Formation of silicate structures in Cu-containing silica xerogels

F. Ruiz

Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, S.L.P., Mexico

J.R. Martínez

Facultad de Ciencias, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, S.L.P., Mexico

J. González-Hernández

Centro de Investigación y de Estudios Avanzados del IPN, Unidad Querétaro, Apdo. Postal 1-1010, C.P. 76010, Querétaro, Qro., Mexico

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Using infrared absorption and Raman spectroscopy, the structure of SiO₂ sol-gel samples containing copper were analyzed as a function of air heat treatments. The weight composition of the samples was 70(SiO₂)–30(CuO) and the thermal treatments were carried out in air at various temperatures in the range of 100–600 °C. It was found that the Cu might be incorporated into the SiO₂ matrix at least in two ways: forming oxide particles and forming metasilicatelike structures. The copper metasilicate found had the chemical formula, Cu₆[Si₆O₁₈] · 6H₂O, which is known as dioptase with a thermal stability at temperatures up to 600 °C.

I. INTRODUCTION

The sol-gel method is a versatile technique for the preparation of glass coatings and powdered samples that allows the incorporation of metals and other materials in their matrixes. The modifications to the glass structure that results from the incorporations of different elements depend on the type of the incorporated elements, post-deposition treatments, and the interactions of the elements with the host matrix.¹ The introduction of transition metals in a SiO₂ glass matrix has a strong influence on the optical visible absorption spectrum.² Nano- and microsized particles of various materials embedded in the glass matrix produce quantum and non-linear optical effects when the particles have some critical size.³

Several authors have reported studies of sol-gel prepared SiO_2 samples containing copper.^{4–8} To our knowledge none of the previous studies observed the formation of metastable copper silicates; instead, they report the formation of oxides or metallic particles, depending on whether the samples are subjected to heat treatments in oxidizing or reducing atmospheres, respectively.^{9–11}

In the present work, we prepared sol-gel SiO_2 glasses containing copper, and the structural evolutions, due to heat treatments in air, have been analyzed using Raman spectroscopy, infrared (IR) absorption, and x-ray diffraction. From these measurements we can conclude that most of the copper precipitates into oxide particles smaller than 50 nm, and that a small amount of the copper atoms form copper silicate structures. According to our results, the copper silicate formed is probably the dioptase, which is a metasilicate with the chemical formula $Cu_6[Si_6O_{18}] \cdot 6H_2O^{12}$ Its chemical structure is formed with sixfold beryl-like rings of the form $[Si_6O_{18}]^{-12}$. According to Belov *et al.*,¹³ the Cu cations with the O atoms and the OH groups form octahedral columns oriented along a threefold screw axis with sixfold silicon-oxygen rings at three levels, while sixfold rings consisting of H₂O molecules are distributed between the columns. The Cu atoms, in dioptase, have (4 + 2)-fold coordination; their four nearest atoms are 4 oxygen of three different Si₆O₁₈ ring surrounding the copper atom in an almost perfect square. The coordination of the Cu atom is raised to 6 by the two O atoms from the water molecules. Our results indicate that, among the two known stable copper silicates, the heat treatments promote the formation of small dioptase structural units, because one of the distinct features of the silica xerogel structures is the presence of the sixfold rings (six oxygen and six silicon atoms).¹⁴

II. EXPERIMENTAL METHODS

The starting solutions were prepared by mixing tetraethyl orthosilicate (TEOS), water, ethanol, and copper nitrate. The molar ratios of ethanol to TEOS and water to TEOS were 4:1 and 11.67:1, respectively. The concentration of Cu nitrates were calculated to obtain 30 wt% of

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cupric oxide. The nitrate used for the incorporation of copper was the $Cu(NO_3)_2 \cdot 2.5H_2O$ and the amount added was such that the sample weight composition was $70(SiO_2)-30(CuO)$, assuming that all the copper forms the cupric oxide. To catalyze the hydrolysis/condensation reactions small amounts of nitric acid were added. The metal nitrate was dissolved in the water, and the TEOS and the ethanol were also separately mixed. A homogenous solution of all components was obtained mixing them for about 15 min using a magnetic stirrer to form the starting solution. This solution was placed in a constant bath temperature of 35 °C. Soft pieces of the glass were obtained after about 48 h. Previously, the bath temperature was fixed at 50 °C during 2 h. For subsequent annealing the samples were introduced in the oven at the desired temperature for 15 min at atmospheric air conditions. Those pieces were ground to form a fine powder.

The Raman spectra were obtained at room temperature using a Labram-Dilor micro-Raman system in which the sample was excited with a He–Ne laser and the signal analyzed with a low-noise charge-coupled device detector. To check for possible changes in the sample induced by laser heating, the laser spot diameter was varied in the $1-10 \mu m$ range and the power density changed using neutral density filters.

The IR spectra were measured in a Fourier Transform infrared spectrometer Perkin Elmer System Model 2000 using the diffuse reflectance mode: For that, 0.05 g of powder sample was mixed with 0.3 g of KBr.

III. RESULTS

Figure 1 shows the IR absorption spectra in the range of 400 and 2200 cm^{-1} for a sample with copper after heat treatments in air at the indicated temperatures. The strong absorption band, at about 1400 cm⁻¹ in the sample heat treated at 100 °C, is associated with vibrations of the nitrate radical NO₃⁻. This band has less intensity in the sample treated at 200 °C and it does not appear in samples treated at 400 and 600 °C. The latter is because the copper nitrate thermally decomposes, and the nitrogen evolves to the atmosphere in the form of nitrogen oxides.¹⁵ The three features identified with the letters R, B, and S are absorption bands related with particular vibrational modes of the oxygen (O) atom with respect to the silicon (Si) atom that they bridge. The rocking (R) of the O atom along an axis through the two Si atoms is associated with the lowest-frequency band centered at about 457 cm^{-1} . The bending (B) of the O atom along a line bisecting the axis formed by the two Si atoms corresponds to the band centered at about 800 cm^{-1} . The band at about 1078 cm⁻¹ is associated with the asymmetrical stretch (S) motion, in which the O atom moves back and forth along a line parallel to the axis along the two Si atoms.^{16,17} This mode has a strong absorption



Fig. 1. IR absorption spectra in the range of 400 to 2200 cm⁻¹ for the 70(SiO₂)–30(CuO) powered samples.

shoulder at its high-energy side. The absorption band at about 950 cm⁻¹, which intensity increases with the annealing temperature, is due to vibrations of the silanol (Si–OH) groups.¹⁸ The absorption band at about 1650 cm⁻¹ has been previously assigned to vibrations of free molecular water.¹⁹

Several reports have been published concerning the high-energy shoulder of the stretching band, in the frequency range of $1150-1300 \text{ cm}^{-1}$; however, its origin is not yet clear. For instance, in previous work IR spectra have been reported in which these subbands can have an amplitude comparable or larger than the main stretching band at 1078 cm⁻¹.^{20,21} This has been achieved in vitreous SiO₂ samples prepared by the sol-gel method from solutions with a large water/TEOS ratio. The enhanced intensity of these subbands has been interpreted as due to the formation of a chain- or ringlike structure. Lange²² has also observed that the intensity of these subbands increases when vitreous SiO₂ thin films are subjected to ion bombardment. He has proposed that the relative increase in the intensity of the subband is due to an increase in the structural disorder.

From Fig. 1 it can be seen that the relative intensity of the bending (B) and rocking (R) bands basically does not change for the former and increases for the latter with the increase in the annealing temperature. This could be due to some absorption from cupric oxide, whose vibrational modes has been reported at 420, 425, and 528 cm⁻¹.²³ The Si–O stretching (S) band at approximately 1078 cm⁻¹ suffers significant modification with the increase in the annealing temperature. An explanation of this will be proposed in next parts of this section.

Several authors have deconvoluted the high-energy shoulder of the stretching band into several bands, which according to them are associated with specific vibrations related to some detail in the SiO_2 structure. Lange and

Kirk,^{22,24} for example, have reported vibrational modes at 1254, 1170, and 1200 cm⁻¹, and related them with disorder-induced modes in amorphous SiO₂ films. Seifert *et al.*²⁵ suggested that the presence of these subbands could be related to two or more structure types present in the fully polymerized glass. Vuckcetich has proposed a two-state model²⁶ for the SiO₂ glass structure, in which there are at least two distinct populations of Si–O–Si angles within the tetrahedral network with value near 138° and 145°. We have assigned these bands to the presence of ringlike structures.^{20,21}

Figure 2 shows the deconvoluted IR spectra in the range of 700–1300 cm^{-1} for the SiO₂ with copper. The spectra were decomposed in six absorption bands, which gave the best fitting to the experimental data. The dotted curve denotes the measured spectra and the solid curve, traced along the data points, is the sum of the six bands (thin lines) obtained from the decomposition. As can be seen from these figures, the positions of the subbands are about 800, 930, 964, 1078, 1168, and 1220 cm⁻¹, labeled with B, 1, 2, 3, 4, and 5, respectively. It is observed that the band assigned to the Si-OH vibration is composed of two bands. This has been explained as due to the existence of at least two different configurations for the Si-OH groups.¹⁸ For annealing temperatures above 200 °C the relative intensity and width of these last two bands increase. This result differs from the observations in other SiO₂ sol-gel samples, including those without copper, in which the relative intensity of these bands clearly decreases with the annealing temperature, as a consequence of the glass densification. 1,15,20,27

From the results in Fig. 2, one can see that the relative intensity and broadness of subbands 3, 4, and 5 change with the annealing temperature. For instance, subband 3 becomes broader and its relative intensity, with respect to the higher energy bands, increases with the increase in the annealing temperature. The linewidth of this band has been directly related with the Si-O-Si bond angle distribution, indicating the degree of structural relaxation of the SiO₂ network.²⁸ The relative intensity and linewidth of subbands 4 and 5 also change; however, to our knowledge, the reason for these changes has not yet been fully understood. In previous publications we proposed that these subbands can be associated with vibrations of rings with a different number of members (Si-O-Si). Thus, the change in the intensity of any of these subbands reflects the change in the statistical population of the particular ring involved.²⁰ According to our observations²⁰ and other investigations,^{14,29–32} the structure of samples annealed at low temperatures are basically formed by four-, five-, and mainly sixfold rings. For higher annealing temperatures the amount of larger rings is decreased and so are the intensities of the corresponding subbands.

Figure 3 shows the IR spectra for a SiO_2 film grown on a silicon wafer by thermal oxidation³³ and for a silica xerogel sample with Cu and annealed at 600 °C for



Fig. 2. Deconvoluted IR spectra of $70(SiO_2)-30(CuO)$ in the $700-1300 \text{ cm}^{-1}$ range. The spectra were decomposed in six absorption bands at: approximately 800 cm⁻¹ (B), approximately 930 cm⁻¹ (1), approximately 964 cm⁻¹ (2), approximately 1078 cm⁻¹ (3), approximately 1068 cm⁻¹ (4), and approximately 1220 cm⁻¹ (5).

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15 min. There are several differences between the two spectra: the relative intensity of the stretching band, in the region of $1100-1250 \text{ cm}^{-1}$, as well as that of the Si-OH vibration band is more pronounced in the xerogel sample, and the rocking mode appears broader, which, at least, in part is due to the absorption of the copper oxides, in the region of $500-650 \text{ cm}^{-1}$. Obviously, the two preparation processes are different. In the sol-gel process, a wet process, the presence of water at high concentrations promotes a high degree of hydrolization, which in turn produces samples with longer Si-O-Si chains or rings with a larger number of members.^{1,18,20} It is known that thermally grown SiO₂ on silicon wafers has a dense structure, formed by a statistical distribution of *n*-fold rings predicted by previous theoretical calculations.14,29-32

Figure 4 shows the Raman spectra in the range of 200 to 1100 cm^{-1} for the same set of samples shown in Fig. 1. For comparison a spectrum is included (top) for a pure, that is, without copper, sol-gel-made SiO₂ sample annealed at 200 °C. For this sample, four major features are observed, characterizing the amorphous SiO₂ Raman spectrum.¹⁶ The position of these bands is at about 430, 495, 850, and 980 cm⁻¹. The sharp band at approximately 495 cm⁻¹, known as D1 band, along with a band at about 606 cm⁻¹, known as the D2 band, have received considerable attention and several interpretations have been proposed $^{29,34-36}$; the most accepted was made by Galeener.²⁹ He has suggested that the D1 and D2 bands correspond to decoupled modes of in-phase breathing motions of oxygen atoms in planar three- and fourmember rings, respectively. In agreement with other Raman results in sol-gel-made samples, our data do not



Fig. 3. IR spectra for a thermal-growth SiO_2 sample and for silica xerogel sample with composition $70(SiO_2)-30(CuO)$, annealed at 600 °C for 15 min.



Fig. 4. Raman spectra in the range of 200 to 1100 cm^{-1} for the same set of samples of Fig. 1. For comparison a spectrum of a nondoped xerogel sample annealed at 200 °C for 15 min is included.

show the D2 mode.^{37,38} According to Riegel et al.,³⁷ in SiO₂ samples prepared using a wet method, the chemisorbed water beaks up the siloxane bridges, especially those under mechanical stress, as in threefold rings, transforming those in rings with a larger number of members with a free hydroxyl group. The Raman band at 980 cm^{-1} supports this interpretation, because it has been previously related with vibrations of SiO₄ units with two nonbridging oxygen, in which these oxygen are bound to OH groups³⁹; this band, 980 cm⁻¹, is absent in the Raman spectrum of fused quartz, because in this material, the four oxygen are bridging atoms. For sol-gel-made samples annealed at higher temperatures the D1 band appears due to the dehydroxylation process. This process transforms some sixfold rings onto three- and fourfold rings.37,38

In Fig. 4 it can be observed that the Raman spectra of the sol-gel sample with copper is quite different from the corresponding fused quartz sample. The spectrum of the 100-°C-treated sample has as the main Raman feature an intense and sharp peak at about 1050 cm⁻¹, which corresponds to vibrations of the NO₃⁻ ions or forming nitrates. The other peaks in the range of 250 and 949 cm^{-1} have the same origin. Notice that, in agreement with the IR results, the intensity of this band is strongly reduced after the annealing at 200 °C and it disappears for annealings above 400 °C. Also, in the Raman spectrum of the 200-°C-treated sample appears a band at approximately 288 cm⁻¹, and weak peaks at approximately 350 and at approximately 430 cm⁻¹. These features are ascribed to vibrations of Cu-O bonds in cupric oxide.⁴⁰ In the same spectrum, two broad bands appear, one in the region of 400 to 700 cm^{-1} and the other above 850 cm^{-1} . On top of this latter band, weak peaks at 918, 949, and 973 can be resolved. The Raman spectra of the samples

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annealed at 400 and 600 °C show basically the same features, but the broad bands are better defined, particularly in the 600-°C-annealed sample.

Figure 5 shows the x-ray pattern of the samples annealed at 200, 400, and 600 °C. In the sample annealed at 200 °C, the sharp lines have been identified with the partially hydrolyzed $Cu_2(OH) \cdot 3(NO_3)$ copper nitrate phase. For the 400- and 600 °C-annealed samples, the nitrate phase disappears and the CuO phase appears.⁴¹

IV. DISCUSSION

The main features in the IR and Raman spectra of Cu-doped samples annealed at 100 and 200 °C are the nitrate band. For samples annealed to 400 and 600 °C the nitrates bands disappear and most of the copper segregates to form CuO particles embedded in the glass matrix. In the IR spectra of samples containing copper (Fig. 1), it is clear that the relative intensities of the Si–(OH) bands at 940–970 cm⁻¹ and of the Cu–O band at around 530 cm⁻¹ increase with the increase in the annealing temperature. The presence of the Si–(OH) groups even after the treatment at 600 °C is contrary to the annealing behavior of similar samples without copper. In these latter samples, the Si–(OH) groups gradually disappear with the increase in the annealing temperature, being basically removed for temperatures around 600 °C.

Several previous reports have pointed out that most Raman spectra of silicates have major bands near 600 and 1000 cm⁻¹.^{42,43} The spectra of crystalline silicates are similar to that of the corresponding glasses, but with narrower lines.^{42,44,45} The Raman results, in Fig. 4 for samples treated at 200, 400, and 600 °C, show two weak but well-defined bands in the ranges of 400–700 cm⁻¹ and 850–1050 cm⁻¹, which may be associated with the



Fig. 5. X-ray pattern for the $70(SiO_2)$ –30(CuO) sample annealed at 200 °C, 400 °C, and 600 °C.

presence of the Cu incorporated into the glass matrix. The latter band is centered at about 950–980 cm⁻¹. Raman vibrations in this frequency range have been associated with SiO₄ units with two nonbridged oxygens (NBOs).³⁹ SiO₄ units with two NBOs may form different kinds of cyclosiloxanes, with structures formed basically by rings with three and six members.¹² Because threefold rings do not exist in the presence of large amounts of OH groups, the main contribution for the 850-1050 cm⁻¹ band could come from SiO₄ units with two NBOs forming rings of six members. The SiO₄ units with two NBOs are the only constant factor in the structure of most silicates. The high-frequency Raman line in crystalline and glass silicates has been related to symmetric silicate stretching motions involving the nonbridged oxygens, and the low frequency to vibrations of the bridged oxygens.42,43

To our knowledge, there are only two stable copper silicates, one the dioptase and the other the shattuckite with the composition $\text{Cu}_5(\text{SiO}_3) \cdot 4(\text{OH})$, which is a single-width unbranched inosilicate with the structural formula $(\text{SiO}_x)^{3+}$. According to previous work,⁴² silicate molecular groups of the form $(\text{SiO}_x)^{3+}$ should give an additional Raman line at about 700 cm⁻¹, which we do not observe in our Raman results. Therefore, comparing our Raman and IR results with previous reports, it is quite possible that in the samples studied in this work there exists the formation of small units that have the structure of dioptase, because one of the essential features in the structure of this silicate is that the sixfold rings are present in the structure of silica xerogel.^{14,37}

As has been mentioned above, six member rings are the basic structural units of the metasilicate known as dioptase. These rings can trap the water molecules that are observed in the IR spectra, being stable to heat treatments at elevated temperatures.

The fact that the two Raman lines related to the formation of structural units of silicates are weak and broad means that in our samples the silicate formation, perhaps around the oxide particles, is still incipient, and therefore without any long-range structural order, the reason why they do not show the characteristic x-ray and/or IR signals of micro- or nanocrystalline dioptase. The broadness of these two Raman lines also agrees with the calculations by Rino et al.¹⁴ They have shown that the Si–O–Si bond angle distribution for nonplanar six-member rings is wide, and therefore, wide bands should be expected in the Raman spectra. The situation is different for the planar threefold and quasi-planar fourfold rings. In these cases, their vibrations are decoupled and the bond angle distributions are narrower, producing sharp peaks in the Raman spectrum at frequencies of about 606 and 490 cm⁻¹, for the three- and fourfold rings, respectively.^{29,34–36}

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V. CONCLUSIONS

It is well known that silica xerogels have an open structure formed basically by regular n-fold rings with n = 4, 5, and 6. When these glasses are heated for densification, the ring statistics change, forming rings with a low number of members including threefold rings. In samples containing copper, the metal avoids the dehydroxylation process preserving the open (polymeric) structure and allowing the formation of metal silicates. From our analysis, we propose that upon thermal annealing at temperatures above 200 °C, there is the formation of small silicate structures corresponding to the dioptase.

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