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The paramagnetic and luminescence properties of single-stage synthesized ZnS:Cu

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The paramagnetic and photoluminescence properties of ZnS with different concentrations of Cu dopant obtained by the self-propagating high-temperature synthesis have been investigated. The temperature-dependent change in electron paramagnetic resonance (EPR) spectrum of ZnS:Cu with copper concentration N_{Cu} ~ 0.6 wt.% has been demonstrated. The phase formation processes in ZnS involving Cu are discussed. It has been shown that clustering of copper ions in the material occurs starting from the concentration N_{Cu} > 0.3 wt.%. Formation of complexes including Cu clusters is accompanied by the appearance of a superparamagnetic subsystem under study that is confirmed in experiment by the appearance of an anomalous EPR signal.

Исследованы парамагнитные и фотолюминесцентные свойства ZnS с разной концентрацией легирующей примеси Cu, полученного методом самораспространяющегося высокотемпературного синтеза. Продемонстрировано изменение спектра электронного парамагнитного резонанса ZnS:Cu с концентрацией меди N_{Cu}≈0,6 масс.% в зависимости от температуры. Обсуждаются процессы формирования фаз с участием Cu в ZnS. Показано, что, начиная с концентрации N_{Cu} > 0,3 массс.%, происходит кластеризация ионов меди в материале. Формирование комплексов, включающих кластеры Cu, сопровождается появлением суперпарамагнитной подсистемы, экспериментальным подтверждением чего служит появление аномального сигнала электронного парамагнитного резонанса.

1. Introduction

The synthesis and research of nanostructured materials exhibiting both "classical" semiconductor and new quantum-dimensional properties is among directions of promise in modern semiconductor physics [1, 2]. These properties are of importance first of all for practical applications, while physical study of the classical semiconductor materials used as a matrix for nanoinclusions is among important problems in the fundamental science. In general, the nanostructured materials can be considered as usual compounds synthesized within artificial borders, in conditions of so-called "limited geometry". The nanocomposites obtained by single-stage synthesis are of a special interest [1–3]. ZnS is the base of high-quality phosphors fabricated by single-stage synthesis, therefore, it is a prospective material for using as a matrix for nanoinclusions. In particular, phosphors on the basis of copper-activated zinc sulfide are widely used among the most effective ones in green-blue spectral region, and the technology thereof is well developed. However, in some cases, the structure of the luminescence centers including Cu ions remains unclear to date [4–7]. This is explained by that oxygen in ZnS gives similar luminescence bands in absence of copper [8] and that, due to recombination interaction, the band characteristics may change essentially in presence of defects or additional (uncontrollable) impurities. As a result, display of the bands related to Cu ions in ZnS:Cu photoluminescence (PL) spectra depends heavily on the synthesis conditions influencing the formation of the active center structure.

Today, the nature of the so-called dark blue and green centers of luminescence caused by Cu in ZnS (bands *B*- and *G*–Cu) [4–7] is studied minutely enough in many aspects. In [9–13], it is shown that the center responsible for *G*–Cu band occurrence is the isolated copper ion substituting zinc in the ZnS lattice. It has been found that the center symmetry is not lower than the regular unit symmetry in cubic or hexagonal ZnS lattice, hence, the coactivator does not involved into the center structure.

The dark-blue luminescence is ascribed to formation of Cu_2S phase nuclei-associates such as Cu_{Zn}–Cu_{Zn} [6,7]. The formation and mutual transformation of the dark-blue and green copper centers under annealing is associated to potential possibility of Cu_2S formation at interblock surfaces as a separate phase. The formation of more complex centers including Cu, such as copper clusters or nanoparticles influencing on ZnS luminescence efficiency, were not considered in literature, among other causes, due to the difficulties related to detection and identification of such objects in a material.

The purpose of this work is to study the influence of Cu impurity concentration on the PL and electron paramagnetic resonance (EPR) characteristics in ZnS samples obtained by a self-propagating high-temperature synthesis (SHS) as well as to make a detailed comparative analysis of changes in the spectral characteristics of photoluminescence and EPR depending on the concentration of copper introduced.

2. Experimental procedures

A set of Cu-doped ZnS-based phosphors was synthesized by SHS in nitrogen atmosphere at the temperatures providing interaction process between sulfur and zinc [14]. Copper was introduced into the material in the form of CuCl. This technique allowed us to introduce the necessary amount of the impurity during synthesis. The Cu concentration in the set varied from 0.1 up to 2 wt. %; initial materials of Zn and S were in the stoichiometric ratio. After synthesis, the obtained material has been separated basing on the granulometry. The powder fraction of about 20 to 50 μm size was used to the study. The PL spectra were excited by 337.1 nm line of LGI-21 laser and registered using a KSVU-23 spectrometer at T = 300 K. The EPR measurements were carried out using X-band ($\nu \cong 9.4$ GHz) of a Radiopan X-2244 EPR spectrometer with 100 kHz modulations of magnetic field.

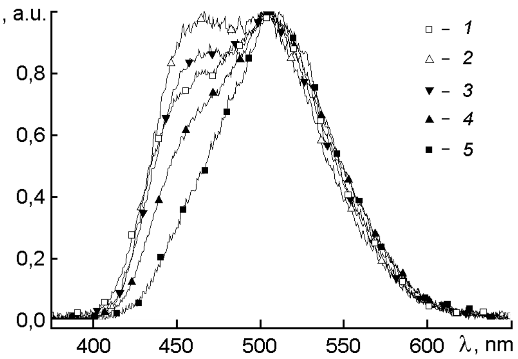

Fig. 1. PL spectra of Cu-doped zinc sulfide powders with Cu concentration: *1* – 0.1 wt. %; *2* – 0.2 wt. %; *3* – 0.3 wt. %; *4* – 0.6 wt. %; *5* – 2 wt. %.

3. Results and discussion

The PL spectra of ZnS:Cu phosphors synthesized with different copper contents (up to 2 wt. %) are shown in Fig. 1. The PL spectra appear to be a complex wide band in the blue-green spectral range; it consists of several individual lines. The change of copper chloride/zinc sulfide ratio during synthesis results in intensity redistribution thereof (see Fig. 1). The copper-free sample exhibits a single PL line at 460 nm. Another PL line with maximum at λ_{max} = 505 nm is appeared for all copper concentrations studied and dominates in the PL spectra of samples with the highest Cu concentration (2 wt. %). The PL line at 460 nm revealed as a wing in a short-wave part of the spectrum for copper-containing samples ($0 < N_{Cu} < 2$ wt. %). Both lines have visually equal intensities in the sample with N_{Cu} = 0.2 wt. % (Fig. 1, curve *3*).

To analyze the PL spectra shown in Fig. 1, we used procedure of spectrum decomposition into elementary components proposed by Alentsev-Fock method [15, 16]. According to this method, the PL spectra including an identical set of elementary components but being obtained for ZnS:Cu samples with different copper contents were chosen for the analysis. The analysis of

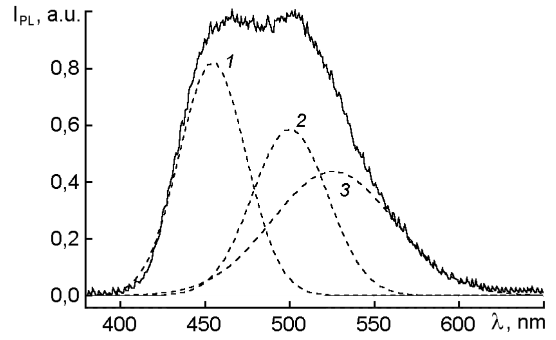

Fig. 2. PL spectrum of the ZnS powder doped by copper with concentration of 0.2 wt. %. The shaped line shows elementary component of the ZnS:Cu PL spectrum.

these spectra has shown the presence of three elementary components with λ_{max} about 455, 503 and 525 nm. Such decomposition of PL spectrum for the sample with 0.2 wt. % copper concentration is presented in Fig. 2 as an example.

The unambiguous identification of the elementary components forming the PL spectrum of ZnS:Cu represents some difficulties. However, although there is no generalized model for the luminescence centers containing Cu ions, it was found that formation of the *B*-band with λ_{max} about 455 nm (Fig. 2, curve *1*) and *G*-band with λ_{max} about 503 nm (Fig. 2, curve *2*) in luminescence spectra of Cu-doped ZnS are caused by the radiative centers including Cu^+ and Cu^{2+}, respectively [6, 7]. The dark-blue and green electroluminescence centers are the best studied ones [17]. It was shown [7, 18] that the formation of dark-blue luminescence centers is related to the ZnS–Cu_2S system while the green luminescence centers are caused by ZnS–CuS system. As all the ZnS:Cu samples were synthesized in identical conditions, except for varying N_{Cu} parameter only, the intensity ratio of *B*-band to *G*-band one can be considered as the amount ratio of radiative centers including Cu^+ to thoset including Cu^{2+}.

Fig. 1 shows that the PL spectra long-wave wings of all copper-containing samples are similar. This points out that the visual variation of PL lineshape in ZnS:Cu phosphors results from change of the intensity ratio between the elementary components forming short-wave part of the spectra, namely change of the relatively intensity ratio between *B*- and *G*-bands. As it will be shown below, the relative *B*-band intensity variation depending on N_{Cu} is nonlinear and correlates well with EPR data.

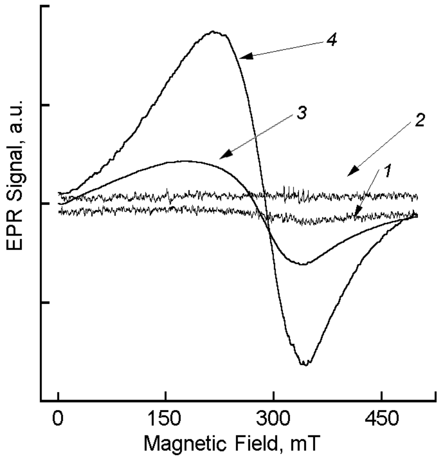

Fig. 3. EPR spectra (T = 300 K) of the ZnS:Cu with Cu concentration: *1* – 0.1 wt. %; *2* – 0.2 wt. %; *3* – 0.6 wt. %; *4* – 2 wt. %.

The EPR measurements were carried out using the same ZnS:Cu samples with copper concentration varying from 0 up to 2 wt. %. Fig. 3 shows the room-temperature EPR spectra of several zinc sulfide powders with different copper concentrations. The phosphors with low copper concentration (0.1 and 0.2 wt. %) do not exhibit any EPR signals related to paramagnetic species including Cu ions. The EPR spectra of these samples consist of six weak lines attributed to uncontrollable Mn^{2+} impurity in ZnS lattice. Increasing of introduced copper concentration results in the appearance of a new broad and intense EPR signal characterized by $g = 2.4\pm0.1$ and $\Delta H_{pp} \approx 130$ mT (see Fig. 3). It arises in the threshold manner and its intensity increases with further rise of introduced copper concentration.

This EPR signal possesses a number of features. First of all, its integrated intensity is very high in comparison with the EPR signals caused by conventional paramagnetic systems. In addition, it demonstrates an unusual temperature behavior. First, with temperature lowering, the integrated intensity of spectrum $I_{EPR}(T)$ increases much weaker than it is to expect from the Curie law for the paramagnetic centers ($I_{EPR}(T) \sim 1/T$). Second, the resonant magnetic field H_{res} is displaced towards lower values, so g factor is 2.75 ± 0.2 at T = 23 K. Finally, in 60 to 200 K interval, an additional narrower EPR line ($g = 2.0\pm0.03$, $\Delta H_{pp} \approx 25$ mT) is revealed; its spectral position being inde-

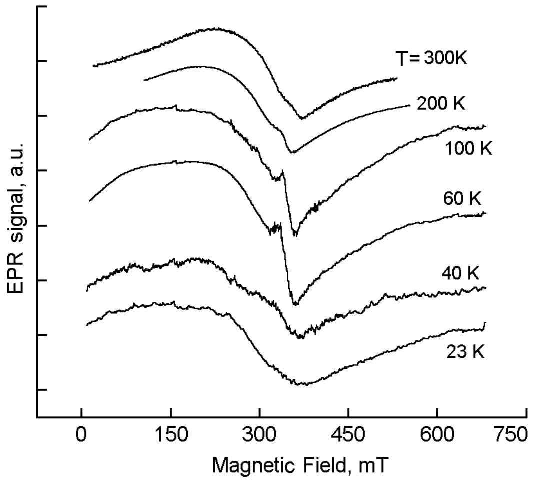

Fig. 4. EPR spectra of ZnS:Cu sample with copper concentration of N_{Cu}≈0.6 wt. % measured at different temperatures.

pendent of the measurement temperature (see Fig. 4).

Let the experimental results obtained be analyzed. Fig. 5 (curve *1*) shows dependence of the EPR spectrum integrated intensity on the introduced copper content at T = 300 K. Curve *2* presents the change of the photoluminescence *B*- and *G*-bands intensity ratio with N_{Cu} increasing. A basic distinction appears to take place in behavior of the ZnS:Cu system at low and high copper concentrations. At low N_{Cu} (area A in Fig. 5) the $(I_B/I_G)_{PL}$ value grows with increasing N_{Cu} and reaches its maximum at N_{Cu}≈0.2 wt %. This growth is caused mainly by increase in relative number of radiative centers responsible for the *B*-band. As the *G*-band is usually attributed to the presence of bivalent copper (<CuS> band [6, 7]), it was possible to expect the corresponding EPR spectrum in ZnS:Cu at N_{Cu}≈0.1 wt. %. However, any copper-containing paramagnetic centers are not revealed in the EPR spectra of the samples with introduced copper concentration $0 < N_{Cu} < 0.2$ wt. % (Fig. 5, curve *1*). This can be explained by broadening of the Cu^{2+} ion EPR lines at room temperatures due to strong spin-lattice coupling caused by Jahn-Teller effect [19] or influence of fast-relaxing paramagnetic oxygen quasimolecules [6]. According to [20], the spin relaxation processes are slowed down by decreasing temperature down to 1–2 K and EPR signals from bivalent copper ions bevome observable.

The situation is drastically changed at further N_{Cu} increase. The $(I_B/I_G)_{PL}$ ratio starts to dropl with N_{Cu} growth (area B in Fig. 5) mainly due to reduction of relative contribution from I_B. This is accompanied by appearance and rapid increase of EPR signal generally consisting of two overlapped lines — wide and narrow (Fig. 4). The radiospectroscopic characteristics of the most intense wide line (*g*-factor and its temperature dependence as well as its anomalous linewidth and temperature behavior) do not agree with published data for Cu^{2+} ions in ZnS [6, 20] that point out another origin of the observed EPR spectrum. Taking into consideration the almost threshold character of its occurrence, it is possible to assume that the EPR spectrum nature is due to essential clustering of copper ions occurring during synthesis when the introduced copper concentration exceeds a certain value. The specific features of the sample synthesis technology appear to be decisive. For each set of the synthesis technological parameters, there will be a specific threshold Cu concentration. Introduction of comparable copper concentrations in the standard technological procedure by sedimentation from aqueous solutions using hydrogen sulfide with the subsequent joint annealing of ZnS powder and Cu was found to do not result in occurrence of such EPR signals [16, 17]. Moreover, the detected correlation between relative drop of I_B PL intensity and increase of the EPR signal (Fig. 5) specifies that the clustering occurs, first of all, due to falling efficiency of Cu_2S phase formation during ZnS:Cu synthesis as compared to the CuS phase.

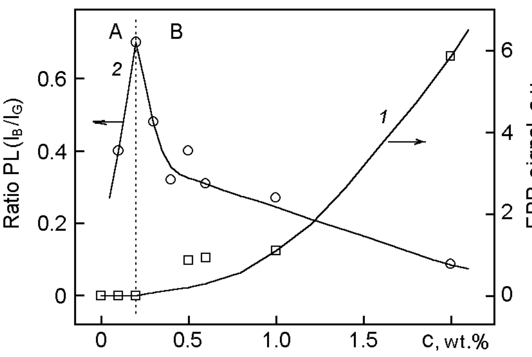

Fig. 5. Integrated intensity of the EPR spectra and intensity ratio of PL *B*- and *G*-bands as functions of N_{Cu} at T = 300°K.

What is nature of new magnetic states in ZnS:Cu samples? The anomalous temperature dependence of the integrated spectrum intensity, reduction of the resonant magnetic field (H_{res}) with decreasing measurement temperature, the specific lineshape with a narrow line observed in a restricted temperature interval — all these attributes are unusual for behavior of spin systems of the isolated paramagnetic centers. On the other hand, such behavior is typical of so-called superparamagnetic systems formed by ensembles of small ferromagnetic particles [21–25]. In our case, the nature of such particles can be attributed to formation of nanosized copper clusters during the crystal synthesis. Indeed, the phenomenon of copper clustering in ZnS:Cu as well as its influence on electroluminescence characteristics was revealed in a number of works [see, for example, 26]. Much more surprising is the fact that copper nanoclusters may show ferromagnetic properties. Nevertheless, occurrence of magnetic properties of Au, Ag, and Cu nanoparticles ($d \sim 2–3$ nm) being initially nonmagnetic on a macroscale, is revealed recently and is interpreted in connection with fundamental problems of magnetism [27].

Within the considered model including superparamagnetic behavior of copper nanoclusters, it is easy to explain the features of magnetic resonance response in ZnS:Cu samples studied. So, the reduction of necessary external field H_{res} observable at the temperature lowering is connected with the action of the internal "superparamagnetic" field increasing in the intensity up to transition to the "blocked", i.e. ferromagnetic state [22]. Another consequence following from this approach is visual subdivision of the magnetic resonance spectrum into a "narrow" line and a "wide" one (see Fig. 4). In fact, both those lines belong to the united magnetic resonance spectrum for an ensemble of nanoparticles with considerably varying size. In this case, the ratio between spectrum contributions from particles of the small and great sizes ("narrow" and "wide" lines, respectively) depends on a set of parameters, including the dispersion characteristics of the particles and temperature [23–25]. It is to note that the narrow line observed in our experiments (Fig. 4) can be attributed not only to small copper clusters, but also to single Cu^{2+} centers due to proximity of their radiospectroscopic characteristics, see [5].

4. *Conclusion*

Thus, the data obtained allow us to conclude that at increasing introduced Cu concentration during SHS synthesis of ZnS:Cu, a certain fraction of copper atoms not only forms radiative centers including Cu^{2+} and Cu^{+}, such as Cu_2S and CuS phases, but is also involved in formation of more complex ensembles. The copper ions clustering involving a large number of Cu atoms occurs at $N_{Cu} > 0.3$ wt. %. The latter process has a threshold character and it is manifested as the occurrence of a superparamagnetic subsystem in researched materials being confirmed in experiment as occurrence of anomalous EPR signal.

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Парамагнітні та люмінесцентні властивості ZnS:Cu, одержаного методом одностадійного синтезу

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Досліджено парамагнітні та фотолюмінесцентні властивості ZnS, одержаного методом самопоширюваного високотемпературного синтезу з різною концентрацією легуючої домішки Cu. Продемонстровано зміни спектра електронного парамагнітного резонансу ZnS:Cu з концентрацією міді $N_{\mathrm{Cu}} \approx 0,6$ мас.% в залежності від температури. Обговорюються процеси формування фаз з участю Cu в ZnS. Показано, що починаючи з концентрації $N_{\mathrm{Cu}} > 0,3$ мас.% відбувається кластеризація іонів міді у матеріалі. Формування комплексів, які включають кластери Cu, супроводжується появою суперпарамагнітної підсистеми, експериментальним підтвердженням чого є поява аномального сигналу електронного парамагнітного резонансу.