Tailoring Glass Properties: Why Chemical Composition and Thermal Treatments Matter

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Architectural use of glass dates back from the beginning of our era when it was used to make windows. Its range of chemical composition was close to that of current flat or hollow glass, illustrating early optimization of both production process and material properties. In modern buildings glass is ubiquitous, highly visible as in facades or hidden as fibers for thermal insulation or for high-speed telecommunication. This short review describes the main factors that have made this variety of uses possible. The fundamental point is the amorphous nature of glass, which allows pieces of any shape and size to be produced and the properties of the material to be tailored through thermal treatments and incorporation of a host of chemical elements in widely different proportions.

Keywords: Glass structure, chemical composition, glass color, fire protection

1. A historical perspective

In architecture, glass made its debuts at the beginning of the Christian era. At that time, a real technological revolution took place thanks to the use of raw materials pure enough to allow glass to become transparent, in thicknesses of a few millimeters, and, especially, to the invention of blowing which allowed pieces of any shape to be made quickly with the pristine surfaces ensured by "fire polish" and lack of contact with a mold [1]. Almost suddenly, glassware of any kind spread throughout the Roman world [2]. Glass windows were even installed in some buildings such as public baths. In this use, however, glass was more translucent than transparent. It could not be made thin and with fire polish because, to get flat panels, the molten glass had to be poured on a solid substrate with which some reaction was taking place. Although these windows were short-lived, glass reappeared no later than the 6th century as small, colored round pieces adorning churches. This was the beginning of stained glass whose subsequent importance in religious architecture is too well known to be discussed here.

In civil architecture, the high cost of glass would very long restrict its use to the wealthy in the form of small pieces mounted within a lead frame, like stained glass, that was so heavy that windows could not be opened. Interestingly, the two processes that were designed, probably around the turn of the millennium, to make flat glass relied on a first stage of blowing (Fig. 1) that ensured the sought after fire polish. But it was only during the 17th century that optimization of glass composition allowed production of the larger, thinner glass panels that made the French window possible. With the passage of time

glass became less expansive and its uses in architecture more extensive, but no fundamental evolution would take place before the 20th century. Then dramatic changes took place. From the late 19th century, a glass science had developed and rapidly gave rise to a variety of important innovations [3, ch. 1].
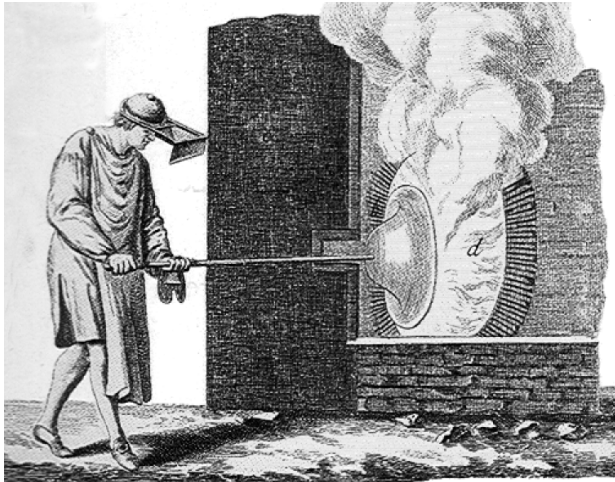

Figure 1: Flat glass as made by the crown process from a vessel that is first blown and then opened and flattened, opposite to the blowing pipe side, through rotation in front of a very hot furnace (engraving from the 18th-century Encyclopédie of Diderot and D'Alembert). In the mantle process, a large cylinder is first blown, cut at both ends and then along one side, and finally opened and flattened in a furnace heated near the softening temperature.

These innovations took advantage of the progress made in the physics and chemistry of glass. With a few exceptions, such as lead glass used in optical instruments and in "crystal" glassware, the composition had for instance not varied much during the 45 centuries of glass history. After a great many new elements had peopled Mendeleev Table, efforts were made, especially in Germany, to determine how these could be incorporated and whether they would result in novel properties. To name a single element, boron gave rise to a new glass family whose importance stems from very low thermal expansion, improved chemical inertness, good fusibility and low melting conditions. The latter advantages made drawing of fibers an industrially possible process and resulted in production of glass fibers for either reinforcement of composite materials or for thermal insulation. Among the great many new glass products that were designed in the 20th century, fibers proved to be remarkably versatile. To mention only two other examples, the aluminosilicate composition of other thermally insulating glass fibers ensured fire protection up to more than 700°C, whereas optical fibers made from ultrapure silica have gained an enormous importance since they transmit information at the speed of light and are thus a key component of the whole Internet revolution.

Considering mainly advances relevant to building design and construction, our main purpose in this short review is to describe why glass lends itself to so diverse applications. In this perspective, the first topic of interest is how the way in which glass is made affects its physical properties. The disordered structure of glass at an atomic level will then be presented to explain how glass formation depends on atomic structure

and why so many different chemical elements can be incorporated and enable glass properties to be engineered almost at will. To illustrate these features, we will first consider how light transmission and, thus, the color of glass, can be designed to meet practical requirements. The second example will be the manner in which fire protection is obtained through optimization of glass composition to trigger specific high-temperature transformations in fibers. Note that mechanical properties will not be considered at all as they have already been dealt with by T. Rouxel in the 2008 Challenging Glass meeting [4]. As to the variety of novel functionalities that result from deposition of thin films at glass surfaces, they would deserve a specific review and are, therefore, beyond the scope of this paper. Suffices it to remind here that they may ensure, for instance, infrared or visible radiation control, variable light transmission, self-cleaning capability or anti-bacterial protection.

2. Glass as a frozen-in liquid

Even though there exist other means to produce amorphous solids, cooling of a melt remains the only significant method to make glass industrially. The transition from a fluid, molten silicate at temperatures of about 1500°C, at which complete homogenization of the starting products and release of gas bubbles are achieved, to the final material at room temperature seems continuous and to manifest itself only by a gradual increase of viscosity. As was already guesstimated by early Babylonian glass makers, viscosity is indeed the key property that controls the various steps of production. In modern S.I. units, melting is performed at viscosities of the order of 100 Pa.s, blowing near 10^6 Pa.s, softening near $10^{6.6}$ Pa.s and annealing at 10^{12} Pa.s (for comparison the viscosity of water is 10^{-2} Pa.s, and that of thick honey 10^5 Pa.s).
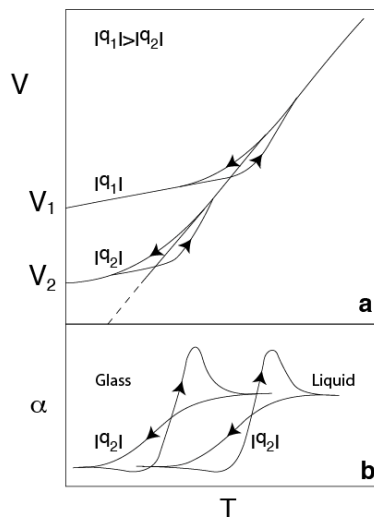

Figure 2: (a) Volume changes of a glass-forming melt on heating and cooling through the glass transition at two different rates q_1 and q_2, causing the density of glass to decrease with faster quench. (b) Associated changes in thermal expansion coefficient, $\alpha = 1/V\ dV/dT$, which also differ on heating and cooling. This hysteresis is another illustration of the nonequilibrium nature of the glass transition.

On closer inspection, however, definite changes in physical properties of a glass-forming melt are detected on cooling. They take place in a temperature interval which is proper to a given glass and narrow enough that these changes can be considered as abrupt. The slope of the volume-temperature relationship, for instance, decreases markedly near temperatures ranging from 450°C, for alkali silicates, to 1200°C for pure SiO_2 in the way pictured in Fig. 2. This *glass transition* unambiguously distinguishes two different states of matter, namely, the liquid and glass at higher and lower temperatures, respectively. Of particular importance is the fact that the temperature of the glass transition depends on the cooling rate (q) of the material, shifting toward lower temperatures with lower cooling rates. As a result, the volume V of the material in the glass domain, and thus its density ($\rho = M/V$ where M is its mass), are not defined only by temperature, unlike that of the liquid, but also by thermal history.
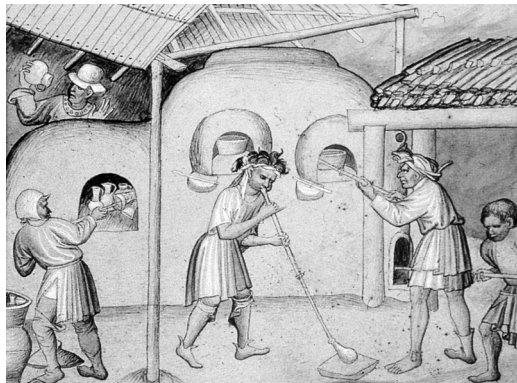

Figure 3: Annealing of glass as practiced in the left-hand side oven, the last step after completion of blowing of the gob of molten glass prepared in the two pots of the bigger oven (detail of a 15th century miniature illustrating The Travels of Sir Mandeville [5]).

This phenomenon demonstrates that the glass transition is an irreversible phenomenon, whose theoretical treatment raises numerous difficulties which are not yet solved [6]. From a practical standpoint, this transition causes practical problems which have been known and empirically solved ever since glass making exists (Fig. 2). These problems stem from the fact that, when brought down to room temperature, any glass piece necessarily cools faster at its surface than in the bulk. Because the glass transition takes place at progressively lower temperatures from the surface to the core, the density increases correlatively within the piece with the consequence that the surface ends up being under compression and the core under extension. Internal stresses thus develop when the glass transition is crossed to the point that the piece may break either spontaneously or under a slight shock during or after cooling to room temperature. The only way to remove these stresses is to homogenize the density from the surface to the core. This is achieved through *annealing*, i.e., through a heating stage lasting a few hours at the lower end of the transformation range of the glass where the rate of density rearrangement has become small, but not yet vanishingly low.

As a matter of fact, glass breaks on cooling because the distribution of internal stresses is generally irregular. If a smooth, homogeneous stress distribution were obtained instead, the glass surface would become extremely resistant to fracture because the

strength of any material increases under compression. Such an improved resistance remained a scientific curiosity until the late 19th century when fast cooling by compressed air came into use and made it possible to cool a piece of *tempered* glass in a uniform way with a surface compression of up to 1000 atmospheres. Resistance to shock is achieved in this way as long as some critical stress is not exceeded, in which case the material shatters as a great many small pieces to release violently the mechanical energy that was stored during the quench. By the way, a stronger still effect can be obtained by chemical means. When small sodium ions, of ionic radius 1.10 Å, are replaced in the first atomic layers of the glass surface by bigger potassium ions, of ionic radius 1.46 Å, the surface is put in a state of compression five times stronger than by rapid quenching. Hence the most shock-resistant glass is produced through ion exchange between the glass and a molten potassium salt. This process is for instance used to make aircraft windows.

3. Glasses as disordered solid materials

In a liquid, atomic mobility prevails as indicated by the ease with which the substance adjusts to the shape of its container. A consequence is that the atomic structure constantly keeps rearranging and can be described only in terms of short, successive snapshots. With decreasing temperature, however, the observed increase of viscosity points to progressively lower atomic mobility. If crystallization is bypassed, the rate of structural rearrangements become eventually so slow that the liquid transforms into a glass, *i.e.*, into a solid whose disordered atomic arrangement reflect that of the liquid which has been frozen in and no longer varies significantly during any experimental timescale.

This statement flatly contradicts the popular story of the century-long flow of stained glass in cathedrals, which has been deduced from the fact that the thickness of panels is often greater at the bottom than at the top. This story thus deserves here a short comment. As a matter of fact, the rate of flow of glass is already very small in the glass transition range. Extrapolation of these rates down to room-temperature indicates that billions of years would not be sufficient to ensure significant flow under the slight stress exerted by the weight of glass [7]. Flow of "cathedral glass" is, therefore, pure legend. As glass of even thickness was not available, the stained-glass masters simply used to place the thickest pieces at the bottom of panels because they knew that images would be distorted if pieces of different thickness were randomly assembled instead.

Turning now to the atomic structure of glass, we note that it strongly depends on chemical composition although its main features can be described in fairly simple terms [3, ch. 3]. First, silicates can be considered as ionic substances in which a single anion, oxygen (O^{2-}), bonds to a wide variety of cations of different sizes and electrical charges. Second, there are always more oxygens than atoms of any other elements and the radius of the oxygen ion, about 1.30 Å, is large compared to the radii of most cations (0.34 Å, for instance, for Si^{4+}, the second most abundant ion). In pure SiO_2, it follows that oxygen atoms occupy 100 times more space than silicon. Hence, deciphering the structure of silicates is tantamount to describing how cations mutually fit in-between oxygen anions.
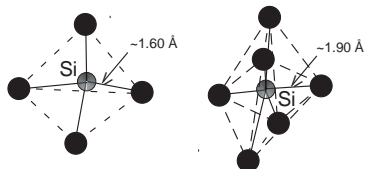
Figure 4a: Individual oxygen coordination polyhedra: SiO_4 tetrahedron (left) and MO_6 octahedron (M = metal cation, right).
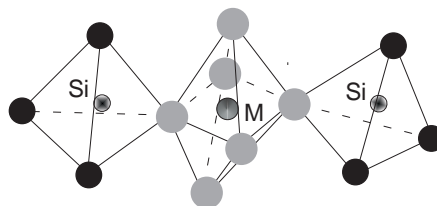
Figure 4b: Connection between differing oxygen coordination polyhedra through sharing of apical oxygens.

This structural description is conveniently done in terms of polyhedra whose apices are the oxygens bonded to the cation they are surrounding. Such *coordination polyhedra* are characterized by their number of oxygen ions and by the various cation-oxygen distances which are both determined primarily by ionic radius ratios between oxygen and the various cations (Fig. 4a). Everything else being equal, small and highly charged cations compete more effectively for bonding with oxygen. Silicon is thus the most efficient because it has the smallest radius and the highest formal charge (4+). Its optimum coordination is achieved in the form of SiO_4 tetrahedra. By forming their own oxygen coordination polyhedra, other cations then share oxygens in the network defined by SiO_4 tetrahedra (Fig. 4b) according to their relative bond strengths with oxygens.

● Bridging oxygen (BO)
● Nonbridging oxygen (NBO)
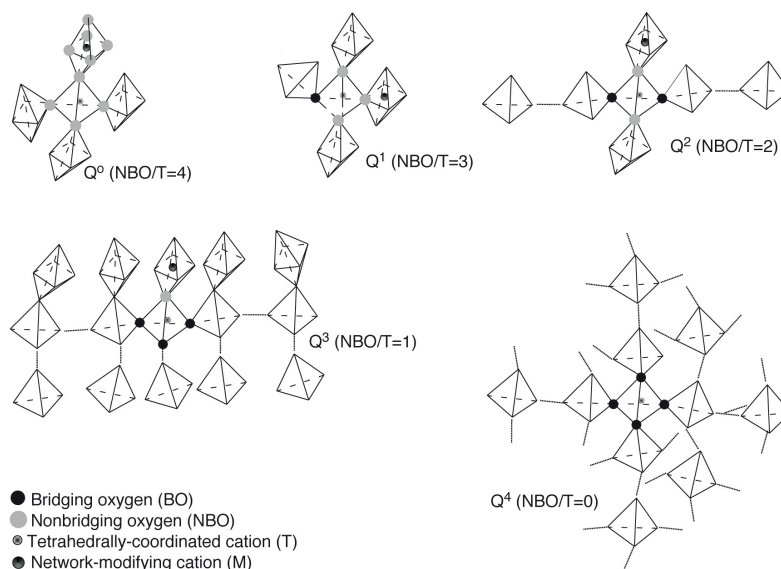◉ Tetrahedrally-coordinated cation (T)
● Network-modifying cation (M)

Figure 5: Schematic representation of interconnected silicate tetrahedra and larger metal oxide polyhedra in the various Q" structural units [3]. In the Q^4 sketch, the short lines indicate effectively infinite extension of the structure. The ratio of nonbridging oxygens over tetrahedrally cations (NBO/T) is a simple measure of the degree of polymerization of the silicate framework.

At longer scales, atomic organization is controlled by the relative amounts of silicon and other metal cations since the manner in which coordination polyhedra are connected depends on the overall Si/O ratio of the material (Fig. 5). In pure SiO_2, all SiO_4 tetrahedra polymerize to form an open, three-dimensional network in which each oxygen is bridging (BO), i.e., is shared by two neighboring tetrahedra. At the other end, one finds isolated SiO_4 tetrahedra where all oxygens are nonbridging (NBO). Between these two extremes, the number of nonbridging oxygens per silicon atom (NBO/T) increases from 0 to 4. This number is an average value that characterizes the degree of polymerization of the silicate framework. Since oxygens are either bridging or nonbridging, the various kinds of SiO_4 tetrahedra may be distinguished by their relative proportions in such a way that a Q^n-species designates an SiO_4 tetrahedron in which n oxygens are bridging and 4-n are nonbridging (Fig. 5).
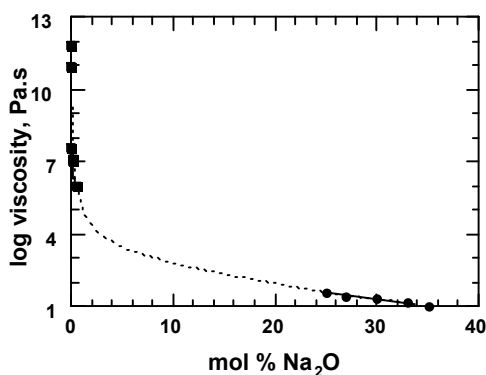

Figure 6: Viscosity decrease due to addition of Na_2O to SiO_2 at 1200°C [3, ch. 6]. Note the 10^{11} viscosity decrease from 0 to 35 mol % Na_2O in this logarithmic scale.

The glass-forming ability of a melt is directly related to the distribution of its Q^n-species. In silica-rich compositions where Q^3- and Q^4-species predominate, the average size of the structural entities is large and the microscopic rearrangements needed to produce the ordered atomic structures of crystals are difficult so that crystallization may be easily by-passed. In silica-poor melts where Q^0- and Q^1-species predominate, the microscopic entities are small and rearrange easily. Glass-formation then is impossible or would require extremely rapid cooling of very small samples of little industrial interest. Correlatively, the viscosity varies in a similar way. At a given temperature, it strongly decreases with decreasing SiO_2 content and decreasing proportion of bridging oxygens but the effect is markedly nonlinear. For Na_2O-SiO_2 melts (Fig. 6), a few mol % Na_2O first lowers viscosity by 8 orders of magnitude whereas an additional 30 mol % reduces it by a comparatively small factor of 1000.

The last point to be emphasized in this section is that coordination polyhedra of a given element are not identical, as they are in a crystal, but show the definite variations of both sizes and shapes that are necessarily associated with the characteristic disordered nature of liquids. This is probably the single most important feature that accounts for the specific properties of glass. If a glass piece can be given any shape, regardless of its size,

it is because its structure represents the frozen-in disordered polyhedral arrangement of the melt. And if a great many different elements can be accommodated in a wide range of proportions, it is because the size and shape distributions of their coordination polyhedra make it possible to fill up space completely through mutual adjustment of such differing polyhedra.

Figure 7: Part of a Roman glass ingot from les Embiez shipwreck, Côte d'Azur, still very fresh after 18 centuries spent in sea water [8]. This glass was likely made near Alexandria where the existence of natural ores of sodium carbonate gave a definite competitive advantage to local glass makers [9]. These exported ingots as well as finished products throughout the whole Mediterranean area, and even in Western Europe, where glass was extensively recycled, remelted and blown again, but not produced from raw materials before the third part of the first millennium [10].

4. Color and glass composition

The compositions of a few types of glasses are given in Table 1. This list is certainly not comprehensive because the composition is adjusted for every special application with a number of oxides which are not considered here. Most commonly, however, glass is primarily made from two natural substances, silica (SiO_2) and limestone ($CaCO_3$), and a synthetic product, sodium carbonate (Na_2CO_3), which mutually react at high temperatures to melt and expel the CO_2 of the two starting carbonates. These *soda lime* compositions are extensively used for making flat glass for windows and hollow glass for bottles. Interestingly, their compositions are strikingly similar to that of Roman ingots found in a shipwreck from the 3rd century near les Embiez (Côte d'Azur) [8] and, more generally, resemble those of a great many glasses made from Antiquity to the middle ages.

This similarity is of course not fortuitous, but the result of an early, complex optimization process that took into account the price and availability of raw materials, the cost of melting and the properties of the glass itself. The first two factors led to soda lime compositions, the last two to the particular composition range actually selected. Glass formation is for instance easier in the Na_2O-SiO_2 system, where melting temperatures are in particular much lower, but the glasses obtained are so hygroscopic that they react rapidly with atmospheric water and even transform, for the most Na_2O-rich glasses, to a sodium silicate solution in a few hours. Calcium is thus needed to

stabilize the product, but in moderate amounts otherwise melting temperatures would increase too much and glass formation would in addition become difficult.

Table 1: Compositions of a few glasses in wt % [3, ch. 1]. For Flat display panel glass, add 4.4 % BaO, 1.2 % SrO and 0.3 % Sb_2O_3.

	SiO2	Al2O3	FeO	Fe₂O₃	MgO	CaO	Na2O	K2O	B₂O₃	TiO₂
Roman (les Embiez)	72.7	1.8			0.4	5.2	19.0	0.4		
Window glass	72.6	0.6	0.8		3.6	8.7	14.3	0.2		
Pyrex	81.1	0.4	0.2		0.3	1.1	1.5		22.0	
Reinforcement	56.5	14.3	0.5		2.6	18.4	0.4	0.4	6.4	0.6
Glass wool	65.0	2.5			2.5	8.0	16.5	0.7	4.5	
Rock wool	46.6	13.3	4.8	6.4	9.1	10.0	5.6	1.4		2.4
Flat Display Panel	69.0	11.5			1.4	5.0			7.3	

The almost infinite diversity of hues is the most ancient illustration of the ability of glass to accommodate different chemical elements. In the visible range of electromagnetic radiations, the absorption of light by soda lime glasses is practically negligible. Transmission is higher than 90 %, the loss being mainly due to reflection at the glass surfaces. That glass remained colored to the point of being opaque during more than two millennia was due to impure starting materials. At an early time where glass makers were producing only beads and other jewels, they had thus been able to color glass long before to mold it. How they figured out that glass could be made not only translucent, but also transparent is unknown. But the difficulties to be overcome to achieve such a goal were formidable owing to the extremely strong coloring power of elements that could be ubiquitous in raw materials. Cobalt oxide, for instance, gives a strong blue hue at contents of 0.01 wt % and is already visible at amounts that are 5 times lower. Although iron is less efficient, its natural abundance is so much higher that it is always present at some level in the starting materials. In side view, this is why iron still gives a characteristically green hue to modern window glass.

Color actually results from different kinds of interactions between matter and light. The most common is absorption of light which takes place in two different ways. At wavelengths within the narrow 400-700 nm range (1 nm = 10^{-9} m) of visible radiations, there exist transitions between electronic states of a given cation as well as electron transfer to a given cation from an anion (besides oxygen, O^{2-}, sulfur, S^{2-}, or selenium, Se^{2-}, when these elements are added). Without delving in the details of these processes, which are rather well understood [11], it will suffice to say here that coloring elements are generally present at low concentrations in glass either as the aforementioned anions or as cations such as Co^{2+} (blue), Ni^{2+} (brown), Fe^{2+} (blue), Fe^{3+} (dark yellow), Cr^{3+} (green in the coordination polyhedra they form to optimize their bonding with anions. When coloring elements are present in a given glass matrix, they absorb light in proportion to their concentration so that it is possible to calculate the resulting transmission as a function of wavelength and, if the sensitivity of the eye is taken into account, to determine also the color as it will be seen.

Such calculations are extensively made in industry to design glass color. Examples are shown in Fig. 8 for cobalt, iron and selenium in window glass. The blue color of cobalt is due to a broad absorption band centered on 600 nm. The role of iron is more complex because this element exists in two different valence states. Ferrous iron (Fe^{2+}) gives a blue hue because it absorbs light in the near infrared whereas ferric iron (Fe^{3+}) undergoes charge transfer with oxygen in the near ultraviolet and thus yields a dark yellow tint. In glass, the proportion of these two cations depends on total iron content, melting temperature and on the oxidizing or reducing conditions prevailing during the melting process. Usually Fe^{2+} is between three and four times less abundant than Fe^{3+} with the result that iron-bearing glasses are slightly green. As for selenium, its brown hue also results from charge transfer, a process whose general effectiveness is illustrated by the important effect observed even at very low concentrations.
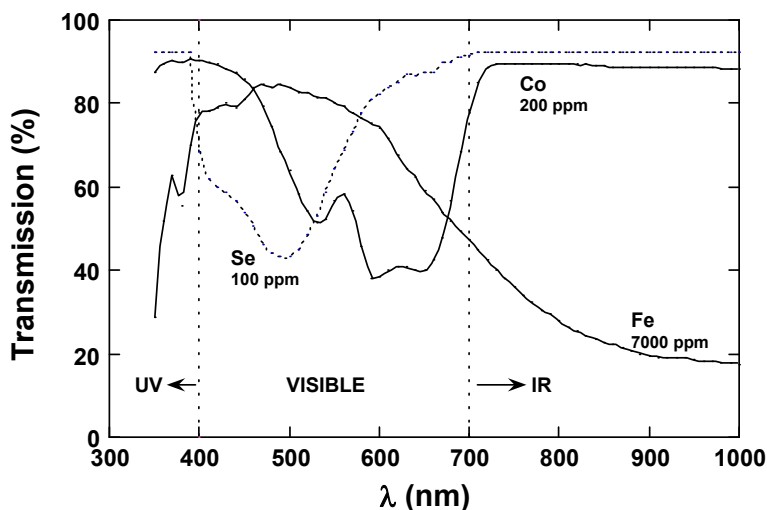

Figure 8: Calculated transmission in the visible range of 4-mm thick window glass doped at the indicated levels (1 ppm = 10^{-6} wt %) with Co^{2+}, Se and Fe with a redox ratio $Fe^{2+}/(Fe^{2+}+Fe^{3+}) = 0.3$. The ultraviolet and infrared ranges lie below 400 and above 700 nm, respectively.

Even when an element dissolves as a single species the color it yields may vary because the size and shape of its coordination polyhedra and, thus, its electronic energy levels, are affected by the nature and proportion of the other ions. The shifts of the absorption wavelengths with varying glass composition are no major but, given the narrowness of the range of visible radiation, they may translate into significant color changes. Nickel is a case in point. Its color is brown with sodium and calcium, but purple with potassium and yellow with lithium, an effect that is usually assigned to a change from primarily tetrahedral to octahedral coordination from potassium to lithium systems. Another complication has to be taken into account when several elements have at least two valence states. In this case, a reaction will take place during melting, modifying the

initial valence state of each element. If manganese is for instance introduced as MnO_2 in an iron-bearing glass, the Mn^{4+} ion reacts with 2 Fe^{2+} to yield Mn^{2+} and 2 Fe^{3+}. Such reactions have of course to be taken into account when predicting glass color from the individual absorption coefficients of cations to make sure that their actual, and not nominal, concentration is used.

5. High-temperature reactivity

To end this short review we will consider an aspect quite different whereby the specific functionality of a glass is designed to be activated under the conditions of its use. The example of fibers for high-temperature protection will illustrate this point. First note that glass wool is totally inappropriate for this purpose because under fire conditions the glass will not only soften but sinter as a result of interfacial forces. Hence, the initial material with a density of a few tens of kg/m^3 will either flow or transform to a piece of hot glass of density higher than 2 tons/m^3. The problem is then to find compositions for glass fibers which allow thermal insulation under usual conditions but are able to sustain temperatures accidentally higher than at least 700°C without losing their insulating properties.
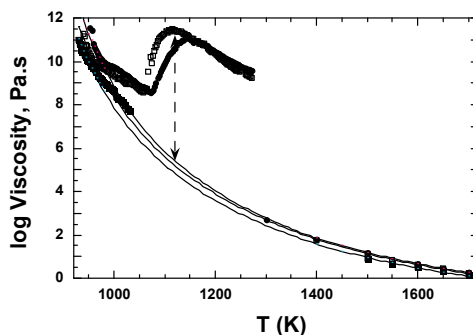

Figure 9: Increases of viscosity of basalt melts on heating due to partial crystallization of the material [12]. The monotonous curves extending to high temperatures show the viscosity decreases that would obtain if crystallization were not taking place. N.B. T (K) = T (°C) + 273.

It happens that glass fibers made from calcium aluminosilicate composition closely related to the basalt volcanic rock do satisfy these constraints. Instead of softening, the material show anomalous variations of viscosity beginning at about 600°C and causing an excess of 6 orders of magnitude at temperatures of about 1000°C (Fig. 9). These abnormal variations imply the existence of a transformation within the material which appears to be partial crystallization of the fibers. This is actually a two-step process, in that a mineral named spinel first precipitates (with compositions intermediate between $MgFe_2O_4$, Fe_2TiO_4 and $FeAl_2O_4$), and then induces crystallization in greater amounts of another well-known mineral, pyroxene, whose composition is unusually poor in SiO2 and rich in Al_2O_3. These two kinds of crystals are readily recognized by Transmission Electron Microscopy (Fig. 10). They have a dual role, inhibiting sintering because they form at the surface of the fibers, and providing the fibers with a rigid framework that prevents them from deforming and flowing at high temperature.
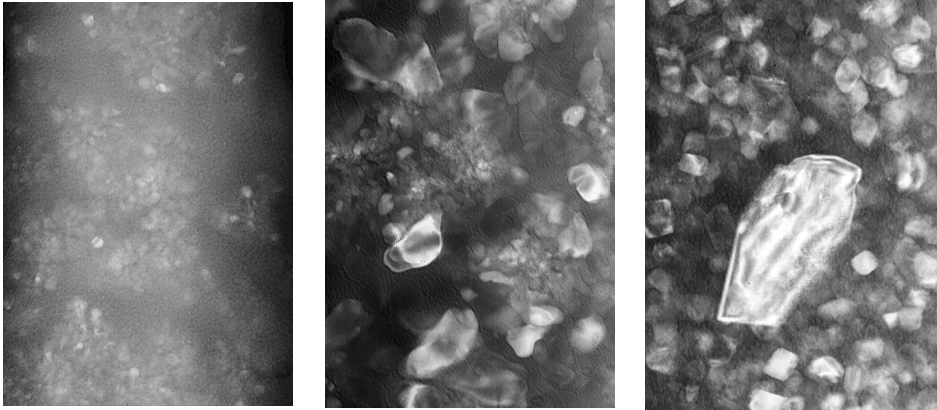
Figure 10: Development of crystallization and increasing crystal size with increasing heating temperature in basalt fibers after heating to 720°C (a), 820°C (b) and 1020°C (c) as seen in Transmission Electron Microscopy [12]. Two kinds of crystals are clearly distinguished in (b) and (c), namely, large spinels and small pyroxenes. Panel widths: 0.5 micron.

Production of such basalt fibers is no longer pursued because of largely unjustified concerns over their biosolubility, but new compositions have been devised and efforts are being made to improve further the properties of these new products. By fine-tuning the glass composition, it is in effect possible to modify the nature and composition of the crystals that form in such a way that they will allow fire protection at higher still temperatures. This example also illustrates the complexity of the optimization that is behind the development of such new materials. For instance, fibers must now be biosoluble to dissolve in lungs, but resistant to weathering under the conditions of their use. The melt must be produced at temperatures as low as possible, its viscosity must be in a narrow range to allow the fibers to be drawn, its reactivity with the superalloy metal plates used for drawing must be minimal and, of course, crystallization must be by-passed before the fibers are drawn. It is no surprise that such constraints often tend to be mutually contradictory and can induce higher production costs. Optimization would thus be problematic without a good understanding of the various physical and chemical processes involved.

Conclusions

In view of its bewildering diversity of uses, glass has found quite new applications in buildings throughout the 20th century. Its transparency and the possibility of forming large panels that withstand meteorological conditions and are readily cleaned remain fundamental assets. Even for such applications, however, new functionalities have been obtained through physical or chemical treatments of glass surface. There is in fact no reason why the complex physical chemistry of glasses and melts should cease to be exploited to create new products and improve existing ones. High-temperature reactions of glass surfaces with reducing atmospheres could for instance yield new properties of practical interest [13]. And work is currently done on reactive systems such as variable glass transparency to prevent warming in summer or cooling in winter. Other progress will be made through association of glass with other materials such as organic polymers, as already practiced in laminated glass. As to the environmental constraints and the

needs to develop renewable sources of energy, they should give an additional impetus to new products and new functionalities of interest to the building industry. The resources of the vitreous state have certainly not been exhausted yet. Combinations of experimental, theoretical and modeling work will make good use of them.

6. Acknowledgements

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