Phase separation in highly-photosensitive tin-doped and codoped silica optical fibers and preforms

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Abstract: Electron microscope analysis has shown that nanoscale phase separation occurs in the SnO₂-doped preform and fibers after UV exposure. This phenomenon has been observed only in Sn-doped germanosilicate and phosphosilicate core glasses when the SnO₂ concentration is high.

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1. Introduction

Hydrogen loading and co-doping with B₂O₃ and SnO₂ have been used to achieve high photosensitivity in silicate optical fibers. Compared to hydrogen loading and B₂O₃ co-doping, the use of SnO₂ keeps the absorption at 1.5 μm low and provides better temperature stability of the grating. So far tin has been shown to increase photosensitivity of silicate [1], germanosilicate [2], phosphosilicate [3], sodium-silicate [4] and alumino-germanosilicate [5] optical fibers and tin-doped silica films [6]. In particular, for SnO₂ concentrations higher that 1 mole %, refractive index modulations (Δn_mod) higher that 10⁻³ have been achieved [2,3]. Lower photosensitivity (Δn_mod~10⁻⁴) has been observed in tin-silicate fibers, where the SnO₂ concentration was much smaller (0.15 mole %). A major problem with tin silicate fiber is the difficulty of its fabrication because of crystallization occurring for SnO₂ concentrations higher than 1% w/w (~0.4 mole %) [7]. When a sol-gel technique is used to produce tin-silicate glasses, the crystal diameter can be easily controlled and glass ceramics with particles smaller than 10 nm can be produced. It has been recently shown that nanometer-scale phase separation can be also induced in germanosilicate glass thin films [8]. Exposure of specimens rich in GeO₂ (30 mole %) to ArF laser irradiation produced nanometer sized particles rich in GeO₂. In this paper we show how phase separation occurs in tin-doped and codoped silica optical fibers and preforms.

2. Experiment

Three compositions of tin-doped fibers with different SnO₂ concentrations have been studied: a tin-silicate fiber with numerical aperture (NA)~0.1 and cut-off wavelength (λ_c)~1.4 μm, a tin-germanosilicate fiber with NA~0.3 and λ_c~1.25 μm and a tin-phosphosilicate fiber with NA~0.23 and λ_c~1.3 μm. Codoping with Ge and P has been used to increase the amount of SnO₂ in silica, which is otherwise limited to 1 mole %. Slices from a tin-doped phosphosilicate preform have been lapped and polished to optical quality. Gratings written in the fiber pulled from the same preform showed that Δn_mod~10⁻³ can be achieved using a KrF excimer laser. A compositional analysis in the most doped region was carried out with energy dispersive X-ray analysis, resulting in a concentration of SnO₂, P₂O₅ and SiO₂ of about 6, 6.5 and 87.5 mole % respectively. One of the slices has been exposed to 6000 pulses of a KrF excimer laser at a repetition rate RR~20 Hz and pulse fluence (I_p)~0.1 J/cm². SEM analysis has been carried out on the gold-coated samples at an acceleration voltage of 20 kV. Fig. 1a and 1b show SEM pictures of the surface in the unexposed and exposed preform samples respectively. As previously observed in rich germanosilicate thin films [8], the unexposed specimen is homogeneous while nanometer-sized particles that give bright contrast developed in the UV treated region. The average particle size is considerably different: whilst in ref. 6 it was of the order of 10 nm at most, in the analyzed preform slice the particle diameters reach 100 nm.
Fig. 1. SEM pictures of tin-doped phosphosilicate optical fiber preforms. While the unexposed sample a) is uniform, the specimen b) exposed to KrF laser shows nanometer-sized phase-separated particles.

A fiber pulled from the same preform was exposed to laser radiation with the same conditions. Exposed and unexposed specimens were gold coated and then analyzed by SEM. Fig. 2a and 2b show the core of the fibers as-pulled and exposed to excimer laser. A quick comparison shows that phase separation has occurred also in the fiber. While the unexposed sample is rather homogeneous, the exposed sample indicates the presence of particles ~50 nm diameter.

Fig. 2. SEM pictures of the cores of fibers pulled from samples presented in fig. 1. The unexposed sample a) is rather uniform while the specimen b) exposed to KrF laser shows phase separated particles with average diameter 50 nm.

Similar analyses have been carried out on other tin doped fibers. A SnO₂ co-doped germanosilicate fiber has been exposed to 6000 pulses of excimer laser radiation at \( I_p \sim 0.1 \) J/cm² and RR=20 Hz. SEM pictures of the doped regions are presented in fig. 3. As previously observed in SnO₂-doped phosphosilicate fiber, the exposed specimen shows segregated particles with an average size of some tens of nanometers. As in the previous sample, the SnO₂ concentration is higher that 1 mole %.

Samples from the tin-silicate optical fiber preform described in ref. 1 have been exposed to a KrF laser beam delivering pulses at RR=30 Hz and \( I_p \sim 0.1 \) J/cm² for up to 30 mins. A different behavior has been observed in this fiber with respect to the previous samples. A few sporadic phase-segregated particles have been detected with an extremely low density (\(<10^2 \) μm²), not comparable to the phenomenon observed in codoped tin-silicate fibers.
3. Conclusions

In conclusion, phase separation associated with UV irradiation has been observed in a SnO$_2$ rich phosphosilicate optical fiber preform. Analogous behavior occurs in the cores of SnO$_2$-doped germanosilicate and phosphosilicate fibers. The complete absence of particles in the exposed tin-silicate fiber seems to indicate that phase separation occurs only at high SnO$_2$ concentrations. In fact, the SnO$_2$ concentration in germano- and phosphosilicate fibers is one order of magnitude greater than in the tin-silicate fiber. The UV radiation in germano- and phosphosilicate fibers can induce a rearrangement of the glass network frozen in a metastable state because of the rapid cooling during preform and fiber fabrication. On the opposite, in low SnO$_2$-concentration fibers the Sn is inserted in the silica network in a stable substitutional position [9] and it does not undergo any structural reorganization when the glass is exposed to UV radiation.

4. References