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# The Preparation of CdS Particles in Silica Glasses by a Sol–Gel Method

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**The sol–gel process has been successfully applied to the preparation of a small-particle-size CdS-doped silica matrix with a significant quantum size effect. Transparent and colorless gels were prepared through the hydrolysis of a complex solution of $Si(OC_2H_5)_4$, $(CH_3)_2SO$, and $Cd(CH_3COO)_2 \cdot 2H_2O$. These gels were heated at 350, 500, 750, and 1000°C to form fine, hexagonal, CdS-microcrystal-doped glasses. The thermal treatments of samples were established by TDA/TGA analysis. Structural evolution of alkoxide silica during densification was followed by infrared spectroscopy. Samples were characterized using X-ray diffraction. The absorption spectra have also been measured and indicate the potential application of this material in optical devices. A simple quantum mechanical model has been used to calculate the particle size from the absorption onset measured for CdS in the $SiO_2$ matrix. The result is interpreted in terms of a quantum confinement effect of small crystal size.**

## INTRODUCTION

The effects of CdS precipitated in silicate glasses on optical properties are well known (1). The formation of CdS and CdS/CdSe in glasses can give rise to luminiscent glasses after thermal development of color centers (2). On the other hand, the spectral transmission of glasses containing Se, CdS, and Zn is modified by the presence of $Zn_XCd_{1-x}Se$ particles (3). Furthermore, these glasses can be interesting in nonlinear optics (4).

The preparation of CdS-doped glasses is difficult to achieve by conventional melting techniques because only a few crystallites of CdS are thermally developed from supersaturated melt-quenched silicate glasses. In fact, previous research carried out by melting and quenching from the CdS–$SiO_2$ system have produced glasses with very low sulfur contents (5).

The sol–gel method has been proposed by different authors because it is a low-temperature process (6), but $H_2S$ is used as the sulfur source. The synthesis of these glasses has many problems due to sulfur oxidation when the samples stay in a open atmosphere (7). The aim of this research has been to obtain a glass in which CdS is effectively included in a $SiO_2$ matrix by a sol–gel process, using dimethyl sulfoxide (DMSO) as the sulfur source, in order to avoid the problems caused by the use of $H_2S$ and its toxicity.

The optical absorption edge is blue-shifted by ~0.2 eV compared to the bulk absorption value of CdS crystals (6).

As shown in (8), the band gap of a semiconductor is, by definition, the energy necessary to create an electron and a hole that are at rest with respect to the lattice and far enough apart to make their Coulombic attraction negligible. If one carrier approaches the other, they may form a bound state (Wannier exciton), approximately described by a hydrogenic Hamiltonian. The confined Wannier exciton Hamiltonian is used in the Schroedinger equation for the crystallite excited state. An approximate solution can be obtained by taking the solution for the first excited state of the particle in a box problem when assuming that the electron and hole are uncorrelated. In spherical coordinates, the energy of the first excited state is

$$\Delta E = \frac{\pi^2\hbar^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} \qquad [1]$$

where $m_h$ and $m_e$ are the effective masses of hole and electron, respectively, and $R$ is the radius of CdS.

This energy $\Delta E$ can be determined by substituting the experimentally determined absorption onset in

$$\Delta E = E_g(R) - E_g(\infty). \qquad [2]$$

λg is obtained from the intersection of the tangent with the wavelength axis in the absorption spectrum. Thus,

$$\Delta E\, R^2 = 2.44 \times 10^{-18} - 4.53 \times 10^{-17} R. \qquad [3]$$

## EXPERIMENTAL

Silica samples of nominal composition 100 wt % $SiO_2$ and 4 wt% CdS in the CdS–$SiO_2$ system were prepared by the hydrolysis of $Si(OC_2H_5)_4$ (TEOS) and

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$Cd(CH_3COO)_2 \cdot 2H_2O$ in DMSO, which acts as a solvent and a source of sulfur at the same time. The experimental procedure carried out can be seen in Fig. 1.

The reagents were commercially supplied and used without further purification. The quantities used to prepare 5 g of dry gels are given in Table 1.

TEOS was previously homogenized in a solution of 3 ml $H_2O$ and 25 ml of DMSO, until a single phase was obtained. The calculated amount of $Cd(CH_3COO)_2 \cdot 2H_2O$ was added to 25 ml of DMSO. This solution was stirred at room temperature until the salt was totally dissolved. Then, both solutions were mixed and refluxed at 100°C until gelation was attained. This took place in approximately 48 hr; transparent and colorless homogeneous gels were obtained.

In order to design the firing treatment, thermal (DTA) and thermal gravimetric (TGA) analysis were performed (Perkin–Elmer Model DTA 1700 instrument) in two steps: First, at temperatures between 50 and 350°C at a heating rate of 10°C/min in air and under $N_2$, and second, at temperatures between 50 and 1000°C at a heating rate of 10°C/min under a nitrogen atmosphere.

From the results of DTA/TGA, the dry gels were thermally treated up to 350°C at a heating rate of 10°C/min in a dry air atmosphere and they were retained at this temperature for 30 min. Additional heat treatments have been carried out at 350, 500, 750, and 1000°C under nitrogen at a heating rate of 10°C/min, where each temperature was maintained for 30 min. The calcination processes were performed in a Model CTF 15/75 carbolite furnace.

After firing, all samples showed a yellow coloration but when temperatures were 750 and 1000°C a loss of yellow intensity was observed; thus the experiments were performed in samples fired at 350 and 500°C.

X-ray diffraction (XRD) patterns of the samples were measured on a Rigaku D-max/B system with rotatory anode dispositive using monochromated Cu*Kα* radiation at 40 kw to 100 mA in the range $2\theta = 25°–50°$ in 0.04° steps and counting for 60 sec.

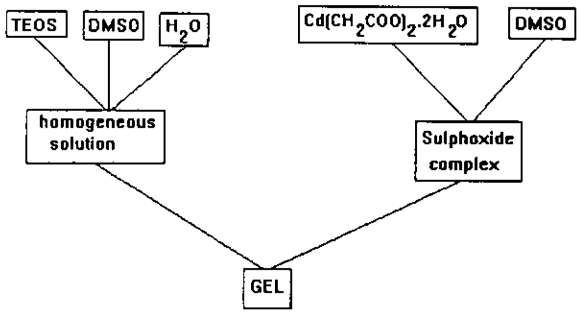

FIG. 1. Schematic representation of the sol–gel process employed.

**TABLE 1**
**Sample Composition**

| Composition | TEOS[a] | $H_2O$[a] | DMSO[a] | $Cd(ac)_2 \cdot 2H_2O$[a] |
|---|---|---|---|---|
| 100% $SiO_2$ | 0.08 | 0.15 | 0.7 | — |
| 4% CdS–96% $SiO_2$ | 0.083 | 0.15 | 0.7 | $1 \times 10^{-3}$ |

[a] In moles.

IR analysis were carried out in the 200 to 7000 $cm^{-1}$ range with a Perkin–Elmer 2000 FT-IR spectrometer, in order to study the evolution of the gelation processes.

The surface area of the 4% CdS–96% $SiO_2$ fired at 350 and 500°C was measured in liquid $N_2$ using a Micromeritics Instrumental (ASAP 2000).

Visible absorption spectra of the ~2 mm thick samples were measured on a Perkin-Elmer Lambda 19 UV/VIS/NIR Spectrometer in the range 400–500 nm.

## RESULTS AND DISCUSSION

Sulfoxides have an ambidentate character in which either the oxygen or the sulfur atom may coordinate to a metal ion. In our system two possible interactions may take place (9, 10). In one, $Cd^{2+}$ links to S and in the other $Si^{4+}$ links to $O^{2-}$ in terms of Pearson's hard and soft acids and bases (11). There are examples in the literature in

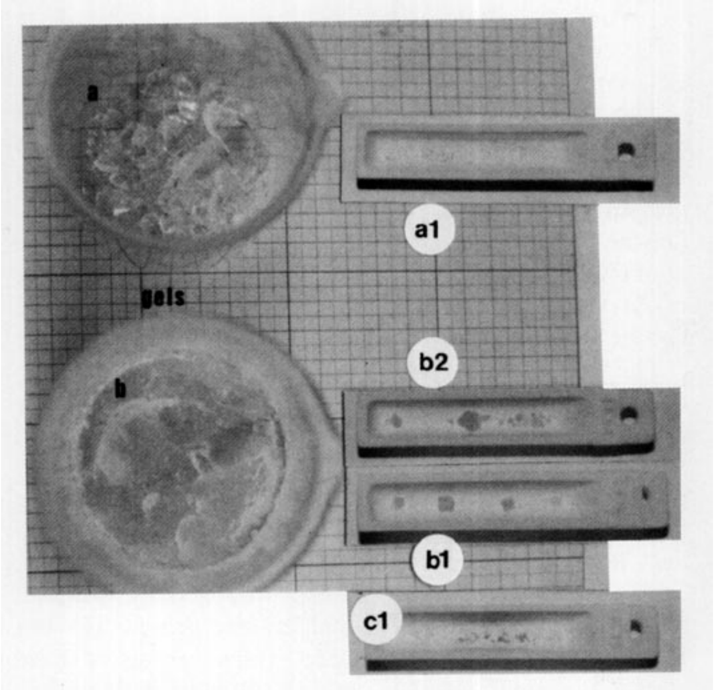

FIG. 2. Physical aspects of gels and fired samples obtained in this process, (a) 100% $SiO_2$ greenbody; (a1) 100% $SiO_2$ at 1000°C; (b) 4% CdS–96% $SiO_2$ greenbody; (b1) 4% CdS–96% $SiO_2$ at 350°C; (b2) 4% CdS–96% $SiO_2$ at 1000°C; (c1) 100% CdS at 1000°C.

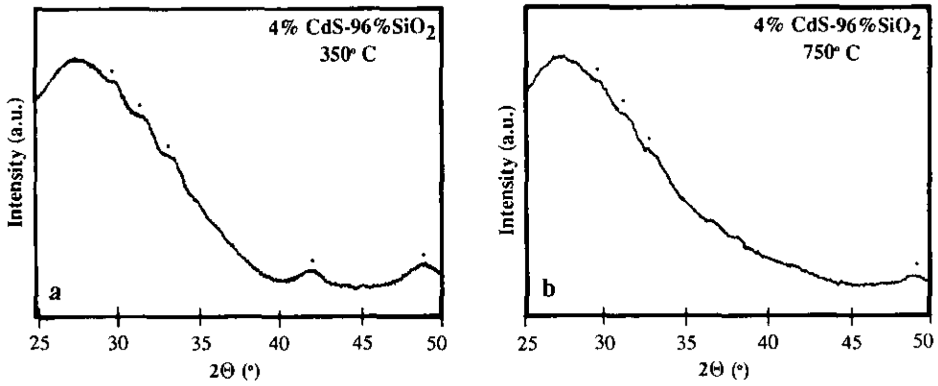

FIG. 3. XRD spectra of 4% CdS–96% SiO$_2$ sample at (a) 350 and (b) 500°C.

which dimethyl sulfoxide acts as a good coordination solvent because of its high polarity, as it tends to strongly coordinate to cations (11). These facts could explain the initial formation of a complex of Cd$^{2+}$ ions with DMSO that decomposes when the temperature increases, resulting in the formation of CdS particles, which are incorporated into the silica matrix.

Gels obtained by this process were large dense blocks (Fig. 2). When the gels were fired, a yellow coloration appeared in the samples with Cd$^{2+}$ that was observed even at 1000°C, although its intensity was less. This fact should be due to the formation of CdS particles that are incorporated into the SiO$_2$ matrix thus avoiding its evaporation and oxidation.

Figure 3 shows the XRD patterns of a 4% CdS–98% SiO$_2$ sample heated at 350 and 750°C. Both samples exhibit the typical amorphous halo and broad peaks at $2\Theta = 29.5°$, 31.2°, 33°, and 49°, indicating the precipitation of very fine, hexagonal, wurtzite CdS crystals.

Figure 4 shows the IR spectra of 100% SiO$_2$ and 4% CdS–96% SiO$_2$ greenbody are shown. The assignments of the infrared absorption peaks are summarized in Table 2 (12). The greenbody of the 100% SiO$_2$ sample shows an O–Si–O bending mode at 470 cm$^{-1}$ and a symmetric Si–O–Si stretching at 793 cm$^{-1}$. The feature at 947 cm$^{-1}$ is due to Si–ethoxide stretching. The strong phonon bands centered at 1075 and 1150 cm$^{-1}$ are from an antisymmetric Si–O–Si siloxane stretching. Deformation vibration and stretching of C–H give rise to the features at 1400 and 3000 cm$^{-1}$, respectively. The absorption at 1620 cm$^{-1}$ comes from the bending of molecular water. SiO$_2$ overtones are found at 1640 and 1690 cm$^{-1}$. Hydrogen bonding between adsorbed species and surface species results in broad bands ranging from 3200 to 3550 cm$^{-1}$ for the OH stretching features. This range overlapped with molecularly absorbed water, which has strong adsorption features between 3400 and 3500 cm$^{-1}$. Free silanol groups (Si–OH) give a sharp OH absorption feature at 3750 cm$^{-1}$. The greenbody IR spectrum of the 4% CdS–96% SiO$_2$ sample is almost identical to that of the 100% SiO$_2$ sample.

When the 100% SiO$_2$ and the 4% CdS–96% SiO$_2$ sam-

TABLE 2
Assignment of Bands in Spectra of Samples 100% SiO$_2$ and 4% CdS–96% SiO$_2$

| | SiO$_2$ | | | | 4% CdS–96% SiO$_2$ | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\nu$(cm$^{-1}$) | Raw | 350°C | 500°C | 750°C | Raw | 350°C | 500°C | 750°C | Assignment (12) |
| 3750 | x | x | x | x | x | x | x | x | Free surface-SiOH stretching |
| 3540 | x | x | x | x | x | x | x | x | H-bonded-SiOH stretching |
| 3400–3500 | x | x | x | x | x | x | x | x | H-bonded H$_2$O<br>H-bonded OH vibration of alcohol |
| 1640 | x | x | x | x | x | x | x | x | SiO$_2$ overtone |
| 1400 | x | x | | | x | x | x | x | C–H deformation vibration |
| 1150 | x | x | x | x | x | x | x | x | Antisymetric Si–O–Si stretching |
| 1075 | x | x | x | x | x | x | x | x | Antisymetric Si–O–Si stretching |
| 946 | x | x | x | x | x | x | x | x | Si–OC$_2$H$_5$ stretching |
| 793 | x | x | x | x | x | x | x | x | Symmetric Si–O–Si stretching |
| 450 | x | x | x | x | x | x | x | x | O–Si–O bending |

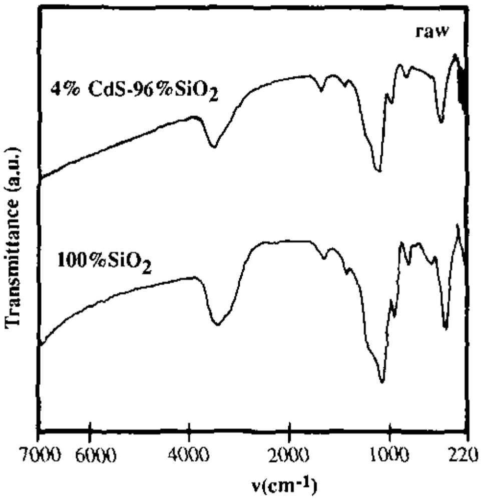

FIG. 4. IR spectra of $SiO_2$ and 4% CdS–96% $SiO_2$ greenbody.

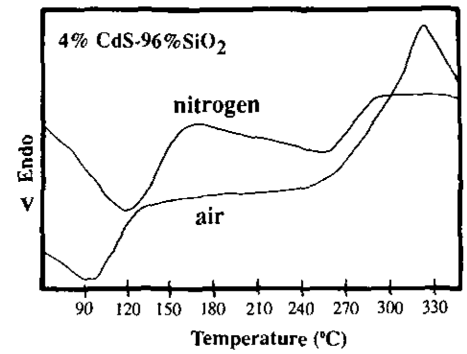

FIG. 6. DTA results of 4% CdS–96% $SiO_2$ in 50 to 350°C in air and in a nitrogen atmosphere.

ples were fired, the C–H bending feature at 1490 $cm^{-1}$ diminished and the Si–O–Si phonon band and overtone became more intense, perhaps due to a greater consolidation of the silica backbone in samples after thermal treatments. Figure 5 shows these observations for samples fired at 500°C.

In order to confirm the results of IR spectra about the densification of $SiO_2$ gels, the surface are (BET) was measured in gels with CdS and the values were less than 0.2 $m^2/g$.

Figure 6 shows the DTA results for the 4% CdS–96% $SiO_2$ sample in air and in a nitrogen atmosphere in the temperature range between 50 and 350°C. A sharp exothermic peak appears for the sample in air that is not observed for the sample in the $N_2$ atmosphere. Thus we fired in air up to 350°C and above this temperature in $N_2$, to avoid sulfur oxidation. The DTA-TGA results in the 50 to 1000°C temperature range under a nitrogen atmosphere are given in Fig. 7 for the 100% $SiO_2$ and 4% CdS–96% $SiO_2$ samples. In Fig. 7a two endothermic peaks can be observed between 100 and 300°C, corresponding to the loss of solvents ($H_2O$ and DMSO) and to the loss of the DMSO link to Si ions, respectively. From Fig. 7b, the same two endothermic peaks can be inferred, but now the second peak is stronger, which is likely due to the loss of the DMSO link to Cd ions. The DTA results are in agreement with the TG measurements (Fig. 7), in which a great loss of weight is observed in the two samples.

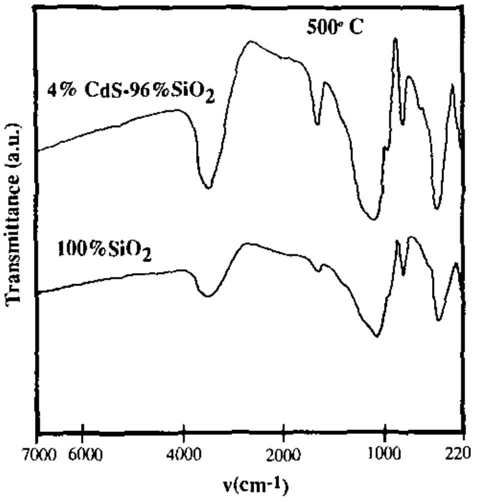

FIG. 5. IR spectra at 500°C of 100% $SiO_2$ and 4% CdS–96% $SiO_2$.

The optical absorption spectrum of 4% CdS–96% $SiO_2$ samples fired at 350 and 500°C (Fig. 8) shows the absorption edges at 460 and 430 nm, respectively, which are located at shorter wavelengths than that of bulk CdS (520 nm). This blue-shift of optical absorption could be due to quantum size effects (13).

The radius of the CdS crystal was calculated by Eq. [3]. $\lambda_g$ is obtained from intersection of the tangent with the wavelength axis in Fig. 8. The size of the CdS particle is ~2.7 nm.

## CONCLUSION

A sol–gel process has been applied in order to prepare CdS particles in silica glasses. Gels were prepared by the hydrolysis of a complex solution of TEOS and cadmium acetate in DMSO, which acts concomitantly as a solvent and a sulfur source, thus avoiding the use of $H_2S$ as indicated in literature. The gels obtained were transparent and colorless and contain cadmium dimethylsulfoxide complexes. These gels were heated from 350 to 1000°C under a nitrogen atmosphere, yielding transparent yellow glasses throughout the range of temperatures but of less intense color at higher temperatures. These results are

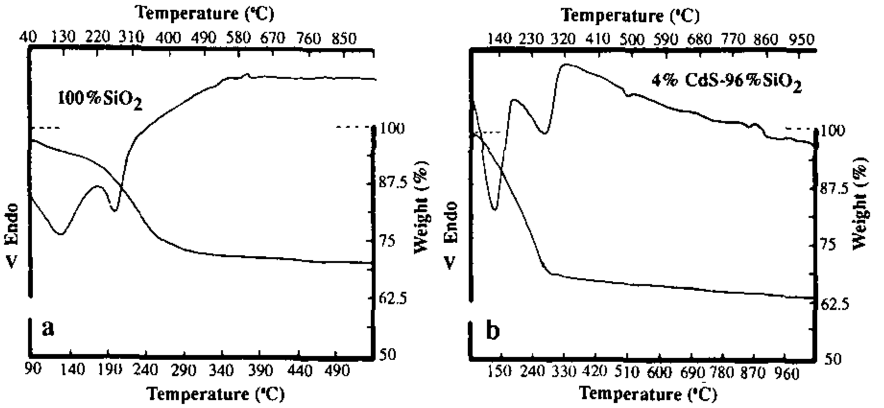

FIG. 7. ATD/TGA results (a) 100% $SiO_2$ and (b) 4% CdS–96% $SiO_2$.

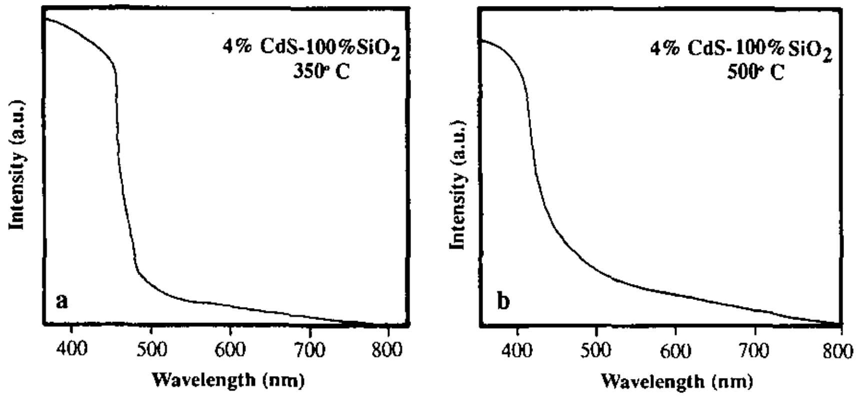

FIG. 8. Optical absorption spectrum obtained of 4% CdS–96% $SiO_2$ (a) 350 and (b) 500°C.

connected with the incorporation of Cd and S ions as CdS into a silica glass matrix under thermal treatments. By IR spectroscopy and BET measurements we inferred a great consolidation in the $SiO_2$ matrix. The results of optical absorption measurements on 4% CdS–96% $SiO_2$ samples fired at 350 and 500°C show that small particles of CdS (about 2.7 nm) are incorporated in to $SiO_2$ glasses, this finding is interpreted in terms of a quantum confinement effect of small crystal size.

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