

PACS 78.55.Et

Luminescent properties of fine-dispersed self-propagating high-temperature synthesized ZnS:Cu,Mg

Yu.Yu. Bacherikov¹, A.G. Zhuk¹, R.V. Kurichka¹, O.B. Okhrimenko¹, A.V. Gilchuk², O.V. Shcherbyna², M.V. Herkalyuk²

¹*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine
41, prospect Nauky, 03028 Kyiv, Ukraine; e-mail: Yuyu@isp.kiev.ua*

²*National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnical Institute"
37, prospect Peremogy, 03056 Kyiv, Ukraine*

Abstract. The influence of magnesium impurities on luminescent properties of ZnS:Cu,Mg using obtained by self-propagating high-temperature synthesis (SHS) has been investigated. Special attention was paid to changes of photoluminescence spectra caused by relaxation processes in ZnS:Cu,Mg-SHS. It was shown that introduction of magnesium into ZnS:Cu-SHS leads to a change in symmetry of ZnS crystal lattice. It leads to relaxation quenching the photoluminescence bands caused by presence of copper impurities in ZnS.

Keywords: self-propagating high-temperature synthesis, photoluminescence spectra, luminescence excitation spectra, electron microscopy.

Manuscript received 12.01.17; revised version received 26.04.17; accepted for publication 14.06.17; published online 18.07.17.

1. Introduction

The increasing flow of information stimulates studies of materials that can be used as luminophores for basic components of display devices [1-3]. At the same time, luminescent characteristics of light-emitting materials largely depend on the material structure [4, 5], ratio of impurities acting as luminescence activators and co-activators [6, 7], *etc.* Studies of the materials obtained using unconventional methods, such as SHS, are of particular interest. Using SHS can reduce the cost of obtained luminophores, because this method is a low-cost technology.

In almost all studies of luminophores, the main task is to increase the intensity of radiation and possibility of using the obtained material in electroluminescent devices. In [8], it was shown improvement of electroluminescent characteristics in thin-film devices based on ZnS:Cu,Mn after doping MgF₂ and MgS. Also,

increasing the intensity of photoluminescence (PL) after introduction of MgS or MgCl₂ in defined concentration was noted [8].

At the same time, the resistance to degradation of luminophores is a necessary condition for their successful use. Most of luminophores loses their efficiency, which may be related both to valence change caused by oxidation, and to degradation of crystal lattice. In the second case, atoms diffuse through material and react with ambient matter. The results of degradation were not only decreasing the quantum efficiency of luminophore, but also changing the spectral characteristics of its luminosity.

The goal of this work was to study the influence of magnesium impurities that were introduced into ZnS as activator and co-activator in fine-dispersed ZnS:Cu obtained using the SHS method, and time evolution of luminescent characteristics of obtained luminophores.

2. Materials and methods

Fine-dispersed undoped ZnS-SHS, Mg-doped ZnS:Mg and doped with magnesium and copper ZnS:Cu,Mg were obtained using SHS. Magnesium and copper doping was carried out by adding Cu and Mg chlorides directly in the process of synthesis. For synthesis, Zn and S were taken in the stoichiometric ratio. Concentration of Cu was close to 1.2 wt.%. For synthesis of ZnS:Mg, the concentration of Mg was ~1.2 wt.%. For synthesis of ZnS:Cu,Mg, the amount of MgCl₂ in the charge was ~5 wt.%. Charge materials were analytical grade.

Photoluminescence spectra were registered at room temperature by using the spectrometer SDL-2.

Investigation of particle sizes and morphology was carried out using the method of scanning electron microscopy with the device REM-106 I. Samples were investigated using the accelerating voltage 20 keV in the regime of backscattered electrons.

Measurements of elemental composition were performed using energy-dispersive X-ray spectroscopy (EDS).

3. Experimental results and discussion

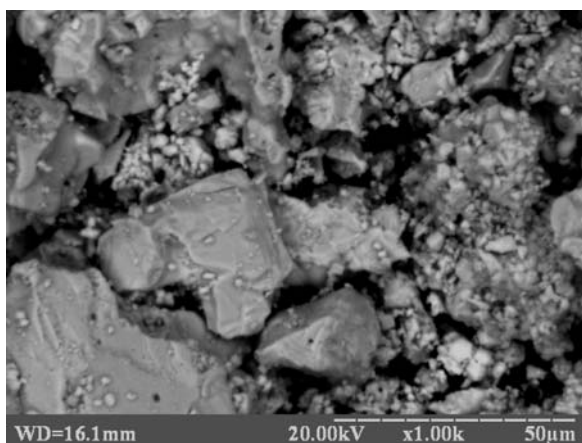
Electron microscopy study of ZnS:Cu,Mg-SHS showed that the synthesized powders consist of two fractions. One fraction consists of large particles with dimensions up to several decades of micrometers. The second fraction consists of particles of micron and submicron sizes (Fig. 1a). The minimum Ferret diameter was chosen as a characteristic particle size. The histogram of particle sizes distribution is shown in Fig. 1b. The function of distribution was approximated by lognormal law and, according to this approximation, the average particle size was $1.32 \pm 0.01 \mu\text{m}$.

According to EDS measurements (Fig. 2), elemental composition of fine-dispersed ZnS:Cu,Mg-SHS is close to the stoichiometric one: Zn_{48.8}S_{49.0}Cu_{0.7}Mg_{1.5}.

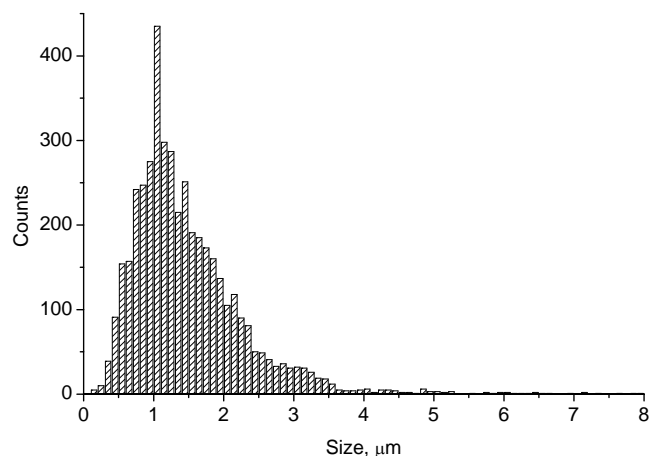
Fig. 3a represents PL spectra of ZnS-SHS, ZnS:Mg-SHS and ZnS:Cu,Mg-SHS. As can be seen from Fig. 3a, curves 1 and 2 in the spectra of undoped ZnS-SHS and ZnS:Mg are almost identical by their spectral composition. This means that luminescence of both powders is self-activated and caused by identical centers. Slight broadening the PL line in the area of long waves can be associated with disturbance in lattice of ZnS during the process of introducing the impurity with very different ionic radius.

The PL spectrum of undoped ZnS-SHS is a broad line in the area of 400 to 650 nm with $\lambda_{\text{max}} \sim 505$ nm. This band is complicated and consists of several individual components. Decomposition of the PL spectrum of ZnS-SHS into components is presented in Fig. 3b. The PL bands with $\lambda_{\text{max}} \sim 455$ -465 nm was related to native defects and their complexes that may include co-activator and oxygen [9, 10]. These complexes are centers of self-activated (SA) luminescence. According to [9, 10], SA-luminescence of undoped ZnS consists of range of closely located and, in general, overlapped bands of PL related with different defects (Fig. 3b).

Investigation of spectral composition of ZnS:Cu,Mg-SHS PL spectra, registered immediately after synthesis, showed a significant difference in comparison with the spectrum of undoped ZnS-SHS and ZnS:Mg-SHS. As can be seen from Fig. 3a, curve 3, spectrum of ZnS:Cu,Mg that was registered immediately after synthesis is a broad asymmetric sub-band with $\lambda_{\text{max}} \sim 530$ nm. This band is complicated and consists of at least three individual components with $\lambda_{\text{max}} \sim 450$, ~ 500 and ~ 520 nm. It is well known that PL band of ZnS:Cu in the blue-green region is complex, and usually is a superposition of several sub-bands related to copper dopant and native defects of ZnS. The nature of the luminescent centers responsible for the blue and green lines is ZnS was studied in sufficient detail in [11-18].



a



b

Fig. 1. a) Electron microscopic image of ZnS:Cu,Mg-SHS powder. b) Size distribution of particles in ZnS:Cu,Mg-SHS.

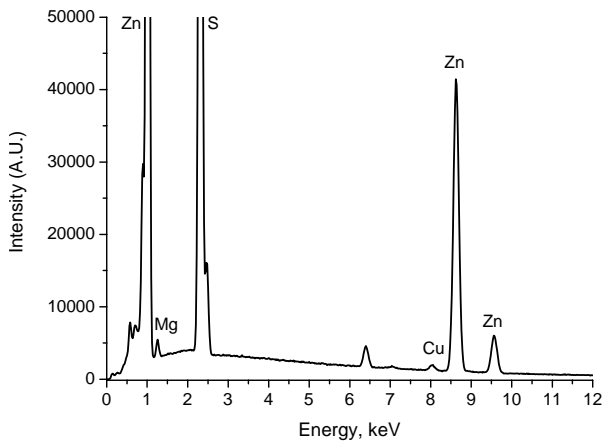


Fig. 2. EDS spectrum of fine-dispersed ZnS:Cu,Mg-SHS.

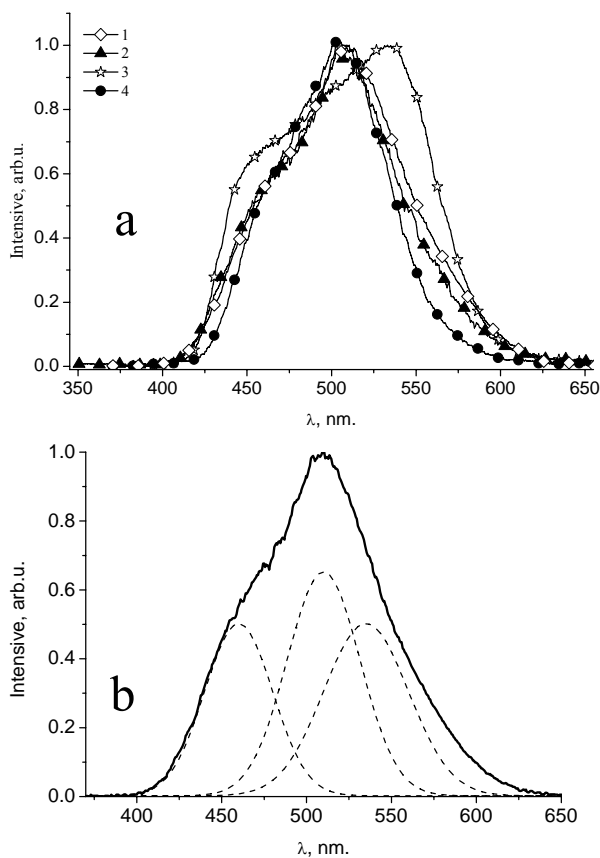


Fig. 3. a) PL spectra of: ZnS-SHS (1), ZnS:Mg-SHS (2), ZnS:Cu,Mg-SHS (3) immediately after synthesis, ZnS:Cu,Mg-SHS 7 days after synthesis (4); b) decomposition of ZnS-SHS spectrum into components.

Authors [11-17] showed that the center responsible for the appearance of Cu green line was insulated copper ion that replaced the zinc one in the lattice of ZnS. It was determined that symmetry of this center is not less than that of the regular lattice point in cubic or hexagonal lattice of ZnS. At the same time, this center doesn't include co-activator. The blue band was related with formation of donor-acceptor type associations Cu_i-Cu_{Zn} [18].

The PL spectrum of ZnS:Cu,Mg-SHS undergoes great changes in 7 days after synthesis (Fig. 3a, curve 4). PL bands caused by copper dopant and presented in Fig. 3a, curve 3, are almost absent in the spectrum registered in 7 days after synthesis (Fig. 3a, curve 4). Comparison of the PL spectrum of ZnS:Cu,Mg-SHS registered a week after synthesis and the PL spectrum of undoped ZnS-SHS showed that PL spectra in these cases can be related to the centers of radiative recombination, which have similar nature. At the same time, the PL band with the maximum in the range of 500 nm, which is related with self-activated PL in ZnS, is dominant in the spectrum of pure ZnS-SHS, ZnS:Cu,Mg-SHS and ZnS:Mg-SHS (Fig. 3a).

These data indicate that centers of radiative recombination which includes copper are destroyed during the relaxation processes in material. Probably, it is caused by increasing in the degree of ZnS lattice deformation in processes of magnesium introduction, because the ionic radius of Mg is much less than that of Zn and Cu. According to [19], Mg ions can partially fill tetrahedral interstitial sites or replace Zn in ZnS lattice. The volume of the unit cell, in which Mg is inserted, decreases due to shorter ion radius of Mg. Consequently, mechanical stress and deformation of ZnS lattice occur. Furthermore, introduction of magnesium can change the phase ratio in ZnS [19]. It is well known [11, 20] that introduction of copper usually stabilizes the cubic phase, but introduction of magnesium stabilizes the hexagonal phase, according to [21]. Therefore, since both copper centers include Cu_{Zn} , it is quite possible that simultaneous decrease of green and blue bands is caused by copper shifting from the main position into the interstitial site due to deformation or to the change of lattice symmetry. Perhaps, this process will be accompanied by dropping out of Cu as separate fraction.

It should be mentioned that SHS – is physical-chemical process that proceeds in extreme conditions at high temperature and with a high rate of heating the substance in a wave of combustion [22, 23]. These factors lead to formation of several phases of material (with different crystal structure, character of bonds, symmetry, etc.) during the process of synthesis in wide temperature and pressure ranges. All this contributes to the appearance of unstable structural states in material.

Therefore, at the beginning of introduction of $MgCl_2$ into the charge, magnesium compounds lead to mass transfer between particles of ZnS, *i.e.* act as a flux [21, 24, 25]. According to [4, 11], it may contribute to introduction of an activator (copper or some other dopants) into lattice of luminophore. In the further relaxation processes (especially if synthesis conditions facilitate the formation of unstable structural states or phases), presence of magnesium promotes deformation processes, which leads to changes in symmetry of ZnS crystal lattice. It becomes a reason for quenching the PL bands, which is caused by presence of copper impurities.

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