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Fabrication and characterization of nanostructured thermoelectric Fe\(_x\)Co\(_{1-x}\)Sb\(_3\)

Abstract: A novel synthesis route for the fabrication of p-type nanostructured skutterudite, FeCo\(_{1-x}\)Sb\(_3\) in large quantity is reported. This scalable synthesis route provides nano-engineered material with less impact on the environment compared to conventional synthesis procedures. Several Fe substituted compositions have been synthesized to confirm the feasibility of the process. The process consists of a nano-sized precursor fabrication of iron and cobalt oxalate, and antimony oxides by chemical co-precipitation. Further thermochemical processes result in the formation of iron substituted skutterudites. The nanopowders are compacted by Spark Plasma Sintering (SPS) technique in order to maintain nanostructure. Detailed physicochemical as well as thermoelectric transport properties are evaluated. Results reveal strongly reduced thermal conductivity values compared to conventionally prepared counterparts, due to nanostructuring. P-type characteristic was observed from the Seebeck measurements while electrical conductivity is high and shows metallic behavior. The highest TE figure of merit of 0.25 at 800 K has been achieved, which is strongly enhanced with respect to the mother compound CoSb\(_3\). This suggests the promise of the utilized method of fabrication and processing for TE applications with improved performance.

Keywords: Skutterudite (CoSb\(_3\)), thermoelectric, iron substituted skutterudite, bottom-up synthesis, SPS

1 Introduction

Thermoelectric (TE) materials are one of the most promising candidates for sustainable energy generation, which are attracting research communities as well as industry [1-4]. Developing TE material in large scale for industrial applications has been one of the bottlenecks of this technology. Having a synthesis route with high yield, reproducibility and low energy consumption is one of the key issues that have to be tackled and overcome. Chemical synthesis routes usually take less energy, time and have less impact on environment [5,6]. CoSb\(_3\), known as skutterudites, exhibit high TE figure of merit. Skutterudites have an effective TE operational range from 650K to 950 K. Among the different types of skutterudites compounds, CoSb\(_3\) based members have attracted by far the greatest interest because of constituents’ abundant availability and less cost [7]. Iron substituted CoSb\(_3\), FeCo\(_{1-x}\)Sb\(_3\), have been reported to display good performance as a p-type TE material, in terms of its TE figure of merit (ZT), and abundance of the constituent elements [8-14]. The ZT can be improved via introduction of dopants, nanoengineering and in case of skutterudites, introducing rare earth elements in the crystal cages to reduce the thermal conductivity [1,4-6] due to rattling of the fillers.

Previous reports on synthesis of bulk powders of iron substituted skutterudites show synthesis routes, which consume high amount of energy, in terms of heat and electricity, as well as long synthesis/processing times. Most of these processes include melting the elemental powders of constituents, using high energy ball milling and finally having a high range of annealing step from 60 hours to almost 200 hours in some cases [8,9,11-16]. Recently, Biswas et al. and Ianniduo et al. have adopted microwave synthesis for skutterudites production. [17,18].
However, the process is fast and effective but it requires very expensive high purity initial powders.

In the proposed route initial oxalate and oxide powders of the constituent elements are precipitated at room temperature. Following this a thermochemical process of no more than 3 to 4 hours of heating will result in high purity skutterudites \([5,19-21]\). In this work, iron has been selected as the substituent element and the materials have been synthesized via a novel chemical synthesis technique. Skutterudites nanopowders with several concentrations of iron (20, 25 and 30% of Co sites) have been fabricated. Structural and thermoelectric transport properties of the fabricated materials are thoroughly investigated.

2 Experimental procedure

The experimental procedure is divided into three major steps, as detailed in our earlier work \([5,19-21]\). First a thermodynamic modeling has been performed to determine the chemical synthesis conditions. After this step the chemical synthesis was performed at room temperature and the oxalate powders of iron and cobalt as well as oxide of antimony were produced. The powders were thermally treated to decompose oxalate compounds and then the nano-oxide mixture material was thermally treated under reducing atmosphere to result in the desired phase.

2.1 Thermodynamic modeling

Thermodynamic modeling was performed with Medusa software \([22]\). This simulation results are obtained from careful consideration of equilibrium constants of aqueous reactions. The results provide predictions of all possible chemical species (solid, complexes, etc.) within all pH ranges. For our experiment purpose a $\text{Fe}^{2+}/\text{Co}^{2+}/\text{Sb}^{3+}/\text{C}_2\text{O}_4^{2-}/\text{OH}/\text{Cl}$ system was simulated to predict the presence of desired precipitated compounds (i.e., iron oxalate, cobalt oxalate and antimony oxide). Fig. 1 presents the fraction of metallic ions in the form of oxalate and oxide crystals. Working pH window for maximum yield for iron oxalate precipitate is between 1.8 and 2.3. The experiments were performed in this pH window as Co$^{2+}$ and Sb$^{3+}$ species also have their maximum yield.

![Figure 1: Thermodynamic modeling showing the speciation of a) Fe$^{2+}$ b) Co$^{2+}$, c) Sb$^{3+}$ species and d) overlay of desired precipitates.](image-url)
Fabrication and characterization of nanostructured thermoelectric $\text{Fe}_{x}\text{Co}_{1-x}\text{Sb}_3$

2.2 Synthesis

Precursor to skutterudite nanopowder was prepared by dissolving stoichiometric amounts of cobalt chloride ($\text{CoCl}_2\cdot6\text{H}_2\text{O}$), iron chloride ($\text{FeCl}_2\cdot4\text{H}_2\text{O}$) and antimony chloride ($\text{SbCl}_3$) in 3 M hydrochloric acid (HCl) (The powders were used as received from Sigma Aldrich). The precipitating agent was 0.3 M ammonium oxalate ($\text{C}_2\text{H}_8\text{N}_2\text{O}_4$). Considering the reaction yield of iron from the results of the thermodynamic modeling, extra 25% of iron was added to the stock solution. The reaction pH was kept between 1.8 and 2.3 with goal of having it at constant pH of 2. This was done by adding acid (3M HCl) or base (ammonium hydroxide, NH$_4$OH). The precipitating process was carried out at room temperature. The metal ion solution as well as the precipitating agent was added to the reaction chamber simultaneously. The reaction was controlled in a way to consume all the reactive elements at the same time. After the precipitations, the powders were washed and filtered to remove unreacted species and further dried at 60°C overnight.

2.3 Thermochemical processes

The powders were calcined in air in a box furnace (Carbolite Furnaces) at 350°C in order to convert them to corresponding oxides. After this step the mixed oxide powders of iron, cobalt and antimony were reduced under hydrogen at 450°C for 3 hours in a rotating tube furnace, producing a batch of ca. 30 g of TE powder. The powders were then consolidated using SPS technique (SPS Dr. Sinter 2050).

2.4 Characterization Techniques

Phase purity was determined by X-Ray powder diffraction (Powder diffractometer Panalytical X’Pert PRO) and morphology of the powder as well as the consolidated pellets were evaluated using Scanning Electron Microscopy (SEM Zeiss Ultra 55). Further elemental analysis of the alloy was performed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES Thermo scientific iCAP 6500 ICP Spectrometer). TE Characterization was performed by an in-house developed ZT-measurement tool by Fraunhofer-Institut für Physikalische Messtechnik (Ph-IPM, Germany) [23-25].

3 Results and discussions

Fig. 3 illustrates the powders. The prepared dried powders are yellowish due to the presence of iron oxalate. The calcined powder is light grey and the final reduced powder is dark grey, which visually confirms the success of different synthesis steps. The following sample tags were used for each sample (KTH_11 with chemical composition of $\text{Fe}_{0.2}\text{Co}_{0.8}\text{Sb}_3$, KTH_12: $\text{Fe}_{0.25}\text{Co}_{0.75}\text{Sb}_3$, and KTH_13: $\text{Fe}_{0.3}\text{Co}_{0.7}\text{Sb}_3$).

Reduced powder was evaluated for the elemental content using EDX analysis, displayed in Fig. 3, which confirms the co-presence and a homogeneous distribution of iron, cobalt and antimony within the fabricated material.

The reduced powders as well as the compacted pellet have been investigated for their structural phase determination using XRD. The patterns show major phase of Skutterudite as well as some elemental antimony and secondary phase of $\text{FeSb}_2$, which forms when saturation of solid-solubility of iron is reached. Fig. 4 displays the XRD patterns for the prepared samples, where peaks for skutterudite structure are indexed with relevant Miller indices (ICDD# 01-083-0055). To further approve the composition of the samples we performed ICP measurements to verify the exact stoichiometric amount of each element. Table 1 shows
the desired sample compositions with respect to precursor composition, and the composition determined from ICP measurements, which confirm the success of the fabrication method within the sensitivity range of ICP technique.

Using the SPS parameters of 70°C min⁻¹ heating rate, compaction temperature of 475°C, holding time of 3 minutes and applied pressure of 75 MPa [26] all the samples reached compaction densities of more than 94% compared to their theoretical density. Fig. 5 shows typical SEM micrograph of the reduced powder as well as the SPS-compacted pellet.

SEM micrograph shows the particle size of the powder in Fig. 5a to be in the range of 200–400 nm. On the other hand, grain growth is visible as SPS-compacted samples exhibit grain size in the range of 250–600 nm, due to the impact of sintering condition on the grain growth. Nearly all samples prior to and resulting in the final samples show the same morphological properties.

The samples were characterized for their TE transport properties; Fig. 6 shows TE evaluation results of the three samples.

Comparing the results from the prepared samples, the Seebeck coefficient follows a trend showing the decrease of the Seebeck coefficient with increase of iron concentration in the sample. Seebeck coefficient, electrical conductivity, thermal conductivity and eventually ZT are within the same range but the trend is visible as the sample with 25% has the highest ZT reaching up to 0.25. Referring to table 1 KTH_11 has 20% iron substituted on cobalt sites and 25 and 30% for KTH_12 and KTH_13 respectively. The electrical conductivity follows a visible trend, which shows an increase with 25% iron doping and then decrease in the case of 30% iron doping, due to the negative effect of the secondary FeSb₂ phase. The formation of FeSb₂ phase is a result of the saturation of solubility of iron in the structure. The electrical conductivity starts about 700 S cm⁻¹ for lowest Fe doping and reaches 1400 S cm⁻¹ in the sample with 25% Fe concentration and then reduces to 900 S cm⁻¹. These values are higher than the reference values such as 590 S cm⁻¹ [9] (with chemical composition of Fe₀.₂Co₀.₈Sb₃) and about 510 S cm⁻¹ [16] (with chemical composition of Fe₀.₁Co₀.₉Sb₃). Electrical conductivity values decrease with increasing temperature, which indicates metallic characteristics of the fabricated materials. Positive sign of Seebeck coefficient reveals success of the doping-process for fabricating p-type TE materials. Although the electrical conductivity of the material is higher, the corresponding value for the Seebeck is fairly low and considering the Seebeck having higher impact on the ZT the final values of Seebeck in case of the same sample (KTH_12, 110 μV K⁻¹) and references (150 μV K⁻¹ [9] and 140 μV K⁻¹ [12]) the ZT value obtained remains in the range of 0.18-0.25 at 800 K. The overall low Seebeck coefficient
can be attributed to the presence of the FeSb₂ phase. FeSb₂ has been reported to be an n-type semiconductor [27] which considering its negative Seebeck coefficient results in a lower net value for the Seebeck of the bulk samples. Thermal conductivity (TC) measurements show that we have been successful in our nano-engineering approach. Its value at room temperature is much lower than the bulk thermal conductivity of skutterudite (10 W m⁻¹ K⁻¹) [6] and the values approve the materials’ TC to be within the range of the state of the art material (2.2 W m⁻¹ K⁻¹ [9]). A sudden rise in the value of the TC can be observed in samples KTH_11 and KTH_13 above 700 K. The TC value at low temperatures consists of only lattice thermal conductivity and the carrier thermal conductivity; at high temperatures another process of ambipolar thermal conductivity, is added to the total value [28]. At high temperatures an electron-hole pair is excited and diffused from the hot side to the cold side, which result in no net current but contributing to the TC of the material.

Figure 5: SEM micrographs KTH_12 a) after reduction, b) after SPS compaction.

Figure 6: Thermoelectric evaluations of SPS’d KTH samples (as detailed in Table 1).
For classical semiconductors Wiedemann–Franz law can be applied to estimate the electronic contribution to the thermal conductivity \(k_e\), and using this value the lattice thermal conductivity \(k_l\) can be estimated by subtracting from the total thermal conductivity \(k_{tot}\). Using Wiedemann–Franz law and the conventional value for Lorenz number, \(L_0 = 2.44 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}\) for metals and \(1.49 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}\) for heavily doped semiconductors) we estimated and plotted \(k_l\) values for the evaluated samples as displayed in Fig. 7. Looking at the ratio it can be seen that \(k_l\) is about 85% of \(k_{tot}\), which means it is still the highest contributor to \(k_{tot}\). We are cautious on reporting these \(k_l\) values, as recently there are some reports on \(L_0\) not necessarily being a constant that can be applied to all metal/semiconductor or bulk/nanoparticle systems. This issue is also raised by Xun Shi et al. [29] in their attempt to calculate \(k_{tot}\), where they calculated the \(L_0\) specific to their particular material based on their assumptions. This discrepancy is raised due to the size dependence of the conductivity behavior.

Considering the electrical and thermal conductivity, they are well within the range of the available literature but the weak part of the material remains to be the Seebeck coefficient and eventually the ZT remains in the range of 0.25.

### 4 Conclusions and future work

Nanostructured p-type iron substituted CoSb₃ skutterudite with high phase purity has been successfully fabricated in large-scale using a novel chemical route. Low thermal conductivity of the material approves the success of the nanoengineering approach. Thorough physicochemical analyses proved the desired content of Fe in the samples. Metallic behavior of the sample may come from the segregated Fe and FeSb₂ phases, which in turn results in a low Seebeck coefficient of the samples, resulting in ZT value of 0.25 at 800 K, which is significantly higher than the mother compound without Fe. Comparing with the available synthesis routes, the method suggested dramatically reduces the time and energy consumed for fabrication of the material. Additionally this method results in high yield (ca 100 g per day in lab scale) with high degree of reproducibility providing a promising route for commercialization of the material.

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