Investigation of zinc sulfide phosphorescent materials obtained by a modified nonco-precipitative method

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Received: June 20, 2023; Accepted: December 12, 2023

The purpose of this project is to investigate the qualities of ZnS-based phosphorescent materials, obtained by a simple wet chemical route, which does not involve co-precipitation of the base material and the modifier used to activate the ZnS. The method is adjusted, so halogenides are introduced as co-activators through the usage of the corresponding activator salt. Experiments, utilizing different activators (Mn, Cu and Ag) or investigating the presence of halogenides (Cl⁻), trivalent cations (Al³⁺) or co-activator, were conducted. The luminescent properties of all modified phosphors were measured in order to determine the optimal doping conditions for ZnS. Out of the determined conditions the peak activator concentrations and the halogenide additions were compared to the corresponding conditions reported in related research, where different synthesis routes have been used.

Keywords: ZnS, phosphors, non-co-precipitative, co-activation, activator halogenide

INTRODUCTION

There are several reported methods for synthesis of ZnS-based luminescent materials, which differ in the method of obtaining ZnS and the procedure of modification. The most common methods used often contain a co-precipitation route, whose main advantages are the homogenous activator distribution and the quality of the produced ZnS nanoparticles [1, 2]. From the large amount of research on this topic, different synthesis routes lead to different luminescent properties under the same doping conditions. The method used in this project involves separate precipitation of ZnS and activator addition. It is therefore expected that the procedure investigated in this project would give distinct results, because of its difference from the commonly used co-precipitation. This difference is related to ZnS purity, the possibility of adding halogenides as a counter-ion of the salt used to introduce the activator (using activator halogenide salts).

The hypothesis, which this project is trying to defend, expects an inhomogeneous glow surface of the prepared phosphors because of omitted coprecipitation. Furthermore, phosphors, being modified with activator halogenide salt, are expected to give better results, compared to other methods of halogenide addition.

A monovalent halogenide anion, when introduced to the ZnS before the firing process, can have its own effect on the efficiency of the incorporation, and therefore, on the quality of the phosphor. Its presence usually resolves the issue of imbalanced charge after an introduction of a foreign atom [3]. Another theory suggests that the halogenide ions begin to act as traps within the forbidden gap, when they become part of the ZnS crystal [4]. Alongside the electron traps formed from S²⁻ vacancies, this effect leads to an increase in the number of electrons in the trapped state, causing more electrons to be excited when the phosphor is exposed to UV light and therefore, increasing the intensity of the emitted light. In the co-precipitation method, both the base compound (ZnS) for the phosphor and its activator are obtained in a sulfide form, which requires additional introduction of the described halogenide anions, often in the form of alkali or ammonia chlorides [5]. The anions can also be included by adding the activator after the precipitation of ZnS and using the corresponding halogenide of the particular activator.

In the case, when a single activator is used, its concentration has a key influence on the phosphor properties. The concentration of the activator, which leads to a material with the best luminescent properties, regarding other variables, is often called peak concentration. A lower concentration implies formation of fewer recombination sites and causes fewer non-UV photons to be emitted, therefore, decreasing the intensity of the emitted light [2]. Using higher than the peak concentration can result in a wide variety of changes. For example, when a higher concentration of copper is used, it is expected to give rise to killer centers [6] leading to a stronger green fluorescence at lower

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temperatures, and sustaining a blue fluorescent emission only at even lower temperatures. This changes the characteristic green-blue emission to yellow for measurements at room temperature.



Scheme 1. Electron transitions in Mn:Cu co-activated phosphor.

A ZnS phosphor, activated with more than one modificator, is considered to be co-activated. The spectrum, emitted by a phosphor, co-activated with an ideal ratio of copper and manganese (peak ratio) consists of the individual wavelengths of the contributing activators, but also a shift towards higher wavelengths can be observed [7] (Scheme 1) The reason for occurrence of this shift can be similar to the effect of using higher than the peak concentration of one of the activators in the system of peak ratio. This shift can become even more evident, if one of the activators is used in excess to the other activator, compared to the peak ratio [3].





The graph (Scheme 2) helps visualizing the effect of Cu-co-doping on the suppression of blue photoluminescence [8] by comparison of the effect of copper recombination sites (denoted as $Cu^{2+}t_2$ (triplet state) and $Cu^{2+}e$ (singlet state)).

EXPERIMENTAL

Materials

The materials used for this project can be divided into chemicals, glassware, and other equipment. Purity grades are marked in brackets. If not otherwise stated, all used solutions are aqueous and all given fractions of solutions are mass fractions.

Chemicals used

ZnSO₄.7H₂O (pure), powdered Zn, activated charcoal, powdered S, powdered Fe, dilute HCl, distilled H₂O (for the ZnS synthesis). CuSO₄.5H₂O (high pure), MnCl₂.4H₂O (high pure), AgNO₃ (high pure), AlCl₃.6H₂O (high pure), conc. HCl (high pure), 25 % NH₃ (p.a.), NaHCO₃. (for the modification process)

Other equipment

For the synthesis: propane furnace, blowtorch, hot plate. For measuring the properties of each sample: camera – Sony DSC-HX400V, UV-vis spectrophotometer Thermo Scientific Evolution, Cary Eclipse fluorescence spectrophotometer, UV 365 nm and 256 nm lamps.

Procedure

The experimental procedure can be divided into three parts: synthesis of pure ZnS, modification process and measuring the properties of the final product.

1. Synthesis of ZnS

Commercially available ZnS is often contaminated with metal impurities, such as Fe, Co, Ni, Pb which can significantly decrease the luminescent properties of a phosphor derived from ZnS [6, 9]. This created the necessity of purifying the starting material – ZnSO₄.

1a. 500 mL of a 37.5 % solution of $ZnSO_4.7H_2O$ was prepared using distilled water.

1b. To the solution were added 30 g of powdered Zn, and the mixture was boiled for 30 min. This step involves a reduction of the metal contaminants, which are worse reducing agents than zinc (which make up the most impurities) back to their metallic forms.

1c. The solution was gravity-filtered, and the filtrate was collected.

1d. To the solution were added 30 g of activated charcoal, and the mixture was boiled for 1 h. This step removes impurities, introduced from the Zn powder in the previous step, as well as other contaminants [9].

1e. The solution was gravity-filtered, and the filtrate was collected.

1f. Using the gas generator, H_2S gas was bubbled through the purified solution. The gas was obtained from the reaction of 120 g of FeS and dilute HCl. ZnS is insoluble in water, which causes its precipitation. lg. The mixture was filtered and the ZnS was collected.

2. Modification process

2a. A certain amount of a salt of the particular activator was dissolved in 100 mL of distlled water and 5 mL of the solution were taken. This step was taken to minimise any errors caused by measuring the weight of the activator salt which was added to a comparatively small amount to ZnS.

2b. A dilute NH₄Cl solution was made by mixing 25 % NH₃ solution and HCl. The amount of NH₄Cl taken, was in 7-fold excess, compared to the molar amount of the activator. (Such solution was not made for $MnCl_2.4H_2O$, because the source of chloride anions is the counterion of the activator in this case)

2c. The solution of co-activator was prepared as described in 2a with a concentration comparable to that of the other used activator.

2d. 2 g of ZnS were measured, and to them were added: the activator solution, the chloride solution (does not apply to Mn-activated samples and samples, showing the effect of absence of halogenides in the phosphor) and the co-activator solution (if such was being used for the particular probe) and distilled water.

Extra step: if Ag is being used as an activator, the previous step would generate a precipitate from AgCl, which will prevent the even distribution of the activator. To solve this issue, a few drops of NH₃ solution were added to dissolve the precipiate, forming a complex.

2e. All of H_2O in the mixture was boiled upon heating using a hot plate. The result of this step consists in an even distribution of the activator on the surface of ZnS.

2f. ZnS was collected and put into a quartz tube. The tube was filled with CO_2 gas produced from the reaction of NaHCO₃ and HCl. The gas acts as an inert atmosphere for the firing process.

2g. The firing process – the quartz tube was put into the preheated propane furnace and was heated for 10 min. After that, the produced phosphor was taken out.

The steps from 2a to 2g were repeated twice for the same concentration in order to yield reproducible results. The average result from the first and the second trial of the probe, was considered to be the most accurate one, and is therefore the type of result, presented in the section "Results".

3. Measuring the characteristics of the phosphor

3a. Measuring the duration of glow. The phosphor was excited for 5 s using the 365 nm and the 256 nm UV lamps. After turning the UV source

off, a RAW video (where each pixel represents an exact value of the light registered in the sensor of the device) of the phosphorescing probe was recorded [10]. The video was used as an input for a computer program, which takes the values, registered by the sensor in each pixel of the area of the phosphor, and takes its average value for each frame. The output of the program is a .csv file which can be used to calculate the duration of glow of a particular sample. The values (ranging from 0 to 255) in the results represent the excitement of the phosphor with the more suitable of the two wavelengths. The duration of phosphorescence was measured as the time, for which the pixel values became equal or smaller than the measured background value.

3b. The spectrum of phosphorescence and the UV-vis absorption spectrum were taken using a dedicated apparatus.

3c. Using the phosphorescence spectrophotometer and the already determined highest intensity wavelength emitted by the measured probe, the most suitable UV wavelength for the excitation of the used activator was determined.

RESULTS

The results, obtained from each conducted experiment, represent the values of the independent variables. The experiments can be devided into three types, depending on the activators and co-activators used:

1. Single activators - the purpose of the experiment is to determine the peak concentrations of each activator used in this project (Mn, Cu, Ag)

2. Co-activation – the purpose of this experiment is to investigate the effect of co-activation of ZnS using both Mn and Cu in different ratios.

3. Influence of halogenides and aluminium – this experiment aims to prove the important role of halogenides and aluminium on the overall properties of the phosphor.

Single activator – Manganese

The properties of six probes with different molar concentrations of Mn (0.14 mol%, 0.7 mol%, 2.1 mol%, 3.5 mol%, 4.9 mol% and 9.8 mol%) were measured.

- Glow duration – the duration of phosphorescence is measured according to the method, described in 3a.

Diagram 1 clearly shows the effect of the activator concentration on the duration of the phosphorescence – the peak concentration (in this case, 4.9 mol%) exhibits the longest glow and the

duration gradually declines, as the concentration gets lower or higher than that peak concentration.



Diagram 1. Comparison of glow duration.

- Color – the color of a particular phosphor is represented by its phosphorescence spectrum as described in 3b.



Graph 1. Phosphorescence spectrum of two Mndoped phosphors

A characteristic change [11] of the color of glow is observed at different activator concentrations – a gradual shift from red (at 0.7 mol %) to green-yellow (at higher and lower than 0.7 mol %) is evident. This effect is also shown on Graph 1, where the wavelength of the light with highest intensity shifts from 582 nm (at 4.9 mol %) to 599 nm (at 0.7 mol %). The change of color can also be explained by the absence of light with wavelength below 550 nm in 0.7 mol %, since its presence contributes to the color of glow to look yellow-green.

Single activator – Copper

The properties of six probes with different molar concentrations of Cu (0.75 mol%, 1.5 mol%, 2.33 mol %, 3 mol %, 5 mol % and 7.5 mol %) were measured.



Diagram 2. Comparison of duration of glow.

Diagram 2 shows again the effect of the concentration of the activator on the duration of glow. Modification with copper has peak concentration of 2.33 mol % and using higher or lower concentration results in decreasing duration of phosphorescence.

- Color

Contrary to manganese-doped, copper-doped ZnS phosphors do not show any color shift, when different concentrations of activator were used. This is also shown in Graph 4 which shows very small deviation between the samples measured, which is smaller than the usually reported in other procedures [12].



Graph 4. Spectrum of Cu-doped phosphor

Single activator – Silver

The properties of five probes with different molar concentrations of Ag (0.33 mol %, 0.75 mol%, 1.33 mol %, 2.66 mol %) were measured.

- Glow duration

Diagram 3. Comparison of duration of glow

The graph shows that the peak concentration for ZnS modification with silver is 0.75 mol %. Probes with silver concentration, different than the peak one, tend to have significantly shorter duration of phosphorescence.



Graph 6. Phosphorescence spectrum of Ag-doped ZnS phosphors.

Silver-doped ZnS phosphors fluoresce and phosphoresce with a strong cyan color. Graph 6, which shows a phosphorescence spectrum of a sample with silver concentration of 0.75 no1%., reveals three wavelength peaks of emitted light – at 457 nm, at 518 and at 587 nm, which contribute to the overall color.

Manganese-Copper co-activation

The properties of five samples with different molar ratios of Mn and Cu (1.5 mol%:1.5 mol % (1:1), 3 mol %: 1.5 mol % (2:1), 4.5 mol %: 1.5 mol % (3:1), 1.5 mol %: 3 mol % (1:2) and 1.5 mol %: 4.5 mol % (1:3)) were measured.



Diagram 4. Comparison of duration of glow

Manganese-Copper co-activated samples are generally short-lasting but give strong fluorescence. It is noticeable that in Diagram 4 the ratio Mn:Cu=1:1 acts as a "peak ratio" for the particular activators, as a ZnS phosphor doped with it, exhibits much longer phosphorescence than the other ratios.

Color



Graph 8. Phosphorescence spectra of three Mn-Cu co-activated phosphors



Graph 11. Comparison of Ag:Al co-activation and activation by Ag

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The phosphorescing color of the sample is related to the ratio of the co-activators. A ZnS phosphor, doped with Mn:Cu-2:1, emits yellow light, with only one peak at 585 nm, which corresponds to the light emitted by a probe doped with Mn only. The sample, doped with Mn:Cu-1:2 emits green light, with two peaks at 525 nm and at 575 nm, which correspond to the two peaks, characteristic for ZnS with only Cu used as an activator. The phosphor with Mn-Cu ratio of 1:1, emits the 585 nm peak, characteristic for manganese, as well the two peaks, characteristic for copper-doped ZnS.

Co-activation Ag-Al

The properties of one probe with Ag concentration of 0.75 mol % (the found peak concentration of silver) and Al concentration of 0.11 mol % were measured.

- Duration of glow - the probe exhibits phosphorescence for a period of 40.6 sec, measured by the method, described in the procedure.

- Color and intensity



Graph 10. Spectrum of a Ag:Al co-activated phosphor

As Graph 10 and Graph 11 show, Ag:Al coactivated emits light with one peak at 598 nm which corresponds to one of the peaks of ZnS doped with only silver. The other two characteristic peaks of silver are absent in the light emitted from the Al coactivated probe.

Homogeneity of the phosphors

The degree of homogeneity can be determined qualitatively, using Photo 1. There are clearly noticeable spots with different intensity of glow and even different color. This is a sign of low degree of homogeneity, caused by local difference of activator concentration.



Photo 1. Inhomogeneous phosphor

DATA ANALYSIS

From the results presented in the previous section, several conclusive statements can be made. First, ZnS phosphors, doped with silver, show the worst luminescent properties, compared to the other phosphors modified with a single activator. This is also a common occurrence in other research, concerning this topic [13], and a number of possible explanations has been reported. The most evident one is caused by the different oxidation state of Ag⁺, compared to that of other activators (Cu^{2+} and Mn^{2+}) and even to the cation of the base material $-Zn^{2+}$. This difference causes imbalance of charge, when silver is incorporated into the crystal lattice of ZnS, and a possible solution for solving the issue is the use of halogenides and trivalent cations [14]. For example, a chloride and a sulfide anion are able to balance the combined charge of a zinc and a silver cation. The situation is similar with the use of trivalent cations like Al³⁺ [15]. However, Ag:Al codoped phosphors show better phosphorescent properties than Ag-doped phosphors with added chloride, both intensity-wise and duration-wise, which is also reported in other procedures, some including co-precipitation [16-19]. This leads to the assumption that the procedure of the addition of halogenides alongside single-activated phosphors is less effective than the addition of alumin

um and also to the direct conclusion of the big importance of balancing the charge of an activator with an oxidation state different from that of the ions of the base material. There are also other reasons for the less effective activation with silver. For example, silver can be easier reduced to its metallic form during the firing process than the other activators. This can lower the degree of retaining the original concentration, and lead to a poor-quality phosphorescent material. Furthermore, the reduction can be enhanced by the presence of organic contamination in the ZnS, which is harder to control than the heavy metal contaminants [9].

Another clearly noticeable phenomenon is the better luminescent properties of the Mn-doped phosphors over the Cu-doped ones. The use of activator chloride (in particular MnCl₂) has shown to yield phosphors with excellent luminescent properties (around 90 s phosphorescence for the peak concentration Mn-doped probe). Moreover, the decrease in properties of the phosphor when the concentration of the activator is different from the peak concentration, seems to be less steep with manganese than with copper. These effects are contrary to most of the results reported in papers, doing similar research - in the usual case copperactivated ZnS phosphors are reported to give a longer lasting, as well as brighter phosphorescence [7, 8, 20, 21]. This deviation from the commonly obtained results can be explained by the *less effective* addition of halogenides via the ammonium salts, compared to using an activator halogenide and it also proves the previously made assumption for the overall ineffectiveness of additional addition of halogenides. This also partially proves the hypothesis, because one of the main opportunities which this method provides, in contrast to other methods, namely the usage of activator halogenide. actually shows to give better results.

The phosphors, co-doped with Mn and Cu, phosphoresce for shorter periods of time, but all of the investigated ratios and concentrations emit light with high intensity (except the ratio Mn:Cu=1:1, where the phosphorescence also lasts longer). It is noticeable that the excess use of one activator over the other, causes suppression of the light with wavelengths characteristic for the activator with lower concentration [22]. This way, the spectrum shows that at 1:1 ratio between the activators, the peaks corresponding to each activator are clearly present; in the Mn:Cu-1:2 co-doped phosphor, the light with wavelengths, emitted from copper (527, 550 and 571 nm) suppress the light, emitted from manganese (which has a peak at 585-590 nm). This effect can be explained by the effect of using one activator in excess to the other in a co-activation system, already discussed in the theoretical background [5].

DISCUSSION

The main purposes of investigating this method of obtaining ZnS modified phosphors in this project were to determine the ideal doping conditions for the phosphors, and the benefits and disadvantages of the method. One of the main disadvantages, associated with this method is the general inhomogeneity of the produced phosphorescent materials. Although the followed procedure gave results proving that

disadvantage, there are a few actions that can be done, in order to reduce its effects. One way of dealing with the issue is mixing the pure ZnS powder and the activator, used to modify it, using an ultrasonic stirrer. This is a much more efficient way of mixing the base material and the solution containing the activator, since ZnS is insoluble in water and the fine dispersion of its particles is crucial to dealing with the resulting inhomogeneity after removing the solvent from the mixture.

The most common sources of error, occurring in this project, are related to measuring different variables and constants.

- Weight - $\pm 1mg;$

- Glassware volume measurement - ± 1 mL;

- UV-Vis and phosphorescence spectrophotometers – negligible source of error;

- Camera sensor – negligible source of error.

The method of using pixel values, taken from a RAW video, to determine the duration of phosphorescence, can be regarded as affordable, but objective and accurate for the purpose of the investigation. The idea of using pixel values has already been investigated and used [1], but the program used for taking and processing the data from the pixel values, was specifically written for the purposes of the project by the author himself.

Another source of error important to mention is the effect of the inhomogeneity of the phosphors, which leads to local differences in the concentration of the activator applied. The method of dealing with this issue when measuring the results is by taking average values of the two probes, made for each altered dependent variable, but still, there is a certain amount of error affecting the final results.

It is important to note that the phosphors, obtained in the followed procedure, are not in the form of nanoparticles. A possible step to be added to the procedure, could also be the addition of a capping agent, which can stabilize the formed ZnS nanoparticles [23-25]. The ZnS nanoparticles are the most widely produced form of the material in recent research, often being associated with coprecipitation being a part of the procedure followed, however, they can also be obtained by slight modification of the method used in this project.

CONCLUSION

The project has fulfilled its main aims. Doping conditions, approximate to the ideal conditions, were determined as the peak concentrations and the peak ratios for single activators and co-activators were found and shown in the table below.

Activator/ Co-activator	Peak concentration/ ratio	Duration of glow(s)
Mn, Cl	4.9 mol %	91
Cu	2.33 mol %	32.6
Ag	0.75 mol %	36.4
Mn:Cu	1.5 mol %: 1.5 mol %	42

The statement of the hypothesis was proven using a chloride activator as a source of both activator and halogenide anion is more efficient than addition of halogenides. the external The opportunity for such addition can be regarded as the most notable advantage of this method, compared to other procedures. The other assumption, concerning the lack of homogeneity of the obtained phosphor, was also proven to be right. Attempts to resolve the lack of homogeneity, being the main source of error and simultaneously the main disadvantage of the method, were proposed and described in the discussion (mixing with ultrasonic stirrer, stabilizing the formation of nanoparticles).

Acknowledgement: The author extends his sincere appreciation to the Inorganic Chemistry Department of the Chemical Faculty, Sofia University "St. Kliment Ohridski." Their generous provision of access to specialized equipment was instrumental in the successful execution of this research.

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