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Properties of mechanochemically synthesized nanocrystalline Bi_2S_3 particles

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ABSTRACT

Nanocrystalline Bi_2S_3 particles have been synthesized from Bi and S powders by high-energy milling in a planetary mill. Structural and microstructural characterization of the prepared particles, including phase identification, specific surface area measurement and particle size analysis has been carried out. The optical properties were measured by spectroscopic methods and the structural stability up to 500 °C was studied by thermal analysis. The production of orthorhombic Bi_2S_3 with crystallite size of about 26 nm was confirmed by X-ray diffraction. The nanocrystals tend to agglomerate due to their large specific surface area. Accordingly, the average hydrodynamic diameter of the mechanochemically synthesized particles is 198 nm. EDS analysis shows that the synthesized material is pure Bi_2S_3. The band gap of the Bi_2S_3 nanoparticles is 4.5 eV which is wider than that in bulk materials. The nanoparticles exhibit good luminescent properties with a peak centered at 490 and 390 nm. Differential scanning calorimetry curves exhibit a broad exothermic peak between 200 and 300 °C, suggesting recovery processes. This interpretation is supported by X-ray diffraction measurements that indicate a 10-fold increase of the crystallite size to about 230 nm. The controlled mechanochemical synthesis of Bi_2S_3 nanoparticles at ambient temperature and atmospheric pressure remains a great challenge.

1. Introduction

The synthesis of one-dimensional (1D) nanostructured metal chalcogenides has been the focus of attention because of their important physical and chemical properties, as well as their applications in semiconductors, pigments, luminescence devices, solar cells, IR detectors, and thermoelectric devices.

Bismuth sulphide, Bi_2S_3 is known to be attractive material for photoelectrochemical applications as it has a reasonably narrow band gap (E_g=1.3 eV) and a reasonable incident photon to electron conversion efficiency. Bi_2S_3 is also a promising semiconductor material for applications in photovoltaic cells and thermoelectric cooling technologies because of its environmental compatibility.

Conventionally, Bi_2S_3 is prepared by methods such as direct reaction of bulk bismuth with sulphur vapour in a quartz vessel [1] and thermal decomposition of various precursors [2]. In these methods, high temperature is required and the final products always contain some impurities [3]. In the recent years, Bi_2S_3 nanowires,

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nanotubes, nanoflowers and nanorods have been synthesized by several groups. Methods such as solvothermal, sonochemical, and hydrothermal processes, microwave irradiation, photochemical synthesis, and electrodeposition have been reported for fabricating Bi_2S_3 nanostructures [4–9].

High-energy milling has been used to synthesize various nanocrystalline chalcogenides [10–15]. We have already published the paper dealing with the synthesis and kinetics of mechanochemical synthesis of Bi_2S_3 nanoparticles by high-energy milling [16]. However, this paper is focused on the study of structural, surface, optical and thermal properties of mechanochemically synthesized Bi_2S_3 particles from the point of view of the possible application of the such as-synthesized Bi_2S_3. The controlled mechanochemical synthesis of nanocrystalline Bi_2S_3 at ambient temperature in the absence of a solvent is still a great challenge.

2. Experimental

Mechanochemical synthesis of Bi_2S_3 was performed in a planetary ball mill (Pulverisette 6, Fritsch, Germany) starting from powders of bismuth (99.5%, Aldrich, Germany) and sulphur (99%, Ites, Slovakia) in an argon atmosphere, according to the reaction

$$2Bi + 3S \rightarrow Bi_2S_3 \quad (1)$$

The reaction is thermodynamically possible, as the enthalpy change is negative, $-\Delta H_{298}{}^{\circ} = 176.6$ kJ/mol [17].

The milling was performed in a 250-mL tungsten carbide milling chamber with 50 tungsten carbide balls, 10 mm in diameter. The rotational speed of the planet carrier was 500 rev/min. The powder charge was 4.06 g Bi and 0.94 g S, corresponding to the stoichiometry of Eq. (1). The milling time was 60 min and the mill was operated at room temperature.

X-ray diffraction (XRD) measurements were carried out using a D8 Advance diffractometer (Bruker, Germany) equipped with a θ/θ goniometer, Cu $K\alpha$ radiation (40 kV, 40 mA), secondary graphite monochromator and scintillation detector. For the data treatment and analysis the commercial Bruker processing tools have been used. Concretely, for the phase identification the Diffrac plus Eva and for the Rietveld analysis and microstructure characterization the Diffrac plus Topas software have been utilized. The crystalline size was estimated by "double-Voight" method, using the integral breadth, since this characteristic is the most comparable to values observed by TEM.

The specific surface area was determined by the low temperature nitrogen adsorption method in a Gemini 2360 sorption apparatus (Micromeritics, USA).

Particle size analysis was carried out employing a Nanophox particle sizer (Sympatec, Germany) using the photon cross correlation spectroscopy method. The light source is a build-in He–Ne laser with a maximum output of 10 mW at the wavelength of $\lambda = 0.6328$ μm. The sample was dispersed in water, ultrasonically de-agglomerated after sedimentation and the spectrum from the fine particles present in the liquid was taken. The measured results were processed with the Windox 5 software.

The morphology, microstructure and composition of the sample were analyzed using LEO 1550 field emission scanning electron microscope (Zeiss, Germany) and TECNAI G2 F30 STEM FEG, field emission scanning-transmission electron microscope, operating at 300 kV, coupled with an energy dispersive spectrometer EDS INCA detector spectrometer. The sample was sufficiently conductive, thus it is not coated with any conductive material in order to avoid charging artefacts.

A small quantity of the powder sample was suspended in acetone and droplets of the suspension were deposited on carbon-coated copper grids for the SEM and TEM (HRTEM) analysis.

Optical studies were carried out using UV–vis spectrophotometer Helios Gamma (Thermo Electron Corporation, Great Britain) in quartz cell by dispersing of synthesized particles in absolute ethanol by ultrasonic stirring.

The photoluminiscence (PL) spectra at room temperature were acquired at right angle on a photon counting spectrofluorometer PC1 (ISS, USA) in the range 370–500 nm with an excitation wavelength of 325 nm. A 300 W xenon lamp was used as the excitation source. The emission is collected in a 25 cm monochromator with resolution of 0.1 nm equipped with a photomultiplier. For measuring the PL intensity, the nanopowders were dispersed in absolute ethanol.

Calorimetric measurements were carried out in a SETARAM differential scanning calorimeter DSC-111 with a sensitivity of 1 mV/s. Samples of 6 to 8 mg were used and subsequently heated under a nitrogen atmosphere from ambient temperature to 500 °C, at a rate of 10 °C/min. An empty crucible was used as a reference sample.

3. Results and discussion

The progress of the mechanochemical synthesis of Bi_2S_3 is illustrated by XRD patterns of the mixture of Bi+S precursors (a) and sample taken after 60 min of milling (b) (Fig. 1). In the starting material (pattern a) only peaks belonging to Bi metal (JCPDS 77-7112) and S (JCPDS 78-1888) are seen. The mechanosynthesized Bi_2S_3 (bismuthinite) has orthorhombic structure (space group 62, *Pnma*), with refined lattice parameters $a = 11.3008$ Å, $b = 3.9855$ Å, $c = 11.1439$ Å. The estimated average crystallite size is $D = 26$ nm. The process is rather straightforward, with Bi_2S_3 (JCPDS-74-9437) being the only solid product (pattern b). The kinetics of the mechanochemical synthesis was studied in paper [16].

The specific surface area of the mechanochemically synthesized Bi_2S_3 nanoparticles is 1.7 m^2/g. This value is about 30 times higher than the corresponding value of the starting Bi+S mixture ($S_A = 0.06$ m^2/g). Particles in the nanometer size range have a strong tendency to agglomerate due to their relatively large specific surface area.

The particle size distribution of the nanocrystalline Bi_2S_3 particles was characterized by photon cross correlation spectroscopy as shown in Fig. 2. The size of the particles is rather uniform with an average hydrodynamic