

## Spectroscopic studies of Cu<sup>2+</sup> ions in sol–gel derived silica matrix

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**Abstract.** The Cu<sup>2+</sup> ion doped silica gel matrices in monolithic shape were prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The absorption, transmittance and fluorescence spectra of the gel matrices heat treated at different temperatures were monitored. The loss of water and hydroxyl group from silica network changes the optical properties of the Cu<sup>2+</sup> ions in the host, noted by the change in colour of monolith and spectral characteristics. The pronounced blue shift observed (700–900 nm to 600–850 nm) for the broad band of the absorption spectra of the samples heated up to 700°C is attributed to the ligand field splitting and partial removal of hydroxyl group from the silica matrices. The results indicate broadband filtering effects of the samples in the wavelength region 400–600 nm. Absorption and fluorescence spectra of the glass matrices heated to 1000°C confirms the conversion of Cu<sup>2+</sup> ion to Cu<sup>+</sup> ion.

**Keywords.** Sol–gel glasses; optical properties; optical materials.

### 1. Introduction

The motivation for sol–gel processing, a relatively new technique for the preparation of glasses is primarily to get potentially high purity and homogeneity and low processing temperatures compared with the traditional glass melting techniques (Hench and John 1990). The primary problem that had to be overcome during drying and aging of the sol–gel materials is cracking due to the large shrinkage that occurs when pore liquids are removed from the gels. For small cross sections such as in powders, coatings or in fibres the drying stresses are small and can be accommodated by the material. One of the best methods used for making sol–gel silica monolith is the hydrolysis and polycondensation of alkoxide precursors followed by aging and drying (Klein 1993). When the pore liquid is removed by thermal evaporation called drying, shrinkage occurs and the monolith is termed as xerogel. The gel is defined as dried when physically absorbed water is completely removed. This occurs in the temperature range 100–200°C. A dried gel still contains large concentration of chemisorbed hydroxyls. Thermal treatment in the range 500–800°C desorbs the hydroxyls resulting in a stabilized gel. Though the porous gel is transformed to a dense glass at 1000°C, micro pores may still be present.

The monoliths processed by sol–gel method allow the incorporation of transition metal ions and rare earth ions

in their matrix. Transition metal ions have been used as colour agents in glass industry along with rare earth for many years (Bever 1987). The rare earth ions colour glass usually to a less degree than metal ions. Their spectra consist of large number of weak bands. Colouring in these glasses occurs due to the atomic transitions in the *d* orbitals of the incorporated metals and due to the formation of metal oxide particles. The absorption bands observed for transition metal ion doped silica matrix are due to the electronic transitions of the 3*d* electrons of the ion. When the transition metal ions are coordinated with other ions, the energy levels of these *d* electrons are split by the electric field of the coordinating ions instead of being degenerate as in free ions. Host matrices embedded with copper have been produced to study their properties as catalytic materials, tunable visible light solid-state lasers and coloured coatings (Ikoma *et al* 1990; De Sanctis *et al* 1990). In a sol of the system CuO–SiO<sub>2</sub> copper enters in the divalent state and the ratio (Cu<sup>2+</sup> + Cu<sup>+</sup>)/Cu<sup>2+</sup> in the gel glasses is close to unity while in melt glass it lies between 0.2 and 0.3 (Demskaya and Pivovarov 1990). Since Cu<sup>2+</sup> is smaller and highly charged it interacts more strongly with water molecules as a result Cu<sup>2+</sup> is more stable in aqueous solution than Cu<sup>+</sup> (Conry and Karlin 1994). The optical properties of Cu doped silica gel in the form of xerogel coatings and powders have been studied extensively (Jones *et al* 1996; Perez-Robles *et al* 1999). The structural evolutions of copper doped porous silica gel treated at different temperatures were also studied (De Sousa *et al* 2000). So far no reports have been seen on the spectroscopic studies of Cu<sup>2+</sup> doped

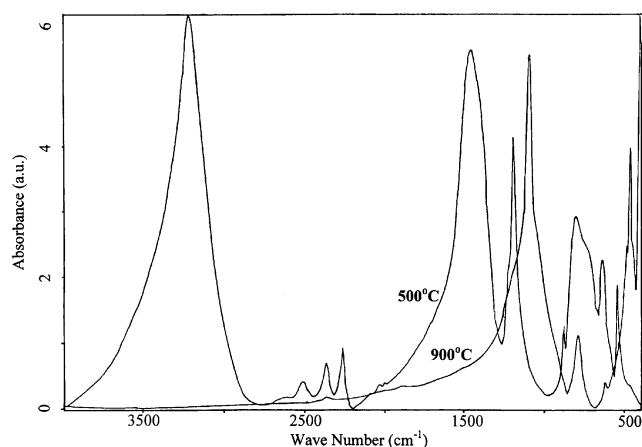
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monoliths heated at high temperatures. The present work aims at understanding the effect of doping copper in the gel structure and heat treatment on the spectroscopic properties of  $\text{Cu}^{2+}$  ion in the matrices.

## 2. Experimental

The samples were prepared by sol-gel method (Hench and John 1990; Perez-Robles *et al* 1999) using tetraethyl orthosilicate (TEOS) hydrolyzed with  $\text{HNO}_3$ , acidified water in molar ratio of  $\text{TEOS} : \text{H}_2\text{O} : \text{HNO}_3 = 1 : 12 : 0.01$ . The required amount of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was added to the solution such that the metal oxide concentrations of the final product were 0.5, 1 and 2 wt% (samples A, B and C, respectively). A homogeneous solution of all components was obtained after mixing them for 15 min using a magnetic stirrer. The final pH value of all the

samples was found to be 3. The resultant solution was then poured into polypropylene container. It was sealed and kept at room temperature for 30 days to form gel monoliths. The gel samples were heated to  $60^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $700^\circ\text{C}$  and  $1000^\circ\text{C}$  at a slow heating rate in a programmable furnace. After each stage the absorption spectra and transmittance spectra of the samples were recorded including the reference sample. Care was taken to irradiate the sample portion having the same thickness and hence the same path length, for glass samples at different temperatures. Fluorescence spectra of samples heated to  $1000^\circ\text{C}$  were also recorded. The absorption and emission spectra were recorded on UV-2401PC Shimadzu spectrophotometer and RF 5301PC spectrofluorophotometer, respectively. The IR spectra of the samples were measured by using Nicolet AVATAR 360 ESP FTIR spectrometer. TEM micrographs were taken using Hitachi H-600 electron microscope.

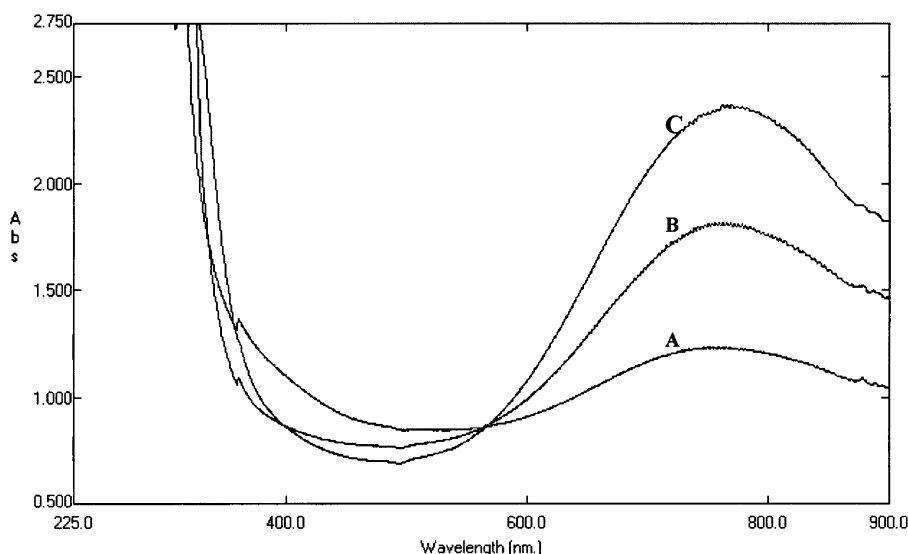


**Figure 1.** FTIR spectra of  $\text{Cu}^{2+}$  doped silica gel heat treated at two different temperatures.

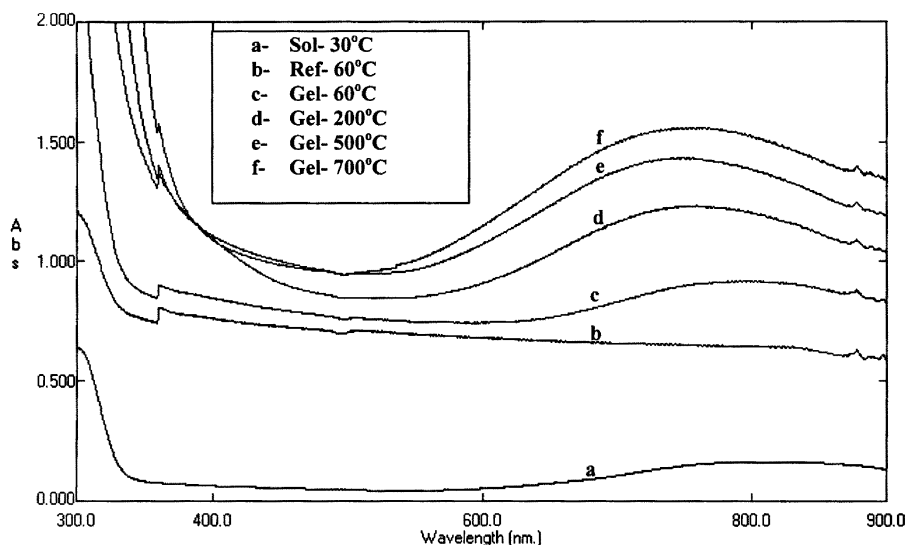
## 3. Results and discussion

### 3.1 Physical properties

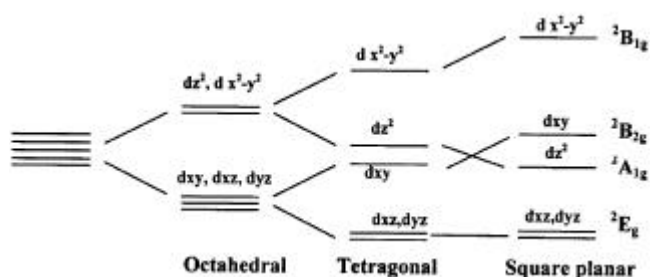
After 30 days all monolithic samples were found to be light blue in colour. The change in volume at  $30^\circ\text{C}$  from solution to gel was  $1/6$  of its initial volume and average density was 1.3. When heated to  $60^\circ\text{C}$  no change in colour was observed but mass changed to  $1/3$  of its initial mass and density increased. Samples heated to  $200^\circ\text{C}$  at a rate of  $6^\circ\text{C}/\text{h}$  showed a colour change to dark blue. The change in size and density was small. The water molecules present in the sample might have been lost at  $200^\circ\text{C}$ . Samples heated to  $500^\circ\text{C}$  and  $700^\circ\text{C}$  at a rate of  $20^\circ\text{C}/\text{h}$  showed no change in colour but a little change in size. All monoliths heated to  $1000^\circ\text{C}$  at a rate of  $50^\circ\text{C}/\text{h}$  showed a



**Figure 2.** Absorption spectra of samples A, B and C heated to  $200^\circ\text{C}$ .



**Figure 3.** Absorption spectra of sample A (0.5 wt%) in solution and heated at different temperatures.

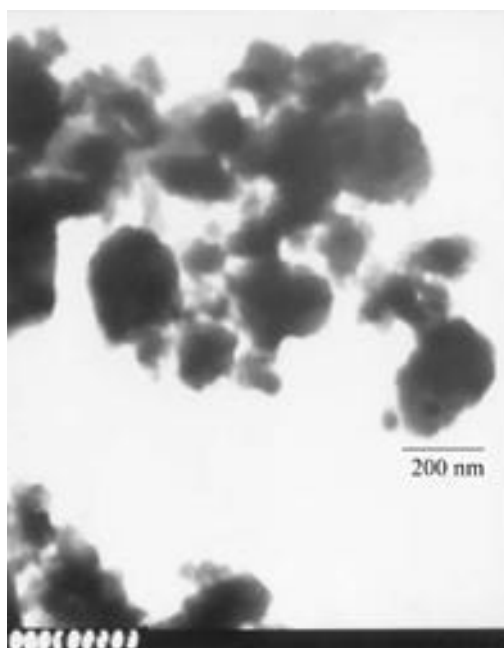


**Figure 4.** Energy level diagram for  $d^9 \text{Cu}^{2+}$  as a free ion in octahedral, tetragonal and square planar coordination.

change in colour and monoliths cracked to small pieces. The sample A changed to dark yellow, sample B to gray and sample C to brown. Molecular water present in the gel can be removed around 200°C. However, hydroxyl group present can be removed only in the range of temperature 800–1000°C. The FTIR spectra of sample B heated to 500°C and 900°C are shown in figure 1. By following the procedure of Pope *et al* (1988), the OH content was evaluated to be ~5000 ppm (500°C) and 2000 ppm (900°C). The cracks observed in the monoliths may be due to the removal of hydroxyl group and the closure of pores with trap water and organic residues (De Sousa *et al* 1999).

### 3.2 Optical properties

From the recorded spectra it is observed that all doped gel samples show an absorption band with a peak around 780 nm which clearly indicates the presence of  $\text{Cu}^{2+}$  ions in the gel matrix (Bever 1987). The absorption intensity also increases for high concentration. This is due to the



**Figure 5.** TEM micrograph of  $\text{Cu}^{2+}$  doped sol-gel silica glass.

presence of more  $\text{Cu}^{2+}$  ions/unit volume. Figure 2 shows the absorption spectra of different samples heated to 200°C and figure 3 shows the absorption spectra of sample A for different temperatures 30°C (sol), 60°C, 200°C, 500°C and 700°C. The broad absorption peak shifts towards shorter wavelength with increase of temperature.

The absorption spectra of the samples can be analysed by invoking the familiar single energy level diagram of  $\text{Cu}^{2+}$  ion (Jones *et al* 1996) and is shown in figure 4. It is

known that the diluted  $\text{Cu}^{2+}$  ions inside glass matrix exhibit a broad optical absorption band around 780 nm, assigned to the  ${}^2E_g-{}^2B_{1g}$  transition due to Jahn-Teller splitting of  $d$  levels of  $\text{Cu}^{2+}$  ions in a ligand field. The broad absorption band was observed in the NIR region for samples heated from 60–700°C, the peak wavelength shifted from 790–746 nm or the broadband shifted from the range (700–900 nm) to (600–850 nm), i.e. high-energy edge of red absorption shifted from 700–600 nm. There are three possible  $d-d$  electronic absorption transitions as per the diagram shown in figure 4. The broadening of absorption band around 780 nm observed is attributed to the three electronic transitions in  $d$  orbitals

corresponding to  ${}^2E_g-{}^2B_{1g}$ ,  ${}^2A_{1g}-{}^2B_{1g}$  and  ${}^2B_{2g}-{}^2B_{1g}$ . Perez-Robles *et al* (1999) suggested that the broad absorption around 750 nm observed in  $\text{Cu}^{2+}$  xerogel are due to the presence of  $\text{Cu}^{2+}$  ions in the interstitial positions in silica matrices. The shifting of broad absorption to low wavelength also shows that as temperature increases removal of water molecules and shrinkage increased the ligand field. Impurity water in oxides in the form of hydroxyl group produces absorption band in the near infrared region (Bever 1987). Here as the temperature increased to 700°C the absorption peak shifts towards shorter wavelength which indicates the partial removal of hydroxyl group.

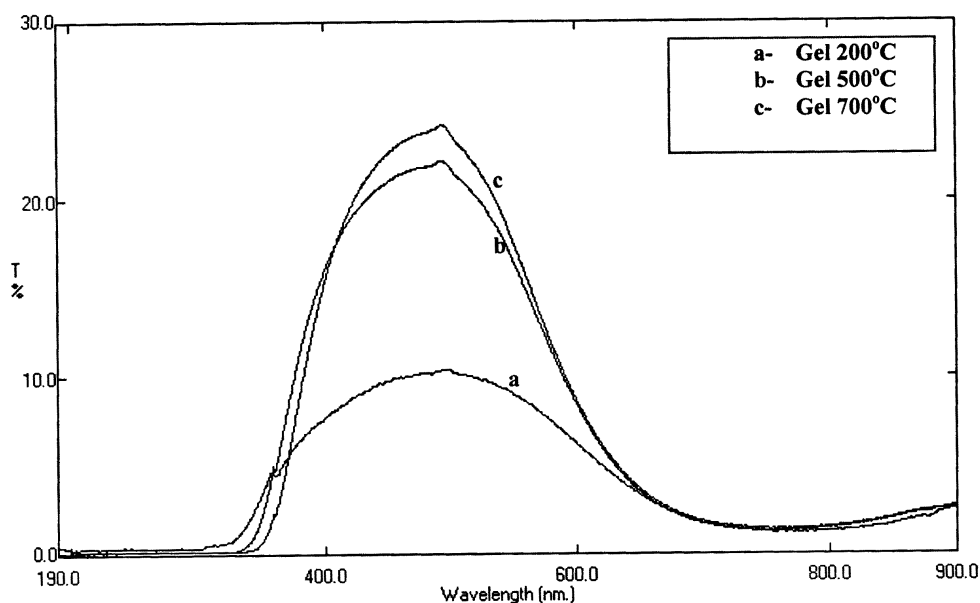


Figure 6. Transmittance spectra of sample B (1 wt%) heated to different temperatures.

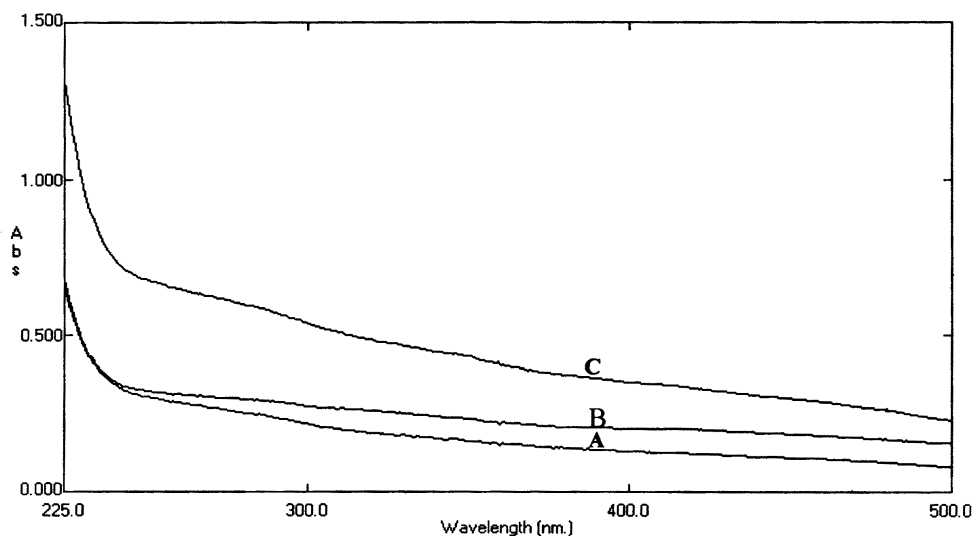
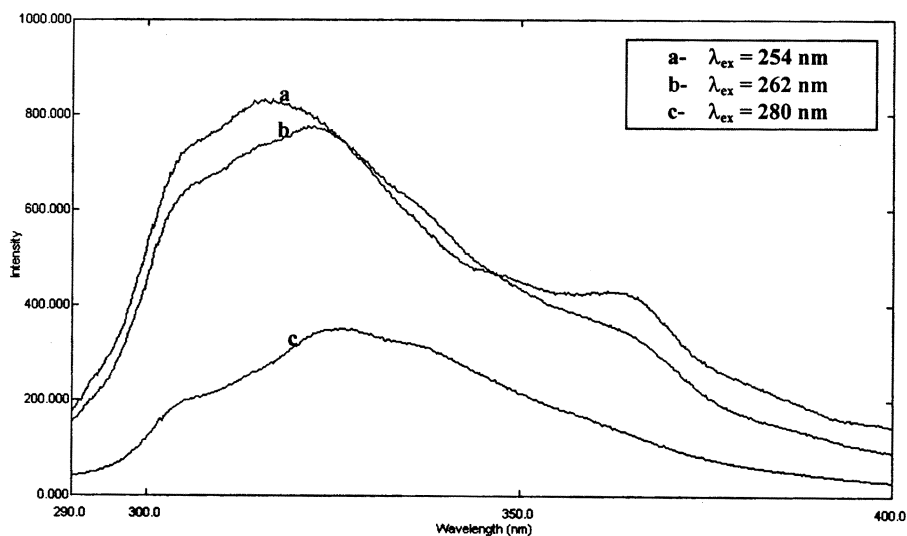


Figure 7. Absorption spectra of samples A, B and C heated to 1000°C.



**Figure 8.** Emission spectra of sample B heated at 1000°C, excited with different wavelengths.

Perez-Robles *et al* (1999) and Jones *et al* (1996) observed an absorption band in the blue region around 400 nm, which was explained in terms of CuO colloidal particles present in the gel matrix. It is surprising to note that in our samples we have not observed any absorption bands around 400 nm, which may be due to the low concentration of  $\text{Cu}^{2+}$  ions and the low pH value in the present samples (Scherer 1987). However, one cannot completely rule out the formation of colloidal particles. The TEM micrograph of dried sample B shown in figure 5, confirms the formation of colloidal particles of average size  $200 \times 180 \text{ nm}^2$ . However, the absorption edge observed in the UV region around 350 nm for Cu doped samples gradually shifts towards 400 nm when the samples were heated up to 700°C. The undoped reference sample and sample A in solution showed the absorption edge around 300 nm. The shifting of absorption edge can be explained as charge transfer between  $\text{Cu}^{2+}$  metals and ligands of the glass matrix.

Figure 6 is a representation of transmittance spectra of sample B heated at different temperatures. The blue colour of the gel samples heated up to 700°C can be explained in terms of the transmittance spectra, which show maximum transmittance in the range 400–600 nm. Because of high purity and low water content these glasses have broad transmission. The present observations indicate that these samples show broad wavelength filtering effect in the region 400–600 nm. It may be noted that shrinkage, size effects and surface morphology might have affected in the peak intensity values for the absorbance and transmittance spectra.

As heat treatment temperature increased to 1000°C the powdered samples showed absorption spectra similar to that of  $\text{Cu}^+$  (figure 7). The broad absorption around 780 nm was completely removed for all the samples.

From this observation we can infer that at 1000°C,  $\text{Cu}^{2+}$  ions may be converted to  $\text{Cu}^+$  ions or  $\text{Cu}_2\text{O}$ .  $\text{Cu}^+$  oxide is more stable than  $\text{Cu}^{2+}$  oxides. Thus the reaction of copper metal ion and oxygen initially yields CuO, which is converted to  $\text{Cu}_2\text{O}$  during longer reaction time or at higher temperature (Sharpe 1981; Conry and Karlin 1994). The emission spectra of powdered samples heated to 1000°C, for different excitation wavelengths are shown in figure 8. The shift of emission peak with excitation wavelength gives substantial support to the presence of  $\text{Cu}^+$  in glass matrices heated to 1000°C (Gan Fuxi 1992).

#### 4. Conclusions

We have studied copper doped sol-gel derived silica matrices in the form of monoliths with different concentrations. Each sample was heat treated to 60°C, 200°C, 500°C, 700°C and 1000°C and spectroscopic properties were investigated. From the absorption studies the incorporation of  $\text{Cu}^{2+}$  ion in the matrix up to 700°C was confirmed. The broadband absorption of  $\text{Cu}^{2+}$  ions around 780 nm was due to the ligand field splitting of  $d$  levels. The interstitial  $\text{Cu}^{2+}$  ions and hydroxyl group in the gel matrix contributed to the broadband absorption. The partial removal of hydroxyl group was confirmed by the shifting of broadband to the high-energy side. FTIR measurements confirm the removal of hydroxyl group from the samples to a large extent in the temperature range 800–1000°C. The TEM image confirms the formation of colloidal particles of size  $\sim 200 \times 180 \text{ nm}^2$ . The transmittance spectra of high temperature treated Cu doped silica matrices indicate the broad band filtering effect. The absorption and fluorescence spectral studies of gel matrices heated to 1000°C confirm the removal

of  $\text{Cu}^{2+}$  ions from the matrices and conversion of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ .

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### References

- Bever B Michel 1987 *Encyclopedia of material sciences and engineering: color and optical absorption of glasses* (New York: Pergamon Press) Vol. 1, p. 731
- Conry R Rebecca and Karlin D Kenneth 1994 *Encyclopedia of inorganic chemistry* (ed.) R Bruce King (England: John Wiley & Sons) Vol. 2, p. 829
- De Sousa E M B, Wellington F de Magalhaes and Mohallem N D S 1999 *J. Phys. Chem. Solids* **60** 211
- De Sousa E M B, Porto A O, Schilling P J, Alves M C M and Mohallem N D S 2000 *J. Phys. Chem. Solids* **61** 853
- Demskaya E L and Pivovarov S S 1990 *Fizika I Khimiya Stekla* **16** 605
- DeSanctis O, Gomez L, Pollegri N, Maragofsky A, Curan A and Parodi C 1990 *J. Non-Cryst. Solids* **121** 338
- Gan Fuxi 1992 *Optical and spectroscopic properties of glass* (Shanghai: Shanghai Scientific and Technical Publishers) p. 159
- Hench L Larry and John K West 1990 *Chem. Rev.* **90** 33
- Ikoma K, Kawakita S and Yokio H 1990 *J. Non-Cryst. Solids* **122** 183
- Jones S M, Friberg S E and Farrington H C 1996 *Phys. Chem. Glasses* **37** 111
- Klein C Lisa 1993 *Ann. Rev. Mater. Sci.* **23** 437
- Perez-Robles J F, Garcia-Rodriguez F J, Yanez-Limon J M, Espinoza-Beltrain F J, Vorobiev Y V and Gonzalez-Hernandez J 1999 *J. Phys. Chem. Solids* **60** 1729
- Pope J A Edward and Mackenzie J D 1988 *J. Non-Cryst. Solids* **106** 236
- Scherer W George 1987 *J. Non-Cryst. Solids* **87** 199
- Sharpe G Alan 1981 *Inorganic chemistry* (England: ELBS Longman) p. 470