

## Effect of the doping method on luminescent properties of ZnS:Ag

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**Abstract.** Effect of doping the method on luminescent characteristics of dispersed ZnS doped with Ag has been studied in this work. The analysis of ratio of the intensity of photoluminescence bands related with the centres caused by Ag impurity and the intrinsic defects has led to the conclusion that formation of dispersed ZnS:Ag prepared using the self-propagating high-temperature synthesis (SHS) has several advantages: doping occurs directly in the process of material synthesis, possibility of simultaneous preparation of two fractions with different particle sizes, in ZnS:Ag-SHS with particle sizes greater than 20 nm there is a lower concentration of defects as compared to that in ZnS:Ag obtained using the thermal doping method.

**Keywords:** self-propagating high-temperature synthesis, thermal doping method, photoluminescence, ZnS, Ag.

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### 1. Introduction

Interest in semiconductor materials of the  $A^2B^6$  group over the past 20 years has increased significantly due to their unique optical and luminescent properties that can be used in various optoelectronic devices as well as to create luminescent screens [1]. The materials of this group are especially attractive due to the fact that their properties can be improved or changed during the doping process. One of the typical examples of the  $A^2B^6$  group materials is ZnS [1-3]. Since ZnS can have both a cubic and hexagonal structure with a wide forbidden band 3.54 and 3.91 eV, respectively, among semiconductors of the  $A^2B^6$  group it becomes the most interesting object for modifying its properties [4-6].

Silver-activated zinc sulfide, ZnS:Ag, is one of the oldest inorganic scintillators and is widely used to measure alpha-radioactivity in samples of environment [7]. In this case, ZnS:Ag has a very high scintillation efficiency, comparable to the efficiency of NaI (Tl). Currently, ZnS:Ag is synthesized only in the form of a

polycrystalline powder by chemical means, so it is usually used for manufacturing thin screens, used mainly for detection of alpha particles or other heavy ions.

The appearance of new methods of synthesis enables to prepare materials with a wider range of properties. However, use of these new methods requires additional research to compare the properties of materials obtained and doped with application of the standard and new methods. One of the new promising methods for obtaining materials is self-propagating high-temperature synthesis (SHS).

The advantages of this method are that it allows to dope the obtained material in one cycle of the synthesis process as well as to immediately obtain two fractions of the material with different sizes. The synthesis of one fraction takes place directly in the combustion zone of Zn and S, and the second one – in the gas phase. Formation of the second fraction in the gas phase occurs as follows. In the course of SHS, due to high temperatures and increase in the pressure inside the ampoule during propagation of the combustion front in the charge, some

of the reagents in the form of vapor exits from the ampoule into the reactor volume. When colliding with inert gas atoms, vapor particles quickly lose their kinetic energy and form nanoparticles.

The purpose of this work was to find out the effect of doping method on the luminescent characteristics of dispersed ZnS doped with Ag. In this paper, two methods of doping were considered: 1) doping directly during the SHS process and 2) thermal doping of pure ZnS obtained using the chemical method.

## 2. Experimental technique

The studied ZnS:Ag was obtained in two ways. In the first case, ZnS was synthesized using the SHS method at temperatures that ensure the process of sulfur and zinc interaction [8, 9]. In this case, Ag doping occurred directly in the synthesis process. The amounts of initial materials were as follows: Zn – 0.45 mol, S – 0.56 mol, AgS – 0.006 mol. Obtained there were two fractions of ZnS:Ag. One fraction is in the combustion zone with the particle sizes 5...20  $\mu\text{m}$  and the second one – in the gas phase zone with the particle sizes approximately 50...100 nm.

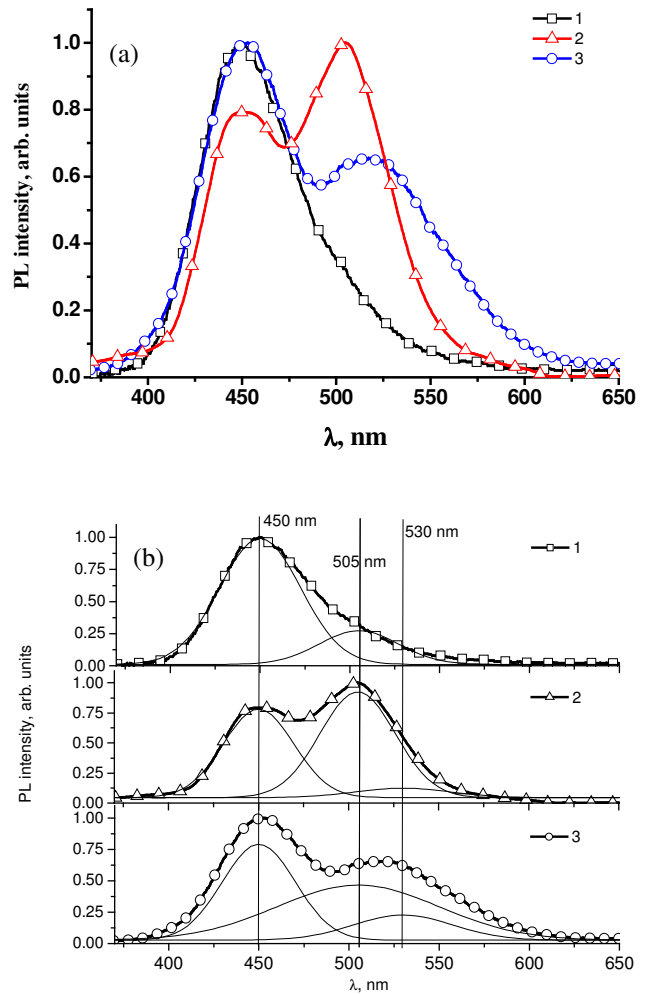
In the second case, thermally doped ZnS:Ag was obtained using thermal annealing of pure ZnS powder chemically synthesized in the presence of silver sulfide with the particle sizes close to 20...40  $\mu\text{m}$ . The impurity concentration of AgS was 0.018 mol. Annealing was carried out in a muffle furnace at the temperature 800 °C for 180 min. The powders were annealed in silica test tubes. To limit the access of atmosphere in the annealing process to the annealed powders, a gas shutter made of activated carbon was used.

The photoluminescence (PL) spectra were measured on a CДЛ-2 setup at  $T = 300$  K. PL was excited with radiation of an LGI-21 nitrogen laser with  $\lambda_{\text{exc}} = 337$  nm.

## 3. Experimental results and discussion

Fig. 1 shows the PL spectra of dispersed ZnS:Ag, obtained using the SHS method (ZnS:Ag-SHS), doped directly in the synthesis process, for two size fractions: micro- and nanofraction, as well as the PL spectrum for ZnS:Ag, obtained using the thermal doping method. As can be seen from Fig. 1, curve 1, the PL spectrum of ZnS:Ag-SHS with micrometer sizes of particles has the form of a wide band with a maximum at the wavelength  $\lambda_{\text{max}} \sim 450$  nm, which is typical for emission of ZnS doped with Ag [10, 11]. At the same time, in the PL spectra of ZnS:Ag obtained using the thermal doping method as well as in the PL spectra of nanosized ZnS:Ag-SHS, there are two bands with  $\lambda_{\text{max}} \sim 450$  nm and  $\sim 500$ –510 nm (Fig. 1, curves 2, 3).

In the work [12], the intense PL band with  $\lambda_{\text{max}} \sim 450$  nm in the PL spectra of ZnS:Ag, regardless of the doping method, is associated with radiative recombination between the levels formed by sulfur vacancies and the levels related with silver impurity.



**Fig. 1.** a) The PL spectra normalized to the maximum of the spectrum for different fractions of dispersed ZnS:Ag doped with Ag directly in the synthesis process: 1 – micrometer fraction, 2 – nanofraction, and 3 – thermal doped Ag. b) Decomposition of the PL spectrum contour for ZnS:Ag into the components.

At the same time, according to [12, 13], in this area (450 nm) there can be observed self-activated (SA) ZnS luminescence caused by several types of intrinsic defects: sulfur vacancies ( $V_S$ ) [14, 15], transitions in oxygen clusters involving impurities [16], radiation centers similar to the center – associate ( $V_{\text{Zn}}-V_S$ )' [17], zinc vacancies ( $Zn_i$ ) [18].

The overlapping of these PL bands leads to broadening the resulting PL band. Since radiative recombination processes related with the presence of intrinsic defects are characterized by a very short recombination time, the radiative recombination channels related with defects can compete with radiative recombination channels caused by the centers related with Ag [12]. On the other hand, some lattice defects can be a source of nonradiative recombination, which leads to a decrease in the energy transfer for photoemission. Thus, the presence of lattice defects in ZnS:Ag can lead to the quenching of luminescence related with Ag [12].

As can be seen from Fig. 1a, the PL spectrum of the micrometer fraction ZnS:Ag-SHS is a narrow and almost symmetric PL band with  $\lambda_{\max} \sim 450$  nm (Fig. 1, curve 1). For smaller sizes of ZnS:Ag-SHS crystallites, in the PL spectrum, the additional band with  $\lambda_{\max} \sim 504$  nm appears, its intensity exceeds the intensity of PL band with  $\lambda_{\max} \sim 450$  nm by approximately 1.3 times (Fig. 1, curve 2).

Fig. 1b shows decomposition of the PL spectra into contour components for two different fractions of ZnS doped with Ag directly in the synthesis process (SHS) and for ZnS:Ag obtained using the thermal doping method.

As can be seen from Fig. 1b (curve 1) for the micrometer fraction, the PL spectrum is a wide complex band in the blue-green spectral region with a radiation maximum at  $\lambda_{\max} \sim 450$  nm and a weak band in the region of 505 nm. In this case, the low-intensity band with  $\lambda_{\max} \sim 505$  nm, apparently, is also complex and is caused by the presence of intrinsic defects in ZnS [19, 20].

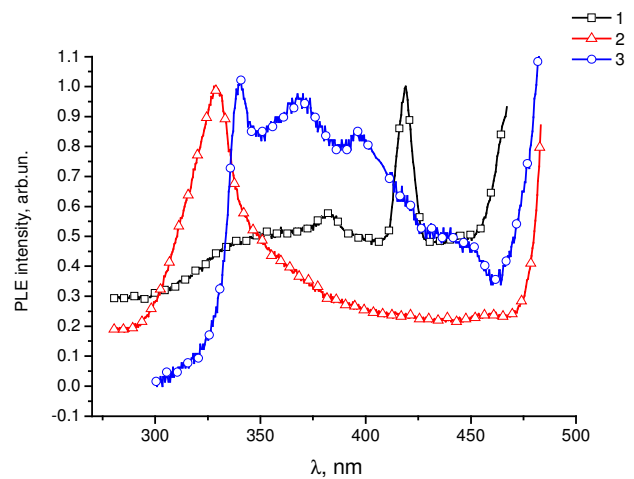
As can be seen from Fig. 1b (curve 2) in the PL spectrum of nanosized ZnS:Ag, in addition to the bands with  $\lambda_{\max} \sim 450$  nm and the dominant PL band with  $\lambda_{\max} \sim 505$  nm, there is a band with  $\lambda_{\max} \sim 530$  nm. The bands with  $\lambda_{\max} \sim 505$  nm and  $\sim 530$  nm are “self-activated”, and their nature has been well studied [16, 19, 20].

Self-activated luminescence in this spectral region is associated with radiative recombination at the PL centers formed by intrinsic defects as well as their complexes that may include a coactivator and oxygen [2, 29-34]. As it was shown in a number of papers [29–31, 35, 36], self-activated luminescence usually consists of a series of overlapping bands related with the defects caused by the presence of oxygen [36], zinc vacancies ( $\text{Zn}_i$ ), as well as defects caused by an excess sulfur in ZnS crystals [35].

Despite the fact that when the visual observing, the PL spectra of the micrometer fraction of ZnS:Ag-SHS and ZnS:Ag obtained using the thermal doping method have the same brightness, as can be seen from Fig. 1 (curves 1, 3), the PL spectrum of ZnS:Ag-SHS has a narrower and almost symmetric PL band with  $\lambda_{\max} \sim 450$  nm. In this case, the additional band with  $\lambda_{\max} \sim 505$  nm appears in the PL spectrum of ZnS:Ag obtained using the thermal doping method. It may indicate that the thermal doped ZnS:Ag contains more intrinsic defects (which is equivalent to the greater amount of self-activated luminescence centers) or quenching of the self-activated PL band occurs in the micrometer fraction of ZnS:Ag-SHS.

Fig. 2 presents the spectra of luminescence excitation for micro- and nano-fractions of ZnS:Ag-SHS (Fig. 2, curves 1, 2) and thermal doped ZnS:Ag (Fig. 2, curve 3). To excite the PL spectrum, the radiation of a He-lamp passing through a monochromator was used.

It should be noted that the luminescence excitation spectra of ZnS:Ag, except the fundamental excitation band, may contain additional bands corresponding to elementary impurity absorption bands. The energy position, distance between them and their spectral shape



**Fig. 2.** Normalized luminescence excitation spectra of micrometer fractions of ZnS:Ag-SHS (1), ZnS:Ag-SHS nanofraction (2) and thermal doped ZnS:Ag (3).

depend on a number of factors: the degree and conditions of doping, symmetry of the intracrystalline field, number of ions forming this field, distance between them, type of neighboring defects, *etc.*

As can be seen from Fig. 2 (curve 1), the luminescence excitation spectrum of micrometer fraction, except the weak band with  $\lambda_{\max} \sim 340$  nm caused by the fundamental absorption in ZnS [21], contains also two bands: a weak band of luminescence excitation spectrum with  $\lambda_{\max} \sim 380$  nm and an intense band with  $\lambda_{\max} \sim 420$  nm related with the presence of an uncontrollable manganese impurity in the charge [22].

The luminescence excitation spectrum of ZnS:Ag-SHS nanofraction contains only one band with  $\lambda_{\max} \sim 330$  nm (Fig. 2, curve 2) that is caused by the fundamental absorption in ZnS [21]. However, the maximum of this band at the wavelength 330 nm is shifted to the shortwave region in comparison with its position in the micrometer fraction and in the thermal doped ZnS:Ag (see Fig. 2).

The observed  $\sim 110$ -meV shift of the fundamental position band can be explained by the presence of nanosized particles in the dispersed ZnS:Ag-SHS, for which the quantum-size effect appears [21]. The 110-meV shift of the fundamental band makes it possible to estimate the size of these particles as  $d < 7$  nm [21]. It should be noted that this fraction consists of two types of particles. These are particles with sizes less than 7 nm and with the sizes of 50 to 100 nm. However, the irradiation of particles with the sizes 50...100 nm is practically absent due to domination of nonradiative recombination channels in them, as it was shown in [23].

In the luminescence excitation spectrum of thermal doped ZnS:Ag, three bands are observed: the narrow one with  $\lambda_{\max} \sim 340$  nm and two broad ones with  $\lambda_{\max} \sim 368$  nm and  $\sim 395$  nm (Fig. 3, curve 3). The band with  $\lambda_{\max} \sim 340$  nm is caused by band-to-band absorption and is characteristic of bulk zinc sulfide [24].

#### 4. Conclusions

The analysis of ratio of the intensity of the PL bands related with the centers caused by Ag impurity and self-activated PL allows us to conclude that, when obtaining ZnS:Ag using the SHS method, the concentration of Ag in the micrometer fraction in the prepared material is maximum. In addition, the PL spectrum of ZnS:Ag-SHS has a narrower and almost symmetric PL band with  $\lambda_{\max} \sim 450$  nm (Ag band), and in the PL spectrum of ZnS:Ag obtained using the thermal doping method, there is an additional band with  $\lambda_{\max} \sim 505$  nm, which indicates a high concentration of intrinsic defects.

A decrease in the particle size leads to a decrease in the concentration of luminescence centers related with Ag impurity, and an increase in the PL centers caused by intrinsic defects of ZnS lattice.

Thus, formation of dispersed ZnS:Ag by using the SHS method has several advantages: doping occurs directly in the process of material synthesis, possibility of simultaneous preparation of two fractions with different particle sizes, in ZnS:Ag-SHS with particle sizes greater than 20 nm there is a lower concentration of defects as compared to that in ZnS:Ag obtained using the thermal doping method.

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