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Article

Effect of electron-beam induced nanostructuring on surface properties and radioluminescence of ZnS:Cu,Br phosphors

Elena Zelenina [1, 2, *], Vadim Bakhmetyev [2] and Maxim Sychov [2]

[1] *Saint-Petersburg State Institute of Technology*; office@technolog.edu.ru
[2] *Khlopin Radium Institute*; radium@khlopin.ru
* Correspondence: elena.v.zelenina@gmail.com

Abstract: Electron beam treatment of ZnS:Cu,Br (Cu activator content 0…0.6%wt.) radioluminescent phosphors as well as charge mixture with the electron energy 900 keV and absorbed dose of 600 kGy resulted in an enhancement of brightness up to 80%. The increased brightness is due to increase of content of wurtzite phase relative to sphalerite one with formation of wurtzite/sphalerite nanocomposite structure. Transformation of crystal structure is accompanied with corresponding change in content of active surface centers characteristic for sphalerite and wurtzite phases. A model describing surface centers of ZnS:Cu,Br radioluminescent phosphor is suggested.

Keywords: radioluminescence; ZnS phosphors synthesis; surface properties; phosphor structure; spectral content; brightness

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1. Introduction

Radio- (β-particles induced) and cathode luminescence are based on the interaction of exciting electrons with the surface of phosphor grains. Consequently, the target properties of radioluminescent phosphors such as their intensity, brightness and luminescence spectra largely depend on the features of the phosphor grains' surface. Surface properties may be modified in various ways. In addition to the optimization of the synthesis conditions, a number of methods can be used for processing the charge mixture or ready phosphor in order to provide needed phosphor structure. The surface properties of phosphors largely influence electrophysical processes occurring in the phosphor grain, such as charge transfer and luminescence [1].

The design of effective radioluminescent (RL) phosphors involves the synthesis of crystalline or polycrystalline powders with special surface imperfections. Radioluminescence and cathode-luminescence processes take place in the surface layer of the phosphor grains. Therefore, the state of the phosphor grain surface, including the concentration and distribution of impurity crystal lattice defects acting as luminescence or quenching centers is one of the key characteristic of the phosphor efficiency [2].

A possible approach to the modification of the surface layers of solids is based on their processing with accelerated electrons or ions, as well as γ-, neutron or laser irradiation. As a result of such exposure, the formation of radiation defects (RD) occurs. The effect of ionizing radiation upon a solid structure is known to involve two main mechanisms, including electronic (excitation and ionization) and impact (displacement of atoms) effects. The predominance of one of them depends on the nature of the solid, as well as on the radiation type and energy. The irradiation of semiconductor materials with the particle energy exceeding the threshold level of atom displacement (E_m = 100–400 keV for accelerated electrons) leads to the appearance of point defects (interstitial atoms and vacancies), as well as associates of defects with impurities and other imperfections of the crystal lattice [3]. Particularly, electron beam, γ-radiation of neutron processing of zinc sulfide causes the formation of Frenkel defects, such as V_{Zn}, Zn_i and V_S, S_i. The interaction of ZnS with high energy (several MeV) electrons provides not only point defects, but also linear and bulk imperfections in the lattice. Linear and bulk defects contribute to the agglomeration of point defects, reducing their total number. This effect can lead to changes in the number of luminescence centers. Such surface imperfections or zones can promote a nonradiative recombination of electrons and holes, reducing the luminescence yield [4]. Radiation-induced point defects on the surface of particles can act as adsorption centers, with their adsorption activity increasing upon electron beam processing (radiation-stimulated adsorption) [5].

In [6] the formation of vacancies in a ZnS crystal under the proton irradiation with an energy of 3 MeV and electron irradiation with an energy of 1 MeV was revealed. A post-irradiation annealing was found to promote the agglomeration of point defects into vacancy complexes of various sizes or into small vacancy pores. The intensity of electron beam (EB) irradiation was shown to affect the structure of zinc sulfide. The increase of accelerated electron flux promoted the recrystallization and phase transformation in ZnS films with sphalerite structure. For some samples a more intensive grain growth and formation of large wurtzite single crystals were observed along with the recrystallization. It was concluded that the increase of irradiation intensity leads to the growth of base crystals, possibly due to the presence of uncontrolled impurities.

In [7, 8] a high-intensity electron beam modification was shown to facilitate the diffusion of activator ions deep into the polycrystalline materials. In [9], a 60 % increase of brightness and longwave shift of electroluminescence spectra was observed for ZnS:Cu,Hal (Hal=Cl, Br) phosphor after 900 keV EB modification of the initial charge mixture before calcination and accounted for the appearance of radiation-induced defects promoting the activator diffusion into the crystal with consequent formation and increased content of green luminescence centers. Also, the comparison of electro- and cathode-luminescence spectra revealed the redistribution of surface and bulk luminescence centers in the phosphor. In [10], 900 keV EB treatment of ZnS:Cu,Al electroluminescent phosphors resulted in a significant increase of the luminescence brightness without any changes in the luminescence spectra.

Electron beam treatment of zinc sulfide based phosphors strongly depends not only on the irradiation conditions (duration, dose rate and absorbed dose) and on phosphor composition (including the nature and content of luminescence activating ions), but also on the conditions of the luminescence excitation and surface properties of phosphors.

The surface properties can be considered in interaction with the reaction medium, which forms a new surface by changing the composition and structure of surface centers. The properties of solids strongly depend on the presence of the surface proton and hydroxyl donor groups or Broensted centers, as well as electron acceptor and electron donor Lewis basic and acidic centers, respectively.

The effects of the distribution and redistribution of active centers on the surface of different photo- and electroluminescent phosphors according to acid-base and donor-acceptor properties, as well as a possibility to enhance the phosphor properties due to electron beam induced modification, was considered in a series of our earlier studies [11-14]. In this study, this concept was applied to a series of zinc sulfide based RL phosphors.

2. Materials and Methods

Several series of ZnS radioluminescent phosphors activated with Cu (up to 0.6 % wt.) and coactivated with Br (0.8 % wt.) were synthesized from the initial charge mixtures comprising ZnS (NPO Lumonophor, Stavropol, Russia), chemical purity grade), CuCl, NH_4Br and elemental sulfur, prepared by mixing of the above components in the rotary drum mixer for 3 hours.

The synthesis was carried out by calcination of the initial blend for 1.5 h in an alumina crucible at 950 or 1100 ^{o}C under a layer of active carbon as a reducing medium. Then the prepared phosphors were purified from the non-luminous particles under a UV-lamp, milled and sieved, followed by washing in aqueous solution of NH_3,

$(NH_4)_2CO_3$ and $(NH_4)_2S_2O_8$ to remove the impurities and particles of ZnO and Cu_xS from the surface. After washing phosphors were dried at 120 °C and sieved again.

Electron beam processing of the charge mixtures and ready phosphors was carried out using a resonance-transforming electron accelerator RTE-1V (produced by Efremov Institute of Electrophysical Apparatus, Saint-Petersburg, Russia) under the following conditions: electron energy 900 keV, beam current 1 mA and absorbed dose about 600 kGy earlier [9]. The optimized for the treatment of ZnS:Cu based electroluminescent phosphors.

All the synthesized phosphors were excited by the tritium β-source (Khlopin Radium Institute, Saint-Petersburg, Russia) comprising a tritium-containing titanium layer (thickness 0.5 μm, source area 1 cm^2, incorporated activity not higher than 0.4 Ci) on a steel plate. The radioluminescence spectra including a relative quantum yield of luminescence in the wavelength range 350-700 nm were measured using a spectrofluorimeter AvaSpec-3648. The obtained spectra were analyzed by deconvolution into Gaussian bands. The radioluminescence brightness was measured using a radiometer IL-1700 (International Light, USA). XRD analysis was performed using a Rigaku SmartLab 3 X-ray diffractometer (Rigaku Corporation, Japan).

A quantitative analysis of the phase composition (particularly, ratio between wurtzite and sphalerite contents) was carried out using the Rietveld method. The grain size and surface quality of the phosphors were estimated by scanning election microscopy using the Hitachi TM3000 (Hitachi, Japan) и Tescan VEGA 3 SBH (Tescan, Czech Republic) installations.

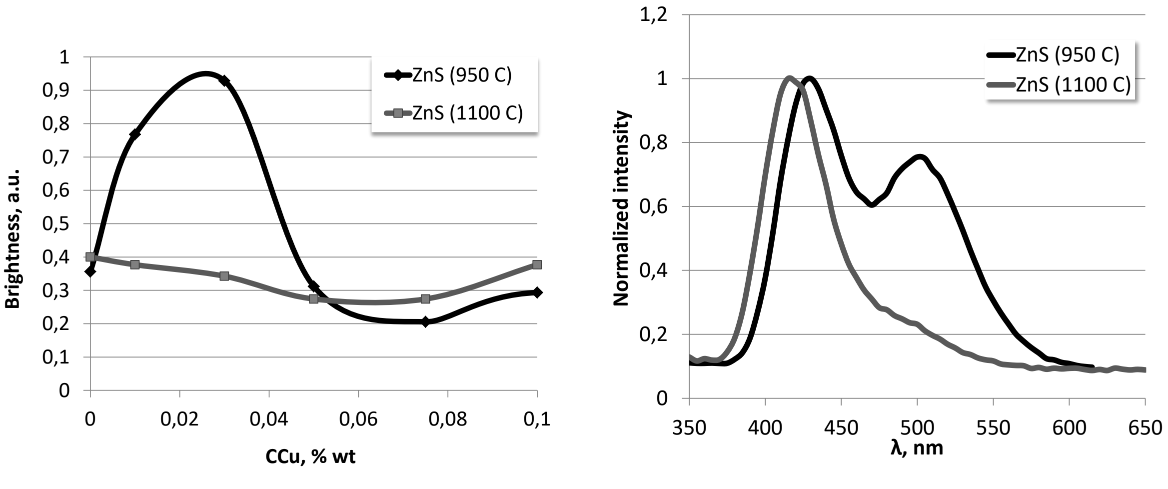
The surface functional composition of the studied phosphors was characterized using the adsorption of acid-base indicators with intrinsic pKa values ranging from -5 to 15 with measurement of the changes in optical density of their solutions upon the interaction with the phosphors according to the procedure described in detail in [15-16]. The optical density of the indicator solutions was measured using a SF-56 spectrofotometer (LOMO, St.Petersburg, Russia) at the wavelengths corresponding to absorption peak for each indicator.

3. Results and Discussion

Brightness depending on the activator (Cu) content and radioluminescence (RL) spectra of the phosphors synthesized at temperatures below (950 ^oC) and above (1100 ^oC) the sphalerite-wurtzite phase transition point (about 1050 ^oC) are shown in the Fig. 1.

According to our previous studies [17] it was expected that the increase of annealing temperature to 1100^oC should provide a growth of the luminescence brightness due to the increase in the content of wurtzite stable upon annealing above 1050-1100 ^oC. Nevertheless, the phosphors synthesized at 1100 ^oC featuring with a single phase wurtzite structure according to XRD data exhibit a significantly lower brightness and a shortwave shift in the luminescence spectrum compared with the sample annealed at 950 ^oC.

Therefore, it was supposed that the improvement of radioluminescence performances requires the formation of a two-phase sphalerite-wurtzite composite structure with an extended phase boundary facilitating the activator (Cu) and coactivator (Br) diffusion with the formation of radioluminescence centers. For this purpose, electron beam treatment with the electron energy 900 keV exceeding the defect formation energy in ZnS (190 keV for S atoms and 235 keV for Zn atoms) was expected to facilitate the hexagonal phase formation in the cubic matrix and to provide a mixed sphalerite-wurtzite structure enriched with the wurtzite phase on the phosphor grain surface.

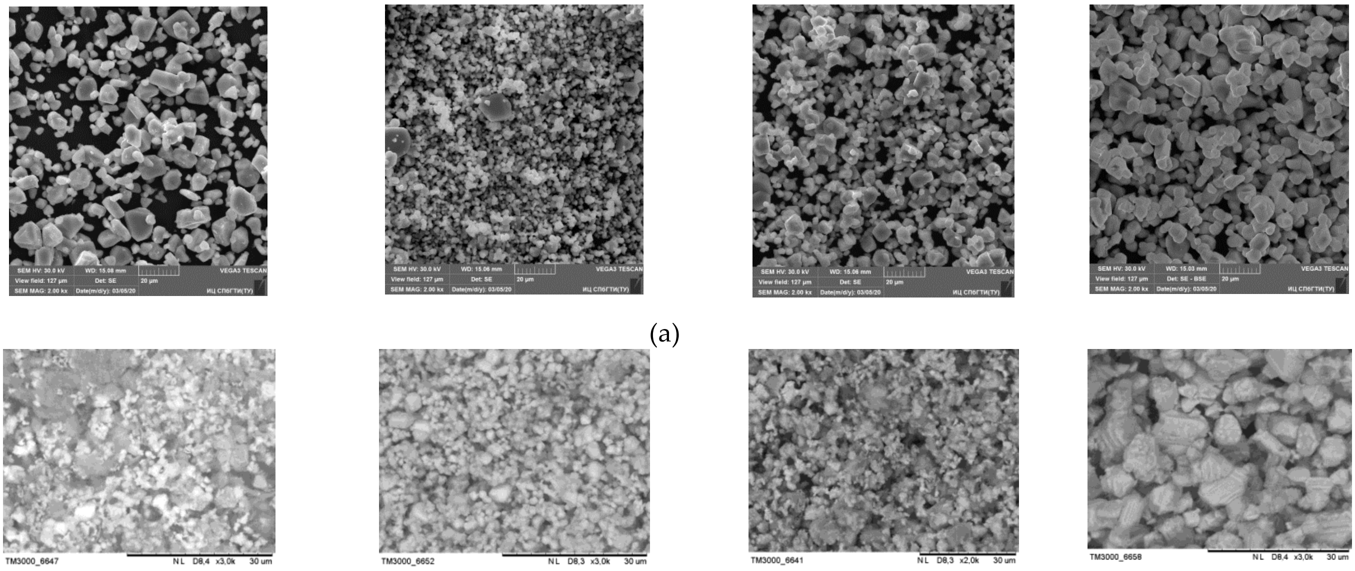


(**a**) (**b**)

Figure 1. Brightness *vs* Cu content (a) and RL spectra (b, Cu content 0.03 %wt.) of ZnS:Cu,Br phosphors synthesized at different temperatures.

To implement this approach, three series of ZnS:Cu,Br RL phosphors with Cu activator content in the range from 0 to 0.6 % wt. were synthesized and compared. The first series was synthesized without EB processing, for the second one only the charge mixture was subjected to EB treatment, and for the third series EB processing was applied to both charge mixture and ready phosphor.

All the phosphors were synthesized in the form of finely dispersed white crystalline powders. Their SEM images (Fig. 2-a) indicate that phosphors synthesized without EB processing have a smooth surface and well-separated particles with well-faced grains suggesting a high crystallinity. The largest size of agglomerates is observed for the sample with the highest Cu content 0.6 % wt.



(a)

(b)

Figure 2. SEM images of ZnS:Cu,Br phosphors with various Cu concentrations prepared from regular (a) and EB processed charge mixture (b).

On the contrary, for the samples obtained using EB treatment particle agglomerates surrounded by smaller particles without prominent grain boundaries are observed (Fig. 2-b). The data on the average grain size for the phosphors synthesized from the non-modified and EB-processed charge mixture are given in the Table 1.

Data in the Table 1 suggest that the addition of the lowest Cu content (0.03 % wt.) results in a decrease of the phosphor grain size to the minimum. However, the further increase of Cu content leads to the growth of the grain size, since CuCl acts as a flux. EB treatment of the charge mixture results in a certain decrease in the grain size of the phosphor in the entire range of the activator concentrations.

Table 1. Average grain size of phosphors with different Cu contents synthesized with and without EB processing of charge mixture.

Cu, % wt.	d_{av}, μm (without EB processing)	d_{av}, μm (EB processing of charge mixture)
0	5 – 10	3 – 5
0.03	3 – 5	1 – 3
0.075	5 – 10	3 – 5
0.2	5 – 10	5 – 7
0.6	10 – 15	7 – 9

The results of XRD analysis (Fig. 3) confirm that EB processing promotes the increase in the hexagonal (wurtzite) phase relative content in the phosphors synthesized below the phase transition temperature (at 950 °C). The size of wurtzite and sphalerite grains is about 1…3 nm. In respect of the target performances, EB pretreatment of the charge mixture provides 20 % increase of brightness, while additional EB processing of the ready phosphor resulted in 80 % brightness growth (Fig. 3, 4). The maximum brightness is observed at Cu content 0.03 % wt. that corresponds to the highest wurtzite phase content in the formed wurtzite/sphalerite nanocomposite structure. The increase of Cu content above this value results in a drastic decrease of the brightness characteristics, that is caused by stabilization of the cubic (sphalerite) phase in ZnS by copper.

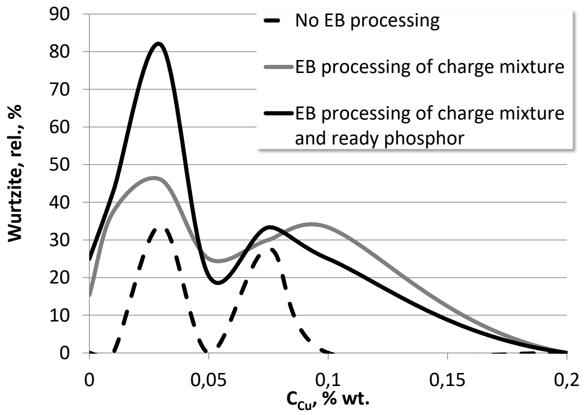


Figure 3. Relative content of wurtzite phase in RL phosphors depending on Cu content and EB treatment.

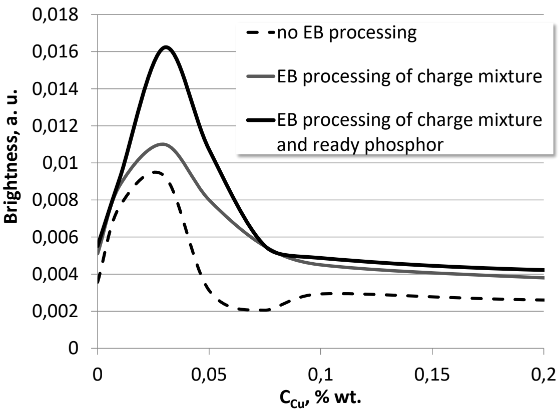
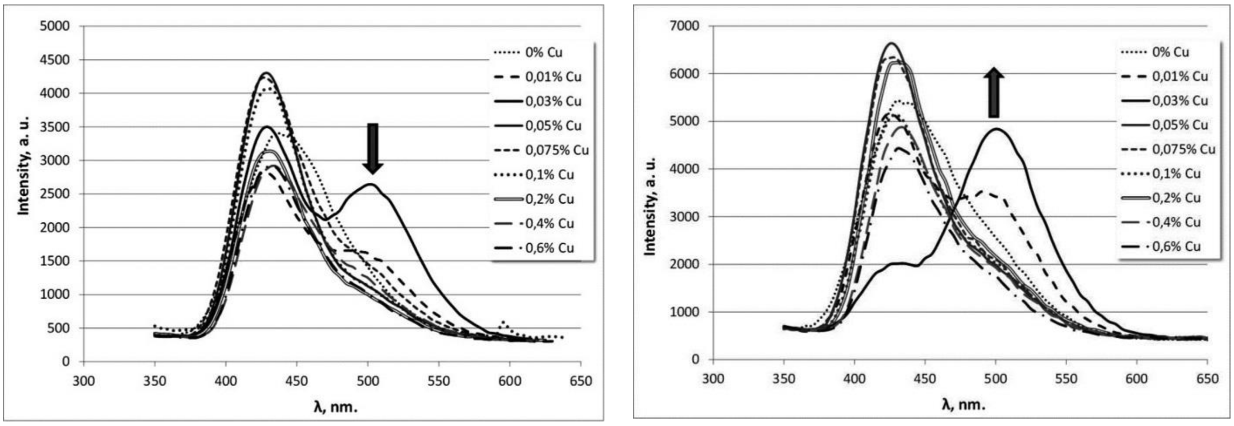


Figure 4. RL brightness of the synthesized phosphors depending on Cu content and EB treatment.

RL spectra of the phosphors synthesized without EB pretreatment and using EB processing only for the charge mixture feature with an intensive luminescence in a "blue" region with the peak at 430 nm (see Fig 5). For the self-activated RL of the non-doped (Cu-free) samples a prominent red shift spectra of luminescence towards the peak at 450 mn was observed, in agreement with reference data [2]. For Cu-activated phosphors this peak is also observed and the overall profile of the spectra is quite complex, involving several bands in the range 350-550 nm. At Cu content 0.01 – 0.075 % wt. common for cathode- and RL phosphors a "green step" at 520 nm appears due to the surface donor-acceptor recombination luminescence and activation of green luminescence centers (such as $V_S^{\bullet\bullet}$ and $Cu_{Zn}'\,Br_S^{\bullet}$ associates) [18].



(**a**) (**b**)

Figure 5. Radioluminescence spectra of the studied phosphors. (a) – no EB processing, (b) – EB processing of charge mixture.

EB processing of the charge mixture provides a significant increase of RL intensity for the phosphors with all Cu contents, while additional EB processing of the ready phosphors promotes the further intensity enhancement. Moreover, EB treatment results in a longwave shift in the RL spectra of the phosphors with Cu content 0.01 – 0.075 % wt. Cu, thus, increasing the "green" luminescence. As shown in Figure 6, for the sample containing 0.03 % wt. Cu and featuring with the highest RL brightness, the additional EB treatment results in a turn from "blue" spectra with the "green" shoulder towards "green" spectra with the "blue" shoulder, whereas for other activator contents this effect was not observed.

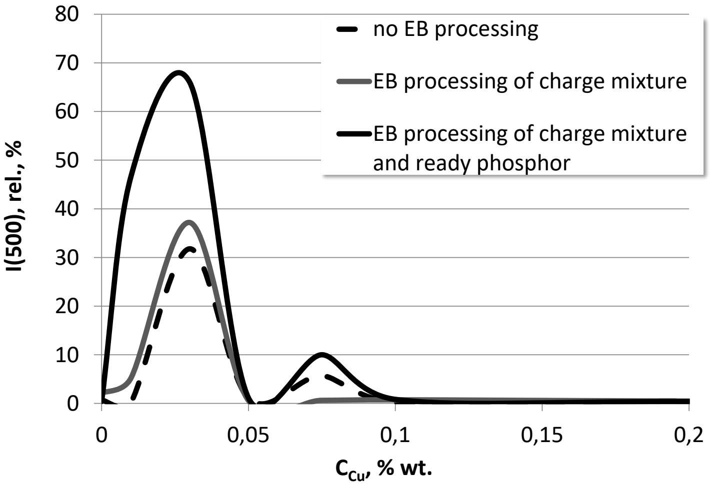


Figure 6. Ratio between the intensities of "green" and "blue" bands in RL spectra of the studied phosphors depending on Cu concentration range and EB treatment.

The effect of wurtzite:sphalerite phase ratio on the relative intensity of the "green" band (about 500 nm) in RL spectra of the studied phosphors depending on Cu content and EB processing is shown in Fig. 7.

For all the samples, a drastic increase of the "green" RL component is observed at wurtzite:sphalerite ratio about 30–40, suggesting that EB-induced phase change promote not only the redistribution of activating agents (Cu and Br) between the bulk and surface of the phosphor but also leads to the spectral bands redistribution causing the brightness growth.

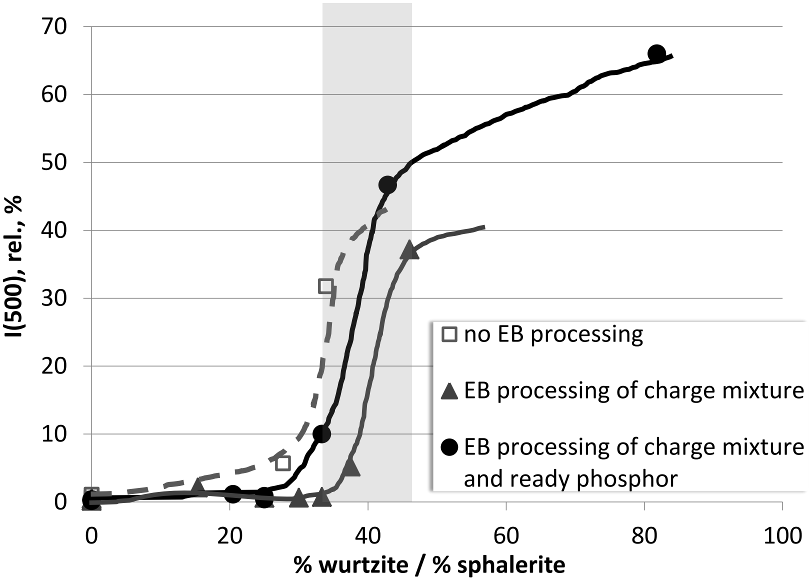
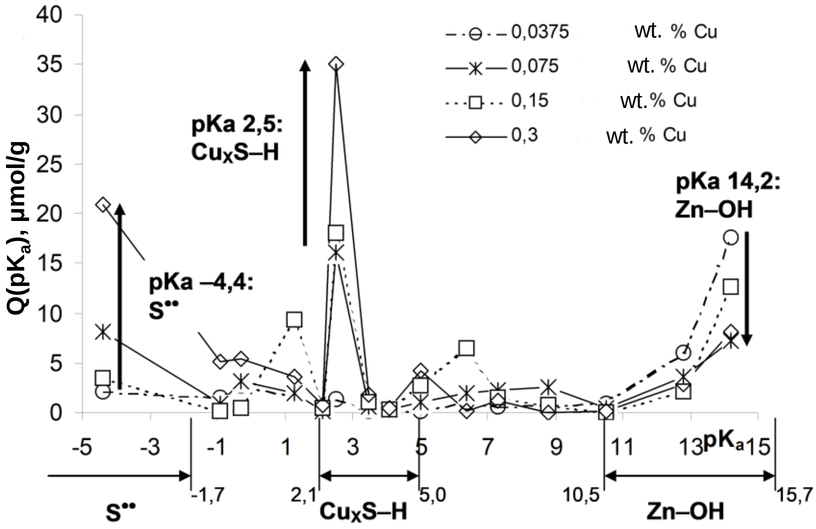
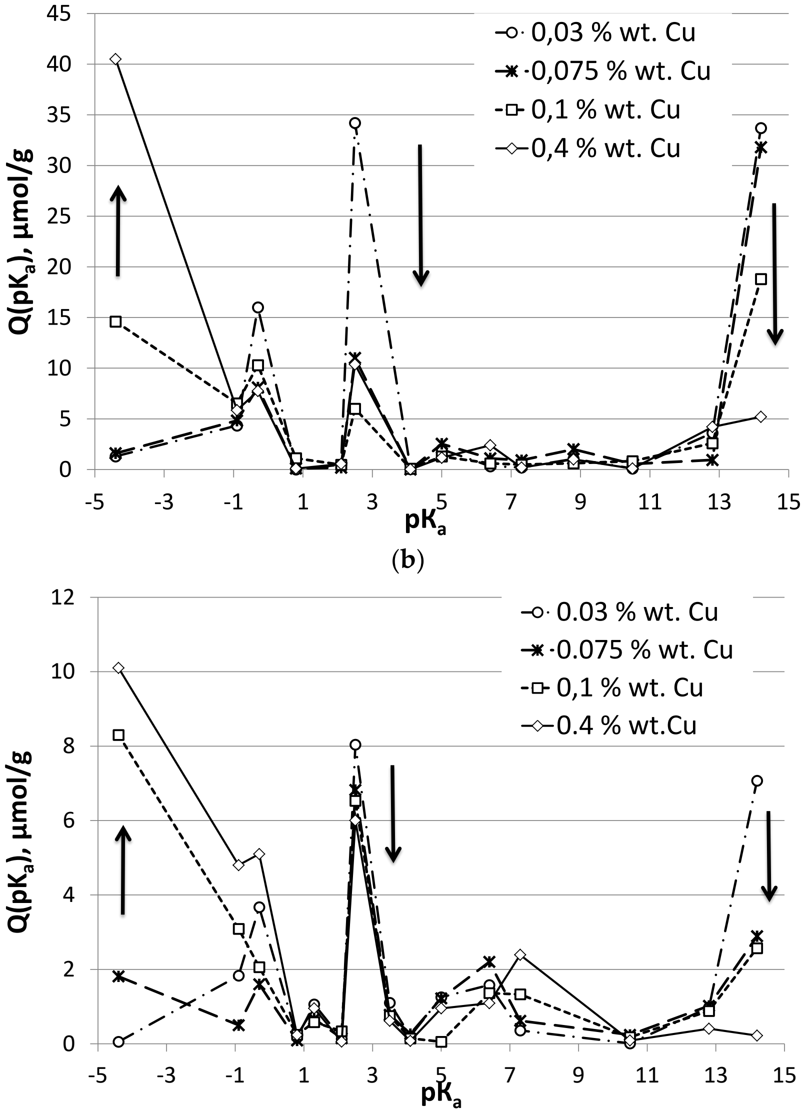


Figure 7. Effect of wurtzite / sphalerite phase ratio on the relative intensity of the "green" RL band.

To analyze the EB-induced changes in the surface chemistry of the phosphors, the irradiated samples were characterized by the adsorption of acid-base indicators in comparison with similar studies for these samples before EB treatment reported earlier in [19]. The obtained distributions of adsorption centers according to pKa values are shown in Fig. 8. Figure 8-a shows the amount of sites with pKa 14.2 zoomed tenfold because number of that sites significantly overshoot the number of other sites.



(a)



(b)

(c)

Note: the content of centers with pKa 14.2 in Fig. 8-a is zoomed 10-fold for the presentation convenience

Figure 8. Distribution of adsorption centers on the surface of the surface of the studied phosphors with different Cu contents: a – without EB treatment after low-temperature annealing [19]; b – synthesized from EB processed charge mixture; c – after additional EB.

For most of the samples, prominent peaks at pKa -4.4…-0.3, 2.5 and 14.2 are observed, as well as relatively intensive peaks at pKa about 6.5…8 in Fig 8-c for the phosphors subjected to repeated EB treatment.

A common trend for all the studied phosphors involves the increase in the content of centers with pKa -4.4 and growth in the content of centers with pKa 14.2 with the increase of Cu concentration. According to the model proposed in our previous studies [19], Lewis basic centers with pKa < 0 correspond to two-electron orbitals of surface sulfur atoms $S^{\bullet\bullet}$, and their amount characterizes the content of surface zinc vacancies V_{Zn}'. The Broensted basic centers with pKa > 10 relate to sulfur vacancies $V_S^{\bullet}$ or Zn-OH groups on the phosphor surface.

The concentration of Broensted acid centers with pKa 2.5 probably corresponding to SH or S-OH groups grows with the increase of Cu content (0.03 – 0.075 – 0.15 – 0.3 % wt.) for non-irradiated electroluminescent phosphors (Fig. 8-a) but drops in the case of EB treated samples (Fig. 8-b, c). The observed difference can be accounted for the following factors. For the samples prepared without EB treatment low-temperature annealing was carried out after the synthesis, probably resulting in Cu_xS phase exudation on the surface of the phosphor grains and formation of Cu-SH groups, while in the absence of annealing this process did not take place. Moreover, as shown in [9] and [20], EB treatment promotes the solubility of the activator (copper) in the primary ZnS matrix and facilitates the penetration of copper deeper in bulk of the phosphor grain. In this case, the centers with pKa 2.5 probably correspond to ZnS-OH groups and Cu addition results in their distortion.

The concentration of surface centers with pKa -0.3, 2.5 and 14.2 is found to correlate with wurtzite phase content, while the concentration of centers with pKa -4.4 correlates with sphalerite. The correlation coefficients between the concentration of certain surface centers with the phosphor phase composition and target performances are summarized in Table 2.

Table 2. Correlation coefficients between the concentration of adsorption centers on the surface of radioluminescent phosphors with their phase composition and target performances.

pK_a of the surface centers	Sphalerite content	Wurtzite content	Brightness	Relative intensity of the "green" RL band at 500 nm	Relative intensity of the "blue" RL band at 450 nm
-4.4	0.70				0.8
-0.3		0.70	0.70	0.90	
2.5		0.95	0.90	0.97	
6.4	0.90				0.85
7.3	0.84				0.80
14.2		0.70	0.60	0.6	

These data show that sphalerite surface is predominantly occupied with Lewis basic centers (pKa -4.4) corresponding to sulfur atoms on the faces of cubic ZnS crystals and nearly neutral or weakly basic Broensted centers with pKa 6…9 probably relating to OH groups. It reflects a regular structure with basic properties stabilized at Cu contents exceeding about 0.1 % wt. On the contrary, wurtzite surface is essentially acidic featuring with a significant content of Broensted (pKa -0.3…2.5) and Lewis acidic (pKa 14.2) centers.

Furthermore, the content of sphalerite and wurtzite phases and corresponding surface centers obviously correlate with the intensity of "blue" and "green" RL bands, respectively.

The overall RL brightness evidently correlates with wurtzite content.

The observed enhancement of RL performances due to EB treatment can be determined by the following factors:

- formation of wurtzite inclusions on the surface of the phosphor grains, promoting a structural disorder at wurtzite-sphalerite boundaries and consequent appearance of defects responsible for the luminescence;

- transformation of "blue" luminescence centers into "green" ones due to EB-stimulated diffusion of interstitial copper ions and their incorporation into zinc vacancies in the lattice (eq. 1-6):

$$Zn_{Zn} \rightarrow V''_{Zn} + Zn_i^{\bullet\bullet} \tag{1}$$

$$(Cu_{Zn}'\text{-}Cu_i^{\bullet}) \rightarrow Cu_{Zn}' + Cu_i^{\bullet} \tag{2}$$

$$Cu_i^{\bullet} + V''_{Zn} \rightarrow Cu_{Zn}' \tag{3}$$

$$S_S \rightarrow V_S^{\bullet} + S_i' \tag{4}$$

$$V_S^{\bullet} + Br \rightarrow Br_S^{\bullet} \tag{5}$$

$$Cu_{Zn}' + Br_S^\bullet \rightarrow (Cu_{Zn}'\text{-}Br_S^\bullet) \qquad (6)$$

EB treatment stimulates the dissociation of donor-acceptor pairs (Cu'_{Zn}-$Cu_i^\bullet$) causing an increase in the number of sulfur vacancies (and Lewis acidic centers with pKa 14.2 in their proximity) followed by their ionization in the wurtzite locations on the grain surface. The resulting vacancies are filled with bromine ions, leading to the formation of "green" luminescence centers (Cu_{Zn}' $Br_S^\bullet$) featuring with RL peak at about 500 nm. "Blue" luminescence centers (Cu_{Zn}' Cu_i) are probably formed due to the incorporation of copper atoms into zinc vacancies corresponding to Lewis basic centers with pKa 14.2.

According to the above considerations, the scheme of interrelated luminescent and adsorption centers on the surface of the studied radioluminescent phosphors is represented as in Figure 9 with a colored indication of sphalerite and wurtzite phases, as well as blue and green luminescence centers.

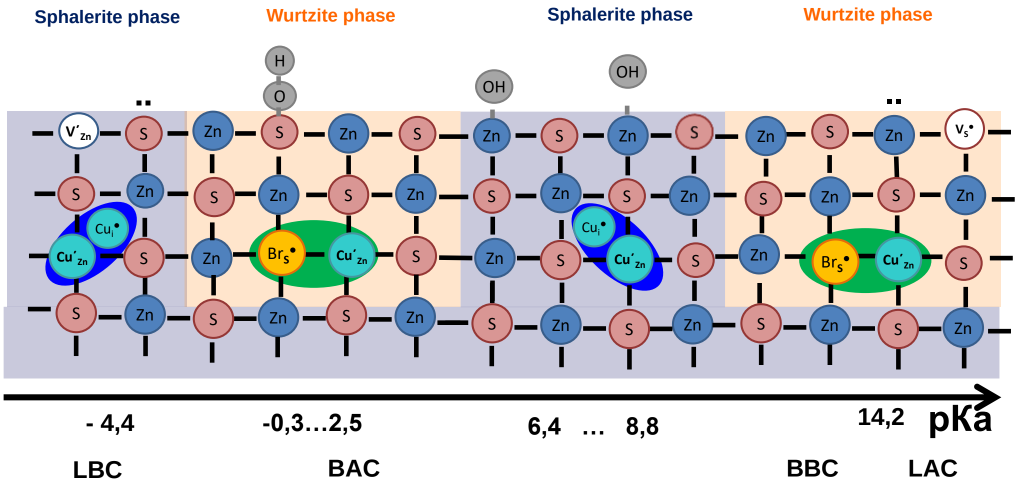


Figure 9. Schematic structure of the studied ZnS:Cu,Br radioluminescent phosphors.

Since according to [2, 21-23] structural defects in solids can undergo a relaxation with a gradual restoration of the initial surface structure, unless the desirable defects are "fixed" using special processing such as annealing, the stability of EB-induced modification of the studied phosphors was studied in the course of their storage. The changes in RL performances of the synthesized phosphors upon storage within 3 months shown in the Figure 10 indicate that their brightness did not drop and even slightly increased in time.

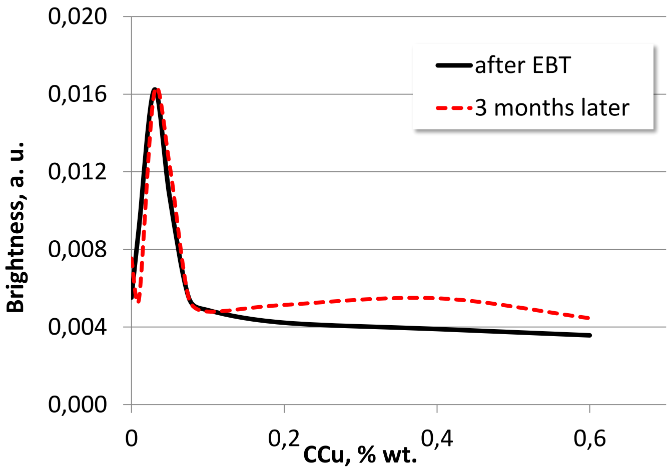


Figure 10. RL brightness for the phosphors with different Cu contents.

4. Conclusions

The radioluminescence brightness of the studied phosphors is found to strongly depend on the activator (Cu) concentration in the phosphors with a prominent maximum at Cu content 0.03 % wt. providing the lowest grain size.

The obtained results demonstrated a possibility to significantly increase the β-radiation stimulated luminescence brightness of ZnS:Cu,Br by electron beam processing of the charge mixture for the phosphor synthesis and further (up to 80 %) enhance their brightness upon the additional EB treatment of the ready phosphors.

Furthermore, the luminescence performances of these phosphors largely depend on their phase composition, with sphalerite and wurtzite phases providing "blue" and "green" luminescence bands, respectively, and the overall brightness growing with the increase in the wurtzite phase content. The highest wurtzite content in the phosphors synthesized below the sphalerite-wurtzite transition temperature is achieved at relatively low (about 0.03% wt.) Cu content corresponding to the maximum brightness, while at Cu concentrations higher than about 0.1 - 0.2 % wt. wurtzite content abruptly drops.

The phase composition of the studied phosphors correlates with the presence of certain centers on their surface. The sphalerite surface features with basic properties being predominantly occupied with Lewis basic and nearly neutral Broensted centers, while wurtzite surface is predominantly acidic featuring with a significant content of Broensted and Lewis acidic centers. A schematic structure of adsorption sites and luminescent centers on the surface of ZnS:Cu,Br radioluminesent phosphors is suggested.

The considered approach is promising for the adjustment of the surface properties, structure and target performances of different phosphors and other materials.

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