

ISTITUTO NAZIONALE DI FISICA NUCLEARE  
Laboratori Nazionali di Frascati

LNF-85/22

M. Emili, L. Incoccia, S. Mobilio, et al.:  
EXAFS AND XANES STUDY OF Ti COORDINATION IN TiO<sub>2</sub>  
CONTAINING GLASSES UPON THERMAL TREATMENT

Estratto da:  
Proc. of an Int. Conf. on Exafs and Near  
Edge Structure III. Stanford p. 317 (1984)

# EXAFS and XANES Study of Ti Coordination in TiO<sub>2</sub> Containing Glasses Upon Thermal Treatment

M. Emili, L. Incoccia, and S. Mobilio  
Laboratori Nazionali di Frascati, I-00044 Frascati, Italy  
M. Guglielmi  
Università di Padova, I-Padova, Italy  
G. Fagherazzi  
Università di Venezia, I-Venezia, Italy

## 1. Introduction

In this work we report an EXAFS-XANES determination of the Ti coordination in TiO<sub>2</sub>-SiO<sub>2</sub> sol-gel glasses for three different percentages of TiO<sub>2</sub> (4.5, 10 and 19 wt% TiO<sub>2</sub>) for thermal treatment of the initial gel up to temperatures which correspond to the glass phase and glass-ceramic phase. Previous studies have been made on TiO<sub>2</sub>-SiO<sub>2</sub> glasses prepared by melt quenching or flame hydrolysis. According to EVANS <sup>1/1</sup> titanium atoms substitute silicon in the SiO<sub>2</sub> network, occupying only T<sub>d</sub> coordinated sites up to 11.5 wt% TiO<sub>2</sub> (stable region). For higher Ti content up to 16 wt% TiO<sub>2</sub>, a fraction of TiO<sub>2</sub> precipitate in the form of O<sub>h</sub> coordinated Ti (metastable region). For concentration greater than 16 wt% TiO<sub>2</sub>, a phase separation-crystallization occur (crystallization region). Recently GREGOR <sup>2/</sup> et al., concluded that the O<sub>h</sub> coordination is always present in this glass also in the stable region. The three different percentages of TiO<sub>2</sub> studied have been chosen in order to clarify which coordination Ti assumes in the sol-gel glasses.

## 2. Experimental

Sample preparation is described elsewhere <sup>3/</sup>. X-ray absorption spectra at the Ti K edge were collected at the bending magnet X-ray beam line of the Frascati Synchrotron Radiation facility. The radiation was monochromatized by a Si(111) channel-cut crystal.

## 3. Results and Discussion

Fourier transforms of the spectra (Fig. 1a, 1b) do not show any significant structure above the first coordination shell with the exception of the samples 19 wt% TiO<sub>2</sub> heated at 1000 and at 1200 °C, that show peaks up the 4<sup>th</sup> coordination shell. Note that 19 wt% TiO<sub>2</sub> heated at 1200 °C is very close to the anatase spectrum, while 19 wt% TiO<sub>2</sub> heated at 1000 °C shows the same peaks but at distances significantly shorter. Also an XRD analysis performed on this sample showed peaks shifted to lower 2θ angles with respect to those of the 19 wt% TiO<sub>2</sub> heated at 1200 °C sample. Moreover some other broad peaks appear at 1000 °C which probably belong to an unknown crystalline phase containing Ti. Table I reports the first shell distances, the coordination numbers and the D.W. factors obtained from a k-space analysis using anatase as model compound. For all non-crystalline samples, the distances range from 1.80 Å up to 1.86 Å, too short to be compatible with an O<sub>h</sub> coordination of Ti. The coordination numbers obtained clearly show that the fraction of O<sub>h</sub> sites for Ti is negligible in the glassy state. It is very interesting to note that the effect of the thermal treatment is a progressive decrease of the Δσ<sub>C</sub>, indicating that one goes from a highly distorted T<sub>d</sub> unit at low temperature, when the material is an essicated gel, to a more ordered T<sub>d</sub> unit in the more densified glasses. To verify in a more quantitative way the possible presence of a small quantity of sixth fold coordinated Ti<sup>4+</sup> ions, a fit has been performed on the inverse Fourier transform of the first peak of the spectra, using both a single and double shell model. An excellent agreement is obtained with a single shell model with an average coordination number of 4 (Fig. 2a, 2b).

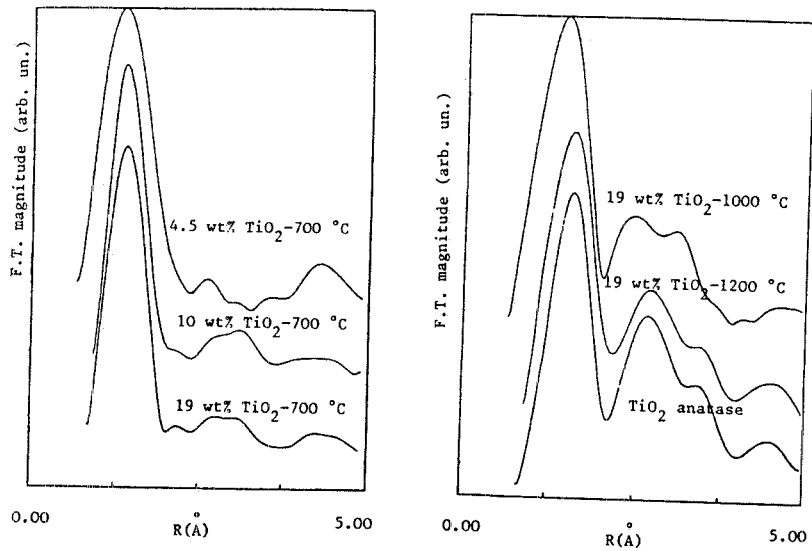


Fig. 1 - Fourier Transform of some EXAFS spectra.

TABLE I - Ti-O R bond distances, coordination numbers N and Debye-Waller factors obtained from the k-space analysis.

Gel-glass composition (wt% TiO <sub>2</sub> )		250 °C	430 °C	700 °C	1000 °C	1200 °C
4.5	R(k)	n.d.	n.d.	1.84	1.81	1.81
	N	n.d.	n.d.	4.6	4.4	4.1
	$\Delta\sigma^2$	n.d.	n.d.	$-0.23 \times 10^{-2}$	$-0.33 \times 10^{-2}$	$-0.41 \times 10^{-2}$
10	R(k)	1.84	1.84	1.83	1.81	1.81
	N	3.6	3.4	3.8	4.3	3.7
	$\Delta\sigma^2$	$0.10 \times 10^{-2}$	$0.13 \times 10^{-2}$	$-0.14 \times 10^{-2}$	$-0.22 \times 10^{-2}$	$-0.29 \times 10^{-2}$
19	R(k)	1.86	1.85	1.84	n.d.	1.93
	N	3.6	3.6	3.8	n.d.	5.9
	$\Delta\sigma^2$	$0.45 \times 10^{-2}$	$0.26 \times 10^{-2}$	$0.09 \times 10^{-2}$	n.d.	$0.6 \times 10^{-2}$

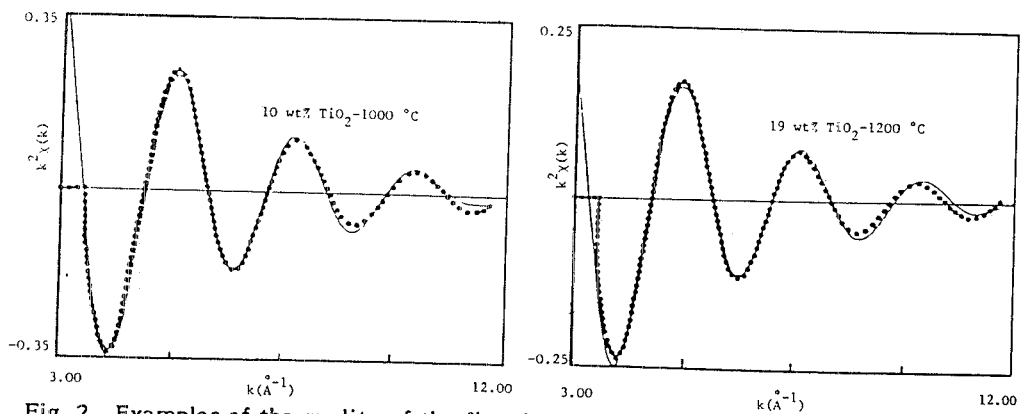


Fig. 2 - Examples of the quality of the fits obtained by using a single shell approach.

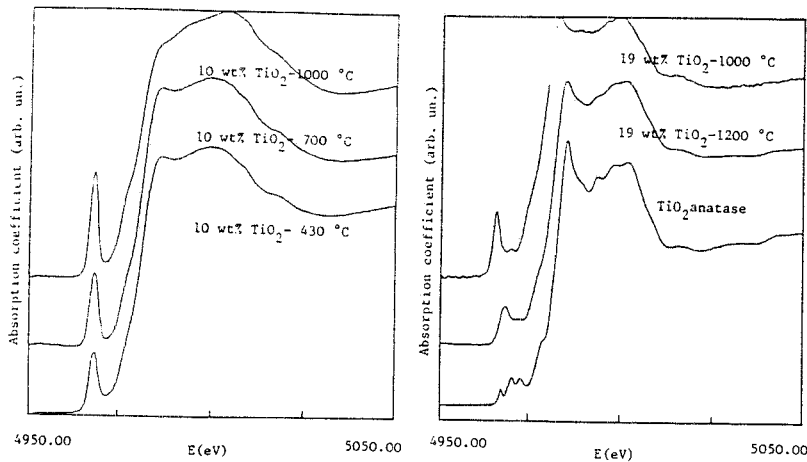


Fig. 3 - Ti K edge absorption coefficient of some of the samples.

In Fig. 3 the near-edge spectra of Ti K edge of some of the samples studied together with  $\text{TiO}_2$  anatase are shown. As known, the 1s-3d transition, that gives rise to the pre-edge peak, is dipole allowed only when the point group of Ti sites has no inversion symmetry: for this reason its intensity has been related to the ratio of  $T_d$  Ti-sites vs  $O_h$  Ti-sites in these glasses.

Table II shows the intensity of this peak normalized to the atomic absorption coefficient. Its magnitude increases with increasing temperature and decreases with increasing Ti content. The low intensity for the sample 19 wt%  $\text{TiO}_2$  heated at 1200 °C together with the similarity of the general features above the edge again clearly show the crystallization of this sample towards anatase.

TABLE II - Intensity of the pre-edge peak normalized to the single atom.

Gel-glasses Composition (wt% $\text{TiO}_2$ )	Heat Treatments				
	250 °C 3h	430 °C 3h	700 °C 3h	1000 °C 3h	1200 °C 3h
4.5	0.38	0.32	0.38	0.60	0.71
10	0.30	0.29	0.32	0.55	0.54
19	0.28	0.32	0.28	0.36	0.19

#### 4. Conclusions

We conclude that the Ti ions occupy only four-fold ( $T_d$ ) sites at any concentration up to the temperature where an "intermediate" ordered phase comes out. Thus, for our sol-gel glasses a complete dissolution of  $\text{TiO}_2$  in the  $\text{SiO}_2$  network occurs, at least up to 10 wt%  $\text{TiO}_2$ ; we think that this is due to the high homogeneity of the sol-gel glasses. The thermal treatment causes a progressive ordering of the  $T_d$  units and the shortening of the bond length resulting in a more ordered and compact structure. The intensity variations of the 1s-3d pre-edge peak are due to the shortening and to the ordering of the tetrahedral units: the increase of the overlap integrals between Ti 3d and O 2p states results in an increased oscillator strength of the transition.

The crystallization occurs only for the 19 wt%  $\text{TiO}_2$  glass towards anatase through an unknown intermediate phase.

#### References

- /1/ D.L. Evans, *J. Non-Crystalline Solids* 52, 115 (1982).
- /2/ R.B. Gregor, F.W. Lytly, R. Sandstrom, J. Wong, P. Schultz, *J. Non-Crystalline Solids* 55, 27 (1983).
- /3/ M. Emili, L. Incoccia, S. Mobilio, G. Fagherazzi, M. Guglielmi, in press on *J. Non-Crystalline Solids*.