

Advanced Characterisation of Atomic and Medium-Range Structural Development of Amorphous Sol-Gel Materials

Overview and Context of Research Programme

This project built on the successful research funded by GR/L28647 developing a comprehensive advanced methodology for improved understanding of the structure and its evolution in amorphous sol-gel materials, and was a collaboration between Warwick (Smith) and Kent (Newport). It is very clear that many of the properties of such materials are determined by structural features formed in the amorphous, precursor materials (e.g. progenitor phase separation). The current pair of tied projects had two distinct strands both encompassing the principal project aim to, (i) enhance the methodology and (ii) increase understanding of gel-formed materials. This work led to new aspects of the leading-edge, advanced methodology, with specific applications targeted on the technologically important TiO_2 - SiO_2 binary system. Our core methodology was applied to new systems such as HfO_2 - SiO_2 , and to more complex systems such the ternary ZrO_2 - TiO_2 - SiO_2 and quaternary Na_2O - ZrO_2 - TiO_2 - SiO_2 . The research carried out provided new insight into the factors that link the chemical nature of the elements involved with the type of structure that evolved, and hence how these convey the properties of these materials. The detailed work on TiO_2 - SiO_2 provided the most complete and accurate structural information yet obtained on such a gel-produced amorphous material. Comparison with HfO_2 (and ZrO_2 under GR/L28647) and the more complex systems gave real insight into the competing structural influences of the different elements, and how for example they determine the structure of the underlying silicate matrix (and hence largely determine their properties) and phase separation. We believe that much of the research carried out was at least internationally competitive, and some aspects, such as the neutron diffraction difference experiments and the ^{17}O and ^{49}Ti NMR, were internationally leading.

Achievements of Scientific Programme: Summary of Outcomes

The main scientific highlights were:

1. The first neutron diffraction (ND) data on $^{46,48}\text{Ti}$ isotopically enriched amorphous gel-produced materials samples was collected. Carrying out difference experiments provided the most accurate description to date of the local titanium environment in these materials. This revealed the coordination changes with composition, allowing improved modelling of the titanium sites.
2. The first solid state NMR was carried out on ^{49}Ti -enriched samples providing the highest quality titanium NMR data from amorphous materials, and indicated differences in the titanium site with composition.
3. The most complete multinuclear NMR data was collected from sol-gel produced materials, and the NMR methodology optimised so that it can be widely used by other workers in this field.
4. The first detailed data from sol-gel prepared $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$ combined FTIR, multinuclear MAS NMR, EXAFS, SAXS and TGA was reported. It was shown that although the behaviour was similar to ZrO_2 added to SiO_2 there were subtle, but significant differences in the silicate network structure and degrees of phase separation.
5. In the ternary $(\text{ZrO}_2)_x(\text{TiO}_2)_y(\text{SiO}_2)_{1-x-y}$ system the individual metals show similar behaviour to their respective binary systems, with the metals being homogeneously distributed up to 750°C and 500°C for ≤ 15 and ≤ 20 mol% metal content respectively. After heating to 750°C in a $\text{Zr}5(= 5\text{mol}\% \text{ZrO}_2)\text{Ti}15$ sample phase separation into X-ray amorphous ZrTiO_4 domains occurs, and for $\text{Zr}15\text{Ti}5$ ZrO_2 phase separates.
6. Ternary samples which have Na_2O added show that the sodium is incorporated into the network lowering the connectivity, and the samples are quite homogeneous at lower heat treatment temperatures ($\leq 500^\circ\text{C}$).

Detailed Description of Work Carried Out

1. Preparation of isotopically titanium enriched precursors for neutron diffraction and solid state NMR experiments

Titanium isotopes were purchased to make samples for both neutron diffraction and solid state NMR experiments, in the form of TiO_2 , as $^{46}\text{TiO}_2$ (72.1 atom% enriched), $^{48}\text{TiO}_2$ (99.8 atom% enriched) and $^{48/49}\text{TiO}_2$ (74.3 and 23.9 atom% enriched respectively). To allow the current studies to be compared with our previous work the conventional sol-gel route was employed, but this required the conversion of the oxides to the corresponding isopropoxides via their chloride analogues. Each chloride was prepared by first grinding the oxide with an excess of carbon and heating ($\sim 1000^\circ\text{C}$) under a controlled atmosphere of chlorine in a fluidised-bed reaction vessel. The resultant TiCl_4 was condensed in a cold trap and purified by distillation. The isopropoxide was prepared by reacting the TiCl_4 with anhydrous isopropanol under a dry nitrogen atmosphere. The HCl by-product was converted to insoluble NH_4Cl by diluting the reaction mixture with anhydrous toluene (to reduce the solubility of the NH_4Cl), bubbling dry NH_3 through for 2 hrs, followed by heating at 60 - 70°C for a further 2 hrs. The solid NH_4Cl was removed by filtration and the toluene

boiled off under vacuum. The resultant $\text{Ti}(\text{OPr})_4$ was purified by vacuum distillation and then used in the sol-gel process.

2. Neutron difference experiments on isotopically-enriched samples

Samples $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ ($x = 0.08, 0.18$ and 0.41) were sol-gel prepared and heated to $250, 500$ and 750°C . ^{46}Ti and ^{48}Ti were selected for the neutron diffraction experiment because of their availability and their nuclear properties, i.e. they are both stable isotopes and possess very different neutron scattering lengths, $b_{\text{Ti-46}} = 4.93$ fm and $b_{\text{Ti-48}} = -6.08$ fm (cf. $b_{\text{natural}} = -3.44$ fm). If the difference in real space data is taken between samples composed of different isotopes of element A the resultant correlation function is of the form

$$\Delta T(r) = T(r) - T'(r) = c_A^2 \left(b_A^2 - b_{A'}^2 \right) t'_{AA}(r) + 2 \sum_{j \neq A} c_A c_j b_j \left(b_A - b_{A'} \right) t'_{Aj}(r)$$

where $t'_{Aj}(r)$ represents the partial pair correlation function for elements A and j , with c and b the respective concentrations and neutron scattering lengths. Thus, only the structural environment of element A is probed. The nature of the difference experiments requires the samples are structurally identical and this was confirmed by X-ray diffraction at station 9.1 of the SRS. This study represents the first time that changes in coordination number, and associated changes in Ti-O bond length, have been directly observed for $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ sol-gel prepared glasses. Such changes have previously been inferred from XANES and ^{17}O MAS NMR measurements. However, it is only the use of neutron diffraction with isotopes and high quality data collected over a wide Q-range (to give good real-space resolution, $\Delta r \sim \pi/Q_{\text{max}}$) available at the ISIS GEM diffractometer that have allowed us to make such observations.

On the basis of the ND data in this study the following conclusions are reached. The $(\text{TiO}_2)_{0.08}(\text{SiO}_2)_{0.92}$ samples exhibit only one Ti-O bond distance of 1.83 Å due to tetrahedrally-coordinated Ti substituted in the silica network, regardless of heat treatment. The $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ sample shows two Ti-O distances suggesting that initially the majority of the Ti is present in a distorted octahedral environment. Heating the $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ sample decreases the longer Ti-O distance until at 750°C it is identical to the bond length in anatase. Hence some phase separation occurs but most of the titanium remains as part of the silicate network (Fig. 1). The $(\text{TiO}_2)_{0.41}(\text{SiO}_2)_{0.59}$ sample shows longer Ti-O distances at all temperatures indicating phase separation of TiO_2 , which crystallises into anatase by 750°C .^{8,9}

Taking the analysis of the neutron diffraction data further, we have used RMC (Reverse Monte Carlo) modelling to construct a model of the structure of the $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ 750°C material which is consistent with all three datasets collected from the samples containing $^{\text{nat}}\text{Ti}$, ^{46}Ti and ^{48}Ti . This model has allowed us to assign peaks at 3.1 and 5.2 Å in the real space difference data from the $^{\text{nat}}\text{Ti}$ and ^{48}Ti samples to Ti-Ti correlations. This is the first time that these distances have been assigned in such a material. Since the RMC model was constructed from an initial configuration in which the Ti was substituted within the silica network, the observation of these distances in the experimental data as well support the conclusion that the majority of Ti in this material is substituted tetrahedrally within the glass network. The RMC model of the $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ is being extended to contain some TiO_6 groups as a minority species, and also the data from $(\text{TiO}_2)_{0.08}(\text{SiO}_2)_{0.92}$ will be modelled as part of an on-going study.¹³

3. TiO_2 - SiO_2 materials studied via titanium NMR and vis-UV

Titanium has two NMR-active isotopes (^{47}Ti (nuclear spin $I = 5/2$) and ^{49}Ti ($I = 7/2$)) but there has been relatively little solid state titanium NMR published to date. The main experimental difficulty is that both isotopes have moderately large electrical quadrupole moments (Q) in the ratio $^{49}\text{Q}/^{47}\text{Q} = 0.8179$, and the ^{49}Ti line is often preferred as it shows less quadrupole broadening, even though it has the lower natural abundance (5.51% (^{49}Ti) vs. 7.28% (^{47}Ti)). Spectral interpretation is complicated as these two NMR-active titanium isotopes have extremely similar γ s, so that even at 14.1 T their resonance frequencies only differ by ~ 9 kHz, which is usually much smaller than the widths of the resonance lines. An initial study examined titanium at natural abundance in sol-gel prepared titania nanoparticles.¹ Below 700°C the lineshape of the titania nanoparticles could be well simulated by taking the interaction parameters of

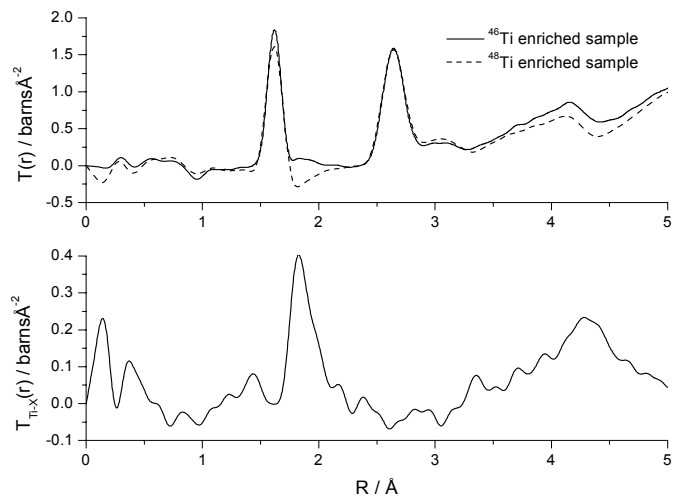


Figure 1 Top: Total correlation functions, $T(r)$, from the ^{46}Ti enriched and ^{48}Ti enriched $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$ samples heated to 750°C . Bottom: Difference correlation function showing clearly two Ti-O bond distances at 1.82 and 2.0 Å. The broad feature at ~ 4.3 Å is associated with 2^{nd} -neighbour correlations involving Ti (e.g. Ti-O-Si).

anatase and applying an additional broadening that was inversely proportional to the particle size. Above 700°C the spectra become more complex as the particles become mixtures of anatase and rutile. XRD can also distinguish these phase components but the NMR information is complementary. At low anatase concentrations XRD fails to pick up any anatase whereas the NMR evidence is unequivocal as to its presence.¹

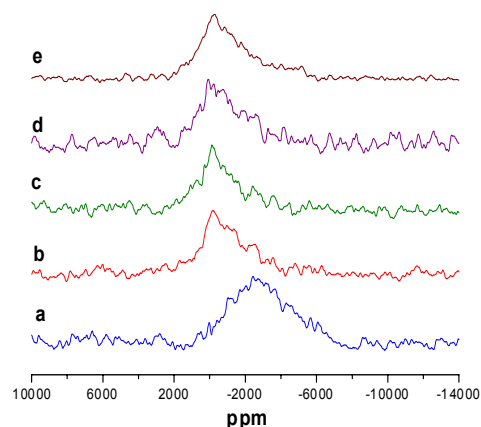


Figure 2. ⁴⁹Ti static NMR spectra from an 8 mol% TiO₂ containing silicate gel (a) unheated and then heated to (b) 120, (c) 250, (d) 500 and (e) 750°C.

Our preliminary studies using diffuse reflectance UV-vis spectroscopy to probe the environment of Ti in (TiO₂)_x(SiO₂)_{1-x} materials have identified a clear correlation between the wavelength of the UV-vis absorption edge and the value of x. Consistent with the literature, as x increases and with it the proportion of 6-fold Ti, so does the wavelength of the Ti UV-vis absorption transition. *In situ* UV-vis studies during heating are currently being undertaken.

(4) Further developments of multinuclear NMR characterisation of gel materials

Further, new developments of the NMR methodology for gel-produced materials have been undertaken, augmenting ²⁹Si MAS NMR information about the network connectivity by using other nuclei. ¹³C monitors the loss of the organic fragments and ¹H MAS NMR is a very sensitive probe of the proton-content.^{3,7} Protons associated with organic and hydroxyls groups can be readily distinguished and the absolute level of protons can be determined from the integrated proton signal compared to a proton standard. The residual proton levels remain significantly above that of surface absorbed protons until relatively high temperature (i.e. between 500 and 750°C), presumably from remaining isolated hydroxyls that are difficult to remove.

⁴⁹Ti NMR (3) offers an alternative NMR view of changes in the titanium coordination. ¹⁷O NMR is the most powerful NMR probe of such oxide materials as it is present throughout the structure and distinct resonances from different fragments M-O-M' (M, M' can be Ti, Zr, etc., and/or Si) are resolved. In TiO₂-SiO₂ materials the field variation and utility of multiple quantum approaches for ¹⁷O NMR were examined, and the optimum experimental approach is to perform normal single quantum MAS experiments at medium field (7.05-9.4T) since this usually provides sufficient resolution of the different M-O-M' fragments.⁷ This means that the technique is widely accessible only requiring access to a standard solid state NMR spectrometer, and the sample does not require the high enrichment necessary for the 2D MQ technique. 1D ¹⁷O MAS NMR was applied to a series of functionalised silicon alkoxides and acetylacetonate modified titanium precursors and the NMR data provided clear evidence for the effects of these changes on the structure of the sol-gel formed.²

To preserve the expensive ¹⁷O label heating was always carried out under nitrogen (not the standard air) and the same sample was successively heated to the temperatures rather than a single target temperature. The need to heat under nitrogen to preserve the oxygen-label is illustrated in Fig. 3. A large difference in loss of signal between the as-made sample and the samples heated to 750°C under nitrogen compared to air is observed, with the ¹⁷O label significantly better preserved under nitrogen. Different atmospheres and heating procedures could lead to the samples being structurally different, but a detailed comparison via multinuclear NMR and some of the other methods (e.g. IR, X-ray based, etc.) suggested that the equilibrium structure develops very rapidly at a given temperature so that the

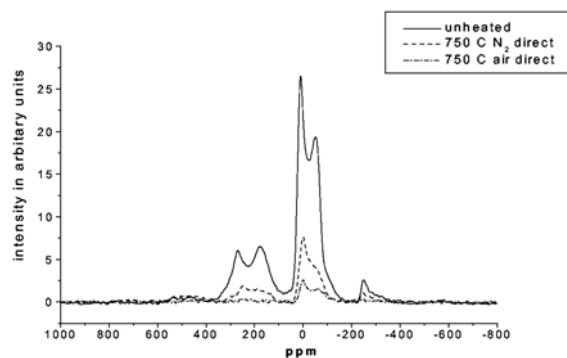


Figure 3. Comparison of ¹⁷O MAS NMR signals from an 18 mol% TiO₂, unheated and 750°C under air and nitrogen.

Enriching the titanium in the samples so that 23.9 at% is ⁴⁹Ti and 73.3 at% is ⁴⁸Ti effectively depletes the sample of ⁴⁷Ti. Two significant advantages accrue through the signal enhancement of ⁴⁹Ti and the simplification of the NMR spectra, as the effects of ⁴⁷Ti can be effectively neglected. This isotopic enrichment means that titanium NMR of amorphous materials can be seriously contemplated with this being the first such report in the literature.⁷

Large differences in ⁴⁹Ti NMR spectra from silica gels containing 8 and 41 mol% TiO₂ are observed. As the samples are heat treated the changes with the 41 mol% sample are relatively small, with some sharpening of parts of the lineshape. The 8 mol% sample shows much more significant changes (Fig. 2). The data can be interpreted as the 41 mol% sample being dominated by TiO₆ environments, largely in phase separated nanocrystalline anatase. The larger change in the ⁴⁹Ti NMR signal from the 8 mol% TiO₂ sample is probably due to the development of structurally integrated TiO₄.^{7,12,13} From this initial work it is clear that solid state NMR could develop into an important new probe of the titanium environment in amorphous materials.

different total amount of heating makes no significant difference.^{3,7} Also there was no marked change of structure under the different heating atmospheres (apart from the ~20-30°C difference at which the residual organic fragments are lost). Small changes in the distribution of intensity between the different M-O-M' fragments as the samples were heated were observed. This is due to T_1 increasing more rapidly at some sites compared to others at elevated temperatures. The large change in ^{17}O T_1 needs to be taken into account using ^{17}O data quantitatively. All the NMR developed in this project established further principles for the use of NMR by non-specialist groups interested in sol-gel materials.

(5) Structural development of the $\text{HfO}_2\text{-SiO}_2$ system and comparison with other binaries

We believe that our work on sol-gel produced $\text{HfO}_2\text{-SiO}_2$ was the first detailed study of this system.^{6,10} There is increasing technological interest in this material, particularly for specialist electronic applications. Multinuclear MAS NMR, FTIR, EXAFS, SAXS and thermal analysis were applied. There is much similarity between the behaviour of HfO_2 and ZrO_2 added to SiO_2 , which might be expected. Both zirconium and hafnium can be dissolved to significant levels into silica, and although homogeneously part of the silicate phase, the high preferred coordinations of zirconium and hafnium means these metals do not become part of the tetrahedral framework. This is a key distinction to titanium, and although the amount of titanium within the silicate phase cannot be sustained at as high a level as zirconium and hafnium, titanium becomes part of the silicate framework itself. ^{17}O NMR is a very sensitive probe of phase separation through the well separated Hf-O-Hf or Zr-O-Zr resonances.^{6,10} Despite the high degree of similarity between the behaviour of zirconium and hafnium there are two notable and subtle distinctions. When phase separation occurs the nanodomains of the oxide are largely amorphous but atomic scale probes (i.e. ^{17}O NMR, EXAFS) show that the structures are tetragonal and monoclinic for ZrO_2 and HfO_2 respectively. Also the Q^n distribution of the silicate network is quite different, with the amount of Q^4 much higher in the case of zirconium. As the amount of zirconium/hafnium added in these samples is the same, the source of the difference in structure is very small changes in the degree of nanoscale phase separation. ^{17}O NMR data can confirm these very small differences but requires high signal-to-noise data.⁷

(6) Structural development in more complex ternary and quaternary sol-gel materials

The influence of competing structural effects were investigated by looking at a series of more complex sol-gel silicates with (a) ZrO_2 and TiO_2 ,^{4,5} and then (b) Na_2O added as well.^{7,11} These systems were fully characterised and it was shown that the metal environments were very similar to those of the individual metals in the separate binaries. With all combinations of Ti/Zr at $\leq 15\text{mol}\%$ added metal remained homogeneous up to $\sim 750^\circ\text{C}$. For $\leq 20\text{mol}\%$ SAXS, XANES and ^{17}O NMR show that phase separation occurs after heating as ZrO_2 and ZrTiO_4 for higher zirconium and titanium contents respectively, but there is no sign of any crystallisation until 1000°C .⁵ Small amounts of added Na_2O had no noticeable effect on the environments of zirconium and titanium. Na_2O enters the silicate phase and creates more non-bridging oxygens as expected.^{8,12} The samples remain homogeneous up to 750°C .

Project Management, Summary of Expenditure and Progress of Research Programme

The two PIs took responsibility for the management of the appropriate parts of the project, and the enrichment in the titanium isotopes was led by Kent. The teams maintained regular (effectively weekly) contact on the progress of the research, making full use of electronic communication for full involvement of the team in project discussions. During the project there were 11 minuted meetings of the complete project team which alternated between Kent and Warwick. The team also met frequently at the central facilities experiments. The expenditure and the use of central facilities on this project were as set out in the original case for support.

The programme of research largely proceeded as expected. Much of the novel technique development was centred around the preparation of isotopically titanium-enriched samples. Since the isotopes could only be purchased as TiO_2 an efficient scheme had to be devised to convert this to the normal precursor used, titanium isopropoxide (see (1) above). This proved to be quite challenging synthetic chemistry and meant that sample preparation of the isotopically enriched samples took longer than anticipated. It meant that Ti isotope experiments (NMR/neutron diffraction) were moved to the second half of the project. *In situ* variable temperature UV-vis work was delayed more than a year by the equipment supplier, and then the heating chamber developed a fault soon after delivery and had to be returned. However all the UV-vis equipment is now fully functional. The parallel studies on other related sol-gel silicate materials proceeded entirely as expected. In the original case 5 specific objectives and 6 new aspects of technique development were identified. Work was carried out on all 11 areas and the tasks were largely accomplished.

Further Research in this Area

Understanding the underlying structural features of sol-gel materials, with a novel characterisation methodology was the core underlying theme of this project. It is generally applicable to amorphous materials and some of the aspects developed as part of this collaboration are already being used by other researchers. Silicate materials have been the emphasis of our research which shows that much of the previous literature often gave a very limited and incomplete

picture of their structural features. For silicates a major follow-up project has been to use this methodology to understand the structural sources of the properties of bioactive sol-gel calcium silicates that are being developed for tissue replacement. This is currently being funded through 3 joined EPSRC grants (GR/R57492, /R57508, /R59298). It is clear that there are many other amorphous materials to which the approach developed here can be applied, such as phosphate-based systems. The mapping of the more specialist techniques (e.g. high field solid state NMR, neutron and synchrotron experiments) onto commonly available techniques such as FTIR and UV-vis make the results obtained here more widely applicable to the target user community. *In situ* work is one of the keys to making characterisation even more attractive to materials and their processing. This work has shown that both FTIR and UV-vis offer much potential for *in situ* work, but it is synchrotron-based methods (both X-ray absorption and XRD) using the highest intensity, highly coherent sources available that offer the route to the highest quality, most unequivocal structural data. An EPSRC/ESRF studentship project (starting 10/02) entitled "Applications of synchrotron radiation to understanding sol-gel processing" was based on the preliminary *in situ* work on sol-gels carried out by the research team. The UV-vis is also proving extremely effectively for *in situ* monitoring of structural changes of CaO-SiO₂ materials reacting with simulated body fluid that is currently being studied.

Personnel and Training

The pair of projects directly employed an experienced PDRA (Dr Pickup, Kent) and a PhD student (Mr Philips Gunawidjaja, Warwick). Dr Pickup's excellent synthetic skills were suitably stretched by the need to prepare the isotopically enriched titanium alkoxides from TiO₂. Dr Pickup coordinated much of the central facilities work, particularly the neutron experiments. The novel isotope difference neutron experiments extended Dr Pickup's experience. The student was a physics graduate and the project gave him very extensive training in solid state NMR, as well as giving him exposure to sample preparation, and other analysis techniques such as XRD, thermal analysis and FTIR. Philips also took part in many of the central facilities experiments. The PhD thesis was submitted in 8/03, 34 months after the beginning of the project, and successfully defended in 10/03. The student attended an EPSRC graduate school. The presentation skills of both workers were enhanced by their having to present their work at the quarterly project meetings, and at both national and international meetings (including the most significant sol-gel meeting during the project - 1 talk, 5 posters see end). This project has given the workers key skills and competencies necessary for a high science-based technological economy. Mr Gunawidjaja is now looking for a postdoctoral position, probably overseas, to gain more skills, and currently intends to follow a science-based career.

Other workers benefited from the opportunities and facilities offered by these grants. Dr Gervais, a Framework 5 Marie Curie fellow at Warwick became partially involved in some aspects of the NMR. Dr G. Mountjoy a PDRA at Kent helped with some of the central facilities work and data analysis on HfO₂-SiO₂ and the ternary system ZrO₂-TiO₂-SiO₂. Both now have permanent lecturing positions, Gervais at the University of Paris IV and Mountjoy at Kent. Mark Holland completed his PhD 12/01 at Kent, looking at both the catalytic activity of TiO₂-SiO₂ and ternary ZrO₂-TiO₂-SiO₂, and now works in the radiation detector industry. An exchange student Armanda van Puten (University of Utrecht) carried out her research internship at Kent (9/00-6/01) and worked on TiO₂-SiO₂ materials on controlled pore development characterisation, and UV-vis studies (on a departmental instrument). She successfully completed this project and now works in the Dutch chemicals industry. The EPSRC/ERSF PhD studentship (filled by Mr K.O. Drake) has made use of the facilities and samples provided by this grant. Several undergraduate final year projects on related sol-gel materials were run in parallel using the facilities funded through these grants. We believe that the funding from this pair of grants has provided good research training opportunities in a leading-edge research project at the materials-physics interface, as well as generic in skills, and it also fed into research-led undergraduate teaching.

Dissemination, Relevance to Beneficiaries and Collaboration

Six publications have already appeared in internationally leading physical chemistry/chemical physics journals, making contact with a wide audience, a specialist solid state journal and in a journal that makes direct contact with the most direct beneficiaries of this work. A number of others have either already been submitted or are in preparation. The work is targeted primarily at materials scientists/technologists interested in understanding sol-gel materials, but is also more widely beneficial to solid state/materials chemists where the synthesis or target product contains amorphous components. The project team very actively disseminated the results from this project giving 13 talks, (8 invited with 1 plenary) and 7 posters, many at meetings where the main users of this research were most likely to participate. Through such dissemination collaborations developed. The follow-on project on CaO-SiO₂ bioactive materials also involves Prof. Hench's group at Imperial, with this contact beginning at one of the UK-Ireland sol-gel meetings. A collaboration aimed at understanding sol-gel prepared dental materials is actively being explored with Prof. Knowles (Eastman Dental Institute). Collaboration with University of Paris IV funded through the CNRS/Royal Society built on the new titanium NMR to understand the structural development of sol-gel prepared non-stoichiometric barium titanates.

Appendix – Details of Publications and Presentations to which GR/N64151/01 and GR/N64267/01 contributed

Publications already published/submitted are numbered directly on the IGR form (1-9), papers in preparation and other forms of dissemination are presented here.

(a) Papers in preparation

10. *Structure of $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$ xerogels ($x = 0.1, 0.2$ and 0.4) from FTIR, ^1H , ^{13}C , ^{17}O and ^{29}Si MAS NMR, EXAFS, SAXS and TGA*
P.N. Gunawidjaja, M.A. Holland, G. Mountjoy, D.M. Pickup, R.J. Newport and M.E. Smith, *J. Mater. Chem.*
11. *Multinuclear solid state NMR characterisation of quaternary $\text{Na}_2\text{O-ZrO}_2\text{-TiO}_2\text{-SiO}_2$ xerogels*
P.N. Gunawidjaja, D.M. Pickup, R.J. Newport and M.E. Smith, *Solid State NMR*
12. *Applications of $^{47,49}\text{Ti}$ enriched samples for solid state NMR of $\text{TiO}_2\text{-SiO}_2$ sol-gel materials*
P.N. Gunawidjaja, D.M. Pickup, R.J. Newport and M.E. Smith, *Solid State NMR*
13. *Neutron diffraction and ^{49}Ti solid state NMR study of $\text{TiO}_2\text{-SiO}_2$ sol-gel glasses using isotopic enrichment*
D.M. Pickup, P.N. Gunawidjaja, F.E. Sowrey, K.O. Drake, R.J. Newport and M.E. Smith, *J. Phys Chem. B*

(b) Invited Conference Presentations

14. *Combining advanced probe techniques to characterise ceramic materials (Plenary)*, M.E. Smith, IOM Ceramics Convention, Cirencester, 4/01
15. *Solid state NMR as part of an advanced characterisation methodology of materials*, M.E. Smith, MSSI Research Forum, University of Limerick, 9/01
16. *Detecting atomic scale ordering in glassy and crystalline materials by solid state NMR*, M.E. Smith, RSC Solid State Chemistry Group, Reading, 12/02
17. *Applications of solid state NMR to the study of technologically significant inorganic materials*, M.E. Smith, IUPAC Congress, Ottawa, Canada, 8/03

(c) Invited Colloquia

18. *Recent advances and applications of solid state NMR to characterisation of inorganic materials*, M.E. Smith, Department of Chemistry, University of Aberdeen, 11/01
19. *Applications of solid state NMR to understanding atomic scale structure of materials*, M.E. Smith, Department of Chemistry, University of Dundee, 02/03
20. *Applications of solid state NMR to understanding atomic scale structure of material*, M.E. Smith, Department of Chemistry, Nottingham Trent University, 03/03
21. *Applications of solid state NMR to understanding atomic scale structure of materials*, M.E. Smith, Department of Chemistry, University of St Andrews, 05/03

(d) Contributed Conference Talks

22. *Transition metal sites in ternary $\text{ZrO}_2\text{-TiO}_2\text{-SiO}_2$ xerogels*, G. Mountjoy, M.A. Holland, P. Gunawidjaja, G.W. Wallidge, D.M. Pickup, R.J. Newport and M.E. Smith, 11th Int. workshop on glasses, ceramics, hybrids and nanocomposites from gels (Sol-Gel 2001), Abano Terme, Italy, 9/01
23. *The effects of different heat treatment on the evolution in structural properties of $(\text{TiO}_2)_{0.15}(\text{ZrO}_2)_{0.05}(\text{SiO}_2)_{0.80}$ xerogels*, P.N. Gunawidjaja, M.E. Smith, M.A. Holland, G. Mountjoy and R.J. Newport, BRS Meeting, London, 11/01
24. *The atomic scale structure of sol gel materials*, R.J. Newport, UK-Ireland Sol Gel Meeting, Cranfield, 5/03
25. *Aspects of multinuclear solid state NMR as a probe of sol-gel produced materials*, M.E. Smith, UK-Ireland Sol Gel Meeting, Cranfield, 5/03
26. *Titanium environment in $(\text{TiO}_2)_x(\text{SiO}_2)_{1-x}$ sol-gel catalysts studied by neutron diffraction with isotopic substitution*, D.M. Pickup, R.J. Newport, F.E. Sowrey, K.O. Drake and M.E. Smith, 1st Int. Conf. Appl. Phys., Badajoz, Spain, 10/03

(e) Contributed Conference Posters

27. *Comparing the atomic structures of binary $\text{MO}_2\text{-SiO}_2$ ($M = \text{Ti, Zr or Hf}$) xerogels*, G. Mountjoy, M.A. Holland, P. Gunawidjaja, D.M. Pickup, G.W. Wallidge, M.E. Smith and R.J. Newport, 11th Int. workshop on glasses, ceramics, hybrids and nanocomposites from gels (Sol-Gel 2001), Abano Terme, Italy, 9/01
28. *The effects of different heat treatment and atmospheres on the NMR signal and structure of $\text{TiO}_2\text{-ZrO}_2\text{-SiO}_2$ xerogels*, P.N. Gunawidjaja, M.E. Smith, M.A. Holland, G. Mountjoy and R.J. Newport, IOM Materials Congress, London, 04/02
29. *Applications of ^{17}O MAS NMR to characterising the structure of silicate-based sol-gel materials*, P.N. Gunawidjaja, M.E. Smith, M.A. Holland, G. Mountjoy, R.J. Newport and D.M. Pickup, Rocky Mountain Conference on Analytical Chemistry, Denver, U.S.A., 8/02
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