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Article

In Situ Observation of the Formation of Si Clathrate Ba_8Si_{46} at High Pressures and High Temperatures

Motoharu Imai[*,†] **and Takumi Kikegawa**[‡]

National Institute for Materials Science, 1-2-1 Sengen Tsukuba, Ibaraki 305-0047, Japan, and
Photon Factory, National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba,
Ibaraki 305-0801, Japan

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X-ray diffraction measurements at high pressures and high temperatures revealed that Si clathrate Ba_8Si_{46} is formed by a solid-phase reaction of an 8:30 molar mixture of $SrSi_2$-phase $BaSi_2$ and Si after $BaSi_2$ undergoes the $BaSi_2$-to-$EuGe_2$ and the $EuGe_2$-to-$SrSi_2$ transitions. The volume reduction during the formation of Ba_8Si_{46} is the largest, 7.6%, among the observed transitions. On the other hand, an 8:30 molar mixture of $SrSi_2$-phase $SrSi_2$ and Si does not result in the formation of Sr_8Si_{46} at high pressures and high temperatures; only $SrSi_2$ transforms from the $SrSi_2$ phase into the α-$ThSi_2$ phase, and Si remains in the diamond phase.

Introduction

Type-I Si clathrate, whose general chemical formula is A_8X_{46}, has a characteristic crystal structure, that is, the Na_8Si_{46}-type structure (space group $Pm\bar{3}n$, $Z = 1$, Figure 1a).[1] In A_8X_{46}, atoms X form X_{20} dodecahedra and X_{24} tetrakaidecahedra, and these polyhedra are linked by sharing faces; atoms A are located in the polyhedra. Because the X_{20} and X_{24} polyhedra are isostructural with fullerenes C_{20} and C_{24}, respectively,[2] and superconductivity with a relatively high superconducting critical temperature (T_C) was observed in alkaline-doped fullerides,[3] a search for superconducting Si clathrates has been underway. The first superconducting transition in Si clathrates was observed in $(Ba,Na)_8Si_{46}$, whose T_C is approximately 4 K.[4] This Si clathrate was synthesized by the thermal decomposition of Na_2BaSi_4 in a vacuum at 773 K. In 2000, a superconducting Si clathrate with a higher T_C (8.0 K), Ba_8Si_{46}, was synthesized by a different method from the thermal decomposition, a solid-phase reaction between an 8:30 molar mixture of $BaSi_2$ and Si at a pressure of 3 GPa and a temperature of 1073 K.[5] Further research on the synthesis conditions demonstrated that Ba_8Si_{46} can be formed from the mixture at pressures above 3 GPa and temperatures above 1073 K.[6] Although the synthesis conditions of Ba_8Si_{46} have been clarified, the formation process of Ba_8Si_{46} at high pressures and high temperatures has not been elucidated yet. $BaSi_2$, one of the starting materials, has four phases at pressures ranging from 0 to 5 GPa and temperatures ranging from 300 to 1273 K,[7,8] although another starting material, Si, has only one phase (the diamond phase) in this pressure-temperature range.[9] The stable phase of $BaSi_2$ has the $BaSi_2$-type structure (space group *Pnma*, $Z = 8$, Figure 1b) under ambient conditions.[10] One of the high-pressure, high-temperature phases has the $EuGe_2$-type structure (space group $P\bar{3}m1$, $Z = 1$, Figure 1c),[11] and the other has the $SrSi_2$-type structure (space group $P4_332$, $Z = 4$, Figure 1d).[12] The crystal structure of the fourth phase, denoted as $BaSi_2$−IV, is unknown. Because Ba_8Si_{46} is

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[*] To whom correspondence should be addressed. E-mail: imai.motoharu@nims.go.jp.
[†] National Institute for Materials Science.
[‡] National Laboratory for High Energy Physics.

(1) Kasper, J. S.; Hagenmuller, P.; Pouchard, M.; Cross, C. *Science* **1965**, *150*, 1713.
(2) Kroto, H. W. *Nature (London)* **1987**, *329*, 529.
(3) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature (London)* **1991**, *1350*, 600.
(4) Kawaji, H.; Horie, H.; Yamanaka, S.; Ishikawa, M. *Phys. Rev. Lett.* **1995**, *74*, 1427.
(5) Yamanaka, S.; Enishi, E.; Fukuoka, H.; Yasukawa, M. *Inorg. Chem.* **2000**, *39*, 56.
(6) Fukuoka, H.; Kiyoto, J.; Yamanaka, S. J. *Phys. Chem. Solids* **2004**, *65*, 333.
(7) Imai, M.; Hirano, T.; Kikegawa, T.; Shimomura, O. *Phys. Rev. B* **1998**, *58*, 11922.
(8) Imai, M.; Kikegawa, T. *Chem. Mater.* **2003**, *15*, 2543.
(9) Bundy, F. P. J. *Chem. Phys.* **1964**, *41*, 3809.
(10) Shäfer, H.; Janzon, K. H.; Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 393.
(11) Evers, J.; Oehlinger, G.; Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 538.
(12) Evers, J.; Oehlinger, G.; Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 659.

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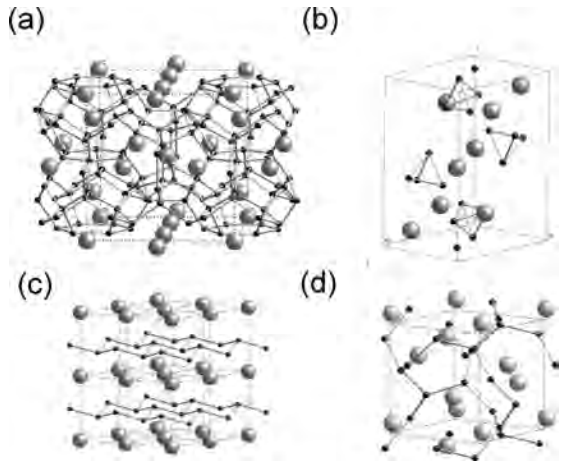

Figure 1. Crystal structure of Ba_8Si_{46} and $BaSi_2$: (a) Ba_8Si_{46}, (b) $BaSi_2$-phase $BaSi_2$, (c) $EuGe_2$-phase $BaSi_2$, and (d) $SrSi_2$-phase $BaSi_2$. The large and small spheres correspond to Ba and Si atoms, respectively.

expected to be formed by a solid-phase reaction of Si with one of four phases of $BaSi_2$, it would be interesting to see which phase of $BaSi_2$ reacts with Si and results in the formation of Ba_8Si_{46}.

In this study, we observed the formation of Ba_8Si_{46} from an 8:30 molar mixture of $BaSi_2$ and Si at high pressures and high temperatures. We also observed the phase behavior of an 8:30 molar mixture of $SrSi_2$ and Si at high pressures and high temperatures for a comparison.

Experimental Section

The starting material was prepared by an Ar-arc melting of an 8:30 molar mixture of $BaSi_2$ (nominal purity 98%) and Si (nominal purity 99.9999%). X-ray diffraction measurements at high pressures and high temperatures were performed in the beam line of the TRISTAN accumulation ring (AR-NE5) at the National Laboratory for High Energy Physics (KEK). High pressure was applied using the multianvil high-pressure apparatus MAX80. WC anvils with a square flat-surface size of 6 × 6 mm^2 were used. A powdered starting material was loaded in the h-BN capsule. The temperature was measured by an alumel−chromel thermocouple attached to the sample capsule. The pressure was evaluated from the lattice parameter of a NaCl internal pressure marker.[13] Details of the sample assembly have been described elsewhere.[8] The X-ray diffraction patterns were measured by an energy-dispersive method using synchrotron radiation from the bending magnet. The lattice parameters were obtained by the least-squares fitting of the indexed pattern.

Results and Discussion

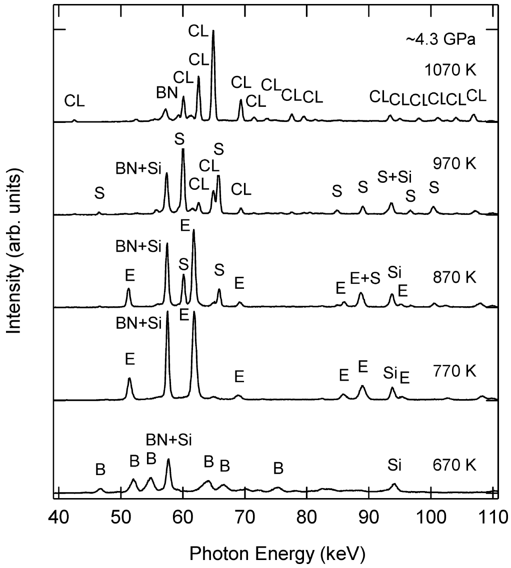

Figure 2. X-ray diffraction patterns of the 8:30 molar mixture of $BaSi_2$ and Si at an approximate pressure of 4.3 GPa and various temperatures ($2\theta = 4°$). The symbols "Si", "B", "E", "S", and "CL" represent reflections from Si, $BaSi_2$-phase $BaSi_2$, $EuGe_2$-phase $BaSi_2$, $SrSi_2$-phase $BaSi_2$, and Si clathrate Ba_8Si_{46}, respectively. The symbol "BN" shows reflections from the h-BN capsule.

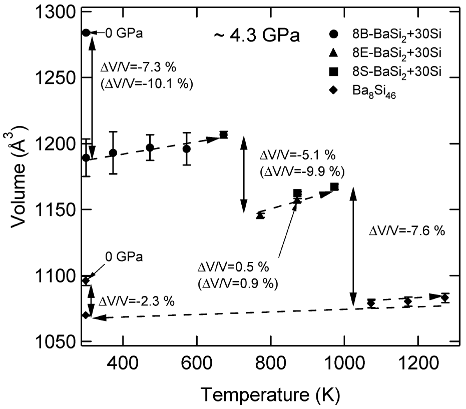

Figure 3. Volume of the 8:30 molar mixture of $BaSi_2$ and Si and that of Ba_8Si_{46} as a function of temperature. The abbreviations "B-," "E-," and "S-" stand for the $BaSi_2$-phase, the $EuGe_2$-phase, and the $SrSi_2$-phase, respectively. The broken lines are guides for the eyes.

Figure 2 exhibits the X-ray diffraction patterns of the 8:30 molar mixture of $BaSi_2$ and Si at an approximate pressure of 4.3 GPa and various temperatures. The diffraction patterns were measured for 300 s for the sample and 100 s for the pressure marker, respectively, at approximate intervals of 100 K. At room temperature and 4.3 GPa, the sample remains a mixture of $BaSi_2$-phase $BaSi_2$ and Si. When the sample is heated up to 870 K, $BaSi_2$ undergoes two phase transitions: the $BaSi_2$-to-$EuGe_2$ transition at 770 K and the $EuGe_2$-to-$SrSi_2$ transition at 870 K; Si remains in the diamond phase. With further heating up to 970 K, the diffraction peaks that can be assigned to the Si clathrate Ba_8Si_{46} appear, which suggests that the formation of Ba_8Si_{46} starts at 970 K. The formation of Ba_8Si_{46} was completed at 1070 K. These results demonstrate that Ba_8Si_{46} is formed by the solid-phase reaction of $SrSi_2$-phase $BaSi_2$ and Si at high pressure and high temperature. The pressure-temperature conditions under which the Ba_8Si_{46} formation starts are consistent with those reported previously.[6]

Figure 3 shows the volume of the sample as a function of temperature. In this figure, the volume corresponds to the volume of the 8:30 molar mixture of $BaSi_2$ and Si, that is, a sum of the 8-fold volume per formula unit of $BaSi_2$ and the thirty-fold atomic volume of Si, or the volume per formula unit of Ba_8Si_{46}. The volume change at the transition $\Delta V/V$ is shown in the figure. The number in the parentheses is $\Delta V/V$ of $BaSi_2$. The volume change at the formation of Ba_8Si_{46}

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(13) Brown, J. M. J. *Appl. Phys.* **1999**, *86*, 5801.

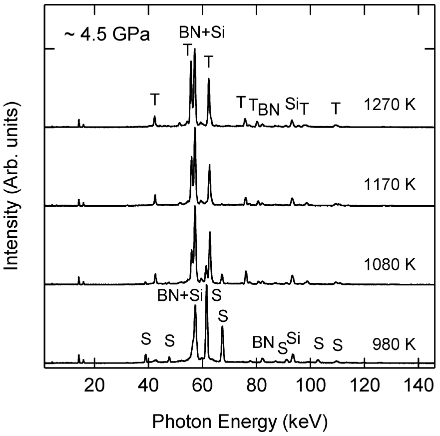

Figure 4. X-ray diffraction patterns of the 8:30 molar mixture of $SrSi_2$ and Si at an approximate pressure of 4.5 GPa and various temperatures ($2\theta = 4°$). The symbols "Si," "S," and "T" represent reflections from Si, $SrSi_2$-phase $SrSi_2$, and α-$ThSi_2$-phase $SrSi_2$, respectively.

from the mixture of the $SrSi_2$-phase $BaSi_2$ and Si is the largest (7.6%) among the observed phase transitions. The volume difference between the starting material, the 8:30 molar mixture of the $BaSi_2$-phase $BaSi_2$ and Si, and Ba_8Si_{46} is large (14.6%) under ambient conditions, which is consistent with a previous report (15%).[5]

The above results demonstrate that Ba_8Si_{46} is formed from the 8:30 molar mixture of $SrSi_2$-phase $BaSi_2$ and Si. Because $SrSi_2$ has the $SrSi_2$-type structure under ambient conditions,[14] we examined what happens in an 8:30 molar mixture of $SrSi_2$-phase $SrSi_2$ and Si at high pressure and high temperature. At an approximate pressure of 4.5 GPa and room temperature, the sample consisted of $SrSi_2$-phase $SrSi_2$ and Si, as it did under ambient conditions. Figure 4 exhibits the X-ray diffraction patterns of the 8:30 molar mixture of $SrSi_2$ and Si at an approximate pressure of 4.5 GPa and various temperatures. The diffraction patterns were measured for 200 s for the sample and 100 s for the pressure marker, respectively, at approximate intervals of 100 K. When the sample was heated at this pressure, only $SrSi_2$ starts to transform into the α-$ThSi_2$-phase[15] at 1080 K and complete the transformation at 1170 K. During this structural transition, the diamond phase Si remains the same. $SrSi_2$ does not react with Si up to 1280 K, the highest temperature in this experiment. Thus, the mixture of $SrSi_2$-phase $SrSi_2$ and Si does not result in the formation of Si clathrate. This result is in contrast to the case of the mixture of $BaSi_2$ and Si in spite of the fact that the crystal structure of the $SrSi_2$-phase $SrSi_2$ is the same as that of the $SrSi_2$-phase $BaSi_2$. The failure to form Sr_8Si_{46} from the mixture of $SrSi_2$ and Si at high pressures and high temperatures is consistent with the report by Toulemonde et al.[16]

Ba_8Si_{46} is formed at pressures above 3 GPa and temperatures above 1070 K. In this pressure-temperature region, $BaSi_2$ has the $BaSi_2$−IV phase.[7,8] The formation of Ba_8Si_{46}, therefore, suggests that Ba_8Si_{46} is more energetically stable than the 8:30 molar mixture of $BaSi_2$−IV phase $BaSi_2$ and Si in this pressure-temperature region. On the other hand, the failure to form Sr_8Si_{46} suggests that Sr_8Si_{46} is less energetically stable than the 8:30 molar mixture of α-$ThSi_2$-phase $SrSi_2$ and Si. The difference in the stability of phases between the Ba−Si and Sr−Si systems can be discussed considering the difference in atomic radii between Ba and Sr atoms and the difference in the crystal structure between $BaSi_2$−IV-phase $BaSi_2$ and α-$ThSi_2$-phase $SrSi_2$. To discuss this, it is necessary to determine the crystal structure of $BaSi_2$−IV-phase $BaSi_2$, which has not been clarified yet. The determination of the crystal structure of $BaSI_2$−IV-phase $BaSi_2$ will, therefore, deepen the understanding of the phase relationship in the Ba−Si and Sr−Si systems. First-principle calculations of the total energy of $SrSi_2$-phase $SrSi_2$, α-$ThSi_2$-phase $SrSi_2$, and Sr_8Si_{46} would also be interesting to identify the pressure-temperature region where Sr_8Si_{46} is stable and thus clarify why Sr_8Si_{46} has not be synthesized yet. Furthermore, an in situ observation of formation of another Ba contained Si clathrate $Ba_{24}Si_{100}$[17] also would be interesting for understanding of Ba−Si phase relationship at high pressures.

Conclusions

We found by in situ X-ray diffraction measurements at high pressures and high temperatures that Ba_8Si_{46} is formed by a solid-phase reaction between an 8:30 molar mixture of $SrSi_2$-phase $BaSi_2$ and Si after $BaSi_2$ undergoes the $BaSi_2$-to-$EuGe_2$ and $EuGe_2$-to-$SrSi_2$ transitions. We also observed that Sr_8Si_{46} is not formed from the 8:30 molar mixture of $SrSi_2$ and Si at high pressures and high temperatures in spite of the fact that the $SrSi_2$-phase $SrSi_2$ is isostructural with $SrSi_2$-phase $BaSi_2$.

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(14) Janzon, K. H.; Schäfer, H.; Weiss, A. Z. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 245.

(15) Evers, J.; Oehlinger, G.; Weiss, A. J. *Solid State Chem.* **1977**, *20*, 173.

(16) Toulemonde, P.; Adessi, C.; Blasé, X.; San Miguel, A.; Tholence, J. L. *Phys. Rev. B* **2005**, *71*, 094504.

(17) Fukuoka, H.; Ueno, K.; Yamanaka, S. J. *Organomet. Chem.* **2000**, *611*, 543.