Mid-infrared Fiber Optics for 1 – 18 µm Range

IR-fibers and waveguides for laser power delivery and spectral sensing

Viacheslav Artyushenko, Alexey Bocharnikov, Tatiana Sakharova and Iskander Usenov

Development of infrared (IR) fibers and hollow waveguides (HWGs) was in good progress to meet growing market demands for laser power delivery, flexible IR-imaging and remote process-spectroscopy in spectral range from 1 to 18 µm. Parameters of IR-glass fibers, polycrystalline IR-fibers (PIR-fibers) from silver halides and HWGs are compared to enable optimal choice for the production of IR-cables, spectroscopy probes and multispectral bundles (Fig. 1).

Fig. 1 Combined 128 fiber bundle of 3 fibers types (UV + NIR Silica fibers + CIR-fibers) to control emission spectra in 0.18 – 6 µm range from various sources.

Well-known fused silica fibers possess high transmission in a broad spectral range from 180 nm up to 2.2 µm (Fig. 2a). They can be used for spectroscopy in UV-Vis and near-infrared (NIR) range, for flexible power delivery of various lasers, for illumination, sensing applications, etc. As silica fibers transmission is limited at longer wavelengths by multi-phonon absorption wing the other types of materials are used to fabricate fibers transparent in mid-infrared (MIR) range, i.e. for the wavelengths longer than 2.2 µm (Fig. 2).

IR-fibers are fabricated by drawing from the different types of IR-glasses, while polycrystalline fibers are extruded from solid solutions of silver halides crystals and single crystalline fibers are grown by pulling from the melt crystals. Hollow waveguides provide an alternative way to IR-fibers for flexible delivery of mid IR-laser power and spectroscopy sensing, while their design is based on thin tubes with metal and dielectric layers deposited on internal wall surfaces.

IR-glass and single crystalline fibers for UV-Vis & NIR up to 4 µm

In addition to the silica fibers which are the best for very broad range from 180 nm to 2.4 µm there is a variety of IR-glass fibers for 1 – 4 µm range which are produced from Ge-oxide, fluoride, chalcogenide and other glasses. The broad range from UV-Vis to 4 µm can be also covered by single-crystalline sapphire fibers. The main features, advantages, drawbacks and key applications of all these fibers are listed in Table 1.

Fluoride glass fibers possess the lowest optical losses in 1.5 – 3.5 µm range (especially zirconium fluoride ZrF_4 fibers) and can be used for power delivery of any lasers in this range, including Er:YAG & Er:YSGG lasers (Fig. 2b). Fiber cables for Er:YAG-lasers enable flexible delivery of high energy pulses at 2.94 µm when either GeO_2 or fluoride glass fibers are used for their assembly. Due to the highest absorption of water and tissue at 2.94 µm medical Er:YAG-lasers are already

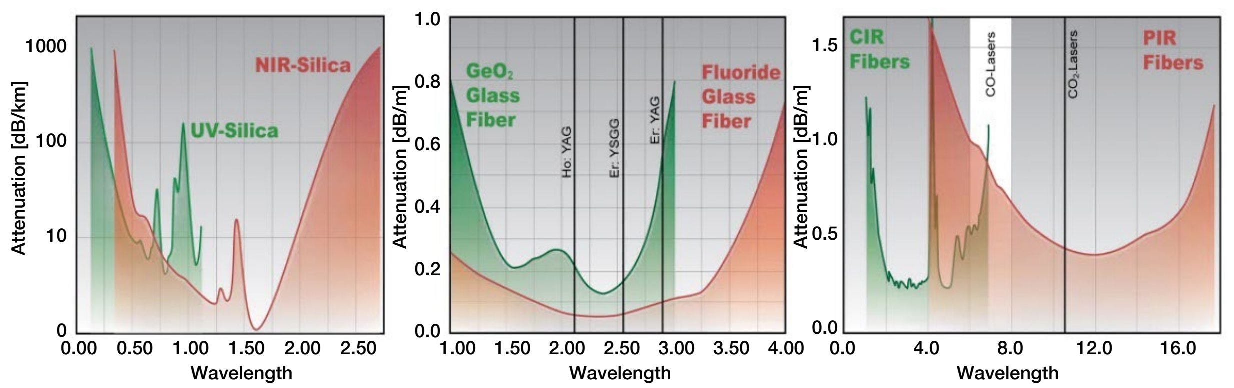

Fig. 2 Attenuation spectra of a) silica fibers; b) IR-glass fibers; c) chalcogenide IR-glass (CIR) and PIR-fibers.

Fiber Type	Advantages	Drawbacks	Applications
Silica fiber Pure silica core & F-doped cladding	■ 0.2 – 2.4 µm ■ Non- toxic ■ Non-hygroscopic ■ Stable up to 600°C ■ Photonic crystals !	■ Brittle without coating	■ Telecom ■ Spectroscopy probes ■ Imaging bundles ■ Laser power delivery up to 10 kW ■ Illumination
POF fiber plastic optical fiber from PMMA, CYTOP, polystyrol, etc.	0,4 – 0,8 µm High flexibility Low cost Easy installation Photonic crystals !	■ Limited transmittance ■ Limited range of temperature: –55°C / +85°C	■ Illumination ■ Local telecom ■ Light control in auto, plane, etc. ■ Fiber sensing for various parameters
Germanate Fiber Fluoride Fiber Ge-O or ZBLAN-glass	■ 1 – 3 µm & 1 – 4 µm ■ Non toxic ■ Stable up to 250°C	Brittle without coating ZBLAN glass is slightly hygroscopic	■ High power delivery for Er:YAG & Er:YSGG laser ■ Surgery
Sapphire fiber single-crystalline	■ 0.5 – 3.4 µm range ■ Non toxic ■ Stable up to 2000°C	■ No cladding ■ Stiff & Brittle	■ High power delivery for Er:YAG & Er:YSGG laser ■ Surgery ■ Spectroscopy probes

Table 1 Advantages, drawbacks and applications of different types of IR-glass and single crystalline fibers.

used in dentistry, plus in orthopedic and dermatological operations. They are also used in laser technology for the processing of plastics and metals. Design of combined cables is based on GeO_2 or fluoride glass fibers, protected by durable tubing and combined in protective sleeve with silica fiber for pilot beam, polymer pipe for water supply plus electrical wires to the distal handpiece – where the focusing optics is fixed together with remote control of laser.

MIR-fibers and waveguides for 2 – 18 µm range

Development of innovative fibers for mid IR spectral range opens a variety of promising fiber applications in 2 – 18 µm range. Main features, advantages, drawbacks and key applications of PIR- & CIR-fibers are listed in Table 2 together with HWGs.

IR-transmitting materials for the spectral range from 2 to 18 µm are known for many years. But only a few types of IR-materials can be used for the manufacturing of uniform long-length IR fibers with low optical attenuation and acceptable mechanical bending properties. Many years of research and development for reliable IR-fiber technologies led to the final selection of the main IR-materials acceptable for production of mid IR-fibers of optical performance good enough for pragmatic applications.

Nowadays the best fibers for 1.5 – 6 µm are drawn from chalcogenide IR-glass (CIR-) based on As_2S_3-composition. Purification technology of this glass enables its high transmission in the specified range [1]. Attenuation spectrum of CIR-fiber is presented in Fig. 2c. Design concept of CIR-fibers is based on step refractive index structure with numerical aperture $NA = 0.3 – 0.37$ defined by refractive index difference between core and cladding glass compositions. To enhance mechanical strength of brittle CIR-fiber its lateral surface is coated with a special double polymer layer, which enables mechanical protection and flexibility. CIR-fiber manufacturing is possible either by drawing using "floating crucible" technique or by drawing from the preform "rod-in-tube". Typical specifications of CIR-fibers are presented in Table 3.

Unique PIR-fibers are fabricated by hot extrusion from crystals of silver halide solid solution $AgCl_{1-x}Br_x$ (where $0 < x < 1$) [2–6] and provide the best flexible solution a broader range 3 – 18 µm compared to IR-glass fibers. PIR-fiber transmission includes so called

Fiber Type	Advantages	Drawbacks	Applications
CIR-fiber chalcogenide IR glasses: As-S or Ge-As-Se-Te chalco-halide glasses Te-Ge-I	■ Transmittance in 0.7 – 6 µm (As-S) or 2 – 10 µm (GeAsSeTe) ■ Stable for 250 – 400 K ■ Non-hygroscopic	■ Fragile ■ Toxic ■ Low T_g (450 K) ■ High dn/dT ■ High N	■ Spectroscopy probes for gases & liquids ■ Flexible radiometry ■ IR-imaging bundles for endoscopy
PIR-Fiber polycrystalline IR crystals from silver halide solid solutions	■ Transmittance in wide 3 – 18 µm range ■ Non-brittle ■ Non toxic ■ Non-hygroscopic ■ Stable in 5 – 600 K	■ High scattering from 0.6 to 3 µm ■ UV-sensitive ■ Corrosive in contact with some metals	■ Spectroscopy ■ Probes for gases & liquids ■ Flexible radiometry ■ IR-imaging bundles ■ Power delivery (50 W) for CO-/CO_2-lasers
Hollow waveguides silica, silver or polymer tubes with reflective inner coating	■ High transmittance ■ Low divergence ■ High damage ■ Threshold (> 2 kW) for Er:YAG / CO_2-lasers ■ Rugged & durable	■ Sensitive to bending (3 dB at 10 cm radius) ■ High losses for transmission of $NA > 0.1$	High laser power delivery (> 2 kW) for Er:YAG / CO_2-lasers Spectral sensors for gas flow through hollow guide cell

Table 2 Advantages, drawbacks and applications of PIR-, CIR-fibers and HWGs.

Company

art photonics GmbH

Berlin, Germany

art photonics GmbH was founded in Berlin in 1998 for development and production of specialty fiber cables, bundles and spectroscopy probes required for various applications in any range from UV to mid-infrared – from wavelengths of 180 nm to 18 µm. Pioneering development of polycrystalline IR-fibers (PIR-fibers) for mid IR provides to art photonics the leading role in production of unique PIR-fiber cables and probes for the 2.5 to 18 µm spectral range. In result flexible solutions for process-spectroscopy can be based now on different fibers types – from silica fibers for 0.2 to 2.5 µm to PIR- & CIR-fibers in mid IR (CIR fibers are drawn from chalcogenide As-S glass).

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"finger-print" region of the spectrum (3 – 16 µm) – the most information rich for specific absorption bands of various molecular vibrations.

In contrast to the most IR materials AgCl:AgBr crystals are non-toxic, non-hygroscopic and can be extruded by plastic deformation under high pressure and elevated temperature. These unique features in combination with a high optical purity of silver halide solid solutions enable fabrication of high quality IR-fibers by extrusion method. Attenuation spectrum of PIR-fiber is presented in Fig. 2c. Design concept of PIR-fiber is based on step refractive index structure defined by difference in refractive indexes of core and cladding. Preforms of "rod-in-tube" type for PIR-fibers are also made by plastic deformation in vacuum to eliminate air bubbles at core/clad boundaries. After extrusion PIR-fibers are inserted into a loose polyetheretherketone (PEEK) tubing for mechanical protection and bending within the elasticity limits, while no polymer jacket is applied directly to the lateral fiber surface. PEEK tubing provides in addition PIR-fiber protection against illumination by UV and visible light and therefore prevents photo-induced Silver formation at fiber surface – together with the possibility to make hermetic PIR-fiber cable assembly. An optimized production technology of PIR-fibers and assembly of durable PIR-cables, bundles and probes result in their high optical and mechanical parameters for reliable exploitation in a broad temperature range from 5 K to > 410 K without deterioration of those all parameters. Industrial type of PIR-cables are also made so robust that they withstand specific climatic and vibration tests. Special development of PIR-fiber technology was done to fabricate the 1st single-mode fibers (Fig. 3) to be used as the wavefront filters in ESA Darwin mission program [7]. Efficient coupling of PIR-fibers with IR-lasers was started from flexible delivery for medical CO2-lasers, while for IR-spectroscopy applications they can be perfectly coupled to quantum cascade lasers (QCL) [8]. Typical specification of PIR-fibers is presented in Table 3.

Fiber Type	CIR-fiber	PIR-fiber
Transmission range, µm	2 – 6	3 – 18
Core/Clad structure materials	Chalcogenide glasses As_2S_3/As-S (amorphous)	Solid solution crystal AgCl:AgBr (polycrystalline)
Core/Clad diameter, µm	250 – 500 / 300 – 550	200 – 900 / 300 – 1000
Core refractive index	2.44	2.15
Optical losses	0.2 dB/m at 2 – 4 µm	0.2 – 0.3 dB/m at 8 – 12 µm
Operation temperature range	From 280 to 370 K	From 5 to 400 K
Max. length available, m	Up to 50	Up to 20 – 30

Table 3 Main parameters of CIR- & PIR-fibers.

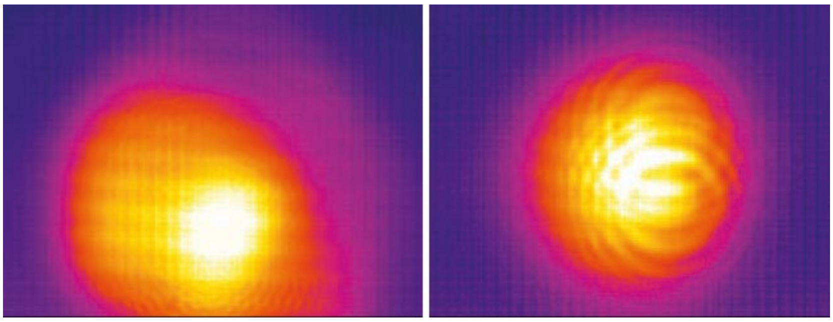

Fig. 3 Output intensity of realized SM-87-7 fibre with 47/500 core/cladding and 2 % composition difference [7].

To enable expansion of a common UV-Vis-NIR spectral range for silica fiber bundles CIR- and/or PIR-fibers can be also included in mixed bundles – extending their range to mid IR (Fig. 1) for delivery of broad spectra or emission spectra control for a various lights sources – from lamps to stars. Flexible 2D & 3D IR-imaging systems is an additional important example for application of coherent IR-fiber bundles coupled with IR-detectors. Such IR-fiber systems enable remote sensing with flexible PIR-fiber cables at long distance from IR-source – up to 20 m. IR-fiber can be coupled with room temperature IR-detectors or with much more sensitive MCT or InSb-detectors fixed in Dewars cooled by liquid nitrogen or helium.

Spectroscopy probes assembled with mid IR-fibers provides real revolution in modern chemical and bio-laboratories

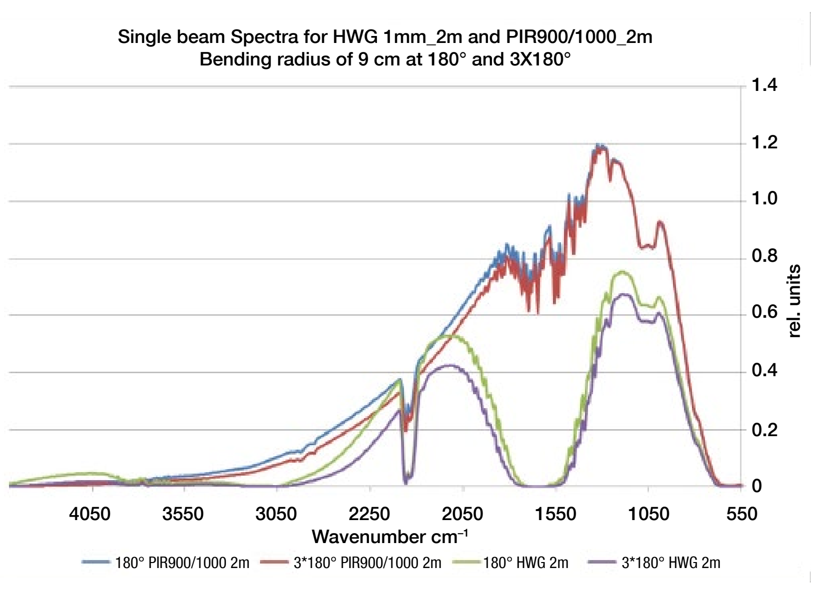

Fig. 4 HWG vs PIR-fiber single beam spectra under different bending conditions.

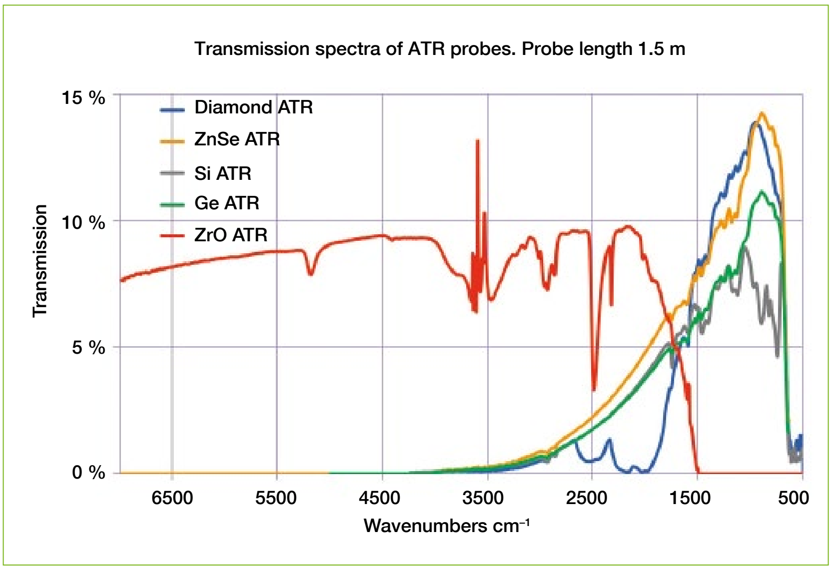

Fig. 5 Transmission spectra of fiber optic probes with different ATR-elements.

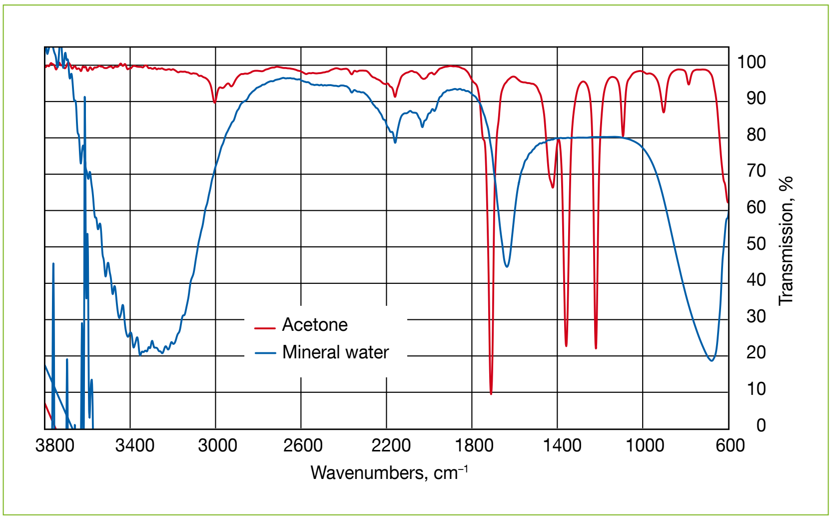

Fig. 6 Transmission spectra of acetone and mineral water.

where mid IR-spectroscopy is the main tool of molecular analysis for all liquid, solid and gas media – as flexible and robust probes enable to monitor chemical reactions in-situ and to provide remote process-control in industrial production in real time for petrochemical, chemical, fermentation, pharma, polymer, food and many other industries. Fiber probes based on IR-fibers can be couple with a single or several spectrometers to enable simultaneous process analysis using various spectroscopic techniques: transmission, evanescent absorption, reflection, fluorescence, scattering and Raman scattering spectroscopy methods.

High power (HP) cables based on MIR-fibers provide flexible delivery of laser radiation in a broad spectral range. They can be used with various IR-lasers – from solid state Ho- & Er:YAG to HF-, DF-, CO- & CO_2-gas lasers. Special design of High Power HP-connectors enables long life of HP-cables made with IR-fibers, while special microstructure anti-reflection treatment (SMART-) at fiber end surface helps to suppress Fresnel reflection – which is quite high (above 30 % for two fiber ends) due to a high refraction index of IR-materials used for IR-fiber production.

Fresnel reflection losses can be eliminated when HWGs are used instead of solid-core IR-fibers – as IR-light propagates through the hole in HWG. Key features of HWG are their ability to transmit long wavelengths above 2 µm and even beyond 20 µm; their inherent advantage of having an air core for high-power laser delivery; and their relatively simple structure and potential low cost [9]. Initially these waveguides were developed for medical and industrial applications, involving the delivery of medical CO_2 laser radiation, but more recently they have been also used to transmit incoherent light for broadband spectroscopic and radiometric applications. In general HWG enjoy the advantages of high laser power thresholds, low insertion loss, no end reflection, ruggedness, and small beam divergence. Drawbacks, however, include an additional loss on bending, small *NA* and relatively short available lengths. Nevertheless, they are today one of the best alternatives for both chemical and temperature sensing as well as for power delivery in IR laser surgery or in industrial laser delivery systems with losses as low as 0.1 dB/m and transmitted CW laser powers as high as 2.7 kW.

Main competitor for HWG in spectroscopy applications are PIR-fibers – as PIR-fiber coupling with IR-light of high divergence is much better and as their transmission is much less sensitive to the probe bending. Fig. 4 shows the comparison of single beam spectra for HWG (from Polymicro [10]) of 2 m length and 1000 µm core diameter versus the same 2 m length of PIR-fiber with 900/1000 µm core/clad diameter under 9 cm bending radius at 180° and 3 × 180°.

Mid-IR ATR fiber probes

Spectroscopy analysis in MIR spectral range (λ = 2 – 18 µm) is the most effective for the remote in-line control of molecular composition in industrial and laboratory processes because characteristic bands of most molecular vibrations (including organic) fall into this range of the spectrum. Therefore IR absorption spectra contain key information about molecular content of liquid, gas or solid substance, which allows to identify its chemical content and, also, to trace the changes in reaction mixture composition in real time. In all practical applications a traditional spectroscopic approach demands a sampling for subsequent measurements. Therefore, the most promising advantages of molecular analysis, namely, real time control of different chemical processes (polymerization, oil distillation, etc.) become unavailable. Also the applied control method must provide a measurement immediately in zone of reaction that takes place usually in wide range of temperature and pressure conditions, in the possible presence of mechanical vibrations, aggressive chemical components, intensive electromagnetic fields, etc. The use of optical fibers allows transmit radiation from the investigated environment to the spectrometer and satisfies all above mentioned conditions. Fiber probes could be connected with FTIR-, TDL-, QCL- or IR-filter spectrometers for molecular analysis of any liquids and gases composition in a wide range of temperatures from 5 K to 500 K and even in a presence of strong electromagnetic fields.

Due to a high absorption of the most of substances in MIR range the attenuated total reflectance (ATR) method is the most suitable to measure their absorption spectra for molecular composition analysis of liquids, polymers or soft surfaces (like tissue in medical diagnostics). Different shapes of ATR elements are known, including: prism, cone, multi-bounce plate and fiber loop. Different materials (AgCl:AgBr solid solution crystals, ZrO_2, ZnSe, Ge, Si and diamond) are used for manufacturing of ATR-elements for different applications and environment. Transmission probes in mid IR range could be used mostly for composition monitoring in gaseous mixtures.

Transmission spectra of ATR probes with ATR-elements, made from different materials and with different fibers are presented in Fig 5. While typical spectra of acetone and mineral water are presented in Fig. 6 when measured with diamond ATR/PIR-fiber probe.

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Authors

Viacheslav Artyushenko received a PhD in physics from the General Physics Institute, Moscow in 1981 with focus on polycrystalline fiber optics for mid IR-range. His results were published in multiple articles and patents on development of IR-optical materials, fiber optics, laser medicine, fiber spectroscopy, optical diagnostic, etc. In 1998 he founded art photonics GmbH in Berlin to produce and develop innovative fiber products for very broad spectral range – from UV to mid-infrared.

Alexey Bocharnikov received his engineer diploma at the Taganrog State University of Radio Engineering in 1999. He joined art photonics in 2004 and took responsibility for quality control of MIR-fiber optic products. Since 2008 he is CTO of the company managing manufacture and quality control of fiber optic products. In 2010 he performed ISO 9001:2008 certification of art photonics. Mr. Bocharnikov was deeply involved in development of mid-IR ATR fiber optic probes for Ex-areas.

Tatiana Sakharova is R&D manager at art photonics GmbH since 2004. She manages development, manufacturing, testing and quality control of optical fibers, fiber optic cables and probes for mid-IR spectral range. In 1994, Dr. Sakharova received a PhD in technology and started her work at the Moscow State Academy of Fine Chemical Technology as Science Fellow. In 2004, she spun-off her scientific lab at MSAFCT to the General Physics Institute of Russian Academy of Science.

Iskander Usenov is R&D specialist at art photonics GmbH. He is engaged in the development, improvement and quality control of products for mid-IR spectral range. In 2013, he graduated from Moscow State University with a diploma in physics, and started his work at art photonics GmbH as R&D specialist. In 2014 Usenov has enrolled in the Technical University of Berlin as a PhD-student in physics.

Dr. Viacheslav Artyushenko, art photonics GmbH, 12489 Berlin, Germany, Tel. +49 30 677-988-777, Fax: +49 30 677-988-799, E-mail: sa@artphotonics.com