Fabrication of bismuth telluride nanotubes via a simple solvothermal process

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Abstract

The unique Bi_2Te_3 tubes were obtained via a simple solvothermal reaction in the presence of ethylenediaminetetraacetic acid disodium salt. The product was characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Bi_2Te_3 nanosheets are vertically grown off the tube wall to form Bi_2Te_3 tubes. A possible formation mechanism is proposed.

1. Introduction

The performance of thermoelectric materials (TE) depends on the figure of merit ZT of the material ($ZT = \alpha^2 T/\rho\kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity, T is the absolute temperature). Excellent TE materials require a perfect combination of electrical and thermal properties, which needs achieve simultaneously high power factor (α^2/ρ) and low thermal conductivity. Interests are then focused on searching for novel and more efficient thermoelectric materials for cooling and power generation applications. Hicks and Dresselhaus [1,2] pointed out that, it may be possible to increase Z of certain materials by a factor of several times of their bulk values if they have a 1D or 2D nanostructure. Thermoelectric properties of low-dimensional structures started to attract attention in the 1990s. Impressive ZT values have been reported in some low-dimensional structures [3–7].

Currently, the bulk material with the highest thermoelectric figure of merit at room temperature (300 K) is Bi_2Te_3 with $Z = 0.003$, but an improvement by about a factor of 2 is necessary for thermoelectric devices to be competitive with vapor-compression technology. Bismuth telluride based alloys have many important applications, for example, used as thermopiles, thermal sensors, or thermoelectric cooler for laser diodes [8]. A few methods have been developed to prepare Bi_2Te_3 nanomaterials by hard templates approach, kinetic control solution growth, and self-assembly process [9–16]. However, the preparation of Bi_2Te_3 nanotubes is seldom reported [5]. The hollow tube channels have a strong phonon scattering effect like the cages in a holey compound, so one-dimensional nanotubes reduce the lattice thermal conductivity further due to the phonon blocking effect of their low-dimensional nature. It is promising to enhance the overall TE properties by preparing Bi_2Te_3 materials in the shape of nanotube. The challenges in this field are still the development of synthetic methods, control of morphology, and assembly of desired nanostructures. Herein, we reported that Bi_2Te_3 nanotubes can be easily obtained using tubular precursor Te tubes as sacrificial template in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA). Bi_2Te_3 nanocrystals show unique tubular structure we call 'sheet-tube'. Bi_2Te_3 nanosheets grows off the wall of the Te tubes by packing them perpendicular to the axis of the Te tubes, and the content of tube wall change from Te to Bi_2Te_3.

2. Experimental

All chemicals were purchased from Beijing Chemical Co. Limited. A mixture of $BiCl_3$ (0.315 g, 1 mmol), tellurium powder (99.99%, 0.191 g, 1.5 mmol) and EDTA (0.744 g, 2 mmol) was put into a 50 ml Telfon-lined autoclave. The autoclave was then filled with *N,N*-dimethylformamide (DMF) up to 80% of its capacity, and stirred for 1 h at room

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temperature. Next KOH (2.225 g, 40 mmol) was added slowly into the autoclave and stirred for 0.5 h at room temperature. The autoclave was maintained at 140 °C for 10–36 h, followed by cooling to room temperature naturally. The products were filtered and washed with distilled water and absolute ethanol in sequence. Finally, the dark products were dried at 80 °C.

Powder XRD data were collected on a Rigaku D/MAX 2200 PC automatic X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm). The grain morphology and size were observed by SEM (FEI Siron 200) and TEM (HITACHI H-8100). Further structural and elemental analyses were performed using HRTEM (FEI Company, Tecnai G2 F20 S-Twin FEG TEM at 300 kV) and selected area electron diffraction (SEDX).

3. Results and discussion

Fig. 1 shows the XRD patterns of the final product obtained at 140 °C for 36 h. It is identified as a rhombohedral of Bi_2Te_3. The obtained lattice parameters for Bi_2Te_3 are $a = 4.384$ Å and $c = 30.49$ Å, which are in agreement with the reported values $a = 4.385$ Å, $c = 30.46$ Å (JCPDS 15-0863). Some Te was present in the products when the reaction time was less than 16 h.

Under our solvothermal treatment, the reaction of Te powders with $BiCl_3$ yields about 30% Bi_2Te_3 tube-like materials and Bi_2Te_3 sheets. The SEM images of the sheet-rod-like materials are shown in Fig. 2. The tubes, consisted of orientation attachment of Bi_2Te_3 rings, have not been achieved so far (Fig. 2(a) and (c)). The hexagonal or triangle channel of the sheet-tubes is clearly observed in the Fig. 2(b) and (c), with the same shape as that of Te tube [17]. The thickness of the hexagonal plates ranges from more than 20 to 50 nm. Energy dispersive X-ray (EDX) analysis of the sheets and the tube wall indicates that the atomic composition is almost the same in whole sheet-tubes, with ratio of Bi/Te about 2.0:3.0, which is in good agreement with that of the stoichiometric composition of Bi_2Te_3. Size control of the Bi_2Te_3 sheet-tubes was achieved by adjusting the growth temperature and the growth time.

The microstructure of the product was further examined using TEM and HRTEM. TEM image as shown in Fig. 3(a) presents that Bi_2Te_3 sheet-tubes are made up of the lamellar sheets but with ordered and aligned arrangement relationship, which
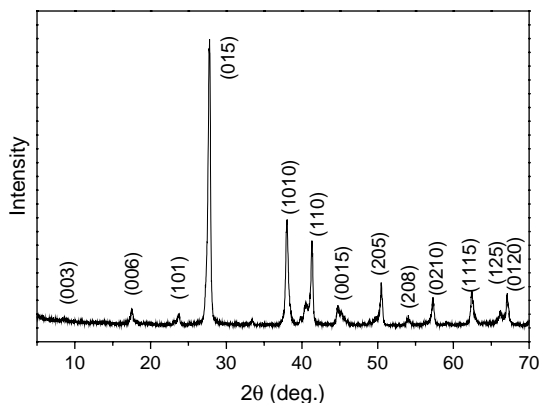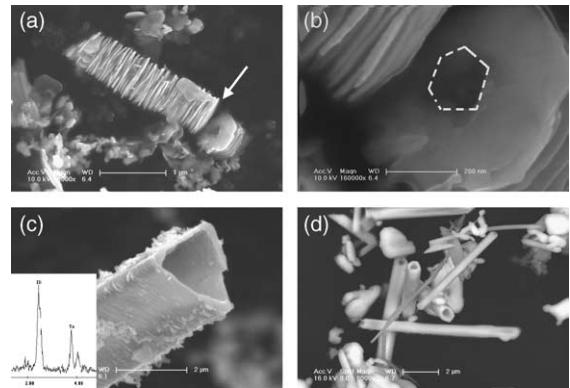

Fig. 2. SEM images of the final product (a) an individual sheet-tube with hexagonal pore; (b) enlarged image taken from the arrow in a; (c) an individual sheet-tube with triangle pore and EDX pattern (inset) taken from wall; (d) Te tubes formed at 140 °C for 24 h.

suggests a possible crystallographic orientation relationship among them. A close examination of the sheet-tubes (Fig. 3(b)) indicates that the sheets grow off a tube and they are mostly attached to the edge of tube wall. The measured wall thickness of the nanotubes is about 10 nm. The selected area electron diffraction (SAED) pattern (inset in Fig. 3(a)) taken from a single sheet-tube indicates that the sheet-tubes are single crystals.

Fig. 3(c) and (d) are representative HRTEM images of a single-crystalline Bi_2Te_3 sheet-tubes shown in Fig. 3(b), which were taken from the area A and B, respectively. An interesting phenomenon was observed in Fig. 3(c) that the lattice planes in the Bi_2Te_3 sheets have almost the same direction with the tube
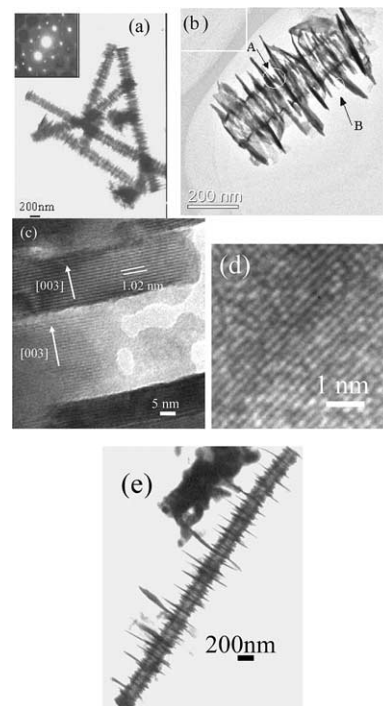

Fig. 3. (a) TEM images of the resulting products and SAED pattern (inset) taken from a single sheet-tube; (b) HRTEM image of an individual sheet-tube; (c) HRTEM image of wall taken from the area A in b; (d) HRTEM image of sheet taken from the area B in b; (e) TEM image of the final product using Te tubes as parent templates.

Fig. 1. XRD patterns of the final product prepared at 140 °C for 36 h.

wall, implying that Bi_2Te_3 sheets epitaxially grow off the tube wall. It is possible to have a long distance epitaxial growth of Bi_2Te_3 sheets on tube wall, and result in the formation of Bi_2Te_3 sheet-tube. A close examination reveals that there is a slight mis-orientation of the lattice fringes between the Bi_2Te_3 sheets and the tube wall (about 1°). The observed fringe pattern of Bi_2Te_3 sheets and tube wall, with spacing of 1.02 nm, is nicely indexed to the (003) plane of the rhombohedral Bi_2Te_3, which indicates that the Bi_2Te_3 sheets grow along the [003] direction. The image shown in Fig. 3(d) indicates the sheets on the tube are a single crystal with a preference growth direction.

The series of starting materials fed, solvent and reaction temperature play a key role in the formation of Bi_2Te_3 sheet-tubes. It is necessary to first mix $BiCl_3$ with EDTA at room temperature for some time to stabilize Bi ions. The sheet-tubes formed only at the temperature range of 120–160 °C. In our reaction process, Te tubes could be prepared under the same solvothermal condition without the using of Bi salts at 140 °C for 24 h, while Te rods would dominative occurred at higher temperature above 180 °C. Typical SEM micrograph of as-prepared Te tubes is shown in Fig. 2(d), the hexagonal pores of the Te tubes indicate that the Te tubes may work as sacrificial template in the formation of Bi_2Te_3 sheet-tubes. The present of Te tubes at the early stage of the reaction might be the key to synthesize Bi_2Te_3 sheet-tubes.

Thus, Bi_2Te_3 sheet-tubes may also be prepared via a two-step process using Te tubes as parent templates. When the Te powders were heated in DMF with KOH at 140 °C, the Te tubes appear to form in the initial heating step, and then Bi_2Te_3 appears to grow epitaxially off the surface of Te tube wall to give Bi_2Te_3 sheet-tubes (shown in Fig. 3(e)) after they were cooled, added by $BiCl_3$ and EDTA and were heated again at 140 °C. Those results further confirm that tubular precursor Te tubes work as sacrificial template to form Bi_2Te_3 tubes in our solvothermal process.

According to the analysis above, the Bi_2Te_3 sheet-tubes in this solvothermal process occur mainly by the following route as a Dissolution–Precipitation–In-site reaction–Growth process to result in such a novel nanostructure. The whole reaction process can be expressed as follow (shown in Fig. 4): When $BiCl_3$, Te powder and EDTA were stirred at room temperature, bismuth ions were first stabled by the coordination of organic ligand EDTA. Te powders would slowly dissolve into solution after the addition of KOH. Then Te nuclei precipitate from the saturated solution and some nuclei quickly grow into Te crystalline tubes. During the next solvothermal treatment at 140 °C, Te tubes are easy to undergo an in-site reaction with Bi^{3+} or $[Bi(EDTA)]^+$ to give Bi_2Te_3 seeds on Te tube wall. The epitaxial orientation relationship of the growth direction between Bi_2Te_3 and Te

is preserved to reduce the lattice mismatch energy. The intrinsic crystal properties dominate the shape of the primary Bi_2Te_3 particles. Due to the anisotropic bonding environment, the crystalline facets tend to develop on the low-index planes to minimize the surface energy, and the Bi_2Te_3 nuclei forming from the solution are tiny thin crystals. Further epitaxial growth of the Bi_2Te_3 seeds perpendicular to the axial direction of Te tubes occurred in the next growth step, in which the consumed Te came from tube wall and solution. Finally, Bi_2Te_3 sheet-tubes formed due to the completely growth of the Te tube wall.

4. Conclusions

In conclusion, single-crystal Bi_2Te_3 sheet-tubes have been synthesized by a simple ligands-assisted solvothermal method at 140 °C. Of interest to note is the formation of the Bi_2Te_3 sheet-tubes is due to in-site reaction of Te tube wall to Bi_2Te_3 sheets. Te tubes are intentionally formed in the first step and epitaxial growth of Bi_2Te_3 nanosheets occurred by packing them perpendicular to the axis of the central Te tubes in the second step. We believe that these well-built structures are desired low-dimensional thermoelectric building-blocks for possibly achieving a high thermoelectric figure of merit. And this facile solvothermal route might make a new generation of sophisticated nanostructures such as Bi_2Te_3–Te sheet-tube possible.

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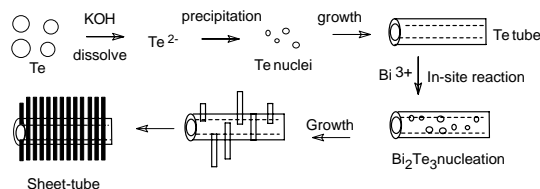[17] G. Xi, Y. Peng, W. Yu, Y. Qian, Cryst. Growth Des. 5 (2005) 326.

Fig. 4. Proposed growth process of the Bi_2Te_3 sheet-tube.