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Influence of aluminum on doping of ytterbium in optical fiber synthesized by vapor phase technique

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The process conditions of vapor phase doping technique for fabricating rare earth (RE) doped optical fiber have been systematically investigated to achieve better control over RE incorporation. Experimental results showed that the amount of RE incorporation can be precisely controlled by adjusting Al ion concentration in the inlet gas mixture. The extent of RE incorporation can also be predicted for any composition of inlet gas mixture if all other process parameters remain constant. The investigation helps to obtain the optimum conditions necessary to produce fibers of given specification and thus achieve greater reproducibility. For the first time co-operative phenomenon has been established through gas phase technique.

1. Introduction

Efficient operation of fiber laser systems demands the use of rare earth (RE) doped fibers with large mode area (LMA) structure, high RE concentration, uniform dopant distribution and good optical properties with low attenuation [1]. Reproducibility is another important factor so far the fabrication of the preforms/fibers is concerned. In this context, conventional solution doping technique has not been so successful as the process suffers from several limitations particularly the difficulty in making large core with high dopant uniformity [2]. The search for an alternate process led to the development of vapor phase doping technique involving supply of the RE-chelate compounds at high temperature [3]. Recently, high success has been reported in producing good quality fibers employing this technique [4,5]. While selection of the process plays an important role in getting the right kind of fiber, another major issue is control over the RE and Al incorporation and optimizing their proportion for improvement in lasing performance of the fiber.

Although the role of Al on RE solubility is well known [6] and is one of the prime requirements for getting good fiber properties, most of the literatures provide qualitative concept about RE incorporation into glass structure. No quantitative relationship was presented to correlate the fabrication conditions with the amount of RE incorporation. For the first time, Dhar et al. [7] presented the mechanism of RE incorporation by solution doping and the role of Al was explained on the basis of adsorption—pore retention factors. On the above background, this paper presents the influence of Al on Yb incorporation in case of fabrication through vapor phase doping technique. The experiments were designed to systematically study the Yb incorporation with variation in Al/Yb ratio and study the effect on final fiber properties.

2. Experimental

The preform fabrication process consisted of SiO_2 cladding layers deposition followed by sintered SiO_2–Al_2O_3–Yb_2O_3 core layers deposition through vapor phase in a Heraeus F-300 silica tube over the length of 400 mm and diameter of 20/17 mm. Yb chelate compound, $Yb(thd)_3$ [thd = 2,2,6,6-tetramethyl-3,5-heptanedionate] and anhydrous $AlCl_3$ were used as precursor materials for Yb and Al respectively. The solid precursor materials were heated at a fixed temperature within individual sublimators to transform into their respective vapors which were then delivered to the reaction zone by passing controlled amount of preheated Helium (He) gas. He flow rate was kept constant for Yb sublimator to deliver $Yb(thd)_3$ as 1.11 mol% of inlet gas mixture while for Al, it was regulated judiciously in the range of 0.15–1.67 mol% to obtain different Al/Yb ratios. All other process parameters were kept constant including $SiCl_4$ flow rate (0.58 g/min), deposition temperature (1850 ± 5 °C), soot box pressure (0.5 Torr), carriage traversed speed (125 mm/min),

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total gas flow rate (1 l/min) and front ribbon burner temperature (260 ± 10 °C). After deposition of two core layers, the substrate tube was collapsed into solid rod in oxidizing atmosphere following soft collapsing technique. SEM analysis (LEO 430i) was performed on unsintered soot layers to get the information on structure and characteristics of deposited soot. Refractive index profile (RIP) of the preforms was measured by preform analyzer (PK-2600). Fibers of diameter 125 ± 0.5 µm were drawn to evaluate the geometry and RIP using fiber analyzer (EXFO, NR-9200). Attenuation spectra of the fibers were measured in the range of 800 to 1100 nm following cut-back technique (Bentham). Average Yb ion concentration in core was determined from the absorption peak at 915 nm in attenuation curve. The concentrations of Al and Yb were also measured by EPMA to have detailed information about the elemental distribution in the core region.

3. Results and discussion

Preforms with length up to 330 mm and diameter of around 10.6 mm have been produced with numerical aperture (NA) in the range of 0.08–0.20 and Yb^{+3} concentration in the range of 4430–7185 ppm. The fiber characteristics obtained from different preform runs are summarized in Table 1. The results show that for a fixed inlet $Yb(thd)_3$ concentration, the variation in Al ion concentration leads to change in the amount of incorporated Yb ions into glass network appreciably. Gradual increment in Al content is also observed with increase of $AlCl_3$ molar ratio as shown in Fig. 1. The tabulated results thus indicate the possibility of controlling the Yb incorporation by manipulating Al/Yb ratio in inlet gas mixture instead of increasing $Yb(thd)_3$ flowrate directly. Thus the decomposition of RE precursor material has been confined to the minimum value. The data is presented in Fig. 2. The curve indicates that for higher $AlCl_3$ concentration the incorporation efficiency of Yb increases initially. This trend is found to be continued up to $AlCl_3$ concentration of 0.46 mol%, after which a sharp decline in the Yb incorporation efficiency has been observed. This declination continued up to $AlCl_3$ concentration of 1.14 mol% after which Yb concentration is found to be steady at around 4450 ppm. The result shows similarity to the observation by Dhar et al. [7] while carrying out similar investigation for solution doping technique. Although they mentioned that RE incorporation efficiency falls down for higher Al concentration, this has not been studied further.

Table 1
Influence of experimental conditions on final fiber characteristics.

Preform ID	At inlet gas mixture		In final fiber			
	$AlCl_3$ concentration (in mol%) with fixed $Yb(thd)_3$ concentration of 1.11 mol%	Ratio of Al/Yb	Al^{+3} Conc. in glass × 10^{-3} (in ppm)	Yb^{+3} Conc. in glass (in ppm)	Ratio of Al/Yb	NA
RE_1	0.15	0.13	14.80	5485	2.70	0.08
RE_2	0.24	0.21	28.61	5775	4.95	0.10
RE_3	0.37	0.33	40.66	6400	6.35	0.12
RE_4	0.46	0.41	53.51	7185	7.45	0.13
RE_5	0.60	0.54	63.13	6980	9.31	0.14
RE_6	0.82	0.74	79.00	5765	13.40	0.15
RE_7	1.09	0.99	110.80	5200	20.15	0.18
RE_8	1.14	1.04	113.02	4430	24.60	0.18
RE_9	1.67	1.53	142.72	4480	31.86	0.20

The variation in Yb ions incorporation efficiency with changing Al/RE proportion can be explained on the basis of co-operative phenomena. Addition of Al ions modifies silica network structure as two local bonding configurations depending on its concentration. These are: (a) tetrahedral bonding configuration of $AlO_{4/2}$ groups which acts as “network former”, (b) octahedral coordination of oxygen atom of $AlO_{6/2}$ groups which acts as “network modifiers” [6]. In the case of $AlO_{4/2}$ groups, due to charge compensation, the RE^{+3} ions are preferentially accommodated near Al rich domain [8,9]. For the network modifier case, Al ion breaks the bridging O_2 sites (Si–O–Si, Si–O–Al and Al–O–Al) and produce non-bridging O_2 which can coordinate the RE^{+3} ions into glass matrix [9,10].

It appears that for the initial cases (Up to RE_7 in Table 1), as Al ion concentration is low ($<$ 12 mol%), it is incorporated into silica network primarily as “network former” as reported by Aksay et al. [11]. During soot formation stage, as the concentration of Al species increases (RE_1 to RE_4 in Table 1), it attracts more and more Yb ions towards soot layer and due to charge compensation Yb ions get bound to near Al rich domain. But this phenomenon is non-linear in nature and decreases after an Al/Yb ratio of 0.41. Due to relatively large excess of Al ions in inlet gas mixture (RE_5 to RE_7 in Table 1), incorporation of Al into silica network preferentially increases which reduces the number of non-bridging O_2 into the silica network and produces bridging O_2 sites of Si^{+4} and Al^{+3} tetrahedra. Similar results were obtained by Bruckner et al. [12]. This leads to decrease of Al assisted Yb incorporation rapidly which leads to sharp declination of Yb concentration in the fiber. This declination also continues up to a certain level and after that Yb concentration becomes steady at around 4450 ppm. At this stage, due to high concentration of Al ions ($>$ 12 mol%), some of

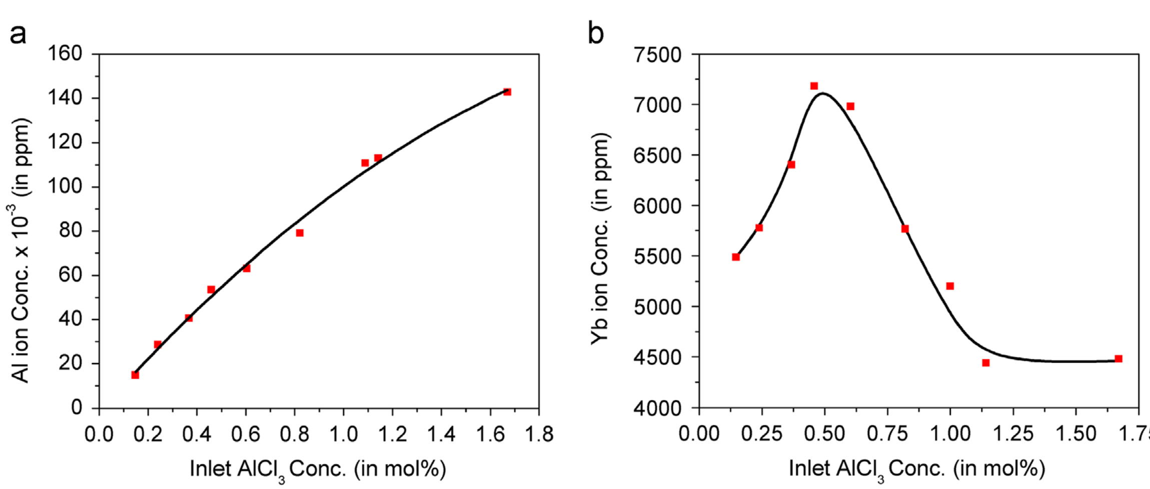

Fig. 1. Effect of inlet $AlCl_3$ concentration on (a) Al and (b) Yb ions concentration in fabricated preforms.