

# Phase Relationship between 3C- and 6H-Silicon Carbide at High Pressure and High Temperature

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**The phase relationship between 3C- and 6H-SiC is investigated in the pressure range 2.5–6.5 GPa and the temperature range 400°–2500°C, by analyzing recovered samples, using X-ray diffractometry and Raman-scattering techniques. The phase transition from 3C- to 6H-SiC occurs at 2200°C and 2.5 GPa. In the pressure range >4.5 GPa, 6H-SiC transforms to 3C-SiC at 2500°C, via an intermediate state, as indicated by broadening peaks in the X-ray diffraction profile. Thermodynamically, 3C-SiC appears to be the low-temperature stable form, and the temperature of transition to 6H-SiC, which is stable at high temperature, appears to increase with pressure.**

## I. Introduction

SILICON CARBIDE (SiC) exhibits many polytypes, which are based on the tetrahedral coordination of carbon and silicon. The structures of the polytypes differ only in the stacking sequences of the atomic planes. However, despite many studies on the structural relationships and transformations among the polytypes, the question of which factors (e.g., stoichiometry, impurity, pressure, or temperature) control the formation or stability of those polytypes is still controversial.

For many years, 3C-SiC with a zinc blende type of cubic structure was accepted as the low-temperature stable form of SiC up to 2100°C, at which temperature it converted to the hexagonal form (6H-SiC).<sup>1</sup> On the other hand, numerous reports of 6H-SiC formation at <2000°C, as well as of 3C formation at temperatures >2200°C and interconversions of 3C and 6H forms, in addition to the coexistence of the two forms, have shown that these phase relationships are not necessarily simple. If we look at the stability diagrams of the polytypes ever proposed, Inomata *et al.* allocated the stable region to 3C-SiC at temperatures below 1700°C<sup>2</sup> while Knippenberg suggested that 3C-SiC is thermodynamically unstable under all conditions.<sup>1</sup> In addition to temperature conditions, the influence of impurities is also crucial when we discuss the stability of SiC polytypes. As Jepps and Page reviewed in their paper,<sup>3</sup> electrically p-type materials to SiC (e.g., B and Al) tend to stabilize  $\alpha$ -SiC and n-type materials (e.g., N and P) stabilize  $\beta$ -SiC. In the presence of high pressures of nitrogen, for instance, “reverse” transformation from 6H- to 3C-SiC was observed in the temperature range 1800°–2500°C where commonly 3C is converted into 6H.<sup>4</sup>

During high-pressure and high-temperature treatments of SiC, Sokhor *et al.*<sup>5</sup> found that 6H-SiC transforms to the 3C form under 3.0–7.0 GPa pressure and at temperatures in the range 1200°–1400°C. In contrast, Whitney and Shaffer<sup>6</sup> failed to identify

interconversion between the 3C and 6H forms in the region of 6.0 GPa pressure and temperatures up to 2000°C. Those researchers ascribed the discrepancy between their results and those of Sokhor *et al.* to impurities contained in the starting material used by Sokhor *et al.* Their further study suggested that impurities which are insoluble to SiC (e.g., Fe) lead to the formation of  $\alpha$ -SiC. On the other hand, Nakamura *et al.*<sup>7</sup> reported that the transition temperature of 6H- to 3C-SiC decreases from 1100° to 500°C as pressure increases from 1 to 4 GPa. However, the X-ray diffraction (XRD) peaks for their sample after treatment at 1000°C and 5 GPa were broad, and peaks from the 6H form seemed to remain in the sample that they claimed had completely converted to the 3C form.

Transformation to the 3C form from the 6H form is difficult to identify by XRD, because the diffraction peak positions of the 3C form are nearly the same as those of the 6H form in the starting sample, and the 3C form, which has a symmetry higher than that of the 6H form, shows no intrinsic diffraction peak.

The purpose of the present study was to investigate the phase relationship between 6H- and 3C-SiC and the stabilities of those forms at high pressure and high temperature, using XRD and Raman-scattering techniques.

## II. Experimental Procedure

In the present study, the sources of the 3C- and 6H-SiC used as samples were  $\beta$ -SiC (Betarandom, Ibigawa Denko Co., Ltd., Japan) and  $\alpha$ -SiC (GC #16, Showa Denko Co., Ltd., Tokyo, Japan), respectively. The structural composition of the  $\beta$ -SiC was determined by XRD as completely cubic 3C-SiC, and it contained only a trace of 2H polytype. The  $\alpha$ -SiC consisted of 6H-SiC with ~6% 14R and 4H polytypes. Recent computer simulation study, however, proposed the possibility that those traces of other polytypes in XRD profile were due to the presence of stacking faults in SiC.<sup>8</sup> Chemical analysis showed inclusion of 0.06% SiO<sub>2</sub>, 0.09% Al<sub>2</sub>O<sub>3</sub>, 0.07% Fe<sub>2</sub>O<sub>3</sub>, 0.07% CaO for the  $\beta$ -SiC, and 0.0005% Fe, 0.0004% Ca, 0.0002% Na, 0.0001% K, N.D. Ni, Cr, Cu, Zn, B, Al, Nb for the  $\alpha$ -SiC.

The experiments were conducted in a 6–8-anvil-type high-pressure apparatus<sup>9</sup> in the pressure range 2.5–6.5 GPa. Pressure calibration of the apparatus was performed using the pressure fixed points of bismuth (I–II, 2.55 GPa; II–III, 2.7 GPa), tellurium (II–III, 3.7 GPa), and barium (I–II, 5.5 GPa) at room temperature. The sample was put directly into a capsule of graphite used as a heater, to avoid the influence of contamination with the wall material and to achieve a C–Si system. A W–Re (3–25%) thermocouple was used to measure the temperature of the sample up to 2300°C; at >2300°C, the temperature was obtained by extrapolating the relationship between temperature and electrical heating power. The sample was compressed in a high-pressure cell of pyrophyllite and heated to the heat-treatment temperature at a rate of 100°C/min. After the sample had been held at temperature for 10 min, it was quenched to room temperature and then recovered at ambient pressure. This treated sample then was examined by powder XRD and Raman-scattering techniques.

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### III. Results and Discussion

#### (1) 3C $\rightarrow$ 6H Transformation

Figure 1 shows a series of powder XRD patterns for 3C-SiC after treatments at 2200°C and 2.5–6.5 GPa. Here we present the results in the range of 29–41° 2 $\theta$  as no considerable change was observed in their diffraction patterns after the treatments in other regions. Two diffraction peaks, other than those of the starting material, appeared at 2.5 GPa and are identified with the diffraction lines of the (101) and (103) planes for 6H-SiC. Those peaks indicate a phase transition from the 3C to the 6H form, and the fraction of that transition was estimated at  $\sim$ 30%, using the method of Ruska *et al.*<sup>10</sup> This result at 2.5 GPa is consistent with those of previous works,<sup>1,11–14</sup> which reveal a 3C-to-6H transition at  $>$ 2000°C and 1 atm pressure.

On the other hand, the diffraction profiles of the samples treated under 4.5 and 6.5 GPa pressure and at temperatures up to 2200°C are the same as that of the starting 3C form. This result is consistent with the experimental data of Whitney and Shaffer,<sup>6</sup> which indicate that the 3C form is stable in the pressure region 4.0–6.0 GPa and up to a temperature of 2000°C. Therefore, our present results suggest that the temperature required to attain the transformation from the 3C to the 6H form tends to increase with pressure.

Here we discuss the influence of impurities contained in our  $\beta$ -SiC sample such as 0.09% of Al<sub>2</sub>O<sub>3</sub> and 0.07% of Fe<sub>2</sub>O<sub>3</sub>. If we follow the rule mentioned in an earlier section of this paper both Al, which is electrically p-type material to SiC, and Fe, which is insoluble to SiC, tend to stabilize 6H rather than 3C. Even if the results described above are influenced by those impurities, therefore, higher stability of 3C-SiC under high pressure is still true. Moreover, the concentration of those impurities was much lower than those reported in the experiments which seemed to be controlled by impurities.<sup>5,6</sup>

#### (2) 6H $\rightarrow$ 3C Transformation

The XRD peaks of 3C-SiC are common to all of the SiC polytypes; hence, it is difficult to identify the 3C form in a mixed

phase of 3C and 6H forms without taking into account the intensity ratio of the diffraction peaks. Diffraction profiles of 6H samples after high-pressure treatment under pressures of 2.5, 4.5, and 6.5 GPa at 2500°C are shown in Fig. 2. The intensities of those lines are normalized with that of the (102) line for the 6H form, which corresponds to the (111) line of the 3C form. The unknown peak designated by an arrow in Fig. 2 is attributed to an aluminum silicate produced by reaction of the SiC with the alumina tube used to protect the thermocouple, because the peak was absent when no alumina tube was used. A comparison of the results with and without the alumina tube confirmed that the contamination had no effect on the transformation of SiC.

For high-temperature treatment at 2500°C, the characteristic diffraction lines of the 6H form, such as the 6H (101) and 6H (103) lines, broadened at 2.5 GPa, and the intensities of the lines at 4.5 and 6.5 GPa pressure were lower than those at 2.5 GPa. The other diffraction peaks appearing at higher diffraction angles, 6H (104) and 6H (105), for instance, also broadened and weakened after the treatment. There was no diffraction peak for SiC polytypes other than the 6H and 3C forms. These results suggest that the 6H form partially transformed to the 3C form and that this transition accelerated under higher pressure.

Figure 3 shows the results for various temperature treatments at 4.5 GPa. The diffraction peaks of the 6H form broadened with increasing temperature, especially at 1000°–1900°C, and then sharpened at 2500°C. This broadening is attributed to “nonrandom insertion of faults” during transformation of the 6H form to the other form, much the same as the transition of the 3C to the 6H form pointed out by Sebastian and Krishna<sup>15</sup> and Kabra *et al.*<sup>16</sup> Those researchers suggested that diffusion of the diffraction peaks takes place during the process of transition, when stacking faults are introduced preferentially into the crystal. Therefore, a series of diffraction profiles shows an intermediate state, characterized by broad diffraction profiles, during transition from the 6H to the other more stable form, as a phenomenon before transition.

Similar broadening also was reported by Sokhor *et al.*<sup>5</sup> and Nakamura *et al.*,<sup>7</sup> although they simply regarded it as a sign of

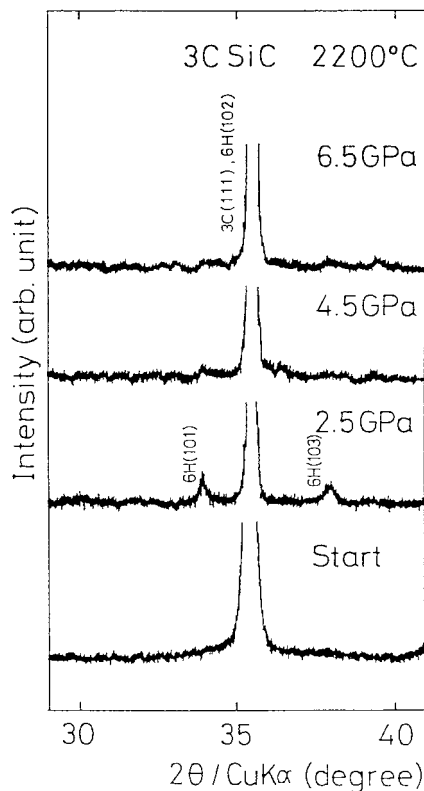


Fig. 1. Powder X-ray diffraction profiles for 3C-SiC retrieved after high-pressure treatment at 2200°C.

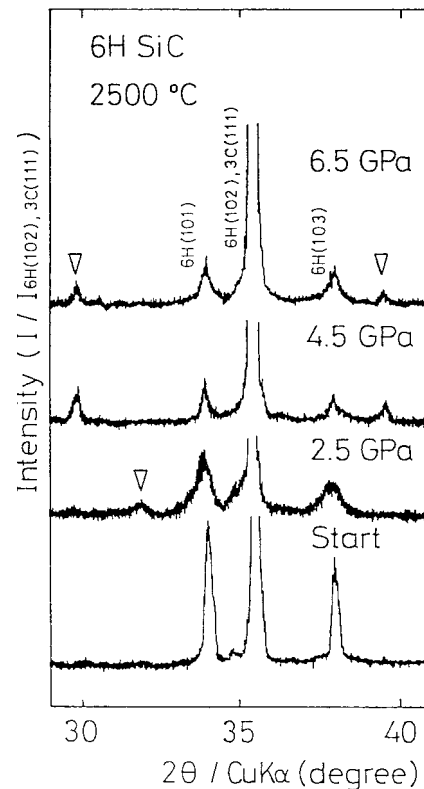
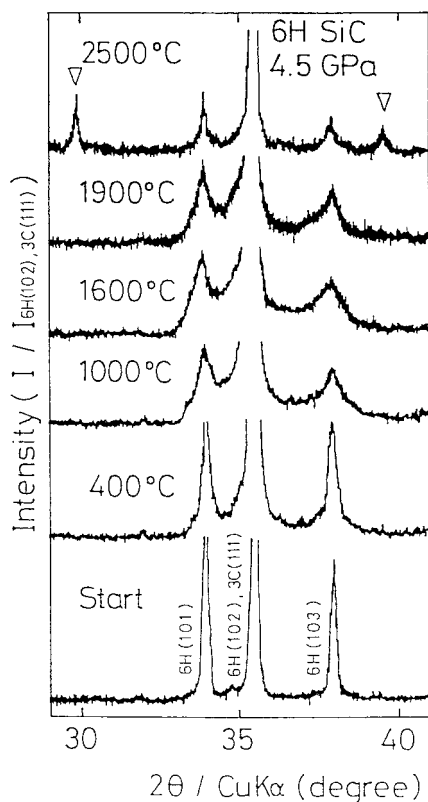


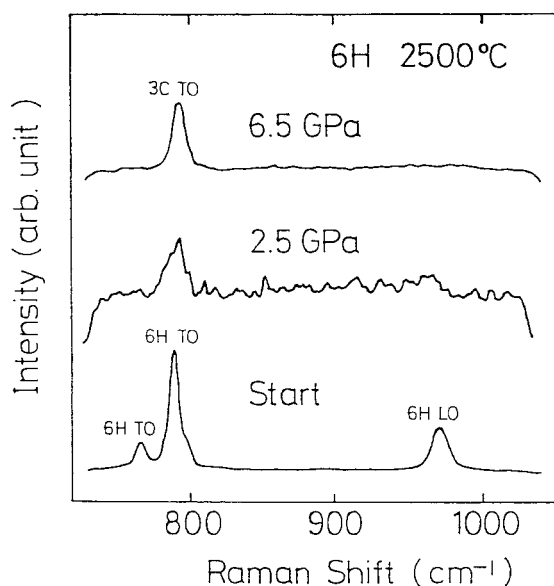
Fig. 2. Powder X-ray diffraction profiles for 6H-SiC retrieved after high-pressure treatment at 2500°C. Diffraction intensities are normalized to the 6H (102), 3C (111) peak.



**Fig. 3.** Powder X-ray diffraction profiles for 6H-SiC retrieved after high-temperature treatment at 4.5 GPa. Diffraction intensities are normalized to the 6H (102), 3C (111) peak.

transition from the 6H to the 3C form. Because the broadening decreased after treatment at higher temperature and resulted in the transition to 3C-SiC in our work, those researchers observed the starting process of the transition.

Figure 4 shows Raman-scattering data for samples retrieved after high-pressure treatment at 2500°C, together with data for the starting sample of the 6H form. The three TO modes of the 6H form (768, 788, and 793  $\text{cm}^{-1}$ ) are reduced to a single peak after



**Fig. 4.** Raman spectrums for starting 6H-SiC and samples retrieved after high-pressure treatment at 2500°C.

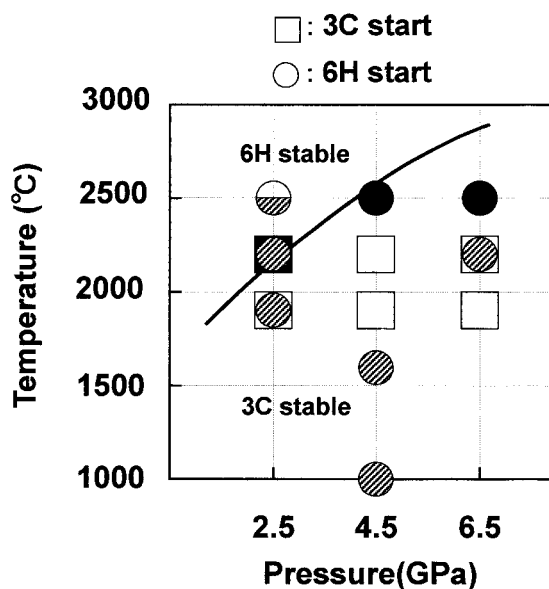
treatment. This 793  $\text{cm}^{-1}$  peak coincides with only one TO mode of the 3C form and occurs in the shoulder of the main peak of 788  $\text{cm}^{-1}$  in a starting sample of the 6H form. However, the LO mode of the 3C form at 970  $\text{cm}^{-1}$ , which is the same as that of the 6H form, is absent in the profile of the retrieved sample. This result might be attributable to a defect in the crystal, because this Raman peak also was absent in other sources of 3C-SiC produced at ambient pressure.

As mentioned earlier, both the XRD results and the Raman-scattering measurements indicate that the 6H form tends to transform to the 3C form at high temperatures, ranging up to 2500°C, under high pressure. The broadening of the XRD peaks at temperatures  $>1000^\circ\text{C}$  implies that the 6H form is a metastable form of SiC and starts transformation to the other form. This broadening in the lower-temperature region can be interpreted as the intermediate state of transition from 6H to 3C, 4H, 15R or other polytypes. However, it is a plausible interpretation that 6H-SiC starts transformation to 3C-SiC at low temperature because no diffraction peak intrinsic to 4H, 15R, or other polytypes was observed in the broadened XRD patterns and XRD and Raman-scattering showed the final product at 2500°C to be 3C-SiC.

As for influence of impurities on the experiments started from  $\alpha$ -SiC, chemical analysis showed that our  $\alpha$ -SiC sample did not contain a considerable amount of impurities and we believe the effect of metals faintly contained in the sample is negligible.

### (3) Phase Relationship between 3C and 6H

The present experimental results for the phase relationship between the 3C and 6H forms are summarized in Fig. 5. At pressures of 2.5 GPa, the 3C form is stable at temperatures up to 1900°C; above 1900°C, it transforms to the 6H form. In contrast, the instability of the 6H form causes a broadening of the peaks in the XRD profiles as the temperature increases above 1000°C. At temperatures  $>2200^\circ\text{C}$ , the intermediate state characterized by the broadening starts an inverse transformation to the 6H form, as it enters a stable  $p$ - $T$  region of the 6H form. However, because the transition proceeds slowly, the intermediate state remains at 2500°C and 2.5 GPa. All of these experimental results suggest that the phase boundary of the 3C and 6H forms exists at a temperature just below 2200° at 2.5 GPa and that the 3C form is a low-temperature phase of SiC and the 6H form a high-temperature phase.



**Fig. 5.** Summary of high-pressure and high-temperature experiments. Black circle (square) indicates phase transition between 3C- and 6H-SiC; open circle (square) indicates no characteristic change; shadow lined circle indicates broadening in X-ray diffraction profile.

On the other hand, at pressures of 4.5 and 6.5 GPa, the 3C form is stable to 2500°C, and the transformation of the 6H to the 3C forms, through the intermediate state, is accomplished at 2500°C. These results indicate that the phase boundary has a positive slope and that the stable region of the 3C form tends to extend to 2500°C with increasing pressure.

#### IV. Conclusions

The phase relationship between the 3C- and 6H-SiC in the  $p$ - $T$  field was examined by the phase analysis of samples recovered after high-temperature and high-pressure treatment, using XRD and Raman-scattering techniques.

3C-SiC transformed to 6H-SiC after treatment at 2.5 GPa and 2200°C. At higher pressures, 4.5 and 6.5 GPa, this transformation was not observed, and the 3C form was stable up to 2200°C. For 6H-SiC, the intensity of the 6H characteristic XRD peaks decreased after treatment at 2500°C under 4.5 and 6.5 GPa pressure, a result ascribed to transformation from the 6H to the 3C form. This transformation also was confirmed by Raman-scattering results. In the temperature range 1000°–1900°C, the XRD peaks of the 6H-SiC broadened, implying that the 6H form started a slow transformation to the 3C form, by the introduction of stacking faults.

The present experimental results led to the following conclusions:

(1) 6H- and 3C-SiC have high- and low-temperature stable regions, respectively.

(2) The phase boundary between the 6H and the 3C forms apparently occurs at just below 2200°C under 2.5 GPa pressure and has a positive slope.

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