Substitution effect on the superconductivity in W$_{5-x}$Ta$_x$SiB$_2$ with the T$_2$ phase structure

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Abstract. We report here the magnetic susceptibility and electrical resistivity measurements of W$_{5-x}$Ta$_x$SiB$_2$. W$_{5-x}$Ta$_x$SiB$_2$ crystallizes in a tetragonal (the Mo$_5$SiB$_2$ (T$_2$ phase) type) structure. We evaluated the effect of the partial substitution of Ta in W$_5$SiB$_2$. The superconductivity was observed below $x = 2$ in W$_{5-x}$Ta$_x$SiB$_2$. As substituted Ta for W, the superconducting transition temperature ($T_c$) clearly enhanced from 5.8 K to 6.5 K. The largest volume fraction exhibits at $x = 0.2$ sample. Thus, this work shows, for the first time, the superconductivity in W$_{5-x}$Ta$_x$SiB$_2$.

Moreover, we determined that the dominant carrier sign of W$_5$SiB$_2$ are the hole from the thermoelectric power measurement and discussed about the enhancement of $T_c$ of W$_{5-x}$Ta$_x$SiB$_2$ system.

1. Introduction

One of major phase of the boro-silicide TM$_5$SiB$_2$ (TM = transition metal element), which is named as the T$_2$ phase (Mo$_5$SiB$_2$-type structure), has a tetragonal structure with the space group of I4/mcm (No. 140) [1]. The TM atoms occupy at the Wyckoff positions of 16l and 4c, and Si and B atoms are positioned at 4a and 8h sites, respectively [2]. The TM$_5$SiB$_2$ compound show the various interesting phenomena, such as ferromagnetic ordering in Fe$_5$SiB$_2$ and Mn$_5$SiB$_2$ [3,4]. Moreover, superconductors have been reported in three compounds of Mo$_5$SiB$_2$ ($T_c$ = 5.6 K), Nb$_5$SiB$_2$ ($T_c$ = 7 K), and W$_5$SiB$_2$ ($T_c$ = 5.8 K) [5,6,7].

We focused on the superconductor of W$_5$SiB$_2$ with $T_c$ of 5.8 K. The electrical resistivity, magnetization, and specific-heat data reveal that the W$_5$SiB$_2$ exhibits a conventional type-II superconductor and can be described by the BCS theory. In addition, W$_5$SiB$_2$ has been reported that the $d$-orbital of W plays an important role for the superconductivity from a viewpoint of the calculated electronic density of state [8]. In the framework of BCS theory, the higher density of state (DOS) near Fermi energy ($E_F$), lighter elements resulting in higher frequency phonon modes, and large electron-phonon interaction strength are needed for enhancing the superconducting state and $T_c$. Considering the existence of these previous studies in the BCS superconductors [9,10], it is expected that the superconducting transition temperature of W$_5$SiB$_2$ is enhanced by the substitution effect which has a increase the DOS near $E_F$.

In this paper, we successfully synthesized the polycrystalline sample of W$_{5-x}$Ta$_x$SiB$_2$ with T$_2$ phase structure using a conventional solid state reaction, and we reported the results of magnetic susceptibility and electrical resistivity measurements of a boro-silicide superconductor, W$_{5-x}$Ta$_x$SiB$_2$, with the maximum transition temperature of $T_c$ = 6.5 K with $x = 0.2$. In addition, we clarify that the
dominant carriers of W$_5$SiB$_2$ at 300 K are whether the holes or electrons by thermoelectric power evaluation.

2. Experimental details
Polycrystalline sample of W$_{5-x}$Ta$_x$SiB$_2$ were synthesized by the conventional solid state reactions following synthesis conditions in Ref. 7.

The synthesized samples were analyzed by a powder X-ray diffraction technique using a conventional X-ray spectrometer with a graphite monochromator. Intensity data were collected with CuK$\alpha$ radiation over a 2$\theta$ range from 5$^\circ$ to 80$^\circ$ at 0.02$^\circ$ step width. The magnetic susceptibilities were determined by a SQUID magnetometer (MPMS-R2, Quantum Design) at temperatures between 1.8 K and 10 K in and applied magnetic fields of $H = 10$ Oe. The electrical resistivity was measured using a conventional dc four-probe method with the measuring current of $I = 1$ mA in the temperature range between 2.5 K and 300 K, using PPMS (Quantum Design) and a laboratory-built apparatus. Electrical leads were fabricated by spot-welding gold wires (25 $\mu$m) onto the polished surface of a specimen. The thermoelectric power measurement was performed by the conventional four-probe method for bar-shape sample.

3. Experimental results and discussion
Fig. 1 displays the powder X-ray diffraction (PXRD) pattern of the synthesized sample of W$_{4.8}$Ta$_{0.2}$SiB$_2$. The diffraction peaks in PXRD pattern from the T$_2$ phase structure was observed as a main contribution. The residual minor peaks were a small amount of impurity phase, which was identified as the WSi$_2$. The PXRD data of W$_{4.8}$Ta$_{0.2}$SiB$_2$ in Fig. 1 is in good agreement with the previous one for the non-doped sample of W$_5$SiB$_2$ [5]. The W$_{4.8}$Ta$_{0.2}$SiB$_2$ can be indexed as a tetragonal unit cell with the space group I4/mcm (No. 140).

The temperature dependence of the magnetic susceptibility of W$_{5-x}$Ta$_x$SiB$_2$ ($x = 0$ and 0.2) under an applied magnetic field of $H = 10$ Oe is shown in Fig. 2. The magnetic susceptibility data were measured on the field cooling (F.C.) process. The magnetic susceptibility of W$_5$SiB$_2$ ($x = 0$) exhibited a marked drop at around 5.8 K, suggesting the occurrence of superconductivity. On the other hand, a sharp transition at around 6.5 K was observed in the data of W$_{5-x}$Ta$_x$SiB$_2$ with $x = 0.2$ in Fig. 2. We confirmed that the solution limit of Ta substitution was $x = 0.2$ because the diffraction peaks of

![Figure 1. (Color online) Powder X-ray diffraction pattern of W$_{4.8}$Ta$_{0.2}$SiB$_2$. Arrows indicate the impurity phase of WSi$_2$.](image-url)
impurity phases in the PXRD patterns increased with $x$ above $x = 0.3$ region in $W_{5-x}Ta_xSiB_2$ system. The largest superconducting volume fraction, $V.F. = \sim 15\%$ defined of $\chi$ data of $W_{4.8}Ta_{0.2}SiB_2$ at 1.8 K was confirmed.

Superconductivity can also be inferred from the result of the electrical resistivity measurements, as shown in Fig. 3. The onset transition temperatures ($T_{c\, \text{onset}}$) and the zero resistivity temperature ($T_{c\, \text{zero}}$) were observed to be 6.6 K and 6.4 K. The transition width is defined to be a temperature interval

Figure 2 (Color online) Temperature dependence of the magnetic susceptibility of $W_{5-x}Ta_xSiB_2$ with $x = 0$ and 0.2 under an applied magnetic field of $H = 10$ Oe (F.C. process).

Figure 3 (Color online) Temperature dependence of the electrical resistivity of $W_{4.8}Ta_{0.2}SiB_2$ with measuring current of $I = 1$ mA. The inset shows an enlarged view of the plot in a low-temperature range ($T \leq 10$ K) of electrical resistivity.
between 10 and 90% of the transition and was observed to be approximately \( \sim 0.15 \) K. Such a sharp transition is characteristic of a sample with a good quality. The residual resistivity ratio (RRR), \( \rho_{300K}/\rho_0 \) (where \( \rho_0 \) is the residual resistivity at \( T_c \) onset), was obtained to be \( \sim 6.5 \), which is a fine value despite the existence of a minor impurity phase in measured sample. The defined \( T_c \) in the electrical resistivity measurement is in good agreement with the magnetic susceptibility result. From the results of both the magnetic susceptibility and the electrical resistivity measurements, \( T_c \) of \( W_{4.8}Ta_{0.2}SiB_2 \) was determined to be 6.5 K.

In order to determine a type of dominant carrier of \( W_{5}SiB_2 \), the Seebeck coefficient, \( S \), was determined at 300 K by using the thermoelectric-power measurement. The value of the \( S \) of \( W_{5}SiB_2 \) at 300 K was to be about \( S = \sim 0.85 \) \( \mu \)V/K. The positive sign of \( S \) indicates that the dominant carriers of \( W_{5}SiB_2 \) are holes. The electrons of \( d \)-orbital in Ta atom are less one electron than that of \( d \)-orbital in W atoms. This fact suggests that the enhancement of \( T_c \) of \( W_{5}SiB_2 \) was induced by increasing a density of hole carriers by partial substituted Ta for W in \( W_{5-x}Ta_xSiB_2 \) system.

In summary, we validated the effect of Ta partial substitution on the superconductivity in \( W_{5-x}Ta_xSiB_2 \) system. The superconducting transitions of \( W_{5-x}Ta_xSiB_2 \) were observed from the electrical resistivity and magnetic susceptibility measurements. The maximum superconducting volume fraction was confirmed from the data of \( W_{4.8}Ta_{0.2}SiB_2 \) with \( T_c = 6.5 \) K. This enhancement of \( T_c \) in \( W_{5-x}Ta_xSiB_2 \) system suggests the results of increment of the density of state near Fermi energy. Further experiments on the superconducting state are necessary and desirable to clarify superconducting state for \( W_{5-x}Ta_xSiB_2 \), such as specific heat measurements and theoretical calculation of electronic state.

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References

[1] R. Sakidja, J. H. Perepezko, S. Kim, and N. Sekido: Acta Materialia 56 (2008) 5223.
[2] C. J. Rawn, J. H. Schneibel. C. M. Hoffmann, and C. R. Hubbard: Intermetallics 9 (2001) 209.
[3] D. M. Almeida, C. Bormio-Nunes, C. A. Nunes, A. A. Coelho, and G. C. Coelho: J. Magn. Magn. Mater. 321 (2009) 2578.
[4] V. Reghavan: J. Phase Equilibria Diffusin 28 (2007) 380.
[5] P. Peshev, G. Gyurov, R. Stoyanchev, Izv. Khim. 19 (1986) 267.
[6] A. Brauner, C. A. Bortolozo, G. Rodrigues, A. J. S. Machado, Solid State Commun. 149 (2009) 467.
[7] M. Fukuma, K. Kawashima, M. Maruyama, J. Akimitsu, J. Phys. Soc. Jpn. 80 (2011) 024702.
[8] M. Fukuma, K. Kawashima, M. Maruyama, J. Akimitsu, Physica C 471 (2012) 714.
[9] E. E. Havinga, H. Damsma and M. H. van Maar, J. Phys. Chem. Solids 31 (1970) 2653.
[10] E. E. Havinga, H. Damsma and J. M. Kanis, J. Less-Common Met. 27 (1972) 281.