

Structural modification on silica glass surface induced by thermal poling for second harmonic generation

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O-K edge XANES spectroscopy evidences structural modification induced by thermal poling treatment in surfaces of bulk Herasil silica glass presenting second harmonic generation. Considering model silicon dioxide clusters, calculations based on full multiple scattering approach have been performed in order to explain accurately the differences observed on XANES spectra at different stage of the poling treatment. These structural modifications on extreme surface affect both network and defects by breaking Si-O-Si bridging bonds. Despite of the formation of bridging bond occurring during the thermal depoling -which erases the SHG inside the glass-, the initial structure of the unpoled sample is not reproduced.

Keywords: Herasil silica glass, thermal poling, Second Harmonic Generation, O-K edge XANES, FTIR spectroscopy.

1. Introduction

In the field of telecommunication or information storage, silica-based glass is one of the most basic engineering materials utilized for passive or active optical devices. Nonlinear features in silicate glasses are also desirable and promise to produce novel opportunities, like efficient and cheap modulators and frequency converters. Because of symmetry consideration, Second Harmonic Generation (SHG) is expected to take place only in non-centrosymmetric structure or anisotropic materials. Nevertheless, using a thermal or UV-assisted poling technique, frequency doubling and linear electro-optical effect can be induced in glass (Myers et al, 1991; Fujiwara et al, 1997). Myers et al. firstly reported that a $\chi^{(2)}$ as large as 1pm/V could be induced in bulk fused silica by thermal poling. The model generally proposed to explain the effect of thermal poling is related to the interaction between the third order nonlinear susceptibility $\chi^{(3)}$ and a strong electrostatic field E_{dc} , eventually followed by reorientation of polarisable dipoles (Mukherjee et al, 1994). The charge transport of mobile ions driven by the poling field from the anode towards the cathode creates a negatively charged depletion layer close to the anodic surface. During or after poling, a charge neutralization or air ion deposition builds up a large frozen-in E_{dc} electrostatic field in a layer near the anodic surface (Kazansky et al, 1994). Eventually, an orientation of polarisable dipole could occur during the creation of this depletion region or

follow the establishment of the frozen-in electrostatic field. The location, spatial extent, charge composition, and electric field profile in this depletion layer depend on the poling voltage, temperature, atmosphere or poling time. Most of the studies proposed that the active nonlinear region is a thin layer about few micrometers thick close to the anodic surface. However, Qiu et al (1999) have recently exposed two different techniques to distinguish SHG from the anode and cathode-side faces of poled glasses: SH signal from cathode-side face is two orders of magnitude lower. In spite of the considerable technological interest in the understanding of the induced SHG origin, the mechanism is not completely elucidated. Much effort has been expended to clarify it, but only few structural characterizations of poled glasses have been performed. In poled fused silica glass, the defect sites like non-bridging oxygen hole center and non-bridging oxygen (NBOHC or NBO, respectively) are often mentioned as involved in the SHG process (Mukherjee et al, 1994). Recently by inelastic neutron scattering studies, Cabrillo et al (1998) concluded to large microscopic alterations involving the opening of Si-O-Si bond angles along the direction of the poling. On the other hand, proton migration is often postulated to explain the conduction properties of the silica glass during poling (Alley et al, 1998).

The object of this paper is to present the interpretation of the slight structural modification in Herasil silica glass surfaces induced by a thermal poling treatment revealed by X-ray Absorption Near-Edge Structure spectroscopy. The XANES experimental results are presented for unpoled, depoled and both poled surfaces.

2. Experimental procedure

The optimization of the SHG signal intensity and homogeneity had been obtained by repeating a cycling poling process (Nazabal et al, 2000). The poling was carried out at 300 °C for 1h with 3 kV voltage applied across the 5mm thick sample with circular stainless steel electrodes. The poling treatment effect could be suppressed by a thermal depoling treatment (300 °C for 1h). The homogeneity of the SHG signal after poling was controlled as described elsewhere (Nazabal et al, 1997).

The O-K edge XANES measurements were performed at the LURE, (Orsay, France) on beam station SA72 by O-KLL Auger electron yield detection under high vacuum with a maximal probed depth about 100Å (Instrumental resolution is 0.3eV). In this investigation, a Full Multiple Scattering (FMS) analysis was performed using the extended CONTINUUM code developed by Natoli and coworkers (1980). The potentials of the initial and final state were built as previously described (Natoli et al 1980). Tests on the construction of the potentials were done by checking the influence of the electronic configuration on the final state, of the muffin-tin radii, and of the cluster size. The best simulations were obtained for the so-called "relaxed and unscreened" potential for the excited state in the (Z+1) approximation and considering the X- α exchange potential.

The choice of an atomic model for the amorphous silica structure representative of the local structure visited by the photoelectron is central to any adequate understanding of its macroscopic properties. Approximations are unavoidable due to the non-periodic structure of the glass and small clusters extracted from the α cristobalite structure are assumed to give an acceptable model for the local structure in silica glasses (Wright, 1995). The structure is made up by corner sharing [SiO₄] tetrahedra, resulting in interconnected rings. Most of these rings in the glass network contain six silicon atoms and six oxygen atoms. Moreover, the structural glass disorder mainly results from the variation of the Si-O-Si angle in a range of 130-160°.

Whereas, the Si-O-Si angles in the cristobalite crystal are about 146.8° for α phase (and 147.7° for β phase), the α and β forms differ by only slight rotations of successive tetrahedra..

3. Results and discussion

The experimental spectrum recorded for unpoled Herasil silica glass presents a usual shape characterized by a prepeak at 534eV and a large absorption line at 540eV with a first EXAFS oscillation at about 20eV after the edge (Figure 1).

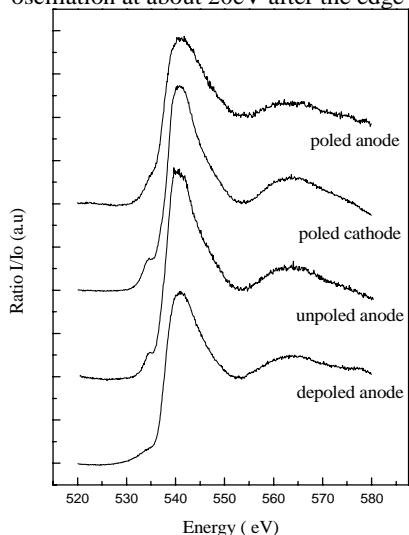


Figure 1: Herasil silica glass O K-edge XANES spectra recorded for the unpoled anode, poled anode and cathode, and depoled anode respectively.

After poling, an increase of the apparent intensity of the prepeak and a broadening of the main absorption edge for both anode and cathode surfaces are observed. These effects are more emphasized on the anodic face. After depoling, the prepeak vanishes, but the main absorption line remains large. So, the unpoled initial structure is not completely restored.

Simulations have been tempted for different spherical clusters extracted from this α cristobalite crystal structure (space group $P4_12_12$). These clusters are presented in Figure 2:

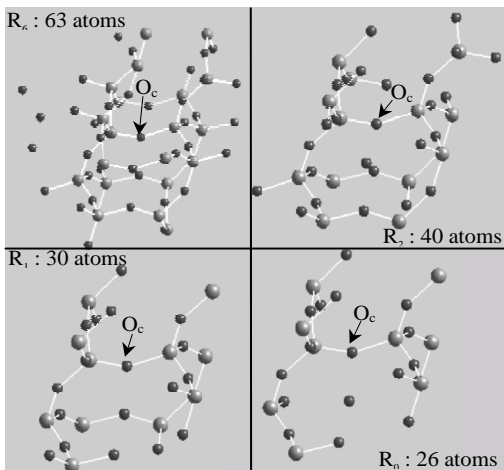


Figure 2 : Relevant spherical clusters with different number of interconnected rings extracted from the α cristobalite structure: R_2 : 40 atoms, 5.01 Å radius; R_1 : 30 atoms, 4.73 Å; R_0 : 26 atoms, 4.45 Å.

They are characterized by an increasing diameter size and consequently by an increasing number of interconnected rings. On one hand, calculations performed for the largest cluster R_6 (63 atoms, 6 rings, 5.86Å in radius) give rise to the worst agreement with the experimental spectrum (figure 3). The theoretical spectrum presents a too large number of well-defined resonances compared to the experimental one. Even by considering a broadening of these structures due to the core hole width, instrumental resolution and inelastic losses of the photoelectron, these structures will not be sufficiently smoothed to disappear.

This result is not surprising since the cluster size is larger than the typical photoelectron mean free path calculated from the imaginary part of the photoelectron self-energy at about 5Å. On the other hand, the calculations performed for clusters R_0 (26 atoms, 4.45Å in radius), R_1 (30 atoms, minimal cluster to form a single ring, 4.73Å) and R_2 (40 atoms, 2 rings, 5.01Å radius) reproduce satisfactorily the experimental spectrum. Among the three calculations, the opened ring cluster R_0 gives a slightly poorer agreement with the experience since the white line width is too large compared to experimental one, and the A prepeak is located at too low energy.

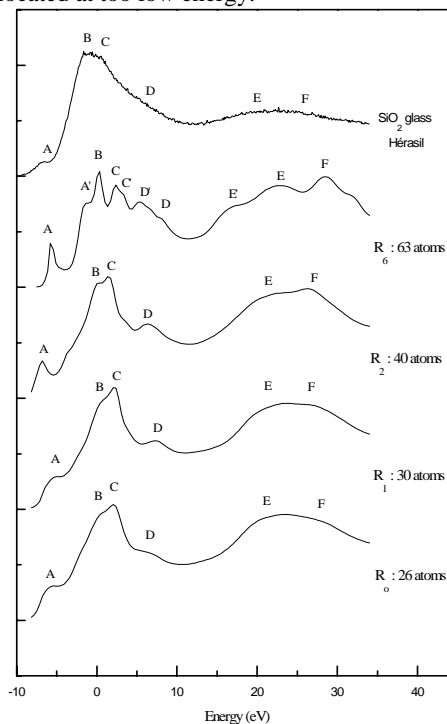


Figure 3 : O K-edge XANES spectrum simulations obtained by FMS calculations (CONTINUUM code) for spherical clusters R_6 , R_2 , R_1 , R_0 , compared to the experimental spectrum of the unpoled Herasil silica glass.

In a second step, the effect of hanging chains branched on the rings has also been investigated by eliminating silicon branching ramifications on original clusters R_1 and R_2 . Then, FMS calculations have been performed on clusters free of hanging chains (R_1' and R_2' , one and two rings respectively). The global structure of the spectra is maintained compared to the simulations performed on original clusters R_1 and R_2 , but the intensity of prepeak A is strongly reduced. This result evidences clearly a correlation of the A prepeak intensity with the presence of hanging branched ramifications in the structure of the glass.

In order to improve the simulation of the disordered glass structure, the structural relaxation for clusters of 40 atoms has been done in two ways:

(i) calculations have been performed on cluster with structure relaxed by the minimum energy calculation using the Cerius 3 code. The relaxed cluster R_2^{Cer} extracted from the cluster R_2 presents average (Si-O) distance and (O-Si-O) angle like the cluster R_2 and different (Si-O-Si) angles with average value about 145° .

(ii) Relaxed structure was used based on clusters obtained by Jesurum and al. (1996). The construction of their initial cluster was obtained by assembling $[SiO_4]$ tetrahedra according to the cristobalite β structure. Some 5° rotation error is introduced randomly, the total stored elastic energy has been minimized to preclude underconnection. A 40 atoms cluster R_2^{Jes} was extracted from this initial cluster giving a comparable structure to clusters R_2 and R_2^{Cer} and used for calculations (Figure 4).

The main effect of the relaxation, whatever the procedure used, is to produce a broadening of the white line. Such trends (broadening of resonances and decrease of intensities) are commonly observed by comparing ordered structures and derived-disordered structures and reflect some differences in phase of the different multiple scattering contributions (V. Briois et al, 1997). On the other hand, due to the broadening of the white line, the prepeak appears less resolved for relaxed clusters than non-relaxed clusters. Among the three models, the relaxed structure obtained from the Cerius program gives the best agreement with the experiment in terms of broadening of the white line.

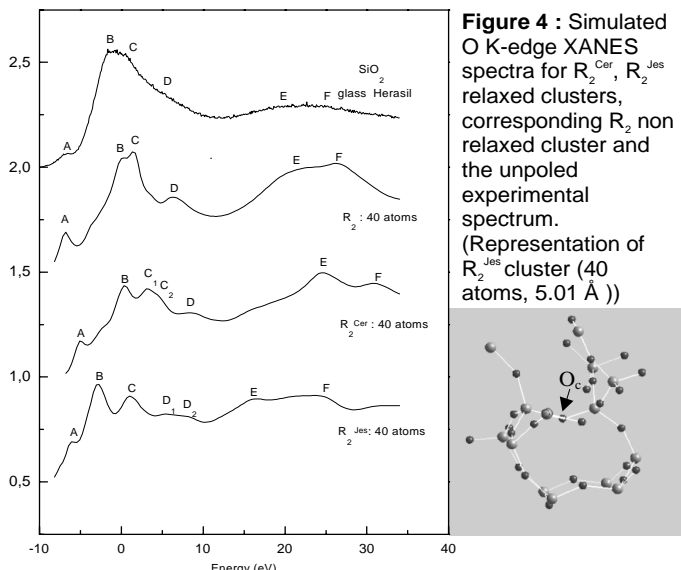


Figure 4 : Simulated O K-edge XANES spectra for R_2^{Cer} , R_2^{Jes} relaxed clusters, corresponding R_2 non relaxed cluster and the unpolished experimental spectrum. (Representation of R_2^{Jes} cluster (40 atoms, 5.01 Å))

Multiple Scattering calculations show that the O-K edge spectrum of Herasil silica glass can be well reproduced by a one or two rings oxygen environment derived from the cristobalite structure. The main results obtained can be summarized as follows: the intensity of the prepeak is correlated to the existence of hanging disconnected ramifications in the glass network, a broadening of the main absorption white line characterizes a relaxation of the structure leading to a more disordered one.

As O-K edge XANES spectroscopy is achieved by Auger electron detection, only the extreme surfaces of silica glass are analyzed. As expected for such discontinuous environment, the intense A prepeak observed, in spite of the high purity of this glass, traduces the presence of some ring bridges broken by polishing for example. Moreover, the FMS study performed in this work is fruitful to explain the structural changes occurring during poling. After poling, the increasing intensity of this prepeak A can be the signature of a more open structure. According to this creation of new broken bridging bonds, separate rings can relax leading to a more disordered structure. Therefore a broadening of the main absorption line is observed, in agreement with the broadening effect which is observed for the relaxed cluster and the Jesurum disordered cluster.

This interpretation is fully confirmed and completed by IR Reflectance and polarization modulation-infrared reflexion absorption spectroscopy (PM-IRRAS) measurements (Nazabal et al, 2000). PM-IRRAS measurements and simulations clearly revealed a structural perturbation of Si-O-Si groups in the region close to the surfaces after poling (T. Buffeteau et al (1999)). The partial structural anisotropy along the direction of the poling electric field inside these layers is correlated to an optical birefringence, in agreement with the results of Fujiwara et al. (1997) in poled germanosilicate glass. Moreover, the mechanism

can be favored if extreme surface adsorbed water molecules react with the network to break Si-O bridging bonds and form Si-OH bonds. During the poling treatment of a silica glass sample, we can suppose that molecular hydrogen or protons could be separated from hydroxyl groups resulting to the formation of NBOHC or NBO sites. Then, these molecular hydrogen or protons can migrate from the anode to the bulk or can be extracted from the near surface of the cathode. The IR Reflectance measurements effectively show a decrease of the $\equiv\text{Si-OH}$ groups on poled surfaces; this is more pronounced on the anodic face. At the same time, an increase of $\equiv\text{Si-O}^-$ groups is observed on the cathodic face. A similar increase could occur on the anodic face but may remain undetected if the formed Si-O⁻ groups were oriented parallel to the dc field during the poling.

Finally, the different shape of the spectrum recorded after depoling can be also interpreted by this FMS study. The weaker intensity of prepeak A for the depoled surface evidences a decreasing number of hanging chains. This explanation is consistent with the fact that a thermal annealing can lead to the reformation of bridging bonds. But the white line remains enlarged, probably because only distorted bridging bonds can occur in this relaxed structure.

4. Conclusion

XANES and IR experimental results and simulations evidence structural reorganizations in the silica glass during poling affecting both network and defect. Bridging (Si-O-Si) bonds have been broken during poling and partly restored after thermal treatment. But these structural modifications on extreme surfaces induced by poling are not completely reversible. At the same time, a decrease of hydroxyl Si-OH bonds associated with an increase of non-bridging oxygen (Si-O⁻) can be interpreted by proton conduction during poling (T.G. Alley et al, 1998). Simultaneously, a structural anisotropy involving the Si-O-Si units has been clearly evidenced in agreement with the results of C. Cabrillo et al (1998).

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References

- T. G. Alley, S. R. J. Brueck, R. A. Myers, J. Non-Cryst. Solids, **242**, 165 (1998).
- V. Briois, C. Brouder, P. Saintavit, A. San Miguel, J.P. Itié, A. Polian, Phys. Rev. B, **56**, 5866(1997).
- T. Buffeteau, D. Blandez, E. Péré, B. Desbat, J. Phys. Chem. B, **23** (1999).
- C. Cabrillo, G. J. Cuello, P. Garcia-Fernandez, F. J. Bermejo, V. Pruneri, P. G. Kazansky, S. M. Bennington, W. S. Howells, Phys. Rev. Lett., **81**, 4361, (1998).
- T. Fujiwara, M. Takahashi, A.J. Ikushima, Appl. Phys. Lett., **71**, 1032, (1997).
- C. E. Jesurum, L. W. Hobbs, A. N. Sreenam, B. A. Berger, Nucl. Instrum. Methods Phys. Res., B **116**, 18 (1996).
- P.G. Kazansky, A. Kamal, P.St.J. Russel, Opt. Com., **110**, 611, (1994).
- N. Mukherjee, R.A. Myers, S.R.J. Brueck, J. Opt. Soc. Am. B, **11**, 665 (1994).
- R.A. Myers, N. Mukherjee, S.R.J. Brueck, Opt. Lett., **16**, 1732 (1991).
- C. R. Natoli, D. K. Misemer, S; Doniach, F. W. Kutzler, Phys. Rev. A, **22**, 1104, (1980).
- V. Nazabal, E. Fargin, J.J. Videau, G. Le Flem, A. Le Calvez, S. Montant, E. Freysz, A.Ducasse, M. Couzi, J. Solid State Chem, **133**, 529 (1997).
- V. Nazabal, E. Fargin, Labrugère C., G. Le Flem, J. Non-Cryst. Solids, **270**, 223, (2000).
- M.Qiu, T. Mizunami, Y. Takagaki, R. Vilaseca, J. Martorell, J. Non-Cryst. Solids, **255**, 250 (1999).
- A.C. Wright, J. Non-Cryst. Solids, **179**, 84 (1994).