

## Research Letter

# Structural Effects of Heat-Treated Silica Xerogel Induced by Incorporation of Chlorophyll Species

J. R. Martínez,<sup>1,2</sup> G. Martínez-Castañón,<sup>1</sup> G. Ortega-Zarzosa,<sup>1</sup> J. A. de la Cruz-Mendoza,<sup>1</sup>  
S. A. Palomares-Sánchez,<sup>1</sup> and Facundo Ruiz<sup>1</sup>

<sup>1</sup>Facultad de Ciencias, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, Mexico

<sup>2</sup>Departamento de Físico-Matemáticas, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, Mexico

Correspondence should be addressed to J. R. Martínez, flash@fciencias.uaslp.mx

Received 29 August 2007; Accepted 5 October 2007

Recommended by G. Q. Lu

Composites containing chlorophyll aggregates dispersed in amorphous silica are of interest because of their optical attractive properties. The silica powders added with chlorophyll species, prepared by the sol-gel method, were studied using X-ray diffraction, IR spectroscopy and differential temperature analysis. Silica xerogel samples were prepared using an ethanol/H<sub>2</sub>O/TEOS molar ratio of 4:11.6:1 and loaded with extracts from frozen spinach leaves. The silica xerogel microstructure of the powders was studied as a function of the annealing temperature. We found in our samples partial crystallization of the glass matrix in form of tridymite and cristobalite phases and quenching centers or nonfluorescing aggregates due to denaturation of photosystem promoted by chlorophyll decomposition after 400°C.

Copyright © 2007 J. R. Martínez et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## 1. INTRODUCTION

Sol-gel chemistry and further processing to xerogels or aerogels allow flexibility in obtaining a great variety of materials based on incorporation of particles embedded in inert matrices such as SiO<sub>2</sub> with specific properties, which are related to the structure of the forming composite materials. These matrices have been also used experimentally as supporting substrates for molecular chemical systems [1] and for artificial photosynthesis [2, 3]; including organic photoactive or electroactive molecules has opened new opportunities for optical and electrooptical applications [4–7].

We have reported that the incorporation of metallic species in the xerogel matrix promotes the devitrification process at relatively low temperatures with the presence of partial crystallization in form of quartz, cristobalite, or quartz and cristobalite [8–13]. The structural changes in the xerogel matrix are induced by the incorporation of particles and by thermal treatment; the phase obtained is related to the structure corresponding to the pure matrix that we produced by controlling the parameters in the preparation process; however, the appearance of specific crystalline form of SiO<sub>2</sub> is not clear. There are not reports about the forma-

tion of tridymite in silica xerogel when inorganic or organic species are embedded into it.

The higher plants are an efficient system to absorb and transfer the energy through photosynthetic apparatus. This situation can be used to take advantage to prepare materials based in extract of plants for eventually design efficient optical- and electrooptical-based sol-gel encapsulated biomolecules [14]. Thus, it is necessary to understand the structural evolution of extracted components of leaves embedded in silica xerogel matrix, as well as the interaction between the pigments embedded into the inorganic matrix under heat treatment in which the matrix undergoes a gel to glass transition, and then correlate all these changes with the optical properties. Chlorophyll is a pigment that has been chemically altered to provide alkoxysilane functionality. This allows the chlorophyll molecule itself to participate in the hydrolysis and condensation reactions along with the other alkoxide precursor. The result is a covalently bonded active molecule within the xerogel structure [14]. In previous work, we compared the spectral characterization of chlorophyll fluorescence of the doped glass and the structural evolution promoted by heat treatment with the spectral characterization of chlorophyll fluorescence of pure barley

leaves. We obtained a higher thermostability for leaves embedded in xerogel matrix than in green leaves, and we observed that at higher temperatures fluorescing aggregates are formed, whereas in the pure leaves those components disappear above nonphysiological temperatures (higher than 100°C) [14]. Thus, the chlorophyll components interact with the SiO<sub>2</sub> matrix while it is formed, promoting the formation of composites and the devitrification process for the matrix.

In this work, we report that the sol-gel amorphous SiO<sub>2</sub> bulk samples containing extract of spinach are partially crystallized into the tridymite and cristobalite phases at temperatures much lower than those specified by the phase diagram. For that, chlorophyll aggregates need to be added to the starting solutions, which upon thermal treatments form small colloidal particles in the glass matrix.

## 2. EXPERIMENTAL METHOD

In order to obtain the organic composites consisting of extract of spinach leaves embedded in xerogel matrix, a precursor material composed of TEOS, water, ethanol, and pigments extract of spinach leaves was prepared. The ethanol to TEOS and water to TEOS molar ratios were 4:1 and 11:1, respectively. This composition has proven to give good quality SiO<sub>2</sub> coating. These quantities correspond to a high water/TEOS ratio, needed to enhance the hydrolysis [16] to assure a close amorphous structure for the as-prepared SiO<sub>2</sub> powder, and to allow us to compare the results with some previous work [8, 10, 12, 15]. The TEOS was dissolved in the ethanol using magnetic stirring for 15 minutes. The suspension of pigments in water was added to the ethanol-TEOS solution to form the starting material.

The X-ray diffraction (XRD) patterns were obtained using a GBC-Difftch MMA diffractometer. The nickel filtered Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation was used. The infrared (IR) spectra were recorded in an FT-IR spectrometer Nicolet system model Avatar 360 using the diffuse reflectance (DR) mode, for which 0.05 g of powder sample was mixed with 0.3 g of KBr. DTA measurements were carried out in a TA instruments system, model Q600, at constant rate of 10°C/min inside DTA analyzer in nitrogen atmosphere up to 1100°C.

X-ray data refinement was made using the program Maud in order to calculate the amorphous/crystalline fraction of the composites [16]. The analysis was started assuming the structure of cubic SiO<sub>2</sub> (cubic, spacegroup P2<sub>1</sub>3) for the amorphous phase. For the crystalline phase of silica, the structures of tridymite (hexagonal, spacegroup P6<sub>3</sub>/mmc) and low cristobalite (trigonal, spacegroup P4<sub>1</sub>2<sub>1</sub>2) were assumed.

## 3. RESULTS AND DISCUSSION

In order to investigate the structural evolution of the compound, the as-prepared powder was heated at constant rate 10°C/min inside a DTA analyzer in nitrogen atmosphere up to 1100°C. As shown in Figure 1, the analyzed sample gives endothermic peaks at 99°C, 222°C, 303°C, 508°C, 549°C, and 848°C, and exothermic peaks at 367°C, 407°C, 631°C, 721°C, and 962°C. After 400°C, a very broad endothermic

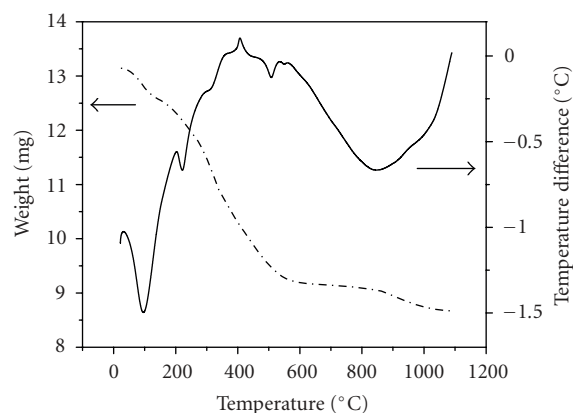


FIGURE 1: DTA and weight-loss curves of chlorophyll species embedded in a silica matrix heat treated in nitrogen.

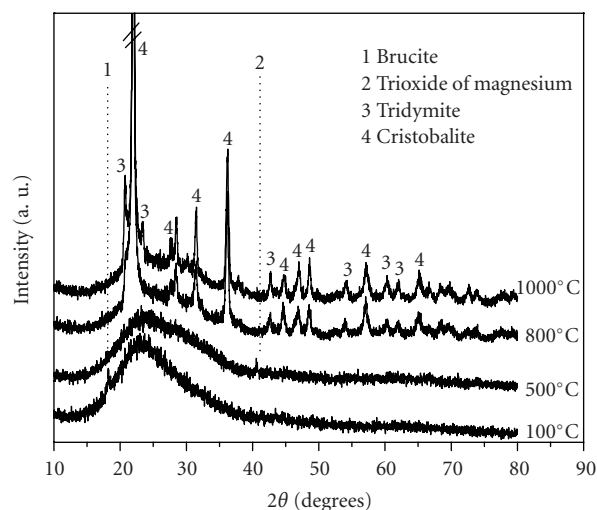


FIGURE 2: X-ray diffractograms of the chlorophyll-containing silica xerogel samples heat treated at the indicated temperatures.

process occurs due to decomposition of chlorophyll species, whereas the formation of phases of oxide and hydroxide magnesium species is initiated, the transformation of gel to glass, and the formation of crystalline phases of SiO<sub>2</sub>, as cristobalite and tridymite.

Figure 2 shows the X-ray diffractograms for the prepared samples. Embedded in amorphous silica xerogel the chlorophyll species decomposed and interacted with the silica matrix promoting the formation of hydroxide magnesium species, quenching centers or nonfluorescing aggregates due to denaturation of photosystem promoted by chlorophyll decomposition, and partial crystallization of the matrix, as it is discussed below.

Using both results, DTA and X-ray diffraction, we can see that at temperatures lower than 800°C the composite powders are in amorphous form; the DTA peak at 99°C corresponds to partial water elimination, whereas water is partially eliminated, brucite layer phase is formed as we can observe the appearance of the peak at 18.2 2-theta degrees.

The exothermic peak at 367°C can be related to the gel to glass transition according to previous work [12]. The chlorophyll species begin decomposing at temperatures around 222°C, in accordance with the endothermic peak in Figure 1. Its decomposition conduces to the formation of magnesium oxide species, organic compound that produce quenching centers, and crystallization of SiO<sub>2</sub> as cristobalite and trydimite; the diffractogram clearly shows the presence of these phases at 18.2 2-theta degrees. The exothermic peak at about 400°C indicates the formation of trioxide of magnesium phase that we can observe with the appearance of a very incipient peak located at 40.5 2-theta degrees in the diffractogram for the sample heat treated at 500°C. For the samples heat treated below 500°C, only the broadband corresponding to the SiO<sub>2</sub> gel is present, which is extended to higher degrees due to the presence of chlorophyll species.

In the 800°C heat-treated sample, we observe peaks corresponding to the cristobalite and trydimite phases. The peaks corresponding to cristobalite phase are more pronounced; the presence of cristobalite phase can be associated to the exothermic peak located at 633°C, Figure 1. The diffractogram for the sample heat treated at 700°C, not shown, shows the incipient peak corresponding to cristobalite phase. It appeared after the water loss and chlorophyll decomposition, and it agrees with the presence of the endothermic peak at 848°C and evidenced by the loss of percent weight in the same figure. Finally, in the 1000°C heat-treated sample, both the cristobalite and trydimite peaks are very well defined and an incipient broadband ascribed to amorphous phase is also observed.

The infrared absorption spectra in the range of 400 to 4000 cm<sup>-1</sup> are shown in Figure 3. The bands at 457 cm<sup>-1</sup>, 800 cm<sup>-1</sup>, and 1078 cm<sup>-1</sup> are associated to absorption bands related to particular vibrational modes of the oxygen (O) atom with respect to the silicon (Si) atoms, which they bridge [17, 18]. The principal band, located at about 1078 cm<sup>-1</sup>, has a strong absorption shoulder at its high-energy side that is more pronounced when the temperature is increased.

Several reports have been published concerning the high-energy shoulder of the stretching band, in the frequency range from 1150 to 1300 cm<sup>-1</sup>. For instance, in a previous work, IR spectra have been reported in which these subbands can have amplitude comparable or larger than the main stretching band at 1078 cm<sup>-1</sup> [15, 19]. The enhanced intensity of these subbands has been interpreted as due to the formation of a chain- or ring-like structure. This band suffers significant modification with the increase in the annealing temperature. An explanation of this will be proposed in next parts of this section.

A band centered at 950 cm<sup>-1</sup> assigned to silanols (Si-OH) is present at the range of temperature from room temperature to 200°C; for temperatures above 400°C the band is incorporate to the main stretching band when the temperature is increased. We can also observe a band at 1600–1690 cm<sup>-1</sup>, assigned to the deformation of molecular water and to alkenyl C=C stretch. This band is found in the spectra of the as-prepared and heat-treated samples at 200°C, upon this temperature the band at 800°C and at 1000°C, the water is eliminated and only the alkenyl and C=C–C stretching

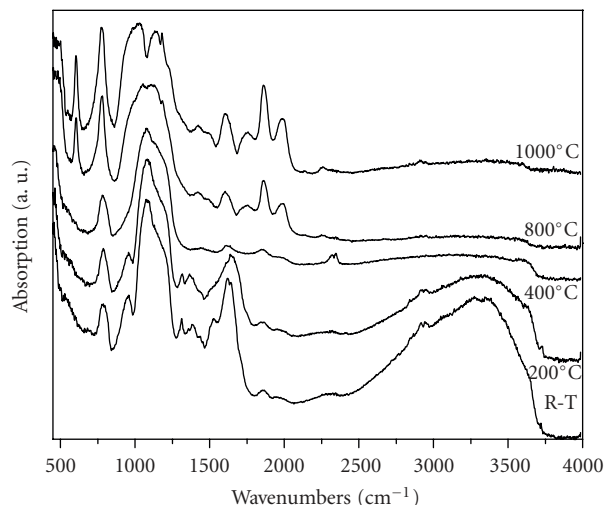


FIGURE 3: Infrared absorption spectra of the chlorophyll-containing silica xerogel samples heat treated at the indicated temperatures.

and bending vibrations are present. It indicates that organic species, typical of green leaves, still exists in the structural conformation.

For samples heat treated below to 200°C IR spectrum, it can be seen a strong absorption band at the range 1270–1560 cm<sup>-1</sup>. This band is associated with a combination of vibrations of the nitrate and CH species. The principal contributions are due to the CH group; from the figure we can observe that according to the temperature increases the band undergoes noticeable changes, indicating the evolution of chemical species. It is possible to see that for the heat-treated samples at 800°C, the band is partially incorporated to the main stretching band. In these temperatures, the composite shows important phases transformation. Their presence at high temperature indicated, among the presence of organic compound in the composite, a preference linear structure for the matrix [20].

The band in the range of 2250 to 3000 cm<sup>-1</sup> corresponds to the fundamental stretching vibrations of different hydroxyl groups [21]. The band is composed of a superposition of Si–O–H stretching vibrations. The weakband observed at around 2800 cm<sup>-1</sup> corresponds to C–H stretching vibrations. This band is related to the band at the 1250 to 1550 cm<sup>-1</sup>. It is noticeable, according to the previous discussion, that for temperatures higher than 1000°C, these contributions are present.

The presence of these IR bands suggests that the structure includes polymerized species predominantly with oligomers. The formation of this kind of polysiloxanes is related to the presence of the IR bands at the range of 1250 to 1550 cm<sup>-1</sup> and 2800 to 3000 cm<sup>-1</sup>; these bands tend to diminish by heat treatments at temperatures higher than 200°C indicating the evolution of the OR groups due to the chlorophyll decomposition. At the same time, the Si–O–Si chains in formation are terminated by OH species, as indicated by the presence of the free surface silanols band (3724 cm<sup>-1</sup>) Si–OH, as an evidence of the linear character. The permanence of these

TABLE 1: Computed fraction of amorphous/crystalline phases, grain size crystallites, and cell parameters.

Phase	800°C	1000°C
<i>Tridymite</i>		
$a(\text{Å})$	4.9187	4.9600
$b(\text{Å})$	8.4165	8.3142
wt%	3.33	7.328
Grain size (Å)	2389.0	2198.8
<i><math>\alpha</math>-cristobalite</i>		
$a(\text{Å})$	4.9818	4.9817
$b(\text{Å})$	6.9775	6.9676
wt%	29.72	32.51
Grain size (Å)	321.3	454.32
<i>Amorphous silica</i>		
$a(\text{Å})$	6.0166	5.9983
wt%	66.89	60.06
Grain size (Å)	302.25	299.8

groups at elevated temperatures promotes the partial devitrification with formation of tridymite phases, no reported previously in xerogels matrix. Only the appearance of cristobalite and quartz has been reported in this kind of matrices, as in the case of incorporation of metal species in xerogel matrix.

The principal band of the IR absorption spectra of the samples heat-treated at 800°C and at higher temperatures, presents well-defined peaks typical of crystalline allotropic varieties of SiO<sub>2</sub>, that in this case corresponds to tridymite phase.

In this characterization, we did not perform full calcinations of the spinach extract pigment as a blank sample study, but as mentioned before, in the pure leaves those components disappear above nonphysiological temperatures. The products due to the calcinations of the extract are involucre in the formation of the composite glass at temperatures above 300°C, for which the extract components, nonembedded in the matrix, almost disappears. Thus the tridymite and cristobalite phases arise from devitrification of the silica matrix.

The presence of the three phases at temperatures above 800°C is corroborated by the Rietveld refinement for amorphous SiO<sub>2</sub> [16]. From a fit of measured X-ray diffraction data by theoretical intensities, the crystal structure can be refined on the basis of an initial assumption for the structure.

Using the above Rietveld process, the Bragg pattern and the peak positions of the diffractogram corresponding to the phases identified according to the spatial group P2<sub>1</sub>3 for the amorphous phase structure of cubic SiO<sub>2</sub>, P63/mmc for the tridymite and P4<sub>1</sub>2<sub>1</sub>2 for the low-cristobalite have a good coincidence. The computed fraction of amorphous/crystalline phases, the grain size crystallites, and the cell parameters are listed in Table 1.

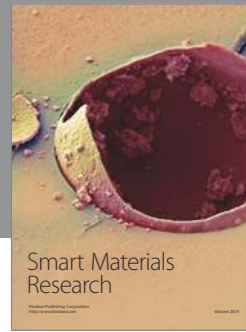
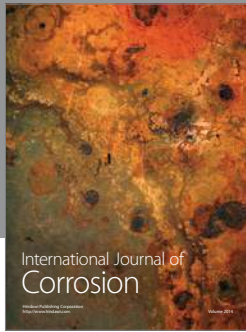
#### 4. CONCLUSIONS

In summary, this work shows that sol-gel-made amorphous SiO<sub>2</sub> bulk samples can be crystallize *simultaneously* into the tridymite, and cristobalite phases at temperatures much lower than those specified by the phase diagram. The tridymite phase has not been reported in this kind of xerogel matrix. For that, chlorophyll aggregates need to be added to the starting solutions. Embedded in amorphous silica xerogel, the chlorophyll species decomposed and interacted with the silica matrix promoting the formation of oxide magnesium species, quenching centers or nonfluorescing aggregates due to denaturation of photosystem promoted by chlorophyll decomposition, and partial crystallization of the matrix.

#### REFERENCES

- [1] L. Persaud, A. J. Bard, A. Campion, et al., "Photochemical hydrogen evolution via singlet-state electron-transfer quenching of zinc tetra(N-methyl-4-pyridyl)porphyrin cations in a zeolite L based system," *Journal of the American Chemical Society*, vol. 109, no. 24, pp. 7309–7314, 1987.
- [2] J. S. Krueger, J. E. Mayer, and T. E. Mallouk, "Long-lived light-induced charge separation in a zeolite L-based molecular triad," *Journal of the American Chemical Society*, vol. 110, no. 24, pp. 8232–8234, 1988.
- [3] M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, and M. Honda, "Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on titanium oxides anchored within micropores of zeolites: effects of the structure of the active sites and the addition of Pt," *Journal of Physical Chemistry B*, vol. 101, no. 14, pp. 2632–2636, 1997.
- [4] D. Levy and L. Esquivias, "Sol-gel processing of optical and electrooptical materials," *Advanced Materials*, vol. 7, no. 2, pp. 120–129, 1995.
- [5] I. Gill and A. Ballesteros, "Bioencapsulation within synthetic polymers (part 1): sol-gel encapsulated biologicals," *Trends in Biotechnology*, vol. 18, no. 7, pp. 282–296, 2000.
- [6] J. Livage, T. Coradin, and C. Roux, "Encapsulation of biomolecules in silica gels," *Journal of Physics Condensed Matter*, vol. 13, no. 33, pp. R673–R691, 2001.
- [7] G. Qian and M. Wang, "Study on the microstructural evolution of silica gel during sol-gel-gel-glass conversions using the fluorescence polarization of rhodamine B," *Journal of Physics D: Applied Physics*, vol. 32, no. 18, pp. 2462–2466, 1999.
- [8] J. R. Martínez, G. Ortega-Zarzosa, O. Domínguez-Espinós, and F. Ruiz, "Low temperature devitrification of Ag/SiO<sub>2</sub> and Ag(CuO)/SiO<sub>2</sub> composites," *Journal of Non-Crystalline Solids*, vol. 282, no. 2-3, pp. 317–320, 2001.
- [9] M. G. Garnica-Romo, J. González-Hernández, M. A. Hernández-Landaverde, Y. V. Vorobiev, F. Ruiz, and J. R. Martínez, "Structure of heat-treated sol-gel SiO<sub>2</sub> glasses containing silver," *Journal of Materials Research*, vol. 16, no. 7, pp. 2007–2012, 2001.
- [10] S. Ponce-Castañeda, J. R. Martínez, S. A. Palomares-Sánchez, F. Ruiz, and J. A. Matutes-Aquino, "Formation of nickel-zinc ferrite embedded in a silica xerogel matrix," *Journal of Sol-Gel Science and Technology*, vol. 25, no. 1, pp. 37–41, 2002.
- [11] G. Ortega-Zarzosa, J. R. Martínez, A. Robledo-Cabrera, G. A. Martínez-Castañón, M. G. Sánchez-Loredo, and F. Ruiz, "Annealing behavior of silica gel powders modified with silver crystalline aggregates," *Journal of Sol-Gel Science and Technology*, vol. 27, no. 3, pp. 255–262, 2003.

- [12] S. A. Palomares-Sánchez, S. Ponce-Castañeda, J. R. Martínez, F. Ruiz, Y. Chumakov, and O. Domínguez, "Quantitative analysis of iron oxide particles embedded in an amorphous xerogel matrix," *Journal of Non-Crystalline Solids*, vol. 325, no. 1–3, pp. 251–257, 2003.
- [13] G. Ortega-Zarzosa, S. A. Palomares-Sánchez, J. R. Martínez, F. Ruiz, and M. G. Sánchez-Loredo, "Structural study of silica xerogel composites containing Pd aggregates," *Journal of Sol-Gel Science and Technology*, vol. 35, no. 1, pp. 5–11, 2005.
- [14] A. Vázquez-Durán, C. Araujo-Andrade, G. Martínez-Castañón, G. Ortega-Zarzosa, F. Ruiz, and J. R. Martínez, "Spectral characterization of chlorophyll fluorescence in extract of barley leaves embedded in silica xerogel matrix," *Journal of Sol-Gel Science and Technology*, vol. 39, no. 3, pp. 223–227, 2006.
- [15] J. R. Martínez, F. Ruiz, Y. V. Vorobiev, F. Pérez-Robles, and J. González-Hernández, "Infrared spectroscopy analysis of the local atomic structure in silica prepared by sol-gel," *Journal of Chemical Physics*, vol. 109, no. 17, pp. 7511–7514, 1998.
- [16] A. Le Bail, "Modelling the silica glass structure by the Rietveld method," *Journal of Non-Crystalline Solids*, vol. 183, no. 1-2, pp. 39–42, 1995.
- [17] P. Sen and M. F. Thorpe, "Phonons in  $AX_2$  glasses: from molecular to band-like modes," *Physical Review B*, vol. 15, no. 8, pp. 4030–4038, 1979.
- [18] F. L. Galeener, "Band limits and the vibrational spectra of tetrahedral glasses," *Physical Review B*, vol. 19, no. 8, pp. 4292–4297, 1979.
- [19] J. R. Martínez, F. Ruiz, J. A. de la Cruz-Mendoza, et al., "Structural evolution of silica-gel in the late stages of the gelation process," *Revista Mexicana de Física*, vol. 44, no. 6, pp. 575–579, 1998.
- [20] G. Ortega-Zarzosa, C. Araujo-Andrade, M. E. Compeán-Jasso, J. R. Martínez, and F. Ruiz, "Cobalt oxide/silica xerogels powders: X-ray diffraction, infrared and visible absorption studies," *Journal of Sol-Gel Science and Technology*, vol. 24, no. 1, pp. 23–29, 2002.
- [21] G. Orcel, J. Phalippou, and L. L. Hench, "Structural changes of silica xerogels during low temperature dehydration," *Journal of Non-Crystalline Solids*, vol. 88, no. 1, pp. 114–130, 1986.



**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

