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# Effects of Nb substitution on thermoelectric properties of CrSi<sub>2</sub>

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# ABSTRACT

The effects of Nb substitution on the solubility range, lattice parameters, and thermoelectric properties of CrSi<sub>2</sub> with a C40-type structure have been investigated. Polycrystalline samples of Nb-substituted Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> ( $0 \le x \le 0.15$ ) have been prepared by a two-step arc-melting process, followed by spark plasma sintering. XRD patterns confirm that single-phase Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> is obtained in the composition range  $0 \le x \le 0.10$ . As *x* increases from 0 to 0.10, the *a*- and *c*-axis lengths increase linearly. For x > 0.10, the *a*- and *c*-axis lengths do not obey Vegard's rule. The electrical conductivity of Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> ( $0 \le x \le 0.10$ ) increases with increasing *x*, although the Seebeck coefficient gradually decreases with increasing *x*, owing to the reduction in lattice thermal conductivity. As a consequence, the dimensionless figure-of-merit *ZT*<sub>max</sub> increases from 0.16 (x = 0) at 600 K to 0.20 (x = 0.05) at 700 K.

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# 1. Introduction

Transition-metal silicides have been widely and extensively investigated as functional materials for various applications [1-3]. Among these silicides, semiconducting  $MnSi_{\gamma}$  [3–5] and  $CrSi_2$ [1-3,6-9] have attracted great interest as promising candidates for p-type thermoelectric (TE) materials, owing to their large power factor, low toxicity, reasonable chemical stability for hightemperature TE applications, and the natural abundance of their constituents. TE performance can be evaluated by the dimensionless figure-of-merit  $ZT = S^2 \sigma T / \kappa$ , where *S*,  $\sigma$ , *T*, and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity, respectively [10]. The binary transition-metal silicide CrSi2 is a particularly strong candidate for a p-type TE material for medium-temperature applications because it intrinsically exhibits a large power factor [6-9]. CrSi<sub>2</sub> is a degenerate semiconducting material [6,11] and has a hexagonal crystal structure (the so-called C40-type structure) with the space group  $P6_222$ , as shown in Fig. 1 [2]. Cr atom is coordinated by 10 Si atoms (6 Si atoms are in the *ab*-plane), and the typical interatomic distance between the Cr and Si atoms is about 2.56 Å. However, the crystal structure of  $CrSi_2$  is relatively simple compared to that of  $MnSi_{\gamma}$  conductivity, regardless of its large power factor. Some attempts have been made at improving the ZT value of CrSi<sub>2</sub> [16–21]. Pan et al. reported the effects of substituting V for Cr on the transport properties of single-crystalline CrSi<sub>2</sub> prepared by the opticalheating floating zone method [19]. They found that the maximum *ZT* value for  $Cr_{1-x}V_xSi_2$  was 0.20 for x = 0.08 at 450 K, owing to the great reduction in thermal conductivity. More recently, the effects of the substitution of the heavy element Mo on TE properties of polycrystalline CrSi<sub>2</sub> samples have been reported by Ohishi et al. [21]. They concluded that Mo substitution is effective in improving the ZT value because of the decrease in lattice thermal conductivity and that the maximum ZT value of  $Cr_{1-x}Mo_xSi_2$  increased from 0.13 to 0.23 for x = 0.30 at 800 K because the phonon-impurity scattering rate increases with increasing *x* as a function of the difference in mass [22]. Thus, we expect that Nb substitution in CrSi<sub>2</sub> will improve the TE performance of CrSi<sub>2</sub>. Because 4d transition-metal Nb has the same valence as V and an atomic radius comparable to that of Mo, the ZT value should increase due to an effective reduction in lattice thermal conductivity. However, there have been no reports concerning the effects of Nb substitution for Cr on TE properties of CrSi<sub>2</sub>. In this paper, we report the effects of the substitution of the heavy element Nb on the solubility range, lattice parameters, and TE properties of polycrystalline  $Cr_{1-x}Nb_xSi_2$ (0 < x < 0.15) samples, obtained by two-step arc-melting followed by spark plasma sintering.

[12–15]. Thus, CrSi<sub>2</sub> has a small *ZT* value due to its high thermal





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Fig. 1. Hexagonal C40-type crystal structure of CrSi<sub>2</sub>.

#### 2. Experimental procedure

Polycrystalline samples with nominal compositions of  $Cr_{1-x}Nb_xSi_2$  (x = 0, 0.01, 0.03, 0.05, 0.07, 0.10, 0.12, 0.15) were prepared by two-step arc melting using an arc-melting furnace (GMAC-1100, G.E.S) under Ar atmosphere using tungsten electrodes and a water-cooled copper hearth. We used stoichiometric mixtures of granular Cr (99.9%, grain size: 2-5 mm), Nb (99.9%, grain size: 2-5 mm), and Si (99.999%, grain size: 2-5 mm). First, we prepared separate ingots of CrSi<sub>2</sub> and NbSi<sub>2</sub> in order to synthesize Nb-substituted CrSi<sub>2</sub>, because we could not obtain single-phase samples of Nb-substituted CrSi2 for the nominal compositions (0 < x < 0.15) by using Cr, Nb, and Si granules and arc-melting. This is because Cr. Nb. and Si have different melting temperatures. The melting temperature,  $T_{\rm m}$ , of Nb (2742 K) is much higher than that of Cr (2136 K) and Si (1687 K) [23]. These mixtures of Cr, Si, and Nb were melted 4–6 times and turned over after each melting run to obtain homogeneous ingots of CrSi2 and NbSi2. Next, the abovementioned raw samples, i.e., CrSi<sub>2</sub> and NbSi<sub>2</sub>, were crushed using an alumina mortar and pestle and stoichiometric mixtures of these raw samples were melted 4-6 times and turned over each time to obtain fully homogeneous polycrystalline samples of  $Cr_{1-x}Nb_xSi_2$ (0 < x < 0.15). The samples used for measuring TE properties were densified by spark plasma sintering (SPS; SPS-511S, Fuji Electronic Industrial) in the temperature range 1153–1253 K under 50 MPa for 20 min. The sintered density was adjusted to around 80% for all samples, by varying the sintering temperature as shown in Table 1, for a proper comparison of the composition dependence of TE

**Table 1** Sintering temperature, density, and relative density of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples.

x	Sintering temperature (K)	Density (g/cm <sup>3</sup> )	Relative density (%)
0	1153	3.99	80.0
0.01	1223	4.12	82.6
0.03	1223	4.01	80.3
0.05	1223	4.04	80.6
0.07	1233	3.98	79.1
0.10	1253	4.08	80.5



**Fig. 2.** Powder XRD patterns of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.15$ ) samples after SPS.

properties of polycrystalline Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> samples. This is because of the decrease in sintered density with increasing Nb content, *x*. All samples after the SPS process were characterized by powder X-ray diffraction (XRD; D8 ADVANCE, Bruker) analysis using Cu K<sub>α</sub> radiation at room temperature. Rietveld refinement was performed on the XRD patterns using the JANA2006 software package [24]. The crystal structure of CrSi<sub>2</sub> was drawn with the VESTA software [25]. The electrical conductivity and Seebeck coefficient were measured simultaneously in He atmosphere from 300 to 1000 K, using an automated thermoelectric tester (ZEM-3, ULVAC-RIKO). The carrier concentration and mobility were determined by Hall measurement with PPMS (Physical Properties Measurement System, Quantum Design) at 300 K under a magnetic field of 5 T by the van der Pauw

4.50 4.45 4.45 4.40 6.40 6.40 6.36 6.36 0 0.05 0.10 0.15x

**Fig. 3.** Effects of Nb content *x* on lattice parameters (a) *a* and (b) *c* of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.15$ ) samples.

method. The thermal conductivity was measured in vacuum using a standard laser flash thermal constants analyzer (TC-7000, ULVAC-RIKO). The TE properties were measured along the pressing axis of SPS.

# 3. Results and discussion

100

(a)

Fig. 2 shows the variation in the XRD patterns of the samples obtained by two-step arc-melting and spark plasma sintering. Single-phase  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples with a C40-type structure were obtained. Small amounts of a Nb-rich (Nb, Cr)Si<sub>2</sub> secondary phase with a C40-type structure were observed in samples with nominal compositions of x > 0.10.

Fig. 3(a) and (b) plot the variation in the lattice parameters *a* and *c* with Nb content, *x*, for  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.15$ ) samples. Both the *a*- and *c*-axis lengths were in good agreement with those of Nb-free CrSi<sub>2</sub> reported previously [21] and increased linearly from a = 4.42776 (3) Å and c = 6.36858 (6) Å for x = 0 to a = 4.4684 (2) Å and c = 6.3853 (2) Å for x = 0.10, which indicates that the Cr sites were partially substituted by Nb atoms according to Vegard's rule up to x = 0.10. On the other hand, neither the *a*- nor the *c*-axis

= 0

-x = 0.01

length changed appreciably for x > 0.10. According to previous reports on V and Mo substitution of the Cr site in CrSi<sub>2</sub>, the solubility limits of each element are 0.40 and 0.30, respectively [19,21]. These results show that the solubility limit of Nb in CrSi<sub>2</sub> is much lower than those of V and Mo in CrSi<sub>2</sub>, even though Nb has the same valence as V and nearly the same atomic radius as Mo. However, the combination of two effects, namely, hole-carrier doping and the change in average atomic radius due to Nb substitution, may improve the TE properties of CrSi<sub>2</sub>.

Fig. 4(a) and (b) show the temperature dependence of the electrical conductivity and the Seebeck coefficient of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples. The electrical conductivity of Nb-free  $CrSi_2$  gradually decreased with increasing temperature from  $63 \times 10^3$  S/m at 300 K to  $28 \times 10^3$  S/m at 700 K, and increased above 700 K. Similarly, the electrical conductivity of Nb-substituted samples decreased with increasing temperature down to a minimum,  $\sigma_{min}$ , in the range of 600-800 K and this  $\sigma_{min}$  value increased with increasing temperature of the Nb-free sample gradually increased with increasing temperature up to a broad maximum,  $S_{max}$ , of around 600 K. This  $S_{max}$  value was 197  $\mu$ V/K for x = 0 at 600 K, which was comparable to the value reported





**Fig. 4.** Temperature dependence of (a) the electrical conductivity  $\sigma$  and (b) the Seebeck coefficient S of Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> ( $0 \le x \le 0.10$ ) samples.

**Fig. 5.** Effects of Nb content *x* on (a) the carrier concentration and (b) the carrier mobility of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples at 300 K.

previously [6]. With increasing hole-carrier concentration due to Nb substitution, the absolute value of  $S_{\text{max}}$  gradually decreased and the sample with x = 0.10 exhibited  $S_{\text{max}} = 113 \ \mu\text{V/K}$  at 650 K. Fig. 5(a) and (b) show the composition dependence of the carrier concentration and mobility of  $\text{Cr}_{1-x}\text{Nb}_x\text{Si}_2$  ( $0 \le x \le 0.10$ ) samples at 300 K. The carrier concentration of Nb-free  $\text{CrSi}_2$  was determined to be 5.7  $\times 10^{20}$  cm<sup>-3</sup>, which is comparable to the literature values [6,19,21], and the carrier concentration increased with increasing *x*. These results are consistent with the increase in electrical conductivity seen in Fig. 4(a) and indicate that Nb substitution for Cr in CrSi<sub>2</sub> has been successful. With increasing *x*, the mobility decreased up to x = 0.07 and then levelled off.

In order to determine the effect of Nb substitution on the TE power factor, we plot the temperature dependence of the power factor  $S^2\sigma$  of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples in Fig. 6. The maximum value of the power factor decreased with increasing *x* from  $1.3 \times 10^{-3}$  W/mK<sup>2</sup> (x = 0) at 450 K to  $0.72 \times 10^{-3}$  W/mK<sup>2</sup> (x = 0.10) at 650 K because the Seebeck coefficient decreased sharply with increasing electrical conductivity.

Fig. 7 plots the temperature dependence of the thermal conductivity measured parallel to the pressing axis of SPS for  $Cr_{1-x}Nb_xSi_2$  (0  $\leq x \leq 0.10$ ) samples. The filled and open circles respectively correspond to the total thermal conductivity,  $\kappa$ , and its carrier contribution,  $\kappa_{carrier}$ . The latter was obtained by applying the Wiedemann-Franz law to the data shown in Fig. 4(a). The  $\kappa_{carrier}$ term can be estimated to be 0.48 W/mK (x = 0) at 300 K, showing that the lattice contribution,  $\kappa_{lattice}$ , dominates in these samples. Over the entire temperature range, the total thermal conductivity of Nb-substituted  $Cr_{1-x}Nb_xSi_2$  (0.01 < x < 0.10) samples decreased, owing to the heavy element substitution with Nb, relative to that of Nb-free CrSi<sub>2</sub>. The *x* value that exhibited  $\kappa$  minima in Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> (0 < x < 0.10) was 0.05. In addition, the total thermal conductivity of  $Cr_{1-x}Nb_xSi_2$  (0.07  $\leq x \leq$  0.10) increased compared to that of Cr<sub>0.95</sub>Nb<sub>0.05</sub>Si<sub>2</sub> because the increase in the carrier thermal conductivity due to Nb substitution was larger than the decrease in the lattice thermal conductivity.

The temperature and composition dependences of the dimensionless figure-of-merit *ZT* of the  $Cr_{1-x}Nb_xSi_2$  samples were estimated from *S*,  $\sigma$ , and  $\kappa$ , as shown in Fig. 8. The Nb-free CrSi<sub>2</sub> sample exhibited a maximum *ZT* value of 0.16 at 600 K, which is larger than



Fig. 6. Temperature dependence of the TE power factor  $S^2\sigma$  of  $Cr_{1-x}Nb_xSi_2$  (0  $\leq x \leq$  0.10) samples.



**Fig. 7.** Temperature dependence of the thermal conductivity  $\kappa$  (filled circles) and the carrier contribution of thermal conductivity  $\kappa_{carrier}$  (open circles) for  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples.



Fig. 8. Temperature dependence of dimensionless figure-of-merit ZT of  $Cr_{1-x}Nb_xSi_2$  (0  $\leq x \leq 0.10$ ) samples.

previously reported values [9,21]. This is most likely due to the nonstoichiometry of Si in CrSi<sub>2</sub> [6,26]. The present Nb-substituted  $Cr_{0.95}Nb_{0.05}Si_2$  samples exhibited a maximum *ZT* of 0.20 at 700 K. However, the maximum *ZT* values of Nb-substituted  $Cr_{1-x}Nb_xSi_2$  (0.07  $\leq x \leq 0.10$ ) samples decreased to 0.13 (x = 0.10), owing to a decrease in power factor and an increase in thermal conductivity. In addition, the temperature at which *ZT* showed a maximum also increased from ~600 K for x = 0 to ~700 K for x = 0.10.

# 4. Conclusions

We studied the effects of Nb substitution on TE properties of

 $Cr_{1-x}Nb_xSi_2$ . Polycrystalline samples of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.15$ ) were prepared by two-step arc-melting, followed by spark plasma sintering. Single-phase Cr<sub>1-x</sub>Nb<sub>x</sub>Si<sub>2</sub> samples were obtained up to x = 0.10. In addition, a secondary Nb-rich (Nb, Cr)Si<sub>2</sub> phase was observed for x > 0.10. Although Nb substitution decreased the power factor, the thermal conductivity of  $Cr_{1-x}Nb_xSi_2$  ( $0 \le x \le 0.10$ ) samples decreased largely. Thus, the maximum ZT increased by a factor of about 1.2 (0.20 in Cr<sub>0.95</sub>Nb<sub>0.05</sub>Si<sub>2</sub>) relative to that of Nb-free CrSi<sub>2</sub>, owing to the large reduction in thermal conductivity. If we can control the power factor so as to maintain a low thermal conductivity, a large ZT value can eventually be obtained.

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