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journal or publication title	Journal of Materials Research
volume	16
number	12
page range	3343-3346
year	2001
URL	http://hdl.handle.net/10097/52138

doi: 10.1557/JMR.2001.0460

High-temperature thermoelectric properties of *n*-type $Ba_yNi_xCo_{4-x}Sb_{12}$

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(Received 21 June 2001; accepted 27 September 2001)

Effects of Ba filling fraction and Ni content on the thermoelectric properties of *n*-type $Ba_yNi_xCo_{4-x}Sb_{12}$ ($x = 0$–0.1, $y = 0$–0.4) were investigated at temperature range of 300 to 900 K. Thermal conductivity decreased with increasing Ba filling fraction and temperature. When y was fixed at 0.3, thermal conductivity decreased with increasing Ni content and reached a minimum value at about $x = 0.05$. Lattice thermal conductivity decreased with increasing Ni content, monotonously ($y \leqslant 0.1$). Electron concentration and electrical conductivity increased with increasing Ba filling fraction and Ni content. Seebeck coefficient increased with increasing temperature and decreased with increasing Ba filling fraction and Ni content. The maximum ZT value of 1.25 was obtained at about 900 K for *n*-type $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$.

For thermoelectric application, both *p*- and *n*-type materials having high thermoelectric figure of merit ZT are required simultaneously.[1] Recently filled skutterudite compounds based on $CoSb_3$ have received great attention as candidate thermoelectric materials because of their high power factor P ($P = \alpha^2\sigma$) and low lattice thermal conductivity due to the rattling of filling atoms.[2–16] To date, many studies have been reported on the synthesis and thermoelectric properties of filled skutterudites. Such efforts have resulted in striking thermoelectric performance especially for *p*-type materials.[4,14] However, few *n*-type skutterudite compounds have been reported so far. In our recent work, we synthesized a series of samples with composition $Ba_yCo_4Sb_{12}$.[17,18] It shows that up to 44% of the voids can be filled with Ba without any charge compensation. These compounds showed low thermal conductivity as compared with the unfilled host.[19–21] However, the lattice thermal conductivity of these samples still remains relatively large in comparison to the skutterudites filled with rare-earth atoms (Ce, La, Yb)[3,4,6,21,22] and others species (Tl, Sn).[23–25] To further decrease the lattice thermal conductivity of $Ba_yCo_4Sb_{12}$-based compounds, substitution of Ni on the lattice sites of Co, which is expected to provide additional phonon scattering and adjust the carrier characteristic, should be one prospective avenue for exploration. In this rapid communication, we synthesized $Ba_yNi_xCo_{4-x}Sb_{12}$ samples and investigated the effect of Ni substitution on the high temperature thermoelectric properties.

Highly pure metals of Ba (99.9%, plate), Sb (99.9999%, powder), Ni (99.9%, powder), and Co (9.99%, powder) were used as the starting materials. Because the reaction between Ba and Sb or Co (Fe) is highly exothermic, it is difficult to directly melt or react a mixture of the constituent elements. In the present study, a two-step solid reaction was used.[17,26] The constituent phases of the samples were determined by powder x-ray diffractometry (Rigaku: RAD-C, Cu K_α, Tokyo, Japan). The chemical compositions of the samples were analyzed by inductively coupled plasma emission spectroscopy. The Hall coefficient (R_H) was measured by using the van der Pauw method with an excitation current of 100 mA and a magnetic field of 5028 G. The carrier concentration (p) was calculated from the Hall coefficient (R_H), using $p = 1/R_He$, where e is the electron charge. The electrical conductivity (σ) was measured by the standard four-probe method in a flowing Ar atmosphere. The thermoelectromotive force (ΔE) was measured under temperature differences (ΔT) of 0 to 10 K, and the Seebeck coefficient (α) was

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obtained from the slope of ΔE versus ΔT plot. The thermal conductivity (κ) was measured by a laser flash method (Shinkuriko: TC-7000, Yokohama, Japan) in a vacuum. All the measurements were performed at temperature range of 300 to 900 K.

Figure 1 shows temperature dependence of thermal conductivity (κ) for $Ba_yCo_4Sb_{12}$. Results are compared to those of $Ce_{0.07}Co_4Sb_{12}$. The thermal conductivity of all samples showed peak values at about 50 K, and those peak values decreased significantly with increasing Ba filling fraction and with rising temperature. Those results indicated that $Ba_yCo_4Sb_{12}$ shows thermal transport properties of the crystal and Ba filled in Sb-icosahedron voids have the remarkable effect of reducing thermal conductivity. The decrease of κ of Ba-filled $Ba_yCo_4Sb_{12}$ was due to that the ionic radius of Ba (Ba^{2+} radius = 1.34 Å) is smaller than the radius of the Sb-icosahedron void (1.892 Å), and thus, Ba is poorly bonded in the structure and rattles about its equilibrium position. The rattling of Ba atom can reduce the mean free path of the heat-carrying phonon, resulting in lowering of the thermal conductivity. Indeed, such rattling was also confirmed by results obtained using Rietveld analysis;[17] i.e., the thermal parameter ($B = 0.61$) of Ba was larger than that of Sb ($B = 0.16$) and Co/Fe ($B = 0.12$). In addition, lowering of the thermal conductivity of $Ba_yCo_4Sb_{12}$ may be the mass disorder scattering associated with the filling Ba versus the unfilled voids.[11] However, at the same filling fraction, the thermal conductivity of $Ba_{0.07}Co_4Sb_{12}$ was larger than these of $Ce_{0.07}Co_4Sb_{12}$.[21] It may be related to that the ionic radius of Ba^{2+} (1.34 Å) is larger than that of Ce^{3+} (1.03 Å). We have found that the lattice thermal conductivity decreased with decreasing ionic radius of the filling atom at the same filling fraction and Fe content for $Ba_yFe_xCo_{4-x}Sb_{12}$, $Ce_yFe_xCo_{4-x}Sb_{12}$, and $Y_yFe_xCo_{4-x}Sb_{12}$; i.e., the rattling effect of the filling atom became stronger with decreasing ionic radius.[26] To reduce thermal conductivity furthermore and adjust carrier properties of $Ba_yCo_4Sb_{12}$, Co sites were substituted by Ni and effects of Ni were investigated further.

The thermal conductivity (κ) of *n*-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$ decreased with increasing Ni content and reached the minimum values at a Ni content of about 0.05. When $x > 0.05$, κ began to increase reversally with increasing Ni content. It was due to that electronic component of thermal conductivity increased with increasing Ni content. The Wiedemann–Franz law ($\kappa_C = L\sigma T$) using a Lorenz number of 2×10^{-8} V^2/K^2 was used to estimate the carrier concentration contribution to the thermal conductivity.[4] The lattice thermal conductivity (κ_L) was obtained to subtract the carrier component (κ_C) from the total thermal conductivity. The effect of Ni content on the lattice thermal conductivity (κ_L) of *n*-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$ is shown in Fig. 2. κ_L decreased with increasing temperature for *n*-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$, and by substitution of Ni at Co sites, κ_L decreased significantly; for example, κ_L of room temperature reduced from 4.6 to 3.7 W m^{-1} K^{-1} though the Ni content was only 0.02. κ_L decreased further with increasing Ni content. The above results indicated that Ni has a remarkable effect on reduction of lattice thermal conductivity of *n*-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$, although the differences of atomic mass and ionic radius of Ni and Co are very small.

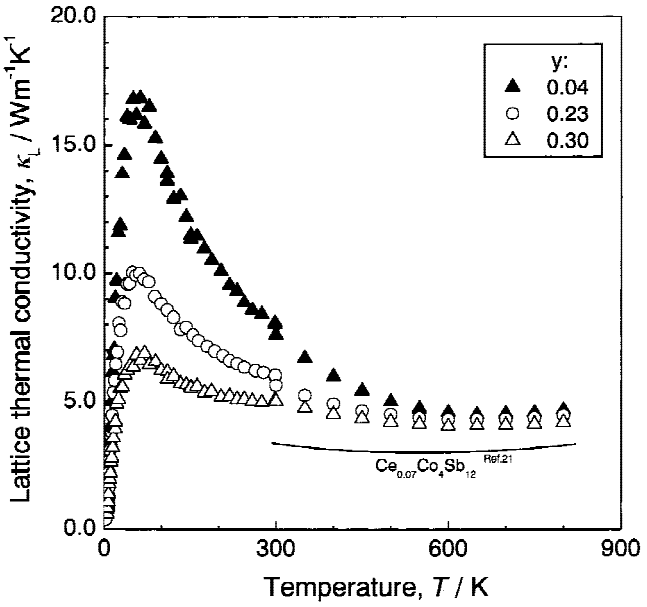

FIG. 1. Temperature dependence of thermal conductivity for $Ba_yCo_4Sb_{12}$.

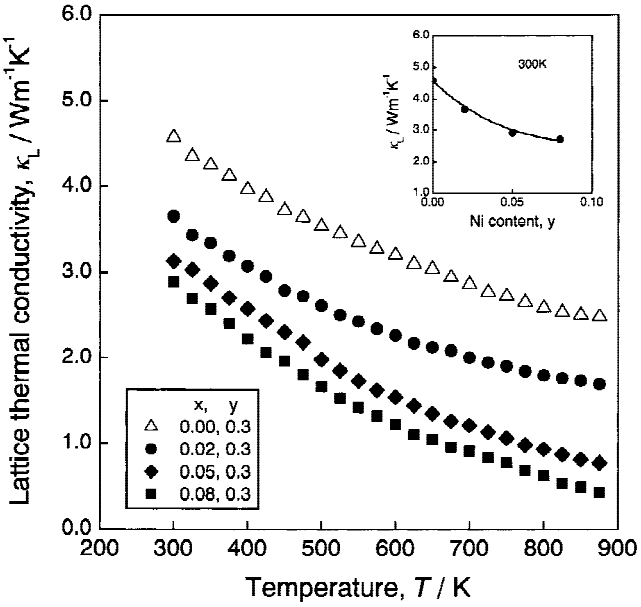

FIG. 2. Temperature dependence of lattice thermal conductivity for *n*-type $Ba_yNi_xCo_{4-x}Sb_{12}$.

When the Ba filling fraction y was larger than about 0.1, n-type filled skutterudite $Ba_yNi_xCo_{4-x}Sb_{12}$ was obtained. Carrier concentration of n-type $Ba_yNi_xCo_{4-x}Sb_{12}$ increased with increasing Ba filling fraction and increased furthermore with increasing Ni content. In general, Ba and Ni are thought of being divalent and quatervalent, respectively;[21] i.e., one Ba^{2+} and Ni^{4+} provide two and four electrons to the skutterudite structure, respectively. Increasing of electron concentration is due to Ba^{2+} and Ni^{4+} providing more electrons to skutterudite structure with increasing Ba filling fraction and Ni content. Temperature dependence of electrical conductivity (σ) is shown in Fig. 3 for n-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$. σ increased with increasing Ni content significantly and decreased with rising temperature when $x \geqslant 0.02$. This is consistent with the change of carrier concentration. Sample $Ba_{0.3}Ni_{0.08}Co_{3.92}Sb_{12}$ showed the largest electrical conductivity, and σ reached 3.31×10^5 S m^{-1} at room temperature. The Seebeck coefficient (α) of n-type $Ba_yNi_xCo_{4-x}Sb_{12}$ increased with increasing temperature and decreased with increasing Ba filling fraction and Ni content. $Ba_{0.3}Co_4Sb_{12}$ which is not substituted by Ni shows the maximum Seebeck coefficient. The above results indicated that filling atom Ba and substituting atom Ni have a remarkable effect on adjustment of carrier concentration and control of electrical transport properties.

The temperature dependence of the dimensionless thermoelectric figure of merit, ZT, of n-type $Ba_yNi_xCo_{4-x}Sb_{12}$ is shown in Fig. 4. ZT increased with increasing temperature for all samples. In the n-type $Ba_yCo_4Sb_{12}$ which is not substituted by Ni, $Ba_{0.3}Co_4Sb_{12}$ shows the maximum

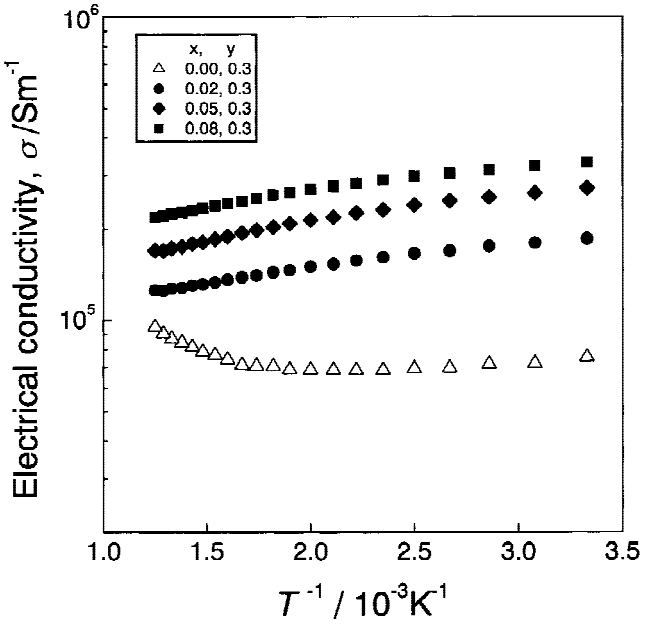

FIG. 3. Temperature dependence of electrical conductivity for n-type $Ba_yNi_xCo_{4-x}Sb_{12}$.

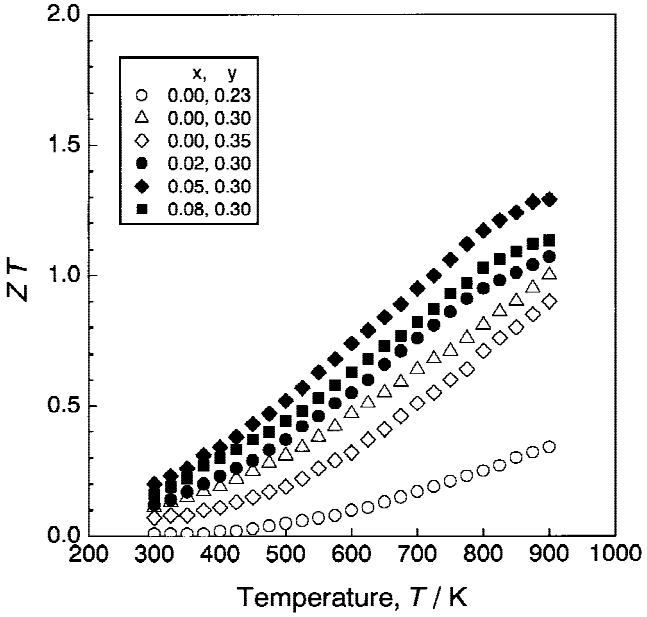

FIG. 4. Temperature dependence of ZT for n-type $Ba_yNi_xCo_{4-x}Sb_{12}$.

ZT. In the n-type $Ba_{0.3}Ni_xCo_{4-x}Sb_{12}$ substituted by Ni, $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$ shows the maximum ZT. The maximum ZT value of 1.25 was obtained at about 900 K.

In conclusion, it was confirmed that filling atom Ba and substituting atom Ni are effective for controlling and optimizing thermoelectric transport properties. Thermal conductivity decreased with increasing Ba filling fraction and temperature. When y was fixed at 0.3, thermal conductivity decreased with increasing Ni content and reached a minimum value at about $x = 0.05$. Lattice thermal conductivity decreased with increasing Ni content, monotonously ($y \leqslant 0.1$). Electron concentration and electrical conductivity increased with increasing Ba filling fraction and Ni content. Seebeck coefficient increased with increasing temperature and decreased with increasing Ba filling fraction and Ni content. The maximum ZT value of 1.25 was obtained at about 900 K for n-type $Ba_{0.3}Ni_{0.05}Co_{3.95}Sb_{12}$.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (A) (No. 12750591) of Japan. The authors are grateful to the staffs of the Technical Services Division of the Institute for Materials Research in Tohoku University, Sendai, Japan, for their continuous support in ICP analysis.

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