

Effect of Soaking Temperature on Erbium Doping of Optical Fiber Core in MCVD Solution Doping Process

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Effect of soaking temperature on erbium doping of the optical fiber core during solution doping procedure, especially in the modified chemical vapor deposition (MCVD) process, was investigated. The concentration of dopants such as Er^{3+} and Al^{3+} in the preforms and the optical fibers measured by the electron probe microanalysis (EPMA) and the optical spectrum analyzer (OSA) was found to increase with decreasing the soaking temperature. The increase in the concentration of the Er^{3+} is attributed to the precipitation of the erbium due to the decrease in the solubility as well as the increase of capillary force and viscosity of the doping solution by decreasing the temperature.

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I. INTRODUCTION

Optical fibers doped with rare-earth ions have been extensively studied for the application of optical amplifiers and optical fiber lasers. [1,2] Since dopant ions in the core of the fibers are active species, several doping processes are developed to incorporate the dopants in large concentration without formation of clusters. Solution doping is one of the popular doping methods and it has been widely used in doping rare-earth ions into optical glass fibers. [3]

In the conventional solution doping method, a saturated doping solution is first prepared at room temperature by dissolving the rare-earth ions in water or alcohol. Aluminum ions are often added in the solution to prevent the rare-earth ions from clustering. [4] Alcohol is preferably used as a solvent although water has larger solubility than alcohol. The reason is that water brings about a higher OH loss in the optical fiber than alcohol does. Then, with the doping solution a soaking process is performed at room temperature to dope rare-earth ions into a fiber preform. In this case, doping concentration of the rare-earth ions within the optical fiber core is determined by two factors. One is the volume of porous region of the partially sintered core layers in the preform that is soaked by the solution containing the rare-earth ions. The other is

the concentration of the doping solution itself. If the total volume of the pores in the layers of the preform increases, the amount of solution remaining in the partially sintered porous core layers increases and so the concentration of dopants into the fiber core does. But, the porous space in the core layers is nearly constant because the reaction temperature for the soot formation is limited during the MCVD process. [5] Moreover, the solubility of dopants also remains constant as long as the temperature of the solution preparation and the soaking process is constant, and so the concentration of the rare-earth ions in the fiber core is limited.

It is well known that the solubility of solute in a solvent depends on temperature and that the viscosity and the surface tension of a liquid are functions of temperature. [6] The surface tension is related to the capillary force, which is the physical quantity keeping a solution in the partially sintered porous core layers and depends on temperature. [6-8] Thus, it is possible to increase the concentration of rare-earth ions in optical fibers by changing the temperature of the doping solution during the soaking process. In this paper, processing parameters for the concentration increase of the rare-earth ions, where erbium element was chosen, in the optical fiber core are investigated and particularly the effect of soaking temperature on the concentration of the erbium ions is discussed.

II. EXPERIMENTS

1. Sample preparation

To investigate the effect of soaking temperature on the concentration of erbium ions in optical fibers, two kinds of erbium solution were prepared. A doping solution of erbium ions, in which the concentration of Er^{3+} was 0.06M and that of Al^{3+} was 0.6M (designated to solution A), was prepared by dissolving ErCl_3 and AlCl_3 into ethanol until the solution was saturated at room temperature (around 15°C). To examine the effect of concentration of the solute itself in the solution on the final concentration of the dopant ions in glasses, the other solution of erbium ion (solution B) with concentration of the same solutes lower than that of the solution A was prepared. The solution B was made by diluting the solution A about 3 times to be 0.019M of Er^{3+} and 0.19M of Al^{3+} , maintaining the same ratio of Er^{3+} to Al^{3+} .

To dope erbium ions by solution doping, tube type preforms with the partially sintered porous layers deposited inside were prepared. Modified Chemical Vapor Deposition (MCVD; SGC) process was used to deposit a partially sintered porous core layer with germanosilicate composition onto the inner side of a silica tube with an inner diameter of 19 mm. The core layer was deposited at 1650°C and the length of the deposited region was about 300 mm. To examine the cross-section of the partially sintered porous layers, one of the silica tubes with the deposited porous layers was carefully cross-cut by fracturing it with a notch. Careful attention was paid for the minimum contamination at the fracture surface of the porous layers. Then the microstructure of the layers in the preform tube was observed using the Scanning Electron Microscopy (SEM; CAMECA). Fig. 1 shows the SEM

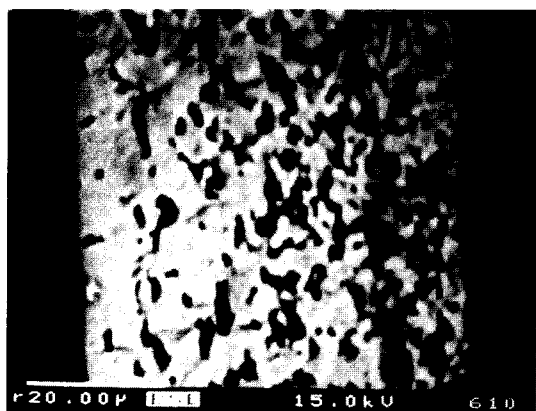


FIG. 1. The SEM microstructure of the cross-section of the partially sintered core layer deposited on the inside of silica tube by the MCVD process.

image of the cross-section of the deposited layers. The white regions are the germanosilicate soots and the dark regions are the pores through which the doping solutions have penetrated. The vertical line in the left-hand side of the image is the inner surface of the silica tube. The line of the right-hand side is the surface of the deposited layers. The thickness of the layers is about $60 \mu\text{m}$ and the size of the pore is $\sim 2 \mu\text{m}$.

2. Soaking treatment

The partially sintered porous layers of the silica tube were soaked in the solutions for an hour at different temperatures; room temperature ($13 \sim 19^\circ\text{C}$), $65 \sim 70^\circ\text{C}$, and subzero temperature (-20°C). The temperatures were chosen arbitrarily between -114.1°C (the freezing point of ethanol) and 78.2°C (the boiling point of ethanol). [6] To keep $\sim 70^\circ\text{C}$, the silica tube was wrapped with a controllable heating tape. To maintain subzero temperature of -20°C , a mixture of designated proportions of water, ethanol and dry ice was used. Even after the soaking treatment, the soaking temperature was kept constant until the doping solution was completely drained out with the rate of about 0.5 mm/sec. Schematic diagram of the experiment setup for the soaking process is shown in Fig. 2. After the soaking treatment, the preform tubes were dried in air for 20 minutes and with the flows of He, O_2 and Cl_2 for 40 minutes by using the MCVD machine. Then the tubes were sintered, and finally collapsed into rod type preforms using the MCVD machine. After obtaining the preforms, concentration of the dopants, Er^{3+} and Al^{3+} , and Ge^{4+} in the core region of the preforms was measured by the electron probe microanalysis (EPMA; CAMECA). However, the amount of erbium doped in the preforms was too small to get reliable data by using the EPMA measurement.

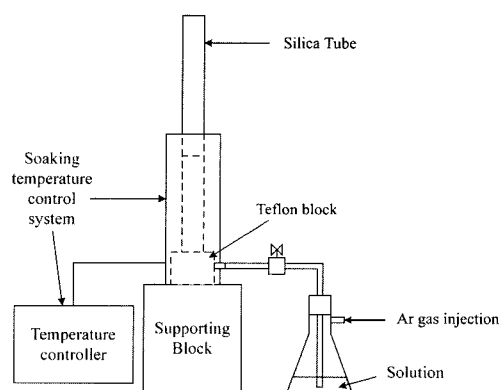


FIG. 2. Schematic diagram of the experiment setup for the soaking process.

TABLE 1. Average concentration of aluminum measured by the EPMA in the preform core.

	Soaking temp. [$^{\circ}\text{C}$]	Average concentration of aluminum [$\times 10^{-19}/\text{cm}^3$]
Solution A	65	16.8
	13	20.6
	-20	40.8
Solution B	70	5.3
	19	6.5
	-20	7.5

After drawing the optical fibers from the preforms we prepared, absorption spectrum of the fibers was measured by using the optical spectrum analyzer (OSA; Ando) with a white light source. [9] The cut-back method was used and the concentration of the erbium ions in the fiber cores was estimated by taking the area of the absorption band between 1350 nm and 1650 nm.

III. RESULTS

1. The dopant concentration in the preform core

Average concentration of aluminum in the core of preforms measured by the EPMA is summarized in Table 1. The relative change of the aluminum concentration with soaking temperature is shown in Fig. 3. In the saturated solution A, the concentration of the aluminum ions in the preform core increased as the soaking temperature decreased. The concentration of the Al^{3+} ions at -20°C increased about 98% and that at 65°C decreased about 18% compared to that at 13°C , respectively. Also, in the unsaturated solution B the concentration of the aluminum ions increased as the soaking temperature decreased even though

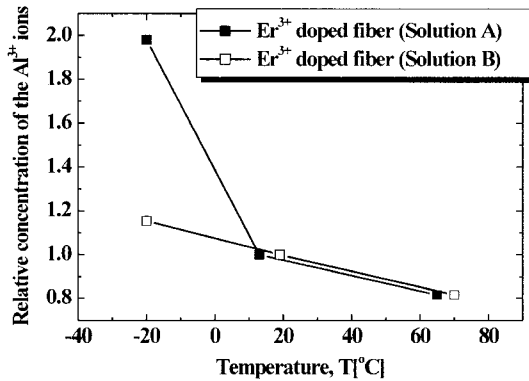


FIG. 3. Relative concentration of aluminum in the optical fiber preforms measured by the electron probe microanalysis (EPMA). The concentration of the aluminum of the preforms soaked at around 15°C was regarded as one.

the amount of the increase was less than that in the saturated solution A. The concentration of the aluminum ions at -20°C increased about 15% and that at 70°C decreased about 18% compared to that at 19°C , respectively.

2. The optical absorption spectra of the optical fiber

The effect of the soaking temperature on the optical absorption spectra of the optical fibers is shown in Figs. 4(a) and (b), where the change of absorption band between 1350 nm and 1650 nm was shown. The

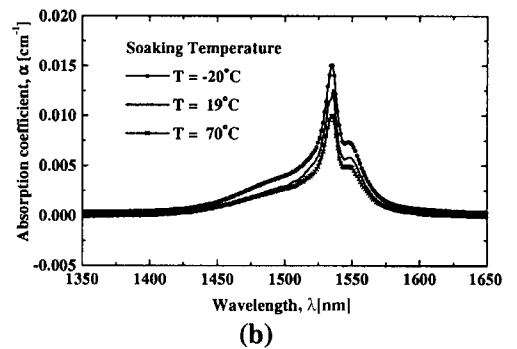
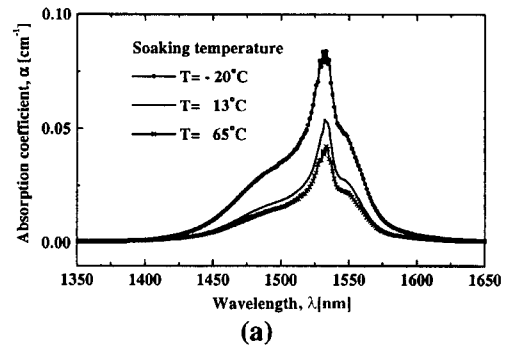


FIG. 4. Optical absorption spectra between 1350 nm and 1650 nm of the erbium doped fibers using the cut-back method: (a) optical fibers soaking treated with the saturated solution A, (b) optical fibers soaking treated with the unsaturated solution B.

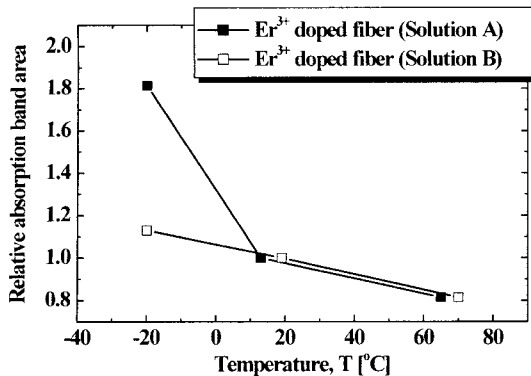


FIG. 5. Temperature dependent relative variation in the absorption band area between 1350 nm and 1650 nm of the fibers doped with the solution A and B. The absorption band area of the fibers soaked at around 15°C was regarded as one.

area of the absorption band between 1350 nm and 1650 nm of the both fibers soaked with the saturated solution A (Fiber A) and the unsaturated solution B (Fiber B), respectively was found to increase with decreasing the soaking temperature. However, the area change with soaking temperature in the Fiber A (Fig. 4(a)) was larger than that in the Fiber B (Fig. 4 (b)).

To clearly examine the change in the area of the absorption band with the soaking temperature, the absorption band area changes are presented as a ratio to the absorption band area at around 15°C and the results are shown in Fig. 5. Since the absorption is linearly dependent on the concentration of the dopants in the fibers, the ratio can be considered as the relative change in concentration of the erbium ions. On the whole, the absorption increased with decreasing the soaking temperature and the concentration of erbium must be increased by the decrease of the soaking temperature.

Similarly to the results of aluminum measured by the EPMA, the absorption band area change with temperature was found to depend on the saturation of a soaking solution. In the case of samples soaked using the saturated solution A, the absorption band area increased as much as 81% and decreased about 18% upon soaking at -20°C and 65°C , respectively. The fiber soaked with the unsaturated solution B showed much smaller area increase (about 13%) with decreasing the temperature and the same decrease (about 18%) with increasing the temperature.

IV. DISCUSSION

The increase in the concentration of Er^{3+} and Al^{3+} ions of the preforms and the fibers upon soaking treatment with decreasing temperature can be related to

factors which affect the amount of the solution (correctly, the dopant materials) soaked into the partially sintered porous layers during the soaking process. Since the soaking solutions penetrated into the porous core layers of the preform tubes, temperature dependent parameters of the soaking solutions are thought to be responsible for the observed temperature dependent concentration of the dopants. They are the surface tension and the viscosity of the solution, and the solubility of the dopants into the ethanol. Since the surface tension and the viscosity of the soaking solution are related to the capacity of retaining the solution in the partially sintered porous layers, both parameters can contribute to the change of the erbium concentration in the preform core with the soaking temperature. Moreover, since the solubility of the dopants in the solution is temperature dependent, precipitation is expected to occur if solution is saturated with the dopants like the solution A.

1. Effect of capillary force and viscosity of the solutions

When the partially sintered porous core layers of the preform were soaked in the doping solution, a part of solution containing the dopants remained in the porous layers even after the draining. The amount of the solution remaining in the partially sintered porous layers depends on the volume of the porous spaces in the core layers. If the pore volume in the layers is constant, the amount of the doping solutions retained in the layers depends on the capillary force exerted from the solutions in the porous region. This capillary force is related to the surface tension of the solution, which is a temperature dependent parameter, in turn. [6,8] The relation between the capillary force and the retaining solution in a capillary tube is given by the following equation. [8,10]

$$H = \frac{\text{Capillary force}}{\pi \cdot a^2 \cdot g \cdot \rho} \quad (1)$$

where H is the height of solution in a capillary tube, a is the radius of the capillary, ρ is the density of a liquid, and g is the gravitational constant. The height of the liquid in a capillary tube is linearly proportional to the capillary force (Eq. (1)). It is noted that the capillary force and the density of the solution in Eq. (1) are temperature dependent. However, the density of the solution can be assumed to be constant in the temperature range of the soaking treatment because the temperature dependence of density in the liquid state is negligible. [6]

To find out the temperature dependence of the capillary force of the ethanol solution, an additional experiment for determining the solution height due to the capillary force was carried out. The height change

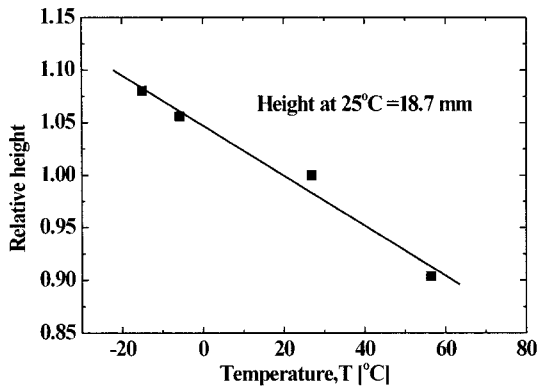


FIG. 6. Temperature dependence of the capillary rise of the solution B in silica glass capillary with inner diameter of 0.4 mm. The capillary height at 25°C was regarded as one.

of the solution B in a silica glass capillary whose inner diameter was 0.4 mm was measured by varying temperature. The relative height measured with various temperatures was plotted as a ratio to the height at 25°C and shown in Fig. 6. The height, i.e., the capillary force, was found to increase linearly with decreasing the temperature. The height of the solution B at -20°C and 70°C was about 10% higher and about 13% lower than that at 25°C, respectively. Thus, it is clear from this experimental result that the change of the soaking temperature indeed affects the amount of the retained solutions in the layers. However, the contribution of the capillary force to the increase in concentration of Er^{3+} or Al^{3+} ions (10%) was a little smaller than that obtained from the absorption data (13%) or the EPMA (15%) as shown in Figs. 3 and 5. Thus, additional contribution to the concentration increase together with that from the capillary force, that is the viscosity change of the solution, is considered.

It is well established that the viscosity of a solution is very dependent on temperature. For example, the viscosity of water is $1793 \mu\text{Pa}\cdot\text{s}$ at 0°C , $1002 \mu\text{Pa}\cdot\text{s}$ at 20°C , and $404 \mu\text{Pa}\cdot\text{s}$ at 70°C . [6] The viscosity is related to transport of the alcohol solution containing the dopants into the pores in the layers of the preform during the soaking treatment. Moreover, when the solution was drained after the soaking, a high viscosity solution is expected to retain more solution in the partially sintered porous layers than a low viscosity solution. Therefore, higher dopant concentration is expected for the preform soaked and drained at lower temperatures and the change of the concentration of the Er^{3+} ions in the fibers can be explained by the temperature dependence of both the capillary force and the viscosity of the soaking solution. Except the case of the large increase of erbium or aluminum concentration in the fiber core soaked with the solution A

at -20°C , the change of the dopant concentration in the fiber core with change in the soaking temperature is well explained by the temperature dependence of those parameters.

2. Effect of solubility of dopants in doping solution

The capillary force and the viscosity are physical parameters that are mainly determined by the kind of solvent, the ethanol in this experiment. From the results of experiments, however, the increase in the dopant concentration after soaking with the saturated solution A was found to be larger than that with the unsaturated solution B. The only difference between the solution A and the solution B is whether the solution was saturated or not. The solution A was prepared by adding the dopants in the ethanol up to the solubility limit at room temperature unlike the solution B. So, the solution A was considered to be saturated with the dopants. Thus a precipitation of the dopants out of the solution is expected to occur if the temperature of the solution decreased below room temperature. The precipitation takes place from the decrease of the solubility of the dopants in the solution at lower temperature.

Unfortunately, the data for the solubility of erbium chloride (ErCl_3) and aluminum chloride (AlCl_3) in ethanol with temperature are not available and the exact quantitative analysis is not possible. However, using the data of aluminum chloride in water, it can be estimated. The precipitation rate of AlCl_3 from a water solution of 100 ml containing AlCl_3 is about 0.5% of its solubility per 10°C . [6] Since the volume of the doping solution residing in the silica tube was about 85 ml during the soaking process, the amount of aluminum in the solution was 1.38 g by considering the doping concentration in the solution A. Because the solution A is saturated, the value is the solubility of aluminum in 85 ml of the solution A at room temperature. If the precipitation rate of aluminum in water is used, the calculated amount of aluminum precipitated from the saturated solution A by decreasing temperature from 13°C to -20°C is about 22.8 mg. On the other hand, the amount of aluminum in the preform was obtained from the density and the EPMA results of the preform core. The actual amount of the Al^{3+} ions in the preform was about 2.2 mg and 4.2 mg at 13°C and -20°C , respectively. Therefore, it is expected that 2 mg of Al^{3+} was obtained by the precipitation of aluminum as well as the contribution of capillary force and viscosity. If the contribution of capillary force and viscosity of the solution, which is the result of experiments with the solution B, is excluded, 1.67 mg of aluminum is expected to be from

the precipitation. The precipitation can be obtained from the amount of 22.8 mg precipitated from the solution. Even though the evaporation of aluminum is considered, the precipitation of aluminum is possible.

Thus, the large increase of the erbium concentration for the experiments with the saturated solution A is expected to be from three causes, the temperature dependence of solubility, capillary force, and viscosity in solution.

V. CONCLUSION

The effect of soaking temperature during the solution doping process on concentration of erbium ions in optical fiber core was investigated. The concentration of the aluminum ions in the preform and that of erbium ions in the optical fiber were measured by the electron probe microanalysis and the optical spectrum analyzer, respectively. For the saturated solution A ($\text{ErCl}_3/\text{AlCl}_3 = 0.06\text{M}/0.6\text{M}$) and the unsaturated solution B ($\text{ErCl}_3/\text{AlCl}_3 = 0.019\text{M}/0.19\text{M}$), the concentration of erbium ions increased up to about 81% and about 13% by decreasing the temperature from $\sim 15^\circ\text{C}$ to -20°C , respectively. The increase in the erbium concentration by decreasing soaking temperature is attributed to the temperature dependence of the capillary force, the viscosity, and the solubility of the erbium in the doping solution. Particularly, the large increase of the erbium concentration upon the soaking at -20°C with the saturated solution results from the precipitation of the erbium due to the decrease in the solubility by the decrease of temperature.

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