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Concentration quenching dynamics in silica glass highly doped with Er^{3+}

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Abstract: In this study, quenching dynamics in RE-doped silica glass were investigated through the measurement of excited-state lifetimes of heavily doped silica micro-hemispheres fabricated directly on the end face of a multimode fiber (MMF).

Rare-earth (RE) oxides have been instrumental for a myriad of industry-relevant applications in the optical field because of their physical, chemical, thermal, electronic, spectroscopic, and photocatalytic properties [1]. In particular active optical components based on RE doped glasses are essential for lasers and amplifiers operating in eye-safe frequency ranges. High doping concentrations of active RE ions are in principle beneficial in optical fibers or waveguides as they allow reducing the length of the gain structure therefore increasing the threshold for the onset of nonlinear effects such as self-phase modulation, stimulated Brillouin and Raman scattering. In a standard Er-doped fiber fabrication process, e.g., using Modified Chemical Vapor Deposition (MCVD), achievable dopant concentrations are limited by the Er-ion clustering and increasingly efficient cooperative upconversion (UC) processes [2]. That causes a well-documented concentration quenching of the optical gain. Alternatively, highly doped Er fibers have been demonstrated using Laser Powder Deposition (LPD) as recently reported in [3]. It is known that the efficiency of UC processes depends on the thermal processing regimes used in the fabrication process. Such dependence needs therefore to be investigated and optimized for specific fabrication process. Here, we will be dealing with LPD-produced Er-doped oxide mixtures that can be used for the fabrication of active fibers and waveguide cores. This way of fabrication enables to reduce high temperature exposure time, that has an impact on dopant mobility [4].

Quenching is typically linked to RE clusters, i.e., two RE ions are sufficiently close to each other that they form a pair of interacting ions. For instance, in the case of Er^{3+} cluster, when the ion pair gets excited to the $^4I_{13/2}$ level, one ion can transfer its energy to the nearby ion and excite it to an even higher state, e.g., $^4I_{9/2}$. This level relaxes quickly back to the $^4I_{13/2}$ state through multiphonon emission resulting in some of the energy dissipating as heat instead of the desired spectral gain. Therefore, excessive clustering associated with nonradiative transitions limits the efficiency of the device. In this work, we utilized Er^{3+} ions excited to the $^4I_{11/2}$ state following a relaxation to the $^4I_{13/2}$ state corresponding to the upper laser level. The lifetime of this level is affected by the UC processes. We therefore investigated its lifetime as a function of thermal treatment using CO_2 laser as a fast and efficient heating pertinent to the LPD fabrication process.

To investigate the full dynamics of the cluster formation during glass fabrication, a prototype fiber structure was developed in the form of heavily doped Er^{3+} hemispheres made directly on the end face of a bare commercial multi-mode fiber (MMF). To obtain such a component, a cleaved end face of MMF was electrostatically covered with Er_2O_3 nano-powder. Subsequently, a focused CO_2 laser pulse ($\lambda = 10.6$ µm, P = 2 W, t = 0.2 s, $M^2 < 1.3$) was used to melt the glass fiber and allowed a gradual diffusion of Er^{3+} into the glass network. The final rounded shape was thus defined by the surface tension, with a typical radius of curvature of approximately 60 µm. The initial Erbium concentration in such hemispheres was highly inhomogeneous, with local maxima up to 70 wt%, measured via energy-dispersive spectroscopy.

To simulate the typical glass-making thermodynamics that involves temperatures above 1800 K, the samples were heated up to the softening point using a focused CO_2 laser beam ($\lambda = 10.6$ µm, P = 2.5 W, cw, spot size of 120 µm), as illustrated in Fig. 1 (a). To grant a deeper understanding of the conditions during laser heating, a heat flow simulation (COMSOL) was used. It showed that the hemisphere typically reaches the equilibrium temperature of up to 1950 K after approximately 100 ms of CO_2 laser irradiation, with similar cooling rates, as shown in the inset in Fig. 1 (a). Utilizing laser heating, each sample was maintained at an elevated temperature for predetermined intervals between 0.2 s and 32 min to observe gradual Er^{3+} diffusion. Subsequently, the sample was cooled down to room temperature. To investigate the lifetime (τ), the sample was then pumped (λ_p) with a pulsed 976 nm diode laser (repetition rate of 2 Hz, t = 100 ms, $P_{avg} = 1.7$ W), while the spontaneous emission (λ_s) was monitored via the MMF using a fiber-coupled fast avalanche photodiode (APD). To remove any in-coupled pump, λ_s was filtered from the pump signal using a low-pass filter. The typically obtained signal is shown in the inset in Fig. 1 (b). To estimate the lifetime (τ), the λ_s signal decay was fitted with an exponential function. For comparison between each sample, τ was normalized to the initial τ obtained post fabrication (t_{exp} = 0.2 s) to compensate for fine material inhomogeneities between the samples.

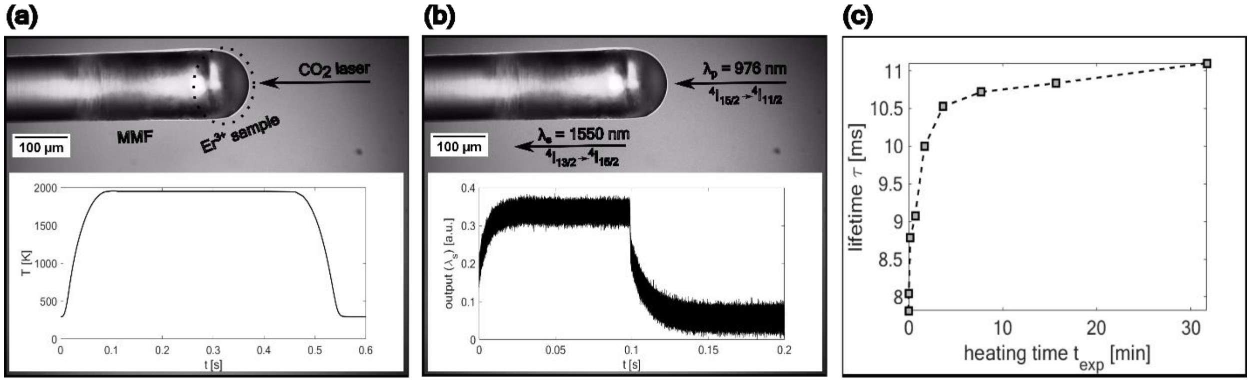

Fig. 1. (a) Micrograph (top) of Er^{3+} hemisphere placed on a fused silica plate. The sample was heated by a focused 10.6 µm laser. Simulated (bottom) temperature of the sample during CO_2 laser heating (pulse duration of 0.5 s). In the second part of the experiment, the sample (b, top) was pumped with a 976 nm pulsed laser while the spontaneous emission was collected via MMF. The typical λ_s decay (bottom) obtained using fiber coupled APD.

When analyzing the lifetimes of Er^{3+} hemispheres subjected to varying laser heating durations, as depicted in Fig. 1 (c), a notable surge is evident. This surge initiates around 8.0 ms following a 0.2-second heating exposure, exhibiting a sharp increase within the initial 4 minutes to approximately 10.3 ms. Subsequently, the rate of increase appears to decelerate, culminating at approximately 11.1 ms after a 32-min heating interval. This signifies an overall lifetime enhancement of approximately 40 %, with 30 % of this enhancement occurring within the initial 4 min.

In summary, we successfully examined the thermal response of Er^{3+}-doped silica glass samples in the early glass fabrication process. By employing a unique approach of heavily doped micro-samples and a time-gated heating source, we delved deeper into the thermal phenomena underlying quenching. In our experiments, the initially obtained excited-state lifetime increased by nearly 40 % (here, up to 11.1 ms) following approximately 30 min of continuous heating. To put our work into further context, such long lifetime in silica fibers is typically obtained by using extremely low ion concentration [2,5]. The obtained results show that the optimization of heat exposure time may have a critical impact on efficiency of highly doped RE doped fibers. This work holds a promise for unlocking the optimal path to producing a new generation of highly doped and efficient gain fibers, that shall be demonstrated in our future activities.

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