

Effect of annealing mode on ZnS–Cu,Cl properties

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Influence of annealing modes on spectral characteristics of photoluminescence, electroluminescence, and electron spin resonance of ZnS:CuCl and ZnS:CuCl₂ powders has been studied. The thermal doping processes and structure properties of ZnS have been shown to be influenced considerably by the sample heating and cooling rates during the anneal. Increasing of the above-mentioned rates results in increased concentrations of double-charged copper and manganese impurities in zinc sulfide. Moreover, it has been shown that the blue ($\lambda_{max} \sim 450$ nm) emission centers are more sensitive to excitation by ac electric field ($U = 250$ V, $f = 5000$ Hz) than to photoexcitation.

Исследовано влияние режимов отжига порошков ZnS:CuCl и ZnS:CuCl₂ на спектральные характеристики их фотолюминесценции, электролюминесценции и электронного парамагнитного резонанса. Показано, что на процессы термического легирования, а также на структурные свойства ZnS, существенное влияние оказывает характер разогрева и остывания образцов в процессе их отжига. Увеличение скорости разогрева и остывания образцов в процессе их отжига приводит к возрастанию концентрации в сульфиде цинка двухзарядных примесей меди и марганца. Кроме того, в работе показано, что центры синего свечения с $\lambda_{max} \sim 450$ нм более чувствительны к возбуждению переменным электрическим полем ($U = 250$ В, $f = 5000$ Гц), чем к фотовозбуждению.

ZnS type luminophors activated with heterovalent impurities contain, besides of activator-related emission centers, a complex system of competitive centers where the charge carrier recombination may occur in both emissive and non-radiative manner, depending on the impurity introduction method. This work is aimed at comparative study of photoluminescence, electroluminescence, and electron spin resonance spectral characteristics of ZnS powders doped with CuCl and CuCl₂ to elucidate the effect of the annealing mode on the zinc sulfide doping process.

The ZnS powders (ETO.035.295 TU) mixed with copper salts, CuCl (1.25 %) or CuCl₂ (1.25 %) were annealed for 1 h at $T = 800^\circ\text{C}$. The sample heating-up time to the anneal temperature was 6.75 h (Rate A) or 15 min (Rate B). The sample cooling down to room temperature was slow (420

and 360 min for A and B Rates, respectively). The samples for electroluminescence (EL) studies were prepared using a standard procedure. A transparent electrode deposited onto glass was coated by light-emitting layer consisting of a mixture of powdered electroluminophor (ZnS:Cu,Cl) and dielectric binder based on ER-96 (TU 6-10-763-75) epoxy varnish. Then opaque metal electrode was deposited in vacuum. The light-emitting layer was about 50 μm thick. Photoluminescence (PL) and electroluminescence spectra were taken using an SDL-2 unit at 300 K. The PL was excited using a DKSSh-150 xenon lamp and a LGI-23 nitrogen laser ($\lambda = 337$ nm). To excite EL, an ac generator was used operated at $0 < U < 750$ V and $0 < f < 5000$ Hz. The electron spin resonance (ESR) spectra were taken at room temperature using an RE-1307 ESR spectrometer operating in 3 cm wavelength range.

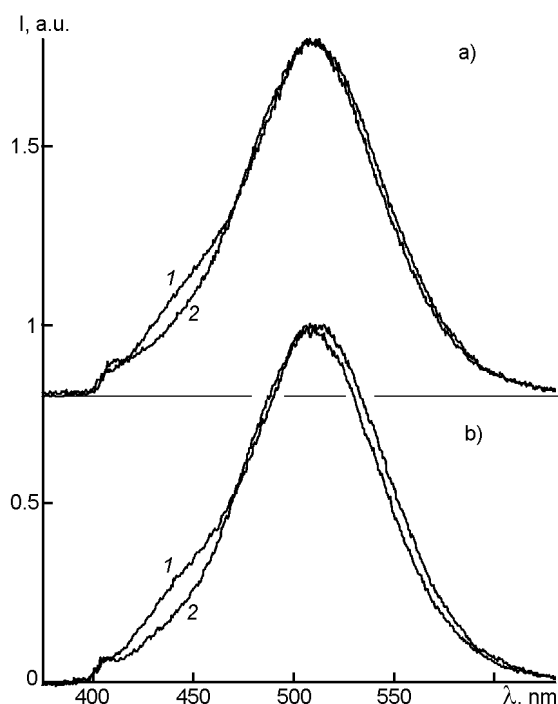


Fig. 1. PL spectra of ZnS:CuCl and ZnS:CuCl₂ powders annealed at the Rate A (1) and B (2).

The PL spectra of studied samples contain three bands. For samples annealed at the Rate A, those are peaked at $\lambda_{max} \sim 450$ nm (2.76 eV) and ~ 508 nm (2.44 eV) answering to blue and green emission centers [1, 2]. In [1], it has been shown that the formation of blue emission centers is related to the ZnS–Cu₂S system while that of green ones, to the ZnS–CuS one. Moreover, a band peaked at $\lambda_{max} \sim 410$ nm (3.02 eV) is also present in PL spectra of all the samples studied (Fig. 1). This band is related to sulfur vacancies, V_S centers [3, 4]. Note that there is no that band in EL spectra. In PL spectra of samples annealed at the Rate B, the $\lambda_{max} \sim 450$ nm band is essentially unobservable. At the same time, that band (450 nm) is present in all the EL spectra, although being weaker for samples treated at the Rate B (Fig. 2a). Thus, the blue emission centers arising, according to [1], as a result of physico-chemical transformation in the ZnS–Cu₂S system are formed at the Rate B in an amount several times lesser than at the Rate A. In other words, the quick heating of ZnS powder when being doped with copper is less favorable for single-charged copper impurity formation. The choice of a salt of both single-charged copper (CuCl) and double-charged one (CuCl₂) as the dopant does not influence

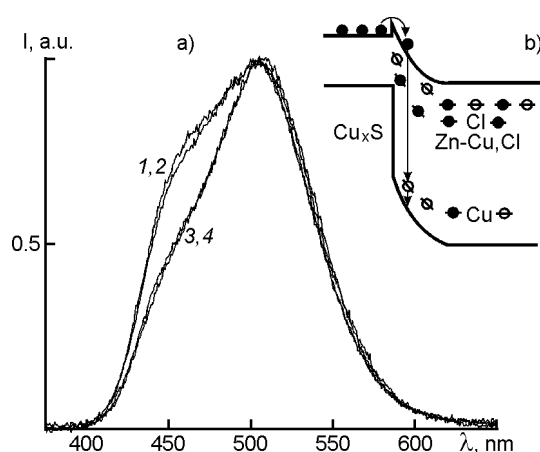


Fig. 2. (a) EL spectra ($U = 250$ V, $f = 5000$ Hz) of ZnS powders annealed with CuCl (1) and CuCl₂ (2) at the Rate A, CuCl (3) and CuCl₂ (4) at the Rate B; (b) energy scheme of heterojunction between copper and zinc sulfides.

the blue band intensity. Perhaps this can be explained as follows. During the annealing, CuCl and CuCl₂ are decomposed into their components still prior to the diffusion into ZnS. Therefore, the only distinction between those cases consists in different chlorine concentrations introduced, that, as is seen from the results, do not effect essentially the shape of both PL and EL spectra.

The results obtained have shown that the blue emission centers are more sensitive to the electric field excitation than to photoexcitation. While the PL spectrum of a sample annealed at the Rate B is similar to a Gaussian, the EL one exhibits a shoulder about 450 nm, thus revealing one more luminescence band. Maybe this is due to what follows. At the PL, the excitation and recombination of non-equilibrium carriers occurs in one and the same point of the crystal. At EL, in contrast, a fraction of the carriers may leave the excitation region and recombine in another crystal point. Basing on the energy scheme proposed for heterojunctions between copper and zinc sulfides in [5] (see Fig. 2b), it can be supposed that in the ZnS–Cu₂S system, the electrons excited in Cu₂S go to the space charge region or to the main material volume where recombine under emission. This situation is observed more clearly at a low concentration of the Cu₂S phase in ZnS when, according to [1], the composition of blue PL luminophors corresponds to $10^{-5} - 10^{-6}$ g Cu per gram ZnS. In our case, it is just the samples annealed at Rate B; then, the emissive transition under consideration is still

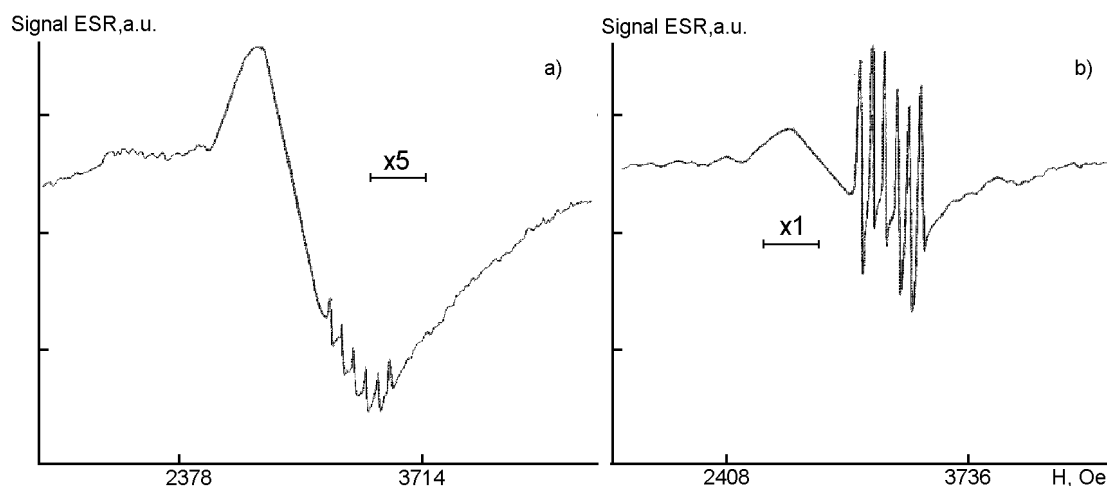


Fig. 3. ESR spectra ZnS:CuCl powder annealed at the Rate A (a) and B (b) ($\nu = 9365$ MHz).

not realized in PL but already observable in EL. As the Cu_2S content in ZnS increases, the amount of excited carriers in the Cu_2S region becomes sufficient to the carriers may attain the recombination point independent of the field action, due to concentration-induced diffusion. The green emission of ZnS- Cu_xS , unlike the blue one, is seen to be manifested itself clearly both in PL and EL spectra. In our opinion, this seems to be due to a high content of CuS phase in ZnS eliminating any priority in the carrier excitation mechanism for the green emission.

That the ESR spectra of all the samples (ZnS:CuCl as well as ZnS:CuCl₂) contain a broad intense line evidencing a large amount of paramagnetic centers (PC), perhaps due to both surface and volume defects, as well as a pronounced six lines characterizing the superfine interaction of manganese ion Mn^{2+} with its nucleus (Fig.3).

The ESR spectrum of Mn^{2+} is described by spin Hamiltonian

$$\hat{H} \rightarrow g\beta\hat{H}\hat{S} + A\hat{S}\hat{I}, \quad (1)$$

where g factor $g = 2.002$ and the superfine constant $|A| = 65.4 \cdot 10^{-4} \text{ cm}^{-1}$. The electron spin S and nuclear spin I are $5/2$.

Note that manganese is an uncontrolled impurity in ZnS due to technological origin. In the initial samples, prior to heat treatment, ESR studies have revealed no PC associated with Mn^{2+} . Perhaps this is ex-

plained to Mn recharging during the anneal. Considering the ESR spectra, it can be stated with certainty that the amount of PC associated with Mn^{2+} is considerably larger in samples annealed at the Rate B than in those treated at the Rate A.

Thus, it follows from the above results that the ZnS thermal doping processes as well as the structure of the material are effected substantially not only by the annealing duration and temperature (being discussed often in literature) but also by the sample heating and cooling rates. The higher are the above rates, the more efficient is the manganese impurity recharging in ZnS, that is, the concentration increase of paramagnetic Mn^{2+} centers. In ZnS doping with copper, this annealing rate is also more efficient in predominating formation of double-charged copper impurity as compared to the single-charged one.

References

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Вплив режиму відпалу на властивості ZnS–Cu,Cl

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Досліджено вплив режимів відпалу порошоків ZnS:CuCl та ZnS:CuCl₂ на спектральні характеристики їх фотолюмінесценції, електролюмінесценції та електронного парамагнітного резонансу. Показано, що на процеси термічного легування, а також на структурні властивості ZnS, значний вплив має характер розігріву та охолодження зразків у процесі їх відпалу. Збільшення швидкості розігріву та охолодження зразків у процесі їх відпалу веде до збільшення концентрації у сульфіді цинку двозарядних домішок міді та марганцю. Крім того, у роботі показано, що центри синього світіння з $\lambda_{max} \sim 450$ нм більш чутливі до збудження змінним електричним полем ($U = 250$ В, $f = 5000$ Гц), ніж до фотозбудження.