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Spectroscopic properties of CdS nanoparticles embedded in sol-gel silica glasses

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Absorption, emission and excitation spectra of CdS nanoparticles embedded in sol-gel silica glasses are reported. Their manufacturing and morphology are described. The effects of temperature on emission behaviour were investigated.

1. Introduction

Recently, a great interest has been observed in studying optical properties of nanosize particles of semiconducting crystals in the form of powders or, embedded in glasses, polymers and thin films. This interest is due to the discovery that the optical and electronic properties depend on size confinement and the intensity of radiative transition increase with decreasing particle sizes. Another important feature of such materials is their potential application in nonlinear optics.

The optical properties of CdS clusters embedded in different glass matrices in the form of bulks and films, as well as powders constituted a subject matter of numerous reports [1]–[7]. However, the nature of electronic properties occurring inside the CdS clusters is not well elucidated.

In this paper, we report on the optical properties of CdS clusters embedded in silica sol-gel glasses. The preparation of films and sol-gel glasses is described. The optical properties of emission and absorption of CdS clusters in silica sol-gel glasses are discussed.

2. Experimental

The samples of CdS embedded in silica gel glasses were prepared by vapour phase deposition. The films have been characterized by TEM measurements. Figure 1 shows a high-resolution micrograph. The average size of the CdS clusters in sol-gel film is approximately 13 nm.

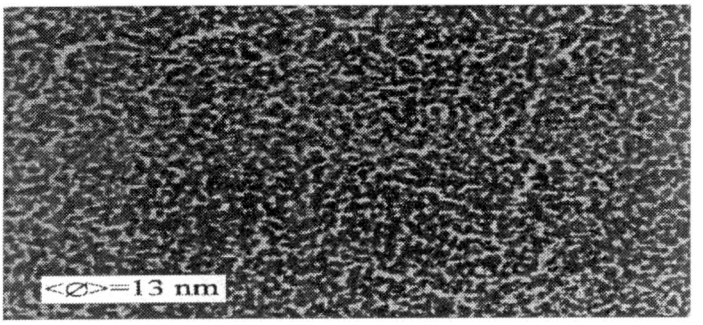

Fig. 1. High-resolution micrograph at CdS.

The silica sol-gel glasses doped with CdS were prepared according to methods known in the literature. The tetraethoxysilane (TEOS), water, ethanol and HCl(aq.) were stirred for 2 h (reagents ratio: 35.4 ml:2.86 ml:9.3 ml:0.05 ml). After the hydrolysis 1 g of $Cd(CH_3COO)_2$ (in 6 ml of methanol) was added to the mixture. Then pH was brought to approximately 5 by means of ammonia solution and gelation took place. After approximately 2 weeks of drying the gels were treated with gaseous H_2S.

Absorption measurements were performed using Cary 5 spectrophotometer. Emission spectra were measured using Jobin Yvon spectrophotometer with Ar^+-ion laser (275 nm) as an excitation source. The emission spectra were measured at room and liquid nitrogen temperatures.

3. Results and discussion

The absorption spectra of CdS doped silica sol-gel glass were measured at both room temperature and 77 K, and are presented in Fig. 2. Both spectra demonstrate the maxima at similar positions (approximately 2.75 eV). They are non-homogeneously broadened.

The luminescence spectra of CdS dopes silica sol-gel glass (at room temperature and 77 K) are presented in Figs. 3 and 4. At both temperatures it can be seen that drying of the glasses results in an increase of the emission intensity and significant blue-shift of the maximum. As expected, the lowering of the temperature narrows the emission features. Moreover, it has been observed that the maxima shift towards lower energies with a decrease in temperature.

We have also measured the emission spectra excited with a different line (351 nm of argon laser). The results are shown in Fig. 5. The emission features of the

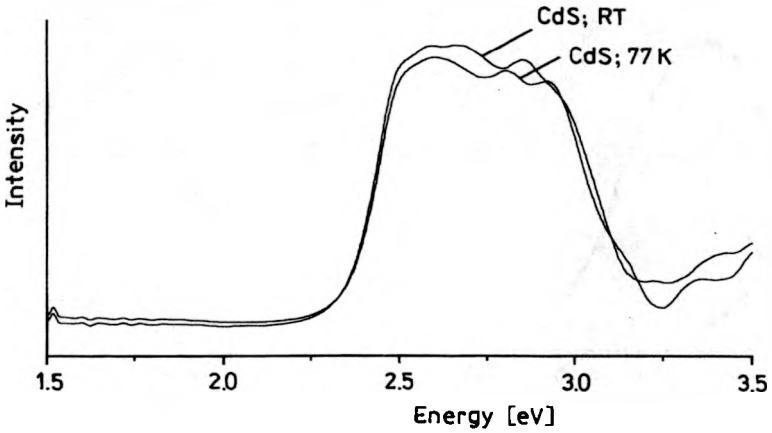

Fig. 2. Absorption spectra of CdS in sol-gel matrices.

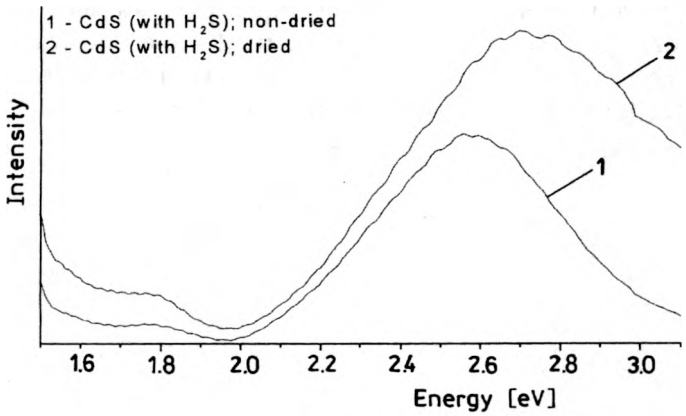

Fig. 3. Emission of CdS in sol-gel matrices at room temperature.

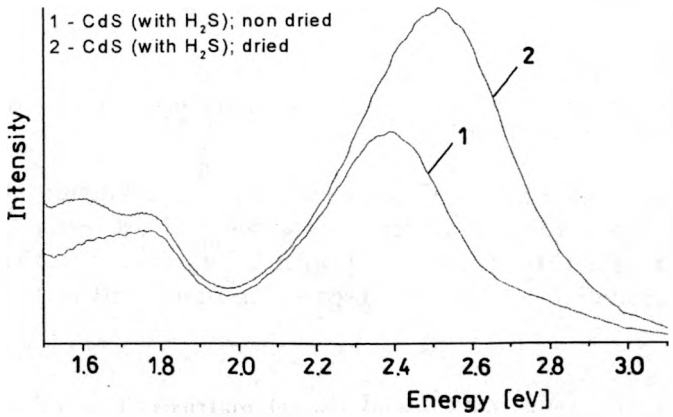

Fig. 4. Emission of CdS in sol-gel matrices at 77 K.

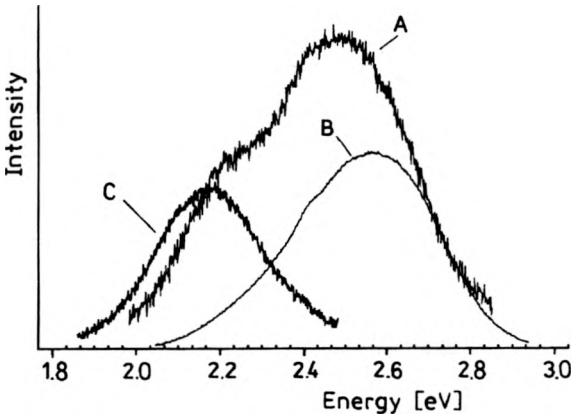

Fig. 5. Luminescence spectra of CdS in sol-gel matrices. A — non-dried sample, B — Cd (acetate), non-dried, C — dried sample; $\lambda_{exc} = 351$ nm.

CdS-containing xerogel samples are generally red-shifted comparing to the starting material (trace B). However, drying of the CdS-doped sample results in a significant red shift and narrowing of the luminescence feature. In the case of the non-dried CdS-doped sample there are at least two overlapping features apparent in trace A.

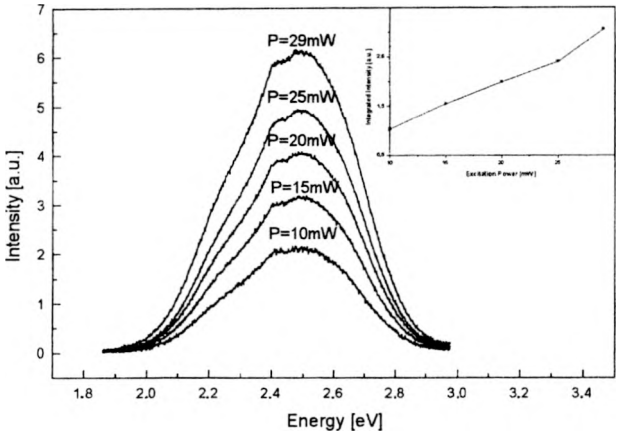

Fig. 6. Effect of excitation power on emission spectra of CdS in sol-gel matrices. Insert shows the intensity dependence of integrated emission on excitation power.

Figure 6 presents emission spectra of the dried CdS-doped sample as a function of the excitation power. As can be seen (insert) the dependence obtained between the laser power and emission intensity is virtually linear. It is interesting to note that the results obtained at the two excitation wavelengths used differ significantly.

4. Conclusions

In this work, we present preparation of CdS-doped sol-gel matrices. The TEM micrographs show the size of the CdS nanoclusters to be approximately 13 nm in

neter. Absorption spectrum of CdS in sol-gel glass shows the absorption edge at roximately 530 nm. It has been observed that annealing of the samples, as well as ering of temperature, shifts the emission maxima towards lower energies. thermore, the luminescence pattern of the CdS-doped samples depends strongly the excitation wavelength. The power dependence of the observed luminscence nsity is approximately linear.

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