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Thermoelectric properties of $Yb_xFe_yCo_{4-y}Sb_{12}$ prepared under high pressure

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Abstract

Thermoelectric materials have received considerable attentions for use as an alternative energy conversion technology. This study focuses on the thermoelectric properties of skutterudite compounds $Yb_xFe_yCo_{4-y}Sb_{12}$ synthesized under high pressure. The properties have been studied by measuring thermal and electrical transport properties. The results clearly indicate that appropriate contents for Yb doping and Fe substitution on Co site could not only enhance Seebeck coefficient but also decrease thermal conductivity. This leads to a further optimized the figure of merit *ZT*. High-pressure synthesis technique has an advantage to tune widely the composition of $CoSb_3$ based skutterudites.

1. Introduction

Thermoelectric (TE) materials are a kind of compounds that can transfer heat power to electric power directly or vice versa. The efficiency of TE materials are evaluated by a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, and κ, the thermal conductivity. An ideal TE material with high ZT should have two desirable features: prevent phonon spread like a glass and conduct electron like a crystal (PGEC).

As one of the most promising thermoelectric materials, the skutterudite compound has been believed to be the PGEC material with flexibly tunable physical properties. Binary skutterudite compound $CoSb_3$, which has received the most interest because of its excellent electric transport properties, has a cubic unit cell (Im-$\bar{3}$) with a cage-like structure with two interstitial voids at the 2a positions (12-coordinated) [1]. However, its high thermal conductivity restricted its application. It is believed that filling atoms, such as rare-earth elements or other metallic elements inside the Sb-icosahedron, can remarkably decrease the thermal conductivity [2, 3].

The high thermal conductivity of $CoSb_3$ is mainly caused by a long-wavelength longitudinal acoustic phonon. Yb atom has been proved as an effective filler for its low-vibration frequency [4]. Since every Yb atom can provide two electrons to conduction band of $CoSb_3$, the majority carrier would gradually change from hole to electron with increasing Yb-doping ratio and the compound would transfer from p-type to n-type accordingly. Many researchers reported the thermoelectric figure of merit of n-type partially filled skutterudites $Yb_xCo_4Sb_{12}$. The thermal conductivity was dramatically reduced for Yb-doped $CoSb_3$. Proper Yb doping ratio was recommended around 0.2 because higher Yb doping causes high electric carrier concentration that would lead to a reduction of Seebeck coefficient and thus low figure of merit. On the other hand, higher Yb doping contributes lower thermal conductivity. In order to achieve higher figure of merit in high Yb doping compound, charge compensation is needed. That is, the excess electrons in $Yb_xCo_4Sb_{12}$ ($x>0.2$) need to be compensated by introducing a hole donor element in Co site. Fe is considered as a p-type dopant in $Yb_xCo_4Sb_{12}$ ($x>0.2$) because Fe has one less 3d electron than Co [5]. It is expected that proper substitution of Fe on Co would improve the thermoelectric properties by compensating the excess electrons in $Yb_xCo_4Sb_{12}$ system.

Fe substitution would affect not only transport properties of the ternary skutterudite $Yb_xCo_4Sb_{12}$ but also the Yb filling fraction. Yb doping ratio of 0.6, which corresponding to the highest actual doping ratio of 0.29, is selected based on our previous results that this filling fraction has minimum thermal conductivity [6].

2. Experiments

Fe substitute $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ ($0\leq y\leq 1$) samples were prepared at high temperature and a high pressure using a cubic-anvil high-pressure apparatus [8]. All the compounds were prepared by reaction of stoichiometric amounts of components at around 590°C and 2GPa. The reaction time was 120 minutes. The crystalline phases of synthesized samples were characterized by powder x-ray diffraction using $CoK_{\alpha 1}$ radiation and silicon as a standard. Scanning Electron Microscope / Energy Dispersive X-ray Spectroscopy (SEM-EDX) was employed to detect the actual components and elements distribution. The resistivity was measured by using a standard dc four-prove method. The Seebeck coefficient and the thermal conductivity were measured by using a thermal transport system (PPMS Quantum Design).

3. Results and discussion

Table I shows the actual composition determined by point analysis of SEM-EDX. As the parent compound, $CoSb_3$ is also included for comparison. By a small amount of substitution of Fe on the Co site, the actual filling fraction of Yb was dramatically increased. The result indicates that Yb atoms can easily enter the voids when Co atoms were partially replaced by Fe atoms. As the filling fraction of filling elements in skutterudite is relevant with the elec-

tronegativity difference between filling atoms and Sb cage, it might be estimated that the replacement of Fe on Co site would influence the charge distribution of adjacent antimony atoms and further the change density of state of the interstitial voids.

Table I Composition and lattice constant for $Yb_xFe_yCo_{4-y}Sb_{12}$

Nominal composition	Actual composition	Lattice constant (Å)
Co_4Sb_{12}	$Co_{4.1}Sb_{12}$	9.0337
$Yb_{0.6}Co_4Sb_{12}$	$Yb_{0.29}Co_{4.1}Sb_{12}$	9.0678
$Yb_{0.6}Fe_{0.5}Co_{3.5}Sb_{12}$	$Yb_{0.5}Fe_{0.5}Co_{3.6}Sb_{12}$	9.0601
$Yb_{0.6}FeCo_3Sb_{12}$	$Yb_{0.5}Fe_{1.1}Co_{3.1}Sb_{12}$	9.0634

Figure 1 shows the Seebeck coefficient and the resistivity of $Yb_xFe_yCo_{4-y}Sb_{12}$ at room temperature. The Seebeck coefficient of $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ compound shows a crossover from n-type to p-type with increasing Fe-substitution ratio. The absolute value of the Seebeck coefficient S initially increases but rapidly decreases with higher Fe ratio, due to excessive charge (hole) compensation. The resistivity ρ increases with increasing Fe-doping ratio.

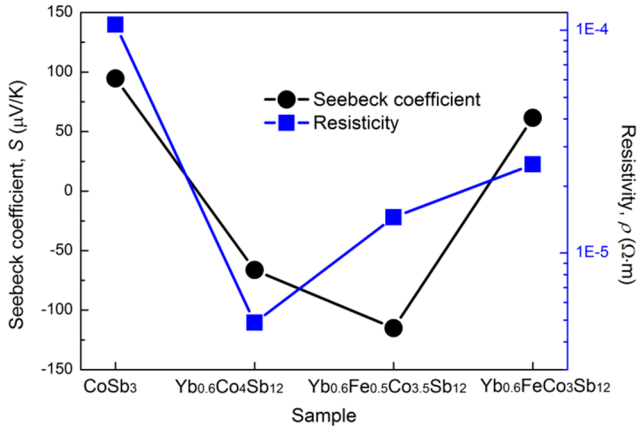

Fig. 1 Seebeck coefficient and resistivity of $Yb_xFe_yCo_{4-y}Sb_{12}$ at room temperature.

Figure 2 shows the figure of merit ZT, power factor ($PF=S^2/\rho$) and the thermal conductivity κ for $Yb_xFe_yCo_{4-y}Sb_{12}$. The increase of Fe-substitution fraction leads to continuous decrease of the thermal conductivity. Taking into account of the increase for the actual filling fraction of Yb by Fe substitution, the 'rattling' of Yb atoms inside the interstitial voids would become remarkable. Therefore, the persistent decrease of thermal conductivity should be induced by the increase of the actual Yb filling fraction. PF was increased in $Yb_{0.6}Fe_{0.5}Co_{3.5}Sb_{12}$ compared with no Fe substitution compound $Yb_{0.6}Co_4Sb_{12}$. However, PF was dramatically decreased with increasing to 1 of Fe-substitution fraction. The balance between electric transport properties (PF) and thermal transport property (κ) results in a maximum of figure of merit ZT in $Yb_{0.6}Fe_{0.5}Co_{3.5}Sb_{12}$. This result confirms that the Fe compensating on the Co site is an effectively approach to tune the thermoelectric property of $CoSb_3$ based skutterudites.

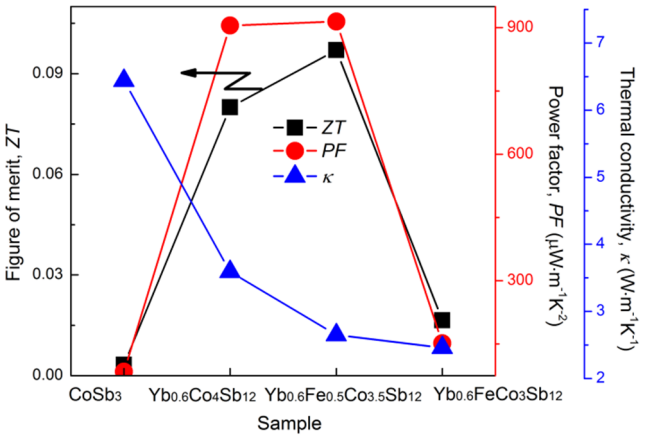

Fig. 2 Figure of merit ZT, power factor PF and thermal conductivity κ for $Yb_xFe_yCo_{4-y}Sb_{12}$.

4. Conclusions

Partially Yb-filled Fe-substituted $CoSb_3$-based n-type skutterudites were synthesized by a high-pressure technique. The thermoelectric properties were investigated at room temperature. Despite the complicated restrictive relationship between thermal and electric transport properties in $Yb_{0.6}Fe_yCo_{4-y}Sb_{12}$ system, both enhanced electric transport properties and improved thermal transport properties were realized with Fe-substitution content of 0.5. With further optimized Fe-substitution ratio, higher figure of merit ZT is expected.

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