Solvothermal synthesis of nanosized cobalt antimonide for thermoelectrics

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Abstract

The present paper highlights the synthesis of cobalt antimonide ($CoSb_3$) micro/nanostructures by following solvothermal technique with water as solvent. Recipe is optimized for preparation of refined $CoSb_3$ compounds and demonstrated that a high processing temperature of 500 °C and long duration of 72 hr indicates presence of $CoSb_3$ phase. The microstructures and composition of the as synthesized $CoSb_3$ nanocomposites are characterized to achieve the optimized phase. The morphologies as imaged using field emission scanning electron microscope resemble granules for the as-synthesized $CoSb_3$. The phase purity and crystallographic structure of the as-synthesized $CoSb_3$ nanocomposites as determined by XRD indicates the formation of the cubic phase of $CoSb_3$ and agrees well with the JCPDS data mentioned for the highly pure $CoSb_3$. The EDX estimates the elemental composition of Co and Sb in 1:3 stoichiometric ratio for the as-synthesized $CoSb_3$. The currently prepared nanosized skutterudite $CoSb_3$ material synthesized by solvothermal method could be utilized as active material for the development of highly efficient thermoelectric devices.

Keywords: Cobalt antimonide, solvothermal synthesis, thermoelectric materials.

Introduction

The nanosized cobalt antimonide ($CoSb_3$) based skutterudites are among the most prospective thermoelectric (TE) materials activated at the intermediate temperature range (300°C to 550°C) for suitable utilization in generating thermopower. The advantages including, high performance, low cost, and accessibility in tailoring the thermal and electrical transport through structural engineering, insists utilization of $CoSb_3$ as a potential material for the next generation thermoelectrics. Among the TE materials investigated **[1]**, the family of skutterudite crystal structures provide promising semiconducting properties and have attracted much attention for showing high performance in typical "phonon-glass-electron crystals" (PGEC) **[2, 3]** that possess electronic properties of a good semiconductor single crystal and thermal properties akin to the amorphous materials, i.e., poor thermal conductor and good electrical conductor. $CoSb_3$ provides a binary skutterudite structure that has a formula of MX_3 (Im3), where M is a transition metal atom (Co, Rh, or Ir) and X is a pnictogen atom (P, As, or Sb), and is characterized as cubic crystalline structure containing large cages and four-membered planar rings of X. Binary skutterudites have superior $S^2\sigma$ due to their appropriate band gaps and high carrier mobilities. The higher thermal conductivities in these materials hinder their applications for fabricating efficient TE devices **[4]**. According to the concept of "phonon-glass-electron-crystal," **[5, 6]** it is possible to reduce the thermal conductivity of $CoSb_3$ by introducing impurities that could fill the voids in the $CoSb_3$ structure and forms partially filled skutterudites. Here, the filler atoms rattle inside the oversized cages and acting as the additional phonon scattering centers, thus reducing the lattice thermal conductivity **[7-9]**. $CoSb_3$ is a narrow band gap semiconductor (0.25 eV) **[10]** with body-centered cubic crystal structure having a space group of Im3, contains elements with low-electronegativity difference and high degree of covalent bonding enabling high carrier mobilities, and exhibits good electron-crystal properties **[11]**.

$CoSb_3$ skutterudite materials are generally processed by mechanical alloying **[11],** ball milling **[11]**, arc melting **[12]**, chemical alloying **[13]**, solid-state reaction **[14]**, ultrasonic spray pyrolysis **[15]**, co-precipitation **[13]**, sol–gel **[16]**, and solvothermal methods **[17, 18]**. However, the solvothermal method is a simple and effective way for the synthesis of nanostructured materials and has advantages such as its relatively low processing temperature, high reproducibility, low cost, large-scale production, and its ability to control the size and morphology of the material **[17, 18]**. The present work reports an attempt for synthesization of $CoSb_3$

micro/nano-structures, suitable for thermoelectric applications following a recipe of cost effective solvothermal method. The effect of annealing on the purity of crystalline structure of the as-synthesized $CoSb_3$ is monitored using the X-ray diffraction (XRD), the composition using electron dispersive X-ray spectroscopy (EDX) and the morphological studies have been imaged using the field emission scanning electron microscope (FESEM), and transmission electron microscope (TEM).

Experimental details

Materials/ Chemicals

All chemicals used in this work are procured from the Sigma Aldrich Co., USA. In the present work, cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$), antimony (III) chloride ($SbCl_3$), sodium borohydride ($NaBH_4$), ethylene diamine tetra acetic acid (EDTA), and sodium hydroxide (NaOH) were used as the precursors for the synthesis of $CoSb_3$ nanocomposites.

Material synthesis/ Reactions

Nanocomposites of $CoSb_3$ are synthesized following the solvothermal process and stepwise recipe is schematically drawn in **Scheme 1**. Analytically pure $CoCl_2.6H_2O$ and $SbCl_3$, in a molar ratio of 1:3 are used as starting materials by placing in a beaker containing 500ml of distilled water (DI-H_2O). A sufficient amount of $NaBH_4$ as reducing agent and 8g of NaOH is added into the beaker. The beaker is heated to 500 ^{0}C on a hot plate and stirred continuously using a magnetic stirrer. The reflux reaction is carried out for 72 hrs. After the reaction, the beaker is cooled naturally to room temperature. The black precipitate is collected, rinsed with DI-H_2O and ethanol for several times, and the resulting precipitate is dried in an oven at 80 ^{0}C, to obtain the as-synthesized $CoSb_3$ in solid form.

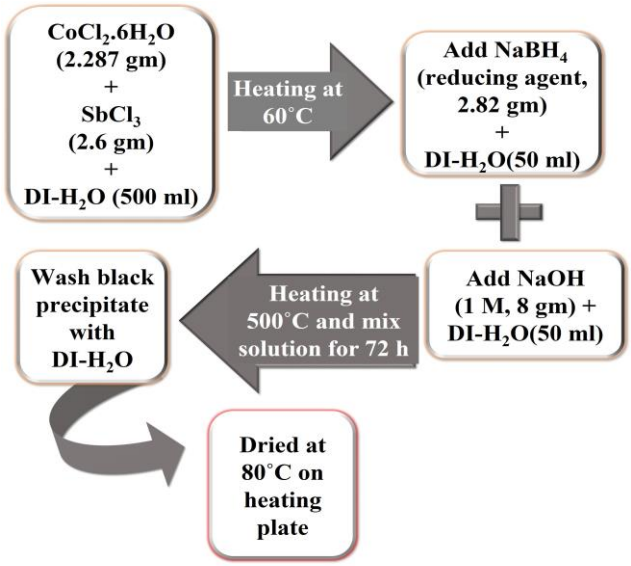

Fig. 1. Schematics of the chemical recipe followed for preparation of $CoSb_3$ nanocomposites.

Characterizations

The surface morphology of the as-synthesized samples are imaged using the field emission scanning electron microscope (FESEM; Jeol JSM 6610LV). Powder X-ray diffraction (XRD) patterns were collected in the 2θ range of, 20^0–80^0 of the as-synthesized and annealed $CoSb_3$ nanocomposites using X-ray diffractometer (XRD; Bruker D8 Discover). The elemental analysis of the $CoSb_3$ is studied using an energy-dispersive analysis of X-rays (EDAX, Jeol JSM 6610LV). Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 UT 30, with an accelerating voltage of 300 kV.

Results and discussion

The chemical reactions for synthesis of $CoSb_3$ is written as:

$$CoCl_2 + 2NaBH_4 \rightarrow Co + 2BH_3 + 2NaCl + H_2\uparrow \quad (1)$$
$$2SbCl_3 + 6NaBH_4 \rightarrow 2Sb + 6BH_3 + 2NaCl + 3H_2\uparrow \quad (2)$$
$$Co + 3Sb \rightarrow CoSb_3 \quad (3)$$

The above reaction mechanism indicates the stepwise formation of the $CoSb_3$ phase. In the beginning of the reaction process, the strong reducing agent $NaBH_4$ rapidly and completely reduces the Co^{2+} and Sb^{3+} ions to Co and Sb atoms, as indicated by the reaction equations (1) and (2), respectively, and combine at high processing temperatures and duration for chemical reaction to form the skutterudite, $CoSb_3$.

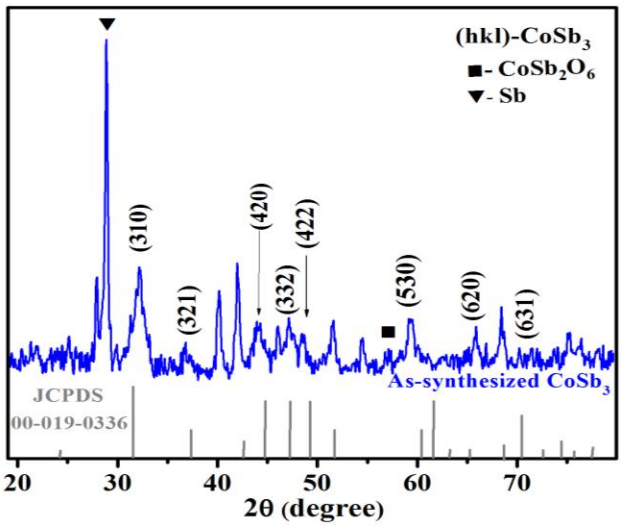

Fig. 2. XRD pattern for the as-synthesized $CoSb_3$ (blue). The lines at the bottom are the various planes assigned for pure $CoSb_3$, as mentioned in JCPDS No. 00-019-0036.

The XRD spectra for the as-synthesized $CoSb_3$ samples prepared solvothermally is shown in **Fig. 2**, indicating a dominant peak for Sb, which is an intermediate product with small peaks for skutterudite phase $CoSb_3$ which can be attributed to the low processing temperature or short duration for the synthesis. The earlier work suggests that a synthesis temperature of around 250 ^{0}C with long reaction duration is necessary for

obtaining pure phase of $CoSb_3$ without the impurities Sb and $CoSb_2$ and the impurities will be formed at low processing temperature and short duration **[17]**. The XRD patterns for post-annealed samples exhibits diffraction peaks corresponding to the skutterudite crystal structure of $CoSb_3$. In addition, the absence of the intermediate product containing Sb is observed except for a trace of $CoSb_2$ and the presence of small amount of oxides. It can be ascribed that during the annealing process, the residual element of Sb starts reconstructing to form $CoSb_2$ and $CoSb_3$ phases in the vacuum ampoule, leading to reduction in the amount of elemental Sb compared to the as-synthesized $CoSb_3$ nanocomposites. The diffraction peaks located for (310), (321), (420), (332), (422), (530), (620), and (631) in all the XRD spectra can be indexed as binary skutterudite $CoSb_3$ with cubic phase, space group Im3 and agrees with the standard XRD profile authenticated among the scientific community (JCPDS File: 000-019-0336) of the cubic $CoSb_3$.

Fig. 3. shows the morphologies of the as-synthesized and post-annealed $CoSb_3$ nanocomposites, respectively, as imaged through the FESEM. The as-synthesized $CoSb_3$ indicates nanocomposites comprising of granules with agglomerated clusters of near-spherical nanoparticles in 20-30 nm dimensions. The EDX measurements, as represented in **Fig. 4**, recodes the contents of elemental Co and Sb in both the as-synthesized and annealed nanocrystals with reduced contents of Sb for the annealed samples. The table in the inset of **Fig. 3b** shows the composition of the elemental Co and Sb contents present in the as-synthesized and post-annealed $CoSb_3$ nanocomposites, confirming the stoichiometric ratio of 1:3 for the as-synthesized and post-annealed $CoSb_3$ samples. The presence of the Cu peak in the EDX spectra is the content of the supporting TEM grid. The initial combined analysis of the FESEM and EDX indicates that the regular features of relatively larger sizes in annealed samples indicate formation of larger crystalline structures originated by removal of elemental Sb from the as-synthesized samples.

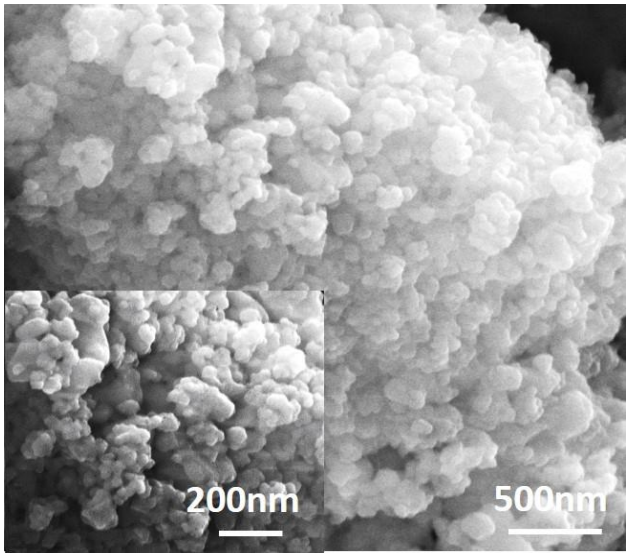

Fig. 3. FESEM images for the as-synthesized $CoSb_3$

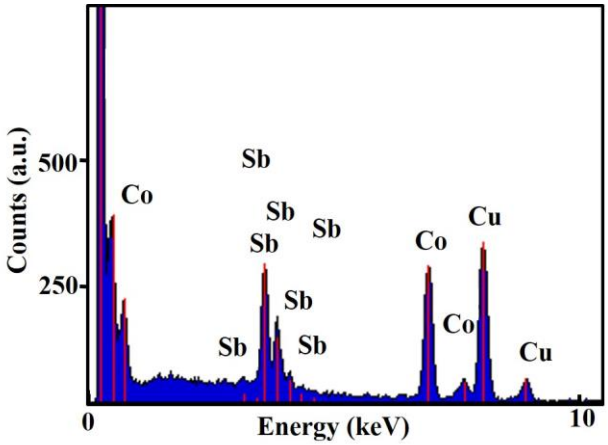

Fig. 4. Energy dispersive X-ray (EDX) spectroscopy for as-synthesized $CoSb_3$ and shows the composition of the elemental Co and Sb content present in the as-synthesized $CoSb_3$ nanocomposites.

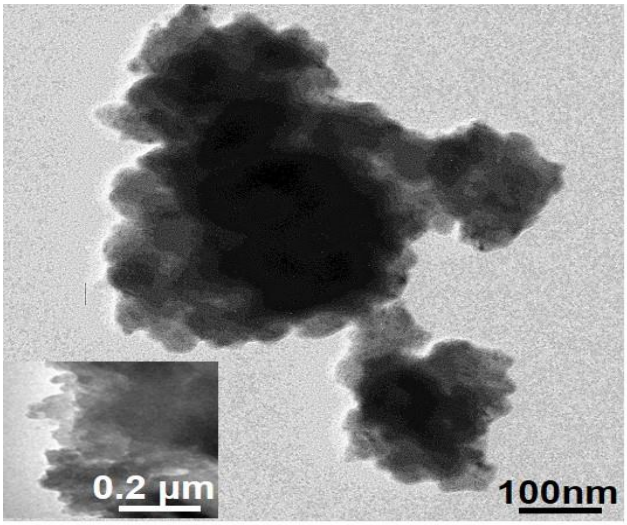

Fig. 5. TEM image of the as-synthesized $CoSb_3$ nanocomposites.

The **Fig. 5** represents the TEM image of the as-synthesized $CoSb_3$ indicating clusters of irregular granule like nanostructure particles of dimensions 10-20 nm with uniform size distribution. The observed crystallographic structure for the $CoSb_3$ based skutterudites have the potential to possess a large unit cell, heavy constituent atoms with low electronegativity differences, and high carrier mobility **[19],** as expected for a good thermoelectric material.

Conclusion

A solvothermal recipe for synthesization of micro/nano-structured $CoSb_3$ skutterudites has been demonstrated, with $CoCl_2.6H_2O$ and $SbCl_3$ as precursors and $NaBH_4$ as reductant. $NaBH_4$ played a key role in the formation of cobalt antimonide because of its energy supply and strong reduction effect. X-ray-diffraction indicates single-phased $CoSb_3$ is achieved for the present solvothermal synthesis, and recipe is refined to remove the elemental Sb that is generally present in the final $CoSb_3$ as residue. The as-prepared $CoSb_3$ powders were composed of irregular

shaped granular nanoparticles (20-30 nm) agglomerated with a uniform size distribution of about 100-400 nm as observed in microstructural analysis. The solvothermal synthesis of nanosized $CoSb_3$ provides a profitable way to develop novel nanostructured skutterudite based thermoelectric materials.

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Author's contributions

Conceived the plan: RPT, AKM, NP; Performed the expeirments: NP, RKG, AKP; Data analysis: NP, AKM; Wrote the paper: NP, AKM. Authors have no competing financial interests.

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