JOURNAL OF MATERIALS SCIENCE **36** (2001) 3247–3251

The effect of Co^{2+} on the structure and colour of silica gel derived materials

M. G. FERREIRA DA SILVA
Departamento de Engenharia Cerâmica e do Vidro, Universidade de Aveiro, UIMC, Aveiro, Portugal
E-mail: gsilva@cv.ua.pt

Undoped and doped Co^{2+} silica gel-derived materials were prepared from hydrolysis and condensation of tetraethylorthosilicate (TEOS). In order to better understand the structural evolution of these samples, with the heat-treatment temperature, ultra-violet (UV), visible (VIS) and near-infrared (NIR) spectrophotometry, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used. The spectroscopic behaviour of Co^{2+} allows us to obtain information about the ability of this ion to act as a network-former and/or as a network-modifier. Above 800°C the samples are opaque and show crystalline phases.

1. Introduction

Many research studies have been done on the colour of cobalt compounds [1–6]. The compounds of divalent cobalt possess a large variety of colours. Pink, red, blue and green can be observed in aqueous solutions and glasses [3]. Cobalt (II) is a transition metal ion with seven 3d electrons. The blue colour of cobalt compounds is attributed to the hexacoordinated Co(II) and the pink colour to the tetracoordinated Co(II) [1–6].

The production of high-quality fused silica, containing transition elements homogeneously dispersed, is extremely difficult due to the high viscosity of silica, even at very high temperature. Using flame hydrolysis techniques, high-purity fused silica was successfully doped with transition elements [4]. Four-and six-coordinated Co(II) were detected in flame-hydrolysed fused silica.

The preparation of silica and doped silica glasses using the sol-gel method provides good chemical homogeneity and easy preparation at low temperatures. The purpose of the present work was to study the colouring mechanism of cobalt in silica gel-derived glasses. Colour and structural changes were correlated with heat-treatment, temperature, porosity and Si-OH groups.

2. Experimental procedure

Silica and silica cobalt doped samples (acid catalysed and not catalysed) were prepared from tetraethylorthosilicate (TEOS), cobalt nitrate hexahydrate, water (or HCl 0.1N) and ethanol as starting material. The solutions were prepared in the molar ratio TEOS : ethanol : water (or HCl 0.1 M) 1 : 3 : 4. The hydrolysis of TEOS taks place in two steps. In the first one a mixture of TEOS, ethanol and water (or HCl 0.1 M) in a molar ratio of 1 : 3 : 1 was stirred for one hour at room temperature. After this first step, water (or HCl 0.1 M) in the case of silica samples or cobalt nitrate dissolved in water (or in HCl 0.1 M) for the cobalt samples was added. The final solution was stirred for one hour, poured into Petri dishes, and allowed to gel and dry at about 50°C. The gels obtained were heat-treated at 120°C. The 120°C samples were heat-treated between 250 and 1200°C (for four hours).

Near-infrared (NIR) and ultraviolet-visible (UV-VIS) spectrophotometry (using an UV-VIS-NIR UV-2101/3101PC spectrophotometer), X-ray diffraction (XRD) (using a Rigaku XDMAX diffractometer) and scanning electron microscopy (SEM) (using a Hitachi S4100-1), were used to study the samples.

3. Results

3.1. Gelation conditions

The samples that were not prepared in acid-catalysed conditions become turbid forming gels with phase separation. The acid-catalysed solutions result in gels and glasses with good homogeneity and transparency. However, the samples undergo an enormous cracking near 700°C.

3.2. Near infrared spectrophotometry

Fig. 1 shows the spectra of the $0.5CoO\text{-}99.5SiO_2$ sample heat-treated between 50 and 650°C. In each figure the spectra with number (1), (2) and (3) corresponds, respectively, to samples not exposed to air humidity (1), exposed to air humidity for approximatly 45 minutes (2) and expose to the air humidity for a long time (one day or more) (3). The spectra of 50°C sample (Fig. 1) present:

- a band near 2300 nm due to the water clusters bonded to silanol groups [7].
- an intense band around 2260 nm that is related to the free OH groups [7, 8]. This band suffers an

intensity decrease with the increased length exposure to air humidity.
- a band near 1910 nm with, a shoulder at 1950 nm, that can be assigned to the vibration of silanol groups hydrogen bonded to water molecules; it is generally used to measure the water concentration of a sample [7–9]. The intensity of this band increases with exposure time to air humidity.
- absorption bands near 1690, 1720 and 1760 nm that were attributed to silanol groups linked to organic substances.
- bands at 1460 and 1415 nm that were associated to the combination of stretching and deformation vibration of silanol groups hydrogen bonded to water. These bands are more intense in the (2) and (3) spectra.

The spectra of the cobalt sample heat-treated at 120, 250 and 500°C (Fig. 1) show the same bands as the 50°C sample but, there is very little difference between hydrated and non-hydrated samples heat-treated at the same temperature. The spectrum of the 650°C sample (Fig. 1) presents new bands centred on 2210 nm and 1360 nm. They can be assigned to vibrations of free silanol groups [7]. The absorption bands near 1690, 1720 and 1760 nm are only present at temperature lower than 500°C, and for this reason were attributed to silanol groups linked with organic substances.

NIR spectra of SiO_2 and $0.5CoO$-$99.5SiO_2$ samples, not exposed to air humidity, are shown in Fig. 2. It is evident that, at 650°C, the silica sample has less silanol groups (and water) than the cobalt sample.

3.3. Ultra-violet and visible spectrophotometry

The blue 50°C sample (not exposed to air humidity) has an absorption spectrum (Fig. 3 - spectrum (1)) with three bands at 660, 624 and 510 nm. The blue colour and the intense band at 660 nm indicates that tetrahedral co-ordinated Co (II) is present in the sample [1–5]. The broad band at 510 nm and the little band at 624 nm can be attributed to Co (II) in octahedral symmetry [1–5, 10]. The colour of the 50°C sample changes with exposure to air humidity. The spectrum number (3) (Fig. 3) was obtained by the 50°C sample with a pink colour. The 660 nm band is not present in the spectrum. This means that all the Co (II) forms octahedral complexes. The 120°C sample suffers a similar evolution with hydration. However, the colour change occurs more gradually and some tetrahedral Co (II) ions are present in the sample exposed to air humidity for a long time. The sample not exposed to air humidity has a violet colour and acquires an amethyst colour after hydration. The violet sample has a stronger 660 nm band (tetrahedral Co (II)) than the amethyst sample. Another band at 590 nm, due to Co (II) in tetrahedral symmetry [1, 16], appears in the violet sample. The spectra of the blue-greyish 250°C sample (Fig. 3 - spectra (1) to (3)) does not show a marked difference with hydration time. After a long time of hydration, the sample has an amethyst-greyish colour. In these spectra the 660 and 590 nm bands are due to Co(II) in tetrahedral coordination and those near 624 and 510 nm to the hexacoordinated Co(II). The blue-greyish 500°C sample does not suffer a change of colour with exposure to air humidity. The spectra present the characteristic bands of tetrahedral (660 and 590 nm) and octahedral (510 nm) Co(II) sites. The 650°C sample has a deep blue-greyish colour that does not change with exposure to air humidity. Fig. 3 shows the spectrum of the 650°C sample. The band around 590 nm (tetracoordinated Co (II)) is more intense in this sample than in the samples at 250 and 500°C. The 510 nm (hexacoordinated Co(II) band is also present in the 650°C sample.

3.4. X-ray diffraction

The SiO_2 sample does not reveal, by XRD, the presence of any crystalline phase up to 1200°C (Fig. 4). However, the sample becomes opaque near 800°C.

The $0.5CoO$-$99.5SiO_2$ sample is transparent up to 800°C and shows (Fig. 4) the formation of α-quartz and α-cristobalite at 1100 and 1200°C.

3.5. Scanning electron microscopy

The SEM micrographs of the 800°C sample reveal a very homogeneous structure. Nevertheless, between 1000°C and 1200°C, it was possible to detect phase separation and crystalline phases (quartz and cristobalite-Fig. 5).

4. Discussion

The turbidity of solutions that were not prepared under acidic conditions is due to the rate of chemical reactions involved in a sol-gel process [11–13]. In acidic conditions the polycondensation rate can be greater than the hydrolysis rate and it lends to precipitation [11]. However, in acidic conditions hydrolysis tends to go to stoichiometric completion [13] and it is possible to obtain homogeneous solutions. The hydrolysis and condensation at low pH results in gels with small pores, which make the drying of monolithic gels very difficult [14]. The pores in the samples studied (gels without separation phases) do not undergo gradual shrinkage but seem to collapse at a temperature near 700°C. The same phenomenon was observed by Elmer [15] in porous glasses. In porous glasses the pore volume is not greatly reduced as a result of the heating from 100 to ~800°C [15]. However, the near infrared results registered in Fig. 1, suggest the presence of close pores at temperatures between 250 and 500°C. In fact, at 250 and 500°C the cobalt sample suffers a slow dehydration because the spectra do not show a great difference between the initial spectrum and those obtained after the exposition to the air humidity (Fig. 1). The hydration phenomenon is evident in the 50 and 120°C samples (Fig. 1) and is not observed in the 650°C sample (Fig. 1). Therefore, the 1910 nm band shows a marked increase in 50 and 120°C (Fig. 1A and B-spectra number 2 and 3). The near-infrared spectra of the dry samples SiO_2 and $0.5CoO$-$99.5SiO_2$ (Fig. 2) suggest that cobalt influences the

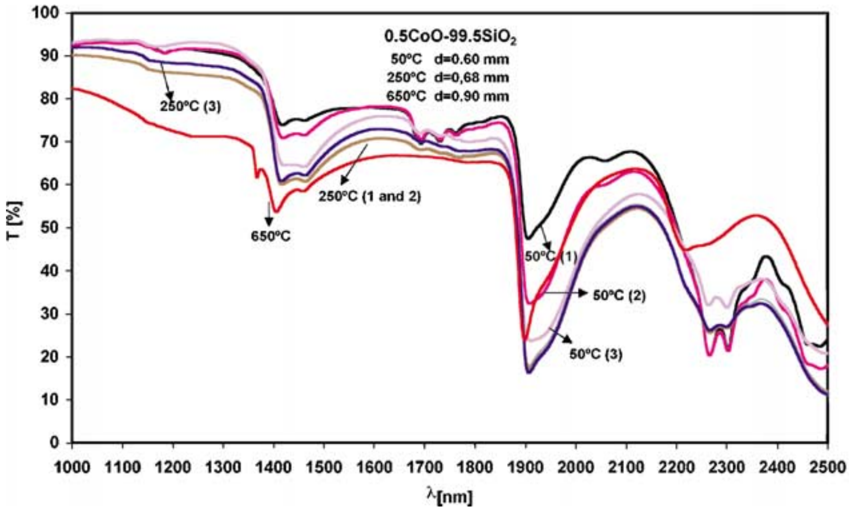


Figure 1 Near infrared absorption spectra of 0.5Co-99.5SiO$_2$ sample heat-treated at 50°C, 250°C and 650°C. (1) – not exposed to air humidity; (2) – exposed ∼45 minutes to air humidity; 3 – exposed a long time to air humidity (one day or more). d – sample thickness.

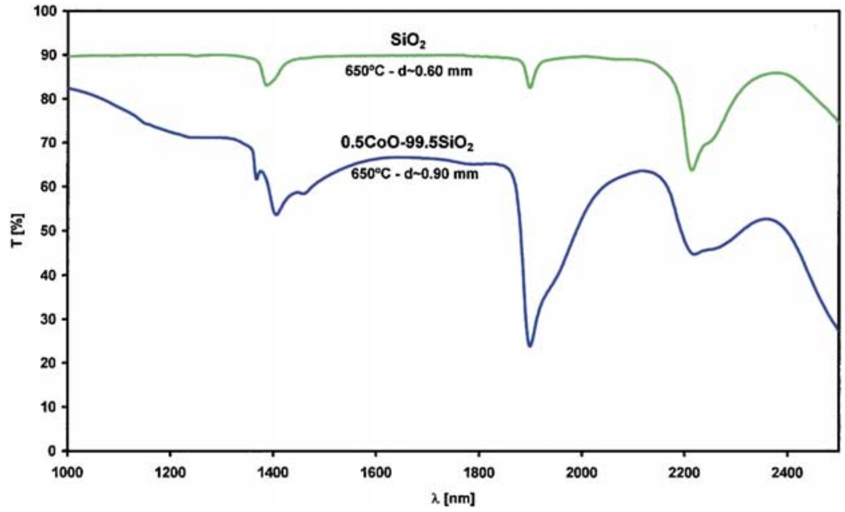


Figure 2 Near infrared absorption spectra of SiO$_2$ and 0.5Co-99.5SiO$_2$ samples heat-treated at 650°C. d – sample thickness.

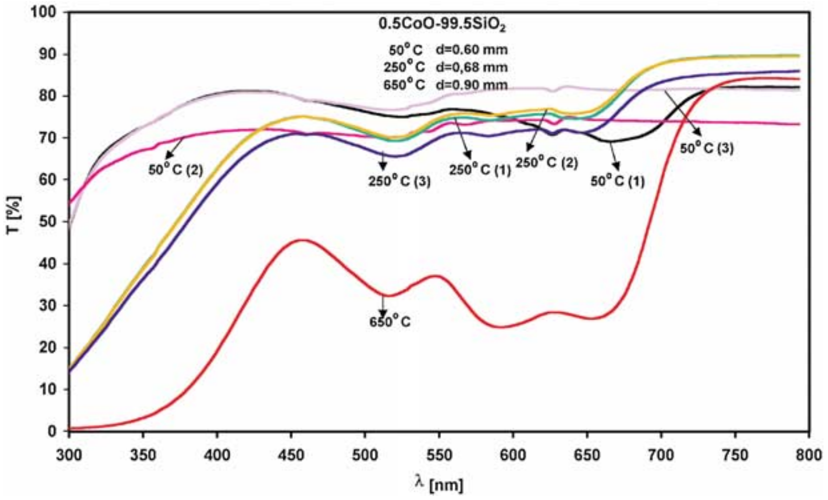


Figure 3 Ultra-violet and visible absorption spectra of 0.5Co-99.5SiO$_2$ sample heat-treated at 50°C, 250°C and 650°C. 1 – not exposed to air humidity; 2 – exposed ∼45 minutes to air humidity; (3) – exposed a long time to the air humidity (one day or more). d – sample thickness.

sintering process. At 650°C the silica sample has less water (band at 1910 nm) and more free silanol groups (bands near 1360 and 2210 nm) than the cobalt sample heat-treated at the same temperature. The colour of the cobalt samples is strongly dependent on heat-treatment temperature and hydration degree. The dry 50°C sample (not exposed to air humidity) has a light blue colour that turns to pink in contact with air humidity. The 50°C

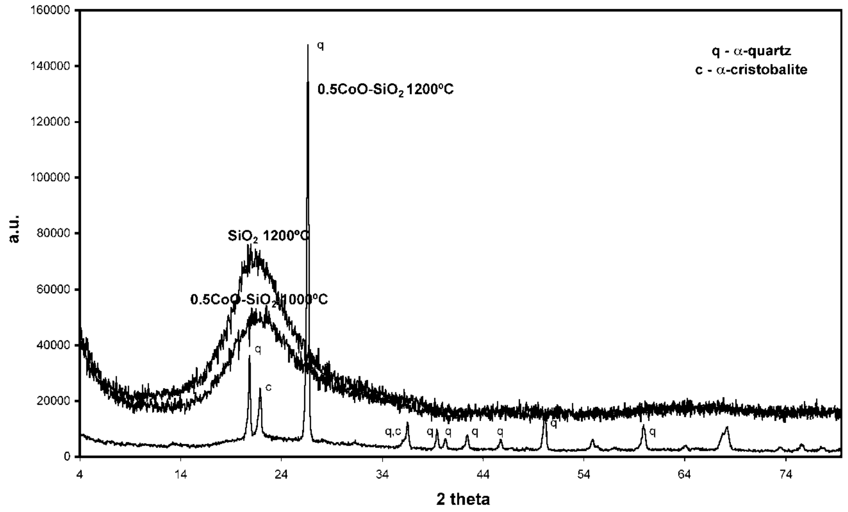
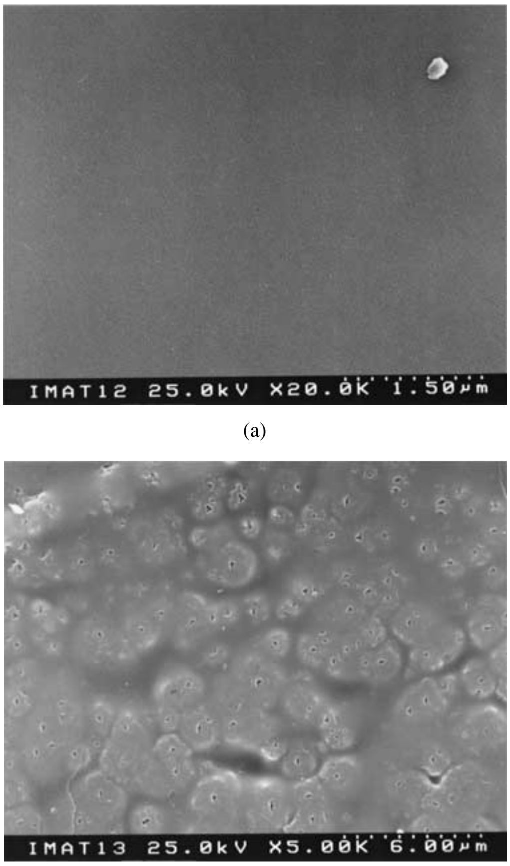


Figure 4 X-ray diffraction patterns of SiO_2 and 0.5Co-99.5SiO_2 samples.



(a)

(b)

Figure 5 SEM micrographs of the 0.5Co-99.5SiO_2 sample. A – heat-treated at 800°C; B – heat treated at 1200°C.

sample spectra (Fig. 3) shows a broad band centred at 510 nm. The $[Co(H_2O)_6]^{2+}$ ions have a similar absorption band [10]. Co (II) hexacoordinated is expected to have, in the visible, a spin allowed d-d transition from the ground state ${}^4T_{1g}(F)$ to ${}^4T_{1g}(P)$ associated with a band at 500–454 nm [1–3, 16]. The 624 nm weak band is also due to hexacoordinated Co(II) but, the electronic transition $({}^4T_{1g}(F) \rightarrow {}^{4A}_{2g}(F)$ associated with this band is forbidden [1]. Therefore, the band is expected to be weak. The Co (II) in tetrahedral co-ordination (present in blue sample) is probably due to the presence of some $[Co(H_2O)_4]^{2+}$ and $Co(OH)_4]^{2-}$ species [17] in the pores. The main absorption bands, in tetrahedral cobalt (II) arise from the ground state ${}^4A_2$ to ${}^4T_2(F)$, ${}^4T_1(P)$ and ${}^4T_1(P)$ states [2, 16]. The very intense absorption band in the visible region is due to ${}^4A_2 \rightarrow {}^4T_1(P)$ transition (between 625 and 500 nm). In silicate glasses, containing cobalt, this band consists of triply-split absorption bands at 540, 590 and 640 nm [16]. It is the spin-orbit coupling that causes the splitting of the tetrahedral band. In the spectrum of the blue 50°C sample an intense band can be detected near 660 nm (Fig. 3). It was not possible to observe the other two absorption bands of tetrahedral Co(II) because they are masked by those of octahedral Co(II). When the 50°C sample undergoes hydration the $[Co(H_2O)_4]^{2+}$ and $Co(OH)_4]^{2-}$ species are substituted by the $[Co(H_2O)_6]^{2+}$ species. The 120°C sample has a similar evolution and their amethyst colour is the result of appropriate quantities of hexa and tetracoordinated Co(II). However, from 500°C, the pores of the cobalt sample appear to be close pores and the hydration is not possible. In this manner, the samples acquire an unchangeable colour. The 650°C sample has a more intense blue colour than the other blue samples. Its spectrum (Fig. 3) has an intense band centred around 590 nm. The same band is present in silicate glasses prepared by melting [1, 2, 16]. Perhaps, at 650°C, many Co(II) ions are inserted into the glass structure. The hexacoordinated Co(II) ions seem to be inside the pores and water coordinated. In fact, the position of 510 nm bands does not change considerably with heat-treatment temperature. At 700 and 800°C the cobalt sample remains transparent and has a dark blue colour but, the negative pressure in the liquid filled pores is much greater than the strength of the solid network and the sample collapses [14]. Crystalline phases were detected in the cobalt sample, by XRD, at a temperature greater than 1000°C (but, were not detected in the silica sample).

5. Conclusions

The results show that:

- the porous structure of silica and cobalt-silica samples does not undergo gradual shrinkage but, collapse at a temperature near 700°C.
- the hydration phenomenon is evident in the 50 and 120°C cobalt sample but, is not observed in 650°C sample.
- the colour of the cobalt sample is strongly dependent on heat-treatment temperature and hydration degree.
- at 650°C tetrahedral Co(II) ions are inserted into the glass structure but, octahedral Co(II) ions are inside the pores.
- the cobalt sample reveals a homogeneous structure at 800°C.
- crystalline phases were detected in the cobalt sample (but not in the sample without cobalt) at temperatures greater than 1000°C (α-quartz and α-cristobalite).

Acknowledgements

The authoress thanks FCT (portuguese Foundation for Science and Technology) for financial support.

References

1. A. PEARSON, Dissertation for the degree of master (Department of Glass Technology, University of Sheffield, Sheffield, 1969).
2. C. NELSON and W. B. WHITE, *J. Mater. Res.* **1** (1986) 130.
3. W. A. WEYL, "Coloured Glasses" (Society of Glass Technology, Sheffield, 1978).
4. P. C. SHULTZ, *J. Amer. Ceram. Soc.* **57** (1974) 309.
5. L. FERRER, M. SALES and J. ALARCÓN, in "Third Euro-Ceramics," Vol. 1, edited by P. Durán and J. F. Fernández (Faenza Editrice Ibérica S.L., Madrid, 1993) p. 285.
6. N. R. WILK JR. and H. D. SCHREIBER, *J. Non-Cryst. Solids* **217** (1997) 189.
7. D. L. WOOD, E. M. RABINOVICH, D. W. JOHNSON JR., J. B. MACCHESNEY and E. M. VOGEL, *J. Amer. Ceram. Soc.* **66** (1983) 693.
8. J. KRATOCHVILA, Z. SALAJKA, A. KAZDA, J. SOUCEK and M. GHEORGHIU, *J. Non-Cryst. Solids* **116** (1990) 93.
9. S. SAKKA, K. AOKI, H. KOZUKA and J. YAMAGUCHI, *J. Mater. Sci.* **28** (1993) 4607.
10. L. E. ORGEL, *The Journal of Chemical Physics* **23** (1955) 1004.
11. H. ZHENG, M. W. COLBY and J. D. MACKENZIE, *Mater. Res. Soc. Symp. Proc.* **121** (1988) 537.
12. E.J. NASSAR, C. R. NERI, P. S. CALEFI and O. A. SERRA, *J. Non-Cryst. Solids* **247** (1999) 124.
13. K. D. KEEFER, *Mater. Res. Soc. Symp. Proc.* **32** (1984) 15.
14. L. L. HENCH and M. J. R. WILSON, *J. Non-Cryst. Solids* **12** (1990) 234.

Received 11 April
and accepted 28 November 2000