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High resolution electron microscopy observations of microcrystalline phases in silica glass

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Abstract. We report high resolution transmission electron microscopy observations of pure silica glass. The sample showed microcrystalline regions which were identified as α-cristobalite, a low temperature form of SiO_2. The results, besides the importance of the presence of microcrystals, show the feasibility of performing atomic resolution-level microscopy in glasses.

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1. Introduction

The detailed study of the microstructure of silica glasses is interesting for a number of reasons. First of all, from a basic science point of view, the microscopic origin of the properties of glasses has been an open question for many years. On the other hand, there exist technological problems related to the crystallization of vitreous silica which demand a complete understanding of the atomic structure of glasses.

One big problem in studying SiO_2 is its property of forming not less than 22 structural modifications [1] from the perfect quartz to the almost completely disordered silica-M. In many practical cases, two or more of such modifications coexist forming an extremely complicated structure.

The extended industrial use of silica glasses has produced different kinds of glasses with distinct properties and uses. Commercially available glasses are fabricated from natural quartz by electrical or flame fusion or by hydrolization of $SiCl_4$ by various industrial methods [1]. Recently, the possibility of employing the so-called sol-gel method in an extended form has been explored for some authors [2–4]. Most industrial processes, however, produce bulk glass with a number of inhomogeneities in the supposed-to-be amorphous structure, since small crystallites have been observed by different means in the past [5–7]. Technologically, the high temperature use of silica glasses is strongly limited by crystallization and a better understanding of the conditions, under which small cristallites are formed in a glassy matrix, would result extremely valuable.

One of the most common sources of inhomogeneities in vitreous silica is an imperfect cooling from the melt. This produces internal stresses that give raise to small inhomogeneities. In particular, the presence of α-cristobalite in certain types of vitreous silica when heated for long periods has been reported in the literature [8]. Also, as was pointed out in a previous report [7], micro-inhomogeneities in several commercial high-purity silica glasses were consistently found by electron microscopy and identified by electron diffraction as corresponding to α-cristobalite, the structure of which belongs to a tetragonal space group. In the present work, further evidence of microcrystalline inhomogeneities in different fused-silica glasses is presented. Also, high resolution electron microscopy of the observed samples allows us to obtain a better insight of the atomic structure of a α-cristobalite microcrystals, and their formation in a glass matrix.

2. Experiment

In this work, Vitreosil (trade mark of a fusion-fabricated glass) samples were prepared for Transmission Electron Microscopy (TEM) analysis. Glasses were pulverized in a common laboratory mortar and pestle, and the powders, containing glass particles ranging from few μm to several hundreds μm in size, as seen in the electron microscope, were ultrasonically dispersed in water in order to obtain uniform suspensions. A drop of the suspension was dried on a carbon film, which was previously deposited onto an electron microscope grid. The effects of electrostatic charging, characteristic of glass specimens, were avoided by carefully dispersing the glass particles on the grids, and, when necessary, by evaporating a small amount of amorphous carbon onto the glass-containing microscope grids.

The TEM observations were carried out in a 300 keV machine (Philips 430). The condenser lenses current was kept in such a way that no radiation damage to the specimens was detected during the TEM analysis. As it is known [9], one of the types of microstructure that arise in silicate glass from electron irradiation is the formation and growth of oxygen-filled gas bubbles, effect not observed in our experiments in any case.

On the other hand, it is important to remark that the use of higher voltages in Electron Microscopy is known to reduce the damage to this kind of materials, since the cross-section values for electrons decreases as the aceleration voltage increases.

3. Results and discussion

Small crystalline regions, tipically in the 700–800 Å range, were found in the Vitreosil samples. Figure 1 shows a low magnification micrograph of a Vitreosil specimen demonstrating again the presence of crystallites embedded in the amorphous matrix. Selected Area Electron Diffraction (SAD) was performed in all

the samples which revealed the cristallites, using a very small SAD aperture to assure that the recorded diffraction pattern corresponds only to the crystallites area. The analysis of the diffraction data has been reported elsewhere [7] and the microcrystals were identified as α-cristobalite.

FIGURE 1. Low magnification TEM micrographs showing a rather large microcrystal in the amorphous structure of a silica glass sample. Notice the regular shape of the cristallites.

Some previous reports on direct observation of glass structure have been strongly criticized, because the preparation of glass specimens suitable for TEM work (thinning, grinding, etc.), usually involve superficial atmospheric attack and its is impossible to make any definitive remark regarding the observed features. In our case, none of the reported artifacts due to the preparation techniques [6] was detected in any case. Also, some defocusing experiments were carried out to assure that the observed crystallites are not small crystal particles on the surface of the glass specimen, but part of the bulk structure. It is also important to point out that the crystalline regions were always found in small proportions in the Vitreosil samples, and never forming big agglomerates.

Another interesting fact observed in the micrograph of figure 1 is that it shows a highly regular crystallite. This result agrees with some earlier reports on the crystallization kinetics of cristobalite in fused silica [8], in which the formation of regular morphologies was observed. In some other cases, however, the crystalline regions are formed by very small crystallites in different orientations, as can be observed in figure 2 (arrows). Thus, what probably happens is that, as a result of the stresses developed during cooling, some nucleation centers are formed and small crystallites are developed. As the glass is further cooled from the crystallization temperature, the coalescence of the microcrystallites forms bigger

crystals that, in some cases, can be observed by optical microscopy [8]. According with this hypothesis, the bigger crystals would present a number of lattice defects (twins, for example) due to the mismatch of the microcrystallites. There is some support for the later, since a high density of twins has been reported previously in similar samples [10].

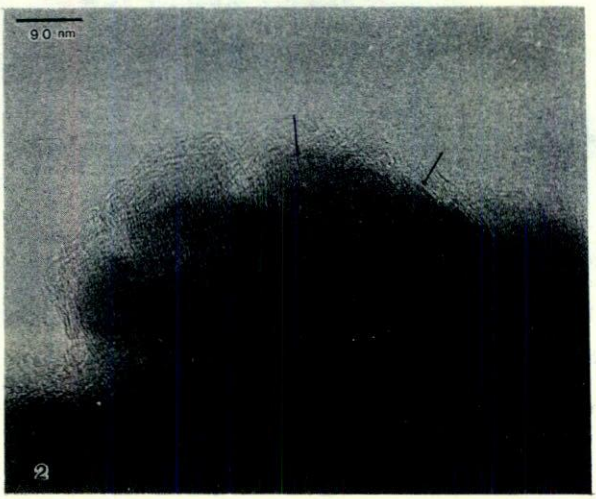

FIGURE 2. TEM picture demostrating several microcrystalline domains (arrows).

On the other hand, the atomic structure of α-cristobalite has been widely studied in the past [10], mainly by X-rays analysis, and there is agreement in the corresponding space group being the $P4_12_1$. However, due to the difficulties in preparing suitable specimens, very little has been done by TEM, in particular at higher levels of resolution, besides the strong charging problems due to the insulating nature of the glass. In order to carry out some high resolution observations, a 400 μm objective aperture was used to produce the image, and all pictures were taken under axial illumination conditions. The nominal aberration coefficient Cs for the microscope used in this work is 1.2 mm. The average thickness of the regions used for high resolution imaging was of the order of a few hundreds of Å.

One big problem in interpreting high resolution images is the evaluation of the contrast in a picture. According to the projected charge approximation [11], for example, the contrast in a high resolution micrographs is proportional to the projected total charge density and to the focusing error. Figure 3, for example, shows fringes with 3.5 Å spacings which correspond to the (1 1 0) planes of the α-cristobalite tetragonal structure. This result demonstrates the feasibility of imaging the glass structure to the atomic level, despite the charging effects and the low ilumination level in the microscope screen used to minimize damage to the

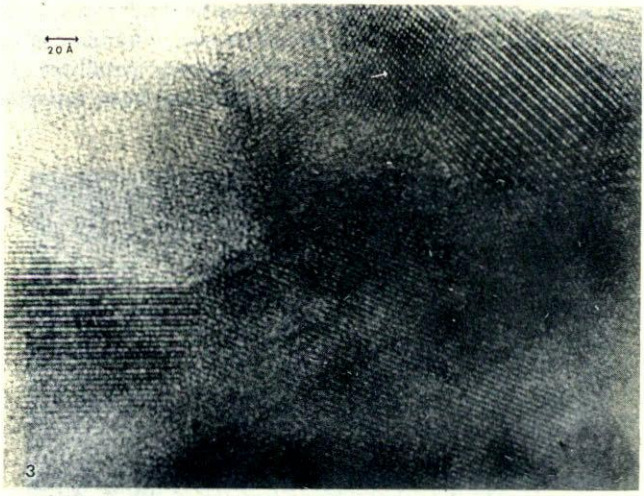

FIGURE 3. High Resolution micrographs showing the lattice structure of the tetragonal structure of a α-cristobalite microcrystal embedded in the glass structure. The arrows point to some dots which correspond to the atomic arrangement of the α-cristobalite.

samples. The fine features (the dots pointed by the small arrow in the picture) in the fringes can be probably identified as corresponding to the arrangement of the silicon atoms in the α-cristobalite structure, according to the projected charge approximation, since the mean thickness of the glass particles was estimated to be of 150 Å or less, so the visualization of atomic positions would result possible for the described conditions.

Some of the contrast changes observed in figure 3 could be attributed to focusing changes due to thickness variations on the samples. However, further TEM work, including computer simulations, must be done in order to fully understand all the details in the high resolution pictures.

4. Summary

Further evidence of α-cristobalite microcrystals in fused silica was presented. Also, the possibility of performing high resolution TEM work in glasses has been established with the results shown in this work. The last point could represent an important contribution for future studies of the microstructure of glasses, since the use of TEM techniques allows the researcher to obtain information out of very small areas, the structure of which could explain some macroscopic phenomena in vitreous materials.

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Resumen. Se detectaron microcristales en vidrios de SiO_2 puro por medio de microscopía electrónica de alta resolución. Además de la importancia de esta observación, que se discute en el texto, el presente trabajo demuestra la posibilidad de analizar la microestructura de vidrios con un alto grado de resolución.