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Glasses for Seeing Beyond Visible

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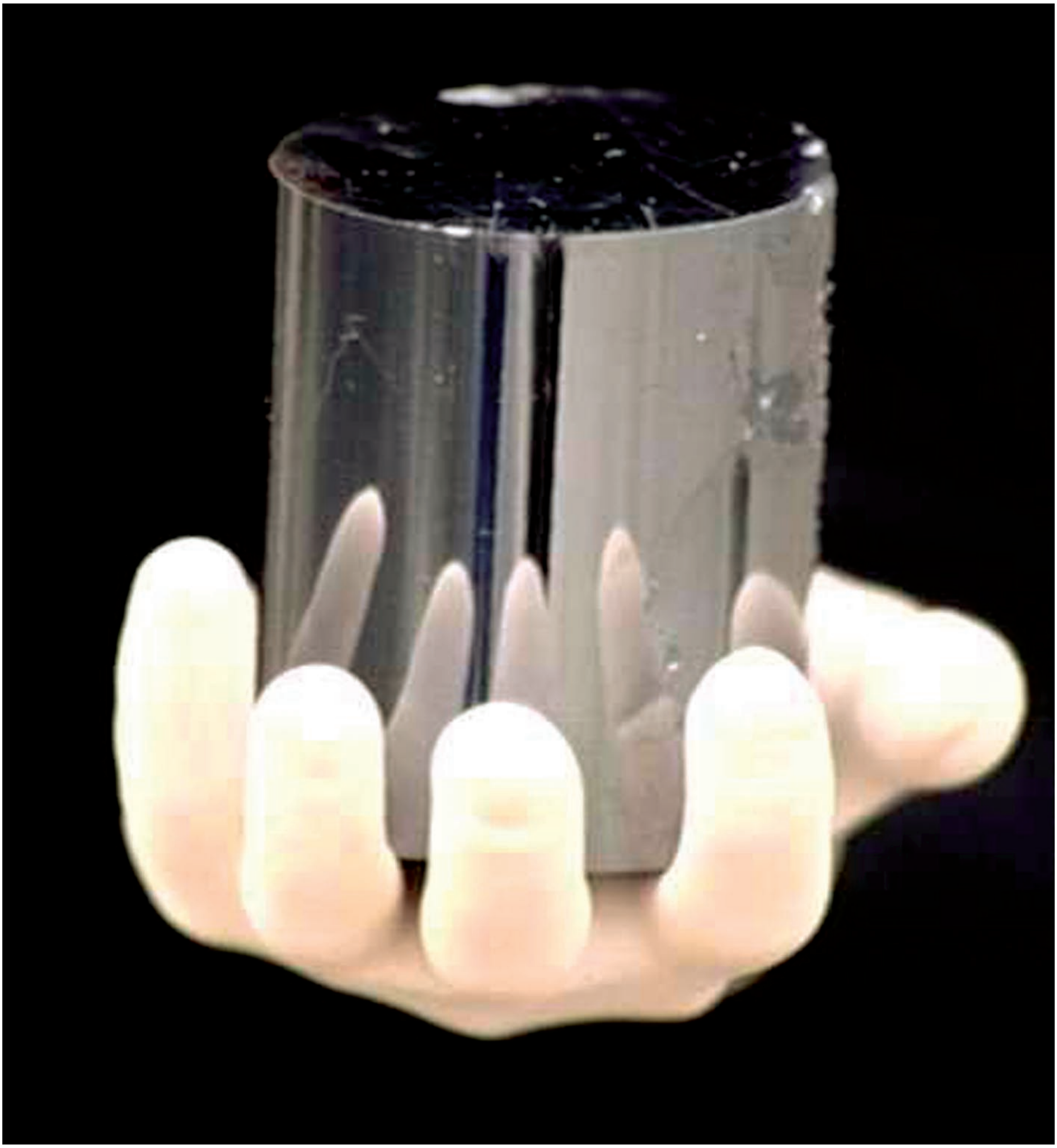

Abstract: Conventional glasses based on oxides have a transparency limited by phonon absorption in the near IR region and have a limited interest for analyzing information located far beyond the visible. The IR spectral domain is nevertheless of prime interest, since it covers fundamental wavelength ranges used for thermal imaging as well as molecular vibrational signatures. Besides spectacular advances in the field of IR detectors, the main significant progresses are related to the development of IR glass optics, such as lenses or IR optical fibres. The field of IR glasses is almost totally dominated by glasses formed from heavy atoms such as the chalcogens S, Se and Te. Their transparency extends up to 12, 16 and 28 μm for sulfide-, selenide- and the new generation of telluride-based glasses, respectively. They cover the atmospheric transparency domains, 3–5 and 8–13 μm, respectively, at which the IR radiation can propagate allowing thermal imaging and night-vision operations through thick layers of atmosphere. The development of new glass compositions will be discussed on the basis of structural consideration with the objective of moulding low-cost lenses for IR cameras used, for instance, in car-driving assistance. Additionally, multimode, single-index, optical fibres operating in the 3 to 12 μm window developed for in situ remote evanescent-wave IR spectroscopy will also be mentioned. The detection of molecular IR signatures is applied to environmental monitoring for investigating the pollution of underground water with toxic molecules. The extension of this technique to the investigation of biomolecules in three different studies devoted to liver tissues analysis, bio-film formation, and cell metabolism will also be discussed. Finally we will mention the developments in the field of single-mode fibres operating around 10 μm for the Darwin space mission, which is aiming at discovering, signs of biological life in telluric earth-like exoplanets throughout the universe.

Keywords: biosensors · glass · IR light · IR spectroscopy

Conventional Oxide Glasses and their Limitations

The concept of glass is usually associated with a transparent material that transmits light in the visible range, typically from blue at wavelengths around 400 nm to the red near 700 nm. This very narrow spectral region corresponds indeed to the sensitivity domain of the retina and constitutes a key factor in our perception of the world. Vitreous materials play an important role in our daily life, since windows or glass containers establish a mechanical barrier between two media, while allowing propagation of light. Savouring fine wine in a Baccarat transparent glass gives us a different feeling than using an opaque ceramic or plastic container. The conventional glasses are dominated by the exceptional glass-forming ability of silica SiO_2, which can be combined with others glass formers such as P_2O_5 and B_2O_3 or glass modifiers such as CaO and Na_2O. The role of the glass formers is to introduce into the polymeric covalent framework building units other than the SiO_4 tetraheda such as PO_4, BO_3, and BO_4 units, which influence many parameters such as the viscosity temperature dependence, resistance to crystallization and so forth. The function of the modifiers is to bring additional oxygen atoms, which results in lowering the unit's connectivity by formation of non-bridging atoms interacting with the modifiers cations by coulombic forces. These oxide-based glasses are ideal for achieving this transparent barrier function, since they transmit light from the near UV to the mid-IR region around 3 μm. The limitation of the transparency in the UV region is due to energy absorption by electrons involved in chemical bonds, while the optical loss in the mid-IR region is attributed to phonon energy absorption coming from the vibrational modes of the glassy network, which can be regarded as a giant inorganic polymer.

The spectral window that extends from the red to the mid-IR region is of limited interest in our everyday life, since our eyes are not sensitive to this range of wavelengths. Nevertheless a remarkable technological development has brought attention to this spectral region with the advent of optical communication.[1,2] Indeed it is now well established that the best way to carry information with high speed and density is to transport binary signals (bits) as an optical signal travelling into the core of a silica optical fibre. Light-propagation studies show that the ultra-low loss optical window of SiO_2 is located near 1.55 μm, far from the UV and the phonon region in the IR region. To reach the ultimate level of transparency, high purity silica is necessary and this objective can be reached by converting high purity $SiCl_4$ vapour into SiO_2 by reaction with oxygen. Ultra-transparent optical fibres are now routinely prepared, reaching the minimum theoretical loss of $0.2\,dB\,km^{-1}$ provided that the transmitted light has a wavelength close to 1.5 μm. In this condition the information propagates at a speed of about $200\,000\,km\,s^{-1}$ and the signal is regenerated and amplified about every 80 km. Our planet is now networked with silica fibres (Figure 1) through which IR light carries

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Figure 1. Part of the undersea telecommunications cable network containing silica-glass optical fibres in which near IR light propagates and carries information.

voices, images and data over very long distances and across oceans. Chemistry has played and continues to play a key role in these fascinating developments.

Overall, the glass industry is dominated by conventional silicate-based glasses that have found markets in many diversified domains such as building, television, car industry, telecommunications, cookware, optics, containers and so forth. However, despite their extremely high level of technological development, these materials suffer from an intrinsic limitations associated with their chemical composition. Silicate, phosphate and borate glasses are all oxide-based materials, made from light elements in the Periodic Table that also exhibit strong chemical bonds. As a consequence the vibrations modes are high in energy, leading to an IR absorption cut-off located in the 3 µm region, which consequently makes these glasses totally opaque beyond this IR edge (Figure 2).

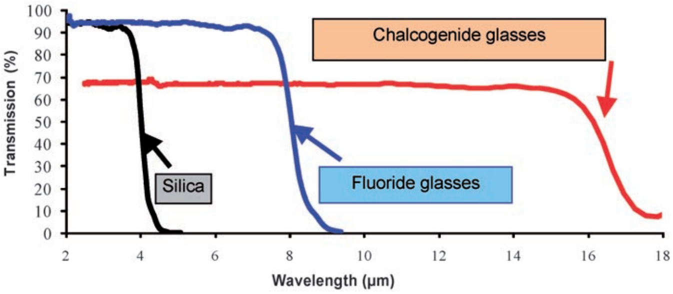

Figure 2. Position of the average IR cut-off for several families of glasses including the oxides represented by silica, fluoride and chalcogenide glasses.

Why Seeing Beyond Visible?

It is not entirely true to claim that the spectral perception of the world for a human being stops beyond red wavelengths. Indeed our skin possesses sensors that are sensitive to invisible light, namely IR radiation, but it is usual to describe this phenomenon by using the concept of heat transfer rather than light, since IR radiation is invisible to the human eye. These sensors are composed of biomolecules that form the epidermis, which exhibit fundamental IR absorption bands lying typically from around 3 µm to 12 µm in the mid-IR region. In fact, all organic molecular species exhibit IR absorption bands due to common chemical bonds, such as O–H, C–H, C–O, C–C, N–H, S–H, that are located in this spectral window. (Figure 3). As a consequence, organic molecules are characterized by a unique IR signature that is at the origin of the powerful analytical method known as IR spectroscopy. The development of instrumentations allowing remote, fast and in situ IR analysis is of prime interest for following chemical reaction in the lab or in industrial processes.

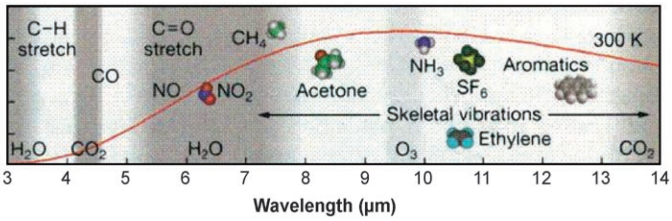

Figure 3. This figure portrays the position of the IR signatures for several chemical species .The figure was supplied by Fibre Photonics Ltd, which develops mid-IR-fibre process-spectroscopy systems.

Another interest of detecting IR light resides in imaging thermal objects around room temperature. Figure 4 represents the black-body emission of solids as a function of temperature and emphasizes two specific cases: the sun emission characterized by a surface temperature of 6000 K and the emission of a human body typically at a temperature of 310 K. For the sun, the maximum of emission is in the visible region, centred on the yellow colour for which our

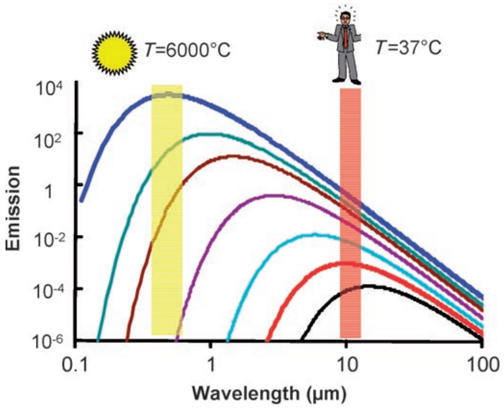

Figure 4. Light emission of several thermal objects at different temperature. The surface of the sun at 6000 °C emits primarily in the visible (blue curve), while a human body at 37 °C has a radiation emission mainly located in the IR near 10 µm (red curve) Just in between are represented the black body emission of thermal objects being, from hot to cold at 2700, 1700, 700 and 250 °C. On the right side the emission curve corresponds to an object at −80 °C.

retina presents the maximum of sensibility. For a thermal object such as a human body, the radiation emission is centred around 10 µm, and it can be noticed that the emitted energy is in the range of 60 W, roughly 1 W kg^{-1}.

Likewise the average temperature of the earth is around 290 K and corresponds to a very similar emissive curve. Special attention is currently being paid to the green house effect, which is partially responsible for global warming. Several molecular species such as H_2O, CH_4, CO_2, O_3, and so forth, which are present in the atmosphere, exhibits strong absorption bands in the mid-IR region and are considered the main causes of global warming, because they prevent IR light emitted by the earth to escape into space. Figure 5 describes the various absorption regions of the atmosphere which are responsible for trapping IR light.

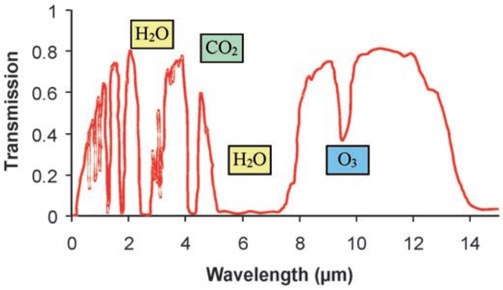

Figure 5. Atmospheric transparency windows in which the IR radiation can propagate: 3–5 and 8–12 µm are the main windows. In the rest of spectral range the atmosphere is opaque due to strong H_2O and CO_2 absorption. Notice that O_3 is only present in the upper part of the atmosphere.

The atmosphere also has several transparency windows that are of technological interest for communication imaging and guiding applications. Except for the visible region, which is most familiar to us, the transparency windows are in the near IR region around 1.6, 2.3 µm distant from O−H absorption as well as in the mid-IR region, typically 3–5 µm and 8–12 µm between the H_2O and CO_2 absorption bands. The ozone molecule O_3 also exhibits absorption in the 10 µm region.

Overall, the growing interest for IR technologies has largely been initiated by defence research programs aiming at developing night-vision systems and recognition devices based on thermal imaging or non-contact temperature measurements. In parallel, the identification of molecules through their IR signatures has also motivated a growing interest for developing IR sensors systems, especially those involved in industrial processes or reaction mechanisms in biology, pharmacy and the food industry. To reach this goal, immense progress has been achieved in the domain of thermal detection and several IR “retina-like” detectors are currently on the market. These systems will not be discussed here, but instead this paper will focus on the IR optics and more precisely on the new generation of glassy materials that transmit light far into the IR region.

The Right Chemistry for Producing IR-Transmitting Glasses

To be of interest for both imaging and sensing, an IR glass must be transparent from the near IR up to the 14 µm region, so as to cover the atmospheric transparency window and the domain of chemical-bond vibrations. In the special case of sensing devices for space exploration the requirements extend up to 20 µm and even beyond.

These specifications can be fulfilled only with low-phonon glasses that exhibit low-energy vibrational modes, in other words glasses made from heavy atoms. Very often, low-phonon characteristics mean weak chemical bonds and consequently poor resistance to chemical attacks from moisture as well as poor thermal properties. This situation is not acceptable for practical applications and excludes heavy halide glasses based on chlorine, bromine or iodine, which suffer from poor resistance to moisture corrosion. The only vitreous materials that survive these requirements are glasses based on sulphur, selenium or tellurium.[3–5]

It must be remembered that a glass has to be regarded as a frozen liquid, or a liquid that has reached an infinite viscosity upon cooling. As a consequence these materials exhibit two major advantages, first they can be produced over a wide range of compositions that can be adjusted to fit a specific property and second they can be reheated above the glass transition temperature T_g, and display a continuous plasticity that allows for easy shaping. The drawback is that, because it is out of thermodynamic equilibrium in comparison to the corresponding crystal, a vitreous material is often prone to crystallization.

The challenge for the chemist is to form an inorganic atomic network with a one-, tow- or three-dimensional space connectivity (or somewhere in between) in which the chemical bonds must have a high degree of freedom; in other words bending and rotations must be permitted without strongly affecting the total bond energy. Upon cooling, these systems can freeze into solids that exhibit a lack of periodicity, but still keep a high bonding energy. In the case of amorphous chalcogenides, glass formation can be described based on three ideal topological situations illustrated in Figure 6.

The elements Se and S, which form infinite covalent chains, are prototypes of one-dimensional glasses.[6] Unfortunately the tendency to form covalent bond is much weaker in Te and the competition to form metallic bond is such that the formation of glass is refrained to the benefit of Te nanocrystal nucleation. Similarly, As_2S_3 and As_2Se_3 represent the two ideal two-dimensional frameworks in which tricoordinate As atoms are linked through bridging S or Se atoms and form flexible sheet-like structures that exhibit excellent glass-forming ability. Networks with higher three-dimensional connectivity can also be produced by linking tetra-coordinate atoms such as Ge. However, in order to conserve structural flexibility each Ge atom is linked by a Se−Se (or S−S) bridge and the structure can be described as interconnected GeS_4 or $GeSe_4$ tetrahedra. These compounds are indeed ex-

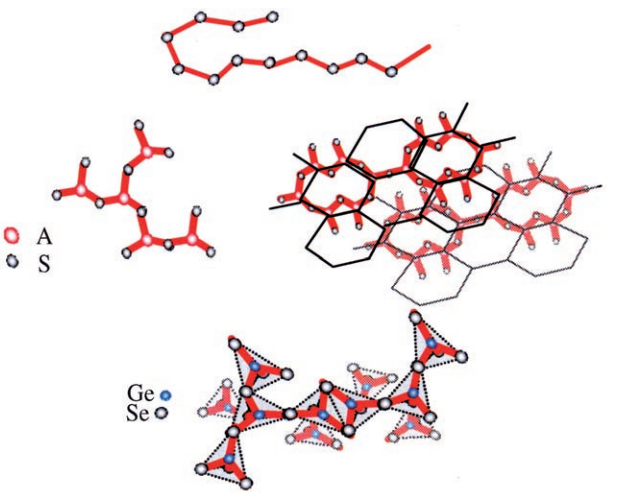

Figure 6. Topological description of the polymerisation processes in amorphous chalcogenide. In vitreous Se, one-dimensional chains are formed (top) while in As_2Se_3 and $GeSe_4$, a two- (middle) and three-dimensional (bottom) connectivity mechanism is observed. Most of the technical glasses are in between these three ideal situations. In the case of the three-dimensional network, the connection is ensured either by one Se or better by a Se–Se pairs which provide more flexibility to the network.

cellent glass formers, because of the flexibility of the Se−Se groups connecting the tetrahedral building units. The investigation of the Ge/Se system shows that glass formation is possible in a very broad range, but that $GeSe_4$ is by far the most stable glass. Out of these stoichiometric situations, a lot of compounds exist in which the reticulation of the polymer is intermediary between one-, two- and three-dimensional. This means that the glassy network will have a more complicated topology, far from a simple composition that could compete with a stoichiometric crystalline form.

The selection of a glass composition for making practical IR devices is usually a compromise in which the three following parameters have to be optimized.

1) A strong resistance towards crystallization, which can be experimentally evaluated by differential scanning calorimetry through the absence of the exothermic peak due to the glass to crystal transformation
2) An appropriate value of T_g, which must be high enough to ensure acceptable thermal and mechanical properties. In chalcogenides this property is directly correlated to the degree of connectivity; for example, one-dimensional Se glasses have T_g values around 40 °C, which is too low for practical applications.
3) The glasses need to contain a large amount of heavy atoms to ensure low-phonon vibrations.

In this paper we will discuss three families of technical glasses that have resulted from these optimizations. The system that has been extensively investigated is the Ge/As/Se system, which offers a vast domain of glass formation and in which several compositions can be selected but not exclusively. The “GASIR glass” $Ge_{22}As_{20}Se_{58}$, which covers the 0.8–12 μm window, has a T_g of 254 °C and corresponds to a structure in which the Ge and As atoms ensure the connectivity of Se chains. Out of a total of 100 connectors, 58 are twofold, 20 are threefold and 22 are fourfold. The reticulation of such a glass is between two- and three-dimensional and it is observed, as expected, that the value of T_g increase with the content of the reticulating elements As and Ge. Since we are here in a liquid-state chemistry it is possible to modify the compositions as long as the required physical specifications are respected. As an illustration the military specifications require that the T_g values need to be superior to 150 °C in order to preserve the glassy state as well as the mechanical properties.

For most of the applications, the Ge/As/Se glasses are fine because they fit with the atmosphere transparency. Nevertheless where IR analysis and space applications are concerned, it is critical to develop glasses that transmit as far as possible in the IR region. This is the case for the two following glass families.

First, the “TAS glass” $Te_2As_3Se_5$, which transmits light in the 1–16 μm window, has a $T_g = 152\,°C$ and corresponds to a network formed from mixed Te/Se chains, reticulated by the trivalent As atoms. Second, the recently discovered “GGT” $Ge_{15}Ga_{10}Te_{75}$[7] and “GTI” $Ge_{20}Te_{73}I_7$[8] glasses, which contain only Te as the chalcogen atom, exhibit the largest optical window ever observed for a glass, extending from 2 to 28 μm. The T_g values for such glasses are located around 150 °C. In contrast to S and Se, the element Te is not a glass former and exhibits a strong tendency to form metallic crystalline species and by consequence the Te-based glasses suffer from a severe glass to crystal competition.

Moulded Glasses for IR cameras

Until recently crystalline germanium was the only material transparent in atmospheric windows that was used for manufacturing lenses for IR-imaging systems. However, Ge has two drawbacks, first the price of the element Ge which is rather rare and second the fact that the production of aspheric or diffractive optics needed in modern cameras requires diamond machining, which is a costly process. Also, Ge is a semiconductor, the transparency of which is highly dependent on temperature and consequently it becomes opaque when heated. To open the way for low-cost IR optics it is then of prime interest to develop a material that contains only a minimal amount of costly Ge. Also it is clearly advantageous to develop a glassy material instead of a crystalline one in order to exploit its plastic behaviour above T_g for developing a moulding process for mass production of high precision optics. It was shown that the GASIR glass fulfils all these requirements and that it exhibits the right viscosity–temperature dependence and the best chemical compatibility with the mould while ensuring outstanding reproducibility and moulding precision.[9] Figure 7 illustrates the surface quality of moulded diffractive lenses mass produced in a form ready to be installed on an IR camera.

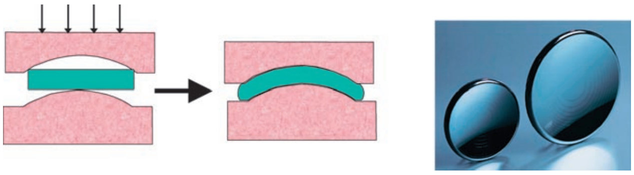

Figure 7. Chalcogenide glasses moulded with high precision leading to lenses ready to equip IR optics.

The fields of application for these IR imaging systems is very wide, running from night-vision systems for the military domain to overheating surveillance devices for electrical systems, and other medical, biological and electronics applications.[10] One of the most promising markets is the night-vision camera containing IR glass optics moulded through this process, which is to be found in high-end BMW vehicles. Car-driving assistance in foggy weather or at night has become a priority for security reasons. Figure 8 shows a night-vision scene in which IR imaging allows an early detection of thermal objects such as pedestrians, animals or others cars.

Figure 8. Night-vision scene obtained from an IR cameras that are used in the car-driving assistance system of BMW cars.

From Glass to Crystal: Composite Glass–Ceramics Materials

As already mentioned, the non-equilibrium thermodynamic nature of glasses often makes these material unstable when heated above T_g. In particular this behaviour is very usual in non-conventional glasses and is considered as a handicap for shaping optical objects that could lose their transparency because of scattering defects due to large crystallites. On the other hand it is known that composite materials in which size-controlled particles have been nucleated offer a mechanical barrier to phonon dissipation and thus a better resistance to fracture propagation. The challenge in the preparation of an optical IR glass–ceramic resides in controlling the devitrification process, in particular nucleating particles that are small enough to make the scattering losses negligible in the IR domain, while exhibiting the mechanical benefit of two-phase composites materials. As an indication it is known that when the size of the crystallites are in the 100 nm range, the optical consequence in the 10 μm spectral domain is negligible, which means that the size of the particles have to be about hundred times smaller than the wavelength.

Most of the time the glass-to-crystal transformation is rather fast and difficult to control and it is of prime interest to developed glass composition in which this phenomenon is slow and easily controllable. Most chalcogenide-based compositions oscillate between either a total resistance to crystallisation, which means that no exothermic peaks are detected by DSC above T_g, or a brutal formation of large crystals. In the end the most appropriate glasses are found in mixed compositions between chalcogenides and halides.[11–13] The key factors in this delicate chemistry are the following. The formation of the nucleating crystallites is governed by coulombic lattice energy formation of the nuclei, which is usually an ionic species such as an alkali halide, for example, CsCl or KCl or occasionally a sulfide. Clearly these species must also be easily accepted by the original glassy matrix, which means that the bonding energy of the corresponding atoms needs to be strong within the glass framework. For instance, for CsCl it is clear that the Cl atoms play the role of terminal atoms in the glassy giant polymer, while the large Cs^+ ions play the role of network modifiers. Finally, during the phase-separation process the glass composition changes continuously; this could have a detrimental effect on the stability of the glassy matrix. This last constraint requires selecting a glass-forming domain as large as possible in which the compositional fraction of the crystalline particles can vary as widely as possible without impeding glass formation. Among others, a good example of a glass–ceramic forming system is given by the ternary compositions $GeS_2/Ga_2S_3/CsCl$ in which the atoms Cs and Cl are perfectly accepted in the glassy matrix, but can also phase separate as CsCl nanocrystallites. Figure 9 represents the evolution of a GeGaSCl glass disk when heated above T_g as a function of time. The glass becomes more and more opaque due to nanoparticle formation, which absorbs visible light. Nevertheless due to the small size of the crystallites, the transparency is not af-

Figure 9. Photographs showing chalcohalide CsGeGaCl glass disks transformed by heating into a composite glass–ceramic in which CsCl nanoparticles have been nucleated. Controlling the particles size permits us to obtain a material that is opaque in the visible but still transparent in the mid-IR region as demonstrated in the transmission spectra.

fected in the mid-IR region as represented on the transmission spectra. These glass–ceramics, in which the glassy fraction is important, are easily mouldable and constitute a second-generation of IR optics.

Infrared Fibres for Evanescent Wave Spectroscopy

As already mentioned, TAS glasses have optimal rheological properties that allows them to be shaped into optical fibres which can guide IR light over distances of a few meters. The methodology developed for the manufacturing of optical fibres will not be discussed here, but routinely prepared fibres have a useful optical window lying from 3 to 12 μm with a maximum of transparency around 9 μm corresponding to an optical loss of about 1 dB m^{-1}.

Due to multiple total internal reflections at the glass/air interface, part of the electric field of the IR light confined within the mono-index fibre extends outside the fibre surface. This fraction of the light, called evanescent wave, can couple to any IR absorbing materials that is put into contact with the fibre surface. As illustrated on Figure 10, analysis of the light transmitted at the fibre output permits collection of the IR signature of the material in contact.

To increase the evanescent wave, the diameter of the fibre is decreased along a sensing zone by mechanical or chemical etching techniques that have been developed for tapering the fibre.[14] The resulting analytical technique, fibre evanescent-wave spectroscopy (FEWS), allows us to perform remote, in-situ analysis of molecules or biomolecules by measuring their IR finger prints. This principle has been applied before to silica fibres, but their poor transparency in the IR region limits their interest. In this case the spectral window 3–12 μm is ideally adapted to the detection of the fundamental vibrational modes of almost all molecules. The intensity of the evanescent wave is a maximum at the surface of the guide, but is still significant at a distance of almost a micron. Consequently this technique is of prime interest for direct contact analysis of biomolecules contained at the surface of biological tissues or for microorganisms such as bacteria. A great number of projects dealing with chemical processes, cellular pathology, environment pollution or food processing have been conducted in order to validate this original analytical method.[15] Four of them have been selected as an illustration and concern the in-situ control of water and soils contaminated by chemicals, the colonisation of a surface by bacterial biofilms, the analysis of liver tissues for monitoring metabolism deregulations and finally the in-situ observation of metabolic reaction of live human cells exposed to chemical agents.

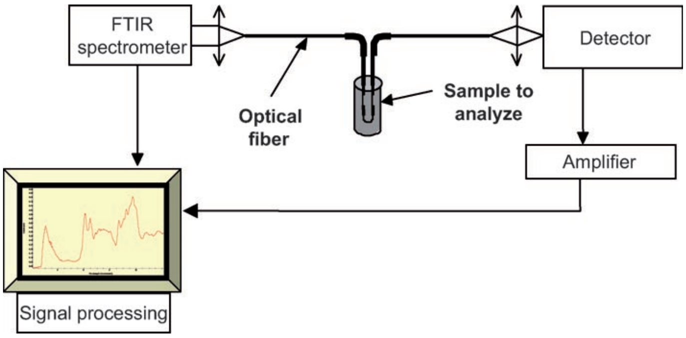

Figure 10. Set-up for remote fibre evanescent-wave spectroscopy. IR light coming from a black body source and coupled inside the fibre is absorbed by the chemical species in contact with the fibre-sensing zone. At the fibre output the light is analysed by a sensitive, cooled, mercury–cadmium–tellurium IR detector. The signal processing coupled with the spectrometer allows the recording of IR signatures.

Figure 11 represents the experimental set-up used for in-situ analysis of underground polluted water.[16] The bent flexible fibre attached to a finger-shaped holder is inserted into a well in order to establish a contact between the sensing zone and the liquid phase. The main target was tetrachloroethylene (TC-en) contamination in water wells. The

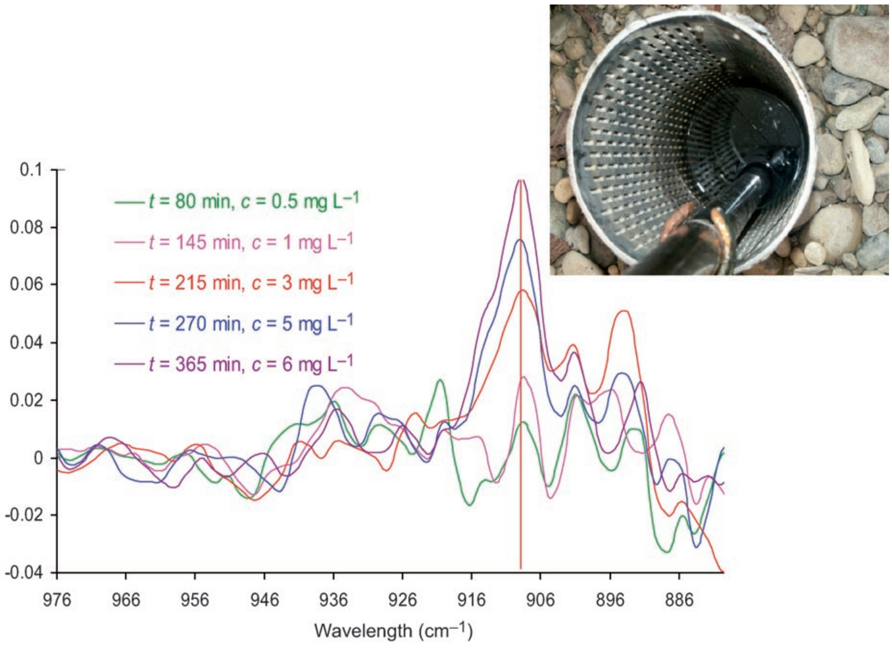

Figure 11. Underground analysis of water polluted with tetrachloroethylene. On the top right the set-up with the bent fibre introduced into the well, underneath the spectra recorded for different concentrations of pollutant introduced in the well.

figure shows IR spectra recorded in situ giving the IR fingerprint of the pollutant for different concentrations of pollutant introduced in the well. The resolution of the detection is in the order of few ppm.

The second series of investigation deals with the formation of a biofilm and was conducted with the aim of controlling the colonization of a surface by bacteria, for instance in hospital environments or in the food industry.[17] The selected target is the pathogen bacteria “proteus mirabilis” and its growing and colonizing ability were investigated on a gelose surface. As shown on Figure 12 the progression of the bacterial biofilm is followed by putting the fibre in contact with the surface of the gelose substrate. Figure 12 also shows details of the IR spectra of the bacteria’s envelope. A detailed analysis of the measurements permits the identification of the presence of two bacterial forms, namely the swarming and vegetative phenotypes.

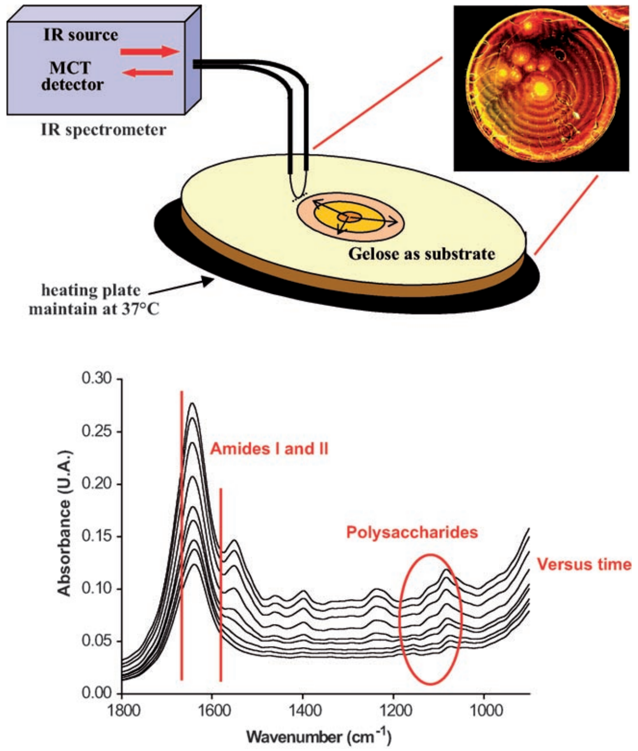

Figure 12. Top: IR fibre set-up used to investigate the colonization of a gelose surface by a bacteria biofilm. Bottom: progression of the IR signature of the Proteus Mirabilis bacteria membrane as the biomass propagates through the substrate.

The third example focuses on liver pathology, particularly the effect of starvation on a mouse liver.[18] This study was performed as part of an intensive cooperation program conducted together with the Rennes university hospital. Figure 13 shows an IR fibre a few millimetres in length coated with enrolled slices of liver tissues that have been cryogenically cut to a thickness of 10 μm. The tissues were taken from a population of animals that had regularly fed as well as from mice that had received no food for 12 h. The IR analysis shown on Figure 13 clearly reveals a strong difference in IR signature between the two groups, especially in the lipid and glucose region; these results demonstrates that starvation has a direct and visible effect on liver metabolism.

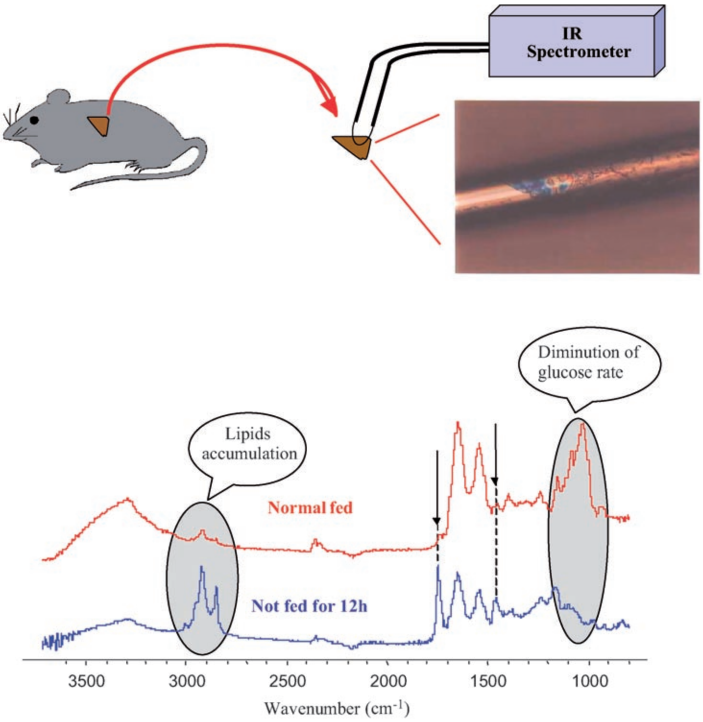

Figure 13. Top: 10 μm thick slice of a mouse liver tissue which has been deposited and wrapped on the fibre surface (iridescent part). Bottom: IR signatures of the tissues for two populations of animals, one regularly fed and the other submitted to a twelve hours starvation period. A significant difference is observed in the sugar and lipid spectral region.

The fourth example involves monitoring living human lung cells coated at the surface of a chalcogenide fibre and their behaviour when exposed to a chemical agent such as a surfactant.[19] To coat a layer of live cells on the fibre surface, the sensing zone was inserted into a pellet of centrifuged cell culture, which showed strong attachment after about an hour. The vibrational spectrum of the cells was then monitored continuously, in particular the phospholipids signal from the cell membrane which lies where the evanescent wave is most intense. Upon introduction of micromolar quantities of Triton X-100 surfactant within the cells environment, a strong and rapid decay in the phospholipids signal was observed (Figure 14). This spectral observation was consistent with the known mechanism of attack of surfactants on cell membranes. Metabolic variations after exposure to various toxic agents were also detected in other spectral regions.[20,21]

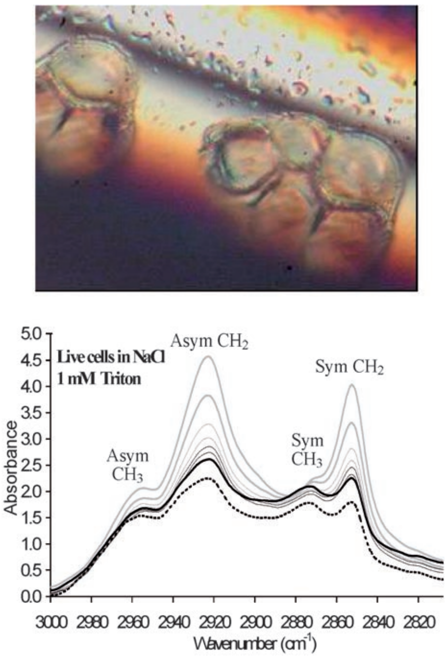

Figure 14. Top: Human live cells forming strong attachment on the surface of a TAS fibre. Bottom: IR signatures of the cell membrane upon introduction of micromolar quantities of surfactant in the cell environment.

Designing Glasses for Space Exploration

The development of glasses transparent to far IR region was conducted in the framework of a space program sponsored by the European Space Agency (ESA) denoted the Darwin mission.[22,23] This program is aimed at detecting signs of life in exoplanets orbiting around stars far in the universe. A similar program "Terrestrial Planet Finder", sponsored by the NASA agency is also running in the US. The aim is to detect exoplanets that have conditions similar to the earth and consequently might be likely to harvest life. If one of these exoplanet is an earth-like planet it must be considered as a thermal object with an average temperature of 15 °C and will therefore emit in the IR region as described in Figure 4. If life exits, this planet must be surrounded by an atmosphere similar to the earth, namely containing water, oxygen and carbon dioxide. As illustrated in Figure 15, the earth's atmosphere contains several gaseous species such as water molecules H_2O absorbing strongly in the 6 μm region, oxygen in the form of ozone O_3 absorbing in the 10 μm region, while CO_2 constitutes a strong barrier to light propagation near 15 μm.

To demonstrate the existence of these IR signatures that are signs of life, a flotilla of telescopes will be launched in space and positioned with high precision to observe the targeted earth-like planets as represented in Figure 16.

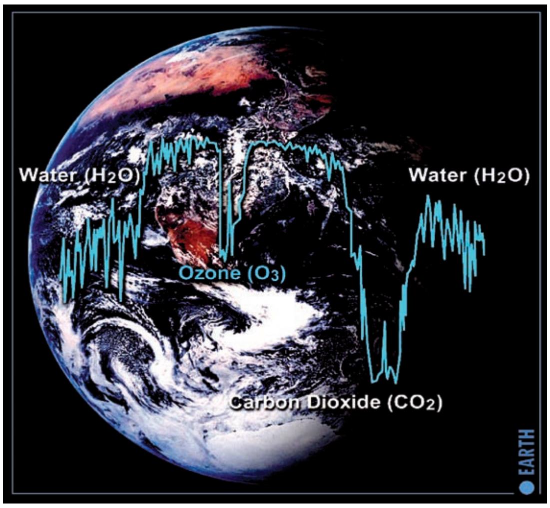

Figure 15. The earth surrounded by the atmosphere composed of several gases such as H_2O, CO_2 and O_3, which are the signs of life. These three biological markers have their IR signature at around 6, 10 and 15 μm, respectively.

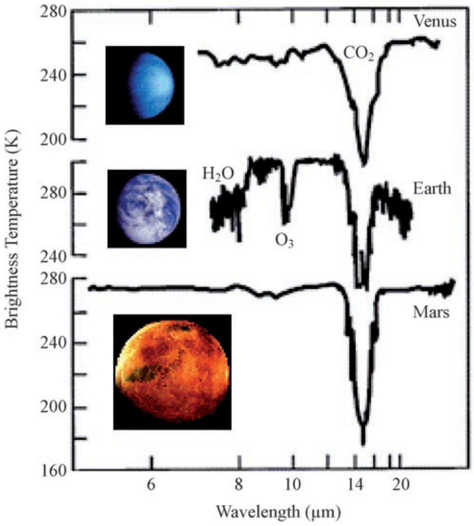

Figure 16. Concept of the Darwin mission: A flotilla of IR telescopes will be positioned in the space to analyse the IR light coming from a targeted exoplanet in order to detect signs of biological life.

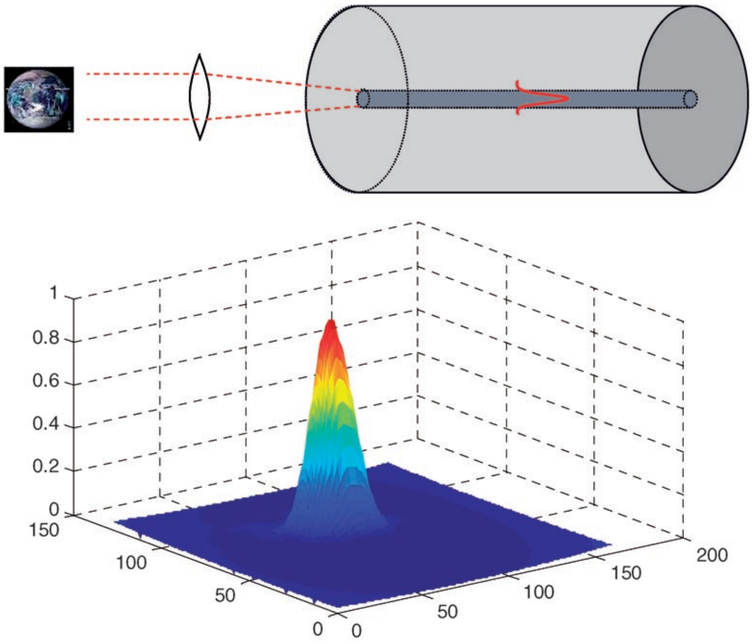

Figure 17. Optical configuration of a single mode, core/clad fibre required for space exploration. The fibre needs to permit the propagation of light only at the three strategic wavelengths 6, 10 and 15 µm. The experimental results obtained with a single mode TAS core/clad fibre are shown below. The Gaussian light output when 10.6 µm CO_2 laser light is injected into the fibre demonstrates the single mode behaviour around 10 µm.

To prevent blinding from strongly emitting nearby stars, efficient filtering is required to collect radiation information specifically from the exoplanet. To fulfil these severe requirements, IR single-mode fibres (SMF) are needed. Their role consists of permitting only the propagation and the selection of light existing in the strategic wavelength window, which extends from 6 to 20 µm. As a consequence the role of the material scientist is to manufacture a fibre or several fibres exhibiting the optical configuration depicted in Figure 17 that are transparent in the required optical domain typically from 6 to 20 µm.

The core of the fibre must be made from an IR glass with a refractive index slightly superior to the clad glass in order to ensure the propagation in the core by total internal reflection. As an example the core diameter is in the range of 25 µm for a clad diameter of about 500 µm. If the propagation of the light is single mode, the light output must have a Gaussian profile as represented in Figure 17. The method for fabricating the single-mode fibre, called rod in tube method will not be discussed here, but SMF have recently been successfully designed from the combination of two TAS glasses.[24]

Concluding Remarks

Looking into the invisible is not a paradox any more thanks to technological advances that permits us to substitute our retina with matrices of IR detectors exhibiting a greater and greater number of pixels, while functioning at room temperature. Chemistry evidently plays a key role in the development of these thermo resistant, microbolometer detectors, which are usually made from silica or vanadium oxides. Chemistry is also central in the development of IR optics; such materials need to exhibit stringent optical properties while being mass produced to reach a large market. Here we have shown that the gap between a fundamental approach to glass chemistry and mass production is not so large. Millions of IR lenses are now under fabrication for the car industry, but it is also expected that the market of thermal detection for firemen or industrial processes, night vision for policemen as well as the field of environmental monitoring through IR pollution control systems will greatly benefit from the most recent developments in IR glass design and manufacturing.

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