STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLV, 2, TOM II, 2010

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

STUDIES ON THE SYNTHESIS OF MANGANESE DOPED ZINC SULPHIDE NANOCRYSTALLINE POWDERS

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ABSTRACT. New synthesis precipitation technique to prepare nanoparticles of Mn-doped zinc sulphide ZnS:Mn^{2+} have been attempted. Various capping agents have been used to control the morphostructural properties of ZnS:Mn^{2+} particles. Infrared absorption spectroscopy (FT-IR), photoluminescence spectroscopy (PL), scanning (SEM) and transmission electron microscopy (TEM) were used to characterise the powder samples. Strong luminescent ZnS:Mn^{2+} nanocrystalline powders could be precipitated at room temperature, from sodium sulphide and zinc-manganese acetate solutions, using the reagent simultaneous addition technique-SimAdd and methacrylic acid or sodium dodecyl sulphate as passivating agent.

Keywords: *ZnS nanoparticles, Mn-doped nanoparticles, photoluminescence.*

INTRODUCTION

In recent times, there have been extensive studies on luminescent semiconductor nanocrystals because of their potential applications in future optoelectronic devices. In undoped II–VI semiconductors (e.g., CdS, CdSe, and ZnS), the bandgap is engineered by control of the crystal size that leads to tunable band-edge emission [1–6]. Following the report of Bhargava and Gallagher [7], doped semiconductor nanocrystals have been regarded as a new class of luminescent material. Among them, ZnS nanoparticles doped with Mn^{2+} exhibit high luminescence quantum efficiency and short luminescence lifetime.

These materials, because they can be obtained in the form of thin films [8], powders and sols [9], have wide range of applications in sensors, displays, electronic devices, laser devices, and nonlinear optical devices, etc. [6-7].

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Having applications in various fields such as optoelectronics, photocatalysis, solar energy conversion, fluorescence microscopy, synthesis of un-doped or Mn-doped ZnS 1D nanostructure have also been reported recently by many researchers [10–13].

The increasing interest in un-doped or doped ZnS nanoparticles has lead to the development of a variety of chemical routes to prepare nanoparticles, including ultrasound [14] and microwave irradiation [15], sol–gel method [16], solid-state reaction [17] and chemical precipitation [18].

The morphostructural and luminescent properties of ZnS powders strongly depend on the specific preparation method and the experimental conditions.

The precipitation of zinc sulphide using the reagent sequential addition technique - *SeqAdd* is the most popular method due to some advantages such as the use of cheap raw materials, easy handling and large-scale-production potential [6].

The present paper reports our attempts to obtain ZnS:Mn nanoparticles by chemical precipitation, using a new wet-chemical synthesis route based on the reagent simultaneous addition technique - *SimAdd,* that was developed for the manufacture of microcrystalline phosphors [19]. In order to control the particle morphology and size, methacrylic acid and sodium dodecyl sulphate were used as passivating/capping agents. The influence of surfactants on the photoluminescence and morphostructural properties of ZnS:Mn^{2+} powders prepared by SimAdd was investigated, using scanning (SEM) and transmission (TEM) electron microscopy, infrared absorption (FTIR) and photoluminescence emission (PL) and excitation (PLE) spectroscopy.

RESULTS AND DISCUSSION

The preparation of ZnS:Mn^{2+} powder was based on the reaction, at room temperature, between zinc acetate and manganese acetate, as metal sources, and sodium sulphide, as chalcogen suplier. When using SimAdd technique, the reagents are simultaneously added into diluted zinc acetate solution containing no additives (C79 sample), sodium dodecyl sulphate – SDS (C80 sample) or methacrylic acid – MA (C81sample) as particle size regulating agent.

The main chemical process for the preparation of ZnS:Mn^{2+} powder i.e. for the formation of zinc-manganese double sulphide is described by the following equation:

$$(1\text{-}x)Zn(CH_3COO)_2 + xMn(CH_3COO)_2 + Na_2S \longrightarrow (1\text{-}x)ZnS \cdot xMnS + 2CH_3COONa$$

Under UV excitation, the as prepared ZnS:Mn^{2+} powders show the characteristic Mn^{2+} emission. Photoluminescence emission (PL) and excitation (PLE) spectra are depicted in Figure 1. Sample C79 prepared with no additive was used as internal standard (I_{600nm}=100%; I_{340nm}=100%).

Photoluminescence emission (PL) spectra consist of two broad emission bands namely, a strong orange one at about 600 nm and a very weak blue one at 400–480 nm.

The characteristic orange emission band can be attributed to the electronic transition between $^4T_1$ and $^6A_1$ energy levels of the Mn^{2+} 3d states. Mn^{2+} d-electron states act as efficient luminescent centres while interacting strongly with s–p electronic states of the ZnS host into which an external electronic excitation is normally directed. The blue emission is characteristic to zinc sulphide and it is usually influenced by many factors e.g. particles size, crystallinity, doping level, surface states of particles etc. Since a large portion of the atoms in nanocrystals is located on or near the surface, the surface properties should have significant effect on their optical properties.

Photoluminescence properties of ZnS:Mn^{2+} powders are influenced by the presence of the passivating agents into the precipitation medium. The use of the sodium dodecyl sulphate increases the orange emission intensity with 25% while the presence of methacrylic acid improves it with only 7%. On the other hand, the intensification of the blue emission is insignificant in the presence of sodium dodecyl sulphate (~0.5%) or methacrylic acid (~0.2%).

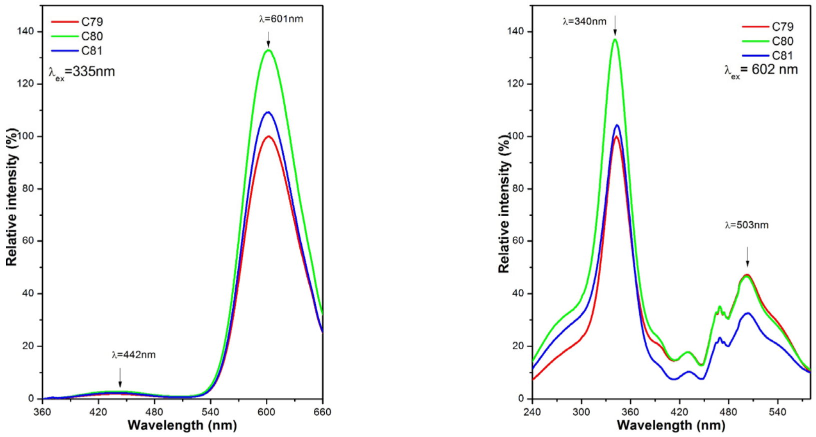

Figure 1. PL (left) and PLE (right) spectra of ZnS:Mn^{2+} powders prepared with no additive (C79), SDS (C80)and MA(C81)

Photoluminescence excitation spectra were registered by monitoring the characteristic orange emission (~ 600 nm) of Mn^{2+} under excitation with variable UV radiation. The highest PLE peak centred at about 340 nm can be attributed to the ZnS host lattice excitation whereas the multiple peaks in the 375-575 nm range can be related to Mn^{2+} presence.

In doped semiconductors, the possible paths for the luminescence excitation of the impurity ions include indirect excitation of the host lattice and direct excitation of impurity ions. This strong excitation absorption peak should arise from the direct excitation transitions of Mn^{2+}. According to the literature [20], the PLE peaks observed around 390, 430, 465, 500, and 535 nm can be attributed to the transitions between the $^6A_1(^6S)$ ground state and the excited states of $^4E(^4D)$, $^4T_2(^4D)$, $^4A_1(^4G)$ and $^4E(^4G)$, $^4T_2(^4G)$, $^4T_1(^4G)$ within the Mn^{2+} $3d^5$ configuration, respectively.

The influence of the passivating agents on photoluminescence properties is also evident in PLE spectra. The strong excitation peak related with the ZnS host (~ 340 nm) is increased with about 37 % in sample with SDS and only with 4 % in sample with MA. SDS seams to do not influence the excitation peaks associated with Mn^{2+} while MA addition decrease them with about 30%, comparative with $ZnS:Mn^{2+}$ without surfactant.

Particle dimensions of $ZnS:Mn^{2+}$ powders were evaluated by electron microscopy.

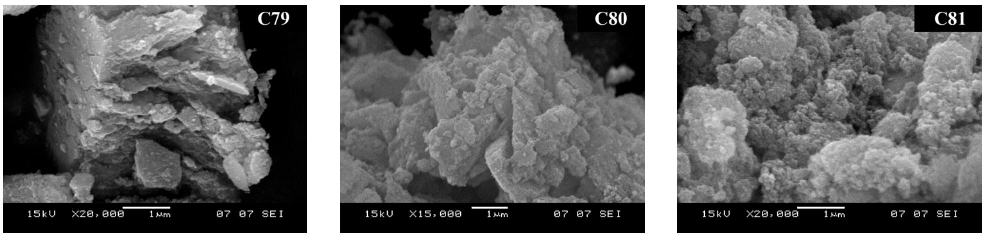

Figure 2. SEM images of different $ZnS:Mn^{2+}$ samples obtained in various experimental conditions.

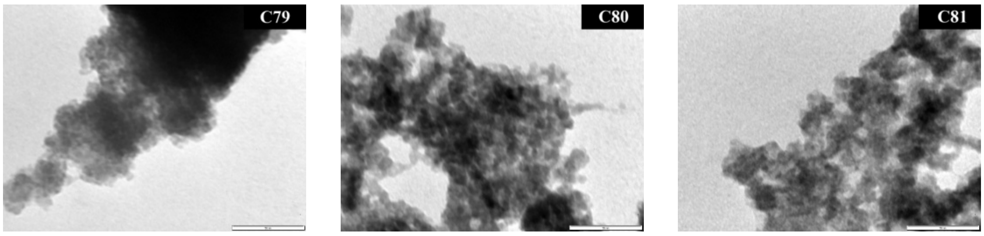

Figure 3. TEM images of different $ZnS:Mn^{2+}$ samples obtained in various experimental conditions (scale bar=50 nm).

SEM investigation of samples prepared with and without surfactants i.e. C80-SDS, C81-MA and C79, shows that ZnS:Mn^{2+} powders consist in large conglomerates formed from tightly packed under-micron particles (Figure 2).

TEM images of samples C79-no surfactant, C80-SDS and C81-MA illustrate the nanocrystalline state of ZnS:Mn^{2+} all powders (Figure 3). The average diameter of nanoparticles is evaluated at 6-10 nm.

The nanopowders obtained by SimAdd technique have a high surface area and energy that account for the strong tendency of particles toward agglomeration. SDS and MA additives seem to increase the powder dispersability; no effect on the particles dimension could be noticed.

The as prepared ZnS nanopowders show a high capacity to absorb impurities and regulating agent from the precipitation medium, as illustrated by the infrared absorption spectra depicted in Figure 4. FTIR spectrum of C80-SDS contains the characteristic absorption bands of sodium dodecyl sulphate i.e. O–H stretching (3800–3200 cm^{-1}) and bending (1700–1600 cm^{-1}), C–H stretching of CH_3 and CH_2 groups (3000–2800 cm^{-1}), C=O asymmetric and symmetric stretching (1600 and 1400 cm^{-1}), C–O stretching (1025 cm^{-1}) and SO_2 stretching (1300–1100 cm^{-1}) vibrations [21].

FTIR spectroscopy illustrates that, in spite of the fact that the precipitate was thoroughly washed, ZnS:Mn^{2+} powders with large surface area contain residual CH_3COO^-, dodecyl sulphate and methacrylate ions.

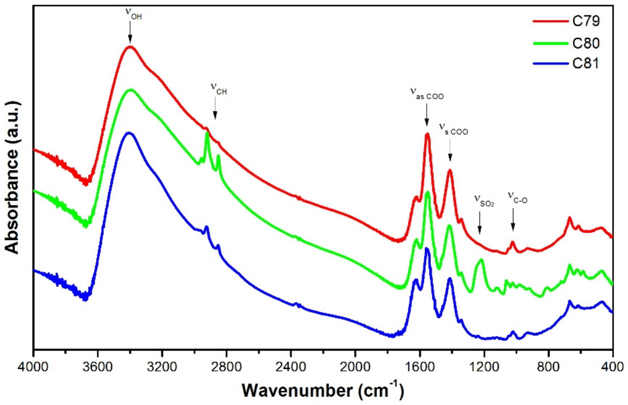

Figure 4. FT-IR spectra of ZnS:Mn^{2+} powders prepared with no additive (C79), SDS (C80) and MA (C81)

CONCLUSIONS

Luminescent manganese doped zinc sulphide (ZnS:Mn^{2+}) nanopowders could be obtained by precipitation, using the simultaneous reagent addition technique-*SimAdd,* with or without sodium dodecyl sulphate or methacrylic acid as particle size regulating agents.

The photoluminescence measurements show that ZnS:Mn^{2+} powders show strong orange luminescence (λ_{pk}~600 nm) characteristic to Mn^{2+}. The strong PL of the un-annealed ZnS:Mn^{2+} powders could be associated with the particle nano-dimension. The strongest photoluminescent powder was obtained in the presence of sodium dodecyl sulphate.

Although ZnS:Mn^{2+} powders are formed from nanosized crystallites (6-10 nm), they are tightly packed into larger and irregular shaped particles. The large surface area explains the high absorption capacity of the ZnS powder, as illustrated by FTIR investigations.

EXPERIMENTAL SECTION

Manganese doped zinc sulphide powders were prepared by precipitation, using the reagent simultaneous addition technique-*SimAdd*, from Zn-Mn acetate and sodium sulphide in aqueous medium, at room temperature. In this respect, equal volumes of 1M aqueous solution of zinc -manganese acetate (8 % mol Mn/(Zn+Mn) and 1M aqueous solution of sodium sulphide were added, under stirring, in water, with or without surfactant addition, sodium dodecyl sulphate and methacrylic acid. The white-pink ZnS powder was separated through centrifugation, washed with isopropyl alcohol and dried at 80ºC.

Infrared absorption spectra (FTIR) were registered on a NICOLET 6700 Spectrophotometer (KBr pellets technique). Photoluminescence emission (PL) and excitation (PLE) spectra were taken with JASCO FP-6500 Spectrofluorimeter (Farbglasfilter WG 320-ReichmannFeinoptik; Sample C79 prepared with no surfactant addition was used as internal standard I_{em}=100%). The transmission electron microscopy (TEM) was performed with JEM JEOL 1010 microscope and the scanning electron microscopy (SEM) images were obtained with a JEOL–JSM 5510LV instrument, using Au-coated samples.

ACKNOWLEDGMENTS

The Romanian Ministry of Education, Research and Innovation (Contract ID-2488/710) supported this research project.

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