Application of Oxygen-17 NMR Spectroscopy to Detection of Atomic Scale Phase Separation in Titania-Silica Gels

Mark E. Smith*[a] and Harold J. Whitfield[b]

[a] Physics Laboratory, University of Kent, Canterbury, Kent, UK CT2 7NR
[b] Department of Applied Physics, Royal Melbourne Institute of Technology, Box 3476W, Melbourne, Victoria 3001, Australia

Oxygen-17 magic angle spinning NMR spectroscopy of TiO_2–SiO_2 gels formed by hydrolysis of alkoxides with [17]O-labelled water provides a novel technique for detecting amorphous or poorly crystalline impurity phases and atomic scale phase separation.

Sol–gel formed SiO_2–TiO_2 materials have many industrially significant applications including dense glasses with low thermal expansion coefficients[1] and tailored refractive indices[2] used as optical coatings, and highly porous samples used as catalyst supports.[3] The properties of such mixtures in these applications vary widely often depending on the atomic scale distribution of the elements which can be subtly controlled by the initial gel preparation conditions,[4] so that it is of key importance to have accurate information regarding this distribution. Extensive spectroscopic work has been carried out on SiO_2–TiO_2 gels including IR,[5] Raman,[6] extended X-ray absorption fine structure,[7] X-ray absorption near-edge structure[7] and [29]Si magic angle spinning (MAS) NMR.[3,6]

Silicon-29 MAS NMR has become one of the most powerful tools for determination of local structure in amorphous silicon-containing systems.[8,9] Extensive ^{29}Si NMR work already exists for SiO_2–TiO_2 gels and their consolidation into dense glasses.[3,6] NMR work has played a crucial role in building models of the structure and distinguishing between intimate mixing (i.e. largely Si–O–Ti linkages) or domain separation (i.e. largely Si–O–Si and Ti–O–Ti linkages).[3,5] The silicon NMR evidence relies on next nearest neighbour effects so is somewhat indirect and has had to be supplemented by IR and Raman work. Oxygen-17 is an ideal probe nucleus for NMR having a large chemical shift range and a relatively small quadrupolar moment. Its only drawback is the low natural abundance of [17]O (0.037%) necessitating isotopic enrichment. However for alkoxide formed gels it has been demonstrated that enrichment using [17]O-labelled water is straightforward and has provided new insight into the crystallisation of ZrO_2[10] and TiO_2[11] gels. It is demonstrated in this communication that single-phase and phase-separated TiO_2–SiO_2 samples give quite different ^{17}O MAS NMR spectra indicating the presence of different oxygen linkages.

The SiO_2–TiO_2 gels were made by taking alkoxide, water, ethanol mixtures in the approximate ratios 1:2:7.5 with varying titania contents. For sample B (7.7 mol% TiO_2) tetraethyl orthosilicate (TEOS), 10% [17]O-labelled water, ethanol and a few drops of acid were mixed before rapidly adding titanium n-propoxide, $Ti(OPr^n)_4$, which resulted in immediate precipitation of some TiO_2. Sample A contained nominally the same amount of titania (7.3 mol% TiO_2) but the ethanol was divided equally between the TEOS–water mixture and $Ti(OPr^n)_4$, the latter then being added slowly dropwise to the TEOS–water–ethanol mixture. Sample C was prepared in an identical manner to B except that it contained 41 mol% TiO_2. All samples were allowed to dry by evaporation under a flow of dry nitrogen for $\approx$48 h after which the remaining excess fluid was removed by evacuation at room temperature. The resulting solid was powdered for MAS NMR. The ^{29}Si and ^{17}O NMR spectra were recorded on Bruker MSL 400 [magnetic field (B_0) = 9.4 T] and ASX 500 (B_0 = 11.7 T) spectrometers operating at 79.47 and 67.8 MHz respectively. Silicon spectra were run with a 7 mm double-bearing (DB) MAS NMR probe at spin-rates of $\approx$4.5 kHz using π/6 tip angle pulses, 30 s recycle delays to allow complete relaxation with about 150 transients added together. For

oxygen a 4 mm DB MAS NMR probe was used spinning at 14 kHz with π/6 pulses and 0.5 s recycle delays. Approximately 80000 transients were necessary to show the minor peaks with adequate signal-to-noise. No high power ^{1}H decoupling was used. The spectra were referenced to $SiMe_4$ ([29]Si) and H_2O ([17]O) at δ 0.

The ^{29}Si and ^{17}O MAS NMR spectra are shown in Figs. 1 and 2 respectively. Samples A and B give ^{29}Si NMR spectra with three peaks at approximately δ −92, −102 and −110 with similar relative intensities. These peaks are attributed to differently connected SiO_4 units termed Q^2, Q^3 and Q^4 (where Q^n designates a tetrahedron having n apical oxygens forming bridging bonds to other tetrahedra[8,9]). The non-bridging bonds in these samples will mostly be OH groups, and this is evidenced by the isotropic chemical shifts which tend to be more negative for Si–OH than for Si–O⁻ non-bridging bonds. Samples A and B contained nominally the same amount of titania ($\approx$7.5 mol%) but the more rapid addition of $Ti(OPr_n)_4$ in B resulted in the immediate formation of a white precipitate around which the sol then slowly gelled. The [29]Si spectra are obviously very similar at this stage suggesting that the network connectivity which determines the silicon spectrum is dominated by the OH (i.e. nearest neighbour) distribution. Sample
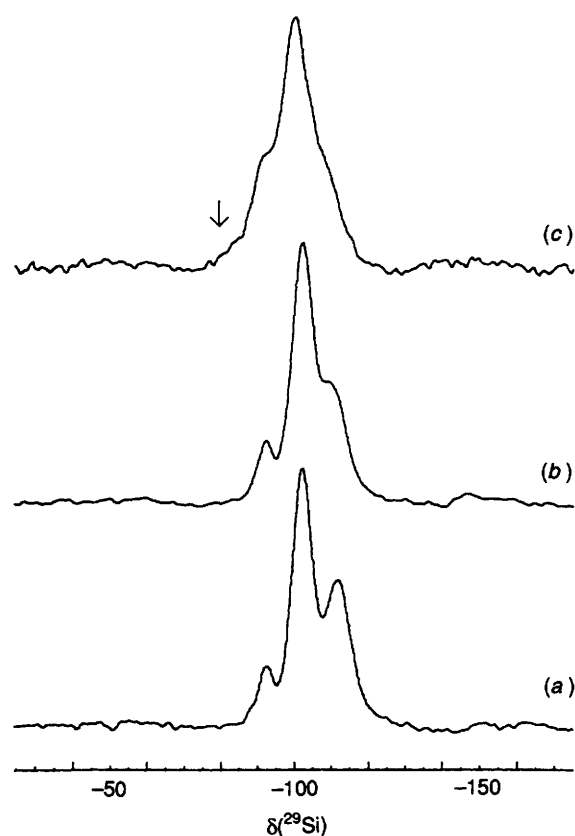

Fig. 1 ^{29}Si MAS NMR spectra of samples (a) A, (b) B and (c) C at 79.47 MHz ($\downarrow$ indicates the resonance at δ 83 in sample C)

C contained four times the titania concentration and the silicon spectrum shows an additional peak at δ-83 [Fig. 1(c)], probably Q^1–OH, and a significantly higher Q^2–OH content than the other two samples. Previous work on SiO_2–TiO_2 suggests that at low titania levels titanium substitutes into the SiO_2 framework whereas beyond 11.3 mol% TiO_2 phase separation of TiO_2 occurs.[6] Hence phase separation is inevitable to some extent in sample C, thus providing a comparison for the lower concentration samples.

In contrast to the ^{29}Si spectra the ^{17}O MAS NMR spectra of samples A and B are strikingly different. In all three samples the ^{17}O spectra are dominated by a resonance with its centre of gravity at $\delta \approx 20$ which shows characteristic second-order quadrupolar structure. The second-order quadrupolar nature of this resonance has been confirmed by repeating the experiment at a magnetic field of 9.4 T resulting in a 20% broader resonance at the lower field due to the inverse magnetic field dependence of this effect.[12] The shape and width of the main resonance agrees with a previous study by Walter et al.[13] for Si–O–Si linkages in amorphous SiO_2, corresponding to an isotropic chemical shift of ≈ 50 ppm. At this stage the ^{29}Si NMR data clearly indicates that there are many Si–OH bonds as well but the ^{17}O resonance from this unit lies under that due to Si–O–Si, as shown by Walter et al.[13] for a pure SiO_2 gel. The major difference in the ^{17}O NMR spectra is that sample A has only one additional resonance at δ 281 (r) while B and C have three additional resonances at δ 542 (p), 371 (q) and 281 (r), and δ 548 (p), 380 (q) and 260 (r) respectively. (It is believed that the shift difference between corresponding peaks in the different samples are beyond experimental error and are the subject of further investigation). Samples B and C give similar ^{17}O NMR spectra apart from the relative increase in the intensity of the peaks associated with titanium (see above) in C, simply reflecting the four-fold increase in the titanium content. These spectra illustrate the sensitivity of ^{17}O NMR in the detection of

amorphous or poorly crystallised impurity phases. Samples A and B have ^{17}O enrichment of only 2.5 atom%, yet the titanium-related peaks which are weak because of the TiO_2 concentration of only 7.5 mol% are clearly observable.

The identity of the coordinations responsible for the smaller resonances is of key importance for understanding the structural significance of the results. Recent work on ^{17}O-enriched TiO_2 gels[11] showed that in the initial gel two major resonances were present at $\delta \approx 530$ and ≈ 370 that were attributed to OTi_3 and OTi_4 coordinations. Heating produced conversion of OTi_4 to OTi_3 until, when anatase crystallised all the oxygen had become OTi_3.[11] The implication for the present gels is that the peaks p and q correspond to OTi_3 and OTi_4. The third resonance (δ 281–260) was never observed in the pure TiO_2 gels, implying that it must be related to Ti–O–Si linkages. This interpretation is reinforced by two pieces of circumstantial evidence. First, the chemical shift is intermediate between Si–O–Si and Ti–O–Ti. Second, the sample A that was manufactured so as to produce an intimate atomic scale mixing (i.e. titanium only as Ti–O–Si) has only this resonance in addition to the major resonance from Si–O–Si. It should also be noted that although samples B and C had visibly phase separated some Si–O–Ti linkages had still formed.

^{17}O NMR spectroscopy offers the possibility for mixed oxide gels of an extremely straightforward method for assigning peaks to different oxide linkages quantitatively. The macroscopic phase separation in the present samples B and C was obvious but confirmed by the ^{17}O NMR spectra with peaks due to OTi_3 and OTi_4. However as NMR is a local probe similar results would have been obtained if nanoscale rather than macroscopic domains had formed. Such information is crucial in understanding and controlling technologically important properties of materials that are related to the local structure. ^{17}O MAS NMR will thus play an important role in characterising such oxide gels by detection of impurity phases and nanoscale phase separation.
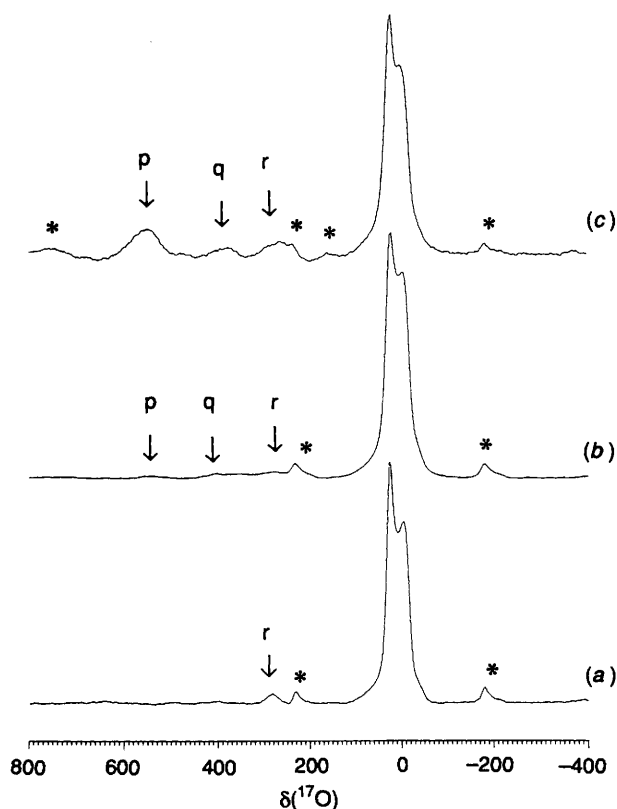
Fig. 2 ^{17}O MAS NMR spectra of samples (a) A, (b) B and (c) C at 67.8 MHz ($\downarrow$, minor isotropic resonance,* spinning sideband)

References

1 Z. Deng, E. Breval and G. C. Pantano, J. Non-Cryst. Solids, 1988, 100, 362.
2 L. Weisenbrock, T. L. Davis, B. J. J. Zelinski, R. L. Roncone and L. A. Weller-Brophy, Mater. Res. Soc. Symp. Proc., 1990, 180, 377.
3 K. L. Walther, A. Wokaun, B. E. Handy and A. Baiker, J. Non-Cryst. Solids, 1991, 134, 47.
4 B. E. Handy, M. Maciejewski, A. Baiker and A. Wokaun, J. Mater. Chem., 1992, 2, 833.
5 C. C. Perry and X. Li in Chemical Processing of Advanced Materials, ed. L. L. Hench and J. K. West, Wiley, New York, 1992, 131.
6 M. Schraml-Marth, K. L. Walther, A. Wokaun, B. E. Handy and A. Baiker, J. Non-Cryst. Solids, 1992, 143, 93.
7 R. B. Greegor, F. W. Lytle, D. R. Sandstrom, J. Wong and P. Schultz, J. Non-Cryst. Solids, 1983, 88, 93.
8 R. Dupree, Expt. Technik. Phys., 1988, 36, 315.
9 H. Eckert, Prog. Nucl. Magn. Reson. Spectrosc., 1992, 24, 159.
10 T. J. Bastow, M. E. Smith and H. J. Whitfield, J. Mater. Chem., 1992, 2, 989.
11 T. J. Bastow, A. F. Moodie, M. E. Smith and H. J. Whitfield, J. Mater. Chem., 1993, 3, 697.
12 M. E. Smith, Appl. Magn. Reson., 1993, 4, 1.
13 T. M. Walter, G. L. Turner and E. Oldfield, J. Magn. Reson., 1988, 76, 106.