Superconductivity of $\text{MI(Al}_{0.5}, \text{Si}_{0.5})_2$ (MI=Sr and Ba, MII=Al and Ga), ternary silicides with the AlB$_2$-type structure

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Ternary silicides $\text{MI(Al}_{0.5}, \text{Si}_{0.5})_2$ (MI=Sr and Ba, MII=Al and Ga) were prepared by Ar arc melting. Powder X-ray diffraction indicates that they have the AlB$_2$-type structure, in which Si and MII atoms are arranged in honeycomb layers and MI atoms are intercalated between them. Electrical resistivity and dc magnetization measurements revealed that $\text{Sr(Al}_{0.5}, \text{Si}_{0.5})_2$ is superconductive, with a critical temperature for superconductivity ($T_C$) of 4.2 K, while $\text{Ba(Al}_{0.5}, \text{Si}_{0.5})_2$ is not at temperatures ranging above 2.0 K. $\text{Sr(Ga}_{0.5}, \text{Si}_{0.5})_2$ and $\text{Ba(Ga}_{0.5}, \text{Si}_{0.5})_2$ are also superconductors, with $T_C$s of 5.1 and 3.3 K, respectively.

Keywords: superconductivity, silicide, AlB$_2$-type structure, $\text{Sr(Al, Si)}_2$
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1. Introduction

Superconductivity at 39 K was recently reported with an intermetallic compound, MgB$_2$ [1]. Magnesium diboride has the AlB$_2$-type (C32-type) structure and, therefore, related compounds are attracting attention because of their potential as new superconductors. The discovery and study of new superconductors with the AlB$_2$-type structure are relevant to our understanding of the origin of the superconductivity of MgB$_2$. Silicides, as well as borides, also contain compounds with the AlB$_2$-type structure or a structure related to it.

Of binary silicides, ThSi$_2$ [2], USi$_2$ [3], and several rare-earth metal disilicides [4, 5] are known to have an AlB$_2$-type structure. Among them, β-ThSi$_2$ is known to be a superconductor with a critical temperature $T_C$ of 2.41 K [6]. A high-pressure phase of CaSi$_2$, which appears above 16 GPa, has an AlB$_2$-like structure in which Si atoms form slightly corrugated honeycomb layers [7]. This phase of CaSi$_2$ is superconductive, with a $T_C$ of 14 K at such pressures [8], while the ambient phase is not [9]. This high-pressure phase cannot be quenched at ambient conditions.

Recently, ternary silicides $M_{Al}(Ga_{x}, Si_{1-x})_2$ ($M_{Al}$=Ca, Sr, and Ba) have been reported to have the AlB$_2$-type structure and to be superconductors with a $T_C$ ranging from 3.3 to 3.9 K [10, 11]. Furthermore, a ternary silicide, Ca$(Al_{0.5}, Si_{0.5})_2$, which has the AlB$_2$-type structure, has been reported to be a superconductor with a $T_C$ of 7.7 K [12]. Ternary silicides $Sr(Al_{x}, Si_{1-x})_2$ and $Ba(Al_{x}, Si_{1-x})_2$ have been reported to have the AlB$_2$-type structure [13-16], though their electrical properties have not been examined yet. It would be interesting to examine whether the $Sr(Al_{x}, Si_{1-x})_2$ and $Ba(Al_{x}, Si_{1-x})_2$ show superconductivity, as $M_{Al}(Ga_{x}, Si_{1-x})_2$ and Ca$(Al_{0.5}, Si_{0.5})_2$ do.

Here, we report the synthesis of ternary silicides $Sr(Al_{0.5}, Si_{0.5})_2$ and $Ba(Al_{0.5}, Si_{0.5})_2$ and demonstrate that $Sr(Al_{0.5}, Si_{0.5})_2$ is a superconductor. We also investigated $Sr(Ga_{0.5}, Si_{0.5})_2$ and $Ba(Ga_{0.5}, Si_{0.5})_2$ for comparison.

2. Experimental

The samples were prepared by Ar arc melting of 1 : 1 : 1 stoichiometric mixtures of $M_I$ ($M_I$= Sr and Ba, nominal purity 99.5 %), $M_{II}$ ($M_{II}$=Al and Ga, nominal purity 99.999 %), and Si (nominal purity 99.9999 %). In the following, ARC-$M_I M_{II}$ denotes the sample prepared by Ar arc melting of 1 : 1 stoichiometric mixtures of $M_I$, $M_{II}$, and Si. Their chemical compositions were determined using electron probe microanalysis (EPMA). The samples for EPMA were prepared by polishing with an oil-based diamond slurry to avoid a reaction with water. The structure of the silicides was examined using a powder X-ray diffraction method. Electrical resistivity was measured by means of the four-probe method at temperatures ranging from 2 to 290 K. Since ARC-SrAl and ARC-BaAl were slightly sensitive to moisture in air, they were covered with insulating varnish (General Electric, 7031) after spark-bonding of Au wires. dc magnetization was measured using a SQUID magnetometer at temperatures ranging from 2 to 12 K.

3. Results

Map analysis by EPMA shows that all the samples consist of almost a single phase, though they contain small amounts of precipitates. Table I lists the average chemical
composition of the main phase determined with EPMA, which confirms that the 
$M_1(M_{II0.5}S_{i0.5})_2$ phase is the main one in all the samples. A small amount of oxygen was 
detected in ARC-BaGa. This would be, however, due to the surface oxidization of samples 
because the amount of oxygen detected was small and it was also detected in the 
precipitates.

Figure 1 shows the powder X-ray diffraction patterns of the samples and calculated 
diffraction patterns for the $M_1(M_{II0.5}S_{i0.5})_2$ phase with the AlB$_2$-type structure. For the 
calculation, we assumed that the compound $M_1(M_{II0.5}S_{i0.5})_2$ would have the AlB$_2$-type 
structure with the observed lattice constants described below, in which the 2d site is 
chemically disordered with occupation probabilities of 0.5 for the element $M_{II}$ and 0.5 for 
$Si$. The major observed reflections are reproduced well by the assumed structure, as shown 
in Fig. 1. These results indicate that the $M_1(M_{II0.5}S_{i0.5})_2$ phase has the AlB$_2$-type structure.

Their lattice constants are listed in Table II, together with those of Ca($Al_{0.5}$, $Si_{0.5}$)$_2$ [12] 
and Ca($Ga_{0.5}$, $Si_{0.5}$)$_2$ [11]. When the alkaline-earth elements are changed, the lattice 
constants change anisotropically: the lattice constant $a$ increases by 2.5 % for $M_1(Al_{0.5}$, 
$Si_{0.5})_2$ and by 3.3 % for $M_1(Ga_{0.5}$, $Si_{0.5})_2$, while the lattice constant $c$ increases by 16.9 % for 
$M_1(Al_{0.5}$, $Si_{0.5})_2$ and 14.9 % for $M_1(Ga_{0.5}$, $Si_{0.5})_2$ when the alkaline-earth elements are 
changed in the sequence Ca, Sr, and Ba.

Figures 2 and 3show the electrical resistivity of $M_1(Al_{0.5}$, $Si_{0.5})_2$ and $M_1(Ga_{0.5}$, $Si_{0.5})_2$ as a 
function of the temperature, respectively. The resistivity starts to decrease at temperature $T_{C \text{ONSET}}$ and becomes negligibly small at temperature $T_{C \text{ZERO}}$ in all the samples except for 
$Ba(Al_{0.5}$, $Si_{0.5})_2$. Table III lists $T_{C \text{ONSET}}$ and $T_{C \text{ZERO}}$ together with those of related materials. 
The resistivity of $Ba(Al_{0.5}$, $Si_{0.5})_2$ decreases continuously with decreasing the temperature 
down to 2 K, the lowest temperature of this experiment. These results suggest that the 
silicides $M_1(M_{II0.5}$, $Si_{0.5})_2$ become superconductive at $T_{C \text{ZERO}}$ except for $Ba(Al_{0.5}$, $Si_{0.5})_2$.

Figure 4 shows the dc magnetization $M$ of $M_1(M_{II0.5}$, $Si_{0.5})_2$ except for $Ba(Al_{0.5}$, $Si_{0.5})_2$ in 
a field $H$ as a function of the temperature. The triangles and circles show data obtained in 
zero-field cooling (ZFC) and those in field cooling (FC), respectively. The samples show a 
Meissner effect (flux exclusion) below a temperature $T_{C \text{MEIS}}$ in FC, which confirms 
the presence of a superconducting phase below the temperature, as indicated by the resistivity 
measurements. Table III also lists $T_{C \text{MEIS}}$, the magnetic shielding fraction in ZFC, and the 
flux exclusion in FC at 2.0 K. These indicate that the superconductivity is a bulk effect. On 
this basis, we conclude that ternary silicides $M_1(M_{II0.5}$, $Si_{0.5})_2$ are superconductors with the 
AlB$_2$-type structure, except for $Ba(Al_{0.5}$, $Si_{0.5})_2$. Therefore, it is revealed that six ternary 
MAE-M$_{II}$-Si systems (MAE=Ca, Sr, and Ba, M$_{II}$=Al and Ga) have compounds with the AlB$_2$-
type structure, and the compounds in the systems are superconductive, except for that in the 
Ba-Al-Si system.

4. Discussion

In the silicides with the same third element $M_{II}$, the $T_C$ depends on the choice of MAE. In 
the silicides MAE($Al_{0.5}$, $Si_{0.5})_2$, the $T_C$ decreases when the element MAE is changed from Ca 
into Sr and finally becomes lower than 2 K, the lowest temperature in this study, when the
element MAE is Ba. On the other hand, in the silicides MAE(Ga0.5, Si0.5)2, the TC becomes the highest when the element MAE is Sr.

In the Bardeen-Cooper-Schrieffer theory, the TC is estimated as

$$T_C = 1.13\Theta_D \exp(-1/N(E_F)V),$$

where $\Theta_D$ is the Debye frequency, $N(E_F)$ is the density of states at the Fermi level, and $V$ is the average electron pairing interaction [17]. In the silicides MAE(B0.5, Si0.5)2, the Debye temperature is expected to be the same because the composition of honeycomb layers is the same in the three compounds. Therefore, the different $T_C$ in MAE(MII0.5, Si0.5)2 would be attributed to the change in $N(E_F)$ under the assumption that $V$ is independent of the choice of MAE. The change of the element MAE affects $N(E_F)$ in two ways. One is the effect on the Fermi energy. When the element MAE is changed in the sequence Ca, Sr, and Ba, the volume of the unit cell increases, as shown in Table II, and the valence electron density decreases. Consequently, the Fermi energy decreases in the sequence because the Fermi energy is proportional to $2/3$ the power of the valence electron density. For instance, the difference in the Fermi energy between Ca(Al0.5, Si0.5)2 and Ba(Al0.5, Si0.5)2 is roughly estimated to be 13 %. The other is an effect on the shape of the density of states (DOS). By analogy with the calculated electronic structure of CaSi2 with the AlB2-type structure [18, 19], the $N(E_F)$ of MAE(MII0.5, Si0.5)2 consists of mixed states of $d$ states of the element MAE and $p$ states of the element MII and Si. The $d$ states are expected to shift upwards when the element MAE is changed in the sequence Ca, Sr, and Ba. The upward shift of the $d$ states changes the shape of DOS. Therefore, the change of the element MAE causes the shift of the Fermi energy, the change of the DOS shape, and, consequently, the change of $N(E_F)$. This would be reflected on the difference in the $T_C$ among MAE(MII0.5, Si0.5)2 with the same third element MII.

In summary, the ternary silicides $M_0(MII0.5, Si0.5)2$ were found to be superconductors with the AlB2-type structure, except for Ba(Al0.5, Si0.5)2. Therefore, silicides with the AlB2-type structure in MAE-MII-Si systems are concluded to be superconductive, except for that in the Ba-Al-Si system. On the other hand, in the binary alkaline-earth metal-boron system, only Mg forms a diboride with the AlB2-type structure. In this sense, these ternary systems are in contrast with the binary alkaline-earth metal-boron system: the ternary alkaline-earth silicides have wider variations of the compounds with the AlB2-type structure than the binary alkaline-earth metal diborides.

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Table I. Chemical compositions of the main phase in the samples.

| Sample   | M_I (at. %) | M_II (at. %) | Si (at. %) | Phase                        |
|----------|-------------|--------------|------------|------------------------------|
| ARC-SrAl | 31.8        | 33.0         | 35.2       | Sr(Al_{0.5}Si_{0.5})_2       |
| ARC-SrGa | 33.8        | 33.2         | 33.0       | Sr(Ga_{0.5}Si_{0.5})_2       |
| ARC-BaAl | 32.7        | 33.3         | 34.0       | Ba(Al_{0.5}Si_{0.5})_2       |
| ARC-BaGa a) | 33.4        | 33.8         | 30.9       | Ba(Ga_{0.5}Si_{0.5})_2       |

a) 1.8 at.% oxygen was detected in ARC-BaGa.
Table II. Lattice constants and theoretical density of \( M_i (M_{II0.5}Si_{0.5})_2 \) phases, together with those of \( Ca(Al_{0.5}Si_{0.5})_2 \) and \( Ca(Ga_{0.5}Si_{0.5})_2 \) phases.

| Phase                        | a(Å)          | c(Å)          | Volume (Å³) | Theoretical density (gcm⁻³) |
|------------------------------|---------------|---------------|-------------|-----------------------------|
| \( Ca(Al_{0.5}Si_{0.5})_2 \) | 4.1905(5)     | 4.3992(8)     | 66.90       | 2.37                        |
| \( Sr(Al_{0.5}Si_{0.5})_2 \) | 4.2475(3)     | 4.7421(6)     | 74.09       | 3.14                        |
| \( Ba(Al_{0.5}Si_{0.5})_2 \) | 4.2973(8)     | 5.1424(17)    | 82.24       | 3.84                        |
| \( Ca(Ga_{0.5}Si_{0.5})_2 \) | 4.1200(8)     | 4.4401(1)     | 65.27       | 3.43                        |
| \( Sr(Ga_{0.5}Si_{0.5})_2 \) | 4.1875(4)     | 4.7447(4)     | 72.05       | 4.29                        |
| \( Ba(Ga_{0.5}Si_{0.5})_2 \) | 4.2587(4)     | 5.1039(9)     | 80.17       | 4.85                        |

a) Reference 12.
b) Reference 11.
Table III. Parameters of silicides $M_{AE}(M_{II}, Si_{1-x})_2$ ($M_{AE}$=Ca, Sr, and Ba, $M_{II}$=Al and Ga) observed in electrical resistivity and magnetization measurements. Units used in the magnetic shielding fraction and flux exclusion are a percentage of the theoretical value of the perfect diamagnetism ($1/4\pi$).

| Silicide                  | $T_C^{ONSET}$ (K) | $T_C^{ZERO}$ (K) | $T_C^{MEIS}$ (K) | Magnetic shielding fraction in ZFC at 2 K (%) | Flux exclusion in FC at 2 K (%) |
|---------------------------|-------------------|------------------|------------------|---------------------------------------------|-------------------------------|
| Ca($Al_{0.5}, Si_{0.5}$)$_2$ a) | 8.0               | 7.7              | 7.7              | 60                                          | 7                             |
| Sr($Al_{0.5}, Si_{0.5}$)$_2$ | 4.3               | 4.2              | 4.2              | >90                                         | 8                             |
| Ca($Ga_{0.5}, Si_{0.5}$)$_2$ b) | 4.5               | 3.3              | 4.3              | 90                                          | 3                             |
| Ca($Ga_{0.37}, Si_{0.63}$)$_2$ b) | 3.6               | 3.5              | 3.5              | 80                                          | 0.6                           |
| Sr($Ga_{0.5}, Si_{0.5}$)$_2$   | 5.2               | 5.1              | 5.1              | 90                                          | 8                             |
| Sr($Ga_{0.37}, Si_{0.63}$)$_2$ b) | 4.7               | 3.6              | 4.2              | 90                                          | 4                             |
| Sr($Ga_{0.37}, Si_{0.63}$)$_2$ c) | 3.5               | 3.4              | 3.4              | 80                                          | 8                             |
| Ba($Ga_{0.50}, Si_{0.50}$)$_2$ | 4.1               | 3.3              | 3.9              | 90                                          | 8                             |
| Ba($Ga_{0.39}, Si_{0.61}$)$_2$ b) | 4.3               | 3.9              | 4.0              | >90                                         | 6                             |

a) Reference 12.

b) Reference 11.

c) Reference 10.
Fig. 1. Powder X-ray diffraction patterns of $M_I(M_{II0.5}, Si_{0.5})_2$ ($M_I=$ Sr and Ba, $M_{II}=$ Al and Ga).

Fig. 2. Electrical resistivity of $M_I(Al_{0.5}, Si_{0.5})_2$ ($M_I=$ Sr and Ba) as a function of the temperature.

Fig. 3. Electrical resistivity of $M_I(Ga_{0.5}, Si_{0.5})_2$ ($M_I=$ Sr and Ba) as a function of the temperature.

Fig. 4. dc magnetization $M$ of $Sr(Al_{0.5}, Si_{0.5})_2$, $Sr(Ga_{0.5}, Si_{0.5})_2$, and $Ba(Ga_{0.5}, Si_{0.5})_2$ measured in field $H$ as a function of the temperature. The abbreviations “ZFC” and “FC” represent the magnetization measured in zero-field cooling and field cooling, respectively.
Fig. 1 M. Imai et al.
Fig. 2 M. Imai et al.
Fig. 3 M. Imai et al.
Fig. 4 M. Imai et al.