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Preparation of uniformly dispersed copper nanocluster doped silica glasses by the sol–gel process

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The synthetic mechanism of uniformly dispersed Cu-nanocluster doped (0.05–1.0 wt%) silica glasses (copper ruby glasses) was investigated by UV–VIS and FTIR spectroscopy, DSC, XRD, surface area and density measurements at different stages of drying/densification up to glass formation. The monolithic gels were prepared from $Cu(NO_3)_2$, $H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$ (DAMO) and acid hydrolysed $Si(OC_2H_5)_4$ (TEOS). DAMO was used to immobilize the Cu^{2+} ions in the silica matrix. The formation and decomposition of Cu–DAMO complexes in the silica gel monoliths were studied. The doped gels were densified under H_2 and He gas atmospheres. A maximum matrix (SiO_2) density of 1.70–1.73 g cm^{-3} (77–79% of the theoretical density) could be achieved in an H_2 atmosphere at 900 °C. However a density close to silica glass 2.17 g cm^{-3} (>98.5% of theoretical) was achieved when the gels were densified in H_2 up to 800 °C followed by He gas at 980 °C. The surface area data also confirmed this densification behaviour. Uniformly dispersed Cu metal nanoclusters were formed during the heat-treatment of the gels and as a result a surface plasmon (SP) band of Cu-nanoclusters (563–580 nm) was observed. The increase of heat-treatment temperature caused the growth of nanoclusters and as a consequence the SP band was blue-shifted. XRD data also confirmed this.

1. Introduction

Metal nanocluster doped glasses are of current interest because of their potential applications[1] in nonlinear optics,[1–5] magnetic devices[6–8] and catalysis.[9–11] Small Cu nanoclusters embedded in a glass matrix leads to a ruby-red colouration of the glass. This colouration is due to the optical absorption arising from the surface plasmon resonance band of the embedded Cu nanoclusters. Cu-nanocluster doped glasses in the form of thin films are promising materials owing to their enhanced nonlinear optical properties.[3–5] The corresponding doped bulk glass might show further increase of optical nonlinearity because of the higher material thickness; as this would allow interaction of light with more Cu nanoclusters along the thickness. Cu-nanocluster doped glasses can be easily prepared by using the sol–gel process.[12–14] However, the conventional doping process (addition of metal salts to a TEOS derived sol) causes migration of dopant cations during the gel drying and densification stages resulting in inhomogeneous distribution of the dopants in the matrix.[15,16] This is severe for cations which do not form –Si–O–M– linkages in the sol and remain as hydrated cations as is the case for Cu. The hydrated cations are easily carried with water or solvents to the surface of the wet gel and some of these ions are expelled with the syneresis liquids.[17] It has been observed that complexing as well as cross-linking agents such as DAMO play a vital role to obtain a homogeneous distribution of metal ions in the bulk silica host.[9,10,18] In a recent communication[19] we also established this in the synthesis of 0.1 wt% Cu–99.9 wt% SiO_2. Considering the potential importance of this material, it was considered desirable to prepare several compositions of Cu-nanocluster doped glasses and examine the reaction pathways more closely. In this paper, the synthesis of Cu nanocluster doped silica gels with copper concentrations of 0.05, 0.1, 0.25 and 1 equivalent wt% are reported using DAMO as a complexing and cross-linking agent. The densification behaviour of the silica matrix in H_2 and He atmospheres is also reported. The reaction pathways have been examined by UV–VIS and FTIR spectroscopy, DSC–TG, XRD, surface area and density measurements.

2. Experimental

Silica gels containing 0.05, 0.1, 0.25 and 1 wt% of copper were prepared following a similar method, with some modifications, as reported earlier.[19] Cu–DAMO complex solutions were prepared by slow addition of DAMO (dissolved in ethanol) to an ethanol–water solution of $Cu(NO_3)_2 \cdot 2.5H_2O$ with stirring. DAMO/Cu molar ratios (r) were set to 0, 1.5, 3 or 5 for 0.05, 0.1 and 0.25 wt% Cu-SiO_2 gels. For 1 wt% copper, the DAMO/Cu molar ratios were set to 0, 1, 1.5 and 2. Parallel to this, a matrix silica sol was prepared by hydrolysing TEOS in the presence of water (H_2O/TEOS = 4) and hydrochloric acid (HCl/TEOS = 0.001). The Cu–DAMO complex solutions were then poured into the matrix silica sols with stirring. In this Cu–DAMO incorporated silica sol, the H_2O/TEOS molar ratio has reached 12 considering the amount of water present in the Cu–DAMO solution and water of crystallisation of the Cu-salt. The sols were then cast into polypropylene containers for gel formation after pH adjustment to 3–3.5. Gel formation took place within 30 to 100 min. Wet gels were kept for 6 days in closed conditions at 25 ± 1 °C. After this period the syneresis liquids[16,18] were decanted and stored for estimation of copper

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content and the wet gels were placed in an air oven (60 ± 2 °C) for drying. Crack-free dried gel monoliths of dimensions 20 mm diameter × 1–2 mm thickness (circular) and 40 × 40 × 2–3 mm thickness (rectangular) were obtained after about 7 days of drying. The gels were first heated in air to 500 °C with 6 h holding time to remove all organic residues. Subsequent heat treatments at different temperatures (*e.g.*, 600, 700, 800, 900 °C with 1–2 h hold) were conducted in H_2 gas for densification of the SiO_2 matrix as well as for reduction of Cu^{2+} to Cu metal. Heat treatment in an He gas atmosphere (up to 980 °C) was carried out beyond 800 °C only for matrix (SiO_2) densification.

The syneresis liquids were analysed for copper by flame atomic absorption spectrometry (Varian SpectrAA-400). Surface areas of the samples was measured on a Nova 1200 (Quantachrome) using 5-point BET method. Absorption spectra of the samples were obtained on a Perkin Elmer UV/VIS/NIR spectrometer (model Lambda 19). X-Ray diffraction measurements of the powdered samples were obtained on a Philips diffractometer (model PW 1880). FTIR spectra in the range 4000–400 cm^{-1} were recorded in a Nicolet (model SX800) spectrometer, with a diffuse reflectance set-up diluting the samples in KBr. Simultaneous DSC–TG analysis of the gels was performed on a Netsch (model STA429) thermal analyser.

3. Results and discussion

3.1 General appearance of the glasses

Crack-free Cu-nanocluster doped silica glasses were obtained after heat-treatments in H_2 and He gas atmospheres. Transparent and uniform ruby-red coloured glasses were resulted when Cu concentrations were 0.05 and 0.1 wt%. Higher Cu concentrations (0.25 and 1 wt%) resulted in red-coloured opaque glasses. The homogeneity of Cu in the densified glasses were verified by comparing the optical density value at 563 nm[3–5] (SP band of Cu nanoclusters) at different positions of the glass block. For this purpose a 0.1 wt% Cu doped glass (densified in H_2 up to 800 °C followed by in He at 980 °C and subsequently ground and polished) of dimensions 20 mm × 10 mm × 0.5 mm was used. The scatter in the optical density value from these different positions was less than 2%, indicating homogeneous distribution of copper nanoclusters in the glass.

3.2 Syneresis liquid

The gels prepared with and without DAMO were aged at room temperature for 6 days under closed conditions. During this period gels underwent shrinkage and the pore liquids were expelled as ‘syneresis liquids’.[17] The amount of copper expelled with the syneresis liquids was analysed by flame atomic absorption spectrometry. These data are presented in Fig. 1. It has been observed that loss of Cu is minimum for a DAMO/Cu ratio of 5 for 0.05, 0.1 and 0.25 wt% Cu series. Thus, 5 mol of DAMO per mol of Cu is required to bond all the copper with the silica matrix in the above series. However for the 1 wt% Cu sample, 1.5–2 mol of DAMO is sufficient to fix all the Cu in the matrix. Moreover, it has also been observed that at a fixed DAMO/Cu mol ratio, the amount of expelled copper decreases with increasing Cu concentration.

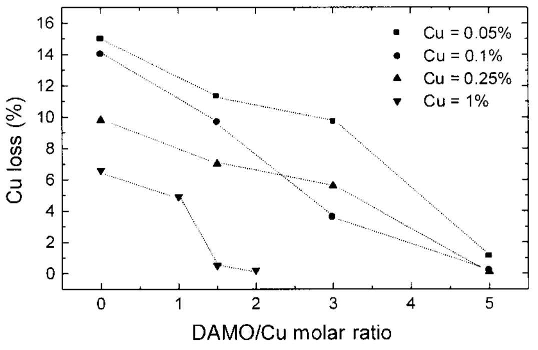


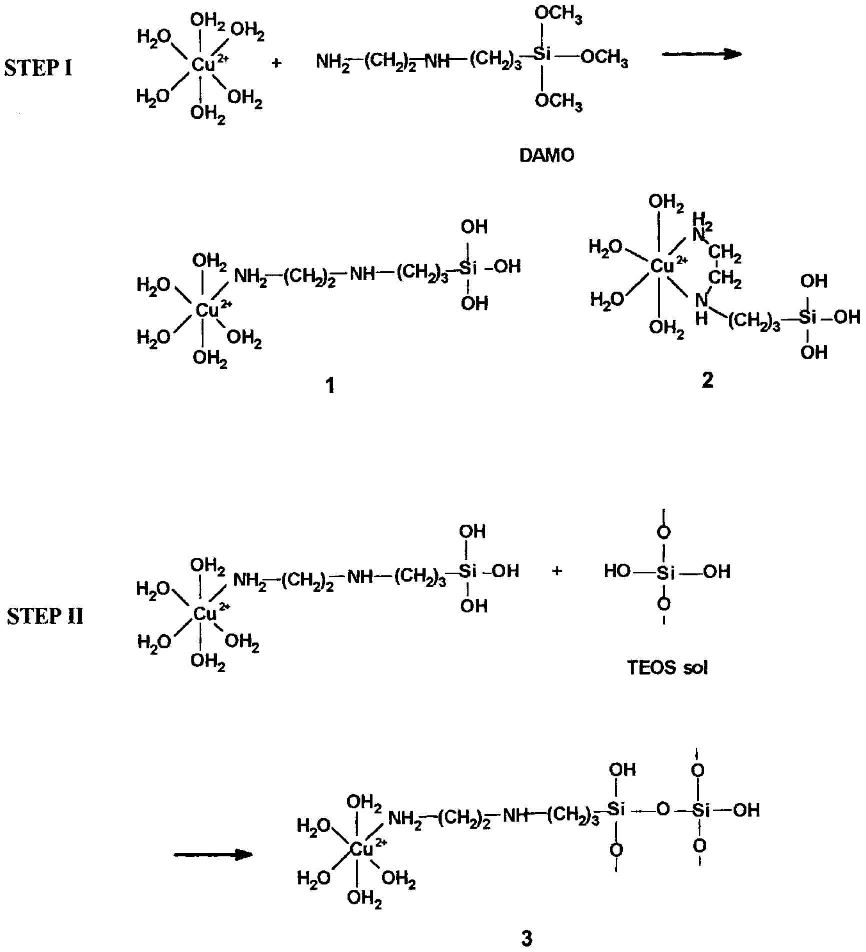
Fig. 1 Percentage of Cu expelled with the syneresis liquid as a function of DAMO/Cu molar ratio for various Cu amounts. The values are calculated with respect to the initial Cu content in the sol. Data points are joined to provide a visual guide.

3.3 Cu–DAMO complexation and cross-linking with the silica backbone

Cu–DAMO complex formation and its fixation in the matrix silica backbone is shown in Scheme 1. As shown in the scheme, the reaction of $[Cu(H_2O)_6]^{2+}$ and DAMO may lead to the formation of two types of Cu–DAMO complexes. Here reaction of only one molecule of DAMO is shown. The bonding of $-NH_2$ groups only with Cu yields a Cu–DAMO complex of type **1**. If both the $-NH_2$ and –NH– groups of DAMO bond with Cu ion a chelate Cu–DAMO complex of type **2** would be obtained. We have noted that for the low concentration series (0.05, 0.1 and 0.25 wt% Cu) only the highest DAMO/Cu mol ratio ($r = 5$) is sufficient to fix all the Cu ions in the matrix. Therefore, we are considering mainly the bonding of $-NH_2$ groups in these cases.[20] If bonding of –NH– groups were also to occur in these cases, a lower amount of DAMO (maximum $r = 3$) could fix all the copper. As a consequence, type **1** Cu–DAMO would be the major reaction product in these low concentration series. By contrast, for 1 wt% Cu, $r = 2$ is sufficient to fix almost all the Cu ions in the matrix. In this case, it is expected that both $-NH_2$ and –NH– groups are taking part in the complexation leading to **2**. This anomaly is due to the change in concentration of Cu in the silica matrix. For the low concentration series, Cu ions are more dilute and there is less scope of bonding of both NH_2 and –NH– groups; whereas Cu ions are relatively more cocentrated in 1 wt% Cu, and bonding of both coordination sites of DAMO is feasible.

It may also be noted here that we have used an ethanol–water solution of copper nitrate and the DAMO solution for the complexation reaction. Under such conditions, the DAMO alkoxy ($Si-OCH_3$) groups would undergo hydrolysis reactions and generate –Si–OH (silanol) groups as shown in **1** and **2**. These silanol groups will form –Si–O–Si– linkages through condensation reactions[21] with the TEOS originated matrix silica as shown in **3** (step II of Scheme 1). The reaction of **1** only is shown in step II. Similarly, silanol groups attached to Cu–DAMO complexes of the type **2** also undergo condensation reactions with the matrix silica. In this way, the DAMO originated Si and TEOS originated Si (matrix) will bond through –O–Si–O–Si– bridging and all Cu ions will be virtually locked in the matrix.

The coordination behaviour of Cu^{2+} ions was studied by optical absorption spectroscopy. Fig. 2(a–c) show the optical absorption spectra of 0.05, 0.1 and 1 wt% series of Cu doped gels (dried at 60 °C) containing different amounts of DAMO. All spectra are normalised to the thickness of the gels. For the 0.05 and 0.1 wt% series a broad absorption band centred at about 760 nm (d–d transition) is observed due to the hydrated Cu^{2+} ion.[22,23] This band gradually shifts to shorter wavelength up to about 600 nm ($r = 5$) and the intensity of the band increases with increasing DAMO concentration. The 0.25 wt% series also showed similar behaviour. The shifting of the band with increasing DAMO indicates increased Cu–amine complex formation.[22,23] This is because the amines produce a stronger ligand field than water, which causes the absorption band to move from the far red to the middle of the red region of the spectrum.[22] The absorption band observed at 600 nm at $r = 5$ for the low concentration (0.05, 0.1 and 0.25 wt%) series indicates that at least four amines are bonded per Cu



Scheme 1 The complexation of $[Cu(H_2O)_6]^{2+}$ and DAMO (step I) and condensation reaction (step II) between the silanols attached to Cu–DAMO and TEOS derived silica.

ion.[22,23] However, for the 1 wt% series the shifting of the peak to 600 nm (Fig. 2c) occurs with a lower amount of DAMO ($r=2$). This clearly indicates that in this case (*i.e.* 1 wt% Cu with $r=2$) the basic coordination chromophore of Cu is similar to that of 0.05/0.1 wt% series with $r=5$. This is possible if both the $-NH_2$ and –NH– groups are bonded with the Cu in the 1 wt% series with $r=2$.

3.4 DSC–TG

1 wt% Cu–99 wt% SiO_2 gel with $r=2$ was analysed by DSC and TG. For a comparative study, 1 wt% Cu–99 wt% SiO_2 without DAMO ($r=0$) and SiO_2 gels containing an equivalent amount of DAMO but without Cu were also analysed. All samples were dried at 60 °C prior to analysis. The DSC–TG results are presented in Fig. 3. The silica gel containing only DAMO shows an endotherm starting from room temperature to about 120 °C due to absorbed water. The corresponding TG also shows weight loss in this temperature range. Further heating leads to a broad exothermic peak at about 250 °C due to the decomposition of DAMO. For gels containing only Cu ($r=0$) only one endothermic peak starting from room temperature to about 120 °C is observed and is due to the loss of absorbed water. The exothermic peak is not seen here because this sample contains no DAMO. For Cu doped gels containing DAMO ($r=2$) the initial endothermic peak is present as in the above samples. On further heating a sharp exothermic peak at 170 °C is observed. The absence of this peak in the undoped samples strongly suggest that this exothermic peak is mainly due to the decomposition of Cu–amine bonds. The corresponding TG shows a small weight loss indicating a partial loss of amines. At this temperature, the sample colour has changed from purple to light bluish-green. After this, decomposition of DAMO results and consequently an exothermic peak at about 250 °C is observed as in silica gel samples containing only DAMO. The evolution of the optical absorption spectra of the above gel with respect to the heat-treatment temperature is shown in Fig. 4. The 60 °C dried sample shows absorption at about 600 nm. This band is shifted to about 675 nm at 170 °C and finally to 750 nm at 350 °C. This shifting is due to the change of coordination geometry around Cu ions from nitrogen donor [Cu–amine] (60 °C) to a mixture of nitrogen–oxygen (170 °C) to oxygen donor (350 °C).

3.5 FTIR

FTIR diffuse reflectance spectra of a 1 wt% Cu–99 wt% SiO_2 gel with $r=2$ was studied with respect to the heat-treatment temperature. The spectra are presented in Fig. 5 and the band assignments are in Table 1. It may be noted here that two sets of spectra are shown in C, D and E. Spectra shown as thinner lines are the corresponding spectra of the samples having no copper but an equivalent amount of DAMO. To show the decomposition of Cu–DAMO complex in the gels, the H–O–H, H–N–H and H–C–H bending vibration regions (1800–1250 cm^{-1}) of A, B and C are expanded and shown in Fig. 6. Curve A (Figs. 5 and 6) shows the 60 °C dried samples (purple in colour). This sample shows a peak at 3672 cm^{-1} due to SiO–H stretching.[24] The peak at 1592 cm^{-1} is due to the bending vibration of NH_2 bonded with Cu ions.[25] Curve B is the spectrum of the 170 °C heated sample (bluish-green). The presence of C–H peaks (1500–1300 cm^{-1}), confirms that the DAMO is still present in the sample. The remarkable feature of this spectrum is the disappearance of 1592 cm^{-1} peak

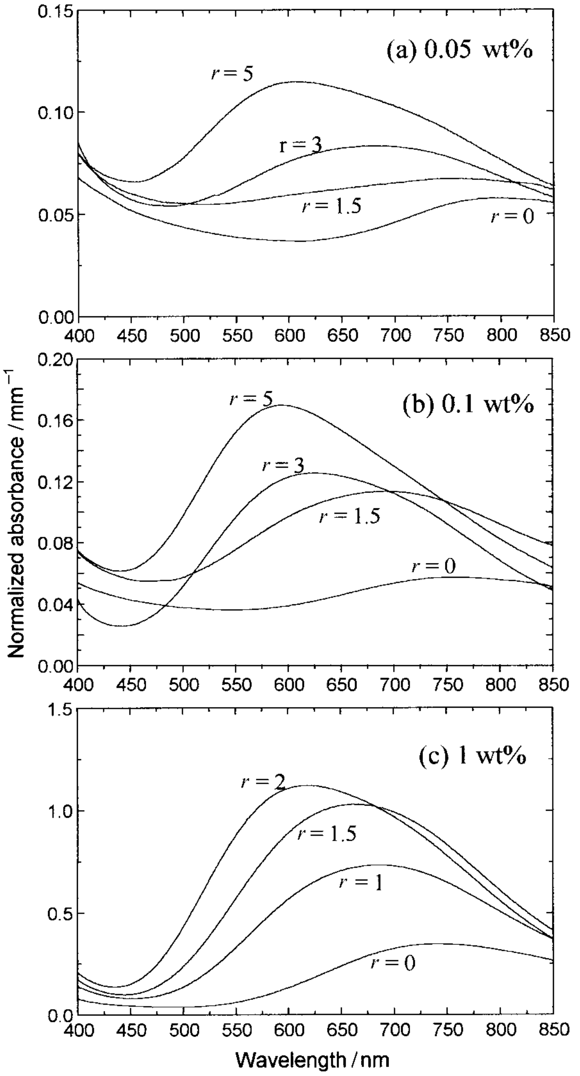


Fig. 2 Optical absorption spectra of 60 °C dried silica gels with a Cu content of 0.05 wt% (a); 0.1 wt% (b) and 1 wt% (c).

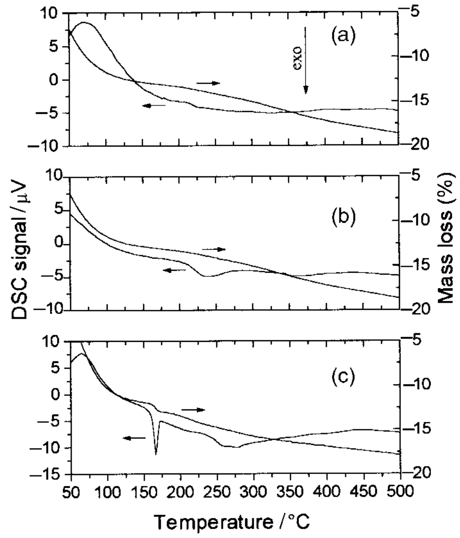


Fig. 3 DSC/TG curves measured on silica gels of differing compositions: (1) gel with 1 wt% Cu without DAMO; (2) gel without Cu but with a DAMO content equivalent to 1 wt% Cu and $r=2$; (3) gel with 1 wt% Cu and DAMO ($r=2$).

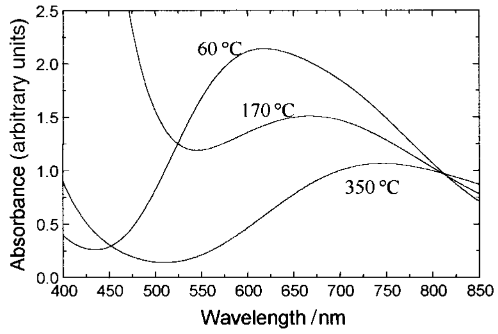


Fig. 4 Evolution of the Cu^{2+} d–d band position with the heat-treatment temperature for a 1 wt% Cu doped silica gel ($r=2$).

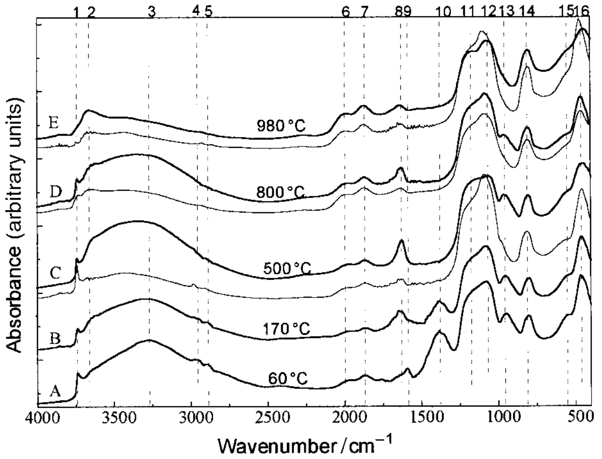


Fig. 5 FTIR diffuse reflectance spectra of 1 wt% Cu–99 wt% SiO_2 gels containing DAMO equivalent to $r=2$ heat-treated at different temperatures: 60 °C/air (curve A); 170 °C/air (curve B); 500 °C/air (curve C); 800 °C/H_2 (curve D) and 980 °C/He (curve E). The spectra (thinner lines) shown under the curves C, D and E are for the corresponding undoped silica gels heat-treated in similar conditions.

Table 1 Assignment of the FTIR peaks shown in Fig. 5

Peak no.	Peak positions/cm^{-1}	Assignment
1	3740	Isolated free ≡SiO–H (silanol) stretching
2	3670	Stretching vibration of H-bonded adjacent silanol groups
3	3600–3000	Stretching vibrations H-bonded silanols with water, N–H
4,5	2970, 2897	C–H stretching
6,7	1977, 1870	Combination mode vibrations of silica
8	1635	H–O–H bending
9	1592	H–N–H bending (bonded with Cu)
10	1500–1300	H–C–H bending
11	1180	Si–O–Si asymmetric stretching (longitudinal optic)
12	1085–1100	Si–O–Si asymmetric stretching (transverse optic)
13	958	Si–OH stretching, Si–O–Cu non-bridging
14	810	Si–O–Si symmetric stretching
15	562	Four-membered siloxane ring vibrations[26]
16	468	Si–O–Si symmetric stretching

indicating the scission of Cu–N (copper–amine) bonds at 170 °C. The NH_2 bending vibration (after dissociation with Cu) is now shifted towards higher wavenumber 1600 cm^{-1} [25] which is however not clearly visible due to the overlap with H–O–H bending (Fig. 6). The sharp exothermic peak observed at 170 °C in DSC also confirms decomposition of Cu–amine bonds. The spectrum of the 500 °C (curve C) heated sample in air shows the absence of organic peaks in the range 1500–1300 cm^{-1} indicating complete decomposition of DAMO. It may be noted here that the intensity of 958 cm^{-1} peak (Si–OH and Si–O–Cu non-bridging vibrations) remains almost unchanged. However, for the corresponding undoped sample, this peak is very weak due to elimination of silanol (Si–OH) groups following condensation reactions. Therefore we conclude that the 958 cm^{-1} peak for the doped sample (curve C) is due to the Si–O non-bridging vibrations arising from Si–O–Cu. Further heat-treatment of this sample to 800 °C in an H_2 atmosphere (curve D) shows weakening of the Si–O–Cu peak due to reduction of Cu^{2+} ions to metallic Cu. It may also be noted here that the silanol peak of the corresponding undoped sample completely vanishes at 800 °C. The reduction of Cu^{2+} is complete when the sample is heated at 800 °C for 2 h or at 900 °C for 1 h in H_2. Spectrum E is that for the sample heated at 800 °C for 2 h in H_2 followed by He up to 980 °C. In this case highest density (2.17 g cm^{-3}) of the silica matrix is achieved. The spectrum (curve E) shows all the usual silica vibrations. However, the Si–O–Si asymmetric vibration appears at 1085 cm^{-1} (lower wavenumber compared to the fully dense silica glass[24]) suggesting the silica matrix is not fully densified. The corresponding undoped sample absorbs at 1102 cm^{-1} for this vibration indicating full densification of silica matrix.[24]

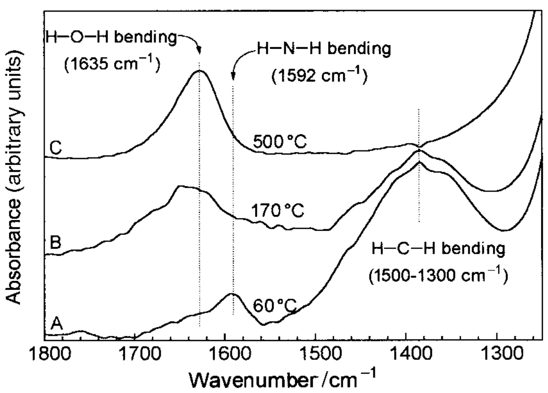


Fig. 6 FTIR spectra showing the H–O–H, H–N–H and H–C–H bending vibration regions of samples A, B and C in Fig. 5.

3.6 Surface area and density

Table 2 shows the BET surface area data of the gels heat-treated at different temperatures up to glass formation. All series show first an increase of surface area up to 500 °C. This is due to elimination of water and organics from the gels resulting in more open surfaces. As a result the surface area values are increased compared to the initially dried samples. A decrease of surface area is observed in all series from 600 °C owing to collapse of pores due to densification. It has been observed that except for the 0.05 wt% series, the surface area of all series are quite high even at 900 °C. At this temperature TEOS derived pure silica gels attain the full density of silica glass.[27] It can be concluded that the presence of Cu in silica retards densification of the silica matrix. The lower surface areas for the 0.05 wt% series at 900 °C is due to the lower amount of Cu present. At 980 °C the surface area of all series drops to 12–20 $m^2\ g^{-1}$. The densification behaviour was further confirmed by density measurements of the 0.1 wt% series. The density values (Table 3) are well corroborated with the surface area data. A slow increase of density up to 900 °C and a sharp increase of density at 980 °C (2.17 g cm^{-3}), close to that of silica glass (2.20 g cm^{-3}) were observed. It may be pointed out here that heat-treatment beyond 900 °C in H_2 causes severe cracking and further densification could not be achieved. Therefore, in all cases samples were heated beyond 900 °C in an He atmosphere.

3.7 XRD characterization

Figs. 7 and 8 show the X-ray diffraction spectra recorded on gels of 0.1 wt% ($r=5$) and 1 wt% ($r=2$) Cu content. For 0.05 wt% Cu the XRD signal of Cu particles could not be detected. In both series increasing the heating temperature results in more intense and sharp diffraction peaks, indicating more effective Cu reduction and growth of particles. It may be noted here that the samples heated at 500 °C in air are amorphous in nature. It is interesting to observe that the presence of crystalline Cu_2O for the 1 wt% sample heated at 600 °C in H_2 (Fig. 8). This result suggests that particle formation occurs through a stepwise process, where Cu^{2+} ions are first reduced to Cu^+ ions, giving rise to Cu_2O particles. Further heat-treatment at higher temperatures results in

Table 2 Evolution of the BET specific surface area[a] with the gel composition and the heat-treatment conditions

Temp./°C (atmosphere)	0.05 wt% series ($r=5$)	0.1 wt% series ($r=5$)	0.25 wt% series ($r=3$)	1 wt% series ($r=2$)
60 (air)	616	702	701	691
500 (air)	627	740	727	727
600 (H_2)	574	541	547	678
700 (H_2)	471	483	484	573
800 (H_2)	388	376	418	452
900 (H_2)	193	330	378	346
980 (He)	14	12	12	20

[a] Experimental error ±1% for surface area values ranging from 702–193 $m^2\ g^{-1}$ and ±5% for surface area values ranging from 12–20 $m^2\ g^{-1}$.

Table 3 Density values of 0.1 wt% Cu–99.9 wt% SiO_2 gels and glasses heat-treated at different temperatures

Temp./°C (atmosphere)	Density/g cm^{-3}
60 (air)	1.40
500 (air)	1.39
700 (H_2)	1.56
800 (H_2)	1.63
900 (H_2)	1.73
980 (He)	2.17

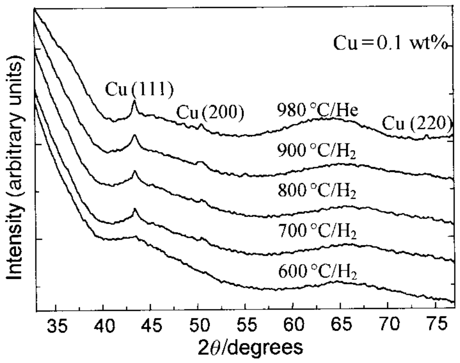


Fig. 7 XRD spectra of 0.1 wt% Cu–99.9 wt% SiO_2 gels ($r=5$) heat-treated at indicated temperatures/atmospheres.

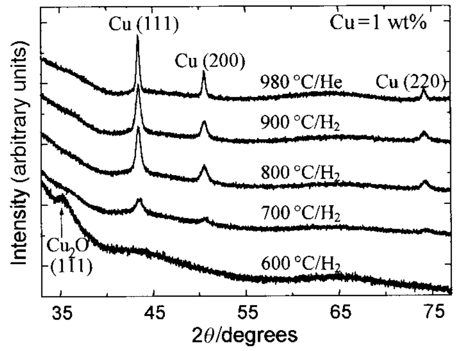


Fig. 8 XRD spectra of 1 wt% Cu–99 wt% SiO_2 gels ($r=2$) heat-treated at indicated temperatures/atmospheres.

Table 4 Evolution of Cu particle size with the heat-treatment temperature

Temperature/°C	1 wt% series	0.1 wt% series
980	28 nm	20 nm
900	17 nm	10 nm
800	16 nm	11 nm
700	9 nm	7 nm

reduction of cuprous oxide, with the formation of Cu particles. The diffraction curves were employed for calculating the mean Cu particle size by fitting the (111) reflection and inserting the FWHM in the Scherrer equation. The results are summarised for both Cu series in Table 4. It is seen that, as expected, increasing the heating temperature results in an increase of the mean particle size. For a given heating temperature the particle size is larger in the 1 wt% series. The size for the 1 wt% series heated at 800 °C is very close to the size found by Nogami *et al.*[13] for a similar Cu content. They reported Cu particle formation after heating in H_2 at 200 °C, while we observe effective particle formation after heating at 700 °C in H_2. As suggested also by FTIR studies (see above), this result can be related with the progressive breaking of bonds between Cu ions and the host matrix. This process delays particle formation, but when most of the Cu ions are released the growth of Cu metal nanoparticles (*via* Cu_2O) can occur.

3.8 Optical characterization

Figs. 9 and 10 show the optical absorption spectra recorded on gels with 0.05 and 0.1 wt% Cu content, respectively. In both the cases $r = 5$ samples were used. The heat-treatments at the indicated temperatures were carried out in an H_2 atmosphere or first in H_2 then in He (980 °C). The measurements could not be carried out on gels with 0.25 and 1 wt% Cu samples due to the extremely intense absorption of such samples. The 0.05 wt% gels show a broad absorption (Fig. 9) at about 580 nm (600 and 700 °C) indicating the presence of Cu nanoclusters. This band intensifies with a blue shifting to 563 nm during heating up to 980 °C. This absorption band (580–563 nm) is due to the excitation of surface plasmon (SP) oscillations[3,4] in the Cu nanoparticles. The corresponding 0.1 wt% series also show similar spectral behaviour. In this case the spectrum of 600 °C samples could not be recorded due to the presence of Cu_2O causing a dark black colour. The evolution of the Cu SP band is useful for studying the growth of Cu particles with the help of the theory of Mie.[28] In both series the increasing intensity of the band is related to the more effective reduction of Cu ions and the consequent particle growth. Heating at temperatures of 700 to 980 °C leads to blue shifting of the SP peak position, which is related to the increase of the particle size. The XRD data also confirmed this. It is interesting that the peak position for the highest heating temperatures is the same for both the 0.05 and 0.1 wt% Cu series, showing that the mean Cu particle size is the same in both cases. The different Cu amount only results in a change of the absorption intensities. The mean particle size deduced from the XRD data was employed as an input parameter for calculating theoretical optical absorption curves using the theory of Mie.[28] Fig. 11 shows a comparison between the theoretical and experimental curves for the sample with 0.1 wt% Cu heated to 800 °C in H_2 for 2 h followed by 980 °C in He. The agreement is good, taking into account that small variations of the matrix refractive index can shift the peak position. In this case the refractive index value of 1.46 for conventional fused silica was used. The agreement shows that the theory of Mie may be effectively used for studying the size of metal particles. Another important information is the amount of reduced Cu. Comparison between the two curves was established by using a theoretical volume fraction of Cu of 1.7×10^{-4}, close to the expected value of 2.5×10^{-4}, calculated by supposing that all Cu has been reduced. This result shows that at such heating temperature indeed all Cu has been reduced and is in the form of nanoparticles.

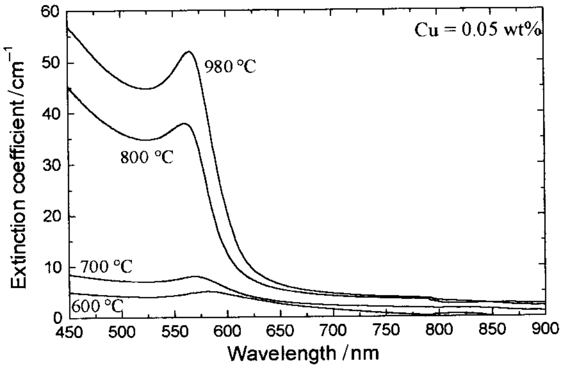


Fig. 9 Optical absorption spectra of 0.05 wt% Cu–99.95 wt% SiO_2 gels ($r = 5$) heat-treated in H_2 up to 800 °C and followed by in He up to 980 °C.

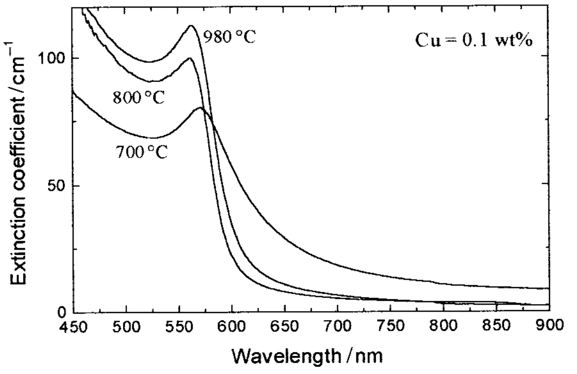


Fig. 10 Optical absorption spectra of 0.1 wt% Cu–99.9 wt% SiO_2 gels ($r = 5$) heat-treated in H_2 up to 800 °C and followed by in He up to 980 °C.

4. Conclusion

Migration of dopant Cu^{2+} ions can be effectively prevented in TEOS derived silica gels using a bifunctional complexing and crosslinking agent, DAMO, at the sol stage. The doped gels, when densified in H_2 up to 800 °C and followed by heating in an He atmosphere up to 980 °C produced Cu metal nanocluster doped silica glasses (Cu-ruby glasses) with Cu concentrations

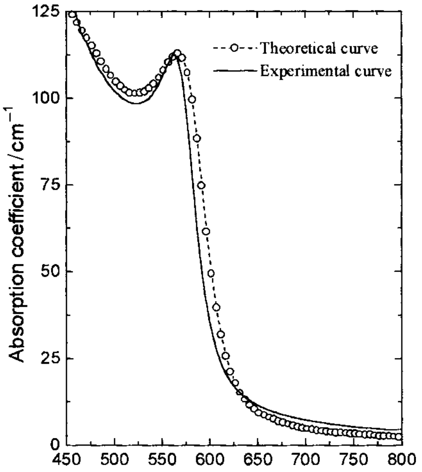


Fig. 11 Optical absorption spectra of 0.1 wt% Cu–99.9 wt% SiO_2 glass heat-treated in H_2 up to 800 °C and followed by in He up to 980 °C and the calculated spectrum based on Mie's theory.

ranging from 0.05 to 1 wt%. This modified sol–gel doping process yielded uniform distribution of Cu nanoclusters in the silica glass matrix, which is essential for any type of optical including nonlinear optical and other applications.

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20 The –NH_2 (primary amine) groups are better ligands than –NH– (secondary amine) groups. Thus bonding of –NH_2 groups with Cu ion is more favourable if only one of the amine groups of DAMO undergoes complexation.
21 It should be mentioned here that the alkoxy groups of DAMO undergo hydrolysis reactions and produce silanols during the complex formation of Cu ions with amine groups of DAMO. Additionally, the silanol groups attached to **1** and **2** may also undergo intramolecular condensation reactions at this stage. However, as the concentration of silica (typically 0.01–0.08 M) in Cu–DAMO solution is low, the probability of intramolecular silanol condensation reactions is less favourable.
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