Melting Behaviour of Bi$_{1-x}$Sb$_x$ Free Standing Alloy Nanoparticles Synthesized via Solvothermal Route

Mayanglambam Manolata Devi†, Krishanu Biswas*†

*Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur-208016, India

†Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur, India

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The present investigation aims at understanding the effect of size on melting behaviour of free standing alloy nanoparticles. Alloy nanoparticles of Bi$_{1-x}$Sb$_x$ (x=0.12, 0.25, 0.50 and 0.75) have been synthesized by solvothermal route using sodium borohydride (NaBH$_4$) as a reducing agent. The samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The melting behaviour of alloys was determined by differential scanning calorimetry (DSC). The formation of different solid solution phases of Bi-Sb alloy has been confirmed by detailed XRD studies. Uniform cuboctahedral as well as spherical morphology of alloy nanoparticles has been observed in TEM with average particle size of 40±9 nm in Bi$_{0.75}$Sb$_{0.25}$ specimen. DSC studies indicate the depression in the melting temperature of the nanoparticles as compared to the bulk alloy of same composition.

**Keywords:** solvothermal route, nanoalloys, X-ray diffraction, transmission electron microscopy, melting, solidification, differential scanning calorimetry

1. Introduction

Melting behaviour of the solids is considered to be one of the most important phase transformations in material science and engineering from both scientific and technological perspective. It has been understood that melting behaviour of any material is strongly dependent on the free surface or interface. In last two decades, there have been tremendous research activities going on the developing of nano-scaled alloys as they exhibit distinctly different properties compared to its constituent elements as well as its counter bulk materials due to its high surface to volume ratio. It has been reported that due to the presence of this high surface to volume ratio in nano-scaled materials, they melt at temperature, which is much lower than that of bulk equilibrium melting temperature. Therefore, thermal stability of any nano-scaled material is an important issue in the development of nanotechnology. Hence, the effect of size on the melting behaviour of the materials is utmost important and thus, it is essential to understand the mechanisms of melting of these solids.

Several attempts have been made in the last two decades to understand the effect of size on the melting behaviour of nano-scaled metals and alloys. However, these studies are mainly focused on the nano-embedded pure metals and alloys. For example, the melting and solidification behaviour of pure nanometric Bi embedded in Al matrix or Zn matrix and nano-embedded Pb-Sn or Pb-In alloys or Pb-Bi alloys in Al matrix have been reported in the literature. It has also been reported that due to the effect of interface between the particle and matrix, the melting temperature of material can be elevated as compared to the equilibrium bulk melting temperature. However, the presence of the matrix limits the study of exact effect of size on melting behaviour of nanoparticle as it is extremely difficult to decouple this in an embedded system. Hence, this is very imperative to study the melting behaviour of free-standing nanoparticles in order to understand the exact effect of size on intrinsic mechanism of melting. Therefore, the investigation on melting behaviour of free standing nano-scaled alloy particles is vital because it will provide an avenue in understanding the exact effect of size on its melting in one way and also help in developing new materials in another way. We have chosen the Bi-Sb system as a model for the study because Bi-Sb alloy exhibit an isomorphous phase diagram with a miscibility gap at low temperature (177 °C) in large composition range of 5 to 95 atom % Sb. However, behaviour of the alloy system depends on the size and thus, it is further necessary to study the alloying at nano-scale.

In the present work, we report some of the salient results on melting behaviour of Bi$_{1-x}$Sb$_x$ alloy nanoparticles, prepared with different reaction conditions. Four different compositions of Bi$_{1-x}$Sb$_x$ alloys (x=0.12, 0.25, 0.50, and 0.75) have been chosen for synthesis via solvothermal route using sodium borohydride (NaBH$_4$) as a reducing agent. X-ray diffraction (XRD) technique has been utilized to identify the phase purity and structure of the samples. Size, shape and morphology of the samples were extensively analyzed with transmission electron microscope (TEM). The thermal characterizations of the alloys were extensively determined with differential scanning calorimetry (DSC).
2. Experimental Procedure

2.1. Materials

Bismuth chloride (BiCl₃) (99.9%, Sigma Aldrich) and Antimony chloride (SbCl₃) (99.9%, Sigma Aldrich) were taken as precursors for Bi and Sb respectively. N, N-dimethylformamidine (DMF) (99.9%, Alfa Aesar), sodium borohydride (NaBH₄) (99.9%, Alfa Aesar) and NaOH has been utilized in the reaction as solvent, reducing agent and pH controller respectively. Distilled water and methanol were used as washing agents. All the chemicals are of analytical grade and were used as received without any further purification.

2.2. Preparation of Biₓ₋₀.₅Sbₓ₀.₅ alloy nanoparticles by solvothermal route

Four different compositions of Biₓ₋₀.₅Sbₓ₀.₅ alloy (with x=0.12, 0.25, 0.50, and 0.75) have been synthesized by solvothermal route. In a typical experiment, 2 mmol of precursor (BiCl₃ and SbCl₃) and 0.72g of NaOH were dissolved in 80 mL of DMF in a beaker and subsequently the transparent solution was transferred into a Teflon-lined container of 100 mL capacity. After that, molar ratio (MR) of precursor/NaBH₄ as 1:0.5 was added in the solution and immediately the colour of the solution turned black. Then, this reactant filled Teflon container was inserted in a stainless steel autoclave which was then heated at 140 °C for 12h inside an oven.

After being cooled down to room temperature naturally, the black coloured products were collected by centrifugation and washing with water and methanol subsequently for several times to remove unreacted chemicals. Finally, the products were air-dried at room temperature and collected for further characterizations.

3. Characterizations

X-ray diffraction (XRD) pattern of all the solvothermally synthesized samples were recorded using Brukers D8 focus X-ray diffractometer with Cu kα radiation (λ=0.15405nm), employing a scan rate of 1º/min in angular range of 20º-80º to identify the phases and structure. The size, shape and morphology of as-synthesized powder products were investigated by transmission electron microscope (TEM, FEI Tecnai G² UT 20 operated at 200kV). The detailed examinations of size, shape and morphology of different specimens, synthesized in the present investigation have been carried out using transmission electron microscope (TEM).

4. Results

4.1. Phase and structural identification

The X-ray diffraction (XRD) patterns obtained from the solvothermally synthesized powder products corresponding to four different alloy compositions, Biₓ₋₀.₅Sbₓ₀.₅, (x=0.12, 0.25, 0.50, and 0.75), synthesized at 140 °C for 12h using molar ratio (MR) of precursor/NaBH₄ as 1:0.5 are shown in Figures 1a-d. All the diffraction peaks of Biₓ₋₀.₅Sbₓ₀.₅, (x=0.12, and 0.25), shown in Figure 1a and 1b were indexed to rhombohedral symmetry (space group=R̅₃m) of Bi-Sb system (designated as (Bi)), which was confirmed by comparing the shift of all the diffraction peak positions as compared to pure Bi (a=0.45475 nm, c=1.18681 nm and, α=90°) (Pearson’s database, 1210759) as well as from pure Sb (a=0.4309 nm, c=1.1286 nm and, α=90°) (Pearson’s database, 1923886). On the other hand, the diffraction peaks of Biₓ₋₀.₅Sbₓ₀.₅ (shown in Figure 1c) can be indexed due to (Bi) and (Sb) whereas that of Biₓ₋₀.₅Sbₓ₀.₅ (shown in Figure 1d) can be indexed due to (Bi), (Sb) and (Sb). The different phase of Bi-Sb solid solutions have been designated as (Bi) and (Sb) corresponding to peak positions, which are the least and the most shifted respectively to higher angle as compared to pure Bi. On the other hand, (Sb) is designated for the peak positions, which are much closed to pure Sb. The inset of Figure 1 shows the enlarged view of (012) diffraction peak of the alloy for more clarity. The diffraction peaks are observed to be broad and shifted to higher 20 as Sb concentration in the alloy increases, indicating distinct change in lattice parameter of different phases of alloy with different amount of Sb.

4.2. Microstructural observations

Detailed thermal characterization of all the alloy nanoparticles using DSC has been carried out. Figure 3a-d shows the DSC thermograms of alloy nanoparticles having
four different compositions \((x=0.12, 0.25, 0.50, \text{and } 0.75)\), prepared solvothermally at 140 °C, for 12h with MR of precursor/\(\text{NaBH}_4\) as 1:0.5. DSC results of these nanoparticles are listed also in Table 1. The solidus and liquidus temperature of Bi-Sb alloy obtained from equilibrium phase diagram\(^{1}\) are also shown for comparison. One can find two different types of thermal behaviour among four alloys. For \(x=0.12\) and 0.25, single melting event is discerned (Figure 3a and 3b). However, the peak temperatures for these melting events vary depending on \(x\), as indicated in Table 1. On the other hand, Figure 3c and 3d show the presence of two melting events for \(x=0.50\) and 0.75. The first melting event in each alloy is

![Figure 2](image1)

**Figure 2.** Bright field TEM images of \(\text{Bi}_{0.75}\text{Sb}_{0.25}\) alloy, prepared 140 °C for 12h using different MR of precursor/\(\text{NaBH}_4\) as (a) 1:0.5, (b) corresponding selected area diffraction pattern and (c) histogram showing particle size distribution.

![Figure 3](image2)

**Figure 3.** DSC Plots of heating cycle of different compositions of alloy (a) \(\text{Bi}_{0.88}\text{Sb}_{0.12}\) (b) \(\text{Bi}_{0.75}\text{Sb}_{0.25}\) (c) \(\text{Bi}_{0.50}\text{Sb}_{0.50}\) and (d) \(\text{Bi}_{0.25}\text{Sb}_{0.75}\) prepared at 140 °C for 12h with MR of precursor/\(\text{NaBH}_4\) as 1:0.5. The upper and lower insets represent the de-convoluted of melting peaks of \(\text{Bi}_{0.50}\text{Sb}_{0.50}\) and \(\text{Bi}_{0.25}\text{Sb}_{0.75}\) respectively, observed on the right end side.
observed to be sharp and symmetrical. However, the later melting events of x=0.50 and 0.75, which are occurring at higher temperature, are found to have shoulder on left side of the peak and need to be de-convoluted to obtain the peak temperatures corresponding to individual events. The detailed results of these de-convoluted profiles (insets of Figure 3) are also listed in Table 1.

In order to decipher the origin of the melting peaks in Figure 3c and 3d, cyclic DSC has been carried out so that the effect of metastability of phases or particle size can clearly be understood. Figure 4a and 4b show the DSC traces for two cycles (1st and 2nd run). One can clearly observe two different types of behaviour. For x=0.75, the first melting peak (as observed in the 1st cycle) vanishes and the second melting peak becomes symmetrical without any shoulder. No significant change in the peak of the second melting is observed in subsequent cycles. On the other hand, cyclic DSC of the nanoalloy with x=0.50 reveals distinctly different behaviour as shown in Figure 4a. The first melting peak becomes more intense and sharp whereas the second peak is observed to be less intense but symmetrical in comparison to the 1st cycle. The detailed origin of these melting events will be discussed in the subsequent section.

5. Discussion

The detailed DSC analysis of all the compositions of alloys prepared by solvothermal route using MR of precursor/NaBH₄ as 1:0.5 reveal the presence of one (x=0.12 and 0.25) or two (x=0.50 and 0.75) melting events depending on their

<table>
<thead>
<tr>
<th>Alloy Compositions</th>
<th>Heating Cycle</th>
<th>Bulk alloys</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Onset Temp. (°C)</td>
</tr>
<tr>
<td>Bi₀.₈₈Sb₀.₁₂</td>
<td>1st melting event (1st cycle)</td>
<td>264.97</td>
</tr>
<tr>
<td>Bi₀.₇₅Sb₀.₂₅</td>
<td>2nd melting event (1st cycle)</td>
<td>265.31</td>
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<tr>
<td>Bi₀.₅₀Sb₀.₅₀</td>
<td>De-convolution of 2nd melting event (1st cycle) Peak 1</td>
<td>614.35</td>
</tr>
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<td></td>
<td></td>
<td>635.62</td>
</tr>
<tr>
<td>Bi₀.₂₅Sb₀.₇₅</td>
<td>2nd melting event (1st cycle)</td>
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<tr>
<td></td>
<td>De-convolution of 2nd melting event (1st cycle) Peak 1</td>
<td>604.07</td>
</tr>
</tbody>
</table>

Figure 4. Comparison of 1st and 2nd heating cycle of (a) Bi₀.₅₀Sb₀.₅₀ and (b) Bi₀.₂₅Sb₀.₇₅ alloys prepared at 140 °C for 12h with MR of precursor/NaBH₄ as 1:0.5. The right inset shows the magnified views of the melting event for clarity. The left inset shows digital photograph of the sample after 1st heating cycle.
Table 2. The detailed of interfacial energies of Bi-Sb alloy nanoparticles.

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Radius of</th>
<th>Density (ρs)</th>
<th>Latent heat (Lm(N))</th>
<th>Melting temp. of nanoparticle (Tm(N)°C)</th>
<th>Melting temp. of Bulk (Tm(B)°C)</th>
<th>Interfacial Energy γsl (mJ/m²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi0.6Sb0.12</td>
<td>22.3</td>
<td>9.61</td>
<td>4028.97</td>
<td>264.97</td>
<td>280.12</td>
<td>23.34</td>
<td>Present study</td>
</tr>
<tr>
<td>Bi0.25Sb0.75</td>
<td>20.5</td>
<td>9.18</td>
<td>5734.93</td>
<td>265.31</td>
<td>291.69</td>
<td>48.82</td>
<td>Present study</td>
</tr>
<tr>
<td>Pure Bi</td>
<td>Bulk</td>
<td>10.05</td>
<td>10.55 × 10⁶</td>
<td>-</td>
<td>271.4</td>
<td>95</td>
<td>Jones21</td>
</tr>
<tr>
<td>Pure Sb</td>
<td>Bulk</td>
<td>6.68</td>
<td>19.89 × 10⁶</td>
<td>-</td>
<td>630.8</td>
<td>137</td>
<td>Jones21</td>
</tr>
</tbody>
</table>

It is to be noted that Tm(N) of different alloys (x=0.12 and 0.25) are obtained from DSC data, whereas Tm(B) of similar compositions were obtained from equilibrium phase diagram. The r(N), ρs and Lm(N) were calculated or measured from XRD, Archimedes method and DSC thermograms respectively. The detailed values are listed in Table 2. Table 2 also shows γsl values for bulk Bi and Sb. To the best of the authors’ knowledge, the γsl values for nano-sized Bi and Sb are not reported in the literature. The calculated γsl values for Bi-Sb alloys nanoparticles are observed to be lower than those corresponding to bulk Bi and Sb. Therefore, the chemistry and size play a significant role in determining the γsl values of Bi-Sb alloy nanoparticles.

6. Conclusion

The present investigation has clearly shown that free standing Bi-Sb alloy nanoparticles can be successfully synthesized by solvothermal route. The experimental findings can be summarized as follows:

- The detailed analysis of XRD patterns indicates that single alloy phase, (Bi), is present in alloy composition with Sb < 50 atom %. On the other hand, (Sb) and (ϕ) along with (Bi) have been observed when Sb concentration in the alloy is ≥ 50 atom %.
- The extensive TEM observation shows that the alloy nanoparticles have cuboctahedral as well as spherical shape with the particle size of 40 ± 9 nm of Bi0.75Sb0.25 alloy.
- The careful and extensive DSC analysis of different compositions of Bi-Sb alloy nanoparticles prepared with MR of precursor/NaBH4 as 1:0.5 reveals the single melting event of (Bi) when the composition of alloy is < 50% of Sb content whereas the multiple melting events have been observed in the alloy samples when the Sb content is ≥ 50%.
- Cyclic DSC events indicated different behaviour for alloys with x=0.50 and 0.75.
- Solid-liquid interfacial energies have been calculated for Bi-Sb nanoalloys with x=0.12 and 0.25 and the values are found to be lowered as compared to bulk Bi and Sb.

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References


