Advanced Powder Technology xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Mechanochemical synthesis, structural, magnetic, optical and electrooptical properties of $CuFeS_2$ nanoparticles

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ARTICLE INFO

Article history:
Received 12 October 2017
Accepted 16 April 2018
Available online xxxx

Keywords:
$CuFeS_2$
Mechanochemical synthesis
Structural properties
Magnetic properties
Optical properties

ABSTRACT

The rapid mechanochemical synthesis of nanocrystalline $CuFeS_2$ particles prepared by high-energy milling for 60 min in a planetary mill from copper, iron and sulphur precursors is reported. The $CuFeS_2$ nanoparticles crystallize in tetragonal structure with mean crystallite size of about 38 ± 1 nm determined by XRD analysis. HRTEM study also revealed the presence of nanocrystals with the size of 5–30 nm with the tendency to form agglomerates. The Raman spectrum confirms the chalcopyrite structure. Low temperature magnetic data for $CuFeS_2$ support the coexistence of antiferromagnetic and paramagnetic spin structure. Moreover, the hysteresis loops taken at temperatures from 5 K to 300 K revealed a presence of very small amount of ferromagnetic phase, which seems to be associated with the non-consumed elemental Fe in as-prepared nanoparticles. The optical band gap of $CuFeS_2$ nanoparticles has been detected to be 1.05 eV, larger than band gap of the bulk material. The wider gap possibly resulted from the nanosize effect. Photoresponses of $CuFeS_2$ nanoparticles were confirmed by I-V measurements under dark and light illumination. It was demonstrated that mechanochemical synthesis can be successfully employed in the one step preparation of nanocrystalline $CuFeS_2$ with good structural, magnetic, optical and electrooptical properties.

1. Introduction

Ternary chalcogenides containing elements, such as sulphur, and selenium exhibit semiconducting properties after bonding with transition metal elements [1]. Recently, these compounds are being extensively studied due to their important physical and chemical properties and promissing applications in solar cells, spintronic and thermoelectric devices, etc. [2–5].

Bulk chalcopyrite $CuFeS_2$ is a typical magnetic semiconductor of the ternary chalcogenide family with unusual optical, electrical and magnetic properties. It has a very small optical energy band gap (0.5–0.6 eV), while nanoparticles of $CuFeS_2$ have a larger band gap depending on their size. It is antiferromagnet with a relatively high Néel temperature of 823 K. The structure can be regarded as double sphalerite cell with an ordered arrangement of Cu and Fe ions in the lattice that are in tetrahedral coordination with sulphur [6].

Nanoparticles and nanocrystals of chalcopyrite $CuFeS_2$ have been recently synthesized by various methods, such as mechanical alloying combining with spark plasma sintering [7], thermal pyrolysis [8], conventional synthesis using single-source precursors [9], facile solution-based method [6,10], cyclic microwave-assisted synthesis [11], thermolysis based wet chemical method [12], etc.

The mechanochemical synthesis has been recognized as an alternative non-conventional method which provides at room temperature an efficient one-step and facile access for preparation of nanomaterials [13]. Using high-energy milling it is also possible to perform reactions which otherwise need supply a large quantum of energy for their proceeding [14].

The nanocrystalline non-stoichiometric $CuFeS_2$ synthesized using high-energy milling for 180–300 min from the nanocrystalline mixture of CuS and FeS_2 has been already performed [15]. $CuFeS_2$ as the final product contained a small amount of FeS_2 phase. In this work, we have reported exhaustive description of

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https://doi.org/10.1016/j.apt.2018.04.018

the preparation of this material by high-energy milling only for 60 min from the metals as precursors. The structural, magnetic, optical and electrooptical properties were investigated studied in detail.

2. Experimental

Nanocrystalline $CuFeS_2$ particles were synthesized in a planetary ball mill Pulverisette 6 (Fritsch, Germany) from 1.73 g of copper (99.7%, Merck, Germany), 1.52 g of iron (extra pure, Merck, Germany) and 1.75 g of sulphur (99%, Ites, Slovakia) in an argon atmosphere, according to the reaction (Eq. (1))

$$Cu + Fe + 2S \rightarrow CuFeS_2 \quad (1)$$

The milling was carried out at 550 rpm using a tungsten carbide milling chamber (250 ml in volume) and 50 balls (10 mm in diameter), composed of the same material, during 5–120 min.

The XRD data were collected using a D8 Advance diffractometer (Bruker, Germany) with a θ/θ goniometer, working with a CuK_α radiation. The data were collected over the angular range 20° < 2 theta < 85° with scanning steps of 0.03° and the measurement step time interval of 6 s. For the data processing, the commercial Bruker tools have been used. For the phase identification, the Diffrac^{plus} Eva and the ICDD PDF2 database and for Rietveld analysis, the Diffrac^{plus} Topas software have been applied.

The zeta-potential (ZP) was measured using a Zetasizer Nano ZS (Malvern, Great Britain). The Zetasizer Nano measures the electrophoretic mobility of the particles, which is converted to the zeta potential by using the Helmholtz-Smoluchowski equation built in the Malvern zetasizer software. The zeta potential was measured in the original dispersion medium and the measurements were repeated three times for each sample.

Elemental sulphur determination was done according below given the procedure. Two grams of sample were placed inside a thick filter paper thimble, which was loaded into the main chamber of the Soxhlet extractor. The Soxhlet extractor was placed onto a flask containing 50 ml of extraction solvent (CS_2, Acros Organics, Belgium). The Soxhlet was then equipped with a condenser. The solvent was heated to reflux. When the Soxhlet chamber was almost full, the chamber was emptied, with the solvent running back down to the distillation flask. This cycle was repeated three times. After extraction the solvent was removed by rotary evaporator, yielding the extracted compound. After weighting the extracted sulphur, the percentage of elemental sulphur in the sample was calculated according the equation (Eq. (2)):

$$S^0\,(\%) = \left(\frac{m_2 - m_1}{m_s}\right) \times 100 \quad (2)$$

where m_2 is a mass of distillation flask after extraction, m_1 is a mass of distillation flask before extraction and m_s is a mass of the sample.

The Micro-Raman measurements were conducted at room temperature in air, with the focus of the beam of an Ar laser (514 nm) using a confocal Raman Microscope (Spectroscopy & Imaging, Germany).

The magnetic measurements were performed by Magnetic Property Measuring System, model MPMS-XL-5 (Quantum Design, USA) equipped with 5 T superconducting magnet.

The granulometric analysis was realized by photon cross-correlation spectroscopy (PCCS) using a Nanophox particle size analyzer (Sympatec, Germany).

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

Transmission electron microscopy (TEM) images and semi quantitative analysis were taken on a 300 kV TECNAI G2 F30 S-twin high-resolution transmission electron microscope (HRTEM) working at 300 kV.

The ultraviolet–visible (UV–Vis) spectrum was taken by a UV–Vis spectrophotometer Helios Gamma (Thermo Electron Corporation, Great Britain).

The micro PL spectra were measured by a UV–Vis-NIR confocal Raman Microscope (Spectroscopy & Imaging, Germany). The excitation at 514 nm was provided using an Ar laser.

The Current-Voltage (I-V) characteristics were measured using semiconductor parameter analyzer Agilent 4155C under dark and white light illumination. The measured sample was separated from crushing pellets to small pieces (thin stripe with dimensions ~200–500 μm) and transferred onto insulating pad. The sample contacts were made by small droplet of silver paste and then annealed together with wiring to the socket. For photocurrent measurements the standard halogen lamp, monochromator and lock-in measurement system between 350 and 1000 nm were utilized.

3. Results and discussion

The progress of the mechanochemical synthesis of $CuFeS_2$ is illustrated by XRD patterns of samples taken after 5–120 min of milling (a-f) (Fig. 1). In the starting material (pattern a) the peaks of Cu (JCPDS 01-089-2838), Fe (JCPDS 03-065-4899) and S (JCPDS 01-083-2283) are seen, while patterns (b-d) represent intermediate states with different ratios of the initial and product phases. After 5 min (b) of milling copper sulphide CuS (JCPDS 03-065-3556) is first formed as intermediate product, while a considerable amount of iron and sulphur remains unreacted. After 15 min (c) of milling there is still a small amount of CuS as well as unreacted Fe present. After 30 min (d) of milling the intermediate CuS phase has almost disappeared. The product phase of $CuFeS_2$ is dominant and only traces of iron are observed. The mechanochemical reaction is completed after 60 min of milling (e). The product was identified as chalcopyrite (JCPDS 037-0471). All the diffraction lines (1 1 2), (2 2 0) and (3 1 2) match well to the JCPDS card of chalcopyrite $CuFeS_2$. The crystal structure has a tetragonal body-centered symmetry belonging to the I42d space group with lattice parameters $a = b = 5.293$ Å and $c = 10.437$ Å. The shape of the peaks indicates that the particles are in nano range and well crystallized. The crystallite size calculated by Rietveld analysis was 38 ± 1 nm. The estimated microstrain is (ε_0 0.35), what points to the presence of defects and distortions in the forming phase. It is noted that no significant change, was observed either in the lattice parameters or in the microstrain after 120 min (f) of milling.

The results from the zeta potential (ZP) measurements of $CuFeS_2$ samples are shown in Fig. 2. The ZP values were recorded in a pH range from 3 to 12. In the case of $CuFeS_2$ milled for 5 min in the pH range 3–5, the ZP values were around 0 mV, which indicate, that the particles with positive and negative ions on their surface are in balance and the Cu, Fe and S elements exist in a sample in unreacted state. In a pH = 6, the sharp increase of ZP to positive value (+30 mV) was registered, which is related with the presence of Fe^{2+} ions originated from iron particles and their transfer into the solution as a consequence of dissolution. With further increasing pH, the particles tend to acquire negative values (up to −43 mV), which is a sign of sulphate and iron hydroxides formation. Two isoelectric points (IEP) were reached, at pH 5.02 and 7.0. In the case of $CuFeS_2$ milled for 15 min, the ZP values are more positive in almost entire pH range in comparison to $CuFeS_2$ milled for 5 min. According to XRD measurements, this shift could be connected with the partial formation of CuS and thus with prevailing Fe^{2+} ions in solution originated from unreacted iron particles presented in a sample. The IEP was established at pH 7.18. Above this

Please cite this article in press as: E. Dutková et al., Mechanochemical synthesis, structural, magnetic, optical and electrooptical properties of $CuFeS_2$ nanoparticles, Advanced Powder Technology (2018), https://doi.org/10.1016/j.apt.2018.04.018