

The synthesis of nanocrystalline electroluminescent chalcogenides

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Zinc and cadmium sulphide is a ternary compound used as a pigment, phosphors and semiconductor material. The paper presents an experimental study regarding the obtaining process of the nanocrystalline compound $Zn_xCd_{1-x}S$. In technical papers there are many recipes for colloidal ZnS and CdS synthesis in different working conditions and from various raw materials. Depending on the chosen recipe one can obtain colloidal $Zn_xCd_{1-x}S$ particles of greater or smaller sizes. The pH and the concentration of the synthesis solution have a great influence on the dimensions and properties of synthesized particles. The method consists in co-precipitation of $Zn_xCd_{1-x}S$ from $CdSO_4/Cd(NO_3)_2$ and $ZnSO_4/Zn(NO_3)_2$ solutions, by adding an exceeding amount of Na_2S at high pH of the solution. The precipitation reaction takes place in the presence of a stabiliser, copolymer styren-maleic anhydride. The stabilizer provides a colloidal state of the synthesized material and does not allow $Zn_xCd_{1-x}S$ nanoparticles to agglomerate. This ternary compound has a high efficiency of the UV exciting energy conversion into visible light, applied in photo and electroluminescent cells.

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1. Introduction

Ceramic films and coating are both active fields of research and widely used areas of technology. The relatively high hardness and inertness of ceramic materials make ceramic coatings of interest for protection of substrate materials against corrosion, oxidation and wear resistance. The electronic and optical properties of ceramics make ceramic films and coatings important to many electronic and optical devices.

We are able to distinguish to mechanisms of electroluminescence: injection due to the cc field effect and intrinsic due to dc field effect. The dc field is applied over powder phosphors in an electroluminescent cell. This one consists of a glass plate covered by a transparent and conductive SnO_2 thin film, a transparent dielectric mass in which the phosphors are dispersed and a metallic film deposited by evaporation. Thus, we obtain a capacitor with one transparent plate. Supplementary, we are able to insert a TiO_2 reflective film. Nitrocellulose and vinyl-polychloride are used as dispersive medium for Cu-doped ZnS. The most used phosphors are: Cu-doped ZnS with blue or green emission and Cu, Mn-doped ZnS with orange emission. We can partly substitute ZnS by ZnSe aiming to obtain a large range of luminescent colour. These cells are the basis for electroluminescent lamps with a relative low efficiency (10-15 lm/W at 600 V) and a low brightness. For this reason, the luminescent lamps are not used in the public illumination but as warning lamps and as lighting of the panels from the different devices. When a vacuum deposited film replaces the dispersion phosphor - dielectric layer, qualitative electroluminescent devices are obtained. The electroluminescent device with a luminescent film and with two insulator layers has a

satisfactory brightness, high chemical stability and long liability. The electroluminescent thin films, due to their liability, brightness and memory function, could be used aiming to obtain plate displays: their future utilization is the achievement of the plate TV and the "fool-colour" panels.

The synthesis of crystalline inorganic nanoparticles is very difficult because in the same time composition and particle size distribution must be controlled. The major problem which appears at nanoparticles synthesis is the obtaining of particle dimensions for every batch, taking into account that physical-chemical properties are dramatically modified when particle dimensions have different values [1, 2, 3]. In this experiment we focused on crystalline pigments of zinc and/or cadmium sulphide [5, 6, 8, 9, 10] for which the modification of particle size distribution, colors and luminescence phenomena was studied.

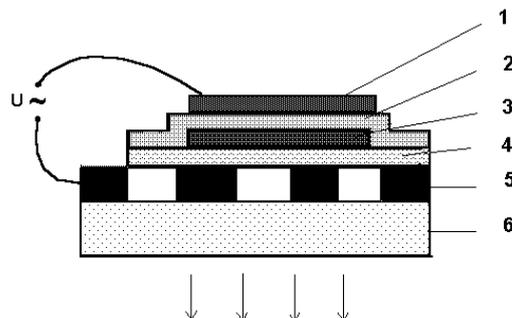
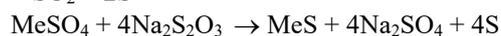
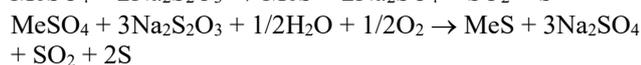
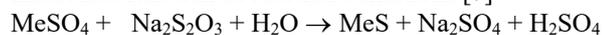


Fig. 1. Electroluminescent cell obtained by vacuum deposition. 1. metal (Al) electrode, 2. insulator layer (200 nm), 3. active layer (600 nm), 4. insulator layer (200 nm), 5. SnO_2 transparent electrode, 6. glass substrate.

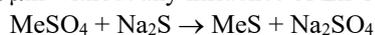
In practice two principal ways are used to obtain [7] $Zn_xCd_{1-x}S$: methods by dried route and methods by wet route. Concerning that chalcogenidical matrix impose advanced purification in order to produce luminescence phenomena, two methods was selected. These methods leading to advanced reagents purification [14] before chalcogenidical matrix synthesis and are: synthesis starting from zinc/cadmium salt and sodium thiosulphate and synthesis starting from zinc/cadmium salt and sodium sulphide. Started from $Zn_xCd_{1-x}S$, varying x value and using different activators and various thermal treatments, we are able to obtain a large range of phosphors:

2. Experimental

The precipitation of zinc and/or cadmium sulphide from sulphate solutions with sodium thiosulphate is a complicated synthesis method. One sulphate molecule ($Me = Zn, Cd$) can reacts with 1, 2, 3 or 4 thiosulphate molecules function of reaction conditions [7].



On the other hand, secondary reactions appear and produce sulphur as by-product in $Zn_xCd_{1-x}S$ precipitate and decrease reaction yield, function of reagents ratio and reaction conditions [7]. For experiments we used saturated de $ZnSO_4$, $CdSO_4$ and $Na_2S_2O_3$ with 1/0, 2/1, 1/1, 1/2 and 0/1 Zn/Cd ratio, sulphate/thiosulphate ratio 1/1, 1/2, 1/3 and 1/4, at room temperature and solutions boiling. Precipitation rate at room temperature is too small in order to apply synthesis process at industrial scale. By increasing solution temperature up to boiling point the precipitation rate significantly increases, but in the same time reaction mechanism become complicated by increasing weight of secondary reactions and by forming polithionates which contaminate the product [7]. By solution boiling particle size distribution of precipitated sulphide increases, covering the influence induce by Zn/Cd ratio. Using zinc nitrate and cadmium nitrate solutions obtained precipitate has fine grains but not so important. By precipitation, at boiling with two hours we obtained sulphide with medium grain size between 1.1-2 μm starting from sulphate solutions and 0.9-1.1 μm starting from nitrate solutions. The zinc and cadmium sulphide precipitation using sodium sulphide as reagent represent a simple and rapid process which take place at room temperature. Particle size distribution is about 0.67 μm without any influence of Zn/Cd ratio.



For particle size decreasing the decreasing of reactants concentrations in the reaction environment was experimented. The antecedent experiments with 1M $ZnSO_4$, $CdSO_4$ and Na_2S solutions was re-established. For accompaniment anion effect study 1M $Zn(NO_3)_2$ and $Cd(NO_3)_2$ was experimented. We can observe that at lower pH we obtain precipitate with smaller particle size. Above

pH=7 from solution precipitate $Zn(OH)_2$ with 0.29 μm particle size. The precipitation from nitrate solutions conduces to smaller particle size graining as opposed to the precipitation from sulphate solution. The precipitated $Zn_xCd_{1-x}S$ powder was thermal treated at different temperatures in order to view the modification of particle size distribution function of thermal treatment time.

One can observe that particle size distribution evolution in time is a linear function, with degree depending of time of thermal treatment and Zn/Cd ratio. Consequently, on the base of experimental results, can be established treatment time for any temperature in order to obtain preset particle size distribution. Calculated pigment particle size distribution has an increasing when quantity of Zn increases in pigment composition.

3. Results

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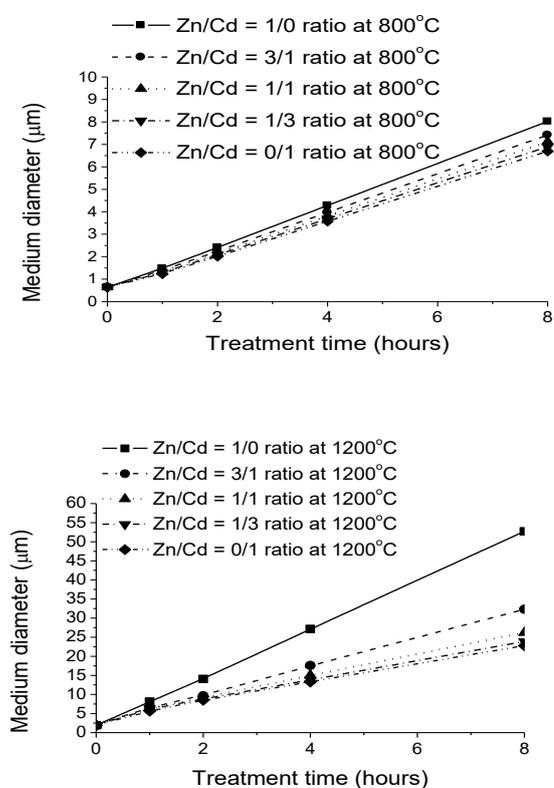


Fig. 3. The evolution of $Zn_xCd_{1-x}S$ (precipitated with sulphide) particle size distribution function of thermal treatment at different temperatures (Fritsch-Analissette 22/ laser granulometry analyzer).

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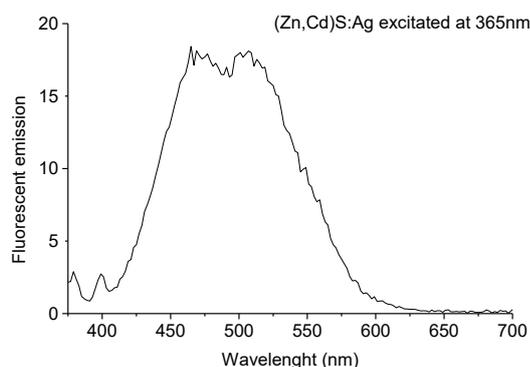


Fig. 4. The fluorescent emission of $Zn_{0.5}Cd_{0.5}S:Ag$ synthesized phosphor (FT-6500 Jasco spectrofluorimeter).

We have synthesized $Zn_xCd_{1-x}S:Cu,Ag,Mn$ with $x = 0, 0.04, 0.1, 0.11, 0.48, 1$ and different concentration of Cu, Ag, Mn dopants.

4. Discussion

Is well known that the agglomeration process of colloidal particles can be stopped using stabilizers because their adsorbent properties stabilizers molecules are seated on colloidal particles breaking closeness of that based on their big molecules.

$Zn_xCd_{1-x}S$ pigment was synthesized by precipitation experiments in 1/1 water-acetone environment and in 1/1/1 water-styrene-maleic anhydride environment. Synthesized pigments can not be retain on filter paper, and consequently they will be separated and washing by sedimentation and decantation. Initially, precipitate washing will be made with deionised water and than with ethylic alcohol or acetone in order to stop reaction products agglomeration and flocculation. After acetone washing pigment is dried in air at $80^\circ C$ for 4 hours. When colloidal $Zn_xCd_{1-x}S$ is synthesized by "at drop" technique, other efficient stabilizers can be utilized such as [1, 2, 3, 11, 12, 13]: styrene-maleic anhydride copolymer (1:1), acrylic acid-maleic anhydride (1:1), diarildimethyl amonium-acrilamide chloride copolymer (1:1), etc.

Because grains dimensions increase in thermal treatment occurrence it will be lead at lower values of temperature and time. Treatment time can be calculated using above presented graphics in order to obtain desired crystalline structure without any increasing synthesized crystals.

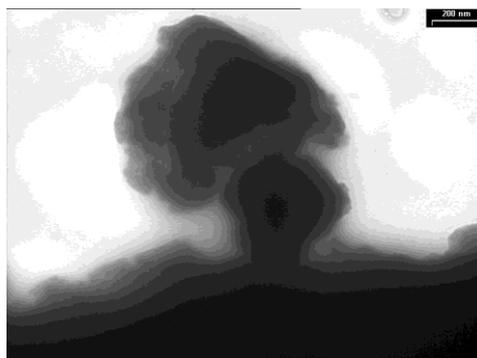


Fig. 2. TEMBF image; $Zn_xCd_{1-x}S$ sample with $x=0$ precipitated with Na_2S without thermal treatment.



Fig. 3. SAED image corresponding micro area from Fig. 2.

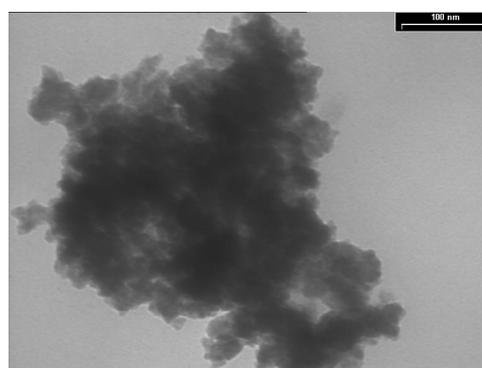


Fig. 4. HRTEM image. $Zn_xCd_{1-x}S$ sample with $x=1$ precipitated with Na_2S without thermal treatment.

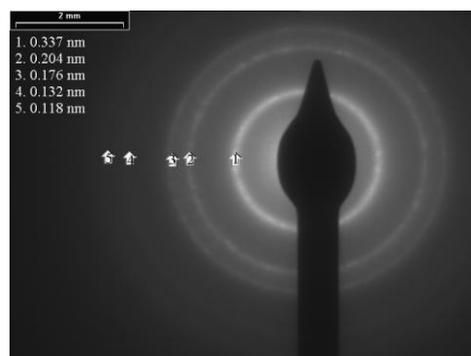


Fig. 5. SAED image for micro area from Fig. 4.

Particle size distribution for $Zn_xCd_{1-x}S$ synthesized by Na_2S method and calcinated at 800 °C for 0.5 hours shows a decreasing when Cd content increases.

We analyzed samples precipitated with Na_2S by electronic microscopy. Transmission electronic microscopy (TEM) was realized with Philips CM 12 microscope having 2Å resolution for precipitated samples. Scanning electronic microscopy was realized with Hitachi S2600N for samples calcinated at 800°C for 0.5 hours.

Image from Fig. 2 shows that particle agglomeration up to tens nanometers. Electrons diffraction presented in Fig. 3 shows diffraction diffuse rings which indicate a crystalline order on nanometer areas, corresponding interlayer distances having small values around values displayed on image. These distances corresponding ZnS compound with cubic crystalline structure (cfc). HRTEM image shows that darkness clusters (about 5nm) with crystalline order are dispersed in thin film which seems to be amorphous material. However Fourier transformed shows high level of local disorder.

Image from Fig. 4 exhibit agglomeration of tens nanometers. Electron diffraction from Fig. 5 presents pronounced diffraction rings which show the existence of crystalline phase, with small crystallites. Interplanar distances from diffraction rings indicate the presence of CdS compound with cubic crystalline structure. HRTEM images exhibit nanometer crystallite with dimensions 10nm.

Comparing obtained experimental results with another obtained in [5] one can observe that by decreasing reagent concentrations, decreasing reaction temperature and using dispersant agents in reaction environment is possible to decrease precipitated pigments particle size distribution down to nanometer level without difficulties.

The influence of (SO_4^{2-} , NO_3^- etc) anions and pH observed in previous works [5] must be take into account in the case of Na_2S method. Colloidal precipitate was hydrothermal treated at 85°C for 8 hours leading to rapid aging of CdS sol, which has as consequence important increasing of particle dimensions. This phenomenon was verified by absorption spectra plotted before and after hydrothermal treatment. The sol absorbance increased by aging on entire range of visible spectra.

Nanometer $Zn_xCd_{1-x}S$ obtaining is not so complicated, bat is very difficult to maintain particle size distribution while powder is conditioned.

To improve the electroluminescence device performances [15], we are able to apply two methods: increasing of the energetic efficiency of the luminescence and achievement of a more efficient electroluminescent device. The used method for luminescent cells obtaining are based on sputtering technologies. The obtaining of stable nanometric phosphor dispersions permits producing these devices on deep-coating technologies, with similar qualities and lower price.

5. Conclusions

For photo and electroluminescent cells, the obtaining of $Zn_xCd_{1-x}S$ nanometer ternary compound into stabilized colloidal suspensions allow the achievement of phosphor coatings by deep-coating method avoiding the problems generated by stoichiometry maintaining necessity at vacuum evaporating methods.

From our experiments we conclude that is possible to obtain doped nanocrystals directly in the synthesis process, without the eventually thermal treatment, by controlling the synthesis conditions. This ternary compound has a high efficiency of the UV exciting energy conversion into visible light, applied in photo and electroluminescent cells.

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