

The preparation of chalcogenide electroluminescent coatings

C. ONOSE^{*}, H. NICIU^a, O. ROBU^b, C. S. ONOSE, D. NICIU^a, M. ELISA^c

Applied Chemistry and Environmental Protection Department, University "Politehnica" of Bucharest, 1 Polizu Street, Sect.1, Bucharest, Romania

^a*National Glass Institute, 47 Th.Pallady Av., Sect.3, Bucharest, Romania*

^b*University "OVIDIUS", 124 Mamaia Av., Constanta, Romania*

^c*INOE 2000, 1 Atomistilor Str., P.O. Box MG-5, Code RO77125, Magurele, Romania*

Alkaline-earth metal silicates as well as many polyvalent metals silicates are prepared usually through aqueous solutions reactions between an alkaline silicate solution and the solutions of metal salts. The oxide composition of the designed glass is established by estimating of the molar ratios of precursors. The vitrification of the oxide compositions takes place directly by the reaction of the chemical precursors on the substrate. This paper presents an experimental study based on obtaining methods of nanocrystalline $Zn_xCd_{1-x}S$ from aqueous solutions. We have investigated the dependence of $Zn_xCd_{1-x}S$ nanoparticles size and properties on composition, pH and concentration of the starting solution. 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 pH high values. The precipitation reaction takes place in aqueous solutions, in the presence of a chemical stabilizer as styrene-maleic anhydride or acrylic acid-maleic anhydride co-polymers. The stabilizer provides a colloidal state of the synthesized material and does not allow $Zn_xCd_{1-x}S$ nanoparticles to agglomerate. The nanocrystalline $Zn_xCd_{1-x}S$ electroluminescent pigments, the vitrification and the quality of the obtained thin films were studied by Optical Microscopy, Transmission Electron Microscopy and Scanning Electron Microscopy.

(Received July 5, 2009; accepted after revision May 26, 2010)

Keywords: Electroluminescence, Nanometric powder, Zn-Cd-S, Coating

1. Introduction

The synthesis of crystalline inorganic nanoparticles is a very difficult process because the composition and the particle size distribution must be controlled concurrently. The main problem that appears is the synthesis of nanoparticles in every batch, taking into account that physical-chemical properties are dramatically modified when particle dimensions have different values [1-5]. In this experiment we focused on crystalline zinc and/or cadmium sulphide [6-17] pigments for which the modification of particle size distribution, colors and luminescence phenomena were studied.

Practically, two main methods were used to obtain [7] $Zn_xCd_{1-x}S$: a) the dried route (preparation of $Zn_xCd_{1-x}S$ by direct combination of Zn and/or Cd with S; preparation of $Zn_xCd_{1-x}S$ by chemical reaction of ZnO and/or CdO with S; obtaining of $Zn_xCd_{1-x}S$ by reaction of ZnO and/or CdO with H_2S ; preparation of $Zn_xCd_{1-x}S$ from Zn and/or Cd salts with S compounds) and b) the wet route (preparation of $Zn_xCd_{1-x}S$ by combination of ZnO and/or CdO with S; obtaining of $Zn_xCd_{1-x}S$ by chemical reaction of ZnO and/or CdO with ammonium sulphide; preparation of $Zn_xCd_{1-x}S$ by reaction of ZnO and/or CdO salts with H_2S ; obtaining of $Zn_xCd_{1-x}S$ by combination of Zn and/or Cd salts with inorganic or organic compounds of S;

preparation of $Zn_xCd_{1-x}S$ by precipitation of Zn and/or Cd salts with $Na_2S_2O_3$).

It must be taken into account that chalcogenide matrix requires an advanced purification of the chemical reagents, in order to generate luminescence phenomena. Two methods were selected for advanced reagent purification before chalcogenide matrix synthesis is done [14]. The routes were: synthesis starting from zinc/cadmium salt and sodium tiosulphate and synthesis starting from zinc/cadmium salt and sodium sulphide.

When colloidal CdS is synthesized by "at drop" technique from $CdSO_4$ and Na_2S , efficient stabilizers can be used, such as [1-5, 15-17]: styrene-maleic anhydride copolymer (1:1), acrylic acid-maleic anhydride (1:1), diarilydimethyl ammonium-acrilamide chloride copolymer (1:1) etc.

The method for obtaining decorative glass through grinding, followed by the transformation of the vitreous powder into a stable suspension is a worldwide studied route. The suspension is deposited on the support layer with special designed piezo cartridges. The image resolution and also the productivity are better than those acquired by serigraphy technique.

Technological limitations are set by the nozzle sprayer with large dimensions, imposed by the granulometry of grinded vitreous material [18,19].

An advanced method is the synthesis of silicates directly on the substrate through the wet method. The deposited silicates are vitrified in the stage of decor fixing on the substrate, which is a necessary technological stage in conventional serigraphy techniques and also in the nonconventional decor digital deposition [20-25].

The silica matrix used in decoration must be carefully chosen in order to ensure the maximum compatibility with the glass substrate and the decor layer.

2. Experiments

Alkaline-earth metal silicates as well as many polyvalent metals silicates can be obtained through aqueous solutions reactions between an alkaline silicate solution and the solutions of metal salts. The oxide composition of the designed glass is established by the calculation of the molar ratios of the precursors. The vitrification of the oxide compositions takes place directly by the reaction of the chemical precursors on the substrate. The sodium silicate viscosity in aqueous solution and the viscosity of nitrogen-containing compounds necessary in the silicates synthesis are compatible with the necessary viscosity for ink-jet cartridges. The chemical synthesis of silicates was studied during the deposition process on the support, so that the functional characteristics of the multicompartiment ink-jet cartridges were used. Different coloring effects were obtained from compositions based on nanocrystalline molecular colorants.

The chemical precipitation of zinc and cadmium sulphide using sodium sulphide as reagent represents a simple and fast process which takes place at room temperature. Particle size distribution is about 0.67 μm without any influence of Zn/Cd ratio.



In order to obtain an Zn/Cd=1 molar ratio, 500 ml 1M purified zinc sulphate solution and 500 ml 1M purified cadmium sulphate were mixed and heated up to the boiling point. In this solution, 500 ml sodium sulphide 1M solution was gradually added by continuously mixing. Then, the solution is mixed and boiled 15 min after sodium sulphide solution adding. Further the solution is cooled up to the room temperature, filtered, washed with deionized water, dried and heated 30 min at 700 °C. The obtained final product is grinded and doped. Five samples of pigment with Zn/Cd = 1/0, 3/1, 1/1, 1/3, 0/1 molar ratios (Rm) were prepared.

The average size of the particles from the precipitated powder is 0.73 μm . The influence of molar ratio Zn/Cd is $\pm 15\%$. The concentration of the solution has an important influence on the particle size distribution.

The agglomeration process of colloidal particles can be stopped by using of stabilizers. These are adsorbed on the surface of the colloidal particles blocking their growth.

When colloidal CdS is synthesized by "at drop" technique from CdSO_4 and Na_2S , efficient stabilizers can be used such as [1-5, 9-15]: styrene-maleic anhydride

copolymer (1/1), acrylic acid-maleic anhydride (1/1), diarildimethyl amonium-acrilamide chloride copolymer (1/1) etc. $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ pigment was synthesized by chemical precipitation experiments in 1/1 water-acetone environment and in 1/1/1 water-styrene-maleic anhydride environment. Initially, the precipitates are washed with unionized water and then with ethylic alcohol or acetone in order to stop the agglomeration and flocculation processes. The washed pigments are separated by sedimentation and dried in air at 80°C for 4 hours.

The particle size distribution of the precipitated powders was investigated by Fritsch-Analissette 22/0.1-600 μm laser analyzer and by electronic microscopy. Transmission electronic microscopy (TEM) was performed with Philips CM 12 microscope having 2Å resolution. Scanning electronic microscopy (SEM) was performed with Hitachi S2600N.

The experiments were directed toward the removal of the resulted segregated suspension. The main goal is that the alkaline-earth silicates and the silicates of many other polyvalent metals can be obtained through aqueous reactions between an alkali-silica solution and the solutions of some metallic salts.

A technique to obtain silicates directly on the deposition support has been set, exploiting the functional characteristics of multi-compartment ink-jet cartridges which can release simultaneously more ink drops. In this way the precursors used in the synthesis of silicates can be isolated, without the apparition of precipitate.

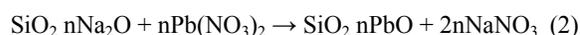
The viscosity of sodium silicate in aqueous solution as well as the viscosity of nitrates or oxalates in the silicates synthesis is compatible with that required for ink-jet cartridges.

Thermal expansion coefficient of the deposited decorative glass must be close to the expansion coefficient of the substrate in order to prevent the tensions in the decorative glass or in the substrate, leading to cracks and finally to the damage of the material. The highest recommended difference of the expansion coefficient between glass and substrate is $\pm 5 \times 10^{-7}/^\circ\text{C}$. Thermal expansion coefficient of lead silicate glasses can be compatible with thermal expansion coefficient of a soda-lime silica glass substrate.

Table 1. The thermal expansion coefficient of different glasses.

Nr. crt.	Glass type	Coefficient of linear expansion (20-200 °C) [10^{-7}K^{-1}]
1	Soda-lime silica glass	90
2	Borosilicate glass	32
3	Lead-silicate glass	85
4	Aluminosilicate glass	40

Basically, the reactions are:



It is mentioned that the replacement of alkaline oxide with lead oxide or other metallic oxide is equivalent. Thus, in order to obtain a lead silicate with a certain $\text{SiO}_2 / \text{PbO}$ ratio, an alkaline silicate with the same ratio between SiO_2 and alkaline oxide must be used. Other soluble metal salts as silicates, sulphates, chlorides, acetates, oxalates can be also used.

The starting alkaline silicate has a $\text{SiO}_2/\text{M}_2\text{O}$ ratio equal to $\text{SiO}_2/\Sigma \text{M}_2\text{O}$ ratio because a mixture of silicates should be prepared. In order to apply this technique, the alkali silicate with the appropriate molar ratio was chosen and a correction for the desired compositions was made. A sodium silicate solution, with 8% Na_2O , 27% SiO_2 , with 1370 g/l density and $R_{\text{mSiO}_2/\text{Na}_2\text{O}} = 3.49$ was used. Compositions with the bellow-mentioned molar ratio were calculated:

$$\frac{R_{\text{mSiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{ZnO}+\text{CoO}}}{R_{\text{mSiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{CdOxS}_{1-x}}} = \frac{R_{\text{mSiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{ZnOxS}_{1-x}}}{R_{\text{mSiO}_2/\text{Na}_2\text{O}+\text{PbO}+\text{CdOxS}_{1-x}}} = 2.22.$$

The compositions of the samples are presented in Table 2.

Table 2. The compositions of the samples.

Glass composition	P1, P7 (wt. %)	P2, P8, P9 (wt. %)	R2 (wt. %)	R3 (wt. %)
Na_2O	18.04	18.01	20.7	18.53
SiO_2	60.87	60.77	54.28	39.73
PbO	12.41	12.39	16.6	24.31
CoO	4.17	2.08	0	0
ZnO	4.51	6.75	0	0
$\text{ZnO}_x\text{S}_{1-x}$	0	0	8.42	0
$\text{CdO}_x\text{S}_{1-x}$	0	0	0	17.43
Total	100	100	100	100

3. Experimental results

The image from Fig. 1 shows particle agglomerations up to ten nanometers. Details presented in Figs. 2 and 3 show inhomogeneous particles groups of nanometer size. SAED image presented in the Fig. 4 shows diffraction diffuse rings, which indicate a crystalline order at nanometer scale. The corresponding interlayer distances have small deviations from the displayed values on the image. These distances correspond to ZnS particles with cubic crystalline structure (cfc). HRTEM image from the Fig. 5 shows that dark crystalline clusters (about 5 nm) are dispersed in a thin film, which seems to be an amorphous material. However, Fourier transform shows high level of local disorder.

The image from the Fig. 6 exhibits an agglomeration of tens nanometers in diameter. Electron diffraction pattern from Fig. 7 presents some pronounced diffraction rings which proves the existence of a small size crystalline phase. The interplanar distances between the diffraction rings indicate the presence of CdS compound with cubic crystalline structure. The crystalline plane is characterized by Miller index (111), (220), (311), (331), (422), in accordance with CdS compound with cubic crystalline structure.

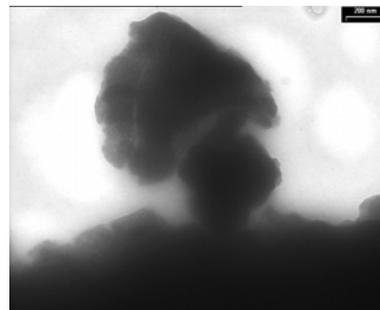


Fig. 1. TEMBF image of ZnS precipitated powder without heat treatment.

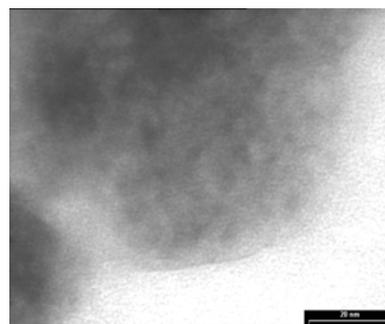


Fig. 2. TEM image (figure 1 detail) of precipitated ZnS without heat treatment.

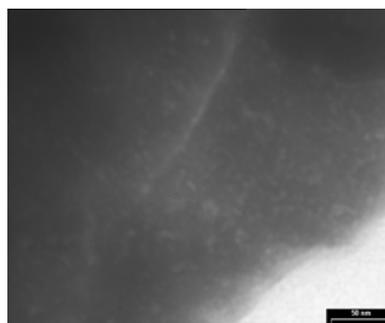


Fig. 3. TEMBF image (figure 2 detail) of precipitated ZnS without heat treatment.

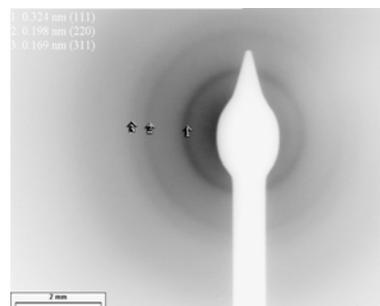


Fig. 4. SAED image micro area from the Fig. 2.

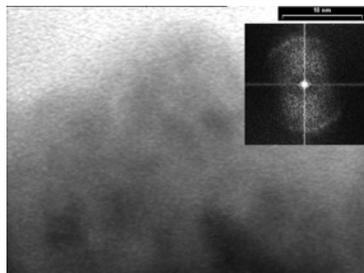


Fig. 5. HRTEM image and Fourier transform of precipitated ZnS without heat treatment.

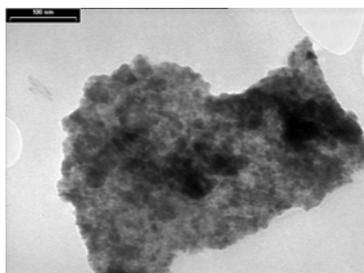
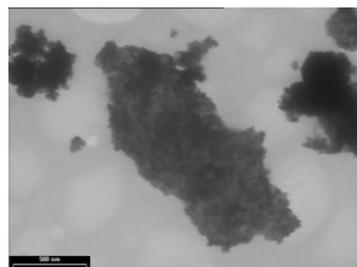


Fig. 6. CdS sample precipitated with Na_2S , without heat treatment (TEMBF).

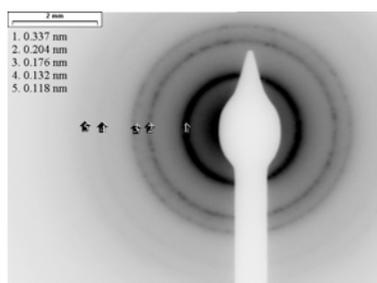


Fig. 7. SAED image associated with micro area of Fig. 6.

HRTEM images exhibit crystallites of 10 nm dimensions. Fourier transform of areas from the image-Fig. 8 shows that crystalline network has an interplanar distance equal to 3.37\AA (plane 111), which belongs to CdS compound.

The supposed particle size distribution is an lognormal type function where A is an arbitrary value depending on the particles number, x_c represents the

maximum of distribution and w represents the dispersion of the diameter values.

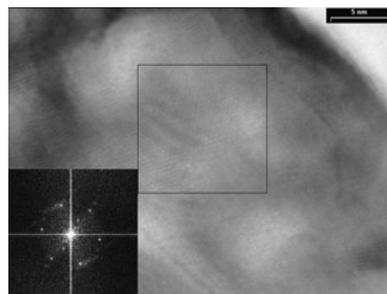


Fig. 8. HRTEM image and Fourier transform of precipitated CdS without heat treatment.

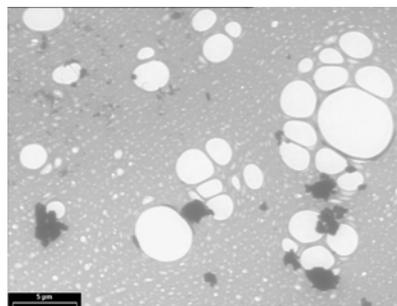


Fig. 9. The distribution of $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ sample onto substrate.



Fig. 10. SAED image for $\text{Zn}_{0.75}\text{Cd}_{0.25}\text{S}$ sample synthesized in water – acetone 1/1 environment.

The diffraction image shows the presence of a polycrystalline substance. The very small dimension of the particles (determined from TEM images), $d = 1.23\text{ nm}$, leads to the formation of some typical bands. Based on this image, we suppose the existence of two phases, having similar structure. The polycrystalline phase appears as clear delimited lines in the Fig. 10. The large bands exhibit the dispersion of particles with very small dimensions. We did not obtain significant HRTEM images for this sample due to the very small size of the particles. The existence of an amorphous phase is also possible.

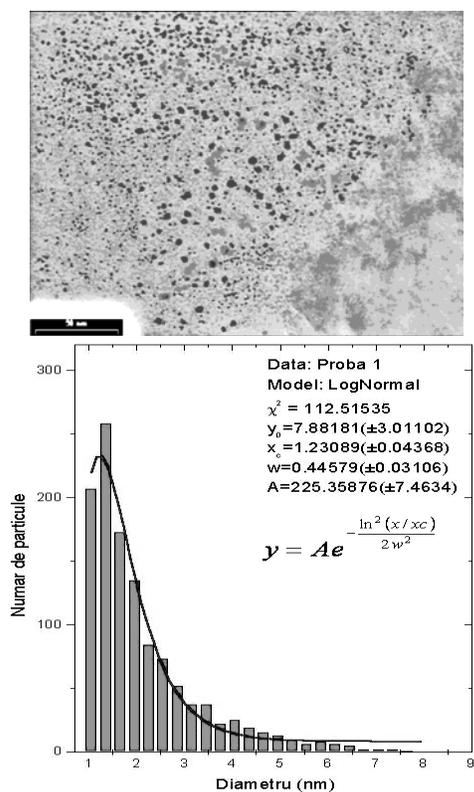


Fig. 11. BFTEM image and the particles diameter distribution for $Zn_{0.75}Cd_{0.25}S$ sample synthesized in water – acetone 1/1 environment.

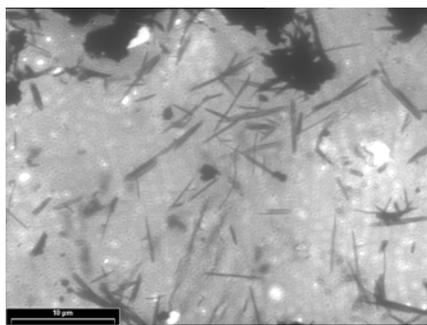


Fig. 12. BFTEM image with $Zn_{0.5}Cd_{0.5}S$ sample distribution.

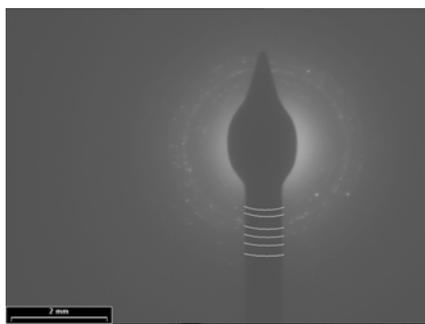
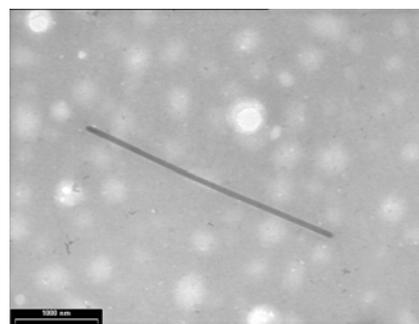
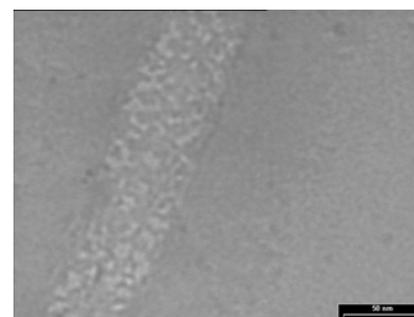


Fig. 13. SAED image for $Zn_{0.5}Cd_{0.5}S$ sample synthesized in water - acetone 1/1 environment.



a



b

Fig. 14. TEM image with one single particle of $Zn_{0.5}Cd_{0.5}S$ (a) and enlarged detail (b) which shows the material instability when exposed at electron beam.

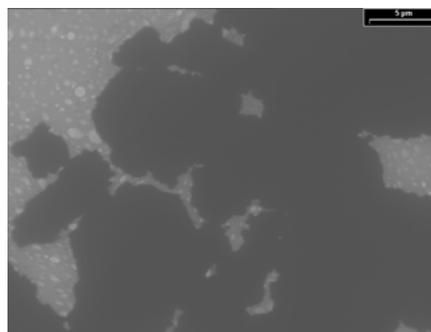


Fig. 15. TEM image which shows an inhomogeneous distribution of particles dimensions in the $Zn_{0.25}Cd_{0.25}S$ sample.

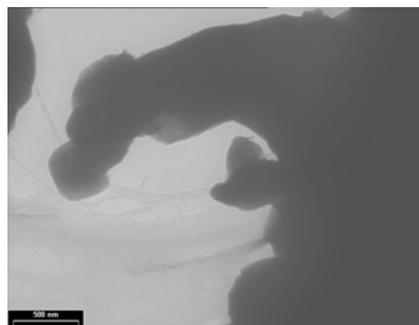


Fig. 16. SEM image on $Zn_{0.25}Cd_{0.75}S$ sample, synthesized in water – acetone 1/1 environment.

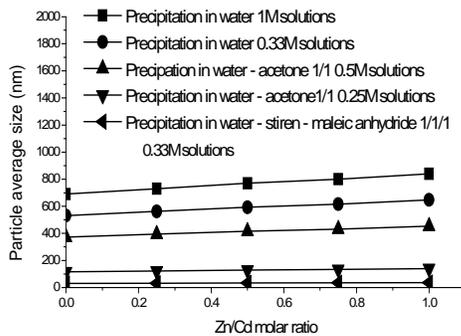


Fig. 17. Particle average size of pigment synthesized at 40 °C, in different dispersion environment.

SAED image shows a polycrystalline material, identified by the diffraction ring, corresponding to the crystalline structure.

It is observed that the particle size of the precipitate increases with the Cd/Zn molar ratio the pigment composition. The pigment particle size decreases when the concentration of the reagent solutions decreases, too.

The pigment precipitated in 1/1/1 water-styrene-maleic anhydride environment exhibits a smaller particle size than the pigment precipitated in 1/1 water-acetone environment. The pigment precipitated in water shows larger size particles.

By controlling the composition of the precipitation environment and the reagents' concentration we are able to decrease the particle average size to 60 nm (measured by sedimentation method).

The thermal treatment at low temperature is needed because the particle size increases by heating. We can calculate the heating time, based on previously obtained graph (fig. 18), to get the desired crystals with small grain size.

The precipitated $Zn_xCd_{1-x}S$ powder was thermally treated at different temperatures in order to evidence the modification of particle size distribution, as a function of thermal treatment time.

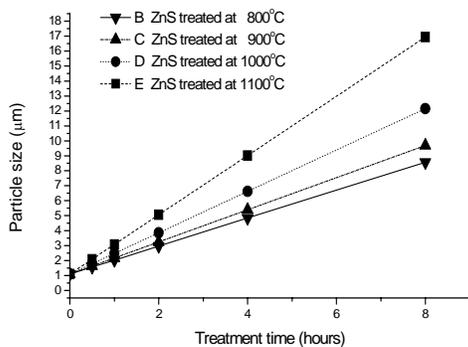


Fig. 18. The increase of ZnS particle size distribution, as a function of thermal treatment at different temperatures (Fritsch - Analisette 22/0.1 - 600 μ m laser particle size distribution analyzer).

One can observe that particle size distribution evolution in time is a linear function, depending on the time of the thermal treatment.

The pigment particle size has a growth tendency when the temperature of the thermal treatment increases. Our experience shows that at 1200 °C we can obtain 40 μ m crystals of zinc sulphide after 8 hours treatment in inert atmosphere. Consequently, on the basis of the experimental results, we can establish the treatment time for any temperature in order to obtain a preselected particle size distribution.

If a good thermal homogeneity of the furnace is not achieved, the sublimated zinc sulphide has a tendency to deposition at the cold zones. This phenomenon is more pronounced when the temperature increases. We can obtain needle-like crystals with 0.2-0.5 mm thickness and large length. After 4 hours treatment at 1200 °C, crystals with 15-20 mm length are obtained.

From the Figs. 19-22, we can conclude that $Zn_xCd_{1-x}S$ crystals grow at $\sim 0.1 \mu$ m after 0.5 hours by heating at 800 °C.

The oxide compositions of the substrate glass were set as a function of the desired linear thermal expansion coefficient required for decoration. The soda-lime silica glass has a coefficient of linear thermal expansion between $90 - 130 \times 10^{-7} K^{-1}$.

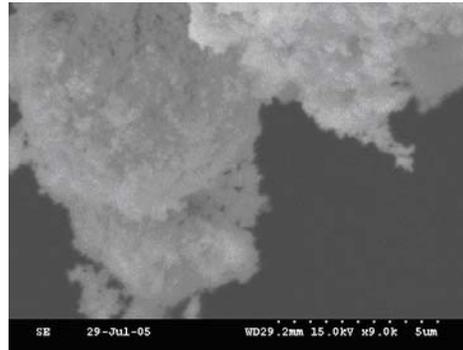


Fig. 19. TEM images of ZnS samples, precipitated with Na_2S and heated 0.5 hours at 800 °C.

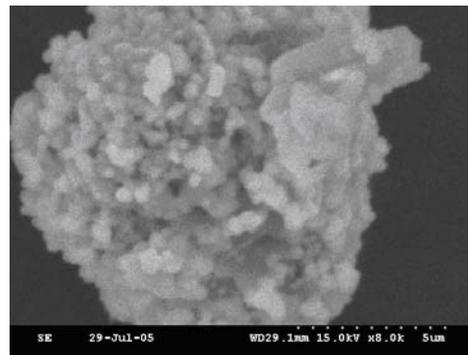


Fig. 20. TEM images of $Zn_{0.75}Cd_{0.25}S$ samples, precipitated with Na_2S and heated 0.5 hours at 800 °C.

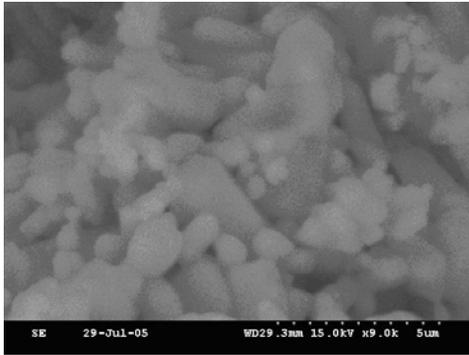


Fig.21. TEM images of $Zn_{0.25}Cd_{0.75}S$ samples, precipitated with Na_2S and heated 0.5 hours at $800\text{ }^\circ\text{C}$.

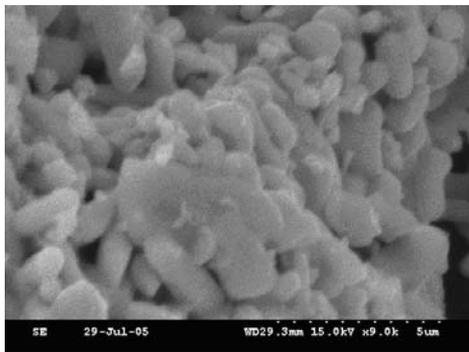


Fig.22. TEM images of CdS samples, precipitated with Na_2S and heated 0,5 hours at $800\text{ }^\circ\text{C}$.

The thermal expansion coefficient is calculated based on the chemical composition of the glass, taking into account the method elaborated by Appen. In the case of P1, P2, P7, P8, P9, R2, R3 samples, it is equal to $117.76 \times 10^{-7}\text{ K}^{-1}$. The vitrifying temperature (Fig. 23) is chosen according to the investigations made by means of the high temperature microscope.

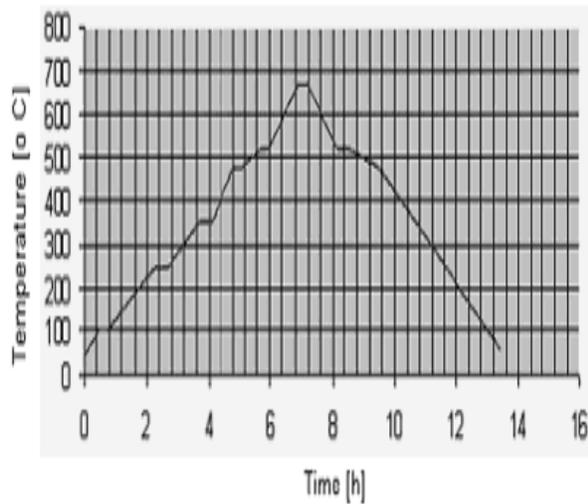


Fig. 23. Vitrification diagram.

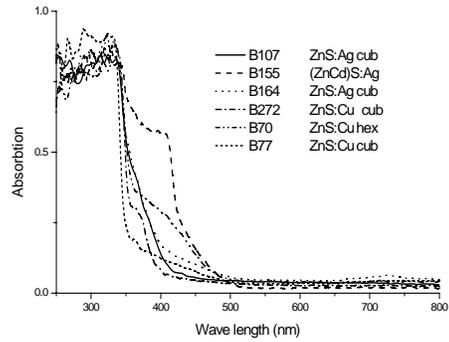


Fig. 24. The optical absorption spectra of different synthesized luminescent powders

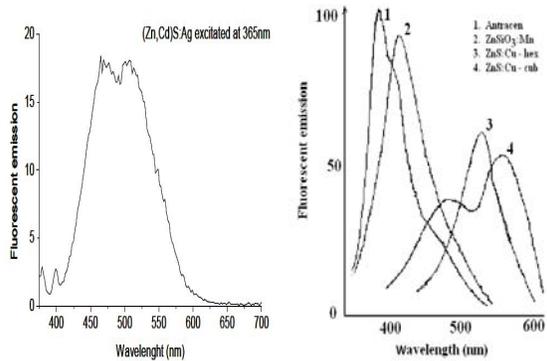
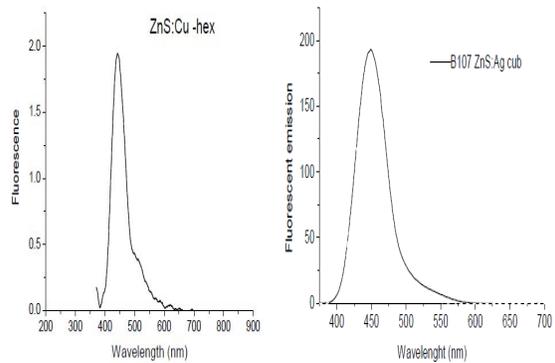


Fig. 24. The fluorescent emission of some synthesized phosphors (excited at 365nm).

4. Conclusions

$Zn_xCd_{1-x}S$ samples with $x = 0 \div 1$ were obtained by precipitation in water – acetone 1/1 environment. The use of 10-20 % acetone in the reaction environment leads to the decrease of the precipitated particle size at 5÷10 nm (in saturated aqueous solutions) and at 800 nm (in diluted aqueous solution). The particles size decreases at 5nm in water – acetone solutions and at 1.23 nm in water – styrene – maleic anhydride solutions.

We can conclude that the particle size of the precipitated pigment decreases at nanometric dimensions

when the concentration of the reagent solutions decreases as well as when the synthesis temperature decreases. The same phenomenon is noticed when dispersant agents in the reaction environment have been used.

The process of getting nanometric pigment precipitate is relatively simple; the problem is to maintain the small particle size and to block the agglomeration during the filtration, drying and heating steps.

The preparation of $Zn_xCd_{1-x}S$ nanometric ternary compound into stabilized colloidal suspensions applied for photo and electroluminescent cells, allows to get/prepare phosphor coatings by deep-coating method, avoiding the non-stoichiometrical compositions in vacuum evaporating methods. We conclude that it is possible to obtain doped nanocrystals directly in the synthesis process, without thermal treatment, by controlling the synthesis conditions.

This ternary compound exhibits a high efficiency of the UV exciting energy conversion into visible light and it is recommended for application in photo and electroluminescent cells.

Alkaline-earth metal silicates as well as many polyvalent metallic silicates can be obtained through aqueous solutions reactions between an alkaline silicate solution and solutions of metal salts.

The oxide composition of the designed glass is ensured by the estimation of the molar ratios of precursors. The vitrification of the oxide compositions takes place directly by the reaction of the chemical precursors on the substrate.

The sodium silicate viscosity in aqueous solution and the viscosity of nitrogen-containing compounds necessary in the silicates synthesis are compatible with the required viscosity for ink-jet cartridges. The silicate forming reactions were studied directly on the deposition support, so that the functional characteristics of the multi-compartment ink-jet cartridges are presented.

Different coloring effects were obtained starting from compositions based on nanocrystalline molecular dyes.

References

- [1] K. Kalyanasundaram, M. Gratzel, J. Philip, J. Kiw, Photochemical system and method of using the same, ZA8005147 / 26.08.1981.
- [2] K. Kalyanasundaram, E. Borgarello, M. Gratzel, *Helv. Chim. Acta*, **64**, 362 (1981).
- [3] K. Kalyanasundaram, E. Borgarello, D. Doungoung, M. Gratzel, *Angew. Chem.* **93**, 1012 (1981).
- [4] M. Gratzel, K. Kalyanasundaram, E. Pelizzetti, E. Borgarello, Method for producing hydrogen and elemental sulphur by photochemical oxidation-reduction of hydrogen sulphide and metal sulphides, BR8203230 / 17.05.1983;
- [5] M. Gratzel, J. Kiwi, J. Philip, K. Kalyanasundaram, Producing H_2 and O_2 from H_2O by photolysis, AU536428B / 10.05.1984;
- [6] M. I. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris: *J. Am. Chem. Soc.*, **110**, 3046 (1988).
- [7] C. Onose, C. S. Onose, M. Dăncilă, The Mechanism of the Synthesis of Zinc Sulphide from Zinc Sulphate and Natrium Tiosulphate, Proceedings of the 13th Romanian International Conference of Chemistry and Chemical Engineering (RICCCE 13), vol. 1, Bucharest, 2003, p. 138-146, ISBN 973-652-823-5
- [8] L. E. Brus: *J. Chem. Phys.* **79**, 5566 (1983). **80**, 4403 (1984).
- [9] Nomoto Shogo, Ishibashi Yoichi – Dispersant for inorganic pigment, JP 2004123903 / 22.04.2004;
- [10] Kumiko Kado, Shigemi Kitamura – Water dispersion containing inorganic pigment-cation resin composite fine particles and ink jet recording material containing said composite fine particles, CN1492008 / 28.04.2004;
- [11] L. Matta Bruce, W. Broadbent Ronald, S. Johnson Grannis, Wiggins Michael S. – Polymeric stabilizer for pigment dispersions, TW593351 / 21.06.2004;
- [12] Nomoto Shogo, Ishibashi Yoichi – Dispersant for inorganic pigment, JP 2004123903 / 2004;
- [13] Kumiko Kado, Shigemi Kitamura – Water dispersion containing inorganic pigment-cation resin composite fine particles and ink jet recording material containing said composite fine particles, CN1492008 / 2004;
- [14] Matta Bruce L., Broadbent Ronald W., Johnson Grannis S., Wiggins Michael S. – Polymeric stabilizer for pigment dispersions, TW593351 / 2004;
- [15] Oike Tomoyuki, Kataoka Naruki, Yano Yoshihiko, Takahashi Masaki, US 2004033363 (2004);
- [16] Wu Long Hai – Method for the fabrication of the electroluminescence element, US 2004224083 / 2004;
- [17] Yamashita Seiji – Electroluminescence device, US 2004227457 / 2004;
- [18] P. F. Blazdell, J. R. G. Evans, *Journal of Materials Processing Technology*, **99**(1-3), 94 (2000).
- [19] X. Zhao, J. R. G. Evans, M. J. Edirisinghe, J. H. Song, *Journal of Materials Synthesis and Processing*, **9**(6), 319 (2001).
- [20] Nomoto Shogo, Ishibashi Yoichi, JP 2004123903 / 2004.
- [21] Kumiko Kado, Shigemi Kitamura, CN1492008 / 2004.
- [22] B. L. Matta, R. W. Broadbent, G. S. Johnson, TW593351 / 2004;
- [23] Nomoto Shogo, Ishibashi Yoichi, JP 2004123903 / 2004.
- [24] Kumiko Kado, Shigemi Kitamura, CN1492008 / 2004;
- [25] Matta Bruce L., Broadbent Ronald W., Johnson Grannis S., TW593351 / 2004.

*Corresponding author: c_onose@yahoo.com