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CYCLIC MICROWAVE ASSISTED SYNTHESIS OF Sb_2S_3 TWIN FLOWERS IN SOLUTIONS CONTAINING A TEMPLATE AND SPLITTING AGENT

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Antimony sulfide (Sb_2S_3) was successfully synthesized from antimony chloride ($SbCl_3$) and sodium thiosulfate ($Na_2S_2O_3$) in ethylene glycol (EG) containing different contents of cetyltrimethylammonium bromide (CTAB) as a template and splitting agent by the 600 W cyclic microwave radiation (CMR). X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy and photoluminescence (PL) spectroscopy revealed the presence of only orthorhombic Sb_2S_3 phase in the shape of twin flowers of single crystalline square nanorod petals, growing along the [001] direction, including the vibration peaks that were in accordance with those of the stibnite with the 435 nm violet wavelength emission peaks.

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Keywords: Sb_2S_3 twin flowers; Cyclic microwave radiation; X-ray techniques; Electron microscopy; Spectroscopy

1. Introduction

Sb_2S_3 is one of orthorhombic V-VI semiconductors with 1.78-2.50 eV energy gap, covering the visible spectrum and NIR range [1]. It has potential applications for solar cells, and thermoelectric and optoelectronic devices [1,2]. Sb_2S_3 products with different morphologies were synthesized by different methods. Among them are single-crystalline Sb_2S_3 nanotubes by EDTA-assisted hydrothermal process [1], double sheaf-like Sb_2S_3 by copolymer-assisted hydrothermal synthesis [2], rod-like Sb_2S_3 dendrites by conventional hydrothermal process [3], Sb_2S_3 peanut-shaped superstructures by hydrothermal process [4], nanocrystalline Sb_2S_3 by microwave-assisted synthesis [5] and orthorhombic Sb_2S_3 dendrites by crystallization of amorphous colloids [6].

In this research, a cyclic microwave radiation (CMR) was used to synthesize Sb_2S_3 twin flowers in solutions containing different contents of cetyltrimethylammonium bromide (CTAB) as a template and splitting agent. This method is fast, extremely effective, inexpensive and environmentally friendly.

2. Experiment

Based on a conventional sol-gel process, 0.002 mol $SbCl_3$ and 0.003 mol $Na_2S_2O_3$ were dissolved in 30 ml ethylene glycol (EG) containing 0.00-1.25 g CTAB with 15 min stirring. Then the solutions were irradiated with 600 W cyclic microwave radiation (CMR) for 15 cycles. Each

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cycle was on for 50 s every 70 s interval. At the conclusion of the process, black precipitates were synthesized, separated by filtration, washed with ethanol and dried at 70 ^{o}C for 24 h.

The products were characterized by an X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV, 15 mA with K_{α} line of a copper target; a scanning electron microscope (SEM, JEOL JSM-6335F) equipped with an energy dispersive X-ray (EDX) analyzer operating at 15 kV; a transmission electron microscope (TEM, JEOL JEM-2010), with a high resolution transmission electron microscope (HRTEM) and selected area electron diffractometer (SAED) operating at 200 kV; a Raman spectrometer (T64000 HORIBA Jobin Yvon) using 50 mW and 514.5 nm wavelength Ar green laser; and a photoluminescence (PL) spectrometer (LS 50B PerkinElmer) excited by 250 nm wavelength at room temperature.

3. Results and discussion

XRD spectra (Fig. 1) of Sb_2S_3, synthesized in the solutions containing different contents of CTAB, were indexed and compared with the JCPDS database no 06-0474 of Sb_2S_3 or stibnite. They were specified as orthorhombic Sb_2S_3 with Pbnm space-group symmetry [7]. Sb_2S_3 phase still formed, no matter the solutions were free of CTAB or contained different CTAB contents. Upon increasing the CTAB contents, the XRD peaks became sharper and narrower, showing that the atomic arrangement was in better order with crystalline degree improvement. In this research, $SbCl_3$ and $Na_2S_2O_3$ were mixed in EG with 15 min stirring and complexes formed. The mixtures were irradiated by a CMR to synthesize Sb_2S_3 black precipitates.

$$SbCl_3 + Na_2S_2O_3 \rightarrow \text{complexes} \quad (1)$$

$$\text{complexes} \rightarrow Sb_2S_3 \text{ (black)} \quad (2)$$

These precipitates were washed with ethanol and thus contain no impurities.

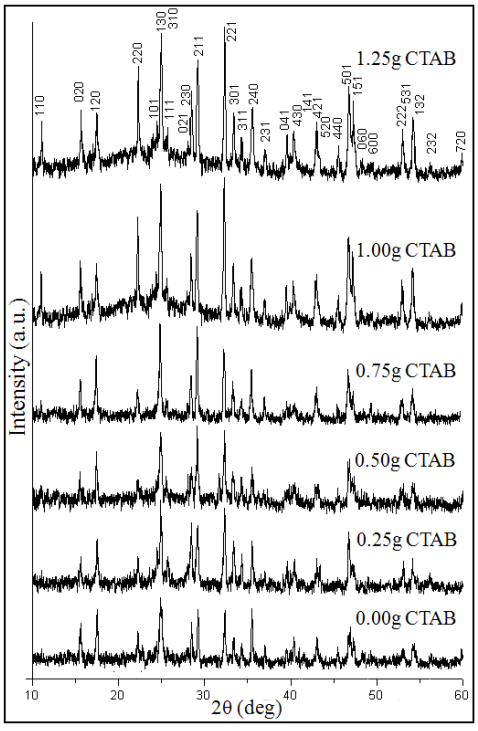

Fig. 1. XRD spectra of Sb_2S_3 synthesized by 600 W CMR of the solutions containing different contents of CTAB for 15 cycles.

The Sb_2S_3 product synthesized in the 0.50 g CTAB-added solution was characterized by EDX and compared with X-ray absorption and emission energies [8]. The spectrum (Fig. 2) appears as the peaks at 3.61, 3.84, 4.10 and 3.19 keV corresponding to L_α, $L_{\beta1}$, $L_{\beta2}$, and L_l lines of Sb, and at 2.31 keV to $K_{\alpha1,2}$ line of S. Due to the quantitative analysis of this product, the atomic ratio of Sb:S was 41.96:58.04, in accordance with the Sb_2S_3 chemical formula. It should be noted that other peaks at 8.04 keV of Cu-$K_{\alpha1,2}$ line and 0.28 keV of C-$K_{\alpha1,2}$ line were also detected - caused by the electronic transition of copper stub and carbon tape used for holding the analyzed sample.

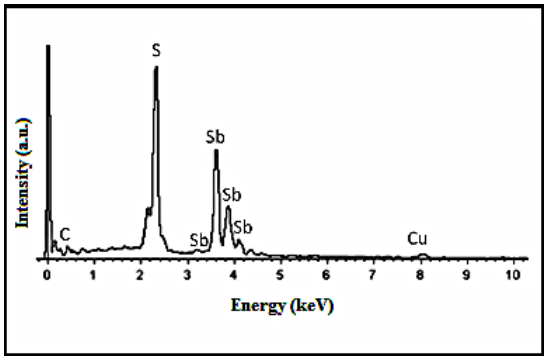

Fig. 2. EDX spectrum of Sb_2S_3 synthesized by 600 W CMR of the solution containing 0.50 g CTAB for 15 cycles.

To further ascertain the presence of the synthesized Sb_2S_3, the product was characterized by Raman spectroscopy. The vibration modes (Fig. 3) were in accordance with the reports of Chen et al. [3] and Makreski et al. [9]. The presence of two peaks at 190 and 252 cm^{-1} revealed that well-crystalline degree of Sb_2S_3 was achieved. The 299 cm^{-1} peak was in accordance with the symmetric vibrations of SbS_3 pyramidal units with C_{3v} symmetry, and the 452 cm^{-1} peak the symmetric stretching of Sb–S–S–Sb bonds of Sb_2S_3 [3].

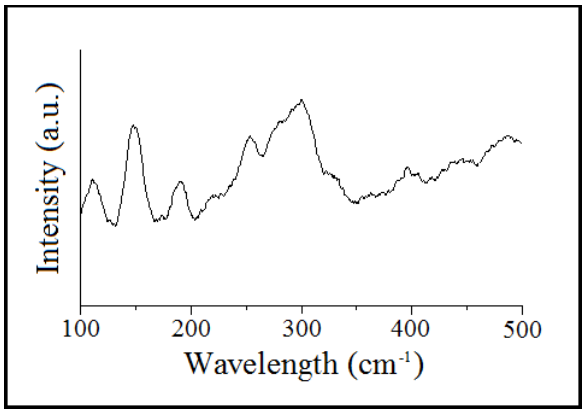

Fig. 3. Raman spectrum of Sb_2S_3 synthesized by 600 W CMR of the solution containing 1.00 g CTAB for 15 cycles.

SEM, TEM and HRTEM images show the development of nanostructured Sb_2S_3 morphologies. In CTAB-free solution, there were a number of nanorods arranging themselves as bundles (Fig. 4a). When different contents of CTAB were added, the nanorods were modeled to be twin flowers (Fig. 4b-i). Their ends were more open, when more CTAB was added. The degree of opening (splitting) was influenced by the contents of CTAB. At the initial stage, Sb_2S_3 molecules of equation (2) nucleated. As time passed, nanorods formed, grew and split at their ends. Each end was independently split, causing these filaments to be entangled with themselves and tied up at the middle (Fig. 4b-f). The twin flowers were composed of a number of square nanorod-like petals

(Figs. 4g-i and 5a). These proved that CTAB functioned as a template and splitting agent. It should be noted that the twin flowers were composed of infinite filaments of stoichiometric Sb_2S_3 running along the [001] direction (Fig. 5b), in accordance with the report of Yang et al. [5]. Their lateral attraction was rather weak, comparing to their internal attraction. Thus the ends of the filaments were not only split but also grew in the [001] direction. The (110) planes (Fig. 5b) parallel to the growth direction were also detected – showing that the nanorod was single crystal. The interpreted SAED pattern (Fig. 5c) also shows that each nanorod was single crystal and corresponded to orthorhombic Sb_2S_3 [7]. To prove the presence of Sb_2S_3 single crystal, its pattern was also simulated [10], and appeared as systematic spots (Fig. 5d) - in good accordance with the interpretation.

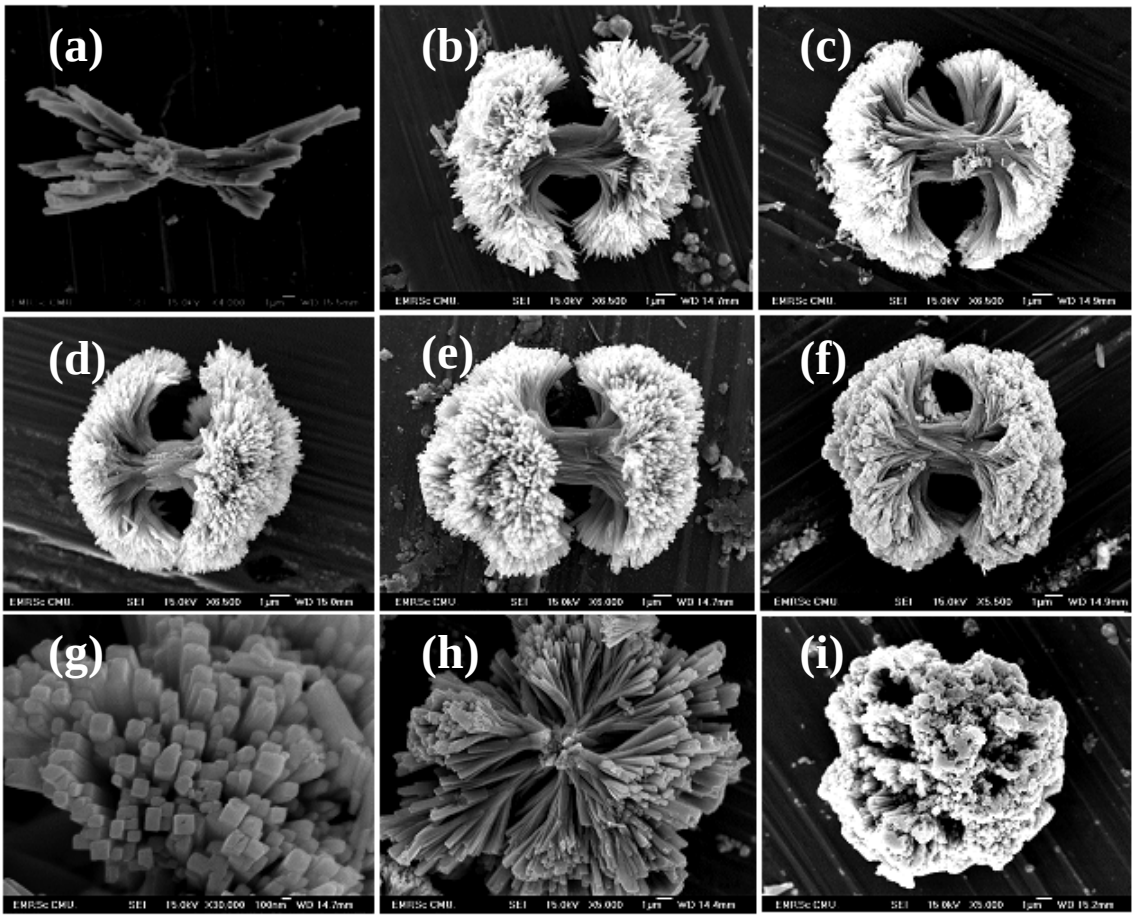

Fig. 4. SEM images of Sb_2S_3 synthesized by 600 W CMR of the solutions containing different contents of CTAB for 15 cycles: (a) 0.00 g, (b) 0.25 g, (c) 0.50 g, (d) 0.75 g, (e, f) 1.00 g and (g-i) 1.25 g.

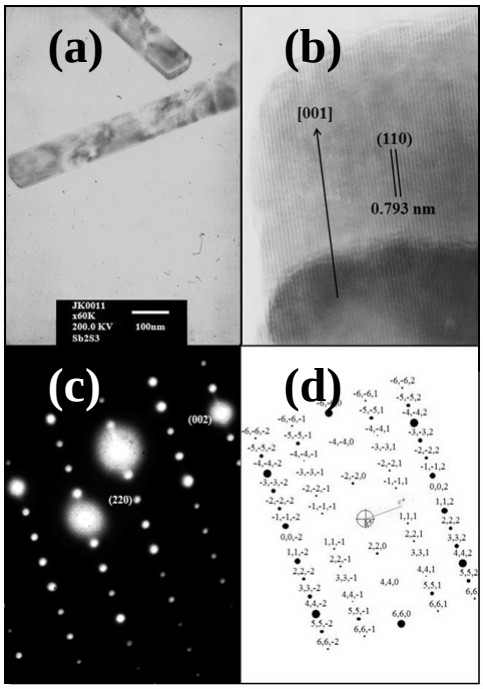

Fig. 5. TEM image, HRTEM image and SAED pattern of Sb_2S_3 synthesized by 600 W CMR of the solution containing 1.00 g CTAB for 15 cycles.

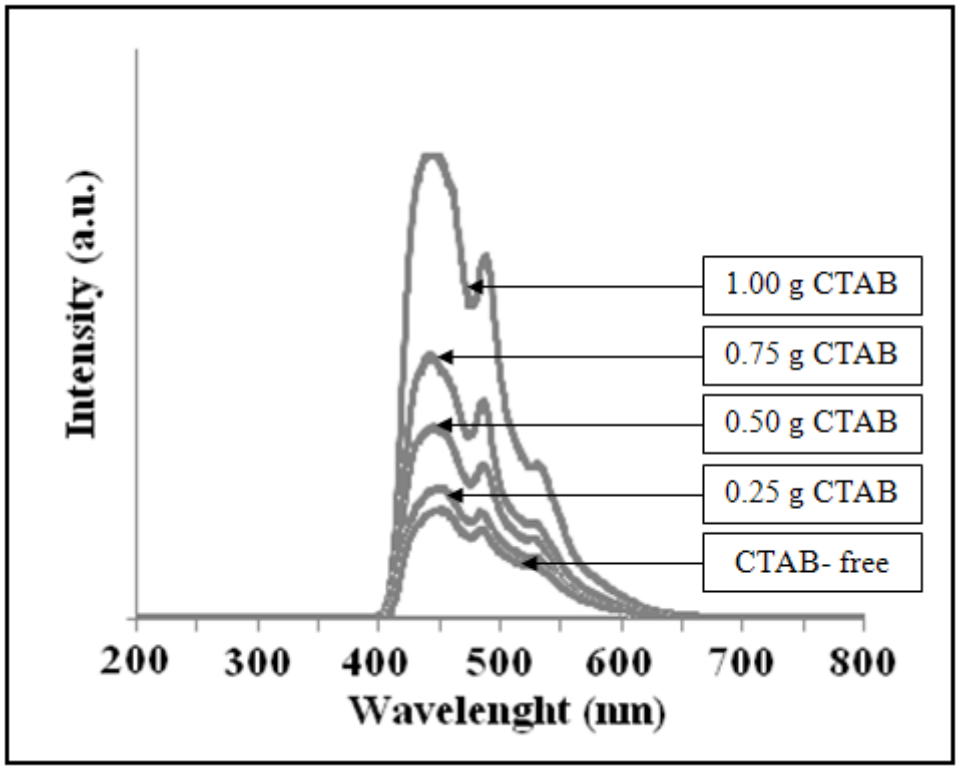

Fig. 6. PL spectra of Sb_2S_3 synthesized by 600 W CMR of the solutions containing different contents of CTAB for 15 cycles.

Optical property of different as-synthesized Sb_2S_3 products was studied using 250 nm excitation wavelength. The emission peaks (Fig. 6) presented broad bands over the 400−600 nm range with strong violet emission peaks centered at the same wavelengths of 435 nm with some

weak shoulders. The luminescence intensity was increased with the increase in the CTAB contents, in accordance with the improvement of crystalline degree characterized by the above XRD analysis.

4. Conclusions

Orthorhombic Sb_2S_3 twin flowers were successfully synthesized by the 600 W CMR. The twin flowers were composed of single crystalline square nanorod petals growing along the [001] direction, including the emission peaks at 435 nm violet wavelength.

Acknowledgement

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