Thermoelectric properties of rare earths filled $CoSb_3$ based nanostructure skutterudite

Peng-Xian Lu [a,b], Fang Wu [a], Hai-Long Han [b], Qian Wang [b], Zi-Gang Shen [a], Xing Hu [a,*]

[a] *School of Physical Engineering, Zhengzhou University, Zhengzhou 450052, China*
[b] *College of Materials Science and Engineering, Hehan University of Technology, Zhengzhou 450007, China*

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ABSTRACT

Nanostructure engineering and rare earths filling were employed to enhance the thermoelectric properties of the $CoSb_3$ based skutterudite. The $CoSb_3$ and the rare earths filled $LaFe_3CoSb_{12}$, $CeFe_3CoSb_{12}$, $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ nano-powders were prepared via a hydro/solvo thermal method and then the nano-powders were used to make bulk samples by hot-press. Our results indicate that besides the nanostructure and the rare earths filling, the existence of a glassy phase in the samples is also an important factor for the enhancement of the thermoelectric properties. The Seebeck coefficients of the samples were improved obviously while their excellent electrical conductivities could be maintained, meanwhile the thermal conductivities of the samples were suppressed significantly. Therefore, the figures of merit were enhanced and ZT values could be reached at 773 K as 0.19, 0.43, 0.62 and 0.82 for $CoSb_3$, $LaFe_3CoSb_{12}$, $CeFe_3CoSb_{12}$ and $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ respectively.

1. Introduction

Thermoelectric materials have important applications such as waste heat transfer to electric power and solid state Peltier coolers [1]. The performance of a thermoelectric material is determined by its figure of merit $ZT = \alpha^2\sigma T/(\kappa_e + \kappa_l)$, where T is the absolute temperature, α is the Seebeck coefficient, σ is the electrical conductivity, κ_e and κ_l are the thermal conductivity of electrons and phonons respectively. Therefore, an excellent thermoelectric material should have a high Seebeck coefficient, a high electrical conductivity, meanwhile a low thermal conductivity. Doping with suitable elements has been used as an effective method to improve the thermoelectric properties of a material. However, due to the correlation between electrical and thermal property, it is very difficult to increase α and σ meanwhile to lower the thermal conductivity [2]. So, a systematical strategy should be considered in order to improve the thermoelectric properties.

Skutterudite compounds are regarded as one kind of the most promising thermoelectric material in high temperature range because they possess a property of an electronic crystal and a phonon glass simultaneously as proposed by Sales [3]. Among the skutterudite the $CoSb_3$ based compounds have been extensively studied in recent years [4]. Due to the strong covalent bonding and the large interstitial voids in the structure, however, the

$CoSb_3$ does not possess the electronic crystal and phonon glass property because it only has a good electrical conductivity but a relatively high thermal conductivity. Therefore, to improve the thermoelectric properties of skutterudite efforts have been focused on elements doping [5] and/or voids filling [6] to reduce its thermal conductivity meanwhile maintaining its excellent electrical properties. Recently a larger figure of merit of 1.4 at 1000 K of $CoSb_3$ based skutterudites has been obtained by filling the interstitial voids with La or Ce atoms [7]. So, filling the interstitial voids in the structure with foreign atoms especially by rare earth atoms is an effective way to reduce the thermal conductivity and meanwhile maintain the electrical conductivity and the Seebeck coefficient of $CoSb_3$ based skutterudites [8].

Nanostructure engineering has been regarded as another possible way to make materials to have a high ZT value [9]. Because, firstly, a nanostructure can increase the density of states near Fermi energy level and thus increase the electrical conductivity. Secondly, nanostructure can lead to a local increase of effective mass of electrons and thus enhance the Seebeck coefficient [10]. Finally, if a bulk sample consists of nanosized grains, more grain boundaries will be introduced, which can increase the phonon scattering and thus reduce the thermal conductivity [11–14].

The purpose of the present work is to optimize the thermoelectric properties of the $CoSb_3$ based skutterudites in further by incorporating the nanostructure engineering and the voids filling. We fabricated the $CoSb_3$ and the rare earths filled $LaFe_3CoSb_{12}$, $CeFe_3CoSb_{12}$, $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ nano-powders by hydro/solvo thermal route and then used such nano-powders to make bulk

* Corresponding author. Tel.: +86 371 67767671; fax: +86 371 67767671.
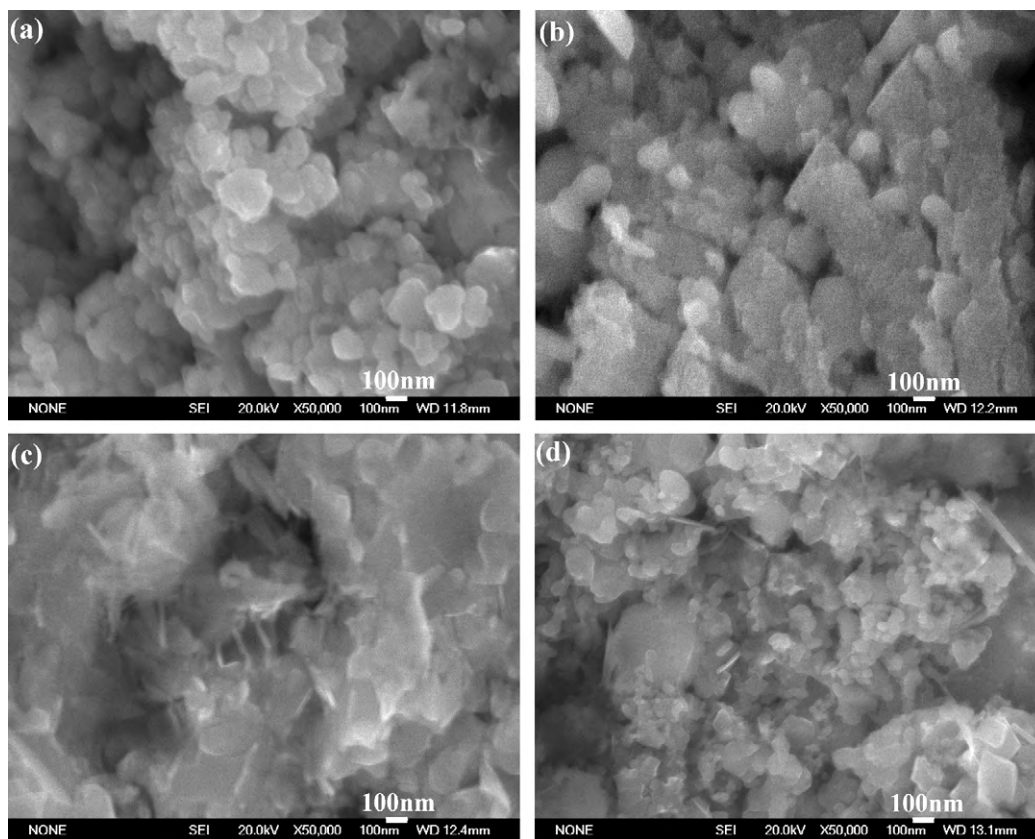*E-mail address:* xhu@zzu.edu.cn (X. Hu).

Fig. 1. SEM images of $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} hot-pressed bulks.

samples by hot-press. Our results showed that by using such a combination of the nanostructure engineering, the voids filling and the coexistence of glassy and crystal phases, a high Seebeck coefficient, a lower thermal conductivity and thus a high figure of merit can be obtained successfully.

2. Experimental

The nano-powders with stoichiometric compositions $CoSb_3$ and (La, Ce, and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} were fabricated via hydro/solvo thermal method. The detailed experimental process has been reported in Ref. [15].

The resultant powders were hot-pressed into pellets with a diameter of 25 mm or 12.5 mm at 843 K for 20 min under a pressure of 60 MPa in a vacuum circumstance. The big pellet was polished and then cut into rectangular sticks with a size of 12 mm × 4 mm × 2 mm for electrical conductivity and the Seebeck coefficient measurements, while the small pellet was used for the thermal conductivity measurement. The electrical conductivity and the Seebeck coefficient were measured at several temperature points by using a four-probe technique on a custom designed apparatus in a tube furnace under Ar gas flow. The thermal diffusion, thermal conductivity and the specific capacity were measured by a thermal diffusivity system (FLASHLINE™ 3000, ANTER Corporation, USA) using Pyroceram (Provided by ANTER) as reference sample at several temperature points.

3. Results and discussion

The properties of $CoSb_3$ and the rare earths filled $LaFe_3CoSb_{12}$, $CeFe_3CoSb_{12}$, $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ nano-powders have been discussed in detail elsewhere [16]. In briefly, XRD and EDS show that major skutterudite phase can be obtained except small Sb secondary phase, and SEM shows that the average size of the nano-powders is about 60 nm. The SEM images of the $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} hot-pressed bulk samples made by such nano-powders are shown in Fig. 1(a)–(d), respectively. From Fig. 1 it can be seen that the average grain size of $CoSb_3$, $LaFe_3CoSb_{12}$, and $CeFe_3CoSb_{12}$ is about 100 nm. While, the average grain size of $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ is about 60 nm. A more promi-

nent phenomenon observed in these hot-pressed bulks may be the coexistence of a glassy phase with the skutterudite crystals. Fig. 2(a) shows the XRD pattern of the hot-pressed $CoSb_3$ and (La, Ce, and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} bulks. It can be seen clearly that besides the peaks of crystals phase there is a wide maximum below 30° for all the four bulks, which is an indication of the glassy phase. Such glassy phase should be resulted from the hot-pressing process. However, the proportion of the skutterudite crystal and the glassy phase in the different bulk is very different. As for the $CoSb_3$ and $CeFe_3CoSb_{12}$ bulks the skutterudite phase is dominant while the glassy phase is small, although some secondary phase such as $CoSb_2$ can be detected in the $CoSb_3$ sample. Dissimilarly, the glassy phase in $LaFe_3CoSb_{12}$ and $La_{0.5}Ce_{0.5}Fe_3CoSb_{12}$ bulks is absolutely dominant and no obvious skutterudite crystal phase can be observed. Moreover, the glassy phase and crystal phase exhibit distinctly different morphologies from the SEM images with low resolution of the bulks. A representative SEM image with the coexistence of the glassy phase and the skutterudite crystal of $CeFe_3CoSb_{12}$ bulk and the EDSs are shown in Fig. 2(b)–(d), respectively. From Fig. 2(b) the continuous and smooth melts should be glassy phase while the crystal grains keep a relatively dispersive and coarse state. The EDSs corresponding to the glassy phase and crystal phases ($Ce_{5.4}Fe_{14.4}Co_{6.2}Sb_{74}$ and $Ce_{4.7}Fe_{15.2}Co_8Sb_{72}$, respectively) suggest that they possess the similar elemental ratios. We believe that the glassy phase should have profound influences on the thermal conductivity, the electrical conductivity and the Seebeck coefficient simultaneously. The thermoelectric properties are expected to be optimized by tuning the proportion of the skutterudite crystal and the glassy phase, and these effects will be studied later.

Fig. 3 shows the electrical conductivities of the hot-pressed $CoSb_3$ and (La, Ce, and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} bulks at several temperature points. All samples exhibit an unusual behavior, which is different from the calculated results [17–19]. It can be also seen
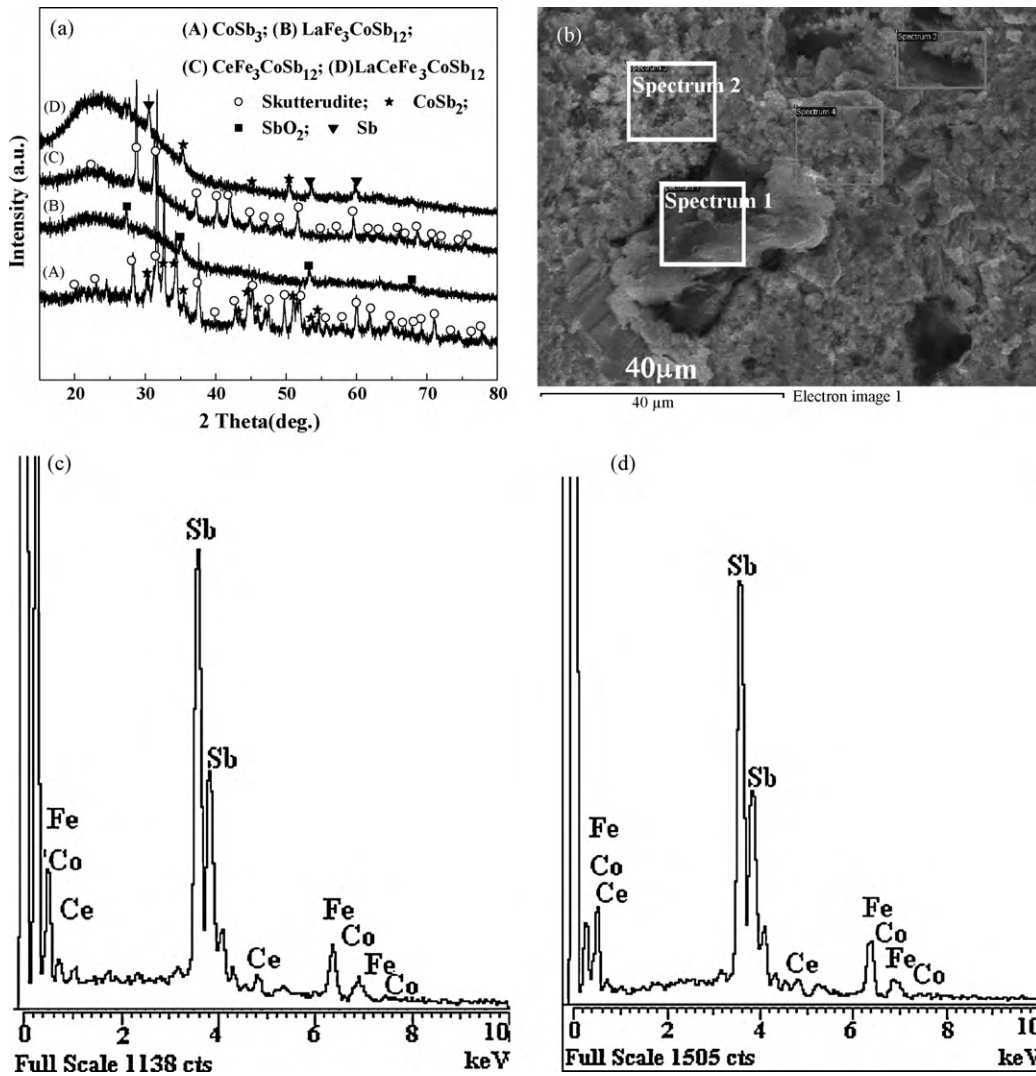
Fig. 2. XRD patterns of $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} hot-pressed bulks in (a), SEM image with the coexistence of the glassy and crystal phase of $CeFe_3CoSb_{12}$ in (b), EDSs in the selected regions in (c) and (d), respectively.

from Fig. 3 that the rare earths filling will result in a reduction of the electrical conductivity, which is disadvantageous for the improving of the thermoelectric properties. It seems that the Ce element filling reduce the conductivity more remarkable than that of La filling. And in the high temperature range the reduction of conductivity caused by rare earths filling is more prominent.

Fig. 4 shows the Seebeck coefficients of the $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} at several temperature points. It can be seen clearly that the rare earths fill increase the Seebeck coefficient, which is beneficial for the improvement of the thermoelectric properties. The increase of the Seebeck coefficient of the filled skutterudites may be understood by the change of electron densities of states (DOS) and effective mass of the electrons [17,20,21]. Moreover, the improved Seebeck coefficient for the unfilled $CoSb_3$ and especially for the filled (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} may be also related closely to the nanostructure of the samples, because the
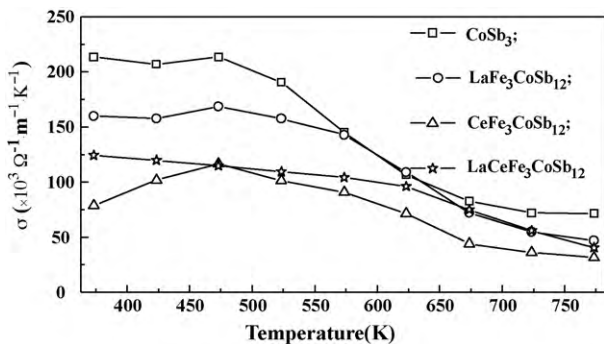

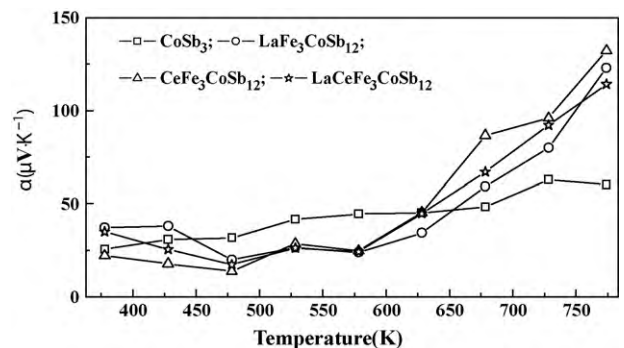**Fig. 3.** The electrical conductivities of $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} bulks.

Fig. 4. The Seebeck coefficients of $CoSb_3$ and (La, Ce and $La_{0.5}Ce_{0.5}$)Fe_3CoSb_{12} bulks.

Fig. 5. The thermal conductivities of CoSb$_3$ and (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ bulks.
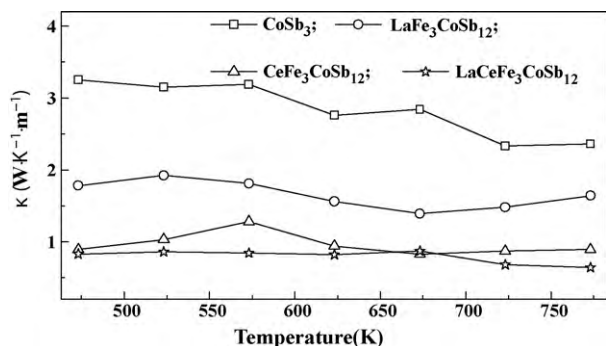
Fig. 6. The figure of merits of CoSb$_3$ and (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ bulks.

nanostructure can increase the carrier mobility due to a sawtooth-like DOS at Fermi energy level and enhancement of the effective mass of carriers [10,11,22].

The thermal conductivities of the CoSb$_3$ and (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ bulks are presented in Fig. 5. As for CoSb$_3$ its thermal conductivity of 2.36 W m^{-1} K^{-1} at 773 K is smaller than the reported values 2.7 W m^{-1} K^{-1} for microsized structures and is close to the reported 2.0 W m^{-1} K^{-1} for nanosized structures [4,23]. In comparison with the unfilled CoSb$_3$, the thermal conductivities of the rare earths filled skutterudites show a significant reduction from 1.64 W m^{-1} K^{-1} to 0.89 W m^{-1} K^{-1} and 0.64 W m^{-1} K^{-1} for LaFe$_3$CoSb$_{12}$, CeFe$_3$CoSb$_{12}$ and La$_{0.5}$Ce$_{0.5}$Fe$_3$CoSb$_{12}$, respectively. In comparison with the reported thermal conductivities of the filled CoSb$_3$ based skutterudites the obtained values in this work are the lowest [6,7,12,14,24]. Such reduction may be resulted from the complex effects of the rare earths filling, the nanostructure engineering and the existence of glassy phase.

In our previous work [16], we have measured the Raman scattering spectra of the unfilled CoSb$_3$ and the filled (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ skutterudites to investigate the effects of the filled rare earths on the thermal conductivity. It was found that the filled rare earths could suppress the thermal conductivity by weakening the covalence bonding between the parent Co and Sb atoms. Moreover, recent advances in the thermal transport in nanostructures show that the thermal conductivity is dominated by the dimensionality, the size and the interface scatter parameter, and the thermal conductivity of materials with smaller grains could be suppressed more strongly due to the enhancement of phonon scattering [25,26]. So, the reduction in the thermal conductivity in our work could also be ascribed to the nanostructure of the samples. More importantly, we believe that the presence of the glassy phase in our samples is also an important factor for the reduction of the thermal conductivity.

The figures of merit of the CoSb$_3$ and (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ bulks are plotted in Fig. 6. With the increase of the temperature the figures of merit begin to increase significantly, and the ZT values of 0.19, 0.43, 0.62 and 0.82 for CoSb$_3$, LaFe$_3$CoSb$_{12}$, CeFe$_3$CoSb$_{12}$ and La$_{0.5}$Ce$_{0.5}$Fe$_3$CoSb$_{12}$ respectively are obtained at 773 K. As for the unfilled CoSb$_3$ the obtained ZT value 0.19 is larger than the microsized structure [4] but is smaller than the nanosized materials [27]. As compared with the unfilled CoSb$_3$ the obtained ZT values for the rare earths filled bulks could be improved significantly, which could be attributed to the improved Seebeck coefficient and the largely reduced thermal conductivity. As for La$_{0.5}$Ce$_{0.5}$Fe$_3$CoSb$_{12}$, its relatively higher ZT value should be ascribed to the smaller grain size and the existence of the glassy phase in this sample. This fact also indicates that besides the nanostructure, rare earths filling, the existence of a
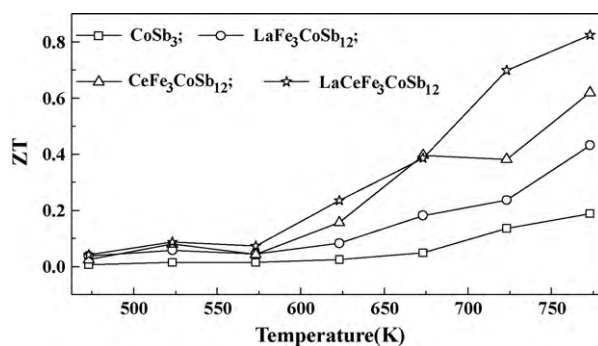
glassy phase in the samples would have an important role on the thermoelectric properties.

4. Conclusions

In conclusion, the unfilled CoSb$_3$ and the filled (La, Ce and La$_{0.5}$Ce$_{0.5}$)Fe$_3$CoSb$_{12}$ nanoparticles can be synthesized via hydro/solvo thermal route successfully. The hot-pressed bulks possess a complex morphology of nanosized skutterudite crystals and the glassy phase. The cooperation of the nanostructure, rare earths filling as well as the glassy phase can improve the thermoelectric properties indeed. The formation mechanism and effects on the thermoelectric properties of the glassy phase deserve further investigation.

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