A Chemical Solution Route to Rapid Synthesis of Homogeneous Bi$_{100-x}$ Sb$_x$ Alloys Nanoparticles at Room Temperature

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A chemical co-reduction route in aqueous solution was developed to synthesize Bi$_{100-x}$Sb$_x$ alloys at room temperature. The hydrolyses of Bi(III) and Sb(III) were effectively avoided by selecting proper raw materials and coordinator. X-ray diffraction analysis indicated that the as-prepared Bi$_{100-x}$Sb$_x$ alloys were homogeneous and phase-pure, and the Bi/Sb ratios in the alloys were very close to those in the aqueous solutions. The transmission electron microscope observation showed that the as-prepared Bi$_{100-x}$Sb$_x$ ($x = 0\sim100$) alloys were particles with a size of tens of nanometers. The selected area electron diffraction patterns confirmed the high crystallinity, the homogeneousness, and the composition controllability of as-prepared alloys. All these characters and the nanometer-scaled size of the alloys are believed to be beneficial to the thermoelectric property of the Bi$_{100-x}$Sb$_x$ alloys.

Keywords: Bi-Sb Alloys, Thermoelectric Materials, Chemical Solution Route, Synthesis, Nanoparticles.

1. INTRODUCTION

Bi and Sb are both semimetals, which belong to the V group of the periodic table with the same rhombohedral crystal structure. They can form binary isomorphous alloys in which only one type of crystal structure is observed over the entire composition range.[1–2] The thermal and electrical properties of the Bi-Sb alloys have been reviewed by Goldsmid.[3] The electrical structure and the transport properties of the Bi$_{100-x}$Sb$_x$ alloy depend strongly on its composition. Those alloys in the composition range $x = 4\sim22$, are semiconductors[3–6] and considered to be the best n-type materials for thermoelectric cooling at temperature ~100 K.[7–10] It is well known that the reduction of the size of the materials can also improve their thermoelectric performance, Devaux, et al. have discussed the influence of the grain size on the phonon scattering and further on the thermoelectric property,[11] so thermoelectric materials in nanometer scale have attracted more and more interests.[12–15]

There have been many studies on the preparation of Bi-Sb alloys. Most of the preparations of the alloys were based on the conventional melt-quench technique,[16–18] including high-pressure injection of the melt of the alloy into a porous template.[19] However, it is difficult to prepare homogeneous Bi-Sb alloys using this technique, because the liquidus and solidus lines are separated from each other in the Bi-Sb phase diagram, resulting in segregation in the melt-grown crystals.[1–2] As the thermoelectric performances are much better in homogeneous materials than in inhomogeneous materials,[20] it is necessary to develop some synthetic methods that can improve the homogeneity of the products. Mechanical alloying and evaporation methods were used to prepare Bi-Sb alloys.[11, 21–22] Molecular-beam epitaxy was also used to fabricate Bi/Sb superlattice alloys.[23] Most recently, Bi-Sb nanowire arrays and thin films were fabricated by electrodeposition.[24–26] However, to the best of our knowledge, there is no report on the preparation of Bi-Sb alloys via non-electro chemical solution route. This might be attributed to the difficulty to obtain homogeneous alloys from solutions of Bi(III) and Sb(III). Some other alloys nanoparticles or films have also been prepared via mechanical alloying technique,[27] polyol process,[28] and sonochemical method,[29, 30] however, synthesis of single-phased alloys with controllable composition still remains a great challenge.

Herein, we focused on the preparation of Bi-Sb alloys nanoparticles by the chemical co-reduction of Bi(III) and

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Sb(III) in aqueous solution at room temperature. Homogeneous nanocrystalline alloys were obtained in large scale, avoiding the segregation in the melt-grown crystals. This method is very fast and simple, avoiding elevated temperature and/or vacuum, which was necessary in melting or evaporating method. And the composition of the alloy can be controlled much more conveniently than in electrodeposition. This method is also very easy to scale up.

2. EXPERIMENTAL DETAILS

All of the reagents were of analytic purity and used without further purification. In a typical procedure, 20 mmol disodium ethylene diamine tetraacetate was dissolved in 120 ml distilled water, then totally 2 mmol bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) and antimony sodium tartrate ($Na(SbO)C_4H_4O_6$) in molar ratio of $Sb/Bi = x/(100-x)$, where $x = 0, 10, 15, 25, 50, 75$, or 100, respectively, were put into the solution, and the pH of the solution was adjusted to 6~7 with potassium hydroxide aqueous solution. This was noted as solution A. Solution B was made by dissolving excessive potassium borohydride (KBH_4) in distilled water. At room temperature and under vigorous stirring, solution B was put into solution A. The black turbidity occurred immediately, and aggregated into black floccules in several minutes. These floccules were centrifuged, washed with water and absolute ethanol in sequence, and dried under vacuum.

X-ray diffraction (XRD) patterns of the products were recorded with a Philips X'pert X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). The transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEM-200CX (JEOL, 200 kV) TEM.

3. RESULTS AND DISCUSSION

The crystal structure and the composition of the products were detected by X-ray diffraction. The XRD patterns shown in Figure 1 indicate that all of the prepared samples are of single-phase rhomb-centered hexagonal structure, including pure Bi and pure Sb. All the peaks of the Bi-Sb alloys appear between the corresponding peaks of pure Bi (JCPDS File No. 44-1246) and pure Sb (JCPDS File No. 35-0732) and shift to the high angle side with increasing Sb concentration. This means that homogeneous solid solutions were formed and no phase separation occurred. Bi and Sb are completely isomorphous, they can form a completely miscible solid solution. It is known that the lattice parameters of Bi-Sb alloys follow Vegard's law,[16–17, 25, 31–33] which assumes a linear variation of the alloy concentration with the lattice constant. According to Vegard's law, the percentages of Sb in the $Bi_{100-x}Sb_x$ alloys were calculated to be 8.91, 13.0, 23.4, 46.2, and 71.0, respectively, while the corresponding ratio of $[Sb(III)]/([Bi(III)]+[Sb(III)])$ in solutions were 10, 15,
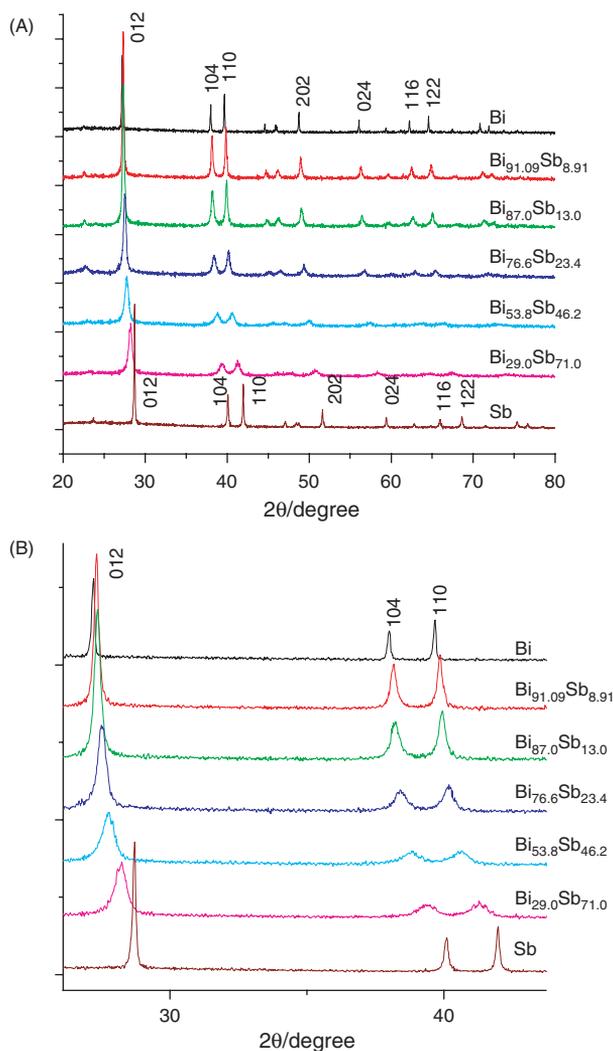

Fig. 1. (A) The XRD patterns of as-prepared pure Bi, pure Sb, and their alloys. (B) The 012, 104, and 110 diffraction peaks of the samples in a higher magnification.

25, 50, and 75 percent, respectively. The percentages of Sb in the $Bi_{100-x}Sb_x$ alloys and the corresponding ratios of $[Sb(III)]/([Bi(III)]+[Sb(III)])$ in solutions were very close.

This closeness between them means the great convenience to control the alloys compositions. On the contrary, there were large differences between them in the case of electrodeposition.[24–26] However, as shown in Figure 2, the molar ratios of Sb to Bi in solid alloys were a little lower than that in solutions, and the difference increased along with the increase of the Sb content. This might result from the fact that Sb(III) is more difficult to be reduced than Bi(III) under this condition, so a little Sb(III) remained in the solutions while the alloys precipitated. The cyclic voltammetric analysis was carried out with a CHI 660 electrochemistry workstation in both Bi(III) and Sb(III) solutions, using indium tin oxide (ITO)-coated glass as working electrode, platinum wire as counter electrode, and aqueous KCl saturated calomel electrode (SCE) as
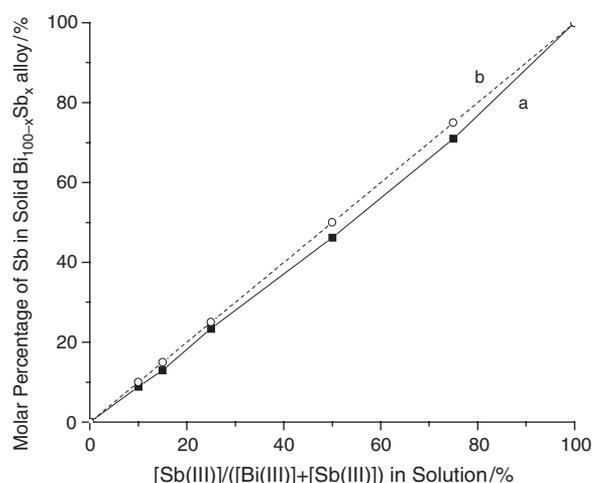
Fig. 2. The relationship between the molar percentages of Sb in $Bi_{100-x}Sb_x$ alloys and $[Sb(III)]/([Bi(III)]+[Sb(III)])$ in solutions. (a) The experimental line. (b) The ideal line, indicating the same molar ratios of Sb to Bi in solid alloys and in corresponding solutions.

Fig. 3. Cyclic voltammetry of Bi(III) and Sb(III) solutions. Scan rate, 0.1 V/s.

reference electrode. From the result shown in Figure 3, we can see that the deposition potential of Sb is obviously more negative than that of Bi, indicating that Sb(III) is more difficult to be reduced than Bi(III).
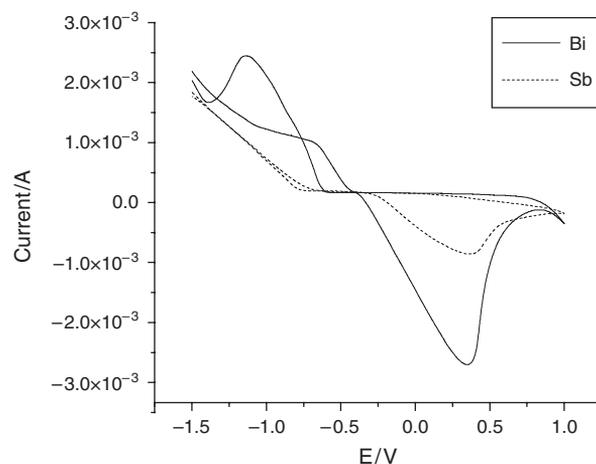
TEM images and the typical SAED pattern shown in Figure 4 indicate that the products were uniform and well-crystallized nanoparticles. The size of the nanoparticles changed along with the composition of the alloy. It was 60~70 nm for pure Sb, and 30~40 nm for pure Bi.
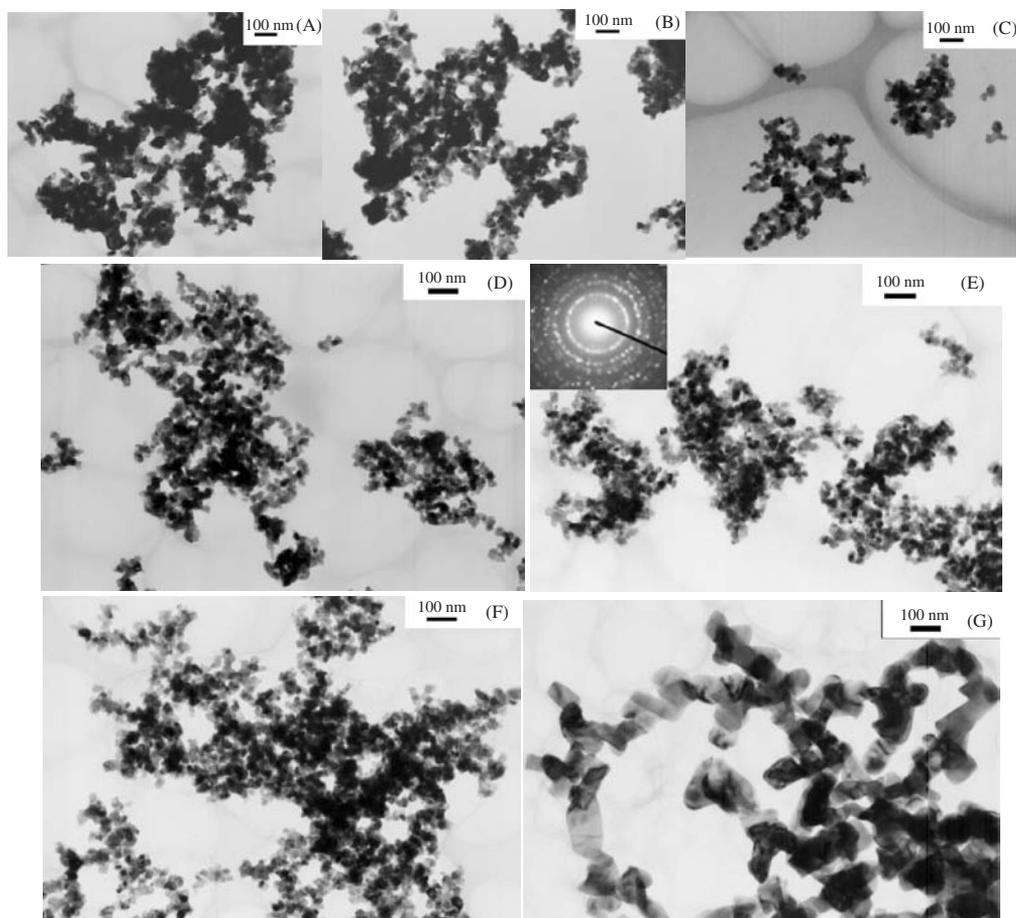

Fig. 4. TEM images of (A) pure Bi, (B) $Bi_{91.09}Sb_{8.91}$, (C) $Bi_{87.0}Sb_{13.0}$, (D) $Bi_{76.6}Sb_{23.4}$, (E) $Bi_{53.8}Sb_{46.2}$, with the insert of its SAED pattern, (F) $Bi_{29.0}Sb_{71.0}$, (G) pure Sb.

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However, when one element was mixed with the other, the particle size prepared decreased, and got to its minimum of 10 ~ 20 nm at $Bi_{53.8}Sb_{46.2}$. The SAED patterns show the high crystallinity of the nanoparticles, and the d values of the alloys calculated from these patterns were between those of pure Bi and Sb, and decreased as the Sb content increased, which was consistent with the XRD results. TEM images also show that these alloys had sheet-like structure, which is mainly related with their crystal structure,[34] and aggregated to make networks.

One of the difficulties in the preparation of Bi-Sb alloys via chemical solution route is how to avoid the hydrolyzation of Bi(III) and Sb(III). In this work, we used water-dissolvable antimony sodium tartrate as antimony source, and added disodium ethylene diamine tetraacetate (EDTA) to coordinate with Bi(III). In a proper range of pH, transparent aqueous solution with any Bi/Sb ratio can be obtained. Subsequently, $Bi_{100-x}Sb_x$ alloys with $x = 0\sim100$ can be prepared. We also tried to add into some other coordinators, such as trisodium citrate dihydrate, tartaric acid, and sodium chloride, but failed to obtain homogeneous solutions containing bismuth and antimony.

To obtain the homogeneous Bi-Sb alloys, bismuth, and antimony should be co-reduced simultaneously. Therefore, a very strong reductant, KBH_4, was selected. The reduction was carried out very fast and was fulfilled only in several minutes. As mentioned above, XRD results indicated that the products were homogeneous Bi-Sb alloys with single phase, and TEM results indicated that products were crystalline particles with size of tens of nanometers. Zinc is also a strong reductant, but not as strong as KBH_4. And, being solid, zinc powder is not so easy to be mixed with the solution A as KBH_4 solution is. The reduction was carried out on the surface of zinc. When zinc powder was used to replace KBH_4, homogeneous Bi-Sb alloys could also be obtained. However, the reduction was slower, and the as-prepared particles were larger, as shown in Figure 5. Another disadvantage of using zinc as reductant is that the excessive zinc is not so easy to remove from the products.
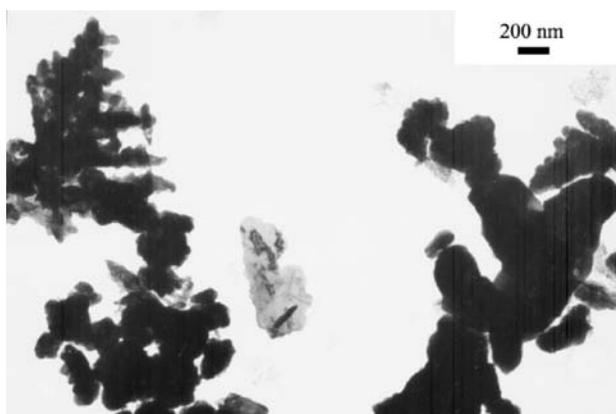

Fig. 5.   The TEM image of the alloy prepared using Zn as reductant.
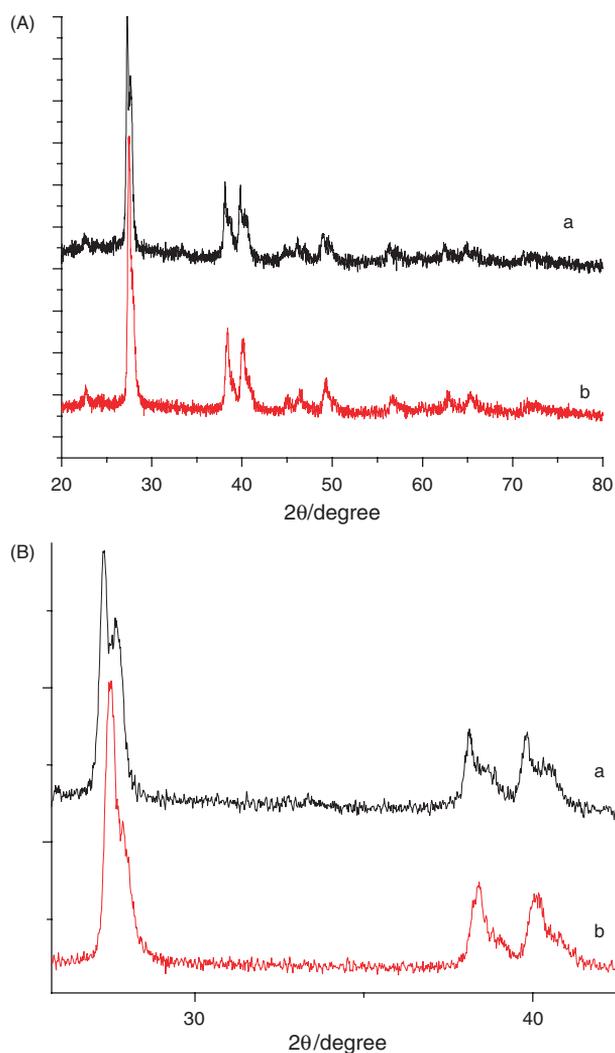

Fig. 6.   XRD patterns of the products obtained (a) under microwave irradiation, and (b) under the hydrothermal condition, without stirring.

Thorough mixture is important to the homogeneousness of the prepared alloys, especially when Zn is used as reductant. Reduction under ultrasonication resulted in the similar products as under stirring. However, the products consisted of two phases when the reduction was carried out under microwave irradiation or under hydrothermal condition without stirring. The XRD diffraction peaks of these products split as shown in Figure 6, and the split peaks corresponded to two alloys with different concentrations.

Since the reduction was carried out very fast, it is difficult to control the morphology of the products. Kinds of surfactants or soft templates, such as polyvinyl pyrrolidone (PVP, K-30), cetyltrimethyl ammonium bromide (CTAB), polyethylene glycol (PEG-400, PEG-2000, PEG-6000), and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) were added respectively into the solutions, but no significant difference was made.

4. CONCLUSIONS

A new chemical solution route was developed to synthesize homogeneous nano-sized $Bi_{100-x}Sb_x$ alloys at room temperature. Proper raw materials and coordinator were selected to avoid the hydrolysis of Bi(III) and Sb(III) in aqueous solution. Strong reductant was used to obtain homogeneous phase-pure alloys. $Bi_{100-x}Sb_x$ alloys with x varies from 0 to 100 can be synthesized by adjusting the ratio of $[Sb(III)]/([Bi(III)] + [Sb(III)])$ in solution, and the alloys obtained were well-crystallized sheet-like nanoparticles with size of tens of nanometers and aggregated to make networks. This method was proved to be very fast, simple and easy to scale up, avoiding elevated temperature and/or vacuum, which was necessary in melting or evaporating method.

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