AD-A266 277

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED
FINAL 15/7/1989-14/7/1993

4. TITLE AND SUBTITLE
Structural studies of sol-gel glasses

5. FUNDING NUMBERS
AFOSR-89-0489

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8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Sponsoring agency: Air Force office of Scientific Research, Bolling AFB, DC 20332-6448
Sponsoring/Monitoring agency: European Office of Aerospace, Research and Development, PSC 802, Box 14. FPO AE 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR-89-0489

11. SUPPLEMENTARY NOTES
FULL Report supersedes reports for the periods 15/7/1989-14/7/1990
Further papers to be published in 15/7/1990-14/7/1991
J. Chem. Soc. Dalton and J.Chem. Soc. Faraday.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release
distribution unlimited

93-14669

13. ABSTRACT (Maximum 200 words)

The research objectives were to relate sol-gel microscopic structural chemistry and silica surface chemistry to the sol-gel process. Detailed studies have been carried out on silica, silica/titania, Co^{2+} Nd^{3+}, dye (RG6) doped silica gel glasses and Sn-Si-O gels. Major conclusions are; (1) On thermal treatment, the gel-glass matrix is strengthened by bond shortening, and a reduction in mean Si-O-Si bond angle and angular distribution for this feature. (2) The incorporation of low levels of titanium lead to more disordered glasses and the addition of tin into the silica matrix enhances the densification process and reduces the thermal treatment temperature by ca. 300°C necessary to remove hydroxyl groups from the surfaces of the gels. (3) Four different water species can be identified on gel-glass surfaces with associated species being formed before completion of the first monolayer. Increasing hydrophobicity for samples at high temperature is attributed to the low concentration of surface silanol groups present and their reduced activity. (4) Cobalt, neodymium and dye (RG6) post-doped homogeneous glasses (for lasing action) were produced. The coordination chemistry of the metal ions depends on the nature of the metal ions and ligands, thermal history and composition of the glass. The silanol groups only play a major role in coordination with the metal ions after sintering. The incorporation of the dye in to the gel-glass matrix results in specific interactions between the glass and the dye and a marked reduction in water content of the glass.

14. SUBJECT TERMS
Sol-gel glasses. Co^{2+} doped glasses. Nd^{3+} doped glasses RG6 doped glasses. Sn-Si-O-gels. FTIR spectroscopy. NIR spectroscopy, UV-VIS spectroscopy, N_2 adsorption, FT Raman spectroscopy

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	unclassified

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

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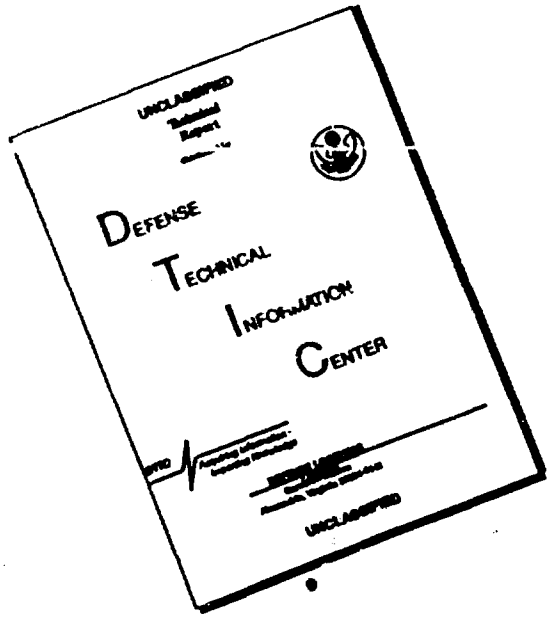

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Proceedings of Euroges II, Elsevier, in press

Spectroscopic Studies of Silica/Titania Gel Glasses

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Abstract

Near and Mid infrared spectroscopy and FT-Raman spectroscopy have been used to study silica/ titania monoliths produced by the sol-gel route which have been subjected to selected heat treatments. Increasing thermal treatment temperature leads to a general strengthening of the gel-glass matrix although the incorporation of low levels (3% by weight) of titanium into tetrahedral sites only, led to more disordered glasses than for silica alone. Evidence has been obtained for the formation of Si-O-Ti bonds principally during the later stages of densification at temperatures between 615 and 1000°C. The addition of titanium also leads to a reduction in surface 'free' silanol levels together with an increase in hydrogen bonded silanol levels and increasing amounts of water associated with the glass. The implication is that the incorporation of titanium onto the surface of the gel matrix leads to tighter binding of water molecules to silanol groups.

Introduction

The sol gel method of glass fabrication is useful in the preparation of optically transparent, porous materials at temperatures lower than 200°C, Controlled thermal treatment at elevated temperatures induces changes in the chemical and physical properties of the gel phase and at the limit, when all the pores are eliminated, the gel glasses are equivalent to those produced by the traditional melt process. Moderation of the heat treatment process can lead to gel glasses with tailored combinations of physical properties such as pore dimensions, interconnectivity and pore surface chemistry.

The addition of heteroatoms such as titanium at the gel synthesis stage leads to glasses with very low thermal expansion coefficients (zero at 7-8% Ti) (1) with increased refractive index. At the molecular level, introduction of titanium into the gel structure (average bond angles, Ti-O-Ti, 159°, Si-O-Si, 152° and bond length Ti-O, 1.8-1.86A, Si-O, 1.6A) yields more readily deformable structures although there are problems to contend with in the presence of elements with different coordination requirements. These problems become more apparent as thermal treatment temperatures are increased and solid state changes including ion migration occur. In addition, the incorporation of electropositive elements provides for variations in charge and surface functional groups. This may well be of importance, particularly for the porous gel glasses where potential applications in the areas of membrane technology, gas separation and catalysis all rely for their efficacy upon the structure and surfaces of the material which are presented to the reaction environment. For all of these applications, it is of fundamental importance to understand the nature of the chemical reactions which occur between gel-glass surface species and adsorbed species. In this paper, information is presented on the effects of the incorporation of titanium on structural changes with thermal treatment and the nature of interactions occurring between gel-glass surface species and water.

Materials and Methods

Silica/ titania glass monoliths provided by Geltech Inc. (USA) were prepared from tetramethylorthosilicate (TMOS) and titanium isopropoxide in a six step process of mixing, casting, gelation, aging, drying and densification. Samples were prepared containing 3 and 15% by weight of titanium and heat treated at temperatures between 180 and 1000°C. Samples had surface areas of the order of 600 m^2g^{-1} at 180°C and 100 m^2g^{-1} at 1000°C. 15mm diameter, 4mm thick discs were used for the majority of the spectral studies although KBr discs prepared from powdered samples were used for the transmittance mid infrared study. A small amount of information is presented for samples containing 0% Ti, for comparative purposes. Mid infrared spectra were collected using a Perkin Elmer 1710 FT infrared spectrometer equipped with a computerised data recording system. Raman experiments were performed using a Perkin Elmer 1720X FT Raman spectrometer. Raman spectra were excited using the 1064nm line of a Nd YAG laser and a 360° scattering configuration was adopted for data collection. Near infrared spectra were collected using a Perkin Elmer Lambda 9 UV-VIS-NIR spectrometer. Further information on experimental procedures is given in references (2,3,4).

Results and Discussion

Figures 1 and 2 show transmittance and reflectance mid infrared spectra for silica and silica/ titania gel glasses. The reflectance features have been assigned to the same vibrational set as the transmittance spectra for which assignments are well established (5).

Figure 1.

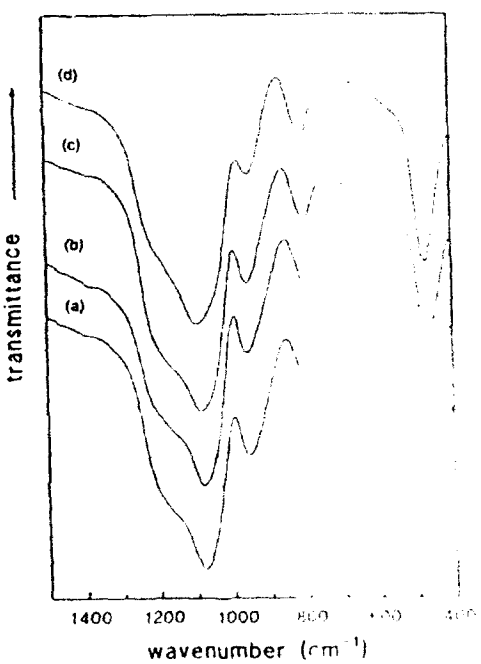

Figure 2.

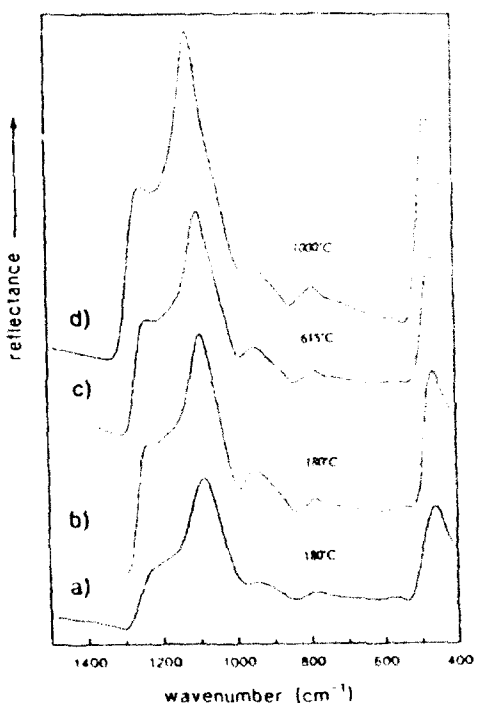

Figure 1. Transmittance mid-infrared spectra of silica/titania gel-glasses. (a) 15% Ti, 180°C, (b) 3% Ti, 180°C, (c) 3% Ti, 615°C, (d) 3% Ti, 1000°C.

Figure 2. Reflectance mid-infrared spectra of silica and 3% titania/ silica gel glasses subjected to increasing thermal treatment. (a) silica, 180°C, (b) silica/titania, 180°C, (c) silica/titania, 615°C, (d) silica/ titania, 1000°C.

A strong band at ca. 1080 cm^{-1} (1085 and 1215 cm^{-1} in the reflectance mode and associated with transverse (TO) and longitudinal (LO) optical modes) is associated with the Si-O-Si antisymmetric stretching vibration. The band at ca. 800 cm^{-1} (790 cm^{-1} in the reflectance mode and split to give TO and LO components at high temperature in the Raman) is associated with the Si-O-Si symmetric stretching vibration and the band at ca. 460 cm^{-1} with a Si-O-Si deformation mode (out of plane bending in the reflectance mode). The band at ca. 960 cm^{-1} (ca. 940 cm^{-1} in the reflectance mode) is associated with Si-OH or Si-O- stretching vibrations. The bands at ca. 1080 and 470 cm^{-1} shift to higher frequency with increasing thermal treatment suggesting a strengthening of the gel-glass matrix. It is noticeable that on thermal treatment a

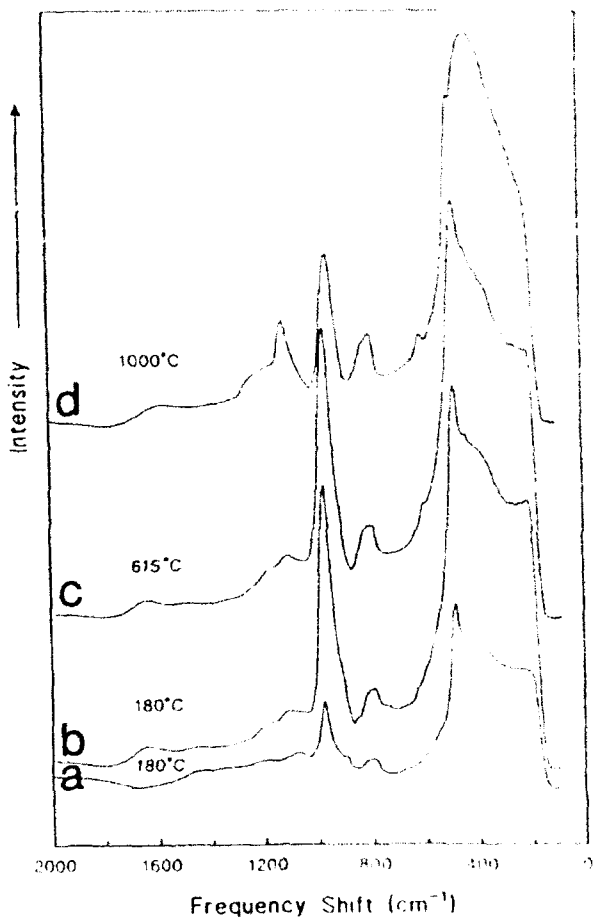

Figure 3. FT-Raman spectra for silica and 3% titania/silica gel-glasses subjected to a range of thermal treaments. (a) silica, 180°C, (b) silica/titania, 180°C, (c) silica/titania, 615°C, (d) silica/titania, 1000°C.

sharpening of none of the spectra is observed suggesting that although thermal treatment leads to a small increase in Si-O bond strength this is not accompanied by a reduction in mean Si-O-Si bond angle and angular spread for this feature. The gel silicas are more open and disordered in the presence of low levels of titanium. Bonds at 1100 and 945 cm^{-1} due to Si-O-Ti motions may be expected (6,7) although they will be of minor significance as the concentration of titanium in the sample is low. In the infrared these bands are not easily seen because of overlap with the Si-O-Si antisymmetric stretch and Si-OH stretching vibration respectively. The band at ca. 940 cm^{-1} is, therefore, a composite feature. At 180°C and 615°C (and for the 180°C sample containing 15% titanium) the band is only marginally more significant than for the silica only glasses and

careful study of this and the second overtone region between 900-1350nm has enabled the identification of both free silanol species and isolated water molecules as well as partly and fully hydrogen bonded species (3). Studies on silica only samples (3) have shown that not only does the silica network strengthen on thermal treatment but that at temperatures up to at least 1000°C there is also a strengthening of the O-H bond of the silanol group which has important consequences for the binding of surface species such as water. Hydration studies have shown that monolayers of water are not laid down sequentially, rather a patchiness in coverage exists. For low temperature treated samples both silanol groups and bound water molecules act as secondary sources for further water binding. In samples treated at 1000°C, the amount of water adsorbed is significantly reduced correlating with the reduction in absolute levels of silanol groups. Some of the remaining silanol groups are not accessible to the external environment and the reduction in dipole moment of the hydroxyl bond for the remaining silanol groups means that the silanol group is not as active in promoting hydration. The importance of water molecules as secondary adsorbing sites within the gel-glass is therefore increased.

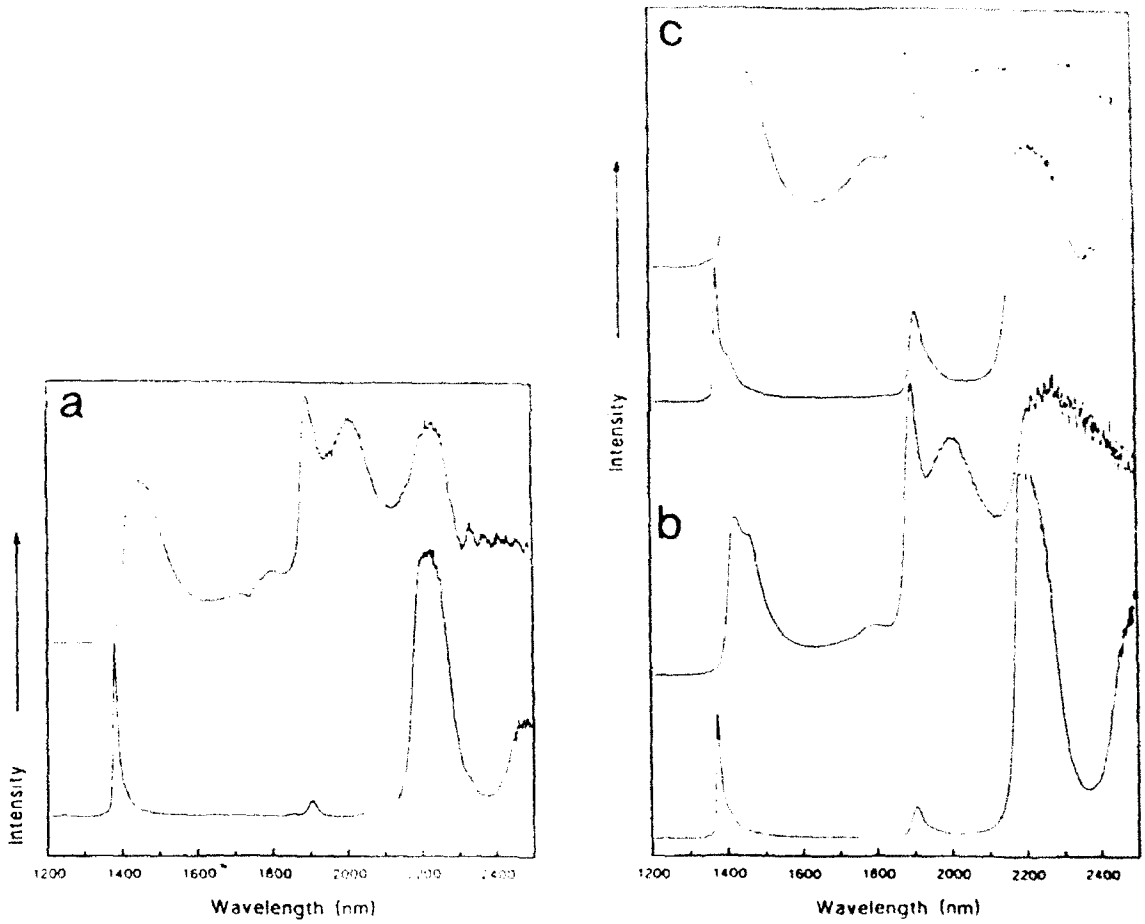

Figure 4. Near infrared reflectance spectra for silica and silica/titania samples thermally treated at 180°C. In all instances, the lower spectrum of the pair arises from a dehydrated sample (dehydration under vacuum for 48 hours) and the upper spectrum from the fully hydrated sample. Reflectance near infrared spectra are used for the study of surface layers of samples. (a) silica only, (b) 3% titania/silica, (c) 15% titania/silica.

The addition of titanium leads to a reduction in free silanol levels and an increase in hydrogen bonded silanol groups, even after extended evacuation figures 4 and 5. Spectral evidence is provided by a reduction in peak intensity for the band at ca. 1370nm, the appearance of a

shoulder at ca. 1400nm and a shift in position of the maximum for the band at ca. 2200nm. In addition, with increasing titanium levels, the amount of water remaining within the glass and the proportion of associated versus monomeric water molecules also increases.

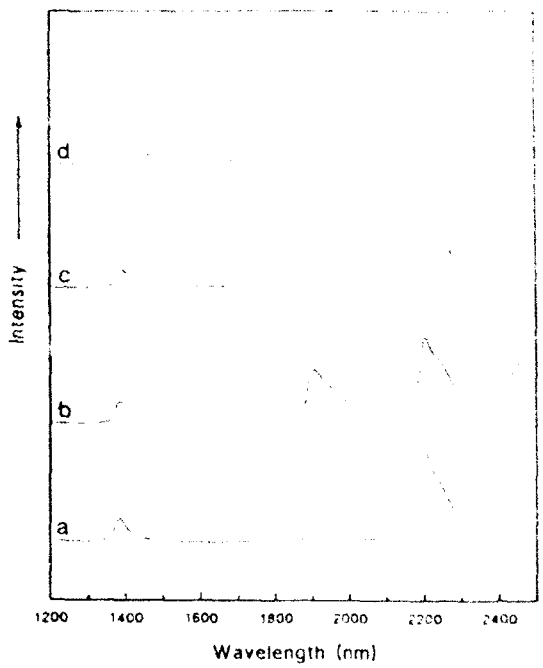

Figure 5. Near infrared spectra for 3% silica/titania gel-glasses treated at 1000°C. (a) and (b) are transmittance spectra ((a) dehydrated sample, (b) hydrated sample), (c) and (d) are reflectance spectra ((c) dehydrated sample, (d) hydrated sample). Reflectance spectra in the near infrared region yield information on the surface layers of the gel glasses, whereas transmittance spectra yield information on the bulk glass structure.

The effect of thermal treatment on gel glass phases containing 3% titanium did not show marked differences until temperatures of 1000°C were reached. At intermediate temperatures spectra merely showed that the relative proportion of hydrogen bonded silanol groups and associated water molecules were marginally higher than for the silica only glasses. After treatment at 1000°C spectra were markedly different to those for silica only samples in that the band shapes of the overtone and combination bands were significantly different. The glass contained fewer free silanol groups, most of which were found in the bulk rather than in the surface layers (in direct contrast to what has been observed for the silica only samples). In addition, the relative amounts of perturbed or hydrogen bonded silanol groups was higher as evidenced by the relative magnitudes of bands at ca. 1400nm vs. 1370nm and ca. 2270nm vs. 2200nm. On hydration, all free silanol groups in the surface layers became hydrogen bonded to water although in the bulk of the glass low levels of silanol groups were unaffected by the hydration process (retention of a band at 1370nm). In addition, any increase in water levels on exposure of the sample to water vapour was significantly reduced in comparison to that observed for the silica only samples. These observations suggest that for glasses containing 3% titanium and heated to 1000°C the silanol groups are largely not accessible to the external environment. They are either perturbed by their immediate matrix environment or have been isolated within pores in association with water molecules. The implication is that the presence of titanium in the gel matrix leads to a tighter binding of water molecules to silanol groups. From these spectra it is

not possible to say anything about the preponderance of SiOH vs. TiOH groups present within the sample as the signal due to the titanium content would be very weak in comparison to that for the silicon species. For samples containing higher relative amounts of another metal species it has proved possible to identify the changeover between surface species of one oxide such as silica and surface species of another oxide such as tin (IV) oxide (15, 16) which was not possible in this system.

Conclusions

The addition of titanium atoms to gel glasses at the mixing stage leads to materials in which the majority of the metal ions are found at the surfaces of the fundamental particles making up the bulk phase. These 'foreign' ions affect the densification of the material and the surface chemistry of the resultant phases. It is only at higher temperatures that, for these systems, incorporation of the titanium ions into the matrix occurs fully. The addition of titanium leads to materials that are significantly more hydrophilic than for similar silica gel-glasses and leads to tighter binding of water molecules to silanol groups.

Acknowledgements

This work was performed under the umbrella of the "Optical Glass and Macromolecular Materials Group" funded by the American Air Force Office of Scientific Research, Grant Number AFOSR 89-0489.

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