

Thermoelectric properties of CoSb₃ and CoSb₃/SiC composites prepared by mechanical alloying and microwave sintering

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Received: 11 October 2016 / Accepted: 22 March 2017 / Published online: 29 March 2017
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Abstract Pure CoSb₃ and 0.1 vol% nano-SiC-composited CoSb₃ were prepared by mechanical alloying and subsequent fast microwave sintering. The electrical transport properties display totally different behaviors in microwave-annealed CoSb₃ and CoSb₃/SiC composites, implying their susceptibility to the preparation conditions or uncertainties. The unique microstructure including the inter-granular and intra-granular precipitates combined with high porosity of the microwave-synthesized CoSb₃ and CoSb₃/SiC composites lead to low thermal conductivity, which compensates the loss in electrical conductivity and results in comparable figure of merit ZT value with those reported for undoped CoSb₃ from conventional method requiring high energy consumption and lengthy synthesis time. The results show that low compactness is not detrimental for the thermoelectric performance and microwave is a highly cost-effective technique for large-scale production of thermoelectric materials possessing nanostructure and low thermal conductivity. In fact, such synthesis route combining mechanical alloying and microwave annealing might be also suitable for other high performance thermoelectric materials. Actually, continuous fabrication can be readily realized

in an upgraded tube microwave heating system for higher energy efficiency ratio.

1 Introduction

Thermoelectric (TE) materials have attracted extensively attention in the past decades because of their important applications in waste heat recovery and environmentally friendly refrigeration. The thermoelectric energy conversion efficiency is mainly governed by the dimensionless figure of merit, defined as $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the total thermal conductivity which is composed of the carrier contribution κ_c and the lattice contribution κ_l . To optimize the ZT value, high α , high σ and low κ are required for high performance TE materials [1–3].

CoSb₃-based skutterudite compounds have been identified as one of the most promising TE materials for intermediate temperature range [4, 5]. CoSb₃ has good σ , large α , but very high κ , which leads to small ZT and inhibits its applications. Many efforts have been made to improve the TE performance of CoSb₃, including doping by partial Co-site or Sb-site substitution, filling structure voids and nanostructuring, from which the κ_l can be significantly reduced due to enhanced phonon scattering [6–13]. Incorporating nanoscale heterogeneity or nano-inclusions (such as Yb₂O₃, ZrO₂ and WO₃) into the CoSb₃ matrix has been proved effective to enhance the ZT [14–16]. Actually, to find a suitable nanodispersion is the key to achieve successful compositing of TE materials, which should reduce the κ while maintain the σ as possible at the same time. Being a promising TE semiconductor with a wide band gap, SiC has large α and relatively high σ , which makes it possible to

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improve the TE performance by adding SiC nanoparticles into other TE materials [17–20]. Moreover, the amount of SiC nanodispersion should be optimized against different TE parent systems to balance the electrical and the thermal properties. For example, Li et al. reported the enhanced ZT value up to 1.33 in $\text{Bi}_{0.3}\text{Sb}_{1.7}\text{Te}_3$ alloys by incorporating 0.4 vol% SiC nanoparticles [18]. However, Akao et al. observed remarkable degradation of the ZT in the Zn_4Sb_3 with 1–5 vol% addition of SiC whiskers [19]. Furthermore, the introduction of hard SiC nanoparticles can improve the mechanical performance of TE materials, which has already been demonstrated [18].

Preparation cost is another key factor to evaluate the feasibility of a promising TE material for applications. During the last decade, various techniques including solid state reaction, mechanical alloying (MA), co-precipitation, sol–gel and solvothermal methods have been used for the synthesis of CoSb_3 . The solid state reaction is a simple process, but it requires heating at high temperature (above 1273 K) with long soaking time (usually 100 h) to obtain pure CoSb_3 because of very slow kinetics [13]. Yang et al. synthesized single phase CoSb_3 easily by annealing the as-MAed elemental powders, and the annealing time could be as short as 1 h for the powders milled for over 10 h [21]. Moreover, in order to get dense bulks maintaining nanostructure, the precursor CoSb_3 powders need to be rapid sintered normally by hot pressing (HP) or spark plasma sintering (SPS), which requires expensive equipments, leading to much high energy consumption but low yield [12–16].

Microwave heating is a volumetric method by converting electromagnetic energy into thermal energy. In advantage over conventional heating, microwave-assisted solid state reaction is a rapid, simple, economically feasible and environmental friendly method [22]. Recently, microwave heating has been applied to fast sintering of the TE materials [23]. Biswas et al. adapted microwave synthesis for In-filled CoSb_3 , reducing the initial calcinations time from 2 days to 2 min [24]. Ioannidou et al. obtained Fe-substituted CoSb_3 using microwave heating within 14 min, while subsequent SPS was still employed to obtain final bulk products [25]. Generally, the microwave-sintered sample has lower density (less than 90%) compared with that (normally above 97%) after HP or SPS, which might increase the Seebeck coefficient and decrease the electrical conductivity due to stronger grain boundary scattering. On the other hand, the lower density can efficiently decrease the thermal conductivity by reducing the phonon transport channels and increasing the phonon scattering. Delaizir et al. carried out a comparative study of SPS, HP and microwave sintering techniques on p-type Bi_2Te_3 [26]. The highest ZT value was obtained for the ceramic processed by microwave, which originates from the very low thermal conductivity due to high porosity. In this work,

bulk CoSb_3 and CoSb_3/SiC composites were fabricated by MA and microwave sintering with the total process being as short as several hours. This method can be an energy-efficient and economical solution to large-scale fabrication of CoSb_3 -based TE compounds.

2 Experiments

Commercial elemental powders of Co (99.9%), Sb (99.9%) and SiC (99%, 0.1 vol% about 0.047 mol% in addition for CoSb_3/SiC composites) were weighted in the desired stoichiometric quantities and fully ground with an agate mortar and pestle. The mixtures of these powders were subjected to MA in a planetary ball milling using a hardened stainless steel vial and ball. The weight ratio of balls to powders was about 20:1 and the mill vial was filled with Ar gas to prevent the powders from oxidation during the milling process. The milling was performed at 500 rpm for 5 h. The MA-derived powders were tablet pressed and then sintered at 873, 923 and 973 K for 30 min, respectively, using a programmable tube microwave heating system (HY-ZG1512, 2.45 G, maximum output 1400 W, Huae Microwave) equipped with an in situ infrared temperature sensor (Raytek). Finally, the obtained pellets were polished first and cut into proper shapes for the subsequent measurements of TE properties.

The phase structure of the products was analyzed using powder X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (Rigaku Miniflex 600). The microstructure and compositions were observed by scanning electron microscopy (SEM, ZEISS ULTRA 55) and energy dispersive spectroscopy (EDS, Bruker Quantax-XFlash 5030), respectively. The Seebeck coefficient and electrical conductivity were determined simultaneously on a commercial ZEM-3 system (ULVAC-RIKO) in the 300–700 K temperature range. The thermal diffusivity coefficient λ and the specific heat C_p were measured utilizing a laser flash system (NETSCZ, LFA-457) and a differential scanning calorimeter (NETSCZ, DSC-204F1), respectively. The thermal conductivity κ was calculated from $\kappa = C_p \lambda d$, d is the bulk density of the sample acquired by the Archimedes method.

3 Results and discussion

Figure 1a shows the XRD patterns of the Co, Sb, SiC mixture after the MA pretreatment and the final bulks after microwave heating to 873, 923 and 973 K, respectively. For the MAed mixture, all the peaks can be indexed to the Co and Sb, indicating no CoSb_3 or CoSb_2 comes into being. No diffraction peaks of SiC were detected owing to its low content. Yang et al. reported that single phase CoSb_3 cannot

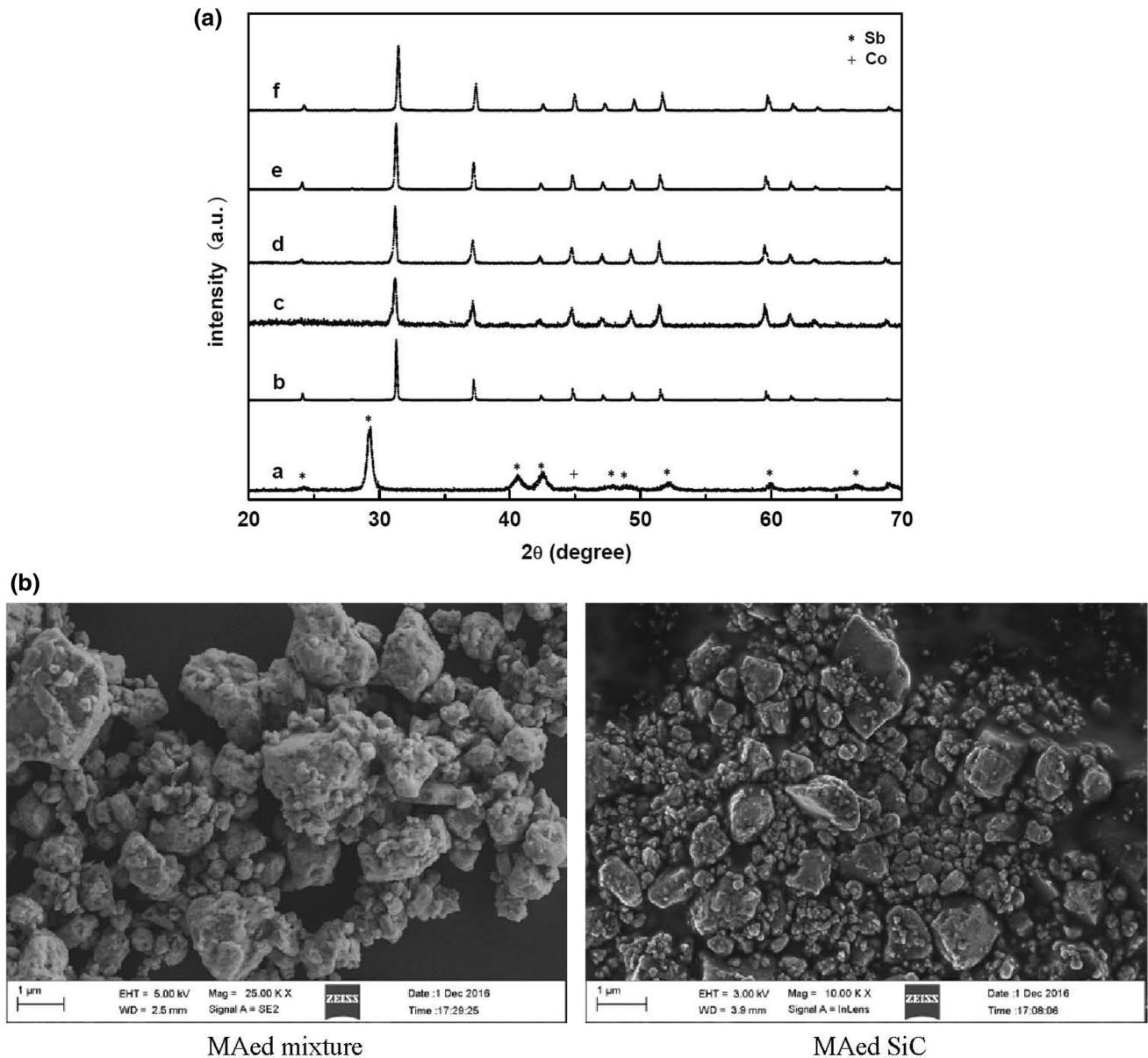


Fig. 1 **a** XRD patterns of the MAed mixture of Co, Sb, SiC (*a*), the reference data of JCPDS: 88-2437 (*b*), the final CoSb₃ products heated at 873 K (*c*), 923 K (*d*), 973 K (*e*) and CoSb₃/SiC heated at 973 K (*f*). **b** SEM images for the solo MAed SiC and the MAed mixture of Co, Sb, SiC

be directly obtained by MA of the mixed raw elemental powders up to 50 h, with the CoSb₃ phase appears after 20 h MA [21]. While Liu et al. obtained single phase CoSb₃ powder by only 5 h MA [27]. Such noteworthy difference may come from different MA conditions, such as the time, the ratio of ball to powder, especially the speed of the mill. For example, Liu et al. utilized the rotating velocity of 1100 rpm, Yang et al. probably used that less than 300 rpm, while we used that of 500 rpm. For the microwave-sintered bulks, the location and strength of most diffraction peaks match with the standard card JCPDS: 88-2437 of CoSb₃ skutterudite structure with space group *Im3* without any

SiC trace. This result indicates that the MAed mixture transforms into CoSb₃ at 873 K, and has the best crystallization and purity after sintering at 973 K. Compared with the previously reported route of MA + annealing [21], the MA pretreatment time is shortened from 10 to 5 h, and the sintering time is reduced from 1 h to 30 min even at lower temperature by microwave. Most important, the final products in this route of MA + microwave sintering are bulks with no need for further fast sintering. Since the SiC particles were expected to work as nanodispersions in the CoSb₃ matrix, it is necessary to characterize their morphology. Figure 1b presents the SEM images for the solo MAed

SiC and the MAed mixture of Co, Sb, SiC for comparison. Having endured the repeated impacting, cold welding and interdiffusion during the MA treatment, both the SiC and the mixture have similar granularity distribution unevenly around several hundred nanometers. Amounts of finer SiC grains with diameters less than 50 nm in the assembly can also be observed.

Figure 2a gives the SEM image for the fractured surface of microwave-synthesized CoSb_3 . Porosity and various grain sizes in the range of 100–200 nm can be readily seen. The microstructure of CoSb_3/SiC composites is almost identical as that of CoSb_3 without obvious suppression on grain size observed. Due to the low content, the SiC particles can hardly be distinguished from the MAed raw mixture or the final sintered product using the SEM or even at its backscattered mode. Alternatively, the EDS, as shown in Fig. 2b, presents tiny trace at 1.7 keV of Si element, indicating the existence of SiC. In addition, a small peak around 6.4 keV corresponding to the Fe $K\alpha$ line can be observed as well. Such subtle Fe contamination is probably introduced during the MA process using stainless steel vial and balls. It has been reported that the Fe substitution into CoSb_3 -based compound may significantly influence the TE performance especially drastically reduce the thermal conductivity, mostly leading to enhancement of the ZT value [28, 29]. From this point of view, the MA technique might have natural advantage to prepare CoSb_3 -based TE material. In earlier study, Delaizir et al. compared the microstructures of Bi_2Te_3 sintered by SPS, HP and microwave, respectively. They observed the intra-granular precipitates in all ceramics processed by SPS, HP and microwave, while some small particles at the surface of grain were only found in the sample after microwave treatment, which were then confirmed to originate from inter-granular precipitates using TEM observation [26]. As marked by the arrows in Fig. 2a, many small particles manifest at the surface of grains. These results suggest that such inter-granular precipitates are particular in microwave-synthesized sample, which may favor to decrease the thermal conductivity combined with high porosity.

Figure 3a gives the Seebeck coefficient α of the microwave-synthesized CoSb_3 and CoSb_3/SiC composites as a function of temperature. The positive α of CoSb_3 indicates that the holes are the major carriers. The α value increases from $67 \mu\text{V/K}$ at 300 K to the maximum value $157 \mu\text{V/K}$ at 650 K and then decreases. This is mainly due to the appearance of an increasing number of thermally excited minority carriers at high temperatures [8]. For the microwave-synthesized CoSb_3/SiC composites, the α is negative at room temperature, reaches the maximum absolute value of $-331 \mu\text{V}$ at 350 K, then increases with temperature and changes to positive near 515 K. This behavior could be ascribed to bipolar effects arising from the positive α

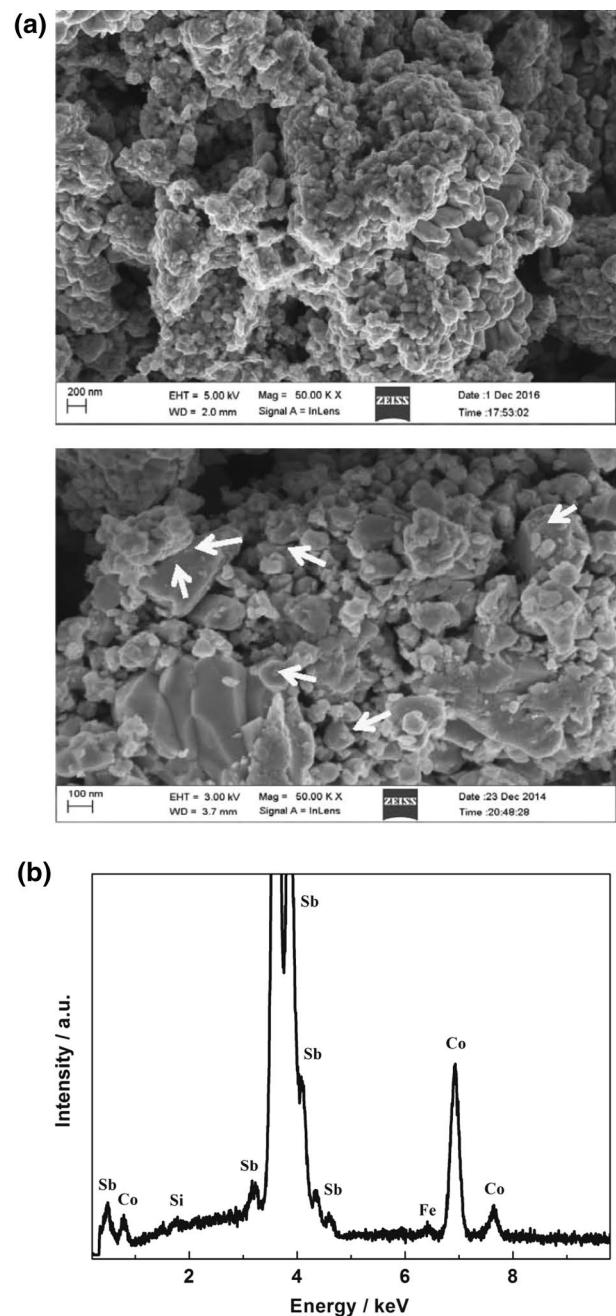


Fig. 2 a SEM images for the fractured surface of the microwave-synthesized CoSb_3 ; b EDS of the microwave-synthesized CoSb_3/SiC composites

of intrinsic holes carriers compensating the negative α of extrinsic electron carriers. At high temperatures, the hole mobility is much larger than the electron mobility [5]. It has been reported that intrinsic CoSb_3 shows p-type conductivity. Theoretical and computational studies reveal the direct and indirect band gaps in CoSb_3 , which would make its majority carriers very sensitive to impurities or small off-stoichiometry [10]. Previous experimental

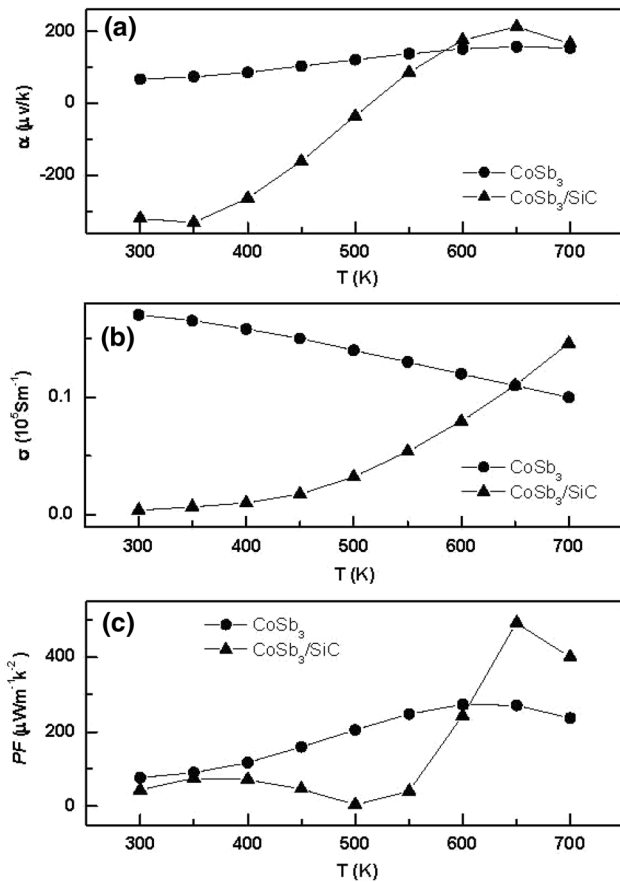


Fig. 3 Temperature dependent Seebeck coefficient (a), electrical conductivity (b) and power factor (c) of the microwave-synthesized CoSb₃ and CoSb₃/SiC composites

investigations have shown that various conditions, such as either tiny Sb or Co deficiency, substituting small amount of Ni in Co sites or Te in Sb sites and even low purity of Co (<99.95%) could bring about the n-type conduction [4, 5, 7, 10, 12, 30]. On the other hand, Sb rich, Fe substitution for Co and appropriate nanostructuring helps to maintain the p-type behavior [6, 8, 25, 28, 29]. It has been revealed that nanodispersion incorporated into a semiconducting matrix might increase the local density of states near the Fermi level and enhance the α value [18]. Because of the p-type semiconducting characteristic of SiC, the α value of the CoSb₃/SiC composites is expected to be positive and increased. However, the opposite result is obtained in this study, which might originate from the uncertainties such as the Sb/Co ratio changed by the sublimation of Sb during the heat treatment. The detailed reason will be studied in the future work. Figure 3b displays the temperature dependence of electrical conductivity σ for the microwave-synthesized samples. With the temperature increases from 300 to 700 K, the σ of CoSb₃ decreased from 0.17×10^5 to 0.10×10^5 S/m, while the σ of CoSb₃/SiC composites

increases sharply from 0.004×10^5 to 0.146×10^5 S/m. The σ behavior of CoSb₃ agrees well with those reported for pure CoSb₃, CoSb₃/WO₃ composites and In_{0.2}Co₄Sb₁₂ where the decrease of σ as temperature increases is attributed to the decrease of carrier mobility [9, 10, 16, 24]. The smaller σ value of the microwave-synthesized CoSb₃ (approximately 40%) may originate from the lower compactness. It should be mentioned that the microwave-synthesized CoSb₃/SiC composites reveals completely different electrical conductivity behavior, indicating an activated type conducting nature. This behavior with comparable value is reminiscent of those reported by Khaliq et al. and Zhu et al. for pure CoSb₃ [7, 12]. Based on the measured α and σ results, the temperature dependence of the power factor, $\text{PF} = \alpha^2 \sigma$, is presented in Fig. 3c. The CoSb₃ and CoSb₃/SiC samples reach the maximum values 274 and 493 $\mu\text{W m}^{-1} \text{ K}^{-2}$ at 600 and 650 K, respectively. The PF value of CoSb₃ is comparable with that of the CoSb₃ sample after SPS the nanoparticles [5]. The remarkable enhancement of the maximum PF value (nearly 80%) in CoSb₃/SiC originates mainly from the higher σ value above 650 K.

In Fig. 4a, the total thermal conductivity κ of the microwave-synthesized samples are plotted vs. temperature. As can be seen, the κ of CoSb₃ decreases from 3.24 W/mK first and then increases slowly with the temperature increasing, reaching the minimum value 2.17 W/mK at 600 K. Similar behavior has been reported in previous literatures, where the preceding decrease of κ could be attributed to the enhanced phonon scattering with the temperature increasing and the subsequent increase of κ may be predominated by intrinsic conduction [16]. For CoSb₃/SiC composites, the κ decreases from 3.11 W/mK monotonically to 2.16 W/mK at 700 K. The minimum values around 2.1 W/mK for both the microwave-synthesized CoSb₃ and CoSb₃/SiC composites are much lower than those reported for pure CoSb₃ and comparable to those of optimized nanostructured or nanocomposited CoSb₃ compounds after SPS or HP [8, 16]. It is worthy mentioned that Ioannidou et al. fabricated Co_{1-x}Fe_xSb₃ by the route of microwave heating, ball milling and SPS, but got the minimum κ exceeding 4.0 W/mK [25]. Since the total thermal conductivity κ consists of the carrier contribution κ_c and the lattice contribution κ_l , the former can be estimated from Wiedemann–Franz law as $\kappa_c = L_0 \sigma T$, where the Lorenz number $L_0 = 2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$, σ is the electrical conductivity and T is the absolute temperature, the lattice thermal conductivity κ_l can be obtained by subtracting κ_c from κ . As shown in Fig. 4b, the κ_l reaches the minimum value 1.99 W/mK at 600 K for CoSb₃, 1.91 W/mK at 700 K for CoSb₃/SiC composites, respectively. From the calculation, the κ_l contributes more than 91% to the κ of CoSb₃ and more than 88% to the κ of CoSb₃/SiC composites. Generally, the grain boundaries, wide or point defects and impurities could

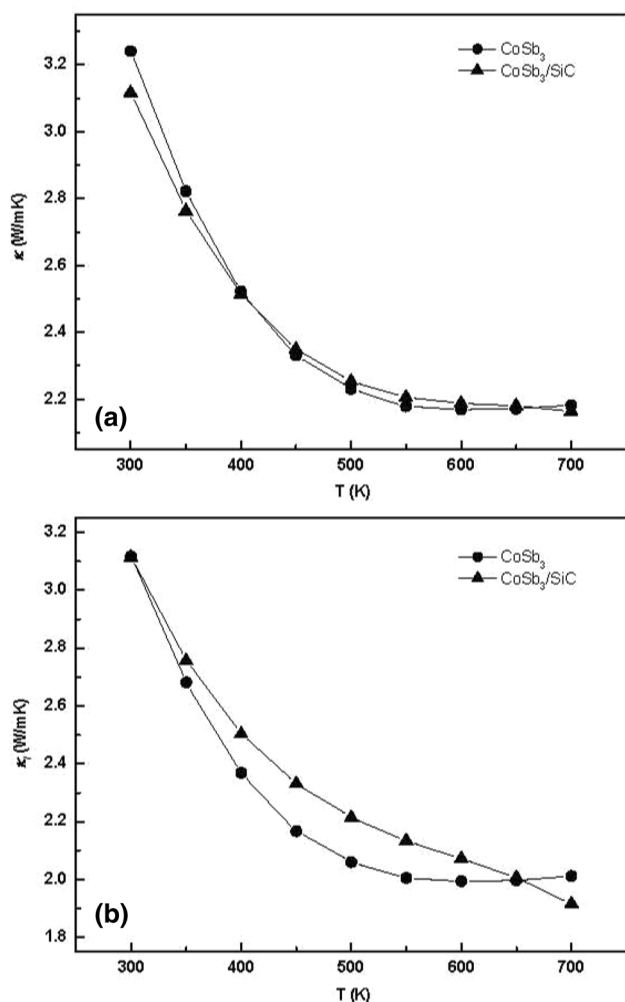


Fig. 4 Temperature dependent thermal conductivity (a) and lattice thermal conductivity (b) of the microwave-synthesized CoSb₃ and CoSb₃/SiC composites

reduce the κ_1 . Like those reported by Delaizir et al. for the microwave-sintered Bi₂Te₃ [26], the special microstructure including the inter-granular precipitates and high porosity (see Fig. 2a) would further decrease the κ_1 due to stronger phonon scattering. Then, one can conclude that the microwave sintering has natural superiority for economical and large-scale fabrication of low κ TE materials with nanostructure. Moreover, as proved previously, small amount of Fe contamination from the MA process in our case might also benefit the decrease of thermal conductivity κ [28, 29].

The temperature dependence of ZT values for the microwave-synthesized samples are given in Fig. 5. Both the CoSb₃ and CoSb₃/SiC composites reach their maximum ZT values at 650 K of 0.08 and 0.15, respectively. The ZT value 0.08 of CoSb₃ is comparable to those of undoped samples prepared by conventional method [5, 12, 13]. This result is also close to the best ZT value of CoSb₃ composited with

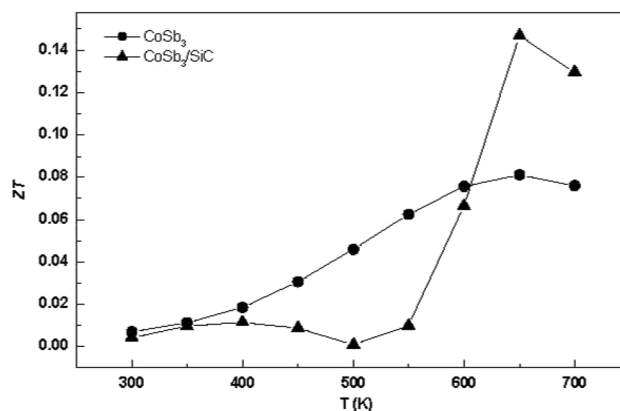


Fig. 5 Temperature dependent figure of merit ZT of the microwave-synthesized CoSb₃ and CoSb₃/SiC composites

CoSb₃ nanoparticles reported by Yang et al. [6]. Ioannidou et al. got the maximum ZT of 0.06 after SPS the microwave-synthesized CoSb₃ because of the high κ [25]. Introducing 0.1 vol% SiC nanodispersion into CoSb₃ matrix in this study increases the maximum ZT significantly, which is mostly due to the improvement of electrical properties at high temperatures. It should be emphasized that the ZT values in this work are still very low in comparison with those of Co₄Sb_{2.85}Te_{0.15} (ZT 0.93) [5], nanostructured CoSb₃ (ZT 0.35) [8], Sm_{0.6}Co₄Sb₁₂ (ZT 0.80) [13] and CoSb₃/2%WO₃ (ZT 0.40) [16]. Considering that current study is a tentative exploring of microwave synthesis of CoSb₃ and CoSb₃/SiC composites, one can expect promising further enhancement of ZT value by optimizing the SiC compositing content, introducing appropriate substitution to improve the electrical properties of CoSb₃ and filling the cages in the CoSb₃ structure to decrease the κ_1 based on present results. In fact, the investigation on microwave-synthesized Te-doped CoSb₃ and optimizing the nanocomposition is in progress.

4 Conclusion

In summary, pure and SiC-composited CoSb₃ were fabricated using mechanical alloying and microwave annealing. The electrical properties including the p-type or n-type conducting were susceptible to the preparation conditions or uncertainties. The particular nanostructure and high porosity in the microwave-synthesized samples leads to low thermal conductivity, which compensates the loss of electrical conductivity and results in comparable ZT value to those prepared with conventional route with high energy consumption and low yield. These results demonstrate the feasibility of high efficient and economical synthesis of CoSb₃-based thermoelectric compounds and promising ZT enhancement by use of microwave heating technique,

which can also be utilized for scale fabricating other thermoelectrical materials.

Acknowledgements This work was supported by the National Natural Science Foundation of China (11404350, 11404348, 11304327, and 11234012), Zhejiang Provincial Science Foundation for Distinguished Young Scholars (LR16E020001) and Ningbo Science and Technology Innovation Team (2014B82004).

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