Rare Metal Materials and Engineering
Volume 48, Issue 10, October 2019
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2019, 48(10): 3118-3123.

ARTICLE

Thermoelectric Properties of Nanostructured $CoSb_3$ Fast Prepared by Solid-State Reaction

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Abstract: Nanostructured p-type $CoSb_3$ was successfully synthesized by solid-state reaction method. The phase composition and crystallographic structure were characterized by X-ray diffraction and scanning electron microscopy, respectively. The electrical properties of the samples prepared with different temperatures and holding time were tested at room temperature. The samples with better power factor at room temperature were selected to study the thermoelectric properties at different temperatures. The results show that the single phase skutterudite thermoelectric materials can be prepared by ball milling combined with solid-state reaction. The obtained samples have many uniform micron-sized pores and the grains are in the nanometer range. The maximum Seebeck coefficient of 222.64 μV/K is obtained at 469.8 K when the sample is synthesized at 863 K. The maximum power factor of 132.17 $\mu W/(m\cdot K^2)$ is obtained at 570 K and the maximum thermoelectric figure of merit ZT of ~0.053 is obtained at 600 K when the sample is synthesized at 903 K.

Key words: $CoSb_3$; solid-state reaction; microstructure; thermoelectric properties

Thermoelectric (TE) material is a kind of semiconductor that can convert heat energy and electric energy directly to each other. TE materials are used to make TE devices. TE materials have wide application prospects in energy crisis, which has become a hot topic in the field of materials research in recent years. The performance of TE materials is characterized by the figure of merit, ZT ($ZT=TS^2/\rho\kappa$), where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the temperature. The electrical properties are determined by the power factor (PF) S^2/ρ [1-5]. A good TE material should have a large power factor arising from high Seebeck coefficient and modest electrical resistivity, and a low thermal conductivity.

As a binary alloy of $CoSb_3$, skutterudites are known as excellent TE materials because they can be used in a wide temperature range, and besides excellent TE quality, they also show stability and have various domains of use. The general preparation methods of $CoSb_3$ include melting-quenching annealing and spark plasma sintering (SPS) [6-8], hydrothermal and solvothermal method [9-11], high pressure and high temperature (HPHT) [12-14], ball milling-hot pressing, solid state-reaction-SPS, etc [15-17]. Except the method of HPHT, other preparation methods are characterized by long preparation period, long annealing period and complex preparation process. The HPHT preparation method has the advantages of speeding up the reaction rate and effectively preventing phase segregation. However, special equipment for producing high-pressure conditions is needed.

This study hopes to explore the simple experimental conditions for the use of ordinary vacuum or atmosphere furnace and planetary ball mill. It is generally believed that the preparation of the $CoSb_3$ requires long time heating, or long time annealing after smelting can be synthesized. This study found that the single phase $CoSb_3$ can be prepared by the vacuum ball milling and solid state reaction at low temperature. The long time heating will lead to grain growth. The nano-structured $CoSb_3$ was prepared by a short-time low-temperature solid-state reaction in this preparation method.

Received date: October 28, 2018
Foundation item: Guizhou Provincial Department of Education Foundation (QianjiaoheKYzi[2016]102); National Natural Science Foundation of China (51764005); Liupanshui Science and Technology Foundation (52020-2018-04-05)

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However, the common nanostructured $CoSb_3$ was prepared by a hydrothermal method or a long-time mechanical alloying method. The high energy consumption of the complex process makes it difficult to achieve industrialization. Vacuum ball milling combined with low-temperature solid-state reaction can produce single-phase $CoSb_3$ with nanometer size in a short time. Nanocrystals is an effective way to reduce the thermal conductivity and to improve the *ZT* value of $CoSb_3$ [15,16].

1 Experiment

In the experiment, Co powder and Sb powder with a purity of 99.99% and an average particle size of about 74 μm were used as starting materials. The chemical metering ratio of chemical $CoSb_3$ was weighed on the analytical balance. After weighing and proportioning, the raw material was quickly put into the cemented carbide ball mill, and the ball material ratio was 30:1. After the vacuum milling of the cemented carbide ball mill, the mixing speed was 350 r/min, the mixing time was 2 h on the planetary ball mill, then raw materials were evenly mixed, and the powder was pressed to form a column with a diameter of 10 mm and a height of 4 mm after being taken out. The sample was placed in a vacuum furnace by a sintering mold and heated to the final temperature for 30 min. After a certain heat preservation time, the sample was removed after the furnace was cooled to room temperature.

The vacuum atmosphere furnace HMZ-1700-20 was used for the sintering of the samples. The phase structures of the products were characterized by X-ray diffraction (XRD) using a TD-2500 X-ray diffractometer (Cu-K radiation, diffraction angle 20º~80º). The microstructure and backscattering test of the samples were conducted by FEI Nova NanoSEM 450 super high resolution scanning electron microscope. The resistivity and Seebeck coefficient of the samples at room temperature were measured by RTS-9 double electric four-probe tester and self-made Seebeck tester with a correction error of 10%. The TE properties in the temperature range of 320~700 K were measured by a Namicro JouleYacht China TE measurement system and Netzsch LFA457 laser flash apparatus.

2 Results and Discussion

Fig.1 shows the XRD patterns of $CoSb_3$ synthesized by the ball milling combined with low temperature solid-state reaction. The XRD patterns of the samples at different preparation temperatures are shown in Fig.1a. As the melting point of Sb is 903 K, the highest temperature 923 K for solid state reaction is selected. The method of preparing samples at different temperatures is mechanical milling for 2 h and soaking for 30 min. At the preparation temperature of 863 K, the XRD patterns of the samples with different soaking time are shown in Fig.1b.

It can be seen from Fig.1a that there is no obvious impurity peak in the prepared sample. The preparation temperature ranges from 723 K to 923 K, and the single-phase skutterudite structure (Im^3) can be prepared. Except at the synthesized temperature of 723 K, the sample contains a small amount of CoSb. The measured peak width of the prepared samples is relatively large, indicating that the samples crystallize well. It can be seen from Fig.1b that single phase $CoSb_3$ can be prepared from 1 min to 180 min. When the holding time is too long for about 300 min, the $CoSb_3$ decomposes, and most of them are decomposed into Sb and $CoSb_2$.

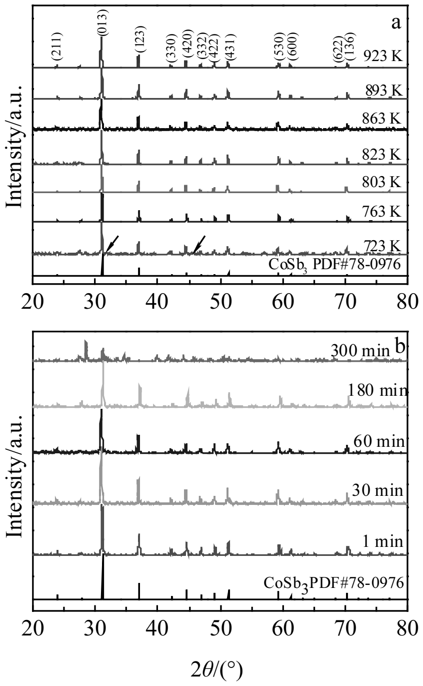

Fig.1 XRD patterns of $CoSb_3$ at different preparation temperatures (a) and with different soaking time (b)

Fig.2 shows the SEM images of the section of $CoSb_3$ samples. It can be seen from Fig.2a that there are many micropores inside the sample, and the micropore diameter is 1~20 μm. This may be due to the high temperature and solid-state reaction, and starting materials constantly react and form a new phase, leading to the formation of micropores in the material. As can be seen from Fig.2b, samples of $CoSb_3$ synthesized by solid-state reaction are uniform and fine, and most of them are nanoscale. Fine grain increases the grain boundary, enhancing the scattering of the phonons, and thus helping to reduce the thermal conductivity of the sample[8,15-17], but the existence of a large number of micropores and grain boundaries can also increase the electrical resistivity significantly.

Fig.3 shows back-scattering electron (BSE) image and EDS results of the $CoSb_3$. Fig.3a shows the BSE image obtained on polished surfaces of sintered samples. Fig.3b and Fig.3c show the EDS analysis of the field emission scanning electron microscope (FESEM) micrographs of $CoSb_3$ bulk sample. It is clear that no contrast can be seen on the back-scattering

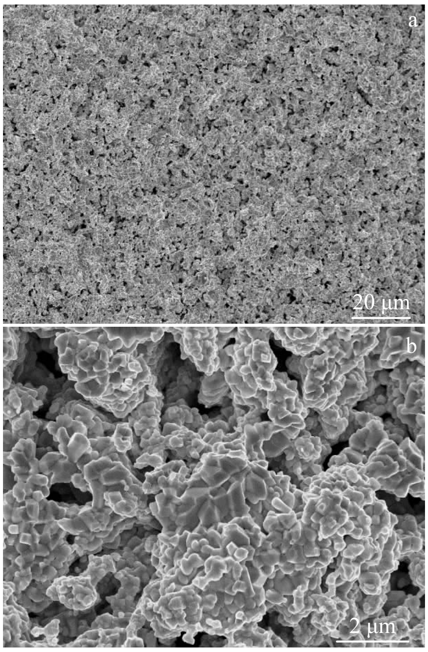

Fig.2 SEM images of inner section plane of $CoSb_3$

electron image of sample, and EDS analysis of the FESEM micrographs is also used to correlate the chemical composition of the bulk skutterudites, indicating that the structure is a homogeneous single phase material.

Fig.4a shows the functional relationship between the sample preparation temperatures and Seebeck coefficient, and electrical resistivity was measured at room temperature. It can be seen that the Seebeck coefficient is positive, which indicates that the sample synthesized by solid state reaction at high temperature is a p-type semiconductor. The Seebeck coefficient of the samples increases with increasing the preparation temperature. When the preparation temperature is 923 K, the maximum Seebeck coefficient 214.74 μV/K is obtained.

With the increase of the preparation temperature, the resistivity of the sample decreases first and then increases slowly. In the preparation temperature range of 723~883 K, the resistivity changes relatively gently, and the resistivity average value is 206.8 mΩ·cm. The minimum resistivity of the $CoSb_3$ is 191 mΩ·cm at room temperature. The power factor (PF) value is shown in Fig.4b. The PF of the samples increases with increasing the preparation temperature. The highest PF value is 21.43 μW/(m·K^2) at 883 K.

Fig.5a shows the soaking time dependence of electrical resistivity and Seebeck coefficients, and Fig.5b shows the power factor of $CoSb_3$. The samples were prepared by vacuum ball milling for 2 h and sintered at 863 K. As shown in Fig.5a, the Seebeck coefficient and electrical resistivity of the samples

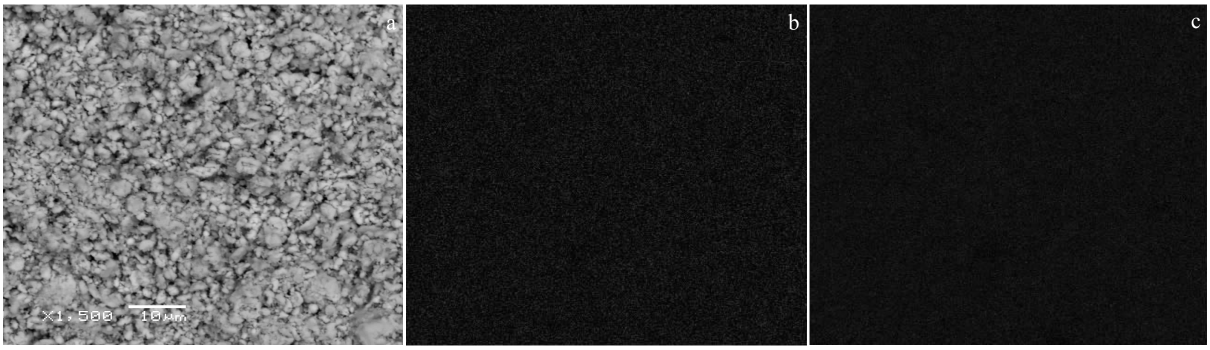

Fig.3 BSE image of polished surface of $CoSb_3$ (a) and EDS mapping of element Co (b) and Sb (c) for the bulk sample

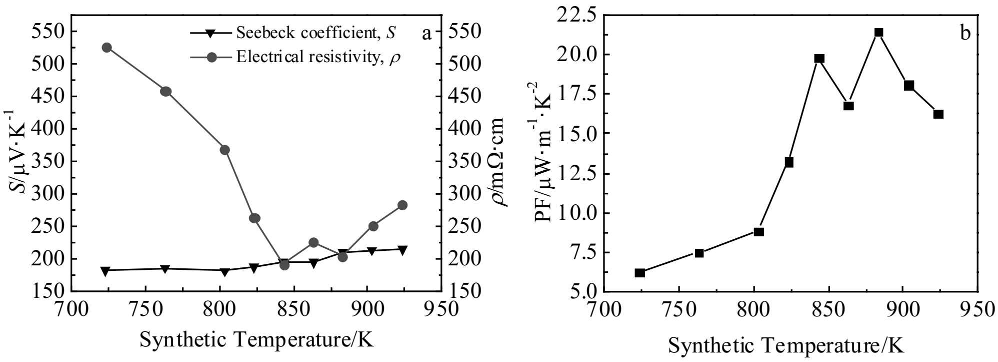

Fig.4 Synthetic temperature dependence of Seebeck coefficient (S) and electrical resistivity (ρ) (a), and power factor (PF) (b) of $CoSb_3$ samples

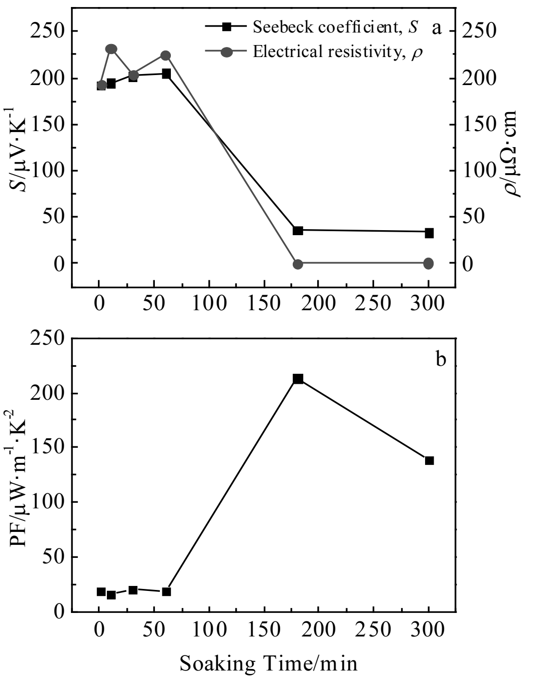

Fig.5 Soaking time dependence of electrical resistivity (ρ) and Seebeck coefficients (S) (a) and power factor of $CoSb_3$ (PF) (b)

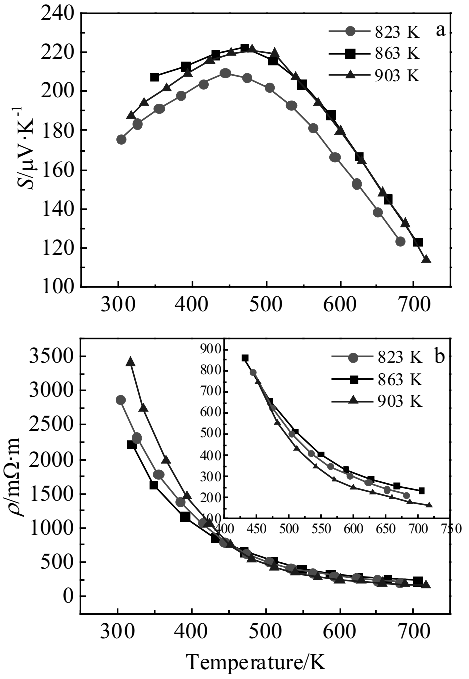

Fig.6 Temperature dependence of electronic transport properties of $CoSb_3$: (a) Seebeck coefficient (S) and (b) electrical resistivity (ρ)

decrease with the prolongation of the soaking time. During the soaking time of 1~60 min, the Seebeck coefficient of the samples is higher, with the average value of 198.61 μV/K, and the resistivity of the samples is also larger. This may be due to the fact that there are many micropores in the structure of nanocrystals, but the nanocrystals can also significantly reduce the thermal conductivity. When the soaking time is more than 180 min, the resistivity of the sample decreases significantly, but the prepared sample is no longer a single-phase Skutterudite structure, so the resistivity of the prepared $CoSb_3$ is higher than that of samples prepared by other methods[6,8,11]. The maximum Seebeck coefficient 205.31 μV/K of the sample is obtained when the soaking time is 60 min.

The PF values shown in Fig.5b indicate that the PF of the sample increases with increasing the soaking time. It is mainly because the resistivity of the samples rapidly decreases with the soaking time. When the soaking time is 180 min, the highest power factor of 213.27 μW/(m·K^2) is obtained.

The temperature dependence of the Seebeck coefficient of $CoSb_3$ with different synthetic temperatures is shown in Fig.6. It can be seen that the Seebeck coefficient is positive, indicating that the sample synthesized by high temperature solid-state reaction is a p-type semiconductor. At near room temperature, the Seebeck coefficient increases first and then decreases with increasing the synthetic temperature. The Seebeck coefficient of samples with different synthetic temperatures tends to be consistent after 400 K. The maximum Seebeck coefficient 222.64 μV/K is obtained when the synthesized temperature is 863 K at the test temperature of 469.8 K.

Fig.6b presents the temperature dependence of electrical resistivity of $CoSb_3$. The electrical resistivity of these samples exhibits semiconductor behavior, and decreases significantly with increasing the preparation temperature. Compared with other preparation methods, the electrical resistivity of $CoSb_3$ prepared by solid-state reaction is higher, which can be attributed to its nanocrystal structure and large grain boundary. When the preparation temperature is 903 K and the test temperature is 717.03 K, the minimum electrical resistivity of $CoSb_3$ of 165.28 mΩ·cm is obtained.

The temperature dependence of the PF for $CoSb_3$ calculated from the measured results is shown in Fig.7. The PF of samples increases first and then decreases with increasing the test temperature. The sample prepared at 903 K shows the highest PF value of 132.17 μW/(m·K^2) at a test temperature of 570.63 K.

Fig.8 shows the temperature dependence of the total thermal conductivity (κ) and the figure of merit ZT for $CoSb_3$. In this study, for the sample's thermal conductivity test, the sample of $CoSb_3$ with the maximum power factor at preparation temperature 903 K and soaking time 30 min was selected. As seen from Fig.8a, κ of $CoSb_3$ at room temperature is about 1.81 W·m^{-1}·K^{-1}, which is lower than that of $CoSb_3$ reported by Ref. [7,13].

The lower thermal conductivity of $CoSb_3$ can be attributed to the micropore and fine grain inside the samples. Fig.8b displays the calculated dimensionless figure of merit ZT of $CoSb_3$.

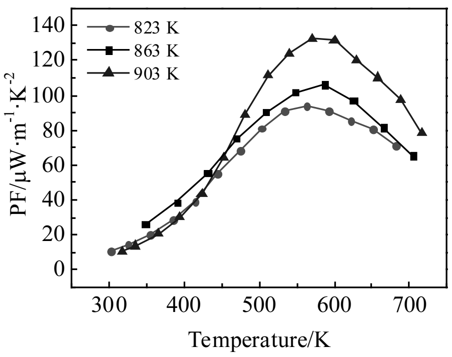

Fig.7 Temperature dependence of power factor (PF) for $CoSb_3$

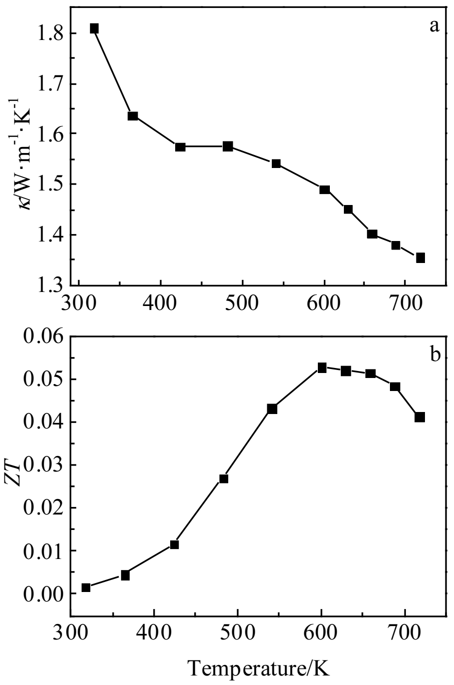

Fig.8 Temperature dependence of thermal conductivity (κ) (a) and figure of merit *ZT* (b) for samples $CoSb_3$

Because of increased electrical resistivity, the *ZT* values of $CoSb_3$ decrease according to Ref.[6], similar to Ref.[12], over the investigated temperature range. The maximum *ZT* value of 0.053 was achieved at 600 K. Better TE performance of $CoSb_3$-based systems can be expected by further and systematic study on effects such as doping and filling[12,14].

3 Conclusions

1) The single phase TE materials $CoSb_3$ can be prepared by vacuum ball milling combined with solid state-reaction. The preparation conditions are vacuum ball milling time more than 2 h and preparation temperature range of 763~923 K.

2) The $CoSb_3$ samples have many micropores and fine grains, and the grain diameter is nanoscale. The samples have high Seebeck coefficient and high electrical resistivity. When the preparation temperature is 863 K, the maximum Seebeck coefficient 222.64 μV/K can be achieved at test temperature of 469.8 K. The highest PF value 132.17 $\mu W/(m \cdot K^2)$ can be obtained when the sample is synthesized at 903 K and tested at 570 K, and the peak *ZT* of 0.053 is obtained when tested at 600 K.

3) As a practical technique for the future industrial-level mass production of skutterudites, vacuum ball milling combined with solid state-reaction is simple, cheap and fast compared with other preparation methods of $CoSb_3$, and thus it is a promising candidate for TE applications.

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固相反应法快速制备纳米结构 $CoSb_3$ 及其热电性能

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摘　要：采用固相反应法成功合成了具有纳米结构的 p 型 $CoSb_3$。采用 XRD 和 SEM 对样品的物相组成和晶体结构进行了表征。在室温下对不同温度和保温时间制备的样品进行了电学性质测试，选择了室温功率因子较高的样品，研究了不同温度下的热电性能。结果表明：采用球磨结合固相反应法可以制备出单相的方钴矿热电材料，所制备的样品内部含有孔径均匀的微气孔，晶粒尺寸在纳米范围。当制备温度为 863 K 时, 在测试温度 469.8 K 时，样品获得最大 Seebeck 系数 222.64 μV/K。当样品制备温度 903 K 时，样品测试温度 570 K 时获得最大功率因子 132.17 $\mu W/(m\cdot K^2)$，且在测试温度 600 K 时得到最大的热电优值 ZT 约为 0.053。

关键词：$CoSb_3$；固相反应；微观结构；热电性能

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