LNF-90/097

M. Benfatto, A. Gargano

THEORETICAL ANALYSIS OF THE XANES SPECTRA OF SiO_2 GLASSES AT THE OXYGEN AND SILICON K-EDGE

Estratto da: Conf. Proc. Vol. 25 XSR-89, A. Balerna, E. Bernieri, S. Mobilio (Eds.)
SIF Bologna, Pag. 43 (1990)

Conference Proceedings Vol. 25
«2nd European Conference on Progress
in X-Ray Synchrotron Radiation Research»
A. Balerna, E. Bernieri and S. Mobilio (Eds.)
SIF, Bologna 1990

THEORETICAL ANALYSIS OF THE XANES SPECTRA OF SiO_2 GLASSES AT THE OXYGEN AND SILICON K-EDGE.

A. Gargano[a], M. Benfatto[b],

a) ENEA C.R.E.- Casaccia, TIB-Divisione Scienza dei Materiali, I-00060 Casaccia Roma (Italy)
b) Instituto Nazionale di Fisica Nucleare, LNF I-00044 Frascati (Italy)

ABSTRACT

Theoretical XANES (X-Ray Absorption Near Edge Structure) calculations at the oxygen and silicon K-edge of SiO_2 glass are reported. The calculations based on the multiple scattering theory have been made for different geometries obtained changing the Si-O-Si bridging angle at the corner sharing two tetrahedra. The calculations are in good agreement with some experimental results taken from the literature.

INTRODUCTION

Due to the great techological importance of the amorphous silicon dioxide a great ammount of research has been devoted to determ its structure. The silica glass is formed by SiO_4 tetrahedral clusters linked togheter in such a way to share a corner. One oxygen is linked to two silicon atoms forming a continuous random network structure [1]. The disorder comes from the random variation of the Si-O-Si angle as well as the dihedral angle. The determination of the mean oxygen bond angle Si-O-Si (referred in the following as θ) is still an open question. A lot of experimental and theoretical results give a spread of values going from 144° to 160° [2].

In this work we investigate the oxygen and silicon site structure by a comparison of theoretical oxygen and silicon K-XANES calculations and some experimental data. The calculation based on the multiple scattering (MS) approach[3] have been made for both edges using five different values of the bond angle θ. Theoretical XANES spectra have been obtained using an X-α potential for the exchange part and Z+1 approximation for the final state potential. In order to compare the experimental data with the theoretical results we have convoluted the latter with a Lorentzian broadening function having a width Γ=2.2eV and 1eV for oxygen and silicon K-edge respectively (these values include both core-hole and experimental width).

RESULTS AND DISCUSSION

In a previous work we have tested the sensitivity of the XANES calculation to the variation of the θ angle[4]. To obtain better agreement with experimental data we have now

enlarged the size of the cluster used in the calculations taking into account two shells beside the photoabsorber. Such a clusters for silicon and oxygen K-edge calculation are depicted in the upper part of Fig. 1 and Fig. 4 respectively. The silicon-oxygen distance is 1.61Å.We start the analysis from the silicon K-edge.

A set of five unconvoluted theoretical silicon K-XANES spectra for the angle θ equal to 130.5°, 144°, 160°, 174° and 180° are shown in Fig. 1. Taking peak A as reference an increase of the intensity of peak B and a decrease of the intensity of peak C can be observed going from 180° to 130.5°. At the same time there is a blue shift of these peaks as summarized in Fig. 2.

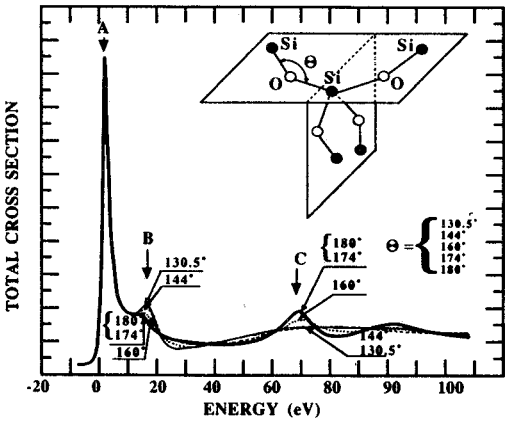


Fig. 1 - Set of theoretical calculations at silicon K-edge for different angles.

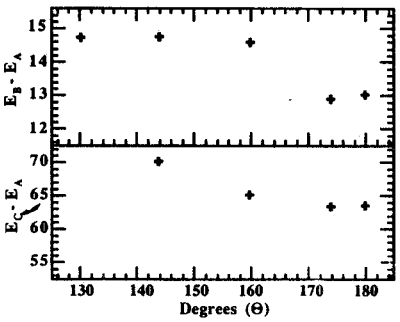


Fig. 2 - Tables with the energy separation between peak A and peak B and C as function of angle.

In Fig. 3 the comparison between an experimental spectrum for a fused quartz and a convoluted theoretical calculation for an angle θ = 144° is reported. The experimental spectrum is taken from Ref. 5. The agreement is rather good indicating a mean oxygen bond angle around 144°.

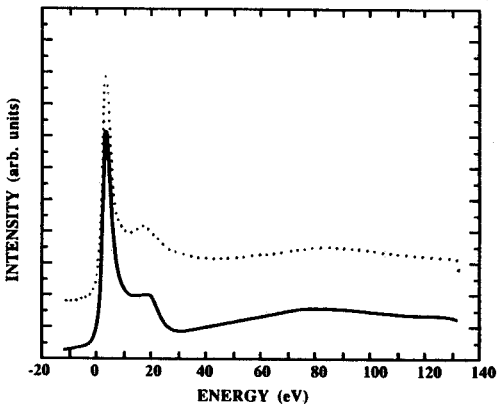


Fig. 3 - Comparison between theoretical calculation (solid line) and experimental data.

Going to the oxygen K-edge, we report in Fig. 4 a set of five unconvoluted theoretical curves calculated for oxygen bridging angles ranging from 130.5° up to 180°.Contrary to what happens at the silicon K-edge both a decrease of the intensity and a red shift of peak B has been found going from 180° to 130.5°. The energy separation between peak A and B as a function af the angle θ has been reported in Fig. 5.

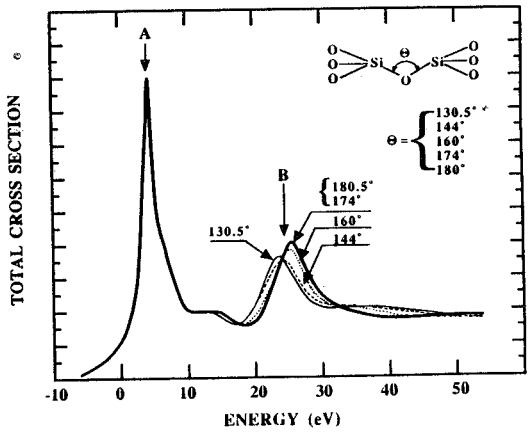
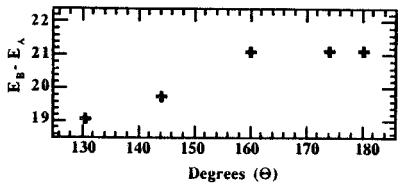


Fig. 4 - Set of different calcluations at oxygen K-edge for various angles.

Fig. 5 - Table with the energy separation between peak A and B as a function of angle.



In Fig. 6 we compare the experimental spectrum (dotted line) of an amorphous sample[6] of SiO_2 detected by partial electron yield technique at the "Grasshopper beam line" of the Frascati Synchrotron Radiation Facility (the experimental resolution was about 2.2eV) with a convoluted theoretical spectrum (full line) obtained adding four spectra calculated for the oxygen bridging angle equal to 130.5°, 144°, 160° and 180° and weighted according to an angle distribution given in the literature[2]. Using other angle distributions we observe only a small variations of the energy separation between peak A and B. These variation are less than 1 eV. Contrary to what happens for the other edge it is difficult to derive in this case some indications around the mean oxygen bridging angle.

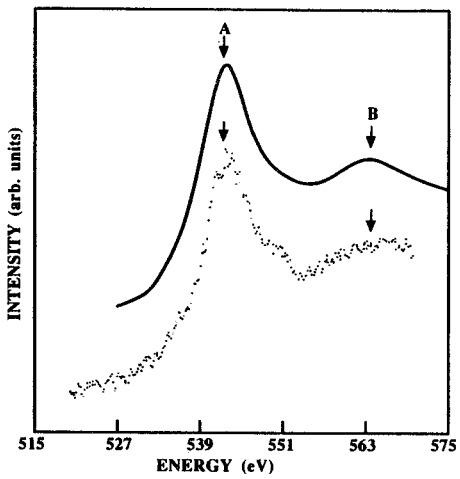


Fig. 6 - Comparison between theoretical result (full line) and experimental data

To conclude the good agreement between experimental data and theoretical calculations for both edges is a clear indication that the size of the cluster used in the calculation is enough to account the main structures presented in the experimental spectra. Although there is a well define sensitivity to the variation of angle θ of the theoretical calculation, the smallness of the differences among the various calculations indicates that it is necessary to have more experimental data with better experimental resolution (better than 1 eV at the oxygen k-edge) in order to discriminate among the different models of structure. Moreover other calculation with a complete different geometry like for example a planar n-fold rings[7] might be useful in this direction.

REFERENCES

(1) W.Zachariasen, J.Am.Chem.Soc.**54**, 3841 (1932).

(2) R.L.Mozzi and B.E.Warren, J.Appl. Crystallogr. **2**, 164 (1969); P.H.Gaskell and I.D.Tarrant, Phil. Mag. **b42**, 265 (1980); G.N. Greaves, A.Fontaine, P.Lagarde, D.Raoux and S.J.Gurman, Nature **293**, 611 (1981); R.Dupree and R.F.Pettifer, Nature **308**, 523 (1984).

(3) C.R.Natoli and M.Benfatto, Jour. de Physique **47**, C8-11 (1986).

(4) A.Marcelli, I. Davoli, A. Bianconi, J.Garcia, A Gargano, C.R.Natoli, M.Benfatto, P.Chiaradia, M.Fanfoni, E.Fanfoni, E.Fritsch, G. Calas and J.Petiau, Journal de Physique **46**, C8-107 (1985).

(5) Z.Hussain, E.Urnbacch, D.A.Shirley, J.Stohr and J.Feldhaus, Nucl.Instr. and Meth. **195**, 115 (1982).

(6) F.A.Seifert, B.O.Mysen and D.Virgo, American Mineralogist **67**,696 (1982).

(7) F.L.Galeener, J.Non Crystalline Solids **49**,53 (1983).