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Solvothermal synthesis and analysis of $Bi_{1-x}Sb_x$ nanoparticles

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ABSTRACT

Bismuth–antimony alloy nanoparticles have been synthesized by a facile solvothermal method using N,N-dimethylformamide and ethylene glycol as solvent/reducing agent; $BiCl_3$, $SbCl_3$ and $Bi(NO_3)_3$ as precursors; and citric acid as a surface modifier/stabilizing agent. The particle size and size distribution of Bi nanoparticles were analyzed as a function of the synthesis conditions: molar ratio of precursor to surfactant, precursor concentration and reducing agent. Synthesis of Sb and $Bi_{0.88}Sb_{0.12}$ under similar conditions was also investigated. The phase purity of nanoparticles was confirmed from X-ray diffraction and thermogravimetry and the nanoparticle morphology was investigated by transmission electron microscopy. A case study of Bi nanoparticles with detailed analysis of the particle morphology and size distribution of the nanoparticles is reported.

1. Introduction

Quantum confined and nanostructured materials are attractive for thermoelectric energy conversion applications due to the predicted and demonstrated enhancements in thermoelectric figure of merit in these materials [1]. Nanoparticles can either be used directly for a single-component material with nanostructured grains, as demonstrated in Bi_2Te_3 [2] or as nanometer-scale inclusions which may enhance the thermoelectric conversion efficiency of a different host material [3]. Bismuth–antimony is a well-known low-temperature thermoelectric material which crystallizes in a rhombohedral structure, and is a semimetal with low effective mass and highly anisotropic fermi surface. The electronic properties of Bi semimetal are sensitive to quantum confinement and can be tuned by reducing the dimensionality, which induces a semimetal–semiconductor transition [4], producing an enhancement in room temperature thermoelectric properties. Nanowires of Bi grown on porous Al_2O_3 and SiO_2 templates have also shown increased thermoelectric power [5], hence there are numerous reports, on the synthesis of Bi nanoparticles, nanowires and nanodots. There are few reports on the synthesis of Bi nanoparticles by reverse micelles/microemulsion methods where a polymer capping agent was used to protect Bi nanoparticles [6,7]. A high-temperature reduction of bismuth 2-ethylhexanoate with an organic capping agent was also reported [8], which resulted in almost spherical nanoparticles of ~30 nm. Further work on synthesis of Bi nanoparticles by polymer assisted polyol process [9] and photochemical polythiol process [10] allow control over shape and size of nanoparticles, resulting in nanocubes, nanoplates, nanobelts, nanorods, nanoribbons of metallic Bi. The synthesis of large, monodisperse spherical colloids of Bi in the size range 100–600 nm diameter has been reported by Wang and Xia [11]. Yu et al. [12] report monodisperse Bi nanoparticles with a narrow size distribution ranging from 8.5 to 12.5 nm, based on a growth method which requires 1.5 nm gold nanoparticles as seeds.

The drawbacks of these synthesis methods are use of large organic molecules or polymers to sequester the growth of the particle and these molecules are difficult (if not impossible) to completely remove. This makes the material unacceptable for many applications requiring high electrical conductivity, since residual organic material impedes electrical conduction and also prevents the material from being fully consolidated. Citric acid, a weak organic acid has proved to be an efficient surface modifier in preventing agglomeration. The use of citric acid as a stabilizer was reported by Goodarzi et al. [13] to achieve a well-dispersed suspension of magnetite (Fe_3O_4) nanoparticles. They have shown that citric acid adsorbs to the surface of nanoparticles via carboxylic groups providing negative surface charges to electrostatically stabilize the colloid. Another report by Padmavathy and Rajendran [14] has shown the use of citric acid as a surface modifier to achieve SnO_2 nanoparticles in a hydrothermal reaction.

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Table 1
Reaction conditions for the solvothermal synthesis of $Bi_{1-x}Sb_x$ nanoparticles.

Sample	Alloy	Precursor	Solvent	$BiCl_3$:citric acid ratio	Temperature	Reaction time
1	Bi	$BiCl_3$	DMF	1:1	160 °C	6 h
2	Bi	$BiCl_3$	DMF	1:5	160 °C	6 h
3	Bi	$Bi(NO_3)_3$	EG	1:5	180 °C	6 h
4	Bi	$BiCl_3$	DMF/2-methoxyethanol (1:3)	1:5	140 °C	12 h
5	Sb	$SbCl_3$	DMF	1:1	160 °C	12 h
6	$Bi_{0.88}Sb_{0.12}$	$BiCl_3 + SbCl_3$	DMF	1:5	160 °C	6 h

In this article, we report a low temperature solvothermal method that has proved to be effective in the synthesis of $Bi_{1-x}Sb_x$ (with $x = 0$, 0.12 and 1) nanoparticles in the 5–50 nm range. The solvothermal method of nanoparticle synthesis allows tunability of various experimental parameters such as reaction temperature, reaction time, stabilizing ratio, reducing agents and concentration of the starting precursors. The choice of a simple molecule is essential, and we have found that citric acid prevents agglomeration of nanoparticles and can be completely removed and hence the resulting nanoparticles, may be used to study properties where a coating of surface modifier is not desired. The different experimental parameters were tuned to achieve Bi nanoparticles with different particle size distributions. The citric acid can be easily removed as shown by Fourier Transform Infrared Spectroscopy (FTIR) and thermogravometric analysis (TGA). Further we demonstrated in a related study that Bi/Bi_2Te_3 nanocomposites, synthesized by incorporating Bi nanoparticles into ball-milled Bi_2Te_3, show electrical conductivities comparable to conventional Bi_2Te_3 compounds [15]. We adopted a similar approach to synthesize Sb and $Bi_{0.88}Sb_{0.12}$ alloy nanoparticles. The size and shape of the nanoparticles was found to be very different in the case of Bi and Sb. The particle size of nanoparticles and particle size distribution can play a significant role in the physical properties of the nanomaterial, and hence an estimate of mean particle size and particle size distribution with the appropriate statistical parameters is essential. We performed particle size distribution analysis on Bi nanoparticles as a case study and we report the estimation of the mean particle size, circularity and particle size distribution. The particle size distribution is represented reasonably well by a log-normal distribution function.

2. Experimental

$BiCl_3$ (Aldrich) and $Bi(NO_3)_3{\cdot}xH_2O$ (Aldrich) were used as precursors for the synthesis of Bi nanoparticles, and N,N-dimethylformamide (DMF) and ethylene glycol (EG) were used as the solvent/reducing agents for the respective Bi precursors. Citric acid (Aldrich) was used as a surface modifier to prevent agglomeration. One mmol of the starting precursor and 1–5 mmol of citric acid were taken for the reaction. Six different synthesis conditions were established to achieve $Bi_{1-x}Sb_x$ nanoparticles (with $x = 0$ for Samples 1, 2, 3, 4 and $x = 1$ for Sample 5 and $x = 0.12$ for Sample 6) as listed in Table 1. Appropriate amounts of the precursor and citric acid were dissolved in 40 ml (total) solvent. The solution was placed in a Teflon-lined autoclave, placed in an oven at 140–180 °C, and allowed to react for 6–12 h. Under all the conditions the final product was washed with methanol thrice and dried for further characterization. The phase purity of the resulting nanoparticles was confirmed by X-ray diffraction studies (Pan Analytical X'Pert) and the stability of nanoparticles investigated by thermogravimetric studies (SDT Q600) on ~25 mg of the sample. The nanoparticles were dispersed in ethanol and deposited on carbon coated copper grids for transmission electron microscopy (TEM, JEOL Model 2010) investigations, operating at 200 kV.

3. Results and discussion

3.1. Synthesis

Table 1 shows the reaction conditions for the synthesis of Bi, Sb and Bi–Sb alloy nanoparticles. Bi nanoparticles synthesized under all reaction conditions mentioned above yielded rhombohedral, phase pure nanoparticles. The synthesis of Sb nanoparticles under similar conditions as discussed in Table 1, also yielded nanoparticles but a spherical morphology could not be achieved in this case. Phase pure Sb nanoparticles could also be achieved, by reducing $SbCl_3$ in ethylene glycol medium at 140 °C for 6 h in an autoclave, with Zn metal flakes as a reducing agent.

3.2. X-ray diffraction studies

The X-ray diffraction (XRD) pattern of Bi nanoparticles in Fig. 1, synthesized by reducing the Bi precursor with an appropriate reducing agent, shows the complete reduction of Bi (III) to Bi (0) and no peaks of oxides or impurities were observed, further emphasizing the role of citric acid in protecting the Bi nanoparticles from oxidation. All the XRD patterns match well with the reported peaks of Bi, JCPDS (05-0519). The synthesized Bi nanoparticles crystallize in a rhombohedral structure ($R\bar{3}m$, 166) and the average grain size calculated by Scherrer's equation, considering full width at half maxima (FWHM) of four major peaks (0 1 2), (1 0 4), (1 1 0) and (2 0 2) were found to be 160 nm, 90 nm, 88 nm and 48 nm for patterns 1 (a), (b), (c) and (d), respectively in Fig. 1. The FWHM of the standard Si peak was subtracted in each case, and the $K\alpha_2$ was stripped for accurate determination of FWHM by pro Fit line profile

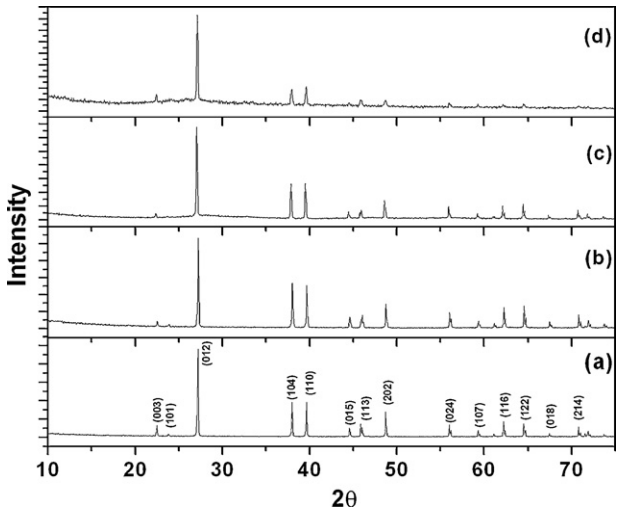

Fig. 1. X-ray diffraction pattern of Bi nanoparticles: (a) $BiCl_3$:citric acid (1:1); (b) $BiCl_3$:citric acid (1:5); (c) $Bi(NO_3)_3{\cdot}xH_2O$:citric acid (1:5) and (d) $BiCl_3$:citric acid (1:5). Samples 1(a) and 1(b) were reduced with 40 mL of DMF, 1(c) was reduced with 40 mL of Ethylene glycol, 1(d) was reduced in a solvent mixture of 10 mL DMF and 30 mL 2-methoxyethanol.