Trimethoxyboroxine as an ‘oxygen-transfer’ reagent: a non-aqueous ‘sol–gel’ route to alkali-free borosilicate glass

Michael A. Beckett,*[a] Martin P. Rugen-Hankey[a] and K. Sukumar Varma[b]

[a] *Department of Chemistry, University of Wales, Bangor, UK LL57 2UW. E-mail: m.a.beckett@bangor.ac.uk*
[b] *Pilkington Group Research, European Technical Centre, Lathom, Lancashire, UK L40 5UF*

Received (in Cambridge, UK) 17th April 2000, Accepted 28th June 2000
Published on the Web 19th July 2000

A synthesis of alkali-free borosilicate gel from $Si(OEt)_4$ and $(MeO)_3B_3O_3$ in non-aqueous solvents is reported; the formation of the gel proceeds *via* rapid transesterification/oxygen transfer with elimination of $B(OR)_3$; removal of volatiles from the gel, followed by drying (60 °C, 12 h) and furnacing in air (600 °C, 20 min) resulted in alkali-free borosilicate glass.

The sol–gel methodology involving hydrolysis and condensation of metal alkoxides is potentially an important low temperature route to homogeneous multicomponent oxide glass thin films and coatings.[1–3] Thus, for example, suitable coatings may be obtained by a ‘dip and furnace’ route without exposure to temperatures required in melt/fusion processes (> 1300 °C). The production of alkali-free borosilicate glass by sol–gel routes have generally used protic solvents and mineral acids, with the silicon source partially hydrolysed by prolonged reflux prior to addition of the boron source as either an orthoborate ester[4–8] or as boric acid.[9–10]. The susceptability of B–O–Si bonds to hydrolytic attack at boron, with subsequent leaching of borate, is a severe limitation of the aqueous sol–gel method.[9] The first synthesis of an alkali-free borosilicate gel carried out at ambient temperature in organic solvents, with exclusion of water and mineral acids and using the metaborate ester trimethoxyboroxine (TMB), has recently been reported by Varma[11] in the patent literature. Here, we report on the underlying chemistry of this new and novel ‘sol–gel’ route to borosilicate materials, in which the TMB functions as both a source of boron and as a non-aqueous ‘oxygen transfer’ reagent.

A transparent gel was obtained when TMB and tetraethoxysilane (TEOS) were dissolved in dry acetone in a 1 : 1 molar ratio (B : Si ratio 3 : 1) and left at room temperature for *ca.* 2 weeks.† We have further noted that (i) the gelation time is decreased by increasing the B : Si ratio (*e.g.* 9 : 1, 1 week), (ii) that gels do not form at B : Si ratios of 1:1 even after prolonged periods, and that (iii) in the absence of solvent neat TMB and TEOS (1 : 1) gelled within a week. The transparent gel was isolated and upon removal of all volatiles and oven-drying (60 °C) gave an opaque/glassy solid. The mass of the dried gel was *ca.* 35% of the combined masses of the added TEOS and TMB. The dried gel lost a further 30–40% of its mass upon firing to 600 °C in air and yielded a silver-grey borosilicate glass with a B : Si ratio of *ca.* 1 : 1.2; TGA showed that most of this mass was lost at 350–400 °C.

The solid products were characterised by elemental analysis,† IR, XRD and solid-state MAS NMR spectroscopy. Elemental analysis confirmed the presence of boron and silicon in both dried and fired samples and the mass balance of the reaction confirms that > 90% of the silicon (added as TEOS), and *ca.* 25% of the boron (added as TMB), remained in the final borosilicate glass. XRD analysis indicated that they were both non-crystalline amorphous solids. The ^{11}B MAS NMR spectrum of the furnaced glass [Fig. 1(b)] exhibited a clear residual quadrupolar ‘doublet’ pattern and was simulated as one signal (δ_{iso} = +14.4 ppm) indicating that the boron atoms were all in equivalent three-coordinate axially symmetrical environments and consistent with them being part of the silica network.[12–14] The dried gel gave a ^{11}B spectrum [Fig. 1(a)] simulated as an 80 : 20 mixture of two signals (δ_{iso} = +15.6 and +10.6 ppm), with the main species at lower field. ^{29}Si MAS NMR demonstrated that the principal species in both the dried gel and the furnaced glass was Q^4 (δ_{iso} = −109 ppm), with the furnaced glass giving an asymmetric signal which was deconvoluted as a 63 : 37 mixture with the lower intensity signal at δ_{iso} = −101 ppm.[14] IR spectra of both the dried and furnaced solids (Fig. 2) showed absorptions at 928 and *ca.* 670 cm^{-1} indicating that

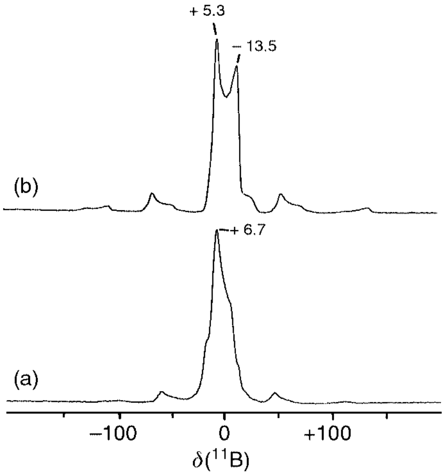

Fig. 1 Observed (96.234 MHz) MAS ^{11}B NMR spectra for (a) the dried gel and (b) the furnaced glass, spinning at 5200 and 5900 Hz, respectively. The dried gel was simulated as two signals: [δ_{iso} (ppm), rel.int, η, C_q (MHz)] 15.6, 80, 0.0, 2.38; 10.6, 20, 0.0, 1.14. The furnaced glass was simulated as a single signal: 14.4, 100, 0.0, 2.63.

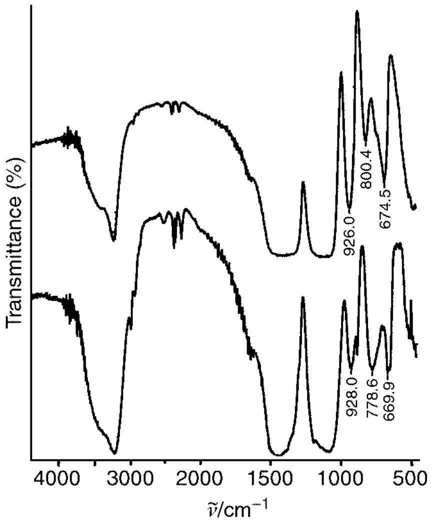

Fig. 2 FTIR spectra (KBr disc) for (a) the dried gel and (b) the furnaced glass.

DOI: 10.1039/b003047n

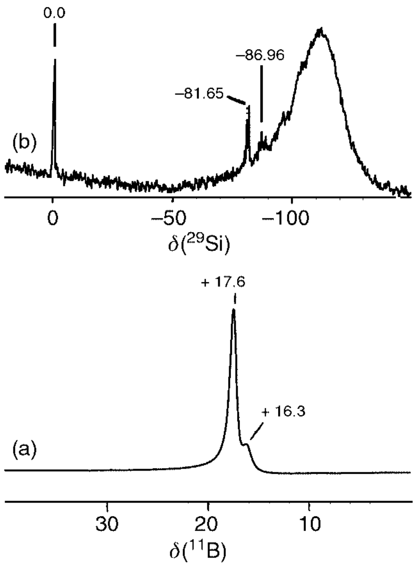

Fig. 3 Solution NMR of the sol diluted with $CDCl_3$ prior to gelling of the TMB:TEOS (1:1) reaction mixture (a) $^{11}B\{^1H\}$ spectrum (80.249 MHz) and (b) ^{29}Si spectrum (49.694 MHz) with $SiMe_4$ added as an internal standard (0.0 ppm).

both samples contain B–O–Si links.[9,15] Strong B–O (br, 1450 cm^{-1}), Si–O stretches (br,1150 cm^{-1}) and Si–O–Si (*ca.* 790 cm^{-1}) were also observed.[9,15] Heating the sample to 600 °C enhanced the relative intensity of B–O–Si bands and produced a weak shoulder (at 740 cm^{-1}) on the lower energy B–O–Si band which may indicate the formation of some B–O–B (720 cm^{-1}) upon furnacing.[15]

The volatile reaction products were investigated qualitatively by GCMS, and ^{11}B NMR and quantitatively by gravimetric boron analysis. ^{11}B NMR showed one peak (*ca.* +17.6 ppm) consistent with a trigonal boron with three oxygen substituents, and GCMS confirmed that $B(OEt)_3$ was the major species present. Gravimetric analysis showed that *ca.* 45% of boron initially added to the reaction mixture as TMB was now in the isolated volatile component.

The above observations demonstrate that orthoborate esters are produced as co-products in the gelling process and an idealised equation for the production of silica from a 2 : 1 B : Si stoichiometry may be written as in eqn. (1). In the preparation

$$Si(OEt)_4 + 2/3(MeO)_3B_3O_3 \rightarrow 1/n\{SiO_2\}_n + 2B(OR)_3 \; (R = Me, Et) \qquad (1)$$

of the gel described above a B : Si ratio of 3 : 1 was used, and it was noted that gels were not formed with B : Si ratios of 1 : 1. The incorporation of boron in the gel, either present as B–O–Si linkages or as occluded borate, appears to be a consequence of the increased B : Si ratio. Occluded metaborate esters would disproportionate to orthoborate esters and boron oxide upon furnacing with the orthoborate esters volatilised at high temperatures.

The initial stages of the reaction (sol formation) were followed by solution ^{11}B and ^{29}Si NMR spectroscopy which show clear evidence for initial B–O–Si bond formation, and oxygen transfer and transesterification, respectively (Fig. 3). The formation of B–O–Si bonds in the sols can be seen by the appearence of a new signal in the ^{11}B spectrum at +16.3 ppm [5] in addition to that for the TMB and $B(OR)_3$ which overlap at *ca.* +17.6 ppm. ^{29}Si NMR of the sols also indicated that transesterification had occurred [Q^0 ester signals at −79.93, −80.82 and −81.65 for $Si(OMe)_2(OEt)_2$, $Si(OMe)(OEt)_3$ and TEOS[5,16]] with strong evidence for Q^1 species (centered at −87 ppm: −85.96, −86.96, −88.56 ppm) but with molecular Q^2, Q^3 and Q^4 species at *ca.* −96, −104 and −112 ppm barely discernable above the broad baseline hump due to borosilicate glass of the sample tube, and gelling sample.[5] Transesterification of orthoborates/orthosilicates has been reported in the literature but several hours at elevated temperature and acid/base catalysis were required for systems to reach equilibrium.[17] In the system described here transesterification is very rapid at room temperature and we believe this to be a consequence of the increased Lewis acidity of the metaborate ester over that of orthoborate esters.[18] It is acknowledged however, that the acetone solvent may play a non-innocent role in this reaction, by functioning as a Lewis base and as a potential catalytic proton source.

Mechanistic aspects of this unusual reaction and detailed studies of these and other multicomponent systems, including applications for the preparation of thin films by 'dip-coating' using the sols, are in progress.

We thank Dr D. Apperley (EPSRC solid-state MAS NMR service, Durham) for spectra and Pilkington plc for financial support.

Notes and references

† TMB (4.16 g; 24 mmol) and TEOS (5.0 g; 24 mmol) were disolved in dry acetone (25 cm^3) and left to stand in a dry, inert atmosphere. The transparent gel, which slowly formed over a 2 week period, was isolated as a solid (4.61 g) after removal of volatiles (25.1 g) (vacuum, RT). GCMS confirmed that $B(OEt)_3$ was the major component of the volatiles and gravimetric analysis (barium borotartrate method[19]) of a hydrolysed aliquot (1.0632 g) gave 0.9689 g of $4BaC_4H_4O_6 \cdot Ba(BO_2)_2 \cdot 4H_2O$ (= 1.35 mmol B), and hence total B of 31.9 mmol. The gel was oven dried at 60 °C for 12 h to yield an opaque glassy solid (3.24 g) with elemental composition Si 21.7; B 10.2; C 14.3; H 3.6; (O ≈ 50.2)%. Firing a sample of the dried gel (0.51 g) to 600 °C in air for 20 min resulted in weight loss (38%) and a silvery–grey borosilicate glass (0.32 g) with elemental composition of Si 31.4 **;** B 10.1; C < 0.5; H < 0.5; (O ≈ 58.0)%.

1 H. Dislich, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 363.
2 I. Artaki, M. Bradley, T.W. Zerda and J. Jonas, *J. Phys. Chem.*, 1985, **89**, 4399.
3 L. L. Hench and J. K. West, *Chem. Rev.*, 1990, **90**, 33.
4 N. Tohge, A. Matsuda and T. Minami, *J. Am. Ceram. Soc.*, 1987, **70**, C13.
5 A. D. Irwin, J. S. Holmgren, T. W. Zerda and J. Jonas, *J. Non-Cryst. Solids*, 1987, **89**, 191.
6 A. Kasgoz, T. Minsono and Y. Abe, *J. Non-Cryst. Solids*, 1999, **243**, 168.
7 N. Pellegri, O.D. Santus and A. Duran, *J. Sol–Gel Sci. Technol.*, 1994, **2**, 519.
8 D. M. Haaland and C. J. Brinker, *Mater. Res. Soc. Symp. Proc.*, 1984, **32**, 267.
9 C. Zha, G. R. Atkins and A. F. Masters, *J. Non-Cryst. Solids*, 1998, **242**, 63.
10 C. Zha, G. R. Atkins and A. F. Masters, *J. Sol–Gel Sci. Technol.*, 1998, **13**, 103.
11 K.S. Varma, *Int. Pat.* WO 98/42627, 1998.
12 M. A. Beckett, P. Owen and K. S. Varma, *J. Organomet. Chem.*, 1999, **588**, 107.
13 G. Engelhardt and D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, Wiley, Chichester, 1987, p. 332.
14 A. D Irwin, J. S. Holmgren and J. Jonas, *J. Non-Cryst. Solids*, 1988, **101**, 249.
15 A. S. Tenney and J. Wong, *J. Chem. Phys.*, 1972, **56**, 5516.
16 J. C. Pouxviel, J. P. Boilot, J. C. Beloeil and J. Y. Lallemand, *J. Non-Cryst. Solids*, 1987, **89**, 345
17 D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, 1946, **68**, 77.
18 M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polymer*, 1996, **37**, 4629.
19 R. S. Braman, in *Encyclopedia of Industrial Chemical Analysis*, ed. F. D. Snell and C. L. Hilton, J. Wiley and Sons, Interscience, 1968, **7**, 384.