A General Hydrothermal Method to V_2VI_3 Thermoelectric Nanomaterials Directly from the Corresponding Elements

Bo Zhou,[1,2] Jian-Ming Hong,[1] and Jun-Jie Zhu*[1]
[1]*Key Lab. of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering,*
Nanjing University, Nanjing 210093, P. R. China
[2]*Jiangsu Key Laboratory of Biofunctional Materials, College of Chemistry and Environmental Science,*
Nanjing Normal University, Nanjing 210097, P. R. China

(Received March 17, 2008; CL-080285; E-mail: jjzhu@netra.nju.edu.cn)

A general hydrothermal method was developed for the preparation of well-crystallized V_2VI_3 (V = Sb and Bi; VI = S, Se, and Te) thermoelectric nanomaterials directly from the corresponding elemental powders. X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) techniques were used to characterize the products and investigate the possible reaction mechanism.

The main-group metal chalocogenides such as V_2VI_3 (V = Sb and Bi; VI = S, Se, and Te) group compounds have attracted much attention owing to their wide application in thermoelectric and optoelectronic devices.[1–4] Many efforts were made to find simple and efficient methods to synthesize the group of compounds, especially their nanomaterials with improved properties.[5] The reported synthesis methods included chemical vapor deposition (CVD), flash evaporation, sputtering, hot wall epitaxy, organometallic complex decomposition, etc.[6] And recently, many wet chemical methods[7] have been successfully developed, such as sonochemical techniques, electrochemical deposition, solvothermal routes, the crystallization of amorphous colloids, polyol process, and microwave-assisted method. However, these methods may require relative high temperature, and may involve the use of expensive and toxic organic agents and the relative complicated procedures may be involved. Therefore, finding convenient and environmentally benign approaches for the production of these V_2VI_3 nanomaterials is still a challenge.

Herein, we report a general and simple hydrothermal method to produce V_2VI_3 nanomaterials directly from the corresponding elements. Few reports used Se or Te powder as source for the preparation of V_2VI_3 nanoparticles.[8] Moreover, direct element reactions of V and VI were only used in the traditional melting–quenching technology and spark plasma sintering technology,[9] where high temperature and high vacuum were needed.

The syntheses of Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3 were similar. Pure products could be obtained via the hydrothermal reactions of corresponding elements[10] as proved by their XRD patterns[11] shown in Figures 1a, 2a, and 3, which were in good agreement with those reported in the literatures (JCPDS No. 15-0863, 71-0393, and 33-0214), respectively. And they were all hexagonal crystals with rhomb-centered lattice.

Two phenomena should be noted in the preparation. One is that the compounds were produced via the direct reactions of the corresponding elements as represented by eq 1. The other is that alkali could accelerate these reactions.

$$2V + 3VI \rightarrow V_2VI_3 \quad (V = Bi \text{ and } Sb; VI = Te, Se, \text{ and } S) \quad (1)$$

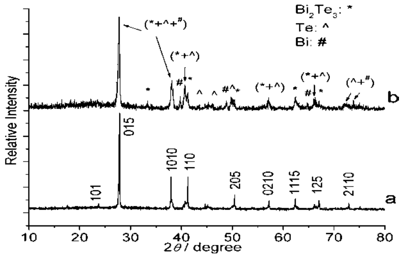

Figure 1. XRD patterns of the products obtained after (a) 10 h and (b) 2 h of reaction in solution containing 1 g of KOH in the syntheses of Bi_2Te_3.

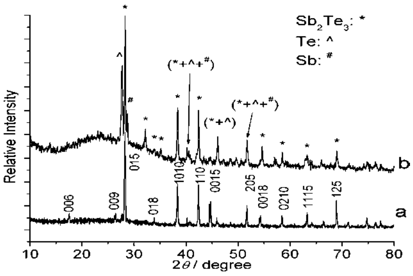

Figure 2. XRD patterns of the products obtained after reacted for (a) 10 h in solution containing 1 g of KOH, and (b) 17 h without KOH, in the syntheses of Sb_2Te_3.

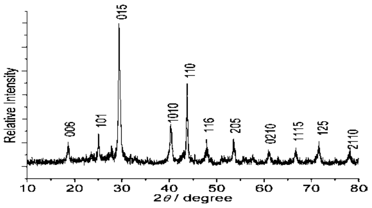

Figure 3. XRD pattern of the product obtained after reacted in alkaline solution (containing 1 g of KOH) for 24 h in the synthesis of Bi_2Se_3.

The direct element reaction can be proved by the following facts: A) If time was not long enough for the reaction to be completed, only the unreacted elements were found besides the expected products. There were no other by-products or mid-products. This suggests that elements directly reacted with each other to produce the corresponding compounds. Figure 1b showed the XRD pattern of the product obtained in the synthesis of Bi_2Te_3 after reaction for 2 h in a system containing 1 g of KOH. All the XRD peaks could be indexed to Bi_2Te_3, Bi or Te (JCPDS File Nos. 15-0863, 44-1246, and 36-1452), which meant that elemental Bi and Te reacted directly to produce Bi_2Te_3. B) Even in a system containing only the elemental powders and water, the corresponding compounds could still be obtained, though slowly. And, similarly, only unreacted elements were found along with the expected compound product. As evidenced by the XRD pattern shown in Figure 2b, after reacted for 17 h without KOH, Sb_2Te_3 was obtained along with some unreacted Sb (JCPDS File No. 71-1173) and Te. This result implied that Sb_2Te_3 was obtained via the direct reaction of elements Sb and Te.

The XRD results shown in Figure 2 also give the evidence of the second phenomenon: alkali could accelerate the reactions. In the synthesis of Sb_2Te_3, the reaction was completed within 10 h (Figure 2a) when 1 g of KOH was added into the system, while it was not completed even after 17 h of reaction without alkali (Figure 2b). This accelerating effect of alkali can be explained as follows: KOH improved the dissolving of Te powder as represented by eq 2, which can be carried out reversely and give out amorphous Te nanoparticles (eq 3).[8,12] These amorphous Te nanoparticles were much more active than the initial powder and reacted more quickly with Sb to produce Sb_2Te_3 (eq 4). The consumption of Te nanoparticles impelled eqs 2 and 3, and accelerated the translation from Te powder into more active α-Te nanoparticles. Thus, the reaction for the production of Sb_2Te_3 was accelerated. The explanation for the acceleration effect of alkali is also consistent with the mechanism of the direct reaction of elements.

$$3\text{Te (powder)} + 6\text{OH}^- \rightarrow \text{TeO}_3{}^{2-} + 2\text{Te}^{2-} + 3\text{H}_2\text{O} \quad (2)$$

$$\text{TeO}_3{}^{2-} + 2\text{Te}^{2-} + 3\text{H}_2\text{O} \rightarrow 3(\alpha\text{-Te}) + 6\text{OH}^- \quad (3)$$

$$3(\alpha\text{-Te}) + 2\text{Sb} \rightarrow \text{Sb}_2\text{Te}_3 \quad (4)$$

The synthesis of Bi_2Se_3 was also similar to those of Bi_2Te_3 and Sb_2Te_3. Pure Bi_2Se_3 was obtained via reaction of elements Bi and Se, and KOH played the same accelerating role.

The morphologies of the as-prepared Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3 were studied with TEM. As shown in Figure 4, they were all well-crystallized sheets or flakes with straight edges. The discrete and bright spots in the corresponding selected area electron diffraction (SAED) patterns indicate the single crystallinity of individual sheets. This sheet-like morphology is strongly correlated with the isomorphic quasi-layered crystal structure they have.[13] The size of the sheets was different for various compounds. The Sb_2Te_3 crystalline sheets were of the largest size of 2–5 μm, the Bi_2Se_3 flakes were of the smallest size of ≈100 nm, and the Bi_2Te_3 sheets were mainly of the medium size of 200–500 nm.

Sb_2Se_3, Bi_2S_3, and Sb_2S_3 can also be obtained via the similar hydrothermal reactions of corresponding elements. However, these reactions were much slower, and alkali worked not so effectively as accelerating agent. And some unexpected reactions might result from the addition of alkali.

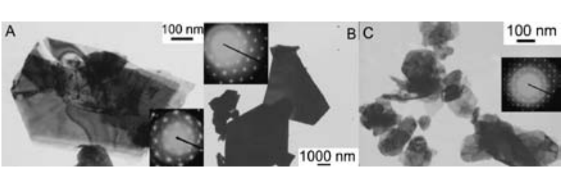

Figure 4. TEM images and the corresponding SAED patterns of the as-prepared Bi_2Te_3 (A), Sb_2Te_3 (B), and Bi_2Se_3 (C).

In summary, a general hydrothermal method has been developed to prepare the well-crystallized nanomaterials of V_2VI_3 group compounds from the corresponding elements. Alkali can accelerate the reactions by improving the dissolving the chalcogens and translating them into much more active amorphous nanoparticles. This work proves that element reaction route can be used in milder hydrothermal technique, though it was formerly used only in melting–quenching technique and mechanism-alloying technique.

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10 The typical synthesis procedure is as follows: Powders of elements of group V (Bi or Sb) and group VI (Te, Se, and S) in molar ratio of 2:3 were put into a Teflon-lined autoclave, following which, 0–1 g of KOH was put into it, distilled water was then added into it up to the 80% of its capacity. The sealed autoclave was kept at 180 °C for a certain time. The products were centrifuged and washed with distilled water and absolute alcohol several times in sequence, and then dried at 60 °C.

11 The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and selected area electron diffraction (SAED) with a Philips X'pert X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) and JEM-200CX (JEOL, 200 kV) TEM, respectively.

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