BABEȘ – BOLYAI UNIVERSITY CLUJ-NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL
ENGINEERING

SEMICONDUCTOR MATERIALS WITH SPECIAL PROPERTIS

Ph.D. Thesis Abstract

Scientific advisor
Prof. Ph.D. Luminiţa Silaghi-Dumitrescu

Ph.D. Student
Eng. Adrian-Ionuţ Cadiş

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Scientific advisor:
Prof. Ph.D. Luminiţa Silaghi-Dumitrescu
Jury:
President:
Prof. Dr. Mureşan Liana-Maria

Members:
Prof. Dr. Eng. Duţă-Capră Anca – Transylvania University of Braşov

Conf. Dr. Eng. Venter Monica – Babeş-Bolyai University, Cluj-Napoca

Prof. Dr. Chicinaş Ionel – Technical University of Cluj-Napoca

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TABLE OF CONTENTS (as in the full text)

Keywords: Manganese doped zinc sulphide, nanocrystalline powder, photoluminescence, wet-chemical synthesis, single-source molecular precursors, microwave-assisted solvothermal decomposition

LIST OF ABBREVIATIONS

BET - **B**runauer, **E**mmett, **T**eller Method
BJH - **B**arrett, **J**oyner, **H**alenda Method
CTAB - **C**etyl-**t**rimethyl-**a**mmonium **B**romide
DTA - **D**ifferential **T**hermo **A**nalysis
DTG - **D**ifferential **T**hermo**g**ravimetry
EGA - **E**volved **G**as **A**nalysis
FT-IR - **F**ourier **T**ransformer **-** **I**nfra **R**ed
ICP-OES - **I**nductively **C**oupled **P**lasma **-** **O**ptical **E**mission **S**pectrometry
IR - **I**nfra **R**ed
LED - **L**ight-**E**mitting **D**iodes
MAA - **M**ethacrylic **A**cid
MW - **M**icro**w**ave
PDF - **P**owder **D**iffraction **F**ile
PEX - **P**otassium **E**thyl **X**anthate
PL - **P**hoto**l**uminescence
QD - **Q**uantum **D**ots
QD-LED - **Q**uantum **D**ots **L**ight-**E**mitting **D**iode
r.m.s. - **R**oot **M**ean **S**quare
SA - **S**elf-**A**ctivation
SDDTC - **S**odium **D**iethyl-**Dit**hio**c**arbamate
SDS - **S**odium **D**odecyl **S**ulphate
SEM - **S**canning **E**lectron **M**icroscopy
SSMP - **S**ingle-**S**ource **M**olecular **P**recursor
STD-MW - **S**olvo**t**hermal **D**ecomposition **M**icro**w**ave Assisted
TAA - **T**hio**a**cet**a**mide
TEM - **T**ransmission **E**lectron **M**icroscopy
TG - **T**hermo**g**ravimetric **A**nalysis
UV - **U**ltra**v**iolet
WCS - **W**et-**C**hemical **S**ynthesis
WCS-SeqAdd - **W**et-**C**hemical **S**ynthesis **- Seq**uential **Add**ition
WCS-SimAdd - **W**et-**C**hemical **S**ynthesis **- Sim**ultaneous **Add**ition
WCS-US - **W**et-**C**hemical **S**ynthesis **U**ltra-**S**ound **A**ssisted
XRD - **X**-**R**ay **D**iffraction
ZDDTC - **Z**inc **D**iethyl-**Dit**hio**c**arbamate
ZEX - **Z**inc **E**thyl **X**anthate
ZMDDTC - **Z**inc and Manganese **D**iethyl-**Dit**hio**c**arbamate
ZMEX - **Z**inc and Manganese **E**thyl **X**anthate

INTRODUCTION

The technical development that we are experiencing in recent years are covering a very large fields belonging to the most varied requirements of life. Among these, in the last decade, a very fast development of the lighting system has been observed. A similar fast evolution is found in the case of visual communication, computers, medical diagnostic systems and others. A lot of components with different structures and properties are need to achieved opto-electronic devices from which an essential role are playing the semiconductor materials with special properties. An good example are the metal chalcogenides and, in particular, the high dispersed zinc sulphide with or without doping.

The opto-electronic properties of high dispersed zinc sulphide depend very much on the structure and morphology of particles, which, in turn, depend on the preparative conditions, precursors and the synthesis method. Because of this, a lot of studies are performed in the field. The aim of the studies are focused on obtaining high dispersed zinc sulphide powders/systems with superior electrical and optical properties, reproducible, as well as explaining the phenomena related to their nanocrystalline structure.

Determination of optical, structural and morphological properties of high dispersed zinc sulphide involve the use of classical and modern techniques, of which the most used are spectroscopic, thermogravimetric, microscopic and diffractographic methods.

The PhD thesis contributes to knowledge development in a topical field on the international level, that of the semiconductor materials with special properties, in particularly, the materials based on zinc sulphide nanocrystalline powders with application in opto-electronic devices. The multiple possibilities of using these materials argues the applicative importance of performed research.

The PhD thesis provide new knowledge about preparation of semiconductor materials with special properties, based on zinc sulphide and manganese doped zinc sulphide nanocrystalline powders with luminescent properties.

The thesis is divided in two parts: “Literature data on zinc sulphide type semiconductor materials, with special properties” and “The original researches on the synthesis and characterisation of zinc sulphide based semiconductor materials with special properties”. Add to this the introduction, general conclusions, reference, curriculum vitae and scientific activity annexes.

The material is divided into 5 chapters and has 269 pages and 361 bibliographic indexes.

The first part gathers information from literature on synthesis and characterisation of semiconductor materials with special properties, which include chapter 1. In this chapter is presented the current state of knowledge in the field and show the motivation the PhD thesis researches.

The second part includes the original scientific contributions on synthesis and characterisation of semiconductor materials with special properties based on zinc sulphide and is divided in 4 chapters.

Chapter 2 is focused on to the methodology used for to realization of the research. In this chapter are reviewed the synthesis methods and procedures used to prepare zinc sulphide powders as well as the investigation techniques and equipments used to characterize the as prepared samples.

Chapter 3 presents the results of research on the synthesis and characterisation of undoped and manganese doped zinc sulphide powders obtained by wet-chemical synthesis method, using different precipitation techniques namely ultrasound-assisted synthesis, sequential addition of reagents method and simultaneous addition of reagent method, respectively. This three studies “monitored” the influence of various preparative factors on optical and morpho-structural properties of zinc sulphide powders.

Chapter 4 is devoted to studies on synthesis and characterisation of undoped and manganese doped zinc sulphide powders prepared by decomposition of single-source molecular precursors. The studies are related to the preparation and characterisation of single-sours molecular precursors and to characterisation of nanocrystalline zinc sulphide powders obtained by solvothermical decomposition microwave-assisted of precursors, respectively.

Chapter 5 reviews the luminescent and morpho-structural properties of zinc sulphide and manganese doped zinc sulphide powders obtained by various synthesis methods used in order to evaluate their applicative potential.

The list of bibliographic references for all the work is attached to the end of thesis.

All thus results were obtained at Faculty of Chemistry and Chemical Engineering, Department of Organic Chemistry, Cluj-Napoca (Prof. Dr. Luminiţa Silaghi-Dumitrescu) and at “Raluca Ripan” Institute for Research in Chemistry from Cluj-Napoca, Solid-State Chemistry Laboratory (CSI Dr. Elisabeth-Jeanne Popovici).

The results presented in this work were published and communicated. A list of woks is attached to the end of the thesis. The studies were made in two research contracts funded by Ministry of Education, Research, Youth and Sport, namely: *Nobel metal nanostructures and nanoparticles with multifunctional plasmonic properties for relevant applications in nanophotonics, biodetection and laser spectroscopy - NANOBIOSPEC (MATNANTECH – CEEX-71/2006; Leader Prof.Dr. S. Astilean)* and *Physical and chemical aspects of synthesis of luminescent micro- and nanostructured materials with controlled properties – MATERLUM (ID 2488-C710/2009; Leader CSI Dr. E.-J. Popovici).*

1.4. The motivation research in the Ph.D. thesis

The synthesis of new semiconductor materials with special properties remains one of the major challenges in now days chemistry, in the field of luminescent material. Field is a fundamental due to the close correlation between the morpho-structural and the special properties manifested. The multiple possibilities of using the materials developed arguments applied importance of researches.

Complexity of the field of semiconductor materials with special properties is due to their interdisciplinary characteristics, combining different aspects of chemistry, physics and engineering. Currently, research in this field is a continuous challenge and knows a strong revival due to the multiple applications of these materials in opto-electronics.

Semiconductor materials with special properties such as nanopowders doped or undoped zinc sulphide show considerable interest in electronics and optoelectronics fields. These materials are difficult to prepare because of the complexity of synthesis factors that affect properties, hence the great interest in research in the field.

The complexity in this domain can be seen in the extremely high number of articles (over 69,000 according to Web of Knowledge) published between 1989-2012 in the field of nanomaterials (nanoparticles, nanopowders) based on zinc sulphide.

The general objective of the PhD thesis is to obtain semiconductor materials with special properties (luminescent) based on nanocrystalline particles of zinc sulphide and manganese doped zinc sulphide by various methods and their characterization in order to establish a correlation between preparation conditions and their specific properties.

The synthesis of ZnS have been made using different methods, such as::

- the wet chemical synthesis method by ultrasound-assisted precipitation – WCS-USA;
- the wet chemical synthesis method, using the sequential addition of reactants technique – SeqAdd;
- the wet chemical synthesis method, using the simultaneous addition of reactants technique – SimAdd;
- the microwave-assisted solvothermal decomposition method of single-source molecular precursors – STD-MW.

The studies presented in this thesis follows to:

- Develop new methods for synthesis of zinc sulphide nanocrystalline powders with luminescent properties;
- Establish the preparative factors that influence the properties of zinc sulphide nanoparticles.

PART TWO.

THE ORIGINAL RESEARCHES ON THE SYNTHESIS AND CHARACTERISATION OF ZINC SULPHIDE BASED SEMICONDUCTOR MATERIALS WITH SPECIAL PROPERTIES

2. Experimental details regarding synthesis and characterization of zinc sulphide with luminescent properties

The experimental procedures used in this study, to obtain nanocrystalline powders of doped or undoped zinc sulphide and for synthesis of single molecular precursors are:

- the wet chemical synthesis method by ultrasound-assisted precipitation – WCS-USA;
- the wet chemical synthesis method, using the sequential addition of reactants technique – SeqAdd;
- the wet chemical synthesis method, using the simultaneous addition of reactants technique – SimAdd;
- the microwave-assisted solvothermal decomposition method of single-source molecular precursors – STD-MW.

To determine the physico-chemical, morpho-structural and luminescent properties of zinc sulphide powders a wide range of measurements can be used. The investigation methods together with the equipment used to characterize the samples are presented below:

- Photoluminescence spectroscopy based on *emission spectra (PL)*, *excitation spectra (PLE)* and *chromatic coordinates*, measurements were made with a JASCO FP-6500 spectrofluorimeter equipped with photomultiplier PMT R3377 or PMT R928.
- *X-ray diffraction (XRD)* measured with a diffractometer Bruker D8 ADVANCE or DRON 3M type.
- *Optical microscopy (OM), scanning electron microscopy (SEM)* and *transmission electron microscopy (TEM)*, which were made with Olympus BX51 microscope, electron microscope JOEL JSM 5510LV, respectively, JEOL JEM 1010.
- *Specific surface area and porosity measurements* based on Brunauer, Emmett, Teller (BET) method, using an analyzer "Tri Star II 3020" - Micrometrics.
- *Inductively coupled plasma optical emission spectroscopy (ICP-OES)*, which was carried out with a spectrometer PERKIN ELMER OPTIMA 2100 DV.
- Fourier transform infrared spectroscopy (FT-IR), performed with a Thermo Scientific FT-IR NICOLETTM^{TM} 6700 or Jasco 610 spectrometer.
- Thermal analysis and gas evolved analysis, based on *thermogravimetric analysis* (TG), *differential thermogravimetric analysis* (DTG), *differential thermal analysis* (DTA) and *gas evolved*

analysis (EGA) measurements were performed in an inert nitrogen atmosphere using thermogravimeter METTLER-TOLEDO TGA/SDTA851 and coupling TGA module of spectrometer Thermo Scientific FT-IR NICOLETTM^{TM} 6700 at thermogravimetric METTLER-TOLEDO TGA/SDTA851.

3. Studies on the synthesis manganese doped and undoped zinc sulphide powders by wet-chemical synthesis methods

The most popular method for the synthesis of zinc sulphide with luminescent properties is wet chemical synthesis (WCS) which has the advantage of allowing the use of cheap raw materials and has great potential for large-scale production [160]. Typically, zinc sulphide nanocrystalline powders are obtained by WCS method using the sequential addition of reactants technique [220]. The microwave and ultrasound assisted WCS are another variants methods reported in literature for the synthesis of ZnS [209, 264].

The studies performed for the preparation of microparticles of luminophores with oxide compositions have shown that powders with well controlled optical and morphological properties can be obtained by WCS method, using the simultaneous addition of reagents, abbreviated WCS-SimAdd [49]. A tempt, to use the WCS-SimAdd method, have been mach for the first time in order to obtaining metal chalcogenides under-micron sized particles.

3.1. Preparation and characterization of doped and undoped zinc sulphide nanocrystalline powders, using wet-chemical synthesis by ultrasonic-assisted precipitation

3.1.1. The aim of the investigation

The aim of the study was to obtain and characterize luminescent nanocrystalline powders of zinc sulphide and zinc sulphide doped with manganese by wet-chemical synthesis with ultrasound-assisted precipitation method (WCS-US). The investigations have pursued to highlight the influence of the concentration and ratio of reactants, pH of the reaction medium and manganese dopant concentration on morpho-structural and photoluminescent properties of ZnS powder and ZnS: Mn^{2+} prepared by WCS-US. The research results were published [98].

3.1.2. Synthesis of the zinc sulphide powders by WCS-US method

In a typical procedure for zinc sulphide [98] synthesis consist on mixing of zinc acetate – $Zn(AcO)_2$ and thioacetamide – TAA solution (0.1 M or 0.5 M) in a volumetric ratio corresponding to desired molar ratios. The pH of medium was adjusted with a solution of hydrochloric acid 6 M. The mixtures were covered and sonicated for 3 hours at 70 °C, cooled to 10 °C and allowed to stand for 24 hours. The resulting white powder was recovered by centrifugation, washed with deionised water and isopropanol and then dried for 2 hours in vacuum at 80 °C.

To synthesis of manganese doped zinc sulphide, was done by the same procedure described above, excepting that the metal acetate solution is a mixture of zinc acetate and manganese acetate in a molar ratio of 19:1, 18:2, 17:3 and 16:4.

3.1.3. The physico-chemical characterisation of zinc sulphide powders obtained by WCS-US method

Investigation aims to determine the purity phase, incorporation degree of manganese, photoluminescence and morphology of particles prepared by WCS-US. Thermogravimetric analysis, infrared spectroscopy, inductively coupled plasma optical emission spectrometry, photoluminescence spectroscopy and scanning electron microscopy have been used for some characterizations.

3.1.3.1. General physico-chemical properties of zinc sulphide powders obtained by WCS-US method

Thermal behaviour of zinc sulphide samples was evaluated by thermal analysis in the range 25-1100 °C in nitrogen flow (atmosphere). In figure 3.4 are represented the TG curves, of some zinc sulphide samples. The values of final weight loss and the temperature ranges together with sublimation temperatures for TG curves are listed in table 3.2.

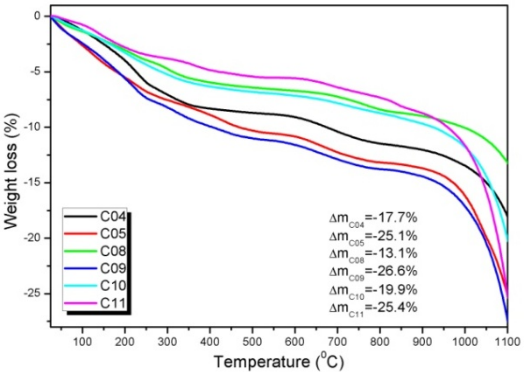


Figure 3.4. TG curves recorded in nitrogen, for some ZnS samples obtained under different conditions of synthesis.

From table 3.2 it is observed that the samples obtained at pH = 2 have, in the temperature range 850-1100 °C, a lower weight loss than those obtained at higher value of pH. This indicates that the samples obtained at pH = 3 are composed by smaller particles. The largest weight loss by sublimation it has the sample obtained from concentrated solution with a 1/3 ratio of zinc acetate/thioacetamide, at pH = 3.

Differences between TG curves of zinc sulphide samples may be associated by different degrees of powders contamination, in direct correlation with particle size and surface area, and thus with different degree of powder dispersion.

Table 3.2. Thermogravimetric analysis data for ZnS powders obtained under different conditions of precipitation

Code	Synthesis conditions			TG weight loss (%)						Sublim. point (°C)
	Sol. conc. of reactants	Reactants ratio	pH	Temperature range (°C)					Total	
				20-185	185-250	250-555	550-850	850-1100		
C04	Conc.	1/1,5	2	3,5	2,5	2,8	2,9	6,0	17,7	1025
C05	Conc.	1/1,5	3	5,1	1,7	3,8	2,8	11,7	25,1	1027
C08	Conc.	1/3	2	2,8	1,1	2,7	2,1	4,4	13,1	1042
C09	Conc.	1/3	3	5,0	2,3	3,9	2,8	12,6	26,6	1031
C10	Diluted	1/3	2	3,0	1,3	2,7	2,2	10,7	19,9	1028
C11	Diluted	1/3	3	2,5	0,9	2,1	2,6	17,3	25,4	1042

The concentration of manganese was measured from manganese doped zinc sulphide samples. According to data obtained by ICP-OES analysis, the ZnS:Mn^{2+} powders prepared from zinc acetate/manganese and thioacetamide, by WCS-US method, contain a very small amount of manganese, about 0.05 mol%.

3.1.3.2. Photoluminescent properties of zinc sulphide powders obtained by WCS-US method

Under UV excitation, all undoped ZnS samples shows a green luminescence, centered at about 540 nm. Emission intensities depending on the conditions of synthesis. Different brightness is evidenced by photoluminescence emission PL spectra recorded at excitation with UV radiation with a wavelength of 354 nm.

Some of the PL spectra of undoped ZnS samples are shown in figure 3.6.

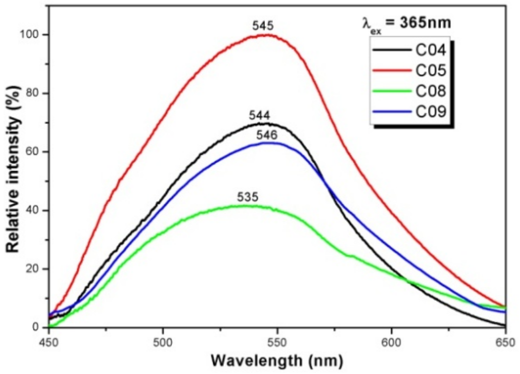


Figure 3.6. PL spectra of ZnS powders obtained in several different synthesis conditions.

In PL spectra is observed that the samples obtained at a molar ratio acetate/thioacetamide 1.0/1.5 have a better photoluminescence than those obtained at a molar ratio of 1.0/3.0. A higher pH favors photoluminescence.

3.1.3.3. Morphological properties of zinc sulphide powders obtained by WCS-US method

SEM images of powders obtained in different experimental conditions, by WCS-US method, are shown in figure 3.8, at a magnification of 15,000 times. For the images shown in medallions, the magnification was increased 3000 times and the scale is 5 mm.

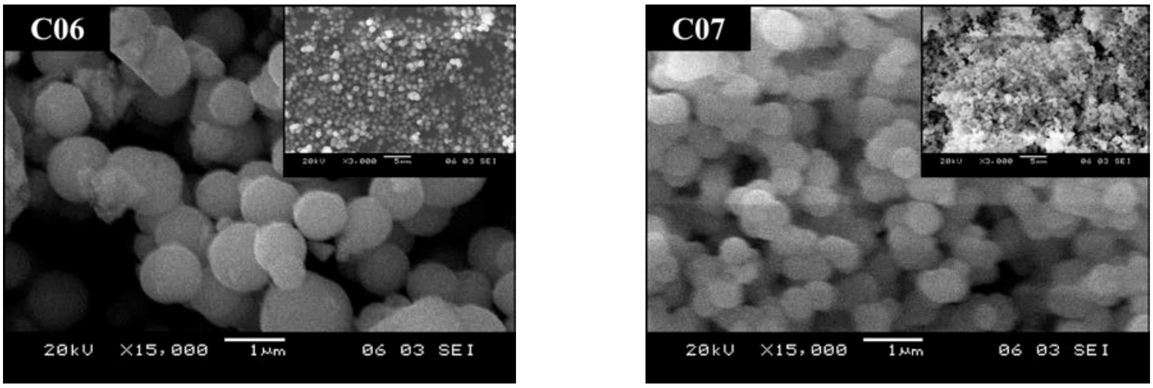


Figure 3.8. The SEM images of ZnS samples obtained in different experimental conditions.

All samples consist of spherical particles composed from small primary particles of nanometric dimensions. The powders with smaller spherical particles are obtained using more concentrated solutions with a molar ratio of 1 to 1.5 and a pH of 3. The sample with the most dispersed particles are obtained using dilute solutions with a molar ratio of 1.0/3.0 and a pH of 3.

3.2. Preparation and characterisation of manganese doped zinc sulphide nanocrystalline powders using wet-chemical synthesis, sequential addition of reactants

3.2.1. The aim of the investigation

The study consists in determining the physico-chemical, morphological, structural and luminescent aspects of manganese doped zinc sulphide nanocrystalline powders prepared by wet-chemical synthesis by precipitation with sequential addition of reagents - WCS-SeqAdd at low temperature. To control the morphology and particle size, two organic additives, namely methacrylic acid – MAA as passivator, and sodium dodecyl sulphate – SDS as surfactant were used.

We studied the influence of both organic additives and manganese concentration on the morpho-structural and photoluminescent properties of ZnS: Mn^{2+} powders. Some results have been published [72, 33].

3.2.2. Synthesis of the manganese doped zinc sulphide powders by WCS-SeqAdd method

The zinc sulphide powders were prepared using WCS-SeqAdd. Precipitation of ZnS and ZnS:Mn^{2+} powders were made at low temperature (5 °C) in an aqueous medium, using on the aqueous solution of zinc acetate-manganese and sodium sulphide 1 M. For this purpose a solution of zinc acetate-manganese was added to deionised water containing organic additive (MAA or SDS), over which has added an aqueous solution of sodium sulphide and it was stirred vigorously for 30 min. Powders of $ZnS:Mn^{2+}$ results were carefully washed with deionised water and isopropanol, centrifuged, and finally dried at 80 °C in vacuum.

3.2.3. The properties of manganese doped zinc sulphide powders

It was investigated the influence of organic additives and manganese concentrations on the physico-chemical, morpho- structural and luminescent characteristics of the ZnS and $ZnS:Mn^{2+}$ powders obtained by wet-chemical synthesis method with sequential addition of precursors in aqueous medium and low temperature. ICP-OES, thermogravimetry, infrared spectroscopy, photoluminescence, scanning and transmission electron microscopy and X-ray diffraction investigations were used.

3.2.3.1. *General physico-chemical properties of manganese doped zinc sulphide powders obtained by WCS-SeqAdd method*

Table 3.4 presents Mn/(Mn+Zn) ratios used in the synthesis and ratios determined by ICP-OES investigation in powers along with the co-precipitation level and main thermogravimetric data of samples obtained under different conditions.

Thermal behaviour of $ZnS:Mn^{2+}$ powders is dependent on the conditions of precipitation (table 3.4, figure 3.10). The three endothermic steps can be associated with:

a) loss of physical adsorbed water, in the temperature range up to approximately 200 °C;
b) remove organic ionic species adsorbed from precipitation medium, in the temperature range between 200 °C and 900 °C;
c) volatilization of zinc sulphide under the cumulative effect of temperature and nitrogen flow at temperatures above 900 °C.

Table 3.4. Manganese concentration (Mn x 100/(Mn+Zn)) and thermogravimetric analysis data for $ZnS:Mn^{2+}$ powders obtained using WCS-SeqAdd method.

Code	Organic additive	Mn conc. (mol%)		Mn co-precipitation level	Weight loss TG (%)				Sublimation point (°C)
		theor.	actual		Temperature range (°C)			Total	
					20-200	200-900	900-1100		
C17	MAA	0,0	0,00	0,00 %	7,4	13,0	3,8	24,2	1042
C19	MAA	5,6	0,07	1,25 %	10,6	13,0	3,6	27,2	1011
C73	MAA	11,0	0,18	1,64 %	6,4	8,5	4,0	18,9	1034
C21	MAA	16,4	0,22	1,34 %	7,5	12,5	3,8	23,8	1021
C77	MAA	25,0	0,45	1,80 %	7,5	9,7	4,0	21,2	1043
C21	MAA	16,4	0,22	1,34%	6,1	16,1	2,0	24,2	1035*
C74	-	16,4	0,67	4,09%	5,4	9,6	2,4	17,4	1040*
C75	SDS	16,4	0,71	4,33%	6,1	19,3	2,9	28,3	1037*

*TG performed with double amount of sample, in relatively large crucibles

The volatilization/sublimation level, expressed by mass loss in the range of 900-1100 °C, depend on the dispersion and particle size of ZnS:Mn^{2+} powders. Sublimation temperature was estimated by the "onset" (starting temperature of weight loss step)after 900 °C, from the TG curves.

Figure 3.11 shows the DTG curves corresponding to the TG curves from figure 3.10.

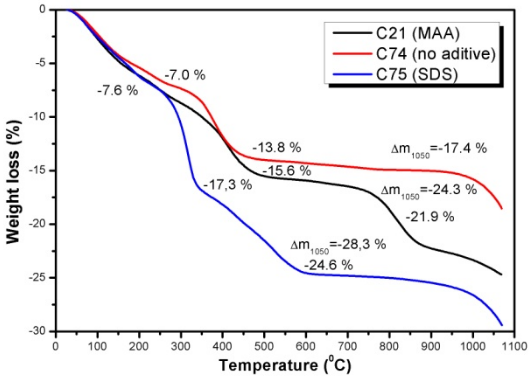


Figure 3.10. TG curves of samples prepared with or without organic additives.

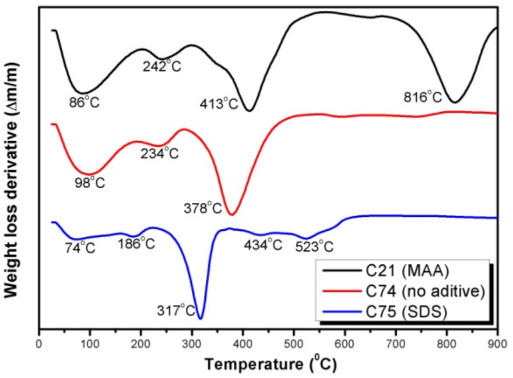


Figure 3.11. DTG curves of samples prepared in the presence of different organic additives.

The influence of size regulation additive on thermogravimetric - TG and differential thermogravimetric - DTG curves is illustrated in figure 3.10 and figure 3.11. It can be seen that in the temperature range 200-900 °C, correlated with the removal of organic compounds, weight loss occurs in:

a) two steps (C74), correlated with decomposition of adsorbed acetate ions;
b) three steps (C21), correlated with decomposition of adsorbed acetate and methacrylate ions;
c) four steps (C75), required for thermal dissociation of acetate and dodecyl-sulphate ions, including SO_2 emissions.

Nature of organic impurities adsorbed on the surface of ZnS:Mn^{2+} particles is evidenced by infrared spectroscopy (figure 3.12). For comparison it is illustrated in the inset the vibrational spectrum of a calcined ZnS:Mn^{2+} sample (C75).

In addition to weak broadband at about 480 cm^{-1} attributed to Zn-S bond, the FT-IR spectra show the characteristic vibration bands of water, surfactant and acetate ions adsorbed from the precipitation medium. The main absorption bands are shown in table 3.5.

The most important absorption bands for ZnS:Mn^{2+} powders obtained without additive (C74), besides those of zinc sulphide from about 480 cm^{-1}, are vibrations of water and acetate ions. The FT-IR spectra of the samples obtained with MAA (C21) and SDS (C75) also contain vibrations of methacrylate and dodecyl sulphate ions, respectively.

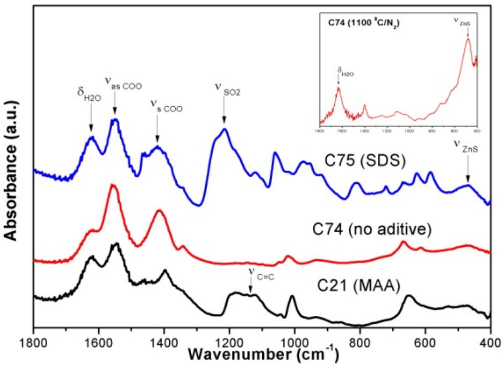


Figure 3.12. FT-IR spectra of ZnS:Mn^{2+} samples prepared with or without organic additives (normalized).

Table 3.5. The FT-IR absorption spectra attribution signals of ZnS:Mn^{2+} samples obtained using WCS-SeqAdd method [257].

Sample	Vibration frequency [cm^{-1}]	Attribution	
		Vibrations tip	Origin
C21, C74, C75	1650	$\delta_{O\text{-}H}$ bending vibration	water
C21, C74, C75	1600	$\nu_{asC=O}$ asymmetric stretching vibration	acetate
C21, C74, C75	1300	$\nu_{sC=O}$ symmetric stretching vibration	acetate
C75	1300-1100	$\nu_{S=O}$ stretching vibration	dodecyl-sulfate
C21	1200-1000	$\nu_{C=C}$ şi $\nu_{=C\text{-}H}$ stretching vibrations	Methacrylate
C21, C74, C75	480	$\nu_{Zn\text{-}S}$ stretching vibration	Zinc sulphide

C21 – with MAA, C74 – without additive, C75 – with SDS

The FT-IR and TG investigations reveal high capacity of ZnS:Mn^{2+} powders to adsorb anionic species from precipitation medium, thus illustrating a large particles surface correlated with their small size.

3.2.3.2. Photoluminescent properties of manganese doped zinc sulphide powders obtained by WCS-SeqAdd method

All samples were excited with ultraviolet radiation with wavelength of 335 nm to record the PL spectra shown in figure 3.13. The PLE spectra is shown in figure 3.14, monitored at 602 nm.

When excited with ultraviolet radiation, all manganese doped zinc sulphide powders exhibits orange photoluminescence with variable brightness, depending on the synthesis conditions, while undoped zinc sulphide powder has a blue photoluminescence.

Photoluminescence emission spectra show that the inactivated sample (C17) have only a weak blue emission band (at approximately 435 nm), associated with defects attributed to the ZnS host lattice. Manganese doped zinc sulphide samples, posses a second emission band centred at approximately 600 nm.

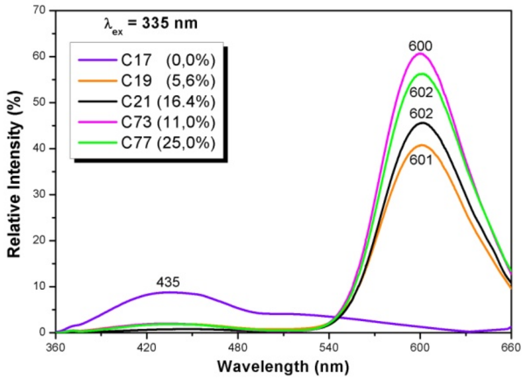


Figure 3.13. PL spectra of ZnS:Mn^{2+} powders prepared with MAA and various amounts of manganese.

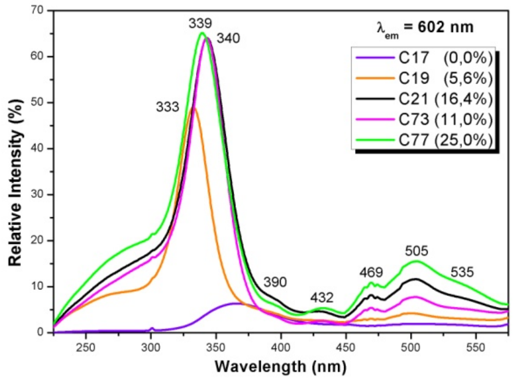


Figure 3.17. PLE spectra of ZnS:Mn^{2+} powders prepared with MAA and various amounts of manganese.

Figure 3.14 shows photoluminescence excitation spectra (PLE) of manganese ions emission from samples with different doping levels. Are highlighted two possible excitation ways of doped semiconductors, an indirect one, that includes host lattice, and a direct one, which involve the doping ions. The maximum excitation signal of Mn^{2+} ions is centred at about 340 nm and related to the ZnS host lattice UV absorption, while relatively small spectral signals in the domain 375-575 nm is due to the directly excitation transitions of Mn^{2+} ions. In this domain, PLE intensity increases with the concentration of Mn^{2+}. According to literature [123], this absorption signals observed in Mn^{2+} ions bands at about 390, 430, 465, 500 and 535 nm are attributed to transitions between the ground state $^6A_1(^6S)$ and excited $^4E(^4D)$, $^4T_2(^4D)$, $^4A_1(^4G)$, $^4E(^4G)$, $^4T_2(^4G)$ and, respectively, $^4T_1(^4G)$ of 3d^5 configuration of Mn^{2+}, levels shown in figure 3.15.

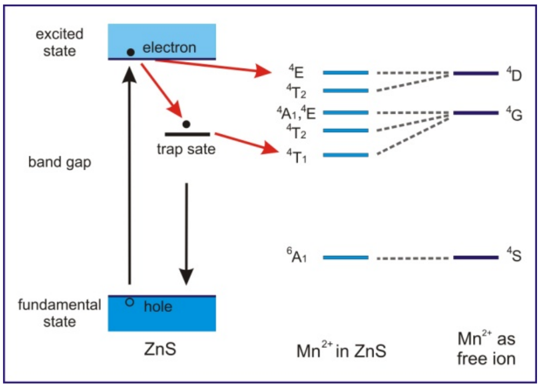


Figure 3.15. Diagram of energy levels of undoped and manganese doped zinc sulphide and from manganese free ions [295].

3.2.3.2. *Morpho-structural properties of manganese doped zinc sulphide powders obtained by WCS-SeqAdd method*

The SEM and TEM images of sample C75, obtained in the presence of SDS are shown in figure 3.19 and figure 3.20. It is observed that powders are composed of large conglomerates, with size between 5-50 μm, consisting of very small particles with diameters less than 5 nm, which have a strong tendency to agglomeration, due to their large surface.

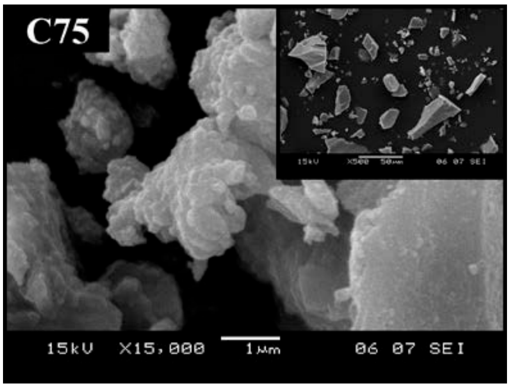


Figure 3.19. The SEM image of the sample prepared with SDS. The bar from inserted picture is 50 mm.

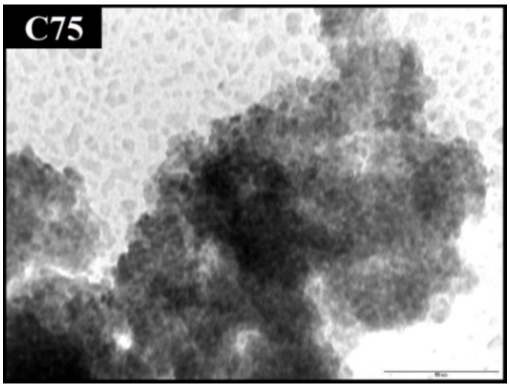


Figure 3.20. The TEM image of the sample prepared with SDS, the bar is 50 nm.

The XRD patterns of ZnS and ZnS:Mn^{2+} powders indicate the formation of a single phase of nanocrystalline ZnS, with cubic structure, regardless of the conditions of synthesis. Figure 3.21 illustrates three specific diffraction bands of cubic zinc-blend structure (PDF 65-0309) from planes (111), (220) and (311).

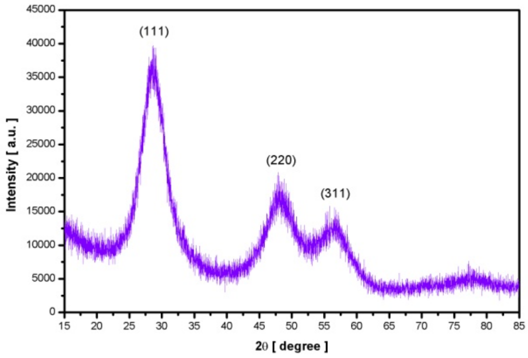


Figure 3.21. XRD pattern of un-doped ZnS sample (C17).

The micro-structural parameters i.e. the effective crystallite mean size (D_{eff}) and the root mean square (r.m.s.) of micro-stress $<\varepsilon^2>^{1/2}$ illustrates that, in our experimental conditions, all powders are composed of ZnS nanoparticles ($D_{eff} \approx 3$ nm), with an average density of packing defects of about 0.01. Effective diameter of the crystallites appears to be independent of the Mn concentration and the presence of organic additive.

3.3. Preparation and characterisation of manganese doped zinc sulphide nanocrystalline powders using wet-chemical synthesis by simultaneous addition of reactants

3.3.1. The aim of the investigation

The aim of the study was to obtain and characterize the luminescent properties of manganese doped zinc sulphide nanocrystalline powders using wet-chemical synthesis by precipitation with simultaneous addition of reagents – WCS-SimAdd. For this purpose, the influence of various factors on general physico-chemical, morpho-structural and photoluminescent properties of $ZnS:Mn^{2+}$ powders was studied, i.e. the nature of the reaction, the manganese concentration, nature and concentration of organic additive.

To control the particle size, the precipitation was carried out in water or water-methanol mixture, a precipitation medium with different dielectric constant (at 20 °C ε_{H2O} = 80.1, $\varepsilon_{CH3\text{-}OH}$ = 33), in the presence of organic additives with different function in process i.e. a capping/passivation agent (methacrylic acid – MAA), an anionic surfactant (sodium dodecyl-sulfate – SDS) and a cationic surfactant (cetyl-trimethyl-ammonium bromide – CTAB). Some results have been published [34, 110, 112, 151].

3.3.2. Synthesis the manganese doped zinc sulphide powders by WCS-SimAdd method

Preparation of zinc sulphide powders doped with manganese was conducted by WCS-SimAdd method at room temperature in aqueous or methanol from aqueous 1 M sodium sulphide and Zn-Mn acetate. For this purpose, equal volumes of Zn-Mn acetate and Na_2S were added simultaneously, with flow control, under vigorous stirring, over a bottom solution (aqueous or alcoholic, with or without organic additives). The amount of manganese was varied between 0 mol% and 16.0 mol% relative to Zn+Mn. Powders obtained were washed with methanol, centrifuged and dried at 80 °C in vacuum.

3.3.3. The properties of manganese doped zinc sulphide powders

It have been investigated the influence of manganese concentration, the concentration of organic additive, additive and bottom solution type on the physico-chemical, luminescent and morpho-structural properties of $ZnS:Mn^{2+}$ powders.

3.3.3.1. *General physico-chemical properties of manganese doped zinc sulphide powders obtained by WCS-SimAdd method*

The study revealed that the manganese doping is dependent on reaction medium, the type and amount of organic additive added to control particle size and also on the initial concentration of manganese. It was found that, the sample with the highest theoretical amount of manganese (C32) has the highest level of co-precipitation (~ 5.9%).

The sample prepared in methanol-water, MAA as passive agent (~ 9.3%) has the highest level of co-precipitation, while the lowest is for the sample prepared in methanol-water with CTAB as cationic surfactant (~ 0.6%). The two additives seem to act differently in co-precipitation of zinc and manganese.

The amount of organic additive changes also the ratio of co-precipitation ZnS-MnS. For example, a small amount of MAA has a favourable effect on the level of co-precipitation, while a large amount of MAA, it decreases drastically.

The samples prepared in water, solvent with relatively high dielectric constant ($\varepsilon = 80$) had a level of co-precipitation better than the corresponding samples prepared using methanol solution, a solvent with relatively low dielectric constant ($\varepsilon = 33$). An exception is the samples prepared with MAA as organic additive. The highest level of co-precipitates for samples prepared in water is for the sample prepared in the presence of MAA (~ 6.0%). It should be noted that when methanol is used as a bottom solution, the precipitation actually occurs in a mixture of methanol (bottom solution) and water (derived from organic precipitant solutions).

3.3.3.2. *Photoluminescent properties of manganese doped zinc sulphide powders obtained by WCS-SimAdd method*

Under UV excitation, all samples of ZnS:Mn^{2+} shows an orange luminescence, specific for manganese ions, or blue luminescence, specific self-activation (SA). Luminescence intensity is variable and depends on the conditions of synthesis. Photoluminescence PL emission spectra of the samples prepared without organic additives in methanol-water medium are represented in figure 3.28, while figure 3.30 presents the variation photoluminescent intensity emission with the concentration of manganese.

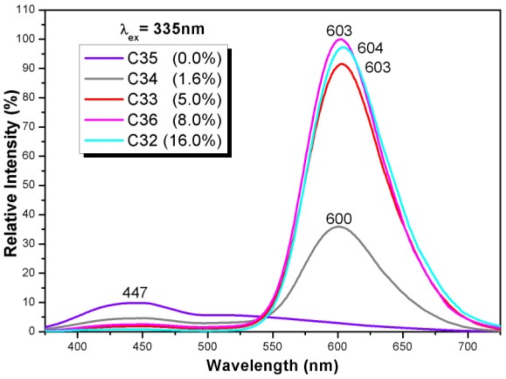


Figure 3.28. The PL spectra of ZnS:Mn^{2+} powders prepared with varying amounts of Mn^{2+} in methanol-water medium.

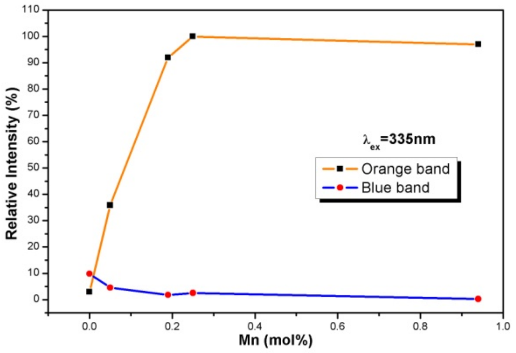


Figure 3.30. Relative intensity of the orange (λ_{em} = 603 nm) and blue (λ_{em} = 447 nm) emission bands depending on the actual concentration of manganese in samples prepared without organic additives in methanol-water medium.

Sample C35 shows a weak emission band centred at around 450 nm, due to the Zn and S vacations and interstitial atoms that an found in the zinc sulphide host lattice. PL spectra of samples doped with manganese (C32-C36) present an additional strong emission band, centred at about 602 nm which tends to move towards higher wavelengths, while the concentration of manganese ions increases. This characteristic orange emission is associated with $^4T_1$–$^6A_1$ electronic transitions within the manganese ion [28].

The PL spectra of ZnS:Mn^{2+} powder, prepared in methanol medium, without additives or with different concentrations of organic additive - MAA (C36, C37 and C59) are shown in figure 3.31. The addition of MAA decreases the emission intensity with about 20%, at concentration of 7.27 g/l, and 70%, when the concentration of MAA is 10 times higher. Gradual reduction of intensity with increasing MAA concentration suggests that the additive has a quenching effect on luminescence.

The influence of MAA is also highlighted in PLE spectra which is presented in figure 3.32. The addition of MAA tends to move toward blue and reduce by about 30% and 75% the peak in the UV (334-339 nm) associated with zinc sulphide host lattice of samples obtained in medium with small (C59) and large (C37) quantities of MAA, compared with a sample obtained without additive.

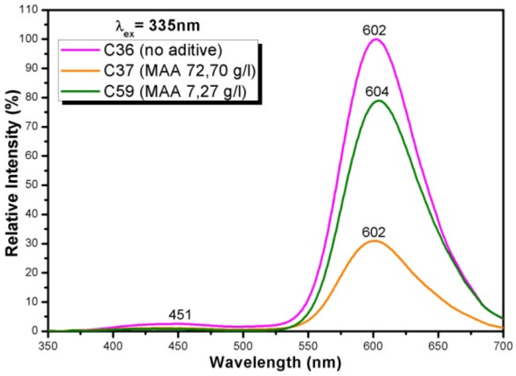


Figure 3.31. The PL spectra of ZnS:Mn^{2+} powders prepared in methanol-water, with varying amounts of organic additive (MAA).

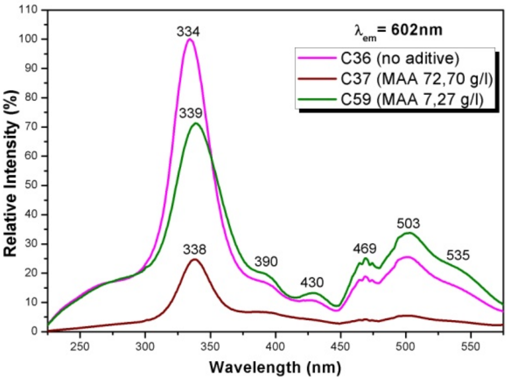


Figure 3.32. The PLE spectra of ZnS:Mn^{2+} powders prepared with varying amounts of organic additive (MAA).

On the other hand, the peaks situated in the range 390-550 nm corresponding d-d transitions are enhanced by about 30%, for the sample with small amounts of MAA, and reduced by about 80%, for the sample with large amount of MAA. This is a normal behaviour if it is considered that these multiple peaks are attributed to 3d^5 intra-configuration transitions of Mn^{2+} ion and that the sample prepared with a smaller amount of MAA contains, according to the analysis ICP-OES, a higher manganese amount.

3.3.3.3. *Morpho-structural properties of manganese doped zinc sulphide powders obtained by WCS-SimAdd method*

In SEM and TEM images of manganese doped zinc sulphide powder prepared by WCS-SimAdd method with SDS in methanolic medium are presented in figures 3.37 and 3.38, respectively.

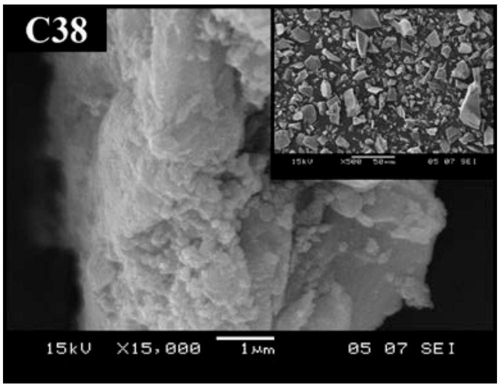


Figure 3.37. The SEM image of the sample prepared in the presence of SDS.
The bar from inserted picture is 10 μm.

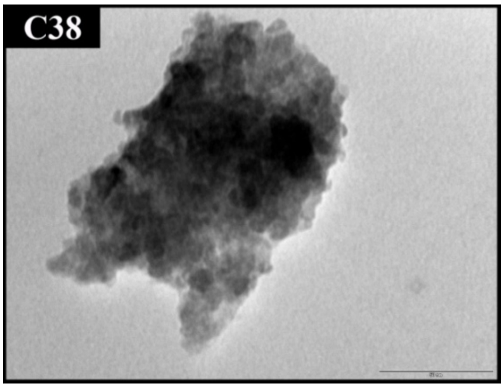


Figure 3.38. The TEM image of the sample prepared in the presence of SDS,
the bar is 50 nm.

SEM images show that all samples are composed of sub-micron particles tightly packed in conglomerates with sizes between 5-50 μm. TEM images put in evidence that the ZnS:Mn^{2+} powders consist from very small particles with diameters below 10 nm with a strong tendency to agglomeration, due to the large specific surface area.

By X-ray diffraction was observed that whatever the synthesis conditions are, by WCS-SimAdd method, it is obtained a single phase nanocrystalline powder with cubic structure of ZnS blend.

Unit cell parameters are in agreement with data from the literature (PDF 65-0309: cub-ZnS; a=b=c 5.40 Å; V = 157.46 $Å^3$). All ZnS powders prepared are composed of very small nanocrystals (3.0-3.1 nm), with a root mean square (r.m.s.) of micro-stress between 0.8×10^{-2} - 1×10^{-2}. Micro-structural parameters are dependent on both the concentration of manganese, and the amount and nature of organic additive used.

4. Studies on synthesis of manganese doped zinc sulphide powders by decomposition of single-source molecular precursors

Lately, new methods for the synthesis of metal sulphides were developed. This methods starts from single-source molecular precursors metal-organic compounds which contain all compound secured for the final product. The method has a number of advantages that justify its use in synthesis of semiconductor materials based on metal chalcogenides.

Preparation of single-source molecular precursors was done by precipitation, using the simultaneous and sequential addition of reagents technique. The synthesis of doped or un-doped zinc sulphide powders was achieved by thermal decomposition (pyrolysis) in nitrogen atmosphere or by microwave-assisted solvothermal decomposition in ethylene glycol medium.

4.1. Preparation and characterisation of single-source molecular precursors of sulphur and zinc/manganese

4.1.1. The aim of the investigation

The aim of the study was to obtain and characterize the single-source molecular precursor powders for the synthesis of zinc sulphide doped or not with manganese. The influence of the synthesis method on the properties of the single-source molecular precursors – SSMP and on the zinc sulphide was also studied. Two types of precursors were obtained i.e. zinc ethyl-xanthate and zinc diethyl-dithiocarbamate. The precursors prepared using wet-chemical synthesis method by sequential - WCS-SeqAdd and simultaneous - WCS-SimAdd addition of reagents.

Characterization of single-source molecular precursor was done by thermal analysis, FT-IR spectroscopy and scanning electron microscopy and by determining the properties of corresponding zinc sulphide powders.

Parts of research results were published [177, 335].

4.1.2. Obtaining the single-source molecular precursors

Zinc ethyl-xanthate (ZEX) and zinc diethyl-dithiocarbamate (ZDDTC) powders were prepared by the reaction between zinc acetate and potassium ethyl-xanthate or sodium diethyl-dithiocarbamate, at molar ratio of 1:2 and at room temperature in an aqueous medium, using WCS-SeqAdd and WCS-SimAdd methods. All samples were washed with double distilled water, filtered and dried at 100 °C, under vacuum.

A series of SSMP powders based on zinc and manganese diethyl-dithiocarbamate - ZMDDTC and zinc and manganese ethyl-xanthates - ZMEX. For this, a part of zinc acetate was replaced with manganese acetate were also prepared by WCS-SimAdd method.

Some of SSMP samples were calcined at 900 °C, to obtain ZnS and ZnS:Mn^{2+} powders, to evaluated the morpho-structural and luminescent properties.

4.1.3. The properties of single-source molecular precursors

The characterization of SSMP samples was carried out by thermogravimetric analysis (TG), differential thermogravimetric (DTG), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and FT-IR spectroscopy coupled with thermogravimetric analysis (FT-IR–TG). The zinc sulphide powders obtained from pyrolysis of SSMP samples were characterized by infrared spectroscopy (FT-IR), photoluminescence emission spectroscopy (PL) and scanning electron microscopy (SEM).

4.1.3.1. *The general physico-chemical properties of precursors powders*

The FT-IR spectra of a zinc diethyl dithiocarbamate powder (pC89) and by the raw materials (zinc acetate dihydrate - $Zn(CH_3COO)_2 \times 2H_2O$ and sodium diethyl-dithiocarbamate trihydrate - $(C_2H_5)_2NCS_2Na$ x $3H_2O$) are shown in figure 4.3.

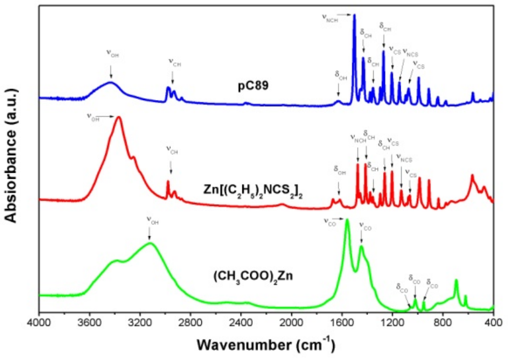


Figure 4.3. The FT-IR spectra of a $Zn[(C_2H_5)_2NCS_2]_2$ sample and the corresponding raw materials.

The vibrational bands of ZDDTC precursor (sample pC89) are systematized in table 4.2 [336]. For ZDDTC precursor (sample pC93) prepared by WCS-SeqAdd method, the situation is similar.

Table 4.2. Attribution of the signals from FT-IR spectrum of ZDDTC sample.

Vibration frequency [cm^{-1}]	Attribution	
	Vibration tip	Origin
3600-3000	ν_{O-H} stretching vibration	water
2990-2850	ν_{C-H} stretching vibration	diethyl-dithiocarbamate
1627	δ_{O-H} vibraţie de forfecare	water
1502	ν_{N-CH} stretching vibration	diethyl-dithiocarbamate
1450-1270	δ_{C-H} bending vibration	diethyl-dithiocarbamate
1210	ν_{C-S} stretching vibration	diethyl-dithiocarbamate
1146	ν_{N-CS} stretching vibration	diethyl-dithiocarbamate
1096-1073	$\nu_{C=S}$ stretching vibration	diethyl-dithiocarbamate

Under thermal treatment up to 700 °C in nitrogen atmosphere, the ZDDTC samples (pC89 - figure 4.7 and pC93 - figure 4.8) shows a mass loss of approximately 93% and decomposition is characterized by two strong endothermic peaks, associated with the change of phase (180-182 °C) and thermal dissociation (310-320 °C). The thermal decomposition of pC89 sample (prepared by WCS-SimAdd) takes place in a single step with a maximum weight loss at 313 °C which is accompanied by a strong endothermic peak at 317 °C. Sample pC93 (prepared by WCS-SeqAdd) decomposes in two step, with a weight loss of 88% in the first step, with a maxim to 306 °C, and

5% in the second step, with maxim to 414 °C. Those two steps of decomposition are endothermic and have maxima at 310 °C and, respectively, 400 °C. This suggests that pC93 sample consists from larger particles than pC89 sample, which prevents the rapid release of gases.

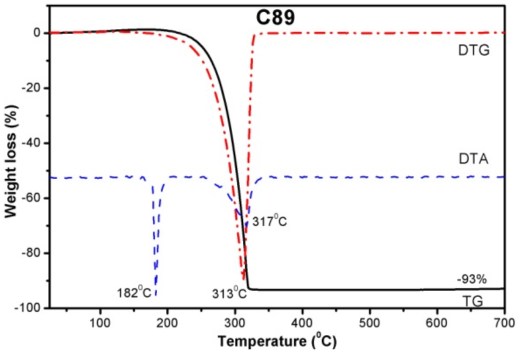


Figure 4.7. The TG, DTG and DTA curves of the sample obtained by WCS-SimAdd ZDDTC.

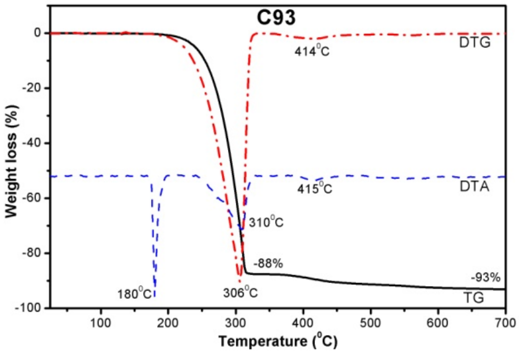


Figure 4.8. The TG, DTG and DTA curves of the sample obtained by WCS-SeqAdd ZDDTC.

The evolved gas analysis (EGA) was used in order to characterize the process of pyrolysis single-source molecular precursors.

In figure 4.14 are presented the results from the thermal decomposition of a ZDDTC sample, pC107.

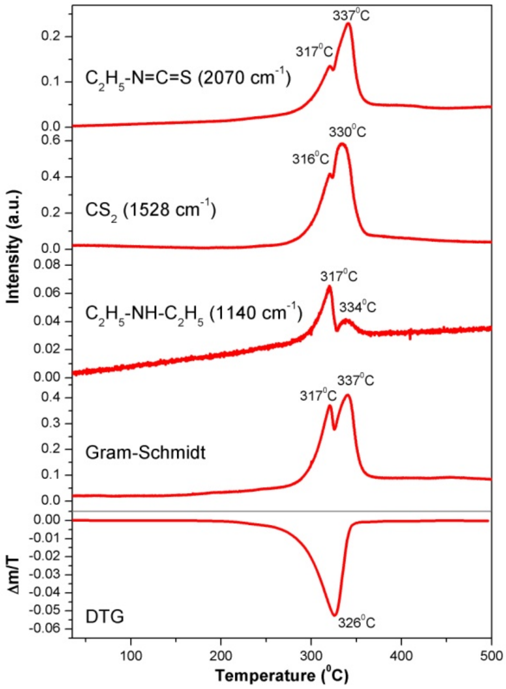


Figure 4.14. The Gram-Schmidt diagram, DTG curve and absorption profiles of groups of substances identified in the gas mixture obtained from decomposition of a ZDDTC sample (pC107).

The DTG curves (with one step of decomposition at 326 °C) are presented together with the Gram-Schmidt diagram (where it is observed that gas flow has two IR absorption maximum) and the IR main absorption profiles (temperature evolution of the absorbance of a specific wavelength). The profiles of ethyl-isothiocyanate at 2070 cm^{-1}, carbon sulphide at 1528 cm^{-1} and diethyl-amine at 1140 cm^{-1} were searched.

Figure 4.15 presents the FT-IR spectra of the gas mixture obtained from decomposition of ZDDTC samples measured in the peaks of the Gram-Schmidt diagram (at temperatures of 317 °C and 337 °C).

The characteristic absorption bands identified in the FT-IR spectra are shown in table 4.5.

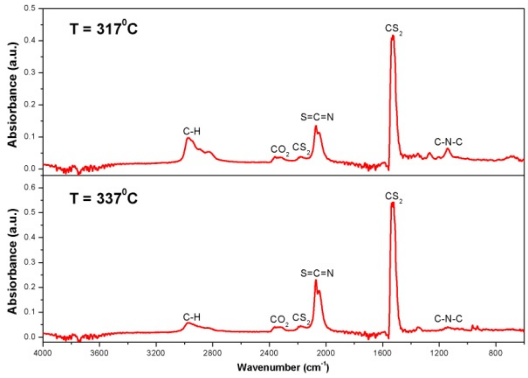


Figure 4.15. The FT-IR spectra at different times (temperature) of the gas resulting from the decomposition of the sample ZDDTC, pC107.

Table 4.5. The attribution of signals from FT-IR absorption spectrum of the gas resulting from the decomposition of the ZDDTC sample, pC107 [336, 339, 340].

Vibration frequency [cm^{-1}]	Attribution	
	Vibration tip	Origin
3200-2770	ν_{C-H} asimetric and simetric stretching vibration	diethyl-amine, ethyl-isothiocyanate
2360-2310	$\nu_{C=O}$ stretching vibration	carbon dioxide
2215-2148	$\nu_{C=S}$ stretching vibration	carbon sulphide
2072	$\nu_{N=CS}$ stretching vibration	ethyl-isothiocyanate
1140	ν_{C-NH-C} stretching vibration	diethyl-amine
1540-1522	$\nu_{C=S}$ stretching vibration	carbon sulphide

In figure 4.16 is presented the 3D image of the temporal variation of infrared radiation absorbance of gases released at thermal decomposition, in nitrogen (flow rate 40 ml/min, 5 °C/min) for ZDDTC sample pC107.

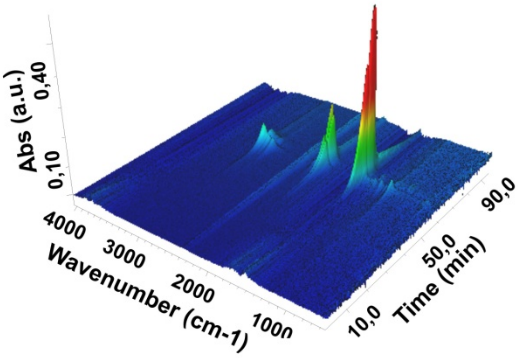


Figure 4.16. The time variation of FT-IR absorbance with time for a ZDDTC sample, pC107 (image 3D).

4.1.3.2. Morpho-structural properties of SSMP and ZnS powders obtained by his pyrolysis

In figure 4.19 are shown the images obtained by scanning electron microscopy (SEM) of fine single-source molecular precursors (left) and ZnS powders obtained by pyrolysis at 900 °C in nitrogen atmosphere (right). The ZDDTC samples pC89 and pC93 were prepared by WCS-SimAdd and, respectively, WCS-SeqAdd methods.

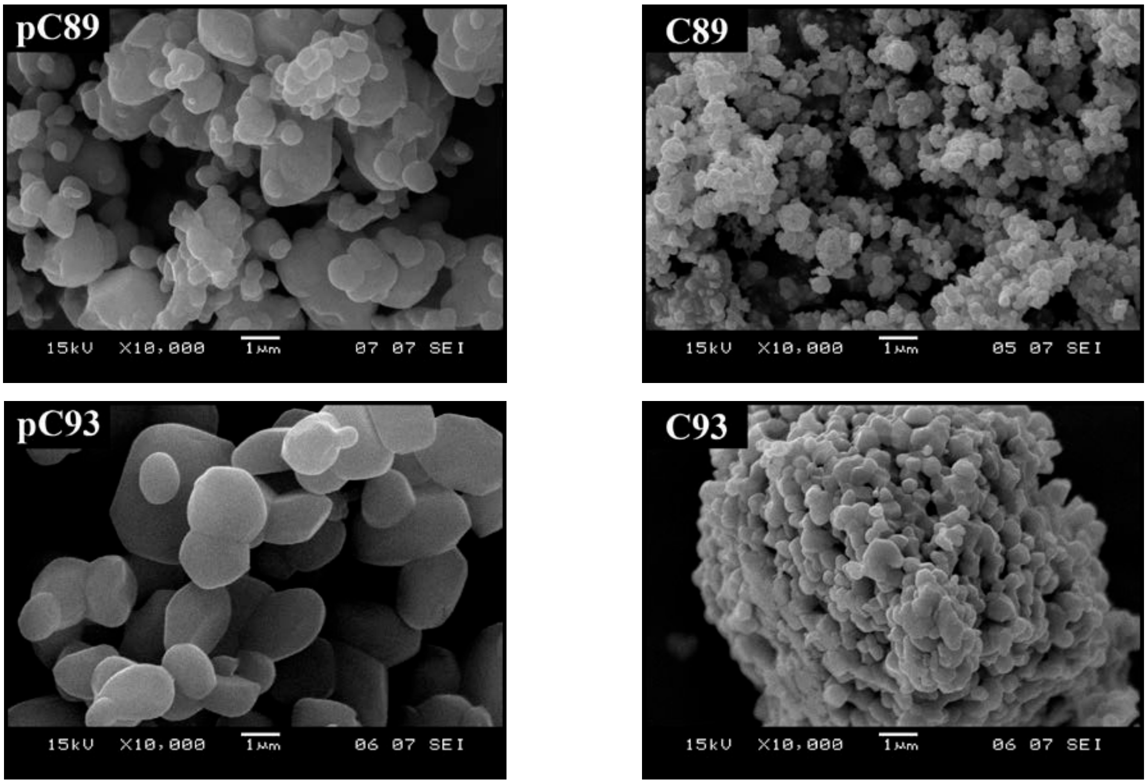


Figure 4.19. SEM images of ZDDTC samples prepared under different conditions (left) and zinc sulphides from their pyrolysis (right).

The particle size depends on the addition of reactants in precipitation step. It is observed that wet-chemical synthesis method with sequential addition - WCS-SeqAdd (sample pC93) leads to larger particles, but with a much narrower particle size distribution.

The zinc sulphide powders obtained from ZDDTC (C89 and C93) are forming conglomerates and the particle dimensions are influenced by the technique used for the preparation of single-source molecular precursors. The ZnS powders obtained from precursors prepared by WCS-SimAdd technique (C89) have the particle size of 0,25 μm, while those obtained by the WCS-SeqAdd technique (C93) have sizes between 0,25 μm and 1,5 μm.

4.1.3.3. Photoluminescent properties of zinc sulphide powders obtained by Pyrolysis of SSMP samples

The luminescent properties of zinc sulphide and manganese doped zinc sulphide obtained from single-source molecular precursor by pyrolysis (900 °C, nitrogen) were measured and compared.

The PL spectra from figure 4.22 shows a broad emission band in the green domain, centred at approximately 505 nm. The band asymmetry and position of the maximum suggests that luminescence is due to the self-activation of zinc sulphide and of its doping with oxygen. The emission bands of zinc sulphide obtained from ZEX exhibit a large shift. Forward green domain that the emission bands of zinc sulphide obtained from ZDDTC. This behaviour suggest a hight oxygen contamination of samples C91 and C94.

In figure 4.24 are shown the PL spectra of the manganese doped zinc sulphide samples, prepared by calcination at 900 °C in an inert atmosphere, of single-source molecular precursors powders based on zinc and manganese diethyl-dithiocarbamate ZMDDTC and compared with ZDDTC precursor without manganese.

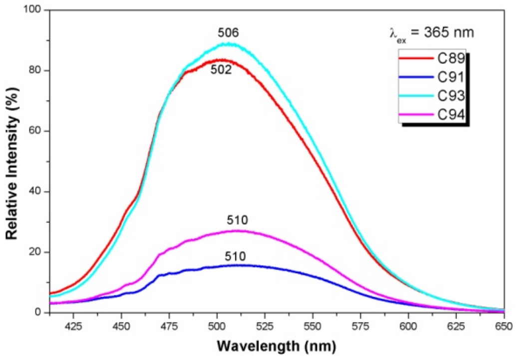


Figure 4.22. The PL spectra of ZnS powders obtained by pyrolysis SSMP.

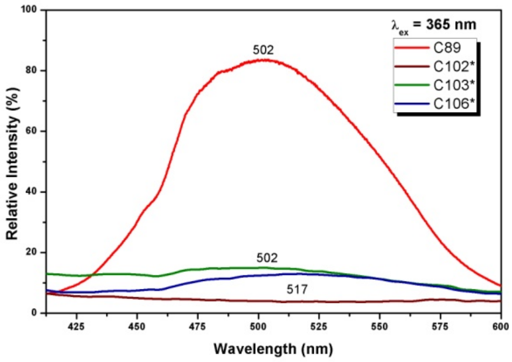


Figure 4.24. The PL spectra of $ZnS:Mn^{2+}$ powders obtained by pyrolysis of ZMDDTC and ZDDTC. * Multiplied ten times.

It is observed that the undoped ZnS powder (C89) obtained from precursor ZDDTC has a relatively strong photoluminescence emission in the green spectral range, with a maximum studied at 502 nm, probably associated with oxygen doping. Samples doped with manganese, has a very small emission in the green domain; in addition the specific manganese emission bands in the orange domain cannot be observed. The very small emission of ZnS:Mn^{2+} powders suggests that the manganese ions act as a quenching species. The decrease of the luminance can be also associated with the self-absorption of emitted light, due to the formation of coloured manganese sulphide on the particle surface. The quenching effect of the emission intensity increases with manganese concentration. It can be sun that above 1.5 mol% Mn the luminescence is completely absent.

The luminescent emission observed for this samples is not-specific, therefore we are say that ZMDDTC or ZMEX precursors does not lead to manganese activated zinc sulphide formation.

It can be concluded that under these experimental conditions, the pyrolysis method of SSMP powders based on diethyl dithiocarbamate is not favourable for the synthesis of manganese doped zinc sulphide powders, with efficient luminescence.

4.2. Preparation and characterisation of zinc sulphide and manganese doped zinc sulphide nanocrystalline powders by solvothermical decomposition microwave-assisted of single-source molecular precursors

4.2.1. The aim of the investigation

The present study aims at obtaining and characterize the zinc sulphide powders and manganese doped zinc sulphide. The synthesis was performed by microwave-assisted solvothermal decomposition - STD-MW of single-source molecular precursors. Are taken into consideration the samples based on zinc diethyl dithiocarbamate (type ZDDTC) and zinc and manganese diethyl-dithiocarbamate (type ZMDDTC) precursors, prepared by wet-chemical synthesis method with simultaneous addition of reagents - WCS-SimAdd.

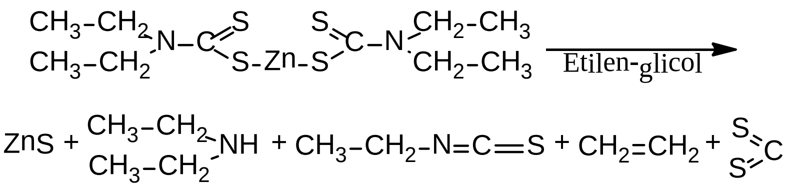
The aim was also to establish the optimal amount of manganese in single-source molecular precursor of sulphide ions and zinc and manganese ions who by solvothermal decomposition microwave-assisted lead to a manganese doped zinc sulphide powder with relatively strong photoluminescence emission. The data obtained in this chapter were partially published [335].

4.2.2. Synthesis of the zinc sulphide powders by STD-MW method

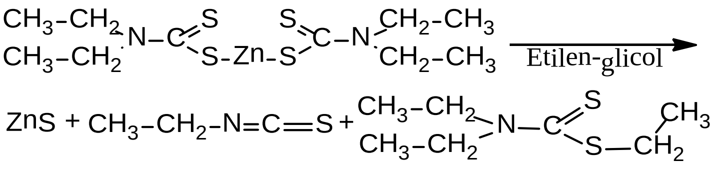
The zinc diethyl-dithiocarbamate and zinc and manganese diethyl-dithiocarbamate powders prepared by method WCS-SimAdd (see chapter 4.1) were dispersed in ethylene-glycol, resulting colloidal solution 0.04 M, heated at 110 °C for 10 minutes under MW irradiation. The yellow-orange suspension was left for 30 minutes to cool, was centrifuged and the white precipitate was washed with absolute methanol and dried at 60 °C for 6 hours.

Based on the gas evolved analysis (chapter 4.1), the solvothermical decomposition reaction have been determined (equation 4.3). the role of ethylene glycol in the reaction was ignored.

According to the literature [344] general equation of solvothermical decomposition of metal diethyl-dithiocarbamate consists of two chemical reactions shown in equations 4.4 and 4.5.



ec. 4.3



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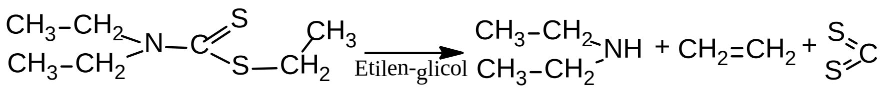

ec. 4.5

4.2.3. The properties of zinc sulphide powders prepared by STD-MW method

Physico-chemical, morpho-structural and luminescent characterisation of zinc sulphide samples undoped and doped with manganese, obtained by microwave-assisted solvothermical decomposition of SSMP type zinc/manganese diethyl-dithiocarbamate was achieved by FT-IR spectroscopy, thermal analysis, photoluminescence spectroscopy (PL), electron microscopy SEM, analysis by ICP optical emission spectroscopy, specific surface area and porosity measurements and X-ray diffraction.

4.2.3.1. General physico-chemical properties of zinc sulphide powders

Concentration of manganese in ZMDDTC precursor samples and ZnS:Mn^{2+} powder was determined by inductively coupled plasma optical emission spectroscopy. The real values of the concentration of manganese in the sample are presented in table 4.7, together with theoretical values.

The concentration of manganese in ZMDDTC powder varies between 42 and 70% of the theoretical value, and also remains approximately the same in ZnS:Mn^{2+} powders. The manganese co-precipitation level varies between 42 and 80%.

Table 4.7. The theoretical and actual molar concentrations of manganese in ZMDDTC and $ZnS:Mn^{2+}$ samples.

Theoretical value (mol%)	SSMP code	Actual value in SSMP (mol%)	ZnS code	Actual value in $ZnS:Mn^{2+}$ (mol%)	Zn-Mn co-precipitare level (% in $ZnS:Mn^{2+}$)	
					ZMDDTC	$ZnS:Mn^{2+}$
0	**pC120**	0	**C120**	0		
0	**pC107**	0	**C111**	0		
0,1	**pC106**	0,07	**C112**	0,08	70	80
0,5	**pC103**	0,21	**C113**	0,21	42	42
1,5	**pC102**	0,73	**C114**	0,84	49	56
15,0	**pC101**	9,96	**C115**	9,24	66	62

4.2.3.2. Photoluminescent properties of zinc sulphide powders

Figure 4.30 presents photoluminescence emission spectra (PL) of ZnS and $ZnS:Mn^{2+}$ samples obtained by solvothermical decomposition of the SSMP samples, under UV excitation 365 nm radiation.

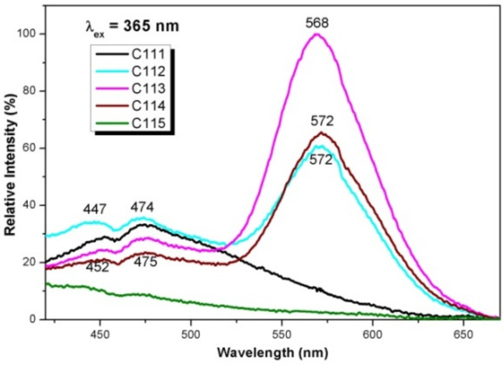

Figure 4.30. The PL spectra of ZnS and $ZnS:Mn^{2+}$ powders obtained by ZDDTC solvothermal decomposition.

The emissions spectra shows a broad self-activated emission band, located at 450-475 nm, in the blue spectral range, due to lattice defects from zinc sulphide host lattice. Tthe "split" form is an artefact due to the instrument optical system, correlated with a relatively weak photoluminescence signal. In addition to the self-activated emission band, the spectra of manganese doped samples contain a intense band located at 568-572 nm, in the yellow spectral range. This emission is due to transitions $^4T_1(^4G)$-$^6A_1(^6S)$ of manganese ions [345].

Asymmetric form of the band centered at ~ 570 nm suggests the existence of overlapped peak at ~ 600 nm, a strong band observed in powders obtained by precipitation.

4.2.3.3. Morpho-structural properties of zinc sulphide powders

The specific surface area of ZnS powder was determined by the Brunauer, Emmett, Taller (BET) method, while by de Boer method was determined surface micropores (t-plot). pore volume, pore area and average pore diameter were calculated by the Barrett, Joyner, Halenda (BJH) method using desorption isotherm. The results are listed in table 4.9 are compared with the values of single-source molecular precursor powder ZDDTC type from which it was prepared.

It is observed that the specific surface area of the ZnS powder is ~ 77 times higher than the precursor, total pore volume is ~ 9 times higher, total pore area is ~ 46 times higher and the average diameter of pore is ~ 5 times smaller. Average particle size of ZnS calculated from the specific surface area is about 10 nm.

Table 4.9. The main characteristics of specific surface area and porosity of ZnS powder and the corresponding SSMP.

Sample	Specific surface area m^2/g	Micropores surface cm^3/g	Pores total volume cm^3/g	Pores total area m^2/g	Pores average diameter nm
pC107	2,04	-	0,0137	1,89	28,92
C120	154,5	22,9	0,1201	86,55	5,55

In figure 4.34 is shown the SEM image of a ZnS powder. The powders consist by uniform spherical conglomerates with size of about 200 nm, which are composed from nanoparticles with sizes below 10 nm. The presence of manganese does not bring major changes in the size and shape of conglomerates or constituent nanoparticles. The ZnS:Mn^{2+} powders seem to be more heterogeneous in terms of particle size and are composed from smaller conglomerates than compound with non-doped samples.

The XRD patterns from figure 4.35 indicate that all the samples obtained in our synthesis conditions are polyphasic materials containing: hexagonal ZnS (JCPDS file no :36-1450; P63mc(186) a=b=3.82098 Å, c=6.2573 Å, V=79.116512 Å^3), cubic ZnS (JCPDS file no. 05-0566, F4¯3m(126) a=b=c=5.4060 Å. V=157.989 Å^3) and hexagonal MnS (JCPDS file no. 40-1289, P63mc(186) a=b=3.9792 Å, c=6.4469 Å, V=88.40424 Å^3). The results are in agreement with literature data [347, 349, 350].

Micro-structural parameters, i.e. the effective crystallite mean size D_{eff} and root mean square micro-stress $<\varepsilon^2>^{1/2}_m$ (table 4.10), are illustrating the incorporation of Mn^{2+} ions in hexagonal ZnS phase lattice. The relative value of micro-stress in all obtained samples reflects the great disorder of ZnS host lattice.

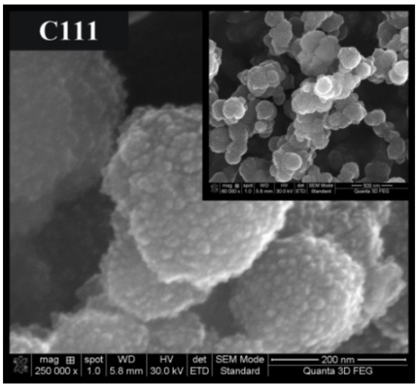

Figure 4.34. The SEM images of ZnS and ZnS:Mn^{2+} powders. Inset bar is 500 nm.

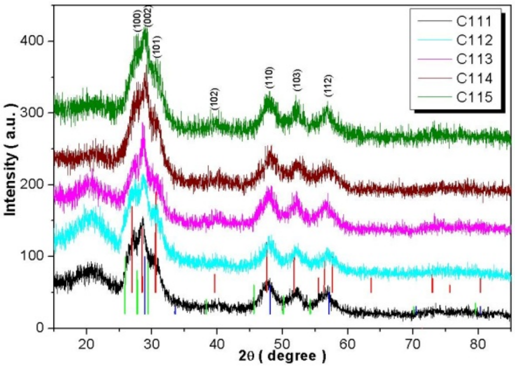

Figure 4.35. The XRD patterns of the ZnS and ZnS:Mn^{2+} samples and positions of diffraction lines of crystalline phases, according to literature data, JCPDS cards: 36-1450 - hexagonal ZnS (red); 05-0566 - cubic ZnS (blue) and 40-1289 - hexagonal MnS (green).

Table 4.10. The effective average crystallite size and root mean square of the micro-stresses calculated by Rietveld refinement.

Sample	Mn conc. (mol%)	hexagonal ZnS		cubic ZnS		hexagonal MnS	
		D_{eff} [nm]	$<\varepsilon^2>^{1/2}_m \times 10^3$	D_{eff} [nm]	$<\varepsilon^2>^{1/2}_m \times 10^3$	D_{eff} [nm]	$<\varepsilon^2>^{1/2}_m \times 10^3$
C111	0,00	8,7	7,162	8,6	7,058	-	-
C112	0,08	8,6	7,458	9,2	7,024	-	-
C113	0,21	8,5	7,858	10,4	6,846	6,4	8,876
C114	0,84	8,4	8,089	14,7	6,579	8,7	8,052
C115	9,24	7,9	8,886	16,7	5,745	14,8	4,246

The XRD patterns of all ZnS:Mn^{2+} samples are characterized by a broadening of the diffraction bands, which is characteristic to nanocrystalline materials. The effective crystallite mean size calculated for hexagonal ZnS phase varies between 8.7 and 7.9 nm. The effective crystallite mean size of cubic ZnS is between 8.6 and 16.7 nm. The values increase with increasing of manganese concentration. The same goes for hexagonal MnS phase.

The unit cell volume increase as the manganese concentration increase for both hexagonal and cubic ZnS (table 4.11). The undoped sample has the smallest unit cell volume of 0.079682 nm^3 hexagonal ZnS and 0.157595 nm^3 for cubic ZnS, respectively. Regarding the MnS phase, it can be observed that the unit cell volume decreases with increasing manganese concentration.

In the case of C112 sample the manganese concentration is so small that hexagonal MnS phase can not be detected.

Table 4.11. The unit cell volume and composition of zinc sulphide samples phases.

Sample	Mn conc. (mol%)	hexagonal ZnS		cubic ZnS		hexagonal MnS	
		% vol.	V [nm^3]	% vol.	V [nm^3]	% vol.	V [nm^3]
C111	0,00	84,0	0,079682	16,0	0,157595	-	-
C112	0,08	81,2	0,079688	18,8	0,157738	-	-
C113	0,21	77,4	0,079694	21,6	0,158222	1,00	0,088751
C114	0,84	74,7	0,079701	22,3	0,158718	3,00	0,088271
C115	9,24	65,4	0,079934	26,6	0,159079	8,00	0,087567

In table 4.11 are also presented the volumetric composition of the three crystallographic phases. The volume percentage of cubic ZnS phase increase for the manganese concentration increase.

5. Comparative studies of the properties of zinc sulphide nanocrystalline powders prepared in different synthesis conditions

The luminescent properties of zinc sulphide and manganese doped zinc sulphide nanopowders are highly dependent on particle size, their surface condition, the concentration of dopant, the degree of crystalline structure, the concentration and type of nanocrystalline lattice defects. In turn, these properties depend on the method and conditions of synthesis used.

This chapter compares the properties of nanocrystalline zinc sulphide samples obtained by various synthesis methods described in previous chapters. For this comparative study we used samples of zinc sulphide ZnS and manganese doped zinc sulphide ZnS:Mn^{2+} which presents the most intense self-activated and manganese characteristic photoluminescence emission.

5.1. Synthesis of zinc sulphide nanocrystalline powders with luminescent properties

The samples, methods of preparation and synthesis conditions are presented in table 5.1. The samples were prepared by the wet-chemical synthesis - WCS, starting from two precursor metal ions and, respectively, sulphide sources, and by decomposition of single-source molecular precursors - SSMP.

A zinc sulphide sample prepared by the method WCS-SimAdd it was calcined, too.

The Mn concentration from manganese in manganese doped zinc sulphide powders (determined by inductively coupled plasma optical emission spectroscopy - ICP-OES) is much smaller than the theoretical amount, due to the difference between the solubility products of zinc and manganese salts. For the comparison of powders with different concentrations of manganese we used the precipitation degree, which is the ratio between the concentration of manganese ions in powder and manganese ion concentration in the precipitation solution.

Table 5.1. The representative ZnS and ZnS:Mn^{2+} samples and their conditions of synthesis.

Crt.	Sample Code	Synthesis method	Precursors	Manganese concentration (mol%)		Synthesis medium	Organic additive	Temperature synthesis of ZnS (°C)	
				Teor.	Pr.			WCS	Pyrolysis
1	**C05**	WCS-US	$Zn(AcO)_2$ TAA	0		water	-	70	
2	**C85**		$(Zn,Mn)(AcO)_2$ TAA	10,0	0,05	water	-	70	
3	**C17**	WCS-SeqAdd	$Zn(AcO)_2$ TAA	0		water	MAA	5	
4	**C75**		$(Zn,Mn)(AcO)_2$ TAA	16,6	0,71	water	SDS	5	
5	**C35**	WCS-SimAdd	$Zn(AcO)_2$ TAA	0		methanol	-	20	
6	**C35c**		$Zn(AcO)_2$ TAA	0		methanol	-	20	900
7	**C38**		$(Zn,Mn)(AcO)_2$ TAA	8,0	0,28	methanol	SDS	20	
8	**C80**		$(Zn,Mn)(AcO)_2$ TAA	8,0	0,37	water	SDS	20	
9	**C89**	SSMP-Pyrolysis	ZDDTC	0		water*	-	20*	900
10	**C103**		ZMDDTC	0,5	0,21	water*	-	20*	900
11	**C91**		ZEX	0		water*	-	20*	900
12	**C104**		ZMEX	15,0		water*	-	20*	900
13	**C111**	STD-MW	ZDDTC	0		ethylene-glycol	-	110	
14	**C113**		ZMDDTC	0,5	0,21	ethylene-glycol	-	110	

* conditions for obtaining SSMP powder.

The samples prepared by STD-MW method have the best co-precipitation level, with values between 42 and 80%. The manganese co-precipitation level in WCS-SimAdd and WCS-SeqAdd methods depends on the initial concentration, precipitation medium and the organic additive type. The co-precipitation level vary between 1.2 and 4.3% for WCS-SeqAdd method and between 0.6 and 9.3% for WCS-SimAdd method. For WCS-US method values are very low, about 0.05%, which show that doping with manganese is failed.

5.2. Photoluminescent properties of zinc sulphide nanocrystalline powders

The photoluminescence emission of zinc sulphide doped or undoped is associated with a number of electronic transitions which involves the defects of lattice. So, the blend or wurtzit type crystalline lattice may contain lattice defects (intrinsic) i.e. sulphur $V_S^{\bullet\bullet}$ and zinc $V_{Zn}^{//}$ vacancies, interstitial zinc Zn_i^x and sulfur S_i^x atoms and the impurity lattice defects (extrinsic) i.e. oxygen O_S^x, manganese Mn_{Zn}^x or chlorine $Cl_S^{\bullet}$ ions. In the Kroger-Vink notation the index is the occupied lattice node and the exponent ^{x}, $^{\bullet}$ and $^{/}$ is the neutral, positive and negative effective electric charge of defect [353]. If the sulphur vacations is partially occupied with electrons it is noted by $V_S^{\bullet}$, while zinc vacantion that is not fully occupied by electrons is noted by $V_{Zn}^{/}$.

The PL spectra for manganese doped zinc sulphide ZnS:Mn^{2+} nanocrystalline powders are shown in figure 5.5. The samples were excited with a UV radiation with 365 nm. The sample (C80) with the most intense emission from the series prepared by WCS-SimAdd method was used as internal standard.

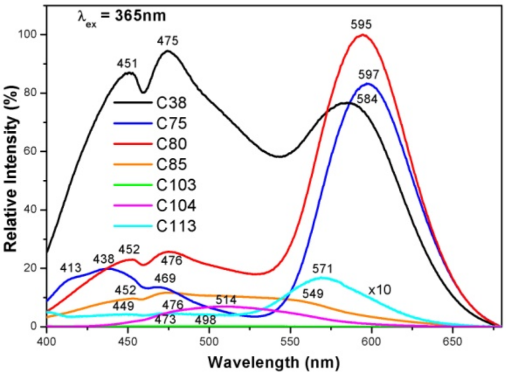

Figure 5.5. The PL spectra of the best ZnS:Mn^{2+} samples from in each series obtained. (C113 emission sample was multiplied by 10).

The zinc sulphide self-activated emission band in the blue domain and the manganese emission band in the orange domain were observed for sample C75 (WCS-SeqAdd), C38 and C80 (WCS-SimAdd). For sample C85 (WCS-US), manganese emission band disappear, expanding the zinc sulphide self-activated emission band in the green domain, probably, due of oxygen doping. For sample obtained from pyrolysis of SSMP powders based on ZMEX (C104) the zinc sulphide self-activated and oxygen doping signal increases. For the sample obtained from pyrolysis of SSMP powders based on ZMDDTC (C103), the emission is in the same domain as that of samples obtained from ZMEX (C104), except that in this case, the signal is almost nonexistent. In exchange for the sample obtained by solvothermical decomposition microwave-assisted of ZDDTC based SSMP (C113), there is only a weak emission in yellow domain.

Comparative analysis of PL spectra indicate their composed nature. The complex shape of the spectra is probably due to the variety of lattice defects involved in the emission process. In the case of ZnS:Mn^{2+} powders the apparent/overall luminescence consists from dopant - manganese characteristic luminescence, superimposed with auto-activated luminescence due to defects in the host lattice - zinc sulphide. The contribution of a parasite luminescence, due to impurification with oxygen is not excluded.

To identify the Gauss components from PL spectra of ZnS:Mn^{2+} samples, it was done the deconvolution of PL spectrum of the C75 sample obtained by WCS-SeqAdd method. This deconvolution is shown in figure 5.6.

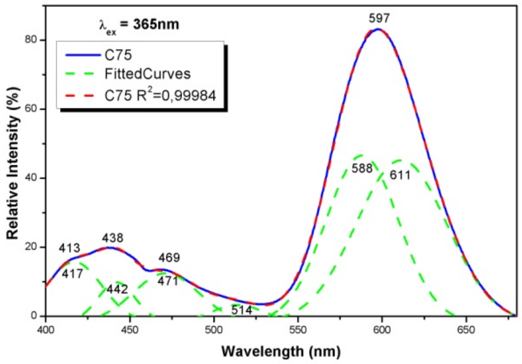

Figure 5.6. The PL spectrum deconvolution of the manganese doped zinc sulphide sample obtained by WCS-SeqAdd method.

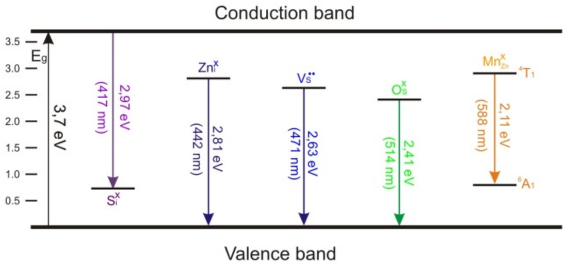

Figure 5.8. The schematic diagram of energy levels in ZnS:Mn^{2+} nanoparticle obtained using WCS-SeqAdd (sample C75).

The PL spectrum of the manganese doped zinc sulphide sample obtained by WCS-SeqAdd (sample C75) was split into 6 overlapped peaks, the coefficient of multiple determination R^2 = 0.99984. Overlapped peaks are located at 417 nm, 442 nm, 471 nm, 514 nm and 588 nm, which are assigned to lattice defects S_i^x, Zn_i^x, $V_S^{••}$, the oxygen doping O_S^x and respectively manganese ions Mn_{Zn}^x [220, 353]. The peak at 611 nm could not be assigned directly.

We explain these emission bands by electron-hole recombination transitions or intra-centre electronic transitions, involving the corresponding defects. Figure 5.8 presents the schematic diagram of energy levels and radiative transitions corresponding to self-activated zinc sulphide and manganese dopant ions proposed for sample C75, adapted from the scheme given by Kripa and collaborators [220].

The band gap energy E_g of zinc sulphide was considered the value commonly used in the literature [16, 145].

It should be noted that the proposed models are based on mathematical deconvolution in Gaussian bands of experimental spectra. Since the peak position obtained by deconvolution is based on a mathematical calculation using Gaussian or Lorentzian functions and the precision with which their positions were chosen, the results are not accurate. These can be used only informative.

5.3. Morpho-structural properties of zinc sulphide nanocrystalline powders

All samples obtained by these methods are composed by conglomerates with similar aspect.

SEM Images for zinc sulphide powders undoped or doped with manganese, representative for different synthesis methods are shown in figure 5.9.

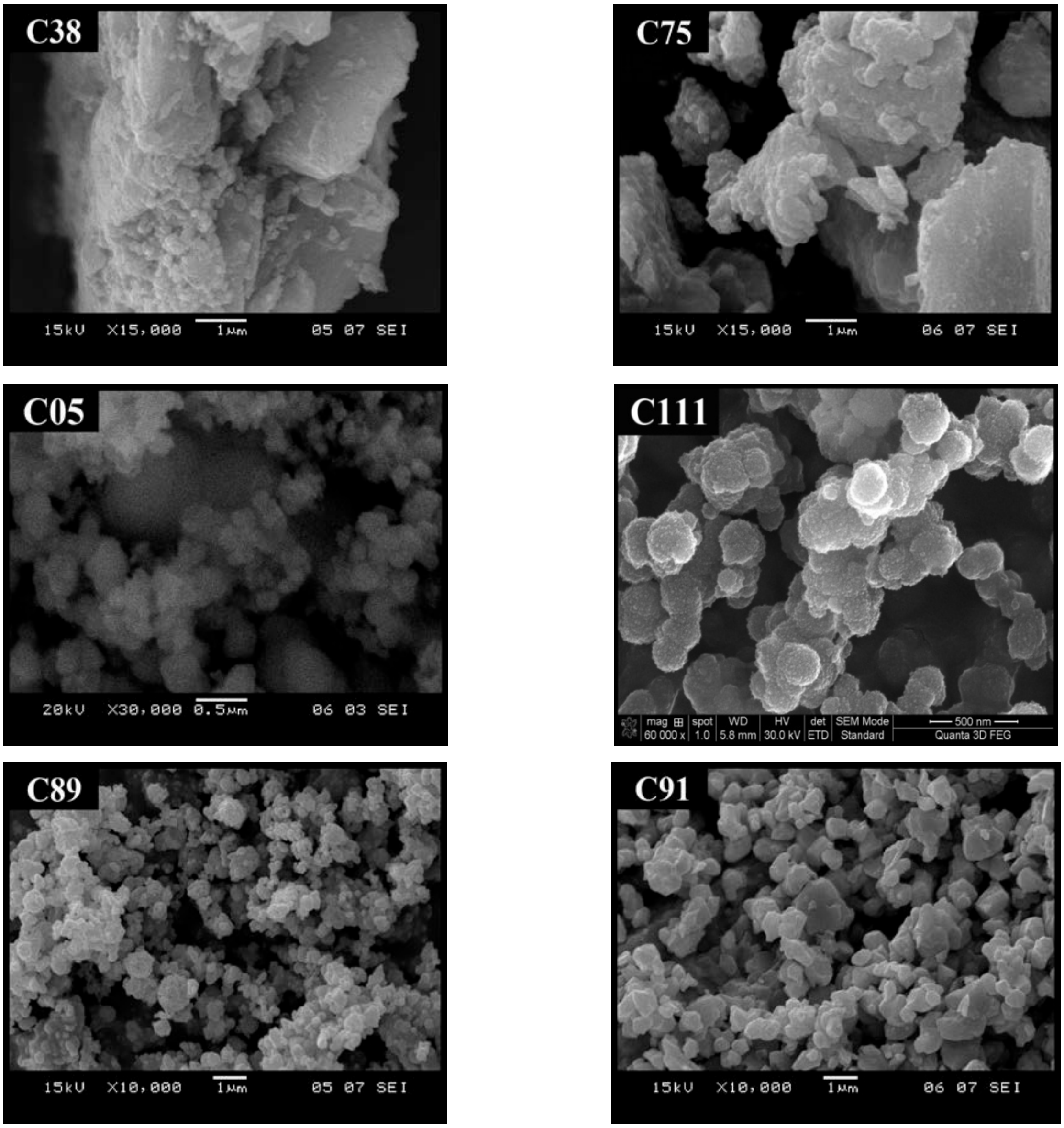

Figure 5.9. The representative SEM images for ZnS and ZnS:Mn^{2+} samples obtained by WCS-SimAdd (C38), WCS-SeqAdd (C75), WCS-US (C05), STD-MW (C111) and SSMP-pyrolysis (C89 - ZDDTC and C91 - ZEX) methods.

From the morphological point of view, the undoped and manganese doped zinc sulphide samples obtained can be classified as follows:

- Powders consisting tightly packed nanoparticles in large conglomerates with irregular form, which includes the samples obtained by the WCS-SeqAdd (C75) and WCS-SimAdd (C38) methods. At drying, the powders have a tendency to create large conglomerates with size between 5 and 50 μm, due to their large surfaces on which are adsorbed organic compounds. The primary particles have sizes less than 10 nm and relatively spherical form of quantum dots;

- Powders consisting tightly packed nanoparticles in spherical under-micron conglomerates, which includes samples obtained by the WCS-US (C05) and STD-MW (C111) methods. The conglomerates dimension are between 0.2 and 1 μm for sample C05 (ultra-fine powder) and 50-100 nm for sample C111 (nano-grained powder). The primary particles have dimensions less than 10 nm and relatively spherical form of quantum dots;
- Powders consisting of under-micron conglomerates, with irregularly form, obtained from SSMP powders pyrolysis (C89 and C91). They have sizes between 100 and 200 nm, for sample C89 (nano-grained powder), and 200 and 2000 nm, for sample C91 (ultra-fine powder).

The samples obtained in our conditions of synthesis are both powder with monophase structure and polyphasic structure (biphasic).

The manganese doped zinc sulphide powders (figure 5.11) can be classified into:

- Monophasic powder with of cubic ZnS structure. Most samples of ZnS:Mn^{2+} powders prepared in this study are of this type. As an example we have X-ray diffractogram of C38 sample, a sample obtained by the WCS-SimAdd method.
- Polyphasic powders consisting from ZnS with cubic and hexagonal structures and MnS with hexagonal structure. These powders are obtained by STD-MW method for synthesis of ZnS:Mn^{2+} and their structure is exemplified by diffractogram of C113 sample.

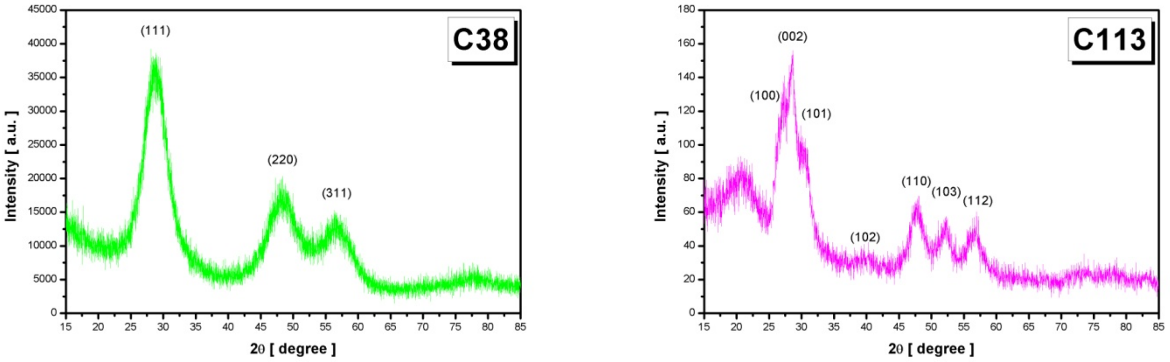

Figure 5.11. The X-ray diffractogram of representative ZnS:Mn^{2+} samples.

The effective crystallite mean size (D_{eff}) of prepared samples by WCS techniques (~ 0.3 nm) is much smaller than that of samples prepared by STD-MW method (~ 0.9 nm).

Packing defects for powders using STD-MW method (~ 9.5) are lower than those of powders obtained by WCS techniques (~ 7.5).

5.4. Evaluation of the applicative potential of zinc sulphide nanocrystalline powders with luminescent properties

In order to evaluate the applicative potential of zinc sulphide and manganese doped zinc sulphide powders, it was estimated emission color at excitation with UV radiation of 365 nm. This was accomplished by determining the chromaticity coordinates, which were plotted in diagrams in figure 5.14 and figure 5.15.

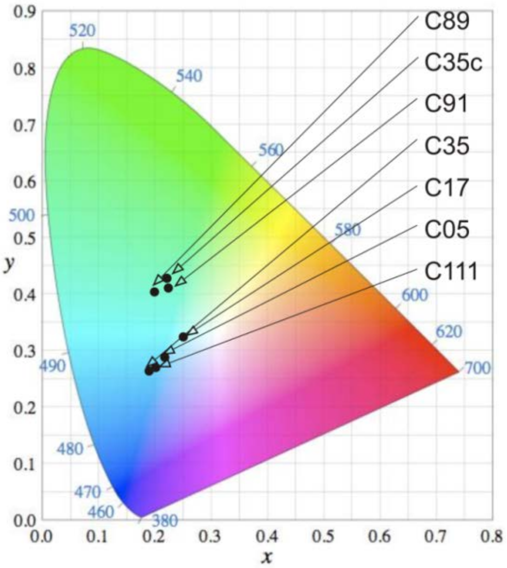

Figure 5.14. The chromatic diagram of ZnS samples at excitation with 365 nm radiation.

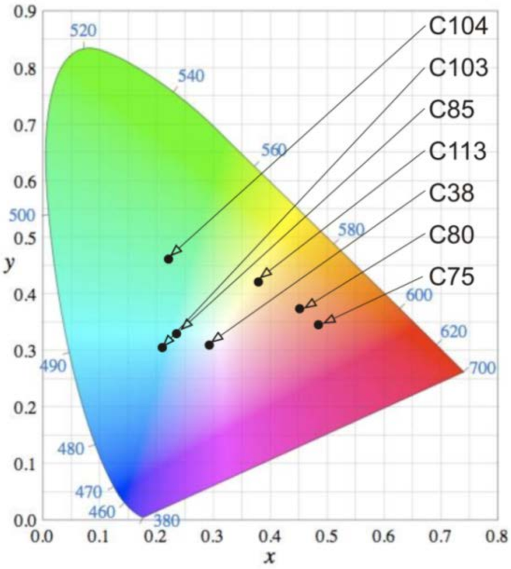

Figure 5.15. Chromaticity diagram of ZnS:Mn^{2+}

samples at excitation with 365 nm radiation.

For the samples based on manganese doped zinc sulphide, the difference between powders calcined and uncalcined is not visible, due to both the small incorporation degree of manganese and the are very weak luminescent signals.

The luminescence colour could be modulated by using controlled concentrations of manganese. For illustration is presented the optical microscopy images, at 1x magnification, for ZnS:Mn^{2+} samples with variable manganese concentration and prepared by WCS-SimAdd method, in methanolic medium, without organic additives. Variation of the manganese amount in samples from 0.05 mol% to 0.94 mol%, lead to change of emission colour from blue to orange (figure 5.16).

The samples were excited with the unfiltered radiation - Rn and monochromatic UV radiations with wavelength of 365 nm and 254 nm. We used these two monochromatic radiation because they are mostly used in UV optoelectronic devices.

The powders emission colour depends on the exciting radiation. This is because by changing the wavelength of the exciting radiation, it changes the nature of excited centers as well, and their excitation level.

The trichromatic coordinates and thus placing of colour on chromatic map of photoluminescent color of nanocrystalline zinc sulphide powders depends on the synthesis method and their conditions of production. From the above data, coupled with PL measurements show that, on excitation with UV radiation of 365 nm, the best method of synthesis of blue luminescent material based on zinc sulphide without dopant is WCS-SimAdd. For synthesis of orange photoluminescent materials based on manganese doped zinc sulphide, the best results are obtained with WCS-SimAdd in aqueous medium, and WCS-SeqAdd methods, while WCS-SimAdd method in methanolic medium can be used to get purple luminescent material.

All the methods leads to nanocrystalline powders with luminescent properties. By WCS-SimAdd and WCS-SeqAdd methods are obtained powders with the most intense photoluminescence emission spectra, while by STD-MW method are obtained the highest dispersible powders.

The wet-chemical synthesis WCS techniques have as result the obtaining of zinc sulphide powders with monophase crystalline structure of ZnS-blend. By the microwave-assisted solvothermic decomposition method STD-MW is obtained, biphasic crystalline powders composed of ZnS-blend and ZnS-wurtzit.

The synthesis methods and procedures described may be used to obtain luminescent materials based on doped/undoped zinc sulphide nanocrystalline, highly dispersed powders (quantum dots - QDs) simple or stratified (core-shell) type. These could be incorporated into polymers to obtain plastics with luminescent and opto-electronics properties, used to obtain quantum dots light-emitting diodes QD-LED. They have the energy consumption comparable to organic LEDs (OLEDs) currently used in mobile phones, while their performance could get the best inorganic LEDs.

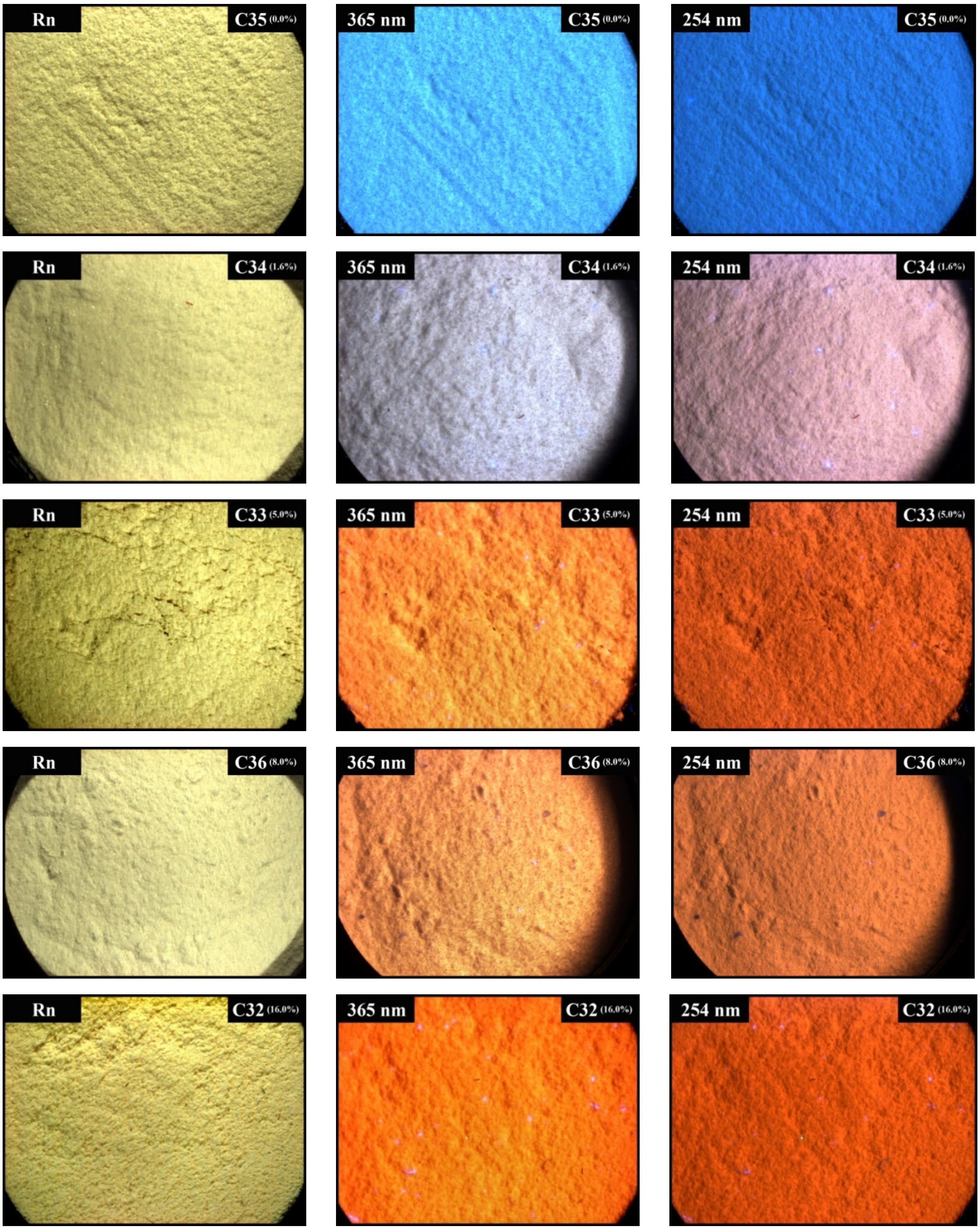

Figura 5.16. The optical microscopy images (taken at a 1x magnification), on samples obtained in methanolic medium by the WCS-SimAdd method excited with ultraviolet and unfiltered radiation, for ZnS (C35) and ZnS:Mn^{2+} with 0.05 mol% Mn (C34), 0.19 mol% Mn (C32), 0.25 mol% Mn (C33) and 0.94 mol% Mn (C36) samples.

The zinc sulphide and manganese doped zinc sulphide powders obtained could be used, after functionalization with organic species, as biological markers for the implementation of new diagnostic systems and minimally invasive treatment effects.

GENERAL CONCLUSIONS

The main aim of the thesis was to obtain semiconductor materials with special properties (luminescent) based on nanocrystalline powders of zinc sulphide (ZnS) and zinc sulphide doped with manganese, by various methods as well as their characterization. Correlation between preparation conditions and their specific properties have been also established.

The first part of the PhD thesis "**Semiconductor Materials with Special Properties**" getter the bibliographic data related to the preparation, characterization and use of ZnS powders. The second part of the thesis includes the results of original research performed in order to obtain highly dispersed luminescent powders based of zinc sulphide and manganese doped zinc sulphide. To establish the synthesis parameters were prepared 120 samples in different experimental conditions.

The work consists of six research studies, five of which are dedicated to synthesis and characterization of luminescent nanocrystalline zinc sulphide and one is for comparative analysis of structural and morphological properties of luminescent materials obtained by different methods/processes of synthesis and evaluation of their potential application. Studies led to the following conclusions:

1. **Wet chemical synthesis method via ultrasound-assisted precipitation WCS-US**, performed at 70 °C, in aqueous medium, from zinc/manganese acetate and thioacetamide, allows to prepare highly dispersed powders of zinc sulphide with luminescent properties. It was determined the effect of concentration and ratio of reactants, pH value and concentration of manganese on morphology and photoluminescence properties.
    - ➢ The luminescent emission of undoped zinc sulphide samples is situated in green spectral domain (λ_{max} ~ 540 nm), is due to a parasite luminescence (result of contamination from the reaction medium) that covers the blue luminescence specific for self-activation. The intensity can be improved by lowering the ratio of reactants and by increasing the pH value.
    - ➢ The samples are composed from ultra-fine powders of tightly packed nanoparticles in spherical and under-micron conglomerates. The conglomerates size can be reduced by lowering the ratio of reactants and increase the pH value. Instead, the particle sizes distribution can be narrowed using dilute solutions of reactants.
    - ➢ The synthesis of manganese doped zinc sulphide with good luminescence it was failed. At manganese addition the luminescent properties greatly decreases and particle size increase.

- ➢ *The best results were obtained* for zinc sulphide powder prepared from zinc acetate and thioacetamide in an aqueous medium, at a temperature of 70 °C, in the presence of ultrasound, using a molar ratio of 1 to 1.5 and pH = 3.

2. **Wet-chemical synthesis method by sequential addition of reagents precipitation WCS-SeqAdd** was performed in an aqueous medium at 5 °C using zinc/manganese acetate and sodium sulphide. The effect of organic additive (methacrylic acid and sodium dodecyl sulphate) and the concentration of manganese on morphology and photoluminescence properties of powders was studied. Nanocrystalline powders of manganese doped zinc sulphide with relatively strong luminescence were obtained.

- ➢ The presence of organic additives are strongly modify the co-precipitation level of manganese in powder. For the same concentration in the reaction medium, co-doping level varies from 1.3 to 4.3% of the theoretical. The sample prepared in the presence of sodium dodecyl sulphate has the highest co-precipitation level.
- ➢ The $ZnS:Mn^{2+}$ powders shows a strong emission in the orange domain (~ 600 nm), which can be improved by adding sodium dodecyl-sulphate and reduced by adding methacrylic acid.
- ➢ The powders are composed of tightly packed nanoparticule with cubic monophase crystalline structure. The effective crystallite mean size is about 3 nm and the mean density of packing defects is about 0.01.
- ➢ *The best results* were obtained for manganese doped zinc sulphide powder prepared from zinc/manganese acetate and sodium sulphide, in aqueous medium, at a temperature of 5 °C, in the presence of sodium dodecyl-sulphate, using a manganese concentration of 16.4 mol%.

3. **Wet-chemical synthesis method by simultaneous addition of reagents precipitation - WCS-SimAdd** was performed using zinc/manganese acetate and sodium sulphide, in methanol or aqueous medium, at a temperature of 20 °C. The effect of reacting medium, organic additive (methacrylic acid, sodium dodecyl-sulphate and cetyl-trimethyl-ammonium bromide) and manganese concentration on the luminescent and morphological properties was studied. The method allows a better control of synthesis parameters on the local concentration of reactants precipitation of about 7.5-5.0 x 10^{-5} mol/L. By carefully choosing the conditions of precipitation can be prepared nanocrystalline powders of manganese doped zinc sulphide, homogeneous with strong orange luminescence (original method).

- ➢ The amount of dopant in $ZnS:Mn^{2+}$ powders is strongly influenced by the nature and amount of organic additive and the nature of the reaction medium. Adding a small amount of methacrylic acid increases the amount of manganese incorporated, while the presence of cetyl-trimethyl-ammonium bromide or large amounts of methacrylic acid decreases the amount of co-precipitated manganese.

- The emission from the orange domain (~ 600 nm) of ZnS: Mn^{2+} powders is enhanced if is added sodium dodecyl-sulphate, regardless the type of reagent. In aqueous medium, methacrylic acid has a weak effect on the photoluminescent emission while in methanolic medium it have an quenching effect. Instead cetyl-trimethyl-ammonium bromide have a strong quenching effect regardless the reaction medium. Use of a large amounts of methacrylic acid has strong quenching effect.
- All samples are composed of tightly packed nanoparticles in supra-micron size conglomerates. They contain a single crystalline phase, i.e. ZnS-blend, with the effective crystallite mean size of about 3 nm and an mean density of packing defects about 0.01.
- *The best results* were obtained for manganese doped zinc sulphide powder prepared from zinc/manganese acetate and sodium sulphide in methanolic medium, at 20 °C, in the presence of sodium dodecyl-sulphate, using a manganese concentration of 8 mol%.

4. Studies regarding **the single-source molecular precursors SSMP** of sulphur and zinc/manganese allowed to choose the best method for preparation of SSMP powders in order to obtain undoped and manganese doped zinc sulphide. The synthesis used zinc/manganese acetate and sodium diethyl-dithiocarbamate or potassium ethyl-xanthate, in aqueous medium at 20 °C, using WCS-SeqAdd and WCS- SimAdd methods (patented method).

- The thermal stability of single-source molecular precursors was studied. Gas evolved analysis was used to establish their composition (original item). The presence of carbon sulphide and carbonyl sulphide was put in evidence from the decomposition of ZEX based samples. The decomposition of ZDDTC based powders shown the presence of carbon sulphide and ethyl-isothiocyanate.
- The methods influence the single-source molecular precursors particle morphology, same as the size and luminescence of zinc sulphide particles prepared by their pyrolysis.
- The SSMP powder pyrolysis leads to highly dispersed powders consisting of micron particles. The samples with smallest particles were obtained by pyrolysis of ZDDTC powder prepared by WCS-SimAdd method. Changing the precursor and the method cause increase the particle size and/or their surface area distribution.
- All zinc sulphide powders obtained by SSMP pyrolysis contain in their crystalline lattice the luminescent centers associated with oxygen impurities, originating either from the precursor molecular structure (eg ZEX) or from the water of crystallization. This determines the position of the emission maximum is at ~ 500 nm.
- The pyrolysis of SSMP samples based on ZMDDTC and ZMEX lead to the formation of zinc sulphide powders in which manganese have a quenching effect. This effect is

probably due to the formation of manganese sulphide is not incorporated into particles, being spread on their surface. This is confirmed by the brown colour of powders.

5. **The solvothermical decomposition microwave-assisted method STD-MW of single-source molecular precursors** allowed to obtain zinc sulphide powders with very good dispersibility. The synthesis was carried out in ethylene-glycol at 100 °C, using zinc/manganese diethyl-dithiocarbamate. It was studied the effect of manganese concentration on photoluminescent and morpho-structural properties of zinc manganese doped sulphide powders.

   - From this method it can be obtained manganese doped zinc sulphide powders. The actual concentration of manganese in $ZnS:Mn^{2+}$ powders is approximately equal to that from single-source molecular precursors used in the synthesis.
   - The photoluminescence emission of manganese doped zinc sulphide powders, with a maximum at ~ 570 nm, is not intense due to the quenching effect of organic compounds adsorbed from medium.
   - The powders consist of nanoparticles tightly packed in uniform spherical conglomerates, with size of about 200 nm. They consist of a mixture of wurtzite and blende. Using conventional methods, wurtzit and blend mixture is obtained by calcination at high temperatures over 1000 °C.
   - *The best results* were obtained for manganese doped zinc sulphide powder prepared by solvothermical decomposition microwave-assisted of the zinc/manganese diethyl-dithiocarbamate, in ethylene-glycol medium, at temperature of 110 °C, using a precursor containing 0.21 mol% manganese.

6. Comparative study of the properties of nanocrystalline zinc sulphide powders produced by different synthesis methods.

   - Sample doped zinc sulphide obtained by the WCS-SimAdd method shows the most intense photoluminescence emission, under UV excitation with 365 nm. In the case of doped zinc sulphide powders, only samples prepared by WCS- SimAdd and WCS-SeqAdd methods has a strong orange emission. The samples obtained by other methods have a much weaker photoluminescence.
   - The deconvolution on emission spectra allowed to propose a model of energy transitions in zinc sulphide and manganese doped zinc sulphide (original item).
   - The calculation of emission colour of ZnS calcined samples, share situated in green - cyan domain, while the uncalcined, in cyan – blue domain. For samples doped with manganese in small amounts, the color points varies in green - cyan – blue domain, and for the samples where the doping with manganese is succeeded, in yellow - orange – pink domain. The only exception is for sample obtained by the WCS-SimAdd method in methanolic medium,

which show an emission colour in blue – pink domain, due to intense self-activated and manganese ions emission.

- All powders are composed of under-micron particles, but only those obtained using WCS- US and STD-MW methods are highly dispersed. In the case of samples obtained through WCS-SeqAdd and WCS-SimAdd methods, the particles are strongly connected in compact, irregular conglomerates. The best method for obtaining highly dispersed powders with small particle size is STD-MW method.
- All ZnS samples prepared by WCS methods are monophase with cubic structure. ZnS samples obtained using STD-MW consist of a mixture of cubic phase and hexagonal phase, with a predominance of hexagonal phase characteristic of high temperature synthesis methods, over 1000 °C.
- The synthesis methods and procedures described may be used to obtain highly dispersed nanocrystalline powders of single or multilayer, doped or undoped zinc sulphide with luminescent properties. The methods can be used to obtain light-emitting diodes with quantum dots QD-LED, used in obtaining of display screens. It can also be used to made economic bulbs with nanoparticles or in medicine as a biological marker.

The studies have contributed to the knowledge of the preparation of zinc sulphide and manganese doped zinc sulphide powders.

Some of the results have been published in eight papers (six in ISI journals) and communicated to national and international conferences. New elements have been identified and a patent application has submitted.

Original contributions

Based on the research results report on the current state of the international research the following original contributions are put in evidence:

1. Development and optimization of new methods for synthesis of semiconductor materials with special properties based on photoluminescent zinc sulphide nanocrystalline powders;
2. Development of new methods for preparation of single-source molecular precursors, used in the synthesis of nanocrystalline powders based on zinc sulphide;
3. Contributions to define the properties of zinc sulphide powders undoped/doped with manganese and single-source molecular precursor powders synthesized by the described methods;
4. Identification of the products of thermal decomposition of single-source molecular precursors, i.e. zinc diethyl-dithiocarbamate and zinc ethyl-xanthate.

5. Achieving/developing a comparative study on morpho-structural and luminescent properties of nanocrystalline zinc sulphide powder undoped and doped with manganese obtained by different synthesis methods;
6. Proposing theoretical models of energy levels and radiative transitions in zinc sulphide powders undoped and doped with manganese.

Recommendations for further studies

1. Studies regarding other solvents and single-source molecular precursors in synthesis of zinc sulphide and manganese doped zinc sulphide by solvothermal decomposition microwave-assisted method.
2. The synthesis of core/shell type nanoparticles using the methods developed in this thesis.
3. To demonstrate the applicative potential of ZnS powders in opto-electronic devices.

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[336] Baza de date HR Nicolet TGA Vapor Phase.

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ANNEX I – Curriculum vitae

1. **First name(s)**: Adrian-Ionuţ
2. **Surname**: Cadiş
3. **Date of birth and location**: 28.03.1981, Cluj-Napoca
4. **Nationality**: Romanian
5. **Marital status**: single
6. **Studies**:

Institution	Babeş-Bolyai University Cluj-Napoca, Faculty Of Chemistry And Chemical Engineering	Babeş-Bolyai University Cluj-Napoca, Faculty Of Chemistry And Chemical Engineering	Babeş-Bolyai University Cluj-Napoca, Faculty Of Chemistry And Chemical Engineering
Dates	October 2000 – June 2005	October 2005 – June 2006	October 2007 – Present
Diploma	Chemical Engineer – University Diploma	Master in Advanced Organic Chemistry	PhD Degree

7. **Scientific title**: Chemist Engineer
8. **Work experience**:

Dates	11.2006 – 11.2007	11.2007 – present
Location	Cluj-Napoca, România	Cluj-Napoca, România
Institution	“Raluca Ripan” Institute for Research in Chemistry	Babeş-Bolyai University, “Raluca Ripan” Institute for Research in Chemistry
Position	Researcher assistant	Researcher assistant

9. **Patents**: 1 patent application
10. **Papers**: 13 papers published (11 in ISI journals, 1 in ISI proceeding, 1 in BDI proceeding), 9 scientific communications
11. **Member of professional associations**: Romanian Society of Chemistry
12. **Languages**: English (average), French (beginner), Italian (beginner)
13. **Other skills**: PC operating knowledge, utilization of editing-image processing software (WORD, EXCEL, POWER POINT, ORIGIN, CHEMDRAW, CORELDRAW, PHOTOSHOP, SOLID EDGE)
14. **Experience accumulated in national/international programs**: member in 2 research projects

ANNEX II – Scientific activity

List of elaborated papers

Scientific papers published in thesis theme

1 A.-R. Tomşa, E.-J. Popovici, **A.-I. Cadiş**, M. Ştefan, L. Barbu-Tudoran, S. Astilean, *Ultrasound-assisted synthesis of nanocrystalline zinc sulphide powders*, Journal of Optoelectronics and Advanced Materials, 2008, 10(9), 2342-2345 (ISI publication).

2 **A.-I. Cadiş**, A.-R. Tomşa, M. Ştefan, R. Grecu, L. Barbu-Tudoran, L. Silaghi-Dumitrescu, E.-J. Popovici, *Studies on the synthesis of Mn-doped ZnS nanoparticles with luminescent properties*, Journal Of Optoelectronics And Advanced Materials - Symposia, 2010, 2(1), 111-114 (BDI proceeding).

3 **A.-I. Cadiş**, A.-R. Tomşa, E. Bica, L. Barbu-Tudoran, L. Silaghi-Dumitrescu, E.-J. Popovici*, Preparation and characterization of manganese doped zinc sulphide nanocrystalline powders with luminescent properties*, Studia Universitatis Babes-Bolyai – Chemia, 2009, 54(3), 23-29 (ISI publication).

4 **A.-I. Cadiş,** E.-J. Popovicia, E. Bica, L. Barbu-Tudoran, *Studies on the synthesis of manganese doped zinc sulphide nanocrystalline powders*, Studia Universitatis Babes-Bolyai – Chemia, 2010, 55(2), 255-264 (ISI publication).

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6 **A.-I. Cadiş**, E.-J. Popovici, E. Bica, I. Perhaiţa, L. Barbu-Tudoran, E. Indrea, *On the preparation of manganese-doped zinc sulphide nanocrystalline powders using the wet-chemical synthesis route*, Chalcogenide Letters 2010, 7(11), 631-640 (ISI publication).

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Other scientific papers published

1. M. Pintea, M. Fazekas, P. Lameiras, **I. Cadiş**, C. Berghian, I. Silaghi-Dumitrescu, F. Popa, C. Bele, N. Ple, M. Darabantu, *Serinolic amino-s-triazines: iterative synthesis and rotational stereochemistry phenomena as N-substituted derivatives of 2-aminopropane-1,3-diols,* Tetrahedron (2008), 64(37), 8851-8870 (ISI publication).
2. L.E. Muresan, E.-J. Popovici, E. Bica, **A.-I. Cadiş**, M. Morar, E. Indrea, *Spectroscopic and structural characterisation of SiO2 -Y2O3 based materials with luminescent properties,* Studia Universitatis Babes-Bolyai - Chemia (2010), 65(2), 255-264 (ISI publication).
3. E.-J. Popovici, M. Morar, E. Bica, I. Perhaiţa, **A.-I. Cadiş**, E. Indrea, L. Barbu-Tudoran, *Synthesis and characterization of cerium doped yttrium-gadolinium aluminate*

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4. L.E. Mursean, E,-J. Popovici, E. Bica, **A.-I. Cadiş**, I. Perhaiţa, L. Barbu-Tudoran, *Investigation of thermal decomposition of yttrium-aluminum based precursors for YAG phosphors*, Journal of Thermal Analysis and Calorimetry (2012), 110(1), 349-356 (ISI publication).
5. A. Saponar, E.-J. Popovici, I. Perhaiţa, G. Nemes, **A.-I. Cadiş**, *Thermal behaviour of some ester derivatives of p-tert-butyl calix[n]arene*, Journal of Thermal Analysis and Calorimetry (2012), 110(1), 349-356 (ISI publication).

List of communicated papers

Communicated papers in the thesis topic

1. A.-R. Tomşa, E.-J. Popovici, **A.-I. Cadiş**, M. Ştefan, L. Barbu-Tudoran, S. Astilean, *Ultrasound-Assisted Synthesis of Nanocrystalline Zinc Sulphide Powders*, Isotopic & Molecular Processes (PIM), 2007, Cluj-Napoca, Romania.
2. A.-R. Tomşa, E.-J. Popovici, **A.-I. Cadiş**, M. Ştefan, L. Barbu-Tudoran, S. Astilean, *Ultrasound-Assisted Synthesis of Nanocrystalline Zinc Sulphide Powders*, Polimeri Hidrosolubili Pentru Aplicatii Avansate, 2008, Iasi, Romania.
3. **A.-I. Cadiş**, A.-R. Tomşa, M. Ştefan, R. Grecu, L. Barbu-Tudoran, L. Silaghi-Dumitrescu, E.-J. Popovici, *Studies on the synthesis of Mn-doped ZnS nanoparticles with luminescent properties.* Advanced Spectroscopies on Biomedical & Nanostructured Systems (NANOSPEC), 2008, Cluj-Napoca, Romania.
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5. **A.-I. Cadiş**, E.-J. Popovici, E. Bica, I. Perhaiţa, L. Barbu-Tudoran, *On the preparation of zinc sulphide powders from single-source molecular precursors: thermal descomposition of zinc diethyldithiocarbamate*, The 5 th International Conference on Amorphous and Nanostructured Chalcogenides (ANC-5), Magurele, Romania.

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1. C. Bele, I. Covaciu, E. Munteanu, **A.-I. Cadiş**, C. Berghian, M. Dărăbanțu, *The Influence of a New N-substituted-2-chloro-4,6-diamino-s-triazine on the Fatty Acids of Polar Foliar Lipids of Raphanus sativus*, The 41th Croatian and 1st International Symposium on Agriculture, 2006, Opatija, Croația.
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3. I. Perhaiţa, E.-J. Popovici, L. Muresan, M. Morar, **A. Cadiş**, *Phisical-chemical properties of precursors for YAG:Ce type phosphors obtained by wet-chemical synthesis*, Chemistry and Life, 2011, Brno, Cehia.
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