VAPOR PHASE DEPOSITION PROCESSES FOR FABRICATION OF SENSOR AND SPECIALTY OPTICAL FIBER PREFORMS

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Key words: vapor phase, fabrication of optical fibre preform, special optical fibres

Abstract: An overview of vapor phase doping methods in fabrication of optical fiber preform using different technologies is presented. Advantages of vapor phase processes are discussed and evaluated based on several samples developed for applications in sensorics, MOEMS and photonic component design. Vapor phase methods have shown good potential and are suitable tools for further development of standard and novel glass structures.

Uporaba tehnologije nanosa v parni fazi za izdelavo senzorjev in posebnih optičnih vlaken

Kjučne besede: parna faza, izdelava preforme optiÄnih senzorjev, posebna optična vlakna

Izvleček: Predstavljena je tehnologija dopiranja in nanosa v parni fazi za izdelavo optičnih vlaken. Predstavimo prednosti nanosa v parni fazi na osnovi mnogih vzorcev, razvitih za aplikacije v senzoriki, MOEMS in načrtovanja fotoničnih komponent. Metode nanosa v parni fazi so se pokazale kot obetavno orodje za razvoj standardnih in novih struktur.

1 Introduction

Optical fibers for sensor and specialty application require silica glass layers to be doped with a number of dopants not used in fabrication of telecommunication fibers/1/. Many such dopants like heavy metal- and rare earth ions, do not offer precursor materials in gaseous form or have very low vapor pressures. One way to deal with this limitation is to use a process, based on soaking of porous silica layers by solution, containing dopant ions (so-called "solution doping" method)/2/. Solution doping technology has some limitations and recently vapor phase doping methods are gaining wider acceptance. These methods rely on presence of dopant precursor vapor in the reaction zone where silica is formed. The advantage of vapor-phase doping methods over soaking is in reduced complexity, improved purity, wide choice of precursors and possibility to produce larger preforms with improved yield.

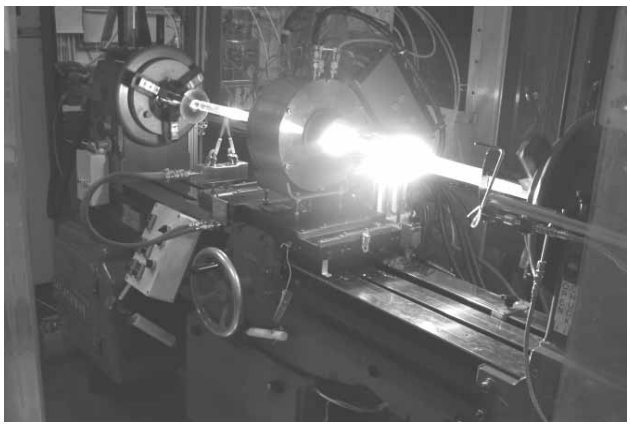

Fig. 1: View of MCVD preform fabrication system.

Vapor phase methods have been known since late 80's but did not gain wider acceptance due to the lack of feasible fabrication equipment. Recently, semi-industrial devices were introduced and several new methods can be used on standard optical fiber preform fabrication equipment.

The first such method is so-called "chelate doping" /3/, based on high temperature evaporation of solids (powders or sands). The second method is so-called "flash vaporization" method, based on impulse evaporation of solutions containing proper precursors.

An option to vapor phase doping method is "aerosol" method, offering advantages of both liquid and vapor phase methods.

Vapor phase methods have shown good potential and are suitable tools for further development of standard and novel glass structures.

2 Chelate doping method

2.1 Raw materials

Precursors in chelate rare earth-doping system are organometalic compounds of the 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) or acetyl acetonate (acac) type. They are widely available from commercial sources, with typical purity between 99.9 and 99.999% in regard to metal impurities.

2.2 Device concept

In a chelate doping system precursors have to be heated over 150°C to provide high enough vapor pressure for use in MCVD process. Powders typically melt at temperatures

over 170°C and they decompose at temperatures over 280°C while boiling.

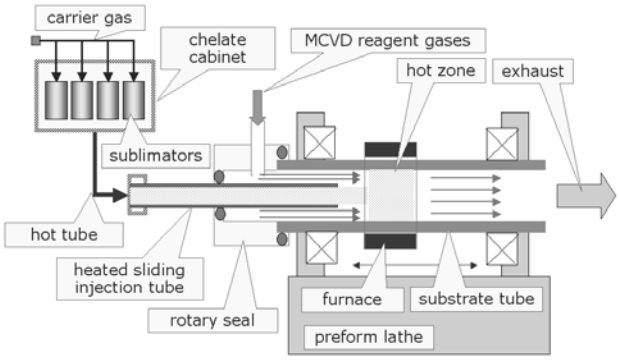

Fig. 2: Schematical view of chelate doping device on MCVD preform fabrication system

Chelates (and AlCl3) are evaporated from special heated vessels called sublimators. A standard sublimator design is shown schematically on Fig. 3A. It is usually filled by powder in bulk, possibly mixed with some inert material as filler. This simple design has been tested by fabrication of several preforms (Yb content results are indicated as area A in Fig. 4) It was found that such devices have poor performance due to small active surface interacting with carrier gas flow and due to agglomeration with prolonged use, preventing repeated use of the same materials.

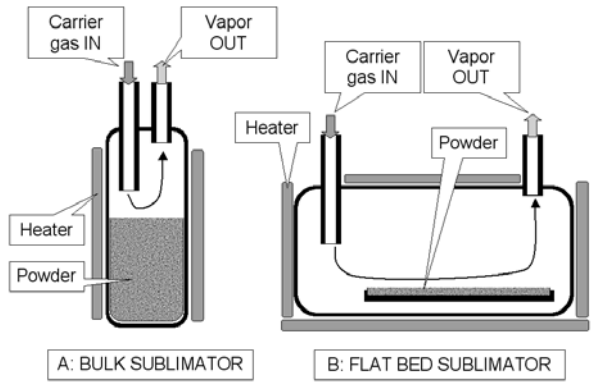

Fig. 3A: Typical design of a bulk sublimator; 3B: design of improved flat bed sublimator.

It was found that for deposition of highly-doped thick core layers, required for LMA fibers, sublimator has to be heated above precursor melting temperature. Therefore, a new type of sublimator (flat bed, Fig. 3B) had to be developed and tested on a series of preforms (Yb content results are indicated as area B in Fig. 4).

Relationship between evaporation rate (normalized to standard SiCl4 vapor flow and carrier flow) and Yb2O3 concentration in fabricated glass (each dot for one measured preform) is shown in Fig. 4. opposite.

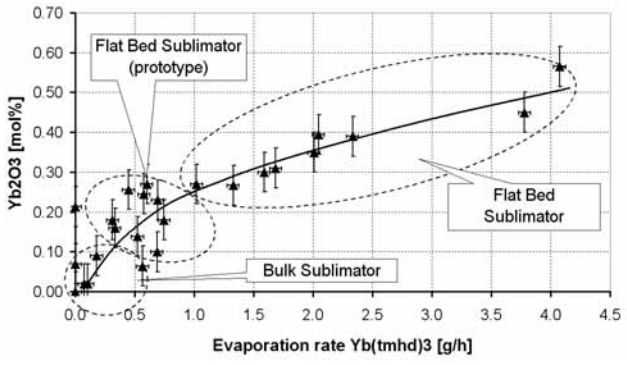

Fig. 4: Evaporation rates and deposition efficiency for different sublimator designs are shown.

2.3 Experimental

An MCVD preform fabrication system equipped with induction furnace was used. Chelate delivery system, connected to preform lathe as add-on device was a prototype of a commercial device. Precursor vapors, volatized at temperatures between 100°C to 220°C, were transported and injected into reaction hot zone by a system of heated conduits, valves, specially constructed high-temperature rotary seal and sliding precursor vapor injection tube.

Each precursor was sent to the hot zone in its own conduit to prevent chemical reaction between them. Each individual conduit (PTFE tube) can be exchanged quickly and conveniently, as it has been noticed that using same conduit for different precursor resulted in cross-contamination.

Preform fabrication was carried out in standard MCVD fashion. Cladding deposition was followed by active core deposition using chelate doping system.. Volatized precursors were transported and injected into reaction hot zone by a system of heated conduits, high-temperature rotary seal and sliding injection tube. An inert gas was used as carrier to prevent chemical reaction between constituents. They were allowed to mix with oxygen and SiCl4 vapors (and other gases and vapors GeCl4, POCl3, BCl3 and fluorine containing gas) delivered from standard MCVD gas cabinet only in the hot zone.

Prototype chelate doping system permitted deposition of multiple layers (up to 20 or more, depending on charge) but typically 5 – 9 layers were used to form core. SiCl4 carrier flow (O2) in core was typically set for 100 to 250 sccm with bubbler temperature 35°C and carriage traverse speed was 100 mm/min. Deposition was typically made over 600 mm and preforms with useful length between 250 and 350 mm and OD of 12 – 15 mm were produced.

After deposition of core layers, substrate tube was collapsed into solid rod preform in the conventional MCVD way, with the exception that furnace was used as heat source, which permitted significant acceleration of collapse process (more than twice faster) with generally improved geometrical characteristics.

3 Flash vaporization doping method

3.1 Flash Vaporization Concept

A new type of high performance vaporizers were developed for ALD, CVD, MOCVD (Metal Organic CVD), PECVD(Plasma Enhanced CVD), PEALD (Plasma Enhanced ALD) and all other gas phase processes containing vapors of solid or liquid compounds. New type of vaporizers can vaporize pure liquid compounds and solid ones dissolved in a carrier liquid (organic solvent). Their operation is based on a very fine atomization of a pulsed liquid flow, mixed with carrier gas prior to injection into vaporizer chamber.

Generated vapors can be used, for instance, for the synthesis by ALD and CVD of thin films, nanoparticles and nano-objects of numerous functional materials such as: dielectrics (low-k and high-k), barrier layers (Ta, Ti and Nb nitrides), ferroelectrics, piezoelectrics, metals (Cu, Ru, Rh, Pd, Ag, Ir, Pt…), III-V, II-V, chalcogenides (GST, CIS, CIGS,…), transparent conductive oxides, photovoltaic ones, low friction coatings, hard coatings and superconductors. In this described case we employed vaporizers as vapor delivery for optical fiber preform fabrication.

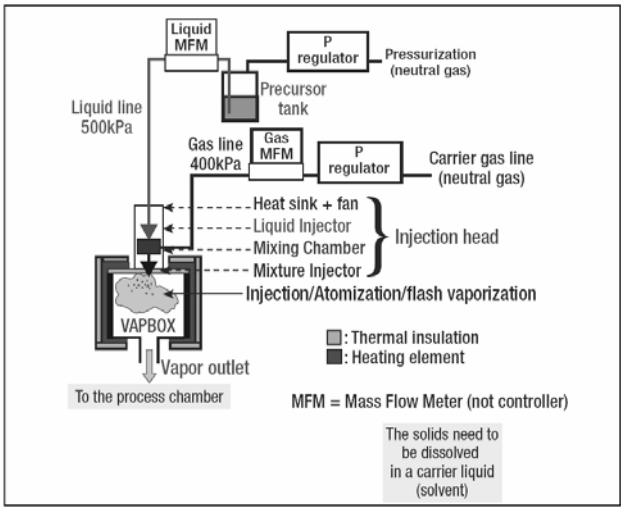

Fig. 5: Flash vaporization principle as employed in VapBox devices, single injector is shown.

VapBox vaporizers employ a proprietary way to deliver and atomize the liquid inside the vaporizer. They feature what is termed an injection head (see Figure 5 opposite). The injection head consists of multiple components: one liquid injector, one mixing chamber and one mixture injector. These three components are surrounded by a heat sink with a cooling fan. This arrangement keeps liquid or solution at room temperature, as long as it is not injected in the vaporizer. Premature precursor decomposition is thus avoided. Both the liquid and mixture injectors are normally closed fast solenoid valves working in a pulsed regime. The liquid to be vaporized is stored at room temperature in a pressurized tank at a higher pressure than the mixing chamber that is maintained under constant inert carrier gas pressure. The liquid injector pulses the cool fluid into the mixing chamber. The mixing chamber blends this fluid with the inert carrier gas. Finally, the mixture injector injects this mixture into the vaporizer in a pulsed regime. Pulsed flow combined with the blasting effect of the carrier gas pressure allows atomization of the blended fluid into an aerosol with extremely small droplets, typically 10 µm in diameter, with narrow distribution.

The surface of evaporation is thus very large. Furthermore, the droplets are very uniformly distributed over the carrier gas volume. Since the carrier gas serves as a heat transfer medium between the hot vaporizer walls and the droplets, heat transfer is very efficient. This provides efficient and truly non-contact flash vaporization to happen. The pulsed two-phase flow regime at the outlet of the mixture injector is highly turbulent and therefore the mean residence time of the droplets inside the vaporizer is largely increased, as compared to a stationary flow situation, avoiding the presence of non-vaporized droplets at the outlet of the vaporizer. A large amount of the droplets vaporize before touching the hot vaporizer walls of the vaporization chamber, limiting the clogging risks and allowing for generation of particle-free vapors. It is thus possible to efficiently vaporize thermally unstable compounds without clogging. These vaporizers can operate from vacuum to atmospheric pressure.

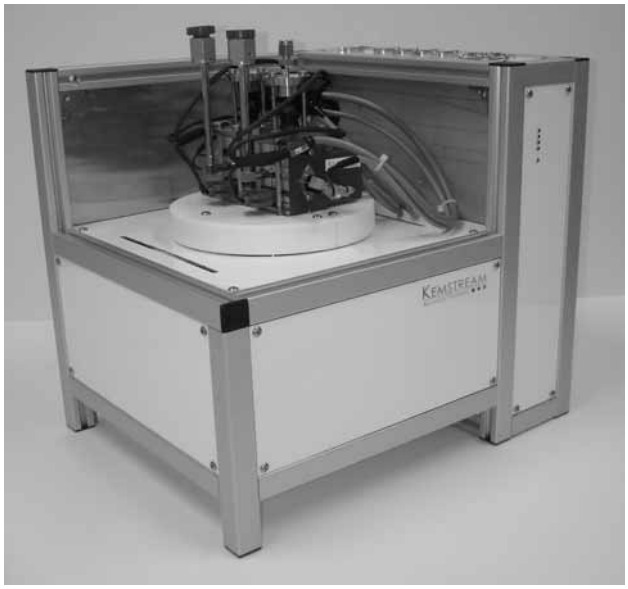

Fig. 6: Commercial version of Vapbox flash vaporization device with two injectors.

Vapbox vaporizer was adopted as vapor source for novel MCVD-like process for deposition of silica layers highly doped by lanthanides or metal ions. Figure 6 shows Vapbox device with two injection heads.

3.2 Raw Materials

Flash vaporization process relies on use of organometallic compounds as precursors for deposition process. It is not possible to combine standard halides like $SiCl_4$ in combination with organometallic materials or organic solvent vapors. Therefore chloride was replaced by TEOS (tetraethyl orthosilicate, Si(OC2H5)4), a material widely used in electronic industry. TEOS easily converts to silica by hydrolysis (sol-gel process) or at higher than 600 °C in presence of oxygen to SiO2 and diethyether. TEOS is readily available in ultra high purity and does not require complex handling.

There are other options, among which octamethylcyclotetrasiloxane (OMCTS or D4) or tetramethylcyclotetrasiloxane (TMCTS, precursor for gate dielectrics in thin-film transistors) have reportedly been used in specialty optical fiber preform fabrication by Morse /5/. They both have much higher content of silicon than TEOS and their reaction with oxygen is strongly exothermic.

β-diketonates have been chosen as organometallic precursors for lanthanide and transition metal ions. The reason for this was good availability from several commercial sources, relatively high purity, simple handling (with exception mentioned below) and good solubility in organic solvents. Most often used materials are chelates (tmhd) or acetyl acetonates (acac) as in case described above in chapter 2.

Organic solvents for preparation of solutions were, i.e. diglyme, 1,3-dimethoxyethane, tetrahydrofuran (THF) or chloroform, p.a. pure. Solution preparation and filling of precursor containers was made under dry and neutral (nitrogen) atmosphere, when necessary.

3.3 Experimental

Standard MCVD preform system has been used for fabrication of preforms. Flash vaporization doping system, connected to preform lathe as add-on device was a prototype of a commercial device. Schematic view of the complete set-up is shown on Figure. 7.

Precursor liquid or solution was injected into Vapbox vaporizer, volatized at temperatures between 180°C and 220°C, transported and injected into reaction hot zone by a system of heated conduits, valves, specially constructed high-temperature rotary seal and sliding precursor vapor injection tube

An inert gas was used as a carrier to prevent chemical reaction between constituents. Precursors were allowed to mix with oxygen and other gases (i.e. fluorine containing gas) delivered from standard MCVD gas cabinet only in the hot zone. Vapor entering substrate tube is shown on Figure 4b.

Standard cladding layers were first deposited on synthetic fused silica tube as barrier against hydroxyl impurity diffusion. Cladding was followed by active core deposition using flash vaporization doping system. Core was deposited in multiple thin layers.

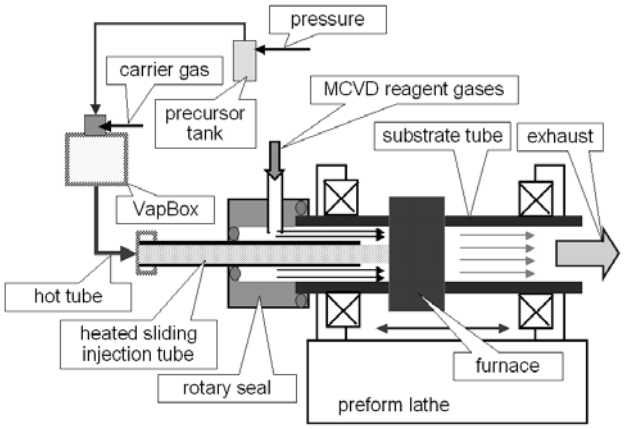

Fig. 7: Flash vaporization principle as employed in VapBox devices, single injector is shown.

Direct comparison with standard MCVD deposition is not possible, as TEOS was used in flash vaporization process as silicon precursor with evaporation rates between 0.25 and 2 g/min.

Core layers were deposited as thin porous doped silica layers (carriage forward motion) with low hot zone temperature of approx. 1450°C. At higher deposition rates, layers were filled with carbon soot (see Figure 8.) mainly from organic solvents and also partially from organometallic materials. At very high deposition rates, silica soot was filled with carbon to such an extent that the adherence to substrate tube wall was minimized and deposited layers detached themselves from the tube inner wall randomly.

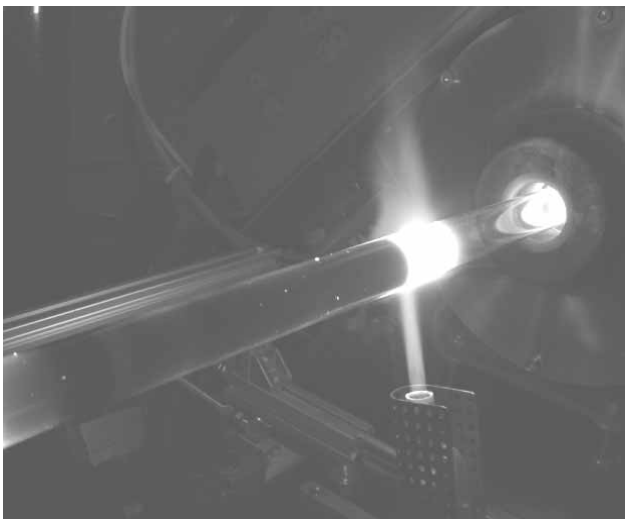

Fig. 8: Deposition of soot-filled layers during high deposition rate process.

Carbon was removed from soot-filled layers in oxygen-rich atmosphere at moderate to high temperatures, leaving

transparent and solid layer of doped silica. Chlorine was sometimes added to gas flow at this stage to remove hydroxyl and other impurities from deposited layers, and to reduce background loss /1/.

After deposition of several core layers, vapor injection tube was retracted and substrate tube was collapsed into solid rod preform. In these experiments furnace was used as heat source, permitting significant acceleration of collapse process (more than twice faster than with H2/O2 burner) with generally improved optical and geometrical characteristics.

4 Aerosol doping method

By modifying construction of flash vaporization doping device, a new type of devices is created. Instead of sending precursor and solvent vapor into process, a finely distributed aerosol is made from precursor-containing solution and guided into reaction by a system of heated conduits. Schematical view of such a doping system is shown on Fig. 9.

Aerosol enters reaction zone as very fine mist and evaporation process is initiated as soon as the substrate tube or burner flame (in outside deposition process) is hot enough. Therefore, vapors are produced on the spot where precursors are reacted with oxygen and other reagents.

Advantage of aerosol process over flash vaporization is in the capacity to use highly aggressive solutions or solutions based on alcohols or even water. Such process open the possibilities to use inorganic precursor materials which are most often available in higher purity.

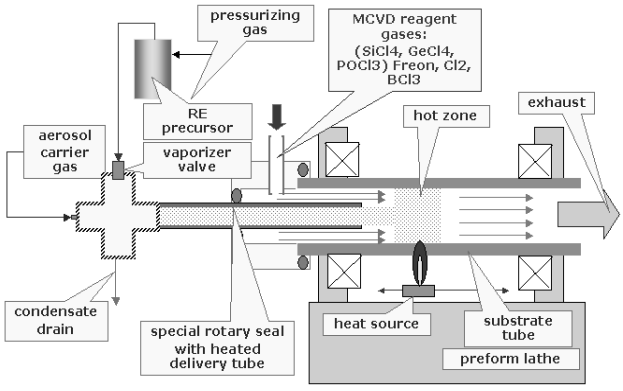

Fig. 9: Schematical view of aerosol doping device, based on flash vaporization process.

And, another important characteristics – due to use of injectors with higher injector orifice cross section, atomization causes no clogging or process problems even with precipitation of solids from solution. In all other aspects, the process is run as by the flash vaporization method.

5 Results and discussion

Most often specialty preforms are produced on request by customers developing new applications or devices. Deposited glass composition and characteristics have to provide behavior required by the sensor device or system. Such characteristics may range from optical to geometrical or even purely mechanical. A wide range of specialty preforms and glass compositions has been made in the recent years, based on above described doping methods and fabrication technologies.

5.1 Rare Earth-doped Performs and Fibers

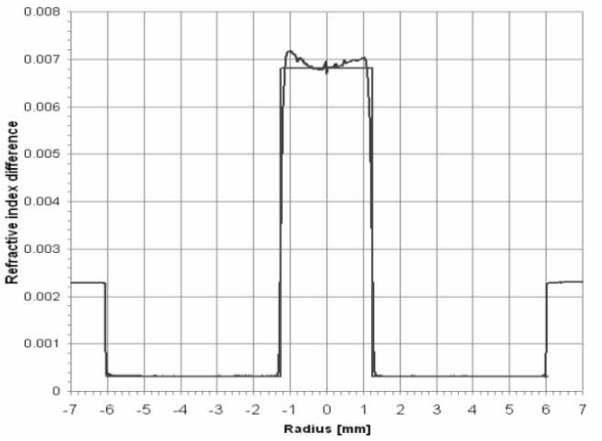

Fig. 10: Typical refractive index profile of a core preform made by flash vaporization doping process.

A number of experiments were carried out during evaluation of flash vaporization process and device. Preforms for laser fiber, co-doped by Yb^{3+} and Al^{3+}, (or phosphorous) were of most interest as they are currently very intensely investigated. A few experiments were made with other rare earth dopants (Er^{3+}, Tb^{3+}) to compare results of flash vaporization process with that of direct chelate evaporation / sublimation. For Yb^{3+}, the doping level achieved ranged from a few thousands to 70,000 ppmw with Al^{3+} or P^{5+} levels in appropriate ratio to rare earth, to prevent clustering.

Fibers were drawn from such preforms and it was demonstrated that chelate or flash vaporization doping can technology provides high quality glass, suitable for amplifier or laser operation.

Further testing is under way to confirm photodarkening characteristics of such glasses, while excellent slope efficiency performance has already been demonstrated. Background losses are well-controlled, both for chelate and flash vaporization made fibers.

Figure 10 demonstrates excellent refractive profile control for flash vaporization method. Figure 11 shows a typical octagonally-shaped preform for laser fiber (preform P0400 from Optacore).

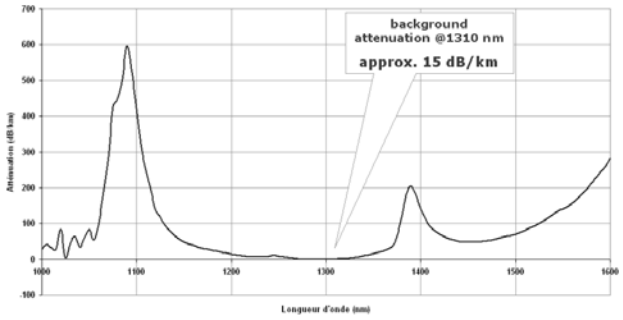

Fig. 11: Spectral atteenuation diagram for P0400 Yb^{3+}/Al^{3+}-codoped dual clad fiber

Fibers drawn from this preform were analyzed and spectral attenuation coefficient is shows on Fig. 12.

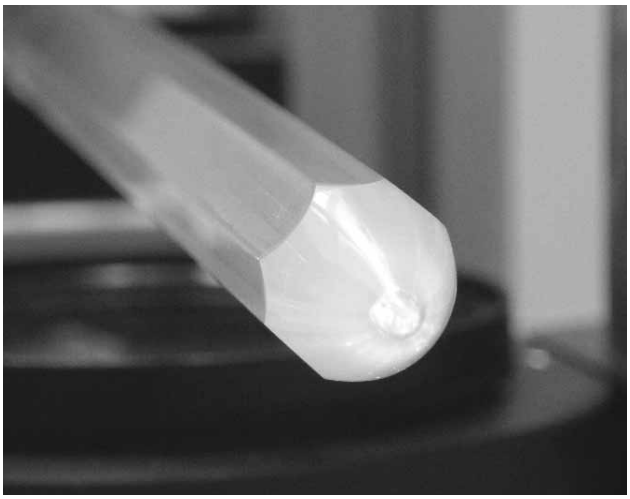

Fig. 12: Yb^{3+}/Al^{3+}-codoped dual clad preform produced in Optacore, ready for fiber drawing

5.2 Bismuth-doped Performs

Large interest in bismuth-doped fibers is related to search for laser white light sources. Bi-doped preforms were made by chelate and flash vaporization methods.

Bi-doping by chelate process is difficult, due to Bi-ion affinity to chlorine, which is always present when chloride is used as Si-precursor. Finding a Bi precursor for flash vaporization process is quite a complex task.

Bismuth chelate Bi(tmhd)3 is a very moisture sensitive compound which has to be handled under strict inert atmosphere and with anhydrous and deoxygenated solvents. Triphenyl bismuth Bi(C6H5)3O was identified as suitable Bi-dopant.

So far analysis of preform samples (slices) by X-ray microanalysis (EDS) has shown that bismuth content is below or at the detection level of the mentioned method (0.02 %at). Some of the preforms have shown bismuth luminescence (measured courtesy of FORC Moscow) but insufficient to proceed with preform or fiber analysis. Based on presented results and publications, new Bi dopants and modifications to precursor preparation process are currently investigated.

5.3 Metal ion-doped Performs and Fibers

Metal ions are used to produce glasses with very specific optical or mechanical characteristics. Vapor phase doping methods were tested with a number of dopants. Elements that are used as part of laser fiber fabrication process were not re-tested.

The following types of glasses have been deposited, and some were drawn to optical fibers:

- pure TiO2 on silica deposition
- highly vanadium-doped silica layers
- ZnO and CuO layer deposition on the inner wall of a quartz glass tube
- Fe-, Co- and Cr – doped preforms

Preforms have shown that significant doping levels, can be achieved while glass quality (in respect to bubbles and inclusion) and opto-mechanical characteristics remain suitable for use of drawn fibers in sensorics and photonic device development and fabrication.

6 Conclusions

Presented results and discussion demonstrate that vapor phase doping methods provide suitable and extremely flexible means for fabrication of different types of optical fiber preforms.

Experimental results have shown that highly rare-earth-doped fibers can be produced with sufficiently high deposition rate and repeatability to permit fabrication of high LMA laser fibers using chelate doping method.

Novel flash vaporization doping method has also demonstrated that fully vitrified transparent preforms without inclusions or bubbles can be fabricated using organometallic precursors for silicon, lanthanides, metal and transition element ions.

Fibers have been produced with suitable refractive index profiles and composition for intended purposes in laser and amplifier applications, for sensor applications and for fabrication of photonic devices. Champion data from such preforms and fibers show their characteristics are at least comparable to those of fibers produced by solution doping.

Wide range of precursors permits fabrication of diverse glass compositions thus making vapor phase methods and aerosol a versatile and reliable research tool, suitable for development and fabrication of novel glass structures and compositions.

Acknowledgments

Author would like to acknowledge support from Center of Excellence "En->Fist" and Slovenia Research Agency for part of the work presented here.

References

/1/ A. Mendez, T.F. Morse, ed., Specialty Optical Fibers Handbook, Academic, Burlington, 2007, Chap 7., 0-12-369406-X

/2/ Townsend, J.E. et al, "Fabrication of low loss optical fibres containing rare earth ions", Electr. Lett. 21, 737-738 (1987)

/3/ R.P. Tumminelli et al., Fabrication of High-Concentration Rare-Earth Doped Fibers Using Chelates, J. Light. Technol., Vol. 8 (1990)

/4/ B. Lenardič et al., Poster P09, ECOC Berlin, 2007

/5/ Materials from www. kemstream. com

/6/ B. Lenardič et al., Paper 1734, APOC Hanzhou, 2008

/7/ B. Lenardič et al., Paper OthK6, OFC San Diego, 2009

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Prispelo (Arrived): 01.09.2010 *Sprejeto (Accepted): 15.09.2010*