

***In situ* measurements of the orthorhombic-to-trigonal transition in BaSi₂ under high-pressure and high-temperature conditions**

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The phase transition in BaSi₂, an orthorhombic structure at ambient conditions, was investigated by *in situ* x-ray diffraction along the paths of compression up to 5.2 GPa at room temperature and subsequent heating up to 873 K at 5.2 GPa. No phase transition occurred during the compression at room temperature. When heated at 5.2 GPa, orthorhombic BaSi₂ transformed into trigonal BaSi₂ at 673 K, whose structure is the same as that of the sample quenched from the same conditions. These results ensure that trigonal BaSi₂ forms directly from orthorhombic BaSi₂ at high pressures and high temperatures and maintains its structure when the pressure-temperature conditions are returned to ambient conditions. The reason why trigonal BaSi₂ is quenched, despite it being a metal, is discussed. [S0163-1829(97)01901-2]

INTRODUCTION

BaSi₂ has three crystallographic forms: orthorhombic, cubic, and trigonal structure at ambient conditions.¹⁻⁴ The first is stable and the latter two are metastable. Each structure has a characteristic Si atomic configuration as shown in Fig. 1: tetrahedra in the orthorhombic structure, a three-dimensional network in the cubic structure, and corrugated hexagonal layers in the trigonal structure. Electrical properties strongly depend on the structure. Orthorhombic BaSi₂ is a semiconductor.⁵ Recently, we found that cubic BaSi₂ is a semiconductor and trigonal BaSi₂ is a metal.⁶ Interestingly, trigonal BaSi₂ shows superconductivity with an onset temperature of 6.8 K.⁷

Evers *et al.* synthesized the cubic and trigonal phases by subjecting orthorhombic BaSi₂ to high-pressure and high-temperature conditions and subsequently returning it to ambient conditions (called quench experiments hereafter).²⁻⁴ They considered that both phases are high-pressure and high-temperature phases and are quenched without changing their structures. They then constructed a pressure-temperature (*p-T*) diagram of BaSi₂ in the temperature range from 773 to

1273 K and pressure range from 0 to 4 GPa.⁴ According to their diagram, the trigonal phase is stable at temperatures above 1100 K and at pressures above 1 GPa. There are two questions concerning their experiments. First, we successfully synthesized trigonal BaSi₂ at 673 K and 5.5 GPa in the same way as Evers *et al.*⁶ This temperature is much lower than that estimated from Evers' phase diagram. Second, since they did not identify both the cubic and the trigonal phases by *in situ* measurements, it is not clear whether both phases, in particular the metallic trigonal phase, are high-pressure phases. It is usually difficult to quench a high-pressure metallic phase synthesized from semiconductors.

In this study, we investigated the phase transition in BaSi₂ by the *in situ* x-ray diffraction technique.

EXPERIMENT

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 National Laboratory for High Energy Physics.^{8,9} Sintered diamond anvils with a square flat surface of 6×6 mm² were

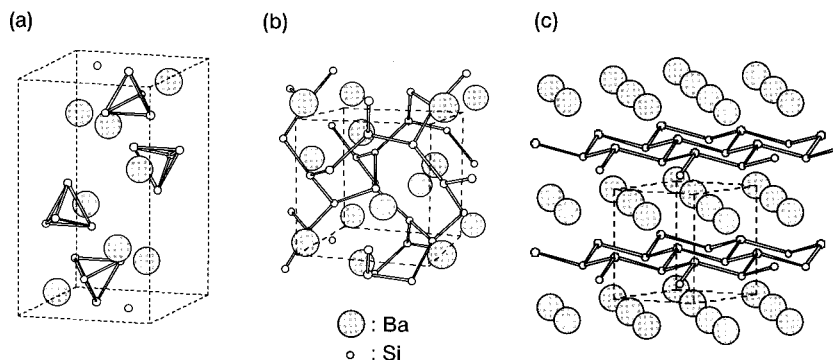


FIG. 1. Crystal structures of BaSi₂. (a) Orthorhombic structure, (b) cubic structure, and (c) trigonal structure.

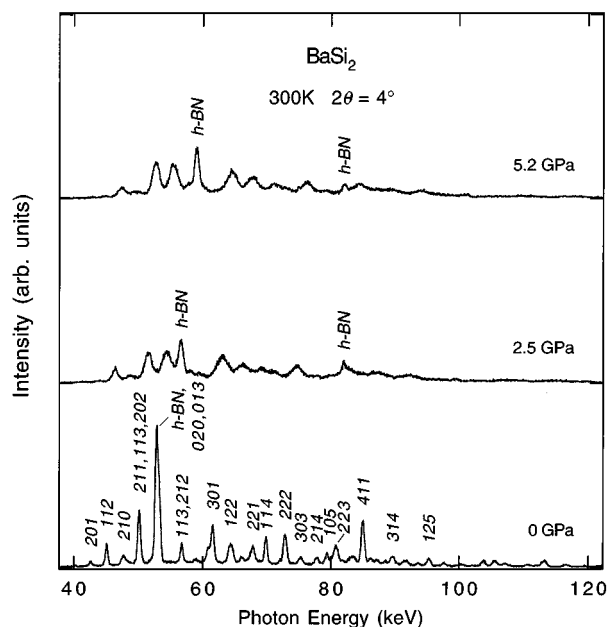


FIG. 2. X-ray diffraction patterns of BaSi_2 when compressed at room temperature.

used. Powdered orthorhombic BaSi_2 , the starting sample, was loaded in the h -BN capsule in the same way as in our quench experiments^{6,7} and the capsule was set in the center of the boron-epoxy pressure transmitting medium. Details of sample assembly were described elsewhere.⁹ 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.¹⁰ The sample was compressed to 5.2 GPa at room temperature and subsequently heated up to 873 K. The path was the same as those along which the quench experiments were done.^{4,6,7} X-ray diffraction patterns were measured by an energy dispersive method using synchrotron radiation from the bending magnet. The diffraction data were measured typically for 500 sec at $2\theta=4^\circ$ and more precisely for 1000 sec at $2\theta=4$ and 6° at the p - T conditions where phase transition occurred. The measurements were performed at intervals of 100 K with a heating rate of about 5 K/sec.

RESULTS

Figure 2 shows x-ray diffraction patterns of BaSi_2 at various pressures and room temperature. At atmospheric pressure, the 020 and 013 reflections of the orthorhombic phase overlap with the reflection of the h -BN sample capsule. When the sample is compressed up to 5.2 GPa, the orthorhombic phase shows no phase transition; only the positions of the diffraction peaks shift to the lower d values and the peak widths become broader.

Figure 3 shows x-ray diffraction patterns of BaSi_2 on heating at 5.2 GPa. When the sample is heated to 673 K, BaSi_2 undergoes phase transition. The peaks from the transformed phase (shown by the arrows) are assigned to a trigonal structure, which agrees well with that of trigonal BaSi_2 obtained by our quench experiments.^{6,7} The results prove that trigonal BaSi_2 is a high-pressure phase and is quenched

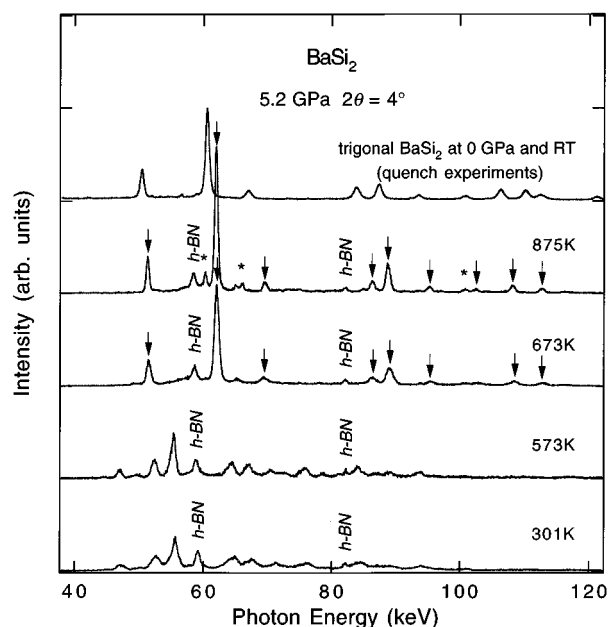


FIG. 3. X-ray diffraction patterns of BaSi_2 when heated at 5.2 GPa. The arrows and asterisks represent the reflections from trigonal BaSi_2 and those from cubic BaSi_2 , respectively. The pattern at the top is that of trigonal BaSi_2 at 0 GPa and room temperature, which was synthesized by our quench experiments (Refs. 6 and 7).

without structural change when the temperature is lowered to room temperature and the pressure is reduced to atmospheric pressure. When the sample is further heated up to 873 K, the second phase transition starts. The peaks from the transformed phase (shown by the asterisks) are assigned to a cubic structure, which is also the same as that of cubic BaSi_2 obtained by our quench experiments.⁶ Thus the results clearly prove that both trigonal and cubic BaSi_2 are high-pressure phases, and can be quenched without structural change. In this paper, we focus on the orthorhombic-to-trigonal transition.

Variations of the x-ray diffraction pattern with time were measured while keeping the temperature at 400 °C and pressure at 5.2 GPa in order to confirm the orthorhombic-to-trigonal transition. Figure 4 shows that the $10\bar{1}1$ reflection of the trigonal phase appears in 500 sec and the reflections of the orthorhombic phase disappear in 1500 sec (25 min), indicating clearly that the trigonal phase forms directly from the orthorhombic phase. No cubic phase is observed in the orthorhombic-to-trigonal transition. The results are consistent with our conditions for synthesizing trigonal BaSi_2 , 5.5 GPa, and 673 K for 120 min.^{6,7}

Figure 5 shows the molar volume of BaSi_2 when heated at 5.2 GPa as a function of temperature. The molar volume is normalized by that of orthorhombic BaSi_2 at ambient conditions. The volume reduces to 87% when compressed to 5.2 GPa at room temperature, and increases slightly (2%) due to thermal expansion when heated up to 673 K. When the orthorhombic-to-trigonal phase transition occurs, the volume reduces by 7%. This volume change is much larger than that at the bcc-to-hcp transition in Ba (2%),¹¹ but smaller than that at the diamond-to- β -Sn transition in Si (20%).¹²

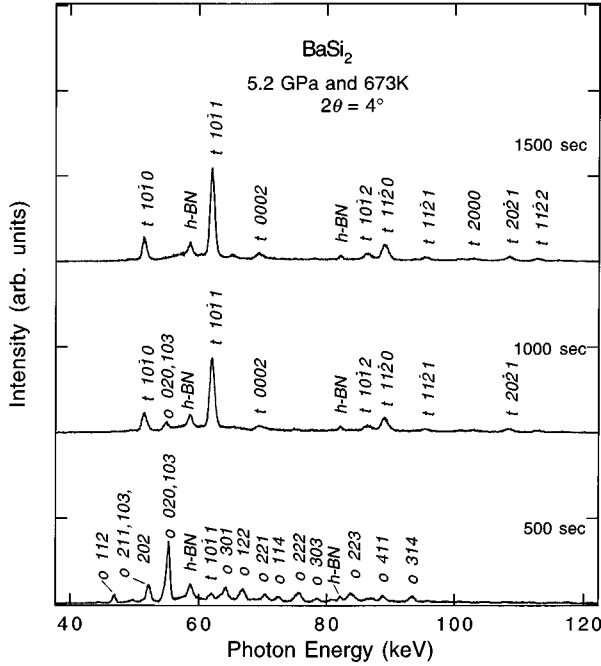


FIG. 4. X-ray diffraction patterns of BaSi₂ at 5.2 GPa and 673 K. The symbols “o” and “t” represent the reflections from the orthorhombic and the trigonal phases, respectively. The indices of the trigonal phase are expressed according to a hexagonal system.

DISCUSSION

The present *in situ* experiments revealed that orthorhombic BaSi₂ transforms into trigonal BaSi₂ at 673 K and then into cubic BaSi₂ at 873 K when heated at 5.2 GPa, indicating that both the trigonal and the cubic phases are high-pressure and high-temperature phases. Therefore, these transition temperatures are consistent with our conditions for synthesizing the trigonal phase by quench experiments, 673 K and 5.5 GPa.^{6,7} Evers *et al.* constructed the *p*-*T* diagram of BaSi₂ in the temperature range from 773 to 1273 K and pressure range from 0 to 4 GPa. According to their phase diagram, orthorhombic BaSi₂ should transform into the cubic phase and then into the trigonal phase, which is quite different from the phase transition sequence that we observed. Since their experiments were performed at temperatures above 773 K, their diagram may not hold true at lower temperatures.

The present results also revealed that both high-pressure and high-temperature phases, trigonal BaSi₂ and cubic BaSi₂, are quenched to ambient conditions. As already mentioned, orthorhombic and trigonal BaSi₂ are a semiconductor and a metal, respectively. This means that the metallic phase synthesized from the semiconductor phase under pressure is quenched. This is quite uncommon. For example, Si, which has the diamond-type structure at ambient conditions, transforms into a metallic phase with the β -Sn-type structure at 11.6 GPa,^{13,14} but this structure cannot survive when the pressure is reduced to normal pressure, and transforms into a body-centered-cubic structure (BC-8).¹⁵ We discuss here the reason in the framework of classical nucleation and growth theory¹⁶ why trigonal BaSi₂ is quenched although it is a metal. Assuming that a spherical nucleus of orthorhombic

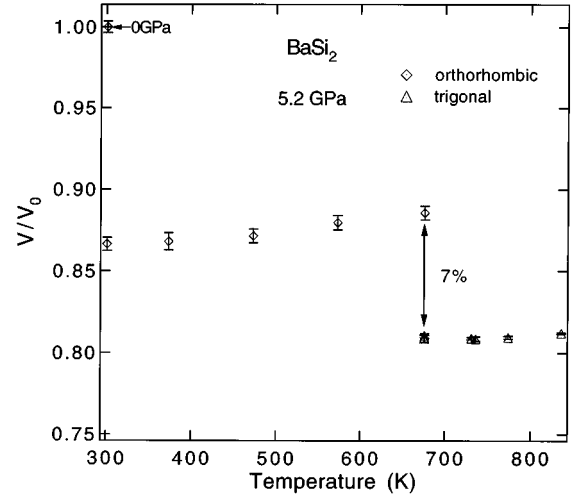


FIG. 5. Molar volume of BaSi₂ when heated at 5.2 GPa as a function of the temperature. The rhombus and triangles represent the volume of orthorhombic BaSi₂ and that of trigonal BaSi₂, respectively.

BaSi₂ is homogeneously formed in a trigonal BaSi₂ matrix, then the thermodynamic energy barrier for nucleation, ΔG_T , is given by

$$\Delta G_T = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G)^2}, \quad (1)$$

where σ is the interfacial energy and ΔG the free-energy difference between the phases. We consider the following quenching path which we actually adopted in the study. First, the sample is cooled from 673 K to room temperature keeping the pressure constant at 5.2 GPa, then the pressure is reduced to normal pressure. At a constant pressure, ΔG near transition temperature T_T can be approximated by

$$\Delta G \approx \frac{\Delta H}{T_T} \delta T, \quad (2)$$

where δT is a temperature deviation from T_T , $\delta T = T_T - T$ and ΔH the enthalpy change at the transition. At a constant temperature, ΔG near transition pressure P_T can be approximated by

$$\Delta G \approx \Delta V \delta P, \quad (3)$$

where δP is a pressure deviation from P_T , $\delta P = P_T - P$ and ΔV the volume change at the transition. Thus the total amount of ΔG is

$$\Delta G \approx \frac{\Delta H}{T_T} \delta T + \Delta V \delta P. \quad (4)$$

The fact that trigonal BaSi₂ was quenched indicates that ΔG_T is sufficiently large compared with thermal energy $k_B T$, where k_B is Boltzmann's constant. Two factors can be considered to contribute to the large ΔG_T .

First, ΔG , which is the driving force for the phase transition, is small. The values for the evaluation of ΔG are listed in Table I. ΔV is obtained from Fig. 5 and ΔH refers to the measurements by Evers *et al.*⁴ The exact T_C at $P_T = 5.2$ GPa

TABLE I. Experimental data for the pressure-induced phase transition of BaSi₂ and Si (Ref. 12). In the case of Si, the data were measured during compression at room temperature because the phase transition occurs at room temperature.

	BaSi ₂	Si
High-pressure phase	Trigonal	β -Sn
Low-pressure phase	Orthorhombic	Diamond
P_T (GPa)	5.2	11.6
T_T (K)	>673	300 (constant)
ΔV (Å ³ /atom)	2.3	4.1
$\Delta V \delta P$ (10 ⁻² eV/atom)	7.46	29.68
ΔH (10 ⁻² eV/atom)	1.59 (at 1 atm) ^a	
$\frac{\Delta H}{T_T} \delta T$ (10 ⁻² eV/atom)	0.95 (at most)	
ΔG (10 ⁻² eV/atom)	8.41	29.68
Remarks	Quenchable	Not quenchable

^aReference 4.

is not known but it is surely below 673 K. Thus ΔG can be estimated to be 8.41 eV at most. Most of ΔG is due to the second term in Eq. (4), $\Delta V \delta P$. The value of 8.41 eV is rather small compared with that of the transition in Si whose high-pressure metallic phase, the β -Sn type structure, cannot be quenched. This is because the orthorhombic-to-trigonal transition in BaSi₂ occurs at relatively low pressures.

Second, σ , which is defined as the work expended upon nuclei to increase the surface area, must be large. We can estimate this work from the spatial distribution of valence charge density. Although the charge density in trigonal BaSi₂ has never been quantified, it is probably similar to that of

CaSi₂ because both alkaline-earth metal disilicides have a similar structure except for a small difference in the stacking sequence of the metal and Si layers. Fahy and Hamann calculated that a Si atom forms three covalent bonds with three Si neighbors in CaSi₂ whose charge is comparable with that in the diamond phase Si.¹⁷ This means that trigonal BaSi₂ has the same covalent bonds as those in the diamond phase Si. When the trigonal-to-orthorhombic transition occurs a drastic change in the Si configuration is required, i.e., from the corrugated hexagonal layers into the tetrahedra. Therefore, the covalent Si-Si bonds in the layers must be broken and then rearranged into tetrahedra. We consider that most of the work for the transition is done in this process. A large amount of work is likely to break and rearrange the covalent Si-Si bonds, leading to a large value of σ .

Consequently, the small ΔG and large σ lead to a large ΔG_T , and therefore trigonal BaSi₂ can be quenched.

CONCLUSION

In situ x-ray diffraction measurements at high pressures and high temperatures confirmed that trigonal BaSi₂ forms directly from orthorhombic BaSi₂ and can be quenched when returning to ambient conditions. The results are consistent with our quench experiments.

ACKNOWLEDGMENTS

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