Materials Research Bulletin 84 (2016) 57–64

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Studies regarding ZnS:Mn nanopowders prepared from single source molecular precursor using microwave-assisted decomposition

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ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form 19 July 2016
Accepted 22 July 2016
Available online 25 July 2016

Keywords:
A. chalcogenides
B. solvothermal
B. luminescence
C. thermogravimetric analysis (TGA)
C. X-ray diffraction

ABSTRACT

Nanocrystalline undoped and manganese doped zinc sulphide (ZnS) powders were prepared by microwave—assisted solvothermal decomposition of zinc-manganese diethyldithiocarbamate as single-source molecular precursor. The precursors are being obtained in aqueous solution, from sodium diethyldithiocarbamate and zinc-manganese acetate mixtures containing variable amounts of manganese. Complementary investigations such as: thermal analysis, X-ray diffraction, SEM and BET were used to characterize both the precursors and phosphors. After the solvothermal treatment, the specific surface area of the powders increases from 2.04 m^2/g to 154.5 m^2/g. Phosphor samples consist of small particles (~12 nm) which present a high tendency to form spherical agglomerations. Photoluminescence spectra show a dominant yellow emission peak at 568 nm accompanied by several weaker peaks. In this paper, we discuss about the manganese incorporation effect in ZnS lattice concerning the morpho-structural and luminescent characteristics of the samples.

1. Introduction

Nano-scale semiconductors have been extensively studied due to their novel properties generated from quantum confinement effect [1,2]. Quantum confinement effect changes both physical and chemical properties of nano-sized semiconductors with different shapes [3–5]. II–VI semiconductors occupy a prominent place in the study of nanomaterials and have various applications in optoelectronics [6,7].

Zinc sulfide (ZnS) is an important II–VI semiconductor with a wide band gap of 3.7 eV used in optoelectronics, photocatalysis, targeted drug delivery, biosensors, light emitting diodes [8–12]. ZnS can act as host lattice for various transitional or rare earth ions (Cu^+; Tb^{3+}, Eu^{3+}; Ni^{2+}; Co^{2+}; Mn^{2+}) because it has a large band gap that is enough to emit visible light without absorption and the efficient transport of high energy electrons [13–15].

The morpho-structural and luminescent characteristics of undoped or doped ZnS, strongly depend on the specific preparation method and the experimental conditions [16]. Therefore, ZnS nanoparticles with different shapes (nanorings, nanowires, nanorods) were obtained using thermal evaporation techniques, hydrothermal methods or thermal decomposition of single source molecular precursor [17–19]. On the other hand, ZnS particle size can be adjusted using a wide variety of surfactants or by changing the S^{2-}/Zn^{2+} ratio [20–23]. Labiadh et all proposed an aqueous route for the preparation of manganese doped ZnS nanoparticles which exhibits a gradual blue shift of luminescent emission from 595 nm to 570 nm as the synthesis conditions are changed [24].

The large majority of the synthesis methods lead to the cubic ZnS phase since it is stable at low temperature. Usually, the hexagonal phase is obtained at around 1020 °C [25]. Hexagonal ZnS is more desirable because the luminescent properties are greater than the cubic's phase [26]. Therefore, finding soft conditions for the synthesis of hexagonal ZnS phase becomes an important task for researchers. Tiwary et all, present a precipitation method followed by annealing of the cubic ZnS phase at 600 °C in order to obtain hexagonal-ZnS nanocrystal of 49 nm [27]. Other synthesis examples of hexagonal ZnS at relatively low temperatures involve prolonged processing [28,29]. The development of low temperature synthesis techniques such as solvothermal decomposition, ultrasound or microwave assisted techniques, represent opportunities for low temperature preparation of hexagonal ZnS [28–32].

The microwave assisted technique has been accepted as a promising method for high purity small inorganic particle

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http://dx.doi.org/10.1016/j.materresbull.2016.07.023
0025-5408/

production with narrow particle size distribution, which presents a short reaction time [33–35].

In this paper, we demonstrate an easy and fast low temperature (110 °C) route for large-scale synthesis of ZnS nanoparticle based on the combination of simultaneous addition of reagent and microwave-assisted technique. The synthesis uses single-source molecular precursors. The goal of this paper is to bring new understandings regarding the incorporation degree of manganese and its concentration effect on the phase composition and luminescent characteristics.

2. Experimental part

2.1. Materials and samples synthesis

Undoped zinc sulphide (ZnS) and manganese doped zinc sulphide (ZnS:Mn) nanopowders were prepared by microwave-assisted solvothermal decomposition of zinc diethyldithiocarbamate—$Zn(DDTC)_2$ and zinc-manganese diethyldithiocarbamate—$(Zn,Mn)(DDTC)_2$ as single-source molecular precursors (coded as SSMP). The synthesis involves two stages namely: (1) preparation of SSMP and (2) solvothermal decomposition of SSMP.

(1) Preparation of SSMP

The synthesis of SSMP was done using a wet-chemical synthesis route named "the reagent Simultaneous Addition technique" (SimAdd), developed in our research group in order to prepare micro and nano-phosphors [36–38].

$Zn(DDTC)_2$ and $(Zn,Mn)(DDTC)_2$ powders were prepared based on the precipitation reaction between zinc acetate or zinc-manganese acetate and sodium diethyldithiocarbamate (Na-DDTC) at room temperature. The starting reagents are: $Zn(CH_3COO)_2{\cdot}2H_2O$ (Merck), $Mn(CH_2COO)_2{\cdot}4H_2O$ (Merck), $C_5H_{10}NS_2Na{\cdot}3H_2O$ (Austranal-Praparate).

The SimAdd method consists in the simultaneous addition of equal volumes of Zn or Zn-Mn acetates (0.25 M) and Na-DDTC (0.5 M) into a diluted bottom solution of acetates (0.025 M) under continuous stirring. The precipitates were washed with double distilled water, filtered and dried at 100 °C, under low vacuum.

(2) Solvothermal decomposition of SSMP

$Zn(DDTC)_2$ and $(Zn,Mn)(DDTC)_2$ powders were dispersed in ethylene glycol (Lach-Ner) and introduced in an Anton PaarSynthos 3000 system. The suspensions were heated for 10 min at 110 °C by microwave irradiation (800W). Thus obtained yellow-orange colloidal solution was allowed to cool for 30 min. The white coloured powders separated by centrifugation were washed with absolute methanol (Penta) and dried at 60 °C.

Several precursors were prepared to obtain phosphors with the general formula $Zn_{1-x}Mn_xS$ ($x = 0.001 \div 0.15$) in order to study the influence of the manganese concentration on the morpho-structural and luminescent characteristics of $ZnS:Mn^{2+}$ nano-powders. The possible reactions during the synthesis process take place in two different stages:

1) Preparation of precursors by simultaneous addition technique:

$$(1-x)Zn(CH_3COO)_2 + xMn(CH_2COO)_2 + 2Na(C_2H_5)_2NCS_2 \rightarrow Zn_{1-x}Mn_x[(C_2H_5)_2NCS_2]_2 + 2CH_3COONa$$

2) Preparation of phosphors by solvothermal decomposition:

$$Zn_{1-x}Mn_x[(C_2H_5)_2NCS_2]_2 \xrightarrow{C_2H_6O_2/T(^\circ C)} Zn_{1-x}Mn_xS + CS_2 + (C2H_5)_2NH + C_2H_5NCS + C_2H_4$$

2.3. Characterisation of samples

The thermal behaviour of the materials was evaluated based on thermal analysis (TG-DTA) and evolved gas analysis (EGA) carried out with a THERMO SCIENTIFIC NICOLET™ 6700 FT-IR spectrometer coupled with a METTLER-TOLEDO TGA/SDTA851 (heating rate 5 °C/min, nitrogen flow 40 ml/min).

Specific surface area and porosity measurements were made on decontaminated samples of any traces of moisture or other adsorbents, using a Micromeritics, TriStar II 3020—Surface Area and Porosity Analyzer. Adsorption—desorption isotherms were measured close to the boiling point of nitrogen (77 K). Gas pressure was gradually increased to the saturation value, when condensation of the adsorbate (N_2) occurs into the powder pores.

The size and morphology of the samples were revealed by electron microscopy scanning (SEM) using an JEOL–JSM 5510LV electron microscope (accelerating voltage of 15 kV, Au-coated powders).

Structure and microcrystalline parameters were evaluated based on X-ray diffraction (XRD) performed using a BRUKER D8 Advance X-ray diffractometer (40 kV and 40 mA, goniometer equipped with a germanium monochromator in the incident beam, step-scanning $\Delta 2\theta = 0.01^\circ$, $\lambda_{CuK\alpha 1} = 1.54056$ Å). The crystalline phases were retrieved after a semi-automatic peak search routine using the Joint Committee on Powder Diffraction Standards (JCPDS) data base.

Luminescent characteristics of phosphors were evaluated based on emission spectra registered with JASCO FP-6500 spectrofluorimeter Wavell, equipped with PMT R928 photomultiplier (glass filter UG1 ReichmannFeinoptik). In order to compare the emission intensities, the sample with the most intense emission was used as internal standard ($I_{em} = 100\%$).

The chemical analysis of $ZnS:Mn^{2+}$ powders was carried out from hydrochloric solutions, by inductively coupled plasma optical emission spectrometry (ICP-OES), using a PERKIN ELMER OPTIMA 2100 DV spectrometer. The manganese and zinc detection was made at 257.61 nm (detection limit 0.4 μg/L) and 206.20 nm (detection limit 1.0 μg/L), respectively.

3. Results and discussion

3.1. Thermal characterisation of samples

Thermal analysis gives information regarding the transformations that occur during the thermal treatment from 25 °C to 1100 °C. Fig. 1 presents the TG, DTG and DTA curves of precursor and corresponding undoped ZnS phosphor.

When the precursor is heated up to 500 °C in nitrogen atmosphere, the TG curve shows one single-step decomposition with a total mass loss of 82.3% and maximum situated at 326 °C. The thermal effects during the heating process are revealed by DTA curve, which exhibits two strong endothermic peaks, corresponding to the melting of the zinc ditiocarbamate at 182 °C and its thermal decomposition at 329 °C.

Because the mass loss (82.3%) is higher than the theoretical value (73.0%), it is supposed that the strong thermal dissociation causes the dispersion of precursor particles and a part of them are carried out by the evolved gases. In comparison, undoped zinc sulphide has a total mass loss of 27.2% which occurs in several small decomposition stages, associated with the removal of: physically adsorbed methanol (55 °C); physically adsorbed ethylene-glycol (278 °C); chemically bonded organic components on the surface (278 °C ÷ 700 °C). When the temperature reaches 940 °C, one can see an abrupt mass loss associated with volatilization of zinc sulfide. Excepting the endothermic peak (onset 940 °C) no other thermal effects are observed on the DTA curve (Fig. 1b).

According to the thermal analysis results, ZnS sample still contains methanol (1.7%), ethylene-glycol (7.3%) and other organic components (8.3%).

Evolved gas analysis provides additional information regarding the thermal stability of the precursors and it is used to identify the