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Time and temperature based gellability zones in modified titanium alkoxide sols

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Abstract

Titanium hydroxide derived from stoichiometrically hydrolysed modified precursors usually takes as much as 14 days to gel under ambient conditions. These systems can however be made to gel within a few hours by raising the sol temperature to above 80°C or alternatively, by lowering it to below 10°C. A gellability zone has been identified between 10°C and 80°C on the temperature axis and between 0 and 14 days on the time axis, for all chelate ratios up to 1:4. The spread of the acetyl acetone gellability zone is wider than that for ethyl acetoacetate leading to a wider range of microstructural controls that may be imposed upon such systems. The locus of gel points on the gellability zone separates the sol state from the precipitated state. Thermoreversible gelling is seen within the titania gellability zone. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

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1. Introduction

Thermoreversible gelling in alumina gels synthesized from aluminium polyphosphates has been recently reported [1]. This paper reports a similar phenomenon occurring in titania gels synthesized from modified titanium isopropoxide precursors.

Alkoxide derived gels are normally synthesized under ambient conditions. Experiments with alumina and boria [2,3] have resulted in gel formation under 28°C conditions. Microstructure control in alkoxides is enhanced by chelating the susceptible alkoxy linkages with stoichiometric chemical additives such as ethyl acetoacetate and acetylacetone [4–12] which introduce a structural reorganization in the alkoxide making it relatively passive to an uncontrolled water attack. Though the processing benefits accruing from microstructure control in sol–gel synthesis are being technologically exploited [13,14], present day understanding on gelling is handicapped by two major weaknesses. The first is the absence of an experimentally confirmed theory on gelling. A recent comprehensive review [15] on gelling mechanisms evaluates entirely statistical and model dependent theories such as the Mean-Field Theory, the Percolation Theory and the Fractal Theory. From a microstructure standpoint, these theories do not account for morphological changes occurring in the sol to gel transition as has been recently reported [2] to occur in chelated alkoxides by a dissolution–nucleation mechanism.

The second gap in the present knowledge-base relates to an understanding of the conditions under which gelling in chelated alkoxides takes place. Gelling in alkoxides was so far thought to be primarily time dependent [16] and though it was suggested [17] that temperature, pH and the presence of enzymes could substantially alter gel-points [18], a scientific investigation into the identification of specific gellability zones based on the contribution from each varied parameter, was noticeably absent. As a result, the capability of the sol–gel process to yield tailored microstructures was severely restricted. Very recently, a gellability zone for aluminium sec-butoxide chelated with ethyl acetoacetate, identified on the basis of pH has been established [19] and this investigation suggests that gelling in chelated alumina occurs only within a pH range of 3.0–8.5. Any pH value outside this regime, irreversibly precipitates

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the alumina, not withstanding any electrostatic or chemical bonding between sol particles which influences the sol–gel equilibrium of phases in the vicinity of the gel point. Further, complete alkoxide hydrolysis is attained only within a pH range of 5.7–7.7 and the extent of hydrolysis is reduced as the acidity/basicity of the system is increased. At a pH of 8.5 or 3.0, though an alumina gel is obtained as a major product of reaction, the extent of alkoxide hydrolysis is only about 55% leading to a porous, gelatinous mass with a high surface area.

However, extending a similar treatment to chelated titania sols was difficult because chelated titania did not gel easily under ambient conditions. Pilot experiments revealed that gelling was a function of chelate ratio and temperature. Moreover, microstructure mechanisms leading to chelated alkoxide gelling are still not well understood.

Therefore, establishing a gellability zone for titania on the basis of sol- temperature, and suggesting microstructure mechanisms leading to chelated alkoxide gelling was the primary objective of this research. The chelating agents chosen were ethyl acetoacetate and acetyl acetone in molar ratios with titanium isopropoxide varying from 0 to 4.0 which, from structural and stoichiometric considerations, is the highest extent of chelation possible in titanium alkoxides.

2. Experimental

2.1. Materials

The titanium isopropoxide (TIP) used in the experiments was of 97% assay (Fluka) and was used as received from the manufacturer. The isopropyl alcohol (IPA) (Fluka) with a 96% assay was dried by a 4 h storage in calcium oxide previously heated to 800°C. The ethyl acetoacetate (EAA) (Spectrochem) and acetyl acetone (AA) both of a 96% assay were used as received. Milli-Q water (18 MΩ-cm) was used to hydrolyse the chelated titania sols. Hydrolysis was done with the stoichiometric amount of water.

2.2. Methods

About 3.0 g of TIP were weighed out in a teflon coated, screw capped sample bottle under inert gas flow in a glove box containing P_2O_5 desiccant. About 15 ml of previously dried IPA were added to it and the mix ultrasonically agitated at 18.750 kHz at an ultrasonic power of 90 w output for approximately 600 s on a Branson-450 probe type ultrasonicator horn, using a 12 mm diameter probe disruptor horn tip. The immersion of the probe tip was adjusted to about 2 mm below the liquid level in order to achieve maximum turbulence and sonication efficiency [20].

In the first batch of five samples chelated with EAA, for TIP/EAA molar ratios varying from 1:0 to 1:4, the amount of EAA added was 0 ml, 1.5 ml, 3.0 ml, 4.5 ml and 6.0 ml, respectively.

In the second batch of five samples chelated with AA, for TIP/AA molar ratios varying from 1:0 to 1:4, the amount of AA added was 0 ml, 1.35 ml, 2.70 ml, 3.05 ml and 5.40 ml, respectively.

Both batches were hydrolysed with water at 28°C at the water addition rate of 0.4 ml/h/g of TIP until the stoichiometric amount of water required for complete alkoxide hydrolysis was introduced into the system. Continuous ultrasonication was maintained during the alkoxide hydrolysis. The hydrolysed samples were sealed and the containers were left undisturbed at temperatures of 10°C to 90°C until they gelled. The temperature controller had a measurement accuracy of ± 2°C. The time taken for complete gelling (characterized by a complete immobilization to inversion of the container) of the sol was recorded for each sample. The data for each chelating agent were recorded and interpreted in an attempt to establish a temperature dependent gellability zone in chelated titania sols. About 100 samples were prepared and analysed during this research and the results of the investigation are presented.

3. Results and discussion

The first batch of samples chelated with EAA was found to show the following behaviour. A 1:1 chelated sample was seen to gel within 6 days when maintained under ambient conditions. However, when the same sample was maintained at 80°C or at 10°C, it was seen to gel within 2 h of mixing. Temperatures lower than 80°C or above 10°C resulted in increasing gelling times and as a representative case, gelling within 96 h was found to occur either at temperatures above 60°C or at temperatures below 20°C. Gelling in this system depended upon time and temperature. It was also possible to control one factor if the other was known. Samples at higher or lower temperatures were seen to gel faster than those maintained under ambient conditions. Further, for any desired process time, gelling could be carried out at two possible temperatures: one above and the other below the ambient. Additionally, sols gelled under the influence of an increased or lowered temperature were found to revert to the sol state on exposure to ambient conditions, i.e. thermoreversible gelling was observed in titania gels. A schematic representation of the temperature versus time graph for the EAA chelated system for differing chelate ratios is shown in Fig. 1.

Similarly, a 1:2 system maintained under ambient conditions was seen to gel in about 7 days. However, when the same sample was maintained above 68°C or below 16°C, it was seen to gel within 96 h.

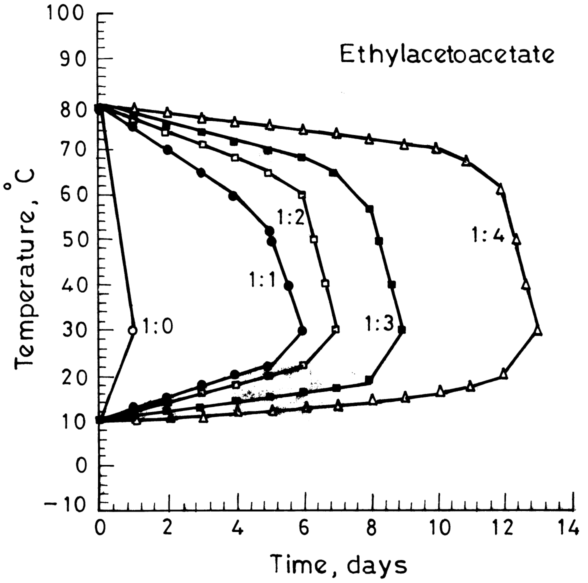

Fig. 1. Gellability zone for stoichiometrically hydrolysed ethyl acetoacetate chelated titanium isopropoxide in chelate ratios varying from 1:1 to 1:4. A 1:0 ratio indicates an unchelated alkoxide precursor. Outside this lamellar zone, titania occurs as a precipitate. Inside the zone, it occurs as a titania sol. A titania gel is obtained at the periphery of this gellability zone.

A 1:3 system maintained under ambient conditions was seen to gel within 9 days. However, when the same sample was maintained above 72°C or below 12°C, it was seen to gel within 96 h.

Lastly, a 1:4 system maintained under ambient conditions was seen to gel within 13 days. However, when the same sample was maintained above 76°C or below 10°C, it was seen to gel within 96 h.

Above 80°C and below 10°C, titania precipitation was seen to occur. Inside the gellability zone shown in Fig. 1, sols in varying stages of gelling were found to occur. The peripheral region, or the boundary of the gellability zone was found to indicate the onset of gelling in such systems. Thermoreversible gelling was a characteristic feature of all sols gelled at any temperature excepting the ambient.

In the second batch of samples chelated with AA, the following behaviour was noticed. A 1:1 chelated sample was seen to gel within 7 days when maintained under ambient conditions. However, when the same sample was maintained at 84 or at 8°C, it was seen to gel within 2 h of mixing. Temperatures lower than 84 or above 8°C resulted in increasing gelling times and as a representative case, gelling within 96 h was found to occur either at temperatures above 64°C or at temperatures below 18°C. Gelling in this system depended upon time and temperature. It was also possible to control one factor if the other was known. Samples at higher or lower temperatures were seen to gel faster than those maintained under ambient conditions. Further, as also seen in ethyl acetoacetate chelated systems, for any desired process time, gelling could be carried out at two possible temperatures: one above and the other below the ambient. Additionally, sols gelled under the influence of an increased or lowered temperature were found to revert to the sol state on exposure to ambient conditions, i.e. thermoreversible gelling was observed in titania gels. A schematic representation of the temperature versus time graph for the AA chelated system for differing chelate ratios is shown in Fig. 2.

Similarly, a 1:2 system maintained under ambient conditions was seen to gel in about 8 days. However, when the same sample was maintained above 72 or below 14°C, it was seen to gel within 96 h.

A 1:3 system maintained under ambient conditions was seen to gel within 10 days. However, when the same sample was maintained above 78°C or below 10°C, it was seen to gel within 96 h.

Lastly, a 1:4 system maintained under ambient conditions was seen to gel within 14 days. However, when the same sample was maintained above 82 or below 8°C, it was seen to gel within 96 h.

Above 84°C and below 8°C, titania precipitation was seen to occur. Inside the gellability zone shown in Fig. 2, sols in varying stages of gelling were found to occur. The peripheral region, or the boundary of the gellability zone was found to indicate the onset of gelling in such systems. Thermoreversible gelling was a characteristic feature of all sols gelled at any temperature excepting the ambient.

3.1. Gelling mechanisms in alkoxides

Several theories which explain gelling mechanisms in alkoxides have been proposed. An excellent review of model dependent statistical gelling mechanisms, such as the Mean-Field theory, the Percolation theory and the Fractal theory has recently been published [15]. However, on the basis of the co-ordinated Bethe lattices, the ultramicroscopic Cayley tree and the fractal parameters, it is difficult to correlate an experimentally observed gelling phenomenon with predictions from these models. Specifically, microscopic changes such as those in particle size, distribution, morphology, rheology and optical transmittance are not accounted for by presently known gelling mechanisms. Moreover, the characterization techniques used [21–27] such as EXAFS, IR, viscosity, QELS, intrinsic deformation, NMR or Raman scattering, on which the classical gelling theories are mathematically based, do not directly reveal microstructural or morphological detail. Frequently, from model-dependent analyses, conflicting microstructural information is reported.

In a recent research attempt [28] on structural reorganization in ethylacetoacetate modified aluminium sec-butoxide, one school of thought proposes that Al

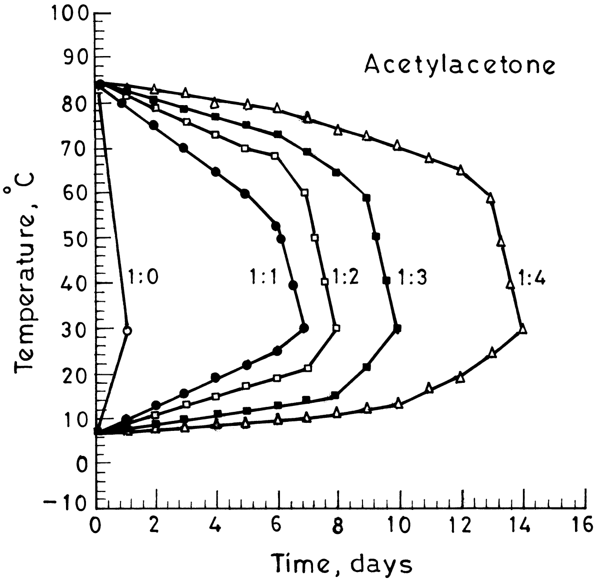

Fig. 2. Gellability zone for stoichiometrically hydrolysed acetyl acetone chelated titanium isopropoxide in chelate ratios varying from 1:1 to 1:4. A 1:0 ratio indicates an unchelated alkoxide precursor. Outside this lamellar zone, titania occurs as a precipitate. Inside the zone, it occurs as a titania sol. A titania gel is obtained at the periphery of this gellability zone.

manifests itself in tetra-, penta-, and hexa-fold coordination in an oligomeric alkoxide species whereas another [29] suggests that the penta-fold Al coordination is not present. The basis of both characterization techniques is a model-dependent ^{27}Al NMR. As a result, presently, much uncertainty prevails on the microscopic composition of the chelated or even unchelated alkoxide microstructures.

The Zarzycki ultrastructural model, recently proposed [24,30,31] on the basis of SAXS and SANS characterization, offers a reasonably good explanation of changing microstructures during gelling by stating that the microstructure becomes decreasingly 'lumpy' and increasingly 'wispy' as the extent of hydrolysis is increased [31]. The polymerization steps leading to gelling have been explained in terms of nucleation of primary particles, particulate growth and Ostwald ripening. It is felt that the initial agglomerated alkoxide microstructures are not equilibrium phase, rigid, dense, colloidal microstructures, but are a first order Fickian diffusing form of particulate clusters with the flux decreasing both with time and the extent of hydrolysis. Gel clusters have been found to show fractal features (corroborating some aspects of the Fractal theory) and follow a 'tip-to-tip' growth mechanism indicative of an increase in the aspect ratio of sol–gel microstructures. It is known that silica systems are extremely amenable to continuous fibre drawing at viscosities above 1 Pa s [32] and increased cross-linking and fibrillar entanglement probably occur at greater hydrolysis points. As per Zarzycki's ultrastructural model [31], the conversion of a sol into a gel is progressive and the growing aggregates (microgels) gradually invade the volume originally occupied by the sol. Additionally, it is felt that the interparticulate networking is initially through a physical cross-linking and the expulsion of interstitial fluid results in a chemically bonded polymeric framework on ageing. However, the driving force and the mechanism behind the expulsion of fluid and the separation of gel–liquid phases is not well understood. These two research investigations [31,33] and variations thereof, account for most of the present understanding in the microstructure evolution during the sol to gel transition in alkoxides. However, it is somewhat surprising that currently accepted gelling models seek to explain transitions and growth mechanisms from a nanometre-scale to a millimetre-scale without considering the contributions from a particulate morphology.

Using light scattering analyses with time and with water added, the cluster dimensions have been seen to increase. In a series of compressive and tensile measurements on gels, in an effort to explore gelling mechanics [27] it was proposed that even when the gel network is purely elastic, gels exhibit a time-dependent behaviour that resembles viscoelasticity which results from fluid flow. The absence of a 'direct' characterization technique to in situ visualize wet sol–gel microstructures which would lay the basis for a directly visualized gelling mechanism is probably the reason for a purely mathematical treatment presently accorded to a purely experimental phenomenon.

A 'wet' characterization technique for imaging labile sol–gel microstructures using the cryogenic-scanning electron microscope (cryo-SEM) has been recently proposed, developed and applied for alkoxide microstructures [2,5,34]. Cryo-SEM observations on controllably hydrolysed aluminium sec-butoxide (ASB) from the sol stage to the gel point were recorded and a dissolution–nucleation mechanism of gelling based on a 'direct visualization' of wet sol–gel microstructures was proposed. Comprehensive details on the proposed gelling mechanism are available elsewhere [2] but the basic tenets of the suggested mechanism of ASB gelling necessary to attempt a preliminary explanation into chelated TIP gelling are as follows.

Ethyl acetoacetate (EAA) encapsulates the ASB species to yield globular microstructures about 6–8 μm in diameter before the start of hydrolysis. As controlled hydrolysis progresses, the large globules break down in size and ultimately dissolve into the alcohol-rich matrix through a range of microstructures: spherical to cylindrical to tape-like to needle-like. Dissolution of species to a distinct morphology has been found to depend upon the extent of hydrolysis. Accompanying the chelated agglomerate dissolution is seen the emergence or nucleation of a spherical aluminium hydroxide species which grow in size and number density and at the sonogelling point, occupies the entire sol volume. Both dissolution and nucleation processes are simultaneous. The Al $(OH)_3$ size increases from about 5 nm at the start of hydrolysis to a final size of about 1046 nm, with the final size depending upon the ASB/EAA mole ratio. Higher chelate ratios yield finer particles. Quasi-elastic light scattering, uv-visible spectrophotometry and rheological measurements were used to corroborate the cryo-SEM data and were used to propose a gelling mechanism from the microscopic to the macroscopic scale i.e. 5 nm to about 8 μm. Alumina gels with an optical transmittance of above 99.99% in the uv-visible region were obtained as the hydrolysed product.

Gelling behaviour in aluminium alkoxides is somewhat different from that seen in titania or silica. Freshly prepared, chelated alumina gels are found to show a reversible gelling behaviour until about 4 h of ageing i.e. a fresh alumina gel is a meta stable state between the sol and the gel states and until polymeric stiffening starts within a few hours of gelling (in the isolated environment of a glove box) even slight variations in temperature or pH may revert the gel back to the sol stage. This is because gelling in alumina is the result of electrostatic interactions, unlike that in silica or titania in which it occurs as a result of chemical bonds. No liquid expulsion from the gel interstices is seen in alumina systems. As a result, there is little or no shrinkage and the volume of an alumina gel is almost the same as that of an alumina sol. In titania systems, however, shrinkage may typically be 60% or higher.

It is felt that gelling in titania follows the same dissolution–nucleation mechanism as seen in alumina. The valency, co-ordination number and electronegativity of the Ti and Al atoms differ. Valency differences permit a chelate ratio of up to 1:4 in titania as against 1:3 in alumina. The Al–O bond has an ionic character of 15.9% and a bond strength of 511 ± 3 kJ/mol [35]. In the case of titania, the Ti–O bond has an ionic character of 8.7% and a bond strength of 672.4 ± 9.2 kJ/mol [35]. Thus, the Ti–O bond has a lesser ionic character and a greater strength than the Al–O bond. During the hydrolysis of chelated titania microstructures, it is thought that a certain amount of electrostatic character in the modified TIP species is retained through the transgression across the morphological forms until the gel point.

ASB gels, irrespective of the chelate ratio are reversible for up to 4 h after preparation after which any change in temperature does not revert the gel back to sol. However, titania gels are reversible to the corresponding sol for as long as 14 days. Titania gels are seen to have a marked temperature dependence on their integrity and may be readily converted to a colloidal state, either by an increase or by a decrease in their temperature. Thermoreversibility may be obtained for a period of about 14 days depending on temperature. The temperature range of thermoreversibility depends upon the time that has elapsed since the fully hydrolysed titania sol was prepared. After extended ageing, the polymeric network becomes sufficiently stiffened and an increased chemical bonding becomes the dominant force in maintaining structural integrity. The titania gel loses thermoreversibility after this period.

Assuming the dissolution–nucleation gelling mechanism to be valid for titania systems as well, it is seen that titania gels occupy about a third of the sol volume whereas alumina gels occupy the entire sol volume. As the gel point approaches, the Ti–O bond which is stronger than the Al–O bond, expels a larger amount of interstitial fluid. A final chemically bonded polymeric framework results only on ageing and this observation agrees reasonably well with predictions from literature [33]. From available literature [36] it is thought that gelling is unlikely to be reversible if shrinkage exceeds about 70% and that gel reversibility decreases as gel consolidation increases.

4. Conclusions

Gel points in chelated titania sols depend upon temperature, chelating agent and chelate ratio. For a fixed chelate ratio, i.e. a fixed chemical composition, the gel point is decided on the basis of the process temperature. For stoichiometrically hydrolysed alkoxides, gelling time at ambient temperature is as long as 14 days. A gellability zone identifying specific time and temperature conditions for gelling in chelated titanium alkoxides has been proposed. Any temperature variations either above or below the ambient only serve to accelerate gelling. Gelling in modified precursors has been found to be thermoreversible. The gellability zone for acetyl acetone has a wider spread than that for ethyl acetoacetate leading to a greater scope for controlling the process from a microstructure standpoint and the sol–gel-precipitate states of titania have been seen to occupy the inside-periphery-outside regions of this zone. The conditions leading to gelling in chelated titania sols have hence been established on the basis of the processing parameters.

References

[1] E.C. Lima, F.J. Galembeck, Colloid Interface Sci. 166 (1994) 309.
[2] M.M. Haridas, J.R. Bellare, Bull. Mater. Sci. 20 (1997) 49.
[3] M.M. Haridas, J.R. Bellare, Sonogelling in modified boron alkoxides and imaging of 'wet' boria microstructures using cryo-SEM, Matls. Charact., in press.
[4] F. Babonneau, L. Coury, J. Livage, J. Non-Cryst. Solids. 121 (1990) 153.
[5] M.M. Haridas, A. Menon, N. Goyal, S. Chandran, J.R. Bellare, Ceram. Int. 26 (1996) 155.

[6] T. Heinrich, F. Raether, H. Marsmann, J. Non-Cryst. Solids 168 (1994) 14.

[7] R.K. Mehrotra, R.C. Mehrotra, Can. J. Chem. 39 (1961) 795.

[8] R. Nass, H. Schmidt, in: H. Hausner, G.L. Messing, S. Hirano (Eds.), Proc. 2nd Int. Conf. on Ceramic Powder Processing Science, Oct. 1988, Deutsche Keramische Gesellschaft, Cologne, 1989, pp. 69–73.

[9] R. Nass, H. Schmidt, J. Non-Cryst. Solids 121 (1990) 329.

[10] C. Sanchez, L. Livage, M. Henry, F. Babonneau, J. Non-Cryst. Solids 100 (1988) 65.

[11] H. Schmidt, J. Non-Cryst. Solids 100 (1988) 51.

[12] J.H. Wengrovius, M.F. Garbauskas, E.A. Williams, R.C. Going, P.E. Donahue, J.F. Smith, J. Am. Chem. Soc. 108 (1986) 982.

[13] M.M. Haridas, J.R. Bellare, A method to synthesize highly transparent sonogels from chelated alkoxides, Indian patent application No. 487/BOM/95, 1995.

[14] M.M. Haridas, J.R. Bellare, A method to synthesize Nordstrandite from chelated alkoxide sonogels, Indian patent application No. 488/BOM/95, 1995.

[15] L.L. Hench, J.K. West, Chem. Rev. 90 (1990) 33.

[16] R. Xu, E.J.A. Pope, J.D. Mackenzie, J. Non-Cryst. Solids 106 (1988) 242.

[17] R.W. Jones, The Fundamental Principles of Sol–Gel Technology, 1st ed., Inst. of Metals, London, 1989.

[18] T. Tanaka, Sci. Amer. (1981) 110.

[19] M.M. Haridas, J.R. Bellare, Sonogelling agents and gellability zone for ethyl acetoacetate modified aluminium sec-butoxide, Ceram. Int., in press.

[20] R. Barenholz, D. Gibbes, B.J. Litman, J. Goll, T.E. Thompson, F.D. Carlson, Biochemistry 16 (1977) 2806.

[21] J.D. Mackenzie, J. Non-Cryst. Solids 100 (1988) 162.

[22] C.J. Brinker, in: J. Fricke (Ed.), Aerogels, Springer-Verlag, Heidelberg, 1986, pp. 37–49.

[23] S. Sakka, H. Kozuka, J. Non-Cryst. Solids 100 (1988) 142.

[24] J. Zarzycki, J. Non-Cryst. Solids 95–96 (1987) 173.

[25] T. Lours, J. Zarzycki, A. Craievich, D.I.D. Santos, M. Aegerter, J. Non-Cryst. Solids 100 (1988) 162.

[26] R. Finsy, Adv. Colloid and Interface Sci. 52 (1994) 79.

[27] G.W. Scherer, Better Ceramics through Chemistry V, in: M.J. Hampden-Smith, W.G. Klemperer, C.J. Brinker (Eds.), Proc. Mat. Res. Soc. Symp., vol. 271, MRS, Pittsburgh, 1992.

[28] L. Bonhomme-Coury, F. Babonneau, L. Livage, J. Sol–Gel Sci. Tech. 3 (1994) 157.

[29] K. Tadanaga, T. Iwami, N. Tohge, T. Minami, J. Sol–Gel Sci. Tech. 3 (1994) 5.

[30] J. Zarzycki, J. Non-Cryst. Solids 121 (1990) 110.

[31] J. Zarzycki, Glasses and the Vitreous State, Cambridge University Press, Cambridge, 1991, pp. 271–279.

[32] S. Sakka, Sol–Gel processing of advanced ceramics, in: F.D. Gnanam (Ed.), Proc. of the Int. Workshop on the Sol–Gel Processing of Advanced Ceramics, Anna University, 8–9 January 1996, Oxford and IBH Publishing Co., New Delhi, 1996.

[33] C.J. Brinker, G.W. Scherer, J. Non-Cryst. Solids 70 (1985) 301.

[34] M.M. Haridas, Microstructure development in ceramic precursors: experimental studies, Doctoral Dissertation, Indian Institute of Technology, Bombay, 1997.

[35] D.R. Lide, H.P.R. Frederikse (Eds.), CRC Handbook of Chemistry and Physics, 75th ed., CRC Press, Boca Raton, FL, 1995.

[36] J.C. Debsikdar, J. Mater. Sci. 20 (1985) 4454.