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Influence of the presence of a fluxing agent and its composition on the spectral characteristics of ZnS(Cu) obtained by self-propagating high-temperature synthesis

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Abstract. Investigated in this work were the photoluminescence spectra and luminescence excitation spectra of powered ZnS:Cu, obtained using the method of self-propagating high-temperature synthesis (SHS) with addition of NaCl and MgCl₂ as a fluxing agent into the charge and without them. It was shown that increasing the amount of fraction with the particle sizes ≤ 5 nm in powdered ZnS:Cu-SHS, where fluxing agents are present in the charge, is caused by the decrease in temperature inside the reactor in the course of the synthesis reaction. Besides, related increasing the intensity of the PL blue band with $\lambda_{\text{max}} \sim 450..465$ nm in powdered ZnS:Cu-SHS/MgCl₂, which is associated with redistribution of the copper impurity in the bulk of microcrystals, probably, occurring as a result of increasing the partial pressure of Cl during synthesis.

Keywords: self-propagating high-temperature synthesis, photoluminescence spectra, luminescence excitation spectra, fluxing agent, powered ZnS, copper impurity.

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1. Introduction

In recent years, more and more attention is paid to non-classical methods of producing materials, to which, inter alia, applied is the method of self-propagating high-temperature synthesis (SHS) [1]. Materials obtained by SHS in their structure, properties, chemical resistance are different from the materials obtained in other ways, even if they have the same chemical composition. One of the problems in studying the SHS-materials is to establish relationships between the properties of SHS-products, on the one hand, and the composition of the charge, on the other hand, which is necessary to optimize the synthesis conditions for

obtaining the single-phase materials having the desired properties [2]. Among the materials, in preparation of which the SHS method is widely used, are phosphors based on ZnS [3, 4]. In particular, this applies to ZnS, doped with Cu, Mn, Al or Ag that act as activators of luminescence in ZnS [4, 5].

A special place in the studies of the effect of preparation regimes on materials obtained using SHS is comprised by the influence of fluxing agents on the course of the process of synthesis, structure and properties of the material [6]. Typically, fluxing agents are used to reduce temperature of synthesis and sintering of the produced material, which in turn leads to a decrease in dispersion of the obtained material [7].

Of particular interest is the possibility of obtaining by the SHS method of low-dispersion ZnS with a particle size close by its value to the radius of exciton (~5 nm) and manifesting the quantum size effects in the obtained material.

The aim of this work was to determine the effect of fluxing agents (NaCl and MgCl₂) introduced into the charge on the luminescence properties of the fine-dispersion ZnS:Cu, prepared using the SHS method.

2. Experimental procedure

Powdered ZnS:Cu was prepared using the SHS method. Doping with copper impurity was carried out from CuCl, directly during synthesis. The ratio of starting materials was: Zn – 62 wt.%, S – 32 wt.%, CuCl – 1 wt.%, the fluxing agent content was 5 wt.% in both cases. As a fluxing agent NaCl and MgCl₂ were added into the charge.

Studies of morphology and the particle size were performed using scanning electron microscopy (SEM) on the microscope JAMP-9500F (Jeol).

Photoluminescence (PL) spectra, electroluminescence spectra and luminescence excitation spectra (PLE) were recorded at room temperature by using the setup SDL-2. For PL, we used radiation of the nitrogen laser LGI-23 ($\lambda = 337$ nm). When recording LES, excitation of samples was carried out with radiation of Xe lamp through the monochromator MDR-12.

3. Experimental results and discussion

Fig. 1 shows typical SEM images for the fine-dispersion ZnS:Cu fractions, prepared using the SHS method. As seen from these SEM images, the synthesized fine-dispersion fraction is a mixture of particles of different sizes, in which both the nanoparticles and particles of micron and submicron sizes are available.

Fig. 2 shows the photoluminescence spectra of ZnS:Cu obtained using the SHS method with addition of NaCl and MgCl₂ as a fluxing agent into the charge and without them. All the spectra have the form characteristic for PL zinc sulfide doped with copper, but with different localization of copper in the lattice of ZnS.

As can be seen (Fig. 2), the spectra are complex broad band in the blue-green area of the spectrum and consist of bands with $\lambda_{\max} \sim 450 \dots 465$ nm and $\lambda_{\max} \sim 505 \dots 535$ nm. Note that these bands may be caused by several types of centers of copper emission [8-10] as well as by centers of oxygen [8, 11] and self-activated radiation [9-11]. To date, the nature of the luminescence centers, causing the blue and green bands of Cu in ZnS, is well studied [8-13]. In the works [11-15], it is shown that the center of the green glow of copper with $\lambda_{\max} \sim 505 \dots 535$ nm is isolated copper ion, replacing zinc ion in the ZnS lattice. The blue band with $\lambda_{\max} \sim 450 \dots 465$ nm is related to formation of associates like to the close DA-pair Cu_i-Cu_{zn} [16]. The

main difference of the PL spectra between them, as shown in Fig. 2, is in redistribution of the intensities of the bands associated with copper impurity. And in ZnS:Cu without fluxing agent, the green band with $\lambda_{\max} \sim 505 \dots 535$ nm is dominant, as well as a wing with $\lambda_{\max} \sim 450 \dots 465$ nm is present. With the introduction of MgCl₂, a significant increase in the intensity of the blue band and a small shift of the maximum into the short-wave region are observed. When introducing NaCl, in the PL spectrum the blue band with $\lambda_{\max} \sim 450 \dots 465$ nm becomes dominant, which leads to a shift of the PL maximum into the blue spectral region.

Increasing the intensity of the blue band (Fig. 2, curve 3) is associated with redistribution of the copper impurity in the volume of microcrystals. Possibly, the presence of a fluxing agent leads to increasing the partial pressure of Cl [17], which increases the solubility of copper in the basis of luminophore and results in additional association of copper ions and formation of centers like to the close DA-pair Cu_i-Cu_{zn} and, accordingly, to combusting of PL blue band.

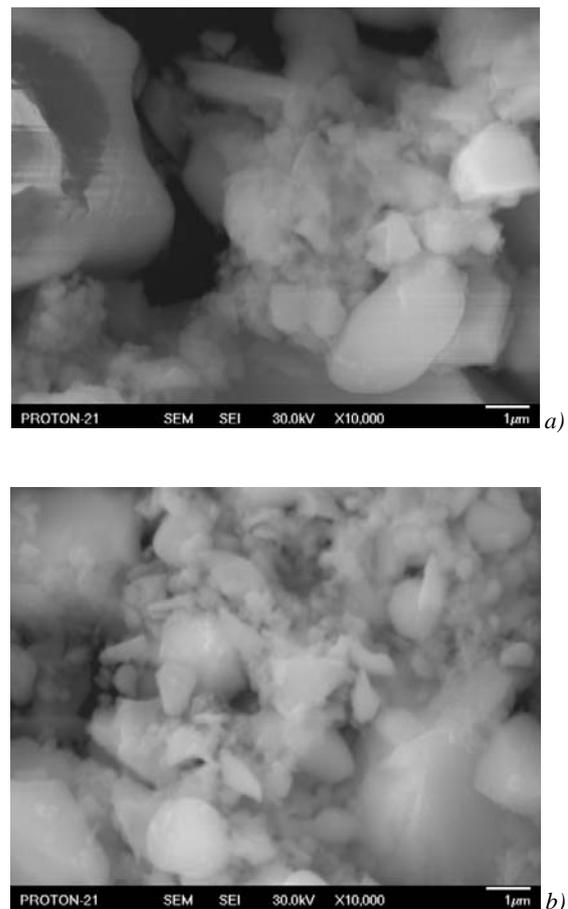


Fig. 1. SEM-images of fine-dispersion ZnS:Cu obtained using the SHS method with addition of NaCl (a) and MgCl₂ (b) as fluxing agents into the charge.

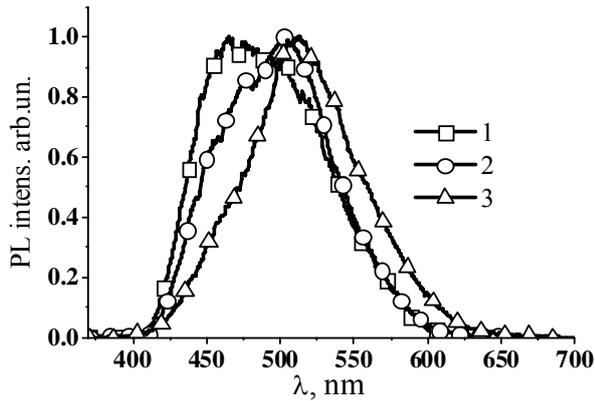


Fig. 2. PL spectra of ZnS:Cu obtained using the SHS method with addition of NaCl (1) and MgCl₂ (2) as fluxing agents into the charge and without them (3).

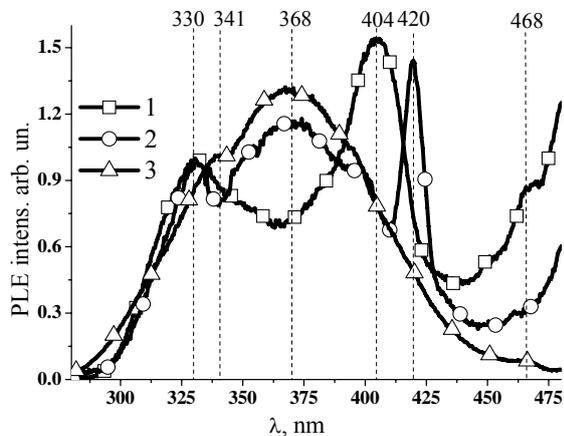


Fig 3. PLE spectra of SHS-synthesized ZnS:Cu, normalized to the intensity of the fundamental absorption band, with addition of NaCl (1) and MgCl₂ (2) as fluxing agents into the charge and without them (3).

Table. Comparative characteristics of NaCl and MgCl₂ fluxing agents [18].

Parameter	NaCl	MgCl ₂
Melting temperature, °C	800.8 °C	713 °C
Boiling temperature, °C	1465 °C	1412 °C
Specific heat of evaporation	170.85 kJ/mol	246 kJ/mol
Specific heat of melting	28.68 kJ/mol	39.7 kJ/mol
Saturated vapor pressure, in mm Hg (750 °C)	0.357	19
Heat capacity	35.79 (g) J/(mol·K)	56.6 (g) J/(mol·K)
Energy of crystal lattice	744 kJ/mol (185 kcal/mol)	2480 kJ/mol (597 kcal/mol)

Effect of Cl, as a co-activator, on the spectral composition and PL intensity is related with necessity to compensate charge of internal defects in material, which is in sufficiently details described in the works [8-14]. In [14], it has shown that even a small amount of the Cl impurity in ZnS conduces introduction of copper into the sites of Zn sublattice, or filling the Zn vacancies, which leads to an increase in contribution of the green band to luminescence. The appearance of the blue band in the PL spectrum, when introducing Cl, is obviously associated with the formation type of the centers similar to close DA-pair Cu_i-Cu_{Zn}.

Fig. 3 shows the spectra of luminescence excitation (PLE) measured for the band with $\lambda_{\max} = 510$ nm normalized to the maximum of band-to-band excitation. It is seen that the excitation spectrum of zinc sulfide doped with CuCl contains three bands with maximum positions 368, 380 and 395 nm in addition to the band of the band-to-band excitation at 334 nm. In spectra of the samples synthesized in the presence of a fluxing agent, there also are the bands of 404, 420 and 468 nm, probably related to both the Na and Mg impurity, respectively. As seen in Fig. 3, curves 1 to 3, the spectra of luminescence excitation for ZnS:Cu-SHS include bands corresponding to transitions of band-to-band excitation in bulk and quantum-sized ZnS. According to [8], the E_g value for ZnS is ~ 3.65 eV, which corresponds to the absorption band of 340 nm. The shift of the maximum of fundamental absorption band by 10 nm indicates the presence in the material of the particles, the size of which corresponds to the manifestation of the quantum sized effect [18]. This indicates the presence of the material of both large particles, dimensions of which are larger than hundreds of nanometers, and particles with the sizes less than 5 nm (*i.e.*, of the order of the Bohr radius for exciton in ZnS), which is clearly seen from the SEM data. Increasing the amount of the fraction with the particle sizes ≤ 5 nm in powdered ZnS:Cu-SHS, in which fluxing agents present in the charge, is caused by the decrease in temperature in the reactor during the course of the synthesis reaction. As seen from Table, the melting temperatures of MgCl₂ and NaCl are close, like to their specific heats of melting [19, 20]. Probably, that's why the particle sizes composing the nanofraction are close. As evidenced by the coincidence of values of band-to-band transitions for ZnS:Cu-SHS in that case when NaCl and MgCl₂ were present in the charge.

4. Conclusion

Thus, as can be seen from these results, introduction of fluxing agents (NaCl and MgCl₂) into the charge results in increase of the amount of material with the particle sizes ≤ 5 nm in the powdered ZnS:Cu-SHS.

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