METAL-SILICA SOL-GEL MATERIALS

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ABSTRACT

The present invention relates to a single phase metal-silica sol-gel glass formed by the co-condensation of a transition metal with silicon atoms where the metal atoms are uniformly distributed within the sol-gel glass as individual metal centers. Any transition metal may be used in the sol-gel glasses.

The present invention also relates to sensor materials where the sensor material is formed using the single phase metal-silica sol-gel glasses. The sensor materials may be in the form of a thin film or may be attached to an optical fiber. The present invention also relates to a method of sensing chemicals using the chemical sensors by monitoring the chromatic change of the metal-silica sol-gel glass when the chemical binds to the sensor.

The present invention also relates to oxidation catalysts where a metal-silica sol-gel glass catalyzes the reaction. The present invention also relates to a method of performing oxidation reactions using the metal-silica sol-gel glasses.

The present invention also relates to organopolymer metal-silica sol-gel composites where the pores of the metal-silica sol-gel glasses are filled with an organic polymer polymerized by the sol-gel glass.

17 Claims, 4 Drawing Sheets
OTHER PUBLICATIONS


* cited by examiner
COLORLESS

COLORED

\[ L = H_2O \]

**FIG. 4**
METAL-SILICA SOL-GEL MATERIALS

This invention was made in the course of work done under NASA Prime Contract NAS 7-918 and is subject to the provisions of Public Law 96-517 (35 U.S.C. §202) under which NASA has certain rights to the invention.

TECHNICAL FIELD

The present invention generally relates to sol-gel glasses containing a relatively low concentration of metal centers, which glass has unique sensor and catalytic properties.

BACKGROUND ART

The application of the sol-gel process to the synthesis of dense oxide glasses and ceramics has been the subject of escalating interest because of the low fabrication temperatures and compositional flexibility provided by these materials. The sol-gel process utilizes the condensation reactions of silicon and/or metal alkoxides to provide a low temperature, synthetically flexible route to optical quality glasses.

The overall reaction for the synthesis of a silica sol-gel glass is:

\[ \text{Si(OR)}_4 + n\text{H}_2\text{O} \rightarrow n\text{SiO}_2 + 4\text{R}_1\text{OH} \]

wherein tetramethyl orthosilicate (TMOS) and tetraethylorthosilicate (TEOS) are the most common silicon alkoxides used. The ultimate production of a glassy material by this route, however, is accomplished in four primary stages: gelation, aging, drying/stabilization, and densification. The general process for forming sol-gels is taught in C. J. Brinker and G. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic Press, Boston, 1990) which is incorporated herein by reference.

The gelation step is composed of a series of condensation reactions in which silicon alkoxide condenses in the presence of water to form a Si—O—Si bonded network and alcohol by-products. The “gel” that forms from the condensation reactions is soft and contains incompletely reacted material (remaining SiOH and SiOR, functional groups), trapped organics (R,OH) and water. Aging of this gel (~3 months) results in further condensation to form Si—O—Si linkages (which is accompanied by a large amount of shrinkage) and the evaporation of water and R,OH. The aged gels are dried (~100°C) and stabilized (~500°C) to remove any remaining organic material and to complete the condensation process.

The material remaining after stabilization, known as “xerogel,” has the properties of a hard, transparent glass, not unlike conventional fused silica glass. However, unlike fused silica glass, xerogel is porous with surface areas on the order of 200 m²/g. This pore structure can ultimately be closed at temperatures above 1000°C to yield a glass that is indistinguishable from fused silica glass.

The undensified silica xerogel material is unique because of its porous nature. Silica xerogels, acting as a host matrix, can be used to entrap and stabilize reactive chemical species while at the same time permitting small molecules to diffuse into the silica matrix and react. This imparts the reactivity of a particular functional group to an otherwise inert matrix. Many of the materials made previously by the co-condensation of transition metals and silicon alkoxides have utilized relatively high metal concentrations and are often sintered into dense glasses. TiO₂/silica sol-gels have been described extensively because of their importance as low thermal expansion glasses. Similarly, a good deal of work has also been reported on ZrO₂ silicas. Recently, the properties of several SiO₂/V₂O₅ materials have also been reported, including the bulk properties of densified glasses. A. Ghosh, et al., Appl. Phys. Lett., 59:855 (1991); N. Tohge, et al., J. Non-Cryst. Solids, 63:95 (1984).

The present invention relates to sol-gel compositions comprising relatively low concentrations of transition metals and uses thereof.

SUMMARY OF THE INVENTION

The present invention relates to a single phase metal-silica sol-gel glass formed by the co-condensation of a transition metal with silicon atoms where the metal atoms are uniformly distributed within the sol-gel glass as individual metal centers. Any transition metal may be used in the sol-gel glasses.

The present invention also relates to sensor materials where the sensor material is formed using the single phase metal-silica sol-gel glasses. The sensor materials may be in the form of a thin film or may be attached to an optical fiber. The present invention also relates to a method of using the metal-silica sol-gel glasses.

The present invention also relates to thermal and photochemical oxidation catalysts where a metal-silica sol-gel glass catalyzes the reaction. The present invention also relates to a method of performing oxidation reactions using the metal-silica sol-gel glasses.

The present invention also relates to organopolymers metal-silica sol-gel composites where the pores of the metal-silica sol-gel glasses are filled with an organic polymer polymerized by the sol-gel glass.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood by reference to the appended Figures, of which:

FIG. 1 depicts changes in the optical absorption spectrum of vanadium-silica sol-gel upon the absorption of water;

FIG. 2 provides a schematic depiction of organic polymers dispersed within a metal-silica sol-gel glass;

FIG. 3 depicts the NMR spectra of a stabilized metal-silica sol-gel containing 0.5 mol % V. FIG. 3a depicts the NMR spectrum of a hydrated vanadium sol-gel. FIG. 3b depicts the NMR spectrum of a desiccated vanadium sol-gel; and

FIG. 4 depicts the proposed structures of hydrated and desiccated vanadium sol-gel.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to metal-silica sol-gel glasses containing relatively low concentrations of metal centers such that a single phase sol-gel glass is formed having a predominantly uniform distribution of individual metal centers. Without being bound by theory, it is believed that the uniform distribution of individual metal centers within the silica matrix imparts unusual properties to the composition. The metal-silica sol-gel glasses of the present invention, and applications thereof, is described in A. E.
particular transition metal, or mixture of transition metals to unusual properties to the composition. The transition metal used to form the single phase sol-gel glass of the present invention is influenced by the particular R₁ and R₂ groups for R₁, one is able slow the rate of the transition metal centers within the silica matrix imparts unusual properties to the composition. The transition metal to silicon ratio at which a single phase sol-gel glass has been processed at temperatures in excess of 500° C. without compromising its properties. The metal-silica sol-gels of the present invention may be prepared by a sol-gel process by the co-condensation of a metal alkoxide (M(OR₂)₃) or an oxo-metal alkoxide (OM(OR₂)₂) with a tetraalkyloxysilicate ((Si(OR₁)₄)). As noted above, it is believed that the uniform distribution of individual metal centers within the silica matrix imparts unusual properties to the composition. The transition metal concentration of the different molecules with the vanadium metal center and the molecules and ligands bound to the metal center. Different molecules produce different chromatic changes for a particular metal center. Thus, by monitoring the light absorption of a particular sol-gel glass, one is able to detect the presence of a variety of different molecules. Table 1 lists some of the molecules that bind to vanadium oxide silica sol-gel and the color caused by the coordination of the different molecules with the vanadium metal center.

As can be seen from Table 1, one can use the metal-silica sol-gel glasses of the present invention to differentiate a wide variety of molecules. Different metal centers have different compound selectivities and exhibit different light absorption patterns for the different metal-molecule complexes. Therefore, by using different metal centers and combinations of metal centers, one can devise metal-silica sol-gel sensors for a wide variety of applications. The choice of a metal center to coordinate, and therefore sense, a particular small molecule can be predicted from known coordination chemistry and by using empirical rules such as hard-soft acid-base theory. For example, vanadium (+5) centers are high-valent early transition metals which would be predicted to coordinate "hard" bases, such as water and hydrogen sulfide, and be unreactive towards "soft" bases, such as pyridine. Thus, with regard to metal-silica sol-gel sensors, vanadium, niobium, molybdenum and tungsten are preferred for detecting H₂S, iron is preferred for detecting SO₂, iron, cobalt and nickel are preferred for detecting CO and iron, and chromium and molybdenum are preferred for detecting NO. Overall, particularly preferred transition metals for use in the metal-silica sol-gels of the present invention include vanadium, rhodium, ruthenium, iridium, lead, platinum, tin, nickel, palladium, niobium, molybdenum, tungsten, iron, cobalt, and chromium. The pore size of the sol-gel can also influence the rate of molecular flow into the glass where an increase in the flow rate into the glass increases the response speed of the sensor. Modulation of sol-gel pore sizes by use of different acid and base catalysts is well known in the art. How one would modify the pore size of the sol-gel in order to achieve different chemical selectivity is similarly well known in the art. The amount of light absorbed by the metal-silica sol-gel at a particular frequency is directly proportional to the concentration of the metal-molecule complexes present in the sol-gel. FIG. 1 depicts changes in the optical absorption spectrum of vanadium-silica sol-gel upon the absorption of water. As can be seen from FIG. 1, the metal-silica sol-gel compositions of the present invention may be used to
quantify the amount of a particular molecule present with great sensitivity.

Ideally, one should be able to incorporate sensor materials directly into electronic or optical components to form the key sensing element of an active environmental control system. The metal-silica sol-gel glasses of the present invention are particularly well suited for use as sensors in view of the ease with which these materials may be molded and manipulated. By using pre-formed molds and allowing appropriately for shrinkage, optical components of any specific shape and size can be readily fabricated by the sol-gel process. In addition, the stabilized sol-gel glass, even though highly porous, can be ground and polished much like a conventional fused silica optic. Sol-gel solutions can also be spin-coated onto a flat substrate to produce thin films of high optical quality. This is extremely significant for micro-instrumentation applications since thin film technology greatly reduces the size of the sensing element and, in principle, allows the sensor component to be integrated into a single microchip which performs the entire sensing/analysis operation.

The excellent optical properties of the materials of the present invention, in conjunction with their ability to be processed into thin films, recommends their integration into an optically driven sensor device. Optical devices offer a number of inherent advantages over other sensing/detection methods. The detection and modulation of light can be performed with great sensitivity while extremely small optical components are commercially available which facilitates the fabrication of very small sensing devices.

Of particular recent interest is the use of fiber optic bundles as in-situ optical sensor devices. Fiber optics can change light intensity, yet remain light weight. The fiber optic element (engineered to detect a specific chemical species), an optical sensor element, has the particular advantages of being flexible and extremely small (the diameter for a single mode fiber core ranges from 2 to 8 microns). Thin films of the silica-gel sensor elements can be easily applied to the end of an optical fiber making them extremely compatible with this type of device. An integrated sensor device, capable of sensing and discriminating between gases in a complex mixture can be prepared using these materials and a fiber optic bundle. By coating each fiber in the bundle with a different sensor element, a single microchip which performs the entire sensing/detection operation is achieved. Irradiation of the vanadium sol-gel under a 1/1 CH₄/O₂ mixture (1 atm) in the ESR cavity revealed the formation of methyl radicals. However, the ESR signal associated with VN was not observed. Yet another use of the invention relates to the formation of new organopolymer-silica nano-composite materials. In many cases, molecular species with desirable nonlinear optical properties have not been utilizable in actual devices due to factors as varied as their thermal and/or oxidative instability, poor optical properties or lack of processibility. Organopolymer-silica nano-composite materials which can be formed using the present invention are particularly advantageous for sensor element material whose enhanced properties combine the unique nonlinear and electro-optical properties of polyacetylene with the superior optical properties and excellent processibility of a silica glass.

Fabrication of these polyacetylene nano-composites is easily accomplished under very mild conditions. To do so, silica-gel optical flats (doped at the 0.5 mol % level with vanadium oxide) are evacuated and subsequently back-filled with the mixture. Such a multifunctional device should be much more accurate than a single sensor or a group of sensors read independently.

Thin optical films of the active sensor element are the most promising configuration for device applications. Films of 1 mm in thickness can be fabricated by dipping or spin coating the metal-silica sol-gel solution onto a substrate. After aging and drying, these films should have optical properties equal to those of monolithic components. The potential advantage of thin-film sensor elements over monolithic components is twofold: the large surface area and shallow depth will saturate quickly with the detectable species yielding a rapid response time while the sensitivity of the detection process will be greatly enhanced by monitoring the process optically through the long path-length of the film. The metal-silica sol-gel glasses of the present invention can also be used as oxidation/reduction catalysts. The choice of metal center to use can be predicted from known coordination chemistry and transition metal catalysis. For example, vanadium-silica sol-gel glass was shown to turn from clear to sapphire blue upon being exposed to hydrogen gas at 490° C. As is known in the art, this color change reflects the reduction of V⁴⁺ to V⁰. The presence of the VH⁴⁺ species was confirmed by electron spin resonance (ESR) spectroscopy due to its characteristic eight-line spectrum resulting from hyperfine coupling to the 5¹¹ V nucleus. Vanadium-silica sol-gel glass has also been shown to activate methane. Photolysis (λ>305 nm) of a 0.5 mol % vanadium-silica sol-gel under an atmosphere of methane turned the clear sol-gel glass a sapphire blue color. The presence of the VH⁴⁺ species was confirmed by ESR spectroscopy. Further, when the reaction is conducted at 77° K, the characteristic spectrum for methyl radicals is detected. Gas chromatographic analysis of the products verified the presence of ethane, the expected product of methyl radical recombination and trace amounts of propane resulting from subsequent atomic-abstraction recombination processes.

It is believed that the organic polymer in these new composites is microscopically dispersed within an optically transparent metal-silica sol-gel glass. This is accomplished by photopolymerizing the polymer precursor within the silica sol-gel matrix. FIG. 2 provides a schematic depiction of organic polymers dispersed within a metal-silica sol-gel glass.

The sol-gel glass matrix, which has the bulk properties of a hard transparent glass, is highly porous on a microscopic level and contains discrete vanadium-oxide centers which photochemically initiate the polymerization reaction. The results of this internal polymerization is a new hybrid material whose enhanced properties combine the unique nonlinear- and electro-optical properties of polyacetylene with the superior optical properties and excellent processibility of a silica glass.
optical switches. The nano-composites of the present invention provide the necessary medium for exploiting and applying this well-established material in an actual device.

In a similar fashion, it is believed that these nano-composites will allow the doped form of polyanacetylene, which is metallic and highly conducting, to be fashioned into electronic or electro-optical devices. For example, it should be possible to draw a polyanacetylene "wire" into the composite with a narrowly focused laser beam which, after doping, will yield a thin "molecular" wire embedded in the optical flat.

It should be emphasized that the procedure by which polyanacetylene nano-composites are made can be used to produce a broad range of polymer containing nano-composites for a number of applications. Examples of nano-composites of other polymers include conducting polymers (e.g., polyaniline, polythiophene) and piezoelectric polymers (e.g., polyvinylidene fluoride). Composites of conventional insulating polymers, such as polycarbonate, polymers sold under the Telon brand, polymethylmethacrylate, etc. are also of interest for the production of graded refractive index glasses by varying the degree of polymerization over the length of an optical flat.

The following examples set forth the preferred synthesis of the sol-gel compositions of the present invention and illustrate some of their physical properties. Further objectives and advantages of the present invention, other than those set forth above, will become apparent from the examples which are not intended to limit the scope of the present invention.

EXAMPLES

1. Synthesis and Fabrication of Vanadium-Silica Sol-Gel Materials

Vanadium-silica sol-gel glasses are synthesized by the sol-gel process by co-condensation of oxovanadium trisopropoxide with tetraethylorthosilicate (TEOS):

$$nSi(OC)3 + 3nCH3CH(OH)CH3 \rightarrow nSiO2 + 3nCH3CH=O$$

Specifically, a solution of oxovanadium trisopropoxide of the desired vanadium concentration in isopropanol is added to 6 ml (0.027 mol) of TEOS. Isopropanol is then added to bring the total volume to 12 ml. 8 ml of a 1/5 isopropanol/water mixture is then added drop-wise while sonication. Four milliliter aliquots of the resulting clear solution are placed into 1 cm polystyrene cuvettes, sealed, and allowed to gel. Sonication was used as the catalyst in this example. However, it should be noted that acid catalysts, such as HCl, and alkaline catalysts, such as NH₄OH, may also be used.

Gelation occurred in approximately two weeks at room temperature. After gelation, the seal was punctured and the materials were allowed to age for six months. Optical transparent vanadium-silica glass flats approximately 0.4x0.4x0.25 cm in dimension remained after the aging process. These optical flats ranged from colorless to dark orange with increasing vanadium concentration. The orange color remained after drying (125°C, 1 week). However, upon stabilization at 500°C, all of the materials, regardless of vanadium concentration, became colorless.

This procedure consistently yields high quality optical monoliths that retain the geometry of the 1.0x1.0x0.0 poly-styrene molds in which they are made. By using pre-formed molds and allowing appropriately for shrinkage, optical components of any specific shape and size can be readily fabricated. Additionally, the stabilized vanadium-silica glass, even though highly porous, can be ground and polished much like a conventional fused silica optic. The sol-gel solutions can also be spin-coated onto a flat substrate to produce thin films of high optical quality.

The specific coordination environment of the vanadium in the silica matrix was probed directly by solid-state $^{51}$V NMR spectroscopy. The NMR spectra of a stabilized metal-silica sol-gel containing 0.5 mol % V is shown in FIG. 3. FIG. 3a depicts the NMR spectrum of a hydrated vanadium sol-gel. FIG. 3b depicts the NMR spectrum of a dehydrated vanadium sol-gel. The static spectrum of the dehydrated material reveals an axially symmetric chemical shift tensor with $\delta$ and $\beta$ values of $-1250 \pm 50$ and $-500 \pm 20$ ppm vs VOCl₄, respectively. Previous studies of discrete vanadium compounds with known local environments have shown that the anisotropic chemical shift properties of the $^{51}$V nucleus are highly diagnostic of the coordination geometry. In particular, the line shape observed for the dehydrated sample, shown in FIG. 3a, is unique to a pseudotetrahedral $\text{VO}_2$ coordination environment and has been previously observed for vanadium oxide monolayers on a dehydrated $\text{SiO}_2$ surface. An intense transition in the FT-IR spectrum at 935 cm$^{-1}$ is also observed. This transition, which is absent in pure silica and whose intensity depends on the vanadium concentration, is characteristic of terminal vanadium-oxygen bonds. Taken together, these results suggest that the structure of the vanadium in the silica framework is one of local pseudotetrahedral geometry possessing a short terminal (V=O) bond and three long vanadium-oxygen bonds which are connected to the silica. The proposed structures of dehydrated and hydrated vanadium sol-gel is shown in FIG. 4.

2. Chemical Sensing Properties

Exposure of the colorless stabilized vanadium-silica flats to humidity results in a rapid weight gain from the uptake of water, as shown in FIG. 1, and a concomitant color change from colorless to orange.

The evolution of UV-Vis spectrum as a function of water absorption is shown in FIG. 1. The spectrum of the dehydrated materials has an intense transition appearing as a shoulder at 235 nm ($\epsilon=8 \times 10^3$) which rapidly diminishes as water is absorbed. Meanwhile, a low energy shoulder at 340 nm emerges as water is absorbed.

These spectral changes are due to direct coordination of water molecules to the vanadium metal center which converts the pseudotetrahedral environment to one of a higher coordination number. The tendency of pseudohedral V-V compounds to increase their coordination sphere by either adding ligands or through oligomerization is well documented as are the color changes associated with it.

Due to the high optical transparency of the silica-glass color change can be monitored quantitatively and with great sensitivity by spectroscopic means, an important prerequisite for solid-state optical sensing applications.

Other small molecules also coordinate to the vanadium center, often imparting a characteristic color to the material. For example, the vanadium sol-gel glass turns deep amber and dark green when exposed to hydrogen sulfide and formic acid, respectively. In addition, ammonia is observed to turn the vanadium-silica sol-gel very pale yellow. Meanwhile, formaldehyde-coordinated material is bright yellow. The vanadium-silica sol-gel also exhibits a distinct coordinating preference along with these chemical sensing properties. The sorption of formaldehyde appears to be favored over that of water, which in turn is clearly favored over that of ammonia.
It has been found that vanadium-silica sol-gel desorbs species such as water, formaldehyde and ammonia at relatively mild elevated temperatures (<150°C) while other species (e.g., H₂S) are difficult to remove.

While the present invention is disclosed by reference to the preferred embodiments and examples detailed above, it is to be understood that these examples are intended in an illustrative rather than limiting sense, as it is contemplated that modifications will readily occur to those skilled in the art, which modifications will be within the spirit of the invention and the scope of the appended claims.

What is claimed is:

1. A sensor material wherein the material comprises a single phase undensified metal-silica sol-gel derived glass, the glass exhibiting chromatic changes that detect the presence of chemical species and comprising tin atoms and silicon atoms wherein the tin atoms are uniformly distributed with the sol-gel derived glass as individual metal centers.

2. A sensor material according to claim 1, wherein the single phase undensified metal-silica sol-gel derived glass is formed according to a method comprising the step of co-condensing a metal complex with a tetraalkylorthosilicate.

3. A sensor material according to claim 2, wherein the metal complex is a metal alkoxide, an oxometal alkoxide or a metal acetylacetonate.

4. A sensor material according to claim 1 wherein the sensor material is in the form of a thin film.

5. A sensor material according to claim 1 wherein the material is attached to an optical fiber.

6. A polymerization catalyst, wherein the catalyst is comprised of a photoresponsive single phase undensified metal-silica sol-gel derived glass comprising tin atoms and silicon atoms wherein the metal atoms are uniformly distributed with the sol-gel derived glass as individual metal centers and wherein the photoresponse of the metal atoms initiates polymerization.

7. A polymerization catalyst according to claim 6, wherein the photoresponsive single phase metal-silica sol-gel derived glass is formed according to a method comprising the step of photopolymerizing a polymer precursor within the silica sol-gel matrix.

8. A polymerization catalyst according to claim 6, wherein the photoresponsive single phase metal-silica sol-gel derived glass is formed according to a method comprising the step of co-condensing a metal complex with a tetraalkylorthosilicate.

9. A polymerization catalyst according to claim 8, wherein the metal complex is a metal alkoxide, an oxometal alkoxide or a metal acetylacetonate.

10. A sensor material according to claim 9, wherein the metal complex is a metal alkoxide, an oxometal alkoxide or a metal acetylacetonate.

11. A single phase undensified metal-silica sol-gel derived optically transparent glass comprising tin atoms and silicon atoms in which the tin metal atoms are uniformly distributed as individual metal centers within the sol-gel derived glass and the glass is formed according to a method comprising the step of co-condensing a metal complex with a tetraalkylorthosilicate.

12. A single phase undensified metal-silica sol-gel derived optically transparent glass according to claim 11, wherein the metal complex is a metal alkoxide, an oxometal alkoxide or a metal acetylacetonate.

13. A sensor material wherein the material comprises a single phase metal-silica sol-gel derived glass, the glass exhibiting chromatic changes that detect the presence of chemical species and comprising vanadium and silicon atoms wherein the vanadium atoms are uniformly distributed within the sol-gel derived glass as individual metal centers and wherein the mole fraction of vanadium is less than 1 x 10⁻².

14. A sensor material according to claim 13, wherein the single phase metal-silica sol-gel derived glass is formed according to a method comprising the step of co-condensing a metal complex with a tetraalkylorthosilicate.

15. An organopolymer metal-silica sol-gel composite comprising a single phase metal-silica sol-gel glass comprising transition metal and silicon atoms wherein the metal atoms are uniformly distributed within the sol-gel glass as individual metal centers and an organic polymer, wherein the metal-silica sol-gel glass has pores filled with the organic polymer.

16. An organopolymer metal-silica sol-gel composite according to claim 15 wherein the polymer is selected from the group consisting of polyacetylene, polyamline, polythiophene and polyvinylidene fluoride.

17. An organopolymer metal-silica sol-gel composite according to claim 15, wherein the glass is optically transparent.