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Antimony sulfide tetragonal prismatic tubular crystals

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Antimony sulfide tetragonal (rectangular) prismatic tubular crystals with dimenions of 6–10 mm in length, 50–60 μm in width, and 5–15 μm in thickness were successfully synthesized for the first time *via* a hydrothermal reaction route from antimony trichloride and sodium thiosulfate in the presence of ammonium chloride at 198 °C.

Studies on the synthesis and growth mechanism of micron- and millimeter-scale objects with open structures have attracted a lot of research interest in recent years.[1–4] Methods including self-assembly,[1–3,5,6] heating of PPy-coated PET,[4] electrodeposition,[7] and carbonization of spun hollow poly(acrylonitrile) fibers[8] have been applied to prepare materials with open structures. Up to now, the synthesis of mesoscale crystals with open structures has been a challenge for the materials scientist. Our research group has synthesized a hexagonal millimeter-sized tubular crystal Ag_2Se[9] by the hydrothermal method. Although nanotubules of metal chalcogenides[10] were synthesized by different methods, no other mesoscale tubular crystals of chalcogenides have been reported to date. Here, we report on the antimony sulfide tetragonal tubular crystals synthesized, for the first time, by a hydrothermal reaction route at 198 °C in the presence of ammonium chloride, in which $Na_2S_2O_3{\cdot}5H_2O$ served as a sulfur source. In these procedures, ammonium chloride played an important role in the formation of the Sb_2S_3 tubular crystals based on the following reaction:[11]

$$\begin{aligned}&2SbCl_3 + 9Na_2S_2O_3 \rightarrow \\ &Sb_2S_3 + 6NaCl + 3Na_2S_4O_6 + 3Na_2SO_3 \qquad (1)\end{aligned}$$

In a typical experiment, an appropriate amount of analytically pure $SbCl_3$, $Na_2S_2O_3{\cdot}5H_2O$ and NH_4Cl (with a molar ratio of 1 : 5 : 2) was added into a Teflon-lined stainless steel autoclave, which was filled to 90% of the total volume (50 ml) with distilled water. After stirring an orange-red color was observed, indicating the formation of amorphous Sb_2S_3.[12] The autoclave was then maintained at 198 °C for 10–30 h and left to cool to room temperature for 20 h. The precipitates were washed sequentially with carbon disulfide, ether, distilled water and absolute alcohol to remove impurities. After drying in a vacuum at 60–70 °C for 4 h, brittle rod-like crystals, metallic gray in color with a high reflective luster, were obtained.

Fig. 1(a) is the X-ray diffraction (XRD)† pattern of the polycrystalline powder ground from the antimony sulfide crystals. A scanning rate of 0.020° s^{-1} was applied to record the patterns in the 2θ range of 10 to 60°. All the reflections could be indexed to the orthorhombic Sb_2S_3 phase with lattice parameters $a = 11.222(5)$, $b = 11.316(5)$, and $c = 3.840(5)$ Å, which are in agreement with the reported data of $a = 11.229$, $b = 11.310$, and $c = 3.839$ Å for Sb_2S_3 (JCPDS Card File, 6-474). No characteristic peaks were observed for the other impurities such as Sb_2O_3, Sb_2S_5 or S. The XRD patterns of a needle crystal exhibit only five peaks at 11.14, 22.34, 33.76, 45.52, and 57.84° in the 2θ range of 10 to 60°, which can be assigned to the orthorhombic 110, 220, 330, 440, and 550, respectively [Fig. 1(b)]. From the XRD pattern in Fig. 1(b) we can see that the as-grown tubular crystals, Sb_2S_3, show single crystal characteristics.

The SEM‡ images of as-grown Sb_2S_3 crystals are shown in Fig. 2. It can be seen that the Sb_2S_3 crystals have a tubular tetragonal (rectangular) prismatic structure. Typically, this structure is 6–10 mm in length, 50–60 μm in width, and 5–15 μm in thickness. It can be observed that the walls of some tubules appear to have different thicknesses.

The binding energies obtained in the XPS§ analysis were corrected for specimen charging by referencing the C 1s peak to 284.80 eV. The Sb 3d core level spectrum [Fig. 3(a)] indicates that the observed value of the binding energy for Sb $3d_{5/2}$ (529.45 eV) is in agreement with the literature value,[13] and no evidence for the existence of Sb^{5+} (529.20 eV) was observed. The kinetic energy of the Sb $M_4N_{45}N_{45}$ peak is 462.20 eV. Therefore the value of the "modified Auger parameter" (a') is 991.65 eV, which is in agreement with the literature observed in Sb_2S_3.[13] The S $2p_{3/2}$ binding energy of 161.80 eV [Fig. 3(b)], given by the S core level spectrum, is consistent with the value observed in WS_2.[13] The contents of Sb and S are quantified by Sb 3d and S 2p peak areas, and a molar ratio of 1 : 1.46 for Sb : S is given. No obvious peaks for N 1s, or elemental sulfur were observed.

Fig. 4 is the transmission X-ray Laue¶ photograph of the crystals. It revealed that the obtained material was a single crystal due to the presence of Laue cones.[14]

Antimony trichloride reacted with sodium thiosulfate at the

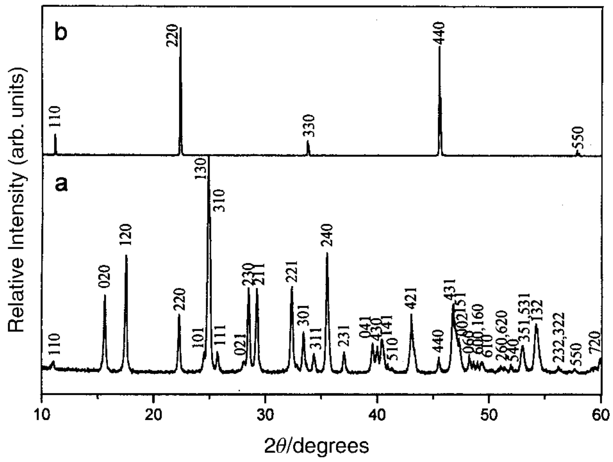

Fig. 1 XRD patterns of the product. (a) X-Ray powder diffraction pattern of ground Sb_2S_3 tubular crystals. (b) X-Ray diffraction pattern of a single Sb_2S_3 tubular crystal.

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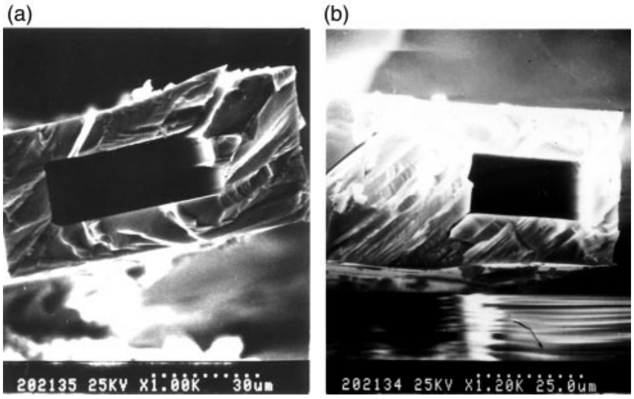

Fig. 2 SEM images of as-produced Sb_2S_3 tubular crystals.

beginning of the process in aqueous solution to form amorphous orange-red Sb_2S_3 according to reaction (1).[11] While ammonium chloride was absent, these newly produced particles could act as nuclei for the growth of Sb_2S_3 crystals, rather than tubules, with the increasing temperature.[15] In the process, the following equilibria existed in solution:

$$NH_4^+ + H_2O \rightarrow NH_3 \cdot H_2O + H^+ \tag{2}$$

$$2S_2O_3^{2-} \rightarrow S^{2-} + S_3O_6^{2-} \tag{3}$$

$$Sb_2S_3 + 3S^{2-} \xrightarrow{NH_4^+} 2SbS_3^{3-} \tag{4}$$

$$2SbS_3^{3-} + 6H^+ \rightarrow Sb_2S_3 + 3H_2S \tag{5}$$

Because of the existence of ammonium chloride combining with the products of equilibrium (3),[16] ammonium sulfide could exist in the reaction system. The as-grown Sb_2S_3 in reaction (1) was partially dissolved due to the effect of ammonium sulfide in equilibrium (4).[12] The process in (4) may form crystal nuclei with minute holes which would maintain the growth of tubular crystals in (5)[17] due to the existence of H^+ and the growth character of orthorhombic Sb_2S_3[18] with a simple chain structure.[19] In the meantime, the orange-red Sb_2S_3 changed to a dark gray color at ~470 K.[12] The feedstock of the reactants was investigated in the experiments and the optimal molar ratio of $SbCl_3$, $Na_2S_2O_3$ and NH_4Cl was 1 : 4–6 : 1.5–2.5. In the products, the yield of the tubular Sb_2S_3 crystals was near to 60% and only about 10% had no tubular open structure, which may be formed due to the reaction (1) proceeding with the decrease in S^{2-} anions. In other words, the use of ammonium chloride in the process established equilibria in the reaction system which gave the opportunity to partially dissolve antimony sulfide with hollow nuclei and refabricate tubules in solution, which is similar to a self-assembly process.

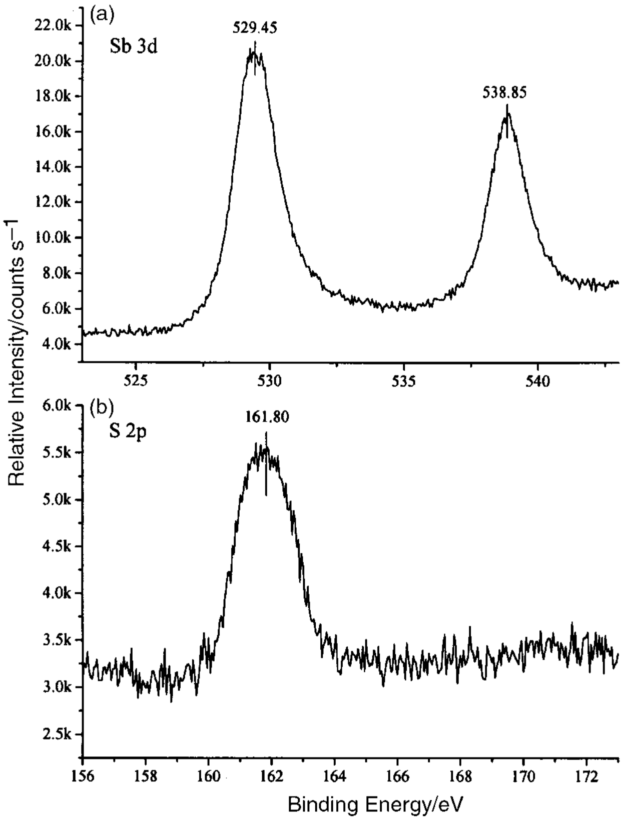

Fig. 3 XPS of the as-produced products: (a) Sb 3d, (b) S 2p.

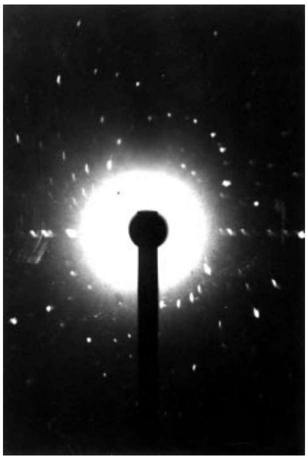

Fig. 4 Transmission X-ray Laue photograph of the single Sb_2S_3 tubular crystal as in Fig. 2(b).

The effect of reaction time and the reaction temperature were also studied. In order to obtain the tubular antimony sulfide crystals, the processing temperature should be no lower than 180 °C and the processing time no shorter than 6 h. The optimal reaction conditions are temperatures ranging from 195 to 200 °C and reaction times ranging from 10 to 30 hours. Processing temperatures higher than 210 °C and reaction times longer than 30 h result in large irregular crystals. In this study, a temperature of 198 °C and reaction periods ranging from 10 to 30 hours were chosen. The 20 h cooling process for the product was good for the growth and the quality of the antimony sulfide tubular single crystals. In solution, varying the pH value from 5 to 8 had no obvious effect on the tubular morphology of the crystals.

In summary, we have succeeded, for the first time, in synthesizing the antimony sulfide tetragonal (or rectangular) prismatic tubular crystals by a simple hydrothermal route at 198 °C. It is believed that these tubular crystals should be expected to have novel properties, and may offer exciting opportunities for potential applications, such as for microsized waveguides,[20] and optical fibers.[21] This method could be applied to the synthesis of Sb_2Se_3, SbSI, and some other tubular chalcogenides.

Acknowledgement

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Notes and references

†XRD patterns were recorded on a MXP18AHF (MAC Science Co Ltd.) rotating anode X-ray diffractometer with graphite monochromatized Cu-Kα radiation ($\lambda = 1.54056$ Å).

‡The morphology and size of the crystals were observed by scanning electron microscopy (SEM), which was performed on a Hitachi X-650 scanning electron microscope.

§X-Ray photoelectron spectra (XPS) were recorded on an ESCALAB MKII X-ray photoelectron spectrometer by using non-monochromatized Mg-Kα radiation as the excitation source.

¶Transmission X-ray Laue photographs were performed on a China JF-1 X-ray generator equipped with a Cu target with films set 31 mm from the sample.

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