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Pressure-induced phase transition in SiC

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X-ray diffraction studies have been made of cubic (3*C*) and hexagonal (6*H*) polytypes of SiC under pressures to 105 and 95 GPa, respectively, using a diamond-anvil cell and an imaging plate technique. 3*C*-SiC undergoes a phase transition into the rocksalt-type structure at 100 GPa or higher accompanied by a volume reduction of 20.3%. The 6*H* polytype of SiC remains stable to the highest pressure studied, with a premonition of a phase transition above 90 GPa. Equation-of-state data for the two polytypes have been found to be essentially the same to 95 GPa, yielding the bulk modulus 260(9) GPa and its pressure derivative 2.9(0.3).

Silicon carbide (SiC) is of considerable practical interest because of its current development for novel electronic devices[1–3] in addition to the traditional use for abrasives and refractories. Various polytypes exist in this material at ambient pressure. The polytypism originates from differences in the stacking sequence of silicon-carbon pair layers arrayed in the cubic (*C*), hexagonal (*H*), or rhombohedral (*R*) structure. Numbers are attached to each polytype according to the number of the layers within the stack. The most common polytypes are 3*C* and 6*H*.

There has been growing interest during the past decade in both experimental[4–12] and theoretical[13–18] studies relevant to the high-pressure properties of SiC. The experiments pursued by x-ray diffraction,[4–6] Raman scattering,[5–11] optical absorption[11,12] as well as luminescence[12] have been limited in most cases to approximately 50 GPa, while the theoretical works[15,16,18] predict an occurrence of a structural transition at around 60 GPa. The structure of the high-pressure phase expected has been either the rocksalt[15,16,18,19] or β-Sn.[20–22]

This paper reports x-ray-diffraction studies undertaken on 3*C*-SiC and 6*H*-SiC in a diamond-anvil cell. The pressure range covered was up to 105 GPa for 3*C* polytype and 95 GPa for 6*H* polytype, respectively.

Our 3*C*-SiC sample with purity higher than 99.43% and particle size in the range 1–2.5 μm was supplied by Ibigawa Denko Co. The 6*H*-SiC sample was provided by Sanyo Electric Co. in the form of a single crystal and was pulverized.

Each sample was pressurized in a gasketed diamond-anvil cell.[23] For 3*C*-SiC, either anvils with flat tops 0.40 mm across (below 80 GPa) or anvils beveled at diameters 0.15 and 0.35 mm (above 80 GPa) were employed. The 6*H*-SiC sample was pressurized with anvils with flat tops 0.40 mm across. A Ni-based alloy was used as the material for the gasket. A mixture of methanol, ethanol, and water was used as a pressure-transmitting medium. Ruby chips to monitor the pressure from the shift of the fluorescence line[24] were incorporated with the sample. The pressure generated on the sample was also estimated from the compression of the gasket in cases when the ruby fluorescence line could not be probed.[25]

For the x-ray source, a Mo $K\alpha$ radiation monochromatized with graphite or a synchrotron radiation at a wavelength of 0.6888 Å from the Photon Factory (BL-6B) at the National Laboratory for High Energy Physics was used. In both cases the x rays impinging upon the sample passed through a collimator with a diameter either 40 or 60 μm and the diffracted x rays were exposed on an imaging plate.[26] The exposure time was typically 12 h for the Mo $K\alpha$ radiation and 3 h for the synchrotron radiation.

Figure 1 shows x-ray-diffraction patterns of 3*C*-SiC recorded both on loading and unloading processes. The patterns shown in Fig. 1(a) were obtained with the Mo $K\alpha$ radiation, while those in Fig. 1(b) were from the synchrotron x-ray studies. The (111), (200), and (220) reflections based on the zincblende-type structure could clearly be observed to 36 GPa, Fig. 1(a) top. At higher pressures the (200) reflection merged into the reflection from the gasket, as exemplified by the pattern taken at 85 GPa, Fig. 1(a) middle. At 100 GPa, a weak peak appeared between the (111) reflection of 3*C*-SiC and the gasket line. This new peak was strengthened upon further increasing the pressure to 105 GPa and, as shown by the arrow in Fig. 1(a) bottom, became as intense as the (111) reflection of 3*C*-SiC.

This same sample under 105 GPa was next x-rayed

with the synchrotron radiation. As shown in Fig. 1(b) top, the gasket lines are perfectly eliminated due to the small divergence of the synchrotron x rays. In addition to the very weak (111) reflection from 3*C*-SiC, three reflections are observed which can unequivocally be assigned to the rocksalt-type structure. Table I shows the observed and calculated interplanar spacings and intensities for the rocksalt phase. The sufficient agreement between the experiment and the calculation indicates that the structure of the high-pressure phase transformed from 3*C*-SiC at 100 GPa or higher is the rocksalt type with a lattice parameter 3.684±0.003 Å and a unit-cell volume 50.0±0.11 cc/mole. This latter value for the volume is 0.603 times of the volume of the zincblende phase at ambient pressure (V_0). From the (111) reflection of the 3*C* phase in Fig. 1, the volume at the transition in the zincblende phase is calculated to be $0.757V_0$. These

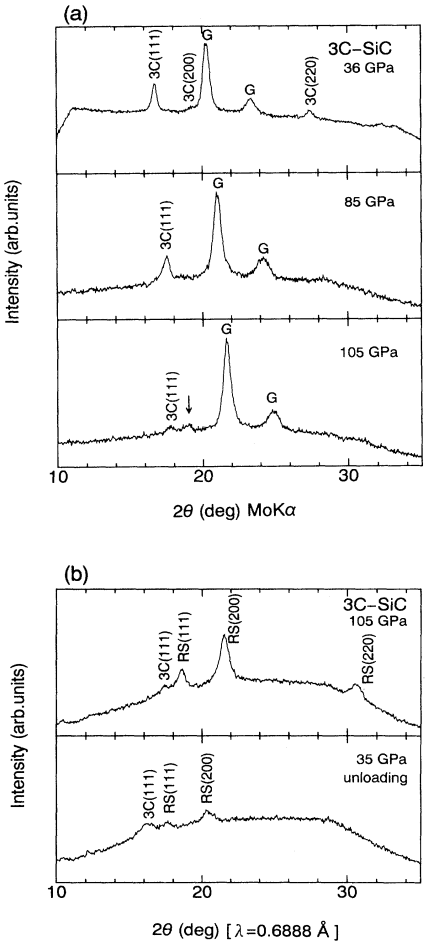

FIG. 1. X-ray-diffraction patterns recorded for 3*C*-SiC using (a) Mo $K\alpha$ and (b) synchrotron radiation for the x-ray source. In the case of synchrotron radiation, a wavelength of 0.6888 Å was employed. The letters 3*C* and RS respectively represent the 3*C* and the rocksalt phases. G denotes reflection from the gasket. The peak labeled by an arrow in the bottom pattern in (a) corresponds to the RS(111) reflection in the top pattern in (b). The two patterns were taken from the same batch of the sample at the same pressure, 105 GPa.

TABLE I. Interplanar spacings (d) and intensities (I) for the high-pressure phase of 3*C*-SiC.

Observed[a]			Calculated[b]	
d_{obs} (Å)	I_{obs}	hkl	d_{calc} (Å)	I_{calc}
2.1288	22	111	2.1269	57
1.8398	100	200	1.8419	100
1.3028	28	220	1.3024	68

[a]At a pressure of $100+\delta$ ($0\leq\delta\leq 5$) GPa.
[b]Calculated on the basis of the rocksalt-type structure of a cubic lattice with $a=3.684$ Å.

lead to a value of 20.3% for the volume reduction accompanying the transition.

Table II compares the present experiment with theoretical studies[15,16,18,20] performed on the transition parameters and the structure of the high-pressure phase of 3*C*-SiC. The transition pressures predicted are around 60 GPa. Our experiment shows that the transition in 3*C*-SiC occurs at 100 GPa or higher, approximately 60% greater than any of the predictions. The calculations[15,16,18] show that the volume of the 3*C* phase at which the transition should take place would be between $0.81V_0$ and $0.84V_0$. These values are 6–10% greater than the measured volume $0.757V_0$. The difference in the transition pressure between the experiment and the predictions does not invalidate the calculations because, as mentioned in our previous papers,[27,28] there is generally an eventual superpressing past the transition in the loading process and hence the observed transition pressure becomes definitely higher than the theoretical equilibrium pressure.

The fact that the high-pressure phase of 3*C*-SiC is the rocksalt type is in agreement with the predictions of Cohen and his colleagues[16,18,19] as well as of Christensen, Satopathy, and Pawlowska.[15] The β-Sn type suggested by Van Vechten[20] and Chelikowsky[21,22] did not appear in the pressure range covered in this study.

In the diffraction pattern taken at 35 GPa (Ref. 29) on the unloading process, Fig. 1(b) bottom, the (111) reflection of the 3*C* phase became a little more intense

TABLE II. Transition parameters and the structure of the high-pressure phase of SiC.

Pressure (GPa)	V_t/V_0[a]	$\Delta V(\%)$[b]	Structure	Reference
		Experiment		
100	0.757	20.3	Rocksalt	This study
		Calculation		
66	0.81	18.5	Rocksalt	16
64			β-Sn	20
60	0.825		Rocksalt	18
59	0.84[c]	19[c]	Rocksalt	15

[a]V_t is the volume of the zincblende (3*C*) phase at the transition, and V_0 is the volume at ambient pressure.
[b]Fraction of volume reduction accompanied by the transition.
[c]These numbers are not explicitly shown in the text of Ref. 15; we have derived them from Fig. 12 of this paper.

than the (111) reflection of the rocksalt phase. This indicates that a backward rocksalt-to-3*C* transition had taken place until the pressure was reduced to 35 GPa. The persistence of the rocksalt phase down to this pressure arises from a big hysteresis associated with the 3*C*-rocksalt phase transition.

Figure 2 shows x-ray-diffraction patterns for 6*H*-SiC. Five to seven reflections from the 6*H* phase are recorded in each pattern and most of them persisted to the highest pressure studied, 95 GPa. With the persistence of such reflections, there appeared two extra peaks at pressures greater than 90 GPa. These peaks, labeled by arrows in the pattern taken at 95 GPa, were not contaminated with the gasket line. The appearance of the new peaks might be an occurrence of other polytype or be premonitory of a phase transition similar to the case observed in 3*C* polytype. There is an ample possibility that 6*H*-SiC would also undergo a phase transition when pressurized to beyond 100 GPa.

The volume-pressure relations for 3*C* and 6*H* polytypes of SiC are shown in Fig. 3. There is no apparent difference between the equation-of-state data for the two polytypes, except for the discontinuity at 100 GPa exhibited by the 3*C* polytype associated with the phase transition. Fitting the data to 95 GPa with the Birch-Murnaghan equation[30] yields the bulk modulus (B_0) 260±9 GPa and its pressure derivative (B_0') 2.9±0.3, common to the two polytypes.

Table III gives the equation-of-state parameters obtained from experiments[4–6,10] and calculations.[13,14,16–18,31] Among the experiments, our B_0 for 3*C* and 6*H* polytypes is close to the value of Strössner, Cardona, and Choyke[4] from an x-ray-diffraction study to 25 GPa. Aleksandrov, Goncharov, Stishov, and Yakovenko[5,6,10] from x-ray diffraction studies to 42.5 GPa show much smaller B_0 for the 3*C* polytype. The calculations[13,14,16–18] are derived from pseudopotential basis except one[31] from macroscopic approach. The bulk moduli given by Dentneer and van Haeringen[14] differ by 108 GPa according to the cutoff energy in the plane-wave approximation, and the mean of the two bulk moduli appears to be close to our B_0. Other calculations[13,16–18,31] give B_0's that are significantly smaller than our B_0. Some of the calculations[13,31] are closer to the experiments[4–6,10] undertaken at lower pressures.

TABLE III. Bulk modulus B_0, and its pressure derivative B_0' for polytypes of SiC.

Type	B_0 (GPa)	B_0'	Pressure range (GPa)	Reference
		Experiment		
3*C*,6*H*	260±9	2.9±0.3	95	This study
3*C*	248±9	3.7±0.3	25	4
3*C*	227±3	3.57±0.1	42.5	5, 6, 10
15*R*	224±3	4.3±0.1	45	6, 10
		Calculation		
3*C*	308	2.1		14[a]
3*C*	200	7.3		14[b]
3*C*	249.4	3.159		13
3*C*	224			31
3*C*	212	3.7		16, 18
3*C*	196.21	3.5722		17

[a,b]Calculation was made for the energy cutoff of 20.6 Ry and 29.7 Ry, respectively, in the plane-wave method.

In conclusion, this study has found a pressure-induced phase transition of 3*C*-SiC into the rocksalt-type structure at 100 GPa or higher and at a volume of 75.7% of that at ambient pressure. The transition pressure is higher by about 60% and the volume is smaller by 6–10% than the recent first-principles calculations.[15,16,18] 6*H*-SiC was found to be stable at least to 95 GPa. Extra peaks appeared in the x-ray-diffraction patterns above 90 GPa, possibly premonitory of a phase transition also in the 6*H* polytype. The bulk modulus

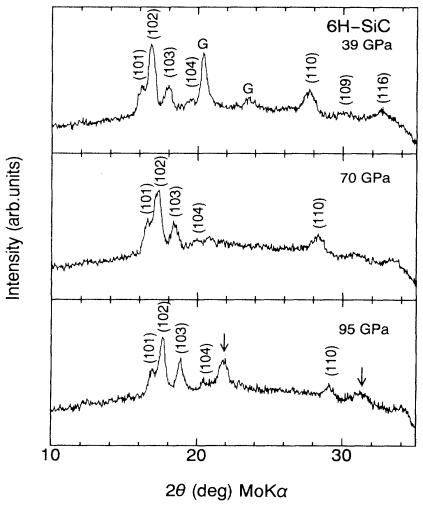

FIG. 2. X-ray-diffraction patterns recorded for 6*H*-SiC. Only Mo $K\alpha$ radiation was employed. G denotes reflection from the gasket. The peaks labeled by arrows are reflections other than from 6*H* phase.

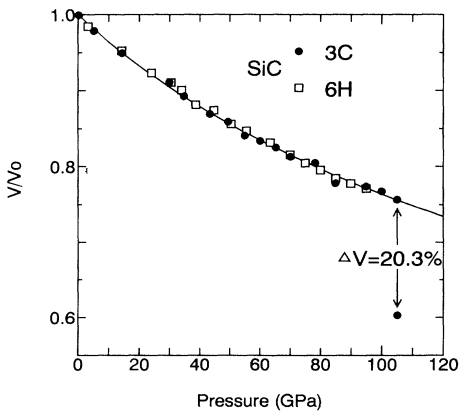

FIG. 3. Change of the relative volume of 3*C* and 6*H* polytypes of SiC as a function of pressure.

260(9) GPa, common to the two polytypes, is larger than any of the previous experiments[4–6,10] performed at lower pressures, and, also larger than most of the calculations.[13,14,16–18,31]

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