \rightarrow ^3\text{H}_4$ ), 480 nm ( $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ) and 650 nm ( $^1\text{G}_4 \rightarrow ^3\text{F}_4$ ). The UV intensity of fluorescence emission originating from  $^1\text{I}_6$  level is magnified twenty times ( $\times 20$ ). This intensity can be increased by increasing the dopant concentration to  $\text{Tm}^{+3}$ . This will reduce the distance between  $\text{Tm}^{+3}$  ions resulting in efficient ETU processes and leading to a strong UV emissions [12,13].

In addition, the measurements of UV emissions originating from  $^1\text{I}_6$  level were taken in few seconds after excitation. The UV fluorescence emission was gradually reduced to the noise level due to formation of color centers and existence of photo-degradation. Usually, this effect can be eliminated almost totally by circulating blue light or wavelength of 514 nm through the fiber core [2,6].

The power dependence of up-conversion fluorescence originating from  $^1\text{G}_4$  level at (480 nm),  $^1\text{D}_2$  level at (365 nm) and  $^1\text{I}_6$  level at (453 nm) were measured by inserting different neutral density filters in the path of the pump



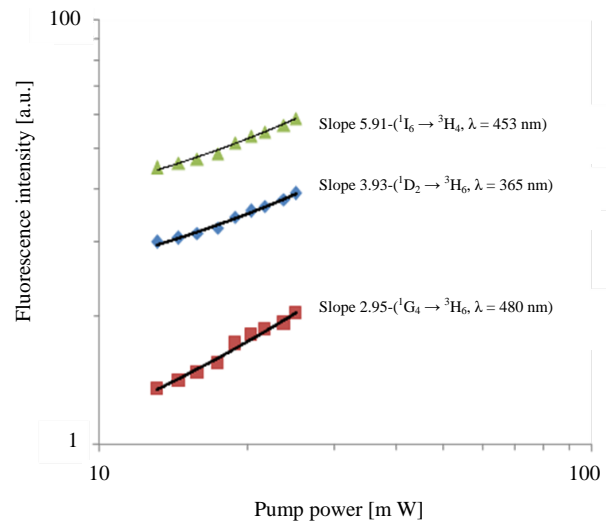
**Figure 4.** Up-conversion fluorescence spectra in 1% molar  $\text{Tm}^{+3}$ -doped zirconium fluoride glass at a pump wavelength of 1.064  $\mu\text{m}$ .

excitation. The wavelength-dependence of the experimental detection system (grating and photodiodes) was taken into account by calibration with the spectrum of a black body.

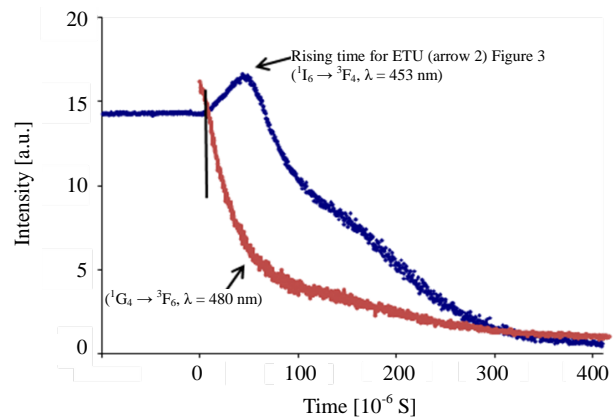
The experimental data have been fit to straight lines in double logarithmic scale with slope about 3 for ( ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ ,  $\lambda = 480 \text{ nm}$ ),  $\sim 4$  for ( ${}^1\text{D}_2 \rightarrow {}^3\text{H}_6$ ,  $\lambda = 365 \text{ nm}$ ) and  $\sim 6$  for ( ${}^1\text{I}_6 \rightarrow {}^3\text{H}_4$ ,  $\lambda = 453 \text{ nm}$ ). As can be seen in **Figure 5** that the blue emission at 480 nm indicates three photon process is involved with slope 3 or fluorescence intensity ( $I_{\text{Fluor}}$ ) is proportional with pump intensity  $P_{\text{Pump}}$  ( $I_{\text{Fluor}} \propto P^3$ ). Moreover, for emission at 365 nm with slopes 4 is considered to be 2 ESAs with 2 ions for ETU (arrow 1 in **Figure 3**) or  $I_{\text{Fluor}} \propto P^4$ . The up-conversion emission at 453 nm is also considered 3 ESAs and 2 ions for ETU (arrow 2 in **fig. 2**) or  $I_{\text{Fluor}} \propto P^6$ .

In order to determine and confirm the excitation mechanism of the up-conversion process, time resolved spectroscopy method is used to analyse the temporal behavior after pumping processes of the 453 nm and 480 nm transitions.

**Figure 6** shows the temporal behavior of fluorescence decays at 480 nm and 453 nm. As can be seen in **Figure 6** that, when the pump excitation is turned off the resulting fluorescence exhibits an exponential decay for 480 nm. Therefore, the mechanism of up-conversion fluorescence can be confirmed as ESA process. Whereas, up-conversion fluorescence decay at 453 nm exhibits an initial rising phase. This is the typical behavior of ETU



**Figure 5.** Power dependence of up-conversion fluorescence at 365, 453, and 480 nm at a pump wavelength of 1.064  $\mu\text{m}$ .



**Figure 6.**  $\text{Tm}^{+3}$ : doped zirconium fluoride fluorescence dynamic monitored at 453 nm ( ${}^1\text{I}_6 \rightarrow {}^3\text{H}_4$ ) and 480 nm ( ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ ) under up-conversion pumping at 1064 nm.

that takes place after the end of the excitation process and have an observable rise time.

As mentioned above the reduction in the fluorescence intensity after few minutes of appearance is mainly due to presence of color centers problem. The photo-curing of the photo-darkening effect is realized by directing a wavelength of a 514 nm on the side of length thought glass sample shown if **Figure 1**. The emitted UV fluorescence emissions did not affected potentially as presented in ref. [6] for fiber lasers. This mainly due to large pump area compared with fiber lasers.

## 4. Conclusion

In conclusion, we have identified experimentally the excitation mechanism of a (1% molar) Thulium ( $\text{Tm}^{+3}$ )-doped Zirconium fluoride glass sample. The sample was pumped at 1064 nm. The dependence of up-conversion

fluorescence intensity versus excitation power at 1064 nm and its temporal behavior have been investigated based on experimental data. The experimental data showed that three ESAs and ETUs processes  $^3\text{H}_4$ ,  $^3\text{F}_2 \rightarrow ^1\text{D}_2$ ,  $^3\text{H}_6$  &  $^1\text{G}_4$ ,  $^1\text{G}_4 \rightarrow ^1\text{I}_6$ ,  $^3\text{F}_4$ . The related problem of photo-degradation associated with formation of color centers that has not been solved yet is also introduced. The presented date is very useful for producing short wavelength fiber lasers.

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