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Thulium-doped nanoparticles and their properties in silica-based optical fibers

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ABSTRACT

Lasers and amplifiers based on thulium-doped silica fibers require improved spectroscopic properties. In this context, one of the most promising approaches is based on the embedding of thulium ions in nanoparticles of tailored composition and structure. This paper presents various methods used to produce thulium-doped nanoparticles inside silica-based optical fibers. Effects of solution doping method during the elaboration of Modified Chemical Vapor Deposition preform and doping solution composition are studied. A comparison is made between the use of solutions containing $\text{LaF}_3\text{:Tm}^{3+}$ or YAG:Tm^{3+} nanoparticles and aluminum-lanthanum-thulium chlorides. Results show that for similar lanthanum content, lanthanum-thulium chlorides doping allows for similar enhancement of $^3\text{H}_4$ level of Tm^{3+} than $\text{LaF}_3\text{:Tm}^{3+}$ doping. Also, effects of aluminum on $^3\text{H}_4$ lifetime enhancement and inhibition of nanoparticle's formation is discussed.

Keywords: Optical fiber, nanoparticles, thulium, silica, aluminum, lanthanum, yttrium

1. INTRODUCTION

Silica-based optical fibers doped with rare-earth (RE) ions are largely used as amplifiers or lasers [1]. Among RE ions, thulium (Tm^{3+}) is widely studied for the 1.9 μm emission band or its others various transitions emitting in the visible and near infrared (0.45-3.9 μm) demonstrated in low phonon materials [2]. Yet, despite the enabling of these emissions, these host materials also possess insufficient properties such as, in the context of fiber lasers, low glass transition temperature and low optical damage threshold. For these considerations, silica glass remains a material of prime quality. Indeed, high power fiber lasers have been demonstrated in silica [1]. However, silica's properties may also represent drawbacks, such as its high phonon energy or low solubility of luminescent ions [3]. In that purpose, the encapsulation of luminescent ions in nanoparticles is envisioned as a way to both combine the beneficial properties of silica matrix and tailored

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spectroscopic response of a more suitable host. In comparison to silica, enhancement of energy transfers, modification of phonon energy and modification of emission spectra have already been demonstrated [4,5,6].

Among thulium's problematics, in silica-based optical fibers, many studies focus on the enhancement of energy transfer, decrease of photodarkening or of the local phonon energy [5,6,7,8]. The effect of $\text{LaF}_3\text{:Tm}^{3+}$ nanoparticles doping in the porous layer of Modified Chemical Vapor Deposition (MCVD) preform has already proved its efficiency to alter the spectroscopic properties of Tm^{3+} ions [6]. To go further, this report discusses about several routes of fabrication of silica-based optical fibers containing thulium-doped nanoparticles. Fiber samples were prepared by different solution doping techniques such as nanoparticles ($\text{LaF}_3\text{:Tm}^{3+}$ and YAG:Tm^{3+}) and chlorides doping. Samples were characterized and compared according to their composition, nanoparticles content, and in terms of optical losses and modification of the $^3\text{H}_4$ lifetime fluorescence. The effect of aluminum on the spectroscopic properties and material features is discussed also. Fluorescence lifetime measurements show that the use of lanthanum chloride allows for a $^3\text{H}_4$ lifetime enhancement similar to that of $\text{LaF}_3\text{:Tm}^{3+}$ nanoparticles doping. Scanning Electron Microscopy (SEM) imaging revealed the ability of both systems to form nanoparticles in the optical fibers for lanthanum content higher than 3000 at. ppm. The co-doping with aluminum lowers the fluorescence lifetimes.

2. EXPERIMENTAL

1. Fabrication of samples

Various sets of optical fibers drawn from MCVD preforms were produced with different doping techniques. Details are reported in Table 1. A first set of samples (LaF0.1-a , LaF0.1-b , LaF1 and YAG) was prepared by injecting $\text{LaF}_3\text{:0.1\%Tm}^{3+}$, $\text{LaF}_3\text{:1\%Tm}^{3+}$ or $\text{YAG:0.1\%Tm}^{3+}$ nanoparticles doping solution into the rotating tube maintained horizontally on the MCVD lathe. The fluoride converts to an oxide (La-rich silicate) during the high temperature lathe and fiber draw processing. For more details on nanoparticle and preform formation, see Ref. 6 and references therein. A second set of fibers (LaCl-a , LaCl-b and LaCl-c) was produced by the conventional solution doping technique with ethanol-based solutions containing various concentrations of TmCl_3 and LaCl_3 [9]. A third set of fibers (Al , AlLa-a and AlLa-b) was prepared using the gradual-time doping method [10]. In this technique, two doping solutions (indicated as solutions A and B in Table 1) are used to obtain a longitudinally varying preform composition. Doping solutions contain AlCl_3 , TmCl_3 and LaCl_3 or CeCl_3 [7,8]. For these samples, no germanium was incorporated to increase the refractive index.

After the doping step, the porous layer was sintered at 1800°C and tube collapse into the final preform was performed at a temperature above 2200°C . The diameter of the final preform was around 10 mm. Fibers were drawn at a temperature of approximately 2000°C and draw tension varying between 0.42 and 0.44 N. The fibers were coated with a UV-curable polymer (Desolite 3471-3-14, DSM). The diameter of the uncoated fibers was 125 μm (core diameter is between 5 and 10 μm).

2. Characterization of samples

Scanning electron microscopy (SEM), Energy dispersive x-ray (EDX) and electron probe microscopy (EPMA) analyses were used to characterize the composition of fiber samples and the presence of nanoparticles. Data of fiber samples are provided in Table 2. SEM measurements were performed on transversal sections of preforms and fibers to investigate the presence of nanoparticles. Samples were polished (preforms) or cleaved (fibers) and carbon coated for the SEM imaging. Both secondary electron imaging and backscattered electrons were used to discriminate coating artifacts. As an example, image of nanoparticles in LaF0.1-b fiber is showed in Figure 1.

EDX and EPMA analyses were conducted in the core of fiber samples to measure La, Al, Ge and Y contents. Maximum concentrations are indicated for all samples in Table 2. Thulium contents were deduced from attenuation measurements performed with the cut-back technique and the use of thulium's attenuation values of reference [11,12]. Two cases prevented the use of the above measurements techniques: high optical losses preventing from measuring Tm^{3+} absorption spectra or La^{3+} content being inferior to detection limit (1 wt. %). For both cases, indicated with a star in Table 2, concentrations were deduced by crossing EDX values and attenuation analyses with the Tm^{3+} content of initial nanoparticles [5].

Spectral attenuation was performed by the cut-back technique on fiber samples measuring between 2 cm and 1 m. Indeed, the wide range of thulium content imposed the use of different lengths to avoid absorption saturation and to

optimize accuracy. Luminescence decays, were measured on centimetric samples pumped at 785 nm and contra-propagative fluorescence was collected on an APD. For more details, see Ref. 7.

Table 1. Details of the MCVD preforms. Doping techniques, doping elements and nominal concentrations in doping solutions are indicated. Core's aspect of the preforms is also reported (white aspect indicating the presence of nanoparticles in the core of the optical preforms).

Sample	Doping Technique	Doping elements	Concentration in doping solution in mol.l ⁻¹ (number of injections)	Core's Aspect
LaF0.1-a	horizontal	LaF ₃ : 0.1 % Tm ³⁺	0.088 (3)	White-Transparent
LaF0.1-b	horizontal	LaF ₃ : 0.1 % Tm ³⁺	0.53 (3)	White
LaF1-a	horizontal	LaF ₃ : 1 % Tm ³⁺	0.0265 (1)	White-Transparent
LaF1-b	horizontal	LaF ₃ : 1 % Tm ³⁺	0.0003-0.03	White-Transparent
YAG	horizontal	YAG:0.1 % Tm ³⁺	0.025 (1)	White-Transparent
LaCl-a	solution	LaCl ₃ -TmCl ₃	0.0003-0.03	Transparent
LaCl-b	solution	LaCl ₃ -TmCl ₃	0.0003-0.03	Transparent
LaCl-c	solution	LaCl ₃ -TmCl ₃	0.0015-0.15	White-Transparent
Al	Gradual-time	AlCl ₃ -CeCl ₃ -TmCl ₃	Sol. A: [AlCl ₃]=0.7, [CeCl ₃]=0, [TmCl ₃]=0.02 Sol. B: [AlCl ₃]=0.7, [CeCl ₃]=0.02, [TmCl ₃]=0.02	Transparent
AlLa-a	Gradual-time	AlCl ₃ -LaCl ₃ -TmCl ₃	Sol. A: [AlCl ₃]=0.7, [LaCl ₃]=0.03, [TmCl ₃]=0.02 Sol. B: [AlCl ₃]=0.7, [LaCl ₃]=0.15, [TmCl ₃]=0.02	Transparent
AlLa-b	Gradual-time	AlCl ₃ -LaCl ₃ -TmCl ₃	Sol. A: [AlCl ₃]=0.7, [LaCl ₃]=0.1, [TmCl ₃]=0.02 Sol. B: [AlCl ₃]=0.7, [LaCl ₃]=0.7, [TmCl ₃]=0.02	Transparent

Table 2. Data of fiber samples. For the values labeled with a star, see the text. Y/Ce and Al contents are indicated in the “[La]” and “[Ge]” columns, respectively.

Sample	[Tm] (at. ppm)	[La] (at. ppm)	Losses à 1300 nm (dB/m)	Lifetime (μ s)	[Ge] (at. %)	Particles in fibers
LaF0.1-a	5	3000	0.02	58	2	Yes
LaF0.1-b	28*	20000	2250	70	0.8	Yes
LaF1-a-1	139*	9800	275	41	1.1	Yes
LaF1-a-2	85*	6100	250	51	1.2	Yes
LaF1-a-3	5	500	0.03	23	2	No
LaF1-a-4	11	1100	0.05	25	2	No
LaF1-a-5	24	1500	0.15	31	1.42	No
LaF1-a-6	20	2200	0.01	32	2	No
LaF1-a-7	34	1700	0.03	36	1.9	No
LaF1-a-8	38	2100	0.03	34	0.7	No
LaF1-a-9	2	130*	0.02	24	N.A.	No
LaF1-a-10	33	2160*	0.06	33	N.A.	No
LaF1-a-11	175*	12300	N.A.	46	0.45	Yes
LaF1-b	40	2620*	0.05	46	N.A.	No
YAG	10	[Y]= 5400	0.5	37	0.28 [Al]= 1.74	No
LaCl-a	3	1000	0.01	29	1.1	No
LaCl-b	26	1200	0.01	24	1.2	No
LaCl-c	22	3300	0.9	64	0	Yes
Al	150	[Ce]=0	1.1	20	[Al]= 0.8	No
AlLa-a1	160	350	0.09	21	[Al]= 0.8	No
AlLa-a2	190	1700	0.4	22	[Al]= 0.8	No
AlLa-b	230	7000	1	30	[Al]= 0.8	No

Figure 1. SEM image of LaF0.1-b fiber.

3. RESULTS

The 1/e-lifetimes of the $^3\text{H}_4$ level are reported in Figure 2. Whatever the doping techniques, the lifetime value without lanthanum is about 20-25 μs and the higher the lanthanum or yttrium content, the higher the lifetime. When doping with $\text{LaF}_3:0.1\%\text{Tm}^{3+}$ and $\text{LaF}_3:1\%\text{Tm}^{3+}$ nanoparticles, the lifetime increases up to 70 and 50 μs , respectively. For the latter doping, the increase is less pronounced when La^{3+} content is higher than 3000 at. ppm. When doping with chlorides salts, the lifetime increases up to 64 and 30 μs for $\text{LaCl}_3\text{-TmCl}_3$ and $\text{AlCl}_3\text{-LaCl}_3\text{-TmCl}_3$ doping solutions, respectively. By doping with YAG:Tm^{3+} nanoparticles, the lifetime is 37 μs .

Figure 2: 1/e-lifetimes of the $^3\text{H}_4$ level of Tm^{3+} . For the sample without lanthanum (sample Al), the lifetime is 20 μs .

Figure 3: Optical losses measured at 1300 nm for samples elaborated by LaF₃: Tm³⁺ horizontal doping and LaCl₃-TmCl₃ solution doping.

The optical losses were measured at 1300 nm by the cut-back technique. This wavelength has been chosen because there is no absorption band due to the presence of Tm³⁺ ions or OH⁻ in this spectral domain. Optical losses increase with La³⁺ content for all sets of samples (see Figure 3). Attenuation is lower than 0.1 dB/m when La³⁺ content is lower than 3000 at. ppm, while above this concentration, attenuation increases drastically, reaching more than 1000 dB/m for 20000 at. ppm of lanthanum (LaF₃:0.1%Tm³⁺ doping). These high optical losses variations were correlated with the presence of nanoparticles in the fibers, detected only for La³⁺ content higher than 3000 at. ppm.

4. DISCUSSION

1. LaF₃:Tm³⁺ vs LaCl₃-TmCl₃ doping method

The doping of the porous core layer with LaF₃:Tm³⁺ nanoparticles can lead to the presence of amorphous particles in the optical fibers [6]. These nanoparticles were evidenced to be lanthanum-rich and fluorine-free. As the fluorine ions evaporate during the MCVD process, we compare the spectroscopic properties of Tm³⁺ ions with fibers prepared according to the standard solution doping process, *i.e.* with LaCl₃ and TmCl₃ chlorides salts. Three features can be extracted from the lifetimes reported in the Figure 2:

- lifetimes increase with lanthanum concentration in the range 0-3000 at. ppm La³⁺, for both LaF₃:1%Tm³⁺ and LaCl₃-TmCl₃ processes. The measured lifetime depends on the radiative lifetime and the non-radiative decay rate. The energy difference between the ³H₄ and ³H₅ levels is less than 4000 cm⁻¹. Then, the fluorescence lifetime depends strongly on the non-radiative decay rate, hence the phonon energy of the environment. As the La₂O₃ phonon energy (~400 cm⁻¹ [13]) is lower than that of silica (1100 cm⁻¹), the increase of the lifetimes can be attributed to the enrichment of lanthanum in the environment of Tm³⁺, even if nanoparticles were not detected for this concentration range of La³⁺.
- for [La³⁺]≈3000 at. ppm, LaF₃:0.1%Tm³⁺ and LaCl₃-TmCl₃ doping processes induce similar lifetimes. This could be surprising as the LaF₃:Tm³⁺ nanoparticles approach would be expected to lead to a higher content of La³⁺ in Tm³⁺ environment, hence a higher Tm³⁺ lifetime. However, a high content of OH⁻ groups was measured in fibers prepared with the LaF₃:Tm³⁺ nanoparticles process (see Figure 4). The content of OH⁻ groups is estimated to be about 10 at. ppm [6]. As these radicals absorb at 1.38 μm, an energy transfer between Tm³⁺ ions (³H₄-³F₄ emission wavelength is about 1.45 μm) can occur, inducing a decrease of the Tm³⁺ lifetime. Then, by removing the OH⁻ groups, the LaF₃:0.1%Tm³⁺ process could lead to a higher Tm³⁺ lifetime.
- for [La³⁺]>3000 at. ppm, LaF₃:0.1%Tm³⁺ doping process lead to higher lifetime than LaF₃:1%Tm³⁺ one. This was attributed to energy transfer which may occur between Tm³⁺ ions [6]. Indeed, it has already been shown that nanoparticles doping induces spatial localization of rare-earth ions and therefore enhances energy transfer [5]. For La³⁺ concentration higher than 3000 at. ppm, Tm³⁺ lifetimes slightly change for a given doping process. This tends to prove that the Tm³⁺ environment should not drastically change.

Figure 4: Absorption spectra of samples prepared with nanoparticles doping (LaF0.1-a and YAG) and standard solution or gradual-time doping (LaCl-a and AlLa-a). Absorption spectra were normalized at 1.21 μm .

2. Effect of aluminum

It has been reported that in silica-based optical fibers, the lifetimes of Tm^{3+} ions increase almost linearly from 14 to 50 μs with the aluminum concentration varying from 0 to 18 mol% $\text{AlO}_{3/2}$ [14]. The lifetimes reported in this article demonstrate that La^{3+} is more efficient to improve Tm^{3+} lifetimes. Indeed, an increase of 40 μs is obtained by co-doping with 3000 at. ppm of La^{3+} , while the same concentration of aluminum would lead to an increase of 5 μs only.

When the samples are co-doped with lanthanum and aluminum, the lifetimes are intermediate values between La-free and Al-free samples. For the fibers prepared according to the $\text{AlCl}_3\text{-LaCl}_3\text{-TmCl}_3$ doping process, the aluminum content is constant (about 8000 at. ppm) which should lead to a lifetime of 20 μs according to the Ref. 14. This is in agreement with the value reported for La-free sample of this set. When La^{3+} content increases (while keeping constant aluminum concentration), the Tm^{3+} lifetime increases, but at a lower rate compare to the Al-free sample (see Figure 2). For the fiber prepared with YAG:Tm^{3+} nanoparticles, the lifetime is 37 μs . Once again, the lifetime is improved compare to Y-free sample. Indeed, the lifetime expected for the same fiber with the corresponding aluminum content (17400 at. ppm) would be 25 μs . All these results clearly demonstrate that there is a competition between lanthanum, yttrium and aluminum to be located on the environment of thulium ions. Structural analyses of these glasses would allow to clarify these modifications.

Aluminum also prevents the presence of nanoparticles. This ion is known to offer a better solubility for rare-earth ions [15]. In the set of $\text{AlCl}_3\text{-LaCl}_3\text{-TmCl}_3$ samples, no nanoparticles were observed in the fibers, even for the highest La^{3+} concentration (7000 at. ppm). Nanoparticles (smaller than 100 nm) were imaged in the preform prepared with YAG:Tm^{3+} nanoparticles (see Figure 5) whereas they were not observed in the fiber. The fiber drawing step has to be carefully studied in the context of the fibers containing nanoparticles as it can degrade the integrity of the nanoparticles [16].

Figure 5: SEM image of YAG preform.

5. CONCLUSION

In conclusion, we have investigated the influence of La, Y and Al elements on the spectroscopic properties of thulium-doped silica-based optical fibers. Several Modified Chemical Vapor Deposition preforms were elaborated by using different doping techniques. Horizontal doping of YAG:Tm³⁺ and LaF₃:Tm³⁺ nanoparticles was performed, as well as gradual-time doping of lanthanum, aluminum and thulium chlorides and standard solution doping of lanthanum and thulium chlorides. Optical fibers were drawn and characterized for their compositions, nanoparticles content and spectroscopic properties. The beneficial effect of lanthanum content on ³H₄ lifetime of Tm³⁺ was demonstrated for all doping techniques and compositions. It was reported that the doping with a solution of thulium and lanthanum chlorides allows to achieve similar lifetime enhancement (64 μs) as for LaF₃:Tm³⁺ nanoparticles doping (70 μs). Moreover, the doping with nanoparticles leads to the presence of a high content of OH⁻ groups, which would decrease the fluorescence lifetime due to possible energy transfer mechanisms. In the case of aluminum, we showed that the presence of this ion reduces the beneficial effect of lanthanum on ³H₄ lifetime and prevents the formation of nanoparticles. All these results provide routes to improve the spectroscopic properties of Tm³⁺ ions.

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REFERENCES

- [1] D. Richardson, J. Nilsson, W. Clarkson, “High power fiber lasers: current status and future perspectives” [invited], JOSA B 27 (11), B63-B92 (2010).
- [2] X. Zhu, N. Peyghambarian, “High-power ZBLAN glass fiber lasers: review and prospect”, Adv. Optoelectron. 2010, 501956 (2010).
- [3] M.C. Gonçalves, L.F. Santos, R.M. Almeida, “Rare-earth-doped transparent glass ceramics”, Comptes Rendus Chim. 5 (12) , 845-854 (2002).

- [4] F. d'Acapito, W. Blanc, B. Dussardier, "Different Er^{3+} environments in Mg-based nanoparticle-doped optical fibre preforms", *J. Non Cryst. Solids* 401, 50-53 (2014).
- [5] C. Kucera, B. Kokuoz, D. Edmondson, D. Griesse, M. Miller, A. James, W. Baker, J. Ballato, "Designer emission spectra through tailored energy transfer in nanoparticle-doped silica preforms", *Opt. Lett.* 34 (15) (2009) 2339-2341.
- [6] M. Vermillac, *et al.*, "Use of thulium-doped LaF_3 nanoparticles to lower the phonon energy of the thulium's environment in silica-based optical fibres", *Opt. Mater.* 68, 24-28 (2017).
- [7] J.-F. Lupi, *et al.*, "Impact of cerium and lanthanum on the photo-darkening and photo-bleaching mechanisms in thulium-doped fibre", *Opt. Mater.* 72, 106-114 (2017).
- [8] J.-F. Lupi, *et al.*, "Steady photodarkening of thulium alumino-silicate fibers pumped at 1.07 μm : quantitative effect of lanthanum, cerium, and thulium", *Opt. Lett.* 41 (12), 2771-2774 (2016).
- [9] J. Townsend, S. Poole, D. Payne, "Solution-doping technique for fabrication of rare-earth-doped optical fibres", *Electron. Lett.* 7 (23), 329-331 (1987).
- [10] J.F. Lupi, M. Vermillac, S. Trzesien, M. Ude, W. Blanc, B. Dussardier, "Gradual-time solution doping for the fabrication of longitudinally varying optical fibres", *J. Lighthwave Technol.* 36, 1786-1791 (2018).
- [11] B.M. Walsh and N.P. Barnes. "Comparison of $\text{Tm} : \text{ZBLAN}$ and $\text{Tm} : \text{silica}$ fiber lasers ; spectroscopy and tunable pulsed laser operation around 1.9 μm ". *Applied Physics B*, 78(3-4), 325-333 (2004).
- [12] Yuen H Tsang, Daniel J Coleman, and Terence A King. "High power 1.9 μm Tm^{3+} -silica fibre laser pumped at 1.09 μm by a Yb^{3+} -silica fibre laser". *Optics communications*, 231(1), 357-364 (2004).
- [13] J. Zarembowitch, J. Gouteron, A. Lejus, "Raman spectra of lanthanide sesquioxide single crystals with A-type structure", *Phys. Status Solidi (b)* 94 (1) 249-256 (1979).
- [14] B. Faure, W. Blanc, B. Dussardier, G. Monnom, "Improvement of the $\text{Tm}^{3+} : ^3\text{H}_4$ level lifetime in silica optical fibers by lowering the local phonon energy", *J. Non Cryst. Solids* 353 (29), 2767-2773 (2007).
- [15] Dignonnet, Michel JF, ed. "*Rare-earth-doped fiber lasers and amplifiers*", revised and expanded. CRC press, 2001.
- [16] M. Vermillac *et al.*, "Fiber-draw-induced elongation and break-up of particles inside the core of a silica-based optical fiber," *J. Amer. Ceram. Soc.*, 100 (5), 1814-1819 (2017).