New Methods in the Technology of Electroluminescent Phosphors

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Abstract
Controlling synthesis conditions of ZnS:Cu,Al and ZnS:Cu electroluminescent phosphors we optimized particle size, color properties and efficiency. Surface properties were studied by new method and showed correlation with luminescence as shown by the analysis of EL spectra with Fok-Alentsev method. Luminance and maintenance improvement was achieved by the electron-beam annealing due to additional decomposition of ZnS-Cu_2S solid solution and formation of centers of blue luminescence.

1. Introduction

Electroluminescent powder phosphor is the key component of electroluminescent light sources (ELP). EL phosphor directly convert electrical energy to the light, it is economical, light-weight, flat and flexible device. ELPs are used for backlighting LC displays for mobile electronics. It is mercury free and does require any disposal. Current situation requires phosphors of different colors to meet market demands. It is also essential to provide high brightness of electroluminescence while keeping voltage and power consumption low hence ELP thickness should be decreased. To achieve that one need small particle phosphor to ensure bright and uniform device luminescence.

2. Phosphor Synthesis

We developed technology of the synthesis of small particle size ZnS:Cu,Al and ZnS:Cu electroluminescent phosphors. For the synthesis of electroluminescent powders high-purity zinc sulfide was mixed with the flux of different composition as well as copper and aluminum compounds. Synthesis was performed in closed quarts crucibles without utilization of any special atmosphere. After synthesis and consequent annealing, excess of copper sulfide phase was washed out of the surface of the powders. Details of the synthesis conditions were published elsewhere[1].

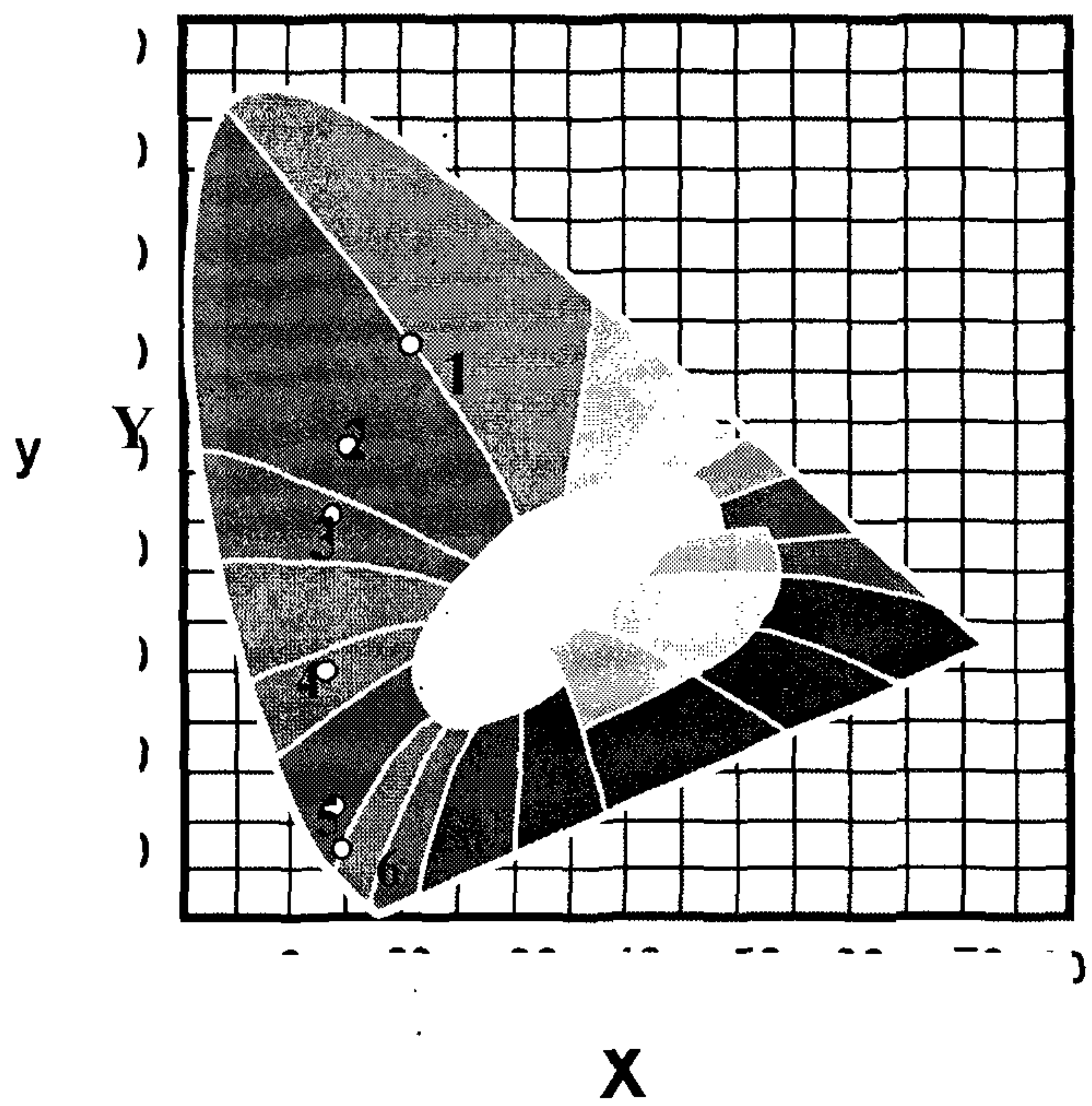


Figure 1 – Color properties of developed phosphors.

By the optimization of the synthesis conditions and flux composition we were able to regulate color of luminescence and improve brightness and stability of phosphor. Figure 1 reflects color properties of the developed phosphors.

To decrease particle size of the phosphor ball milled zinc sulfide was used and synthesis temperature was decreased. Grains of synthesized phosphor are quite regular and phosphor has relatively narrow particle size distribution with average particle size of 14μ comparing to 25μ for the commercial sample[2].

3. Phosphor Fractionation

For the purpose to further decrease particles size we developed fractionation technique based on gravitational sedimentation in the viscous media. Conditions were found allowing to separate three fractions of the green phosphor: small size particles (0-10μ), middle size (10-20μ) and large size (20-30μ). Initial and fractionated samples were tested for the brightness and stability (defined as half-brightness time in the accelerated aging test). Results are shown on the figure 2. One can see that small size fraction has about two time higher brightness comparing to the initial phosphor while its stability is almost same. Yield of the small particle fraction is up to 70%.

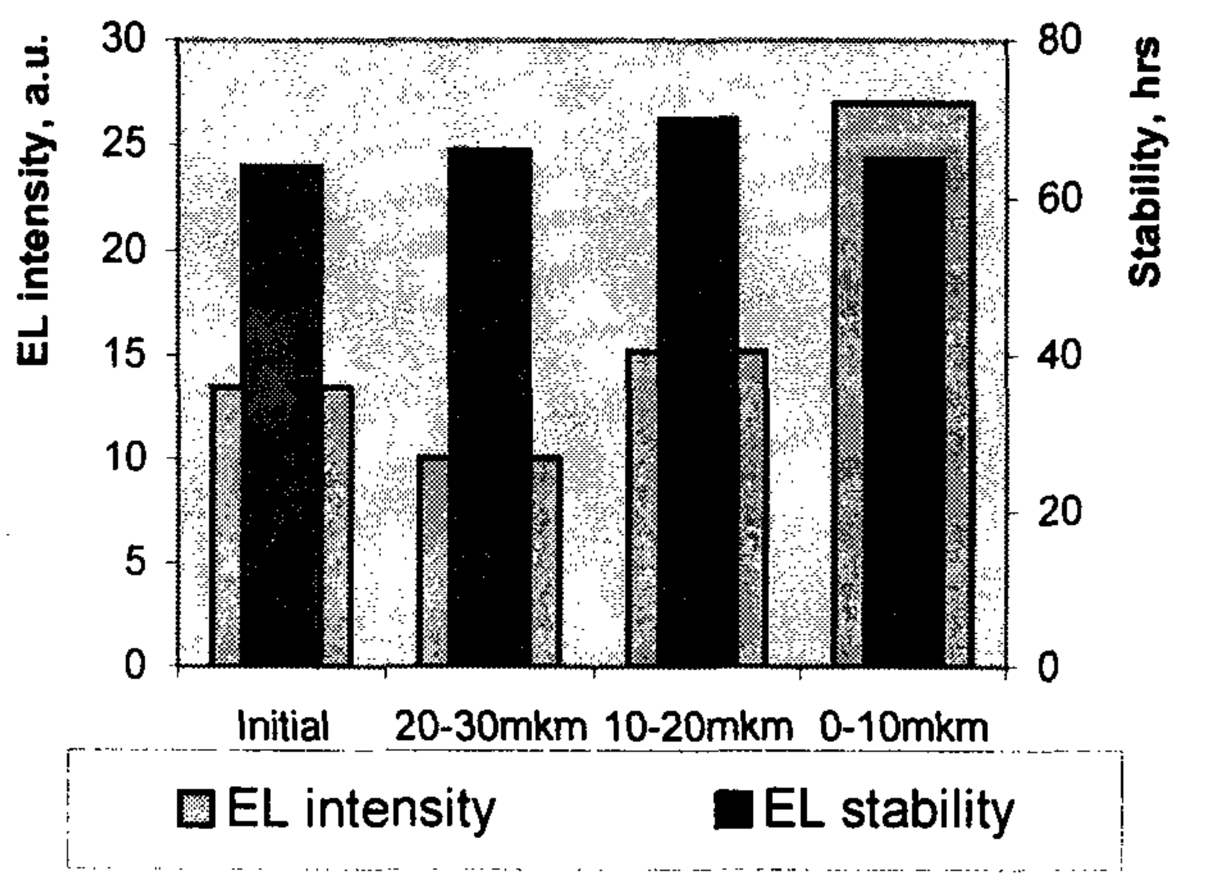


Figure 2 – Characteristics of phosphor fractions.

Fractionation also eliminates "dust" – smallest particles which have low brightness and stability and which have largest sedimentation times.

3. Surface Properties of Phosphors

3.1 Measurement Technique

Since surface of the phosphor play important role in the luminescence processes it is important to control and regulate its properties. We studied distributions of absorption centers (DAC) of fabricated phosphors measuring amounts of specific active acid-base centers on the surface of powders. Technique is based on adsorption of probe indicators from water solutions as described elsewhere[3]. Resulting distribution reflects amounts of absorption centers with certain pKa values (constant of acid-base properties of the center).

3.2 Correlation with Luminescence

In the previous publications it was shown that change of the sulfur content in the flux for the phosphor synthesis allows to maximize EL brightness by the regulation of gas-phase processes. At the same optimal conditions total amount of surface active centers minimizes[3]. It was suggested that surface adsorption centers may be related to the structural defects and thus serve as surface non-radiation recombination centers.

To investigate the idea we studied EL spectra of phosphors prepared with different amount of sulfur in the flux at low and high drive frequencies (400 and 2500Hz). With the utilization of the Fok-Alentsev method it allowed us to decompose EL spectra on three bands – blue and green ones with maximums at 455nm and 505nm, as well as very low-intensity one at about 410nm – figure 3. The last one was attributed to the structural defects – sulfur and zinc vacancies.

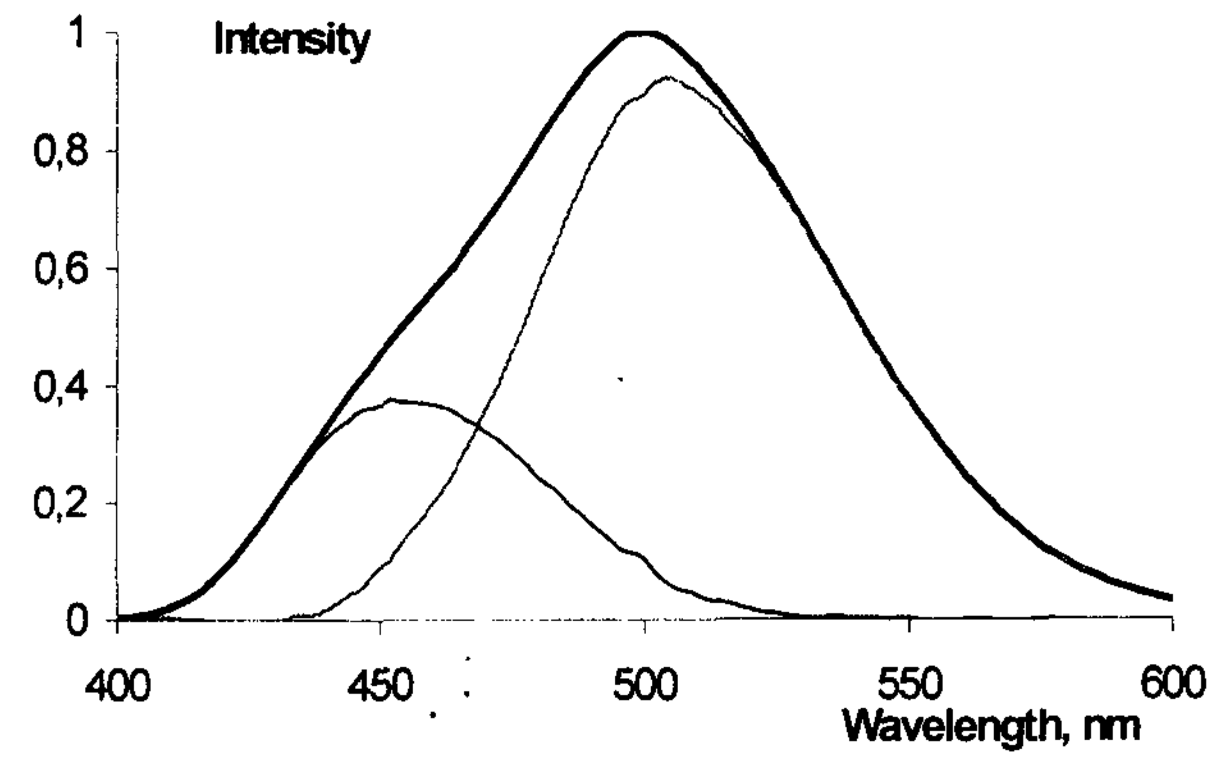
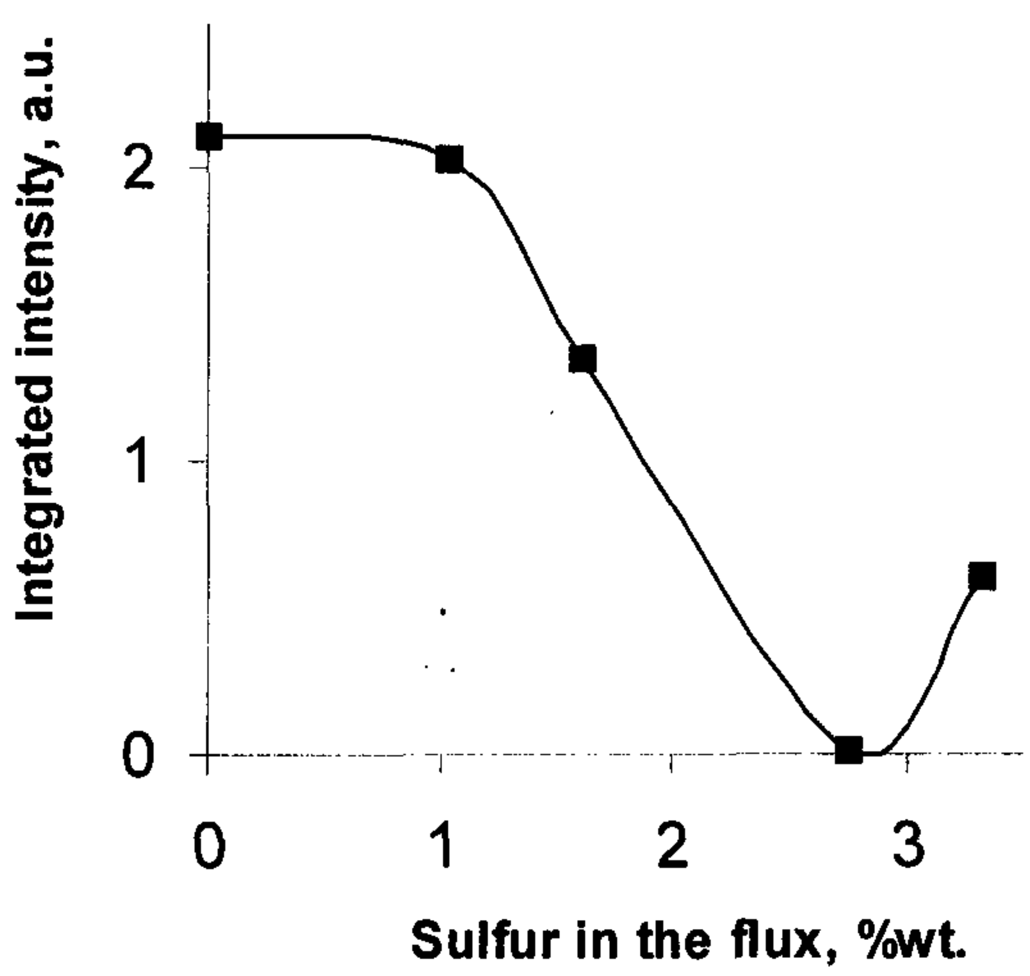


Figure 3 – Example of EL spectrum decomposition.

The dependence of the integrated intensity of the



410nm band on the sulfur content in the flux is shown below.

Figure 4 – Intensity of 410nm band depending on synthesis conditions.

The minimal amount of the defects has sample prepared with 2.7 %wt. sulfur in the flux, same conditions at which EL brightness has maximum and total amount of absorption center has minimum. Thus the experiment directly proves that DAC technique allows to obtain data related to the surface structural defect and to forecast phosphor's performance.

4. Electron-Beam Irradiation

4.1 Background

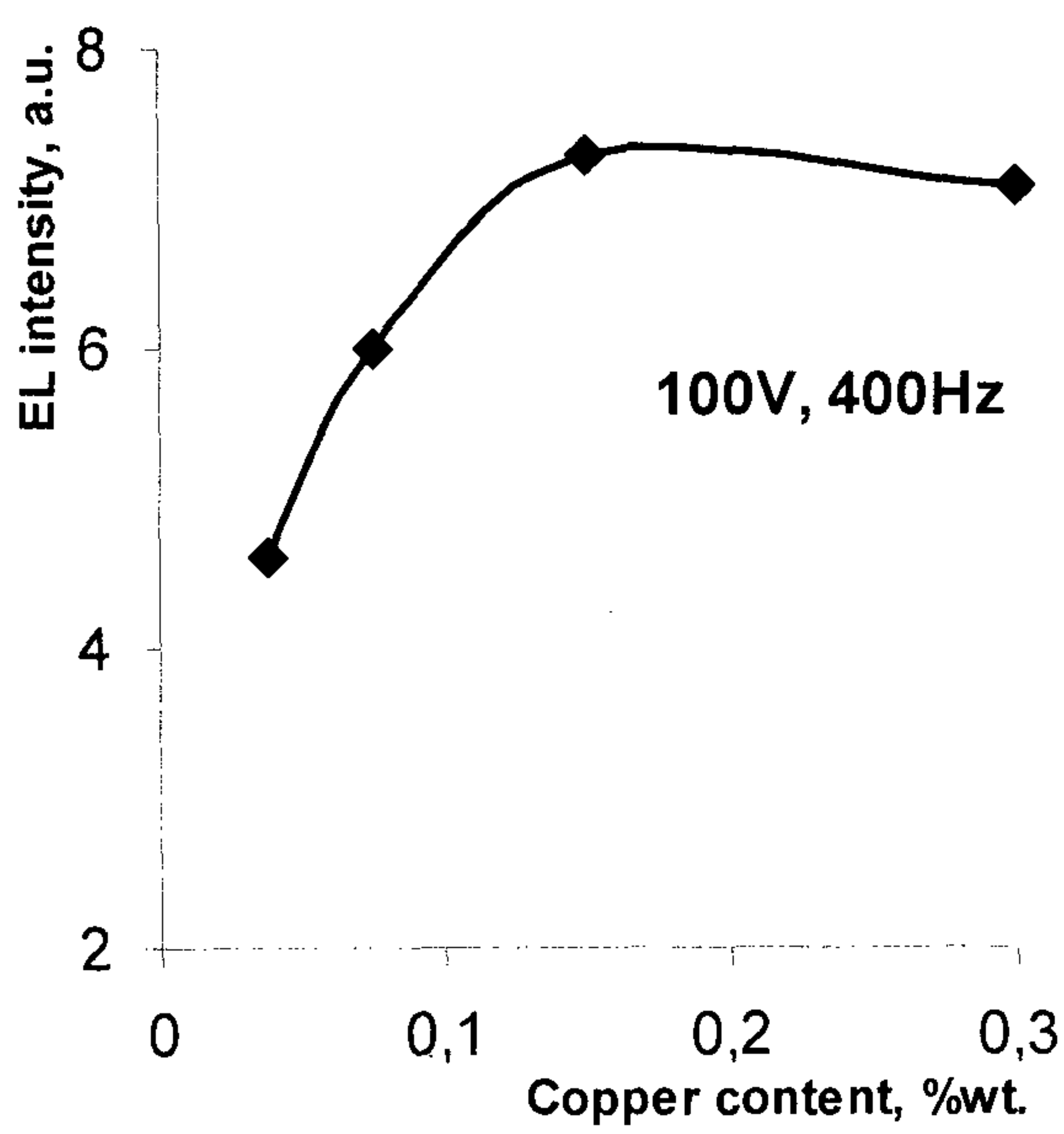
In works[2,4] we reported increase of the EL brightness of ZnS:Cu,Al phosphors by the irradiation with middle-energy electrons. For the irradiation we utilized industrial resonance-transforming electron accelerator. As a result brightness of ZnS:Cu phosphor was improved up to 100% while no change of spectra was registered.

To explain obtained results we suggest following explanation. During phosphor synthesis at high temperature formation of zinc sulfide/copper sulfide solid solution occurs with the help of gas phase reactions between the ZnS and copper-containing flux. During cooling after the syntheses solid solution partly decomposes with the formation of ZnS-Cu_2S heterojunctions which serve as charge carriers generators when external voltage is applied to the phosphor. Additional decomposition takes place during phosphor's annealing but its temperature and time is limited due to oxidation of the zinc sulfide. Thus system is not at thermodynamic equilibrium that limits brightness and stability of the phosphor.

We suggested that increase of the brightness after EB irradiation is connected to the additional decomposition of solid solution ZnS-Cu_2S with formation of new heterojunctions and probably luminescent centers. Since processes of formation and decomposition of solid solution depend on the content of copper in the phosphor, for the verification of the stated assumption in the present work influence of an irradiation on properties of ZnS:Cu EL phosphors with various Cu contents was investigated. Four samples with different copper content were fabricated. The radiation dose was 5Mrad – optimal value find in the previous experiments. 900keV electron energy was chosen to ensure uniform irradiation of exposed layers of phosphor powders.

4.2 Characterization of Samples

Dependence of the phosphor brightness on copper



content is shown on the figure 5.

Figure 6 – EL intensity of phosphors depending on the copper content.

As one can see from the figure 6, brightness increases with increase of the copper content and then saturates. Main reason of the brightness increase is the change of EL spectra – figure 7. EL spectra shows well-known shift of emission to the longer wavelengths with higher copper content due to the presence of green and blue bands in the spectra. The centers of green luminescence are donor-acceptor pairs $[Cl_S]^d$-$[Cu_{Zn}]^a$, and the centers of a blue luminescence – donor-acceptor pairs $[Cu_i]^d$-$[Cu_{Zn}]^a$. Shift of spectrums to green is connected to the formation of the centers suppressing blue luminescence.

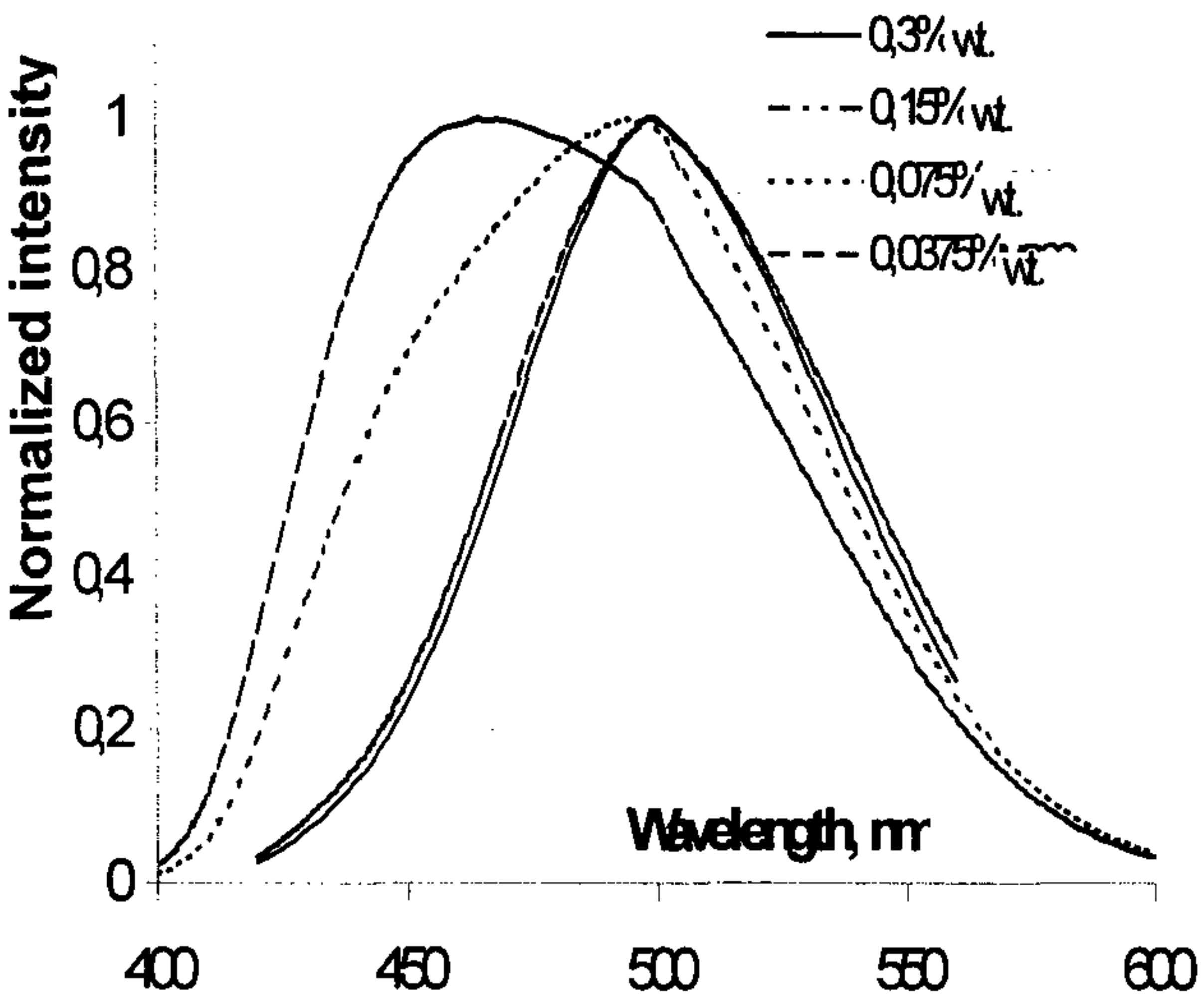


Figure 7 – EL spectra of phosphors depending on the copper content.

4.3 Irradiation Influence on Brightness

It was further found, that with increase of the copper content brightness of phosphor after irradiation has increased to a higher extent, reaching maximum value for a 0,15 %wt copper sample – figure 8.

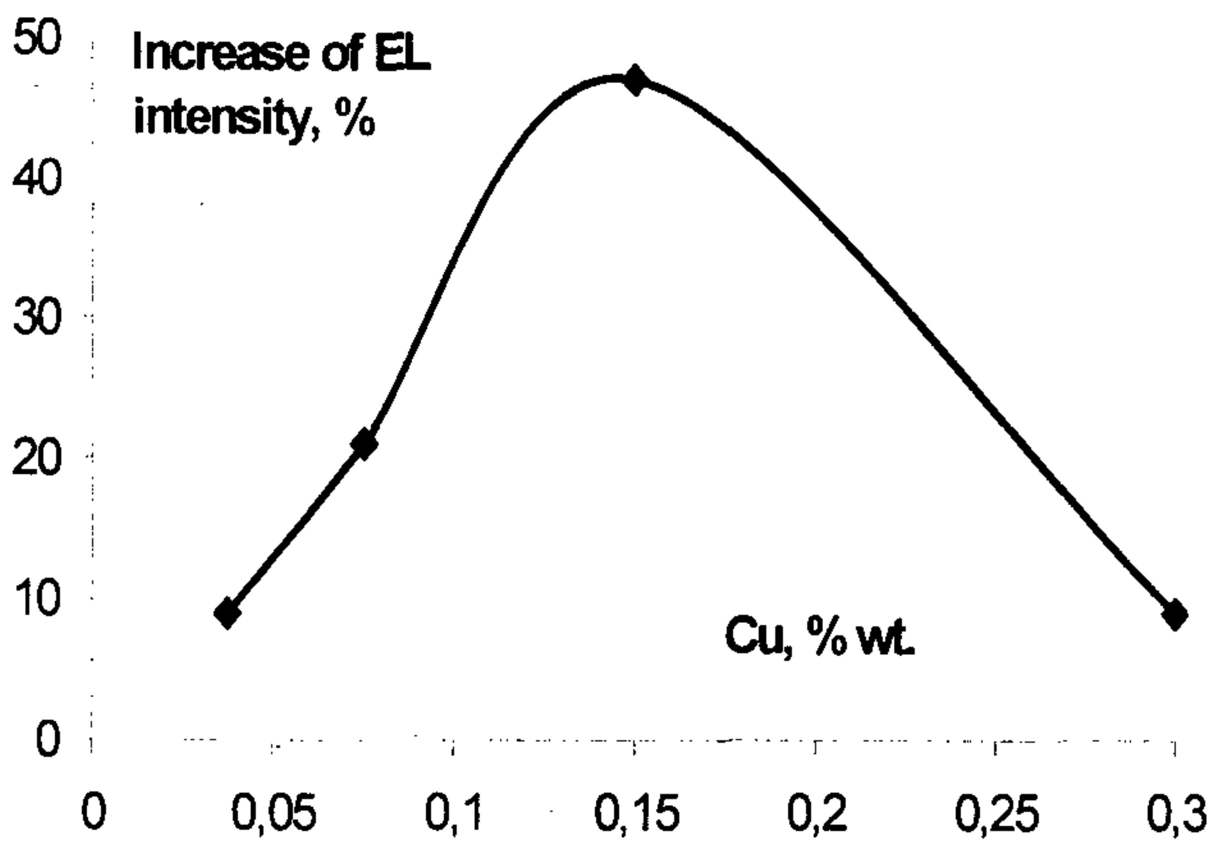


Figure 8 – Increase of phosphor's EL intensity depending on copper content.

These data confirm the assumption of decomposition of solid solution since the more Cu content in the phosphor, the more supersaturated solution is obtained after synthesis and the more non-equilibrium will be the system and therefore the higher will be possibility to improve brightness by addition decomposition. In case of a sample with the maximum content of copper, certain decrease in improvement of brightness should be attributed to the formation of surface Cu_2S phase which absorbs emitted light and is not removed completely by washing.

4.4 Irradiation Influence on EL Spectra

Study of EL spectra of samples before and after the EB irradiation has shown that for the 0.15 %wt. copper sample there is shift of emission to shorter wavelength – figure 9. For all other samples both with higher, and with lower contents of copper, position of maximums in spectra practically did not change with irradiation.

All these facts also confirm the assumption of decomposition of solid solution with formation of copper sulfide. It is known, that formation of this phase is accompanied by the formation of associates of two copper atoms (forming blue centers $[Cu_i]_d$-$[Cu_{Zn}]_a$). It shifts to shorter wavelength maximums in spectrum of the 0.15 %wt. of Cu phosphor. In spectra of phosphors with the smaller content of copper maximums already lay in the blue region, therefore formation of the additional blue centers does not change position of maximums. In the phosphor with the highest content of copper centers of suppression which extinguish blue band of electroluminescence exist, therefore irradiation of phosphor does not result in shift of maximum to the blue region.

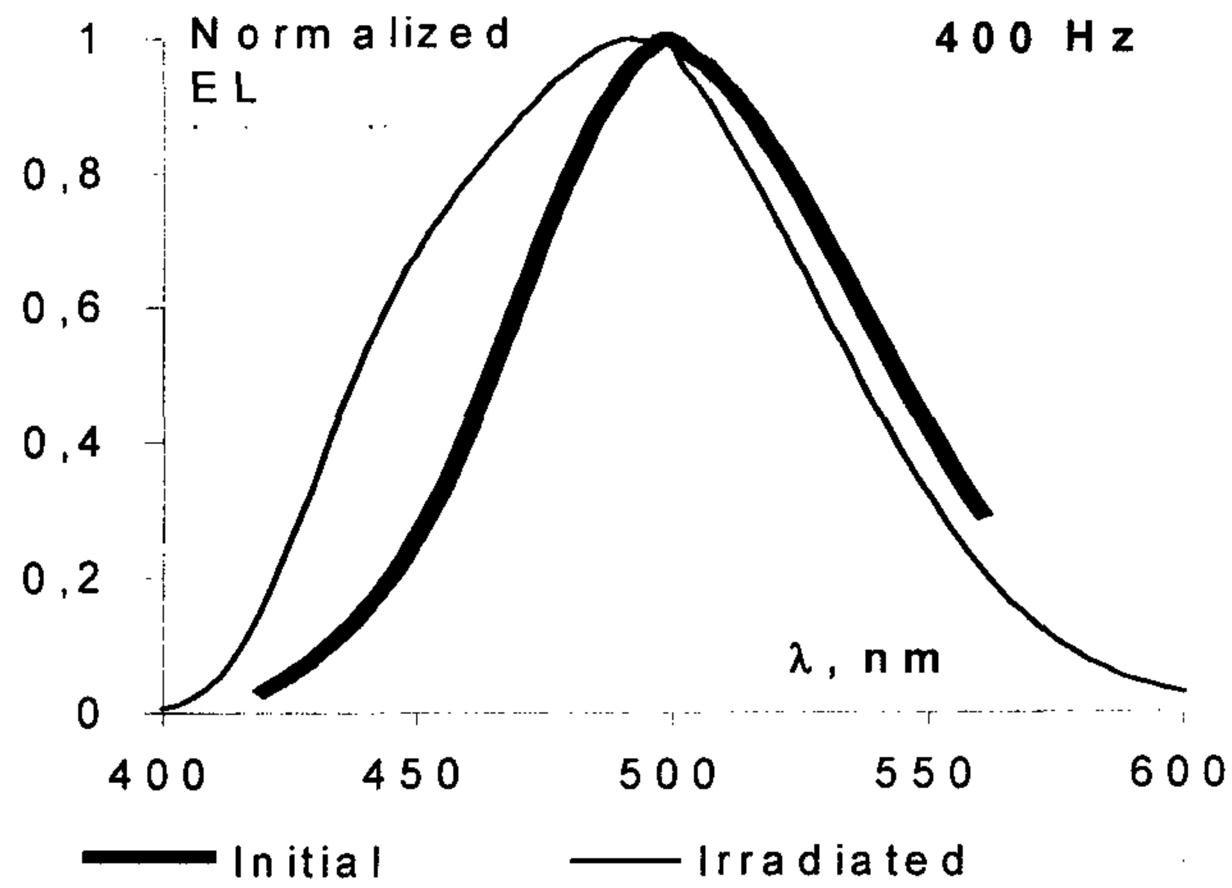


Figure 9 – EL spectra of 0.15%wt. Cu sample before and after EB irradiation.

Thus electron-beam irradiation allows to improve EL phosphor brightness simultaneously making its luminescence bluer – color coordinates changed from x=0.138&y=0.41 to the x=0.153&y=0.283 for the 0.15 %wt. of Cu phosphor (400Hz drive).

4.5 Irradiation Influence on Stability

Influence of the irradiation on the phosphor's stability was also studied – figure 10. It is clear that stability of phosphors increased as a result of irradiation, except for the phosphor with the maximum content of copper.

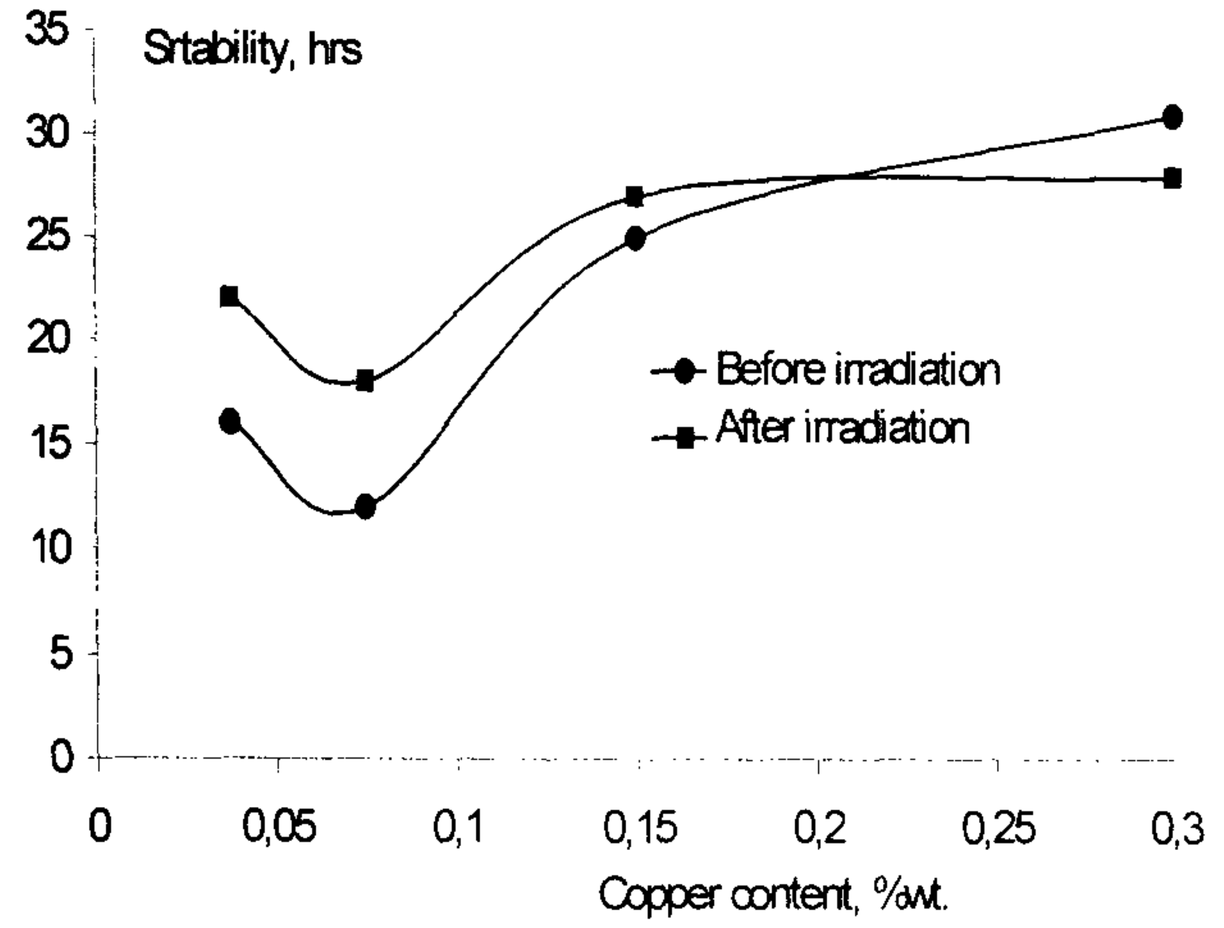


Figure 10 – Relative phosphor's stability depending on copper content.

Analysis of electroluminescence spectra of aged phosphors has shown that spectra of the irradiated samples practically did not change except for a sample with the minimum contents of copper– see figure 11. As for the nonirradiated phosphors, aging led to the increase of bandwidth to the green region due to faster degradation of blue centers.

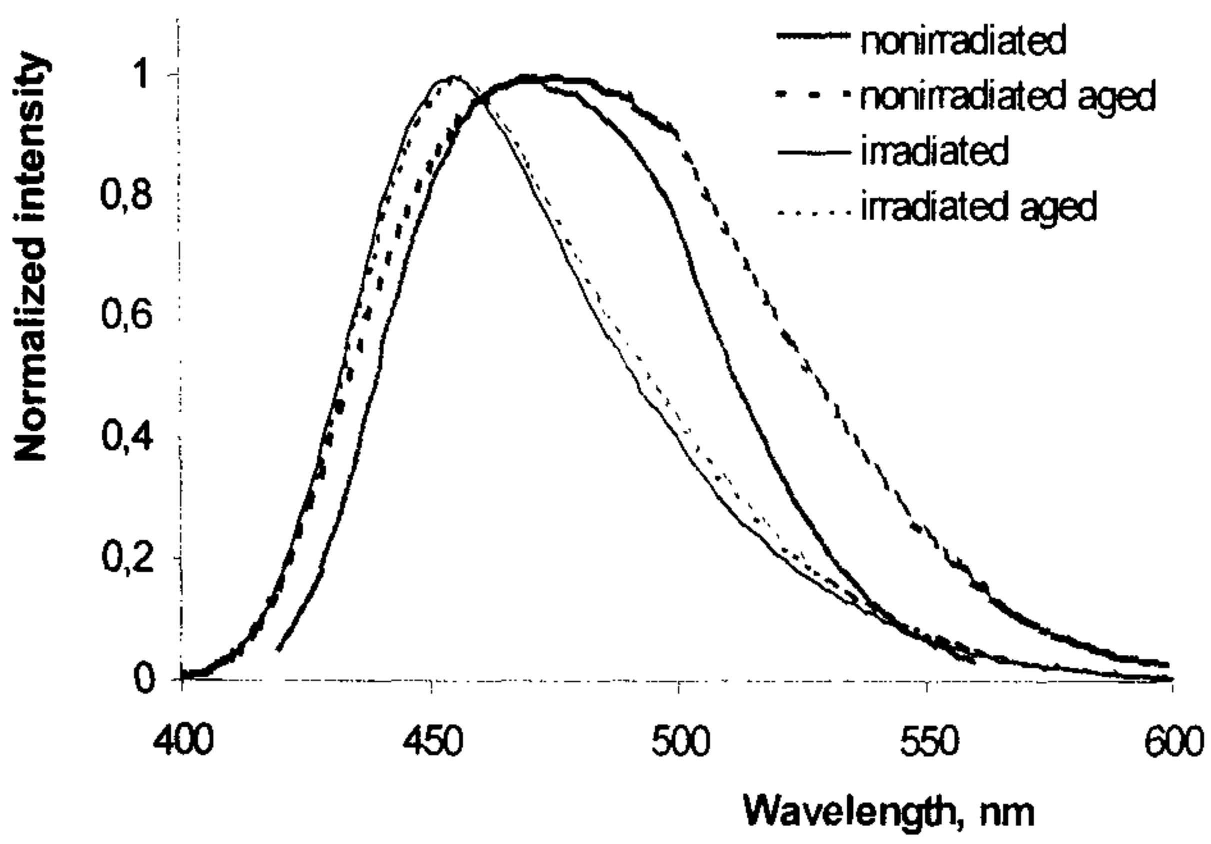


Figure 11 – EL spectra change for the sample with maximum copper content.

This results confirm suggestion that irradiation led to the formation of addition blue centers, that in turn led to the increased stability of the shape of the EL spectra after aging. As for the electroluminescent phosphor with the maximal contents of copper, as discussed it contains plenty of the centers of the suppression of blue luminescence, so irradiation and possible formation of blue centers did not lead to the improved stability. Moreover, stability decreased, probably due to formation of copper sulfide phase on the grain surface what is known to negatively influence stability.

7. Conclusions

The developed thechnology of the synthesis and fractionation of the powder EL phosphors yields small particle phosphor with improved brightness, color of luminescence may be regulated in a wide range.

It was shown that that DAC technique allows to obtain data related to the surface structural defect and to forecast phosphor's performance.

By the method of electron beam irradiation brightness and stability of the phosphor was improved. It was shown that effect is due to decomposition of Cu_2S-ZnS solid solution and formation of additional centers of blue luminescence.

Acknowledgements

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