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OXYGEN K EDGE AND LOCAL STRUCTURE OF AMORPHOUS SiO_2

A.Gargano[x], M.Benfatto[*], A.Bianconi[o], P.Chiaradia[*], I.Davoli[+], M.Fanfoni[o], J.Garcia[o§], A.Marcelli[*] and C.R.Natoli[*]

(x) ENEA, CRE-Casaccia, TIB, Divisione Scienza dei Materiali, 00060 Casaccia, Italy
(o) Dip. di Fisica, Universitã "La Sapienza" di Roma, 00185 Roma, Italy
(+) Dip. di Matematica e Fisica, Universitã di Camerino, 62032 Camerino, Italy
(*) INFN-PULS and CNR, Laboratori Nazionali di Frascati, 00044 Frascati, Italy
(§) Permanent address: Dept. of Thermology, Univ. of Zaragoza, Spain

We report the results of the investigation of the oxygen K-XANES (X-ray absorption near edge structure)[1] spectra of crystalline and amorphous SiO_2. In a previous work the Si tetrahedral site in amorphous SiO_2 layer has been studied by Si L-edge[2]. Here, by measuring the oxygen K-edge spectra, the oxygen site structure is investigated. In fact, by multiple scattering processes, XANES probes higher order correlation functions of atomic distribution around the absorbing atom. Our preliminary results show the sensitivity of XANES to bond angle and bond distance variation at the oxygen site in a "natural" and a suprasil silica glasses.

The oxygen soft X ray absorption spectra of quartz and of silica glasses have been measured at the Frascati "Grasshopper" beam line. The absorption cross section has been measured by partial electron yield technique. The secondary electrons emitted at 2 eV kinetic energy are selected by a cilindrical mirror analyser and their intensity as function of the photon energy is measured. The crystalline and amorphous samples were held in an ultra-high vacuum system and the spectra were recorded on untreated samples and on surfaces sputtered by argon ion beam.

In Fig. 1 we show the XANES spectra of quartz crystal, of the natural and of Suprasil silica glasses. The oxygen K XANES shows in all spectra a weak shoulder on the rising absorption edge, a main line with a shoulder on its high energy side and a broad resonance at about 21 eV above the main line. We show here the spectra of sputtered samples. There is a variation going from the crystal to the glass spectra concerning the intensities of the main line and of the resonances at higher energy.

The XANES spectra have been interpreted using the multiple scattering

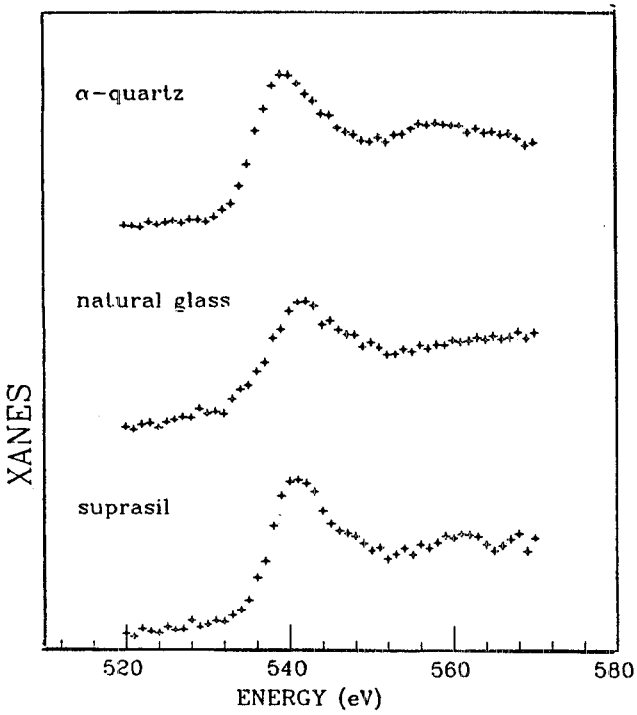

Fig. 1 - Oxygen K-XANES of α-quartz, of "natural" silica glass and of suprasil WII.

theory[3] for a small cluster formed by the central oxygen atom and two neighbouring Si atoms with different Si-O-Si bridging bond angles. In the energy region where the expansion of the cross section in terms of contributions of multiple scattering pathways which begin and end at the oxygen site (classified according with the number of scattering events n=2(EXAFS),3,4,..) is possible, the total cross section a_t can be factorized into

$$a_t = a_o(1 + \Sigma_n \varkappa_n) \ .$$

The total a_t, the atomic absorption coefficient a_o and the partial contributions $\varkappa_n$ for n=2,3,4,5 have been calculated for several configurations. The theoretical spectrum for a simple Si-O-Si collinear cluster shows that the higher order contributions (n=3,4,..) are very important up to high energy because of strong forward scattering but they are neglected by cancellation effect for a destructive interference. The spectrum shows only one bound state which appears as a weak shoulder on the low energy side of the main line observed also in the experimental data. The main line is a multiple scattering resonance in the full multiple scattering regime below the energy limit E_c=0.4 Ryd, above which the expansion is possible. The calculations of the total absorption coeffi-

cient for a set of clusters with different bridging bond angles have been performed. Going off collinear configuration the destructive interference effect is suppressed. Two multiple scattering resonances (MSR) appear. Theory shows that bridging bond variation induces a change on the intensities of multiple scattering resonances. The effect of bond distance changes are very strong on MSR[4,5] and a blue shift of 1 eV for 0.02 Å contraction of the Si-O distance has been observed.

In conclusion these results show the advances in the measure of geometry of local structure in silica glasses by XANES. The experimental spectra in the difficult oxygen K-edge energy range are reported and XANES is shown to be sensitive to the different local structures in the glasses. The theoretical analysis has shown that XANES by probing multiple scattering photoelectron pathways is sensitive to bridging bond angle and distance variations.

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