

## Phase transitions of BaSi<sub>2</sub> at high pressures and high temperatures

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*In situ* x-ray diffraction measurements reveal that BaSi<sub>2</sub> has three high-pressure, high-temperature phases: a trigonal, a cubic, and an additional phase, at pressures up to 7 GPa and temperatures up to 1300 K. The trigonal phase exists at lower temperatures than previously reported, and the additional phase appears in the pressure-temperature region reported as the trigonal region previously. The structures that appear at high pressures are the same as those at ambient conditions of the other alkaline-earth-metal disilicides with a smaller atomic number metal. This is different from structural sequence for pure elements or for AB<sub>2</sub>-type compounds such as dioxides of 4A group elements. [S0163-1829(98)07841-2]

### INTRODUCTION

Silicides have attracted attention as potential constituents of microelectronic and optoelectronic devices. Some silicides can have different crystal structures from the stable one at ambient conditions, and the electrical properties are dependent on their structure. BaSi<sub>2</sub> has three crystallographic forms at ambient conditions: orthorhombic, cubic, and trigonal.<sup>1-4</sup> Recently, it has been shown that the electrical properties strongly depend on the crystal structure: orthorhombic and cubic BaSi<sub>2</sub> are semiconductors, and trigonal BaSi<sub>2</sub> is a metal which shows superconductivity with an onset temperature of 6.8 K.<sup>5-7</sup>

The orthorhombic form is stable at ambient conditions, and the others are metastable.<sup>4</sup> The metastable phases are synthesized by subjecting orthorhombic BaSi<sub>2</sub> to high-pressure, high-temperature conditions and subsequently returning it to ambient conditions rapidly (called quench experiments hereafter).<sup>2-7</sup> Evers used this technique to construct a pressure-temperature (*p-T*) diagram of BaSi<sub>2</sub> in the temperature range from 773 to 1273 K and pressure range from 0 to 4 GPa, assuming that both observed phases are high-pressure, high-temperature phases, and are quenched without a change in their structures.<sup>4</sup> Recent *in situ* x-ray diffraction studies have confirmed that both the trigonal and the cubic phases exist as high-pressure, high-temperature phases, and are quenched without a change in their structures.<sup>8</sup> The *p-T* diagram of BaSi<sub>2</sub> is, however, still unclear. The *p-T* conditions where the trigonal phase appears in the *in situ* experiments (5.2 GPa, 673 K) are consistent with those of our previous quench experiments,<sup>5-7</sup> but the temperature is much lower than that estimated from Evers' phase diagram. Since the previous *in situ* experiments were carried out only at 5.2 GPa and temperatures from 300 to 873 K, further investigation in a wider *p-T* region is still needed to clear the *p-T* diagram of BaSi<sub>2</sub>.

In this study, the *p-T* diagram of BaSi<sub>2</sub> is investigated by the *in situ* x-ray diffraction technique at pressures up to 7

GPa and temperatures up to 1300 K. The observed structural sequence at high pressures is discussed in comparison with those known already for the elements and other AB<sub>2</sub>-type compounds.

### EXPERIMENT

Details of the experiments have been described previously.<sup>8</sup> High pressures were applied using the multianvil high-pressure apparatus MAX80, which is installed in the beam line of the TRISTAN accumulation ring (AR-NE5) at the National Laboratory for High Energy Physics.<sup>9,10</sup> Powdered orthorhombic BaSi<sub>2</sub>, the starting sample, was loaded into a *h*-BN capsule and the capsule was set in the center of the boron-epoxy pressure transmitting medium.<sup>8</sup> Temperature was measured by an alumel-chromel thermocouple attached to the *h*-BN sample capsule. Pressure was evaluated from the lattice constant of an NaCl internal pressure marker.<sup>11</sup> X-ray diffraction patterns were measured by an energy dispersive method using synchrotron radiation from the bending magnet. X-ray diffraction patterns of CaSi<sub>2</sub> and SrSi<sub>2</sub> at high temperatures were measured under He atmosphere with the conventional angle dispersive method using a Cu *K*α line.

### RESULTS

When BaSi<sub>2</sub> is compressed up to 7.1 GPa at room temperature, the orthorhombic phase shows no phase transition; only the positions of the diffraction peaks shift to lower *d* values and the peak widths become broader. When the sample is heated at 0.8 GPa, it shows no phase transition up to 873 K.

Figure 1 shows x-ray diffraction patterns of BaSi<sub>2</sub> for various temperatures at 5.2 GPa. BaSi<sub>2</sub> undergoes the orthorhombic-trigonal transition at 673 K and the trigonal-cubic transition at 873 K, as reported in Ref. 8. The trigonal-cubic transition is sluggish. At 973 K, a large part of the sample transforms into the cubic phase, but the trigonal

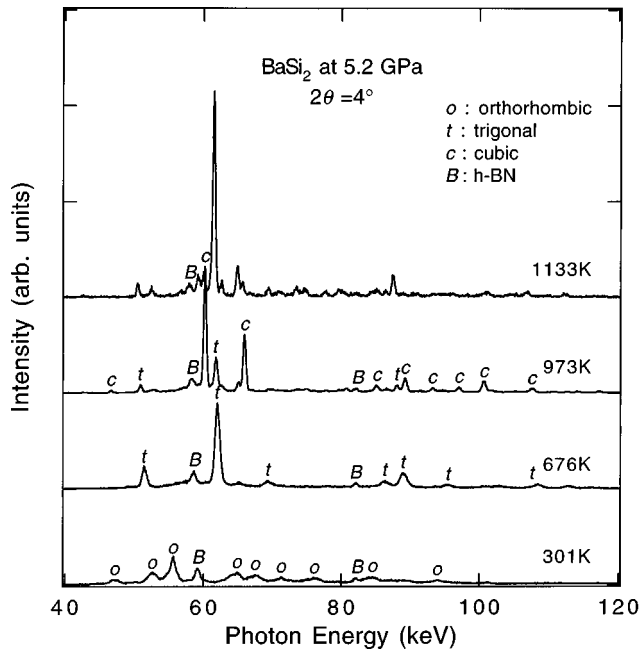


FIG. 1. X-ray diffraction patterns of  $\text{BaSi}_2$  for various temperatures at 5.2 GPa. The symbol “B” represents reflections from the *h*-BN sample capsule.

phase still remains. When the sample is heated up to 1073 K, there appears another phase that is different from both the cubic phase and the trigonal phase. Its crystal structure has not been determined yet. We shall refer to it subsequently as  $\text{BaSi}_2\text{-IV}$ . Details of  $\text{BaSi}_2\text{-IV}$  are under investigation. A similar series of phase transitions was observed when orthorhombic  $\text{BaSi}_2$  was heated at about 3 and 4 GPa.

At 7.1 GPa, orthorhombic  $\text{BaSi}_2$  transforms into trigonal  $\text{BaSi}_2$  at 723 K. When the sample is further heated, the trigonal phase transforms into  $\text{BaSi}_2\text{-IV}$ . The cubic phase does not appear upon heating at this pressure.

Figure 2 shows the  $p$ - $T$  diagram of  $\text{BaSi}_2$ . In the  $p$ - $T$  region investigated,  $\text{BaSi}_2$  has three high-pressure, high-temperature phases: trigonal, cubic, and  $\text{BaSi}_2\text{-IV}$ . The orthorhombic phase, which is stable at ambient conditions, exists over a wide pressure range at temperatures below 673 K. At pressures from 2.9 to 5.2 GPa, heating induces a series of phase transitions: orthorhombic  $\rightarrow$  trigonal  $\rightarrow$  cubic  $\rightarrow$   $\text{BaSi}_2\text{-IV}$ . When heated at 7.1 GPa,  $\text{BaSi}_2$  undergoes the following phase transitions: orthorhombic  $\rightarrow$  trigonal  $\rightarrow$   $\text{BaSi}_2\text{-IV}$ ; the  $p$ - $T$  region for the cubic phase disappears at this pressure. The present  $p$ - $T$  regions for cubic and trigonal  $\text{BaSi}_2$  are consistent with those for quench experiment synthesis done previously by our group,<sup>5-7</sup> as shown by the solid square and triangle in Fig. 2. The broken lines show phase boundaries determined by Evers with quench samples at temperatures from 773 to 1273 K and pressures from 0 to 4.4 GPa.<sup>4</sup> The  $p$ - $T$  regions for the orthorhombic and the cubic phases are consistent with the diagram of Evers. On the other hand, the  $p$ - $T$  region for the trigonal phase is different. We find the trigonal phase at temperatures above 400 K lower than those where Evers synthesized the trigonal samples. Furthermore, we observe  $\text{BaSi}_2\text{-IV}$  in the  $p$ - $T$  regions where Evers synthesized trigonal  $\text{BaSi}_2$ .

Figure 3 shows the volume per formula unit of  $\text{BaSi}_2$  as a

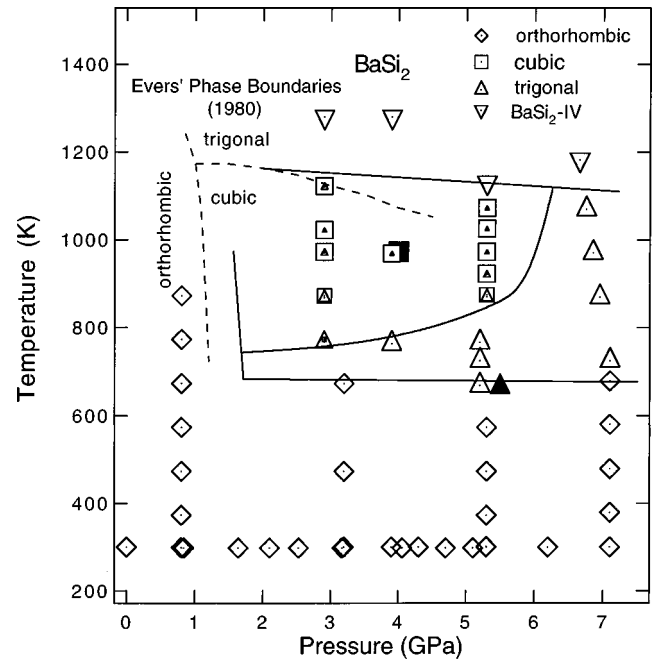


FIG. 2. Pressure-temperature diagram of  $\text{BaSi}_2$ . At the  $p$ - $T$  conditions where two phases are observed, the size ratio of symbols is proportional to the intensity ratio of the strongest lines in the diffraction pattern. The solid square and the solid triangle show the  $p$ - $T$  conditions where the cubic and the trigonal phases were synthesized with our quench experiments, respectively (Refs. 5–7). The solid lines are visual guides. The broken lines are phase boundaries determined by Evers (Ref. 4).

function of temperature. When  $\text{BaSi}_2$  is compressed to 7.1 GPa at room temperature, its volume decreases by 17%. At the orthorhombic-to-trigonal transition for a given pressure, the volume decreases by a large amount (7% at 5.2 GPa). On the other hand, the volume increases by a small amount at the trigonal-to-cubic transition (1% at 5.2 GPa). The volume of the cubic phase is about 1% larger than that of the trigonal phase also in the region of coexistence.

## DISCUSSION

$\text{BaSi}_2$  undergoes the phase transitions when heated at high pressures. The resultant high-pressure, high-temperature phases are quenched to the ambient conditions. Furthermore, it is reported that both the cubic and the trigonal phases return to the orthorhombic phase when heated at atmospheric pressure.<sup>4</sup> These facts suggest that the high-pressure, high-temperature phases are quenched as metastable phases, and the energy barriers for the transitions from the high-pressure, high-temperature phases to the orthorhombic phase are large compared with room temperature. We think the energy barriers for the orthorhombic to high-pressure, high-temperature phase transition are also large. When  $\text{BaSi}_2$  is compressed at room temperature, the diffraction peak height becomes lower and the width becomes broader. When heated at high pressures, the height becomes higher and the widths become narrower. This suggests that compression distorts  $\text{BaSi}_2$  inhomogeneously, and heating relaxes this inhomogeneous distortion. It means  $\text{BaSi}_2$  needs higher temperature than room temperature even in order to relax distortion. There-

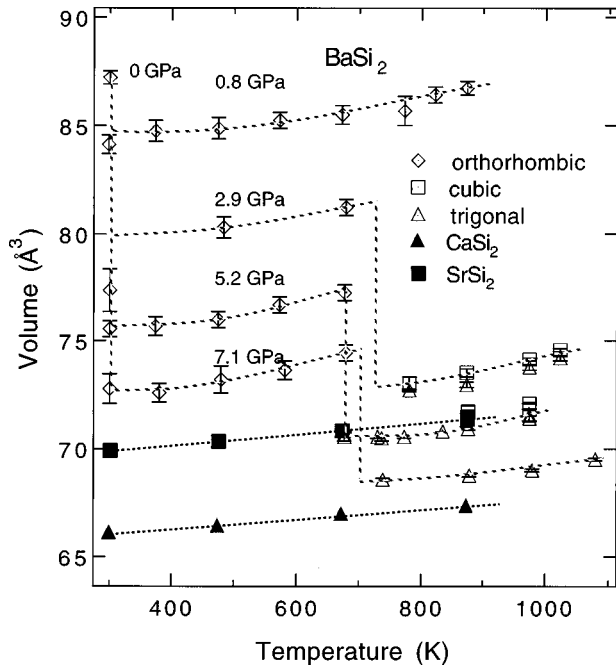


FIG. 3. Volume per formula unit of  $\text{BaSi}_2$  at various pressure-temperature conditions. Solid squares and triangles are the atmospheric pressure volume per formula unit of  $\text{SrSi}_2$  with the cubic structure and  $\text{CaSi}_2$  with the trigonal structure, respectively. The broken and dotted lines are visual guides.

fore,  $\text{BaSi}_2$  is expected to need higher temperature to undergo phase transitions where atomic configuration changes more drastically. Thus we think pressure changes stability of the phases, and temperature plays an important role to overcome the energy barriers for the transitions. Probably this is a reason why  $\text{BaSi}_2$  shows the phase transitions when heated.

The present results show that the structure of  $\text{BaSi}_2$  changes from orthorhombic to trigonal and cubic at high pressures, and that the cubic phase disappears but the trigonal phase remains at the highest pressure of our experiment. The structure of cubic  $\text{BaSi}_2$  is the same as that of stable phase of  $\text{SrSi}_2$  at ambient conditions.<sup>3,4</sup> The structure of trigonal  $\text{BaSi}_2$  consists of layer-by-layer packing in which corrugated Si hexagonal layers alternate with hexagonal Ba layers along the [001] direction,<sup>2,4</sup> and this is the same as the structure of stable phase of  $\text{CaSi}_2$  at ambient conditions except for a small difference in the stacking sequence of the metal and Si layers.<sup>12</sup> This means that, in  $\text{BaSi}_2$ , the structures that appear at high pressures are the same as those of the other alkaline-earth-metal disilicides with a smaller atomic number metal. On the other hand, it is known that an element at high pressures transforms into the structure of elements with a larger atomic number in the same group.<sup>13,14</sup> For example, in the case of 4A group elements, C with the graphite-type structure transforms into the diamond-type structure at high temperature and high pressure, Si and Ge with the diamond-type structure transform into the  $\beta$ -Sn-type structure at high pressure, and Sn has the  $\beta$ -Sn-type structure at room temperature and atmospheric pressure. Although the investigation on structural sequence of compounds at high pressures is scarce, this relationship is observed also in  $AB_2$ -type compounds such as the dioxides of 4A group elements:  $\text{SiO}_2$ ,<sup>15-17</sup>  $\text{GeO}_2$ ,  $\text{SnO}_2$ ,<sup>18,19</sup> and  $\text{PbO}_2$ .<sup>20,21</sup> Therefore,

TABLE I. The interatomic distances in the three phases of  $\text{BaSi}_2$  (Ref. 5), in  $\text{SrSi}_2$  (Ref. 22), and in  $\text{CaSi}_2$  (Ref. 23) at atmospheric pressure. The numbers in parentheses are average interatomic distances.

	Metal-Metal	Metal-Si	Si-Si
Orthorhombic	4.25–4.76	2.95–3.68	2.32–2.47
$\text{BaSi}_2^a$	(ave. 4.52)	(ave. 3.47)	(ave. 2.40)
Cubic $\text{BaSi}_2^a$	4.11	3.37	2.45
Trigonal $\text{BaSi}_2^a$	4.05	3.28	2.45
$\text{SrSi}_2^b$	4.00	3.25	2.39
$\text{CaSi}_2^c$	3.86	3.01–3.03	2.45
		(ave. 3.01)	

<sup>a</sup>Reference 5.

<sup>b</sup>Reference 22.

<sup>c</sup>Reference 23.

the structural sequence of  $\text{BaSi}_2$  at high pressures is different, in fact opposite, from the structural sequence known already in elements or other binary  $AB_2$ -type compounds.

The solid triangles and squares in Fig. 3 represent the atmospheric pressure volumes of  $\text{CaSi}_2$  and  $\text{SrSi}_2$ , respectively. Since the atomic volumes of Sr and Ca are each smaller than that of the Ba atom, the replacement of Ba with Sr and Ca should reduce the volume of the silicides. Indeed we observe that the volumes of  $\text{SrSi}_2$  and  $\text{CaSi}_2$  are smaller than that of orthorhombic  $\text{BaSi}_2$  at atmospheric pressure. The volume of  $\text{SrSi}_2$  is in the volume region where cubic  $\text{BaSi}_2$  is observed and that of  $\text{CaSi}_2$  is in the region where only trigonal  $\text{BaSi}_2$  is observed. The same structure is, therefore, observed at the same volume in the alkaline-earth metal disilicides regardless of the kind of alkaline-earth metals.

Table I lists interatomic distances of the three known polymorphs of  $\text{BaSi}_2$ ,<sup>5</sup>  $\text{SrSi}_2$ ,<sup>22</sup> and  $\text{CaSi}_2$  (Ref. 23) at atmospheric pressure. It shows that for the three polymorphs of  $\text{BaSi}_2$ , the interatomic distance between Ba atoms and that between Ba and Si atoms change greatly compared with that between Si atoms. Comparison among orthorhombic  $\text{BaSi}_2$ ,  $\text{SrSi}_2$ , and  $\text{CaSi}_2$  shows the same tendency: the metal-metal and metal-Si distances change largely while the Si-Si distance almost remains unchanged. Therefore, changes in the interatomic distances by replacement of Ba with Sr and Ca are similar to the changes made during the phase transitions of  $\text{BaSi}_2$  at high pressures and high temperatures. Among the alkaline-earth-metal disilicides, the decrease of metal-metal and metal-Si distances seems to reflect the reduction in atomic volume of the alkaline-earth metal, because the atomic volume of the metal decreases in that order. Therefore, the decrease of Ba-Ba and Ba-Si distances observed in polymorphs of  $\text{BaSi}_2$  can be considered as the reduction of atomic volume of Ba atoms by pressure. It indicates that Ba atoms are compressed selectively at high pressures. Additionally, Fig. 3 shows that the same structure appears at the same volume. We believe, therefore, that the reduction of the Ba atom volume by pressure alters the interaction between atoms, and causes structural change when the Ba atom volume goes below some value.

The small change of the Si-Si distance is interpreted as follows. Each structure has a characteristic Si atomic configuration: tetrahedra in the orthorhombic structure, a three-

dimensional network in the cubic structure, and corrugated hexagonal layers in the trigonal structure. Analysis of x-ray diffraction patterns of orthorhombic BaSi<sub>2</sub> with the maximum entropy method revealed that a Si tetrahedron has face-centered bonding charge and Ba atoms make no bond with other Ba atoms.<sup>24</sup> *Ab initio* calculations of the electronic structure of CaSi<sub>2</sub> with the same structure as trigonal BaSi<sub>2</sub> show that a Si atom forms three covalent bonds with three neighboring Si atoms.<sup>25</sup> Although the charge density distribution in trigonal BaSi<sub>2</sub> has not been quantified, it is probably similar to that of CaSi<sub>2</sub> because both have the same structure. These facts suggest that a Si atom forms some kinds of covalent bonds with neighboring Si atoms in the polymorphs BaSi<sub>2</sub>. Covalent bonds have lower compressibility than metallic bonds generally. In fact, the bulk moduli of alkaline-earth-metal elements [8.93 GPa for Ba, 11.83 GPa for Sr, and 17.4 GPa for Ca (Ref. 26)] are much smaller than that of Si (97.88 GPa),<sup>27</sup> which is covalently bound. Therefore, covalent bonds between Si atoms are the reason why the change of Si-Si distance is smaller than that of metal-metal distance.

Finally, we consider how pressure affects the structure of elements and other AB<sub>2</sub>-type compounds, and compare it with BaSi<sub>2</sub>. In pure elements, the pressure is expected to affect all atoms equally because the solid consists of only one kind of atom. Since among AB<sub>2</sub>-type compounds, the structural sequence of dioxides of 4A group elements are well investigated, we compare it with BaSi<sub>2</sub>. The structure of 4A group dioxides can be represented by packing of one type of unit.<sup>28,29</sup> The 4A group-element atoms are surrounded by oxygen atoms and the resultant cluster is a polyhedron where the oxygen atoms are at its corners. The polyhedra are joined by a shared corner or a shared edge. For example, α-quartz has a Si-centered tetrahedron as a unit and the tetrahedra are joined by a shared corner. The rutile-type structure, which is a form of the high-pressure phase of SiO<sub>2</sub> and low-pressure phase of GeO<sub>2</sub>, SnO<sub>2</sub>, and PbO<sub>2</sub>, has an Si-centered octahedron as a unit and these are connected at a shared edge.<sup>29</sup> Since the structure can be regarded as packing of one type of

unit and the unit contains both 4A group-element and oxygen atoms, pressure is expected to affect both kinds of atoms in almost the same way. On the other hand, BaSi<sub>2</sub> is considered to consist of two types of units: Ba atoms, and Si units of either the tetrahedra, the three-dimensional network, or the corrugated layers of the three forms. Pressure affects the two kinds of units in different ways: Ba atoms are compressed more than the Si units under pressure. Therefore the response of the structure to compression in BaSi<sub>2</sub> is expected to be different from that in the elements and other AB<sub>2</sub>-type compounds such as the 4A group dioxides. For this reason, the observed structural sequence of BaSi<sub>2</sub> at high pressures is found to be different from the structural sequence known already for elements and other AB<sub>2</sub>-type compounds.

## CONCLUSION

The *in situ* x-ray diffraction technique shows that BaSi<sub>2</sub> has three high-pressure, high-temperature phases at pressures up to 7 GPa and temperatures up to 1300 K. The trigonal phase exists at temperatures lower than those reported by Evers and an additional phase, BaSi<sub>2</sub>-IV, exists at the *p-T* region which was reported as the trigonal region. The details of BaSi<sub>2</sub>-IV are under investigation. The observed structural sequence at high pressures is different from that known already in the elements and other AB<sub>2</sub>-type compounds. We conclude that this is due to the fact that the same structure is observed at the same volume in the alkaline-earth-metal disilicides regardless of the kind of alkaline-earth metals.

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