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Multiple solution-doping in optical fibre fabrication I – Aluminium doping

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Abstract

This work is part of a study of solution-doping in Modified Chemical Vapour Deposition, as used in fabrication of specialty silica optical fibres. The present paper concentrates on aluminium solution-doping and the effects of introducing additional heat-treatment stages into the process. The behaviours of the aluminium salt when heat-treated independently and after deposition in the silica soot have been studied by X-ray diffractometry, thermo-gravimetric analysis with mass spectrometry, electron microscopy and microanalysis. It has been shown that a procedure involving multiple cycles of solution-soaking and heat-treatment of the soot layer increases the level of aluminium doping obtainable. Efficiency of aluminium incorporation has been measured in the soaked soot, the sintered glass layer and in the final collapsed preform. An interpretive model of the multiple cycle soak/heat-treatment process is suggested.

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1. Introduction

Solution-doping as a means of extending the basic Modified Chemical Vapour Deposition (MCVD) [1] process is widely utilised to fabricate rare-earth doped silica-based optical fibres, since most rare-earth compounds are insufficiently volatile to be easily vaporised. In solution-doping the silica soot deposited on the substrate tube is immersed in an aqueous or alcohol solution of salts of the desired dopant elements. After drying to remove the liquid component, the soot is sintered to form glass impregnated with the dopants. We have previously reported on the micro- and nano-structures of undoped silica soot and of aluminium-doped silica soot and glass [2,3]. The ultimate object of this research is efficient incorporation of rare-earth ions to create optically active glasses which can be used in fibre lasers.

When silica is solution-doped with rare earths beyond a critical concentration, clustering of the rare-earth ions occurs, leading to unwanted rapid fluorescent decay [4] and 'quenching' of laser emissions. Al^{3+} ions can enter a silica glass matrix either as 'network formers' via tetrahedral coordination or as 'network modifiers' via hexahedral coordination [5], depending on the aluminium concentration. The presence of aluminium appears to suppress clustering of the rare-earth ions [1]. Arai et al. [6], in a study of co-doped Al and Nd, suggest that the incorporated aluminium forms a 'solvation shell' which isolates the rare-earth ions

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from each other in the glass network, preventing interaction between them and thus greatly reducing clustering. This explanation is supported by more recent work [7] involving the incorporation of Er^{3+} ions into aluminosilicate glass where X-ray absorption fine structure spectroscopy showed that the rare-earth ion has an average coordination number of 6.3 with respect to adjacent oxygen atoms in the first coordination shell.

Aluminium can be co-doped simultaneously with the rare-earth by immersion of the porous soot layer in a mixed aqueous or alcohol solution of the chlorides of both aluminium and the rare-earth. However, as a preliminary to rare-earth solution-doping of silica, it would be useful first to study solution-doping of aluminium alone and investigate how this can be done most efficiently.

Few publications have addressed the mechanisms by which dopant ions are incorporated into a soot layer from a liquid solution since the first report in 1987 by Townsend [8], whose sponge model [9] involved incorporation dominated by capillary action and chemical adsorption of the dopant on the silica soot surface. Recently, Khopin et al. [10] have studied solution retention in a porous soot layer as a function of the deposition temperature and the soot layer composition. Partial sintering of the soot occurred immediately after deposition, so that the solution was less able to penetrate the soot layer. These authors correlated lower deposition temperatures with higher dopant content in the glass. Kim et al. [11] reported that both aluminium and erbium levels in a preform core can be doubled if the immersion temperature in a saturated ethanol solution during solution-doping is lowered from 65 °C to −20 °C but that less improvement was observed in a dilute solution. They suggested that this could be explained by capillary effects, solution viscosity and dopant solubility.

In the present study the mechanisms by which aluminium ions are incorporated into a partially fused silica soot layer have been studied by X-ray diffractometry, thermogravimetric analysis with mass spectroscopy and electron microscope examination and microanalysis. The effects of controlled heat-treatment, in addition to drying to remove the liquid components, have been investigated. It is demonstrated that the aluminium content of the soot layer can be greatly increased if it is repeatedly soaked in an aluminium salt solution, each soaking followed by drying and heat-treatment, before sintering and preform collapse. The aluminium content can be increased to the point where Al-rich crystallites are precipitated in the soot and acicular alumina crystals can be seen in the glass.

2. Experimental procedures

Two materials were considered in this study, the silica soot deposited by the MCVD process and a soluble aluminium bearing salt, in this case an hydrated aluminium chloride ($AlCl_3 \cdot xH_2O$). The silica soot has already been studied in some detail [2,3]. The next step is the study of the aluminium salt itself and of the soot layer at various stages in the solution-doping process.

2.1. Preparation of aluminium-doped silica soot

A high quality synthetic silica tube (typically OD = 20 mm, ID = 17 mm) was mounted in the MCVD glass lathe and its inner surface cleaned by etching with fluorine gas. Several fluorophosphosilicate ‘cladding’ layers were then deposited and fully consolidated at high temperature into pore-free transparent glass. A mixture of silicon tetrachloride ($SiCl_4$) and oxygen was then fed into the substrate tube and converted into silica (SiO_2) soot particles by an oxy-hydrogen burner traversing the length of the rotating tube. The soot was carried downstream of the burner and deposited on the inner wall by thermophoresis and partially sintered as the burner passed over it. A porous soot layer suitable for solution-doping was formed. Deposition temperature was measured by an optical pyrometer directed at the exterior of the substrate tube near the hottest region and moving with the burner. Such temperature measurement is indicative rather than absolute, although widely accepted to be accurate to within ±15 °C. Two categories of soot layer were fabricated, one deposited at 1480 °C with $SiCl_4/O_2$ flow rate of 50 ml/min and the other at 1530 °C with a 100 ml/min flow rate, both from a bubbler system at 35 °C.

An approximately 1 M Al^{3+} solution in ethanol was prepared using high purity aluminium chloride hydrate ($AlCl_3 \cdot xH_2O$) where x was between 6 and 7 (Aldrich). The soot layer was soaked in this solution for one hour with the substrate tube in a vertical position. After draining the solution the tube with the impregnated soot layer was dried for an hour in a nitrogen stream at room temperature. Most of the soot layer fabricated at 1480 °C peeled off the inner surface of the silica tube during the drying stage. Bulk samples of this solution-soaked soot layer material were obtained by grinding the peeled layer into small fragments. Similar bulk samples were obtained of Al-solution soaked soot layer fabricated at 1530 °C by carefully scraping it off the inner surface of the substrate tube and grinding it up.

2.2. X-ray diffraction

The crystallinity of the aluminium chloride hydrate used to prepare the ethanol solution and of the bulk Al-solution soaked silica soot layer samples deposited at 1480 °C and 1530 °C were studied by X-ray diffraction (XRD: Shimadzu S6000), using Cu Kα radiation at a scan speed of 0.5°/min (2θ) between diffraction angles 10° and 75° at room temperature. Samples of each material were heated to 800 °C at a rate of 5 °C/min and allowed to cool slowly in a tube furnace. The residue of the aluminium salt after this heat-treatment was examined by XRD at a scan speed of 0.2°/min (2θ) between 10° and 75°. Finally, changes in crystallinity with temperature, of the aluminium chloride