



Rapid fabrication and low-temperature transport properties of nanostructured p-type $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ ($x=0.15, 0.20$ and 0.30) using solvothermal synthesis and evacuated-and-encapsulated heating

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Abstract

Polycrystalline p-type $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ with $x=0.15, 0.20$ and 0.30 are fabricated using a combination of solvothermal synthesis at 260°C for 24 h and evacuated-and-encapsulated heating at 600°C for 5 h. The X-ray diffraction patterns reveal that all the compositions are of single phase. The thermopower of all the samples is positive, indicating that the predominant carriers are holes over the investigated temperature range of 80–300 K. The electrical resistivity and thermopower simultaneously decrease with increasing Ce filling content. Analyses of the temperature dependence of both electrical resistivity and thermopower indicate that all the samples obey the variable range hopping transport mechanism. Among the samples, $\text{Ce}_{0.20}\text{Co}_4\text{Sb}_{12.04}$ exhibits the highest power factor of $0.29 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 300 K. This value represents an improvement of about 556% compared to pristine $\text{Co}_4\text{Sb}_{12.04}$.

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1. Introduction

Thermoelectric materials and devices have great potential of providing alternative energy by converting waste heat into electric energy without using moving parts and without producing carbon dioxide gas, toxic substances or other emissions. The performance of thermoelectric materials is expressed by the dimensionless figure of merit $ZT = S^2T/\rho\kappa$, where S , ρ , κ and T are the thermopower, electrical resistivity, total thermal conductivity, and absolute temperature, respectively. In order to obtain a high value of ZT , the materials need to have large S , low ρ and low κ [1]. The figure of merit can be improved by either increasing the electrical power factor (S^2/ρ) or decreasing the thermal conductivity. Skutterudite compounds are considered as potential candidates for thermoelectric applications [2–4]. Binary skutterudites can be represented by MX_3 ($\text{M}=\text{Co}, \text{Rh}, \text{Ir}$; $\text{X}=\text{P},$

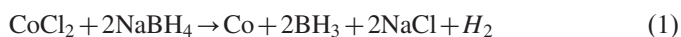
As, Sb), and they have a body-centered cubic structure with a space group $\text{Im}\bar{3}$ symmetry. Among the skutterudite compounds [5], $\text{Co}_4\text{Sb}_{12}$ has attracted much attention in recent years because it exhibits large thermopower and good electrical conductivity [6]. However, its thermal conductivity is too high [7]. There are two effective approaches to reduce the thermal conductivity. The first approach is to fill guest atoms into the voids (or cages) of the skutterudite structure and form a filled-skutterudite. The guest atoms are somewhat weakly bonded in the voids and ‘rattle’ at their equilibrium positions [7]. Another approach is to synthesize nanostructured thermoelectric materials [8].

Synthesis of $\text{Co}_4\text{Sb}_{12}$ was reported by various methods such as solid state reaction [9,10], co-precipitation [11], sol-gel [12], spark plasma sintering [13], polyol, hydrothermal, and solvothermal methods [14–16]. The solid state reaction is a simple process but requires high temperature treatment with long soaking time to obtain pure $\text{Co}_4\text{Sb}_{12}$ phase [9,10,17]. Solvothermal processes transform precursor reactants in the presence of a solvent within a closed vessel and at a temperature higher than the boiling point of the solvent. This

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method provides a promising way of synthesizing nanocrystalline materials and has several advantages such as simplicity, products with high crystallinity, relatively low reaction temperature, large surface area of as-prepared particles, and high efficiency. In order to obtain single phase of p-type $\text{Co}_4\text{Sb}_{12}$ in a short period of time, we carefully investigate the effects of the reaction temperature and its heating rate in the solvothermal synthesis as well as the sintering temperature on fabricating single phase of $\text{Co}_4\text{Sb}_{12+\delta}$, and find that pure phase of p-type $\text{Co}_4\text{Sb}_{12+\delta}$ can be obtained using a combined process of solvothermal reaction with a controlled heating rate of $3^\circ\text{C}/\text{min}$ to reach the reaction temperature of 260°C (holding for 24 h) and the sintering temperature at 600°C . It is interesting to note that the ramp rate to reach the target reaction temperature of solvothermal synthesis plays a role in the fabrication process. Moreover, nanograins of 10–20 nm can be obtained using this fabrication process (Fig. 1). Formation of $\text{Co}_4\text{Sb}_{12}$ phase might undergo multiple steps as described in the following [18–19]:



In this study, we adopt similar procedures to fabricate Ce-filled $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$. As a result, we find p-type $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ can be fabricated with high temperature heating period less than 30 h using a combination of solvothermal synthesis at 260°C and evacuated-and-encapsulated heating at 600°C . We also find that the temperature dependence of both electrical resistivity and thermopower for all the samples obey the variable range hopping transport process in the investigated temperature range of 80–300 K.

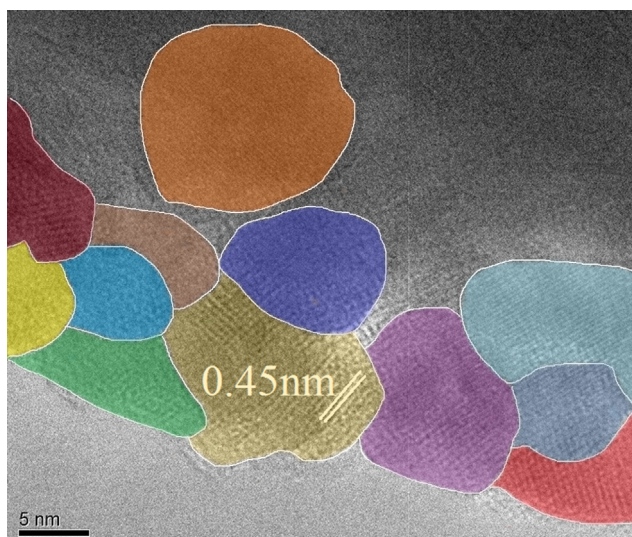


Fig. 1. High resolution TEM images of $\text{Co}_4\text{Sb}_{12.04}$.

2. Experimental details

The reactants of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, SbCl_3 and CeCl_3 were weighted in appropriate stoichiometric ratio. Nominal composition of $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ with $x=0.15$, 0.20 and 0.30 of the starting reactants were placed in Teflon-lined autoclave, which was filled with tetraethylene glycol up to 85% of its total volume. Sodium borohydride (NaBH_4) was used as reducing agent. A sufficient amount of NaBH_4 was slowly added into Teflon-lined autoclave and then autoclave was immediately sealed. The autoclave was transferred to a pressure bomb and heated to 260°C at a heating rate of $3^\circ\text{C}/\text{min}$ and kept at that temperature for 24 h, followed by cooling to room temperature naturally. The resulting suspension was filtered using suction filtration, washed several times with distilled water and ethanol, and dried at 80°C . The black powders were obtained and then powders were compacted into parallelepipeds. The prepared parallelepiped was then loaded into a Pyrex ampoule, which was evacuated using a diffusion pump to reach 10^{-5} – 10^{-6} Torr and then sealed. The parallelepiped in the encapsulated ampoule was then sintered at 600°C for 5 h. The phase purity of resulting powders was examined by a Shimadzu XRD-6000 powder X-ray diffractometer equipped with $\text{Fe K}\alpha$ radiation. The morphology of the samples was examined using a Zeiss AURIGA field emission scanning electron microscope (FE-SEM). Electrical resistance measurements were carried out using standard four-probe techniques. Thermopower measurements were performed between 300 K and 700 K using steady-state techniques with a temperature gradient of 0.5–1 K across the sample. A type E differential thermocouple was used to measure the temperature difference between hot and cold ends of the sample [20], which was measured using a Keithley 2182 nanovoltmeter. The thermopower of the sample was obtained by subtracting the thermopower of the Cu Seebeck probe. The uncertainty for the electrical resistivity and thermopower is about $\pm 3\%$ and $\pm 4\%$ respectively.

3. Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) patterns of $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ with $x=0.15$, 0.20 and 0.30. All the diffraction peaks of the samples can be indexed based on the cubic structure with the space group $\text{Im}\bar{3}$ (No. 204) (PDF Card: 03-65-3144) without secondary phase detected, indicating successful synthesis of single phase of $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$. Similar results were reported by earlier researchers [21–22]. The refined lattice constants are $a=9.061(4)$ Å, $9.062(2)$ Å and $9.064(6)$ Å for $x=0.15$, 0.20 and 0.30, respectively. The lattice constant of $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ is higher than that of pristine $\text{Co}_4\text{Sb}_{12}$ reported by Sofo and Mahan [3] (PDF Card: 03-65-3144, $a: 9.034(6)$ Å), which could be attributed to the Ce filled into voids of CoSb_3 . The lattice constant increases with increasing Ce content, indicating that Ce is filled into voids of the CoSb_3 cage structure and gives rise to lattice expansion [23]. The bulk density was measured by applying the Archimedes principle at room temperature. The density of $\text{Ce}_x\text{Co}_4\text{Sb}_{12.04}$ is 5.28 g/cm^3 , 5.41 g/cm^3 and 6.33 g/cm^3 for $x=0.15$, 0.20 and 0.30, respectively, which

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