Enhanced photorefractivity and rare-earth photoluminescence in SnO_2 nanocrystals-based photonic glass-ceramics

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Abstract. This work presents state of the art rare-earth activated SnO_2 nanocrystals - based transparent glass-ceramics. With combined enhancements in both photorefractivity and rare-earth photoluminescence, the glass-ceramic has unique benefits as a lasing material. It exhibits high photorefractivity with UV induced refractive index modifications in the order of 10^{-3}. Exploiting its high photorefractivity, optical gratings are fabricated on the glass-ceramic under an energy-efficient direct UV writing process. Furthermore, SnO_2 semiconductor nanocrystals are also employed as efficient rare-earth sensitizers enhancing drastically the rare-earth photoluminescence.

1 Introduction

Optical materials and photonic structures are strategic for many applications, e.g., sensing, integrated photonics, light sources, quantum technologies, and green energy systems. Such research activities pave the way for tackling current challenges, opening new scientific knowledge and technological advancements. To design and tailor various interesting functionalities, nanocomposites are among the more appealing materials. Transparent glass-ceramic are two-phases systems constituted by nanocrystals distributed in a glass matrix [1,2]. When the nanocrystals are activated with rare earth ions, photonic glass-ceramics exhibit unique properties such as [1,3](i) the high absorption and emission cross-sections, (ii) the reduction of the non-radiative relaxation processes thanks to the lower phonon cut-off energy, and (iii) the tailoring of the ion-ion interaction by the control of the rare-earth ion partition[3]. Furthermore, the desired properties can be tuned on the base of composition, material, and respective volume fractions of crystalline and amorphous phases.
In this work, Er^{3+}-activated SiO_2-SnO_2 glass-ceramics are discussed. This system uniquely merges two interesting properties: (i) high photorefractivity, and (ii) SnO_2 nanocrystals act as efficient rare-earth luminescent sensitizers. Therefore, this photorefractive glass-ceramic can settle the issue of rare-earths' low absorption cross-section. Furthermore, it can provide strategic fabrication approach for defining channel waveguides and optical gratings with minimal losses using direct UV writing technique[4-6].

2 Sol-gel derived SnO_2 nanocrystals-based photonic glass-ceramics

SnO_2-doped glasses and glass-ceramics can be fabricated by several techniques [7-11]. However, issues of SnO_2 volatilization during the high temperature preparation [9], or α-Sn nanoclusters and nonstoichiometric SnO_x nanoparticles [12,13] raised a challenge of finding a reliable synthesis approach. Sol-gel route showed profitability in synthesizing such glasses with higher SnO_2 content [3,10,12]. Thus, in this work, we present a versatile and reliable sol-gel synthesis route to obtain transparent glass-ceramics with high content of SnO_2. We fabricated SiO_2-SnO_2 transparent glass ceramics as monoliths with a SnO_2 content up to 12.5 mol% and as planar waveguides with a SnO_2 content up to 30 mol%.

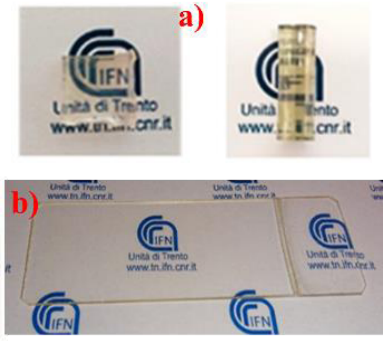

Fig. 1. Pictures of the densified SiO_2-SnO_2:Er^{3+} transparent glass-ceramics in forms of a) monoliths [15] and b) planar waveguides[7].

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3 Enhanced photorefractivity

Attracted by potentials of SnO_2-doped glasses and glass-ceramics for applications in optical fibers and integrated photonics, numerous researches have investigated their photorefractivity. However, due to the low amount of SnO_2 content in the glass matrices (maximum up to 5 mol%), the reported UV-induced refractive index changes are limited to the order of 10^{-4}[16]. In the last years, we have demonstrated: a) that we can fabricate SiO_2-SnO_2 transparent glass ceramics with high content of SnO_2 nanocrystals (from 20 to 30 mol%), and b) that those achieve highly efficient photorefractivity[16-18] (see Fig.2), sufficient for applying direct UV writing technique to fabricate channel waveguides and optical gratings. In such glass-ceramics, refractive index modification, induced by UV irradiation, is $4x10^{-3}$ [5,16-18] (see Fig.2). The fabrication of optical gratings on SiO_2:SnO_2:Er^{3+} glass-ceramics using UV direct writing technique is also recently realized [5]. It is worthy to note that the energy employed to write a grating on SiO_2:SnO_2:Er^{3+} glass-ceramics is much lower compared to those necessary to write the gratings on hydrogen loaded germanoborosilicate glasses [5].

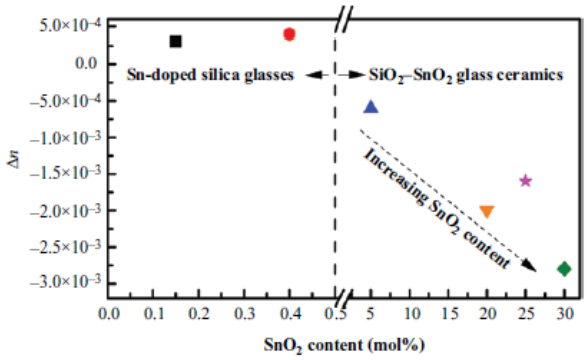

Fig. 2. The refractive index change under UV irradiation of the sol–gel derived tin-dioxide-based glass-ceramics and the tin-doped silica glasses as a function of SnO_2 content[18].

4 Enhanced rare-earth luminescence

The low absorption cross section of the electronic states of the rare earth ions is an important drawback for their application in photonics. In this contest, employing luminescence sensitizers is a robust approach. As reported in our works on different rare-earth-activated SiO_2-SnO_2 glass-ceramic systems, e.g., monoliths, thin films, and waveguides [3-5,7,15-16], we have proved the role of SnO_2 nanocrystals as efficient rare-earth sensitizers. As an example, Figure 3a shows the excitation spectrum recorded at 1530 nm emission of Er^{3+} of a SiO_2-SnO_2:Er^{3+} glass-ceramic monoliths containing 10 mol% of SnO_2 and activated by 0.5 mol% Er^{3+}. This spectrum demonstrates that when the glass-ceramic monolith isexcited at SnO_2 bandgap centered at 360 nm, Er^{3+} luminescence is drastically enhanced in comparison with directly exciting at Er^{3+} electronic states, e.g., $^2H_{11/2}$, $^4F_{7/2}$, or $^2F_{9/2}$. Furthermore, in Figure 3b, the 1.5 µm emission spectrum of Er^{3+} under SnO_2 bandgap excitation (λ_{ex} = 360 nm) reveals Stark splitting and narrow peaks. This again puts in evidence the location of Er^{3+} ions in SnO_2 crystalline local environment as well as the energy transfer from SnO_2 to the rare-earth ions[3,4,15].

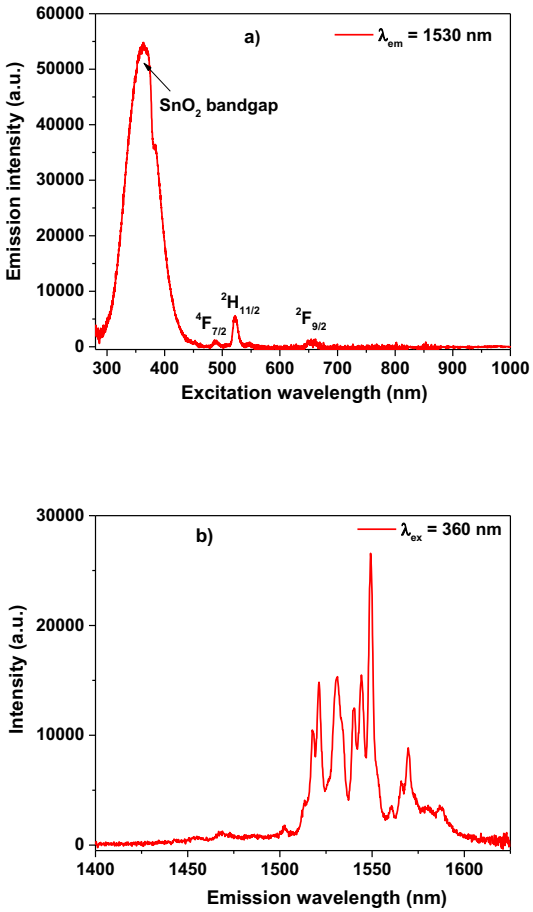

Fig. 3. a) Excitation spectrum monitored at emission λ_{em} =1530 nm of Er^{3+} and b) emission spectrum under excitation at UV SnO_2 bandgap (λ_{ex} = 360 nm) using Edinburgh FLS980 spectrofluorometer of the SiO_2-SnO_2:Er^{3+} glass-ceramic monolith containing 10 mol% SnO_2 and activated by 0.5 mol% Er^{3+}

Acknowledgements

The research activity is performed in the framework of the projects CNR-PAS "Flexible Photonics" (2020-2021), PRIN 2019 "NOMEN" (2020-2022), and ERC-H2020 PAIDEIA GA 816313.

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