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SYNTHESIS AND CHARACTERIZATION THE SULPHIDES TYPE $ZnS_{(1-x)}MS_x$

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Abstract

$ZnS_{(1-x)}MS_x$(x=0.01 and M=Mn^{2+}, Cu^{2+} and Eu^{2+}) compounds have been obtained by precipitation from homogeneous solutions of zinc, copper, manganese and europium salts, with S^{2-} as the precipitating anion, formed by the decomposition of thioacetamide. The thermal study of the milled zinc acetate, thioacetamide, copper acetate, manganese acetate and europium nitrate, respectively, was studied for thermal analyis TG/DSC. XRD respect exhibits a zinc blend crystal structure.

Keywords: decomposition, thioacetamide, zinc sulfide

Introduction

Metal sulfides show novel optical and electrical properties, and some of them are used for the fabrication of devices. A variety of methods can be used to prepare the semiconductor metal sulfide nanoparticles, such as direct element reaction in a quartz vessel at high temperature [1, 2], ball mill solid-state metathesis reaction [3], the chemical deposition method [4], Spray pyrolysis [5–6], Combustion regime [7].

A new kind of luminescence material-doped semiconductor has been the focus of the research. ZnS is a good host because of its large band gap (E_g~3.6 eV). It has been used commercially as a phosphor and a thin film electroluminescent device, especially if doped with transition metals or rare earth ions acting as luminescent centers [8]. In 1994 Bhargava *et al*. [9] gave the first report on the luminescence properties of Mn-doped ZnS nanocrystals. These spectacular results suggested that doped semiconductor nanocrystals form a new class of luminescent materials, with a wide range of applications, in displays, lighting and lasers [10]. Since the work of Bhargava *et al.*, there have been few reports on investigating photoluminescence properties of Mn-doped ZnS nanocrystals [10] and Cu-doped ZnS nanocrystals [11–13] prepared by using different techniques.

This work reports the preparation, characterization and thermal stability of Cu-doped ZnS, Mn-doped ZnS and Eu-doped prepared by precipitation from homogeneous solutions of zinc, copper, manganese and europium salts, with S^{2-} as the precipitating anion formed by the decomposition of thioacetamide.

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Experimental

Zinc sulfide nanoparticles doped with Mn^{2+}, Cu^{2+} and Eu^{2+} were prepared by precipitation from homogeneous aqueous solutions of zinc, copper, manganese and europium salt compounds, with S^{2-} as precipitating anion formed by the decomposition of thioacetamide (TAA). The precipitation of doped ZnS nanoparticles was performed starting from homogeneous solutions of zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$], copper acetate [$Cu(CH_3COO)_2 \cdot 2H_2O$], manganese acetate [$Mn(CH_3COO)_2 \cdot 2H_2O$] and europium nitrate [$Eu(NO_3)_3 \cdot 6H_2O$] at 0.5 M and TAA at 0.5 M for each precipitation reaction. The reaction temperature was fixed at 353 K, and the solutions were acidified (pH=2) to control the decomposition of TAA that generated the sulfide anions. The precipitated doped ZnS nanoparticles were washed with water to eliminate TAA, and were washed with isopropyl alcohol. The cleaned powders were dried for about 10 h at 353 K until the complete evaporation of the solvent was achieved. Afterwards, the powder was heated in an oven EDS at 673 K for 4 h and 873 K for 4 h. The influence heated temperature of $ZnS_{(1-x)}MS_x$ has been investigated using XRD. Thermogravimetric curves were obtained on a Shimadzu 50-H at a heating rate of 10 K min^{-1} in nitrogen flowing at a rate of 50 cm^3 min^{-1}. DSC curves were obtained using a Shimadzu 50 in N_2 atmosphere (heating rate 10 K min^{-1} and gas flow of 50 cm^3 min^{-1}). X-ray powder diffraction (XRD) patterns were recorded using a Shimadzu X-ray diffractometer CuK_α irradiation (=1.5418 Å). The distribution of particles was measured using CILAS-1064 laser granulometer with ultrasonic treatment in pure water for 120 s.

Results and discussion

XRD patterns of the samples are shown in Fig. 1. It reveals that the doped ZnS phase obtained 353 K and heating at 673 K respect exhibit a zinc blend crystal structure.

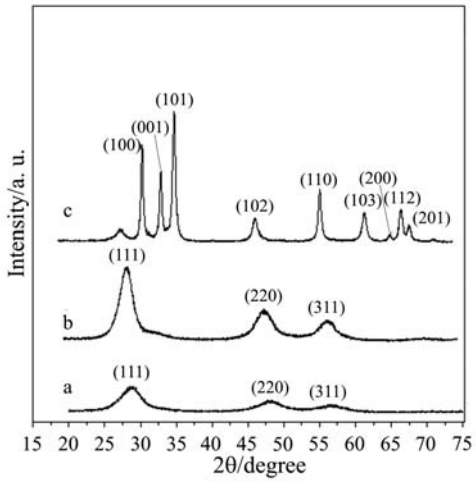

Fig. 1 XRD patterns of doped ZnS prepared at a – 353 K, b – heated at 673 K and c – 873 K for 4 h, respectively

The three diffraction peaks correspond to (111), (220) and (311) planes of the cubic crystalline ZnS (β-ZnS), respectively. The patterns of Fig. 1 of the samples the doped ZnS heating at 873 K for 4 h exhibit the lines of ZnO phases.

To provide more information on the mechanism of the formation of ZnS nanoparticles, we carried out a thermal study of the mixture of milled acetate zinc, copper acetate, manganese acetate, europium nitrate and thioacetamide. The corresponding DSC curve shown in Fig. 3, two endothermic peaks can be observed accompanied by a small mass loss about 18.27% and 16.26% in the TG curve shown in Fig. 2, respectively. The first endothermic peak at 393 K probably corresponds to the melting of thioacetamide (melting point 380.5 K), and corresponds to the vaporization of acetic acid (boiling point 391.7 K). Other small volatile components and the ZnS nanoparticles formed during these processes since the reaction of formation of ZnS takes place at 353 K. As for the small endothermic peak at 637.04 K accompanied by a small mass loss about 16.26%, the mechanism is not clear. We suspect it may represent the decomposition of a by-product and the formation ZnO [14]. The reaction may be described as follows:

$$Zn(CH_3COO)_2+salts+CH_3CSNH_2 \rightarrow ZnS_{(1-x)}MS_x+CH_3COOH+by\text{-}product$$

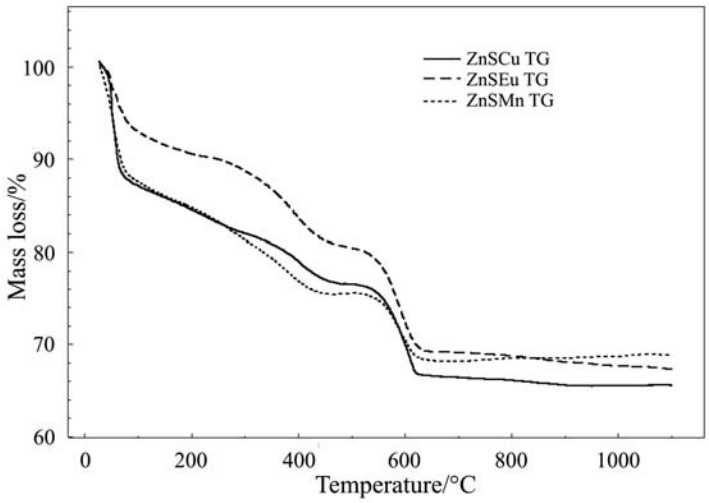

Fig. 2 TG curves of the mixture of the thioacetamide, zinc acetate, copper acetate, manganese acetate and europium nitrate, respectively

The particle size distribution of the sample is shown in Fig. 3. The average particle size is about 2.64 μm. From Fig. 3, it can be seen that particle sizes ranged from 0.1 to 10 μm, and the largest percentage is in the size range of 1.0 to 8.0 μm, this reveals that the size distribution was relatively narrow.

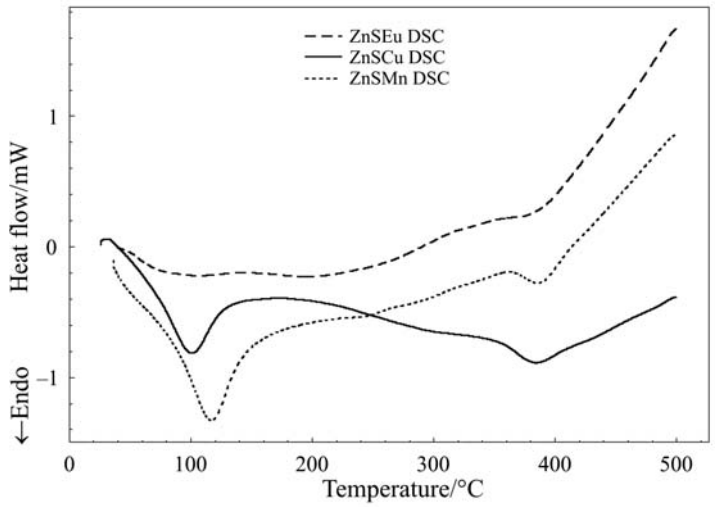

Fig. 3 DSC curves of the mixture of the thioacetamide, zinc acetate, copper acetate, manganese acetate and europium nitrate, respectively

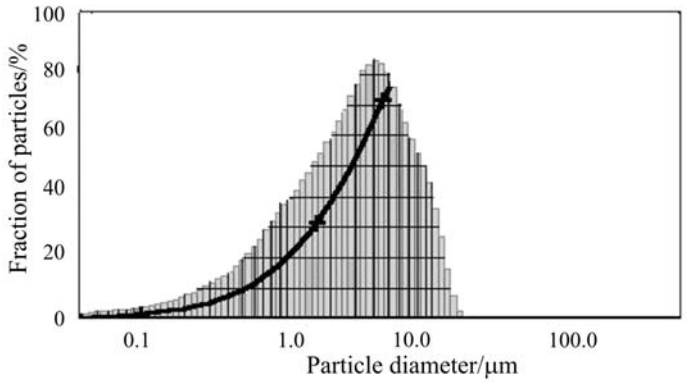

Fig. 4 Particle size distribution of doped ZnS obtained at 353 K

Conclusions

Doped ZnS with cubic phase was prepared at low temperature by precipitation from homogeneous aqueous solutions of zinc, copper, manganese and europium salt compounds, using thioacetamide as sulfur sources. The three diffraction peaks of the doped ZnS in Fig. 1 correspond to (111), (220) and (311) planes of the cubic crystalline ZnS (β-ZnS), respectively. The samples of the doped ZnS present good uniformity in the size. The synthesis method is applicable for the synthesis of a wide range of metals sulfide. Moreover, it has significant potential for a large scale production due to its high efficiency and the low cost process. Due to the promising perspectives, investigations on this class of materials are beginning to be carried out by the method described in this work.

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