Synthesis of ZnS:Cu,Br radioluminescent phosphors using the electron-beam treatment and studying their characteristics

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Abstract. ZnS:Cu radioluminescent phosphors find their applications in medicine non-destructive testing, safety control and can be used as a part of the solid-state radioluminescent light sources (SRLS). This devices are very promising technology due to their independence longevity and safety compared to the gas-filled RLS. Because of the fact that tritium (the most popular radioisotope for RLS) has a very short range in substances, the improving the operating performances of radiophosphors is a crucial task for SRLS. In our study we used the electron-beam treatment to increase the brightness of radioluminescence of ZnS:Cu phosphors. It was found that bombardment of the phosphors initial charge with electrons of 900 kEv energy improves the brightness of radioluminescence by 15 – 20%. Double modifying of the initial charge and ready phosphor cause the 80% increase of brightness. The effect of electron-beam treatment on the phase content and the surface properties was studied at varying the content of activator (Cu) in the range of 0 – 0.6 % mass. As a result the model describing structure of the acid-base sites on the ZnS:Cu phosphor surface was suggested.

1. Introduction
Radioluminescent light sources (RLS) are the devices consisting mainly of the emitting isotope, and the phosphor, giving the visible light affected by ionizing radiation. Tritium, having the half-life period of 12.5 years and emitting beta-particles with the average energy of 5.7 keV, is the most common isotope for RLS for its cheapness and low radiation hazard. Nowadays the gas-filled RLS, using the gaseous tritium in the glass tubes, are the most known configuration. However the main disadvantages of such construction are the glass tubes breakability causing the tritium leakage and the size limitation due to the tritium self-absorption. The solid-state configuration of RLS (SRLS) was suggested in our later studies [1, 2]. This device involves tritium bounded in the solid spongy titanium matrix forming the thin layer on the steel plate and the ZnS powder phosphor layer connected with the TiT₂ in the silicate matrix. This configuration excludes the tritium leakage and increases the safety; however the key problem is the tritium betas path length of several μm in the solid matrix decreasing the brightness of radioluminescence. We can raise the brightness by increasing the incorporated activity of tritium but it may cause the radiation damage and self-absorption processes. On the other hand we can raise the effectivity of the radiophosphor constituted in SRLS. Our previous studies demonstrated the possibility of increasing the electroluminescent performances of the ZnS:Cu and ZnS:Cu,Al phosphors using the electron-beam treatment [3 – 8]. In this paper this technique was applied for ZnS:Cu radiophosphors having the different content of the doping agents and the different excitation mechanism of luminescence. Electroluminescence involves the whole volume of the ZnS crystal, but the radioluminescence is surface donor-acceptor recombination process. And as far as here...
we have only the surface interaction between the electrons and the centers of luminescence, the
surface condition and characteristics are the key for understanding the processes forming the spectral
and brightness performances. Previous studies [9 - 11] have demonstrated the correlation between
the phosphor surface characteristics and their luminescence effectiveness. The model describing the nature
of all surface acid-base sites for the ZnS:Cu and ZnS:Cu,Al electroluminescent phosphors was suggested;
and the direct interrelations between the proper acid-base sites and phosphor centers of luminescence
was found. This study suggests the likewise model was constructed for ZnS:Cu, Br radiophosphors. The
correlations between the phase content of the phosphors and their radioluminescent performances
was found and the effect of the electron-beam treatment was studied.

2. Experimental
The series of ZnS:Cu,Br radiophosphors synthesized from the initial charge consisting of ZnS,
containing 0.8% of Br and 0 – 0.6 % wt. of Cu are the objective of the research. ZnS manufactured by
scientific-production association NPO Lumonophor, Stavropol, Russia, CuCl, NH₄Br and the
elemental sulphur were the starting materials. The initial charge was cooked by 3 hours mixing of the
starting materials in the rotary drum mixer.

Synthesis was conducted by annealing the initial batch in the alumina crucible at 950 °C in a
reducing atmosphere under the active carbon bed [9] for an hour and a half. Then phosphors were
cleaned from the non-luminous particles under the UV-lamp, milled and screened. After that
phosphors were washed in the water solution of NH₃, (NH₄)₂CO₃ and (NH₄)₂S₂O₈ to remove the
impurities and particles of ZnO and CuₓS from the surface. After washing phosphors were dried at
120 °C and screened again.

Electron-beam treatment was done for the initial charge and for the ready phosphors by the electron
flux bombardment using the medium-energy resonant transformer electron accelerator RTE-1V
(produced by Efremov Institute of Electrophysical Apparatus, Saint-Petersburg, Russia). The electron
energy was of 900 keV and the beam current of 1 mA. The absorbed dose was about 600 kGy. The
conditions of treatment were taken as an optimal conditions from our later studies [6].

Now therefore three series of phosphors including the Cu concentration range of 0 – 0.6 % wt.
were synthesized:
1. Phosphors synthesized without using the electron-beam treatment (non-modified, N);
2. Phosphors synthesized from the electron-beam treated initial charge (modified, M);
3. Electron-beam treatment of the ready phosphors synthesized from the electron-beam treated
   initial charge (double-modified, 2M).

To explore the radioluminescent performances of the phosphors they were excited by the tritium β-
source, represented as a tritium-contained titanium layer on the steel plate. Thickness of the layer was
0.5 μm, source area was 1 cm²; the incorporated activity was 0.4 Ci. The brightness of
radioluminescence was measured using a radiometer IL1700 (International Light, USA). The X-ray
diffraction analysis was done using a Rigaku SmartLab 3 X-ray diffractometer (Rigaku Corporation,
Japan). The quantitative analysis of the phase content was done using the Rietveld method. The grain
size and surface quality of the phosphors were estimated by the scanning electron microscopy using
the Hitachi TM3000 (Hitachi, Japan) and Tescan VEGA 3 SBH (Tescan, Czech Republic).

For differentiation of the acid-base sites on the surface of the phosphor grains we used the
adsorption of a series of acid-base indicators with different pKa values in the range from -5 to 15
according to the method described in [12…14]. The calculations was carried out using the SF-56
spectrophotometer (LOMO (Leningrad Optical Mechanical Association), Russia) at the wavelength
of maximum absorption peak of the indicator solution. The list of indicators let define the acid-base sites
in the range of pKₐ from -4.4 to +14.2. using this data the spectra of adsorption sites distribution on
the phosphor surface become available as a function in coordinate representation q_{pka} = f(pKₐ).

3. Results and discussion
Figure 1 represents the microphotographs of the phosphors synthesized from the non-modified and
EB-modified charge. Non-modified phosphors has smooth surface and looks like grained separated
particles, so we can say that they have a good crystallinity. Samples synthesized from the EB-modified
charge looks as a small agglomerates surrounded by the smallest particles without good facet and separation. Obviously their crystalline structure has lowered the degree of perfection.

**Figure 1.** Microphotographs of the ZnS:Cu,Br phosphor samples doped with Cu 0 – 0.6 % wt.

Table 1 gives the data of the average grain sizes for non-modified and EB-modified series of phosphors. It’s apparent that doping phosphors with Cu at first causes the decreasing of the grain size and then, when Cu concentration exceeds 0.1 % wt., effects the grain growth, due to the Cu$_x$S phase formation. At the same time, the EB-treatment of the charge effects the decreasing of the grain size of the samples through the whole concentration range.

**Table 1.** The average grain size of phosphors synthesized from the non-modified and EB-modified initial charge.

| Cu, % wt. | N (non-modified) $d_{av}$, µm | M (modified) $d_{av}$, µm |
|----------|-------------------------------|--------------------------|
| 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 phase content of all synthesized samples was investigated with the XRD analysis. The phosphors has complex phase content with two main phase modifications of ZnS crystalline host – cubic (sphalerite) and hexagonal (wurtzite). The percentage content of each phase counted by the Rietveld method is given in the table 2.

The phase-transition temperature between sphalerite and wurtzite is nearly 1050 °C [15], so wurtzite is a high-temperature modification of ZnS. Nevertheless the data from the table 2 shows that EB-treatment effects the wurtzite formation up to the 45% in the phosphors that were synthesized below the phase transition temperature.
The less amount of the hexagonal modification was found in the non-modified samples and the highest amount in the 2M series – the phosphors prepared from the EB-modified charge and repeatedly modified after synthesis.

Presumably, we can say, that electron-beam treatment leads to the phase changes in ZnS; and the strongest changes were observed in the phosphors with the Cu concentration not exceeding 0.1 % wt. It correlates to the literature data [16, 17] saying that Cu doping promotes the stabilization of the cubic phase.

Table 2. The phase content of the phosphors.

| Cu, % wt | Phases, % | Phases, % | Phases, % |
|---------|-----------|-----------|-----------|
|         | N series  | M series  | 2M series |
|         | Sphalerite| Wurtzite  | Sphalerite| Wurtzite  |
| 0       | 100       | 0         | 86.7      | 13.3      |
| 0.01    | 100       | 0         | 72.7      | 27.3      |
| 0.03    | 74.7      | 25.3      | 68.5      | 31.5      |
| 0.05    | 100       | 0         | 80        | 20        |
| 0.075   | 78.3      | 21.7      | 76.9      | 23.1      |
| 0.1     | 100       | 0         | 75        | 25        |
| 0.2     | 100       | 0         | 100       | 0         |
| 0.4     | 100       | 0         | 100       | 0         |
| 0.6     | 100       | 0         | 100       | 0         |

Figure 2 represents the brightness of radioluminescence for the non-modified, modified and double-modified series of phosphors. It can be seen that the EB-treatment (of the charge and of the ready phosphors) causes the extreme increasing of brightness. For the samples doped with 0.03 % wt. of Cu electron modification of the charge effects the 20% increase of brightness and the repeated electron modification of the ready phosphor effects the 80% increase of brightness. At raising the Cu concentration over the 0.1 % wt. rapid decline was observed probably due to the formation of the quenching solid solution of Cu₃S.

Figure 3 gives the comparison of the spectral data of three series of phosphors for the concentration of activator, giving the maximum brightness (0.03 % wt.). There are two main spectral bands – at 450 nm and 520 nm – «blue» and «green», respectively. It is known that «blue» spectral band is relative to the copper associative centers of luminescence, consisting of two copper ions – one in the lattice point and another in the interstitial lattice site (Cu₂z, Cu'). «Green» spectral band is relative to another type of associative centers of luminescence – copper atom in the zinc lattice point and halogen atom in the sulphur lattice point (Cu₂z, Br$\,$S') [11].

It’s apparent from the figure, that after the EB-treatment of the charge the emission at 520 nm turns higher than 450 nm emission, and the «green» band became predominant in the spectra. None of the other spectra of all synthesized samples with other concentrations of copper give such an effect.

The most probable factor of all brightness and spectral changes in the non-modified and EB-modified series, is the phase and structural changes caused by the electron bombardment. It leads to the redistribution of the doping agents (Cu and Br) – constituents of the «green» centers of luminescence – between the volume and the surface of the crystal. Also it’s possible that the EB-treatment facilitates the ZnS matrix restructuring that decreases the basic degree of perfection of the crystal lattice. This process causes the ionization of the lattice defects, such as sulphur vacancies and promotes the other vacancies formation when sulphur leaves the crystal surface. Bromine radius is bigger than chlorine and in perfect ZnS crystals it’s hard for Br to incorporate into the lattice.
Formation of the wurtzite phase under the EB-treatment facilitates bromine incorporation into the surface layers of the ZnS lattice, filling the sulphur vacancies and forming the \((\text{Cu}_{x}\text{Br}_{y}\text{S}_{z})\) associates.

Figure 2. Brightness of the radioluminescence for the phosphors doped with different amounts of Cu, for non-modified, modified and double-modified series of phosphors. (Inset figure shows the concentration range 0 – 0.1 % wt. of Cu).

Figure 3. Radioluminescence spectra of non-modified, EB-modified and double-modified series of phosphors with Cu concentration 0.03 % wt.

In our later studies [11] we have constructed the model describing the nature of active surface sites of ZnS:Cu phosphors. That phosphors were synthesized without EB-treatment and using the low-
temperature (600…650 °C) baking in air after synthesis but before washing. Low-temperature baking is the necessary step for the electrophosphors synthesis for the formation of the CuₓS phase for effective electroluminescence excitation. This model is given at the figure 4. The analogous investigations of the surface characteristics were made for EB-modified phosphors, using the acid-base indicator method. Figure 5 shows the distribution of the adsorption sites (DAS) on the surface of phosphor with various concentrations of Cu.

![Figure 4](image1.png)
**Figure 4.** Model of active surface sites of ZnS:Cu electrophosphors with different concentrations of Cu (synthesized without EB-treatment and using the low-temperature baking in air) [11].

![Figure 5](image2.png)
**Figure 5.** Model of active surface sites of ZnS:Cu radiophosphors with different concentrations of Cu (synthesized with EB-treatment of the initial charge and without the low-temperature baking).

It’s apparent that in the both cases, at the figures 4 and 5 there are peaks at pKₐ -4.4; 2.5 and 14.2. According to our previous model for electrophosphors at pKₐ -4.4 ... -1.7 we have Lewis’s basic sites consisting of two-electron orbitals of the surface sulphur atoms S⁻. The number of these sites indicates
number of the surface zinc vacancies $V_{Zn}$. $pK_a$ 10.5…15.7 refers to the Broensted basic sites and have an architecture $Zn-OH$. Their number characterizes the amount of the sulphur vacancies $V_S$. Comparing figures 4 and 5 one can see that strong Lewis basic and strong Broensted basic adsorption sites behavior is similar at raising the activator concentration for the both series of phosphors. The number of sites with $pK_a -4.4$ increases and the number of sites with $pK_a 14.2$ decreases. This fact reinforces our conclusions about the nature of these sites from the work [11].

There again, pursuant to the model for electrophosphors, Broensted acidic sites with $pK_a 2.1 – 5.0$ have an architecture $Cu_S-H$ and their number characterizes the amount of the copper sulphide on the surface. And consequently it should increase at increasing of the copper concentration (see figure 4). But for ZnS:Cu,Br radiophosphors synthesized in present study we can see the inverse relation for the Broensted acidic sites with $pK_a 2.5 – q_{pK_a}$ decreases at increasing of the copper concentration (see figure. 5). Obviously, it’s due to the fact of the low temperature baking (in the first case) inducing the $Cu_S$ exudation on the surface and without baking we don’t have the $Cu_S$ on the surface. Moreover, the EB-treatment raises the solubility of the activator in the host ZnS matrix [11] and promotes the copper to penetrate deep into the crystal. Thus, for the radiophosphors series from the figure 5 the amount of the copper on the surface would be much lower than for the electrophosphors from the figure 4. And at high concentrations of Cu (exceeding 0.1 % wt.) the number of the active sites at $pK_a 2.5$ would be much lower too.

Obviously, when the copper concentration on the surface is residual at this $pK_a$ value we may have the $ZnS-H$ sites. And furthermore, the correlation of this active sites with the wurtzite phase content was found (see figure 6). So, we may suggest that hexagonal ZnS modification forms these sites.

Figure 6. Correlations between active sites with pKa 2.5 and wurtzite/sphalerite content relation for ZnS:Cu,Br phosphors at changing the Cu concentration.

4. Conclusions
Therefore, as a result of our study the technique of synthesis of the ZnS:Cu,Br radiophosphors with enhanced brightness was developed. The optimal concentration of the activator in radiophosphor (Cu) was defined as 0.03 % wt. It was found that EB-treatment of the initial charge results the 20 % brightness of radioluminescence increasing and repeated EB-modification of the ready phosphor gives the 80% brightness increasing.

The activator concentration effect on the ZnS:Cu,Br phosphors dispersity, phase content, spectral and brightness changes as well as the surface characteristics was studied.
It has been established that EB-treatment promotes forming of the extra luminescence centers \((\mathrm{Cu}_{\text{a}}\mathrm{R}_{\text{b}} ' 3')\) causing the brightness increasing. In turns, forming of these associative centers is caused by structuring the hexagonal (wurtzite) phase of ZnS at EB-treatment both the initial charge and the ready phosphor.

The investigation of the surface characteristics using the acid-base indicator method resulted the descriptive model of the nature of the active sites on the surface of radiophosphors ZnS:Cu. According to the model, the adsorption sites with \(pK_a \sim 4.4\) and 14.2 has the same nature with the electrophosphors ZnS:Cu. Lewis’s basic sites \(pK_a \sim 4.4\) consists of two-electron orbitals of the surface sulphur atoms \(S^2\); Broensted basic sites with \(pK_a \sim 14.2\) have an architecture of Zn–OH.

Broensted acidic sites with \(pK_a \sim 2.5\) has different nature for electro and radiophosphors. In electrophosphors they are relative to the copper sulphide presence on the surface and has \(\mathrm{Cu}_S\mathrm{S–H}\) architecture. In radiophosphors this sites has an architecture ZnS–H and relative to the ZnS hexagonal (wurtzite) phase presence on the surface of phosphors.

References

[1] Zelenina E, Bakhmetev V, Pechertseva E and Sychev M 2019 Journal of Sol-Gel Science and Technology 92 (2) pp 467–473 DOI: 10.1007/s10971-019-05022-2.

[2] Zelenina E, Pechertseva E 2019 Proc. 35 Int. Conf. «EuroDisplay-2019» (Minsk, Belarus) p 65.

[3] Sychev M M, Bakhmetiev V V, Mjakin S V, Nakanishi Y, Vasile’eva I V, Havanova L V, Cheremisina O A and Korsakov V G 2002 Proc. Electronics Display Conf. EDC’02 (Nagasaki, Japan) pp 67–71.

[4] Sychev M M, Bakhmetiev V V, Komarov E V, Mjakin S V, Vasile’eva I V, Nakanishi Y, Korsakov V G and Kuznetsov A I 2004 Proc. Int. Conf. ADT-04 (Raubichi, Belarus) pp 151–154.

[5] Bakhmetiev V V, Sychev M M, Korsakov V G, Komarov E V, Vasile’eva I V and Mjakin S V 2004 Proc. of the Display Optics 2004 Int. Seminar (St. Petersburg, Russia) p 45.

[6] Sychev M M, Nakanishi Y, Kominami H, Mjakin S V, Bakhmetiev V V, Grigoryev L V, Komarov E V, Korsakov V G, Sokolov I V and Usacheva V P 2005 Proc. of the 1st International Symposium on Nanovision Science (Hamamatsu, Japan) pp 160–166.

[7] Sychev M M, Korsakov V G, Bakhmetiev V V and Komarov E V. 2007 Proc. of ISDLPM 2007 Meeting (Tokyo, Japan) pp 24–25.

[8] Sychev M M, Bakhmetiev V V, Korsakov V G, Mjakin S V, Botchkareva N N, Dorofeev A A and Vasiljeva I V 2010 Proc. of the 15th Int. Workshop on Inorganic and Organic Electroluminescence & Int. Conf. on the Science and Technology of Emissive Displays and Lighting & XVIII Advanced Display Technologies Int. Symposium EL 2010 & ADT 2010 (St. Petersburg, Russia) pp 191–193.

[9] Sychev M M, Bakhmetiev V V, Nakanishi Y, Mjakin S V, Havanova L V, Cheremisina O A and Korsakov V G 2003 Journal of the SID 11 (1) pp 33–38.

[10] Sychev M M, Mjakin S V, Nakanishi Y, Korsakov V G, Vasile’eva I V, Bakhmetiev V V, Solovjeva O V and Komarov E V 2005 Applied Surface Science 244 (1-4) pp 461–464.

[11] Bakhmetiev V V, Sychev M M and Korsakov V G 2010 Russian Journal of Applied Chemistry 83 (11) pp 1903–1910.

[12] Cheremisina O A, Sychev M M, Myakin S V, Korsakov V G, Popov V V and Artsutanov N Yu 2002 Russian Journal of Physical Chemistry A 76 (9) pp 1472–1475.

[13] Myakin S V, Korsakov V G, Panova T I, Sosnov E A, Fomchenkova Yu C, Sychev M M and Shilova O A 2011 Glass Physics and Chemistry 37 (6) pp 624–628.

[14] Sychev M M, Zakharova N V and Mjakin S V 2013 Ceramics International 39 pp 6821–6826.

[15] Yen W M, Shionoya S and Yamamoto H 2006 Fundamentals of phosphors (CRC Press, Taylor & Francis Group LLC) 328 p.

[16] Skinner B J and Barton B B 1960 Amer. Mineral 45 p 612.

[17] Aven, M and Parodi J A 1960 Journal of Physics and Chemistry of Solids 13 (1–2) pp 56–64.