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## Erbium spectroscopy in photosensitive tin-doped silica glass

Norberto Chiodini<sup>\*a</sup>, Alberto Paleari<sup>a</sup>, Giorgio Spinolo<sup>a</sup>, Gilberto Brambilla<sup>b</sup>, Alberto Chiasera<sup>c</sup>,  
Maurizio Ferrari<sup>c</sup>

<sup>a</sup>Istituto Nazionale Fisica della Materia-University of Milano-Bicocca, 20125 Milano, Italy;

<sup>b</sup>Optoelectronics Research Centre - University of Southampton, Southampton, SO17-1BJ, UK

<sup>c</sup>Istituto nazionale Fisica della Materia-University of Trento, 38050 Povo-Trento, Italy

### ABSTRACT

There is considerable interest in Er-doped silica-based materials with photosensitive properties for lasing and photorefractive applications. Tin doping has been recently found to induce strong and stable photosensitivity in silica glass. In this work, Er co-doped Sn-doped silica samples are obtained by sol-gel method by hydrolysis and condensation of TEOS and tin dibutyl diacetate,  $\text{Er}(\text{NO}_3)_3$ , or  $\text{Er}(\text{CH}_3\text{COO})_3$  as dopant precursors. Samples with Er content ranging between 0.1 and 1 mol% are investigated. Sn doping (0.4 mol%) is employed to induce photorefractivity properties in the glassy host. Time resolved photoluminescence, optical absorption and refractive index measurements are carried out and analyzed as a function of the Er content. The specific effects of Er content and Sn doping on the rare earth emission efficiency and photosensitivity of the glass are discussed. In particular it is shown that the Er emission shows the typical features of Er doped sol gel silica and the strong photosensitivity induced by tin doping is not affected by rare earth ions.

**Keywords:** Erbium, tin, glass, luminescence, photosensitivity.

### 1. INTRODUCTION

Signal amplification and signal processing functions are important aims in the design of new silica-based materials for applications in optical telecommunications [1]. In particular, it is interesting to obtain multiple functions in the same device by means of a single type of material. This aim, for an active lasing optical fiber or planar waveguide comprising mirrors, filters and dispersion compensators, implies the design of a material with two main features: high permanent photosensitivity for writing Bragg gratings or waveguide patterns by selective exposure to UV radiation and good solubility of active ions emitting in the telecom windows. Heavy Ge-doping and other post-synthesis treatments, such as hydrogen loading, are usually employed to achieve photosensitivity in silica-based optical devices. Nevertheless other doping processes and material treatments are currently investigated in this field [1-3]. Recently, Sn-doping has been found to induce comparable and stable photosensitivity at concentrations lower than those used in Ge-doped photosensitive fibers [4,5]. During last years we have investigated Sn-doped silica looking for the possibility of obtaining high Sn-doping levels free from material crystallization or phase segregation. We have analyzed the thermal and chemical parameters assuring the dilution of tin substitutional atoms through the densification process of xerogels [6,7]. We found that Sn concentrations up to about 0.5 mol% can be obtained following a modified sol-gel method. The resulting material is similar to an over-saturated system where the content of dopant atoms is well above the solubility level in the silica network. Nevertheless, the particular choice of tin molecular precursors and synthesis route enable to prepare heavy doped silica glass. This approach may be useful for embedding rare earth ions too, whose solubility in silica is very low. For this reason, the fabrication of active fibers usually employs erbium ( $\text{Er}^{3+}$ ) doping, limited at concentrations of about 1000 ppm [8] and difficulties are encountered in increasing the rare earth ion content without clustering processes in silica [6-8]. In fact it is known that in silica, rare earth ions, including erbium, tend to cluster when present in sufficient concentration. The clustering reduces the excited state lifetime of the ions, which is detrimental to the performance of a gain medium optical component. Significant interaction between  $\text{Er}^{3+}$  ions has been observed in silica containing erbium concentration as low as 100 ppm [8]. The undesirable reduction in lifetime caused by the interactions is known as concentration quenching. An effect of this is that the useful level of rare earth doping in gain media is limited to below that at which clustering occurs. In turn, this limits the minimum size of the optical components to that at which the desired quantity of rare earth ions can be accommodated at concentration that does not cause clustering. Several studies were carried out on  $\text{Er}^{3+}$  (and other rare earth ions) doping of

silica by sol-gel methods [9-14], potentially enabling to embed a wide class of ions in oxide matrices. In this paper we present the results we have obtained on Er-doped tin-silicate from sol-gel route, and a comparison is proposed between materials obtained from different erbium molecular precursors.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Material synthesis

Tin doped silica samples were prepared with 2500 and 4000 ppm of tin content and co-doped with up to 1 mol% of erbium by the sol-gel route. The preparation is based on the hydrolysis of tetraethyl orthosilicate  $\text{Si}(\text{OEt})_4$  and dibutyl tin diacetate following a variant of the method already described in reference 7. This method is modified (see Fig.1) by addition of an alcoholic solution of  $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  or  $\text{Er}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$  to the sol, assuring the doping of the glass matrix. The preparation of the dopant solutions is obtained by dilution of  $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  in absolute ethanol at room temperature, whereas it is useful to heat the ethanol at 50-60 °C under ultrasonic treatment in the case of  $\text{Er}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ .

#### Method 1

#### Method 2

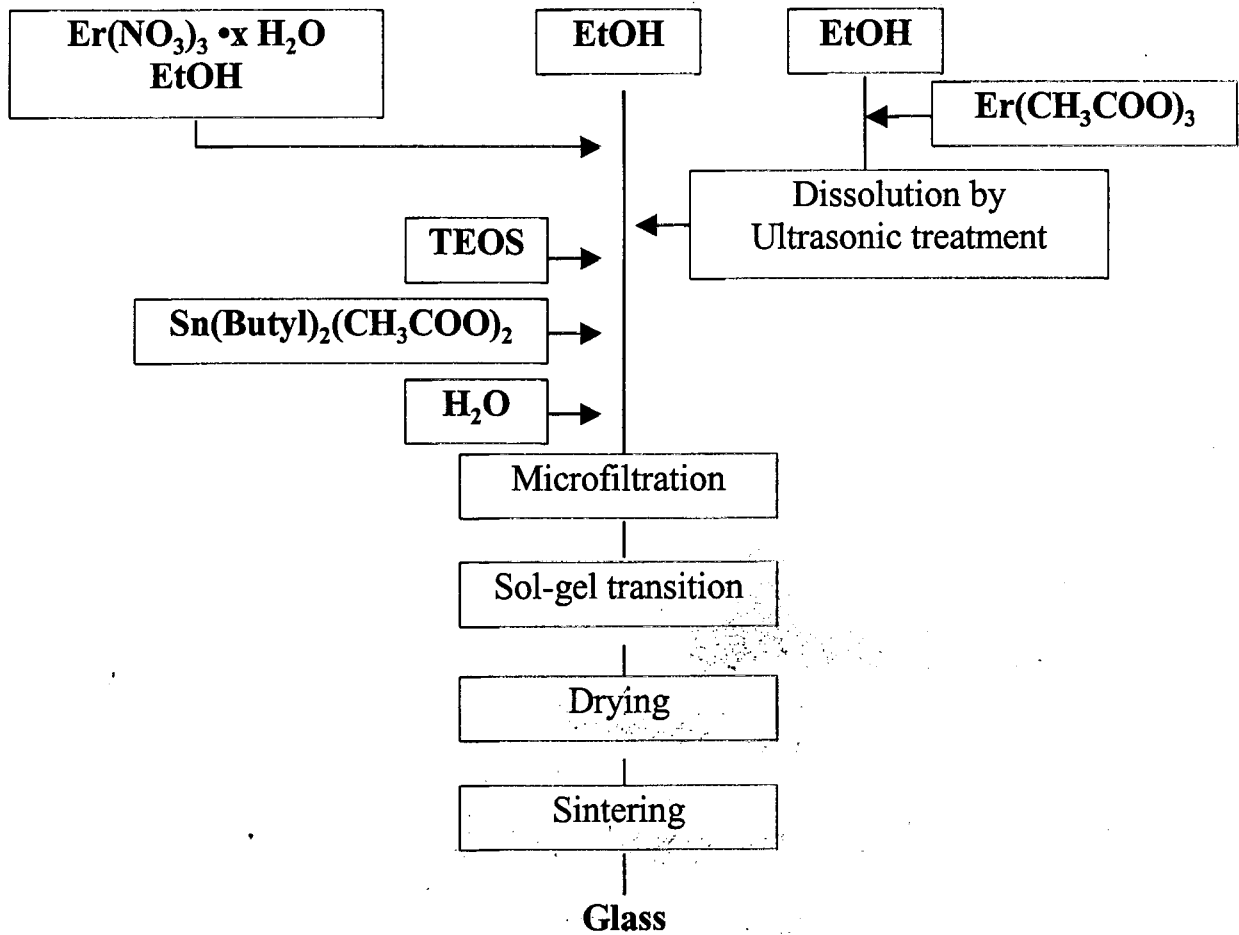


Figure 1: Block diagram of the sol-gel synthesis employed for obtaining erbium-doped tin-silicates

In this instance, owing to the low solubility of  $\text{Er}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$ , the obtained solution is used as the solvent for the sol. Gelation of the sol occurs in few days, without any acid catalysing agent, the needed time depending on the content of dibutyl tin diacetate (which decreases the reaction time) and on the content of  $\text{Er}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (which increases the reaction time). Unlike the Er nitrate, the use of  $\text{Er}(\text{CH}_3\text{COO})_3 \cdot x\text{H}_2\text{O}$  does not affect the reaction kinetics. The solvent is then removed from the alcogel so prepared by slow evaporation for few weeks. Xerogel samples obtained thereof are then treated at  $1050^\circ\text{C}$  by a very slow thermal program (according to Fig.2), obtaining complete densification at  $1050^\circ\text{C}$  [7]. Such a treatment allows to obtain monolithic transparent disks (about 15mm in diameter and 1mm thick).

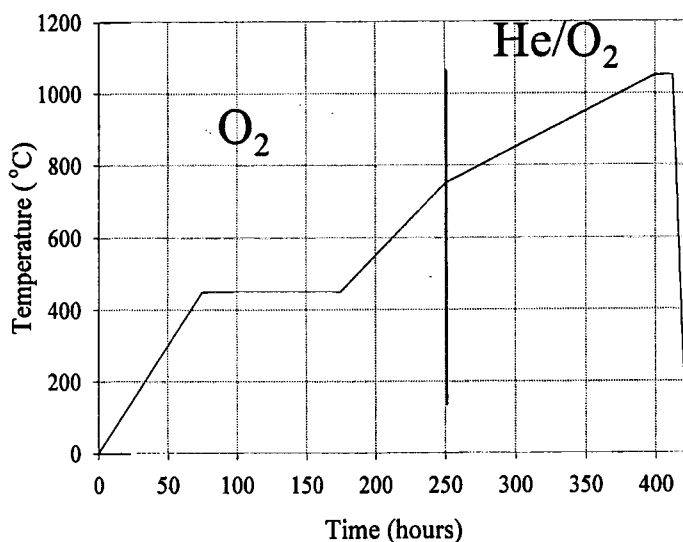


Figure 2: Thermal treatments employed for the synthesis of sol-gel samples of Er-doped tin-silicates. The treatment atmosphere is oxygen during the first 250 hours, then is 1% oxygen in helium.

## 2.2 Experimental measurements

The optical properties of erbium ions and the structural, optical and photosensitive features induced by tin-doping in Er doped Sn-doped silica samples have been investigated as a function of erbium and tin concentration and kind of erbium molecular precursor. The UV-visible absorption of the material was investigated by means of a Cary50 Varian spectrophotometer in the range 200-800 nm. Raman scattering measurements excited at 488 nm were also collected to control the full densification of the glass matrix and the absence of crystallization. Infrared photoluminescence (PL) and infrared PL lifetime measurements excited at 514 nm with a CW  $\text{Ar}^+$  laser. Crystal field (CF) structure of the visible PL was analysed by exciting at 488 nm with the same  $\text{Ar}^+$  laser and detecting the signal at high resolution by means of a micro-Raman Labram Dilor spectrometer. Refractive index measurements at 980 nm were performed by using the prism coupler technique. In these measurements, samples with optically polished surfaces were mounted on a high resolution rotary table with step size 0.3 minutes and nominal resolution of refractive index  $3 \times 10^{-5}$ . Statistical treatment of data sampling was carried out, with a final uncertainty of about  $1 \times 10^{-4}$ . The effects of exposure to intense UV beams were studied by using the fourth harmonic at 266 nm of a pulsed Nd-YAG laser (repetition rate 10 Hz) at pulse fluence ranging from 60 to 340  $\text{mJ}/\text{cm}^2$ .

## 3. RESULTS AND DISCUSSION

The Figure 3 shows the visible-UV absorption spectra of Er-doped tin-silicate samples with different content of erbium obtained from erbium nitrate and erbium acetate precursors, after complete densification at  $1050^\circ\text{C}$ . The narrow peaks due

to f-f electronic transitions of erbium ions are superimposed to a flat background. The background of samples obtained from Er-nitrate is similar to that of pure silica, provided that Er content is kept sufficiently low (samples with 2500 and 4000 ppm of Er doping). No evidence of SnO<sub>2</sub> absorption edge, expected at 3.6 eV (344 nm) [6,7,15], is detected in these samples. Moreover, no absorption band is observed at about 5 eV (250 nm) originated by oxygen-deficient-centres (ODC) [16,17], typically observed in doped silica prepared by melting or chemical vapour deposition [17,18] or xerogel sintered at high temperature in reducing atmosphere. The lack of this band is a direct consequence of the synthesis process carried out in oxidizing atmosphere to minimize the content of ODC [19]. On the other hand a clear absorption edge, reminiscent of the SnO<sub>2</sub> edge with a shift towards higher energy, appears in samples with higher Er doping level. This absorption edge is instead present in all samples prepared starting from the Er-acetate precursor, no matter the erbium content.

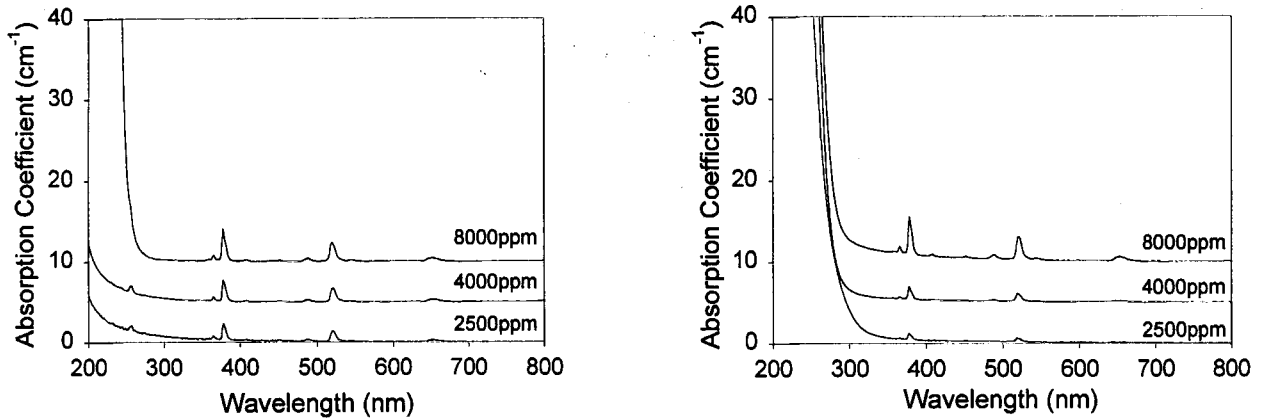


Figure 3: Optical absorption spectra of Er-doped (with the indicated Er content) tin-silicate samples (4000 ppm of Sn content) obtained from sol-gel synthesis starting from the Er-nitrate precursor (left) and Er-acetate precursor (right). The vertical axes of samples with 4000 and 8000 ppm of Er are shifted for clarity by 5 and 10 cm<sup>-1</sup> respectively.

The Raman spectrum (Fig.4) shows the characteristic features of the silica ( $\omega_1$ ,  $\omega_3$  and  $\omega_4$  at 440, 800 and 1100-1200 cm<sup>-1</sup> respectively [20]) and the Si-OH peak just below 1000 cm<sup>-1</sup> [21]. The intensity of D<sub>1</sub> and D<sub>2</sub> peaks at 495 and 605 cm<sup>-1</sup>, sensibly dependent on the medium range structure of the amorphous SiO<sub>2</sub> [22,23], is consistent with that observed in reference [24].

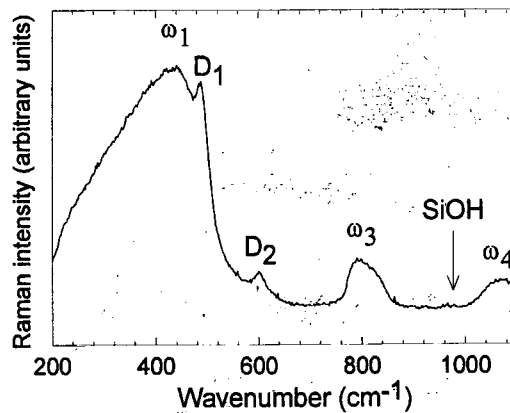


Figure 4: Representative Raman spectrum of one of the investigated sample excited at 488 nm. Vibrational modes of silica are highlighted together with the peak due to the stretching mode of Si-OH.

No other structure from different phases is observed. Taking into account the detection limit of the instrument and the Raman spectrum expected from  $\text{SnO}_2$  phase (characterized by one main peak at  $630\text{ cm}^{-1}$ , quite narrow [25]), the absence of structures distinct from those of the silica spectrum rules out segregation of phases whose fraction is larger than few %. This suggests that the absorption edge in Fig.3 is caused by a partial clustering of tin in  $\text{SnO}_2$  submicrometer-sized segregates, whereas the  $\text{SiO}_2$  matrix maintains a glassy structure.

Figures 5 and 6 report infrared photoluminescence (PL) and infrared PL lifetime measurements, respectively, collected by exciting at  $514\text{ nm}$  by means of an  $\text{Ar}^+$  laser. The PL spectra in Fig.5 show the typical features corresponding to the  $^4\text{I}_{13/2}$ - $^4\text{I}_{15/2}$  transition of  $\text{Er}^{3+}$  ions.

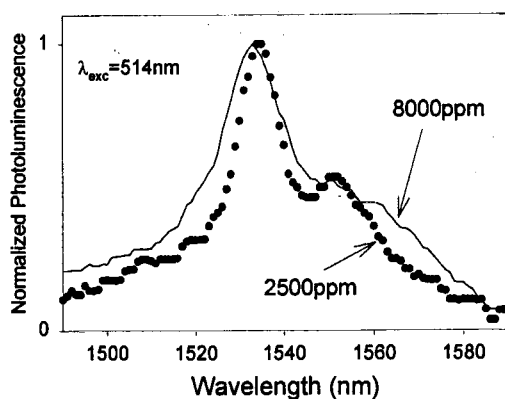


Figure 5: Infrared photoluminescence excited at  $514\text{ nm}$  of Er-doped (with the indicated Er content) tin-silicate samples (4000 ppm of Sn content) obtained from sol-gel synthesis starting from the Er-nitrate precursor.

The comparison between spectra of samples with different erbium content evidences a slight change of the shape. In particular, a clear broadening of the effective bandwidth follows the increase of erbium content, suggesting a larger dispersion of distinct kinds of possible Er sites inside the material.

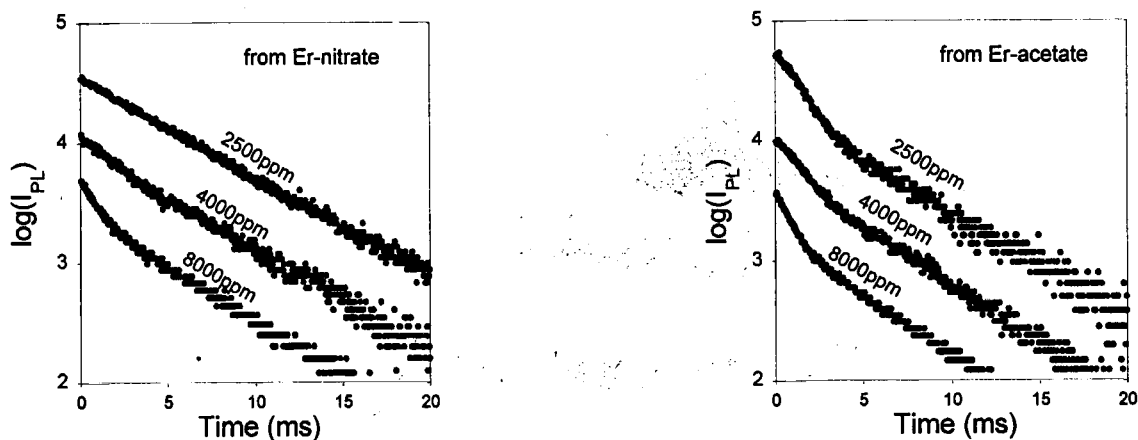


Figure 6: Decay of the infrared photoluminescence excited at  $514\text{ nm}$  of Er-doped (with the indicated Er content) tin-silicate samples (4000 ppm of Sn content) obtained from sol-gel synthesis starting from the Er-nitrate precursor (left) and Er-acetate precursor (right). The vertical axes are shifted for clarity.

The data of time decay of the  ${}^4I_{13/2}$ - ${}^4I_{15/2}$  infrared emission of  $\text{Er}^{3+}$  ions in Fig.6 give a complementary indication. In fact, a strict correlation emerges between a non-linear behavior of the PL decay in semi-logarithmic plot (indicating deviations from single-exponential decay) and the presence of the  $\text{SnO}_2$ -related absorption edge (Fig.3).

The PL decay curves in samples showing the  $\text{SnO}_2$ -related absorption edge are composed by a fast decay with characteristic lifetime lower than 5 ms, and a slower decay of about 10-12 ms, similar to that observed in Er-doped pure silica [8]. The PL lifetime values - roughly estimated by linear fitting the linear parts of the decay curves - are reported in Table 1. The emission properties of Er ions appear to be determined by the synthesis method.

Table 1. PL decay time in Er-doped tin-silicates synthesized from different Er-precursors

| Er-precursor         | Er-nitrate |         |         | Er-acetate |         |         |
|----------------------|------------|---------|---------|------------|---------|---------|
|                      | 2500ppm    | 4000ppm | 8000ppm | 2500ppm    | 4000ppm | 8000ppm |
| fast decay time (ms) | -          | -       | 4.5     | 4.5        | 6.0     | 3.9     |
| slow decay time (ms) | 12.4       | 11.6    | 11.0    | 11.7       | 10.7    | 10.4    |

A trend of  $\tau_{\text{PL}}$  values appears in Tab.1 as a function of the Er-doping, suggesting that the main source of the observed dependence may be a mechanism related to the concentration quenching. This trend is in turn accompanied by an increasing contribution to the near-UV absorption edge due to  $\text{SnO}_2$  clustering (Fig.3). Because of the low solubility of Sn in silica, the interaction between Er clustering and Sn doping in Er co-doped Sn-doped silica is expected to cause the segregation of Sn dioxide, driven by aggregation of Er ions acting as nucleation centers. In fact we have recently shown that Sn doped silica with doping level above 0.05 mol% behaves as an over-saturated system [7]. Nevertheless, in Er co-doped Sn-doped samples from Er-nitrate precursor, the absence of absorption edge at 3.6 eV (Fig.1) suggests that Er-clustering does not occur, avoiding the crystallization of  $\text{SnO}_2$  phase. This interpretation is also suggested by chemical argumentations based on hydrolysis of erbium salts. In fact it is known that the stabilization of erbium ions in solution is favored by acid pH. Therefore the nitrate precursor, more acid than acetate, gives a better stabilization than acetate. Hydrolysis probably prevails in acetate owing to the more basic character, favoring the auto-condensation in segregated phases. Photosensitivity measurements on samples obtained by Er and Sn co-doping of silica samples by sol-gel are shown in Fig.7 where values of refractive index change are reported after different UV exposure time.

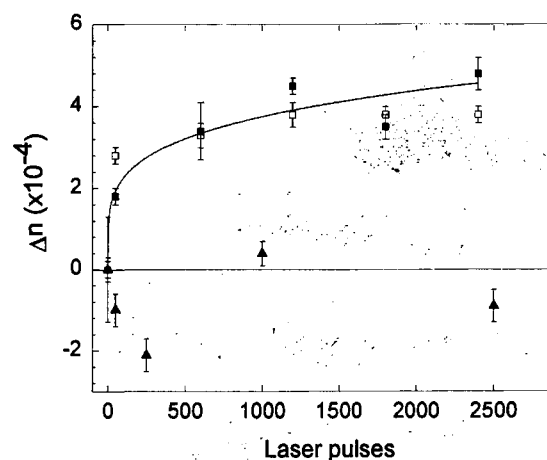


Figure 7: Changes of refractive index in Er-doped tin-silicate samples (4000 ppm of Sn content) without (squares) or with (triangles)  $\text{SnO}_2$ -related absorption edge.

Refractive index changes of about  $4 \times 10^{-4}$  are observed after 2500 UV pulses at a power density of 0.34 W in samples free from the SnO<sub>2</sub>-related absorption edge (such as the samples with low Er content produced from Er-nitrate in Fig.3). By contrast, alternate and non-reproducible behaviour vs. exposure time is observed in the other samples.

Once more a correlation is observed between a specific property of the material - its photosensitivity - and the lack of absorption edge from Er-induced SnO<sub>2</sub>-clustering. As a result, the erbium aggregation appears to inhibit the photosensitivity of the material.

#### 4. CONCLUSIONS

Our results show that the peculiar photosensitivity of Sn-doped silica, recently found to be a valid improvement with respect to that of germanosilicate glass [4,5], can be preserved in Er co-doped silica produced by sol-gel method as luminescent glass. Indeed, the collected data indicate the absence of significant interaction between the two properties, provided that a suitable molecular precursor of erbium is employed via a modified sol-gel route. This makes the investigated material a promising candidate for applications with double functionality, as lasing and photorefractive material.

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#### REFERENCES

1. P. Niay, M. Douay, P. Bernage, W.X. Xie, B. Leconte, D. Ramecourt, E. Delevaque, J.F. Bayon, H. Poignant, and B. Pommellec, "Does photosensitivity pave the way towards the fabrication of miniature coherent light sources in inorganic glass waveguides?", *Optical Materials* **11**, pp.115-129, 1999.
2. J. Albert, "Permanent photoinduced refractive-index changes for Bragg gratings in silicate glass waveguides and fibers", *Mater. Res. Soc. Bull.* **23**, pp.36-41, 1998.
3. B.G. Potter Jr., and K. Simmons-Potter, "Photosensitive point defects in optical glasses: science and applications", *Nucl. Instr. Meth. Phys. Res. B* **166-167**, pp. 771-781, 2000.
4. G. Brambilla, V. Pruneri, and L. Reekie, "Photorefractive index gratings in SnO<sub>2</sub>:SiO<sub>2</sub> optical fibres", *Appl. Phys. Lett.* **76**, pp.807-809, 2000.
5. N. Chiodini, S. Ghidini, and A. Paleari, "Mechanisms responsible for the ultraviolet photosensitivity of SnO<sub>2</sub>-doped silica", *Phys. Rev. B* **64**, pp.73102-73104, 2000.
6. N.Chiodini, F.Morazzoni, A.Paleari, R.Scotti, and G.Spinolo, "Sol-gel synthesis of monolithic tin-doped silica glass", *J.Mater.Chem.* **9**, pp.2653-2658, 1999.
7. N.Chiodini, F. Meinardi, F.Morazzoni, J. Padovani, A.Paleari, R. Scotti, and G.Spinolo, "Thermally induced segregation of SnO<sub>2</sub> nanoclusters in Sn-doped silica glasses from-oversaturated Sn-doped silica xerogels", *J. Mater. Chem.* **11**, pp.926-929, 2001.
8. W.J. Miniscalco, "Erbium-Doped Glasses for Fiber Amplifiers at 1500 nm" *J. Lightwave Tech.* **9**, pp. 234-250, 1991.
9. E.M. Yeatman, M.M. Ahmad, O. McCarthy, A. Martucci, M. Guglielmi, "Sol-gel fabrication of rare-earth doped photonic components", *J. Sol-Gel Sci. Techn.* **19**, pp. 231-236, 2000.
10. M. Benatsou, and M. Bouazaoui, "Fluorescence properties of sol-gel derived Er<sup>3+</sup>-SiO<sub>2</sub>-GeO<sub>2</sub> planar waveguides", *Optics Commun.* **137**, pp. 143-150, 1997.
11. Y. Zhou, Y.L. Lam, S.S. Wang, H.L. Liu, C.H. Kam, Y.C. Chan, "Fluorescence enhancement of Er<sup>3+</sup>-doped sol-gel glass by aluminium co-doping", *Appl. Phys. Lett.* **71**, pp. 587-589, 1997.
12. C. Strohhofer, S. Capecchi, J. Fick, A. Martucci, G. Brusatin, M. Guglielmi, "Active optical properties of erbium-doped GeO<sub>2</sub>-based sol-gel planar waveguides", *Thin Sol. Films* **326**, pp. 99-105, 1998.

13. C. Duverger, M. Montagna, R. Rolli, S. Ronchin, L. Zampedri, M. Fossi, S. Pelli, G.C. Righini, A. Monteil, C. Armellini, and M. Ferrari, "Erbium-activated silica xerogels: spectroscopic and optical properties", *J. Non-Cryst. Sol.* **280**, pp. 261-268, 2001.
14. B.T. Stone, and K.L. Bray, "Fluorescence properties of Er<sup>3+</sup>-doped sol-gel glasses", *J. Non Cryst. Solids* **197**, pp. 136-144, 1996.
15. J. Robertson, "Electronic structure of SnO<sub>2</sub>, GeO<sub>2</sub>, PbO<sub>2</sub>, TeO<sub>2</sub> and MgF<sub>2</sub>", *J.Phys. C* **12**, pp. 4767-4776, 1979.
16. L. Skuja, "Isoelectronic series of twofold coordinated Si, Ge, and Sn atoms in glassy SiO<sub>2</sub>", *J. Non-Cryst. Solids* **149**, pp.77-95, 1992.
17. A. Anedda, C.M. Carbonaro, A. Serpi, N. Chiodini, A. Paleari, R. Scotti, G. Spinolo, G. Brambilla, and V. Pruneri, "Vacuum ultraviolet absorption spectrum of photorefractive Sn-doped silica fiber preforms", *J. Non-Cryst. Sol.* **280**, pp.287-291, 2001.
18. M.J. Yuen, "Ultraviolet absorption studies of germanium silicate glasses", *Appl. Optics* **21**, pp. 136-140, 1982.
19. N. Chiodini, F. Meinardi, F. Morazzoni, A. Paleari, R. Scotti, "Optical transitions of paramagnetic Ge sites created by X-ray irradiation of oxygen-defect-free Ge-doped SiO<sub>2</sub> by the sol-gel method," *Phys. Rev. B* **60**, pp. 2429-2435, 1999.
20. F.L. Galeener, "Band limits and the vibrational spectra of tetrahedral glasses", *Phys. Rev. B* **19**, pp. 4292-4297, 1978.
21. A. Bertoluzza, C. Fagnano, M.A. Morelli, M. Guglielmi, G. Scarinci, and N. Maliavski, "Raman spectra of SiO<sub>2</sub> gel glasses prepared from alkoxide, colloidal and amine silicate solutions", *J. Raman Spectroscopy* **19**, pp. 297-300, 1988.
22. F.L. Galeener, "Planar rings in glasses", *Sol. St. Commun.* **44**, pp. 1037-1040, 1982.
23. A. Pasquarello, and R. Car, "Identification of Raman defect lines as signatures of ring structures in vitreous silica", *Phys. Rev. Lett.* **80**, pp. 5145-5147, 1998.
24. M. Ferrari, C. Armellini, S. Ronchin, R. Rolli, C. Duverger, A. Monteil, N. Balu, P. Innocenzi, "Influence of the Er<sup>3+</sup> content on the luminescence properties and on the structure of Er<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> xerogels" *J. Sol-Gel Sci. Techn.* **19**, pp. 569-572, 2000.
25. C. Xie, L. Zhang, and C. Mo, "Characterization of Raman spectra in nano-SnO<sub>2</sub> solids", *Phys. Stat. Sol. (a)* **141**, pp. K59-K61, 1994.

\* norberto.chiodini@mater.unimib.it; phone +39-02-6448-5164; fax: +39-02-6448-5400; Dipartimento di Scienza dei Materiali, Universita' di Milano-Bicocca, via Cozzi 53, 20125 Milan, Italy.