Materials Letters 93 (2013) 219–222

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

# The impact of synthesis pressure on the thermoelectric properties of $CoSb_3$

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ARTICLE INFO

*Article history:*
Received 19 October 2012
Accepted 22 November 2012
Available online 1 December 2012

*Keywords:*
Electrical properties
Thermal properties
$CoSb_3$

ABSTRACT

A novel chemical alloying method of high pressure and high temperature (HPHT) has been used for the synthesis of bulk-skutterudite $CoSb_3$. Through this method, the processing time can be reduced from a few days to half an hour. The Seebeck coefficient, electrical resistivity and thermal conductivity of $CoSb_3$ were all measured in the temperature range of 327–661 K. The Seebeck coefficient of $CoSb_3$ increased with increasing synthesis pressure; a substantial reduction in the thermal conductivity was observed with increasing synthesis pressure. These results indicated that the HPHT technique may be helpful for optimizing electrical and thermal transports in a relatively independent way.

## 1. Introduction

Thermoelectric material is a kind of function material that can convert electricity and heat directly. As stated earlier, skutterudite compounds have been extensively studied as a group of promising thermoelectric materials over the last decade. Interest in these materials was greatly increased by the introduction of the phonon glass electron crystal (PGEC) concept [1–3]. $CoSb_3$ belongs to a broad family of materials with the skutterudite structure which have been recently identified as potential new thermoelectric materials. Binary skutterudite $CoSb_3$ crystallizes in a body-centered-cubic structure with space group Im3 and has interstitial voids at the 2*a* positions (12 Sb-coordinated) in the lattice. The properties of thermoelectric materials are characterized by the dimensionless figure of merit, $ZT=\alpha^2\sigma T/\kappa$, where $\alpha$, $\sigma$, $\kappa$ and $T$ are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively.

Despite their favorable features such as high electron mobility and high Seebeck coefficient, which gives skutterudites a high power factor, the $CoSb_3$-based skutterudites are disadvantaged by their inherently large thermal conductivity which lowers their ZT value [4,5]. The thermal conductivity contains two parts, one is the carrier thermal conductivity and the other is lattice thermal conductivity. The phonon scattering mechanism has proven to be effective for reducing lattice thermal conductivity of skutterudite and clathrate compounds, thereby improving their thermoelectric properties. Guest atoms can be introduced into the crystal structure to form filled skutterudites; the "rattling" motion of the filled atoms can effectively scatter phonons and cause a significant decrease of the lattice thermal conductivity [6,7]. $CoSb_3$ is one of the most studied skutterudite materials as well as the mother compound for extrinsic atom filling. Spark plasma sintering (SPS) [8], arc melting, nanotechnology [9] and hot pressing have been employed to prepare $CoSb_3$ bulk samples.

It has been reported that the ZT value for many thermoelectric materials could be improved by high pressure [10,11]. In our previous reports [12], the HPHT method has been used to synthesize skutterudite compounds successfully and obtain desired results. Compared with other methods, the HPHT method has many advantages, including rapid tune ability and being clean, typically without introducing disorder, phase separation or other complicating factors. Moreover, through this method, the thermoelectric properties of the materials can be effectively optimized by changing synthesis pressure without using any other technologies, including nanotechnology. If reduction of the thermal conductivity is observed, this will be a "proof of concept" and the technique will then be applied to more optimized filled skutterudites that already have a high ZT.

## 2. Experimental procedure

The $CoSb_3$ samples were prepared with Sb and Co (99.9% in purity) powders as sources, which were weighed according to the stoichiometry. After being uniformly mixed in an agate mortar under argon protection, the mixtures were shaped by pressing. The mixtures were shaped to a cylinder about 3 mm thick and 10 mm in diameter by pressing. The cylinder samples were assembled for HPHT synthesis. The samples were prepared in a cubic anvil high pressure apparatus (SPD 6 × 1200) with a sample chamber of 23 mm on an edge at 900 K. X-ray diffraction (XRD)

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http://dx.doi.org/10.1016/j.matlet.2012.11.089

measurements with Cu-$K_\alpha$ radiation were performed on an X-ray diffractometer (D/MAX-RA). The Hall coefficient ($R_H$) and carriers concentration ($N_p$) at room temperature were measured by the van der Pauw method by using a Hall measurement system (HMS 3000). The Seebeck coefficient and electrical conductivity were measured simultaneously by a ZEM-3 apparatus, and they were measured in the temperature range of 327–661 K. The thermal conductivity was measured on a Netzsch LFA 427 laser flash thermal constants measuring apparatus in the temperature range of 327–661 K.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of $CoSb_3$ synthesized by HPHT. The XRD patterns of $CoSb_3$ prepared at different synthesis pressures are nearly the same. All of the diffraction peak positions and *hkl* values match very well with the standard diffraction data of $CoSb_3$ which indicates that the sample prepared by HPHT is near single phase. Fig. 1(b) shows the optical image of $CoSb_3$ synthesized at 1.5 GPa directly after 30 min HPHT reaction. Compared with the traditional method, the processing time of HPHT method reduced from a few days to half an hour.

The corresponding XRD cell parameters in Å, unit cell volume, Hall coefficient ($R_H$), carriers concentration ($N_p$), thermal conductivity ($\kappa$), electrical resistivity ($\rho$), Seebeck coefficient ($\alpha$) and density of $CoSb_3$ at room temperature are listed in Table 1. The Hall coefficients of all samples are positive, indicating *p*-type conduction at room temperature. As expected, with increasing synthesis pressure, the density, Seebeck coefficient and Hall coefficient all increased while the thermal conductivity and carriers concentration decreased. These results indicate that the HPHT technique may be helpful to prepare thermoelectric materials with enhanced thermoelectric properties.

Fig. 2(a) presents the temperature dependences of electrical resistivity of the samples. The electrical resistivity of the samples of $CoSb_3$ increases with increasing synthesis pressure in the temperature range of 327–600 K. The figure shows that the electrical resistivity of the sample synthesized at 1.5 GPa increases with increasing temperature, indicative of degenerate semiconductor character. On the other hand, the electrical resistivity of the sample synthesized at 4.5 GPa decreases with increasing temperature, indicative of semiconducting transport behavior.

The relationship between the Seebeck coefficient ($\alpha$) and temperature is displayed in Fig. 2(b) for $CoSb_3$. All samples exhibit *p*-type conduction as they have positive $\alpha$. The Seebeck coefficient of $CoSb_3$ increases gradually with an increase of the synthesis pressure in the temperature range of 327–500 K. The highest $\alpha$ near room temperature is 187 $\mu V\,K^{-1}$ for the sample synthesized at 4.5 GPa, which increases almost linearly to 200 $\mu V\,K^{-1}$ at 400 K. At $T > 400$ K, $\alpha$ tends to a maximum and then decreases presumably due to an increasing number of thermally excited minority carriers at higher temperatures which tend to decrease the Seebeck coefficient [13].

The most interesting aspect of these $CoSb_3$ samples is the thermal conductivity measurements. The thermal conductivity ($\kappa$) of $CoSb_3$ is plotted in Fig. 3(a) versus synthetic pressure. It can be seen that the thermal conductivity decreased significantly with an increase of the synthesis pressure. The minimum value of $CoSb_3$ synthesized at 4.5 GPa is 2.5 $W\,m^{-1}\,K^{-1}$, which is about 3 times lower than that of nano-engineered $CoSb_3$ [14] and nearly as low as those of double-filled samples [15]. Unfortunately, so far, we have not found the exact reason for this. Maybe this is because the higher synthesis pressure can increase the plastic strain of the crystal, cause an increase of the average dislocation density which increases linearly in a crystal with the plastic strain [16], and finally reduce the thermal conductivity [17]. These

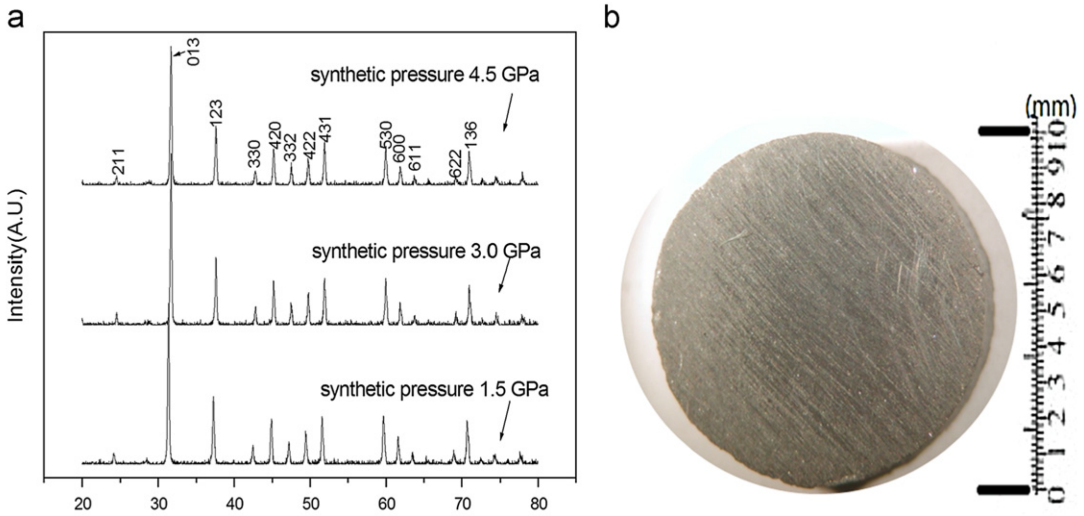

**Fig. 1.** (a) XRD patterns of $CoSb_3$ prepared by HPHT, and (b) optical image of $CoSb_3$ synthesized at 1.5 GPa.

**Table 1**
Comparison of some properties of the three samples, synthesized at 1.5–4.5 GPa, at room temperature.

| Synthesis pressure (GPa) | Density ($g\,cm^{-3}$) | $\alpha$($\mu V\,K^{-1}$) | $\rho$ ($10^{-3}\,\Omega\,cm$) | $\kappa$ ($Wm^{-1}\,K^{-1}$) | $N_p$ ($10^{19}\,cm^{-3}$) | $R_H$ ($cm^{-3}C^{-1}$) | Unit cell parameters (Å) | Unit cell volume (Å$^3$) |
|---|---|---|---|---|---|---|---|---|
| 1.5 | 7.38 | 122 | 3.8 | 5.1 | 1.32 | 0.47 | 9.0383 | 738.3 |
| 3.0 | 7.41 | 139 | 16.8 | 3.5 | 1.09 | 0.57 | 9.0359 | 737.7 |
| 4.5 | 7.48 | 188 | 79.5 | 2.8 | 0.52 | 1.21 | 9.0353 | 737.6 |