

Ti K-edge XANES study of the local environment of titanium in bioresorbable $\text{TiO}_2\text{--CaO--Na}_2\text{O--P}_2\text{O}_5$ glasses

David M. Pickup · Ensanya A. Abou Neel · Robert M. Moss ·
Kate M. Wetherall · Paul Guerry · Mark E. Smith ·
Jonathan C. Knowles · Robert J. Newport

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Abstract Ti K-edge XANES (X-ray absorption near edge structure) spectroscopy has been used to study the local coordination of titanium in biocompatible and bioresorbable $\text{TiO}_2\text{--CaO--Na}_2\text{O--P}_2\text{O}_5$ glasses. Both conventional melt-quenched glasses of composition $(\text{TiO}_2)_x(\text{CaO})_{0.30}(\text{Na}_2\text{O})_{(0.20-x)}(\text{P}_2\text{O}_5)_{0.50}$, where $x = 0.01, 0.03$ and 0.05 , and sol-gel derived $(\text{TiO}_2)_{0.25}(\text{CaO})_{0.25}(\text{P}_2\text{O}_5)_{0.50}$ glass have been studied. The results show that in all the materials studied, titanium is surrounded by an octahedron of oxygen atoms. Further analysis reveals that the TiO_6 site in the amorphous samples is not heavily distorted relative to that in rutile, anatase or CaSiTiO_5 . The spectra from the $(\text{TiO}_2)_{0.25}(\text{CaO})_{0.25}(\text{P}_2\text{O}_5)_{0.50}$ sol-gel samples reveal greater distortion in the TiO_6 site in the dried gel compared to the heat-treated sol-gel glass. The XANES spectra from melt-quenched glass samples soaked in distilled water for various times do not show any evidence of degradation of the titanium site over periods of up to 14 days.

1 Introduction

Phosphate-based glasses containing calcium and sodium can be classed as both biocompatible and bioresorbable [1]. They have predictable dissolution rates which can be varied by changing the composition of the glass [2, 3]. Melt-quenched glasses in the ternary system $\text{CaO--Na}_2\text{O--P}_2\text{O}_5$ show excellent *in vitro* biocompatibility with high CaO content (46–48 mol%) and low dissolution rate glasses supporting the attachment, growth and differentiation of human osteoblasts and fibroblasts [4].

The properties described above make phosphate-based glasses suitable for a host of potential biomedical applications. Bioresorbable glasses offer interesting solutions as reinforcement phases for composite materials, drug delivery systems [5], antibacterial materials [6, 7] and cavity fillers for maxillofacial surgery [8]. Further to this, there has been significant interest in these glasses when manufactured as fibres for potential use in tissue engineering, and in particular for any tissue with a medium to high anisotropy, such as muscle and ligament [3, 9].

One drawback of ternary $\text{CaO--Na}_2\text{O--P}_2\text{O}_5$ glasses is that for applications requiring longer-term stability, this system is still too soluble. To circumvent this problem several metallic oxides, including TiO_2 , Fe_2O_3 and ZnO_2 have been added as stabilizing agents [10–13]. It was found that additions of TiO_2 not only reduced the solubility, but also improved the mechanical properties of the glasses [11]. Furthermore, the inclusion of titanium has major importance for cellular activity as suggested by a number of studies of Ti metal and other Ti alloys, both *in vitro* and *in vivo* [14–17]. In fact, a recent *in vitro* study of the behaviour of phosphate-based glasses has shown that addition of TiO_2 enhances MG63 cell proliferation and causes significant gene up-regulation [18]. It has also been

D. M. Pickup (✉) · R. M. Moss · K. M. Wetherall ·
R. J. Newport
School of Physical Sciences, University of Kent,
Canterbury CT2 7NH, UK
e-mail: dmp@kent.ac.uk

E. A. Abou Neel · J. C. Knowles
Division of Biomaterials and Tissue Engineering, UCL Eastman
Dental Institute, 256 Gray's Inn Road, London WC1X 8LD, UK

P. Guerry · M. E. Smith
Department of Physics, University of Warwick,
Coventry CV4 7AL, UK

shown that adding TiO_2 to bioactive calcium phosphate coatings improves the adhesion of the coatings to metallic substrates [19].

The aim of the work presented herein was to better understand the properties of these biocompatible TiO_2 – CaO – Na_2O – P_2O_5 glasses by probing the structural environment of the titanium ions using Ti K-edge XANES (X-ray absorption near edge structure) spectroscopy. Both conventional melt-quenched glasses of composition $(\text{TiO}_2)_x(\text{CaO})_{0.30}(\text{Na}_2\text{O})_{0.20-x}(\text{P}_2\text{O}_5)_{0.50}$, where $x = 0.01, 0.03$ and 0.05 , and sol-gel derived $(\text{TiO}_2)_{0.25}(\text{CaO})_{0.25}(\text{P}_2\text{O}_5)_{0.50}$ glass, both before and after heat treatment, were studied. Also studied were samples of the melt-quenched glasses that had been soaked in distilled water for 7 and 14 days in order to look for structural evidence of glass dissolution.

2 Experimental procedures

2.1 Sample preparation

The melt-quenched glasses of composition $(\text{TiO}_2)_x(\text{CaO})_{0.30}(\text{Na}_2\text{O})_{0.20-x}(\text{P}_2\text{O}_5)_{0.50}$ ($x = 0.01, 0.03$ and 0.05) were prepared using sodium dihydrogen orthophosphate (NaH_2PO_4), calcium carbonate (CaCO_3), phosphorus pentoxide (P_2O_5) and titanium dioxide (TiO_2) (BDH) as precursors. These precursors were placed in a Pt/10%Rh crucible (Type 71040, Johnson Matthey) which was introduced into a preheated furnace (Carbolite, RHF 1500) at 700°C to allow for removal of H_2O and CO_2 , followed by melting at $1,300^\circ\text{C}$ for 3 h.

The $(\text{TiO}_2)_{0.25}(\text{CaO})_{0.25}(\text{P}_2\text{O}_5)_{0.50}$ sol-gel sample was prepared from the reaction of a mixture of mono- and di-substituted ethyl phosphate $\text{OP}(\text{OH})_2(\text{OEt})$ and $\text{OP}(\text{O}-\text{H})(\text{OEt})_2$ with titanium isopropoxide ($\text{Ti}(\text{OPr}^i)_4$, Aldrich, >95%) and calcium methoxyethoxide (Ca-methoxyethoxide, ABCR, 20% in methoxyethanol) as described previously [20]. The dried gel was heated to 350°C to remove solvent, water and organic molecules.

2.2 Ti K-edge XANES

Ti K-edge XANES measurements were made at room temperature on Station 7.1 at the SRS, Daresbury Laboratory, UK, with a ring-energy of 2 GeV and a stored current of 150–250 mA. The spectra were recorded in transmission mode using a double crystal Si(111) monochromator ($d = 3.136 \text{ \AA}$) and ionisation chambers to detect the incident and transmitted beam intensities. Finely ground samples were diluted in polyethylene (Aldrich, spectrophotometric grade) and pressed into pellets to give a satisfactory absorption and edge step. A titanium foil and a

third ionisation chamber were placed after the sample to allow an absorption spectrum of the foil to be collected simultaneously for the purpose of calibrating the energy scale. The energy scale was defined by assigning the most intense peak in the derivative of the Ti foil spectrum to 4965.0 eV. XANES spectra were collected from 150 eV below to 350 eV above the Ti K-edge in order to allow accurate background subtraction. A fine energy step of 0.15 eV, i.e. comparable to the monochromator's resolution, was used around the edge. The data processing comprised conversion of the data to absorption versus energy, calibration of the energy scale, removal of the pre-edge background by straight-line fitting and removal of the post-edge background by fitting with a second order polynomial. All the spectra were normalised to have an edge-step of 1. Each spectrum consisted of the sum of between 2 and 12 scans, depending on the concentration of titanium in the sample. As well as the data from the titania-doped phosphate glasses, spectra were also collected from a series of reference materials containing Ti^{4+} ions in different coordination geometries: 4.5 mol% TiO_2 -doped cristobalite (fourfold), $\text{Na}_2\text{TiSiO}_5$ (fivefold), and anatase, rutile and CaSiTiO_5 (sixfold). The anatase sample was purchased commercially (Aldrich, 99.9%) and the rutile prepared by heating the anatase to 1000°C . The other reference materials were prepared by solid state reactions using oxide starting materials [21–23].

3 Results and discussion

Ti K-edge XANES spectra are characterised by peaks just to the low energy side of the main X-ray absorption edge in the energy range known as the pre-edge region. The pre-edge features in the spectra from the reference materials are shown in Fig. 1a, and the corresponding features in the spectra from the melt-quenched phosphate-based glasses in Fig. 1b. No significant variation in the spectra from the melt-quenched samples is observed as a function of titanium content. Figure 2a shows the pre-edge features in the spectra from the 3 mol% TiO_2 -doped melt-quenched glass that had been soaked in distilled water for various times. Figure 2b shows the pre-edge regions of the spectra from the $(\text{TiO}_2)_{0.25}(\text{CaO})_{0.25}(\text{P}_2\text{O}_5)_{0.50}$ sol-gel sample, both before and after heat treatment. The intensities, positions and shapes of the pre-edge features in the spectra from the glasses soaked in distilled water show no significant variation as a function of soaking time suggesting that the glasses are stable in water, at least in terms of the titanium environment, over long periods.

The work of Waychunas [24] and Farges et al. [25] demonstrated that the pre-edge peaks in Ti K-edge XANES spectra give information on the coordination geometry of

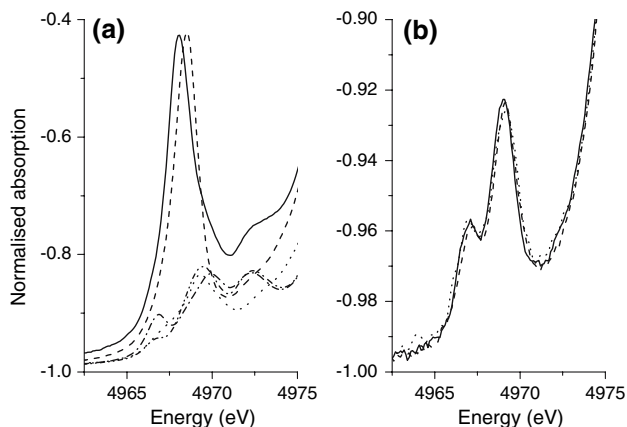


Fig. 1 Ti K-edge XANES spectra in the region of the pre-edge features. (a) Reference materials: 4.5 mol% TiO₂-doped cristobalite (—), Na₂TiSiO₅ (- - -), CaSiTiO₅ (···), anatase (-·-·) and rutile (-·-·). (b) Melt-quenched phosphate-based glasses (TiO₂)_x(CaO)_{0.30}(Na₂O)_{0.20-x}(P₂O₅)_{0.50}: x = 0.05 (—), 0.03 (- - -) and 0.01 (···)

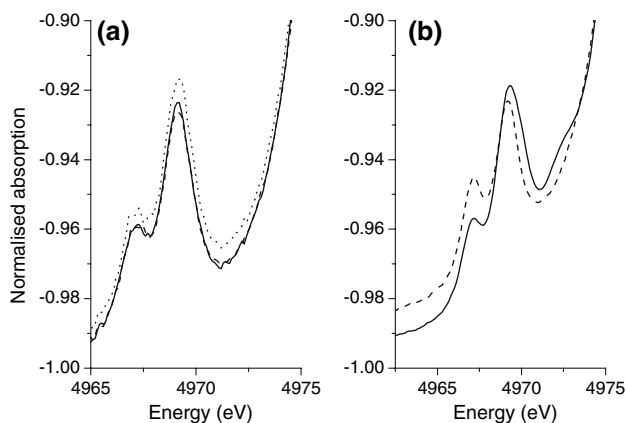


Fig. 2 Ti K-edge XANES spectra in the region of the pre-edge features. (a) 3 mol% TiO₂-doped melt-quenched glass samples that had been soaked in distilled water for 0 (—), 7 (- - -) and 14 days (···). (b) (TiO₂)_{0.25}(CaO)_{0.25}(P₂O₅)_{0.50} sol-gel sample: dried gel (—) and heat-treated sol-gel glass (- - -)

the titanium ions. Figure 3 shows the Gaussian deconvolution of the pre-edge region of the XANES spectrum from rutile TiO₂. In this region, three peaks, labelled **A1**, **A2** and **A3**, are observed. These electronic transitions are assigned according to the literature [26, 27]. The **A1** peak is due to a quadrupolar *1s* → *3d* transition whereas the **A2** and **A3** peaks are due to dipolar *1s* → Ti *3d/O 2p* transitions to states that are mainly *t_{2g}* in character. These dipolar transitions are forbidden in a centrosymmetric environment (Laporte’s rule) as in a regular octahedron. It has been shown that the intensity of the dominant **A2** peak decreases, and its energy increases, as the degree of centrosymmetry around the titanium ions increases due to a reduction of *pd* mixing [24, 25]. Consequently, the **A2** peak becomes more intense and shifts to lower energy as the

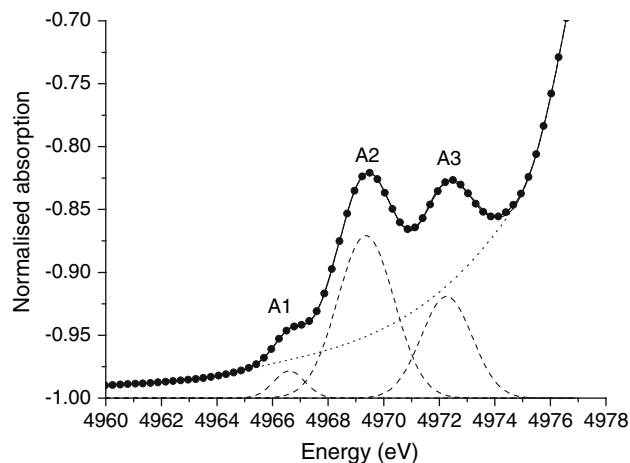


Fig. 3 Pre-edge Ti K-edge XANES spectrum from rutile TiO₂ showing Gaussian deconvolution. The symbols (●) show the overall fit which is composed of three Gaussian functions (- - -) and a cubic spline background (···)

coordination of titanium changes from sixfold → fivefold → fourfold. By measuring the intensity and position of the **A2** peak and comparing the results with those from reference materials with various Ti coordination geometries, it is thus possible to determine the coordination environment of titanium in amorphous materials [28].

Figure 4 shows a plot of dominant pre-edge peak area against position (as determined by Gaussian fitting) for both the reference compounds and TiO₂–CaO–Na₂O–P₂O₅ sol-gel and glass samples. This plot clearly shows that the pre-peaks for the reference materials containing four and fivefold coordinated titanium occur at a lower energy and are more intense than those from the sixfold reference

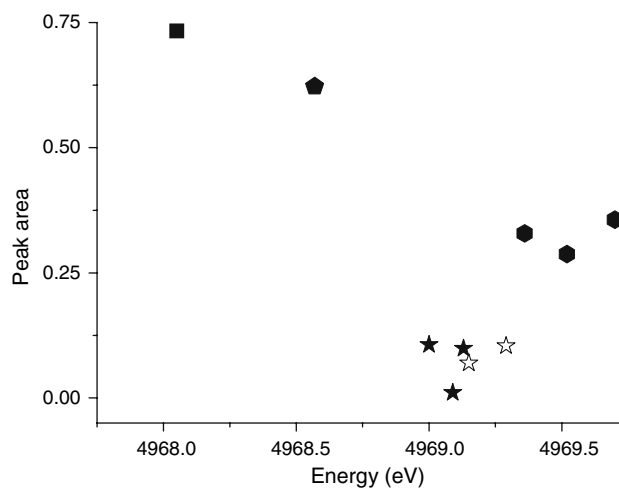


Fig. 4 Plot of Ti K-edge pre-edge peak area versus position (as determined by Gaussian fitting) for both the reference compounds and TiO₂–CaO–Na₂O–P₂O₅ sol-gel and glass samples: 4-coordinate (■), 5-coordinate (●) and 6-coordinate (●) reference materials, melt-quenched glasses (★) and sol-gel samples (☆)

materials. Comparison of the data from the sol–gel and melt-quenched glass samples with that from the reference materials containing octahedrally coordinated titanium shows that the pre-peak intensity and positions are similar, suggesting that the sol–gel and melt-quenched glass samples contain sixfold coordinated titanium. No significant variation in pre-peak parameters is observed between the sol–gel prepared or melt-quenched samples. These results also indicate that there is no variation in the Ti–O coordination number in the melt-quenched samples as a function of titanium content and in the sol–gel samples as a function of heat treatment. Although the pre-peak parameters for the sol–gel and melt-quenched glass samples are similar with those from the reference materials containing sixfold titanium, it can be seen from the clustering of the points in Fig. 4 that the pre-peaks in the XANES spectra from the amorphous samples are slightly less intense and occur at lower energy. It is likely that this difference is related to the degree of distortion of the TiO₆ octahedron [29]. The occurrence of the shoulder **A3** on the high energy side of the dominant pre-edge peak, as in the spectrum from rutile, is attributed to the out-of-centre distortion of the TiO₆ octahedron. The resultant tetragonal symmetry of the crystal field leads to a splitting of the *t*_{2g} orbitals into *e*_g (*d*_{xz} and *d*_{yz}) orbitals with a lower energy (**A2**) and a *b*_{2g} (*d*_{xy}) orbital with a higher energy (**A3**). Thus, the occurrence and shape of **A3** peak provides a sensitive probe for the degree of the distortion. The fact that the **A3** shoulder is not observed in the XANES spectra from the heat-treated sol–gel and melt-quenched glass samples suggests that the degree of distortion around the titanium ions is lower than in the crystalline reference materials. The lower distortion around the Ti site in the heat treated sol–gel and melt-quenched glass samples also accounts for the lower intensity of the dominant pre-edge peak in the XANES spectra from these samples compared to the 6-coordinate reference materials.

Although analysis of the dominant pre-edge peak reveals no variation in the Ti–O coordination number between samples, there are differences between the XANES spectra from the dried sol–gel and heat-treated sol–gel glass shown in Fig. 2b. The XANES spectrum from the dried gel exhibits an extra pre-edge feature at a position close to that of the **A3** peak in the spectrum from rutile. This result suggests a more distorted titanium site in the dried gel compared with both the heat-treated sol–gel glass and the melt-quenched glass samples, and demonstrates that the heat-treatment of the sol–gel causes a structural relaxation around the titanium site, possibly due to the loss of adsorbed water, unreacted alkoxide groups and hydroxyl groups. Further support for this is provided by the observation of a reduction in intensity of the dominant **A2** pre-edge peak upon heat treatment. However, the intensity

and position of the dominant peak still suggest that the degree of distortion around the titanium ions in the dried gel is less than that in rutile, anatase and CaSiTiO₅.

4 Conclusions

Analysis of the pre-edge region of the Ti K-edge XANES spectra from the melt-quenched glasses and sol–gel samples reveal that the titanium ions occupy an octahedral structural environment in all samples. Further comparison of the shape and intensity of the pre-edge features with those measured from reference materials containing octahedrally coordinated Ti suggest that the TiO₆ site in the amorphous samples is not heavily distorted relative to that in rutile, anatase or CaSiTiO₅. The spectra from the (TiO₂)_{0.25}(CaO)_{0.25}(P₂O₅)_{0.50} sol–gel sample reveal greater distortion in the TiO₆ site in the dried gel compared to the heat-treated sol–gel glass. The pre-edge features of the XANES spectra from the 3 mol% TiO₂-doped melt-quenched glass samples that had been soaked in distilled water for various times are all very similar suggesting that the titanium environment is stable in water over long periods, as expected since the addition of titanium is known to improve the chemical durability of phosphate-based glasses.

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