Hydrothermal growth of β-Ag_2Se tubular crystals

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Millimeter-sized tubular crystals of Ag_2Se are successfully grown for the first time *via* a hydrothermal reaction route from AgCl, Se and NaOH at 155 °C.

The synthesis of large three-dimensional (3D) mesoscale (millimeter- to centimeter-scale) objects has recently been the focus of much attention.[1–3] Existing technologies for making 3D microstructures are the limited stereolithography,[4] free-form laser sintering (slow)[5] and traditional casting, machining and assembly which are difficult with a complex or porous structure. Whitesides and coworkers reported the fabrication of open regular 3D mesostructures by self-assembly.[1–3] The newly discovered fullerene-like nest polyhedra (NP) and nanotubules have been observed for metal dichalcogenides[6–8] and micrometer-sized hexagonal, hollow needles of CdSe have been prepared by electrodeposition from molten salts.[9] However, a mesoscale crystal with open structure is, to the best of our knowledge, hitherto unknown for Ag_2Se. Here we report for the first time the growth of millimeter-sized tubular Ag_2Se crystals by a known hydrothermal reaction route.

The synthesis was carried out in an autoclave and was based on the disproportionation reaction of Se:

$$4AgCl + 3Se + 6NaOH \rightarrow 2Ag_2Se + Na_2SeO_3 + 4NaCl + 3H_2O \qquad (1)$$

An appropriate amount of AgCl (0.383 g), Se (0.160 g) and NaOH (0.20 g) was put into a Teflon-lined autoclave (50 mL capacity). The autoclave was then filled with distilled water to 80% of the total volume, maintained at 155 °C for 10 h and then allowed to cool to room temperature. The products were filtered off and washed sequentially with distilled water and absolute ethanol to remove the residual impurities. After drying in a vacuum at 70 °C for 2 h, metallic-gray crystals were obtained.

Fig. 1 shows the X-ray diffraction (XRD)† pattern of several Ag_2Se crystals that were crushed. All the reflections could be indexed to the orthorhombic Ag_2Se phase with lattice constants $a = 4.333$, $b = 7.062$, $c = 7.764$ Å, in agreement with the reported data for Ag_2Se (JCPDS Card File, 24-1041). No characteristic peaks of other impurities such as Ag_2O, Se or AgCl were observed.

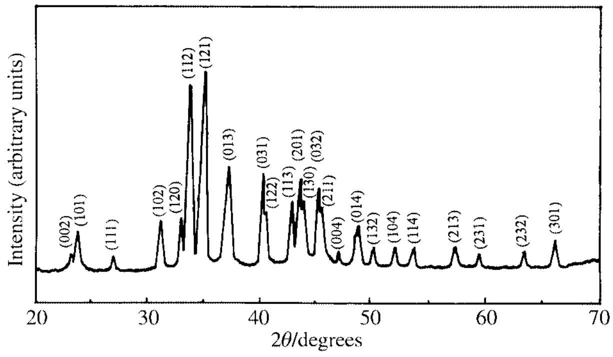

Fig. 1 X-Ray powder diffraction pattern of several Ag_2Se crystals that were crushed.

Fig. 2 shows the scanning electron microscopy (SEM)‡ images of as-grown Ag_2Se crystals. It can be seen that Ag_2Se crystals show tubular hexagonal prism structure. Typically, this structure is 10–15 mm in length, 80–120 μm in diameter and 20–25 μm in thickness. It is of considerable interest that some tubes appear to have one closed-round end [Fig. 2(*b*)], and others show hollow cavities which run through the whole length [Fig. 2(*c*) and 2(*d*) are two undersides of one prism crystal]. From these SEM images, we can see that the as-grown tubular Ag_2Se crystals may show near single crystal nature.

To confirm that single crystals of Ag_2Se were obtained, we recorded the transmission X-ray Laue§ photographs of the tubular crystals. Fig. 3 shows one of these Laue photographs of the Ag_2Se samples. It revealed that the crystal obtained was nearly a single crystal. From the eight-fold symmetrical patterns of the X-ray Laue photographs, we can deduce it is due to the (121) patterns of the characteristic X-ray (Cu-Kα and Cu-Kβ) diffraction. This result was in good agreement with the strong (121) reflection in the XRD pattern.

To provide further evidence for the formation of Ag_2Se crystals, the samples were also characterized by X-ray photoelectron spectra (XPS).¶ The two strong peaks in the spectra (spectra not shown) at 368.00 and 53.65 eV corresponding to Ag 3d and Se 3d binding energy, respectively, are consistent with the formation of Ag_2Se.[10] Quantification of the XPS peak intensities gave elements with a stoichiometry of $Ag_2Se_{1.03}$. No

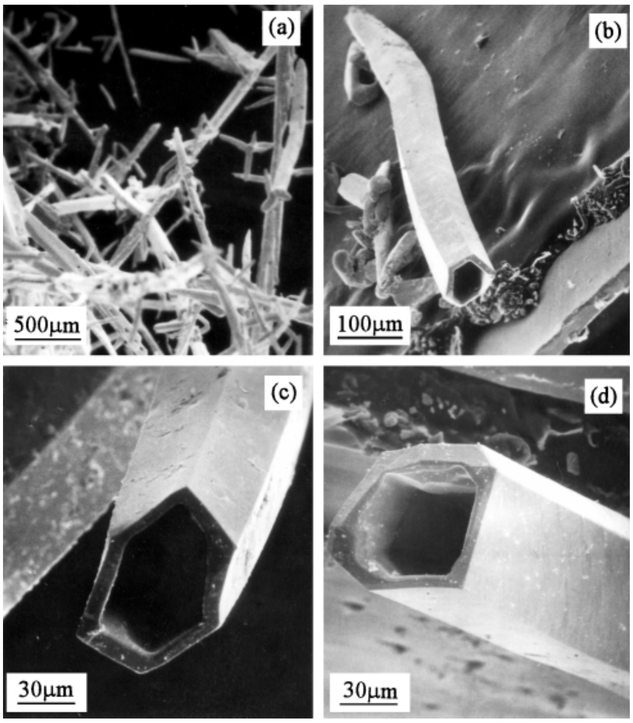

Fig. 2 Scanning electron microscopy images of the as-grown Ag_2Se crystals.

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Fig. 3 Transmission X-ray Laue photograph of the single crystal Ag_2Se as in Fig. 2(*c*).

obvious peaks for silver or selenium oxides were detected, which indicated a high purity of the Ag_2Se crystals produced.

Although the growth mechanism for the tubular crystals is unclear, the reaction temperature and the change of pH were critical factors in the formation of this morphology. Structural studies indicate that Ag_2Se exists as a low-temperature phase β-Ag_2Se (orthorhombic structure) and a high-temperature phase α-Ag_2Se (cubic structure) and the transition from β to α takes place at *ca.* 136 °C.[11] In our hydrothermal route, the essential temperature range for the tubular form was at 150–160 °C. However, the tubular Ag_2Se crystals existed as the low-temperature phase. It may be concluded that the temperature condition falls into the growth thermodynamic stability range of the tubular morphology. According to Korczynski *et al.*,[12] we first prepared the Na_2Se solution (pH 8–9) through the reaction: $3Se + 6NaOH \rightarrow 2Na_2Se + Na_2SeO_3 + 3H_2O$, and then obtained Ag_2Se by the reaction of AgCl with Na_2Se in aqueous media at 150–160 °C. However, the Ag_2Se obtained deviated from its theoretical composition and did not show the tubular morphology. For the growth of tubular crystals of Ag_2Se, we selected a one step hydrothermal reaction from AgCl, Se and NaOH. An initial feedstock pH (NaOH solution) above 13 was needed. In the hydrothermal process, the pH value of the reaction system decreased. So, it is believed that the change of pH value was matched with the nucleation and growth of crystalline Ag_2Se. This matching effect may be beneficial to the formation of the tubular morphology.

In summary, tubular β-Ag_2Se crystals were synthesized successfully for the first time through a hydrothermal reaction at 155 °C. Group 11 chalcogenides have wide applications in semiconductors, pigments,[13] luminescence devices,[14] solar cells, IR detectors and optical fiber communication.[15] It is believed that hollow tubular crystals should be expected to have novel properties, and may offer exciting opportunities for both fundamental research and technological applications. Deeper understanding of the growth mechanism of tubular Ag_2Se crystals and controlling the reaction kinetics are clearly needed.

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Notes and references

† XRD patterns were obtained on a Japan Rigaku Dmax-γA X-ray diffractometer with graphite-monochromatized Cu-Kα radiation (λ = 1.5418 Å).

‡ SEM images were taken with a Hitachi X-650 scanning electron microscope, using a Ni–Co alloy plate.

§ Transmission X-ray Laue photographs were obtained from a China JF-1 X-ray generator equipped with a Cu target with films 31 mm from the sample.

¶ XPS spectra were recorded on an ESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg-Kα ($h\nu$ = 1253.6 eV) radiation as the excitation source.

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