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Influence of NaOH on the synthesis of Bi_2Te_3 via a low-temperature aqueous chemical method

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Abstract NaOH was used to adjust the pH of the solution in the synthesis of nanostructured Bi_2Te_3 alloys via hydrothermal and solvothermal process. However, it is still elusive whether NaOH is necessary and how it affects on the size and morphology of Bi_2Te_3 which contributes a lot to the thermoelectric figure of merit ZT. The present work suggested that bulk quantity of nanostructured Bi_2Te_3 with considerable uniform morphology of nanoflake could be yielded without NaOH when the reaction time ranged from 6 h to 48 h. These nanoflakes have about 10–30 nm thickness and 50–300 nm width. When adding NaOH, the morphology of Bi_2Te_3 becomes various.

Introduction

Considerable attention has been focused on bismuth telluride alloys which are known as the best thermoelectric materials at room temperature [1, 2] with high potential application in power generator, cooler, thermochemistry-on-a-chip, DNA microarrays, fiber-optic switches, and microelectrothermal systems [3–6]. All these applications owe to their high thermoelectric figure of merit $ZT = \alpha^2\sigma T/\kappa$, where α, σ, κ, and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively.

It was suggested [7, 8] that the ZT of nanostructured thermoelectrics in low dimensional form would be significantly enhanced compared with their bulk counterparts. Venkatasubramanian et al. [5] reported on Bi_2Te_3 thin-film superlattices which demonstrate a significant enhancement in ZT at 300 K by controlling the transport of phonons and electrons. Harman et al. [7] found that quantum dot superlattice structures have a potentially more favorable carrier scattering mechanism and a much lower lattice thermal conductivity. Cao et al. [9] indicated that the nanoscale laminated structure improved the thermoelectric performance of the nanocomposites which were hot pressed from Bi_2Te_3 and Sb_2Te_3 nanopowders.

Among current methods for synthesis of low dimensional nanostructure Bi_2Te_3, solvothermal and hydrothermal method gains an advantage of low synthesis temperature and fine grain size over other processes. Zhang et al. [10] showed that Bi_2Te_3 crystals ranging from 20 to 25 nm could be yielded at 373 K. Ji et al. [11] reported that rare earth containing Bi_2Te_3 nano-powders were synthesized in ethanol at 423 K for 24 h by solvothermal processes, and ZT $\approx$ 0.22 was obtained for a sample of Ce–Bi_2Te_3 at about 450 K. Cao et al. [9] found that nanotubes of quasilayered Bi_2Te_3 compound could be prepared by hydrothermal synthesis. The addition of nanotubes results in a remarkable decrease of the thermal conductivity, while the electrical conductivity is much less affected, and thus ZT increases. However, most of these study [12, 13] have emphasized the importance of alkali modifiers (NaOH, KOH, for instance) during the growth process of nanocrystal via a solvothermal and hydrothermal process. One of them pointed out that [14] OH^- is used to change Te powder into Te^{2-}, and Zhao [15] even concluded that Bi_2Te_3 could not be synthesized in a solution without alkaline additives. Actually, the exact role played by NaOH is still elusive. For example, it is not clear whether the alkali modifier is necessary and how it effects on the size and morphology of Bi_2Te_3 which contributes a

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lot to the ZT. The aim of this article is to address these two issues by providing some new experimental evidence using a low-temperature aqueous chemical method [16] belonging to hydrothermal process.

Experimental

Tellurium powder (5 N purity, ≤30 μm), bismuth chloride ($BiCl_3$), sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), and ethylenediamine-tetra-acetic disodium salts (EDTA) are analytical grade without further purification. In a typical procedure, 0.0015 mol Te powder, 0.4 g $NaBH_4$, 0.1 g EDTA, and 0.001 mol $BiCl_3$ were mixed with 150 mL distilled water in three-necked round bottom flask subsequently. The temperature was adjusted to keep the mixed solution boiling and being stirred simultaneously through the total process. In this work, the experiments were divided into two parts: S0-6, S0-24, S0-36, and S0-48 represented samples prepared without NaOH and reacted for 6, 24, 36, and 48 h, respectively; while S11.9, S12.2, S12.5, S12.7, S13.2, and S13.5 represented those synthesized with different concentrations of NaOH in the solution, of which the initial pH values were 11.9, 12.2, 12.5, 12.7, 13.2, and 13.5, respectively. And the reaction time of these six samples were kept 48 h unchanged.

The phase structures of the products were investigated by X-ray diffractions (XRD) with a Rigaku D/MAX-2550P diffractometer using Cu*Kα* radiation ($\lambda = 0.154056$ nm). The powder morphology and fine structure were observed using a JEM-2010 transmission electron microscope (TEM) and FEI-Siron field emission scanning electron microscope (FESEM).

Results and discussion

The XRD patterns in Fig. 1 indicate that Bi_2Te_3 could be yielded without the addition of NaOH when the reaction time was enough, for instance, 24, 36, or 48 h. When time was relatively short (S0-6, 6 h), there were clear diffraction peaks of Bi beside Bi_2Te_3. Therefore, the results from XRD patterns, even synthesized in a shorter reaction time, disprove the previous argument that Bi_2Te_3 could not be synthesized in the solution without alkaline additives [15]. Previous researchers believed that the disproportionating reaction of Te, which is described as equation

$$3Te + 6OH^- \Leftrightarrow 2Te^{2-} + TeO_3^{2-} + 3H_2O \quad (1)$$

would not proceed without NaOH [17, 18]. However, the reaction of Eq. 1 could actually never take place spontaneously from the left-side to the right-side of the equation.

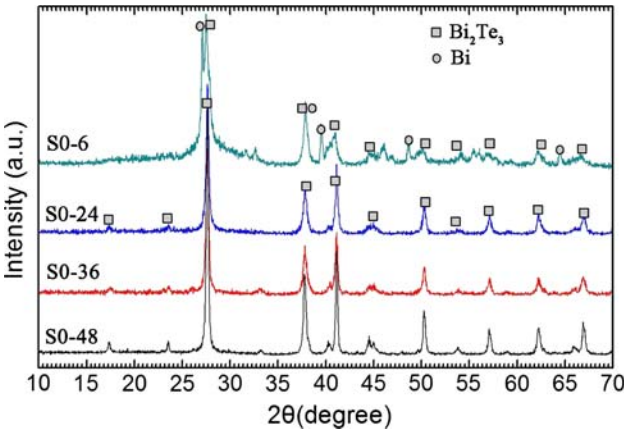

Fig. 1 X-ray diffraction (XRD) patterns of Bi_2Te_3 synthesized in different reaction time without addition of NaOH. S0-6, S0-24, S0-36, and S0-48 represent the samples produced in reaction times of 6, 24, 36, and 48 h, respectively

The standard positive electrode potential in this cell reaction is $E^0_{Te/Te^{2-}} = -1.143\,V$, while the standard negative electrode potential is $E^0_{Te/TeO_3^{2-}} = -0.57\,V$, thus the electromotive force of the cell (abbreviated as e.m.f.) is $E^0 = -1.143 - (-0.57) = -0.573v < 0$, and then the free energy change $\nabla G = -nFE > 0$ (n is the number of electrons transferred; F is the Faraday (96500C)). So the reaction is not spontaneous from the left to the right according to the criteria of spontaneity in terms of G (Gibbs function). Instead, the reverse reaction could occur [19, 20], for the e.m.f. is positive from the right to the left. Hence, NaOH which yields OH^- is not necessary for the synthesis of Bi_2Te_3.

The synthesis mechanism of Bi_2Te_3 is illustrated as follows (Eqs. 2, 3, and 4):

$$BiCl_3 + H_2O \Leftrightarrow BiOCl + 2H^+ + 2Cl^- \quad (2)$$

$$4BiOCl + 3BH_4^- + 5H_2O \Leftrightarrow 4Bi + 3H_2BO_3^- + 6H_2\uparrow + 4H^+ + 4Cl^- \quad (3)$$

$$2Bi + 3Te \Leftrightarrow Bi_2Te_3 \quad (4)$$

This deduction is based on the fact that the reduction half reaction of overall cell reaction Eq. 3 can be described as

$$BiOCl + 2H^+ + 3e^- \Leftrightarrow Bi + Cl^- + H_2O \quad (5)$$

$$E = E^0 - \frac{RT}{zF}\ln Q \quad (6)$$

The e.m.f. of a cell is given by the Eq. 6 according to the Nernst Equation. Take 0.0005 mol $BiCl_3$ as an example, the e.m.f. in Eq. 3 is a positive value calculated by Eqs. 5 and 6. Based on the Gibbs function criterion, BiOCl could be reduced to the corresponding metallic state though in an acidic solution, and it was also proved by diffraction peaks of Bi in S0-6 XRD pattern. In the following step, these metallic particles Bi and Te continue to absorb energy to form binary compound Bi_2Te_3.

Figure 2a and b show TEM images of sample S0-48 synthesized for 48 h without NaOH. The bulk quantity of hexagonal nanoflake with uniform morphology was yielded. Meanwhile, some nanoscale hollow spheres with hexagonal border (Fig. 2b) were synthesized. It is the first time to report this Bi_2Te_3 core-shell nanostructure using the hydrothermal process, and its exact formation mechanism is still under investigation. SEM images of sample S0-48 (shown in Fig. 2c, d) clearly indicate that the nanoflake has about 10–30 nm thickness and 50–300 nm width. And these nanoflakes could radially form a flower-like nanostructure. According to the model of "nucleus saturation" [21] proposed by Ji et al., Bi_2Te_3 crystal will grow faster in *a*- or *b*-axis directions than in *c* direction in Bi^{3+} dilute solution caused by the chelation of Bi and EDTA. The low-magnification SEM image (Fig. 2e) of sample S0-24 shows that Bi_2Te_3 nano thin sheets with bulk quantity have been successfully synthesized without addition of NaOH when reacting for 24 h. The considerable uniform morphology, compared with the ones reported by our group previously [21], may lead to an enhancement of thermoelectric property.

The nanocrystal Bi_2Te_3 can all be yielded when the pH values of reaction solutions ranged from 11.9 to 13.5. The XRD patterns of these products in Fig. 3 show no significant difference from each other, except for sample S13.5. Its final products contained a small amount of Zeolite, P(Na) which is generated by the reaction between the glass

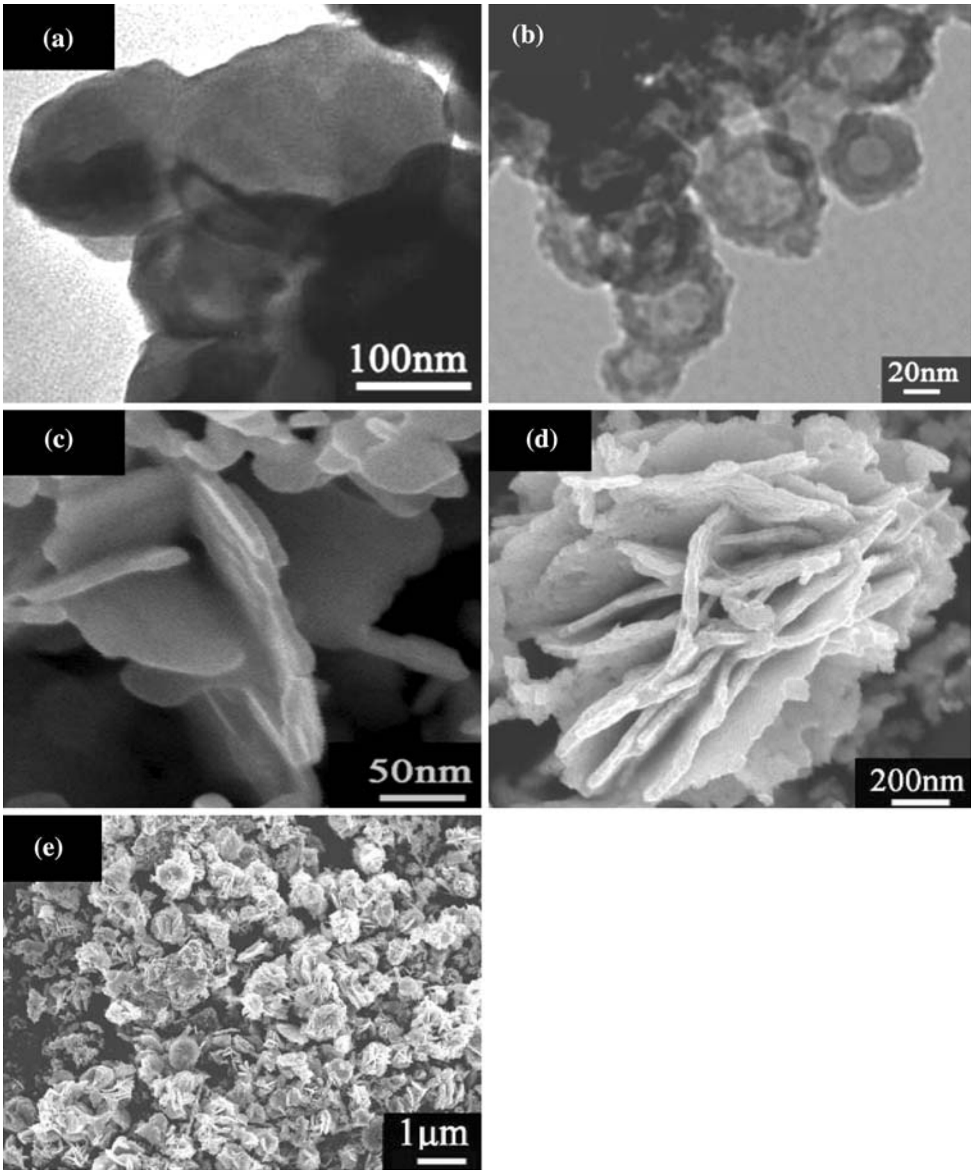

Fig. 2 **a**, **b** Transmission electron microscopy (TEM) images of Bi_2Te_3 synthesized for 48 h in the absence of NaOH; **c**, **e** Scanning electron microscopy (SEM) images of Bi_2Te_3 synthesized for **c** 48 h, **d,** 48 h and **e** 24 h, respectively, without addition of NaOH

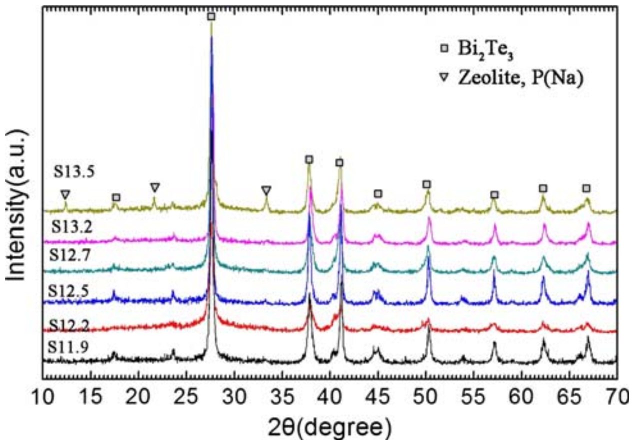

Fig. 3 XRD patterns of Bi_2Te_3 synthesized in solutions with different pH values adjusted by the concentration of NaOH. "SX" means that the pH value of the solution is X

wall of the container and the high concentration NaOH at high temperature for a long reaction time. The addition of NaOH also changes the morphology of the products. Each sample is composed of at least three different shapes, i.e., nanoparticles, microrods, nanorods, etc. For instance, both nanoparticles and microrods were formed in sample S12.7 (Fig. 4). The "continuous nucleation" model is considered suitable for explanation of the formation of different morphology [21]. The changes of the size and morphology are irregular when the concentration of NaOH increases gradually. NaOH is able to change the chemical reaction rate mentioned above by reacting with H^+, and the pH value of the solution plays an important role in controlling the morphology and size of crystals and the chelation of EDTA.

Conclusions

Bi_2Te_3 could be yielded in the absence of alkali modifier (NaOH, for instance) via a low-temperature aqueous chemical method, when reacting for 6–48 h. Bi_2Te_3 nanoparticles have a considerable uniform morphology of nanoflake with about 10–30 nm thickness and 50–300 nm width. OH^- is not necessary during synthesis of Bi_2Te_3 alloys through hydrothermal and solvothermal process. The previously declared reaction of $3Te + 6OH^- \Leftrightarrow 2Te^{2-} + TeO_3^{2-} + 3H_2O$ could not occur spontaneously from the left-side to the right-side, and the bismuth cation could be reduced to the metallic form even in an acidic solution, thus Bi_2Te_3 was synthesized. The morphology of nanostructured Bi_2Te_3 became diverse when the concentration of NaOH changed.

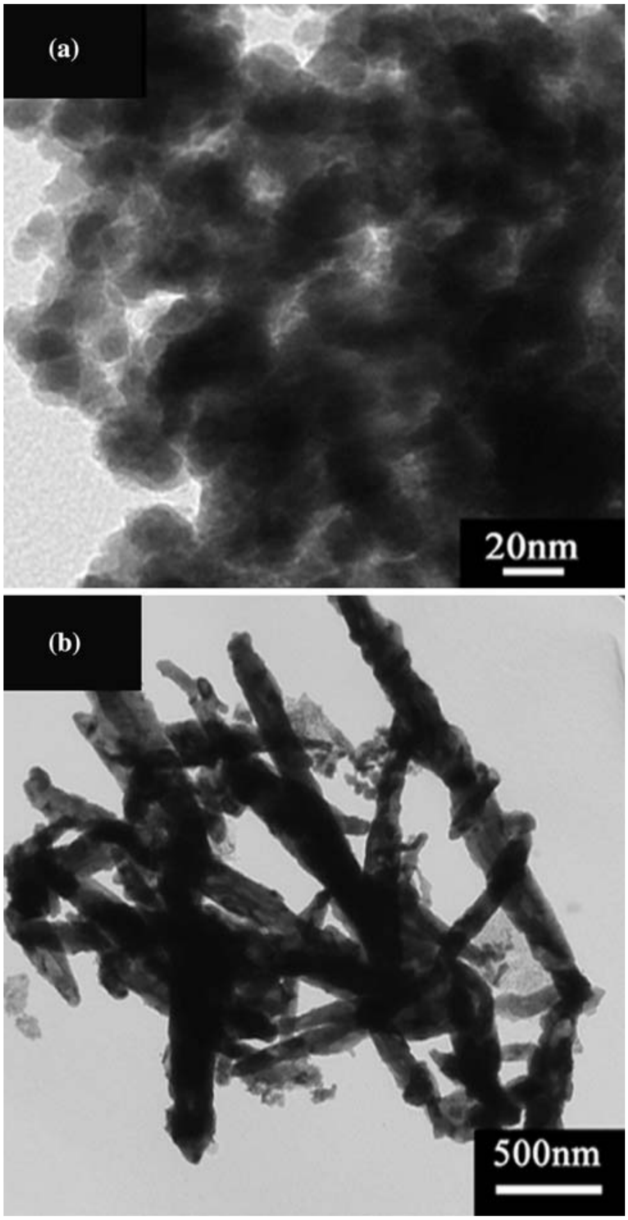

Fig. 4 TEM images of sample S12.7: **a** nanoparticles; **b** microrods

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