

Preparation and study properties of xerogel silica using sol-gel method

Sinaa Ibrahim¹, Harth Ibrahim²

University of Bagdad, college of science, department of physics

Abstract

In This study synthesis of inorganic oxide material by a sol-gel technique through the formation of colloidal suspension (sol) and gelation of the sol into the gel enables incorporation of heat-sensitive active substances into the material during processing. Sol can be further processed into forms, such as monoliths (rod shape). The objectives of this study were to evaluate sol-gel derived silica gel as an implantable (monoliths). The structural properties of the prepared samples were studied, using X-ray diffraction (XRD) and Fourier transform infrared (FTIR), UV-VIS. Spectroscopy of xerogel silica and liner shrinkage of the samples. The sample prepared by mixing TEOS, ethanol, water, and HCL, TEOS and ethanol were mixing and stirred for 10 min at room temp. then 0.1 MHCL was gradually added to the solution until a water to TEOS molar ratio of R=2, R=5. The results shows that, silica xerogel has amorphous structure, FTIR spectroscopy has been used to find the amount of water (OH), it was found that when increase in temperatures the R (R=water:TEOS molar ratio) (R=2, R=5) the decrease intensity of H₂O absorbance are consistent with loss of physisorbed water. Transmission spectra shows that the final samples have good transparency and homogeneity (the reflective index about sample R=2, n=1.41 and R=5, n=1.45), and the linear shrinkage for sample R=5 less about the R=2. it was found that, increase in temp. for (R=2, R=5) will decrease intensity of H₂O absorbance which indent that the water will defused outside the sample.

Key words:- TEOS, sol-gel, monoliths,

1. Introduction

The sol-gel process has been widely shown to be a very flexible route for the fabrication of a large variety of photonic materials in various configurations such as monoliths, coatings, fibres and films for optical device applications. [1] SiO₂ is widely used for optical materials, resistance film, passivation film, etc. usually, SiO₂ is fabricated by a fusion method, chemical vapor deposition or sputtering method. But the fabrication processes for SiO₂ have some disadvantage, e.g. a high temperature is needed. Sol-gel processing is attractive because SiO₂ can be obtained under 1000°C without need for large scale processing [2] This technique uses metal alkoxides as precursors for the synthesis and production of glasses, ceramics, and composites through a series of chemical-physical processes, including hydrolysis, condensation, and thermal treatment [3] A *sol* is a colloidal suspension of solid particles in a liquid. A *colloid* can be defined as a suspension in which the dimension of the dispersed phase is so small (1-1000 nm) that gravitation forces can be neglected and interactions are dominated by short-range forces (van der Waals or surface charges). A suitable definition of a *gel* is a two-component system that consists of a continuous solid and fluid phase of colloidal dimensions. The sol-gel process thus involves the formation of a colloidal suspension (*sol*) and further polymerization of the sol to form an inorganic network in a continuous liquid phase (*gel*) [4]. The hydrolysis and condensation of the metal alkoxide leads to the formation of a colloidal phase, consisting of relatively higher molecular weight polymeric intermediates. This is what is known as the sol phase. These intermediates undergo further polycondensation reactions, which lead to the formation of a cross linked macroscopic three dimensional gel material. The role of the sol-gel method in inorganic ceramic and glass materials has been studied since the mid-1800's. While studying silica gels, Ebelman and Graham observed that tetraethyl orthosilicate, Si(OC₂H₅)₄, underwent hydrolysis in acidic conditions to form SiO₂, in a glass-like form [5]. The method enabled a significantly low temperature processing of glasses and ceramics [6]. When the hydrolysis followed by condensation occurs, clusters and polymeric chains of clusters will be formed. An increase in the quantity of these structures is directly proportional to the sol viscosity. The polymeric chains react all sides of the container at which point there is a sharp rise in the viscosity and the sol is considered (*alcolgel*), where it consists of two parts, a solid part formed by the three-dimensional network of linked particles, which is sufficiently stiff to resist the compressive force of surface tension, yet still full with solvent, and the liquid part (i.e. solvent) fills the free space (nanopores) surrounding the solid part. This liquid part is removed by evaporation (during aging and drying processes), and the alcolgel will become the so-called "Xerogel" [7] The first metal alkoxide were prepared in 1864 by Ebelmen [8] using SiCl₄. He noticed that upon exposure to the atmosphere, these chemicals formed a gel. This is the first form of the sol-gel process as known today. This process was used in the 1930 by the Schott glass company in Germany to produce metal alkoxides. A renewed interest surfaced in the early 1970 when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process [9]. Klein and Garvey [10] observed that, in bulk gels, increased water increases the hydrolysis rate in both acid- and base-catalysed solutions. They also found that in acid-catalysed solutions water has a strong effect on surface area and porosity, while acid addition has little

effect. Tatsuhiko adachi, Sumio sakka [11] preparation of monolithic silica gel and glass by the sol-gel method using N,N-dimethylformamide without cracks when drying the sample.

aim of the research :-

preparation of silica xerogel and study The effect of change molar ratio (R=H2O:TEOS) about silica xerogel properties and study effect the temperature about silica xerogel structure.

Experimental:-

Synthesis of silica xerogel monolithic Samples:-

sol-gel solutions were prepared by mixing tetraethylorthosilicate (TEOS, ≥98% purity), ethanol, water and HCl. Equal volumes of tetraethylorthosilicate (TEOS) and ethanol were mixed and stirred vigorously for 10 min at room temperature. Then 0.1M HCl was gradually added to the solutions, until a water to TEOS molar ratio of R=2 was attained. Additional deionised water was added to give solutions with R =5 so that for all solutions the molecular ratio TEOS:HCl was maintained, as summarised in Table 1. The solutions were placed in the refluxing bath immediately after mixing, and the temperature of the bath was increased to 60°C in 15 min, while stirring, and kept there for 2 h and then cooled to room temperature. drying the sample at 100° c and 200° c . The refractive index is an important parameter for optical applications. Thus, it is important to determine optical constants of the sample studied and the complex optical refractive index is expressed as,

$$n^{\wedge} = n(\omega) + i k(\omega)$$

where n is the real part and k is the imaginary part of complex refractive index. The optical properties of the Silica xerogel are characterized by refractive index. The refractive index can be obtained from the following equation [12],

$$n = \{4R/(R-1)^2 - K^2\}^{0.5} - R+1/R-1$$

Table 1:- Reagent volumes used in sol preparation

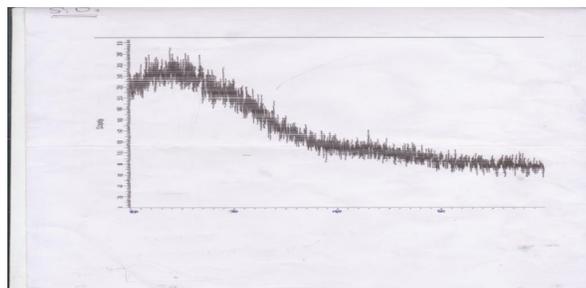
Sample ratio)	(R	TEOS ml	ethanol ml	H2O ml	HCl (0.1M) ml
2		5.0	5.0	10	0.81
5		5.0	5.0	25	0.81

Many tests were calculate to evaluate to the sample :-

- 1- The x-ray diffraction The samples structure were analyzed with a Shimadzu 6000 X-ray diffractometer using Cu Kα radiation (λ=1.5406 Å) in reflection geometry. The XRD patterns display no peaks indicating that the samples structure was in amorphous phase.
- 2- Mid-IR spectra, from 4000 to 400 cm⁻¹, were obtained for some pure samples using FTIR-Spectrometer, supplied by Shimadzu, on KBr pellets of the samples
- 3- UV-Visible transmittance measurement on xerogel sample were performed using spectro UV/VIS., Spectral bandwidth :2 mm, and scan range 190-900nm.
- 4- Linear shrinkage

Results and discussion :-

1- X-ray diffraction pattern of all samples were prepared have same pattern as shown in fig.(1) as it is seen from the figure ,the broad peak ranging from 20-40 in 2θ angle confirms the amorphous nature of the silica xerogel.[13]



Figure(1) : XRD structure of sample silica Xerogel.

2- Fourier transform infrared (FTIR) spectroscopy is used to analyze the composition of the silica sol-gel FTIR spectra of Xerogel samples ,figure (2a,3a,4a) present IR spectra, the sample (R=2) and figure(2b,3b,4b) present IR spectra, the

sample (R=5) collected at room temp. and after drying the sample were heated at 10 °C/min held for 1 h at 100 °C, and 200 °C.

a) 4000 cm^{-1} - 3000 cm^{-1} : In this spectral range, the bands are mainly due to overtones and combination of vibration of H₂O. The position and intensity will variant with increase in temp. for temp. 25 °C The sample (R=2) The band at 3379.05 cm^{-1} , drying 100 °C band 3600.85 cm^{-1} and 3425.34 cm^{-1} at drying 200 °C and the sample (R=5) at 25 °C the band 3348.19 cm^{-1} , the band 3419.3 cm^{-1} for sample drying 100 °C and 3440.77 cm^{-1} for sample drying 200 °C for corresponds to molecular water hydrogen bonded to O-H stretching group [14].

According to this fig.(2,3,4), the increase temp., the decrease in intensity of the H₂O and Si-OH Transmittance are consistent with loss of physisorbed water.

b) 3000 cm^{-1} - 1200 cm^{-1}

: In this spectral range, the bands are due to the overtones and combination of vibration of organic residue, molecular water .for sample (R=2) The band at 1638 cm^{-1} corresponds to vibration of molecular water. In spectra, water bands observed at around 1637.45 cm^{-1} 25 °C, the band at 1633.59 at drying 100 °C, and the band at 1635.5 at 200 °C, and the sample R=5 the band 1625.88 cm^{-1} at room temp., the band 1641.31 cm^{-1} at drying 100 °C, and the band 1637.45 cm^{-1} at drying 200 cm^{-1} , corresponding to bending vibrations [15]

c) 1200 cm^{-1} - 400 cm^{-1}

This spectral region is associated with combinations of vibration of silica network. The band at (1060.78-1078.13-1066.56) cm^{-1} for sample R=2 at 25 °C, drying 100 °C, and 200 °C respectively and the band at (1080.06-1083.92-1074.28) cm^{-1} for sample R=5 at 25 °C, drying 100 °C, and 200 °C assign to asymmetric stretching vibrations of Si-O-Si bridging sequences. The weak band at (958.6-956.6-956.63) cm^{-1} for sample R=2 and the band at (962.41-954.7-950.84) cm^{-1} is due to stretching vibration of silanol (Si-OH) groups [16]. The band at (794.62-800.40-811.98) cm^{-1} for sample R=2, and the band at (804.26-794.62-802.3) cm^{-1} attributed to stretching vibrations of free silanol group on surface of silica network. The band at (451.31- 466.7-466.7) cm^{-1} for sample R=2 and the band at (441.67-457.1-443.6) cm^{-1} for sample R=5, associated with Si-O-Si bond bending vibration.

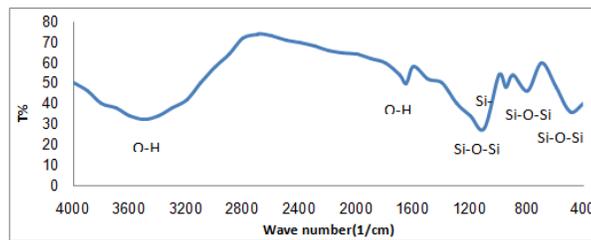


Figure (2a): FTIR transmission spectra of Silica Xerogel(R=2) at room

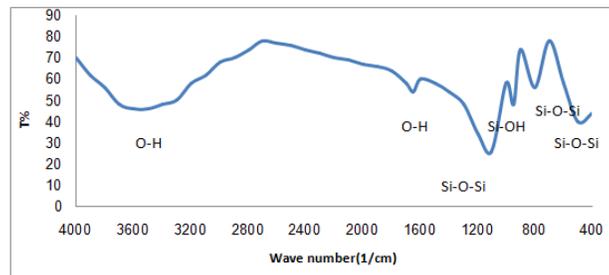


Figure (3a): FTIR transmission spectra of Silica Xerogel(R=2) at 100 °C.

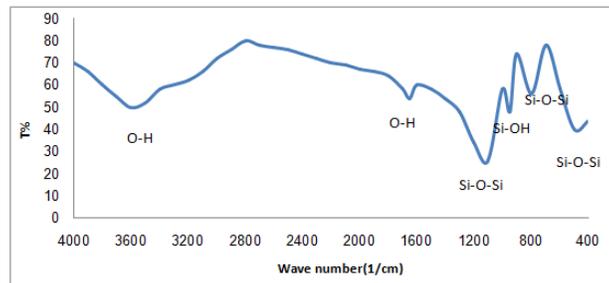


Figure (4a): FTIR transmission spectra of Silica Xerogel(R=2) at 200 °C.

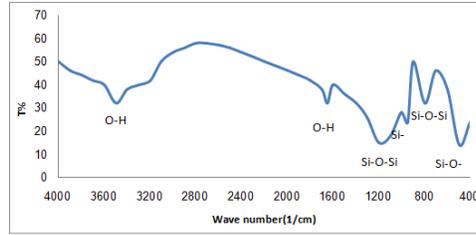
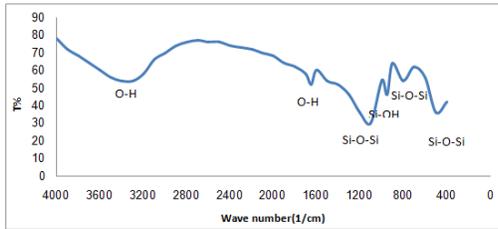
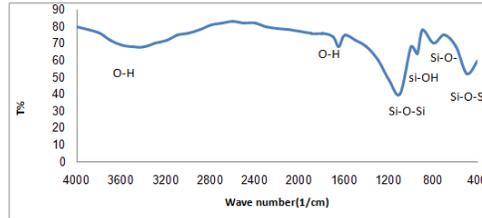


Figure (2b) FTIR transmission spectra of Silica Xerogel(R=5) at room temperature



Figure(3b) FTIR transmission spectra of Silica Xerogel(R=5) at 100°C



Figure(4b) FTIR transmission spectra of Silica Xerogel(R=5) at 200°C

3-Xerogel silica are well known for its high transparency in visible region ,and the transparency was enhanced by increase of water ratio.figure (5) shows the optical transmittance spectra in wavelength range between 190-900 nm .The refractive index values of the silica xerogel were calculated from the T and R spectra of the silica xerogel ,the $n(R=2)=1.41$ and the $n(R=5)=1.45$, the refractive index of all samples decreases with the increase of the wavelength, agreement with the theory of refraction in glass systems[17]

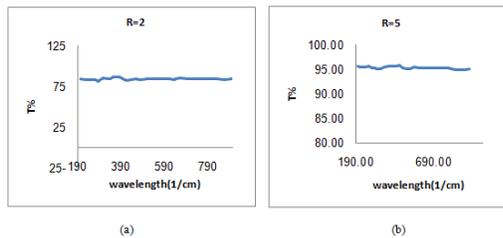


Fig.(5) the transmittance of silica xerogel (a)R=2,(b) R=5

4- The sample shrinkage about the days fig(6) shows how the sample shrinkage at room temperature, it was found that the shrinkage decrease with increasing R [18] .

$$\text{Linear shrinkage \% (R=2)} = \frac{\text{initial length} - \text{final length}}{\text{final length}} * 100$$

$$= \frac{4.5 - 1.3}{1.3} * 100\% = 2.4$$

$$\text{Linear shrinkage \% (R=5)} = \frac{5.5 - 2.2}{2.2} * 100\% = 1.5$$

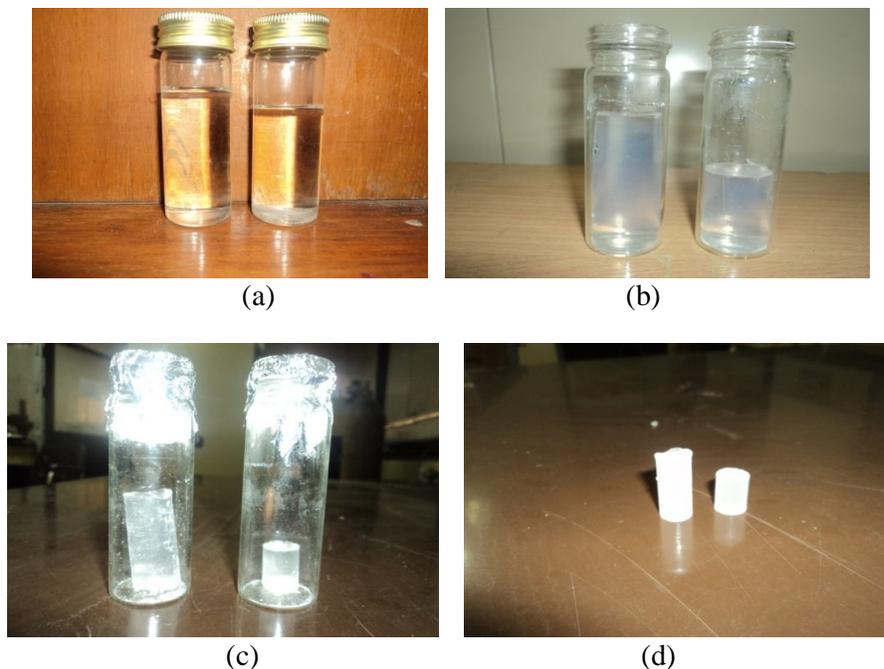


Fig.(6) shows the sample (a) silica xerogel sol (b) shrinkage sample about 20day (c) about 45 day (d) about 60 day

Conclusions:-

- 1- All samples were prepared have same pattern the amorphous nature of the silica xerogel.
- 2- Increasing molar ratio (R) will increase water contain
- 3- Increasing temp. will reduce water contain for $R=2, R=5$.
- 4- high transparency in visible region ,and the transparency was enhanced by increase of water ratio for silica xerogel.
- 5- it was found that the shrinkage decrease with increasing of molar ratio (R).

References :-

- [1] M. A. Fardad "Catalysts and the structure of SiO_2 sol-gel films", journal of materials science (35),pp.1835 – 1841,2000.
- [2] Sachiko Okuzaki,Kojiro Okude,Tomoji Ohishi "photoluminescence behavior of SiO_2 prepared by sol-gel processing"journal of non-crystalline solids (265),pp.61-67,2000.
- [3] Sura Salah.M.Al-Saidi " Spectroscopic Study for Sol-Gel Doping by Rh610 Dye Laser" A Thesis Submitted to the College of Science University of Baghdad in partial fulfillment of the requirements for Master Degree of Science in Physics,2012
- [4] Giovanni Schiavon, "*Sol-Gel Derived Nanocomposites synthesis Spectroscopy, Atomic Force Microscopy*", Ph.D. ThesisTechnisched München University, *Chemie*,, 2000.
- [5] L.L. Hench, J.K. West, The sol-gel process.Chemical Reviews, 90(1): pp.33-72,1990.
- [6] Tahira Pirzada "Synthesis of Polymer Silica Hybrid Xerogels andNanofibers through Sol Gel Processing and Electrospinning",Doctor of Philosophy in Physical Chemistry,2012
- [7] Firas Jawad " prepration and stuy of rare earth laser active media using sol-gel technique ", A Thesis Submitted to the College of Science, University of Baghdad In partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy In Physics ,2007.
- [8] Kirk Othmer "Encyclopedia of chemical technology", Wiley Interscience Vol No. 22,pp. 503, 1994.
- [9] C.J Brinker and G.W. Sherer, "*Sol-Gel Science*", Academic press, San Diego, 1990
- [10]L.C. Klein and G.J. Garvey, in: Better Ceramics Through Chemistry III, ed. C.J. Brinker, D.E. Clark and D.R. Ulrich,Mater. Res. Soc. Symp. Proc. 32,pp.33, 1984.
- [11]Tatsuhiko adachi ,Sumio sakka" preparation of monolithic silica gel and glass by the sol-gel method using N,N – dimethylformamide " journalof material science ,1987,4407
- [12]B. Gündüz *, M. Cavaş , F. Yakuphanoglu"Quality Controlling of SiO_2 Thin Films by Sol Gel Method",6th International Advanced Technologies Symposium (IATS'11),pp. 16-18 May 2011, Elazığ, Turkey>
- [13]A.Gungor,H.Demirtas,I.A.tilgan and M.Yasar "synthesis and characterizationsof SiO_2 films coated on stainless steel by sol-gel method ",intemational iron &steel ,pp. 697,2012

- [14] R.K. Satvekar, M.R. Phadatare, V.A. Karande, R.N. Patil, B.M. Tiwale and S.H. Pawar *"Influence of Silane Content on the Optical Properties of Sol Gel Derived Spin Coated Silica Thin Films" *International Journal of Basic and Applied Sciences*, 1 (4) ,pp.468-476,2012.
- [15] S. Duhana, N. Kishore, P. Aghamkar, S. Devi, "Preparation and characterization of sol-gel derived silver-silica nanocomposite", *Journal of Alloys and Compounds* 507,pp. 101-104,2010.
- [16] X. Song, N. Jiang, Y. Li, D. Xu and G. Qiu, "*Synthesis of CeO₂-Coated SiO₂ Nanoparticle and Dispersion Stability of its Suspension*", *Mater. Chem. And Phys.*, Vol.No. 110 ,pp.128-135, 2008.
- [17] J.Zschokke, "Optical Spectroscopy of Glasses", Reidel, Dordrecht, 1986.
- [18] M.A. Fardad , E.M. Yeatman , E.J.C. Dawnay a Mino Green , F. Horowitz "Effects of H₂O on structure of acid-catalysed SiO₂ sol-gel films " *Journal of Non-Crystalline Solids* 183, pp. 260-267,1995.