

Preparation of flower-like PbS nano-structures using cyclic microwave radiation

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Flower-like PbS nano-structures were successfully prepared from different mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$ in propylene glycol, using the cyclic process of 600 W microwave power for 15 minutes. PbS (cubic) was detected using X-ray diffraction (XRD) and selected area electron diffraction (SAED). The experimental and simulated patterns are in good accord. A Raman spectrometer revealed the presence of vibrations at 134, 275 and 431 cm^{-1} . Flower-like PbS nano-structures were also characterized using a scanning electron microscope (SEM) and a transmission electron microscope (TEM), although the products were prepared using different mole ratios of the starting agents.

Key words: Cyclic microwave radiation, Flower-like PbS nano-structures.

Introduction

Generally, different morphologies of luminescent materials have an influence on their properties [1]. Preparation of such materials is now increasingly important. PbS is a material which has a small band gap (0.41 eV) and large exciton Bohr radius (18 nm) [2-4]. It has novel semiconducting and optical properties [5], which are very sensitive to a quantum-size effect [2, 3]. There are different nano- and micro-structures of PbS that have an influence on its properties. Among them are nanocubes [6], nanoparticles [7], dendrites [6, 8], star-shapes [9], flower-like crystals [10], nanotubes [11] and nanorods [11, 12]. They can be prepared by different methods, such as microwave radiation [10], a hydrothermal process [4], solvothermal synthesis [6], electroless chemical deposition [13] and a sonochemical process [11].

Microwave radiation [14] is a very attractive method used for preparing materials. It is able to reduce time scales of the reactions, and accelerate the reaction process. When microwave radiation is supplied to chemicals, one or more of them is capable of coupling with the radiation. This can lead to a high temperature faster than that achieved by a conventional method. Microwave radiation can solve the problems of temperature and concentration gradients. By focusing large amounts of microwave radiation into solutions, the vibrating electric field applies a force on charged particles which vibrate accordingly. Vibrations of the reactants have an influence on the reaction to proceed with efficiency. Subsequently, pure product is produced.

At present, there are a few reports on the preparation

of flower-like PbS using microwave radiation. For the present research, flower-like PbS nano-structures were prepared from different mole ratios of Pb and S sources, using a cyclic microwave radiation. The final products were then analyzed for further discussion.

Experiment

Flower-like PbS particles were prepared from 1 : 4, 1 : 1 and 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$ in propylene glycol, using 600 W microwave power for 15 minutes. The process was repeated many times and always happened in the same order. For every 100 s, microwave radiation was on for 30 s and off for 70 s. At the conclusion of the test, the products were washed with water and ethanol, and dried at 80 °C for 12 h. The final products were characterized using an X-ray diffractometer (XRD) operated at 20 kV, 15 mA and using $\text{Cu K}\alpha$ radiation in the 2θ angular range of 15-60 degrees, a Raman spectrometer using a 50 mW Ar laser with $\lambda = 514.5\text{ nm}$ at room temperature, a scanning electron microscope (SEM) operated at 15 kV and a transmission electron microscope (TEM) as well as the use of the selected area electron diffraction (SAED) technique operated at 200 kV. The electron diffraction pattern was simulated [15] and compared with that obtained experimentally [16].

Results and Discussion

XRD

XRD spectra Fig. 1(a) were indexed using Bragg's law for X-ray diffraction and compared with that of the JCPDS software (reference code : 05-0592) [17]. They were specified that the products were cubic PbS ($a = b = c$, $\alpha = \beta = \gamma = 90$ degrees) with the Fm-3 m space

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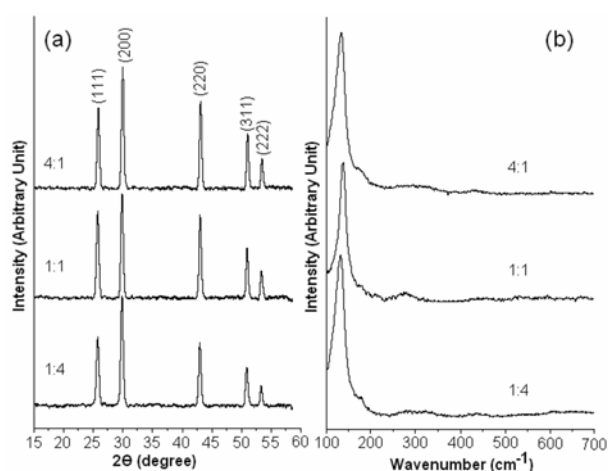


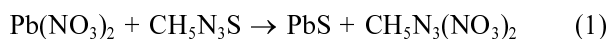
Fig. 1. (a) XRD and (b) Raman spectra of the products prepared using different mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_3\text{N}_3\text{S}$.

Table 1. Calculated lattice parameters of PbS (cubic) prepared using different mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_3\text{N}_3\text{S}$

Plane	Lattice parameter (Å)		
	1 : 4	1 : 1	4 : 1
(111)	5.9670	5.9611	5.9675
(200)	5.9456	5.9531	5.9620
(220)	5.9447	5.9436	5.9476
(311)	5.9391	5.9380	5.9415
(222)	5.9416	5.9405	5.9422
	5.9476 ± 0.0111	5.9473 ± 0.0096	5.9522 ± 0.0119

group. The strongest intensity is at $2\theta = 30.1$ degrees and diffracted from the (200) planes of the crystalline products. The spectra are very sharp showing that well-crystallized crystals were successfully synthesized [18, 19]. The products are composed of a number of atoms aligning in a periodic lattice. No characteristic peaks of impurities were detected showing that each of the products is a pure phase. Atoms were involved in violent vibration with the microwave frequency. They aligned in a systematic and symmetric order, which led to high intensities. Their lattice parameters were calculated from the equation of plane spacing for the cubic crystal system and Bragg's law for diffraction [20]. The parameters corresponding to different crystallographic planes of the products are summarized in Table 1. The averages and standard deviations are 5.9476 ± 0.0111 , 5.9473 ± 0.0096 and 5.9522 ± 0.0119 Å for the products prepared using 1 : 4, 1 : 1 and 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_3\text{N}_3\text{S}$, respectively. They are very close to those of the JCPDS software [17].

To form PbS (cubic), the reaction [21] proceeded according to the following :



Theoretically, 1 mol $\text{Pb}(\text{NO}_3)_2$ and 1 mol $\text{CH}_3\text{N}_3\text{S}$ were used to produce 1 mol PbS and 1 mol $\text{CH}_3\text{N}_3(\text{NO}_3)_2$. For the present research, PbS was able to be produced even when either of the reactants was in excess.

Raman analysis

A definite existence of PbS (cubic) was analyzed using a Raman spectrometer. These test specimens are not destructed and are able to be re-used for other purposes. Their Raman spectra Fig. 1(b) contain prominent bands at the same wavenumbers. They are influenced by some parameters, such as atomic masses of Pb and S, and vibration constant of bonding between Pb and S atoms residing in the lattice. Among the different spectra, their peaks are at 134, 275 and 431 cm^{-1} . The peak below 150 cm^{-1} is tentatively attributable to the so-called plasma line of the excitation laser [5, 22]. The 275 cm^{-1} peak corresponds to two-phonon process [5]. The peak at 431 cm^{-1} is allowed in the rock-salt structure [23]. It is specified as the first overtone mode [22], which involves two phonons with equal but opposite wave vectors ($\mathbf{k}$) [23]. The fundamental longitudinal optical (LO) mode of the rock-salt structure at approximately 215.5 cm^{-1} was unable to be detected due to the rising in intensity of baseline (disorder in PbS lattice) at low wavenumbers. The baseline intensity covered the fundamental LO mode, which was forbidden [22, 23].

SEM

SEM images Fig. 2 show that the products are micro-sized flowers over the whole range of $\text{Pb}(\text{NO}_3)_2$ and $\text{CH}_3\text{N}_3\text{S}$ mole ratios. Flower-like PbS nano-structures were able to be produced even when either of the reactants was in excess. The flower-like products are made up of several petals, which slope up to a point. They have two halves that are the same in size and shape. Each of the petals is composed of a number of small plates arranged in a systematic order. The distance between two apices of the two petals across the center of the flower is 1.7-5.8 micrometers long. The micro-flower is the most complete at 1 : 4 mole ratio.



Fig. 2. SEM images of the products prepared using (a) 1 : 4, (b) 1 : 1, and (c) 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_3\text{N}_3\text{S}$, respectively.

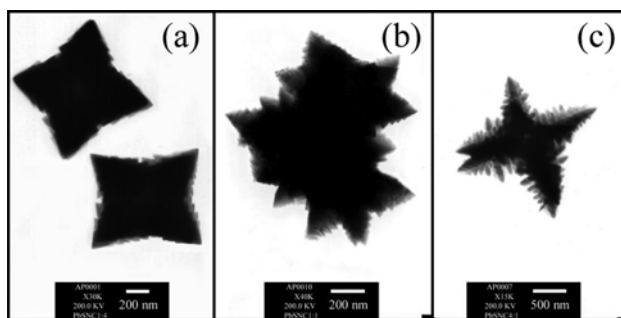


Fig. 3. TEM images of the products prepared using (a) 1 : 4, (b) 1 : 1, and (c) 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_3\text{N}_3\text{S}$, respectively.

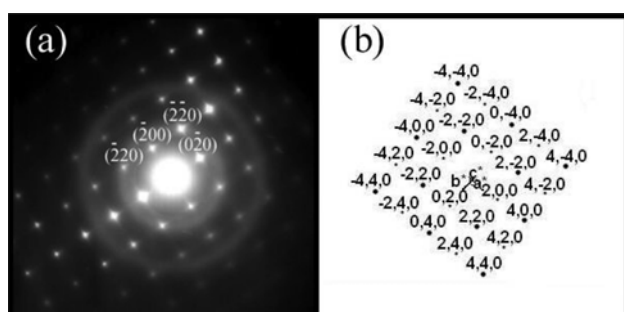


Fig. 4. (a) SAED and (b) simulated patterns of the product prepared using 4 : 1 mole ratio of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$.

TEM, SAED and simulation

TEM images Fig. 3. were used to specify the morphologies of the products. They have a flat shape with four or more acute angles. The results characterized using TEM are in accord with those characterized using SEM. A SAED pattern Fig. 4(a) of the product prepared using a 4 : 1 mole ratio of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$ appears as a symmetric and systematic array of bright spots showing that a number of atoms are arranged on their crystal lattices. The pattern was interpreted [16], and specified as cubic PbS [17]. The calculated electron beam used for the analysis is in the [001] direction. A diffraction pattern of the product with the electron beam in the [001] direction was simulated by respective use of a^* , b^* and c^* lattice vectors in [100], [010] and [001] directions [15]. The simulated pattern Fig. 4(b) is composed of systematic and symmetric bright spots, and is in good accord with the experimental pattern. Additional concentric rings were also detected in the experimental pattern. They were caused by the C supporting grid in the TEM chamber.

Conclusions

Flower-like PbS nano-structures were successfully prepared from 1 : 4, 1 : 1 and 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$ in propylene glycol, using cyclic microwave radiation. XRD and SAED analyses revealed the presence of PbS with a cubic structure. For the present analysis, the experimental and simulated patterns are in good accord. Calculated lattice parameters are 5.9476 ± 0.0111 , 5.9473 ± 0.0096 and 5.9522 ± 0.0119 Å for the products prepared using 1 : 4, 1 : 1 and 4 : 1 mole ratios of $\text{Pb}(\text{NO}_3)_2$ to $\text{CH}_5\text{N}_3\text{S}$. Both SEM and TEM analyses revealed the presence of flower-like PbS nano-structures which were prepared using different mole ratios of Pb and S sources. The 431 cm^{-1} first overtone mode was detected using a Raman spectrometer, but the fundamental one was forbidden.

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