GLASS MATERIALS FOR OPTICAL FIBERS

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Submitted August 20, 2019; accepted October 14, 2019

Keywords: Optical fibers, Silica glass, MCVD, Fiber lasers

Optical fibers represent the key component of modern optical telecommunication networks. Such fibers are based on silica glass of high purity usually modified with several percent of glassforming oxides such as GeO$_2$ and P$_2$O$_5$. These materials with minimum optical losses around 1.5 µm are transparent up to ~2 µm. In this paper, the attention is focused on silica glass materials doped with ions of rare-earth elements for fiber lasers and fiber amplifiers. Since rare earths cause phase separation only in small amount incorporated into silica glass, ternary systems containing P$_2$O$_5$ or Al$_2$O$_3$ have been investigated. Latest results in GeO$_2$-based glasses transparent in mid infrared region are also presented.

THEORETICAL

Conventional silica-based glass materials with minimum optical losses around 1.5 µm for telecommunications

In 1966 Charles Kuen Kao published a paper called „Dielectric-fibre surface waveguides for optical frequencies“ [1] in which he outlined fundamentals of optical communications based on highly transparent silica glass optical fibers. For this groundbreaking paper and lifework in the field of optical fibers he was awarded by the Nobel Prize in 2009. Kao predicted that modern and fast optical communications can be performed only with thin silica-based fibers of ultra-high purity leading to their minimum optical losses in near infrared region around 1500 nm. He also noticed that impurities as for example Fe$^{3+}$, Cu$^{2+}$, Cr$^{3+}$, OH$^{-}$ etc. can be present in such silica glass maximally in ppm amount otherwise the optical losses are unacceptably increased making the fibers useless. It was a challenge for technologists since it is extremely difficult to achieve such level of purity especially during high-temperature processes which in the case of processing of silica glass are of around 2000 - 2100 °C. Therefore, an alternative research was guided to find a suitable multicomponent glasses or polymers of much lower processing temperature. However, two orders higher optical losses were achieved with polymer or multicomponent based fibers [2-3]. Kao’s requirements finally answered in Corning and fabricated silica glass rod (so called preform) of high purity from which the first optical fiber of acceptable optical losses < 20 dB·km$^{-1}$ was drawn [4].

The essential optical rule of higher refractive index of optical core than that of cladding was achieved in this case by coating of the silica glass core with a polymer of lower refractive index. Such generation of optical fibers drawn from single component silica rods – preforms was called Polymer-Clad-Silica (PCS) and their structure was characterized by a simple step-index profile of refractive index. Production of more complex fiber structures with glass cladding and glass core of tailored refractive-index profile required more sophisticated technology. Diffusion of multicomponent core of higher refractive index into silica cladding tube was tested [5] but without a significant impact. Next breakthrough in this field introduced elaboration of the Outside Vapor Deposition [6] and of the Modified Chemical Vapor Deposition (MCVD) methods [7]. The MCVD was presented for the first time by J.B. McChesney [8] at the 10th International Congress on Glass in Kyoto 1974; the ICG was at that time a usual platform for presentation of achievements in this field.

The MCVD method is based on sintering of smooth silica particles onto inner wall of rotating silica substrate tube. Fine SiO$_2$ particles („soot“) are formed by oxidation of SiCl$_4$ vapors at temperatures around 1600 - 2000 °C. Since SiCl$_4$ is a volatile liquid of boiling point of around 60 °C, by its distillation it is possible to achieve high level of purity and to produce a silica glass of ultra-high purity. The glass is deposited gradually into substrate tube in form of layers of thickness of 1 - 20 µm; finally the tube with layers is collapsed into a preform. High quenching rate (~10$^2$ °C·s$^{-1}$) accompanies the deposition because of small dimensions of the layers.
A difference of refractive index of silica fabricated by melting (Heraeus F300) and silica deposited by the MCVD can be seen in Figure 1.

When the layers are doped with compounds modifying refractive index, preforms of complex refractive-index profile can be produced. Number of glass compositions was investigated for this purpose. Conditions such as good miscibility with silica glass, glassforming, close expansion coefficient, low optical losses, availability of starting materials and reasonable dependence of refractive index on glass composition belong to basic criteria for choice of glass composition of the layers [9]. Silica doped with B$_2$O$_3$ or fluorine exhibit lower refractive index than pure silica [10-11]. Binary or ternary systems, E.g. GeO$_2$–SiO$_2$, P$_2$O$_5$–SiO$_2$, TiO$_2$–SiO$_2$, Sb$_2$O$_3$–SiO$_2$, Al$_2$O$_3$–SiO$_2$, GeO$_2$–P$_2$O$_5$–SiO$_2$ exhibit higher refractive index [12-17]. Finally, GeO$_2$-doped silica cores and P$_2$O$_5$-doped silica claddings were globally established as materials transparent in visible and near infrared spectral region of minimum optical losses suitable for telecommunications.

The Czechoslovak and Czech footprint in this field followed the global leaders with a little delay. Multi-component soft-glass-based fibers of typical composition K$_2$O–As$_2$O$_3$–PbO–SiO$_2$ were investigated in Glass Research Institute, Hradec Kralove [18]. Another team for investigation of silica optical fibers was established within Joint Laboratory Silicates of the Czechoslovak Academy of Sciences and the Institute of Chemical Technology in 1979. The first technology of PCS optical fibers was completed in 1982 employing the US Centorr graphite resistive furnace for 2100 °C [19]. Technology of graded-index (GI) and single-mode (SM) telecom fibers based on ternary GeO$_2$–P$_2$O$_5$–SiO$_2$ materials [20] was developed nearly at the same time. Spectral attenuations of discussed materials can be found in Figure 2.

Independently, intensive research of chalcogenide glasses of Ge–Se–Te, Ge–As–Se–Te composition for optical fibers transparent in infrared spectral region up to 10 µm was performed [21]. Optical losses of these materials prepared by conventional melting were not suitable for long-haul optical communications but sufficient for many other applications such as spectroscopy, optoelectronics etc.

New materials for fiber sensors, fiber lasers and amplifiers operating up to 2 µm

Later on, after telecommunication crisis at the beginning of new millennium, optical fibers penetrated to the field of optical fiber sensors, fiber lasers and amplifiers. Low optical losses are not so important in these applications since only short lengths of fibers are used. But specific properties like tailored refractive index or fluorescence are appreciated. Among others, specialty fibers drawn from GeO$_2$-highly-doped silica preforms with inverted refractive index were developed for evanescent-wave sensors. Cores of such fibers contained 50 mol. % GeO$_2$ [22] or even 97 mol. % GeO$_2$ [23]. Such binary glass cores were surrounded by silica substrate tube F300 of more than one order lower expansion coefficient and preforms of centimeters dimensions had to be carefully annealed to prevent crashing (Figure 3). Transparency of such highly-doped fibers stayed limited to cca 2 µm.

High content of GeO$_2$ in silica glass enhances photorefractive properties of the fiber cores and so supports inscription of Fiber Bragg Gratings (FBG) into these fibers. This effect is widely used in FBG sensors and for formation of laser cavity of fiber lasers.
Optical fibers drawn from F2 Schott glass preforms (of refractive index 1.62 and of Na₂O–K₂O–As₂O₃–PbO–SiO₂ composition) were successfully prepared and used for monitoring of polymer composites [24]. An increase of several orders of attenuation of such F2 fiber in comparison to silica glass fibers can be seen from Figure 4 and Figure 2.

Boom in fiber lasers and amplifiers started at Optoelectronics Research Center University of Southampton [25] a long time after publication of the pioneering work of E. Snitzer [26]. Significant part of these devices is based on materials doped with ions of rare-earths elements (RE). These fluorescent agents are capable to withstand high processing temperatures of silica glass. Materials doped with erbium were investigated at first because of their fluorescence around 1550 nm which is the conventional wavelengths used in telecommunications. However, only small amount of around hundreds of ppm of RE in silica glass leads to phase separation [27] and to devastation of optical properties of the material. So, in order to achieve higher RE content in glass the matrix had to be modified with modifiers supporting dissolution of RE and compensating their charge. Modification of the silica matrix with GeO₂ did not lead to fundamental progress [28]. But introducing of Al₂O₃ was highly effective and made doping of fibers with higher content of RE possible. Aluminum oxide is able to exist in modifications of Al₂O₃ as well as of [Al₂O₃]²⁻ depending on its vicinity and in this way it can compensate the RE ions. Glassforming properties of ternary RE–Al₂O₃–SiO₂ systems of bulk samples were investigated by Shelby [29]. Al₂O₃ also positively increases refractive index of glass and so it is widely used for modification of core of optical fibers up to 10 - 12 mol. % typically [17], [30]. Al₂O₃ is also used for modification of silica glass matrix doped with thulium or holmium ions because of its positive influence on fluorescence lifetime of the materials [31]. Since starting materials for Al₂O₃ and RE doping are available only in solid state, number of modifications of the MCVD technology were developed [32-34]. Glass matrices of fibers for ytterbium fiber lasers are usually co-doped with several molar percent of P₂O₅ [35]. In vicinity of Yb³⁺ the double bond P=O is
split and compensates the ions in glass structure. Fibers of composition \( \text{Yb}^{3+} - \text{P}_2\text{O}_5 - \text{SiO}_2 \) are frequently used for kW-class fiber lasers operating at around 1060 nm. Excitation and fluorescence spectra of \( \text{Er}^{3+}, \text{Yb}^{3+}, \text{Tm}^{3+} \) and \( \text{Ho}^{3+} \)-doped silica optical fibers can be seen at Figure 5.

An idea of enhancement of fluorescence of RE by means of nanoparticle technology was brought up a decade ago. Metallic nanoparticles were implemented at first, later fluorides, ceramics and finally a nano-phase separation processes were developed [36]. This issue is still widely investigated [37-39] with ambiguous conclusions. According to [40] when alumina nanoparticles are incorporated into silica matrix, mullite phase is formed after high temperature processing (preform collapsing and fiber drawing) in agreement with \( \text{Al}_2\text{O}_3 - \text{SiO}_2 \) phase diagram [41] and no significant improvement of lasing properties was observed. This conclusion can be indirectly supported by the results observed with sapphire-core fiber drawing [42].

Latest trends

Silica-based optical glasses have been employed for decades as fundament for optical applications in spectral region up to \( \sim 2100 \) nm. Requirements for materials transparent at longer wavelengths has appeared namely in relation to the latest advance in infrared lasers. Optical fibers from such materials should be capable to transmit infrared radiation or to produce stimulated infrared fluorescence as fiber lasers. Extensive research has been executed in fluoride, chalcogenide, telluride and other non-oxide glasses transparent in infrared region and suitable for fiber drawing, including domestic research of \( \text{As}_2\text{S}_3 \) passive optical fibers [43].

\( \text{GeO}_2 \)-based glasses were investigated from the group of oxidic glasses potentially transparent in mid infrared region. Such glass matrix could be suitable for embedding of RE and could be a suitable medium for transmission of their fluorescence up to \( 4 - 5 \) \( \mu \text{m} \). However, it is not easy to fabricate such glass because of its relatively high processing temperature around \( 1500 \) °C. Therefore, \( \text{GeO}_2 \) glass matrix was modified with \( \text{PbO} \) up to 32 mol. % at the beginning. Transparent samples of good optical quality and preform shape were produced (Figure 6a) but lead oxide cannot be considered a perspective material because of its toxicity. Pure \( \text{GeO}_2 \) glass samples were melted in extra dry atmosphere and results were presented again at ICG [44]. Homogeneous transparent samples were obtained as expected but intensive hygroscopicity was observed later (Figure 6b).

Fluorescence spectrum of \( \text{Er}^{3+} - \text{PbO} - \text{GeO}_2 (68) \) glass sample containing 400 ppm \( \text{Er}^{3+} \) can be seen in Figure 7. Despite a good homogeneity and transparency of \( \text{GeO}_2 \) glass samples already prepared, a search for suitable modifier decreasing the processing temperatures and keeping transparency in mid infrared region is a challenge for future research.

Small dimensions of optical fibers and their flexibility make them perfectly suitable for use in medicine. Number of diagnostic or therapeutic tools based on optical soft glass fibers or silica fibers have been widely produced. Recently, requirements for biodegradable optical fibers has appeared. Using of biodegradable fibers for in-vivo applications would significantly decrease the
risk of consequences of potential breaking of fiber-optic tools. Phosphate-based optical fibers could be an answer to this call [45] as an alternative to fibers from biodegradable polymers [46].

CONCLUSIONS

A survey on glass materials used for optical fibers was given with accent on results achieved within 40 years of fiber-optics research in Joint Laboratory of Silicates, later Institute of Chemistry of Glass and Ceramics Materials ASCR, later Institute of Radioengineering and Electronics CAS, later Institute of Photonics and Electronics CAS and Laboratory of inorganic materials of the Institute of Rock Structure and Mechanics CAS. From this survey, it can be concluded that the pioneering vision of Charles K. Kao was extraordinarily viable and predicted trends in optical communications for decades. Silica-based optical fibers are nowadays object of mass production as well as of intensive research and related technologies, thus representing symbols of matured economies.

Acknowledgement

This research has been supported by the Czech Science Foundation, project. No 17-20049. Authors would like to ask for understanding of high portion of self-citations related to commemoration of 40 years anniversary of the research of technology of optical fibers conducted in the Czech Republic.

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