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On the preparation of zinc sulphide powders from single-source molecular precursors: thermal descomposition of zinc diethyldithiocarbamate

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Zinc sulphide (ZnS) nanocrystalline powders were synthesised by thermal decomposition of zinc diethyldithiocarbamate used as single-source molecular precursor (SSMP). Two samples of SSMP were prepared in aqueous medium, from sodium diethyldithiocarbamate and zinc acetate solutions, using two different precipitation methods, namely the reagent sequential addition technique (SeqAdd) and the reagent simultaneous addition technique (SimAdd). Attempts to prepare manganese doped zinc sulphide powders (ZnS:Mn^{2+}) from zinc-manganese diethyldithiocarbamate precursors were also performed. The SSMP and un-doped and Mn-doped zinc sulphide powders were characterized by thermal analysis, infrared absorption spectroscopy, photoluminescence measurements and scanning electron microscopy. It was revealed that luminescent ZnS powders with under-micron particles could be prepared by both the precipitation technique; SimAdd route seems to be favourable to the synthesis of smaller particles. No efficient luminescent ZnS:Mn^{2+} powders could be obtained by our synthesis route.

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1. Introduction

Nanocrystalline chalcogenides have electronic properties intermediate between those of macrocrystalline solids and molecular entities. The properties of such materials are intriguing and have formed the subject of intense research in recent years [1-2]. One interesting possibility is the use of particle size as a control parameter in order to tailor bandgap, which provides a novel approach to the development of materials for various applications as photocatalysts [3], phosphors for light-emitting diodes [4], biological markers [5], photovoltaics for solar cells [6], etc.

Because zinc sulphide is one of the most important II-VI semiconductors, various methods have been developed for the preparation of un-doped or doped ZnS nanoparticles in the past few years, including vapour-liquid-solid process [7], solvothermal route [8], hydrothermal method [9], chemical precipitation [10] and ultrasound [11] or microwave [12] assisted synthesis routes. To increase the chalcogenide performances, they are doped with transition [13] or rare earths metals [14]. However, the synthesis of high quality ZnS nanostructures with uniform size, shape, and good optical properties is still a challenge.

Recently, a new method for synthesizing metal sulphide particles of high quality was developed, using one single-source molecular precursor (an individual molecule containing all the elements required in the final product). This route has several appealing features in the synthesis of semiconducting chalcogenide materials. First of all, it offers the potential advantages of mildness, safety and simplified fabrication procedure and equipment, when compared with the use of multiple sources requiring exact control over stoichiometry. Moreover, these single-source molecular precursors (SSMP) can be used in various methods such as spray pyrolysis deposition [15] or solvothermal decomposition, at low temperature [16]. Another important motivation for the utilization of SSMP may be found in the observation of unusual crystal growth selectivity or metastable phase formation of the resultant products, which are sometimes unattainable with conventional synthetic techniques [17]. Among the SSMP, metal alkyl xanthates [18], dithiocarbamates [19] and thiols [20] are of interest for zinc sulphide synthesis.

Our paper is devoted to the synthesis of zinc diethyldithiocarbamate $Zn(DDTC)_2$ used as SSMP to prepare luminescent ZnS powders. The goal of our studies was to evaluate the effect of the precipitation method i.e. reagent sequential addition technique -SeqAdd [21] and reagent simultaneous addition technique -SimAdd [22], on the properties of ZnS powders obtained *via* the thermal decomposition of $Zn(DDTC)_2$ precursor. Additional samples of zinc-manganese diethyldithiocarbamate samples (Zn,Mn) $(DDTC)_2$ were prepared and investigated in relation with the luminescent properties of the thermal dissociation products (ZnS:Mn^{2+}).

$Zn(DDTC)_2$ as well as the ZnS and ZnS:Mn^{2+} nanocrystalline powders were characterized by Fourier transform infrared absorption spectroscopy, thermal analysis, photoluminescence spectroscopy and scanning electron microscopy.

2. Experimental

Crystalline powders of single-source molecular precursors $Zn(DDTC)_2$ and $(Zn,Mn)(DDTC)_2$ were prepared through the reaction of zinc acetate or zinc-manganese acetate and sodium diethyldithiocarbamate, at room temperature, in water, using SimAdd and SeqAdd precipitation methods.

The SimAdd procedure consists in the simultaneous adding of equal volumes of reagents solutions into a bottom solution, under stirring. The precipitation was carried out using zinc or zinc-manganese acetate and sodium diethyldithiocarbamate (SDDTC), in 1:2 molar ratio. The SeqAdd method consists in the stepwise addition of SDDTC aqueous solution into the zinc or zinc-manganese acetate solution; precipitation was carried out in similar experimental conditions. Precursor powders were water washed, filtered and dried at 100°C, under low vacuum.

ZnS and $ZnS:Mn^{2+}$ powders were prepared from $Zn(DDTC)_2$ and $Zn(DDTC)_2$ - $Mn(DDTC)_2$ powders, by thermal decomposition at 900°C, in N_2 atmosphere. The SSMP powders obtained without or with manganese exhibit white or light grey colour, respectively. The corresponding calcined powders have colours from white (ZnS) to beige ($ZnS:Mn^{2+}$), depending on the manganese amount.

The thermogravimetric and differential thermal analysis (TGA-SDTA) was carried out with a METTLER-TOLEDO TGA/SDTA851 instrument, under nitrogen flow, with a heating rate of 5°C/min. The infrared absorption spectra (FT-IR) were registered on a THERMO SCIENTIFIC NICOLET™ 6700 FT-IR spectrometer (KBr pellets). Photoluminescence emission (PL) spectra were registered with JASCO FP-6500 spectrofluorimeter Wavell, equipped with PMT R928 photomultiplier (interference filter BandPass 365 nm). The internal standard (I_{em} = 100 %) used is a sample of ZnS (C35) prepared previously from sodium sulphide and zinc acetate with SimAdd method and calcined at 900°C [22]. The scanning electron microscopy (SEM) images were obtained with a JEOL–JSM 5510LV electron microscope, with an accelerating voltage of 15 kV, using Au-coated powders.

3. Results and discussion

Zinc diethyldithiocarbamate crystalline powder was used as SSMP for the obtaining of luminescent of zinc sulphide powders. In order to study the effect of the precipitation procedure on the properties of both SSMP and ZnS powders, two $Zn(DDTC)_2$ samples were prepared using SimAdd (pC89) and SeqAdd method (pC93), respectively. Additionally, zinc-manganese diethyldithiocarbamate samples were prepared using SimAdd technique, from zinc-manganese acetate solutions with various Mn/(Mn+Zn) ratios namely 0.001 (pC106), 0.005 (pC103) and 0.015 (pC102). Un-doped ZnS powders C89 and C93 and $ZnS:Mn^{2+}$ powders C106 (0.1%Mn), C103 (0.5% Mn) and C102 (1.5% Mn) were obtained at 900°C.

FT-IR spectra of the precursor (pC89) and the corresponding zinc sulphide powder (C89) are presented in Fig. 1, in comparison with the spectra of the raw materials, $Zn(CH_3CH_2O)_2$ and SDDTC.

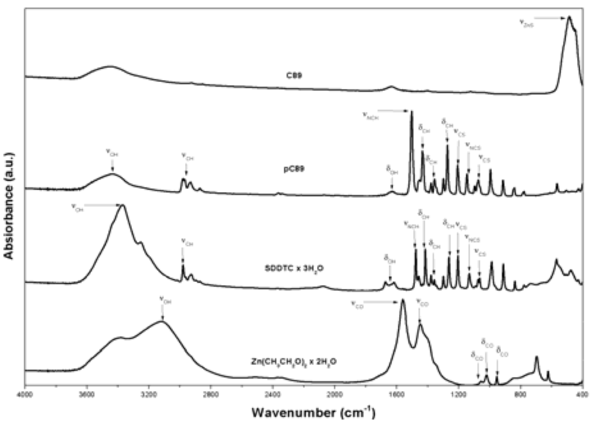

Fig. 1. FT-IR spectra of $Zn(DDTC)_2$ precursor (pC89) and ZnS calcination product (C89), in comparison with the raw materials.

FT-IR spectrum precursor show the characteristic bands in the ranges: 3600-3000 cm^{-1} (the valence vibrations of OH bond from water); 2990 - 2850 cm^{-1} (valence vibrations of CH bond from CH_2 and CH_3 groups); 1627 cm^{-1} (deformation vibrations of OH bond from water); 1502 cm^{-1} (valence vibration of the N-CH bond); 1450-1270 cm^{-1} (deformation vibrations of CH bond from CH_2 and CH_3 groups); 1210 cm^{-1} (valence vibration of CS bond); 1146 cm^{-1} (valence vibration of N-CS_2 bond) and 1096-1073 cm^{-1} (valence vibration of C=S bond) [23]. The spectrum of C89 shows the characteristic Zn-S vibration band at 485 cm^{-1}. One notes that, when sodium ions are replaced with zinc ions, the vibration peaks of NCS_2 group shift toward higher wavenumbers.

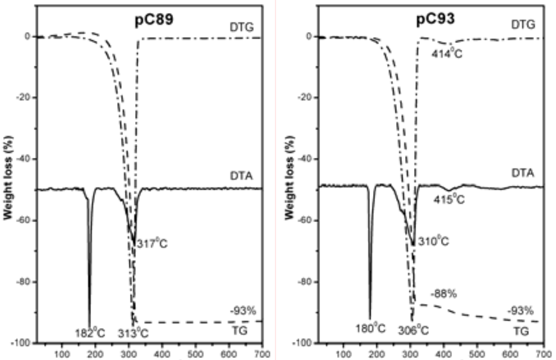

Fig. 2. Thermal analysis curves for precursors obtained using SimAdd (pC89) and SeqAdd (pC93) techniques.

Similar spectra were obtained for SeqAdd prepared samples pC93 and C93.

Fig. 2 illustrates the thermal behaviour of pC89 and pC93 precursors. When heated up to 700°C in inert atmosphere, both samples show a total weight loss of 93% and two strong endothermic peaks related, correspondingly, to a phase change (180-182°C) and thermal decomposition (310-320°). For pC89 (SimAdd sample), the thermal decomposition takes place in a single-step, with a maximum of weight loss at 313°C that is accompanied by a strong endothermic peak at 317°C. Precursor pC93 (SeqAdd sample) decomposes mainly in two steps, with weight loss of 88% and 5% at 306°C and 414°C, respectively. The two decomposition stages are endothermic, with maxima at 310°C and 400°C. This suggests that the decomposition is hampered by the powder compactness.

Mention has to be made that, in both cases, the weight loss (93%) is higher than the theoretical value (73%). One supposes that, the abrupt and strong thermal dissociation causes the dispersion of precursor particles and part of them are carried by the evolved gases.

Fig. 3 shows the SEM images of SSMP powders obtained with SimAdd and SeqAdd methods, and of the corresponding calcination products, ZnS powders. Zn(SDDTC)$_2$ powders consist from micro-particles with dimensions between 0.3 and 5 μm whereas the ZnS powders obtained from their thermal decomposition, are under-micron powders, with particle dimensions between 0.1 and 1 μm.

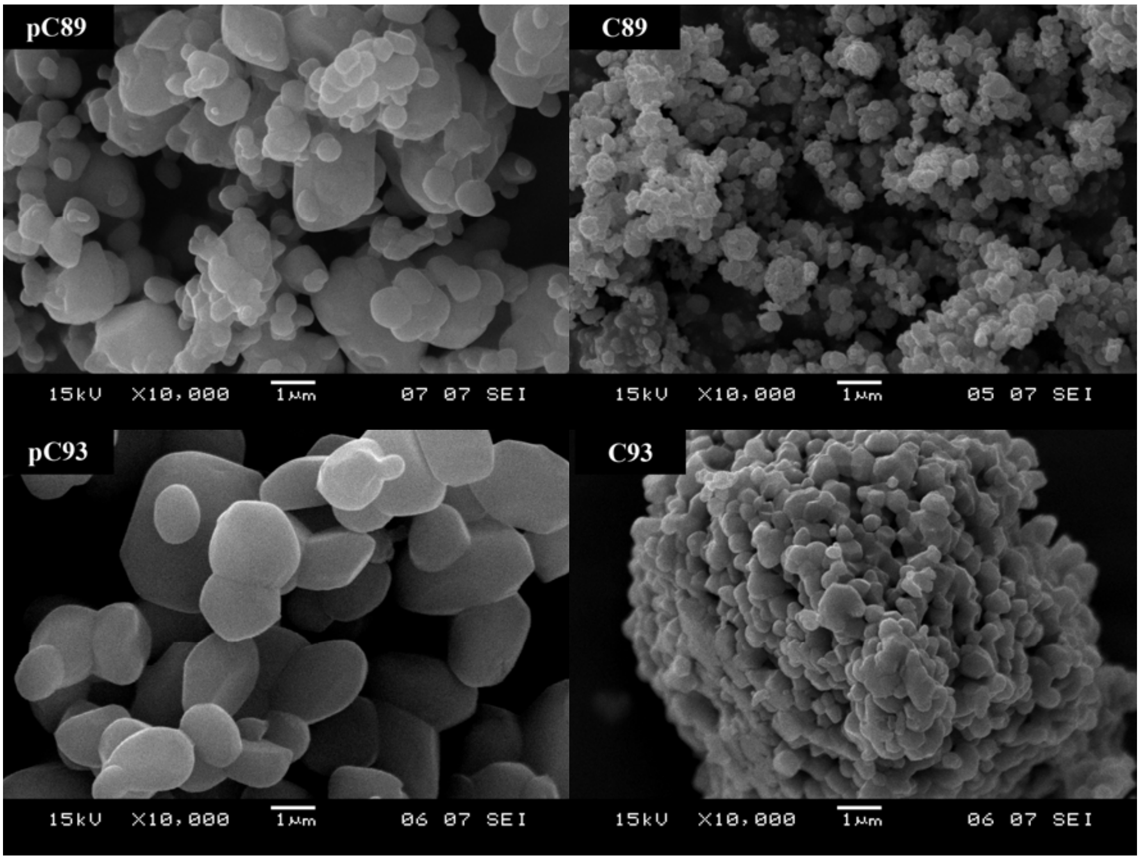

Fig. 3. SEM images of precursors Zn(DDTC)$_2$ (left) and calcination products ZnS (right) prepared using SimAdd (up) and SeqAdd (down) precipitation routes.

Zn(SDDTC)$_2$ powder obtained with SimAdd method (pC89) is more heterogeneous in comparison with the precursor obtained using the SeqAdd precipitation route (pC93), but particle dimensions are smaller. Similarly, the ZnS powders obtained from SSMP prepared with SimAdd method (C89) consists in much smaller particles.

The photoluminescent emission spectra of the un-doped and Mn-doped zinc sulphide powders, ZnS and ZnS:Mn^{2+} samples, are depicted in Fig. 4. A relative strong emission in the green spectral domain (502-506 nm) is observed for the ZnS samples. This emission is probable due to the oxygen doping of zinc sulphide, resulting from the thermal dissociation of the oxygen containing precursor. ZnS:Mn^{2+} samples exhibit weak luminescent emission in the green spectral domain (O-doping). The very low emission intensity suggests that in this case, the manganese ions act as quenching species for the luminescence of the un-doped ZnS powders. The luminescence attenuation can be also related with the self-absorption of the emitted light, in correlation with the coloured manganese sulphide particles separated on powder particle surface. The quenching effect increases with the amount of manganese used for the precipitation of $Zn(DDTC)_2$ - $Mn(DDTC)_2$ precursor.

One can conclude that, in our experimental conditions, the SSMP powders obtained with sodium diethyldithiocarbamate are not favourable for the synthesis of efficient luminescent manganese doped zinc sulphide powders.

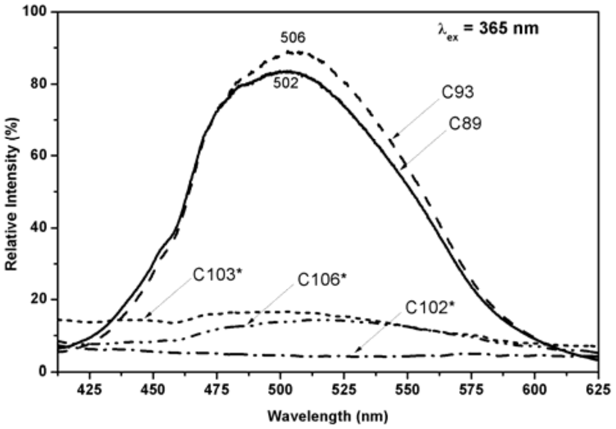

Fig. 4. PL spectra of un-doped ZnS powders C89 (SimAdd)and C93 (SeqAdd), and ZnS:Mn^{2+} powders C106 (0.1%Mn), C103(0.5%Mn) and C102(1.5% Mn);
** 10 time multiplied intensity.*

4. Conclusions

Luminescent under-micron of zinc sulphide were synthesised by the thermal decomposition of zinc diethyldithiocarbamate used as SSMP,, prepared using the reagent sequential addition technique (SeqAdd) and the reagent simultaneous addition technique (SimAdd).

The precipitation technique influences the thermal behaviour and particle morphology of SSMP and consequently, the particle size distribution and luminescence characteristics of ZnS powders generated by their thermal decomposition, in an inert atmosphere. SimAdd technique seems to be favourable to the synthesis of smaller ZnS particles. Both ZnS samples obtained from $Zn(DDTC)_2$ contain luminescence centres associated with oxygen impurities, originating from the oxygen-containing single-source molecular precursor.

In our experimental conditions, no efficient luminescent ZnS:Mn^{2+} powders could be obtained from the SSMP powders prepared with sodium diethyldithiocarbamate.

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