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PHOTOLUMINESCENCE AND STRUCTURAL PROPERTIES OF NANO-SIZE CdS INCLUSIONS IN POROUS GLASSES

Cadmium sulphide nanometer-formations in porous glass matrix are obtained. Results of electron-microscopic, XRD and EDS investigation of these formations are presented. The photoluminescence spectra of obtained samples are investigated, and features of these spectra are explained.

INTRODUCTION

Progress of modern microelectronics and optoelectronics demands increasingly miniaturization, operation speed and reduction of power consumption. It results in necessity of sizes reduction of the microcircuits discrete elements up to the nanometer range. Thus, the development of the semiconductor nanometer-sized clusters formation and their sizes control methods is very important for creation of media with the quantum effects are necessary for imparting of new useful properties to known substances. Necessity of microcircuits discrete elements miniaturization explains escalating interest of researchers to this problem. Till recently almost all researches were carried out within the planar technologies. It limits their possible use and, besides, it does not allow adjusting the formed cluster sizes in a wide range. In present paper we try to depart planar technologies, using porous glasses as a matrix, and to unit opportunities both uses of the volumetric environment and extending the sizes of particles into the nanometer range. It is well known that properties of these nanometer-sized crystallites differ from those of bulk substances [1—3]. New physical properties of corresponding complex materials depend on the sizes and the shape of nanometer-sized crystallites. Reduction of the particles size results in quantum confinement effect which leads to occurrence or amplification of such practical important properties as electro- and the photoluminescence, or influences existing luminescent properties of material essentially. For example, it appears a shift of the photoluminescence spectrum [3, 4], an essential increase in its quantum yield, etc. The preparation, physical properties and potential application of semiconductor nanoparticles in polymers [5], sol-gel glasses [3, 4] and zeolites [6] are intensively studied. Porous glasses obtained by traditional methods (from phase separated silicate glasses) are attractive materials for hosting nanoparticles, because their interconnected pores with narrow size distribution allow easy incorporation of different semiconductors. The dimensions of pores can be changed from few to hundred nanometers.

Cadmium sulphide nanoparticles have photoelectrical properties that allow their application in optoelectronic, photocatalytic, solar conversion systems [3, 4]. We report a novel technique of CdS nanocrystals formation in the matrix of a silica porous glass. The technique is based on a chemical deposition process that allows to form CdS semiconductor nano-clusters in the pores of the silica glass matrix.

Two types of glasses differing in pore diameter were used. EDS measurements indicate that CdS distribution is uniform over the thickness of the wafer. The photoluminescence studies after multiple chemical deposition treatments are presented.

EXPERIMENTAL

Porous glasses were obtained by etching off the borate phase from sodium borosilicate glasses [7]. The glasses were annealed before leaching to enhance phase separation at 763 K (*glass B*) and 933 K (*glass D*). After leaching in hydrochloric acid, porous glasses were immersed in KOH for removing of secondary silica from the pores. The porous glasses differing in texture were formed. The porosity of the glasses (measured as the decrement of mass after the technological procedure) reached 50% and 48% for glass B and D, respectively. The data on texture parameters were obtained using the porosimetry method. The average pore radius was 23 and 160 nm for glass *B* and *D*, respectively. The average pore volume was 364 mm^3/g for glass *B* and 470 mm^3/g for glass *D*; whereas the average surface area was 28.9 m^2/g and 5.9 m^2/g for glass *B* and *D*, respectively. The sizes of porous glass wafers under investigation were $10 \times 10 \times \times 0.5$ mm^3.

CdS clusters were formed inside the porous matrix in the following procedure. Cadmium nitrate (0.3085 g) was dissolved in deionized water (2.5 cm^3). Aqueous solution of $(NaPO_3)_3$ (0.2448 g in 2 cm^3) was added to this solution.

The mixture was stirred for 0.5 h at room temperature. Then, the porous glass samples were immersed into the mixture for 2 h and after that dried at 150°C for 0.5 h. The sulfidation was performed by reaction of Cd^{2+} in the pores with gaseous H_2S at room temperature for 2 h. The procedure was repeated 3 or 8 times. Therefore the samples are labeled B-3 (D-3) or B-8 (D-8). Finally, the yellow color samples were dried at 150°C for 0.5 h.

EDS-technique was used for the studies of CdS content in porous glasses after subsequent chemical depositions.

The crystalline structure of CdS inside pores was studied by the X-ray diffraction (XRD) method using X'PERT diffractometer (Philips/ Panalytical. Holland).

The excitation and photoluminescence spectra were recorded with a Perkin-Elmer LS spectrofluorimeter by excitation with power 235 nm UV-laser at the room temperature. In order to remove the adsorbed water, all samples were heated at 150°C for 0.5 h prior to the measurements.

RESULTS

Figure 1 shows SEM micrographs of cleaved samples: pure B and D glasses.

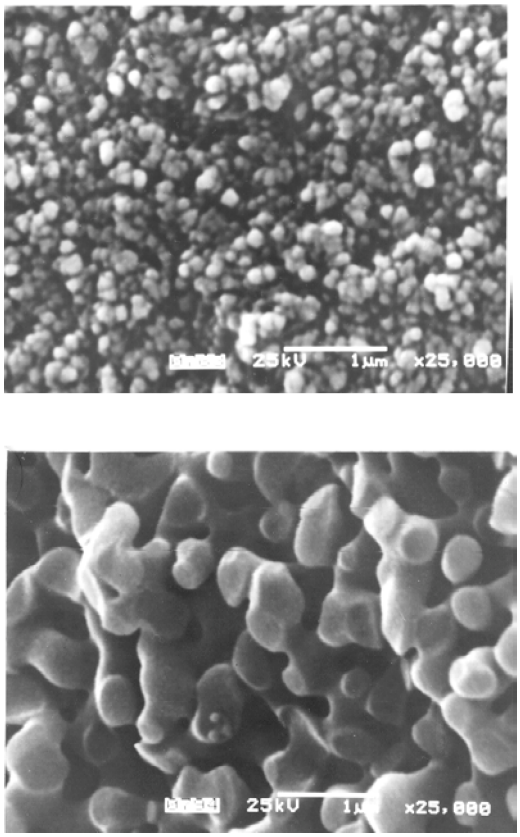

Fig. 1. SEM images for pure B-(*above*) and D-(*below*) porous glasses

The elemental content of Cd and S was obtained on cleave of porous sample. Five points were taken for each cleave. The CdS distribution is uniform over the thickness of samples (on cleave). In Fig. 2, the EDS curve for B-8 (inside in the sample) is presented.

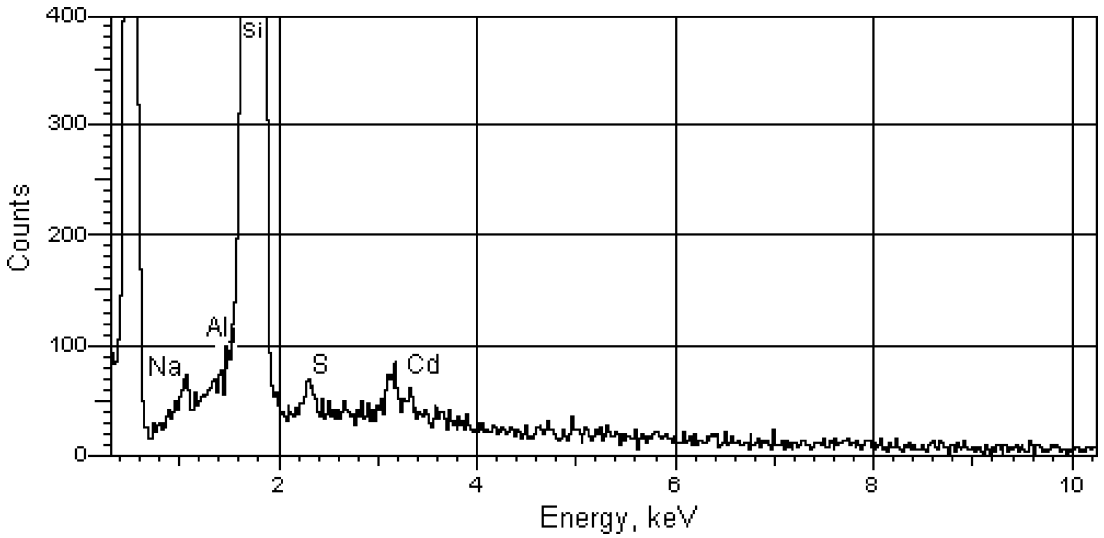

Fig. 2. EDS spectrum of B-8 glass

The average content of Cd and S (in atomic %) is shown in Table 1 for the investigated glasses.

Apparently from the table, CdS content inside the pores rises if the quantity of treatments is increasing.

Table 1

The elemental content of cluster in B and D glasses filled with CdS

Sample	Cd [ат. %]	S [ат. %]
B-3	0.31	0.34
B-8	0.44	0.41
D-3	0.28	0.30
D-8	0.42	0.43

The X-ray diffraction (XRD) pattern of D-8 glasses filled with CdS is presented in Fig. 3. The XRD pattern of B-8 sample is almost identical. The CdS particles inside pores show the same diffraction peaks as in bulk case. The peak at 24°, 26.4°, 28°, 35.5°, 44°, 48°, 52.5° are assigned to the (100), (002), (101), (102), (110), (103) and (112) diffractions of CdS wurtzite polytype, respectively. The XRD peak around 23° is typical for silica porous glass matrix (halo pattern) [8, 9]. It can concluded that CdS particles in the investigated glasses have form of microcrystallites.

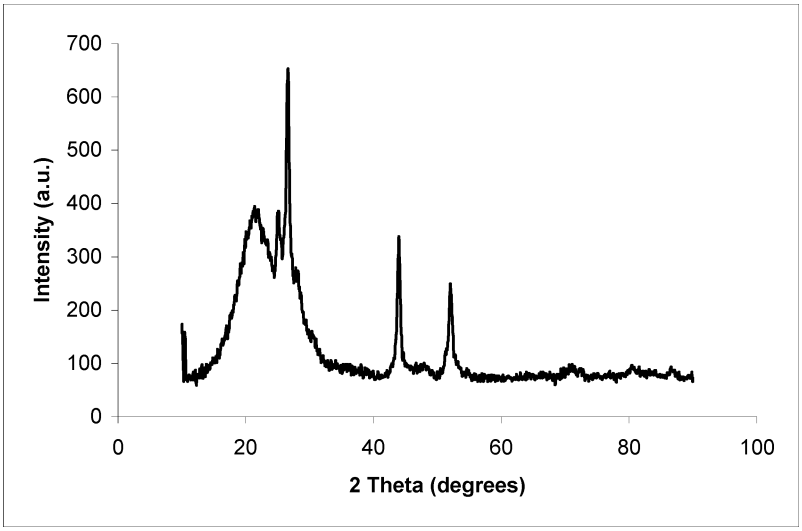

Fig. 3. X-ray diffraction pattern of the D-8

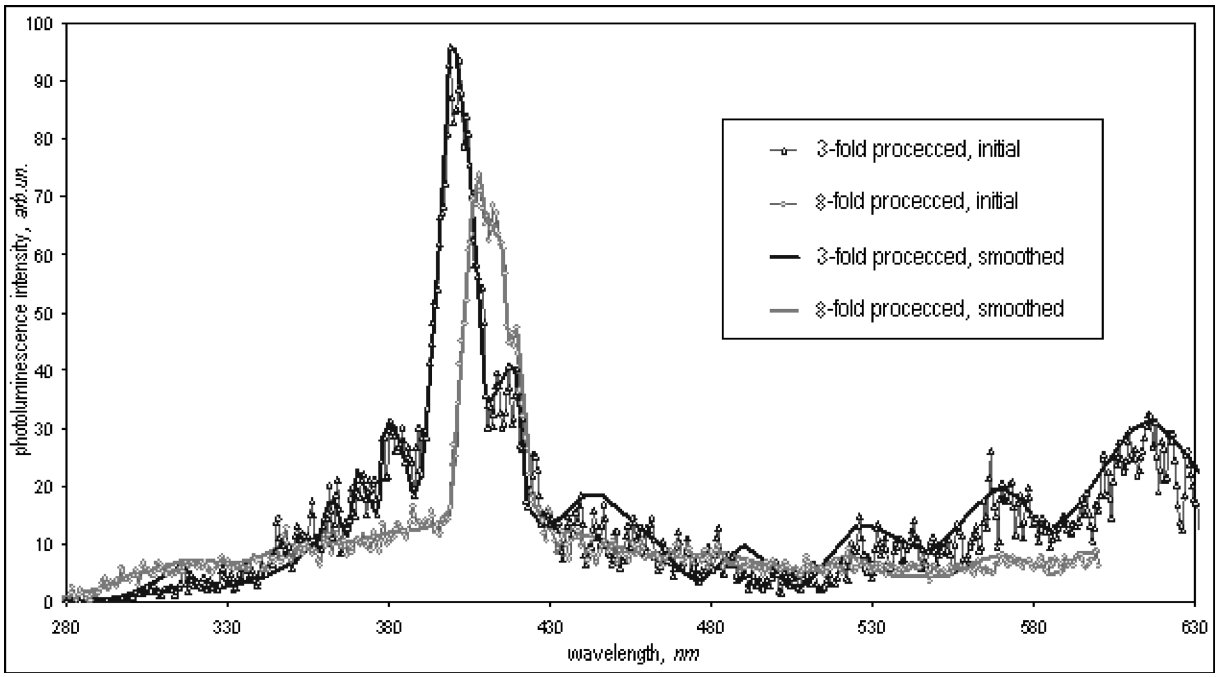

Fig. 4. Initial and smoothed luminescence spectra for B-glasses

Photoluminescence spectra of CdS doped glasses *B* and *D* after three and eight stages of chemical treatment are shown with thin marked lines in figures 4 and 5, respectively. It is clearly, that the existing intensity "pulsations" are not concerned by any image to the processes

occurring in a material at creation of clusters or their excitation. These are especially instrument effects which do not bring any information on structure of a material. Of course, if our purpose was to create any device on the basis of the received luminescence spectra, we had to take into account the instability of spectra and the presence of "pulsations" even at change of wavelength on 5A. But our aim is not working of any luminescence device. We want to investigate the formation mechanism of semiconductor nano-clusters in the porous glass matrix, using the luminescence techniques. Thus the "pulsations" are extraneous information for us, and we shell put aside this by piecewise smoothing. It will allow us to keep all features of the spectrum, namely they are defined by structure of the material and correlate with it. Results of processing spectra by the specified image are shown in figures 4 and 5 with thick continuous lines.

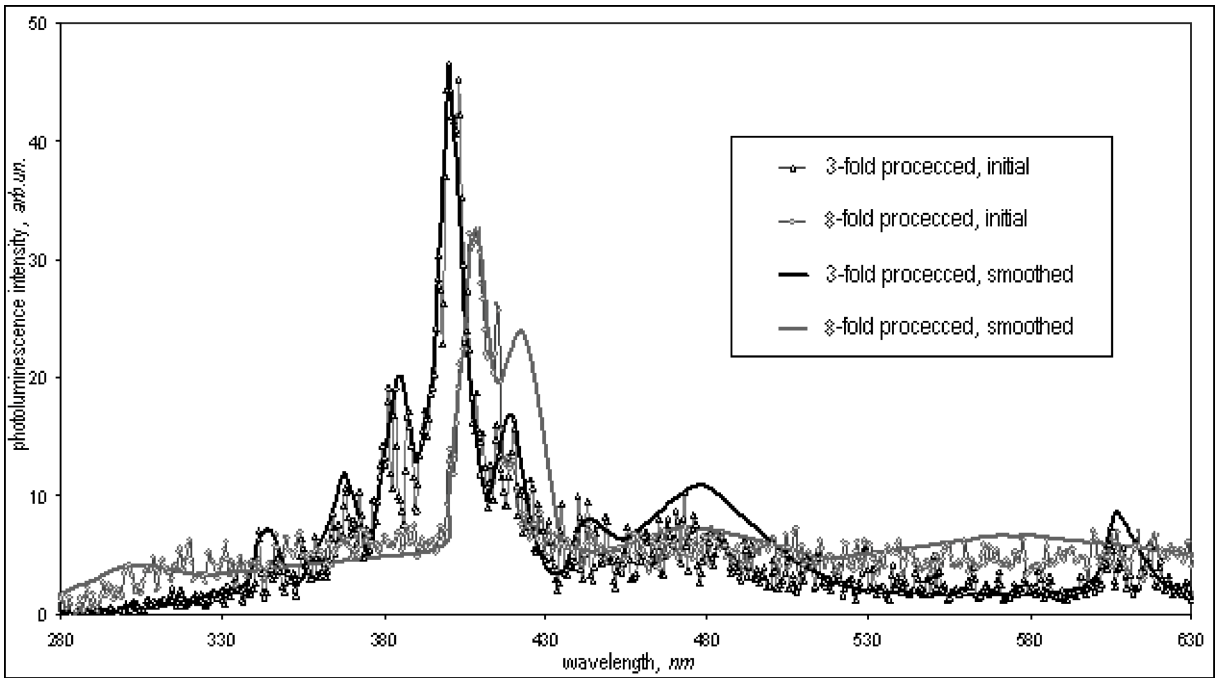

Fig. 5. Initial and smoothed luminescence spectra for D-glasses

DISCUSSION

CdS-clusters provide rather rich spectrum of a luminescence. The nature of its peaks is various. *Firstly*, it is result of band-edge transitions, i. e. direct recombination between conduction electrons and valence holes inside same CdS-cluster. The band gap increases with reduction of the cluster sizes, and, thus, concrete position of corresponding peak depends on the sizes of nano-formations and on the quantum confinement effects [3, 10]. *Secondly*, it is result of transitions "impurity-band". CdS "prefers" to be doted by copper best of all. Such peaks can arise in our spectra hardly, as we did not use any copper catalysts of during formation of nanoparticles, and there was no place to appear this impurity. *Thirdly*, it is the peaks concerned to surface defects (i. e. vacancies arising due to dangle bonds). The luminescence concerned to surface traps, occurs due to recombination between the trapping by sulfur vacancies electrons and valence band holes inside CdS nanoparticles [8]. And, at last, *fourthly*, these are the exciton series due to quantum confinement effects too.

It is energetically preferable to CdS substance to keep an arrangement of atoms intrinsic to crystal at cluster growth. The peak corresponding to band-edge transition, disposed at about 600 nanometers for bulk CdS. As a result of quantum confinement effect this peak should be shifted strongly to the left for small clusters. There is the red shift of the band-edge peak as far as value about 600 nanometers, if the cluster size increases. This effect is rather sufficient, when the cluster size is smaller 14 nm, and it subsides quickly after obtaining 20 nm sizes. If cluster diameter is more 50 nm, it is a crystal practically, but a little one (crystallite) [1].

On the other hand, cluster surface is rich defects such as vacancies and dangling bonds at the first stages of the cluster growth. These defects should not be steady because their presence raises total energy of system. Therefore it is energetically preferable during the cluster growth, first of all, to heal available defects, and only then to increase sizes of cluster. Besides, the surface of the big cluster is always less than the total surface of two small clusters having the same volume. Thus, the contribution of de-

fects on nanoformations surfaces into their photoluminescence spectrum should decrease with growth of the cluster sizes, and it should result in violet shift of corresponding peaks and reduction of their intensity. This quite conforms to results presented in [1].

Thus, the peak presented in spectra of at 600 nanometers, can indirectly testify to existence of crystallites in the pores. Comparison of two smoothed spectra both on fig. 4, and on fig. 5 shows, that such peak is present in the photoluminescence spectrum after three treatments, but after 8 ones it spreads and shifts into short waves. As the clusters hardly break to pieces in result of more quantity of treatments, and grew more likely, the specified peak should be concerned to surface defects and its position should be considered as casual one. And, it is clearly from energy reasons, that the available defects will be healed at first at increase of treatments quantity, and then the cluster begins its increasing. Therefore the quantity of defects becomes less, and it explains reduction of intensity of the specified peak simultaneously with its violet shift. Thus it spreads, that there corresponds to more disorder of the clusters *surface/volume* relation at more quantity of treatments. The system of peaks at 450 and 480 nanometers on the spectrum for D-glass behaves similarly after 3 treatments (fig. 5 shows). After 8 treatments both the peaks lose its intensity (1-st one disappears practically), spread and shift aside short waves. Such behaviour is characteristic for maxima concerned on surface defects.

Apparently, the basic peak, disposed about 400 nanometers on the spectrum after 3 treatments, corresponds to band-edge transition inside small-size clusters. The presence of "satellite" on the right from the basic peak testifies to formation mainly two sizes of clusters. This conclusion confirm by presence of both peaks in the spectrum after 8 treatments, their shift to the right and their intensities redistribution. Besides the peak corresponding to the less wave length is shifted more. Apparently, the less clusters grow faster, but something prevents bigger ones. The pore-sizes distribution spectrum gives the basis to believe, that it is the walls of the big-size pores. The Figure 1 shows, that there are a lot such pores in D-glass and a few ones in B-glass. It follows from the general reasons (see per example [11]), that the clusters, growing inside these pores, do not give any noticeable contribution to the photoluminescence spectrum excited by the UV-laser with wavelength of a 235 nanometers. Nevertheless, walls of these big pores are penetrated numerous small-size pores, and the fine CdS-clusters, arising in them, provide for D-glass a spectrum similar to one for microporous B-glass. At the same time, spectra for D-glass have almost twice smaller intensity. It testifies that, there are less of small pores (and hence fine CdS-clusters giving the contribution to intensity) in this type of glasses on a background bigger volume of intraporous space. Increasing of the clusters size also is accompanied by convergence of band-edge peak and one, concerned to surface defects, in the reference [1]. It confirms the peaks interpretation given here.

After three treatments the system of peaks disposed to the left of the basic one is very similar on an exciton series which are described in reference [12]. Exciton series are concerned on that the energy of some carriers can not suffice for band-edge transition inside a small cluster, so it will result in excitons formation. These excitons will give the corresponding contribution to the spectrum as satellites of frustrated band-edge transition. The exciton peaks system has the typical shape on which they are easy for distinguishing: these peaks are equidistant practically and their intensity decreases in the typical image [12]. Additional treatments will result in increase in the cluster sizes, i.e. in reduction of the band gap in it. Now the exciton bonding energy can suffice for band-edge transition which will be non-radiative one in this case, and, thus, the cluster growth will result in disappearance of the exciton series from the photoluminescence spectrum. Just such effect is observed in the spectra represented on fig. 4 and 5 for the 8 processings.

The above analysis is applicable for the both *D*-glass (fig. 5 shows) and *B*-glass (fig. 4 shows). Therefore the primary size of pores in a porous matrix influences formation process of the semiconductor nanoclusters inside it. The analysis of photoluminescence spectra of both samples types allows to conclude about the predominating role of the small-size pores in formation of CdS-nanoclusters. The preservation of the main maxima (with a small shift) without dependence on quantity of the sample processings testifies this conclusion.

CONCLUSIONS

1. The way of CdS-nanoclusters formation in a porous-glass matrix is developed. These formations have the wurtzite structure and are distributed uniformly inside a porous sample. It confirms by electron-microscopic researches of cleaved samples and by EDS-spectra, and also, by appearance of sharp maxima in the short-wave range of the photoluminescence spectrum, which are typical for nanoformations.
2. The band-edge peaks in the photoluminescence spectra are shifted towards the red range, whereas the peaks, corresponding to surface defects, are shifted towards the violet range at growth of the clusters size.
3. To the left of the band-edge peak there is an exciton series, disappearing at increase in the cluster sizes, in photoluminescent spectra; weakening of quantum confinement effects explains this phenomenon.

4. Change of spectra photoluminescence at increase in quantity of samples processings specifies forming role of the primary pores-size, which limits the maximal clusters size, and allows using the porous glasses as a modeling medium for creation of semiconductor-compound nanoclusters, which have the sizes correlating with the prevailing pore sizes.

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Cadmium sulphide nanometer-formations in porous glass matrix are obtained. Results of electron-microscopic, XRD and EDS investigation of these formations are presented. The photoluminescence spectra of obtained samples are investigated, and features of these spectra are explained.

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ФОТОЛЮМІЕСЦЕНТНІ ТА СТРУКТУРНІ ВЛАСТИВОСТІ НАНОРОЗМІРНИХ ВКРАПЛЕНЬ CdS У ШПАРИСТІ СТЕКЛА

Здобуто нанорозмірні утворення сульфіду кадмію в матриці шпаристого скла. Презентовано результати електронно-мікроскопічного та рентґенівського досліджень зазначених утворень, а також їхній елементний склад. Досліджено фотолюмінесценцію отриманих зразків та пояснено особливості їхніх люмінесцентних спектрів.

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ФОТОЛЮМИНЕСЦЕНТНЫЕ И СТРУКТУРНЫЕ СВОЙСТВА НАНОРАЗМЕРНЫХ ВКЛЮЧЕНИЙ CdS В ПОРИСТЫХ СТЁКЛАХ

Получены нанообразования CdS в матрице пористого стекла. Представлены результаты электронно-микроскопического и рентгеновского исследования указанных образований, а также их элементный состав. Исследована фотолюминесценция полученных образцов и объяснены особенности их люминесцентных спектров.