

To be submitted to
J. Non-Cryst. Solids

ISTITUTO NAZIONALE DI FISICA NUCLEARE
Laboratori Nazionali di Frascati

LNF-84/41(P)
14 Giugno 1984

M.Emili, L.Incoccia, S.Mobilio, G.Fagherazzi and M.Guglielmi:
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METHOD

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ABSTRACT

In the present paper we have clarified by both EXAFS and near-edge spectroscopies in TiO_2 - SiO_2 very homogeneous glasses, having three different TiO_2 concentrations (4.5, 10.0, 19.0 wt%), and obtained by the sol-gel method, that the coordination of Ti^{+4} ions is only tetrahedral. An "intermediate" ordered phase, not yet well defined, has been observed at the beginning of the crystallization process. Also in the essicated gels the coordination of Ti^{+4} is tetrahedral. Moreover, the thermal treatment causes a progressive ordering of the T_d tetrahedral units going from the essicated gels to more and more dense glasses. The presence of six-fold Ti-sites has been clearly observed by both EXAFS and near-edge spectroscopies only in a partially crystallized glass containing the highest TiO_2 content (19 wt%), at 1200°C. On the contrary, in all the glasses having the lowest TiO_2 content (4.5 wt%) a four-fold Ti coordination has been observed up to 1200°C. The crystalline phase, which appears at high temperatures, is anatase having a crystallite size in the range 50-100 Å for thermal treatments in the range 1000-1200°C for the sample richer in TiO_2 . An appearance of crystallinity at higher temperatures for lower TiO_2 concentrations has been observed by XRD analysis, in agreement with other authors.

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1. - INTRODUCTION

The importance of $\text{TiO}_2\text{-SiO}_2$ glasses, either from an industrial or from a scientific point of view, is well known. A low content of TiO_2 decreases the thermal expansion coefficient of vitreous silica. It is possible to obtain a zero expansion composition (7.6 wt % TiO_2) which, for instance, is useful for optical telescope mirrors⁽¹⁾.

The systematic modifications of silica properties as a function of TiO_2 content have been investigated by Schultz and Smyth⁽²⁾. Schultz⁽³⁾ showed a discontinuity of properties like viscosity, refractive index and density between 11 and 12 wt % TiO_2 composition which is very close to the eutectic point in the $\text{TiO}_2\text{-SiO}_2$ phase diagram⁽⁴⁾. According to Evans⁽¹⁾ in the ideal continuous random network, the TiO_2 larger tetrahedra (the Ti^{+4} radius is 0.68 \AA , while the Si^{+4} one is 0.41 \AA) can be dissolved in a statistical way up to about 15 to 16 wt % TiO_2 . This is the upper limit of a "metastable" region which begins at about 11.5 wt % TiO_2 , whereas the composition in the range 0-11.5 wt % TiO_2 correspond to the "stable" region for an ideal substitutional solution of TiO_2 in SiO_2 . In this phase the 4:2 network connectivity scheme between oxygens and cations is supposed to be fully maintained also at relatively high temperature ($\sim 1000^\circ\text{C}$). This interpretation of the observed properties of $\text{TiO}_2\text{-SiO}_2$ glasses is also supported by a previous work of Evans⁽⁵⁾ who completely crystallized low TiO_2 silica glasses (10.8 wt % of TiO_2 as a maximum) at very high temperature (1540°C). She obtained by a careful X-ray diffraction (XRD) analysis of the lattice parameters expansion, that titanium goes completely into solid solution within the cristobalite tetragonal structure. It is worth noting that the above studies and properties concern homogeneous $\text{TiO}_2\text{-SiO}_2$ glasses prepared by the controlled flame hydrolysis process.

In contrast, Sandstrom et al.^(6, 7) have shown, by direct structural techniques like the extended X-ray absorption fine structure (EXAFS) and the near-edge (XANES) spectroscopies, that, while the coordination geometry of Ti^{+4} in low TiO_2 content - SiO_2 glasses is primarily four-fold, i. e. tetrahedral (T_d), a small fraction of these ions show also a six-fold, i. e. octahedral (O_h) coordination, with a longer Ti-O bond length. In three $\text{TiO}_2\text{-SiO}_2$ glasses, containing 3.4, 7.5 and 9.5 wt % TiO_2 , respectively, the authors noted that the six-fold oxygen coordination increases with increased TiO_2 content up to a value of 18% for the 9.5 wt % TiO_2 composition.

The existence of octahedrally coordinated Ti as a former cation in the vitreous network was directly shown in alkali titanite glasses by a X-ray diffraction study on the electron radial distribution function by Zarzycki⁽⁸⁾. Also Rao⁽⁹⁾ suggested for the glassy system $\text{K}_2\text{O}\cdot\text{SiO}_2\cdot\text{TiO}_2$ a dual role for titanium which assumes a predominantly tetrahedral coordination in the high silica region and a predominantly octahedral

coordination in the low silica region.

The aim of the present work is to clarify whether in $\text{TiO}_2\text{-SiO}_2$ glasses, obtained by the sol-gel process, the coordination of Ti^{+4} is only tetrahedral, as suggested by Evans⁽¹⁾, or also partially octahedral, as suggested by Sandstrom et al., as long as the glass composition belongs to the "stable" or to the "metastable" region above indicated. The EXAFS and XANES spectroscopies, the sole direct structural techniques adequate to the present purposes, have been here employed. In fact, as shown by Jose and Urnes⁽¹⁰⁾ in the system $\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{TiO}_2$, the electron radial distribution obtained by XRD was unable to resolve the Ti-involving distances which superimpose onto the corresponding Si-involving distances.

Furthermore, the present work follows the structural evolution of the materials essicated from the gel state towards the vitreous state and, afterwards, towards partially crystallized glasses (here named also glass-ceramic materials) as a function of temperature from 250°C up to 1200°C. The XRD analysis has been used in order to detect and structurally characterize the crystalline phases obtained at high temperature.

Three different compositions have been investigated: 4.5, 10 and 19 wt% TiO_2 . The first two refer to glasses belonging to the "stable" region, the second one being very close to the eutectic composition. The third composition barely exceeds the "metastable" region, in a range where it can be argued that the 6:3 connectivity scheme can be induced by the more numerous Ti-O-Ti bridges. Bearing in mind a possible dual coordination and a possible dual rôle of titanium, the environment of this cation was studied by EXAFS and XANES, comparing the short and intermediate range order of the initial essicated gels with those of the more and more dense glasses, in which microporosity has progressively decreased as a function of the thermal treatment.

2. - EXPERIMENTAL PART

2.1. - Preparation of the $\text{TiO}_2\text{-SiO}_2$ glasses by the sol-gel method and their thermal treatment

In the recent years, glasses from the sol-gel technique have been successfully prepared in a wide range of systems and compositions and their properties have been studied often in comparison with the correspondent glasses obtained from classical fusion techniques⁽¹¹⁾. In the sol-gel method a gel is obtained by hydrolyzation of organo-metallic compounds in alcoholic solution and by subsequent condensation reactions.

Glass is then obtained from the gel by a controlled heat treatment which enables the elimination of liquid phases, the condensation of unreacted groups and the densification of the material microstructure.

The preparation of TiO₂-SiO₂ gel-glasses has been described⁽¹²⁻¹⁷⁾ in many papers for obtaining fibres^(13, 14), films⁽¹⁵⁾ and many properties have been studied^(16,17). In the present work titanium n-butoxide and silicon tetraethoxide were dissolved in a mixture of ethanol and butanol with small amounts of acetylacetone. After 2h stirring at 80°C under reflux, the solutions were left in air until gelation. A subsequent heat treatment was performed with a heating rate of 1° min⁻¹ and with a permanence at 430°C for 40h in order to eliminate the solvent and the unreacted organic radicals. The materials thus obtained as white powders were treated at different temperatures in the range 430-1200°C for 3h (430, 700, 1000 and 1200°C). Table I reports the chemical compositions in mol % and wt % of the three TiO₂-SiO₂ gel-glasses prepared by the sol-gel method.

TABLE I - Chemical compositions in mol % and wt % of the three TiO₂-SiO₂ gel-glasses examined.

Oxide	Chemical composition of the gel-glasses					
	I		II		III	
	mol %	wt %	mol %	wt %	mol %	wt %
SiO ₂	93.6	95.5	92.3	90	85	81
TiO ₂	3.4	4.5	7.7	10	15	19

2.2. - DTA measurements

DTA experiments were carried out under the following conditions : heating rate 10°C min⁻¹; sensitivity 0.1 mV for a full scale expansion; weight 200 mg of sample vs. 200 mg of alumina in specimen holders of sintered alumina.

2.3. - XRD analysis

The crystallinity content was determined by using a version of the Ruland method⁽¹⁸⁾, subsequently computerized by Vonk⁽¹⁹⁾ and modified by Vonk and Fagherazzi⁽²⁰⁾ whereas the crystallite size distributions were calculated by means of Fourier analysis, following the Warren-Averbach procedure⁽²¹⁾.

The diffraction curves of the powdered partially crystallized glasses were obtained with $\text{CuK}\alpha$ radiation and were recorded from $2\theta = 9^\circ$ to $2\theta = 130^\circ$ with a vertical diffractometer which was equipped with a graphite focussing monochromator. Measurements were made at steps of 0.1° and 0.2° , varying with 2θ , and were collected by means of a programmed step scanner. The X-ray intensities were corrected for polarization effects taking into account the formula found by Takeshi and Hiroshi⁽²²⁾. Air and background scattering were suitably subtracted according to standard procedure⁽²³⁾. The atomic scattering factors and the incoherent scattering power data were entered into the original program using the analytic functions reported by Moore⁽²⁴⁾ and by Palinkas and Radnai⁽²⁵⁾, respectively. The original basic computer program for crystallinity determination, kindly provided by C. G. Vonk, has been accordingly modified. Since the incoherent radiation is attenuated by the monochromator, it was necessary to find its pass-band function $M(\lambda)$ in order to correct the intensity as function of λ .

As regards the Fourier analysis of the crystalline peaks present in the X-ray diffraction patterns of the glass-ceramic materials, the deconvolution from instrumental and spectral effects was performed according to Stokes method using a Hanning window function in order to minimize the spurious oscillations due to series truncation effects⁽²⁶⁾.

2.4. - X-ray absorption measurements

The samples, in the form of finely ground powders, were suspended in distilled water and deposited onto a polycarbonate membrane (thickness = $6\ \mu\text{m}$) by using a standard filtration technique. Several tests were made in order to verify samples homogeneity. The optical density of the whole set of samples varied in the range $\mu x = 1.5-2.0$. The X-ray absorption spectra at the Ti K-edge were collected at the X-ray beam line of the Frascati Synchrotron Radiation Facility^(*), utilizing the radiation emitted by the storage ring Adone working at 1.3 GeV with a typical current of 50 mA. The radiation was monochromatized by a Si(111) channel-cut crystal, at an average resolution of ~ 1 eV for the EXAFS spectra and of ~ 0.5 eV for the near edge spectra. The measurements were taken in vacuum at room temperature. Fig. 1 shows some of the experimental curves.

(*) The Synchrotron Radiation Facility is sponsored by CNR (Consiglio Nazionale delle Ricerche) and INFN (Istituto Nazionale di Fisica Nucleare).

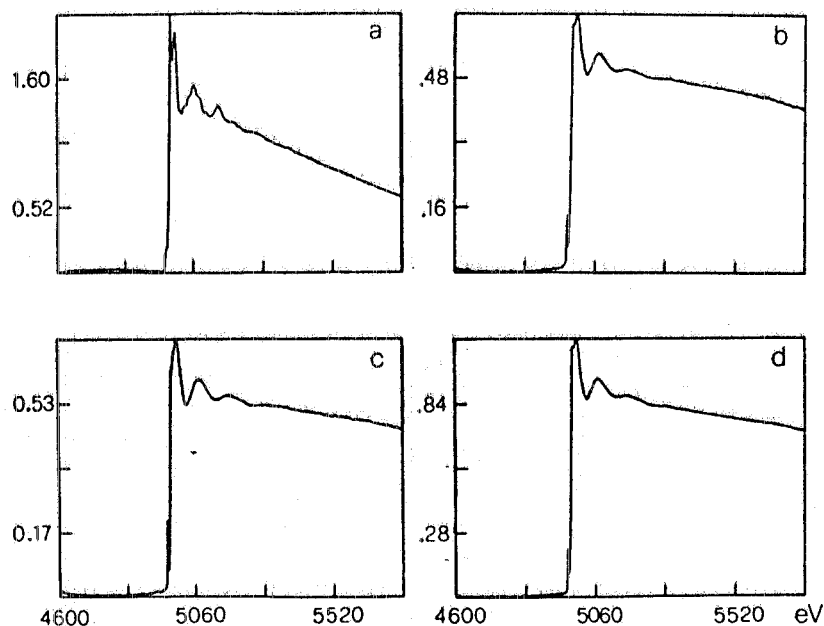


FIG. 1 - Typical Ti K-edge absorption spectra after pre-edge background removal. a) TiO_2 anatase; b) gel-glass II heated at 250°C ; c) glass II heated at 1000°C ; d) glass III heated at 700°C . All thermal treatments are for 3h.

3. - RESULTS AND PRELIMINARY DISCUSSION

3.1. - DTA measurements

At 250°C the materials appeared strongly coloured owing to the formation of carbonaceous products. This darkening completely cleared up after the heating stage at 430°C for 40h. At relatively low temperatures DTA curves similar to those described by Gonzalez-Oliver⁽²⁷⁾ were found. An endothermic peak appeared at about 130°C due to the physical desorption of water and alcohol from gels and an exothermic peak appeared at about $260\text{-}290^\circ\text{C}$, due to the combustion of carbonaceous materials. No trace of exothermic peaks for all the three compositions, due to the crystallization of the glasses, were revealed up to 1300°C .

3.2. - XRD analysis

By XRD analysis it was possible to ascertain that all samples remained amorphous up to 700°C . Glass I in particular did not crystallize up to 1200°C . On the contrary, increasing the TiO_2 content, the crystallization temperature decreased, as already verified by Gonzalez-Oliver et al.⁽²⁷⁾. In fact, crystallinity due to anatase begins to appear at 1200°C for the composition II and is well present at 1000°C for the

composition III.

Table II gives the so-obtained values of crystallinity obtained by the already mentioned computerized procedure^(19, 20). No disorder was detected in the crystalline phases using this method.

TABLE II - Values of anatase crystallinity (wt %) in the glasses heat treated at high temperature.

Gel-Glasses compositions	700°C 3h	1000°C 3h	1200°C 3h
I	amorphous	amorphous	amorphous
II	amorphous	amorphous	<1
III	amorphous	3(*)	11

(*) For this sample the crystallinity was determined taking into account all the observed XRD peaks, included some ones not attributed to anatase.

It is interesting to note that the glass III heated at 1000°C shows broad XRD peaks slightly shifted to lower 2θ angles (expansion of the anatase tetragonal unit cell), with respect to those of the same glass heated at 1200°C. Moreover, some other intermediate broad peaks (four in the $2\theta = 10^\circ$ -70° range) appear at 1000°C (see Fig. 2, where the XRD diagrams of these two samples are reported). Very likely, these extra XRD peaks belong to another crystalline phase containing titanium,

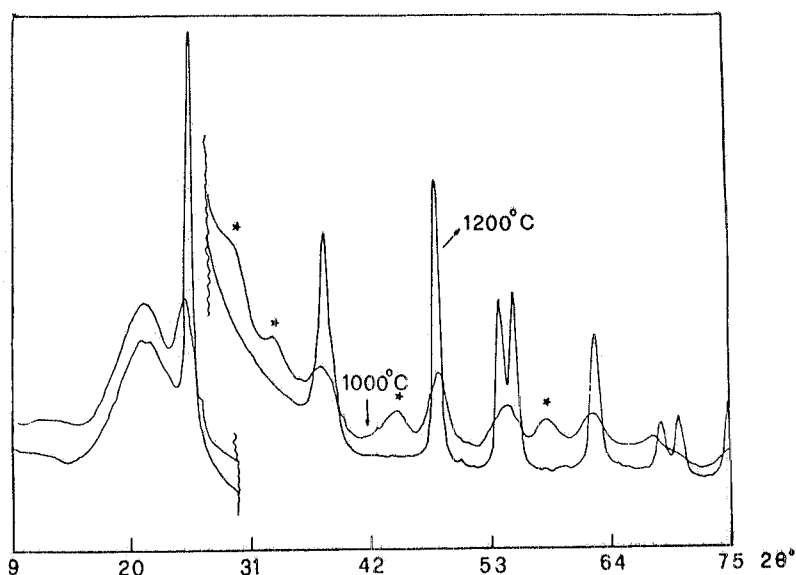


FIG. 2 - XRD diagrams of the partially crystallized glass III heated at 1000°C and at 1200°C for 3h. The extra peaks not belonging to the anatase phase are denoted by an asterisk.

which could not be identified.

A Fourier analysis of the X-ray line broadening was carried out on the glasses III, partially crystallized at 1000 and 1200°C. For both samples the anatase 111 peak

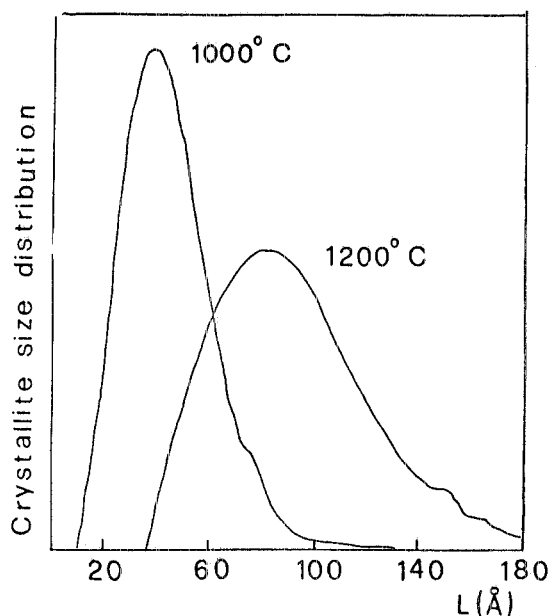


FIG. 3 - Crystallite size volume distributions, $p_v(L)$, obtained according to the equation: $p_v(L) = L(d^2 A^P(L)/dL^2)$ where $A^P(L)$ are the corrected Fourier coefficients for the (111) XRD peaks. The line broadening was attributed only to microcrystallinity.

Note that a Fourier analysis, based on the Warren-Averbach method^(21, 26), performed on the pair of 200-400 anatase reflections of glass III heated at 1200°C did not show any presence of lattice disorder. In fact, the Fourier corrected coefficients plots of the two peaks were closely superimposed to each other. This confirms the result previously obtained using the completely different Ruland method.

3.3. - EXAFS and XANES results

X-ray absorption spectra are usually divided in two parts, according to the energy of the photoelectron and consequently to the theoretical framework used to interpret them⁽²⁸⁾. The near-edge spectra extend up to 30-40 eV above the absorption edge, while the EXAFS spectrum is at higher energies.

3.3.1. - Near-edge (XANES) spectra

In Fig. 4 the near-edge spectra of the Ti K-edge in the TiO₂-SiO₂ gel-glasses heat treated at various temperatures are shown. The near-edge spectrum of TiO₂ (anatase)

was investigated. Fig. 3 reports the two crystallite size distributions obtained from the second derivative of the Fourier coefficients $A^P(L)$ plotted as a function of the L distance (in Å), defined in the direct space. The mean values of the anatase crystallite sizes are 50 Å and 100 Å for the two samples partially crystallized at 1000 and 1200°C, respectively. These values are similar to those found by Gonzalez-Oliver et al. after heat treatments at about 1000-1100°C, carried out on TiO₂-SiO₂ partially crystallized glasses obtained with the sol-gel method too. The crystallite size increases with increasing temperature thus indicating that "diffusion controlled growth and probably precipitate coarsening effects were occurring"⁽²⁷⁾.

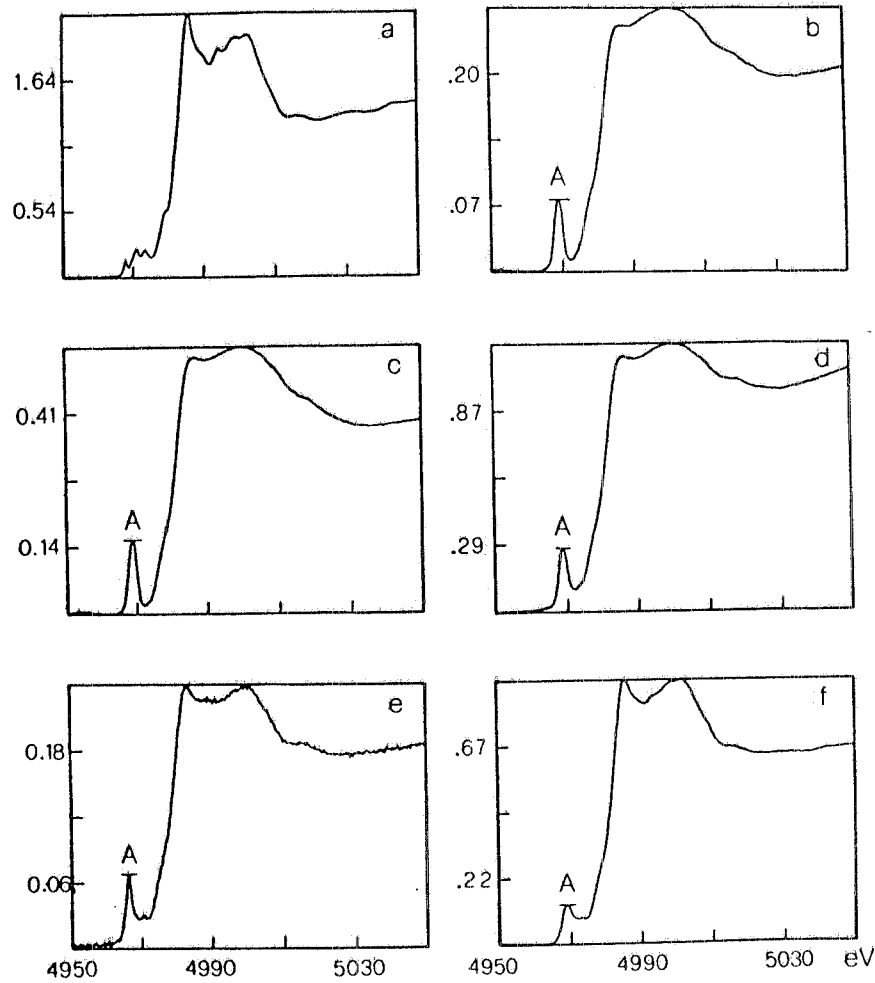


FIG. 4 - Near edge spectra of: a) TiO₂ anatase; b) glass I heated at 700°C; c) glass II heated at 700°C; d) glass III heated at 700°C; e) glass III heated at 1000°C; f) glass III heated at 1200°C.

is also reported. The rather complicated shape of the edge reflects transitions of the photoelectron to both discrete and continuous final states. The sharp rising edge is due to transitions to states in the continuum, while the following structures are due to multiple scattered photoelectron state functions, and are related to the local geometry around the Ti - sites (XANES)^(29, 30).

The XANES structures can be used to investigate the local geometry up to the third and fourth coordination shell^(31, 32). The peak labelled A in the spectra is due to transitions to final states localized around the Ti⁺⁴ ions due to the overlap of the Ti 3d states with the O2p states. These transitions are dipole allowed only when the point group of the Ti-site has no inversion symmetry. For this reason the intensity of peak A has been related⁽⁶⁾ to the ratio of T_d Ti-sites versus O_h Ti-sites in this class of materials.

Table III shows the intensity of peak A for the glasses studied in the present work; the intensities were normalized to the atomic absorption coefficient as measured far from the edge when the EXAFS oscillations die out, in order to eliminate their

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

Gel-Glasses compositions	Heat Treatments				
	250°C 3h	430°C 3h	700°C 3h	1000°C 3h	1200°C 3h
I	0.38	0.32	0.38	0.60	0.71
II	0.30	0.29	0.32	0.55	0.54
III	0.28	0.32	0.28	0.36	0.19

thickness dependence. Note that the intensity of the peak increases with increasing temperature and decreases with increasing Ti content. Only the glass III heated at 1200°C shows an anomalous behaviour, exhibiting the smallest intensity of peak A. This sample shows also significant differences in the XANES pattern due to a strong contribution to XANES spectrum given by the presence of O_h Ti-sites, thus demonstrating a partial crystallization. No chemical shift has been observed in any of the sample studied.

3.3.2. - EXAFS spectra

The EXAFS spectra were extracted from the raw data using the procedure described elsewhere⁽³³⁾. Some of the resulting $\chi(k)$ are shown in Fig. 5. The EXAFS spectra are described^(34, 35) in the one electron approximation by

$$\chi(k) = \sum_{j=1}^n (N_j/kR_j^2) e^{-2\sigma_j^2 k^2} |f_j(k, \pi)| \sin(2kR_j + \phi_j) \quad (1)$$

where N_j is the number of neighbours of the j^{th} shell at a distance R_j from the origin, whose backscattering function is represented by $f_j(k, \pi)$; ϕ_j is a phase term due to the scattering of the photoelectron from both the j^{th} neighbour potential and the central atom potential; σ_j^2 represents the mean square deviation of the j^{th} neighbour distance with respect to the central atom. In eq. (1) no term has been considered to take into account inelastic losses^(36, 37).

By Fourier transforming the experimental spectra one obtains the partial pair distribution functions: Ti-other component⁽³⁸⁾. In Fig. 6 the Fourier transforms (F. T.) of the EXAFS spectra of Fig. 5 are shown. The F. T. of the EXAFS spectrum of

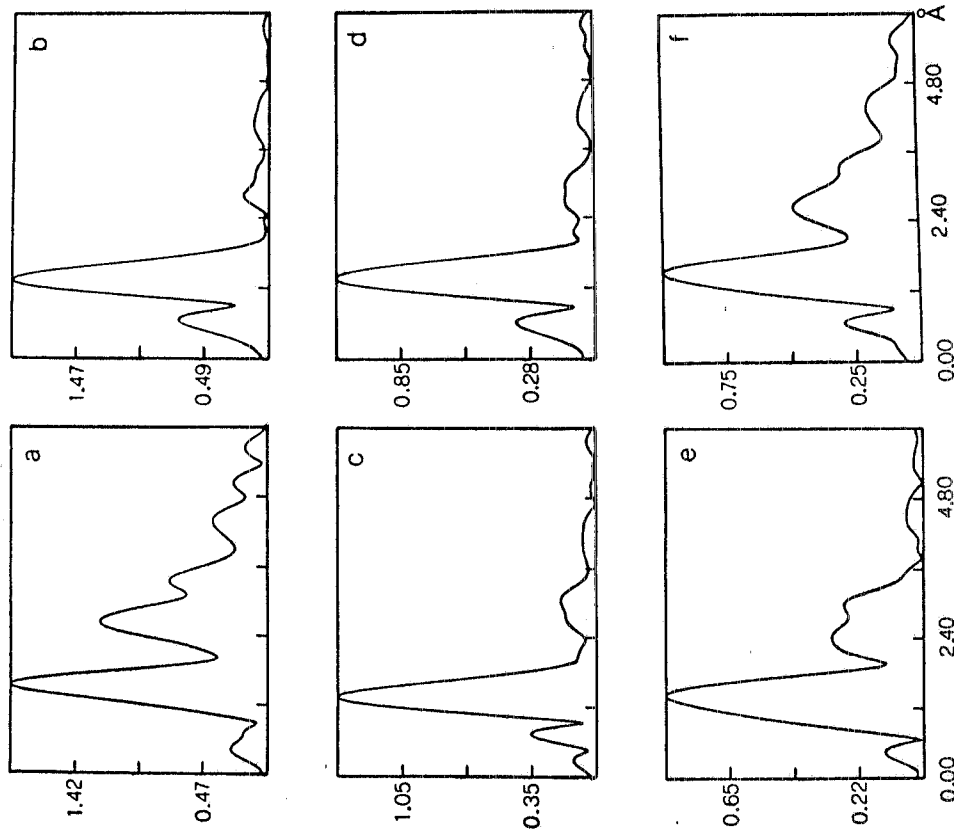


FIG. 6 - Fourier transforms of some EXAFS spectra. a) TiO_2 anatase; b) glass I heated at 1200°C ; c) glass II heated at 700°C ; d) glass III heated at 700°C ; e) glass III heated at 1000°C ; f) glass III heated at 1200°C . All spectra have been transformed in the range $3 \times 12.5 \text{ \AA}^{-1}$ using a gaussian window function and a k^2 weight.

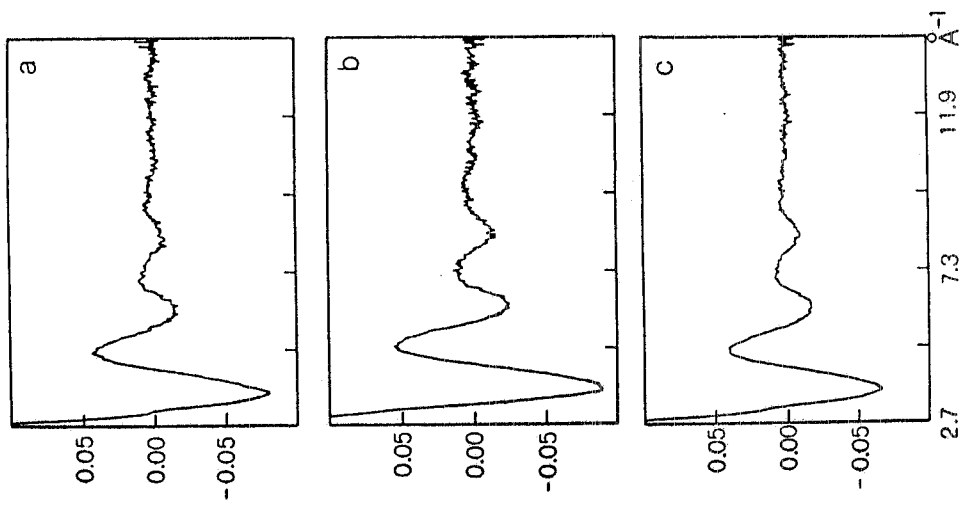


FIG. 5 - Examples of EXAFS spectra: a) glass II heated at 250°C ; b) glass II heated at 1000°C ; c) glass III heated at 700°C .

anatase sample is also reported. As can be noted, the glasses studied do not show any significant structure above the first coordination shell, indicating a lack of intermediate and long range order in these glassy materials.

In Table IV the bond distances obtained from the F. T. 's are reported. The positions of F. T. maxima R_E are related to the bond distances in the glass, R_G , by the relation

$$R_G = R_E + \delta R_{\text{phase}} \quad (2)$$

where δR_{phase} is a phase-shift induced in R-space by the term $\phi_j(k)$ in eq. (1). This term is inherent to a given pair absorber-scatterer atoms, and can be transferred from a system to another one, provided they are chemically alike⁽³⁹⁾.

TABLE IV - Ti-O R_G bond distances obtained from the FT maxima a), and from the R_G vs. k linear trend b). All the values reported are in Å.

Gel-Glasses compositions (wt % TiO ₂)	Heat treatments									
	250°C 3h		430°C 3h		700°C 3h		1000°C 3h		1200°C 3h	
	a)	b)	a)	b)	a)	b)	a)	b)	a)	b)
I (4.5)	n. d.	n. d.	n. d.	n. d.	1.84	1.84	1.81	1.81	1.82	1.81
II (10)	1.84	1.84	1.84	1.84	1.84	1.83	1.82	1.81	1.82	1.81
III (19)	1.85	1.85	1.84	1.85	1.84	1.84	1.85	n. d.	1.95	1.93

For the Ti-O pair the δR_{phase} term was derived from the TiO₂ anatase and rutile crystals, obtaining a value of

$$\delta R_{\text{phase}} = 0.42 \pm 0.01 \text{ \AA}.$$

With the exception of the sample III heated at 1200°C, the values thus obtained range from 1.80 Å up to 1.86 Å, distances too short to be compatible with an O_h coordination of Ti-sites and in agreement with the Ti-O bond distances in Ba₂TiO₄, the only known crystalline Ti compound exhibiting a T_d coordination around Ti⁺⁴ ions⁽⁴⁰⁾. On the contrary, for the glass III heated at 1200°C, the Ti-O distances agree with an octahedral coordination, as measured in anatase and rutile⁽⁴¹⁾ and also in some glasses⁽⁸⁾.

As it is possible to see in Fig. 6, the F. T. of the glass III heated at 1000°C, as well as the F. T. of the same glass heated at 1200°C, shows peaks up to the 4th coordination shell, typical of a long range ordered material. Moreover these F. T. resemble the anatase one even though a greater amount of disorder around the equilibrium positions is present. It is worth noticing that in the glass III heated at 1000°C the Ti-O distances

are significantly shorter and the disorder higher than in the glass heated at 1200°C. This result which may correspond to an intermediate ordered phase parallels the presence of the extra unidentified XRD peaks observed in this sample.

3.3.3. - k-space analysis

By back transforming the first peak of the F. T. , one selects the contribution to the $\chi(k)$ due only to the first coordination shell in eq. (1)⁽⁴²⁾. In this way it is possible to analyze the phase function of $\chi_1(k)$ given by

$$\phi_G(k) = 2kR_1 + \phi_1(k) , \quad (3)$$

separately from the amplitude function given by

$$A_G(k) = \frac{N_1}{kR_1^2} e^{-2\sigma_1^2 k^2} \left| f_1(k, \pi) \right| , \quad (4)$$

The above relations are valid if there is only one shell (even if distorted) contributing to the first peak in the F. T.

The general method employed to extract the R_G values from the phase function (eq. (3)) is the comparison of the total phase function (eq. (3)) with the one of a model compound with known crystallographic R_M value⁽⁴²⁾. Indeed the quantity

$$(\phi_G(k) - \phi_M(k))/2k$$

is phase shift independent, constant over the k range measured and equal to $R_G - R_M$. Table IV shows the R_G values obtained for the glasses using the approach described and TiO_2 anatase as model compound. An excellent agreement with the R_G values obtained from F. T. 's is evident.

The comparison with the amplitude function A_M of a model compound is used to extract N_1 and σ_1^2 information from the spectra^(*)(42). By plotting the function $\ln | A_G(k)/A_M(k) |$ vs. k^2 one should get a straight line whose slope is given by

$$-2(\sigma_G^2 - \sigma_M^2) = -2(\Delta\sigma_G^2)$$

and whose extrapolation to $k^2 = 0$ is

$$\ln \left[(N_G/N_M) \cdot (R_M^2/R_G^2) \right] .$$

(*) These and the subsequent derived symbols N_G , N_M , σ_G^2 and σ_M^2 are referred to the first coordination shell.

Systematic deviation from the straight line behaviour indicate the presence of more than one shell contributing to the first peak of F. T. (43). This is not the case for all the glasses studied in the present work, provided they have not been partially crystal

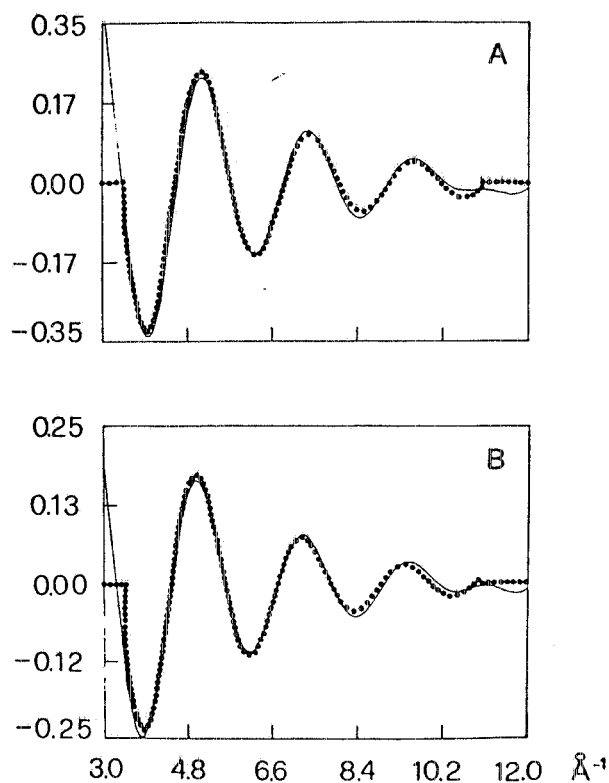


FIG. 7 - Examples of the quality of the fits obtained by using a single shell approach as described in the text in the case of glass II heated at 1000°C (A) and glass III heated at 700°C (B). The continuous lines are the experimental ones, while the big points (●) represent the output of the fitting procedure.

The results on N_G and $\Delta\sigma_G^2$ thus obtained are summarized in Table V. It is very interesting to note that the effect of the thermal treatment is a progressive decrease of $\Delta\sigma_G^2$, indicating that one goes from a highly distorted T_d unit at low temperature when the material is an essicated gel to a more ordered T_d unit in the more densified glasses. The value of $\Delta\sigma_G^2$ in the glass I heated at 1200°C is negative, which means that the first coordination shell in the glass is more ordered than in TiO_2 anatase. Since the structural disorder in anatase is negligible (we estimate $\sigma_{static}^2 \approx 0.1 \times 10^{-2} \text{ \AA}^2$ for the first shell) it can be deduced that the bond distance fluctuations in this glass are negligible, and the tetrahedral units almost perfect.

lized. This indicates that the presence of O_h sites for Ti^{+4} is negligible in the glass state, the essicated gels at 250-430°C included.

To verify in a more quantitative way the possible presence of a small quantity of sixth fold coordinated Ti^{+4} 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, together with the TiO_2 anatase phase and amplitude functions(44). An excellent agreement is obtained with a single shell model with an average coordination number of 4, as shown in Fig. 7.

Thus, the present results both on bond distances and coordination numbers clearly indicate that Ti^{+4} ions occupy T_d sites, when crystallinity is not present. In all these samples a presence of O_h -coordinated Ti-sites greater than the compressive error of the method ($\sim 3\%$ of the total Ti content) can be excluded.

TABLE V - Coordination number N_G , and $\Delta\sigma_G^2$ differences, for the gel glasses. Anatase TiO_2 has been used as reference compound.

Gel-Glasses compositions	Heat treatments					
	250°C 3h	430°C 3h	700°C 3h	1000°C 3h	1200°C 3h	
I	N_G	n. d.	n. d.	4.6	4.4	4.1
	$\Delta\sigma_G^2$	n. d.	n. d.	-0.23×10^{-2}	-0.33×10^{-2}	-0.41×10^{-2}
II	N_G	3.6	3.4	3.8	4.3	3.7
	$\Delta\sigma_G^2$	0.10×10^{-2}	0.13×10^{-2}	-0.14×10^{-2}	-0.22×10^{-2}	-0.29×10^{-2}
III	N_G	3.6	3.6	3.8	n. d.	5.9
	$\Delta\sigma_G^2$	0.45×10^{-2}	0.23×10^{-2}	0.09×10^{-2}	n. d.	0.6×10^{-2}

Then it is possible to infer that in this glass the Ti^{+4} ions occupy completely ordered T_d sites with all bond distances alike. Bearing this in mind, and assuming that the dynamical parameters are comparable, both in the glassy and in the crystalline phase, we calculated the root mean square deviations for all the glasses studied (Table VI), with the exception of glass III heated at 1000°C. In this latter sample an intermediate ordered phase, very likely, was originated, at the beginning of the crystallization process as deduced from the F. T. spectra. For this sample a one-shell fit did not give good results, while a two-shell fit showed too high a correlation between parameters. More refined models to explain this "intermediate" phase are under study.

TABLE VI - δR_G fluctuations of Ti-O bond distances obtained by the $\Delta\sigma_G^2$ values of Table V. All the values are reported in Å.

Gel-Glasses compositions	Heat treatments				
	250°C 3h	430°C 3h	700°C 3h	1000°C 3h	1200°C 3h
I	n. d.	n. d.	0.030	0.020	0.0
II	0.050	0.050	0.035	0.030	0.025
III	0.065	0.060	0.050	n. d.	0.055

4. - FINAL DISCUSSION AND CONCLUSIONS

Taking into account the previously reported EXAFS and XANES results concerning the behaviour of the coordination geometry, the bond distances and the $\Delta\sigma_G^2$ values as functions of heat treatment and Ti concentration, it is possible to conclude that Ti^{+4}

ions occupy only four-fold (T_d) sites at any concentration up to the temperatures where an "intermediate" ordered phase comes out. Thus, the Evan's suggestion of a complete dissolution of TiO_2 in the SiO_2 network has been here confirmed and extended out of the upper limit of the "metastable" region as defined by Schultz and by Evans.

This fact may be thought to be due to the high homogeneity characteristic of glasses obtained from the sol-gel method and considered of great importance for the validity of the assumptions made by Evans.

It must be observed that the described picture is already clear in the essicated gels and the thermal treatment causes a progressive ordering of the T_d units, as shown by the smaller δR_G fluctuations of the Ti-O bond distances obtained by the $\Delta\sigma_G^2$ values (Table VI). This effect is seen also from the progressive increase of the intensity of the peak A in the pre-edge region (Table III). In our materials these variations are not to be attributed to different percentage of T_d vs. O_h (octahedral) sites, as it was supposed by Sandstrom et al. in their glasses, which could be less homogeneous than the present ones. This picture is indeed a simplified scheme since in determining the strength of the transition one has to take into account not only the symmetry of the site but also the geometrical details of the cluster like bond lengths and bond angles. In fact, the shortening of the bond length implies a more compact structure and an increasing of the overlap integrals between Ti 3d and O 2p states, resulting in an increased oscillator strength of the transitions.

The crystallization of the TiO_2 - SiO_2 glasses towards anatase, having very small crystallite sites in the range 50-100 Å has been here confirmed for heat treatments in the range 1000-1200°C. Also an appearance of crystallinity at higher temperature for lower TiO_2 concentration has been confirmed.

It is worth noticing that for the partially crystallized glass III, heated at 1200°C, a crystallinity content of 11 wt% has been computed instead of the total 19 wt% TiO_2 content, as it would be possible to assume on the basis of the almost perfect six-fold coordination (Table V) and the Ti-O bond distance (1.93-1.95 Å) found in this sample. This apparent contradiction can be explained on the basis of a presence of clusters, nuclei, very small crystallites (≈ 25 Å) or paracrystallites which do not contribute to the XRD peaks. Clearly, in these ordered segregate phases as well as in a possible initial glassy segregate phase, the titanium ions have an octahedral coordination coming out from the silica network owing to the opening of the Ti-O tetrahedral linkages.

Furthermore, the "intermediate" ordered phase seen both by XRD and EXAFS in the glass III heated at 1000°C, which is likely to appear also in the glasses I and II at higher temperatures, as some preliminary evidences are showing, will be better investigated in a work to come.

ACKNOWLEDGMENTS

The assistance in the X-ray absorption measurements by Mr. Moretto is very appreciated. Thanks are due to Dr. Alvise Benedetti and Dr. Stefano Polizzi for their contribution in the XRD investigations.

Prof. V. Gottardi is very acknowledged for the initial suggestions on the aims of the present work.

The assistance of the Laboratori Nazionali di Frascati is gratefully acknowledged.

Italian Research Council (CNR, Rome) has partially supported this research (Progetto Finalizzato Chimica Fine e Secondaria, and Comitato Tecnologico).

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