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Progress in the fabrication of Rare earth doped Optical fiber by sol-gel derived granulated oxides

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Abstract

We produced active optical fibers by the doped granulate silica-method. The granulates were derived from the sol-gel technology. We determined volume percentage and distribution of chemical elements in the fabricated glasses fiber by the analytical technique of Energy-Dispersive X-ray (EDX), Scanning Electron Microscopy (SEM), Electron Probe Microanalysis (EPMA) and the degree of crystallization by X-Ray Diffraction analysis (XRD). Furthermore we measured fluctuations of the Refractive Index Profile (RIP) and scattering losses of the fiber core. It was observed from the RIP measurement that the average index difference with respect to the undoped silica was $5.3*10^{-3}$, and thus the optical fiber has a numerical aperture of 0.12. XRD measurements and investigations with SEM showed that the manufactured optical fiber has an amorphous structure. The dopant and co-dopant elements in the core region were uniformly distributed. Although we found strong isolated scattering centers in the fabricated fiber, the loss of the fibers was determined to be 0.35- 3dB/m for selected fiber pieces. Here we present our progress of improving the optical quality of fibers produced from granulates.

Introduction

Fibers fabricated from doped granulates suffer from significant higher scattering losses compared to fibers produced with the conventional technique of modified chemical vapor deposition method (MCVD). Nevertheless, the granulated-silica method offers the advantage of rapid fiber prototyping for arbitrary micro-structured fibers. Furthermore the granulated-silica method targets optical fibers for applications where only a few meters of specialty optical fibers are needed, e.g. highly doped active fibers for high power fiber lasers, amplifiers, and sensing applications.

Up to now a number of fabrication methods for doped optical silica fibers have been developed [1-6]. The solution doping method [7- 9] in combination with the modified chemical vapor deposition (MCVD) technique is the most conventional technique to incorporate rare earth ions into the core of a silica optical fiber preform. This method allows the fabrication of fibers with high optical quality, but has drawnbacks in terms of fiber geometry and homogeneity [10]. However it has been shown that doped fiber preforms can also be produced by the granulated oxides method [11-13]. For the granulated oxides method rare earths oxides (in powder form) are mixed with silica powder. The detailed manufacturing process of this can be found in [12].

The sol-gel method is currently one of the techniques that arose great interest in the preparation of thin films for integrated optical devices [17]. In the recent years, sol-gel doped with rare earth and metal ions have shown to play important role in the development of optical fibers and photoluminescence materials [18-20]. It offers several advantages over the other competing technologies. To name but a few, it is potentially cheaper and simpler, especially for multicomponent glasses, and leads to a high homogeneity, since it is a chemical process, where the different species are mixed at a molecular scale [21, 22]. It is reported that silica powder made by the sol-gel method has much lower impurities compared with natural quartz powder which is commonly used for silica glass melting [23]. By using the sol-gel method a high doping level of rare earth ions in silica glass with minimal formation of clusters of rare earth ions can be achieved [24]. The main drawback of this method in terms of optical properties is the high content of OH^- ions. The OH bonds which are always present in this kind of material are strong energy quenchers for the rare earth ions, resulting in very short a excited state lifetime, which in turn decreases the probability to generate stimulated emitted photons [25].

The sol-gel method eases the inclusion of materials with a low melting temperature (e.g. P_2O_5). Thus, it is possible to incorporate a higher dopant concentration of Ytterbium (Yb) and Erbium (Er) into host material. Furthermore, by sintering the sol-gel material at a high temperature the formation of bubbles in the fiber are reduced. In addition, an

iterative melting and milling procedure for the sol-gel material improves the optical quality of the fabricated optical fibers.

In this work, we present our progress in reducing the scattering losses in the active optical fiber core, which is fabricated by sol-gel derived granulated oxides. We followed two strategies in order to reduce the scattering losses and increase the homogeneity. On one side, we produce the granulated material by the sol-gel method, where the dopants are added as soluble compounds during the liquid stage [26, 27], instead of mixing various pure oxides powders. This results in a higher level of homogeneity (refractive index uniformity) and hence in lower scattering losses. On the other side we increase the homogeneity by iterantive milling and re-melting processes.

Active core material preparation and fiber drawing

Production of doped granulated core material by the sol-gel method

The active fiber core material composed of SiO_2, P_2O_5, $Al2O_3$, and Yb_2O_3 is prepared by the sol-gel method from tetraethyl orthosilicate (TEOS: $Si(OC_2H_5)_4$), trimethyl phosphate (TMP: $(CH_3)_3PO_4$), aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$), and hydrated ytterbium chloride ($YbCl_3{\cdot}6H2O$, 99.99% from S. Aldrich).Ethanol and de-ionized water were used as solvents and hydrochloric acid as catalyst. The glass matrix concentration of the above input precursor materials were in the molar percentage ratio of SiO_2: Al $(NO_3)_3{\cdot}9H_2O$: TMP: $YbCl_3{\cdot}6H_2O$ = 94.7: 3.0 : 2.0 : 0.3. This results in a phosphorus to aluminium Al ratio of 0.6, which increases the refractive index of the doped fiber core compared to the undoped cladding as well as suppressing clustering [28]. In addition to the optical active ion of the ytterbium, the ytterbium also contributes to the refractive index contrast of the core and cladding, which is essential for the guidance of light based on total internal reflection.

The solution was prepared in separate stages. First, TEOS was dissolved in ethanol and thoroughly stirred at room temperature until clear solution was formed. Secondly, TMP, $Al(NO_3)_3{\cdot}9H_2O$ and $YbCl_3{\cdot}6H_2O$, were dissolved in ethanol and then added to the solution containing TEOS. This mixture was then stirred at 450 rpm. In the beginning the mixture of the two solutions is a milky solution, which turns into a clear stable solution due to the stirring. In a next step, 18 mole of di-ionized water (D-I H_2O) was added. Subsequently 0.1 mole of hydrochloric acid, HCL, was added to keep the doped silica sol at a pH value lower than 6. The sol was stored in a loosely closed glass container and heated to an elevated temperature of 70 – 150°C. The gelation occurred after 36 hours resulting in a xerogel-material. This material was then slowly dried in an oven by increasing the temperature at a rate of 2 °C/min until a temperature of 300°C. In a next step, the material was heated to a temperature of 1200°C in order to completely burn out any organic residues. Subsequently the material was sintered at a temperature of 1500 - 1600°C for 3 hrs.

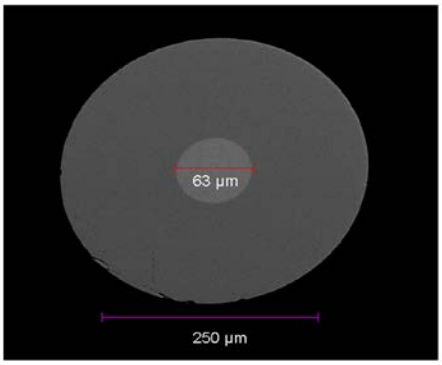

Figure 1: Microscope image of the cleaved fiber end fabricated by sol-gel method

For achieving a more uniform distribution of the matrix elements in the host glass, the mixture was filled in a graphite box and exposed to a CO_2-laser beam of 600 W (beam diameter of ca. 2cm) for about 25s. With this procedure we produced so called pellets with a diameter of ca. 2 cm. To get a uniform vitrification of the pellets, the back side was also irradiated in a similar way. The produced pellets were then milled with a planetary small ball milling machine (with three 1.4 cm and three 0.9 cm zirconium balls) for 5 minutes. Iterative melting and milling was applied (at least 3 times) until the produced pellets appeared homogenous and transparent. Finally the pellets were milled to coarse grained powder and sieved to a size of 100 - 200 µm. The size of the powder grains is important parameter for the evacuation process of the preform during the fiber drawing process. The concentration ratio of the active core fiber preform is 3 mol. % Al_2O_3, 2 mol. % P_2O_5 and 0.3 mol. % Yb_2O_3.

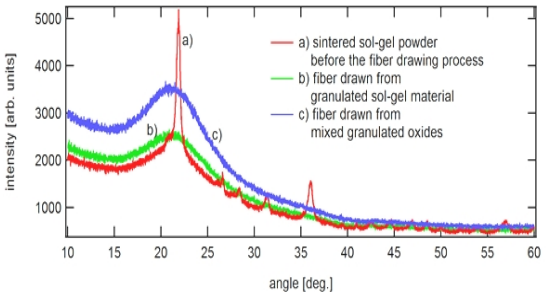

Figure 2: XRD patterns of Yb doped and P-Al co-doped silica glass prepared by sol-gel and granulated silica methods: (a) sol-gel powder was sintered at the temperature of 1600 °C for 3 hr and (b) sintered sol-gel powder after drawn to optical fiber and (c) granulated oxides powder repeatedly melted by CO2-laser and milled and drawn to optical fiber

Sintering, Milling and CO_2-Laser melting to improve glass quality

The material nature of xerogel which is produced from the standard sol-gel process is very porous. It is extremely prone to adsorb water and impurities, which in turn is results in high background losses.

As mentioned before, to improve the optical quality of the xerogel material, a temperature up to 1500-1600°C (heating rate of 2°/min) is required. Treating xerogel material at this temperature range can consolidate the material density which leads to a reduced material porosity [29]. After this stage, the sintered doped xerogel is milled and melted by a CO_2-laser. The pellets obtained with this method are very transparent and suitable for fiber drawing. We have observed in our production facility that fibers drawn without sintering the sol-gel material contain more micro-bubbles which contribute to signal scattering losses.

Fiber drawing

The fabricated active powder material was filled into a silica preform (silica tube with closed bottom) with a outer diameter of 12 mm and an inner diameter of 4 mm. The size of the dopant grains for active core material is about 100-200µm. The preform was evacuated to a pressure of 10^{-3} mbar. In a next step the preform was preheated to a temperature about 1000°C for 30 min in order to outgas the powder, followed by a preheating stage at 1500 °C for another 30 min. Finally the oven temperature was raised to about 1900°C to draw a fiber from the perform. The preform was drawn to a fiber with a diameter of about 250µm (as shown in Fig. 1).

Results

Crystallinity test of core material before and after fiber is drawn

Since the preform was thermally treated, we investigated whether noticeable crystal formation occurred during the cooling-down process. To detect the exact crystalline phase formation during the heat treatment, x-ray diffraction (XRD) measurements were performed on a STOE diffractometer equipped with Ge monochromator and Cu-Kα-radiation at 40kV and 30mA. Powder x-ray diffraction patterns of glass preform and glass fiber were recorded in the range of diffraction angle 2θ from 10° up to 60° with a step size of 0.01°.

Fig. 2 shows XRD patterns of Ytterbium doped and aluminophosphosilicate co-doped silica glass preform fabricated by sol-gel and granulate silica methods. As shown in Fig. 2 (a), material prepared by the sol-gel method and heated at 1600°C for 3 hrs has shown several crystalline peaks. The material fabricated by granulated oxides mixing and sol-gel methods as in Fig. 2 (b and c) was drawn to an optical fiber. The XRD patterns show that the materials that were prepared using the two methods after drawn to optical fiber results in an amorphous doped core material (see Fig.2. a and b). The broad band at about 23° is typical for amorphous structures. This indicates that the fast cooling rate during fiber drawing does not lead to crystal formation in the glass matrix.

The SEM photograph of the synthesized Yb^{3+}, Al^{3+}, P^{5+} is shown in Fig.3.(a-c). The SEM specimens were prepared by dispersing fine powder of sol-gel in ethanol, followed by ultrasonic agitation and then deposition onto a carbon-enhanced copper grid. The sample shown in Fig.3 (a) was slowly heated at 1600 °C and cooled slowly at the rate of 3°/min for 3 hrs. Under this condition, the SEM image shows there is an evidence of phase separated nano-particles formation observed. Heating this material at the same temperature for 4 hrs. and cooling rapidly resulted in amorphous material (as seen in3b). After the fiber was drawing, the optical fiber was crushed and the glass powder was dispersed in ethanol liquid. The copper grid was rinsed into the liquid ethanol and the glass powder was dried then was sticked on the surface of the carbon film. The sample morphology was investigated under SEM and was observed that the material was amorphous in structure. Therefore, the result of XRD in agreement with SEM result

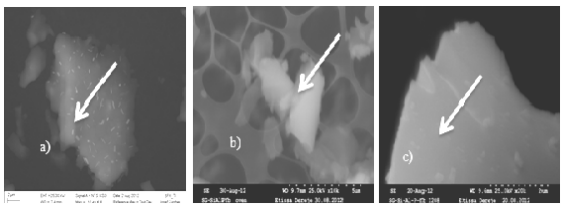

Figure 3: Scanning Electron Microscopy (SEM) images of Yb-doped and P-Al co-doped optical fiber core synthesized by sol-gel: a) Crystalline material was formed by Slowly heating the sol-gel material to 1600°C and slowly cooling before fiber is drawn b) quenching the sol-gel material after heating at 1600 for 4 hrs confirms its amorphous nature and c) sample (a) was drawing to optical fiber, the resulting material was found amorphous

Refractive Index Profile of sol-gel derived granulated silica fiber

The refractive index profile of the fiber was obtained with NR- 9200 (Index Profile Analyzer, Xlim). From the measured refractive index profile (see Fig. 4), the average index difference with respect to the undoped silica was, $\Delta n = 5.3.\ 10^{-3}$ and the numerical aperture (NA) of this fiber was calculated to be 0.12. The standard deviation of the

variation of the profile was 4. 10^{-4} and no central dip is visible.

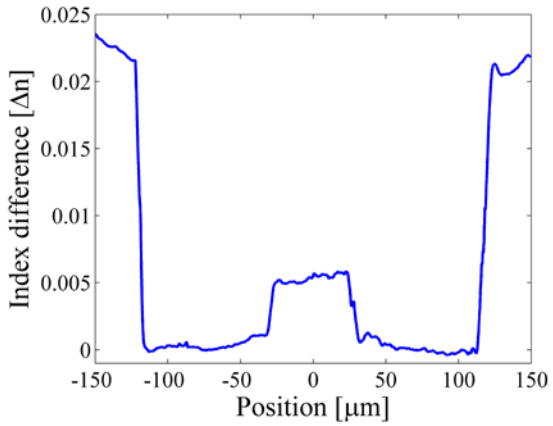

Figure. 4: Refractive index profile of the Yb +3, Al +3, P +5 doped optical fiber.

Element distribution in the fiber core of the sol-gel derived granulated silica fiber

In Fig.5, the distribution of Al, P, and Yb in the fiber core detected by electron microprobe analysis is shown. Fiber core materials were randomly taken for analysis. The doping level of the fiber core is almost comparable with the starting precursors. The variation of Al and P ions along the fiber core was observed with the standard deviation of 0.12 % and 0.09 %. One can see that Yb ions are uniformly distributed having a standard deviation of 0.01 %. Though there is a slight variation of average doping level in the central core region, the fiber consists of the original composition of the dopant incorporated in the sol-gel preparation. This shows that the material prepared using sol-gel method is stable to the exposure at high temperatures.

Attenuation measurement of the fiber core using cutback method

To measure the scattering loss of Yb^{3+} doped aluminophosphosilicate active optical fibers, produced by sol-gel method, we used a He – Ne laser (632.8 nm) laser source at a wavelength that is not close to the one of the absorption bands of Yb (800 – 1100 nm). One of the most typical sources for this purpose is the He – Ne laser (632.8 nm) where there is no absorption band of Yb at this wavelength.

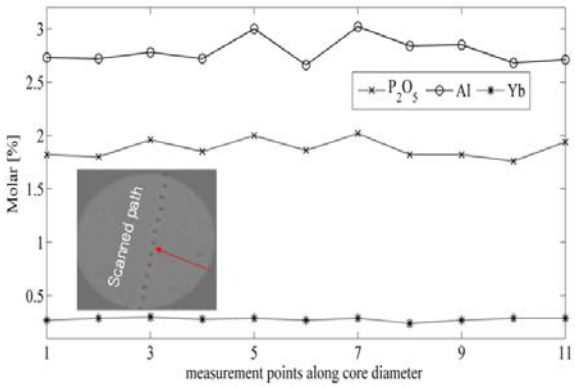

Figure 5: Average elements distribution along the active fiber core measured by electron probe microanalysis (EPMA)

While guiding the light through the active fiber core there are some scattering centers periodically located causing forward scattering. Scattering centers are 10 - 40 cm far apart from one scatterer to the next one, i.e. piecewise there were homogeneous and scattering center free fiber pieces between adjacent successive points. Taking a good piece of fiber between nearby scattering centers, attenuation losses were measured. The average scattering loss measured by using cutback method was 0.35 dB/m.

Conclusions

Yb $^{3+}$ doped and Al $^{3+}$ and P $^{5+}$ co-doped optical fiber core materials, which is suitable for the production of waveguides, have been produced. Improvement of the homogeneity of the active core preform material was done by repeated melting using CO_2-laser and milling process. Finally, sol-gel derived doped granulated silica with improved optical quality of the core material was manufactured. The elimination of bubbles due to the material porosity was another achievement. XRD results showed that the preform crystallized during the sintering process, however, it was again amorphous after the perform was drawn to an optical fiber. This result agrees with SEM image results. Our measurements using electron probe microanalysis revealed that the starting precursor elements constituting the core material were evenly distributed, yielding a flat index profile with low transversal fluctuations and without central dip.

Piecewise, the fiber was homogenous with little scattering centers. The average scattering losses measured on such pieces between consecutive strong scattering centers was 0.35dB/m.

In further work we will study the origin of these residual scattering centers to further improve the fiber quality.

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