研究简报

微波加热制备空心和锯齿形貌 Bi_2Te_3 晶体

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关键词: 微波加热; 纳米结构; 离子液体
中图分类号: O613.53; O614.53+2 **文献标识码**: A **文章编号**: 1001-4861(2010)09-1695-04

Preparation of Well-Crystallized Bi_2Te_3 Hollow Spheres and Nanosaws by Microwave Heating Method

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Abstract: Well-crystallized Bi_2Te_3 hollow spheres and nanosaws were prepared by microwave heating. Both the ionic liquid and the microwave heating play important role in the formation of the above nanostructures. Hollow spheres can not be obtained only by electronic stove heating, while the addition of ionic liquid leads to fast preparation of nanosaws structure under microwave heating conditions. The similar experimental results have been observed in the preparation of Bi_2S_3, Sb_2S_3 and Bi_2Se_3 nanostructures.

Key words: microwave heating; nanostructures; ionic liquid

Bismuth telluride has been one of the most important semiconductor thermoelectric materials (E_g=0.15 eV) at room temperature since the report of its thermoelectric properties[1-3]. Some properties of Bi_2Te_3 prepared by mechanic alloying[4-5], physical evaporation[6-7], ultrarapid quenching[8], hot-pressing[9] have been particularly studied. Studies have proved that the figure of merit of Bi_2Te_3 could be improved by structural modification. The theoretical calculations indicate that it is possible to enhance the thermoelectric properties by using nanomaterials[10-12]. Then, Bi_2Te_3 with different nanostructures (such as quantum-well structrue, superlattice thin film and nanowire array) were synthesized by methods of reverse micelle[13], chemical deposition[14], template[15-16], solvothermal[17-18].

Microwave heating has been applied in synthetic chemistry for years. In microwave field the rapid volumetric heating can result in higher reaction rates and reduction in reaction times often by orders of magnitude. On the other hand ionic liquids are very good media for absorbing microwaves, thus leading to a very high heating rate. By combining the advantages of both microwave heating and ionic liquid, we have synthesized Te nanowires and nanorods[19], ZnO flower-like structure[20], CdS and ZnS nanoparticles[21], Bi_2S_3, Sb_2S_3 and Bi_2Se_3 nanostructures[22-23], $PbCrO_4$ and Pb_2CrO_5

收稿日期:2010-04-16。收修改稿日期:2010-06-12。
西南交通大学科技发展基金,西南交通大学青年教师科研起步项目(No.2009Q052) 资助项目。
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rods[24] in relatively short time.

In this work, Bi_2Te_3 nanostructures were prepared by microwave heating in the presence of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]). Bi_2Te_3 nanosheets and hollow spheres were prepared using ethylene glycol (EG) as solvent under microwave heating conditions. Harpeness et al.[25] tried to synthesize Bi_2Te_3 by the polyol method in microwave field, but Bi_3Te_4 was obtained instead of Bi_2Te_3. In the presence of ionic liquid, Bi_2Te_3 nanosaws was prepared instead of hollow spheres under microwave heating conditions. The Bi_2Te_3 nanostructures with distinctive morphologies were prepared in electronic stove at 150 ℃ for much longer time for comparison.

1 Experimental

The conditions for preparation of some typical samples at 150 ℃ are listed in Table 1.

As indicated in Table 1, Sample **1** and **2** were prepared with the same reaction system but sample **1** was prepared in electronic stove for 24 h, and sample **2** was prepared by microwave heating for 30 min. The experimental reagents for Sample **3** was similar to that of sample **1** and **2**, but [BMIM][BF_4] (0.5 mL) was added. In a typical procedure for preparation of Bi_2Te_3, the reagents were mixed by a magnetic stirrer at room temperature, and were heated to 150 ℃ in electronic stove for 24 h or by microwave heating for 30 min without stirring. Finally, heating was terminated and the solution was cooled to room temperature. Black suspension was obtained after heating. The products were separated by centrifugation, washed with absolute ethanol three times and dried at 60 ℃ in vacuum.

The microwave oven used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). XRD was performed with a Rigaku D/max 2550V X-ray diffractometer using graphite monochromatized high-intensity Cu $K\alpha$ radiation (λ=0.154 178 nm). The TEM micrographs and the electron diffraction (ED) patterns were taken with a Hitachi H800 electron microscope with an accelerating voltage of 200 kV.

Table 1 Conditions for preparation of some typical samples at 150 ℃

Sample No.	Reaction system	Heating		Morphology
		Method	Time	
1	TeO_2 (0.015 g)+EG (0.9 mL) +5mol·L^{-1} HNO_3 (0.9 mL)+ $Bi(NO_3)_3$ (0.032 g)+EG (7.5 mL)	Electronic stove	24 h	Nanosaws & nanosheets
2	TeO_2 (0.015 g)+EG (0.9 mL) +5mol·L^{-1} HNO_3 (0.9 mL)+ $Bi(NO_3)_3$ (0.032 g)+EG (7.5 mL)	Microwave	30 min	Hollow sphere
3	TeO_2 (0.015 g)+EG (0.9 mL) +5mol·L^{-1} HNO_3 (0.9 mL)+ $Bi(NO_3)_3$ (0.032 g)+EG (7 mL)+[BMIM][BF_4] (0.5 mL)	Microwave	30 min	Nanosaws

EG=ethylene glycol.

2 Results and discussion

Fig.1 shows XRD patterns of sample **1** and **2**. From Fig.1 one can see that the products are a single phase of well-crystallized Bi_2Te_3 with hexagonal structure (PDF 82-0358). The result indicates that in microwave field Bi_2Te_3 product can be synthesized in 30 min at 150 ℃, and it requires less time for preparation. The yield of Bi_2Te_3 powder is up to 81% after the product is washed with absolute ethanol three times and dried at 60 ℃ in vacuum.

Fig.2 shows the TEM micrographs of Bi_2Te_3 samples consisting of hollow spheres, sheets and

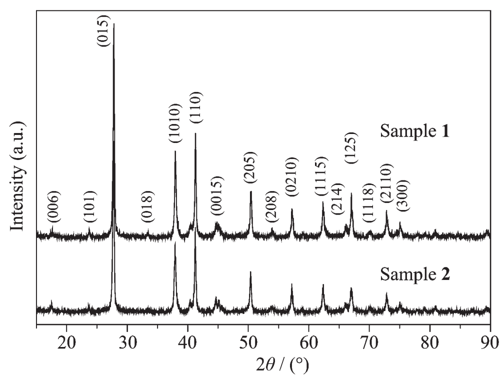

Fig.1 XRD patterns of sample **1** prepared in electronic stove at 150 ℃ for 24 h, and sample **2** prepared by microwave heating at 150 ℃ for 30 min

nanosaws. Fig.2a and b show the TEM micrographs of nanosheets, and nanosaws from sample **1** prepared without [BMIM][BF_4]. The nanosheets are derived from element Te reduced by EG from TeO_2 below 150 ℃. Fig.2c and d show the TEM micrographs of sample **2**. Bi_2Te_3 hollow spheres with diameters from 100~200 nm and fewer nanosheets. Fig.2d shows that the size of the hollow sphere wall is 10~20 nm and there are some particles attaching on the surface of the sphere. The inset indicates that the hollow sphere is polycrystalline. [BMIM][BF_4] (0.5 mL) is added in preparation of sample **3**, and the morphology of nanosaws in sample **3** is greatly different from that of hollow spheres in sample **2**.

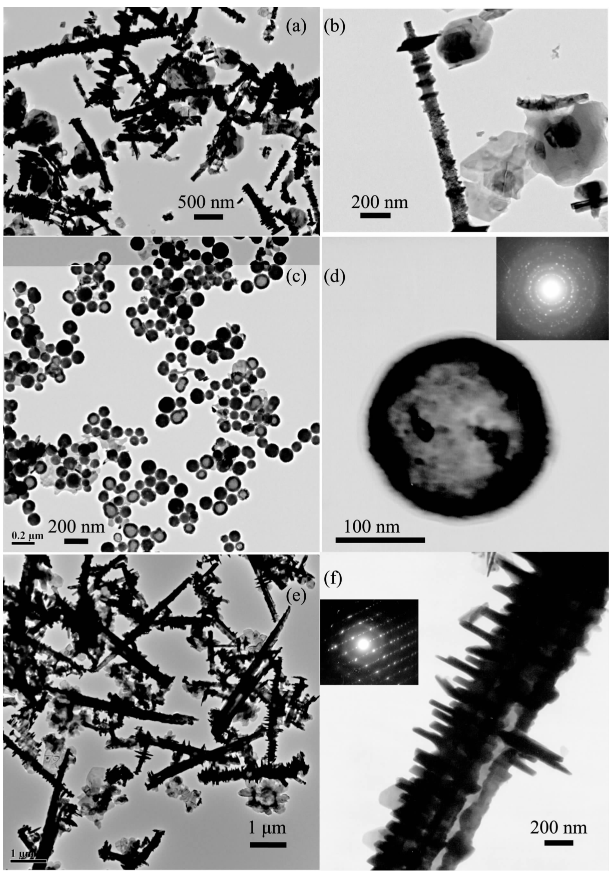

Fig.2　TEM micrographs of Bi_2Te_3 samples: (a) and (b) sample **1**, (c) and (d) sample **2**, (e) and (f) sample **3**; Insets of (d) and (f) show the electron diffraction pattern

Microwave heating and electronic stove heating have different temperature-time curves, which has great effects in the formation of Bi_2Te_3. According to the curves shown in Fig.3, one can see that microwave heating rate is higher than electronic stove one. In microwave heating at 150 ℃ after 10 min the black Bi_2Te_3 is formed and after 30 min well-crystallized single phase Bi_2Te_3 could be obtained. While in furnace heating after 45 min white Bi_2TeO_5 is observed, after 90 min the color is darkening slowly and after 7 h the color turns into black entirely. In the sample of as-prepared Bi_2Te_3 by electronic stove heating at 150 ℃ for 11 h, there are several impurity phase peaks. While, after 24 h the impurity phase peaks disappear and the XRD pattern shows single phase of well-crystallized Bi_2Te_3 (Sample **1**) with the hexagonal structure (PDF 82-0358). The addition of ionic liquid ([BMIM][BF_4]) could make the temperature-rising faster under microwave heating conditions, thus promoting the growth of Bi_2Te_3 nanosaws.

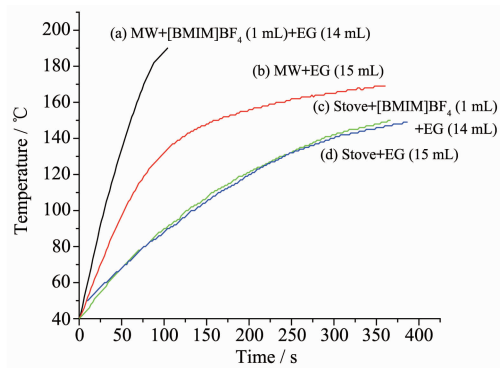

Fig.3　Temperature-time curves of microwave heating and electronic stove heating: (a) Curve of Sample **3**, (b) Curve of Sample **2**, (c) Curve of electronic stove heating with [BMIM]BF_4 used, (d) Curve of Sample **1**

In many papers, Bi_2Te_3 nanostructures were reported to be prepared using Te powder, OH^- (basic reagent), Bi^{3+} and reducing agent (such as $NaBH_4$ and N_2H_4) by solvothermal method[17,26-27]. OH^- was used to change Te powder into Te^{2-} and the reducing agents were used to reduce Bi^{3+} to elemental Bi. Then Te^{2-} and Bi^{3+} or Te and Bi could react to form Bi_2Te_3 by heating. Zhu et al.[28] synthesized Bi_2Te_3 nanorods and nanosheets using $Bi(NO_3)_3 \cdot 5H_2O$, Te powder, KOH, EG and glycerol by microwave heating, in which process, elemental Bi was reduced from Bi^{3+}, and then Bi reacted with Te. In the present work, acidic HNO_3 aqueous solution was used instead of basic environment reported in the literature, and EG was used as a co-solvent. In the preparation of samples, a white intermediate product (Bi_2TeO_5) was obtained, and at last it transformed to black Bi_2Te_3. This white intermediate product could not change to Bi_2Te_3 at temperatures below 130 ℃ by microwave heating. We suggest that the intermediate product Bi_2TeO_5 acts as the core for the formation of Bi_2Te_3 hollow nanospheres. Bi_2Te_3 nanoparticles derived from Bi_2TeO_5 are on the Bi_2TeO_5 surface, forming the shell of the hollow nanosphere. When the Bi_2TeO_5 cores were completely decomposed, the hollow nanospheres formed. The ionic liquid [BMIM]BF_4 acts as surfactant[29], which benefits the formation of nanosaws.

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