研 究

Thermoelectric Properties of $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 Composite

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SYNOPSIS

We have prepared a sintered $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 composite and investigated the Seebeck coefficient, electrical resistivity, and thermal conductivity in order to estimate the corresponding figure of merit. The thermal conductivity of the composite whose molar ratio of $\text{CeFe}_3\text{CoSb}_{12}$ to FeSb_2 is 0.9 : 0.1 is as large as that of $\text{CeFe}_3\text{CoSb}_{12}$ while the lattice contribution of the thermal conductivity of the composite is somewhat smaller than that of $\text{CeFe}_3\text{CoSb}_{12}$, which is ascribed to the enhancement of the phonon scattering caused by the additive material. With increasing FeSb_2 content the thermal conductivity of the composite is enhanced. The Seebeck coefficient and electrical resistivity of the composite generally decrease with increasing FeSb_2 content. These behaviors in the thermal conductivity, Seebeck coefficient and electrical resistivity with increasing FeSb_2 content is considered to be ascribed to the physical properties of FeSb_2 . As a result, the composite whose molar ratio of $\text{CeFe}_3\text{CoSb}_{12}$ to FeSb_2 is 0.9 : 0.1 shows somewhat larger figure of merit than $\text{CeFe}_3\text{CoSb}_{12}$ in the whole temperature range from 373 K to 773 K.

KEY WORDS

Seebeck coefficient, electrical resistivity, thermal conductivity, filled skutterudite

1 Introduction

Skutterudite compounds have been known as potential thermoelectric materials^{1,2)}. Skutterudite Compounds are represented by MX_3 , where M is Co, Rh or Ir and X is P, As or Sb. Most of the binary skutterudite compounds possess reasonably large Seebeck coefficient (S) and good electrical conductivity (σ), resulting in large power factor values ($S^2 \times \sigma$), comparable to state-of-the-art thermoelectric materials. However, their thermal conductivity, especially the lattice thermal conductivity, remains too high to make these materials efficient thermoelectrics³⁾.

One approach to the achievement of the reduction of the thermal conductivity of the skutterudite is to make a formation of a solid solution. It has been shown that the thermal conductivity of CoSb_3 or IrSb_3 can be substantially reduced by making the solid solutions $\text{Co}_{0.88}\text{Ir}_{0.12}\text{Sb}_3$ or $\text{Co}_{0.12}\text{Ir}_{0.88}\text{Sb}_3$, from 9–10 to 3–3.5 W/m/K at room temperature⁴⁾. We have also reported that the thermal conductivity of CoSb_3 is reduced by the substitution for Co by Fe, especially in the high iron content region⁵⁾. Another approach to the achievement of the reduction of the lattice thermal conductivity is to prepare the filled skutterudite compositions^{6,7)}. The composition of the filled

skutterudite compounds can be represented by the formula RM_4X_{12} , where R was La, Ce, Pr, Nd, or Eu. In these compounds, the empty octants of the skutterudite structure which are formed in the MX_3 framework are filled with a rare earth element. X-ray and neutron structure refinements indicate that the R atoms tend to exhibit exceptionally large thermal parameters, corresponding to the “rattling” of these atoms in an oversized atomic cage^{8,9)}. This rattling markedly reduces the thermal conductivity of these filled skutterudite compounds. These approaches correspond to the ways to reduce the thermal conductivity of materials by controlling the microscopic structure in the atomic level.

On the other hand, the extra reduction in the thermal conductivity for sintered materials can be attained by the increase of the phonon scattering at grain boundaries. The existence of an additive compound in the sintered material is effective for the enhancement of the phonon scattering at grain boundaries resulting in the reduction of the thermal conductivity^{10,11)}. This approach corresponds to the way to reduce the thermal conductivity of materials by controlling the microscopic structure in the grain size level.

The combination of the above two approaches, i.e., in the atomic level and in the grain size level, may be more effective for the reduction of the thermal conductivity of

thermoelectric materials. Therefore, we have tried to prepare the composite thermoelectric materials composed of the matrix compound and the additive compound. We have chosen $\text{CeFe}_3\text{CoSb}_{12}$ with a filled skutterudite structure as a matrix compound and FeSb_2 with a marcasite structure as an additive compound. In our previous report, we have shown that the addition of FeSb_2 is very effective for the reduction of the thermal conductivity for CoSb_3 with maintaining moderate Seebeck coefficient and electrical resistivity¹¹⁾. In this study, we have prepared $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 composite and investigated its thermoelectric properties.

2 Experiments

The compounds $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 were synthesized by the direct reaction of their elements. For $\text{CeFe}_3\text{CoSb}_{12}$, Ce (99.9 at.% pure), Fe (99.9 at.% pure), Co (99.9985 at.% pure) and Sb (99.9999 at.% pure) powders with the stoichiometric composition were mixed and evacuated in a quartz ampoule. The ampoule was heated at 1273 K for 20 h via holding at 873 K for 3 h, then quenched into ice water and the ampoule was again heated at 973 K for 30 h. For FeSb_2 , Fe and Sb powders were heated at 973 K for 48 h in an evacuated quartz ampoule. After the reaction was completed, the ampoules were opened and the products were ground by mortar and pestle into fine powders. The obtained $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 powders were weighed in the desired ratios of $\text{CeFe}_3\text{CoSb}_{12}$ to FeSb_2 of $1-x:x$, where $x=0, 0.1$ and 0.2 . The mixed powders were packed into graphite dies and hot-pressed at 923 K for 1 h at a pressure of 10 MPa under a vacuum of 10^{-3} Pa. The phase identification of the obtained samples was made by x-ray diffraction at room temperature. The microscopic structure of the samples was examined using a scanning electron microscope (SEM). The Seebeck coefficient (S) and the electrical resistivity (ρ) were simultaneously measured by the standard four probe dc method in a flowing Ar gas atmosphere in the temperature range from 373 K to 773 K. The thermal diffusion coefficient (D) and the specific heat (C_p) of the samples were measured by the laser flash method. The density (d) of the samples was measured by the Archimedes method.

3 Results and discussion

The x-ray diffraction patterns for the sintered $\text{CeFe}_3\text{CoSb}_{12}$ mainly consist of the diffraction peaks of the skutterudite $\text{CeFe}_3\text{CoSb}_{12}$ phase, and traces of Sb and FeSb_2 were detected. The x-ray diffraction patterns for the sintered body of the mixture of $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2

showed the coexistence of $\text{CeFe}_3\text{CoSb}_{12}$, FeSb_2 and Sb, and the relative intensity of FeSb_2 increases with an increase of the content of FeSb_2 . Fig. 1 shows the SEM photograph for the sintered body of the mixture of $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 whose molar ratio of $\text{CeFe}_3\text{CoSb}_{12}$ to FeSb_2 is 0.8:0.2. Here, we will designate this composite $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$. It is observed that the sintered body consists of two kinds of crystal grains with different contrast. The analysis by the energy dispersive x-ray analysis (EDX) shows that bright and dark grains are $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 phases, respectively. The crystal grain size of $\text{CeFe}_3\text{CoSb}_{12}$ is much larger than that of FeSb_2 . From the results of x-ray diffraction and SEM observation, it has become clear that the sintered body of the mixture of $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 is a composite consisting of $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 grains.

Fig. 2 shows the temperature dependence of the Seebeck coefficient for $\text{CeFe}_3\text{CoSb}_{12}$, $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$, together with the data for FeSb_2 . All the Seebeck coefficients are positive, i.e., the $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 composite system is p type. At lower temperature, the Seebeck coefficient for the $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ composite is somewhat larger than that for $\text{CeFe}_3\text{CoSb}_{12}$. While, the Seebeck coefficient for the $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ composite is the smallest among these samples in the whole temperature range investigated. The reduction of the Seebeck coefficient for the $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ composite is ascribed to the low Seebeck coefficient of FeSb_2 as shown in Fig. 2.

Fig. 3 shows the temperature dependence of the electrical resistivity for $\text{CeFe}_3\text{CoSb}_{12}$, $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$. The data for FeSb_2 are also shown in the figure. The electrical resistivity for the

Fig.1 SEM photograph for the $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ composite.

Fig.2 Seebeck coefficient for $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ and FeSb_2 as a function of the temperature.

Fig.3 Electrical resistivity for $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ and FeSb_2 as a function of the temperature.

composite is generally smaller than that for $\text{CeFe}_3\text{CoSb}_{12}$, which is remarkable in $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ at high temperature. The reduction of the electrical resistivity for the composites is also ascribed to the low electrical resistivity of FeSb_2 . The reason for the somewhat increase of the Seebeck coefficient in $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ at low temperatures, nevertheless with its low electrical resistivity, is not clear. Similar behavior was previously observed in

Fig.4 Thermal conductivity for $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ and FeSb_2 as a function of the temperature.

Ag -added $\text{Na}_x\text{Co}_2\text{O}_4$ system by us¹²⁾. The additive FeSb_2 may affect the composition of the $\text{CeFe}_3\text{CoSb}_{12}$ matrix, which optimizes the carrier concentration of the material.

The thermal conductivity for $\text{CeFe}_3\text{CoSb}_{12}$, $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$, $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$, and FeSb_2 is shown in Fig. 4 as a function of temperature. The thermal conductivity was calculated from the measured thermal diffusivity D , specific heat C_p , and density d using the relationship $\kappa = DC_p d$. There is almost no difference in the thermal conductivity between $\text{CeFe}_3\text{CoSb}_{12}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$, but the thermal conductivity of $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ is much larger than other two samples in the whole temperature range investigated. The enhancement of the thermal conductivity of $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ is considered to be ascribed to high thermal conductivity of FeSb_2 as shown in Fig. 4. This result seems to indicate that the addition of FeSb_2 is not so effective for the reduction of the thermal conductivity. In order to investigate this phenomenon more precisely, we have made a following analysis.

When a single sign of charge carrier is predominant, the thermal conductivity, κ_{total} , of the material can be written as

$$\kappa_{\text{total}} = \kappa_{\text{car}} + \kappa_{\text{ph}}$$

where, κ_{car} is the carrier contribution and κ_{ph} is the lattice

contribution. κ_{car} and κ_{ph} for $\text{CeFe}_3\text{CoSb}_{12}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ were estimated by the Wiedemann-Franz relationship following our procedure in a previous report¹³⁾. The temperature dependence of κ_{car} and κ_{ph} for $\text{CeFe}_3\text{CoSb}_{12}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ is shown in Fig. 5. κ_{ph} of $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ is smaller than that of $\text{CeFe}_3\text{CoSb}_{12}$. While, κ_{car} of $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ is larger than that of $\text{CeFe}_3\text{CoSb}_{12}$. This result shows that the addition of FeSb_2 is somewhat efficient for the reduction of the lattice thermal conductivity of $\text{CeFe}_3\text{CoSb}_{12}$, i.e., the increase of the phonon scattering. The slight increase in κ_{car} for $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ is considered to be due to the high thermal conductivity of FeSb_2 as shown in Fig. 4. The enhancement of the thermal conductivity by FeSb_2 is remarkably recognized on the $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ composite.

The dimensionless figure of merit $ZT (= S^2T/(\rho\kappa))$ was calculated from the Seebeck coefficient, electrical resistivity, and thermal conductivity. Fig. 6 shows the ZT for $\text{CeFe}_3\text{CoSb}_{12}$, $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ as a function of the temperature. ZT monotonously increases with temperature up to 773 K. In the whole temperature range investigated, ZT of $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ exceeds that of $\text{CeFe}_3\text{CoSb}_{12}$ as well as $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$. The obtained maximum ZT was 0.62 at 773 K.

Fig.5 (a) κ_{ph} and (b) κ_{car} for $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ as a function of the temperature.

4 Conclusion

$\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 composites, $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ where $x=0, 0.1$ and 0.2 , were prepared and their thermoelectric properties were examined. The Seebeck coefficient for the $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ composite is comparable to that for $\text{CeFe}_3\text{CoSb}_{12}$, but $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ shows smaller Seebeck coefficient than other two samples. The electrical resistivity for the composite is generally smaller than that for $\text{CeFe}_3\text{CoSb}_{12}$. There is almost no difference in the thermal conductivity between $\text{CeFe}_3\text{CoSb}_{12}$ and $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$, but the somewhat decrease of the lattice thermal conductivity is recognized in the $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$, which is accompanied with the increase in the phonon scattering at grain boundaries. The thermal conductivity for $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ becomes larger than that for $\text{CeFe}_3\text{CoSb}_{12}$. The behaviors in these thermoelectric properties for $(\text{CeFe}_3\text{CoSb}_{12})_{0.8}(\text{FeSb}_2)_{0.2}$ are ascribed to the physical properties of FeSb_2 , i.e., low Seebeck coefficient, low electrical resistivity, and high thermal conductivity. As a result, $(\text{CeFe}_3\text{CoSb}_{12})_{0.9}(\text{FeSb}_2)_{0.1}$ shows maximum ZT of 0.62 at 773 K, which is somewhat larger than $\text{CeFe}_3\text{CoSb}_{12}$.

Thus, we have succeeded in somewhat increasing the ZT of $\text{CeFe}_3\text{CoSb}_{12}$ by the formation of the composite with FeSb_2 . On the other hand, there remain some problems to be examined. As shown in Fig. 1, the crystal grain sizes of $\text{CeFe}_3\text{CoSb}_{12}$ and FeSb_2 are rather large and the precipitated FeSb_2 particles are segregated in the $\text{CeFe}_3\text{CoSb}_{12}$ matrix. Since the phonon is scattered at grain boundaries, smaller

Fig.6 ZT for $(\text{CeFe}_3\text{CoSb}_{12})_{1-x}(\text{FeSb}_2)_x$ as a function of the temperature.

and more dispersed particles are more effective for the phonon scattering resulting in the reduction of the thermal conductivity of the materials¹¹⁾. If we could make the precipitated FeSb_2 particles more widely dispersed, the thermal conductivity of the composite might be more reduced. Mechanical grinding (MG) is a process of grinding alloys and intermetallic compounds into a powder using a ball mill or vibrating mill, by which fine and well-mixed powders are generally obtained. By using powders treated by MG, we can synthesize a sintered material with small grains and dispersed additive materials. And so, we are planning to prepare the $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 composite, where the FeSb_2 particles are finely dispersed in the $\text{CeFe}_3\text{CoSb}_{12}$ matrix, by MG technique. Furthermore, the ZT of our sample of $\text{CeFe}_3\text{CoSb}_{12}$ is relatively small comparing with values previously reported by other researchers^{6,7)}. More examination on the optimum conditions about the synthesis of $\text{CeFe}_3\text{CoSb}_{12}$ is necessary. There remain some problems to be solved, but we believe that we have proposed the efficiency of forming the composite of $\text{CeFe}_3\text{CoSb}_{12}$ - FeSb_2 for the enhancement of the performance as the thermoelectric material.

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References

- 1) T.Caillat, A.Borshchovsky and J.-P.Fleurial: "Novel Transition Metal Compounds with Promising Thermoelectric properties", Proceedings of the 12th International Conference on Thermoelectrics, Yokohama, Japan, (1993)132-134.
- 2) G.A.Slack and V.G.Tsoukala: "Some Properties of Semiconducting IrSb_3 ", J. Appl. Phys., **76**(1994)1665-1671.
- 3) J.W.Sharp, E.C.Jones, R.K.Williams, P.H.Martin and B.C.Sales: "Thermoelectric Properties of CoSb_3 and Related Alloys", J. Appl. Phys., **78**(1995)1013-1018.
- 4) A.Borshchovsky, J.-P.Fleurial, E.Allevato and T.Caillat: "Solid Solution Formation: Improving the Thermoelectric Properties of Skutterudite", Proceedings of the 15th International Conference on Thermoelectrics, Pasadena, CA, (1996)112-116.
- 5) S.Katsuyama, Y.Shichijo, M.Ito, K.Majima and H.Nagai: "Thermoelectric Properties of the Skutterudite $\text{Co}_{1-x}\text{Fe}_x\text{Sb}_3$ System", J. Appl. Phys., **84** (1998)6708-6712.
- 6) B.C.Sales, D.Mandrus and R.K.Williams: "Filled Skutterudite Antimonides: A New Class of Thermoelectric Materials", Science, **272**(1996)1325-1328.
- 7) J.-P.Fleurial, A.Borshchovsky and T.Caillat: "High Figure of Merit in Ce-Filled Skutterudites", Proceeding of the 15th International Conference on Thermoelectrics, Pasadena, CA, 1996, 91-95.
- 8) D.J.Braun and W.Jettschko: "Preparation and Structural Investigations of Antimonides with the $\text{LaFe}_4\text{P}_{12}$ Structure", J. Less Common Met., **72**(1980) 147-156.
- 9) B.C.Sales, B.C.Chakoumakos and D.Mandrus: "Thermoelectric Properties of Thallium-filled Skutterudite", Phys. Rev., **61**(2000)2475-2481.
- 10) S.Katsuyama, H.Kusaka, M.Ito, K.Majima and H.Nagai: "Thermoelectric Properties of CoSb_3 with Oxide Particles Dispersion", Proceedings of the 18th International Conference on Thermoelectrics, Baltimore, MD, (1999)348-351.
- 11) S.Katsuyama, Y.Kanayama, M.Ito, K.Majima and H.Nagai: "Thermoelectric Properties of CoSb_3 with Dispersed FeSb_2 Particles", J. Appl. Phys., **88**(2000) 3484-3489.
- 12) M.Ito, D.Furumoto, S.Katsuyama and S.Hara: "Thermoelectric Properties of CoSb_3 of $\text{Na}_x\text{Co}_2\text{O}_4/\text{Ag}$ Composites", Proceedings of the 23rd International Conference on Thermoelectrics, Adelaide, Australia, (2004), #87.
- 13) S.Katsuyama, Y.Tanaka, H.Hashimoto, K.Majima and H.Nagai: "Effect of Substitution of La by Alkaline Earth Metal on the Thermoelectric Properties and the Phase Stability of γ - La_3S_4 ", J. Appl. Phys., **82**(1997) 5513-5519.