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Optical properties of copper-doped silica gels

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Abstract

Copper-doped silica xerogels, obtained by the sol-gel process, have been submitted to various thermochemical treatments. Depending on copper concentration, treatment time, temperature and atmosphere, different copper species are present in the final product: Cu^+ ions (isolated or dimers), cuprous oxide nanoparticles and metallic copper. These species have been characterized by their optical properties (absorption and luminescence). Some of the materials obtained could be useful for applications or fundamental studies. © 1997 Elsevier Science S.A.

Keywords: Sol-gel; Monovalent copper; Cuprous oxide; Metallic copper; Nanoparticles

1. Introduction

Copper is one of the most studied transition metals when embedded in an insulating matrix [1]: luminescent properties of monovalent copper and optical properties of copper nanoparticles have been widely investigated in a wide range of host matrices [2-5], including glasses [6-12]. However, information on the optical properties of copper species in pure silica glass are seldom because of the difficulties encountered in the preparation of these kinds of materials.

On the other hand, the sol-gel method applied to silica is known to enable the preparation of compounds that are not accessible by classical ways of synthesis. Moreover products of very good optical quality and homogeneity can be obtained. This is essential for optical studies or applications.

This paper describes the synthesis of copper-doped silica by the sol-gel process and the characterization of the copper species in the glasses by optical spectroscopy.

2. Synthesis

The gels are prepared using the sol-gel method, starting from tetramethoxysilane (TMOS), methanol, nitric acid 0.01 N and formamide in the ratio 1:4:4.5:1. The copper is introduced in this mixture in the form of nitrates. The solution is stirred for 1 h at room temperature, then put in UV-cuves and aged for 3 days in an oven at 60°C. At that time, the gels are removed from the mold and dried under argon flow. After this stage of the process, copper is mainly present in these gels in the form of Cu^{2+}, as shown by their optical spectra.

The gels are then submitted to a multistage heat treatment: 100°C (water removal), 250°C and 450°C (organics evaporation and burning out), 750°C (removal of OH groups) and 1000°C (densification). This last stage is necessary to close the porosity and hence to prevent the reoxidation of monovalent or metallic copper when reexposed to air after treatment. But it must be short enough to avoid crystallization of cristobalite since copper is known to promote the devitrification of silica glasses. Using a carefully ad-

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justed heat treatment profile it is possible to obtain densified monolithic blocks ($8 \times 4 \times 1.6$ mm^3) of average density of 2–2.2 g/cm^3 and with a molar ratio Cu/Si up to 0.5%.

Depending on the atmosphere under which this treatment is performed and on the copper content, the final products contain different copper species as described below.

3. Results and discussion

The UV-visible spectra of our gels were taken on a Shimadzu U-3000 spectrophotometer at room temperature, and on a home-made set-up at 77 K. When necessary the samples were thinned by grinding and polishing in order to maintain the absorbance between 0 and 3 in the zones of interest.

Luminescence spectra were taken on a home-made set-up with a photon counting detection.

3.1. Monovalent copper

Gels containing less than 0.1% copper and heat treated under an argon flow give clear colorless monoliths. Their absorption spectra exhibit two bands at 228 and 290 nm (Fig. 1). The intensities of these two bands vary differently with increasing copper loading of the gels, suggesting that there is more than one optically active species present. However, it is well known now that monovalent copper tends to form pairs in solid insulators. This trend has been confirmed by theoretical calculations [13] as well as by EXAFS measurements of copper-copper distance in $CuZr_2(PO_4)_3$ [14] and phosphate glasses [15]. The so-formed copper dimers have specific luminescent properties, quite invariant whatever the host, and differing from those of isolated monovalent copper [8].

Luminescence properties of our gels have been investigated. They exhibit a broad emission band, as generally seen in glasses, centered at 550 nm when excited either at 245 or 300 nm (Fig. 2). Varying the initial concentration of copper does not induce great changes in the shape of the emission spectrum. The excitation spectrum is composed of two bands at 245 and 300 nm, corresponding to the absorption bands. The features of the luminescence (low energy position, large Stokes shift) are close to those of dimers in other insulating matrices. However, the evolution of the excitation bands with the copper concentration does not allow us to attribute the luminescence to monomers or dimers.

3.2. Cuprous oxide nanoparticles

High temperature treatments of gels containing more than 0.1% copper give yellow to red colored gels, depending on the initial copper concentration. Since it is established that, under certain thermal treatment, cuprous oxide (Cu_2O) precipitates in glasses [16] and since the gels are more colored when heated under oxidizing conditions, we attribute this coloration to the precipitation of Cu_2O nanoparticles. This is confirmed by UV-visible spectroscopy performed at room and liquid nitrogen temperature. The obtained spectra (Fig. 3) clearly show the spectroscopic signature of Cu_2O [17]: we observe, at room temperature, two bands peaking at 455 nm and 478

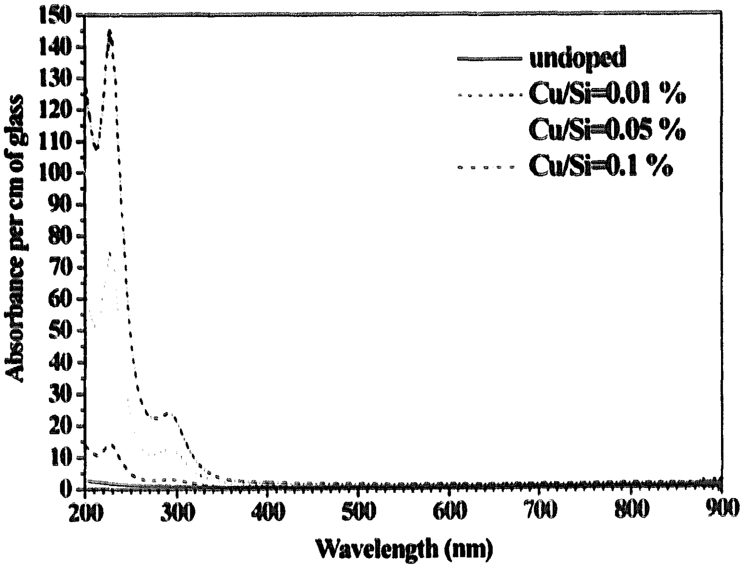

Fig. 1. UV-Visible absorption spectra of gels heated up to 1100°C under argon for various Cu/Si molar ratios.

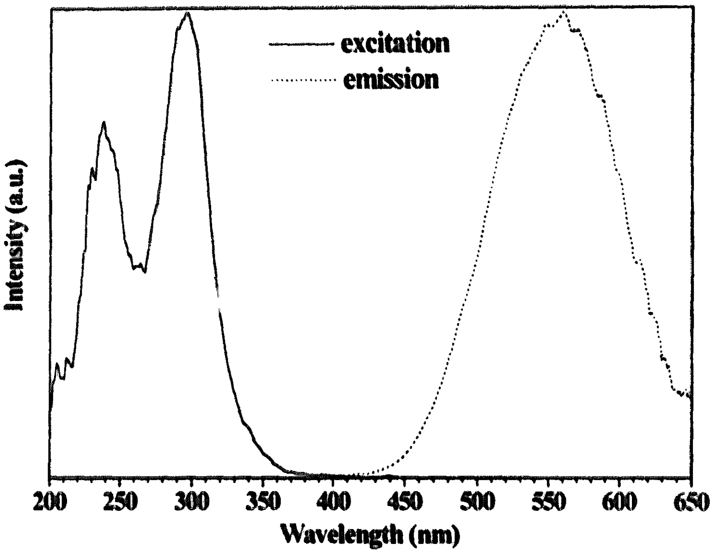

Fig. 2. Normalized excitation and emission spectra of a 0.1% copper-doped gel heated up to 1100°C under argon.

nm. This later band splits, at 77 K, into two bands situated at 475 and 480 nm. The band at 455 nm does not move upon cooling, but it is better resolved at lower temperature. The band at lower energy can be attributed to the $n = 1$ exciton transition of the blue-green series [18]. It is accidentally decomposed, probably by matrix-induced strain [17]. The band at 455 nm can be attributed to the 1s exciton transition of the blue series [18]. The other expected but weak transitions of Cu_2O, in the red to green region, are not resolved and appear as a continuous background [19].

This is the first evidence, to our knowledge, of the synthesis of cuprous oxide nanoparticles in a silica matrix. It is of great interest to be able to prepare such materials, because they could be used to study the quantum confinement effects that are expected when semiconductor nanoparticles are small enough.

3.3. Copper nanoparticles

Once densified, the xerogels can be heated under hydrogen to obtain metallic nanoparticles. Absorption spectra of a 0.1% molar doped xerogel treated for 60 min at different temperatures in the 700–1000°C range are given in Fig. 4. The transparent samples obtained, more or less deep red-ruby colored, give a strong absorption around 560 nm due to the surface plasmon resonance (SPR) of the Cu metal nanoclusters. Similar optical properties of Cu nanoclusters in silica or

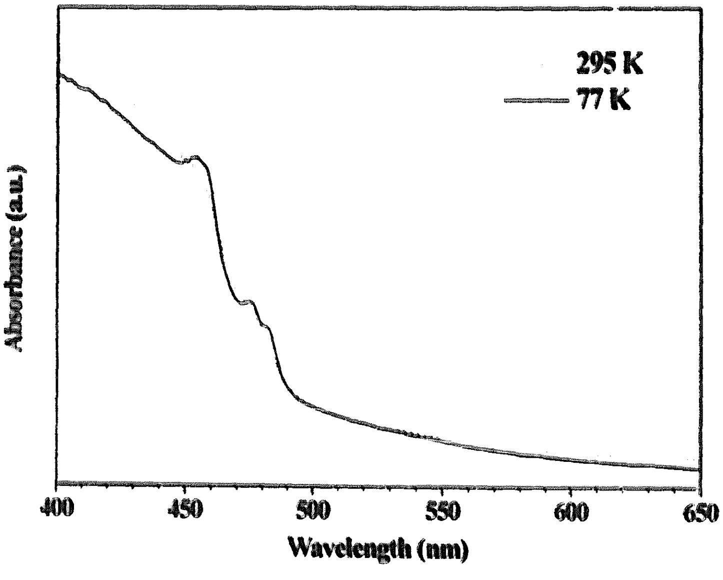

Fig. 3. UV-Visible absorption spectra of a 0.5% copper-doped gel heated up to 1000°C under air.

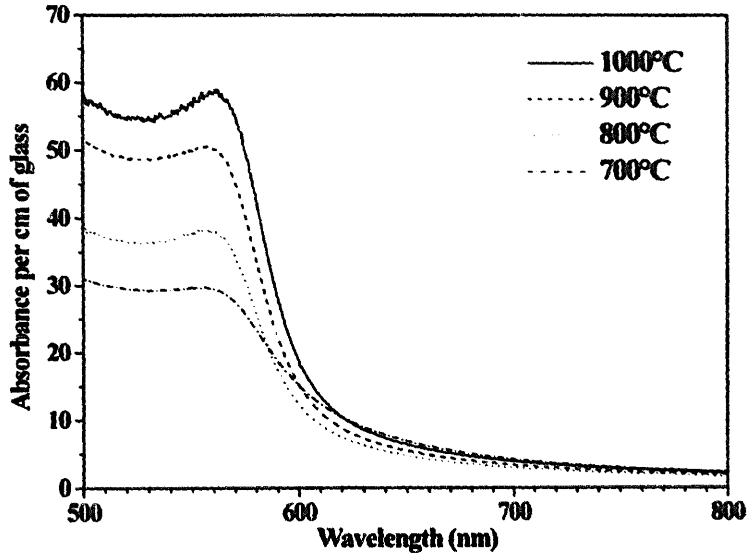

Fig. 4. Absorption spectra of 0.1% copper-doped gels reduced for 60 min under hydrogen at different temperatures.

soda-lime silicate glasses [10,11,20,21] have been reported and their non-linear effects have been studied. However, some authors [22] have claimed that the red-ruby color of copper glass results from cuprous oxide particles in the sample. The absorption of cuprous oxide nanoparticles dispersed in the same matrix, as mentioned previously, is weak in this wavelength range. Obviously, the above comparison shows that the optical absorption band results from small metallic copper particles.

The evolution of the intensity and the shape of this peak with increasing reduction temperatures reflects the change in the size of the particles. Indeed, Ruppin [23] and Trotter et al. [24] have shown, for copper colloidal particles in photochromic glasses, that the increase of the particle size induces an enlargement of the intensity and a shift to shorter wavelengths of the absorption peak.

Moreover, the specific optical properties of silica allow us to observe some of the structures in the UV absorption spectrum of copper particles that had been theoretically predicted [24] but never observed before (Fig. 5). In particular, the singularity near 300 nm can be attributed to an interband transition [25]. Its well contrasted shape suggests that the metallic copper is of good crystallographic quality.

4. Conclusion

By using the sol-gel method, we are able to synthesize silica glass samples doped with either luminescent copper species (Cu$^+$ monomers or dimers), cuprous

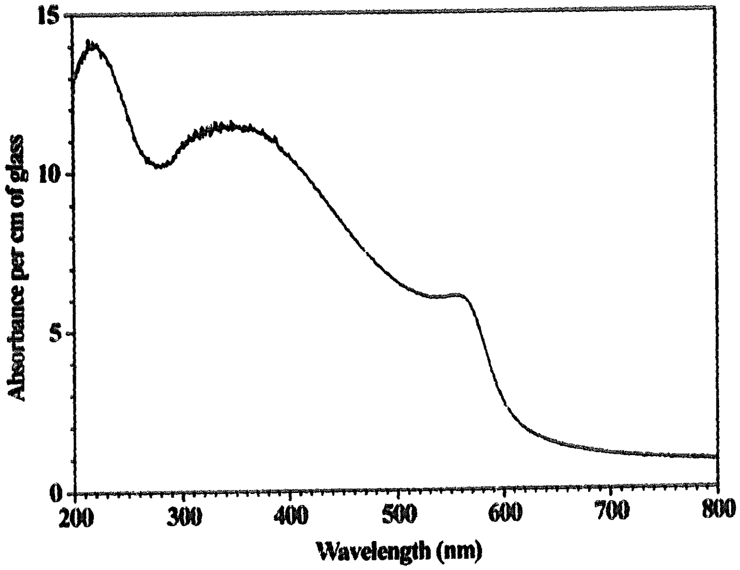

Fig. 5. Absorption spectrum of a 0.01% copper-doped gel reduced for 60 min at 900°C under hydrogen.

oxide nanoparticles or metallic copper nanoparticles. By choosing the concentration and the heat treatment conditions, samples containing only one kind of the above species are obtained, and the size of the nanoparticles can be varied.

The high optical quality of the glasses and their specific properties made them attractive materials for applications such as solid laser sources in the visible range or for further studies, like the size dependence of the non-linear and dynamical optical response.

References

[1] G. Le Flem, J. Alloys Comp. 188 (1992) 36–41, and references therein.
[2] J.P. Doumerc, C. Parent, J.C. Zhang, G. Le Flem, J. Less-Common Metals 148 (1989) 333–337.
[3] J. Texter, D.H. Strome, R.G. Herman, K. Klier, J. Phys. Chem. 81 (1977) 333–338.
[4] P. Boutinaud, C. Parent, G. Le Flem, C. Pedrini, B. Moine, J. Phys. Condens. Matter 4 (1992) 3031–3042.
[5] S.A. Payne, L.L. Chase, L.A. Boatner, J. Lumin. 35 (1986) 171–177.
[6] J.C. Zhang, B. Moine, C. Pedrini, C. Parent, G. Le Flem, J. Phys. Chem. Solids 51 (1990) 933–939.
[7] B. Moine, C. Pedrini, E. Duloisy, P. Boutinaud, C. Parent, G. Le Flem, Journal de Physique IV, Colloque C7, supplément au Journal de Physique III 1 (1991) 289.
[8] P. Boutinaud, E. Duloisy, C. Pedrini, B. Moine, C. Parent, G. Le Flem, J. Solid State Chem. 94 (1991) 236–243.
[9] R. Debnath, S. Kumar, J. Non-Cryst. Solids 123 (1990) 271–274.
[10] R. Doremus, S.C. Kao, R. Garcia, Appl. Optics 31 (1992) 5573–5778.
[11] C. Estournès, N. Cornu, J.L. Guille, J. Non-Cryst. Solids 170 (1994) 287–294.
[12] C. Estournès, N. Cornu, J.L. Guille, Phys. Chem. Glasses 37 (1996) 177–181.
[13] P. Boutinaud, D. Garcia, C. Parent, M. Faucher, G. Le Flem, J. Phys. Chem. Solids 56 (1995) 1147.
[14] E. Fargin, I. Bussereau, G. Le Flem, R. Olazcuaga, C. Cartier, H. Dexpert, Eur. J. Solid State Inorg. Chem. 29 (1992) 975–980.
[15] A. Jacob, E. Fargin, C. Parent, G. Le Flem, J. Alloys Comp. (1997).
[16] A.A. Ahmed, G.M. Ashour, Glass Technol. 22 (1981) 24.
[17] R.J. Araujo, J. Butty, N. Peyghambarian, Appl. Phys. Lett. 68 (1996) 29.
[18] J.P. Dahl, A.C. Switendick, J. Phys. Chem. Solids 27 (1966) 931–942.
[19] S. Nikitine, Progress in Semiconductors, vol. 6, Heywood, London, 1962, p. 235.
[20] G. De, M. Epifani, A. Licciulli, J. Non-Cryst. Solids 201 (1996) 250.
[21] R.H. Magruder III, R.F. Haglund, Jr, L. Yang, J.E. Wittig, R.A. Zuhr, J. Appl. Phys. 76 (1994) 708.
[22] A. Ran, S.N. Prasa, in: American Ceramic Society (Eds.), Advances in Glass Technology, Plenum, New York, 1962, p. 256.
[23] R. Ruppin, J. Appl. Phys. 59 (1986) 1355.
[24] D.M. Trotter, Jr, J.W.H. Schreurs, P.A. Tick, J. Appl. Phys. 53 (1982) 4657.
[25] H. Ehrenreich, H.R. Philipp, Phys. Rev. 128 (1962) 1622.