

Transport properties of undoped and Sb-doped half-Heusler compounds NbCoSn

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Transport properties of NbCoSn_{1-x}Sb_x ($x=0, 0.01, 0.02$ and 0.05), half-Heusler compound and its alloys, have been studied in the temperature range from 80 K to 850 K. As-prepared samples exhibit metallic conduction and similar Seebeck coefficients near 300 K ($S = -100 \mu\text{VK}^{-1}$). Except for NbCoSn_{0.95}Sn_{0.05}, both electrical resistivity, ρ , and the absolute value of S appreciably increase during the annealing for 6 days at 1123 K. Unusual increase in ρ of annealed NbCoSn is found at about 200 K. ρ - T curves of the other annealed samples remain metallic over the measured temperature range and the ρ value noticeably decreases with increasing Sb content, x . In the annealed samples, the maximum power factor, $25 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 850 K, is obtained for NbCoSn_{0.95}Sb_{0.05}.

Key words: half-Heusler compound, thermoelectric material, NbCoSn, Sb-doping, annealing effect, band structure calculation

1. INTRODUCTION

The ternary intermetallics with the formula, $M\text{NiSn}$ ($M=\text{Ti, Zr, Hf}$), frequently referred to half-Heusler compounds, have attracted much attention in recent years due to their potential thermoelectric properties [1-7]. M and Sn atoms form rock-salt type arrangement and Ni atoms occupy interstitial positions in an ordered array [8], i.e., MgAgAs-type structure (space symmetry, F43m). In these compounds, high Seebeck coefficient, S , and low electrical resistivity, ρ , yield a large power factor, S^2/ρ , in the range from 5 to $20 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 450 K [1]. Sb-doping to $M\text{NiSn}$ ($M=\text{Ti, Zr, Hf}$) greatly enhances the power factors, e.g., $69 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 650 K for TiNiSn_{0.95}Sb_{0.05} [3] and $34 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 700 K for ZrNiSn_{0.99}Sb_{0.01} [5].

The half-Heusler compounds such as $M\text{NiSn}$ ($M=\text{Ti, Zr, Hf}$) and TiCoSb are narrow-gap indirect semiconductors because they have 18 valence electrons

per formula unit (VEC=18), while the other compounds with VEC=17 and 19 are metals [9,10,11]. Despite of VEC=18, NbCoSn is a semimetallic compound with significantly lower electrical resistivity than those of TiNiSn and TiCoSb [10,11]. The Seebeck coefficient of NbCoSn has not been reported yet. In this paper, we study the effects of Sb-doping on the transport properties of NbCoSn.

2. EXPERIMENTAL

Polycrystalline samples, NbCoSn_{1-x}Sb_x ($x=0, 0.01, 0.02$ and 0.05), were prepared by mixing and arc melting of pure metals, Nb (99.9%), Co (99.9%), Sn (99.9%) and Sb (99.7%). Raw powder materials were mixed with an appropriate molar ratio, pressed into pellets and melted under argon atmosphere. The alloy buttons were remelted after turning upside down. To

ensure chemical homogeneity, this procedure was repeated four times. A portion of the sample was sealed in an evacuated quartz tube and annealed for 6 days at 1123 K. Powder X-ray diffraction measurement was carried out for all samples using a Rigaku RAD-X diffractometer (CuK α) equipped with a curved graphite monochromator. The structure parameters of NbCoSn $_{1-x}$ Sb $_x$ with $x=0$ were refined by a Rietveld analysis program, RIETAN 2000 [12], using the observed X-ray diffraction data. Between 80 K and 290 K, the electrical resistivity and Seebeck coefficient were measured under He atmosphere by a dc four-probe method and a temperature-gradient technique, respectively. The measurements of ρ and S from 300 K up to 850 K were performed in vacuum using an Ozawa Science RZ2001i automated Seebeck coefficient measuring apparatus. Based on the refined structure parameters, the electron band structure of NbCoSn $_{1-x}$ Sb $_x$ with $x=0$ was calculated by the generalized-gradient approximation full-potential linearized augmented plane-wave (GGA-FLAPW) method using the WIEN2k package [13].

3. RESULTS AND DISCUSSION

3.1 Crystal structure

A few weak impurity peaks (Sn and Nb $_3$ Sn) were detected in powder X-ray diffraction patterns of both as-prepared and annealed samples, probably due to the large difference in the melting points of pure Nb and Sn. But, the intensities of the impurity peak are negligibly small relative to those of the half-Heusler phase. Tobola

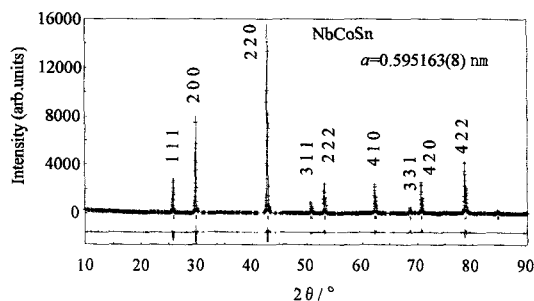


Fig.1. Observed (+) and calculated (solid line) X-ray diffraction intensities of NbCoSn. Tick marks represent the positions of possible Bragg reflections. Solid line at the bottom is the difference between the observed and calculated intensities.

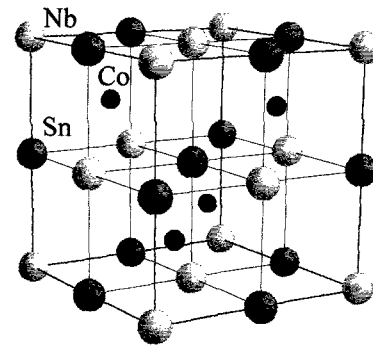


Fig.2. Crystal structure of NbCoSn

et al. [9] also reported the difficulty in preparing single-phase NbCoSn by the arc melting. Figure 1 shows the result of Rietveld pattern fitting for annealed NbCoSn, where the impurity peaks were removed during the calculation. There is good agreement between the observed and calculated intensities ($R_{wp}=15.14\%$, $R_I=5.55\%$ and $R_F=3.24\%$).

Figure 2 shows the crystal structure of NbCoSn with space symmetry F43m (No.216). Nb, Co and Sn atoms sit on 4a(0,0,0), 4c(1/4,1/4,1/4) and 4b(1/2,1/2,1/2) sites, respectively. Lattice parameter, $a=0.595163(8)$ nm, is nearly equal to the previously reported value, $a=0.5947$ nm [9]. The isotropic thermal parameters for Nb, Co and Sn atoms are $B=0.32(7)$, $0.82(9)$ and $0.14(6) \times 10^{-2} \text{ nm}^2$, respectively.

3.2 Electrical resistivity and electron band structure

Figure 3 shows temperature variation of the electrical resistivity, ρ . In the as-prepared samples, intermixing of Nb, Co and Sn atoms possibly occurs at each site due to the rapid cooling after the arc melting. Metallic conduction of these samples ($d\rho/dT > 0$) results from a modification of the electronic states by the intermixing [9,10]. The ρ values appreciably increases during annealing process, suggesting an improvement of the intermixing. Unusual increase in ρ at about 200 K was observed only for NbCoSn. In the annealed samples, the ρ value noticeably decreases with increasing Sb content, x . Partial substitution of the group-V element, Sb, for Sn site causes an introduction of electrons. Accordingly, the increase in carrier (electron) concentration leads to lowering of ρ in the Sb-doped samples.

Figure 4 shows the calculated band structure of

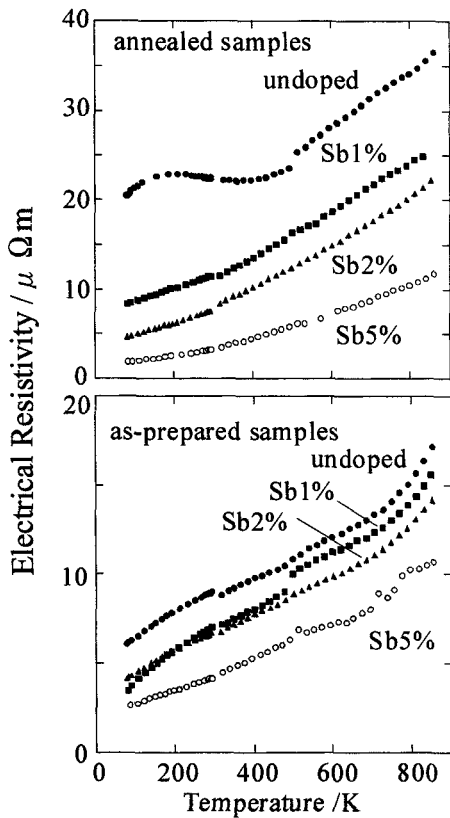


Fig.3. Electrical resistivity vs. temperature (ρ - T curves) for as-prepared and annealed samples. ●: NbCoSn, ■: NbCoSn_{0.99}Sn_{0.01}, ▲: NbCoSn_{0.98}Sn_{0.02} and ○: NbCoSn_{0.95}Sn_{0.05}.

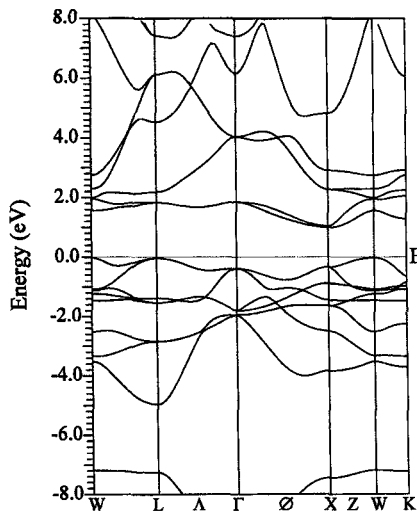


Fig.4. Band structure of NbCoSn.

NbCoSn. This compound is an indirect semiconductor with a band gap of approximately $E_g=1$ eV, which is comparable to that of TiCoSb [14]. However, as shown in Fig.3, the ρ - T curve observed for annealed NbCoSn is metallic above 400 K. The discrepancy may arise

from the residual intermixing of Nb and Co because the calculated density of states near the gap mainly come from Co3d and Nb 4d states. This situation is similar to the case of VFeSb ($E_g=0.39$ eV between L and X points), which also exhibits metallic conduction and relatively high Seebeck coefficient, $S=-70 \mu\text{VK}^{-1}$ near 300 K [15]. From the band structure calculation, Jodin et al. [16] pointed out that the energy gap of VFeSb is closed by about 10% intermixing of V and Fe, i.e., semimetallic electronic states.

3.3 Seebeck coefficient and power factor

Figure 5 shows temperature variation of Seebeck coefficient, S . All samples are n-type thermoelectric materials with $S=-60 \sim -130 \mu\text{VK}^{-1}$ near 300 K. The absolute value of S increases with increasing temperature. Enhancement of S by the annealing treatment is a remarkable feature in NbCoSn_{1-x}Sb_x, becoming less obvious with increasing Sb content. No enhancement of S was observed for the annealed

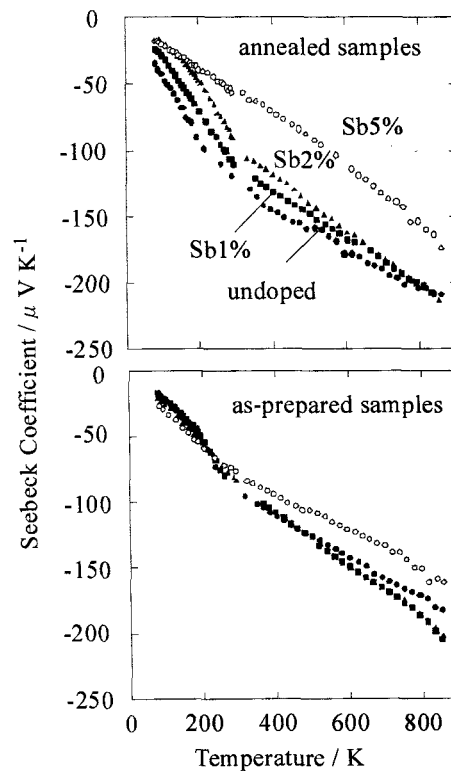


Fig.5. Seebeck coefficient vs. temperature for as-prepared and annealed samples. ●: NbCoSn, ■: NbCoSn_{0.99}Sn_{0.01}, ▲: NbCoSn_{0.98}Sn_{0.02} and ○: NbCoSn_{0.95}Sn_{0.05}.

NbCoSn_{0.95}Sn_{0.05}. The S values of annealed NbCoSn_{1-x}Sn_x ($x=0, 0.01$ and 0.02) at 850 K are almost the same ($-210\mu\text{VK}^{-1}$).

The power factors of all samples are plotted in Fig. 6. The power factors above 400 K are larger than $10\times 10^{-4}\text{Wm}^{-1}\text{K}^{-2}$. The maximum power factor, $29\times 10^{-4}\text{Wm}^{-1}\text{K}^{-2}$ at 850 K, was obtained for as-prepared NbCoSn_{0.98}Sn_{0.02}, but this value decreased to $20\times 10^{-4}\text{Wm}^{-1}\text{K}^{-2}$ after the annealing. NbCoSn_{0.95}Sb_{0.05} exhibits the maximum power factor, $25\times 10^{-4}\text{Wm}^{-1}\text{K}^{-2}$ at 850 K, among the annealed samples.

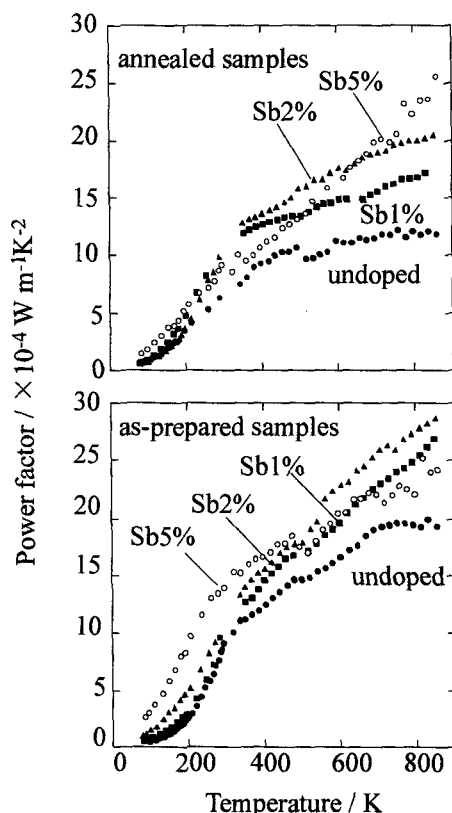


Fig.6. Power factor vs. temperature for as-prepared and annealed samples. ●: NbCoSn, ■: NbCoSn_{0.99}Sn_{0.01}, ▲: NbCoSn_{0.98}Sn_{0.02} and ○: NbCoSn_{0.95}Sn_{0.05}.

4. CONCLUSION

The Sb-doping effects on transport properties of NbCoSn have been studied in the range from 80 K to 850 K. All samples are n-type thermoelectric materials. Both the electrical resistivity and Seebeck coefficient depend on a degree of the intermixing of Nb and Co as well as Sb content. The power factors larger than $10\times 10^{-4}\text{Wm}^{-1}\text{K}^{-2}$ were observed for all samples above 400 K.

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