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Short communication

Morphology-controlled synthesis and characterization of bismuth sulfide crystallites via a hydrothermal method

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Abstract

Bismuth sulfide (Bi_2S_3) crystallites with various morphologies have been successfully synthesized via a hydrothermal process assisted by KOH mineralizer. X-ray diffraction (XRD) and scanning electron microscopy (SEM) indicated that the mineralizer played a key role in the crystallization and morphology-controlled synthesis of Bi_2S_3 crystallites. The room temperature photoluminescence spectra (PL) showed that uniform rod-shape morphology resulted in better luminescence.

Keywords: Hydrothermal method; Bi_2S_3 crystallites; Mineralizer

1. Introduction

V–VI compound semiconductor materials have drawn much attention because of their excellent properties such as photoconductivity, photosensitivity, infra-red (IR) spectroscopy and thermoelectric effect [1–5]. Among these materials, bismuth sulfide (Bi_2S_3), with a direct band gap E_g of 1.3 eV [6], is a potential candidate for applications in thermoelectric devices, electronic, optoelectronic devices and IR spectroscopy [2,4].

Conventionally, Bi_2S_3 is prepared by the direct reaction of bismuth and sulfur vapor in a quartz vessel at high temperatures [2,7]. In previous reports, many techniques have been developed to synthesize Bi_2S_3 such as hydrothermal/solvothermal methods [8,9], thermal decomposition [10], chemical deposition [11], spray pyrolysis deposition [12], and so on.

Recently, crystallites with special size and morphology have attracted extensive attention due to their potential applications in various fields including catalysis, medicine, electronics, ceramics, pigment, cosmetics, etc. [13–18]. However, control on both the particle size and morphology of Bi_2S_3 crystallites is still a challenge. Furthermore, to our knowledge, hydrothermal study assisted by the mineralizer to control the morphology of Bi_2S_3 crystallites has not yet been reported.

2. Experimental procedure

The chemical reagents were bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), thiourea ($CS(NH_2)_2$) and potassium hydroxide (KOH). All the chemicals were analytical grade purity, and used as received without further purification.

Appropriate amounts of $Bi(NO_3)_3{\cdot}5H_2O$ and $CS(NH_2)_2$ with 1:2 molar ratio were added into a Teflon-lined autoclave of 100 ml capacity, filling the autoclave with 50 ml distilled water. The autoclave was sealed, heated up to 200 °C and kept for 15 h, then cooled to room temperature naturally. The mineralizer-assisted hydrothermal experiment was performed by repeating the above procedure under the same condition but adding 0.025 mol KOH in the autoclave. After the hydrothermal process, the products were filtered, washed with distilled water and absolute ethanol for several times, and dried at 70 °C for 4 h for characterization.

X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (XRD, D/max, Rigaku, Japan) with Cu Kα radiation (λ = 1.5406 Å), at a scanning rate of 6° min^{-1} in the 2θ range from 10° to 60°. The morphology of the product

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was observed by a JSM-840 scanning electron microscope SEM (JEOL Ltd., Japan). The room temperature photoluminescence (PL) spectra were obtained on a Fluorolog-3 spectrofluorometer (USA), at power of 450-W (Xenon lamp) and resolution of 0.2 nm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples synthesized under different hydrothermal conditions. Fig. 1(a) presents the XRD pattern of the sample obtained by the direct hydrothermal reaction of $Bi(NO_3)_3{\cdot}5H_2O$ and $CS(NH_2)_2$. All diffraction peaks match well with the standard data of Bi_2S_3 (JCPDS: 06-0333), and no impurity can be found. It means that a pure phase of Bi_2S_3 with orthorhombic structure could be easily synthesized by the present hydrothermal process. It can be also found that the presence of the mineralizer KOH in the hydrothermal process would promote the crystallization and development of Bi_2S_3 crystallites, as shown in Fig. 1(b), where all the diffraction peaks can be indexed to orthorhombic Bi_2S_3 with no any other impurities present. It is noteworthy that some diffraction peaks, especially (1 1 1), increase greatly in intensity in Fig. 1(b). The comparison between Fig. 1(a) and (b) XRD patterns indicates that better crystallization and anisotropic growth of Bi_2S_3 crystallites can be realized in the hydrothermal process assisted by the mineralizer KOH.

SEM images of the Bi_2S_3 powders prepared under the different hydrothermal conditions are given in Fig. 2. As shown in Fig. 2(a), only irregular and agglomerated particles of Bi_2S_3 crystallites with average size of ca. 1–2 μm could be prepared by the direct hydrothermal process without using any mineralizer. Nevertheless, when KOH as a mineralizer was introduced to the hydrothermal process, large changes in the morphology of Bi_2S_3 crystallites could be observed. The presence of KOH resulted in the formation of perfect rod-shaped Bi_2S_3 crystallites with average diameter of ca. 200 nm and length of ca. 10 μm. The anisotropic growth of the Bi_2S_3 crystallites further confirmed the previous XRD analysis.

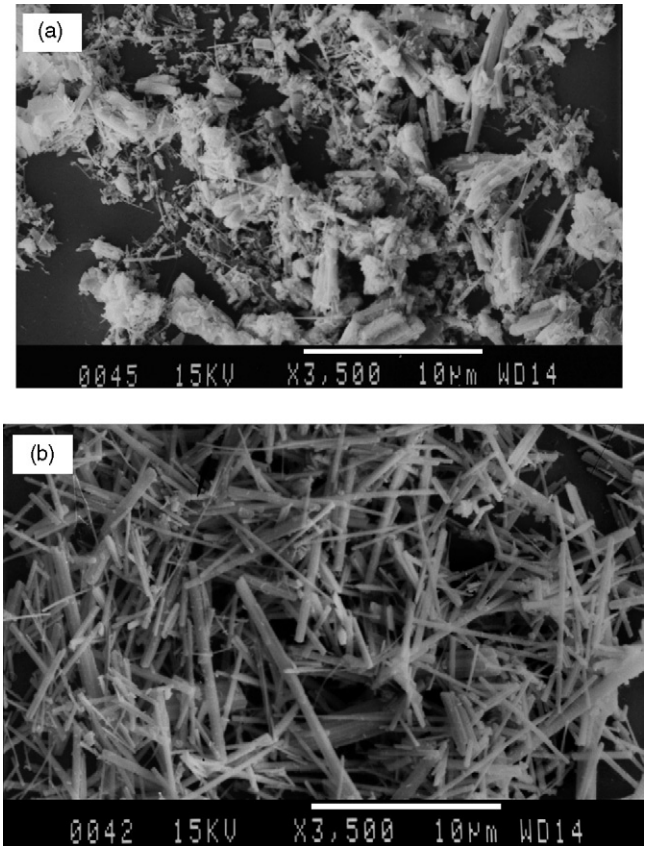

Fig. 2. SEM images of samples produced at 200 °C for 15 h (a) without any mineralizer; (b) adding KOH as a mineralizer.

Room temperature photoluminescence spectra of the as-prepared Bi_2S_3 crystallites are shown in Fig. 3. With the excited wavelength at 325 nm, the corresponding broad emission peaks at 385 nm (corresponding to 3.22 ev) can be observed for both Bi_2S_3 samples prepared by the hydrothermal process with or

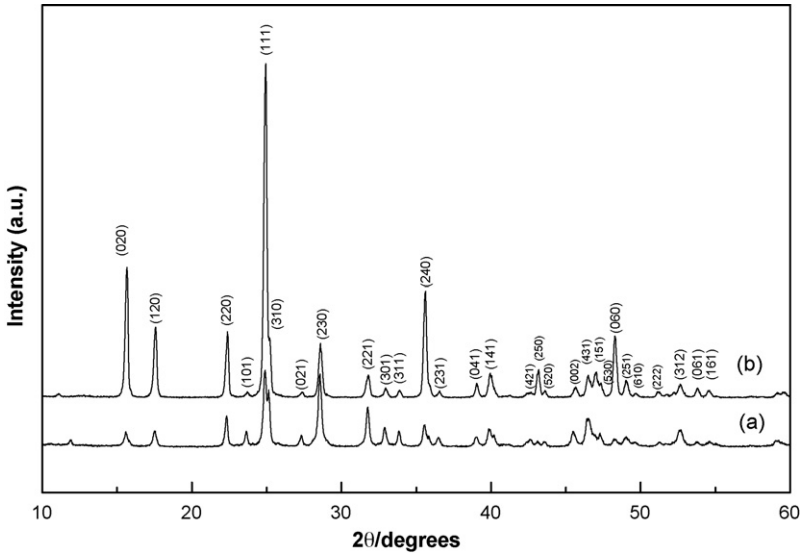

Fig. 1. XRD patterns of the samples synthesized at 200 °C for 15 h (a) without any mineralizer; (b) adding KOH as a mineralizer.

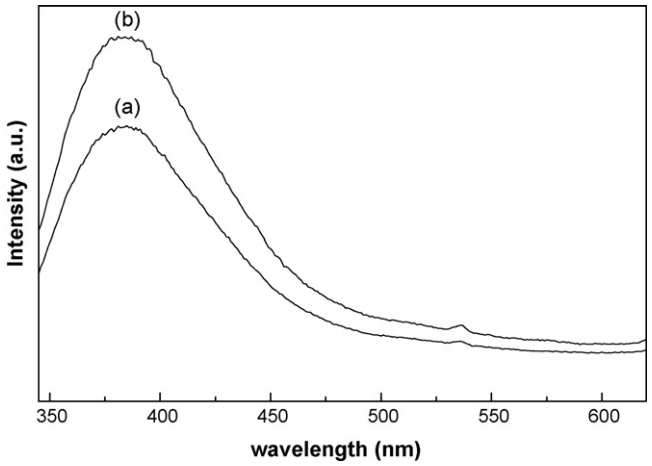

Fig. 3. PL spectra of the as-prepared samples at 200 °C for 15 h (a) without any mineralizer; (b) adding KOH as a mineralizer.

without using KOH. The PL emission intensity of the Bi_2S_3 crystallites obtained by using KOH mineralizer (Fig. 3(b)) is much stronger than the product prepared by the direct hydrothermal process (Fig. 3(a)). It implies that the PL emission intensity of Bi_2S_3 crystallites depends strongly on their particle size and morphology.

4. Conclusions

The size and morphology-controlled synthesis of Bi_2S_3 crystallites has been successfully achieved at 200 °C for 15 h via a hydrothermal process by adding KOH as a mineralizer. In the absence of mineralizer a pure phase of Bi_2S_3 crystallites with aggregated and irregular morphology was obtained. Once KOH was introduced into the hydrothermal process, regular rod-like Bi_2S_3 crystallites could be easily prepared. The morphology-controlled synthetic approach described in this paper may be extended to other kinds of semiconductor materials.

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