Molecular Template Preparation of $AgBiS_2$ Nanowhiskers

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α-$AgBiS_2$ nanowhiskers have been prepared by a solvothermal method at 160 °C. The characterized results showed that the product was α-$AgBiS_2$ which was well crystallized as uniform nanowhiskers. The chain type structure of Bi-S compound under the circumstance of ethylenediamine was found crucial in the formation of α-$AgBiS_2$ nanowhiskers in the possible mechanism.

Currently, developing well-controlled synthesis methods of low-dimensional semiconductor nanomaterials such as nanowires and nanotubes have sparked increasing interest because of their important roles both as interconnecting and active components in optoelectronic nanodevices.[1–5] Thereinto, I-V-VI ternary chalcogenide compounds including $AgBiS_2$ are technologically important in the usage in linear, nonlinear, optoelectronic, thermoelectric devices and optical recording media.[6–8] In addition, its unusual electronic and magnetic properties of $AgBiS_2$ revealed promising applications as a novel mineral semiconductor.[9–11] Based on reports,[12,13] the low temperature phase β-$AgBiS_2$ has a hexagonal structure, which can transform into cubic phase α-$AgBiS_2$ above $468\,K \pm 5\,K$.[12–14] Usually, $AgBiS_2$ can be prepared through solid-state reaction, solid solution technique and flux technique.[15–17] However, the synthesis of low-dimensional $AgBiS_2$ has seldom been reported. In this communication, we report a new route to $AgBiS_2$ nanowhiskers by a moderate molecular template reaction.

All the reagents were of analytic grade. In a typical procedure, 0.01 mol AgCl, 0.01 mol $BiCl_3$ and 0.02 mol K_2S were put into an autoclave with a capacity of 50 mL, then ethylenediamine was filled in until 80% of the total volume was reached. The sealed autoclave was maintained at 160 °C for 24 h and cooled to room temperature on standing in the furnace. The precipitate was collected by vacuum filtration and washed several times with distilled water and absolute ethanol, and then vacuum dried at 50 °C for 6 h.

The obtained sample was characterized by X-ray powder diffraction (XRD) patterns using a Japan Rigaku Dmax γ-A X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). And TEM images were taken with a Hitachi Model H-800 transmission electron microscope using an accelerating voltage of 200 kV.

All the peaks of XRD pattern shown in Figure 1 could be indexed to the cubic phase α-$AgBiS_2$ with cell parameter $a = 5.641$ Å, which is in good agreement with the reported value (JCPDS 21-1178). There is no peak attributable to β-$AgBiS_2$ or impurities. The main morphology of α-$AgBiS_2$ indicated from TEM images (Figure 2) was uniform nanowhiskers with an average diameter of 35 nm, and the length of the nanowhiskers is in micrometer scale.

In this reaction, the formation of α-$AgBiS_2$ nanowhiskers may undertake the following steps: (1) AgCl and $BiCl_3$ are dissolved in ethylenediamine to form Ag^+, Bi^{3+} complexes; (2) The complex of Bi^{3+} and S^{2-} may be ordered under the template effect of ethylenediamine and result into the chain type structure of Bi-S compound;[18,19] (3) Small-sized ions, in this case, Ag^+ released from the complex, attack the Bi-S compound and substitute some Bi in the complex, so they may be able to insert into the chain type structure of Bi-S compound and form ternary chalcogenide nanowhiskers.

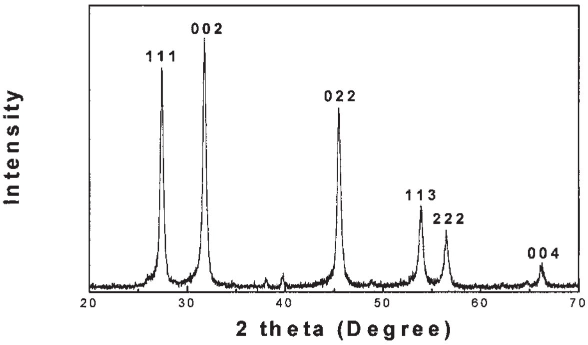


Figure 1. XRD pattern of α-$AgBiS_2$ sample prepared via the solvothermal process.

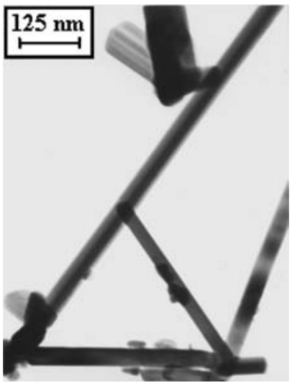
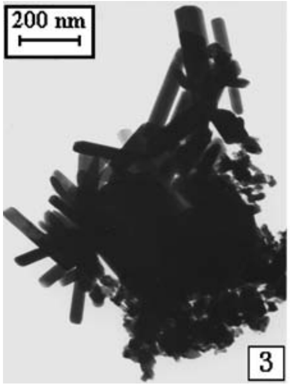


Figure 2. TEM image of the α-$AgBiS_2$ nanowhiskers obtained from solvothermal process.

In order to prove the suggested formation mechanism, we made two different experiments: (1) $BiCl_3$ reacted with K_2S in ethylenediamine first and AgCl was added later; (2) AgCl reacted with K_2S in ethylenediamine first and $BiCl_3$ was added later. Although the XRD analysis of the products of these two experiments proved that both products were α-$AgBiS_2$, the TEM observations showed that the main morphology of the product obtained in the first experiment shown in Figure 3 is nanorod-shaped, while the main morphology of product obtained in the second experiment is nanoparticle-shaped from Figure 4. Based on the above results, we believe the formation mechanism of $AgBiS_2$ is just like what we assume: small-sized ions of Ag^+ insert into the chain type structure of Bi-S compound, which serves as a molecular template in the growth of $AgBiS_2$ nanowhiskers. While Ag-S compound does not have the similar chain structure as Bi-S compound, even Bi^{3+} ions can insert into the crystal structure of Ag-S compound, only nanoparticles can be obtained. The results can be presented in the following way:

$$Bi^{3+} + S^{2-} \xrightarrow[\text{ethylenediamine}]{Ag^+} AgBiS_2 \text{ (nanorods)}$$

$$Ag^{+} + S^{2-} \xrightarrow[\text{ethylenediamine}]{Bi^{3+}} AgBiS_2 \text{ (nanoparticles)}$$



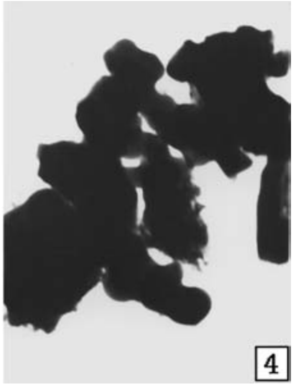


Figure 3. TEM image of the nanorods obtained from the experiment between $BiCl_3$ and K_2S first and AgCl later.

Figure 4. TEM image of the nanoparticles obtained from the experiment between AgCl and K_2S first and $BiCl_3$ later.

To improve our understanding of template effects, we replaced ethylenediamine with benzene or toluene, which have no coordination ability, keeping the other reaction condition constant. The mixtures of Ag_2S and Bi_2S_3 binary sulfides were produced according to XRD analysis. With regard to the pyridine, which has a relatively weak N-coordinating ability but lacks of bidentate coordination ability, TEM observations revealed that only α-$AgBiS_2$ nanoparticles were obtained. Therefore, in the formation of α-$AgBiS_2$ nanowhiskers, ethylenediamine played a very important role as a bidentate ligand to form the relatively stable Ag^+, Bi^{3+} complex and leads to the relatively stable Bi-S rod-like complex.

Moreover, the influences of reaction time and reaction temperature on the reaction process cannot be neglected. It was found that a suitable reaction temperature for the formation of α-$AgBiS_2$ was 160 °C. When the reaction was carried out below 160 °C, the product was a mixture of α-$AgBiS_2$ and β-$AgBiS_2$. Although further prolongation of the reaction time is not very important, the reaction time should be at least 24 h to make the synthetic reaction proceed completely.

In summary, nanocrystalline α-$AgBiS_2$ with uniform nanowhisker morphology has been successfully prepared in ethylenediamine at 160 °C after 24 h solvothermal reaction. The formation mechanism is discussed in detail. The synthesis technique can be easily controlled and is expected to be applicable to the preparation of other multinary chalcogenides containing Bi.

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