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Peculiarities of the mid-infrared evanescent wave spectroscopy based on multimode chalcogenide fibers

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ABSTRACT

Output characteristics of the evanescent wave sensor have been studied in experiment by measurement of the transmittance of a chalcogenide fiber submerged into an aqueous solution of acetone in the range of wavelengths 5–9 μm. The minimum concentration of 1 mol% of acetone has been detected at the wavelengths of 7.33 μm and 8.18 μm. By using a theoretical approach based on the electromagnetic theory of optical fibers, we have revealed that dependence of the transmittance logarithm versus the length of the fiber immersed into the solution is not linear because of the greater attenuation of the evanescent modes having greater radial orders. As calibration curves of the higher-order modes are steeper they are more suitable for the sensitive detection of chemicals. Water absorption as a factor limiting the sensitivity of spectroscopic measurements in mid-infrared has been discussed.

1. Introduction

Transparency of chalcogenide glasses in the mid-infrared (MIR) at the wavelengths $\lambda = 3$–$25\ \mu m$ makes them attractive for development of the fiber-based evanescent wave MIR spectroscopy that provides an efficient tool for chemical analysis of gases and liquids. Strong vibrational bands of inorganic and organic molecules in the MIR are much more suitable for spectroscopic analysis than the absorption spectra in the near-infrared (NIR) and visible (VIS) ranges where generally weak and complicated overtone absorption bands are located.

Using of chalcogenide glass fibers for chemical sensing [1,2] is often based on absorption of evanescent waves in a surrounding medium. Due to this absorption, power transmitted by a fiber at the wavelengths corresponding to characteristic absorption bands of molecules in the medium decreases. Absorption spectra of various chemical substances in aqueous solutions were measured in [3–6] in the MIR by using multimode chalcogenide fibers. In [3], the fibers of the 380 μm diameter, made of $Ge_{27}Se_{18}Te_{55}$ glass were used for detection of acetone, ethyl alcohol and sulfuric acid in aqueous solutions in the range $\lambda = 5$–$9\ \mu m$. The minimum acetone concentration measured at $\lambda = 5.83\ \mu m$ was equal to 5 vol%. In [4], even smaller concentrations of analytes have been detected. The concentration of 2% was measured by using the $Ge_{30}As_{10}Se_{30}Te_{30}$ fiber of the 200 μm diameter in the range $\lambda = 3$–$16\ \mu m$ for the mixtures of water and methanol, ethanol, isopropanol and acetone.

For efficient interaction of the evanescent waves with an external absorbing medium, unclad fibers are to be used or, otherwise, fiber cladding can be removed over some length. The amount of radiation propagating in an external medium is the key parameter for the evanescent wave spectroscopy. In comparison with the silica glass, chalcogenide glasses have much greater refractive indices ($n > 2.4$). As refractive indices of the aqueous solutions of acetone, oil and some other analyted are around 1.3–1.5, propagating radiation is generally more confined in a chalcogenide unclad fiber than in a silica one being immersed into the solutions. Design of fiber sensing elements is a special task in development of the MIR evanescent wave spectroscopy.

Some designs of fiber sensors were proposed for optimisation of the evanescent wave spectroscopy in mid-, near- IR or VIS. In [6], detection of the weak concentrations of pollutants C_2Cl_4 in the groundwater became possible through the use of the bent chalcogenide fiber with the tapered 100-μm zone. It was demonstrated in [7,8] for a sensing element based on a straight silica fiber that using of multimode fibers allows obtaining high sensitivity and linear logarithmic output in VIS. In [8], the evanescent-wave sensor based on a multimode silica fiber was acting as a logarithmic detector. Due to microbends created in the fiber over a length of 6 cm, the sensor had large dynamic range (> 6 orders of magnitude).

In [9], we have proposed an efficient theoretical approach, which

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can be used for design of the evanescent wave sensors. This approach is based on electromagnetic theory of optical fibers and modal representation of the radiation propagating in an optical fiber [10]. An absorbing liquid medium is considered as a fiber cladding. The refractive indices of the fiber core $n_{co} = n_{co}' + i \cdot n_{co}''$ and of the fiber cladding $n_{cl} = n_{cl}' + i \cdot n_{cl}''$ are complex in general with the nonzero imaginary parts n_{co}'' and n_{cl}'' appearing due to losses in the fiber and due to absorption in the surrounding medium. Then longitudinal propagation constants $\beta_m = \beta_m' + i \cdot \beta_m''$ of guided modes of the fiber immersed into the absorbing medium are complex-valued and all the guided modes are evanescent. Magnitudes of the propagation constants can be found from the numerical solution of characteristic equations [10]. Longitudinal component $P_m(z)$ of a power flow of the m-th evanescent mode is decreasing along the fiber axis z:

$$P_m(z) = P_{0m} \cdot \exp(-\eta_m \cdot z) \tag{1}$$

Here $P_{0m} = P_m(0)$ is defined at the fiber input facet, $\eta_m = 2 \cdot \beta_m''$ is the mode attenuation coefficient. Its magnitude depends on the fraction of the evanescent mode radiation propagating in the absorbing medium (outside the unclad fiber core). For a fiber with the core radius R, this fraction depends on the ratio R/λ for each fiber mode [10]. For a fixed λ, this fraction increases with decrease of R until the mode cut-off. For a given R, this fraction increases with wavelength.

In this paper, we study peculiarities of the fiber-based evanescent wave spectroscopy in the MIR both in theory and in experiment. Experimental results have been obtained for a chalcogenide fiber immersed into an aqueous solution of acetone by the measurement of the fiber transmittance spectra in the range λ = 5–9 μm. This range of wavelengths is suitable for acetone solutions because some vibrational bands of acetone do not overlap here with the main absorption bands of the water at λ ≈ 3 μm and λ ≈ 6 μm. Aqueous acetone solutions were also used in [3–6,9,11] as liquid analytes for the evanescent wave chemical sensing in the MIR with the use of chalcogenide fibers.

2. Fiber and aqueous acetone solutions characterization

Chalcogenide glass of the $Ge_{26}As_{17}Se_{25}Te_{32}$ composition was prepared by using a chemical and distillation purification technique as described in [12,13], in the form of a monolithic rod of the diameter of 12 mm and the length of 100 mm. This composition has been chosen especially to fit the transparency range λ = 5–9 μm. With this composition, the optical losses are low and permanent in the range as shown in Fig. 1 inset. The prepared glass had low concentrations of limiting impurities: oxygen < 0.1 ppm (wt), carbon < 0.5 ppm (wt), hydrogen < 0.04 ppm (wt), silicon < 0.5 ppm (wt), transition metals < 0.05 ppm (wt). Concentrations of the residual gas-forming impurities in the fiber were determined by means of the IR spectroscopy from the intensities of absorption bands in the optical loss spectrum using the known values of extinction coefficients [14–16]. The rod of $Ge_{26}As_{17}Se_{25}Te_{32}$ glass was drawn into a single-index fiber by using a single crucible method. The temperature of thermostat was 430 °C, and the drawing rate was of 1.5 m/min. An inert gas (special pure Ar) pressure of 0.5 atm was used to create the necessary melt flow through the die. We did not observe glass crystallization during the fiber drawing. For determination of the optical losses γ of the fiber, several fiber pierces of 2 m length were measured through the cut-back method.

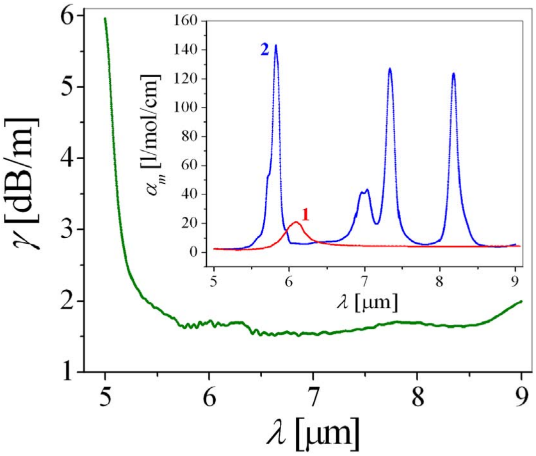

Fig. 1. Optical losses in the $Ge_{26}As_{17}Se_{25}Te_{32}$ fiber; Inset: molar absorption coefficients of water (1), acetone (2).

For evaluation of the molar absorption coefficients of water and acetone in bulk from their absorption spectra, a Fourier-Transform Infrared Spectrometer (FTIR) has been used. Wavelength dependencies of the molar absorption coefficients are shown in Fig. 1 (inset). In the range λ = 5–9 μm, four absorption bands attributed to acetone molecular vibrations (λ = 5.83 μm (α = 1942 cm^{-1}), λ = 7.02 μm (α = 589 cm^{-1}), λ = 7.33 μm (α = 1725 cm^{-1}) and λ = 8.18 μm (α = 1681 cm^{-1})) have been observed [4]. Here α is the absorption coefficient. The path-length d of radiation in a zinc-selenide cell was chosen rather small (10 μm < d < 20 μm). With a bigger d, radiation was totally absorbed because of the strong absorption in the bands. With a smaller d, due to an interference of radiation in the absorbing layer, the relation $A = -\mathrm{Log}\,(T)$ between transmittance T and absorbance A is incompatible with the phenomena. For testing of the obtained results, digital absorption spectrum of water available in [17] has been used.

For characterization of the fiber waveguiding properties, number of the guided modes propagating in the fiber is to be evaluated. Total number of guided modes of a fiber depends on the fiber parameter $\mathrm{V = k \bullet R \bullet \sqrt{n_{co}'^2 - n_{cl}'^2}}$, where $k = 2\pi/\lambda$, R is the fiber core radius [10]. If the fiber input facet is illuminated uniformly by a light beam coaxial with the fiber axis, the HE_{1m} modes are predominantly excited in the fiber. The fundamental HE_{11} mode belongs to this family of the fiber modes. The number N of the HE_{1m} guided modes can be evaluated by using cut-off conditions for the modes. For each HE_{1m} mode, the parameter V_c^{m} at the cut-off obeys the condition $J_1(V_c^{\mathrm{m}}) = 0$ where J_1 is Bessel function of the first kind of order 1. The HE_{1m} mode is classified as a guided mode provided that $V_c^{\mathrm{m}} < V$. Then N is equal to the maximum m, for which this latter condition is satisfied. In fact, this is the N-th zero of $J_1(\mathrm{x})$. If an unclad fiber is immersed into an absorbing medium with the same real part of n_{cl}, all guided modes of the fiber become evanescent, but their number keeps the same.

As the fiber parameter V depends on the wavelengths, number of the guided modes propagating in the fiber at different spectral components varies over the spectrum of input radiation. The magnitudes of N calculated for the $Ge_{26}As_{17}Se_{25}Te_{32}$ fiber used in the experiments are shown in Fig. 2 depending on the wavelength. It is worth to notice that real part of refractive index vary significantly near vibrational absorption bands of a substance. Spectral dependence of the refractive index of water [18] is shown in Fig. 2 inset, demonstrating typical ranges of normal and anomalous dispersion near the absorption band at λ = 6.09 μm. In this range, N varies accordingly (line 2 in Fig. 2). As spectral dependence of acetone refractive index is not available in this range, a mean value n_a = 1.35 (taken from [19] at λ = 0.83 μm) is used in our computer model. Refractive index of the $Ge_{26}As_{17}Se_{25}Te_{32}$ glass is approx. equal to 2.8 in the MIR [20]. By comparison of the lines 1 and 2 in Fig. 2, we can notice that N is greater in the fiber sections outside the solution (in the air) than in the fiber sections submerged into the solution. This means that some transformations of the higher-order modes at the border of the liquid create additional losses in the sensing element.

3. Measurements of the fiber transmittance

For measurement of the fiber transmittance, the same arrangement