GLASSES A MATERIAL OF YESTERDAY, TODAY AND TOMORROW

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Abstract. Glasses play a fundamental role in our daily lives, both economically, culturally, socially, energetically and geologically. Geological glasses bear witness to the Earth's igneous activity and represent an important source of tools and ornamental objects from the Paleolithic to the present day. Today, glasses are also used to manufacture technical materials, such as containers (dishes, drinking glasses, jars, carafes, etc.), screens (television, computer, smartphone, etc.), fibers with multiple applications (reinforcement, information transport, energy, health, etc.), to ensure the storage of domestic or nuclear waste and, more recently, biomaterials (dental or bone implants, etc.). Consequently, silica-based glasses are at the heart of the history of the Earth and humanity. The variation in composition of natural and industrial glasses is vast but its structure is generally based on a tetrahedral framework of SiO4 units, the backbone of more than 90% of the glasses that surround us in our daily lives. Around this silica framework, the other chemical elements are divided into network modifiers, charge compensators, dyes, volatiles, and the whole constitutes a material or substance each time unique. This article proposes to review the links between the structure, properties and chemical composition of glasses, essentially based on silicate.

Key words: glass, structure, properties, fibers, crystalline.

Introduction. Glass is a homogeneous material that can be formed from all elements of the periodic table and all types of chemical bonds. This material is distinguished from other states of matter (crystalline solid, liquid, gas and plasma) firstly by its solid state characterized by an absence of long-range order and, secondly, by the presence of a second-order transition, called glass transition. The reader will find a comprehensive and recent publication on all families of glasses and their properties in the recently published Handbook of Glass. In this article, we will simply present some general concepts, accepted by the entire scientific community and taught in universities and engineering schools. A glass is an amorphous solid. The term solid implies a high viscosity, generally greater than 1011 Pa.s. This viscosity limits the flow of the body. The term amorphous implies the absence of long-range order which reveals an analogy with the liquid state. A glass is therefore a solid whose properties are close to those of liquids. Parks and Huffman even speak of "a fourth state of matter" [2]. The glass state can occur for many chemical compositions as long as the crystallization phenomenon is avoided. There are mineral glasses and other common glasses, glasses of oxides, salts, aqueous solutions, metallic, organic glasses such as gels, caramels, candies, etc. In fact, it is possible to obtain glasses regardless of the type of chemical bond: covalent, ionic, metallic, Van der Waals or hydrogen. The glass state therefore corresponds to a characteristic of condensed matter and there can be an infinite range of chemical compositions of glasses, each having its own structure. As we will see, each of them, individually, can be defined as a material or substance in its own right with its own physical and chemical characteristics such as the glass transition temperature, Tg, an X-ray diffraction pattern or a Raman spectrum, an elemental chemical analysis, a density, a refractive index, etc. Many preparation methods make it possible to obtain an amorphous material. The latter is generally produced by rapid cooling of a liquid phase, but it is also possible to obtain them from a gas phase, by amorphization of a crystalline phase or by sol-gel methods [3]. The most classic method of forming a glass is the freezing of a liquid during rapid cooling (called quenching). During the cooling of a liquid, a continuous increase in viscosity is observed up to a value such that the material can be considered a solid. We can therefore imagine the structure of the glass as being similar to that of a liquid in which all atomic movements would be blocked. Glasses, like liquids, have a disordered structure with only short- and medium-range order. For example, silica, a glassy phase, is made up of SiO4 tetrahedra, linked together by an oxygen atom but without long-range periodicity of the network, unlike crystals. The oxygen atom connecting two silicon atoms is said to be bridging.

Unlike the case of a crystallized solid, we cannot speak of a melting temperature for a glass. Conversely, the solidification of a glass corresponds to a continuous and progressive increase in viscosity during the cooling of a liquid, without the appearance of a crystalline structure. There is no break in the viscosity curves between the values obtained at high temperature and those at low temperature. This clearly shows the continuous transition from glass to liquid for a property such as viscosity. The glass transition, defined by its temperature Tg, is a kinetic phenomenon that characterizes the loss of internal thermodynamic equilibrium. Indeed, the properties of a glass no longer depend solely on pressure and temperature, but also on the speed, |q|, at which the glass transition occurs.

Conclusion

The simplest and oldest characterization of this transition is due to Parks and Huffmann [4]. They note from Nernst (1911) that on heating a glass, "it passes continuously from the amorphous to the liquid state, its properties changing regularly with temperature, without any discontinuity." In fact, as they write, "while there is no precise temperature comparable to the melting point of a crystal, there is nevertheless a distinct and reproducible temperature range over which many properties change with a rapidity approaching that observed in the melting of a crystal. In short, there is a softening range instead of a melting point. The glass as it exists below this softening range differs so markedly from the liquid which exists above it that it may well be considered a different state of the substance."

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