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One-step, ambient-temperature synthesis of antimony sulfide (Sb_2S_3) micron-size polycrystals with a spherical morphology

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Abstract

Antimony sulfide microspheres were prepared for the first time via a one-step, ambient-temperature reaction in a non-toxic solvent. The morphology, composition and crystallinity of the product was characterized by SEM, EDX and XRD.

Keywords: Antimony trisulfide; Scanning electron microscope (SEM); Energy dispersive X-ray (EDX)

1. Introduction

Antimony trisulfide (stibnite) is a semiconductor with high photosensitivity and high thermoelectric power [1]. It has been used in television cameras, microwave devices and various optoelectronic devices [2–4]. The band gap (≈1.78−2.5 eV) covers the visible and near infrared range of the solar spectrum [5,6], and in conjunction with its good photoconductivity, stibnite has received some attention as a potential candidate in solar energy conversion. Microspheres of Sb_2S_3 have also been used as substrates for radiolabeling in routine clinical applications [7,8].

Sb_2S_3 has been synthesized by various methods, including vacuum evaporation [9], direct elemental reaction [10], thermal decomposition [11], solvothermal reaction [12] and other chemical reaction approaches [13–15]. For the vacuum evaporation and direct elemental reaction methods, it is difficult to obtain exact stoichimetric compositions because of the differences in the vapor pressures of the reacting species. All thermal decomposition methods require high temperature, and the final products usually contain impurities. Even the reactions conducted at low temperature (120−180 °C), using solvothermal synthesis typically employ toxic solvents, such as benzene and methanol [12]. Herein we report for the

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first time a one-step, ambient-temperature reaction in a non-toxic solvent for the preparation of exact stoichimetric composition Sb_2S_3 micro crystals having a spherical morphology.

2. Experimental

In a typical synthesis, 0.2281 g antimony(III) chloride (Aldrich, 99.9%) was dissolved in 20 ml absolute ethanol in a test tube equipped with a cap and 0.1503 g thioacetamide (Aldrich, 99.9%) was added to the clear ethanol solution. The above solution was stirred until an orange colored precipitate appeared. Then the test tube was kept at room temperature for 24 h without stirring, and the color of the precipitate became scarlet red. The precipitate was washed with ethanol several times, and vacuum dried at 70 °C for 10 h.

The morphology and composition of the samples were determined using a scanning electron microscope (SEM; JEOL-6300, 15 kV) in conjunction with energy dispersive X-ray spectroscopy (EDX). Samples for SEM and EDX studies were prepared by placing droplets of the ethanol dispersion on silicon wafers and letting the ethanol evaporate in air. The crystallinity of the samples was studied by X-ray diffraction (XRD) measurement (Rigaku multiflex diffractometer, Cu Kα, 40 kV, 40 mA).

3. Results and discussion

Fig. 1 shows SEM images of polycrystalline antimony sulfide with a spherical morphology. Fig. 1(a) is the SEM image of the product formed from a Sb^{3+} starting concentration of 0.05 mol/l. The distribution of sphere sizes appears bimodal: at the low starting concentration (0.05 mol/l, Sb^{3+}), the 1-μm diameter spheres are the dominant product and the sphere size distribution is rather narrow. When the Sb^{3+} concentration was increased to 0.07 mol/l, the larger (∼8-μm diameter) spheres are more abundant and begin to dominate the volume fraction of the Sb_2S_3 sample (Fig. 2).

Fig. 3 shows the XRD pattern of the antimony sulfide spherical polycrystals. A scanning rate of 0.02°/s was used to record the patterns in the 2θ range of 10−65°. All the reflections can be indexed to the orthorhombic Sb_2S_3 phase with lattice parameters $a = 11.225$ Å, $b = 11.314$ Å and $c = 3.838$ Å, in

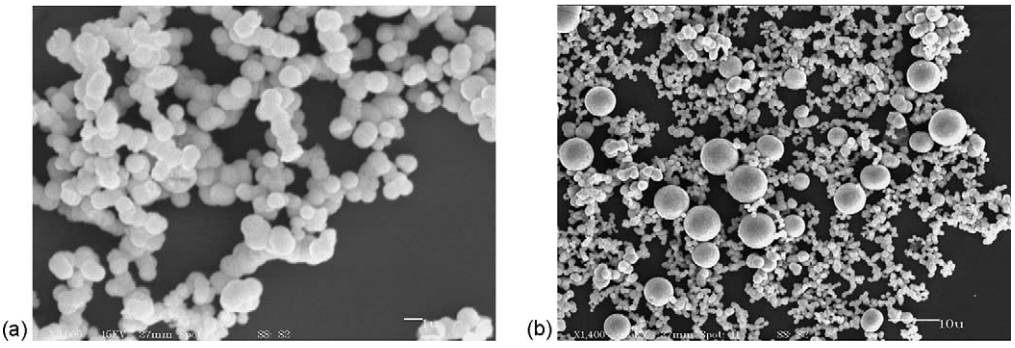

Fig. 1. SEM images of as-prepared Sb_2S_3 spherical polycrystals; (a) initial Sb^{3+} concentration: 0.05 mol/l, scale bar: 1 μm; (b) initial Sb^{3+} concentration: 0.07 mol/l, scale bar: 10 μm.

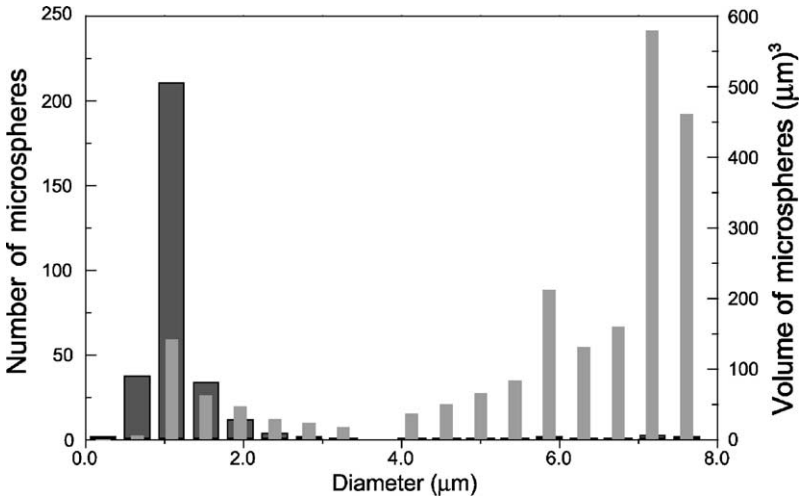

Fig. 2. Histogram of size distribution of as-prepared Sb_2S_3 spheres for the 0.07 mol/l starting concentration of Sb^{3+}. The dark histogram is the number of microspheres vs. diameter; the grey histogram is the amount (by volume) of Sb_2S_3 microspheres vs. diameter.

good agreement with the reported data for Sb_2S_3 ($a = 11.229$ Å, $b = 11.310$ Å and $c = 3.839$ Å, JCPDS File, 6-474).

Fig. 4 shows the EDX spectrum. Besides the peaks of Sb and S, there are peaks for Si and Cl. The Si peak is from the substrate (a silicon wafer), however, the peak for Cl is from the starting material, $SbCl_3$. This reagent could not be removed even when the sample was washed several times in ethanol. In Table 1, the atomic ratio of Sb/S is 54.80/34.44 (=1.59), very close to the anticipated 3/2 stoichimetric composition.

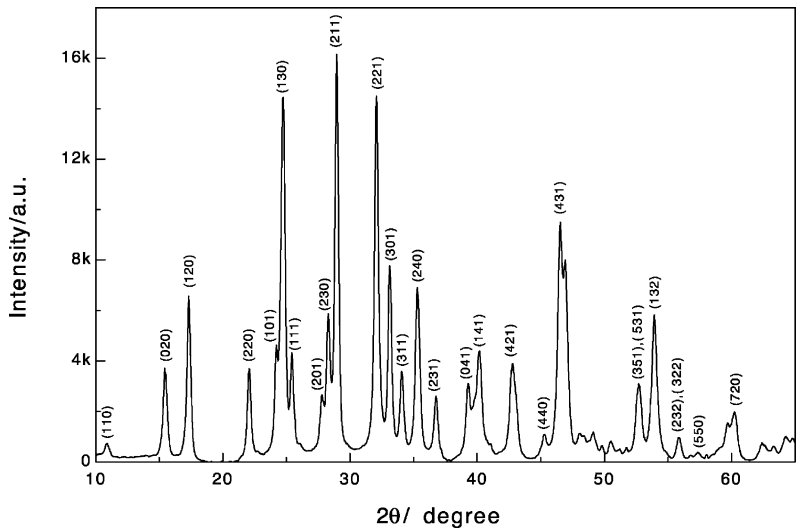

Fig. 3. X-ray diffraction pattern of as-prepared Sb_2S_3 spherical polycrystals.

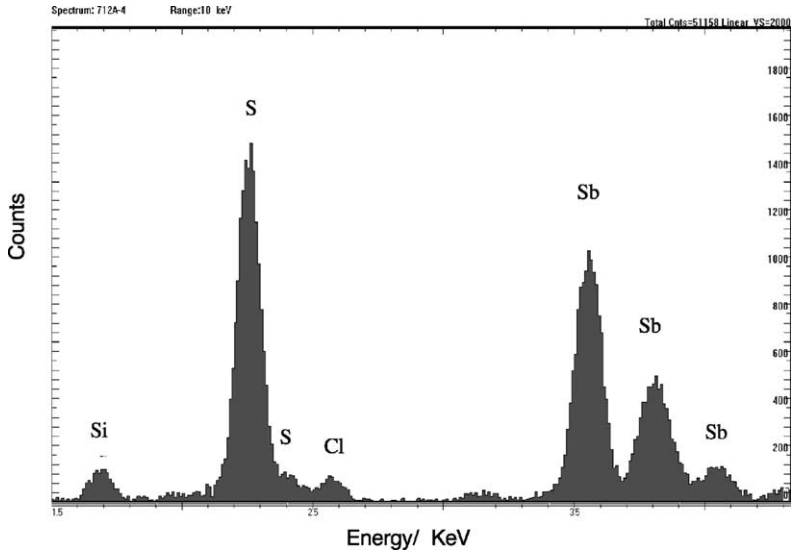

Fig. 4. The EDX spectrum of Sb_2S_3 spherical polycrystals on a silicon wafer substrate.

Table 1
Results of EDX spectrum measurements

Element	Line	In wt.%	*K*-ratio	Counts/s	In at.%
Si	Kα	2.96	0.0192	14.88	6.61
S	Kα	27.97	0.2403	166.70	54.80
Cl	Kα	2.34	0.0174	11.49	4.15
Sb	Lα	66.74	0.5626	127.73	34.44

Since $SbCl_3$ hydrolyzes easily in an aqueous solution, a non-aqueous solvent (absolute ethanol) was used as the reaction medium. When the Sb^{3+} ions encounter S^{2-} ions released from thioacetamide, aggregates of Sb_2S_3 polycrystalline nanocrystals are probably formed. And such aggregates might act as template seeds for growing the larger, micron-size, spherical polycrystals. Irrespective of the detailed mechanism, this simple, convenient method provides an effective route to synthesize antimony sulfide microspheres.

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