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Abstract. Chalcogenide glasses are a matchless material as far as mid-infrared (IR) applications are concerned. They transmit light typically from 2 to 12 μm and even as far as 20 μm depending on their composition, and numerous glass compositions can be designed for optical fibers. One of the most promising applications of these fibers consists in implementing fiber evanescent wave spectroscopy, which enables detection of the mid-IR signature of most biomolecules. The principles of fiber evanescent wave spectroscopy are recalled together with the benefit of using selenide glass to carry out this spectroscopy. Then, two large-scale studies in recent years in medicine and food safety are exposed. To conclude, the future strategy is presented. It focuses on the development of rare earth-doped fibers used as mid-IR sources on one hand and tellurium-based glasses to shift the limit of detection toward longer wavelength on the other hand. [DOI: 10.1117/1.OE.53.2.027101]

Keywords: chalcogenide glasses; infrared fibers; evanescent wave spectroscopy; early diagnosis; food safety.

Paper 131641 received Oct. 30, 2013; revised manuscript received Jan. 8, 2014; accepted for publication Jan. 9, 2014; published online Feb. 6, 2014.

1 Introduction

The glass-forming ability of systems rich in chalcogen elements has been known for several decades but compared with oxide glasses, especially silicates, this class of vitreous materials is just emerging from its infancy. Emerging technologies related to thermal imaging, as well as infrared (IR) sensors, have nucleated new projects involving IR transmitting materials including chalcogenide glasses.

The main attention paid to these materials relies on their large optical window extending in the mid-IR and covering usually the two atmospheric windows ranging from 3 to 5 and 8 to 12 μm.[1–4] This situation leads to fundamental vibrational modes shifted far in the IR, and rendering these glasses interesting for the fabrication of thermal-imaging systems. This exceptional transparency, associated to suitable viscosity/temperature dependence, creates a good opportunity for the development of optical fibers. The most exciting application for this fiber consists in implementing fiber evanescent wave spectroscopy (FEWS).[5,6] Indeed, the optical sensors operating in the mid-IR region, where the main IR signatures of molecules and biomolecules are located, play an important role in the development of analytical techniques giving *in situ* information on metabolic patterns.[7–12]

Chemical detection using chalcogenide glass fibers was initially reported in the late 1980s with the characterization of butanone.[13] Chemical analyses were then performed on acetone, ethanol, and sulfuric acid using Ge-Te-Se fibers.[14,15] A wider range of organic species, including carcinogens such as benzene, toluene, and trichloroethylene, were later detected.[16–19] In parallel, AgCl/AgBr polycrystalline fibers have also been developed as sensors.[20–23] They possess the required optical quality and transmit light up to 20 μm in the IR spectral domain. However, polycrystalline fibers are very sensitive to air contamination, losing their properties of transparency. Moreover, they are obtained by extrusion methods, which are costly and difficult to implement. Last, their sensitivity is lowered due to their large diameter of about 1 mm.

During the past decade, new chalcogenide glasses transparent from the visible to the far IR domains have been developed in order to fabricate some optical fibers for IR sensing. Thus, numerous works have been carried out in different domains of application such as detection of pollutants in waste water,[24,25] monitoring of chemical processes,[26,27] detection of bacterial contamination in food,[28] monitoring of bacterial biofilm spreading,[29,30] and metabolic imaging of tumorous tissues[31,32] and human biological fluids such as serum, plasma,[33] or human cells.[34–39] The aim of the present article is to give an overview of the works that have been carried out, demonstrating the potential of chalcogenide glass fibers for implementing mid-IR FEWS experiments.

2 Mid-IR FEWS

The advantage of the FEWS is to perform remote, real-time analyses *in situ*. The principle of this IR spectroscopy is based on the fact that the light propagating in the optical fiber provides an evanescent wave at the interface between the fiber and the surrounding area. If a chemical or biological

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species is in direct physical contact with the fiber and has absorption bands in the IR spectral region, then the evanescent waves will be partially absorbed at each reflection, leading to a reduction of the fiber transmission which can then be measured.

The FEWS method is quite simple to implement, since the measurement necessitates only a standard spectrometer equipped with special kits to focus the light and an MCT detector cooled by liquid nitrogen. The beam, produced by a blackbody source, is focused at the input of the fiber by two off-axis parabolic mirrors coated with gold. At the output of the fiber, the signal is again focused by two parabolic mirrors on the sensitive part of the MCT detector. The absorbance spectrum A is obtained by using Eq. (1):

$$A = \log\left(\frac{I_{\mathrm{ref}}}{I_s}\right), \tag{1}$$

where I_{ref} corresponds to the intensity when the fiber is in the air, and I_s when the fiber is in contact with the sample to analyze. The critical point is to fabricate the optical fibers transmitting light in the mid-IR, which contains the signature of most chemical and biological molecules through the fundamental vibration modes of their functional groups.

A large range of glass formulations are available to obtain suitable optical fibers with large IR transparency ranges and low energy losses. Among chalcogens, selenium is a good glass former, providing very stable glasses quite easy to shape. In particular, the $Te_2As_3Se_5$ glass composition (TAS glass) is an interesting compromise with a $T_g = 137°C$, which enables implementing experiments at room temperature. This glass offers a large spectral window, typically ranging from 2 to 16 μm for a bulk with a thickness of 1 mm. Moreover, this glass composition exhibits an excellent resistance to devitrification, thus permitting to shape it into an optical fiber. The attenuation curve of the fiber is given in Fig. 1. The minimum of attenuation is less than 1 dBm^{-1} and is located between 6.5 and 9 μm. Obviously, this value is far from the one obtained with silica glass fiber, but the light transmission is sufficient for short distance applications such as remote spectroscopy. Overall, the fiber spectral window encompasses the mid-infrared domain, since transparency is observed from 800 to 4000 cm^{-1} on FEWS spectra.

On the other hand, the optical index of a TAS glass is high ($n_1 = 2.8$). Thus, the optical conditions for total internal reflection are fulfilled for all optical rays entering the TAS glass fiber. The number of bound modes M for a circular fiber, depending on the wavelength λ, is estimated by the following equation:

$$M(\lambda) = \frac{2\pi^2 r^2 (n_1^2 - n_2^2)}{\lambda^2}, \tag{2}$$

where r is the fiber radius, n_1 is the index of the fiber core, and n_2 is the index of the cladding. With a diameter of 400 μm, a fiber index of 2.8 and the index of the air of 1, and the number of modes can be estimated approximately between 37,500 at 12 μm (833 cm^{-1}) and 135,000 at 2 μm (5000 cm^{-1}). Thus, the light propagation in a multimode TAS glass fiber is complex. To cope with this complexity, a background spectrum (called I_{ref} above) is collected before each experiment. So, many effects can be neglected: the entrance and exit conditions of the IR beam, the interaction and attenuation along the optical signal transportation section, the transition of the modes during the taper to the sensing zone, the absorption due to the fiber, and any effect related to fiber bending or surface roughness.

The number of reflections over a length L of a fiber with a diameter d depends on Eq. (3):

$$N(\theta, d, L) = L \cdot \frac{\tan(90 - \theta)}{d}, \tag{3}$$

with θ being the angle of incidence from normal. In the present situation, it is known that the propagation within waveguides can be efficiently described by classical geometric optics. With these considerations, a model of the fiber optic probe's response was presented to help in predictions and to simulate data.[41] It was shown that to improve the sensitivity of the sensor, the diameter of the fiber should be locally reduced to create a tapered sensing zone, which will be brought into contact with the sample to be analyzed. This could also be easily understood by considering that the number of reflections into the fiber is much higher when the fiber diameter decreases, as depicted in Fig. 2. For the following application, the diameter of the fiber has been locally reduced from 400 μm to about 100 μm in the sensing zone, where the targeted samples are brought into contact with the fiber. This design is absolutely essential to benefit of an enhanced signal-to-noise ratio.

Note that the evanescent wave intensity decays exponentially with distance from the surface of the fiber. So, the sensitive area is mostly localized within 1 μm from the fiber surface. Also, the penetration depth is a function of the glass index as well as of the wavelength of the propagating light, according to Eq. (4):[5,6]

$$dp = \frac{\lambda}{2\pi\sqrt{n_2^2 \sin^2\theta_i - n_1^2}}, \tag{4}$$

where λ is the wavelength, n_2 and n_1 are the refractive indices of the glass and surrounding area, respectively, and θ_i is the angle of incidence of the wave in the fiber. The penetration of the evanescent wave increases linearly with the wavelength. So, the spectra collected in evanescent mode show typically lower intensities at shorter wavelengths in comparison with those of transmission spectra. This is clearly visible in spectra collected in attenuated total reflection (ATR) mode using a flat ATR plate, where θ_i is strictly equal to 45 deg. For FEWS, one has also to consider the complex geometry of the optical fiber, in which the distribution of angle of incidence into the fiber makes the dp influences more difficult to analyze and anticipate.

In order to illustrate the efficiency of the methods, various applications have been selected in the frame of two health strategic fields of application.

3 Application in Early Diagnostics

The biomedical domain is always searching for new diagnostic methods using noninvasive approaches and, when possible, in real time. The diagnosis of a disease requires aggregation of positive clinical, biological, and imaging criteria, and other negative criteria excluding other diagnosis. This is the reason new methods that enable physicians to

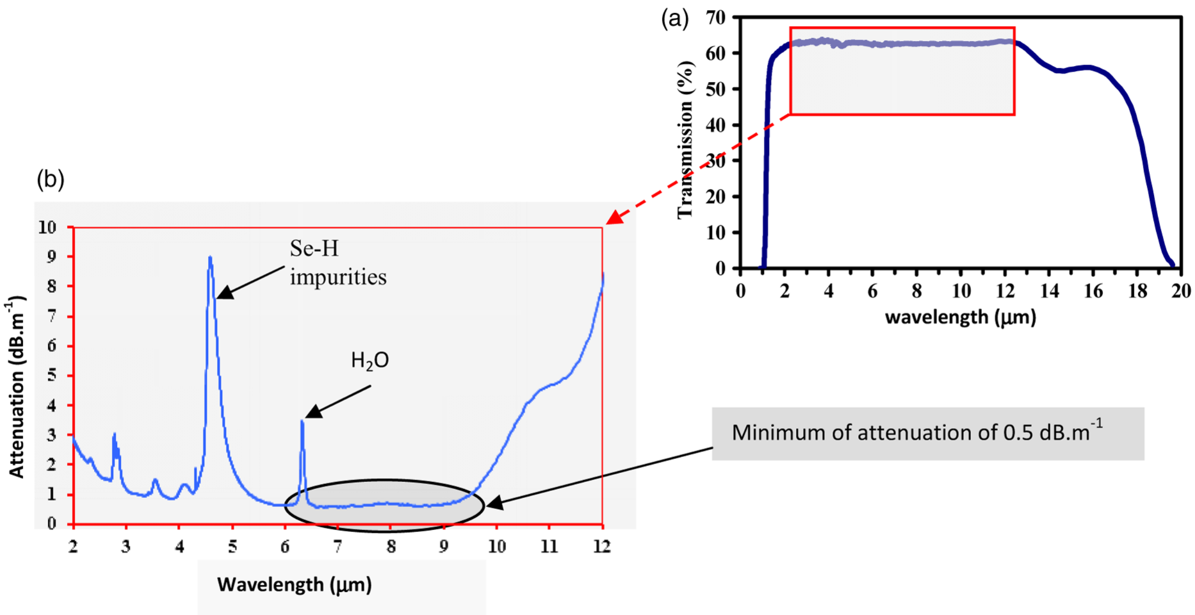

Fig. 1 (a) Transmission window for a bulk of $Te_2As_3Se_5$ glass (thickness 1 mm) together with the attenuation curve of the TAS glass fiber (b).[40]

obtain fingerprints of the disease are under development. This will yield gain of time for patient and physician and also in terms of health cost. IR spectroscopy is a well-adapted technique, permitting the characterization of complex substances like proteins, nucleic acids, and lipids which are the main constituents of the biological systems. Moreover, FEWS carried out with chalcogenide glass fibers increases the signal-to-noise ratio and the sensitivity of the method compared with classical transmission or ATR mode acquisition. This is due to the ability of shaping the fiber with very small diameter (as explained above) and also to the hydrophobicity of chalcogenide glasses which are built with chemical elements strongly covalently bonded to each other.[37]

The benefit of using chalcogenide glass to the signal-to-noise ratio is illustrated by Fig. 3, which compares a FEWS spectrum to a conventional transmission spectrum of mouse liver. The unique difference observed deals with the bands' intensities, which arise from the penetration depth of the evanescent wave in the low-refractive index medium. From this comparison, it appears that the sensitivity and the resolution with the FEWS mode are very good and no spectral distortion or parasitic signal is visible.

Among numerous FEWS medical studies carried out with chalcogenide glasses, including liver tumors[32] or living human lung cells,[34,38,39] the most promising concerns probably work dealing with biological fluids like urine, blood, or sera. For example, FEWS using glass fibers could analyze metabolic abnormalities by placing only 10 μL of serum in contact with the fiber. Most of the time, some unsupervised statistical analyses like partial least squares regression (PLS-R) or principle component analysis (PCA) have to be implemented to discriminate between ill and healthy patients and to fully validate the efficiency of these spectroscopic tools.

Following this strategy, Keirsse et al.[29] reported the first study on sera from mice developing obesity related to a homozygous mutation in the leptin gene, leading to hyperphagia and type II diabetes. The FEWS and PCA carried out

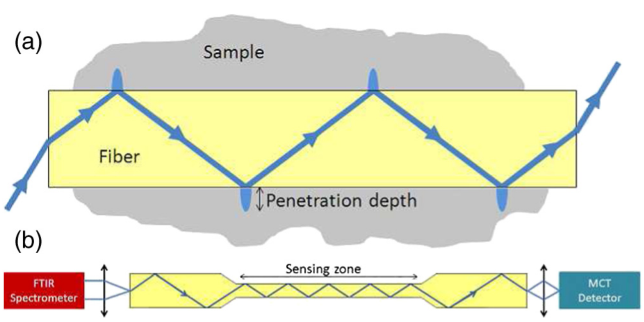

Fig. 2 (a) Mechanism of fiber evanescent wave spectroscopy (FEWS). (b) General setup of FEWS and the scheme of a tapered fiber.[4]

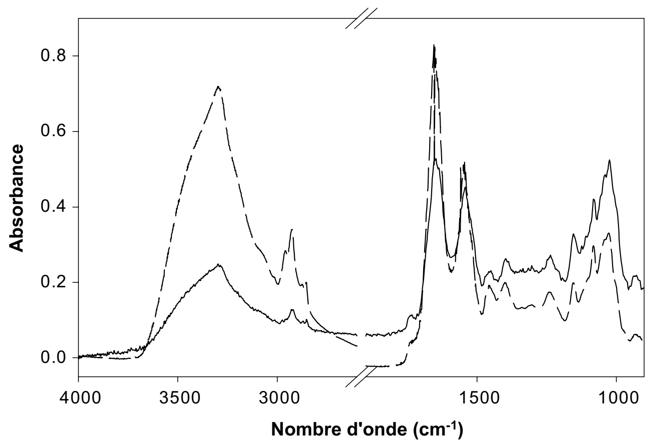

Fig. 3 Comparison between the mouse liver spectra recorded in transmission mode (solid line) and with the optical fiber (dashed line).[42]

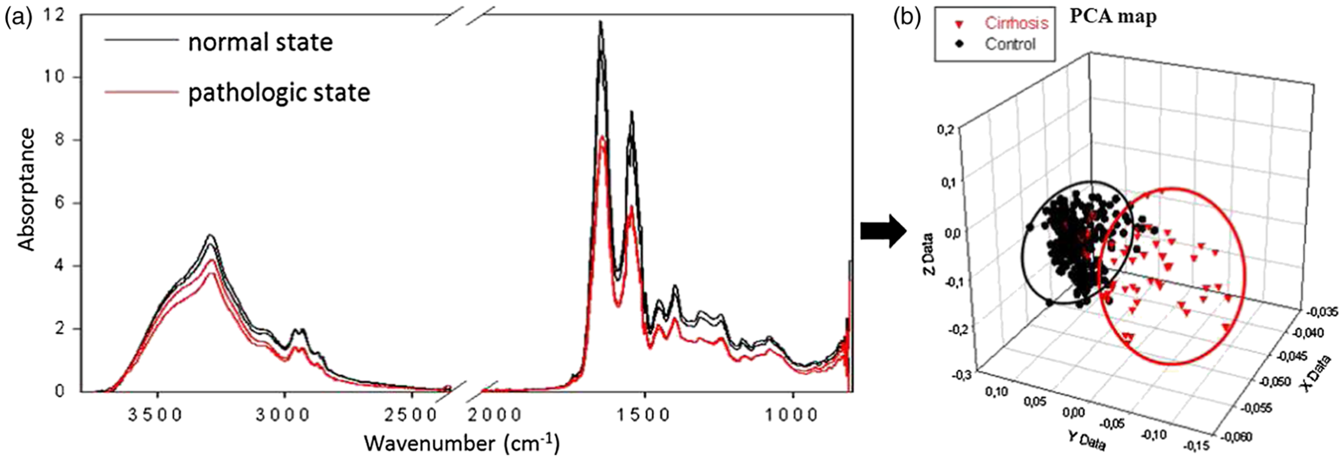

Fig. 4 (a) FEWS spectrum of human serum with and without cirrhosis. (b) The corresponding principal component analysis (PCA) map.[4,33]

in 1100 to 1000 cm^{-1} range, which corresponds to the sugar ring vibration bands, have permitted discrimination of pathological sera from control.

Then, a study was conducted to evaluate whether mid-IR FEWS was able to discriminate metabolic diseases in patients. The serum of one control group and three groups of patients exhibiting chronic liver diseases [genetic hemochromatosis, alcoholic cirrhosis, and dysmetabolic hepatosiderosis (DYSH)] was studied. These metabolic disturbances potentially impact serum quality, thus giving rise to mid-IR signature in the related patient's serum. PLS-R, applied to the recorded spectra, has allowed discrimination of patients with cirrhosis and DYSH from a control patient group. These results strongly suggest that the concept of metabolic profiling using mid-IR FEWS could be a way to investigate diseases having metabolic consequences in patients. Figure 4 better illustrates the discriminant ability of the protocol. Figure 4(a) shows the FEWS spectra collected from human sera with and without cirrhosis. Classical analysis methods are not able to differentiate between the two groups of spectra. On the other hand, Fig. 4(b) shows the PCA map which enables one to fairly distinguish between the metabolic states, i.e., control or cirrhotic.

Thus, chalcogenide glass FEWS possesses aptitudes for early characterization of metabolic anomalies in different pathologic environments. Hopefully, in the future, thanks to the inertia of chalcogenide glass fibers toward biological substances,[29] the fibers may be implemented directly on patients by guiding the probe light onto the area of interest, *in situ* and *in vivo*, rather than performing biopsies.[32,33,43,44]

4 Application in Food Safety

For more than two decades, "food scandals" have been brought up in the international press and arouse a legitimate and durable fear in populations. Assessing food microbiological safety, traceability, health allegations, or adulteration is becoming a major challenge and must be considered as a public health matter. A preliminary work had been carried out in 2006 on the spreading of bacterial biofilm in a Petri plate, namely *Proteus mirabilis*.[30] It had been shown that mid-IR FEWS without any statistical study, permitted one to distinguish between the swarming and the vegetative phenotypes of the contaminant biofilm. More recently, a complete work showed that the protocol exposed in Sec. 3, including PCA, enabled the identification of some contaminants in food matrices: milk, minced meat, and

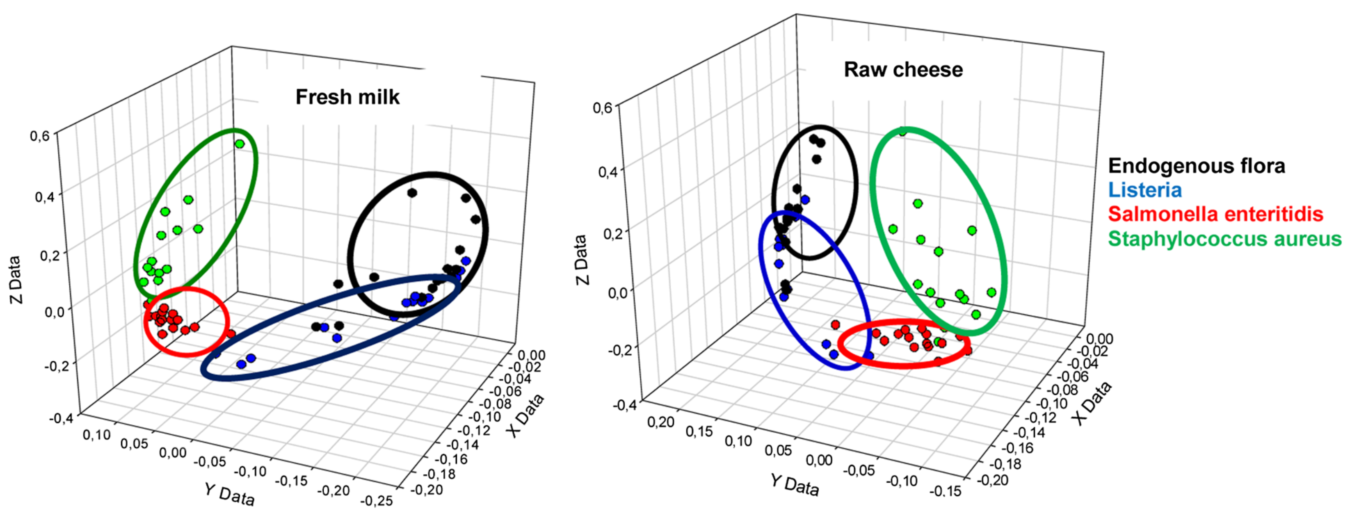

Fig. 5 Mid-infrared (IR) FEWS PCA map for milk and cheese contaminated by various pathogens.[28]

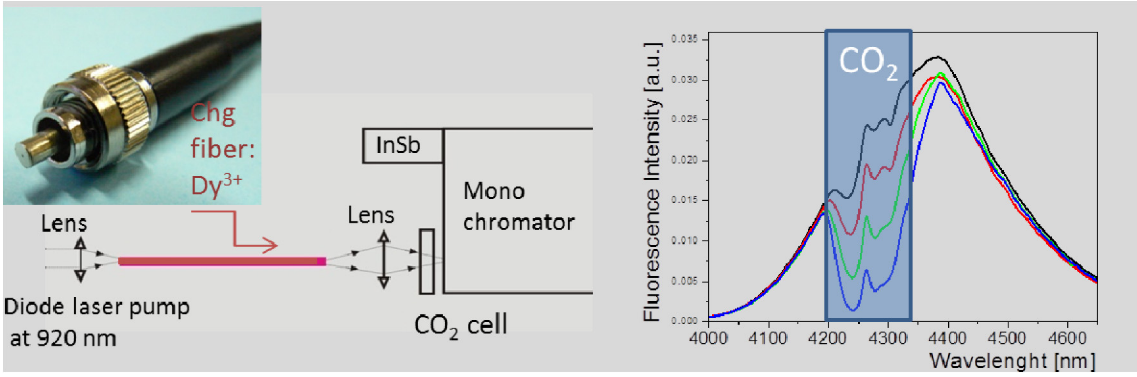

Fig. 6 Fluorescence spectra of Dy^{3+}-doped chalcogenide glass showing the CO_2 absorption bands around 4.3 μm pumped by commercial diode laser at 920 nm.

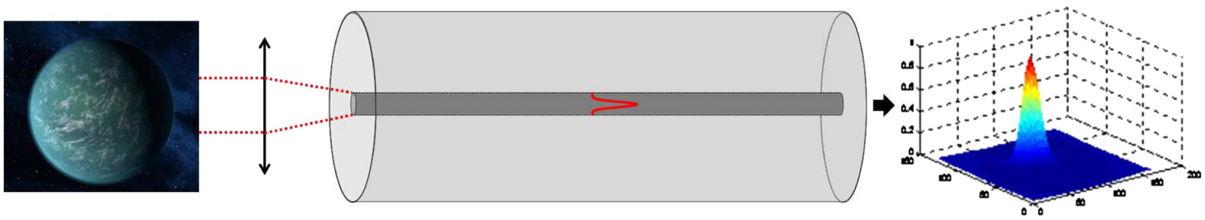

Fig. 7 Optical scheme of the detection of the mid-IR signal coming from an exo-planet through space. The beam profile on the right corresponds to a single-mode TAS glass at 10 μm.

cheese.[28] For each, two experimental conditions were tested. First, enrichment by endogenous flora, which are naturally present in the samples and, second, enrichment by three pathogenic germs: *Listeria*, *Staphylococcus,* and *Salmonella*. Although these pathogens have the same biochemical constituents, namely proteins, polysaccharides, phospholipids, and nucleic acids, the biochemical diversity within these biochemical classes from one strain to another are sufficient to provide distinct FT-IR spectra for each pathogen. The most useful FT-IR features for bacterial identification appear at wavenumbers around 1000 to 3000 cm^{-1} and correspond to the deformation, bending, stretching, and ring vibrations of various functional groups. Also, the statistical analyses were performed on the regions 1000 to 1800 cm^{-1} and 2800 to 3000 cm^{-1}, providing the greatest contribution to the total variance in the FT-IR spectral data. As examples, Fig. 5 depicts the PCA map for contaminated milk and cheese by bacterial germs.

Concerning the differentiation between the pathogens, the best results were obtained for milk and cheese, likely due to a better physical contact between the fiber and the samples, than when studying meat.

So, from the PCA maps, some trends can be pulled out. In addition, logistic-PLS go farther with the discrimination of the pathogens strains with a classification error lower than 3.5%. These results permit optimism in the potential of FEWS for early detection of pathogens in food matrices, which could be extended to various applications in the health field.

5 Conclusion and Perspectives

In the future, there are plans to develop alternative IR optical fibers to be tested for medical diagnosis and food safety. Two routes will be explored: first, tellurium glasses and second, rare earth (RE)-doped chalcogenide glasses. These perspectives are clearly upstream and will need strong progress in material sciences before developing any prototype. Nevertheless, the work has already been initiated in the two following frameworks.

5.1 *RE-Doped Chalcogenide Fibers*

Thus, recently, some innovative optical fibers have been developed for CO_2 detection.[45–47] The ability to detect and quantify CO_2 has become increasingly critical for the monitoring of global warming. Since the emission of this greenhouse gas increases every year, some solutions must be found to reduce or control these CO_2 emissions. One of them is the capture and the storage of CO_2 in natural underground geological formations, but this requires specific monitoring of the storage wells. In that frame, some RE-doped chalcogenide glass fibers have been developed to perform a mid-IR source, pumped by a commercial laser diode and used as a remote mid-IR optical sensor. Indeed, the RE trivalent ions incorporated in chalcogenides host matrix with low-phonon energy can generate light from visible to mid-IR.[48–50] Dy^{3+} ions were selected because, after being optically pumped at 920 nm, the glassy fiber exhibits a mid-IR broad emission corresponding to the transition between ${}^6H_{11/2}$ and ${}^6H_{13/2}$ levels, encompassing the CO_2 absorption bands centered at 4.3 μm (Fig. 6). A mid-IR sensor prototype has been, hence, designed, which enables detecting CO_2 in a wide concentration range from 100% to lower than 500 ppm.[47] It will be very interesting to test the efficiency of this spectroscopic "active" tool for medical applications by selecting the appropriate RE to the targeted metabolic deregulation. The main benefit of this technology, as compared with "passive" selenide fibers, lies in the compactness of the final devices and the brightness of the mid-IR fluorescent sources.

5.2 Germanium Telluride Fibers

Alternatively, much effort has been paid in the development of IR glasses transparent far in the IR in order to detect signs of life on earth-like planets. The presence of life is materialized by the presence of water, ozone, and CO_2 in the planet atmosphere. The three molecules absorb in the IR region around 6, 9, and 15 μm, respectively, and one needs to develop fiber transmitting light from 6 to 20 μm to detect them following the scheme displayed in Fig. 7.[51] The most efficient strategy to expand the spectral window of chalcogen glasses is to use the heavy atoms such as tellurium in order to lower the phonon energy and to shift the multiphonon cut-off to longer wavelengths. Thanks to European Space Agency supports in the frame of the DARWIN program, new chalcogen glasses, exclusively based on tellurium, have been developed for the making of these single-mode fibers.[52–57]

Among telluride glasses, the Te-Ge-X, with X = As, Ga, Se, or I, systems have shown good glass-forming stability, and optical fibers have recently been successfully produced which transmit light up to 15 μm compared with a 11-μm limit for selenide glass fibers. In the future, this spectral widening could be crucial to detect relevant mid-IR signatures that are not reachable with the TAS glass in biology and medicine.

Acknowledgments

The authors thank the French ANR (Emergence, TECSAN, and OPTIC CO_2), the ADEME, the European Space Agency, National Science Foundation under Grant Number ECCS-1201865, the CNRS International Associated Laboratory for Materials & Optics, and the Partner University Fund for financial grants and supports.

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