Synthesis, structure and optical properties of Indium filled CoSb₃ nanomaterials

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Abstract. The nano-sized In₀.₃CoSb₃ skutterudites (y = 0.0125, 0.025, 0.0375 and 0.0625) were synthesized by solvo-/hydrothermal method at 240 °C for 24 hours. The surface morphology of as-synthesized samples analyzed by Field Emission Scanning Electron Microscope (FESEM) shows nanoparticles with size of around 50 nm depicting narrow size distribution and Electron X-ray diffraction spectroscopy (EDX) spectrum confirms the purity of the In-filled CoSb₃ nanomaterials. The powder X-ray diffraction (pXRD) pattern reveals all the compositions showing diffraction peaks indexed to cubic phase of CoSb₃ with Space group Im³. However, no significant variation in the pXRD pattern of In filled CoSb₃ as compared to pure CoSb₃ justifies the successful filling of voids in cage-like structure of CoSb₃ with Indium. FTIR spectra of In filled CoSb₃ presents vibration modes below 1000 cm⁻¹ corresponding to Co-Sb bonding and Cobalt complex. A significance of In filling into CoSb₃ structure is also evident. A wide absorption has been witnessed from UV region to large part of visible region, hence indicating the effect of nanoparticle, agglomeration and filling.

Keywords: Skutterudites; Solvo-/hydrothermal; Nanostructure; Filling; Optical properties.

1. Introduction:
The field of thermoelectrics is growing progressively because of its capability of direct and reversible conversion of thermal energy into electricity and it has been recognized as a potentially transformative power generation technology. Thermoelectric devices would have many advantages such as no moving parts, inexpensive and environmentally friendly. The efficiency of TE materials is defined by the dimensionless quantity so-called figure of merit, ZT = S²σT/k, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, k is the total thermal conductivity (k= ke + klat, where ke and klat are the electronic and lattice thermal conductivities, respectively) [1, 2]. Because of its low energy conversion efficiency, the applications of TE devices are still limited. Hence to improve the efficiency of thermoelectric devices, materials with high ZT value are required. Minimizing the k value and maximizing the power factor, defined as (S²σ) can results in the high ZT value [3]. Many researchers have developed various strategies to reduce the lattice thermal conductivity by creating structural disorder, complex crystal structure and nanostructuring [4] etc. Based on the above criteria, among various TE materials, skutterudite compounds are promising candidates due to their tuneable transport properties. The skutterudite compound can be represented by MX₃ where M is a metal atom and X is a pnictogen atom. It belongs to cubic structure, space group Im³ and there are two relatively large voids per unit cell in the structure. When third atom is inserted into the void they form a filled skutterudite represented by RMX₃, which supports the Phonon-glass
electron-crystal (PGEC) concept. This filled atom introduces additional phonon scattering to reduce lattice thermal conductivity and also donates electrons into the CoSb$_3$ structure thereby enhancing electrical conductivity of the material [5]. Various elements like rare-earth elements (La, Ce, Yb), alkaline-earth elements (Ba, Sr, Ga) and other (Sn, In, Ge) have been used to fill the large voids in the crystal to search for better thermoelectric materials [6-8]. The basic criterion for choosing Indium as a filler is because covalent radius of indium (1.06Å$^0$) is smaller than the void radius (1.892Å$^0$), it is easily go on to the void site, rattle well and also indium containing CoSb$_3$ shows large negative seebeck coefficient [9]. Over the recent years many researchers have synthesized the In filled CoSb$_3$ by various methods. He et al., prepared In$_x$Co$_{4}$Sb$_{12}$(0<x<0.3) by solid state reaction, maximum ZT 1.2 was achieved in In$_{0.25}$Co$_{4}$Sb$_{12}$ at 575K [9]. Mallik et al., fabricated In$_{0.25}$Co$_{4}$Sb$_{12}$ by encapsulated induction melting method and reported ZT of 1.12 at 650K [10]. Andreas et al., reported that short-term sintered bulk materials show improved ZT value [11]. The above synthesis techniques requires a long duration, high synthesis temperature, ultra-high vacuum condition in the order of 10$^{-5}$ to 10$^{-6}$ Torr and are also cost effective. For commercial applications, the cost of TE materials is important and also short duration synthesis is required [12]. Solvothermal technique is a reliable synthesis technique because of its comparatively low synthesis temperature, low cost and high reliability [13, 14]. In the present study, Indium filled CoSb$_3$ nanomaterials were prepared by Solvol-/Hydrothermal method and their structural, optical properties are studied. Variation of the lattice parameter as a function of the In filling ratio of In$_x$CoSb$_3$ is investigated.

2. Experimental Procedure:

Indium filled CoSb$_3$ skutterudites (In$_x$CoSb$_3$, with y= 0.0125, 0.025, 0.0375, 0.0625) were prepared by solvo-/hydrothermal method. CoCl$_2$.6H$_2$O, SbCl$_3$, InCl$_3$ and NaBH$_4$ were used as starting materials. The precursors CoCl$_2$.6H$_2$O and SbCl$_3$ were weighed in the stiochiometric ratio (1:3) along with InCl$_3$ as filler and dissolved in water then the solutions are sonicated 20 minutes for better dispersion. The solution of NaBH$_4$ is taken in a burette; added drop wise and reduction reaction was carried out for 15 minutes. After the completion of reduction reaction, the solution is transferred to PPL-lined autoclave (50 mL) and filled with DMF as solvent up to 70% of its volume. The autoclave was sealed properly and placed in wide-mouth muffle furnace maintained at 2400 C for 24 hrs. After the reaction is completed, temperature of the furnace was brought down to room temperature naturally. The samples were filtered and washed with distilled water and ethanol in sequence for several times, then dried at a temperature slightly above room temperature for 30 minutes. The obtained black powder is taken in a quartz boat and placed in a tubular furnace, annealed at 300$^0$ C for 5 hrs in inert atmosphere (Argon).

3. Results and Discussion:

3.1 Structural analysis of CoSb$_3$ nanomaterials

Figure 1. (a) SEM micrograph of CoSb$_3$ nanomaterials. (b) pXRD pattern for CoSb$_3$ nanomaterials. Inset of 1(b) represents the EDX spectrum of the above compound.
Structural characterization was studied by powder X-ray diffraction (pXRD) using Rigaku Ultima IV Powder X-Ray Diffractometer with CuKα radiation (λ=1.54178 Å). The surface morphology of as-synthesized sample was investigated by Field Emission Scanning Electron Microscopy (FESEM; JEOL JSM-7100F) employed with energy-dispersive X-ray (EDX) analysis to obtain the chemical composition information. The UV–VIS absorption spectrum was measured using Perkin Elmer UV/VIS LAMBDA 365 instrument. Perkin Elmer Spectrometer was used to record IR spectrum of the compounds in the range 400 to 4000 cm⁻¹ in KBr medium at room temperature.

Figure 1(a) shows the surface morphology of CoSb₃ nanomaterials synthesized by solvo-/hydrothermal method. The nanoparticles are found to be uniform in shape and particle size varies from 50-100 nm with some agglomeration. Figure 1(b) represents the XRD and EDX spectrum of CoSb₃ nanomaterials. Almost all the peak positions and hkl values match very well with the binary skutterudite CoSb₃ compound and were indexed to JCPDS File No. 76-0470 with cubic phase and space group Im3. A peak corresponding to CoSb₂ secondary phase exists due to chemical synthesis technique [15]. J.L. Mi et al., [16] reported that the secondary phases (CoSb₂) acts as an intermediate product during the formation of CoSb₃ phase. However, these secondary phases are often reduced or can be completely removed by high temperature and high pressure treatment before transport measurements [15]. Inset of Fig. 1(b) shows the EDX spectrum of CoSb₃ nanomaterials. It indicates that presence of Co, Sb and small amount of oxygen impurity that is anticipated to be originated during the sample processing.

3.2 Structural analysis of Indium filled CoSb₃ nanomaterials

The powder XRD patterns of InₓCoSb₁₂ (x= 0, 0.0125, 0.025, 0.0375, 0.0625) are as shown in Fig. 2. It reveals that all the main diffraction peaks are indexed to the CoSb₃ phase with space group Im3 (JCPDS File No. 76-0470). In addition to that peaks corresponding to CoSb₂, InSb, Sb secondary phases were observed in all the filled samples. Guanghe et al., reported that filling fraction limit of voids in InₓCo₄Sb₁₂ should be in the range of 0.05 < x < 0.10 and when the filling limit exceeds the range InSb, CoSb₂, Sb impurity phases are formed [17]. However, the formation of InSb phase in nanoscale is expected to enhance the TE properties [18]. Using the pXRD data different parameters such as d-spacing, lattice parameter (a) and crystalline size (Dₚ) can be calculated as shown in Table 1. The Crystalline size Dₚ, lattice parameter (a) and d-spacing have been calculated using the following equation:

\[ D_p = k\lambda/\beta \cos\theta, \]

\[ a = \left( d^2 (h^2 + k^2 + l^2) \right)^{1/2} \]

and

\[ n\lambda = 2d \sin\theta, \]

respectively.
Table 1. d-spacing, lattice parameter and crystalline size of In$_y$CoSb$_3$ ($y = 0, 0.0125, 0.025, 0.0375, 0.0625$) samples.

| Nominal Composition | 2θ (degrees) | d-spacing ($\AA$) | Lattice parameter $a$ ($\AA$) | Crystalline size D$_p$ (nm) |
|---------------------|--------------|------------------|-----------------------------|--------------------------|
| CoSb$_3$            | 31.2491(8)   | 2.8620           | 9.0504                      | 41.75                    |
| In$_{0.0125}$CoSb$_3$ | 31.4061(9)   | 2.8481           | 9.0064                      | 36.75                    |
| In$_{0.025}$CoSb$_3$ | 31.4087(9)   | 2.8479           | 9.0058                      | 34.24                    |
| In$_{0.0375}$CoSb$_3$ | 31.2674(3)   | 2.8604           | 9.0453                      | 36.11                    |
| In$_{0.0625}$CoSb$_3$ | 31.5280(2)   | 2.8373           | 8.9723                      | 34.46                    |

Table 1 interprets variation of lattice parameter with increasing In filling fraction. It is revealed that lattice parameter ($a$) decreases with an increase in filling concentration. From Table 1 it is also observed that crystallite size and d-spacing significantly decreases as compared to the unfilled CoSb$_3$ due to increasing grain boundaries in CoSb$_3$. The reduction in crystallite size is due to the atomic radii of In (1.06Å) is smaller than the void radius (1.892Å) of CoSb$_3$. This confirms the successful filling of voids in the CoSb$_3$ with Indium. A similar result has been reported by Mallik et al., for Sn-filled Sn$_x$Co$_8$Sb$_{24-x}$Te$_x$ and Yadi et al., for Ce-filled Ce$_y$Fe$_{4-x}$Co$_x$Sb$_{12}$ skutterudite [19, 20].

Figure 3. (a-d) FESEM photographs of In$_y$CoSb$_3$ ($y = 0.0125, 0.025, 0.0375, 0.0625$) nanomaterials. Inset shows corresponding EDX spectrum.

A typical FESEM images for Indium filled CoSb$_3$ nanomaterials with various concentration are shown in Fig. 3. These images show that Indium filled CoSb$_3$ have slightly irregular shape but uniformly distributed particles with size of 50 - 70 nm. Inset of Fig. 3 (a-d) shows the EDX spectrum which confirms the presence of Co, Sb and Indium in all the In filled CoSb$_3$ nanomaterials.
3.3 Optical Characterization by FTIR Spectroscopy

Figure 4. FTIR analysis of $\text{In}_y\text{CoSb}_3$ ($y = 0, 0.0125, 0.025, 0.0375, 0.0625$) samples.

Figure 4 displays the (chemical bonds) compositional analysis of Indium filled CoSb$_3$ with various concentrations carried by the FTIR measurement at room temperature in the range of 400-4000 cm$^{-1}$. Based on the theoretical studies, the vibrational modes of CoSb$_3$ are available below 400 cm$^{-1}$ [21, 22]. Due to the measurement limitations low frequency phonon vibration modes are not obtainable and hence the information shown in the range 400 to 4000 cm$^{-1}$ as shown in the Fig. 4. In both filled and unfilled CoSb$_3$ nanomaterials, broad absorption peak and small peak found from 2000 to 4000 cm$^{-1}$ indicates the presence of O-H bonding which arises due to the moisture in the KBr pellet or surface absorption of moisture during the sample processing [23]. For all the samples ($y = 0$ to 0.0625), weak peak is found in the regions 1600, 1625, 1623, 1631, 1628 and 1767 cm$^{-1}$, respectively corresponds to metal-oxygen bonding. The peaks at 1387, 1384, 1383, 1384 for samples ($y = 0$ to 0.0625), assigned to Cobalt complex and O-H in plane bonding. All the other peaks below 1000 cm$^{-1}$ are assigned to CoSb bonding. The peaks at 739, 738, 740 and 741 can be attributed to cobalt complex and which also confirms Indium filling in the void site of CoSb$_3$ [24]. From the FTIR spectra, it is also clear that with increase in Indium substance there is no substantial impact on the vibrational modes in CoSb$_3$ structure, except slight variation in position and intensity. In further studies, FTIR spectrum below 400 cm$^{-1}$ is expected to provide more information about the phonon modes of vibration in the CoSb$_3$ samples.

3.4 Optical Characterization by UV-Visible Absorption Spectroscopy

The UV-Visible absorption spectra of Indium filled CoSb$_3$ ($y = 0$ to 0.0625) recorded in the wavelength range 200 to 800 nm are shown in Fig. 5. It reveals that, no absorption peaks available in the wavelength range 300–800 nm. Therefore, the material is suitable for manufacture of NLO (non-linear optical) devices [25]. The unfilled CoSb$_3$ sample have broad absorption peak in the wavelength range 270 nm and filled samples have single absorption peak in range 271 – 282 nm. This indicates the material is suitable for UV filters [24]. Also from the Fig. 5 it is observed that with increasing filling fraction the absorption peak shift and also reduction in the peak intensity is observed in all the filled samples due to nanostruturing [26] and exceeded filling fraction of Indium into the CoSb$_3$ voids. Our further studies on UV-VIS spectroscopy effectively depicts the band gap evaluation.
4. Conclusion:
Solvo-/hydrothermal method was employed to prepare $\text{In}_y\text{CoSb}_3$ ($y = 0, 0.0125, 0.025, 0.0375, 0.0625$) nanomaterials and their structure and optical properties were investigated. The Powder X-ray diffraction (pXRD) pattern shows that both unfilled and filled samples have cubic structure with space group $\text{Im} \bar{3}$. A FESEM study shows the surface morphology of $\text{In}_y\text{CoSb}_3$ nanomaterials with particle size in the range 50-70 nm. FTIR analysis shows the chemical bonds below 1000 cm$^{-1}$ corresponding to Co-Sb with the effect of Indium filling. UV-absorption data reveals that, there is a shift of the absorption peak towards the higher wavelength and also reduction in the peak intensity in all the filled samples.

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Figure 5. UV-Visible absorption spectra for $\text{In}_y\text{CoSb}_3$ ($y = 0, 0.0125, 0.025, 0.0375, 0.0625$) nanomaterials
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