Structural evolution of silica-gel in the late stages of the gelation process

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Infrared spectroscopy has been used to analyze the structural changes in samples prepared by the sol-gel method. Silica gels were prepared from alcoholic solutions of tetraethylorthosilicate (TEOS) keeping the H_2O/TEOS and Et-OH/TEOS molars ratios constant and equal to 11.66 and 4, respectively. The IR spectra was carried out in the wet state, before or after gelation while the gel was still impregnated by pore liquor. The IR spectra of these gels, measured as a function of the gelation time, confirm that the final structure of the material is in relationship with the pattern in the late stages of this gelation process. The preliminary results of IR allows some structural considerations to be advanced about the final SiO_2 glasses obtained.

Keywords: Sol-gel; infrared spectroscopy; glasses; structure

Se presenta un estudio de la estructura local de SiO_2 preparado por la técnica sol-gel, utilizando espectroscopía infrarroja. Muestras de sílica gel fueron preparadas utilizando como precursor ortosilicato de tetraetilo (TEOS). Las muestras analizadas corresponden a composiciones con una relación molar constante de etanol (Et-OH)/TEOS de 4 y de H_2O/TEOS de 11.66. Las mediciones de infrarrojo fueron efectuadas para tiempos de gelación intermedios en los cuales las muestras aún se encuentran húmedas. Se presentan espectros infrarrojos en función del tiempo de gelación y se discute la evolución estructural de las muestras para las etapas finales del proceso de gelación; estas mediciones confirman que la estructura final de la sílica gel está determinada por la estructura que presentan en estas etapas del proceso.

Descriptores: Sol-gel; espectroscopía infrarroja; vidrios; estructura

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1. Introduction

Because of their excellent properties, silica glasses have been receiving considerable attention. The sol-gel process is particularly suitable for the preparation of oxide glasses and in recent years has gained scientific and technological importance [1, 2]. The sol-gel route is recognized as a good technique for forming thin films, coating and for the preparation of fibers and catalysts [3–5].

It is still difficult to prepare massive glasses, using the sol-gel route, with desirable shapes because of both fracture and bloating during firing. It is therefore of scientific and technological interest to study the structural developments occurring at various stages of the entire sol-gel to glass process and investigate the factors influencing structure and hence properties [6].

The rheological data demonstrate that there is a major evolution of structure during the sol-gel transition [7]. The system evolves from a sol, where there are individual particles more or less weakly interacting with each other, to a gel, which basically becomes a continuos molecule occupying the entire volume. Consequently, it is important to characterize the evolution of the structure of the sol during the gelation process.

According to Iler [8], the final structure occurs in three stages: 1) Polymerization of monomers to form particles; 2) Growth of particles; and 3) Linking of particles into chains, then networks that extend throughout the liquid medium, thickening it to a gel. During the development of these stages, the structure of silica gel goes from monomers that include isolated tetrahedral units, passing through molecules chains that are occasionally cross-linked and finally these molecules chains entangle and form additional branches resulting in gelation; that is, a three-dimensional interconnection of the SiO_4 tetrahedral units. In this process the final structure is in relationship with the sample preparation conditions, mainly the water contents [3, 9]. The average value of the Si-O-Si angles in the fundamental structural units, determines very important features in the main structure of the silica gel, features such a: the presence of a predominant linear structure (linear chain of molecules) [9] or the presence of three- and four-members rings structure [10–13].

The IR spectroscopy has proven to be a very successful technique to follow the gelation process in silica and silicate systems [14] and in a general way the IR technique helps to understand the evolution and conformation of the SiO_2 structure [6–13].

Several authors have reported detailed studies of the SiO_2 structure, using mathematical deconvolutions of the IR absorption main bands. Some of them have reported that the shoulder of main stretching SiO_2 band can be composed of a set of sub-bands. Kirk and Lange [15, 16], for example, have reported vibrational modes at 1254, 1170, and 1200 cm^{-1}. These additional bands have been related to disorder-induced modes in amorphous SiO_2 films. Seifert *et al.* [17] have suggested that the presence of two or more sets of SiO_2 stretching bands that could be associated with the presence of two or more structure types present in the fully-polymerized glass, they found two component at 1157–1160 cm^{-1} and 1209–1215 cm^{-1} for the main stretching band shoulder at 1254 cm^{-1}. Vukcetich has proposed a two-state model [18] for the SiO_2 glass structure, in which there are at least two distinct populations of Si-O-Si angles within the tetrahedral network, with values near 138° and 145°. The relatives proportion of Si-O-Si angles with this values can be inferred with the position and band intensities of the IR spectra. The position of the band in the IR spectra is in relationship with the θ angle bond. The changes of frequency can be explained in terms of changes in the bond angle at the oxygen atom site, agree with Lucovsky [19], and the width of the bond-stretching band derives from a sum over a distribution of narrow modes, each associated with a particular Si-O-Si bond angle in the statistical distribution, and centered around the average value.

Other authors found that the central frequency of the mean stretching band 1070–1080 cm^{-1} scale monotonically with the oxygen atom concentration with values of 1075 cm^{-1} in stoichiometry site to 940 cm^{-1} in O doped amorphous silicon [20]. Boyd [21] reported a deconvolution of the main stretching band consistently in two distinct separate Gaussian profiles at 1050 and 1085 cm^{-1}. He related this sub-bands to the existence of two different structure models of amorphous SiO_2 disclaiming the generally accepted continuous random network arrangement (CRN).

In the present paper we study by IR spectroscopy the evolution of the local structure of SiO_2 in the late stages of the gelation process, prepared with the sol-gel method. In this contribution, the kinetics studies have been conducted in the wet state, *i.e.*, before gelation or after gelation while the gel was still impregnated by pore liquor. The purpose of the present study is: 1) to follow the structural evolution of the silica-gel during the gel-glass transition and 2) using a detailed deconvolution of the IR absorption bands, to give a qualitative interpretation of this structural evolution, on the base of variation of the position and relative intensities of founded sub-bands, that correspond to the coexistence of populations of different Si-O-Si angles, that determine the structural features of the silica gels.

2. Experimental procedure

The starting solutions were prepared by mixing tetraethyl orthosilicate (TEOS), with distilled water and ethanol. We use a constant molar ratio of ethanol to TEOS of 4:1 and also a constant molar ratio of water to TEOS of 11.66. This last quantity corresponds to a percentage of water of 70 percent. These quantities correspond to the compositions used for coatings [22]. The solution was prepared mixing the TEOS and the ethanol separately, a homogenous solution of all the components was obtained mixing them, together with water, for about 15 minutes using magnetic stirrer. The process of gelation was carried out at room temperature. When the viscosity that accompanies the gelation reached a specific value the solid phase starts to appear (for these preparation conditions this point was reached 72 hours later). Pieces were dried at room conditions to form a powder. Various samples were prepared under the same conditions at different times of gelation. The time in which the samples and IR spectrum were obtained corresponds to the order of days between one to other. The first sample (T_1) was taken 72 hours after the solution was prepared; the second one (T_2) 36 hours later, the third one (T_3) 36 hours after the second one, and so on with the rest of the samples: Two additional samples were taken: one of them (T_L), one month later of the T_5 and the last one (T_T) two months later of T_5; The T_T sample was annealed at 350°C for 30 minutes in order to remove organic residues and liquor of pores.

The infrared (IR) spectra were carried out in a Nicolet IR spectrometer model 205 FT-IR using the KBr pellet technique. We prepared the samples for IR measurements grounding the solid samples and the KBr finely, after that sample and KBr were mixed and grounded as little as possible to achieve good mixing in order to minimize the KBr contribution on the IR spectrum. The sample concentration in the mixture that we used was 0.4%. The disc was prepared under pressure using a hand operated press.

3. Experimental results and discussion

The infrared absorption spectra of gels in the range 400 to 4000 cm^{-1} obtained at different gelation times are presented in Fig. 1. From this figure is possible to observe well defined absorption bands. In these spectra, the band in the range 2500 to 4000 cm^{-1} (indicated by the number 1) corresponds to the

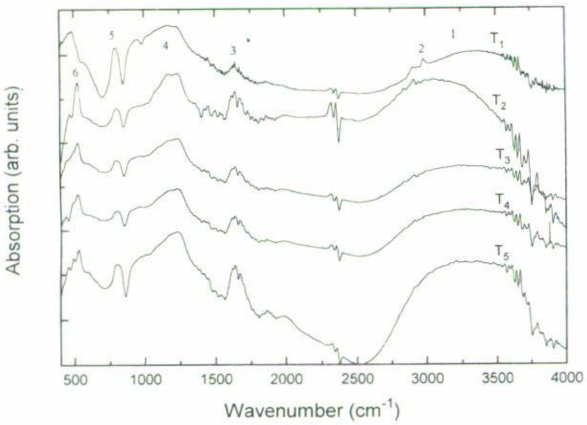

FIGURE 1. IR absorption spectra for samples at gelation times of T_1 to T_5.

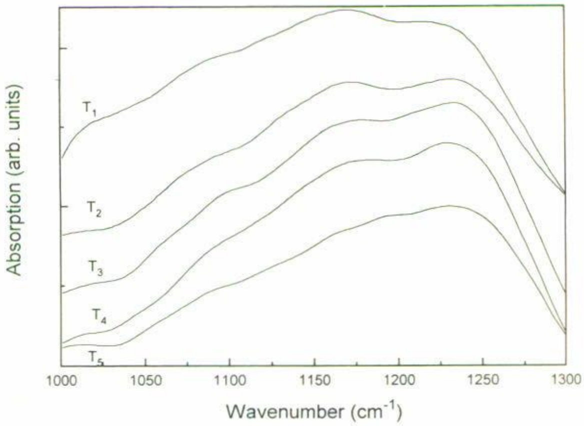

FIGURE 2. IR absorption spectra at 1000–1300 cm^{-1}, for samples at gelation times of T_1 to T_5.

fundamental stretching vibrations of different hydroxyl groups [14]. It is composed of a superposition of SiO-H stretching vibrations and very small contribution from the hydration of the KBr. The weak bands observed at around 3000 cm^{-1} (indicated by the number 2) correspond to C-H stretching vibrations as evident from the TEOS [23]. The relative amplitude of these bands decreases with the increase of the gelation time, indicating the evolution of chemicals reactions. It is possible to observe, from this figure, a small residual features near 2900–3000 cm^{-1} due to organic residues (ethanol or TEOS).

In the interval between 3600 and 4000 cm^{-1} the bands are mainly due to overtones or combinations of vibrations of Si-OH or H_2O. The broad absorption band between 3000 and 3600 cm^{-1} correspond to fundamental stretching vibrations of different hydroxyl groups. It is generally composed of a superposition of the following stretching modes: 3400 to 3500 cm^{-1} correspond to absorbed water; 3540 cm^{-1} correspond to silanol groups linked to molecular water through hydrogen bonds; 3660 cm^{-1} correspond to pair of surface Si and OH mutually linked by a hydrogen bond and internal Si-OH; 3750 cm^{-1} correspond to free Si-OH on the surface of the gel.

The band at 1620–1650 cm^{-1} (indicating by the number 3) is assigned to the deformation of molecular water 1620 cm^{-1} [14], the presence of this band indicates that very little molecular water, if any, remained in the gels at this stage; besides the KBr hydration contributes to this band [24]. An additional and very weak band near 1650 cm^{-1} is observed, which could be due to residual ethanol [14].

In all the IR spectra of the gels studied in this work show two absorption bands at around 450 and 850 cm^{-1} (indicated by number 5 and 6, respectively), which are characteristic of silicon oxides [25]. The lowest frequency vibration at 450 cm^{-1} is a rocking mode in which the oxygen atom motion is out of the plane of the Si-O-Si bond; the band absorption at 800 cm^{-1} is a bending vibration in which the oxygen is in the plane of the Si-O-Si bond and along the direction of the bisector of the Si-O-Si angle [26].

During the formation of a gel from the reaction of tetraethylorthosilicate (TEOS) and H_2O in alcoholic medium, a broad IR band appear from 950 to 1350 cm^{-1} (indicated by the number 4) composed for two shoulders. The left shoulder at 950 cm^{-1} is assigned to the vibration of Si-OH [27] and the right shoulder from 1000 to 1350 cm^{-1} corresponds to asymmetric Si-O-Si stretching motions [26]. The right shoulder or band is more intense and is named the main band. This band indicates the formation of the SiO_2 network, their intensity increase very rapidly according to the increase of connectivity of the SiO_2 network (polymerization) produced by condensation reactions [14]. From the Fig. 1 is not evident to observe that this band could be composed of a combination of various sub-bands with a dominant peak or sub-band at 1070–1080 cm^{-1}; this band is a distinctive of the SiO_2 IR spectra [15].

In Fig. 2 we show the spectra of the main IR band for samples T_1 to T_5. In this figure we can observe that the shape of main IR band is changing according to the evolution of the gelation process, there is noticeable decrement at the left and central part of the band. The behavior of the main band, at 1000 to 1350 cm^{-1}, reflects that at these stages of the gelation process, the chemical reaction is still present and the structural conformation is carrying out derived of the polymerization of monomers; forming and growing of particles; and linking of particles into chains.

In Fig. 3 a deconvolution on the IR spectra was carried out, for samples T_2, T_5 and T_L at the range corresponding to the main band. The spectra were decomposed in five absorption bands, which gave the best fitting to the experimental data. The dashed curves correspond to the measured absorption and the solid ones are the sum of the five absorption bands (doted ones) obtained from the decomposition. As can be seen from these figures, the position of the bands are at about 1010, 1075, 1160, 1200, and 1240 cm^{-1} (indicated by sub-band 1 to 5 respectively); with variation of the order of 25 cm^{-1}. We can observe that the relative amplitude of the bands strongly depends of the gelation time, indicating a structural evolution.

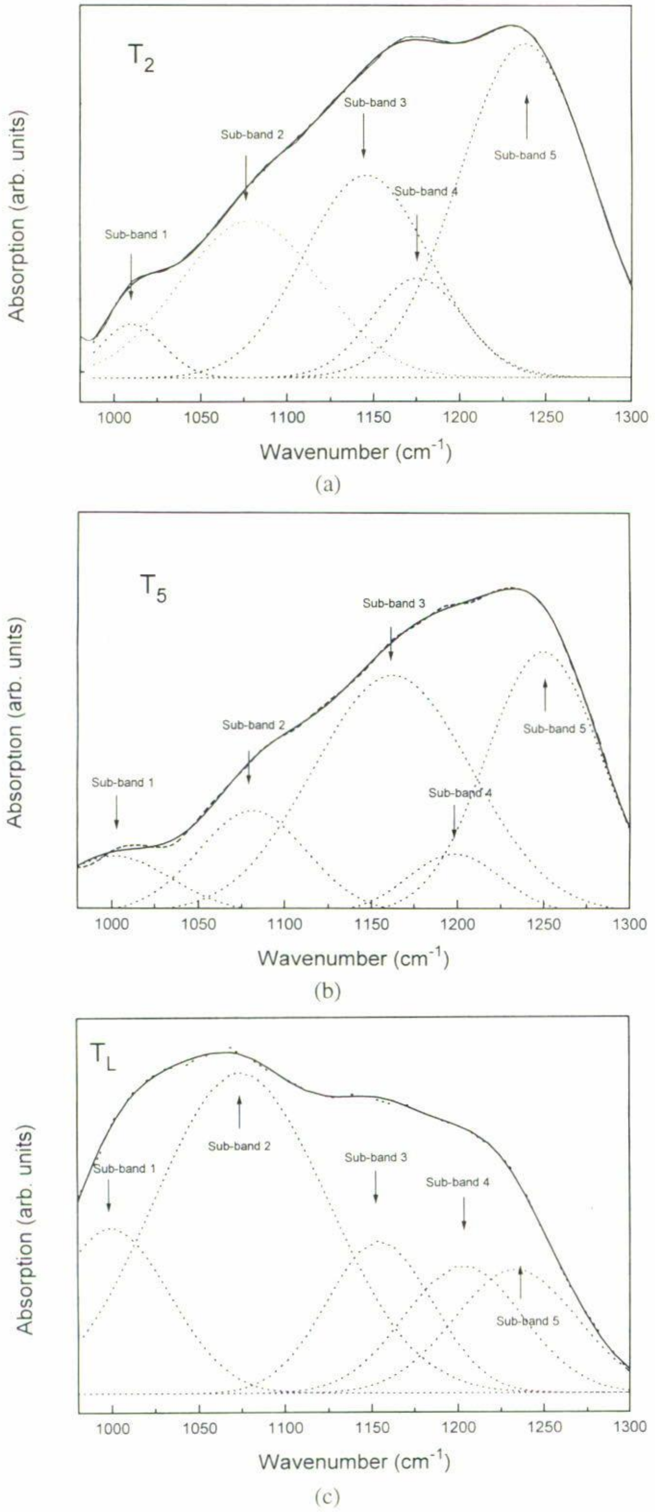

FIGURE 3. Deconvolution of the main IR absortion band at 970-1300 cm^{-1} for: a) samples at gelation time of T$_2$, b) samples at gelation time of T$_5$, and c) sample at gelation time of T$_L$.

The band at about 1075 cm^{-1}, sub-band 2, is the well-known stretching Si-O-Si band assigned to a optically active oxygen asymmetric stretch TO mode (in-phase motion of adjacent oxygen atoms) [19]. The 1010 cm^{-1}, sub-band 1, can be reflecting the existence of SiO$_x$ species [20], the existence of these non-stoichiometric SiO$_2$ species is very probable during the processes of hydrolysis and condensation.

The bands at 1160, 1200, and 1240 cm^{-1}, indicated by sub-band 3 to 5, are very similar to the bands reported previously for thermally prepared SiO$_2$ samples and have been assigned to: 1) disorder-induced modes coupling in amorphous SiO$_2$ [15, 16]; 2) the presence of two or more structure types present in the fully-polymerized glass [17]; and 3) distinct populations of Si-O-Si angles within the tetrahedral network [18].

For the first stages in the gelation process (samples T$_2$ and T$_5$, in Fig. 3) the sub-band at about 1240 cm^{-1} is predominant over the band at about 1070–1080 cm^{-1}, whereas for very much higher times of gelation (sample T$_L$), the situation is inverted and the band at about 1070–1080 cm^{-1} start to be dominant. Assuming that, the relative intensity of sub-band in the our IR spectra is in relationship with the numbers of sites with a particular Si-O-Si bond angle, we associate for the band at 1240 cm^{-1} a near 180° Si-O-Si angle. This assignment is in agreement with Olsen *et al.* for the case of SiO$_2$/Si interface [28] and is also consistent with the simple force constant model [25, 29] that predicts an increase in frequency with increasing bond angle.

The variation in the relative intensities of the band at 1070–1080 cm^{-1} is in relationship with the formation of Si-O-Si angles of about 144° [9] and with existence of a CRN structure. At T$_2$ and T$_5$ the band at 1240 cm^{-1} is large respect to the band at 1070–1080 cm^{-1}, at T$_L$ this fact is inverted and the intensity of the band at 1070–1080 cm^{-1} start to be predominant. It is possible to observe, from the Fig. 3, how the relative intensity of the sub-band at 1160 cm^{-1} (sub-band 3) decrease according to the increasing of the gelation time. This fact can be associated to evolution of the chemical reaction still present at this stages of gelation, also is associated to the increment of sites with Si-O-Si angles near to 180° and O-Si-O bonds angles greater that 110°. On the contrary, the sub-band 4 has an increment of its relative intensity according to the gelation time.

The bands, 1160 and 1240 cm^{-1}, have been associated to the presence of populations of sites with angles of Si-O-Si greater than 144°, and are interpreted as due to the formation of a linear or chain-like structure which is obviously a highly disordered structure. These conditions obviously results in a more open structure [9] very different to the well accepted CRN structure of SiO$_2$ prepared by thermal methods.

Figure 4 shows a deconvolution of the main IR absorption band for the sample T$_T$ (the annealed sample), in this figure it is possible to appreciate the great similarity of this band with the IR reported for silicon oxides prepared by thermal methods [19], for this figure we can observe that the dominant feature of this band is the sub-band at 1070–1080 cm^{-1}, the bands at 1160, 1200, and 1240 cm^{-1} are still present, but their intensities have diminished respect to the intensities that we observed at T$_2$, T$_5$, and T$_L$. This indicates that the final

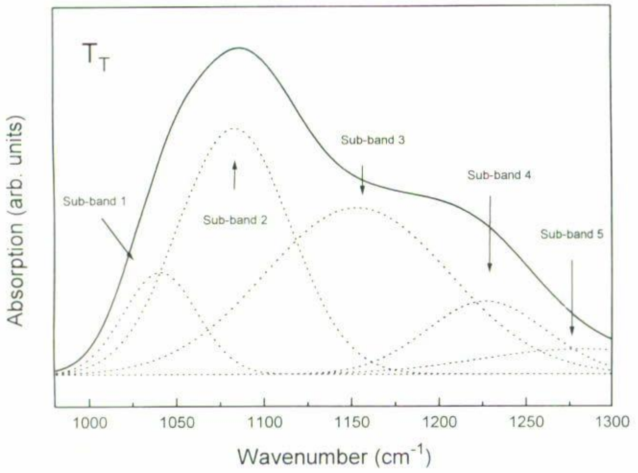

FIGURA 4. Deconvolution of the main IR absorption band at 970–1300 cm^{-1} for the sample at gelation time of T_T and annealed at 350°C for 30 minutes.

structure for this sample is like a CRN structure, and the 144° Si-O-Si bond angle are majority favoring the three-dimensional interconnection of tetrahedral SiO_2 units.

The results, we show, indicate that the material for the stages with times of gelation between T_1 and T_L, it is not fully hydrolyzed, presents a structure deviate from SiO_2 stoichiometry, and the sites with Si-O-Si bond angle greater than 144° are majority. For these sample the spectra reflect the co-existence of different structures and presence of out of stoichiometry SiO_X species. For samples with a large time of gelation and annealed, the dominant structure is the CRN structure and the dominant specie is the SiO_2.

4. Conclusion

The IR spectra can be a useful tool to follow the structural changes which occur when the gelation is in course. The results presented in this work indicate that when the gelation process occurs an evolution in the structure takes place, in which the number of sites with Si-O-Si bonds angles greater than 144° and O-Si-O bond angles greater that 110° are increased with the gelation time, becoming to a linear chain structure in the late stage of gelation.

The results indicate us that the presence of the bands at 1160, 1200, and 1240 cm^{-1} are very similar to the bands due to a disorder-induced mode coupling in amorphous SiO_2 and to the presence of two or more structure types consequence of distinct populations of Si-O-Si angles within the tetrahedral network.

We conclude that, during the gelation process: the structure presents a polymeric character and a predominant linear chain structure.

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