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Clustering of Yb in silica-based glasses synthesized by SPCVD

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ABSTRACT

Light absorption and scattering are studied in silica-based slab lightguides with different contents of aluminum, ytterbium and phosphorous in the silica core. The slab lightguides used in the experiments were fabricated from the structures of doped silica deposited on the inner surface of a substrate silica tube via surface-plasma chemical vapor deposition (SPCVD). The synthesized glasses contained 0.004 −0.4 at. % of Yb, as well as various contents of Al and P ranging from 0 to 1 at. %. Loss spectra of the slab lightguides are measured in the 300−1050 nm wavelength band, with the influence of the profusion of deposited glass on the loss spectra investigated by means of substrate tube external processing at a temperature of ~1600 °C in the flame of a hydrogen-oxygen burner. We found that a combination of the temperature of the inner surface of the substrate tube during the deposition process and the subsequent profusion of the deposited structure essentially influence the distribution uniformity of ytterbium ions in the glass volume. If aluminum and phosphorous are present in the glass, such profusion can influence the formation of ytterbium clusters in opposite ways.

1. Introduction

It is widely known that the non-uniform distribution of ions of an activator in the glass or crystal volume represents one of the main origins of quantum efficiency decay in solid-state lasers and amplifiers. A limit case for such non-uniformity is the formation of clusters with abnormally proximal ions of an activator, which leads to luminescence quenching, with the main precondition for the formation of these clusters being a high concentration of the activator's species and their poor solubility in the host material.

From this viewpoint, amorphous silicon dioxide is not the best host for rare earth ions, even though the solubility of rare earth elements in quartz glass can be improved by the addition of aluminum and/or phosphorus [1–4]. Nevertheless, silica yields a unique possibility for the fabrication of optical fibers and thus currently remains the ground for the fabrication of fiber lasers and amplifiers (see e.g. Ref. [5]). For this reason, a topical research objective would be to determine the largest concentration of an activator, in particular ytterbium, that is reachable in a silica-based fiber without resulting in a decrease in optical gain efficiency.

Conventional technologies employed in the fabrication of activated silica-based fibers possess several specific features that immediately impact the formation of rare earth element clusters [6]. Usually, rare earth activators are incorporated in a fiber preform by means of the solution doping technique or via metal-organic vapors, using the medium of porous glass synthesized by MCVD or OVD from silicon tetrachloride. In the subsequent stage of preform fabrication, the obtained porous glass is subjected to profusion, yielding a transparent preform ready for fiber drawing. Two contrary processes take place simultaneously during this stage, the first being diffusive concentration equalization of the activator initially locked in the pores, and the second including phase separation, cluster formation and crystallization, which can take place in an oversaturated solution-melt. The latter process also depends on the preform cooling rate. Research has shown that the use of a silica host with aluminum and phosphorous additives is much more self-standing with respect to the formation of rare earth element clusters [7].

A variation on the above processes has been adopted in the synthesis of activated preforms via SPCVD technology, first proposed and implemented for erbium [8] and subsequently for ytterbium [9] and bismuth [10].

While similar in general terms, the chemistry of oxide synthesis from chlorides, a stage of porous layer formation, is absent in SPCVD. Reactions take place in a mixture of metal halide vapors and oxygen at a total pressure of about 1 Torr, the glass being formed on the inner surface of a substrate tube as a uniformly doped transparent layer [11]. However, in SPCVD, transit from the tube

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structure to a rod-like preform and further to a fiber is also accompanied by the profusion of the deposited layer. In this regard, the previous question concerning the impact of such profusion again arises.

The term "profusion" in the case of SPCVD first needs some specification. Regardless of keeping the temperature of an outer surface of the substrate tube wall below 1140–1190 °C, the temperature of the inner surface of the tube wall can potentially just exceed this threshold. This phenomenon occurs because of extra energy deposition on the inner surface of the substrate tube, caused by exothermal coupling reactions between oxygen and chlorine atoms available in the plasma during the steps of corresponding molecule formation, an excess of momentum being accumulated by the tube wall. According to the bound energies [12], the fixation of oxygen and chlorine atoms to O_2 and Cl_2 molecules would yield energies as high as 493.58 and 239.53 kJ/mol, respectively.

Previously it was shown [13] that the profusion of Yb-doped silica containing a small amount of phosphorous leads to the formation of clusters in the form of amorphous or crystalline ytterbium orthophosphate causing a significant increase of the loss coefficient in a short wavelength part of the spectrum. Extending the research described in Ref. [14], in the current work we present and discuss experimental data regarding the impact of the profusion stage on the formation of clusters in amorphous silica containing various amounts of ytterbium, aluminum and phosphorous synthesized via SPCVD. For this purpose, we performed a comparative study of light absorption and scattering in slab lightguides fabricated from fused and unfused SPCVD glasses.

2. Experimental

Measurements were performed using samples in the form of 2 cm long slab lightguides cut lengthwise from silica substrate tubes with an outer diameter of 18 mm, wall thickness of 1.5 mm and with three-layer structures of SiO_2:F/SiO_2:Yb/SiO_2:F deposited on their inner surface. Plasma-chemical synthesis of active layer took place in scanning with a frequency of 8 Hz plasma column along a section of the substrate tube ~25 cm in length. For the synthesis of SiO_2:F cladding layers, gas mixture of $SiCl_4$ vapors, CF_4 and O_2 at a pressure of 1 torr was used. In the course of the active layer deposition, vapors of $YbCl_3$ and $SiCl_4$ mixed to O_2 for all samples as well as additives of $POCl_3$ and/or $AlBr_3$ for phosphorus and/or aluminum doped silica, respectively were applied. In these structures, 3.5 at. % F-doped silica layers 30 microns in thickness functioned as light-reflecting cladding. The Yb-doped core had a 150 × 150 microns cross-section. Two opposite lateral and face plane surfaces of the cut slabs were mechanically polished. Further details regarding slab fabrication can be found in Ref. [13].

All samples under investigation, with the exception of sample #7f, can be nominally devided into two groups (Table 1). The first group, denoted "uf" (after "unfused"), constitutes those slabs, cut from the substrate tube section immediately after deposition by the SPCVD glass structure. The temperature of the outer surface of the tube during deposition was measured by a pyrometer and was maintained at 1140–1190 °C. The second group of samples, denoted as "f" (after "fused"), includes those slabs made from another section of the same tube, but in this case after uniform outside profusion accomplished with the help of an oxygen-hydrogen burner at an outer surface temperature of about 1500–1700 °C.

Fig. 1 illustrates the experimental setup used to measure the transmission spectra of slab lightguides. The light of a halogen or deuterium discharge lamp is launched via a section of a standard pure silica core/fluorine doped silica cladding fiber #1 (core diameter 105 μm, numerical aperture >0.2) onto a flat end of the slab lightguide under study. From the opposite flat end of the slab lightguide, transmitted light is delivered to the input slit of a spectrometer by means of pure silica core fiber #2 (200 micron core diameter, NA = 0.2).

A different method was employed to investigate sample #7, which was obtained from a completely collapsed preform derived from the substrate tube and deposited by the SPCVD glass structure. The preform was pulled into a fiber with an outer diameter of 125 μm and an activated core diameter of 17 μm, with the loss spectrum measured via a standard cutback method.

X-ray microprobe analysis and SEM images of the samples were obtained with the help of a Quanta 200™ scanning electron microscope equipped with an EDAX™ energy-dispersive spectrometer. X-ray diffraction analysis, TEM images and microanalysis of the samples were carried out using a JEOL JEM-2100™ transmission microscope equipped with an X-Max 100TLE energy-dispersive spectrometer. This part of the research was carried out in the shared equipment center at the Moscow Institute of Physics and Technology.

According to [14], at temperatures of 1500 °C and 1700 °C, a pure silica host is able to melt down ytterbium in a cluster-free manner for levels up to 0.11 at. % and 0.23 at. %, respectively. Therefore, one can expect that while the Yb concentration does not exceed 0.11 at. %, the profusion of the SPCVD samples obtained under the conditions of our experiments led to the complete decomposition of any possibly clustered Yb, even without the addition of aluminum and phosphorous to the glass. It is clear that in the presence of aluminum and/or phosphorous in the glass network, the maximum cluster-free Yb concentration should be greater.

Fig. 2 shows an SEM view of the activated core class regions for different slab lightguides before and after profusion. Brighter stains

Table 1
Chemical composition of Yb-activated glasses.

Sample	Yb concentration, at. %	P concentration, at. %	Al concentration, at. %	Method used
1uf	0.043 ± 0.012	–	–	X-ray microanalysis
1f	0.054 ± 0.012	–	–	
2uf	0.19 ± 0.01	–	Trace	
2f	0.16 ± 0.01	–	Trace	
3uf	0.22 ± 0.03	0.26 ± 0.03	–	
3f	0.20 ± 0.03	0.24 ± 0.03	–	
4uf	0.068 ± 0.006	0.16 ± 0.02	0.43 ± 0.04	
4f	0.057 ± 0.004	0.15 ± 0.02	0.37 ± 0.03	
5uf	0.37 ± 0.04	Trace	1.03 ± 0.05	
5f	0.24 ± 0.03	Trace	0.70 ± 0.04	
6uf	0.15 ± 0.02	0.12 ± 0.01	0.67 ± 0.05	
6f	0.13 ± 0.02	0.11 ± 0.01	0.59 ± 0.04	
7f	0.004–0.005	–	–	Yb^{3+} absorption (see paragraph 3.3)