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LOW-TEMPERATURE SOLID-STATE PHASE TRANSFORMATIONS IN 2H SILICON CARBIDE

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16. Abstract

Single crystals of 2H SiC were observed to undergo phase transformations at temperatures as low as 400° C. Some 2H crystals transformed to a structure with one-dimensional disorder along the crystal c-axis. Others transformed to a faulted cubic/6H structure. The transformation is time and temperature dependent and is greatly enhanced by dislocations. Our observations indicate that the transformation takes place by means of a slip process perpendicular to the c-axis. Cubic SiC crystals were observed to undergo a solid-state transformation above 1400° C.

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SUMMARY

Silicon carbide is a wide band gap semiconductor with much potential for high-temperature application. Because of high strength in whisker form and excellent chemical stability, it is also a potential fiber-reinforcement material. A serious problem with this compound is that it forms many crystalline structures, some of which are unstable. Recently, it was reported that the pure hexagonal form, 2H SiC, transforms to the cubic form, 3C SiC, above 1400° C by a solid-state process.

This report shows that 2H SiC is unstable at much lower temperatures and that 2H crystals with dislocations will transform at temperatures as low as 400° C. Both optical and X-ray techniques were used to observe the results of solid-state phase transformations in 2H SiC single crystals that had been heated to temperatures in the range 400° to 1800° C. The structure after transformation was either one-dimensional disorder along the crystal c-direction or a faulted cubic or 6H structure. The rate of transformation, besides being dependent on dislocations, is also dependent on time and temperature. The transformation takes place by means of a slip process perpendicular to the c-axis.

The report also shows that cubic SiC underdoes a solid-state phase transformation at temperatures above 1400° C. Under the same conditions the 4H and 6H crystalline forms of SiC do not show any evidence of a transformation.

INTRODUCTION

Silicon carbide is a refractory compound with much promise for certain electronic and structural applications. Its wide energy bandgap and high mobility should make it a useful high-temperature semiconductor (refs. 1 and 2). Because of high strength in whisker form and excellent chemical stability, it may find use in fiber-reinforced materials (ref. 3). A serious problem which has been encountered is that SiC forms many crystalline structures, some of which are unstable.

Since polymorphism in SiC is one-dimensional, the various crystalline forms are called polytypes (ref. 4). These polytypes are built up by the stacking of hexagonal close-packed layers with the stacking sequence in the [0001] direction (also called the c-axis). Because of the close-packed stacking there are only three possible positions for a layer, and these are arbitrarily called A, B, and C. Polytype structures are usually designated by a number followed by a letter. In the designation 2H, 3C, 15R, etc. the number refers to the number of layers in the unit cell. The letters H, C, and R refer to the type of lattice (hexagonal, cubic, or rhombohedral). The stacking sequence can vary from a pure hexagonal (2H structure) to a pure cubic (3C or β) structure. The 2H structure has an ABAB . . . stacking sequence, and the 3C structure has an ABCABC. . . stacking sequence. A mixture of these stacking sequences gives rise to a large number of other polytypes. The most common polytype (6H) has an ABCACB. . . stacking sequence. Frequently the stacking sequence will vary in a single crystal resulting in distinct layers of different polytypes. In some cases the stacking sequence is random for some distance along the c-axis so that there is one-dimensional disorder (ref. 5).

There has been no satisfactory explanation for the formation of the various SiC polytypes. There have been indications that impurities play a role in the formation of the polytypes (ref. 6). Most polytypes are grown by a vapor (Lely) process in the temperature range 2300° to 2700° C (refs. 7 and 8). The 2H polytype has only been grown by a chemical reduction process at about 1400° C (refs. 9 to 12). Cubic SiC has been grown over the temperature range 1200° to 2500° C by a variety of techniques (refs. 11 and 13 to 15).

The question of the relative stability of the various SiC polytypes has not been completely answered. However, recent observations of phase transformations in SiC have provided some answers. Krishna, Marshall, and Ryan (refs. 16 and 17) reported that needle-shaped single crystals (up to 1-mm diam.) of 2H SiC convert to the 3C structure above 1400° C by means of a solid-state transformation. When heated to temperatures above 2200° C, the crystals further transformed to a heavily faulted 6H structure. These authors suggested that the 3C structure was the stable modification in the temperature range 1400° to 1800° C. Bootsma et al. (ref. 18) observed phase transformations in the 2H, 3C, 4H, and 15R polytypes. Their 2H crystals were in the form of thin whiskers 1 to 2 micrometers in diameter, and these transformed to small platelets with the 3C structure in the temperature range 1500° to 1700° C. When heated further to the temperature range 1800° to 2400° C, the platelets transformed to the 6H structure. In both steps, 2H → 3C and 3C → 6H, the transformation was by means of a regrowth process; material was transported by surface diffusion. At temperatures above 2000° C the other polytypes, 4H and 15R, transformed to the 6H structure. This was also a regrowth process rather than a solid-state transformation.

A hexagonal to cubic SiC transformation has been found to occur in nitrogen at high pressures and temperatures around 2500° C (ref. 14). It is not clear whether or not this was a solid-state transformation.

This report is a result of an effort at the Lewis Research Center to develop high-temperature semiconductor devices. Initially 2H SiC appeared to be a promising material for this purpose (ref. 19). However, after growing and evaluating 2H SiC crystals, they were found to be unstable above 400° C. Thus, 2H SiC is unsuitable as a high-temperature semiconductor and possibly unsuitable as a reinforcing fiber in composite materials.

Both optical and X-ray techniques were used to observe the results of solid-state phase transformations in 2H SiC single crystals. These crystals had been heated to temperatures ranging from 400° to 1800° C. Solid-state phase transformations were observed to take place in cubic SiC above 1400° C. The optical property of birefringence was a very sensitive method for detecting structural changes in SiC crystals. Interference microscopy was used to observe deformation of the crystals. X-ray diffraction showed the gross structure changes which occurred.

EXPERIMENTAL PROCEDURE

The 2H silicon carbide crystals used in this investigation were grown by the chemical reduction of methyltrichlorosilane at 1400° C (ref. 19) and were similar to those described by Krishna, Marshall, and Ryan (ref. 17). The crystals grew in the shape of tapered needles up to 3 millimeters long and had hexagonal cross sections up to 0.5 millimeter in diameter. The c-axis was along the axis of the needles.

A ball-shaped deposit of polycrystalline cubic silicon carbide was frequently found attached to the pointed end of the needles. Near the base of the needle there often were thin regions (perpendicular to the needle axis) where the structure was a mixture of highly disordered cubic and 2H silicon carbide. Similar disordered regions occurred less frequently near the small end of the needle. The major portion of each crystal was clear and colorless. The highly disordered regions and the ball-shaped deposits were yellow.

The transformation in the 2H SiC crystals were studied with the crystals fabricated into thin wedges or in the as-grown condition. The condition in which they were broken from the growth susceptor will be called the as-grown condition. The thin wedges were fabricated so that changes in the birefringence could easily be measured. As will be shown later, the process of making the wedges apparently changed the transformation behavior of the crystals. The wedges were made by grinding with diamond paste against a glass plate with the resulting wedge angle varying from 5.7° to 8.8°. The orientation and shape of the resulting wedge is shown in figure 1. The 2H SiC wedges in this report

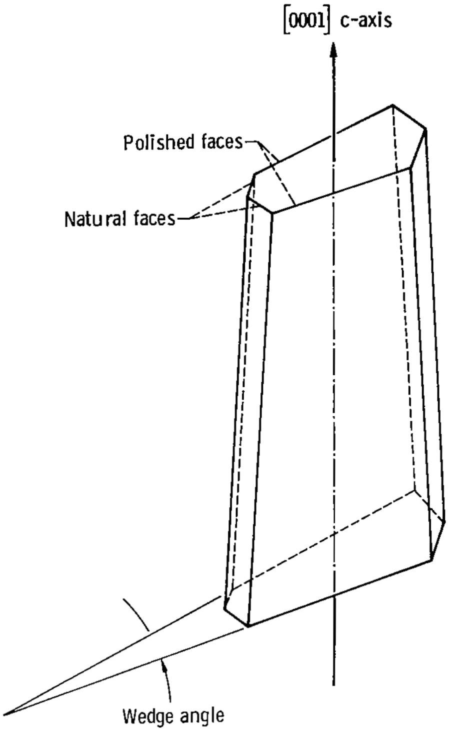


Figure 1. - 2H silicon carbide wedge.

are the same as those for which index of refraction measurements were reported in reference 20. Wedges were also prepared from two cubic SiC crystals and a SiC crystal containing both 4H and 6H regions.

All of these crystals were put through various heat cycles. The heating experiments were all performed in a vacuum. For heat cycles up to 1000° C a small resistance heater was used. The crystals were contained in a graphite crucible with a Chromel-Alumel thermocouple at the base to measure the temperature. For heating above 1000° C a graphite crucible containing the crystals was placed in a graphite split-tube resistance heater. In this case an optical pyrometer sighting on the inside of the crucible was used to measure the temperature. The estimated error in the temperature measurements is less than $\pm 20^{\circ}$ C.

The techniques used to measure the effect of heating the SiC samples to various temperatures included X-ray diffraction and optical, interference, and scanning electron microscopy.

The X-ray technique used to examine the structure of the crystals was the rotating crystal method. Rotation was about the c-axis of the crystal. The incident radiation was CuKα with a nickel filter to reduce the Kβ intensity. The film cassette radius was 3 centimeters, and the beam collimator diameter was 0.28 millimeter. This produced a beam diameter considerably smaller than the crystals, thereby allowing sections of a crystal to be examined separately. The interpretation of the X-ray rotation photographs is discussed in appendix A. The information needed to determine the particular polytype and to detect the presence of stacking disorder is essentially contained in the row of ($10\cdot \ell$) diffraction spots on the X-ray photograph. Therefore, only the ($10\cdot \ell$) row will be given in this report to illustrate the structure of the crystals.

Birefringence observations were also used to detect the structural changes in the crystals. The technique was as follows: A wedge was placed between crossed polarizing filters and illuminated with monochromatic light ($\lambda = 633$ nm with a bandwidth of 1.0 nm). Because of the varying thickness of the wedge, interference fringes formed that were parallel to the intersection of the wedge faces. Similar interference fringes were observed for the as-grown crystals since they also have reasonably flat natural faces and are tapered. A list of the heat cycles for the various samples is given in tables I to III.

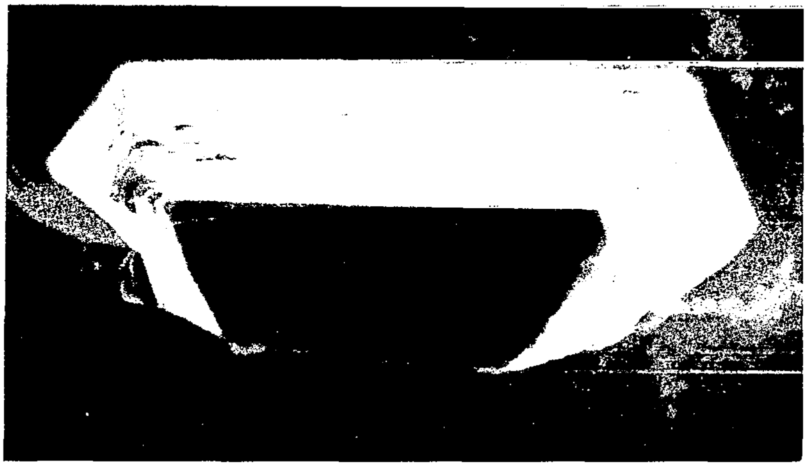
EXPERIMENTAL RESULTS

Transformation of the Wedges

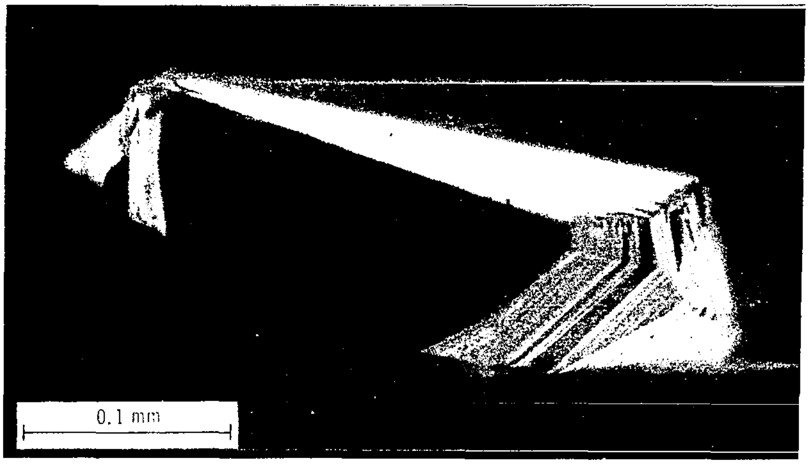
The first change in the 2H SiC wedges which was observed after heating was their physical appearance. As the 2H wedges were heated to successively higher temperatures or for longer periods of time at a given temperature, a twist about the c-axis gradually developed. Also, ridges approximately perpendicular to the c-axis developed on the polished faces.

The twist that developed in wedge 79-3 is shown in figure 2. These photos were taken with a scanning electron microscope operating in the secondary electron mode. The viewing direction is approximately along the c-axis so that the twist can be clearly seen. Figure 3 shows a series of photos of one of the polished surfaces taken with a noncontacting interference microscope. Because of the twist, the number of fringes counted along a direction perpendicular to the c-axis varies along the length of the wedge. The twist can be calculated from the change in the number of fringes along the length of the wedge and the wavelength of the light. In wedge 79-3 a change began at 300° C or below (fig. 3(b)). At 600° C (fig. 3(d)) the twist increased to a maximum of 12° per millimeter, and at 1000° C (fig. 3(e)) the twist decreased to 6.4° per millimeter.

X-ray diffraction was used to determine the structure of the crystal lattice. The results for wedge 79-3 are shown in figure 4. The before-heating X-ray pattern (fig. 4(a)), which was taken after the crystal had been fabricated into a wedge, shows by the lack of streaking along the ($10\cdot \ell$) row and the well-defined diffraction spots that there was very little stacking disorder. After heating to 450° C (fig. 4(b)), the well-defined diffraction spots smeared out indicating a change to a more disordered structure. As

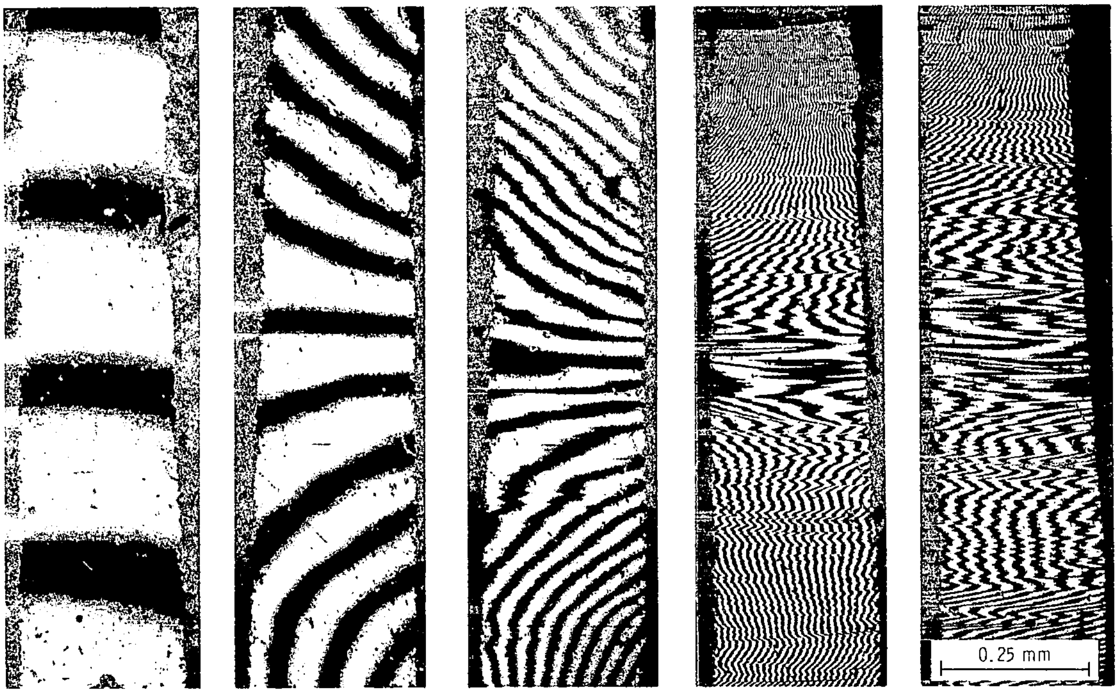


Before heating.



After 800° C heat treatment; note the twist that developed on heating.

Figure 2. - Scanning electron microscope photograph (secondary electron mode) of wedge 79-3. These views are sighting down along the c-axis.



(a) Before heating (λ = 592 nm).

(b) After heating to 300° C for 1 hour (λ = 592 nm).

(c) After heating to 450° C for 1 hour (λ = 592 nm).

(d) After heating to 600° C for 1 hour (λ = 633 nm).

(e) After heating to 1000° C for 1 hour (λ = 633 nm).

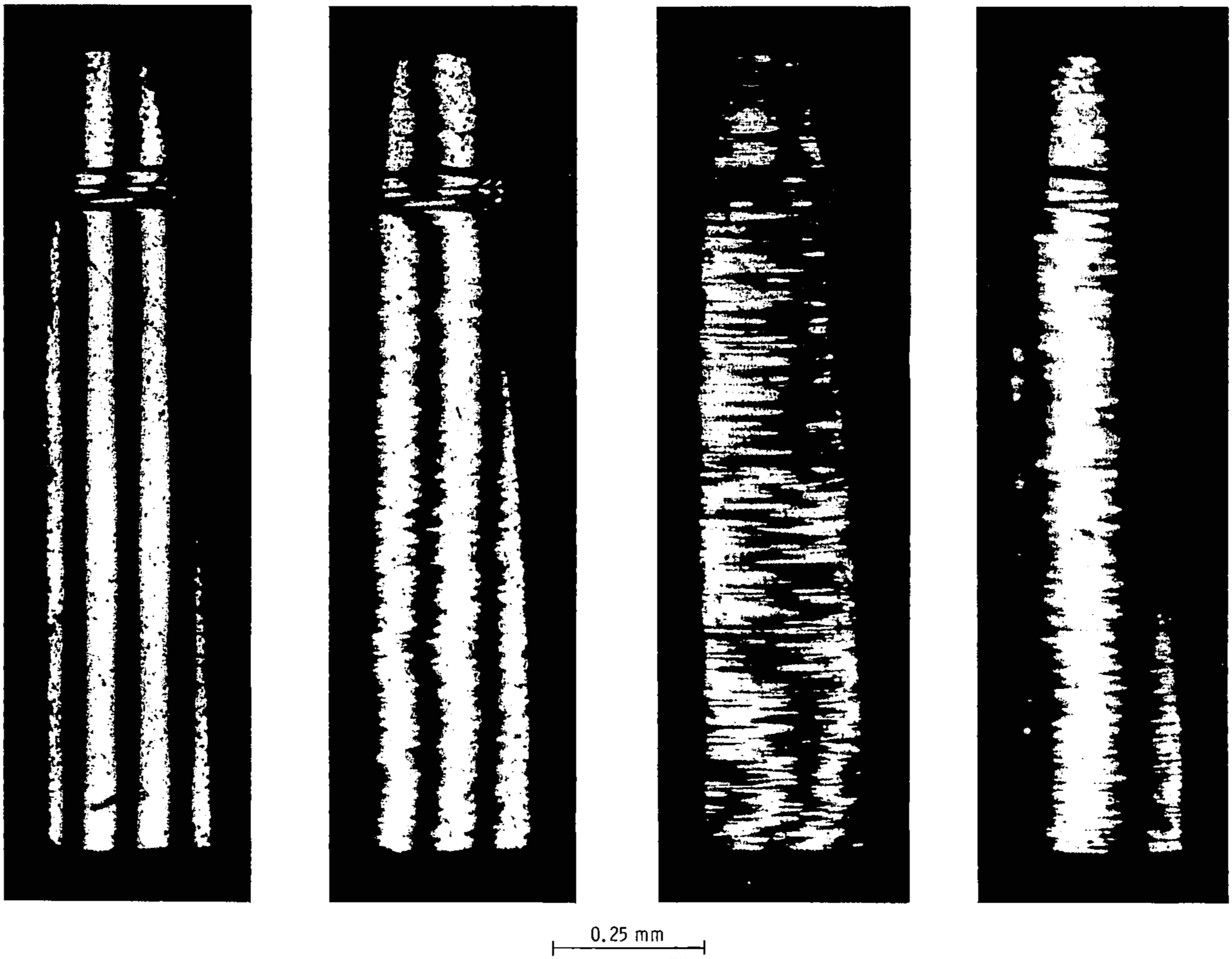
Figure 3. - Interference photographs (reflected light) of polished surface of wedge 79-3. (Small end of crystal is at top of photographs.)

(a) Before heating. (b) After heating to 450° C for 1 hour. (c) After heating to 800° C for 1 hour. (d) After heating to 1200° C for 24 hours.

Figure 4. - The (10·ℓ) row of c-axis X-ray rotation pattern for 2H wedge 79-3. Copper Kα radiation; camera radius, 3 centimeters.

the crystal was heated to higher temperatures (figs. 4(c) and (d)) the streaking along the (10· ℓ) row fanned out. Many different orientations of the wedge with respect to the X-ray camera rotation axis were tried to insure that the fanning out of the diffraction streaks was not caused by misalinement of the wedge. The conclusion was reached that the c-axis direction varied throughout the crystal.

Changes in the birefringence of wedge 79-3 also indicated that a structural change was occurring on heating. Figure 5 shows successive photos of the interference fringes due to birefringence for this wedge. Up to a temperature of 300° C the interference bands did not change. At 450° C the birefringence started to decrease (fig. 5(b)). The decrease is indicated by a wider fringe spacing. At 600° C the bands became very distorted (fig. 5(c)). Upon heating to 800° C the distortion reverted back to distinguishable bands. Above 800° C there was no further change except for a slight decrease in the birefringence.



(a) Before heating.

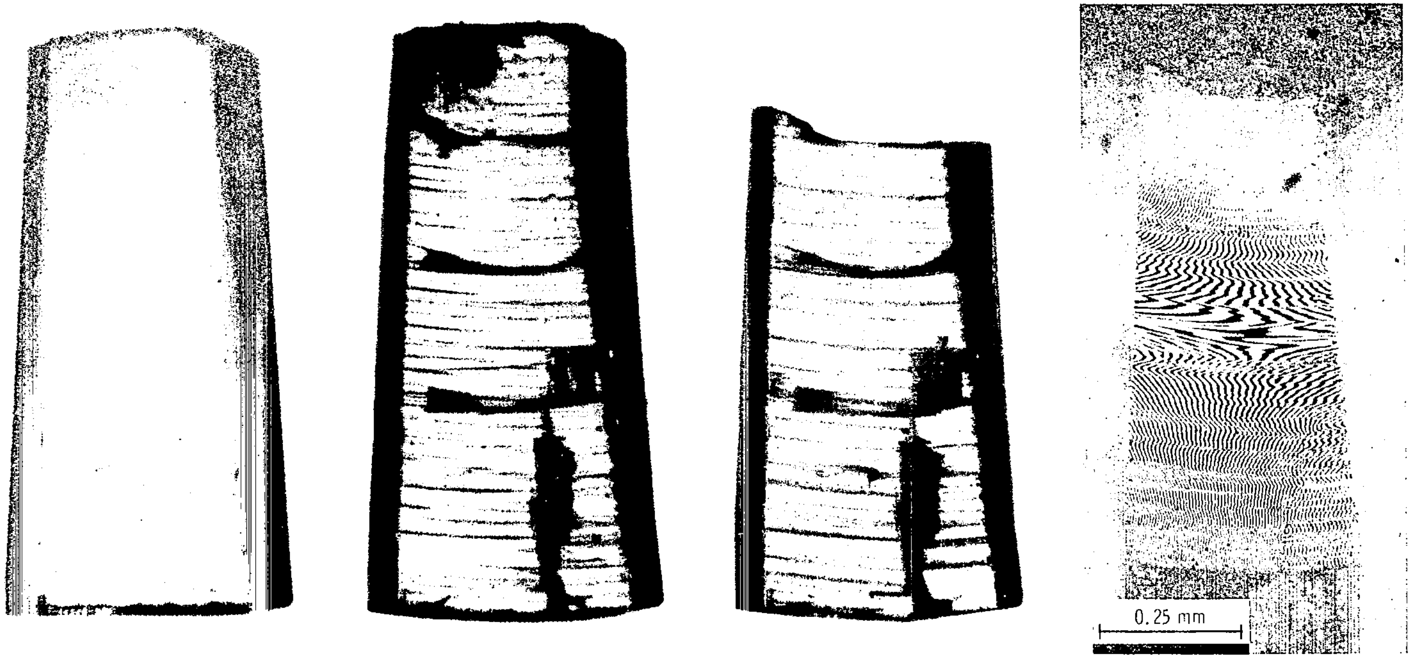
(b) After heating to 450° C for 1 hour.

(c) After heating to 600° C for 1 hour.

(d) After heating to 800° C for 1 hour.

Figure 5. - Interference fringes due to birefringence for wedge 79-3. Transmitted light; wavelength, 633 nanometers; wedge between crossed polarizers.

It was found that the 2H SiC wedges will fracture when the crystal is heated for long periods of time at 400° C. Wedge 75-8 was heated to 400° C for various lengths of time. After being heated for 24 hours at this temperature the crystals exhibited a twist of about 12° per millimeter and a crack had started. After 72 hours the crystal was as shown in figure 6(b). The three nonuniform horizontal dark lines and one short vertical line are cracks. In addition to the cracks, there are parallel ridges that developed on the polished face (figs. 6(b) and (c)). These ridges, which are indicated by the zig-zag pattern of the interference fringes in figure 6(d), curve slightly. This effect was observed in all three 2H wedges.



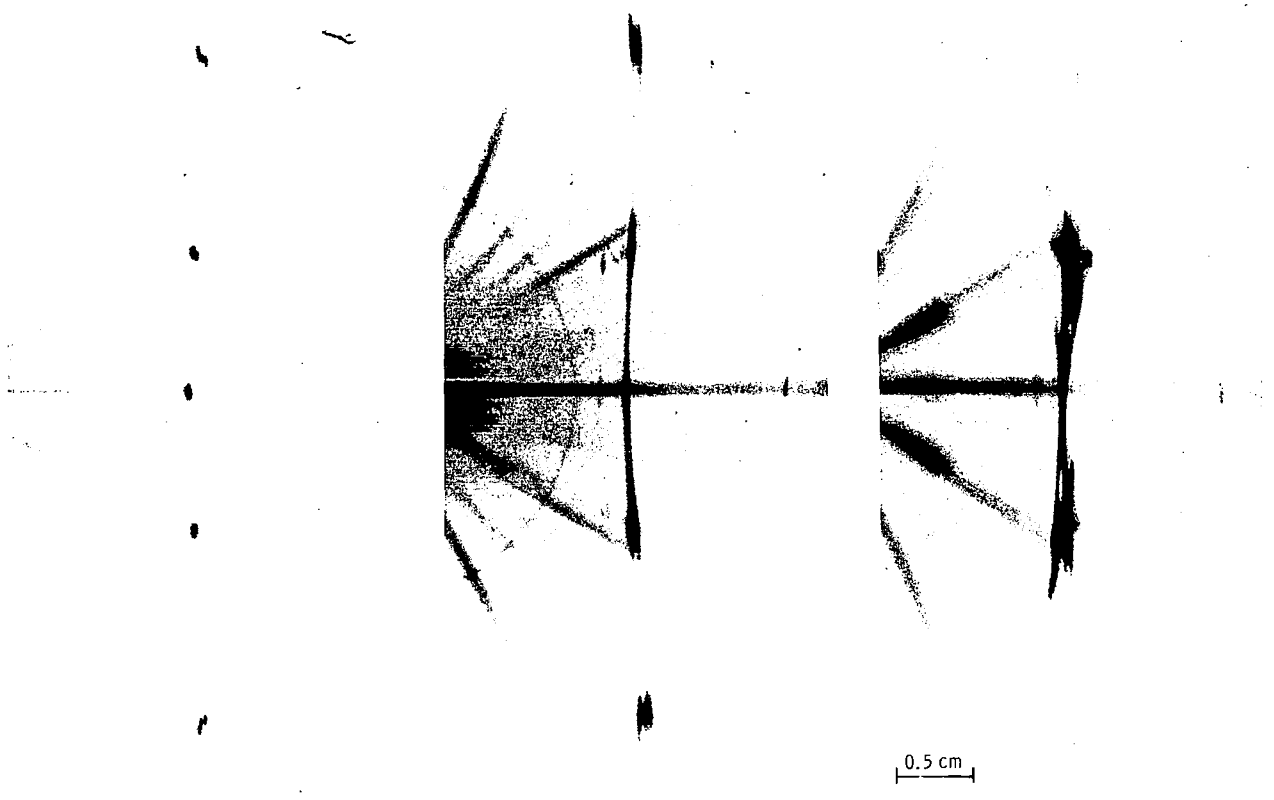
(a) Before heating; transmitted light photograph.

(b) After heating to 400° C for 72 hours; transmitted light photograph.

(c) After heating to 1400° C for 72 hours; transmitted light photograph.

(d) After 1400° C heat cycle (λ = 633 nm); interference (reflected light) photograph.

Figure 6. - Photographs of Wedge 75-8.

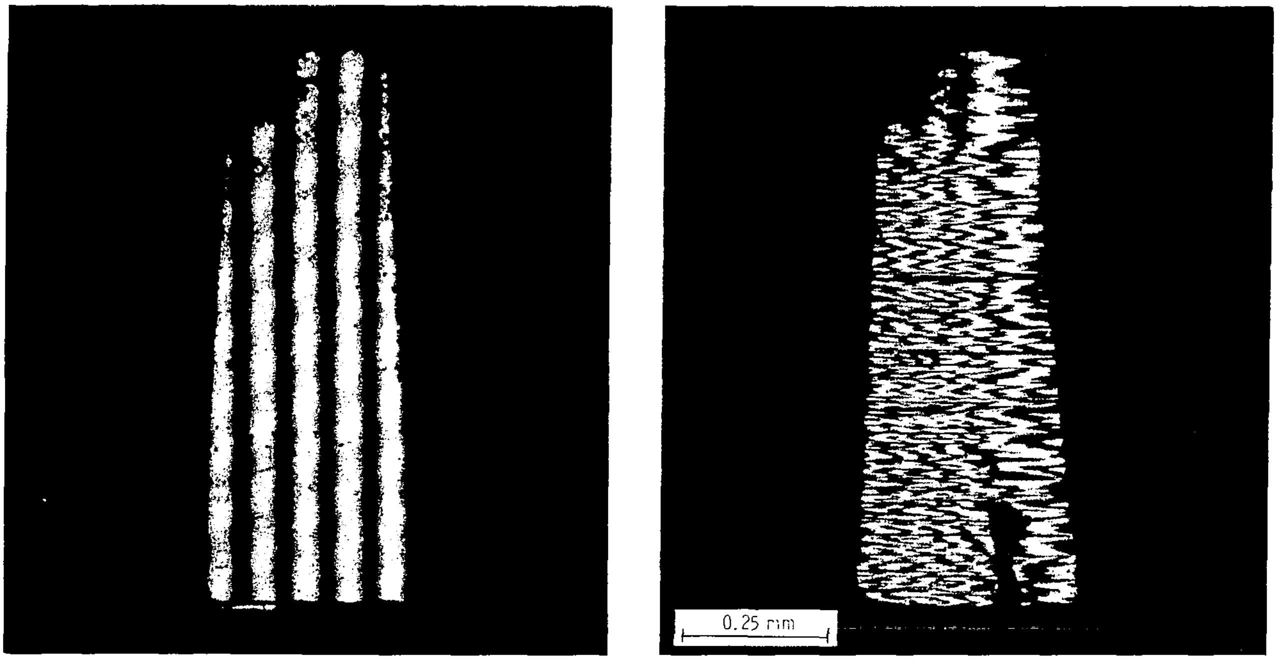


(a) Before heating. (b) After heating to 400° C for 24 hours. (c) After heating to 400° C for 72 hours.

Figure 7. - (10·ℓ) row of c-axis X-ray rotation pattern for 2H wedge 75-8. Copper Kα radiation; camera radius, 3 centimeters.

The structure change of wedge 75-8 is indicated by the X-ray pattern shown in figure 7. Initially this wedge had only a slight trace of stacking fault disorder. After heating to 400° C for 24 hours (fig. 7(b)), the (10·ℓ) reflections became noticeably diffuse. After an additional 72 hours at 400° C (fig. 7(c)) there was nearly a continuous streak along the (10·ℓ) row. There was also fanning out of this streak due to the deformation of the crystal.

The first and second heating cycles (5 min and 1 hr) at 400° C produced only a slight decrease in the birefringence of wedge 75-8. There was no distortion of the interference fringes due to birefringence. However, continued heating at 400° C for 24 hours caused the interference bands to become very distorted as shown in figure 8. This distortion started to revert back to distinguishable bands when the wedge was heated to 1600° C. However by this time the polished surfaces had become frosted making the bands very blurred.



(a) Before heating.

(b) After heating to 400° C for 24 hours.

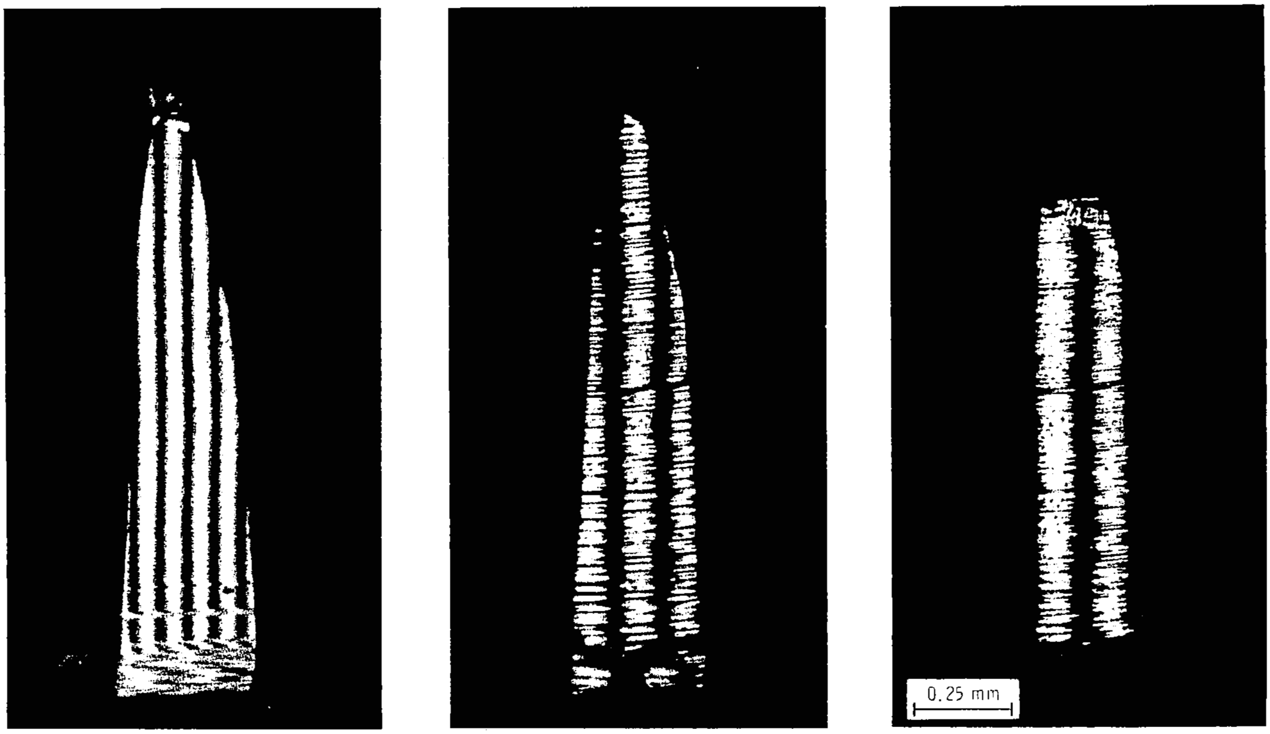
Figure 8. - Interference fringes due to birefringence for wedge 75-8. Transmitted light; wavelength, 633 nanometers; wedge between crossed polarizers.

The first heat cycle for wedge 79-2 was at 1000° C for 5 minutes. The wedge developed a twist of 8.3° per millimeter and then fractured near the wider end. As with many of the 2H crystals, wedge 79-2 contained thin yellowish layers near the base, which were a mixture of highly disordered 2H and cubic structure. These layers most often occur at the base of a crystal where it had been attached to the graphite growth susceptor. (See ref. 12 for 2H crystal growth.) Most of wedge 79-2 was clear and colorless, but, after being heated to 1000° C, it was yellowish in color.

An X-ray rotation pattern of the disordered region near the base of wedge 79-2 indicated that before heating this was a region of random stacking order. The rest of the crystal was determined to be a well ordered 2H structure from the X-ray rotation pattern. After heating to 1000° C the entire crystal transformed to a random stacking sequence. These X-ray results were the same as for wedges 79-3 and 75-8.

The interference pattern due to the birefringence for wedge 79-2 is shown in figure 9. The interference fringes did not appear to go through a stage of gross disorder; however, the crystal did fracture at both the top and bottom.

The results of the heat cycles for the wedges are shown in tables I and II.



(a) Before heating. (b) After heating to 1000° C for 5 minutes. (c) After heating to 1000° C for 24 hours.

Figure 9. - Interference fringes due to birefringence for wedge 79-2. Transmitted light; wavelength, 633 nanometers; wedge between crossed polarizers.

Transformation of Undoped As-Grown Crystals

Five as grown 2H crystals were studied in detail; two of these were nitrogen doped and will be discussed in the next section. The three others were clear and colorless with ball-shaped deposits of polycrystalline β-SiC on the end. These will be called the undoped crystals in the following discussion.

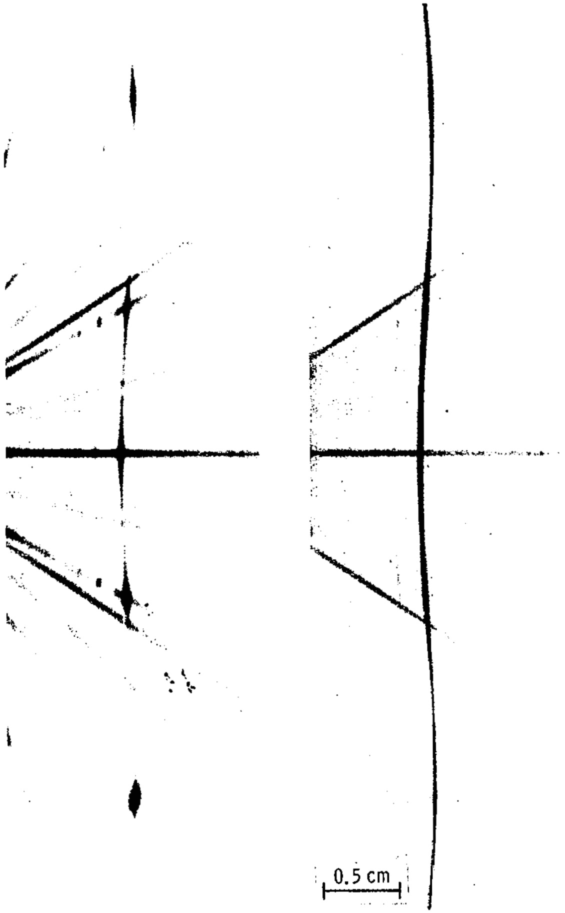
Although the transformation starts at around 400° C in the as-grown crystals, it was much slower than in the wedges. Figure 10 shows the birefringence in undoped crystal 76-1 before and after being heated. The interference fringes due to the birefringence were only slightly distorted after the crystal had been heated to 400° C for 96 hours (fig. 10(b)). An additional heat cycle at 1000° C for 24 hours completely washed out the fringes (fig. 10(c)). In this crystal the $(10 \cdot \ell)$ X-ray diffraction spots for the 2H structure showed only a slight increase in the streaking along the row of spots after being heated to 400° C (fig. 11(a)). After the 1000° C heat cycle (fig. 11(b)) the $(10 \cdot \ell)$ row of diffraction spots became a continuous line. Additional heat cycles at 1400° and 1600° C had no effect on the birefringence or X-ray rotation patterns. The lack of fan out of the

(a) Before heating.

(b) After heating to 400 C for 96 hours.

(c) After heating to 1000 C for 24 hours.

Figure 10. - Interference fringes due to birefringence for as-grown crystal 76-1. Transmitted light; wavelength, 633 nanometers; crystal between crossed polarizers.



(a) After heating to 400° C for 96 hours.

(b) After heating to 1000° C for 96 hours.

Figure 11. - (10·ℓ) row of c-axis rotation pattern for 2H crystal 76-1. Copper Kα radiation; camera radius, 3 centimeters.

(10· ℓ) row in the X-ray pattern (fig. 11(b)) also shows that heating the crystal did not cause bending of the c-axis as was observed for the wedges.

Two other undoped 2H crystals (68-1 and 79-4) were subjected to 24-hour heat cycles at 1000° and 1400° C, then 7-hour heat cycles at 1600° and 1800° C. As with crystal 76-1, the interference fringes due to the birefringence washed out completely after the crystals were heated to 1000° C. The X-ray patterns of these two crystals showed only a small amount of streaking along the (10· ℓ) row after being heated to 1800° C. The diffraction spots for the 2H structure were still clearly present, although somewhat diffused.

The natural faces of crystals 68-1 and 79-4 were sufficiently flat that good surface interference photographs could be taken. Ridges perpendicular to the c-axis could be detected on both crystals with the surface interference photographs after these crystals were heated to 1400° C. These ridges were straight and not curved as were the ridges observed on the polished faces of the wedges. Figure 12 shows some of the ridges that appeared on the surface of crystal 68-1. The 1600° C heat cycle did not affect the height or number of ridges, and the 1800° C heat cycle "frosted" the surface too badly for surface interference pictures to be taken.

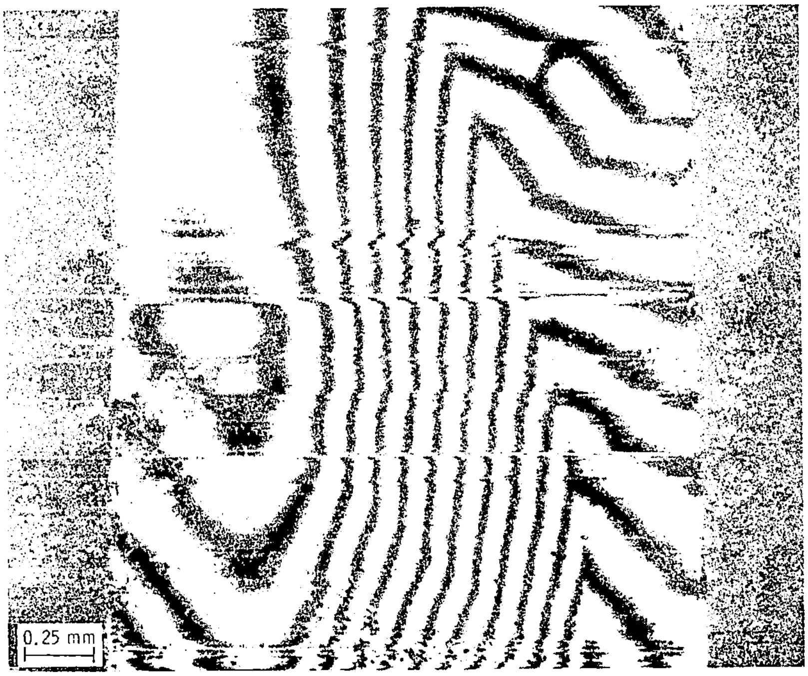
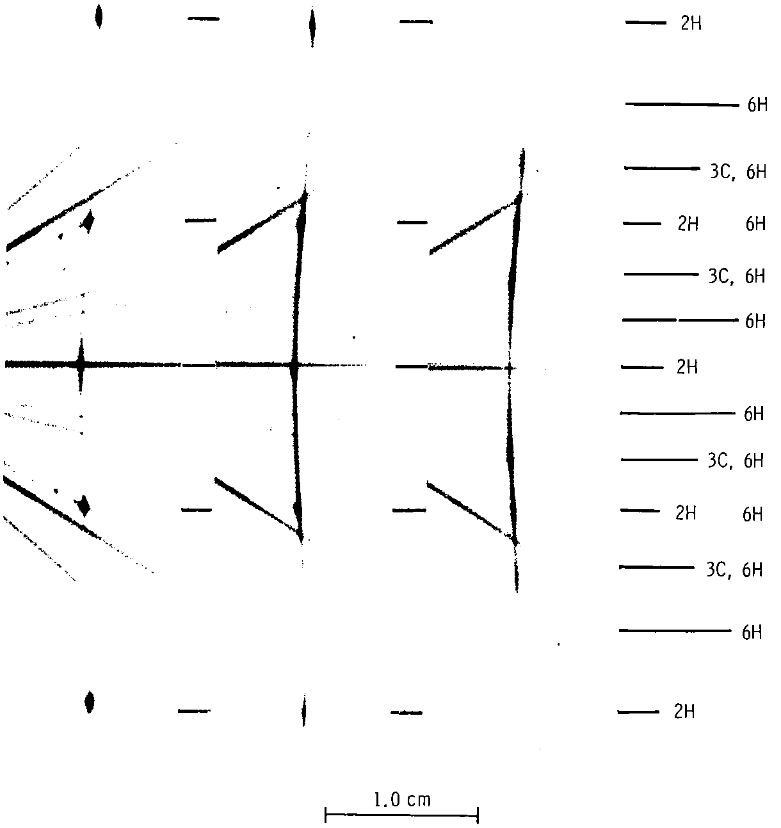


Figure 12. - Interference photograph (reflected light) of one of the natural faces of crystal 68-1 after being heated to 1400° C for 24 hours (λ = 633 nm).

These results indicated that only a partial transformation had taken place in crystals 68-1 and 79-4. Since dislocations were suspected of largely determining the transformation temperature, the following experiment was performed. After the 1800° C heat cycle the two crystals were rubbed lightly against some 6-micrometer diamond paste on a glass plate. The purpose was to scratch the SiC crystals and hence cause surface dislocations. The crystals were then subjected to a 1000° C heat cycle for about 2 hours. They changed from colorless to very yellow. X-ray rotation patterns before and after the heat cycles for crystal 79-4 are shown in figure 13. The X-ray results for crystal 68-1 were the same. The crystals had transformed from a faulted 2H to a structure that produced diffraction spots of both cubic and 6H SiC. These crystals, which had only partially transformed after being heated to 1800° C, underwent a gross transformation at 1000° C as a result of the surface dislocations.



(a) Before heating.

(b) After heating to 1800° C for 7 hours.

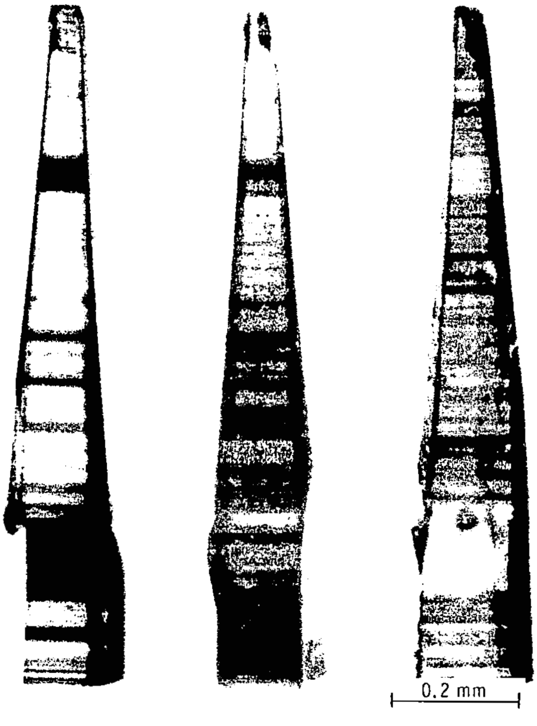
(c) After being scratched with diamond powder and then heated to 1000° C for 2 hours.

Figure 13. - (10·ℓ) row of c-axis X-ray rotation pattern for 2H crystal 79-4. Copper Kα radiation; camera radius, 3 centimeters.

Transformation in Nitrogen-Doped As-Grown Crystals

During one crystal growth run, nitrogen was intentionally added to the carrier gas. The resulting crystals were light violet in color and some of the crystals had blue-green bands perpendicular to the c-axis. When the crystals were examined with polarized light it was found that, when the direction of polarization was parallel to the c-axis (extraordinary ray), the colors were enhanced. However, when the direction of polarization was perpendicular to the c-axis (ordinary ray), the crystal became colorless as both the violet color and the blue-green bands disappeared. This optical effect, called dichroism, has been reported for other nitrogen doped SiC polytypes (ref. 21). The colors vary with polytype, ranging over the full visible spectrum.

Two of these nitrogen-doped 2H crystals (52-1 and 52-2) were subjected to various heat cycles. Their transformation behavior as determined from the birefringence and X-ray patterns was similar to crystal 76-1. The interference fringes due to the birefringence were almost completely washed out after the 1000° C heat cycles. Also, the



(a) Before heating.

(b) After heating to 400° C for 96 hours.

(c) After heating to 1000° C for 24 hours.

Figure 14. - Photographs of crystal 52-2 in polarized transmitted light. Polarization is parallel to c-axis (along length of crystal).

(10·ℓ) row of diffraction spots on the X-ray pattern became a continuous line after the 1000° C heat cycles. Further heat cycles to 1400° and 1600° C did not change the birefringence or X-ray results.

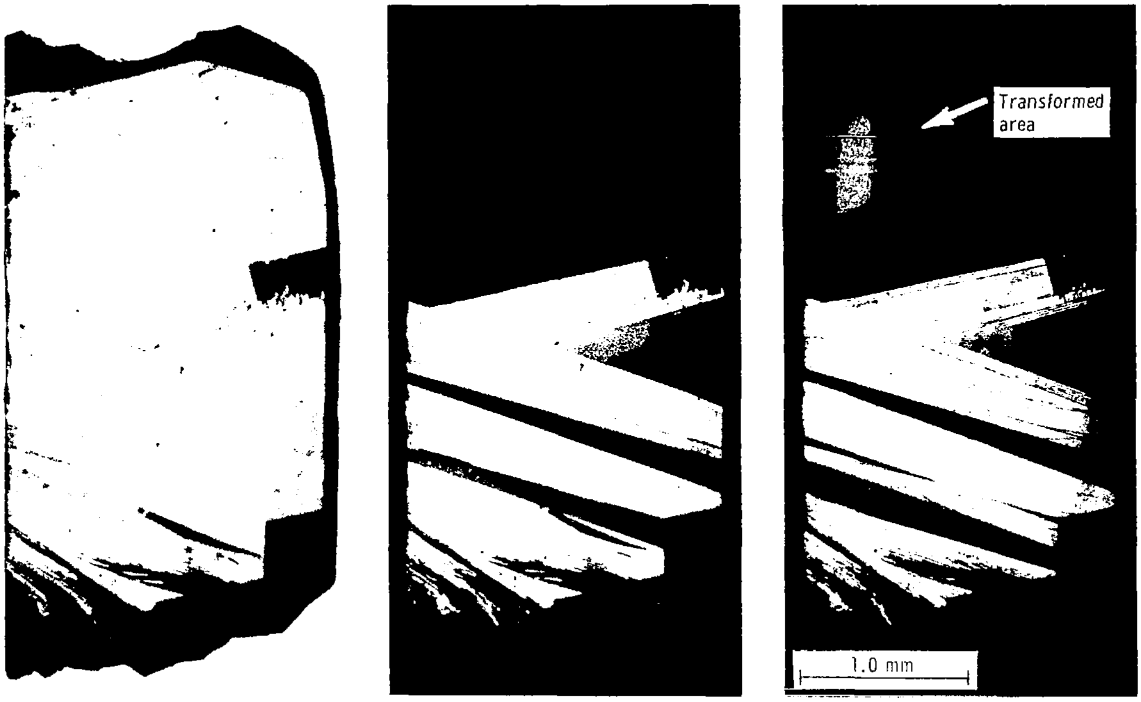
Some interesting color changes were observed in crystal 52-2. Figure 14 shows this crystal (a) in the as-grown condition, (b) after being heated to 400° C for 96 hours, and (c) after being heated to 1000° C for 24 hours. In these photos the crystal was illuminated with polarized light with the direction of polarization parallel to the c-axis. The dark regions were blue-green and the lighter regions were violet. After the crystal was heated to 400° C, it became almost totally blue-green. But after being heated to 1000° C, the regions which were blue-green in the as-grown condition became colorless. No violet color was noted after the 1000° C heat cycle.

The results of the heat cycles for the as-grown crystals are shown in table III (p. 31).

Other Polytypes of Silicon Carbide

Three other polytypes of SiC (6H, 4H, and cubic) were subjected to temperature cycling. A SiC crystal containing both 6H and 4H polytype regions was polished into a wedge shape. The crystal was then heated to 1400° C for 20 hours. Birefringence measurements on the crystal indicated that heating to 1400° C has no apparent effect on the 6H and 4H polytype of SiC.

Cubic SiC was observed to undergo a solid-state transformation. Two samples of cubic SiC (grown by vacuum sublimation technique, Carborundum Co.) were also made into wedges. The orientation of these wedges was not determined. These crystals were found to contain intergrowths of the hexagonal polytypes. The hexagonal polytypes were detected by rotating the crystal between crossed polarizers. The cubic region remains dark as the crystal is rotated, whereas the hexagonal regions extinguished every 90°. Figure 15 shows a cubic SiC wedge before and after heating to 1400° C for 7 hours. Note the arrow in figure 15(c) pointing to a dimly lighted area of the crystal. This area, which changed from light to dark as the crystal was rotated, did not exhibit birefringence in the unheated sample. Other transformed areas were observed but they were not bright enough to show up on the photograph. These observations indicate that part of the cubic SiC crystal had transformed to a noncubic stacking sequence at 1400° C.



(a) In white light. (b) Before heating. Wedge in crossed polarizers; wavelength, 633 nanometers. (c) After heating to 1400° C for 24 hours. Wedge in crossed polarizers; wavelength, 633 nanometers.

Figure 15. - Photographs of wedge from cubic crystal 239 in transmitted light.

DISCUSSION

The data show that 2H SiC undergoes a solid-state phase transformation when heated. This transformation can occur at temperatures as low as 400° C. X-ray diffraction patterns indicate that the structure of the transformed crystals is either one of almost complete stacking disorder along the c-axis or a cubic or 6H structure with some stacking disorder. Other than the bending or twisting none of the crystals grossly changed shape during the heating process. Thus, the phase transformation is certainly not a regrowth process, as observed by Bootsma, Knippenberg, and Verspui (ref. 18), but is similar to the transformation reported by Krishna, Marshall, and Ryan (ref. 16).

The transformation is time and temperature dependent. Wedge 75-8 transformed gradually when heated to 400° C for various periods of time. As the heating temperature was increased the rate of transformation increased. Wedge 79-2 transformed after being heated only 5 minutes at 1000° C.

The transformation temperature is dependent on dislocations in the crystals. The behavior of crystals 68-1 and 79-4 is convincing evidence. These crystals transformed only slightly after being heated to 1800° C, but, after being scratched with diamond grit, they underwent a gross transformation at 1000° C. The difference in behavior of the wedges and as-grown crystals is also evidence for the dependence on dislocations. The process of grinding and polishing the wedge faces certainly introduced many surface dislocations. As a result, all three wedges had essentially completed their transformation at 1000° C, while two of the five as-grown crystals retained some 2H structure even after being heated to 1800° C. The process of breaking the crystals from the growth susceptor may also have introduced some dislocations. The number of dislocations introduced from this source probably would vary greatly from crystal to crystal. So, as might be expected, the transformation temperature for the as-grown crystals observed by the present authors and by Krishna, Marshall, and Ryan (ref. 16) varies from crystal to crystal.

The dependence of the transformation temperature on dislocations has been observed for zinc sulfide (ZnS). Piper and Roth (ref. 22) found that the transformation temperature of highly perfect 2H ZnS crystals was about 750° C, while for faulted crystals it was about 400° C. Also, Singer (ref. 23) observed that faulted 2H ZnS crystals transformed at temperatures of 400° and 530° C.

It appears that for both SiC and ZnS the phase change is nucleated at dislocations. In most whisker crystals, the dislocation density is very low (ref. 22). This may explain why the crystals do not transform during growth and cooling. However, when the crystals are broken from the growth susceptor and handled such that dislocations are introduced, they are then susceptible to transformation.

Mardix, Kalman, and Steinberger (ref. 24) have shown that the most common transformation mechanism in ZnS is a periodic slip process. The slip is by a movement of one hexagonal layer (parallel to the (00.1) plane) with respect to another. The process is transmitted by a rotation and climb about a screw dislocation. When a periodic slip process takes place, the crystal faces develop atomic-sized steps that appear as ridges on the crystal on the macroscopic scale. The ridges that appeared on the faces of the wedges and the as-grown 2H SiC crystals indicate that such a periodic slip process has taken place.

The bending and twisting of the wedges was probably caused by nonuniform transformation throughout the crystal. There are probably orders of magnitude more dislocations in the wedges than in the as-grown crystals. At the lower temperatures these slowly propagate by a slip process at a nonuniform rate into the crystal. As the crystal transforms it shrinks in the c-direction since the spacing between the stacked hexagonal layers is less for 6H and 3C SiC than it is for 2H SiC (ref. 25). The situation might be compared with the thermal expansion of two dissimilar metal plates welded together. Because the two metals expand at different rates the "metal sandwich" will bend and/or twist. If in the case of the 2H wedges we assume that no slip takes place along the c-axis, then the wedges will bend or twist when there is a nonuniform transformation.

As the transformation nears completion, the amount of twist should decrease. This decrease in the twist was observed for wedge 79-3. After the 600° C heat cycle the twist for this wedge was 12° per millimeter, and after the 1000° C heat cycle it was 6.4° per millimeter. In the case of wedge 75-8 the twist apparently caused the crystal to exceed its yield strength resulting in fracture.

The birefringence of the 2H wedges changes from 0.072, the initial value, to a final value in the range 0.034 to 0.037 after transformation (see table I). Caution must be exercised in interpreting this change. There have been attempts to relate the birefringence to the hexagonal characters of both ZnS and SiC polytypes. In the ABC. . . sequence notation of SiC polytypes, any particular double layer of silicon and carbon atoms (perpendicular to the c-axis) is in either a cubic or hexagonal nearest-neighbor environment. As mentioned in the INTRODUCTION, the stacking sequence for 2H is ABAB. . ., for cubic (3C) it is ABCABC. . ., and for 6H it is ABCACB. . .. A layer is in a cubic environment if the two adjoining layers have different orientations and is in a hexagonal environment if the two adjoining layers have the same orientation. For each polytype the fraction of layers in a hexagonal environment h can be computed. Thus, we get $h = 0$ for 3C, $h = 0.33$ for 6H, $h = 1.0$ for 2H, etc. Brafman, et al. (ref. 26) found that, in ZnS crystals that were free of stacking fault disorder, birefringence was a linear function of h. However, Singer (ref. 23) using ZnS crystals with stacking fault disorder obtained very erratic results when he attempted to correlate birefringence with structure.

In the case of SiC the birefringence does not appear to be a linear function of h (ref. 21), but it does increase with increasing h. About the only conclusion that can be reached from the birefringence decrease during the transformation, is that the crystals have a structure which is more cubic in character than it was originally.

The observed instability in 2H SiC apparently rules out its use in a number of applications. Since the 2H structure transforms to a very disordered structure, its use as a high-temperature semiconductor is certainly ruled out. It might be expected that the disordered structure is weaker than any of the perfectly ordered structures. This places a question mark on the use of 2H SiC as a reinforcing fiber in composite materials.

CONCLUSIONS

This report shows that 2H SiC is unstable above 400° C. The 2H polytype transforms into either a structure with one-dimensional disorder (random stacking sequence) along the crystal c-axis or a faulted cubic or 6H structure. The observations show that the process is a solid-state transformation involving a slip of the SiC layers perpendicular to the c-axis. The slip process is nucleated on dislocations and is probably propagated by a rotation and climb about an axial screw dislocation.

This report also shows that cubic SiC undergoes a solid-state phase transformation at temperatures above 1400° C. Under the same conditions the 4H and 6H polytypes do not show any evidence of a transformation.

Because high-temperature processes are usually involved in making semiconductor devices, the 2H polytypes and, possibly, the cubic polytype are unsuitable for device applications. Since the tensile strength of a transformed 2H SiC whisker may be degraded, the material is probably unsuitable for fiber-reinforced composite materials. From a stability standpoint the 4H and 6H polytypes should be suitable for such applications.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 29, 1971,
112-27.

APPENDIX A

X-RAY ROTATION PHOTOGRAPHS OF SiC

The primary X-ray technique used for crystal structure identification in this report was the rotating crystal method. In this method a monochromatic X-ray beam is incident on a single crystal, which is rotating about a major crystallographic axis normal to the incident beam. A cylindrical film is placed around the crystal such that the film axis coincides with the rotation axis. As the crystal rotates, a particular set of lattice planes will, for an instant, make the Bragg angle for reflection of the incident X-ray beam, and at that instant a diffracted beam will form. The diffracted beams lie on the surface of cones that are coaxial with the rotation axis. Thus, the spots on the film lie along horizontal lines as can be seen from figure 16. This is the c-axis rotating crystal pattern of a 2H SiC crystal with CuKα radiation using a nickel filter. The curved streaks emanating from the center of the film are due to white radiation not removed by the filter.

For a complete discussion of X-ray photographs of SiC, the reader is referred to reference 4 (ch. 6). However, a few comments are in order here. The first vertical row of spots to the left and to the right of the film center are due to diffraction from the lattice planes $(10 \cdot \ell)$. The value of ℓ increases with the distance away from the baseline. For those spots on the baseline, $\ell = 0$; for the next set of spots along these rows,

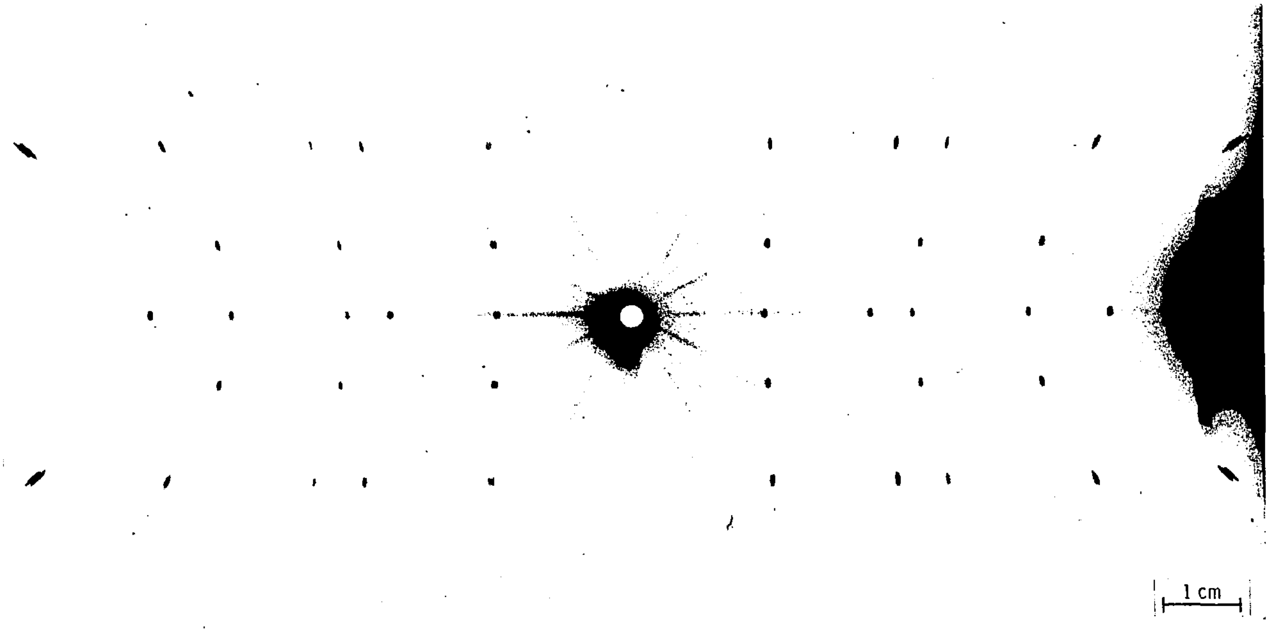


Figure 16. - c-axis rotation pattern of 2H silicon carbide. Copper Kα radiation; camera radius, 3 centimeters.

$\ell = 1$, and so on. Actually each spot is due to diffraction from six crystallographically equivalent sets of lattice planes. For example, each $(10\cdot\ell)$ diffraction spot is also due to diffraction from $(01\cdot\ell)$, $(\bar{1}1\cdot\ell)$, $(\bar{1}0\cdot\ell)$, $(0\bar{1}\cdot\ell)$, and $(1\bar{1}\cdot\ell)$. In this report, reference to diffraction from one set of lattice planes implies diffraction from the other five.

The distance between spots along a vertical row is determined by the repeat distance of the particular polytype stacking sequence (i.e., the height of the unit cell). The larger the repeat distance, the smaller the distance between points. For a structure with a completely random stacking sequence, the repeat distance is infinity, and the vertical rows on the rotating crystal pattern become continuous lines.

The information needed to determine the particular polytype and to detect the presence of random stacking disorder is essentially contained in the row of $(10\cdot\ell)$ diffraction spots on the rotation photograph. Therefore, only the $(10\cdot\ell)$ row need be given to illustrate the structure of the crystals.

APPENDIX B

BIREFRINGENCE MEASUREMENTS ON SiC

All noncubic SiC structures exhibit birefringence. Light passing through a noncubic SiC polytype in a direction other than along the c-axis will split into two rays, each traveling with a different velocity. The ray with the electric vector perpendicular to the c-axis is called the ordinary ray. The other ray with the electric vector parallel to the c-axis is called the extraordinary ray. In the case of SiC, the ordinary ray travels faster. Thus, the ordinary refractive index n_o will be less than the extraordinary refractive index n_e. The difference between the two refractive indices $(n_e - n_o)$ is the birefringence. This property varies with polytype and is very useful for examining the structure of SiC crystals (refs. 27 and 28).

The birefringence phenomenon is observed by placing a SiC wedge (fig. 1) between crossed polarizers of a polarizing microscope. Normally two polarizers rotated 90° to one another will produce a dark field. That is, light passing through the first polarizer will be blocked by the second polarizer. If the silicon carbide wedge is rotated about an axis perpendicular to the c-axis, then light passing through the crystal extinguishes every 90° where the c-axis is parallel to one of the polarization directions. When the c-axis is at 45° to the polarizers the crystal is bright in a dark field.

As a result a noncubic SiC crystal will appear to change from bright to dark as it is rotated between crossed polarizers. This effect is obtained only when the direction of light propagation in the crystal is not parallel to the c-axis. Cubic SiC has only one refractive index and remains dark for all orientations when placed between crossed polarizers. Birefringence measurements can be easily made on wedge-shaped samples with the polarizing microscope. With crossed polarizers and the crystal illuminated with monochromatic light, interference bands will appear on the polished crystal faces. The interference bands will be parallel to the intersection of the two polished faces. The spacing between bands is related to the birefringence δ of the crystal by (ref. 28)

$$\delta = (n_e - n_o) = \frac{\lambda \cot \alpha}{d}$$

where d is the spacing between fringes, λ is the wavelength of light, and α is the wedge angle.

REFERENCES

1. O'Connor, J. R.; and Smiltens, J., eds.: Silicon Carbide, A High Temperature Semiconductor. Pergamon Press, 1960.
2. Henisch, H. K.; and Roy, R., eds.: Silicon Carbide - 1968, Proceedings of the International Conference on Silicon Carbide. Pergamon Press, 1969.
3. Levitt, Albert P., ed.: Whisker Technology. John Wiley & Sons, Inc., 1970.
4. Verma, Ajit R.; and Krishna, P.: Polymorphism and Polytypism in Crystals. John Wiley & Sons, Inc., 1966.
5. Golightly, J. P.; and Beaudin, L. J.: Some Aspects of Disorder in Silicon Carbide. Silicon Carbide - 1968, Proceedings of the International Conference on Silicon Carbide. H. K. Henisch and R. Roy, eds., Pergamon Press, 1969, pp. S119-S128.
6. Knippenberg, W. F.; and Verspui, G.: The Influence of Impurities on the Growth of Silicon Carbide Crystals Grown by Gas-Phase Reactions. Silicon Carbide - 1968, Proceedings of the International Conference on Silicon Carbide. H. K. Henisch and R. Roy, eds., Pergamon Press, 1969, pp. S33-S44.
7. Lely, J. A.: Darstellung von Elinkristallen von Silicium carbid und Behrrschung von Art und Menge der Eingebauten Verunreinigungen. Ber. der Deutschen Keramischen Gesell., vol. 32, no. 8, Aug. 1955, pp. 229-231.
8. Knippenberg, W. F.: Growth Phenomena in Silicon Carbide. Philips Res. Repts., vol. 18, no. 3, June 1963, pp. 161-274.
9. Merz, Kenneth M.; and Adamsky, Robert F.: Synthesis of the Wurtzite Form of Silicon Carbide. J. Am. Chem. Soc., vol. 81, no. 1, Jan. 5, 1959, pp. 250-251.
10. Patrick, Lyle; Hamilton, D. R.; and Choyke, W. J.: Growth, Luminescence, Selection Rules, and Lattice Sums of SiC with Wurtzite Structure. Phys. Rev., vol. 143, no. 2, Mar. 1966, pp. 526-536.
11. Ryan, Charles E.; Berman, Irving; Marshall, Robert C.; Considine, Dennis P.; and Hawley, John J.: Some Factors Affecting the Growth of Beta Silicon Carbide. Rep. AFCRL-66-641, Air Force Cambridge Research Labs., Sept. 1966.
12. Powell, J. Anthony: Crystal Growth of 2H Silicon Carbide. J. Appl. Phys., vol. 40, no. 11, Oct. 1969, pp. 4660-4662.

13. Kern, E. L.; Hamill, D. W.; Deem, H. W.; and Sheets, H. D.: Thermal Properties of β Silicon Carbide from 20° to 2000° C. Silicon Carbide - 1968, Proceedings of the International Conference on Silicon Carbide. H. K. Henisch and R. Roy, eds., Pergamon Press, 1969, pp. S25-S32.

14. Kieffer, A. R.; Ettmayer, P.; Gugel, E.; and Schmidt, A.: Phase Stability of Silicon Carbide in the Ternary System Si-C-N. Silicon Carbide - 1968, Proceedings of the International Conference on Silicon Carbide. H. K. Henisch and R. Roy, eds., Pergamon Press, 1969, pp. S153-S165.

15. Ellis, Ray C., Jr.: Growth of Silicon Carbide from Solution. Silicon Carbide, A High Temperature Semiconductor. J. R. O'Connor and J. Smiltens, eds., Pergamon Press, 1960, pp. 124-129.

16. Krishna, P.; Marshall, R. C.; and Ryan, C. E.: The Discovery of a 2H-3C Solid State Transformation in Silicon Carbide Single Crystals. J. Crystal Growth, vol. 8, 1971, pp. 129-131.

17. Krishna, P.; and Marshall, R. C.: The Structure Perfection and Annealing Behavior of SiC Needles Grown by a VLS Mechanism. Presented at the Conference on Crystal Growth and Epitaxy from the Vapor Phase, Zurich, Switzerland, Sept. 23-26, 1970.

18. Bootsma, G. A.; Knippenberg, W. F.; and Verspui, G.: Phase Transformations, Habit Changes and Crystal Growth in SiC. J. Crystal Growth, vol. 8, 1971, pp. 341-353.

19. Powell, J. Anthony: Growth of 2H Silicon Carbide Crystals. NASA TN D-5313, 1969.

20. Powell, J. Anthony: Refractive Index and Birefringence of 2H Silicon Carbide. NASA TN D-6635, 1972.

21. Golightly, J. P.: The Birefringence and Dichroism of Silicon Carbide Polytypes. Can. Mineral., vol. 10, pt. 1, 1969, pp. 105-108.

22. Piper, William W.; and Roth, W. L.: Perfect Crystals of Zinc Sulfide. Phys. Rev., vol. 92, no. 2, Oct. 15, 1953, p. 503.

23. Singer, Joseph: Study of the Bands of Uniform Birefringence in Faulted ZnS. J. Phys. Chem. Solids., vol. 24, 1963, pp. 1645-1649.

24. Mardix, S.; Kalman, Z. H.; and Steinberger, I. T.: Periodic Slip Processes and the Formation of Polytypes in Zinc Sulphide Crystals. Acta. Cryst., vol. A24, 1968, pp. 464-469.

25. Gomes de Mesquita, A. H.: Refinement of the Crystal Structure of SiC Type 6H. Acta. Cryst., vol. 23, 1967, pp. 610-617.

26. Brafman, O.; and Steinberger, I. T.: Optical Band Gap and Birefringence of ZnS Polytypes. Phys. Rev., vol. 143, no. 2, Mar. 1966, pp. 501-505.

27. Shaffer, P. T. B.: Use of the Microscope in the Operation and Identification of Silicon Carbide Structures. Microscope, vol. 18, July 1970, pp. 179-191.

28. Hartshorne, N. H.; and Stuart, A.: Practical Optical Crystallography. American Elsevier Pub. Co., 1964, pp. 175-176.

TABLE I. - HEAT CYCLES AND BIREFRINGENCE RESULTS FOR THE SiC WEDGES

Heating cycle	Sample									
	79-3		75-8		79-2		239		238	
	Structure									
	2H		2H		2H		Cubic		4H/6H	
	Treatment	Birefringence	Treatment	Birefringence	Treatment	Birefringence	Treatment	Birefringence	Treatment	Birefringence
Before heating	--------------	0.070	--------------	0.072	--------------	0.072	--------------	0	--------------	0.051 (4H) .041 (6H)
1	200° C for 1 hr	.070	400° C for 5 min	.072	1000° C for 5 min	.039	400° C for 24 hr	0	400° C for 24 hr	.051 (4H) .041 (4H)
2	300° C for 1 hr	.070	400° C for 1 hr	.071	1000° C for 24 hr	.034	1400° C for 7 hr	>0	1400° C for 20 hr	.051 (4H) .041 (6H)
3	450° C for 1 hr	.062	400° C for 24 hr	(a)	1400° C for 7 hr	.037	1400° C for 24 hr	↓	--------------	---------
4	600° C for 1 hr	(a)	400° C for 72 hr	(a)	1600° C for 7 hr	.037	1600° C for 7 hr	↓	--------------	---------
5	800° C for 1 hr	.038	1400° C for 7 hr	(a)	--------------	-------	--------------	-------	--------------	---------
6	1000° C for 1 hr	.034	1600° C for 7 hr	(a)	--------------	-------	--------------	-------	--------------	---------
7	1200° C for 24 hr	.034	--------------	-------	--------------	-------	--------------	-------	--------------	---------

[a] Not measured because of fringe distortion.

TABLE II. - RESULTS OF HEATING SILICON CARBIDE WEDGES

[Fringes, refers to fringes caused by birefringence when wedge was observed between crossed polarizers with monochromatic light; spots, refers to (10· () row of diffraction spots on X-ray rotation pattern; streaking, refers to streaking along (10· () row of X-ray diffraction spots; fanning, refers to fanning out of (10· () row of X-ray diffraction spots; twist, refers to twisting of crystal about c-axis; α refers to noncubic polytype of SiC.]

Heating cycle	Sample									
	79-3 (2H)		75-8 (2H)		79-2 (2H)		239 (cubic)		238 (4H/6H)	
	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results
Before heating	---------	Fringes present; distinct spots; no twisting	---------	Fringes present; distinct spots; no twisting	---------	Fringes present; distinct spots; some streaking; no twisting	---------	No fringes; intergrowths of α material in cubic	---------	Fringes present; no twisting
1	200° C for 1 hr	No change	400° C for 5 min	No change	1000° C for 5 min	Slight fringe distortion; X-ray fanning; twist; fracture	400° C for 24 hr	No change	400° C for 24 hr	No change
2	300° C for 1 hr	Slight twist	400° C for 1 hr	No change	1000° C for 24 hr	Fringe distortion; twist; fracture	1400° C for 7 hr	Appearance of more α in the cubic	1400° C for 20 hr	No change
3	450° C for 1 hr	Fringe distortion; X-ray streaking; more twist	400° C for 24 hr	Fringes very distorted; X-ray streaking; very twisted; slight fracture	1400° C for 7 hr	No change	1400° C for 24 hr	More α	--------	---------
4	600° C for 1 hr	Fringes very distorted; maximum twisting	400° C for 24 hr	Extreme fringe distortion; X-ray fanning	1600° C for 7 hr	No change	1600° C for 7 hr	No change	--------	---------
5	800° C for 1 hr	Less fringe distortion; X-ray fanning; some untwisting	1400° C for 7 hr	Top of crystal broke off	-------	---------	-------	---------	--------	---------
6	1000° C for 1 hr	More untwisting	1600° C for 7 hr	No change	-------	---------	-------	---------	--------	---------
7	1200° C for 24 hr	No change	-------	---------	-------	---------	-------	---------	--------	---------

TABLE III. - RESULTS OF HEATING AS-GROWN 2H SILICON CARBIDE CRYSTALS

[Fringes, refers to fringes caused by birefringence when wedge was observed between crossed polarized with monochromatic light; spots, refers to (10·ℓ) row of diffraction spots on X-ray rotation pattern; streaking, refers to streaking along (10·ℓ) row of X-ray diffraction spots.]

Heating cycle	Undoped crystals						Nitrogen doped crystals			
	Sample									
	68-1		79-4		76-1		52-2		52-1	
	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results	Heat treatment	Results
Before heating	---------	Distinct fringes and 2H X-ray spots	---------	Distinct fringes; well-defined 2H X-ray spots with slight streaking	---------	Distinct fringes; well-defined 2H X-ray spots with some streaking	---------	Some distortion of fringes; slightly smeared 2H X-ray spots; violet color with blue-green bands	---------	Distinct fringes; well-defined 2H X-ray spots with slight streaking; violet with blue-green bands
1	1000° C for 24 hr	No fringes; some X-ray streaking	1000° C for 24 hr	No fringes; some X-ray streaking	400° C for 96 hr	Slight fringe distortion; some smearing of X-ray spots	400° C for 96 hr	More fringe distortion; violet regions turned blue-green	1000° C for 24 hr	No fringes; continuous X-ray streak, no spots; many new blue-green bands
2	1400° C for 24 hr	Ridges appeared on crystal faces	1400° C for 24 hr	Ridges appeared on crystal faces	1000° C for 24 hr	No fringes; continuous X-ray streak, no spots	1000° C for 24 hr	No fringes; continuous X-ray streak, no spots; color change (see text)	1400° C for 24 hr	Crystal nearly all blue-green
3	1600° C for 7 hr	More X-ray streaking	1600° C for 7 hr	No change	1400° C for 24 hr	No change	1400° C for 24 hr	No change	1600° C for 7 hr	No change
4	1800° C for 7 hr	More X-ray streaking but 2H spots still present	1800° C for 7 hr	More X-ray streaking but distinct 2H spots still present	1600° C for 7 hr	No change	1600° C for 7 hr	No change	-------	---------
5	1000° C for 2 hr	Cubic 6H X-ray spots[a]	1000° C for 3 hr	Cubic 6H X-ray spots[a]	-------	---------	-------	---------	-------	---------
6	1000° C for 24 hr	No change	-------	--------------	-------	---------	-------	---------	-------	---------

[a] Crystal scratched with diamond before this heat cycle.