An estimate of shape-distribution of small CdS particles with luminescence spectra

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Abstract. The luminescence spectra of CdS particles obtained by sedimentation method are studied. The comparison of measured and calculated photoluminescence spectra was used as the base of the method defining the shape distribution of the particles. For this purpose one can use the symmetry rule for absorption and luminescence spectra. Absorption spectra were calculated via dissipative function in terms of local field theory. The experimental spectra of the photoluminescence were measured during the process of sedimentation in the CdS nano-composite powder. The modification of luminescence spectra detected during sedimentation time is associated with changing the dimension and shape distributions of CdS suspension. As a result, the particles shape distribution was estimated for sizes less then 1 \( \mu \)m.

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1 Introduction

The development of nano-technologies requires the effective methods to control the parameters of nano-systems. There are numerous methods, which are used for this purpose, such as electron microscopy [1], X-ray [2] and optical spectroscopy [3], etc. Optical methods are the most demanded in characterization of nano-composites. The widely used optical methods such as luminescence and absorption spectroscopy allow studying of numerous characteristics of materials. However, the standard approaches to luminescent and absorption spectroscopy become invalid for nano-composites. This is because, as it is known, optical properties depend on both the dimension and shape of nano-particles [4–6]. Moreover, one needs to measure the extremely weak signals. Then, the methods of these signals analysis should allow discriminating the usable parts of the signals. This means that the role of theoretical modeling increases. Theoretical approaches have to take into account the essentially inhomogeneity and shape dependence of the system under consideration. Photoluminescence is a simple, sensitive, non-destructive technique [7]. In particular, photoluminescence is used to study physical properties of semiconductors [8]. Due to its high sensitivity, this method does enable to study dilute solutions, composite materials with small contents of emitted component, etc. The bulk CdS crystals concern to a class of crystal-phosphorus with a high quantum yield of the luminescence [9]. The CdS films are widely used as a component of solar devices [10]. The usage of CdS nano-particles as luminescent markers in modern biology is widely discussed as well [11]. Thus, the obtaining of composites based on CdS nano-crystallites in a neutral matrix is perspective for the development of new technologies.

The dependence of absorption and luminescence spectra on the shape and dimension of particles [5,6,12] needs to separate the particles both on the shape and on the dimension. The sedimentation method could allow succeed in it. In the case of submicron particles the dependence on shape is prevalence. Then, one should separate the heavy particles, which dimensions are sufficiently large. The sedimentation of the small particles suspension in the non-polar liquid can lead to the remaining of particles which are mainly characterized by the same shape and linear dimensions in fixed cross-section of the sell. Then, the small particles with the approximately same dimensions will be prevalent in the layer of suspension in the system under consideration (see Fig. 1). Then, the luminescence spectra will mainly depend on shape distribution of the particles. We can use this fact for definition of shape distribution in this work.

2 The separation of nano-particles by dimension and sharp with sedimentation method

To obtain nano-particles of definite shape and dimension one can use the sedimentation method, the main idea of
which consists in settling out the nano-crystallite powder by gravity [13–16]. Obviously the heavy particles have to settle more quickly. Then the heavy particles will not be presented at fixed cross-section of the cell at appointed time. Due to hydrodynamic properties the particles characterized by stick-like and cub-like shapes have to settle more quickly than the plate-like particles (see, Fig. 2) of the same weight. Taking into account these circumstances we can suppose that differences of luminescence of the particles from appointed cross-section of the sedimentation column are caused by different shapes of the particles. The process of sedimentation was performed by the next steps. The first step consisted in dust preparation. Particularly, high cleanliness and milled in an agate mortar powder of CdS was intermixed with alcohol for homogeneous suspension. The next step was the settling of the suspension. For 60–120 min heavy fractions of CdS powder settled on the bottom of the cell. As a result, the suspension of submicron dimensions particles was obtained. As the water is a dipole medium, the electrostatic interaction between the water and crystallites can lead to the meshing of particles with each other, and aggregates of the particles could arise. As a result, the spectrum of luminescence can disfigure. Therefore the study should be carried out in non-polar liquid, for example, in alcohol. For this case the sedimentation happens much faster. Then, the process of experimental measurements should be carried out during not long time. This fact leads to the request for use of the automatic high sensitive experimental equipment for the registration of weak signals from luminescent particles.

To make sure that the sedimentation process allows us to obtain sufficiently homogeneous on the weight suspension we simulated numerically this process, where the initial distribution of particles obtained by a mechanical refinement was supposed as Gaussian, with the average of distribution of the dimension $R_0 = 0.35 \mu m$ [17], namely it was supposed as $N_0 = (N_0/\sigma \sqrt{2\pi}) \exp \left[-(R-R_0)^2/\sigma^2\right]$, with $\sigma$ dispersion of particle distribution over size. Then, the concentration of particles with the average dimension $R_0$ at the height $h$ is described by equation

$$N_i(h,t) = N_0 \cdot \left(\frac{\text{sign}(h-x_i) + 1}{2}\right),$$

(1)

where $x_i = U_i t$ is the depth at which the particle falls for time $t$. To obtain the velocity $U_i$ we have written the motion equation for the particle with the radius $R_i$ in the form

$$\rho V_i g = 6\pi \rho_v \nu R_i + \rho_v g V_i,$$

(2)

where $V_i = (4/3)\pi R_i^3$ is the volume of particle with the radius $R_i$, $\rho_v$ and $\nu$ are the density and viscosity of solvent and $g$ is the acceleration of gravity. Solving equations (1) and (2) one obtains the number of particles with the radius $R$ which are situated at the h depth of the sell

$$N(R,h,t) = \frac{N_0}{2\sigma \sqrt{2\pi}} e^{-(R-R_0)^2/\sigma^2} \cdot \text{sign}(h)$$

$$-(2/9)R^2 g ((\rho - \rho_v)/\rho_v) t),$$

(3)

where normalization factor is

$$N_0 = 3M/(4\pi \rho l),$$

(4)

with $M$ the mass of the particle and $l = \int_0^\infty \zeta e^{-(\zeta/R_0-1)^2}d\zeta$.

This dependence of particles distribution on time is shown in Figure 3. One can see that the particles, which remain in the suspension after 8 h of sedimentation, will be less than 0.2 $\mu m$. Then, it could be supposed that investigated suspension consists of nano-particles which luminescent properties are defined by its shapes. The study of suspension with optical microscopy has given us an additional corroboration of nano-dimension of the particles under consideration. Indeed in Figure 4 one can see that the dimensions of the particles in the suspension are about or less than 0.1 $\mu m$. Due to the crystalline lattice of CdS (we used CdS crystals with a zincblend lattice), the grinding of CdS crystals will lead to obtaining the powder characterized by the rectangular shape particles with different ratios between the edges (it is well visible at the AFM image). Then, one can suppose that three types of the shape of the particles will form the suspension after sedimentation — cube-like, plate-like and stick-like. Taking into account that absorption and luminescence spectra of the particles depend on the particles shape, one can estimate the shape distribution of the particles in the suspension using the experimentally obtained luminescence spectra.

The luminescence spectra were measured in the experiment, set-up of which is shown in Figure 1. The photoluminescence was excited by the xenon lamp of wavelength