Glass and glass products *

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It was apparently by chance that, about 4000 years ago, glass as an artificial material was discovered. Actually natural glass exists in nature and has been used since a very long time. Fulgurites, produced by the impact of a lightning on sand seems never to have been used, but obsidian, of volcanic origin has been used by men to make arrows tips, and by women to make mirrors... supposed to reflect also the soul!

But it was when natron blocks, a sodium carbonate largely used in antiquity to desiccate the body in the process of mummification, were put by accident in contact with sand in the preparation of a meal, that is with a fire, that the fusion point of silica (actually sand) was sufficiently lowered as to obtain the melting of this mixture, and with its further solidification to realise the first man-made glass. One may say that the whole glass industry started from this event.

Pure silica, SiO_2, exists under two different atomic structures: quartz, a trigonal crystal also found in nature and vitreous silica the structure of which is disordered, that is "amorphous" or glassy".

This article does not examine the exact nature of the amorphous structure. This is a complex issue, still not completely understood by physicists. In its February 2005 issue, the "journal du CNRS" put the "obscure nature of glass" amongst the 10 main enigmas of physics! Neither shall the industrial processes for making glass and glass products be described. They are actually in constant improvement, thanks in particular to the progress in mathematical modelling [1]. This article will concentrate on industrial glass products, and on the trends in these technological developments.

As opposed to silica, a pure material (SiO_2), glass has a complex composition. A composition of 8 to 10 different oxides gives it its properties: fusion point, viscosity at high temperature, mechanical properties, surface hardness, chemical stability, colour, etc.

When comparing ancient compositions with some modern glasses, actually glass bottles, it appears that they are surprisingly similar (over 16 centuries, SiO_2 went from 70.5 to 72.5%, Na_2O from 15.7 to 13% and CaO from 8.7 to 9.3%, the other oxides, K_2O, MgO, Al_2O_3 and Fe_2O_3, changing only slightly their small proportions) although some properties have been enormously improved throughout time. That is the case with transparency: the first glasses were relatively opaque due to a high level of impurities. In the 17th century, the secret of making transparent glasses in order to make mirrors was a monopoly of the Venetians, and to protect the secret the glass manufacturers were installed on the island of Murano, in the Laguna of Venice... where they still are. To break this monopoly, Louis XIV and Colbert, his minister, decided to establish in 1666 the "Manufacture Royale des Glaces de Miroir", to become the "Compagnie de Saint-Gobain". The secret was eventually stolen from the Venetians by means that would certainly not be considered fully ethical today [2]. More recently, silica glasses used to make optical fibres have been subject to the necessity to extend the transparency of this kind of glass to such an extreme value that they are as transparent over tens, or even hundreds of kilometres, as a window glazing over a few millimetres! (Fig. 1)

But let us examine the parameters on which one may play to develop new glass products. We shall examine five of them, although there may be many more:

The composition of glass
- The structure of the glass matrix
- The surface of glass
- Thin films deposition on this surface

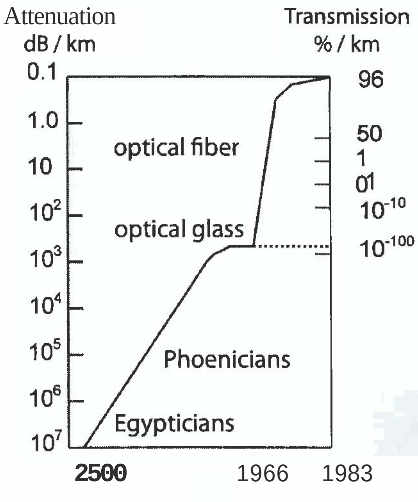
Complex glass products

We shall only consider a few examples in each of these categories.

Glass composition

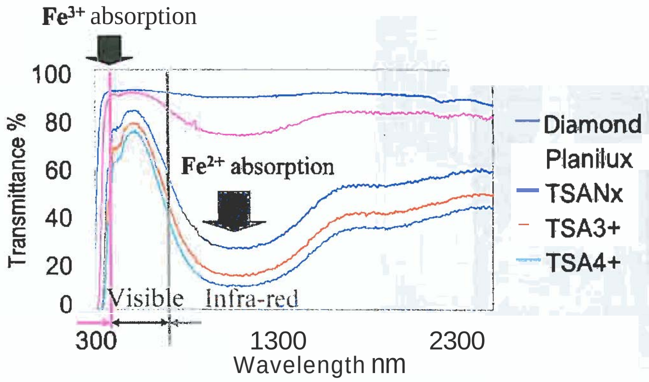
A glass composition is so complex that it is extremely difficult to predict by mathematical simulation the actual properties of a given glass. However the long experience of the glass makers gives them the ability to have a good idea, at least for the most classical compositions, of what will be the properties and how they will change with small modifications of a given constituent. This is part of the "art" of glass making.

A good example of this mastery of the art is what has been an issue for the past ten years for the producers of glass wool for thermal and acoustical insulation: The fact that this product is made of short fibres of small diameters (a few micron of diameter and a few millimetre of length), has raised the question of their behaviour in the lung in case of inhalation. However, from the beginning it was known that contrary to asbestos, a crystallized silicate, the glass used to make these fibres was more or less soluble in



◄ Fig. 1: Improved glass transparency through centuries

▼ Fig. 2: Transmittance of various glasses versus wavelength. Compositionnal . changes by adding Fe induces a wide Fe^{2+} absorption band in the near infrared (900-1200 nm), and a Fe^{3+} absorption shoulder near 450 nm.



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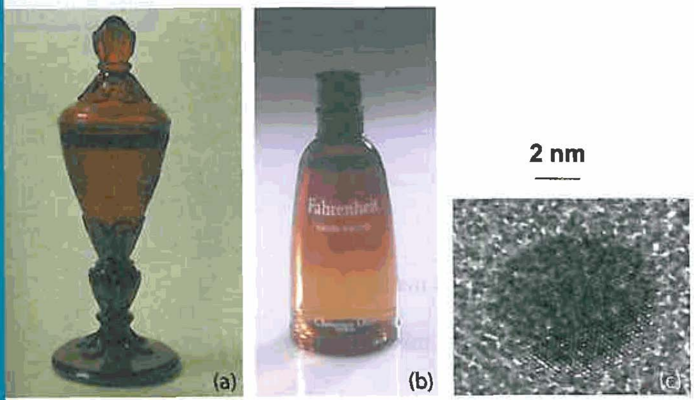
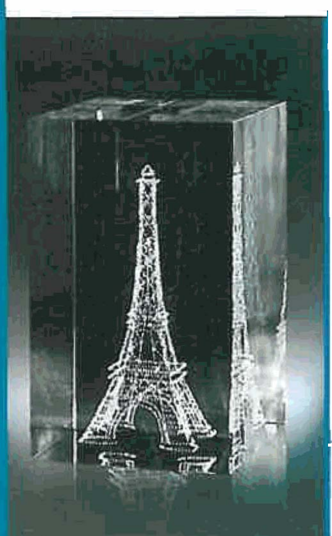


ruby glass bottle (Murano) Fahrenheit bottle Cu cluster

A Fig. 3: (a, b) Two examples of colored glasses. (c) Nanometric Cu clusters inducing the red color in the fig. 03b glass.

the pulmonary liquid. This solubility depends, however, on the precise composition of the glass. The glass initially used for this application disappears totally from the lung after a few months, whereas asbestos fibres are still present 30 years after their imposition. By playing on very small changes in composition (a standard glass becomes bio-soluble by decreasing its Al_2O_3 from 3.4 to 2.2±0.2%, Na_2O from 15.75 to 15.5% while MgO is increased from 3.0 to 3.2%), it has been possible to produce glass wools which, although perfectly stable in the humid air of the walls of a house, are dissolved in the lung, an acid medium, in a few weeks or even a few days. A very large number of tests, as well as epidemiological studies, have now been conducted that have led to the official conclusion that this glass wool is totally safe in term of the risk of cancer.

Another example of progress made by simply changing the composition of glass is that of the simple window glazing. A window-is mostly supposed to isolate from the exterior, while being as transparent as possible. However, if the transparency in the visible is indeed what is desirable, infrared transparency brings in a few inconveniences: On one hand the near infrared is transporting most of the solar energy and heat, therefore in summer it may heat up too much the interior of a building or of a car. Conversely in winter, the black body radiation of the interior of a building, at 20°C has a peak energy around 10 microns, in the far infrared, and if this radiation can also go through the windows, generally by a process of absorption-reemission inside the glass, it gives rise to a high wastage of heat from the interior of the building and therefore to excessive heating energy and discomfort near the window. What are the solutions? The first one is to develop glass compositions as transparent as possible in the visible, but absorbing in the near and in the far infrared. Figure 2 shows the progress made recently. The "TSA 4$^+$" composition is almost perfect, its transparency being strictly limited to the visible spectrum. However, the "ideal" window should be still perfectly transparent in the visible, but reflecting rather than absorbing in the infrared to insure both summer comfort, by reflecting out the heat of the sun, and winter comfort, by reflecting back the blackbody radiation at 10 microns. We shall see later that this has become actually possible by the deposition of complex coatings on glass.



▲ Fig. 4: Example of mass engraved glass using focussed laser pulses.

Glass structure and nano-particles

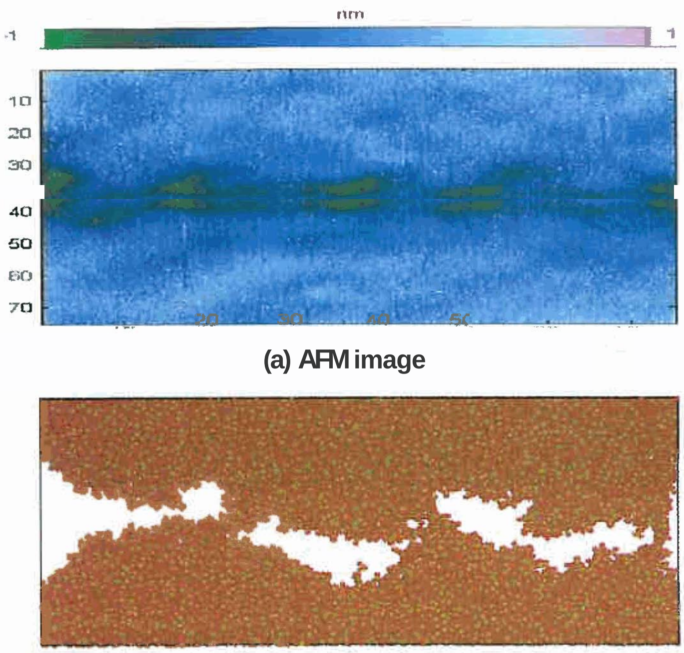
The molecular structure of glass is in itself a complex issue: What does it means to be a disorderly medium? Is there a short distance order, and which one? What is the homogeneity of a composition, at short and medium distance? ...etc. It actually happens that under specific conditions of annealing or illumination, some phenomena of demixing may take place right inside the volume of the glass, and this modifies deeply the local structure. It is the case in the well-known "photochromic" effect in which an ultra-violet illumination induces the dissociation of nanometric aggregates of silver halides, created during the initial annealing of the glass. When the illumination is turned off, the atoms, which did not have the possibility to fly very far from one another, recombine, and the coloration due to atomic silver fades out.

Another well known example is that of the "ruby" glass of the Murano glass blowers. Its very specific red colour (figure 3a) is due to small gold clusters formed during the heat-curing of the glass. A modern version of this colour, due to a plasma resonance of aggregates, is the perfume bottle "Fahrenheit" (for men), the degraded red colour of which (figure 3b) is due to a differential heat-curing along its height, producing copper or copper oxide aggregates of different sizes (figure 3c). The absorption frequencies of their plasma resonances give to the glass the complementary colours.

Finally, over the last few years several laboratories in the world have become interested in the engraving of shapes inside the glass matrix. This can be done by focusing a laser picosecond pulse on successive spots inside the glass, which induces very local changes in structure. The exact nature of these changes (micro-cavities, micro-crystallites, local changes in composition...) is still to be studied precisely. Used today to make decorative objects (figure 4), this technique is also studied with a view to making three-dimensional optical memories.

What can one say about the surface of glass?

The surface is in a way the "Achilles heel" of glass. Indeed, it is the propagation of micro-cracks along the surface that eventually ends up with the fracture of the glass piece. It is therefore from the surface that the brittleness of glass comes, a material which on the other hand has a very high tensile strength modulus. The way that these cracks propagate, at the beginning extremely slowly, is now better understood. The role of water vapour is important, the water molecules being located at the bottom of the crack, therefore leading to the breaking of covalent bonds in the glass. It is well known that the ancient glass workers, to break a piece of glass, would first make a crack with a diamond (which is still actually done, even on industrial lines), and would then spit on this crack to increase its speed of propagation and help the rupture of the glass. Recent experiments using atomic forces microscopy have permitted one to produce a "movie film of the propagation of a crack [3] (Figure 5a). Mathematical modelling has, on a simplified model material, shown a similar behaviour, and in particular the formation of cavities appearing in front of the crack head itself. [4, 5] (Figure 5b).



(a) AFM image

(b) computer simulation

A Fig. 5: (a) Atomic force microscope view of a nanocrack propagation. On top, color code to get the cavity depth. (b) Computer simulation of a crack propagation.

In addition, glass manufacturers are observing complex, or even paradoxical, phenomena. For example, it is mostly the quality of the external surface of a glass bottle which implies its resistance to internal pressure (which is important for champagne bottles!), and it is the quality of the internal surface which governs the shock resistance, which is important during the transport and filling of the bottles.

Thus, a glass product to be strong would require a perfect surface, which is quite hard to maintain in practical situations. It is, however, already almost the case for glass fibres used to strengthen composite materials, the rupture coefficient when it comes out from the bushing being about 3.5 10^9 Pascal, close to the theoretical value for a defect-free silica of 10 to 15 10^9 Pascal. A more realistic approach, which can be generalized, is to block the propagation of the cracks. This can be achieved by different approaches: Tempering is a good way to do it by putting the surface in compression. Thermal tempering is largely used but has a limited performance. Chemical tempering, in which the glass piece is immersed into a hot bath of potassium salts, is far more expensive. The sodium ions of the glass are partially substituted by bigger potassium ions, therefore inducing a compression of the surface, which eventually makes the glass practically unbreakable. Two swords blades made for the uniforms of two members of the French "Institut de France": that of Yvan Peyches, R&D Director of Saint-Gobain from 1944 to 1966 and a member of the Academy of Sciences, and that of Commandant Cousteau, elected in 1988 at the prestigious "Académie Française", have been made by Saint-Gobain in chemically tempered glass!

Other techniques are presently being developed to prevent the cracks from propagating, thanks to appropriate coatings.

Coatings on glass

This brings us naturally to a few considerations on glass coatings. A large variety of functionalities are brought to glass products, especially glazing for windows, by the deposition of simple or complex coatings. As was mentioned earlier, a first target is to realize a "perfect" glazing, transparent in the visible and reflecting in the near and far infra-red.

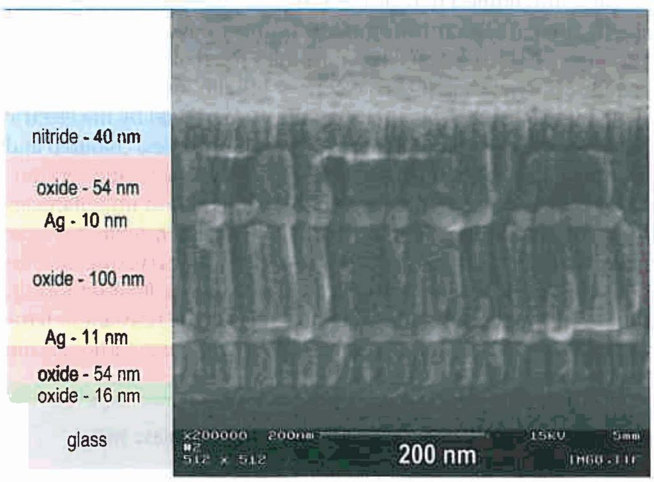
This can be achieved by deposition of a carefully calculated multilayer interference filter at the surface of the glass. It must not only insure one or both of these properties of reflection and transparency, [illegible] especially the glass be manipulated safely while introduced into a double glazing, in which it is eventually protected. And this must be realized at moderate cost. The main technique used to make these coatings is vacuum deposition by sputtering, which gives the possibility to deposit several layers, the structure and thickness of which being perfectly calculated and controlled. The simplest coated glasses would have half a dozen layers, with thicknesses going from a few nanometres to a few tens of nanometres (figure 6). The cost in this case remains low enough to be accepted in the construction market. The most complex may have more that twenty layers. This is the case for example for solar protective glass for car windshields, which reflects the near infra-red while being perfectly transparent in the visible, and able to stand without damage the cycle of heating and cooling necessary to realize the complex shapes of modern car windshields.

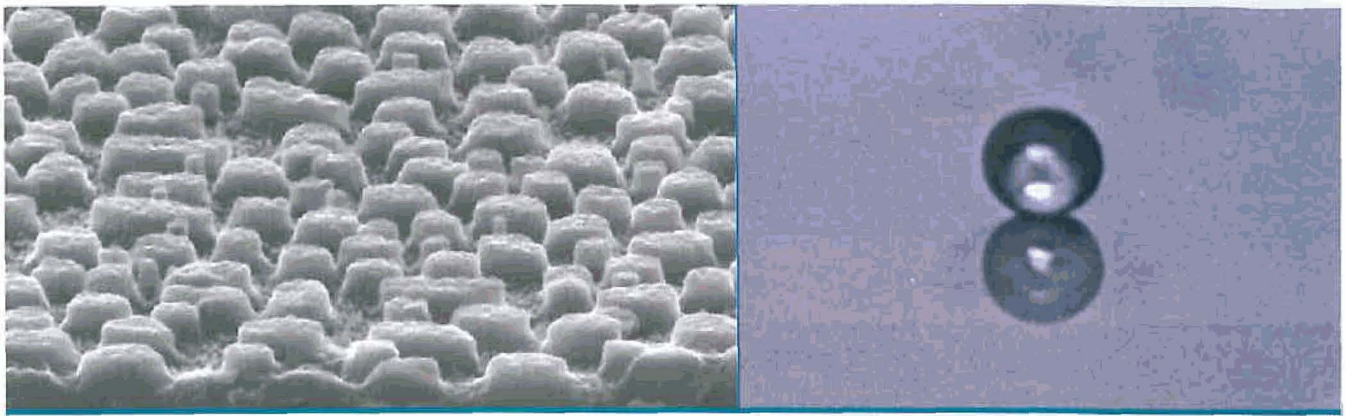
Mastering the various techniques of glass coating gives the possibility of many other functionalities: antireflective, hydrophilic or hydrophobic, antifrost... etc. Hydrophobic layers, especially, automatically assembled organic layers, are already used for airplane windshields, and for some lateral car glazing. The strong constraints imposed, however, by the necessity of keeping the wipers, make it still unsuitable for application in car windshields.

An interesting property that has also been studied is that of "super-hydrophobia": Studies of the hydrophobic property of the leaves of water lilies, which never get wet even under a heavy rain, have shown that this is due to a structure of the surface on a scale of a few hundred nanometres. Reproduced at the surface of a glass piece, it gives rise to a spectacular hydrophobic effect [6] (figure 7).

The latest glass product enriched by thin film deposition is the self-cleaning glass: in this case the cover is a thin coating of titanium oxide TiO_2. In the crystalline phase, called "anatase", it dissociates the greasy dust by a photo-catalytic cracking effect, the cleaning being further assisted by the rain flowing on this coating which is also hydrophilic (figure 8). Such products are now available commercially. Depending on the exact nature of the film they are efficient under UV radiation, or even under ordinary visible light.

▼ Fig. 6: Micrograph of the section of a multilayer cover





▲ **Fig. 7:** Micrograph (left) of a super-hydrophobic glass surface. The efficiency of the wetting decrease is shown (right) by the water drop (R=100 micrometres) which remains nearly spherical.

Complex glass products

The next step in term of glass products is to make complex, glass-based products. Two examples will illustrate this approach. They both are in the category of "electricity-driven" products.

The first example, the "Privalite", a commercialised product, is such that it commutes instantaneously from a transparent to a translucent state (figure 9). While not absorbing the energy of the light, it provides privacy, keeping the inside of a room out of sight from the outside. The applications of such a glazing are in offices, meeting rooms, hospitals (care rooms), etc. Its principle is the following: between two pieces of glass, each one covered by a transparent conductive film (in most cases SnO_2 doped with fluorine), is laminated a plastic film in which are imbedded small droplets of liquid crystal. The whole structure is such that when they are oriented by the electric field produced under an applied voltage, the droplets have, in the direction perpendicular to the glazing, an index of refraction equal to the index of the plastic sheet in which they are embedded. The system is therefore transparent. In the absence of electric field, the droplets are disoriented, presenting a variety of indexes of refraction in a direction perpendicular to the glazing. Their sizes being of the order of the wavelength of the visible light, a fraction of a micron, the light is diffused and the glazing becomes translucent. The commutation time is fast, of the order of a millisecond. Considering the nature of the liquid crystal molecules, this kind of product is not very resistant to ultra-violet radiation, and is therefore mostly used in the inside of buildings and not for outside windows. In the translucent state, it can become an excellent screen for optical projection.

Far more complex to realize is a large-sized "electrochromic" glazing (figure 10): Electrochromism is nothing but a battery between two glass plates. It is actually a thin solid film battery of which the mobile electrical charges are protons or lithium ions. Depending on the battery layer in which these charges are pushed by the electric field, the system, while still transparent, is more or less coloured and absorbing. The migration of ions being a slow process, the commutation time is slow and progressive. If it seems almost instantaneous for a small rear mirror in a car, it can reach several minutes for a car glass roof of 0.5 m^2. The difficulties of manufacturing such an object of this size are considerable. It must change colour uniformly, for a large number of times without aging, and be resistant to temperatures up to 100°C and to intense W light...etc. Although the principles have been known for several decades, it has required about 20 years of development by Saint-Gobain to put the first electrochromic car roof on the market! The applications of such a product in the building industry are very promising, in terms of permanent control of the energetic and luminous transmission through windows. However, the large size necessary and the cost issues specific to its construction make it still a product for the future.

Where will the future progress of glass come from?

In the first instance from the composition itself. We have shown a few examples above, but the number of possible compositions is practically infinite. Only a microscopic fraction of the multi-dimensional space of possible compositions has actually been explored. In just the Aubervilliers research laboratory of Saint-Gobain alone, 200 new compositions are formulated and tested each year. More systematic methods of exploration, inspired by "combinatory chemistry": give today the possibility to greatly increase the number of compositions explored. In addition, the modelling by molecular dynamics, in association with the huge amount of empirical knowledge accumulated by the glass makers over several centuries, should dramatically improve our ability to predict the properties of a glass of a given composition. Then new glassy materials will be developed, either with better performance in existing applications, or adapted to rapidly expanding new applications such as substrates for flat panel displays for television, or in photovoltaic cells. Other applications, such as micro-fluidic or biosensors, may also use glass substrates in the future. To take but one example, the glass used for active matrix liquid-crystal flat TV screens is quite different from the one used for Plasma displays.

► **Fig. 8:** Compared transparencies of an ordinary glass and a self-cleaning one, after one year.

Mastering the surface of glass is the next big challenge. If we are now beginning to really understand the phenomenon of crack propagation, we have very few practical ways of blocking this propagation, at least at an acceptable cost. On the other hand we have seen that by structuring the surface of the glass, it becomes possible to give it new properties such as super hydrophobia, and this can be done locally, opening the door to new elaborate substrates. The propagation of surface waves also gives the possibility to make touch-sensitive glasses, identifying precisely the position where it has been gently pressed.

As for the structure of glass in the bulk itself, exciting new possibilities are opening up. It has been known for a very long time how to grow aggregates or micro-crystallites inside some glass matrices. We have also seen that it is possible to "write" inside the glass by using focused laser pulses. This opens the way to the realisation, inside the matrix, of elaborate patterns giving rise to new optical properties, comparable to those actually obtained by complex thin-film deposition, or to write information with a view to making three dimensional memories, or even to include inside the glass matrix molecular species which could be later released in a controlled way.

Another approach for new materials is that of material "construction" at the molecular level. Hybrid materials in which inorganic and organic molecules are combined to create an amorphous network begin to be developed. Such materials have at the same time the mechanical and thermal properties of minerals, and functionalities which can be brought by organic molecules. It appears to be a very promising approach.

The biocompatibility of glass, or even the bio-solubility of some compositions, opens the way to medical applications. Already, glass micro-spheres, full or empty, are being tested to bring in situ, by ingestion or injection, therapeutic or radiation treatments, or simply to block the circulation of the blood in micro-vessels nourishing a tumour.

In summary,

- the infinite variety of compositions that offer the possibility at best of adapting the glasses to applications that exploit its basic characteristics,
- the mastering of the surface structure and the deposition of thin layers,
- the beginning of an industrial approach to structuring the bulk of the glass,
- the realization of the first truly hybrid materials and
- the making of complex products in which glass is the main component,

▲ **Fig. 9:** Electrocontroled glass wall: opaque (left), transparent (right)

all ensure a brighter and brighter future for this ever expanding material.

The importance of active, ongoing fundamental research on glass must also be stressed, to better understand what is actually an amorphous material, what happens at its surface, how to predict its properties by molecular dynamics, how to realize hybrid materials, how to structure in a controlled way its volume, etc..

Finally, being a physicist who has become modestly a glass manufacturer, I cannot but mention in closing the fascination that this material holds, for its beauty and the diversity of the products that can be made with it.

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▼ **Fig. 10:** (a) Example of electrochromic glass; (b) Changing the ion distribution modifies the optical absorption.