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Letter

Hydrothermal synthesis of double sheaf-like Sb_2S_3 using copolymer as a crystal splitting agent

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ABSTRACT

Double-sheaves of antimony sulfide were synthesized by the 200 °C and 24 h hydrothermal reaction in the acidic solution, containing copolymer – a crystal splitting agent. Using X-ray technique, electron microscopy, and Raman as well as UV–visible NIR absorption spectroscopy, the products were specified as orthorhombic Sb_2S_3, composing of Sb and S with five vibration modes, in the shape of spears in bundles with the [0 0 1] growth direction and 2.38 eV direct energy gap. A diffraction pattern was also simulated, and is in good accordance with that obtained by the interpretation.

1. Introduction

Antimony sulfide (Sb_2S_3, stibnite), a chain-structured V–VI chalcogenide semiconductor with orthorhombic crystal structure [1,2], has good photosensitivity and high thermoelectric power [1,3], and has 1.78–2.50 eV direct band gap – in the visible and near IR range [3]. Its property is generally controlled by the morphologies with different defects and concentrations. A number of methods have been used to synthesize antimony sulfide with different morphologies: nanocrystals by a microwave synthesis [3], dendrites by the crystallization of amorphous colloidal microspheres [4], and straw-tied-like architectures, nanoribbons and sub-microwires by a hydrothermal process [1,5,6].

In the present research, double-sheaves of Sb_2S_3 crystals were hydrothermally synthesized using copolymer as a crystal splitting agent – another function of the copolymer. This method is extremely effective, inexpensive, environmentally benign and appropriate for large-scale synthesis.

2. Experiment

To synthesize Sb_2S_3, 0.005 mol antimony acetate and 0.01 mol thiourea were dissolved in 60 ml H_2O containing 0.5 ml HNO_3. Different amounts of copolymer, poly (vinyl-butyral-co-vinyl alcohol-co-vinyl acetate), were added to the mixtures with continuous stirring. The products were hydrothermally synthesized in home-made stainless steel autoclaves at 200 °C for 6–24 h, and further characterized to determine their phase both by interpretation and simulation [7], morphologies, vibrations and energy gap.

3. Results and discussion

XRD pattern (Fig. 1a) was indexed and specified as orthorhombic Sb_2S_3 phase (Pbnm space group) with no detection of any impurities such as Sb_2O_3. Calculated lattice parameters ($a = 11.25$ Å, $b = 11.34$ Å and $c = 3.82$ Å) are in good accordance with those of the JCPDS no. 42-1393 [2].

For the present research, thiourea was hydrolyzed in acidic solution at elevated temperature to produce S^{2-} [8].

$$NH_2CSNH_2 + H_2O \rightarrow NH_2CONH_2 + S^{2-} + 2H^+$$

Simultaneously, Sb^{3+} reacted with S^{2-} in aqueous (aq) solution containing acid to form Sb_2S_3 (s).

$$2Sb^{3+}(aq) + 3S^{2-}(aq) \rightarrow Sb_2S_3(s)$$

EDX spectrum (Fig. 1b) proved that there are antimony and sulfur existing in this product. Cu and C, stem from copper stub and carbon tape, were also detected. Quantitative analysis shows that the atomic ratio of Sb:S is 21.67:31.16 – in accordance with antimony sulfide chemical formula.

Its Raman shift (Fig. 1c) was specified as five vibration modes. Sharp peaks at 188.8 and 253.4 cm^{-1} proved that the product

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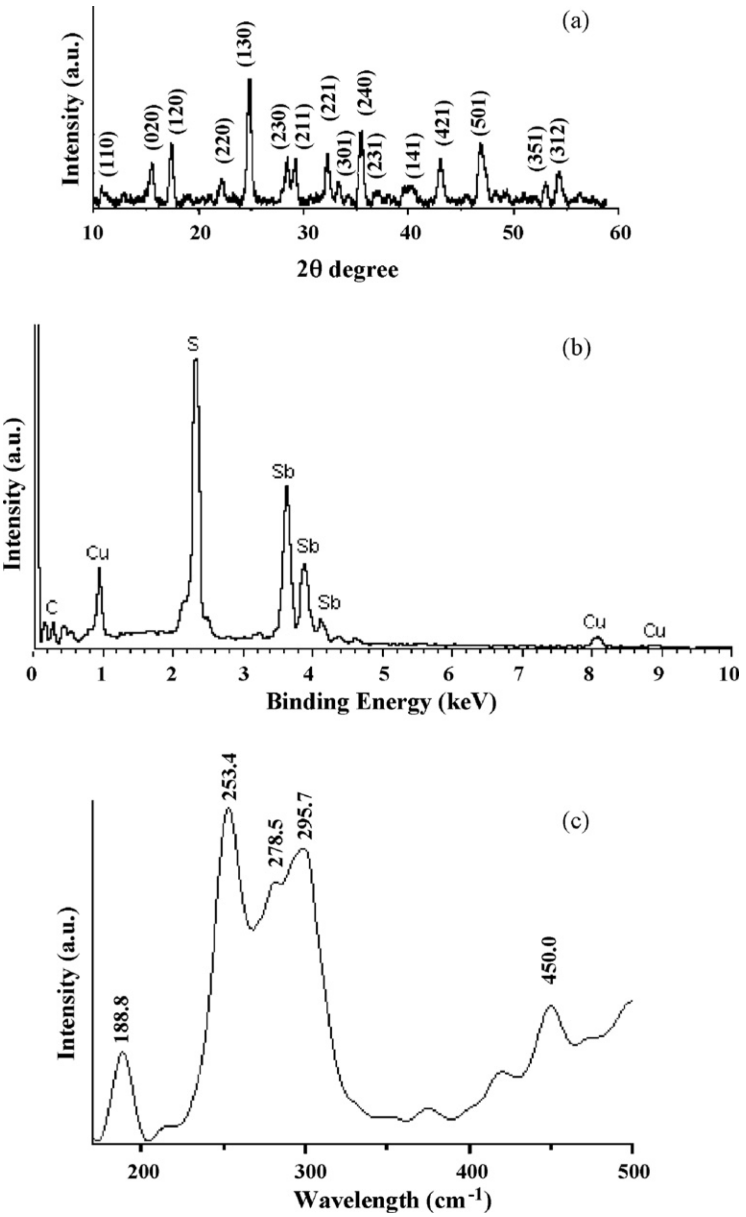

Fig. 1. (a) XRD pattern, (b) EDX spectrum, and (c) Raman shift of Sb_2S_3 synthesized by the 200 °C and 24 h hydrothermal reaction in a solution containing 1 g copolymer.

is good crystalline. Two peaks at 278.5 and 295.7 cm^{-1} are in accordance with the symmetric vibrations of SbS_3 pyramidal units having C_{3v} symmetry [9,10], and the 450.0 cm^{-1} peak the S–S vibrations [9] or the symmetric stretching of Sb–S–S–Sb structural units [10].

SEM images (Fig. 2) show external morphologies of the products synthesized under different conditions. For 6 h and 1 g copolymer synthesis, the product is composed of bunches of oval plates tied together at the middle. When the time was lengthened to be 12 h, these plates slowly developed into branches, remaining fastened at the middle with both sides spreading out – similar to a wheat sheaf or a bundle of filamentary crystals. For 24 h and 1 g copolymer, more filamentary crystals were produced on each bundle and the extent of spreading became wider. The bundles have the shape of double sheaf-like structures. Each of the filamentary or ribbon-like crystals has sharp point, having the shape of a spear. Incomplete sheaf-like bundles were synthesized for 24 h and 0.5 g copolymer, and a number of nanorods with different sizes and orientations for 24 h in copolymer-free solution. These sheaf-like structures could form by crystal splitting during their growth and grew along the preferential direction into ribbon-like branches. The degree of spreading depends on their splitting ability which increases with the prolonged time increase. The splitting ability was also controlled by copolymer in the solution. By reducing its amount, the degree of splitting became lowered and the sheaf-like bundle was incomplete. In copolymer-free solution, there were a number of nanorods with different sizes and orientations appearing as the product [11].

Fig. 3 shows TEM and HRTEM images, SAED and simulated patterns of Sb_2S_3 synthesized using 1 g copolymer at 200 °C for 24 h. Its TEM image shows an individual ribbon in the shape of a spear, growing along the [0 0 1] direction. HRTEM analysis on a ribbon-like crystal proved that the ribbon is single crystal, composing of the (2 2 0) parallel crystallographic planes with 0.39 nm apart in parallel with the [0 0 1] growth direction. The SAED pattern shows the systematic array of diffraction spots of orthorhombic

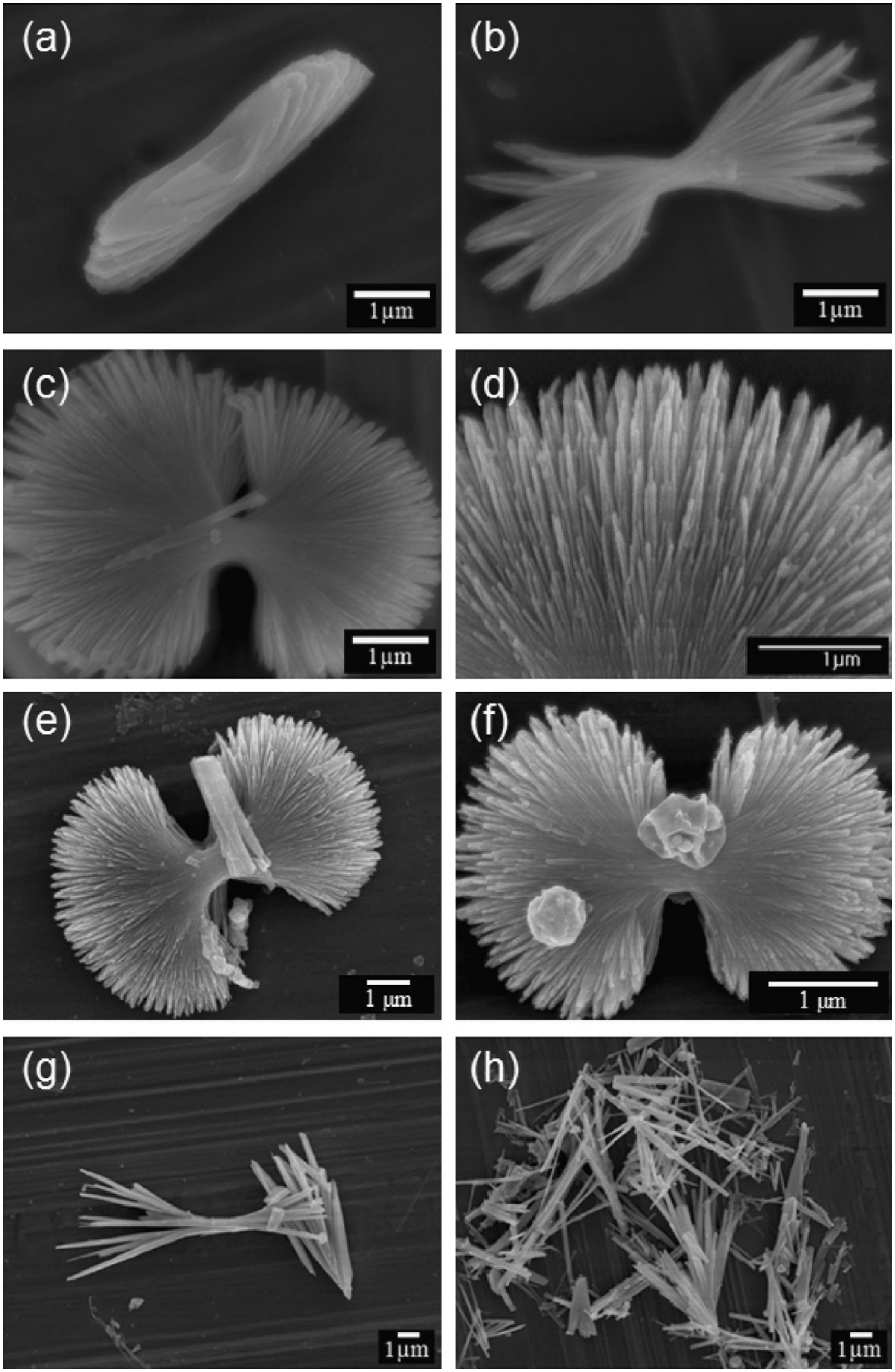

Fig. 2. SEM images of Sb_2S_3 synthesized at 200 °C for different lengths of time and amounts of copolymer (a) 6 h, 1 g; (b) 12 h, 1 g; (c–f) 24 h, 1 g; (g) 24 h, 0.5 g; and (h) 24 h, copolymer-free.

Sb_2S_3 single crystal [2] with electron beam in the [1 0 3] direction, corresponding to the diffraction pattern obtained by simulation [7].

To get an insight into the growth mechanism of sheaf-like structure, its crystal structure (Fig. 4) was simulated [7]. It is made up of infinite chains of stoichiometric composition of atoms running normal to the b axis. The binding of these Sb_2S_3 structure chains in the b direction is considerably weaker than the one along the chains – leading to easily cleavage along its (0 1 0) planes. Thus, the growing crystal was split. Crystal splitting is also associated with

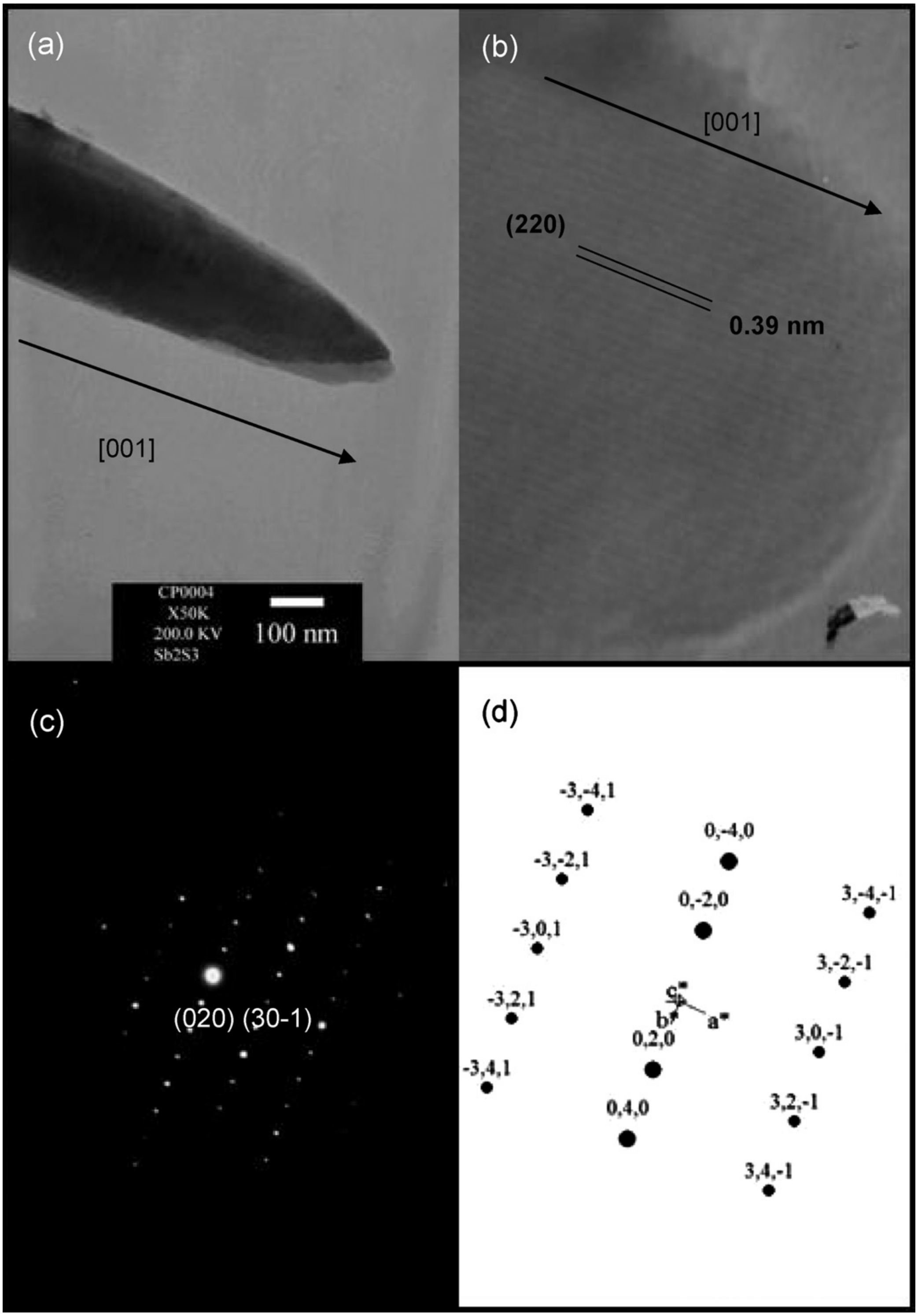

Fig. 3. TEM and HRTEM images, and SAED and simulated patterns of Sb_2S_3 nanoribbons synthesized by the 200 °C and 24 h hydrothermal reaction in a solution containing 1 g copolymer.

rapid crystal growth, due to the supper saturation that exceeds a certain critical value; especially, for some specified condition [11].

Fig. 5 shows the relationship of $(\alpha h\nu)^2$ and photon energy ($h\nu$) for the direct allowed transition, where α (=−(log T)/t) is the total absorption coefficient, T the transmittance of photon through the suspension in ethanol (C = 0.001 g/cm^3) containing in the Spectroscopy cell with the path length (b) of 10.00 mm, t (=bC/ρ) the effective thickness, and ρ the density of Sb_2S_3 [12]. The absorption edge energy, determined by extrapolation the curve to $\alpha = 0$, corresponds to the 2.38 eV energy gap. This value is in the 1.78–2.50 eV energy gap range of nano-Sb_2S_3 determined by other researchers [13].

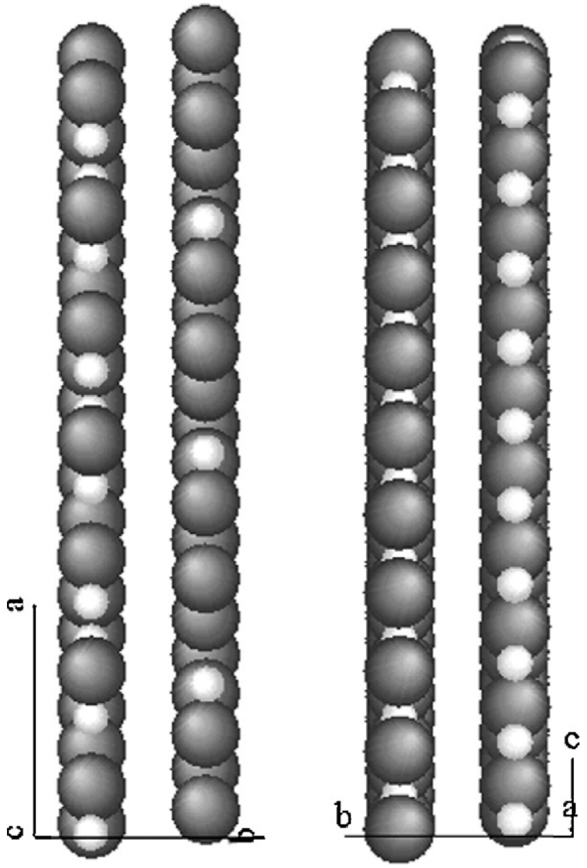

Fig. 4. Crystal structure of Sb_2S_3, composing of Sb (white balls) and S (black balls).

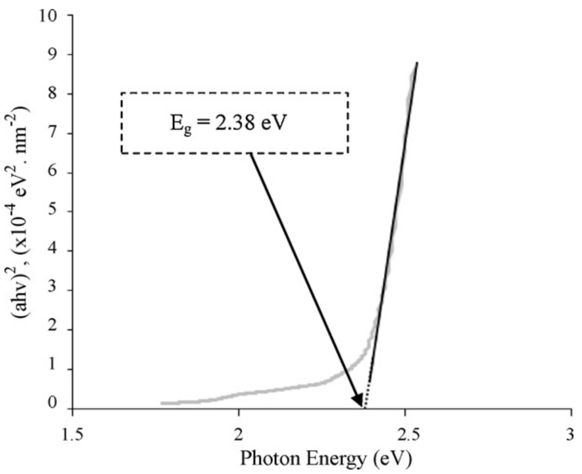

Fig. 5. The relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$) of Sb_2S_3 synthesized by the 200 °C and 24 h hydrothermal reaction in the solution containing 1 g copolymer.

4. Conclusions

Pure double sheaf-like structured Sb_2S_3 was successfully synthesized in acidic solution containing 1 g copolymer by the 200 °C and 24 h hydrothermal reaction – the environmentally benign process. Its phase, constituents, morphology and Raman vibrations – including its 2.38 eV direct energy gap were clearly detected.

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