High pressure synthesized Ca-filled CoSb_3 skutterudites with enhanced thermoelectric properties

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ABSTRACT

Ca-filled CoSb_3 skutterudites were synthesized under high pressure. The structural, electrical, and thermoelectric properties were investigated. $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples show the skutterudite structure of $\text{Im}\bar{3}$ symmetry. The maximum filling fraction of calcium was substantially increased in the high-pressure synthesized samples compared with the ambient-pressure synthesized samples. As a result, the power factor was greatly increased and a maximal PF value of *ca.* $5400 \mu\text{Wm}^{-1}\text{K}^{-2}$ was reached in $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$. The highest ZT of 1.15 was achieved in the optimal $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ at 840 K. Compared with the traditional solid state reaction method, high pressure synthesis can substantially shorten the reaction duration and extend fillable elements (or increase filling fraction), thus provide us an effective pathway for thermoelectric materials fabrication.

Keywords: Skutterudites; High pressure synthesis; Thermoelectric properties

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1. Introduction

Thermoelectric materials have attracted extensive research interests in the past decade due to their prospective applications in energy conversion. The performance of thermoelectric materials is characterized by the dimensionless figure of merit, $ZT = S^2T/\rho\kappa$, where S , T , ρ , and κ are the Seebeck coefficient, temperature, electrical resistivity, and thermal conductivity, respectively. To make the thermoelectric device competitive to other energy conversion devices, thermoelectric materials with high ZT in the working temperature range must be fabricated. Elemental filled CoSb_3 -based skutterudites, a prototype of phonon-glass electron crystal (PGEC) concept proposed by Slack [1], is one of the most promising thermoelectric materials working in the intermediate temperature region [2]. In this class of thermoelectric materials, the loosely bonded filler atoms donate electrons to improve the power factor ($PF = S^2/\rho$) meanwhile rattle inside the crystal voids to strongly scatter phonons and reduce the thermal conductivity.

Various filling elements have been explored to improve the thermoelectric performance of CoSb_3 -based materials [3-10]. Calcium with a small ionic radius and proper electronegativity is an alternative filling element. $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ was synthesized under ambient pressure [11]. However, the filling fraction is relatively low [11, 12], which limits the thermoelectric performance of Ca-filled CoSb_3 . For example, the highest ZT of 0.45 was achieved for $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12}$ at 800 K, mostly due to the very low power factor in this material [11]. Previous works highlighted pressure as a fundamental thermodynamic variable in synthesizing elemental filled CoSb_3 [13-17]. High pressure can lower the reaction temperature, and facilitate the synthesis of metastable phase by shifting reaction equilibrium [18]. Moreover, the pressure induced stress can

increase power factor to some extent, which can be partially trapped after quenching the sample to ambient conditions [19].

In this paper, we report the fabrication of Ca-filled CoSb_3 with high pressure synthesis (HPS) method. The produced $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples were characterized for the structural and thermoelectric properties. Compared with the ambient-pressure synthesized samples, the filling fraction of calcium in CoSb_3 is substantially increased, leading to greatly improved thermoelectric performance of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$. The optimal $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ shows significantly enhanced power factor and substantially suppressed lattice thermal conductivity due to increased filling fraction, and a ZT value as high as 1.15 is achieved at 840 K.

2. Experimental section

Pure Ca (99%, granules), Co (99.8%, powder), and Sb (99.999%, powder) were mixed according to an atomic ratio of $a:4:12$ ($a = 0, 0.2, 1.0$). The mixture was loaded into a mould and shaped into a cylinder with cold press. The as-prepared bulk was inserted into an h -BN crucible and loaded into a **six-anvil** high pressure apparatus (**CS-1B, working pressure: 1–6 GPa, working temperature: 20–2300 K**) for a two-step HPS. The first step of HPS was carried out at 1123 K and 1 GPa for 0.5 h. Then the product was ground into powders under argon atmosphere, shaped with cold press, and loaded into the high pressure apparatus again for the second step of HPS (873 K and 1 GPa for 3 h). The obtained product was ground into powders and washed in acidic solution to remove the excessive Ca. The dried powders were sintered into dense pellets by using spark plasma sintering (SPS) at 60 MPa and 953 K for 0.5 h. Rectangular blocks ($2 \times 2 \times 6 \text{ mm}^3$),

disks ($\phi 6 \text{ mm} \times 1 \text{ mm}$), and slices ($2.5 \times 6 \times 0.4 \text{ mm}^3$) were cut from the final pellets for the electrical transport, thermal conductivity, and Hall coefficient measurements, respectively.

The chemical compositions of the final SPS products were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo IRIS Intrepid II). The crystal structure was characterized by the X-ray diffraction (XRD, Rigaku D/MAX/2500/PC) measurement. **The sample densities were measured with the Archimedes method.** The Seebeck coefficient and electrical resistivity were measured with a ZEM-3 (Ulvac-Riko) apparatus, and the thermal conductivity was measured with a TC-9000H (Ulvac-Riko) apparatus. **The uncertainty in S , ρ , and κ measurements is within 5%.** The Hall coefficient measurements were performed between 2 and 300 K with a Physical Property Measurement System (PPMS, Quantum Design). The heat capacity measurements were carried out between 2 and 25 K with the heat capacity option of PPMS.

3. Results and discussion

The actual calcium filling fractions, x , determined from ICP-AES are 0.14 and 0.31, respectively, for nominal filling fractions of 0.2 and 1.0. Different parts of the final product were checked and a constant x was determined, indicating a uniform chemical composition. The highest x of 0.31 achieved in HPS samples is obviously larger than the maximal x of 0.2 achieved in ambient-pressure synthesized Ca-filled CoSb_3 samples [11], indicating high pressure can promote calcium filling in CoSb_3 . XRD patterns of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples ($x = 0, 0.14$, and 0.31) are presented in Fig. 1 with the characteristic peaks indexed. All samples are dominated with the skutterudite structure of $\text{Im}\bar{3}$ symmetry. No significant diffraction peak from second phases

was observed from these samples. The diffraction peaks show systematical shift to smaller angle with increasing filling fraction, as illustrated in the inset for the magnified (013) peak. This systematical shift indicates that the lattice parameter increases monotonically with increasing Ca filling fraction, as shown in Table 1. The identical skutterudite crystal structure, absence of secondary phase XRD patterns, and continuous expansion of the lattice parameter with increasing Ca filling fraction evidence the successful synthesis of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$, which is further confirmed by the low temperature heat capacity measurements discussed later.

The room temperature electrical properties, carrier concentration and mobility for different samples are summarized in Table 1. After Ca filling, the charge carrier changes from hole to electron due to the extra electrons donated from Ca. Also, the carrier concentration increases with elevating Ca filling fraction, leading to decreasing ρ and S (absolute value). ρ decreases by at least one order of magnitude compared with the unfilled CoSb_3 sample at room temperature. The carrier mobility (μ) decreases with increasing filling fraction, which is consistent with other elements filling [4, 20-24].

The temperature dependent electrical transport properties of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples are shown in Fig. 2. The unfilled CoSb_3 is an intrinsic p -type semiconductor with a large electrical resistivity and a positive Seebeck coefficient, while Ca-filled CoSb_3 samples show a heavily doped n -type semiconductor behavior. The electrical resistivities of Ca-filled CoSb_3 samples, which decrease dramatically after Ca filling, increase with elevating temperature due to stronger scattering (Fig. 2a). Ca-filled CoSb_3 samples possess a negative Seebeck coefficient due to the extrinsic charge carriers of electron from calcium (Fig. 2b). It is noted that, as the carrier concentration increases

with larger Ca filling fraction, a decrease in the Seebeck coefficient (absolute value) occurs. This is consistent with the electrical resistivity measurement results. The temperature dependent PF is demonstrated in Fig. 2c. PF is smaller than $1000 \mu\text{Wm}^{-1}\text{K}^{-2}$ for pure CoSb_3 , while it increases substantially for Ca-filled samples. A maximal PF value of *ca.* $5400 \mu\text{Wm}^{-1}\text{K}^{-2}$ is achieved in $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$.

The temperature dependent carrier mobility for $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ is presented in Fig. 2d. The observed $T^{-3/2}$ dependence of μ at temperatures higher than 70 K clearly indicates that the acoustic phonon scattering is the main scattering mechanism for charge carriers in Ca-filled CoSb_3 samples. The carrier concentration and Seebeck coefficient can then be related with each other using a simple single parabolic band model:

$$n = 4\pi \left(\frac{2m^*k_{\text{B}}T}{h^2} \right)^{3/2} F_{1/2}(\xi),$$

and

$$S = \frac{k_{\text{B}}}{e} \left(2 \frac{F_1(\xi)}{F_0(\xi)} - \xi \right),$$

where ξ is the reduced Fermi energy and $F_j(\xi) = \int_0^\infty \frac{x^j dx}{1 + e^{x-\xi}}$ is the Fermi integral of order j with x being the reduced carrier energy [25].

On the basis of this model, an effective mass $m^* \sim 3.3 m_e$ is deduced for $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ with a carrier concentration of $5.8 \times 10^{20} \text{ cm}^{-3}$, almost the same as other single-element filled CoSb_3 at comparable carrier concentration [7, 11, 13]. The electrical transport properties can usually be characterized with the weighted mobility, $U = (m^*)^{3/2} \mu$, where m^* and μ are the effective mass

and the carrier mobility, respectively [1]. For $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$, a carrier mobility of $34 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was measured, which is a relatively high value among the single elemental filled CoSb_3 materials with comparable carrier concentration ($5.8 \times 10^{20} \text{ cm}^{-3}$) and contribute to the large PF for Ca-filled CoSb_3 [24].

Fig. 3 shows the temperature dependent thermal conductivity of CoSb_3 and Ca-filled CoSb_3 samples. The total thermal conductivity (κ) is a sum of the electronic contribution (κ_e) and the lattice thermal conductivity (κ_L). κ_e can be estimated with the Wiedemann-Franz law $\kappa_e = LT / \rho$, where L is the Lorenz number and a value of $2 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ is used here [26]. For skutterudite materials, κ (or more accurately, κ_L) can be greatly suppressed by the strong phonon scattering from the rattling modes of the filling atoms, as confirmed in Fig. 3 for Ca-filled CoSb_3 samples. The lattice thermal conductivity for $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ reaches a value of *ca.* $1.1 \text{ Wm}^{-1}\text{K}^{-1}$ at 840 K, comparable with other element filled CoSb_3 samples at similar filling fraction [13, 15, 27, 28], and approaching to the lattice thermal conductivity minimum, $\kappa_{L,\min}$, of CoSb_3 calculated with Cahill's formulation [29]. This significant reduction in thermal conductivity can be attributed to the strong resonant phonon scattering by the localized incoherent vibrations associated with Ca atoms in the voids of host lattice.

One of the effective techniques to confirm such kind of localized vibrational modes is the low temperature heat capacity (C_P) measurement [30-32], which was performed on $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ and CoSb_3 samples in the temperature range of 2–25 K. The contribution of calcium to the heat capacity has been determined by measuring the difference in the molar heat capacity of $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ and CoSb_3 . As shown in Fig. 4, this difference below 20 K is fully accounted for

by an Einstein oscillator:

$$\Delta C_p = C_{p, \text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}} - C_{p, \text{Co}_4\text{Sb}_{12}} = \gamma T + Ax^2 e^x / (e^x - 1)^2,$$

where γT is the electron contribution to the molar heat capacity ($\gamma = 0.04 \pm 0.001 \text{ JK}^{-2} \text{ mol}^{-1}$), $A = 5.72 \pm 0.16 \text{ JK}^{-1} \text{ mol}^{-1}$, and $x = \Theta_E / T$ with an Einstein temperature $\Theta_E = 84.5 \text{ K}$. The fitting quality is significantly good with $\chi^2 = 3.1 \times 10^{-4}$ and $R = 0.99954$. The Einstein temperature determined in this work is comparable with that (88 K) reported previously [33]. The heat capacity measurements therefore imply the localized incoherent motions of the Ca atoms in CoSb_3 lattice voids, which can effectively scatter phonons and reduce the thermal conductivity.

$\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples were successfully synthesized under high pressure. The filling fraction of Ca was substantially increased compared with those samples synthesized under ambient pressure. For the optimal $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ sample, ZT shown in Fig. 5 increases with temperature and reaches the maximum value of 1.15 at 840 K. In comparison, the highest ZT of ambient-pressure synthesized samples is less than 0.5 ($\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12}$, 700 K) [11]. The significantly enhanced thermoelectric performance of $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ can be attributed to the enhanced power factor and decreased lattice thermal conductivity due to larger filling fraction of Ca under high pressure. Further thermoelectric performance improvement of Ca-filled CoSb_3 may be achieved through nickel substitution of cobalt atoms [34].

High pressure synthesis not only can broaden elemental species that can be filled into voids of CoSb_3 [13-16], but also increase the filling fraction of elements (specifically here, calcium) to achieve better thermoelectric performance. In addition, high pressure can significantly accelerate

the fabrication process. Compared with the time-consuming solid state reaction method at ambient pressure, HPS can shorten the total reaction duration to several hours. The synthesis conditions (pressure and temperature) of elemental filled CoSb_3 can easily be realized in industrial production [35], another advantage for massive production for thermoelectric applications.

4. Conclusion

n-type $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ skutterudites were successfully synthesized under high pressure. The compositional analysis indicates high pressure can substantially increase the filling fraction of calcium in CoSb_3 compared with ambient-pressure synthesized samples. Consequentially, the thermoelectric performance of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ can be greatly enhanced. The optimal $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ shows significantly enhanced power factor and substantially suppressed lattice thermal conductivity due to increased filling fraction, leading to a *ZT* value as high as 1.15 achieved at 840 K. High pressure synthesis thus provides an alternative method for fabricating elemental-filled skutterudites, with the advantages of fast process, broadening fillable elements, and increasing the filling fraction.

Acknowledgments

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Table 1 Room temperature lattice parameter (a), Seebeck coefficient (S), electrical resistivity (ρ), carrier concentration (n/p), and carrier mobility (μ) for HPS $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples.

x (nominal)	x (ICP)	a (Å)	S ($\mu\text{V/K}$)	ρ ($\mu\Omega\text{m}$)	n/p (cm^{-3})	μ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
0	0	9.034	232	108	5.3×10^{18}	109
0.2	0.14	9.042	-160	7.78	2.2×10^{20}	41
1.25	0.31	9.054	-103	3.10	5.8×10^{20}	34

Fig. 1. XRD patterns for $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples. The inset shows the magnified (013) peak. Standard Si powders were used for calibration purpose.

Fig. 2. Electrical transport properties of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples as a function of temperature. (a) Electrical resistivity ρ . (b) The Seebeck coefficient S . (c) Power factor PF . (d) Carrier mobility μ .

Fig. 3. Temperature dependent thermal conductivity of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples. The inset shows the lattice thermal conductivity κ_L .

Fig. 4. Molar heat capacity divided by temperature vs. temperature square for unfilled CoSb_3 and filled $\text{Ca}_{0.31}\text{Co}_4\text{Sb}_{12}$ (see maintext for the fitting details).

Fig. 5. Temperature-dependent thermoelectric figure of merit (ZT) of $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ samples. The ambient-pressure synthesized $\text{Ca}_{0.2}\text{Co}_4\text{Sb}_{12}$ is shown for comparison.