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Ph. Jonnard[1,a], J.-P. Morreeuw[2], and H. Bercegol[2]

[1] Laboratoire de Chimie Physique-Matière et Rayonnement, Université Pierre et Marie Curie, UMR-CNRS 7614,
11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
[2] CEA/CESTA, BP 2, 33114 Le Barp, France

Abstract. The physico-chemical environment around the aluminum impurity atoms in commercial Herasil silica is studied by electron-induced X-ray emission spectroscopy. Despite the low concentration of aluminum and the charging effect occurring upon electron irradiation, we have been able to characterize the environment of the Al atoms. We show that the Al atoms are in an octahedral environment, *i.e.* surrounded by 6 oxygen atoms. The presence of Al clusters, whose metallic character would make them candidates to be ultraviolet absorption centers, is ruled out.

PACS. 78.70.-g Interactions of particles and radiation with matter – 78.20.-e Optical properties of bulk materials and thin films – 71.55.Jv Disordered structures; amorphous and glassy solids

1 Introduction

The identification of absorption centers in silica (SiO_2) glass is of major importance. Indeed, high quality silica glasses are used for their optical properties in high power ultraviolet lasers. They are essential for lasers that are now under construction like MégaJoule [1] and NIF [2] facilities. Because of the high peak power density (>5 GW/cm^2) and fluence (>12 J/cm^2) involved in the laser transport line of these experiments, even a low concentration of defects can produce damages in the optical systems. In this work, we focus on aluminum impurity in amorphous silica.

2 Experiment

2.1 Sample

The glass sample is a commercial Herasil silica polished to an optical finish, with a bulk Al concentration of 10–50 ppm in weight. A superficial layer of a few μm was removed by etching, *i.e.* by dipping one face of the sample in HF 40% for 5 min. Thus, it is expected that any contamination left by the alumina powder used in the polishing process would be removed by this etching. Herasil silica is one of several possible materials in Mégajoule optics. It

has been chosen in this study because of its relatively high impurity concentration.

2.2 EXES

In electron-induced X-ray emission spectrometry (EXES) [3], the sample is irradiated by an electron beam, causing the ionization in the core shells of the atoms. Photons are emitted during the radiative recombination of the ionized atoms. The transitions can take place from another core level or from the valence band, leading to the emission of characteristic X-rays giving rise to spectral lines or bands, respectively. Because of the local character of the core hole involved in the transition and of the dipole selection rules, the observed spectral densities depend on the element and on the symmetry of states.

Because of the low aluminum concentration, we selected for the analysis the most intense emission of the Al spectrum. It is the Al $K\alpha_{1,2}$ doublet (transitions $2p_{3/2,1/2} \rightarrow 1s$, around 1487 eV). The position of the maximum of this emission is sensitive to the physicochemical environment around the Al atoms [4]. The X-ray spectra are registered with a high resolution wavelength dispersive spectrometer [5], using a quartz ($10\bar{1}0$) crystal at the first reflection order. In our experimental conditions, the relative spectral resolution $E/\Delta E$ is about 5000.
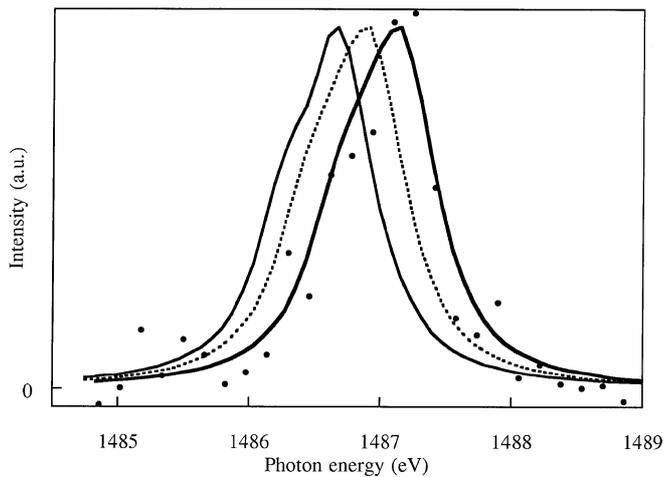
[a] e-mail: `jonnard@ccr.jussieu.fr`

Fig. 1. Al $K\alpha_{1,2}$ emission of Al in silica glass sample (dots). Comparison with reference spectra: Al metal (thin solid line), Al in octahedral environment (thick solid line) and Al in tetrahedral environment (dashed line).

The conditions of the electron bombardment were: energy of 8 keV and current density of 1 mA/cm^2. Note that this electron current density is much lower than that used in classical electron probe microanalysis (typically 1 nA in a 100×100 nm^2 spot, *i.e.* 10^4 mA/cm^2). The electron beam forms a 1 cm diameter spot on the sample. The spectra were accumulated during about 1 h. The total duration of the experiment was 2 days. Because of the charging effect occurring with this insulating sample, some spectra were disturbed by large intensity variations. These spectra were rejected and the presented spectrum results from the accumulation of 13 spectra obtained under stable conditions. Note that the energy of the emitted photons is not sensitive to the charging effect.

The analysed thickness is estimated to be 500 nm, by using a semi-empirical simulation model dedicated to the simulation of the generation of the characteristic X-rays under electron irradiation [6,7]. Due to the charging effect, one expects this value to be an upper limit, because the trapped electrons inside the sample produce an electric field which slows down the electron beam [8]. This prevents the use of the intensity measurement, as is conventionally done in electron probe microanalysis, to quantify the Al concentration in the silica.

3 Results and discussion

We present in Figure 1 the Al $K\alpha_{1,2}$ emission from the aluminum impurities in the Herasil sample. The background emission has been subtracted. The full width of the peak at half maximum is 0.93 ± 0.06 eV and the position of its maximum energy is at 1487.16 ± 0.10 eV. This emission is compared to reference spectra of aluminum metal and aluminum in two different oxide environments. The spectra are normalized with respect to their maximum.

For the metal, the peak's width is 0.86 ± 0.03 eV and its maximum energy is 1486.71 ± 0.03 eV. Two oxides

have been studied: the α-alumina where all the aluminum atoms are in octahedral environment (surrounded by an octahedron of oxygen atoms) and a poorly crystallized γ-alumina where the aluminum atoms are both in octahedral and in tetrahedral environment (surrounded by a tetrahedron of oxygen atoms) [9]. The width and maximum energy for the α-alumina sample are respectively 0.92 ± 0.04 eV and 1487.15 ± 0.03 eV. Concerning the γ-alumina, the Al $K\alpha$ spectrum can be decomposed into the sum of two doublets, one corresponding to that of the α-alumina (Al in octahedral environments) and another corresponding to the Al atoms in tetrahedral environment. For this last environment, the width is 0.92 ± 0.05 eV and the maximum is located at 1486.91 ± 0.04 eV. These positions of the maximum for the octahedral and tetrahedral sites are in agreement with the previous determination as a function of the coordination of the Al atoms in a series of compounds [4].

From the energy position of the Al $K\alpha_{1,2}$ line characteristic of the impurities in the glass, the presence of metallic Al in Herasil can be ruled out. From the energy position and the width of the observed spectral density, it can be concluded that more than 90% of the Al atoms are in octahedral environment and the rest could be in tetrahedral environment. Indeed, because of the counting statistics, a weighted sum of the doublets corresponding to the octahedral and tetrahedral environments would lead to a reasonable fit of the Herasil spectrum, provided that the tetrahedral contribution is less than 10%. In the case of a tetrahedral environment, the Al atoms would be in substitution of the Si atoms. It seems more reasonable to think that the aluminum impurity atoms are located in insertion positions, inside the large voids of the silica glass structure. Indeed, the local structure (over a 1 nm length scale) of amorphous silica has similarities with that of the β-cristobalite [10]. In the voids surrounded by oxygen octahedrons of such a structure, the aluminum atoms would have an environment close to that they have inside the α-alumina, in term of Al-O bond length and O-Al-O angle.

4 Conclusion

The physico-chemical environment of the Al impurity atoms in a Herasil glass has been studied by EXES. Within the analysed thickness, the presence of aluminum metallic clusters, which would be candidates for absorption in the ultraviolet can be ruled out. From the position of the Al $K\alpha_{1,2}$ maximum, it is deduced that the major part of the Al atoms are in octahedral environment, *i.e.* each surrounded by 6 oxygen atoms.

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