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# IN-SITU GROWN ERBIUM-DOPED DIELECTRIC NANOPARTICLES IN SILICA-BASED TRANSPARENT OPTICAL FIBERS

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**Abstract:** An efficient method to fabricate transparent glass ceramic fibers containing in-situ grown Er<sup>3+</sup>-doped oxide nanoparticles is presented. Characterization of the drawn fibers exhibits low loss (0.4 dB/m) and broadened Er<sup>3+</sup> emission spectrum. This attractive method offers new scopes for fiber amplifiers.

## 1. INTRODUCTION

Developing of new rare-earth (RE)-doped optical fibers for power amplifiers and lasers require continuous improvements in the fiber spectroscopic properties (like gain and efficiency characteristics, resistance to spectral hole burning and photodarkening,...) besides reduction in device size and economical efficiency. Silica glass as a host material for fibers has proved to be very attractive. However some potential applications of RE-doped fibers suffer from limitations in terms of spectroscopic properties resulting from clustering or inappropriate local environment when doped into silica. Several mixed-oxide and non-oxide alternatives to silica have been successfully proposed to obtain spectroscopically improved amplifying singlemode fibers, however inducing fabrication difficulties and high cost.

The route of interest here consists of using silica as a mechanical host and support of the fiber optical waveguide, and of embedding RE-ions within oxide nanoparticles of composition and structure different from those of silica, and small enough to reduce scattering loss below an acceptable, application-dependent level. When nanoparticles have a crystalline structure the term Transparent Glass Ceramics (TGC) is used [1]. However the nanoparticle may also be amorphous, such as those obtained by phase separation [2]. In the following we use the term TGC in both cases for convenience.

Scarce reports on RE-doped TGC singlemode fibers use low melting mixed oxides prepared by a rod-in-tube technique [3], or mixed oxyfluorides using a double-crucible technique [4], both with a subsequent ceramming stage. However the low melting point of these materials causes low compatibility with silica components. Transition metal-doped silica-based TGC fibers were prepared by MCVD (modified chemical vapor deposition) and using a slurry method [5], i.e. the particles were synthesized before insertion into the silica tube-substrate. We have proposed a more straightforward technique allowing to embed RE ions within in-situ

grown oxide nanoparticles in silica-based preforms [6]. The implemented principle is the spontaneous phase separation process [2]: Silicate systems can exhibit strong and stable immiscibility when they contain divalent metals oxides (MO, where M= Mg, Ca or Sr). For example, if a silicate glass containing few mol% of MO is heated it will decompose into two phases : one silica-rich and one MO-rich in shape of spherical particles. Two key advantages of this process are that (i) nanoparticles are grown in-situ during the course of the fabrication process and (ii) there is no need (and associated risks) of nanoparticles manipulation by an operator. Further, the process takes advantage of the high compositional control and purity typical of the MCVD technique. The role of CaO in the formation of nanoparticles in fibers has been already reported [6,7]. However their typical diameter was > 100 nm, causing very high scattering losses. A similar phenomenon was observed when incorporating SrO.

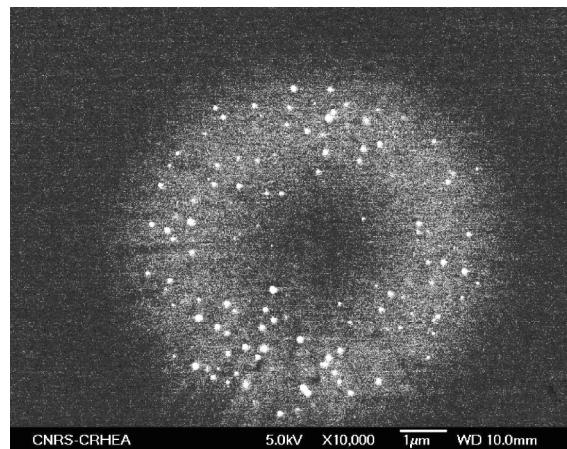


Fig 1: SEM picture of a Mg-doped fiber (fiber A).

In the present paper, we aim at showing the potential of a simple technique to produce silica-based fibers with the core made of a spectroscopically-modified RE-doped TGC. We

report on the growth of erbium-doped MgO-silicate nanoparticles using the MCVD and solution doping techniques, and on the demonstration of nanoparticle stability after the fiber drawing stage. The nanoparticles mean diameter within the fiber is less than 50 nm, inducing scattering loss of 0.4 dB/m at 1350 nm. Such loss would be acceptable for fiber amplifier or laser applications, where few meters of fiber are used. Further it is shown that the Er<sup>3+</sup> emission band is broadened when compared to a standard Er-doped fiber. This demonstrates the potentiality of this fabrication technique for applications such as fiber amplifiers.

## 2. EXPERIMENTALS AND RESULTS

### 2.1. Fiber fabrication

Silica preforms were prepared by the usual MCVD process. Germania along with a small amount of phosphorous was added during the fabrication of the preforms to raise the refractive index of the core and for ease in fabrication, respectively. The series of preforms had a refractive index contrast in the range  $\Delta n = 1.7$  to  $4 \times 10^{-3}$ . A detailed description of the technique adapted for DNP growing was reported elsewhere [7]. Magnesium and erbium elements were incorporated through the solution doping technique. Here the critical process parameter is the concentration of magnesium in the soaking solution. We report on two particular samples labeled Fiber A and Fiber B, doped with solutions containing 0.1 and 1 mol/l of Mg salts, respectively. The erbium concentration in the solution was kept constant at 0.01 mol/l. The preforms were stretched into 125  $\mu\text{m}$  fibers using a conventional drawing tower. The resulting fiber core radius was  $\sim 8 \mu\text{m}$ . The attenuation coefficient due to absorption by Er<sup>3+</sup> ions at 1.53  $\mu\text{m}$  was measured to be 9 dB/m in Fiber A.

### 2.2. DNP characterizations

The fibers were characterized through scanning electron microscopy (SEM, backscattered electrons). One typical SEM picture from the exposed core section of a cleaved fiber (Fiber A) is shown on Fig. 1. The nanoparticles are visible as bright spots, showing the important composition contrast compared to the silica background. The fiber core corresponds to the gray disk. The dark central part of the core is caused by the evaporation of germanium and magnesium elements; this is a common artifact of the MCVD technique that can be easily corrected by process optimization. Analysis of MEB images reveals the nanoparticle mean size  $\sim 40$  nm, and the inter-particle distance within the 100-500 nm-range. The nanoparticles formation is linked to the addition of Mg. No particle bigger than 100 nm was observed in these MgO-doped fibers, unlike the case of CaO-doped fibers [8]. When the solution concentration

increases from 0.1 to 1 mol/l, the density of particles remains nearly the same but the mean particle diameter almost doubles to  $\sim 80$  nm.

### 2.3. Low attenuation fiber

The scattering loss in fibers A and B was measured through the cut-back method. The fiber bending radius was kept  $> 20$  cm to minimize bend loss. The fiber A attenuation spectrum is displayed in Fig. 2. The wavelength range on this figure is limited by the Er<sup>3+</sup> absorption bands at 980 and 1535 nm. At the wavelength of 1350 nm, losses were measured to be 0.4 dB/m only. This value is comparable with the attenuation measured in low-melting temperature TGC fibers [3] and is compatible with amplifier applications. Increase in loss with decrease in wavelength is attributable to stronger light scattering induced by the nanoparticles. Due to the small particle size we assume Rayleigh scattering to be the major source of scatter loss, which was estimated according to the formula:  $\alpha(\text{dB}/\text{m}) = 4.34 \times C_{\text{Rayleigh}} \cdot N \cdot \Gamma$ , where  $N$  is the DNP density ( $\text{m}^{-3}$ ),  $\Gamma$  is the overlap factor between the field and the core containing the DNP ( $\Gamma = 0.3$  in fiber A) and  $C_{\text{Rayleigh}}$  ( $\text{m}^2$ ) is the Rayleigh scattering coefficient [9]:

$$C_{\text{Rayleigh}} = \frac{(2\pi)^5}{48} \times \frac{d^6}{\lambda^4} \times n_m^4 \times \left( \frac{n_n^2 - n_m^2}{n_n^2 + 2n_m^2} \right)^2 \quad (1)$$

where  $d$  is the nanoparticle diameter,  $n_m$  and  $n_n$  the host material and particles refractive indices (assuming same index in particles as in the bulk material), respectively. The actual particle composition is not known but a high content of MgO is expected [10]. Their refractive index is estimated at  $\sim 1.65$ , like that of Mg-based oxide such as Mg<sub>2</sub>SiO<sub>4</sub> [11]. Under these considerations, fitting of

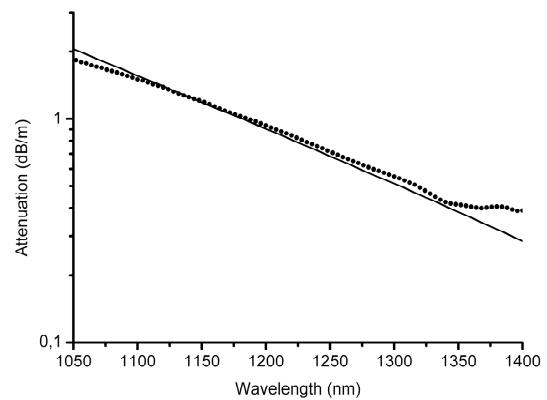


Fig. 2: Transmission spectrum of a Mg-doped fiber (fiber A). Dots: experimental data, full line: calculated Rayleigh scattering curve.

the experimental data with Eq. 1 yields a particle density  $N \sim 0.4 \times 10^{20} \text{ m}^{-3}$ , or equivalently a mean inter-particle distance  $\sim 300 \text{ nm}$ . These values agree well with the results collected from the SEM pictures taken from cleaved fibers.

At 1350 nm, the normalized frequency  $V$  was lower than 1.3 ( $LP_{11}$  mode cut-off wavelength is 700 nm). The difference between experimental data and Rayleigh scattering curve above 1350 nm is attributed to bending loss only. However for practical application, the presented fabrication technique allows any necessary waveguide optimization without preventing the TGC growth. The attenuation of Fiber B was extremely high (several 100s dB/m), in agreement with the Rayleigh formula (120 dB/m) assuming large monodisperse 100 nm particles. This shows that the particle mean size must be less than 50 nm for potential applications, and that the technique presented here is able to produce fibers with acceptable scattering loss.

#### 2.4. Spectroscopic characterization of $\text{Er}^{3+}$

The emission spectra and lifetime from Fibers A and B were measured at room temperature around 1.55  $\mu\text{m}$  under 980-nm excitation. The shape of the emission spectrum from Fiber A (Fig. 3) is broadly similar to the one of a fiber without particles (not shown). Fiber B shows a distinct broadening of its spectrum by as much as  $\sim 50\%$  compared to Fiber A. Moreover, on the spectrum from Fiber B the shape of the curve between the peaks at 1.53 and 1.55  $\mu\text{m}$  decreases monotonically; further the characteristic dip in the emission spectrum (in conventional erbium doped fibers) at 1.54  $\mu\text{m}$  is also absent. These

features are attractive for realizing intrinsically gain flattened fiber amplifiers.

Both fibers A and B produced exponential fluorescence decay curves (not shown). The fitted lifetimes are 11 and 7 ms, respectively. In particular, no fast component at short times was observed, showing that no effect of cross-relaxation occurred and hence no ions pair or cluster was formed. The lower lifetime obtained from Fiber B is tentatively interpreted as an effect of the modification of the erbium ions average local field. In other words erbium ions in Fiber B are, in average, located in a medium with higher local field compared to Fiber A. This induces stronger spontaneous transition probability, and hence a shorter lifetime [12]. Therefore the confinement/embedding of Er ions in nanoparticles is stronger in Fiber B than in Fiber A.

Modifications of the  $\text{Er}^{3+}$  spectroscopic properties in the TGC optical fibers are clearly evident from the above results when the Mg concentration increases, as it was observed in Ca-doped preforms [8]. Here this is observed in optical fibers for the first time. The broadening is attributed to the modification of the  $\text{Er}^{3+}$  ions environment due to its presence in the Mg-rich region particularly in Fiber B, whereas in Fiber A a great part of erbium ions stay in the silica glass host. The difference between spectra from Fiber A and B shows that accurate partitioning of ions in or out of particles is possible by adjusting fabrication parameters. Further process optimization is under way to increase the control of the spectroscopic properties of rare-earth ions within TGC fiber core with a strict control of nanoparticle diameter below the 50 nm limit, so that fibers of type Fiber B would have reduced loss acceptable for applications.

### 3. CONCLUSIONS

A method to fabricate nanostructured  $\text{Er}^{3+}$ -doped fibers entirely through the MCVD process is demonstrated. By adding magnesium to the silica-based composition, nanoparticles of 40 nm in diameter are obtained through in situ growth without requiring a separate process to realize nanoparticles (such as post-process ceramming). Fibers with relatively low Mg content and small nanoparticles have low-loss. Moreover, by increasing the content in Mg, we have observed a broadening of the emission spectrum by as much as almost 50 % and a sensible change of the band curve shape. These are attractive features to realize gain flattened fiber amplifiers. More generally, this concept has great potentials as possible solutions to nowadays issues in amplifying fibers, including (but not limited to) amplifiers intrinsic gain flattening and/or spectral hole burning, amplifiers irradiation strengthening, photodarkening in fiber lasers, etc.

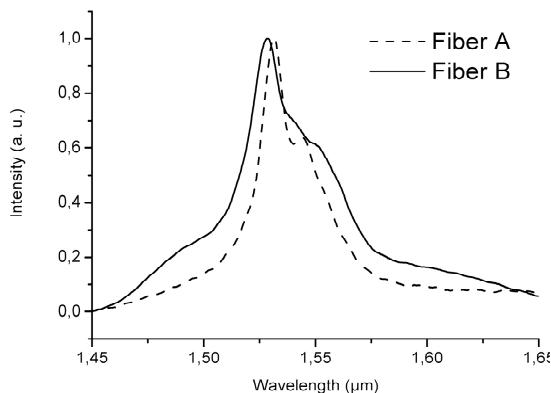


Fig. 3: Room temperature emission spectra from fibers A and B. The Mg concentration in the doping solution is 0.1 and 1.0 mol/l, respectively. Excitation wavelength is 980 nm.

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## REFERENCES

- [1] M. Clara Gonçalves, L. F. Santos and R. M. Almeida, « Rare-earth-doped transparent glass ceramics », *C. R. Chimie*, **5**, 845 (2002).
- [2] J. Zarzycki, in *Glasses and the vitreous state* (Cambridge University Press, 1991).
- [3] B.N. Samson, L. R. Pinckney, J. Wang, G. H. Beall and N. F. Borrelli, “Nickel-doped nanocrystalline glass-ceramic fiber”, *Opt. Lett.*, **27**, 1309(2002).
- [4] B. N. Samson, P. A. Tick, and N. F. Borrelli, «Efficient neodymium-doped glass-ceramic fiber laser and amplifier », *Opt. Lett.*, **26**, 145(2001).
- [5] S. Yoo,U.-C. Paek,W.-T. Han, «Development of a glass optical fiber containing ZnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass-ceramics doped with Co<sup>2+</sup> and its optical absorption characteristics », *J. Non-Cryst. Sol.*, **315**, 180 (2003).
- [6] F. d'Acapito, C. Maurizio, M.C. Paul, Th. S. Lee, W. Blanc and B. Dussardier, “Role of CaO addition in the local order around Erbium in SiO<sub>2</sub>-GeO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> fiber preforms”, *Mater. Sci. Eng.*, **B 146**, 167 (2008).
- [7] W. Blanc, B. Dussardier and M.C. Paul, “Er doped oxide nanoparticles in silica based optical fibres”, *Glass Technol.: Eur. J. Glass Sci. Technol.*, **A 50**, 79 (2009).
- [8] W. Blanc, B. Dussardier, G. Monnom, R. Peretti, A.-M. Jurdyc, B. Jacquier, M. Foret and A. Roberts, “Erbium emission properties in nanostructured fibers”, *Appl. Opt.*, **48**, G119 (2009).
- [9] C.F. Bohren and D.R. Huffman, in *Absorption and scattering of light by small particles* (Wiley, 2004).
- [10] J.F. Stebbins, N. Kim, M. J. Andrejcak, P. M. Boymel and B. K. Zoitos., « Characterization of Phase Separation and Thermal History Effects in Magnesium Silicate Glass Fibers by Nuclear Magnetic Resonance Spectroscopy », *J. Am. Ceram. Soc.*, **92**, 68(2009).
- [11] Z. Burshtein and Y. Shimony, “Refractive index dispersion and anisotropy in Cr<sup>4+</sup>:Mg<sub>2</sub>SiO<sub>4</sub>”, *Opt. Mat.*, **20**, 87 (2002).
- [12] B. Henderson and G. F. Imbusch, in *Optical Spectroscopy of Inorganic Solids* (Clarendon, Oxford, 1989) p. 173.