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## *"Growth of Single Crystal Beta Silicon Carbide"* *Phase I*

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## 1. SUMMARY

$\beta$ -SiC is a promising, wide bandgap material for high power electronic devices capable of operation at high temperatures. Its high saturation velocity, high breakdown electric field, and high thermal conductivity point to superior performance for high frequency applications. The successful fabrication of  $\beta$ -SiC devices requires high quality films to be epitaxially grown on lattice-matched substrate materials. Single crystals of  $\beta$ -SiC offer the optimum substrate material for lattice matching.

The major problem to be overcome in the growth of large single crystals of  $\beta$ -SiC is polytype  $\alpha$ -SiC formation. Cubic  $\beta$ -SiC crystallizes only below 2000°C. Above this temperature, SiC undergoes a phase transformation from the  $\beta$ - to the  $\alpha$ - phase.

In Phase I, we investigated two crystal growth techniques: sublimation and gas-vapor transport. We were able to grow small 3C-SiC crystals by both methods. The sublimation method did not yield pure 3C-SiC, but only crystals with a few percent of 6H-SiC. Crystals grown by the gas-vapor transport method were pure 3C-SiC; however, the growth rate was very low, a few microns per hour. The gas-vapor transport technique appears promising for the preparation of pure 3C-SiC single crystals.

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## 2. BACKGROUND

### 2.1 IMPORTANCE OF THE PROBLEM

The U.S. Navy's demands for high frequency power generators which can operate at high temperatures have required the development of suitable semiconductor materials. Beta silicon carbide is a promising wide bandgap semiconductor material, uniquely suitable for the high power electronic devices capable of operation at high frequencies and high temperatures. This particular material possesses an unusual combination of material properties important for high power, high frequency devices: high saturated electron drift velocity, low dielectric constant, high thermal conductivity and excellent chemical stability.

The successful fabrication of  $\beta$ -SiC electronic devices requires high quality films epitaxially grown on lattice-matched substrate materials. However, substrates whose lattice parameters are closely matched to that of  $\beta$ -SiC are not readily available. In addition,  $\beta$ -SiC films grown on materials other than  $\beta$ -SiC do not demonstrate high theoretical Hall mobility. Thus, a promising approach to obtaining  $\beta$ -SiC electronic devices of high quality is to prepare thin films on  $\beta$ -SiC wafers.

In growing large single crystal boules of  $\beta$ -SiC, the major problem to be overcome is polytype  $\alpha$ -SiC formation. It is known that the cubic form (beta phase) of SiC crystallizes only below 2000°C. Above this temperature, SiC undergoes the phase transformation from  $\beta$ - to  $\alpha$ -phase. Thus this is a crucial limiting factor in designing a crystal growth system and in determining all the growth parameters.

### 2.2 PRESENT STATE-OF-THE-ART

$\beta$ -SiC has a large energy gap (2.2 eV), high electron mobility (1000 cm<sup>2</sup>/V-s), high saturation drift mobility (2.7 x 10<sup>7</sup> cm/s), and excellent chemical stability. Since the maximum operating temperature for semiconductor devices is approximately proportional to their band gap,  $\beta$ -SiC as a wide band gap semiconductor, is well suited for high temperature applications.  $\beta$ -SiC also has the advantage of high thermal conductivity, which is needed for high power electronic devices operating at high temperatures.

Both  $\alpha$ - and  $\beta$ - phases of SiC have excellent material properties for the application of high power, high temperature electronic devices. However, more attention has been given to  $\beta$ -SiC devices than  $\alpha$ -SiC because of the higher electron mobility of  $\beta$ -SiC.

Silicon carbide has more than 200 crystal structures, called polytypes, which have the same chemical composition.<sup>[1,2]</sup> These polytypes arise from different stacking arrangements of the close-packed carbon and silicon layers. The most popular polytypes of SiC are 3C (zincblende) and 6H (hexagonal) types. The cubic form, called  $\beta$ -SiC, is formed by the

reaction between silicon and carbon below 2000°C. The highest growth temperature of  $\beta$ -SiC, 2700°C, was reported by Scace and Slack,<sup>[3]</sup> however, it was mixed with other polytypes.

The hexagonal form, called  $\alpha$ -SiC, has at least six variations of its basic structure. These types, designated  $\alpha$ -I, II, III, IV, V, VI, are formed in the temperature range from 2400 to 2600°C.<sup>[4]</sup>

Several techniques have been employed for the growth of SiC single crystals. Among these techniques, the most successful method for the preparation of single crystalline ingots of SiC with a large area is sublimation. However, this method has been mostly used to grow  $\alpha$ -SiC. Currently  $\alpha$ -SiC single crystals of 1 inch diameter grown by this method are commercially available. Recently, sublimation growth of large single crystals of  $\beta$ -SiC was accomplished by Yoo et al. in 1987.<sup>[5]</sup> They were able to grow  $\beta$ -SiC crystals of 0.4 mm in thickness on CVD-grown  $\beta$ -SiC  $\langle 100 \rangle$  substrates by sublimation. The reported growth rate is 0.2 mm/hr at a system pressure of 400 torr and a growth temperature of 2000°C.

For sublimation, the growth rate is proportional to the substrate temperature and inversely proportional to the system pressure. For instance, the growth rate of  $\alpha$ -SiC prepared by gas transport sublimation was about 1.0 mm/hr at a pressure of 2 torr and about 0.2 mm/hr at 5 torr with the same growth temperature of 2100°C.<sup>[6]</sup> In addition, it was observed that at a growth temperature of 2000°C and a pressure of 2 torr the growth was 0.6 mm/hr.

Most crystal growth of  $\beta$ -SiC has been carried out by chemical vapor deposition (CVD) on substrate materials other than  $\beta$ -SiC (heteroepitaxy). The growth rate of this method is also very slow, and only films have been produced. Silicon has been the substrate commonly chosen because it is readily available and also because it is one of the components of the final product. However, a large lattice mismatch between Si ( $a_0=5.430 \text{ \AA}$ ) and  $\beta$ -SiC ( $a_0=4.358 \text{ \AA}$ ) creates large numbers of dislocations and other defects.<sup>[7]</sup>  $\beta$ -SiC grown on Si  $\langle 100 \rangle$  showed very poor carrier concentrations and Hall mobilities compared to theoretical values.<sup>[8]</sup> Various approaches to solve these problems have been investigated, including the use of Si substrates oriented 2° to 4° off the  $\langle 100 \rangle$  axis<sup>[9,10]</sup> and the use of substrates whose lattice parameters are more closely matched to that of  $\beta$ -SiC, such as  $\alpha$ -SiC<sup>[11,12]</sup> and TiC.<sup>[13]</sup> These approaches have resulted in improved film quality, however, problems still exist.  $\beta$ -SiC films grown on off-axis Si substrates still exhibit some lattice defect structures. The quality of  $\beta$ -SiC films grown on lattice-matched materials is markedly improved, but the availability and quality of the currently available substrates have limited their routine use.

The reduction of the growth temperature of SiC films is another important issue in increasing the feasibility of electronic device applications. The typical growth temperature range for the CVD method is 1300-1400°C. Lowering growth temperatures has been attempted by Molecular Beam Epitaxy (MBE),<sup>[14-15]</sup> Gas Source Molecular Beam Epitaxy (GSMBE),<sup>[16]</sup> Molecular Ion-Beam Epitaxy (MIBE),<sup>[17]</sup> Reactive-Ion-Beam Deposition (RIBD),<sup>[18]</sup> and CVD using a special gas system ( $\text{SiH}_2\text{Cl}_2/i\text{-C}_4\text{H}_{10}/\text{HCl}/\text{H}_2$ ).<sup>[19]</sup>

$\beta$ -SiC crystals have been also grown from solution. Disadvantages of this method are slow mass transport in the condensed phase of a liquid and low solubility of carbon in a silicon melt, which result in slow growth rates and in small crystal size, respectively. Several attempts to increase the solubility of carbon have been made using solvents other than Si, such as Fe,<sup>[20]</sup> Cr,<sup>[21]</sup> and Co<sup>[22]</sup>. However, solvent atoms are mostly incorporated in the crystals and then form microscopic or macroscopic inclusions of solvent.

The silicon-carbon binary system contains only three condensed phases: silicon, silicon carbide, and graphite. The phase diagram of the silicon-carbon binary system at one atmosphere is shown in Figure 1.<sup>[23]</sup> In this phase diagram, the phase transformation temperature of SiC from  $\alpha$ -to- $\beta$  phase is also shown by the horizontal line at about 2000°C. It was believed that the  $\alpha$ -to- $\beta$  phase transformation takes place in the solid state. However, Slack<sup>[24]</sup> found that the phase transformation occurs with reasonable velocity only via the vapor phase. The measurements of Humphrey et al.<sup>[25]</sup> and the work of Taylor and Laidler<sup>[26]</sup> indicate that both the hexagonal ( $\alpha$ -phase) and cubic ( $\beta$ -phase) forms are stable phases, although energy differences between the crystal forms at high temperatures are very small, and therefore, a large uncertainty in the assignment of a transformation temperature results.

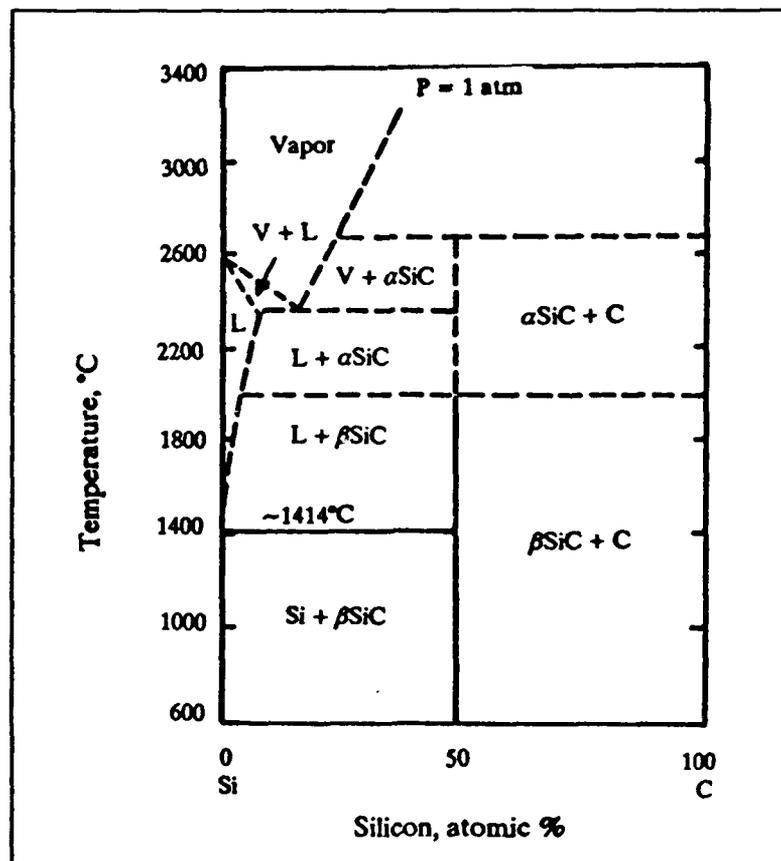


Figure 1. Carbon-Silicon phase diagram at 1 atmosphere.

As shown in the phase diagram of Figure 1, the liquid field is very small at one atmosphere. However, this liquid field expands with atmospheric pressure. Scace and Slack<sup>[3]</sup> studied the solubility of carbon in silicon as a function of reciprocal temperature at an argon pressure as high as 35 atm. The result is shown in Figure 2. This figure shows two points of particular interest: the solubility of carbon in liquid Si at the Si melting point is  $5 \times 10^{-3}$  atomic percent ( $5 \times 10^{17}$  C/cm<sup>2</sup> Si) and the solubility increases with temperature up to 19 atomic per cent at the decomposition temperature of 2830°C.

As indicated in these phase diagrams at different pressures, SiC cannot be melted without bulk decomposition in a certain pressure range. Only at higher pressures, perhaps on the order of 100,000 atm,<sup>[4]</sup> can SiC be melted without decomposition. This is the reason why SiC crystals cannot be grown from the stoichiometric melt. However, the increased solubility of carbon at high temperatures and pressures indicates that crystal growth from solution is feasible. In addition, the sublimation of SiC at low pressure indicates the possibility of growing SiC crystals through the vapor phase.

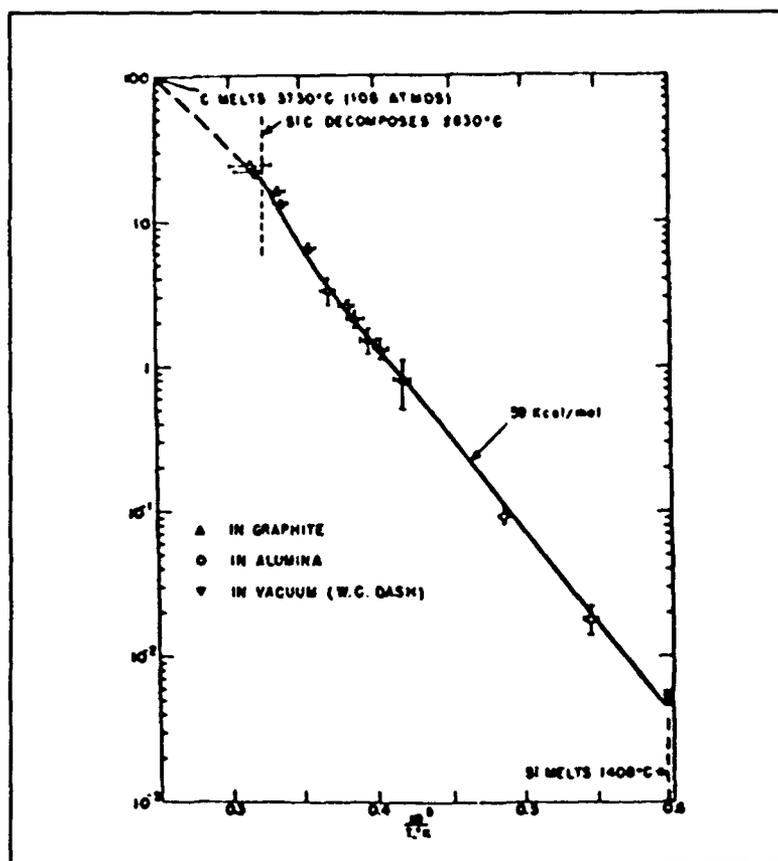


Figure 2. The solubility of carbon in silicon as a function of reciprocal temperature at 35 atmospheres.

### **3. PHASE I TECHNICAL OBJECTIVES**

- 1. Investigate two promising techniques for the growth of  $\beta$ -SiC: top-seeded solution and sublimation. Demonstrate the feasibility of at least one of these techniques.**
- 2. Design and build growth stations, one for top-seeded solution and one for sublimation, capable of producing  $\beta$ -SiC single crystal wafers.**
- 3. Identify the critical growth parameters for high quality  $\beta$ -SiC devices.**
- 4. Establish a growth method to produce  $\beta$ -SiC single crystal boules of 10 mm in diameter, suitable for use as substrates for epitaxial growth of  $\beta$ -SiC thin films.**
- 5. Characterize selected crystal samples using x ray diffraction, x ray topography, mass spectroscopy, and optical microscopy.**

## 4. PROPOSED GROWTH TECHNIQUES

### 4.1 *SUBLIMATION METHOD*

The feasibility of growing single crystals of SiC by sublimation was demonstrated in 1955 by Lely.<sup>[27]</sup> Using this technique, the starting materials (SiC crystallites or even Si and C) are heated to 2500-2700°C and sublime on the walls of the growth cavity. The main disadvantages of this method are the high temperatures required for crystal growth and lack of control over the process of nucleation. Due to these disadvantages, the process of crystal growth was practically uncontrollable, with only small needle- or platelet-shaped crystals being produced (on the average, up to 3-5 mm). Important advantages over the Lely scheme have been obtained by the use of a seed crystal so that the nucleation process becomes controllable.

Tairov et al.<sup>[28]</sup> carried out detailed studies concerning mass transfer and crystallization of silicon carbide by the sublimation method in the temperature range of from 1500 to 2600°C, both under vacuum and in atmospheres of argon, hydrogen, carbon monoxide, nitrogen, and other gases. The results indicate that mass transfer was affected by the fluxes of the gas phase components; Si, Si<sub>2</sub>C, and SiC<sub>2</sub>, formed at the first stage as a result of decomposition of the sintered or powdered silicon carbide source. Drowart et al.<sup>[29]</sup> studied the vapor pressures of gaseous species in the systems, graphite + SiC and Si + SiC, using a mass spectrometer. The results show that the silicon vapor pressure exceeds the pressure of the gaseous phase components Si<sub>2</sub>C and SiC<sub>2</sub> in the system of SiC + graphite. The silicon vapor reacts with the graphite walls of the growth cell, and subsequently yields additional Si<sub>2</sub>C and SiC<sub>2</sub>.

Silicon acts as a carbon transporting agent in this system and plays an active role in the formation of the mass fluxes impinging on the growing crystal. In the case of crystal growth, the most important factor is that the mean free path of the Si, Si<sub>2</sub>C, and SiC<sub>2</sub> vapor species is large enough to reach the seed in the growth cavity. The mean free path of the gas species is inversely proportional to the system pressure. Calculations performed by Tairov<sup>[30]</sup> show that, under a vacuum of 10<sup>-4</sup> to 10<sup>-5</sup> torr, high growth rates of silicon carbide ingots (mm/h) at initial source-to-seed separations larger than 10 mm were obtained due to fluxes from the side walls of the growth cavity, whereas at smaller separations (0.5-10 mm) the principal contribution to the resultant flux is provided by the fluxes that arise due to the dissociative evaporation of the silicon carbide source.

The sublimation method has been successful for growth of  $\alpha$ -SiC bulk crystals, but few investigations have been made on growth of  $\beta$ -SiC crystals. This is probably due to the limiting factors for growing  $\beta$ -SiC mentioned in the previous section.

## 4.2 TOP-SEEDED SOLUTION GROWTH

Top-seeded solution growth is a well known technique<sup>[27]</sup> for growth of single crystals from a high temperature solution which is supersaturated by the constituents of the material. The supersaturation may be promoted by cooling the solution or by a transport process of the solute from a hotter to a cooler region of the solution. The high temperature solution consists mainly of the solvent and the solute; we can consider the less refractory phase as the solvent while the solute is the phase which crystallizes first upon cooling. The main requirement of a solvent is that it will dissolve the solute to an appreciable amount, i.e. the high solubility of the solute in a solvent, a practical minimum being on the order of one percent. The solvent must not react with the solute to form solid compounds or, if it does, these compounds must not be stable in the crystallization temperature range of the phase required. Furthermore, the range of solid solutions between solute and solvent should be as small as possible.

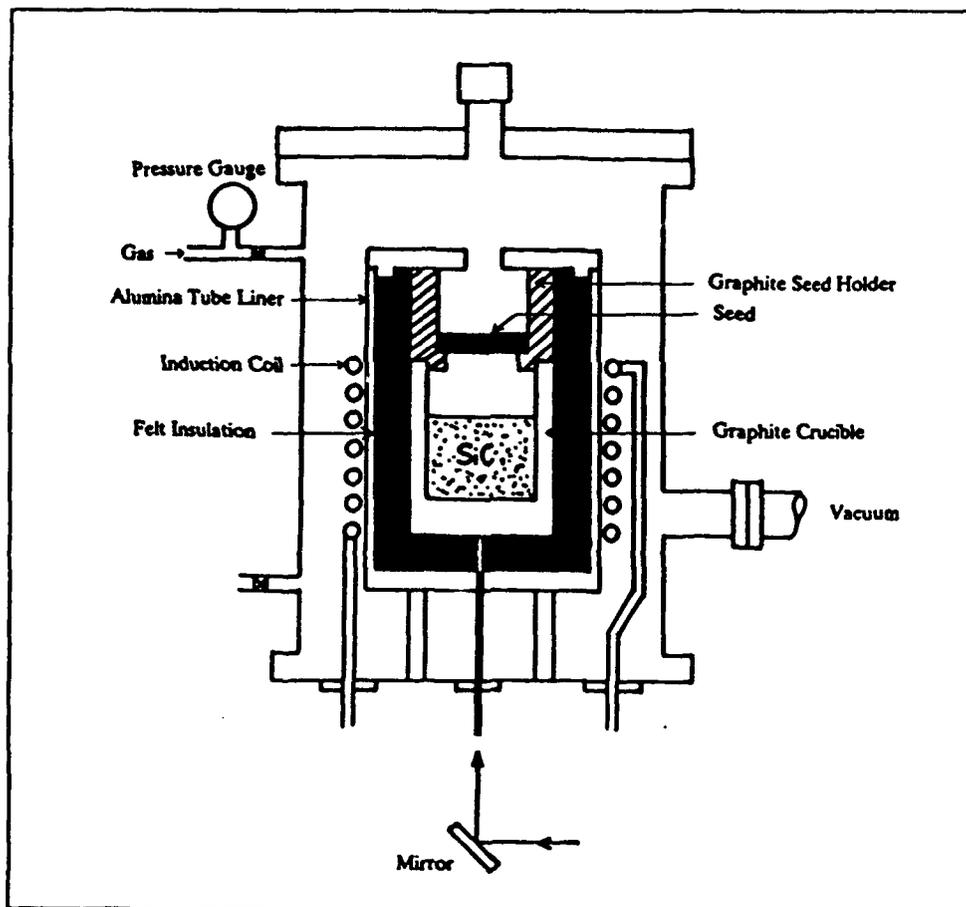
An advantage of crystal growth from solution is that the growing crystal is not exposed to steep temperature gradients, so that the crystal can grow free from thermal constraints. In addition, crystals can be grown at a relatively low growth temperature compared with the melting point of the solute, often resulting in a better crystal quality compared to crystals grown directly from their own melt.

SiC crystals also have been grown by top-seeded solution using solvents of Si,<sup>[30]</sup> Fe,<sup>[20]</sup> Cr,<sup>[21]</sup> and Co/Si.<sup>[22]</sup> However, the size of the crystals was very small, just a few millimeters. In growing  $\beta$ -SiC single crystals by this method, it is crucial to prepare a high temperature solution which can provide a high solubility and no contamination to the crystals. We chose a Si/C solution as our system.

## 5. WORK PERFORMED

### 5.1 SUBLIMATION

We designed and built a new vacuum crystal growth station, shown schematically in **Figure 3**. The SiC charge, contained in a 2.5" diameter graphite crucible, is heated by a 20 kW, 10 kHz Pillar rf generator through a 6" diameter water cooled copper coil. The chamber is made of aluminum and is kept cool by water circulating through copper tubing that jackets the chamber. The graphite crucible is surrounded by an insulating layer of zirconia grog that provides thermal insulation and a clean environment without interfering with the coupling of the rf energy from the coil. The grog is contained within an alumina tube.



*Figure 3. Schematic drawing of crystal growth station utilizing the sublimation technique.*

Initial tests showed that the growth chamber was vacuum tight and could maintain a pressure of about  $10^{-7}$  torr at room temperature. Tests on the coupling of the graphite crucible to the rf generator showed that we had sufficient power to operate over the desired temperature range.

In general, the growth cycle went through the following steps:

1. Pump down of the growth chamber to  $\approx 10^{-6}$  torr. Backfill with Ar to 1 atmosphere. Repeat three times.
2. Pump down to the desired operating pressure.
3. Gradually increase the seed temperature to the range of 1700–1900°C over a period of about 10 hours.
4. Crystal growth.
5. Cool down.

#### 5.1.1 RUNS SB01 AND SB02

A small TiC single crystal seed was placed on the graphite lid, the chamber was pumped down to  $10^{-6}$  torr, and purged by three successive backfillings with argon to 1 atmosphere. The  $\beta$ -SiC powder was then heated to the growth temperature under 250 torr of Ar. The first growth run (SB01) was carried out at 1830°C and the second (SB02) at 1930°C. The growth time for each run was 52 hours.

In Run SB01, the TiC seed moved from its original position on the graphite lid during the run, so that growth occurred on the lid, not the seed. The multicrystalline growth layer was analyzed using our Philips x ray diffractometer and the spectrum is shown in Figure 5, compared with the JCPDS reference pattern for  $\beta$ -SiC.

The product was principally  $\beta$ -SiC, but several extra peaks were observed. We were unable to identify the phase that contributed to these extra peaks. We believe, however, that some of the extra phases were due to the starting material, as we did observe some of these peaks in the  $\beta$ -SiC powder as shown in Figure 6.

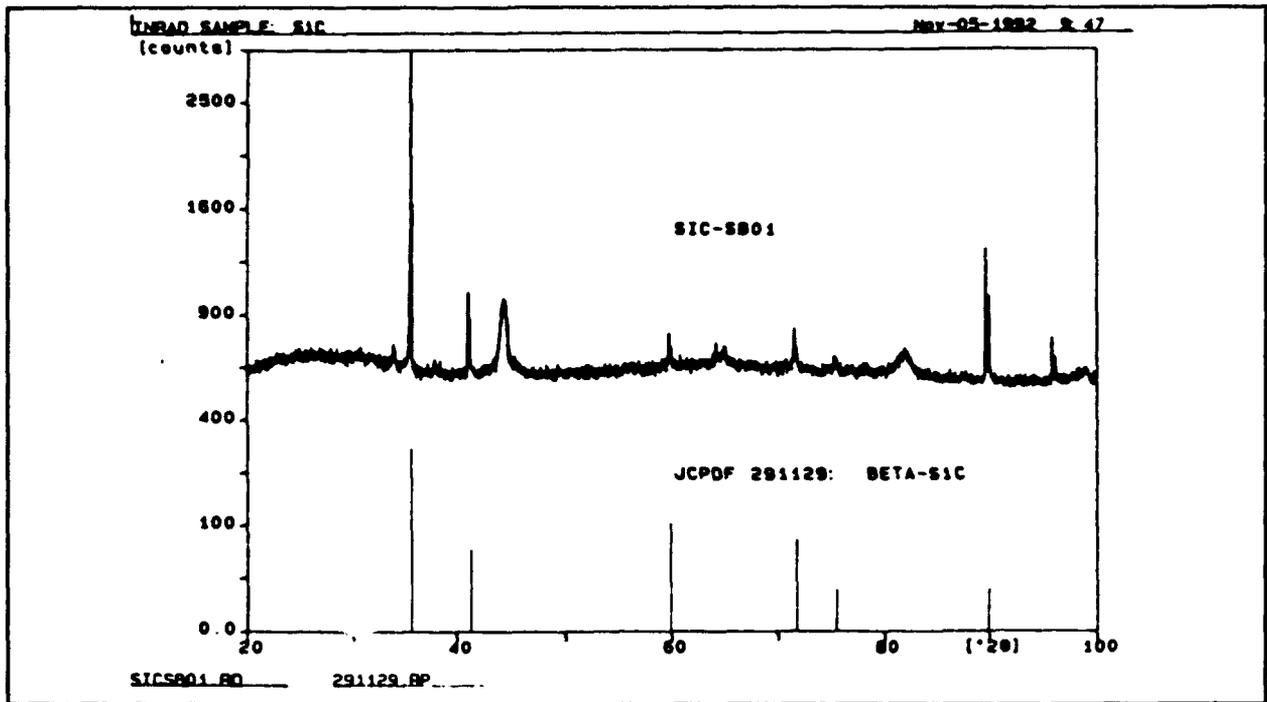


Figure 5. X ray powder diffraction spectrum obtained from Run SB01.

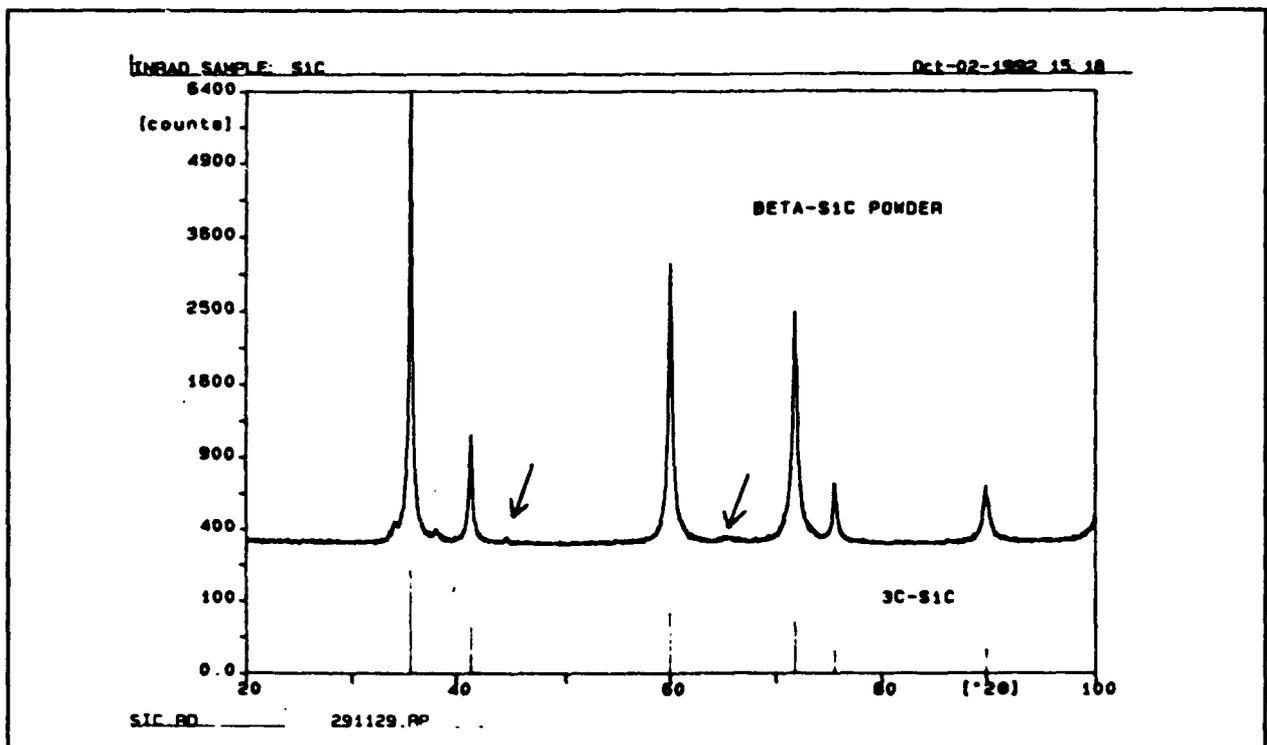
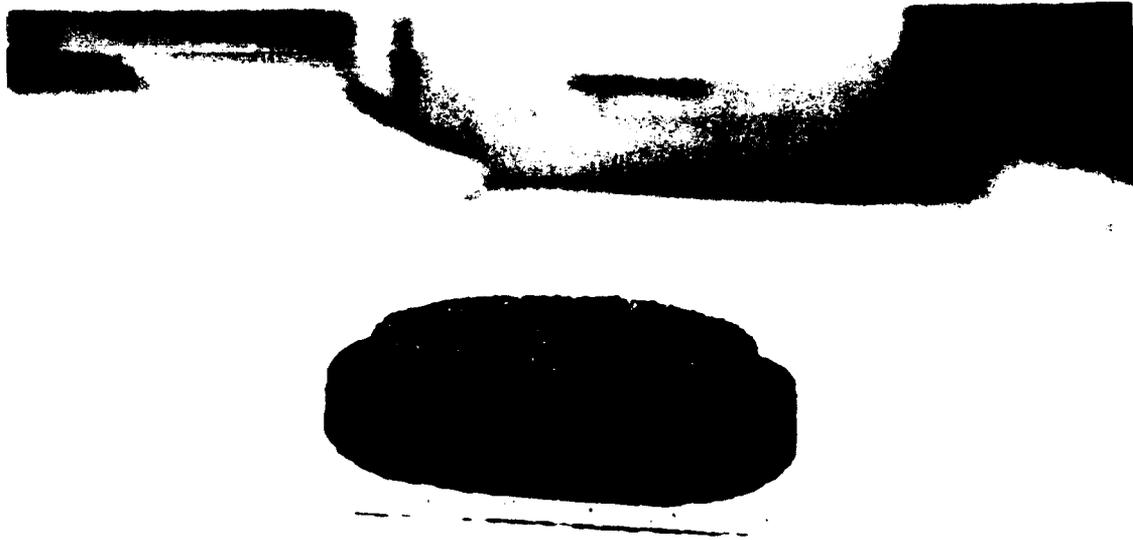


Figure 6. X ray powder diffraction spectrum obtained from  $\beta$ -SiC starting material. Arrows indicate the same extra peaks found in the x ray diffraction pattern of Run SB01.

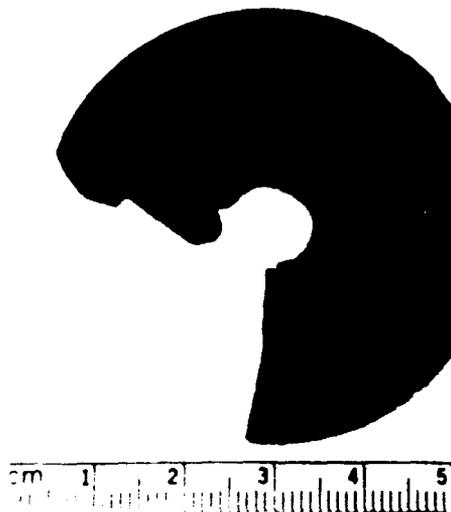
The second growth run, SB02, was carried out under the same conditions as Run SB01, except that the growth temperature was 1930°C. In this run, we were able to grow a SiC layer on the seed as shown in Figure 7. A thick layer of SiC was also grown on the seed holder lid as shown in Figure 8. The SiC layer was separated from the graphite seed holder by oxidizing the graphite at 1000°C. The separated SiC layer is shown in Figure 9. The thickness of the SiC layer was 3 mm. We analyzed a piece of this SiC layer by x ray powder diffraction, and found that the pattern, shown in Figure 10, matched the JCPDS reference for  $\alpha$ -SiC. However, since the x ray diffraction pattern of  $\beta$ -SiC overlaps the one for  $\alpha$ -SiC as shown in Figure 11, it may be a mixture of alpha and beta phases. Thus, a growth temperature of 1930°C is higher than the phase transition temperature from beta to alpha phase of SiC. Therefore, further sublimation experiments were confined to lower temperatures, from 1770°C to 1900°C.



*Figure 7. Thick SiC layer deposited on a TiC seed (5X magnification) in Run SB02.*



*Figure 8. Thick SiC layer grown on the graphite seed holder in Run SB02.*



*Figure 9. Thick SiC layer after removing the graphite seed holder (SB02).*

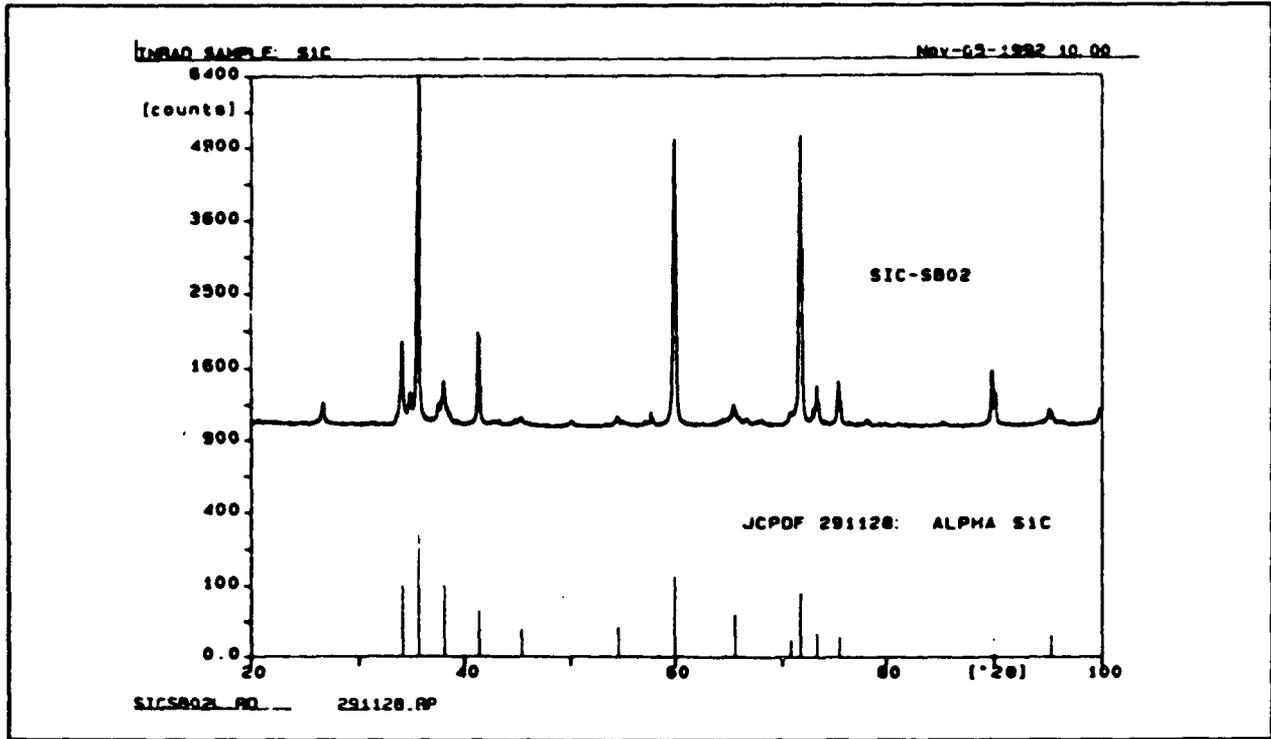


Figure 10. X ray powder diffraction spectrum obtained from Run SB02

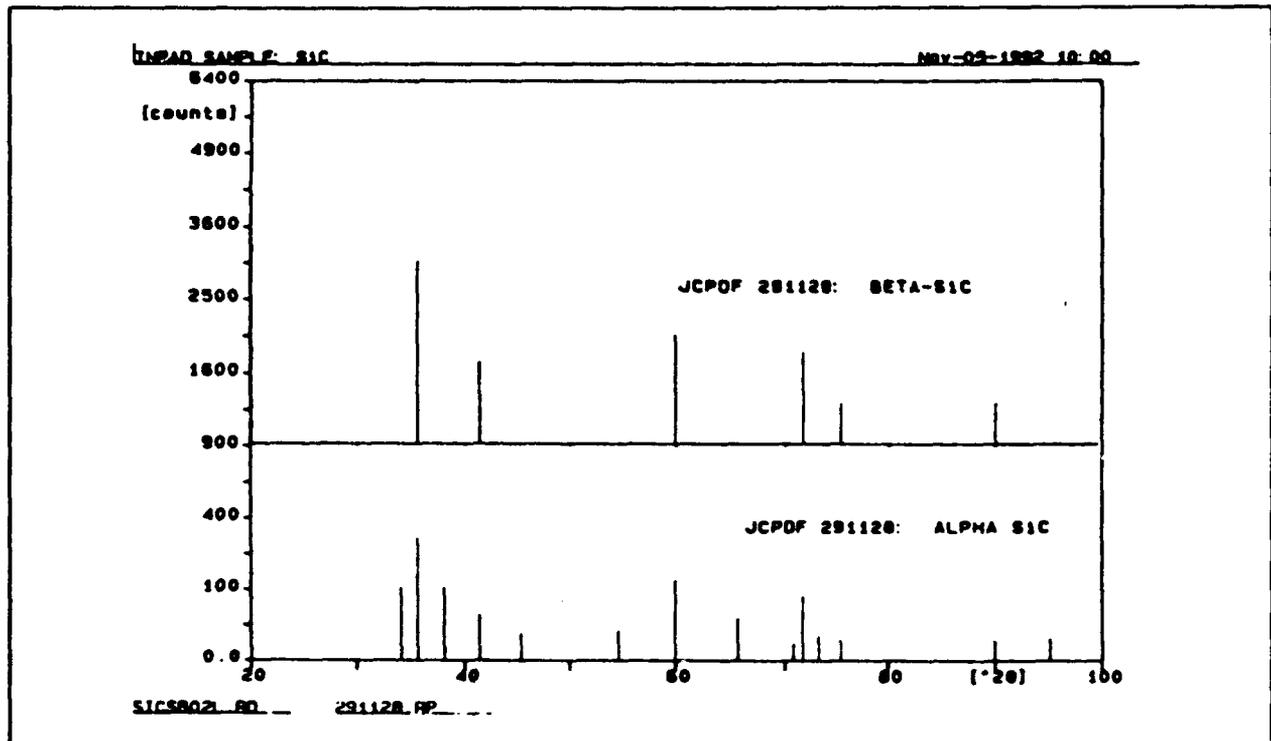


Figure 11. Comparison of JCPDS reference pattern for  $\beta$ -SiC and  $\alpha$ -SiC. All peaks of  $\beta$ -SiC overlap with  $\alpha$ -SiC.

### 5.1.2 RUNS SB03 THROUGH SB08

Six additional sublimation crystal growth runs were carried out and are summarized in Table 1, along with the first two runs described above.

Table 1. Summary of Sublimation Crystal Growth Runs.

RUN	GROWTH TEMPERATURE	SEED	ATMOSPHERIC PRESSURE	GROWTH TIME
SB01	1860°C	TiC	250 torr (Ar)	52 hrs
SB02	1930°C	TiC	250 torr (Ar)	52 hrs
SB03	1900°C	none	760 torr (Ar)	48 hrs
SB04	1830°C	none	0.05-0.1 torr	65 hrs
SB05	1810°C	TiC	0.05-0.1 torr	72 hrs
SB06	1790°C	TiC	0.05-0.1 torr	72 hrs
SB07	1780°C	TiC	0.05-0.1 torr	72 hrs
SB08	1770°C	TiC	0.05-0.1 torr	72 hrs

In Run SB03, no significant layer was deposited. Figure 12 presents the results from Runs SB04 through SB08 in the form of sketches of the contents of the crucibles. Figures 13 through 18 show the x ray diffraction patterns for the products of Runs SB03 through SB08 compared with the JCPDS standard for 3C-SiC. In general, the crystals obtained in the sublimation growth runs were not pure 3C-SiC, but contained a few percent of 6H-SiC.

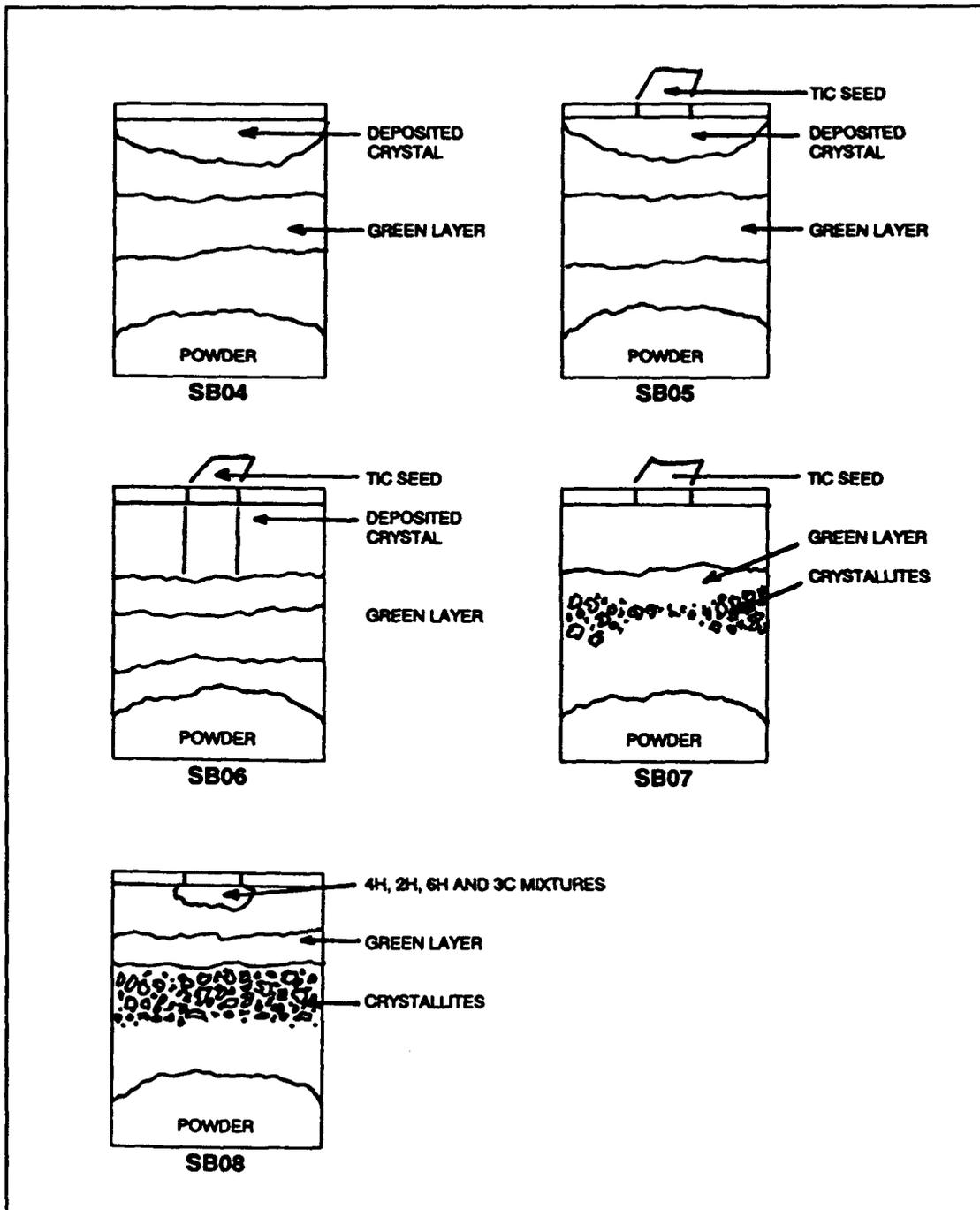


Figure 12. Products obtained in Runs SB04 through SB08.

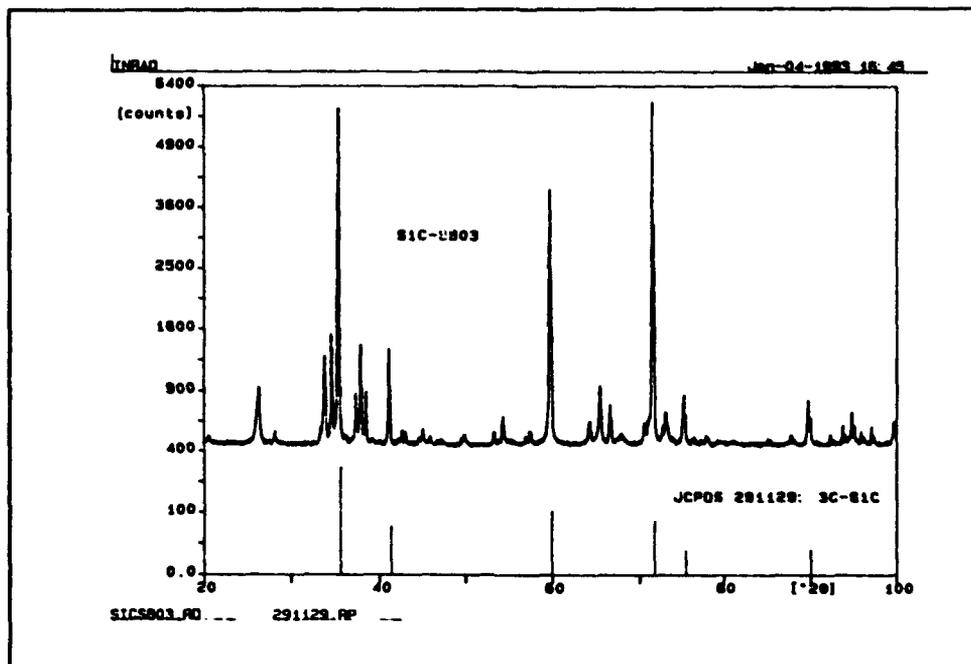


Figure 13. X ray diffraction pattern for Run SB03.

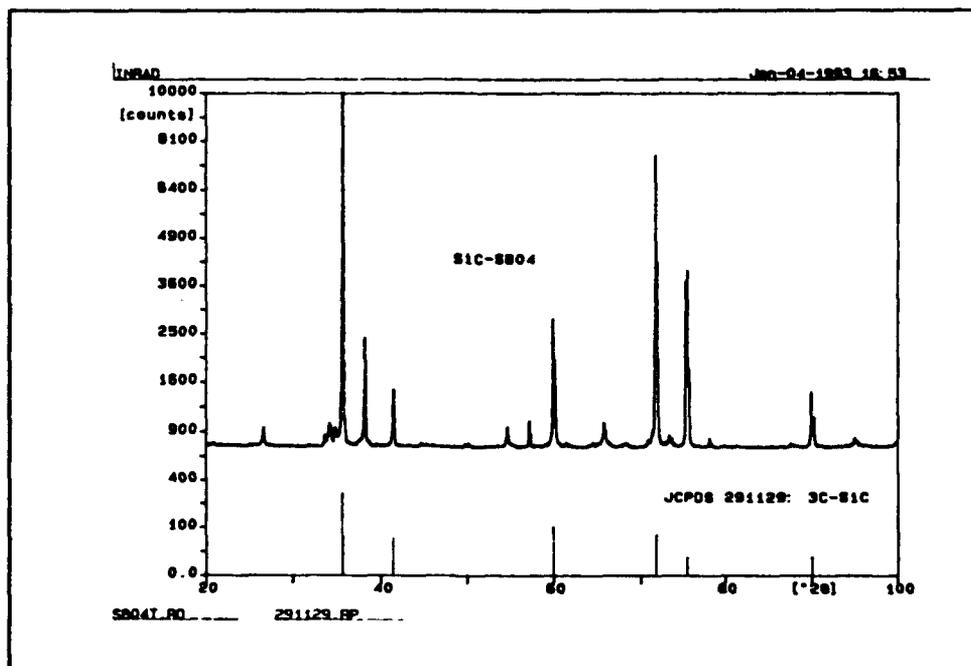


Figure 14. X ray diffraction pattern for Run SB04.

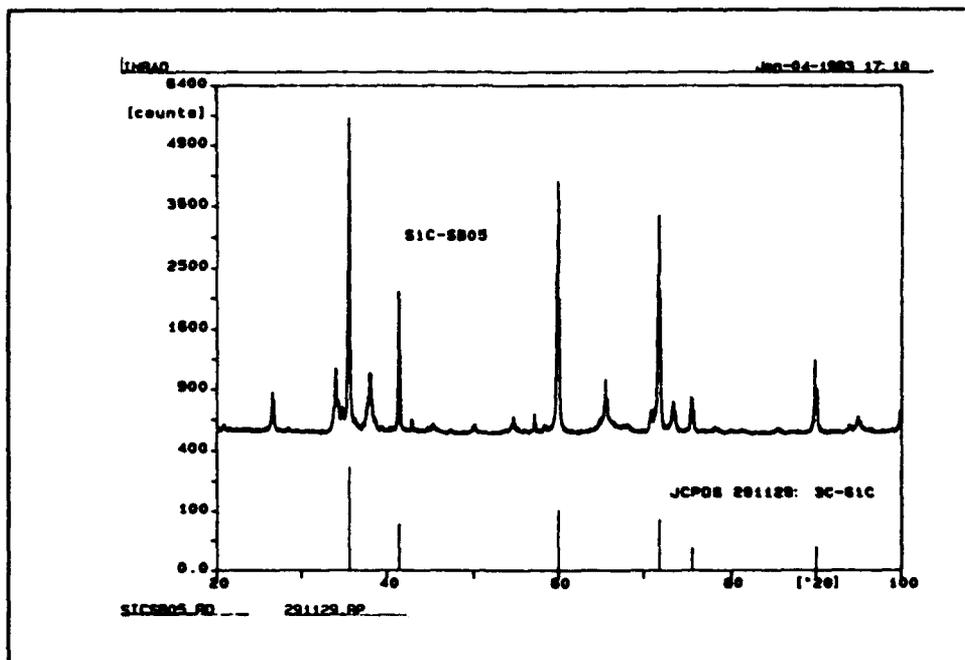


Figure 15. X ray diffraction pattern for Run SB05.

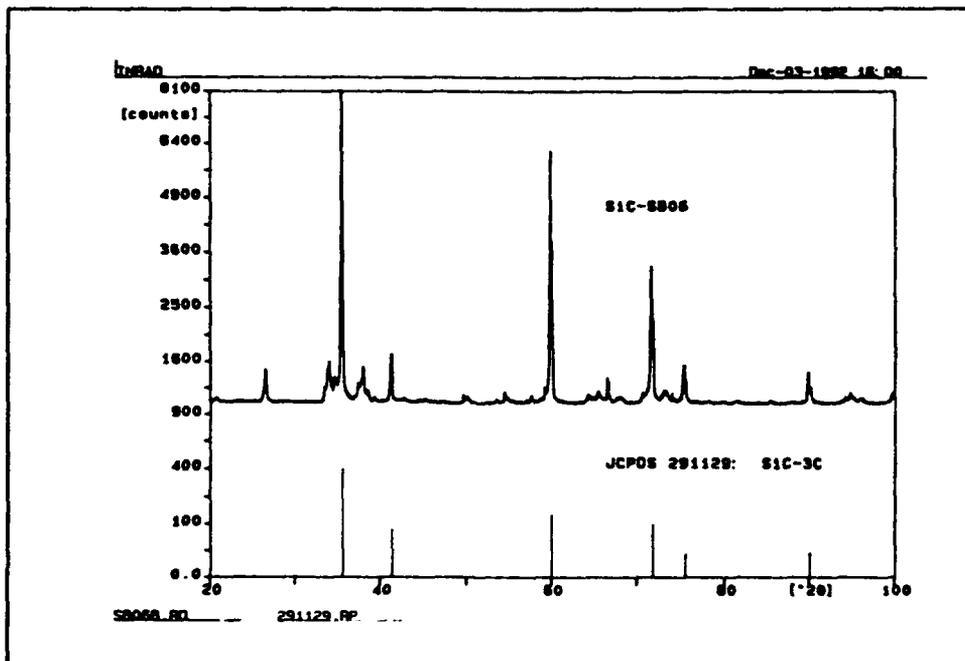


Figure 16. X ray diffraction pattern for Run SB06.

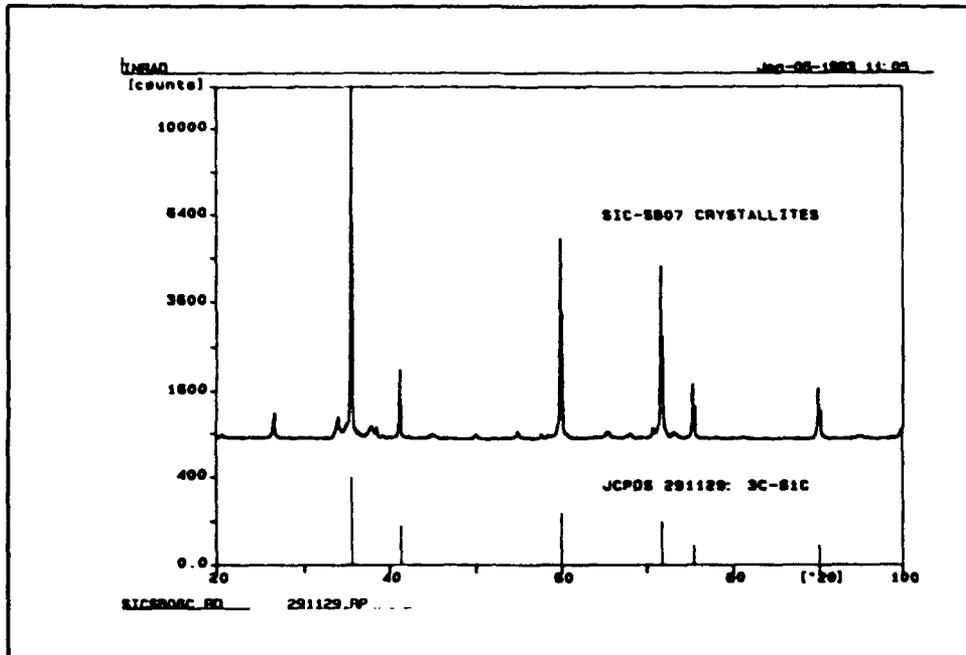


Figure 17. X ray diffraction pattern for Run SB07.

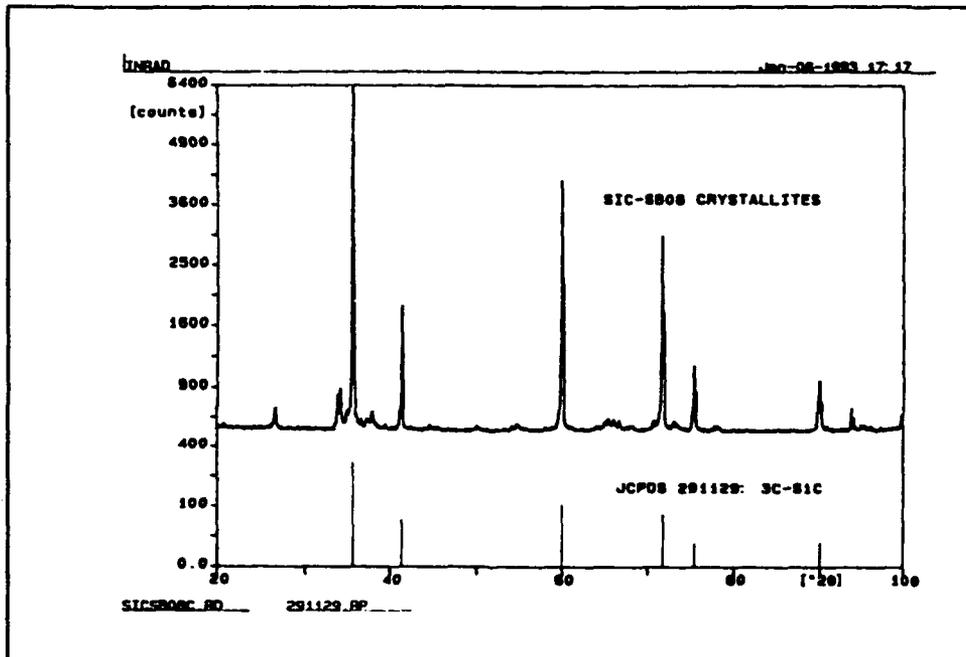


Figure 18. X ray diffraction pattern for Run SB08.

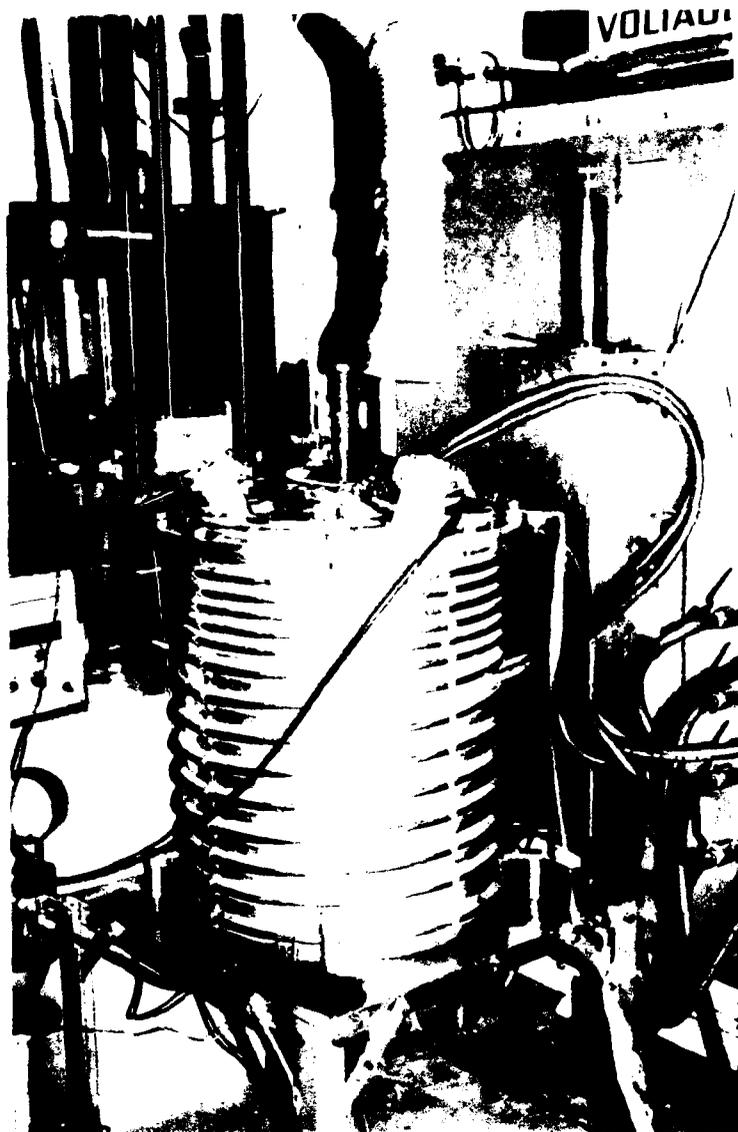
## **5.2 TOP-SEEDED SOLUTION GROWTH**

We were unable to evaluate the top-seeded solution crystal growth process because the delivery of the high pressure crystal growth chamber was delayed. During the construction, we had to change some of the specifications such as thickness of the chamber walls as well as the bottom and top plates to ensure that the maximum design pressure of 1500 psi could be used safely. In the interim period, we were able to carry out some experiments on a gas-vapor transport method that looked promising.

## **5.3 GAS-VAPOR GROWTH**

Recent research on crystal growth techniques for TiC at INRAD showed that  $\beta$ -SiC single crystals might be grown by the reaction of Si vapor and a hydrocarbon gas such as methane. Since Si has a high vapor pressure at high temperatures, 1700–2000°C, this technique appears promising for  $\beta$ -SiC. Although not included in our proposal, we explored the feasibility of this technique using existing equipment at INRAD.

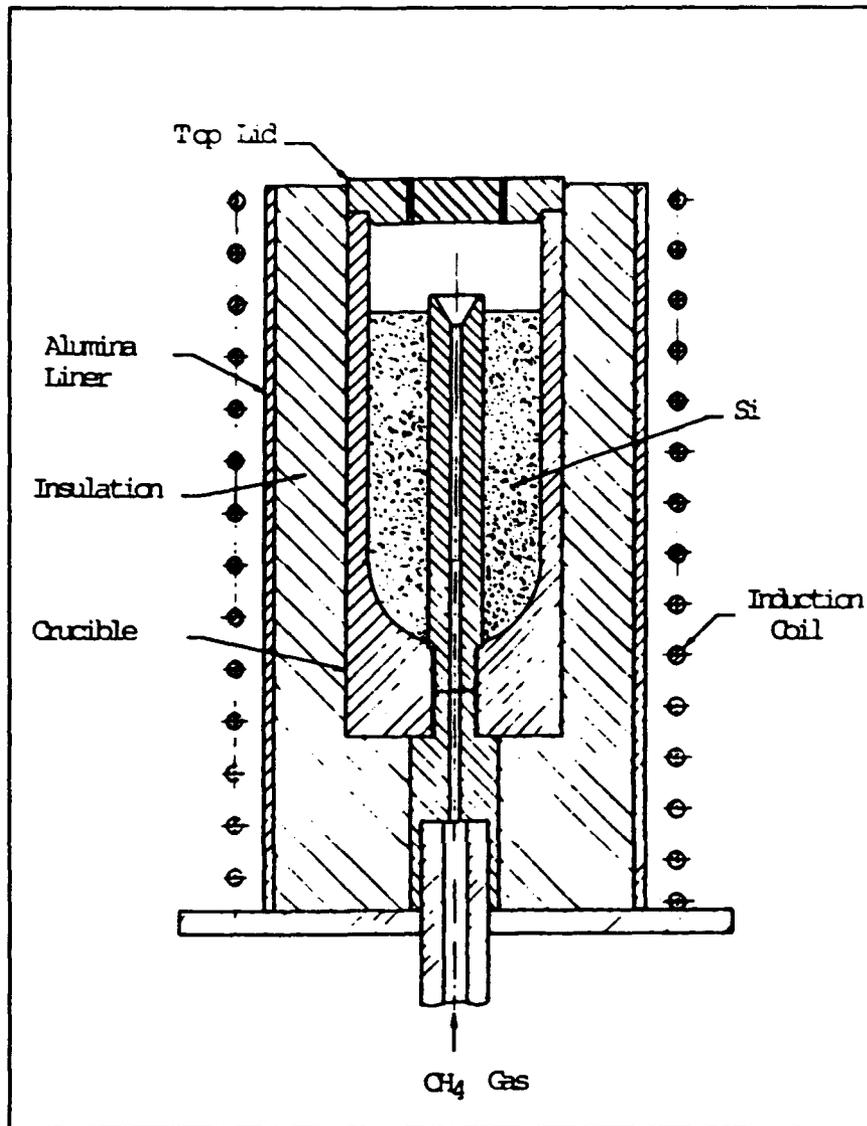
**Figure 19** shows a crystal growth station for vapor transport consisting of a gas-tight chamber, 20 kW, 10 kHz Pillar rf generator, and a computerized temperature control system. A graphite crucible was designed and built to provide for vaporization of Si by rf induction heating and reaction of the vapor with CH<sub>4</sub> gas.



*Figure 19. Photograph of gas-vapor transport  $\beta$ -SiC crystal growth station.*

We attempted to grow  $\beta$ -SiC crystals by the reaction of Si vapor and a hydrocarbon gas such as methane. Since Si has a high vapor pressure in the temperature region of 1700°C to 1800°C, it is a promising method by which to grow  $\beta$ -SiC crystals, if the silicon vapor can react efficiently with methane gas.

A graphite crucible was designed and built to provide for the vaporization of Si by rf induction heating and the reaction of the vapor with CH<sub>4</sub> gas introduced through a graphite pipe as schematically shown in Figure 20.



*Figure 20. Schematic diagram of vapor phase growth of SiC crystals.*

Since molten silicon is very reactive with graphite, we sought to protect the inner surface of the crucible with metal carbide coatings such as ZrC or TaC, which are known to protect graphite from direct reaction with molten silicon. A coating thickness of 0.05 mm was considered adequate. Properties of a variety of metal carbides are shown in Table 2. The graphite crucibles fabricated in our shop were sent to Prazir Surface Technology for coating with ZrC by CVD.

Table 2. Properties of Metal Carbides.

	NbC	TaC	TiC	ZrC
Formula Weight, g/mol	104.93	192.96	54.91	103.23
Density, g/cc	7.85	14.99	4.94	6.66
Structure Type	FCC	FCC	FCC	FCC
Lattice Constant, Å	4.47	4.46	4.32	4.69
Color	Silver-Rose	Gold	Blue-Gray	Silver-Gray
Emissivity (1)	0.85	0.75	0.36	0.40
Melting Point, °C	3760	3880	3140	3540
Eutectic with Carbon, °C	----	3300	2900	2430
Oxidation Limit, °C	800	700	800	800
Electrical Resistivity, micro-ohm cm	30-70	20-40	50+	40-60
Thermal Conductivity, W/mK	13	22	15	21
Th. Exp. Coefficient, 10E(-6)/°C (2)	6.65	6.29	7.80	6.73
Hardness, Kg/mm <sup>2</sup> (Knoop 100 g)	2400-2700	2100-2500	2500-2900	2100-2600
Young's Modulus, GPa	350-500	300-500	450	350-400
Tensile Strength, MPa	----	----	686	196
Compressive Strength, MPa	2352	----	1372	813
Poisson's Ratio	----	0.17	0.19	0.26

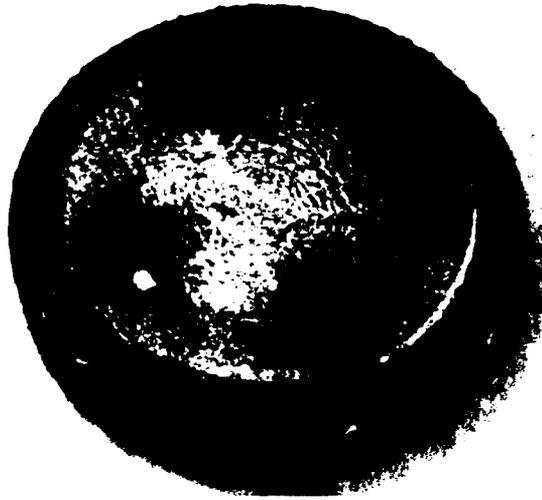
(1) Normal Spectral Emissivity, 800-1600°C.

(2) RT - 1100°C.

Two experiments, VT02 and VT03, were conducted by the gas-vapor transport method at a growth temperature of 1800°C. We placed about 250 grams of Si lumps in a 2.5" diameter crucible and purged with Ar gas for 2 hours. The silicon lumps were heated by rf induction heating to 1800°C for 10 hours. We also flowed Ar gas through the graphite gas-feeding pipe instead of CH<sub>4</sub> gas during the heating. As soon as the temperature reached 1800°C, we switched the Ar gas to CH<sub>4</sub>. The growth time for both runs was 50 hours. In these preliminary experiments, we grew a SiC layer on the ZrC coated graphite top lid.

We found from the experiments that the gas-feeding pipe was blocked by molten silicon that flowed into the gap between the pipe and the crucible. However, we were unable to identify how long CH<sub>4</sub> gas flowed into the crucible during the run before being blocked. In order to overcome this problem, we found it necessary to redesign the crucible.

Figure 21 shows the layer that deposited on the top lid. The four small holes were made to provide for the escape of excess gas in the crucible. This layer was separated from the graphite, and is shown in Figure 22. Its thickness was about 0.7 mm. We analyzed it by x ray powder diffraction, and compared it with JCPDS reference patterns for Si and β-SiC. The spectra indicate that the grown layer is a mixture of Si and β-SiC, as shown in Figure 23. We believe that a SiC layer formed initially, until the gas-feeding pipe was blocked; subsequently, only Si vapor was deposited on the lid.



*Figure 21. SiC-Si layer grown by gas-vapor transport on the graphite top lid.*



*Figure 22. SiC-Si layer after removing the graphite top lid.*

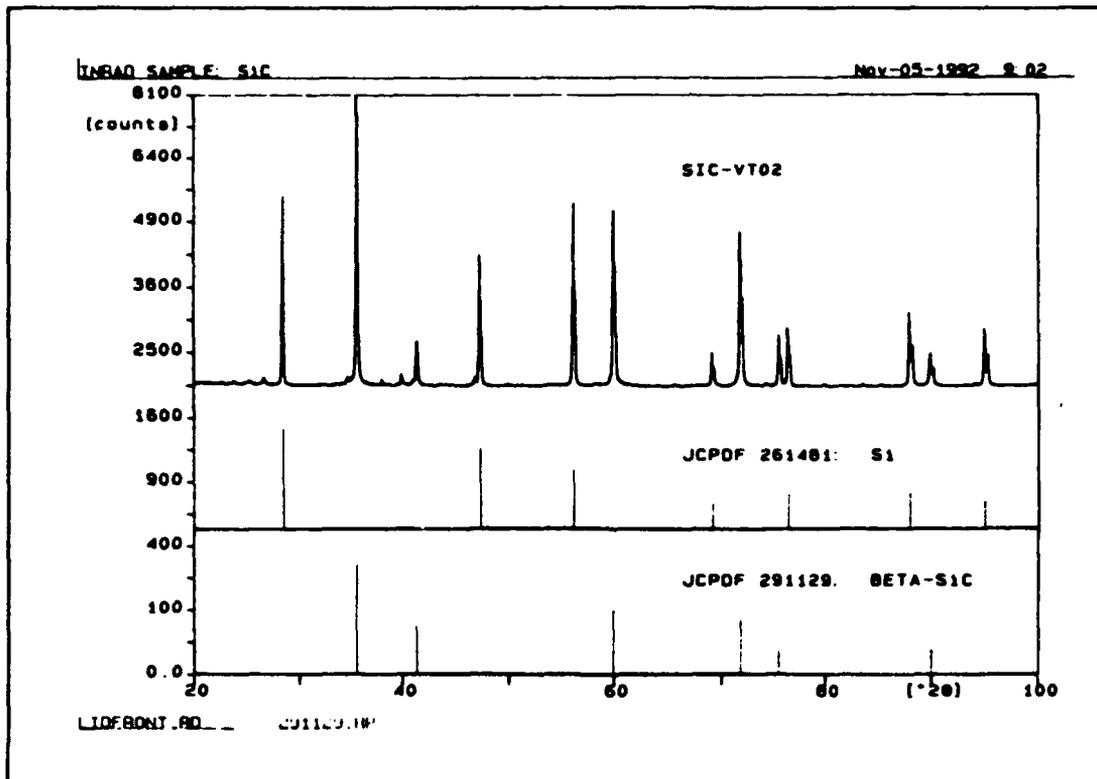


Figure 23. X ray powder diffraction spectrum obtained from a sample grown by gas-vapor transport (VT02).

Three gas-vapor transport crystal growth runs that were carried out are summarized in Table 3.

Table 3.

RUN #	TEMPERATURE	COMMENTS
VT01	1544°C	Not enough rf coupling
VT02	1800°C	Gas line was clogged
VT03	1800°C	Growth occurred in the atmosphere of Ar and CH <sub>4</sub>

The x ray diffraction pattern of the product from VT0-3 is shown in Figure 24, and consisted of 3C-SiC with relatively very little other phases.

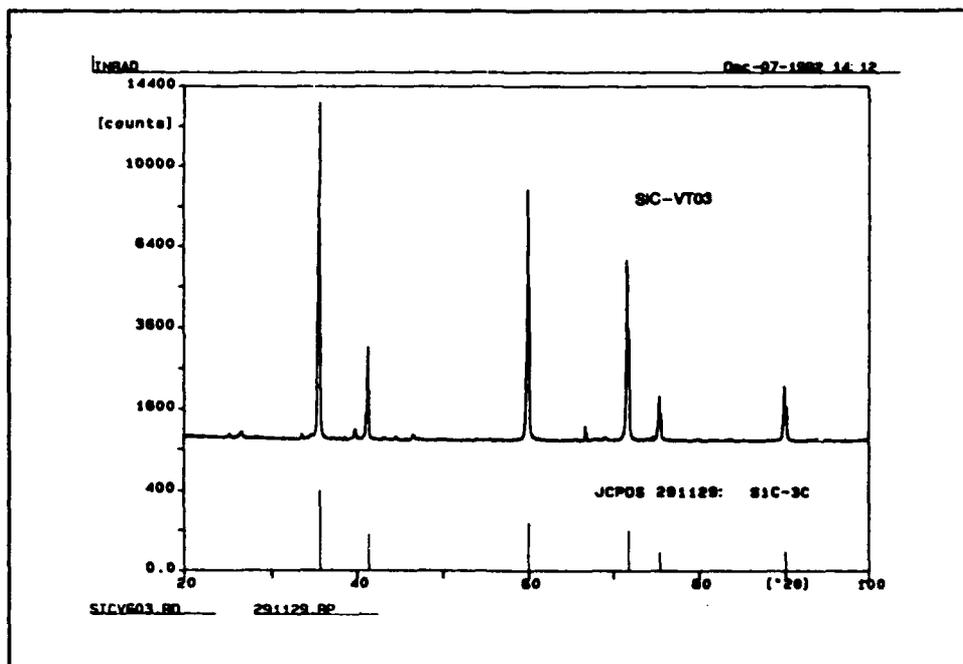


Figure 24. X ray diffraction pattern from Run VT03.

## 6. PUBLICATION AND REPORTS

Two progress reports were submitted to the Office of Naval Research.

## 7. KEY PERSONNEL

**PRINCIPAL INVESTIGATOR:** *DR. KEE-CHANG YOO*

### **EDUCATION:**

Ph.D., Engineering, Brown University, Providence, Rhode Island, 1981

M.S., Physics, Tohoku University, Sendai, Japan, 1975

B.S., Physics, Korea University, Seoul, Korea, 1972

### **EMPLOYMENT:**

1991-Present *Manager, High Temperature Crystal Research, INRAD, Inc.*

1986 - 1991 *Senior Scientist, Westinghouse Science and Technology Center, Pittsburgh, PA.*

1984 - 1986 *Senior Staff Scientist, Solarex Corporation, Rockville, MD.*

1982 - 1983 *Consultant (Part Time), Solarex Corporation, Rockville, MD.*

1981 - 1983 *Research Associate, University of Maryland, College Park, MD*

1978 - 1981 *Research Assistant, Brown University, Providence, RI*

1980 - 1980 *Guest Worker, National Bureau of Standards, Gaithersburg, MD*

1975 - 1977 *Guest Research Associate, Brookhaven National Laboratory, Upton, NY Energy Research Fellow, SUNY at Stony Brook, Stony Brook, NY*

### **SUMMARY OF EXPERIENCE:**

Dr. Yoo's previous position was Senior Scientist with Westinghouse Science and Technology Center, Pittsburgh, PA. Much of his research activities at Westinghouse focused on growth and characterization of nonlinear optical crystals, such as  $Tl_3AsSe_3$  and  $AgGaSe_2$ . Both of these crystals are useful for doubling  $CO_2$  lasers and as active crystals in infrared optical parametric oscillators (OPO).  $Tl_3AsSe_3$  finds application as an acousto-optic material.

While at Westinghouse, Dr. Yoo also worked on monolithic integration of microwave magnetic components with GaAs MMIC's, needed for next-generation compact radar systems. He accomplished LPE growth of Bi-YIG and Ba-hexaferrite needed for magneto-optic device applications. As part of the same project, he performed Czochralski growth of oxide crystals for use as LPE substrate materials.

Dr. Yoo specializes in growth of single crystals by Czochralski, Bridgman, an physical vapor transport methods, in characterizing crystal imperfections, and correlating them with needed improvements in the growth process. He is also experienced in preparing thin films by liquid phase epitaxy, spin spray plating, and vapor deposition.

**SELECTED PUBLICATIONS:**

Dr. Yoo has published several papers in the field of crystal growth and crystal characterization. A selected list is given here.

"Growth of Subgrain-Free  $Tl_3AsSe_3$  Crystals for Efficient MID-IR Harmonic Frequency Conversion," Yoo, K.C., Storrick, R.P., Henningsen, T., Spitznagel, J.A. and Hopkins, R.H., *J. Crystal Growth*, to be published, 1991

"Thallium Arsenic Selenide (TAS): Status of Growth and Application", Henningsen, T. and Yoo, K.C., Proceedings of the 1990 IRIS Speciality Group Meeting on Infrared Materials, Applied Physics Laboratory, JHU, MD, August, 1990.

"Anisotropy Effects on Fracto-Emission from  $MgF_2$  Single Crystals", Yoo, K.C., Rosemeier, R.G., Dickinson, J.T. and Langford, S.C., *Appl. Phys. Lett.*, **55**, 354 (1989).

"X ray Reflection Topographic Study of Growth Defect and Microindentation Strain Fields in an RDX Explosive Crystal", Elban, W.L., Armstrong, R.W., Yoo, K.C., Rosemeier, R.G. and Yee, R.Y., *J. Matls. Sci.*, **24**, 1273 (1989).

"Studies of the Plastic Deformation of  $Tl_3AsSe_3$  Single Crystals by Hardness Indentation", Yoo, K.C., Spitznagel, J.A. and Hopkins, R.H., *J. Materials Research*, **3**, 1404 (1988).

"Effects of Subgrain Structure on the Optical Homogeneity of  $Tl_3AsSe_3$  Single Crystals", Yoo, K.C., Henningsen, T., Grimmett-Dawson, K.D., Singh, N.B. and Hopkins, R.H., *J. Appl. Phys.*, **65**, 827 (1988).

"Investigation of Growth Conditions for the Liquid Phase Epitaxy of Hexaferrite Films Using  $Bi_2O_3$ - $BaO$ - $B_2O_3$  Flux", Yoo, K.C., Storrick, R.P., Kramer, W.E., Stewart, A.M. and Hopkins, R.H., *J. Crystal Growth*, **85**, 389 (1987).

"Stereoscopic Observation of Dislocation Polygonization by X ray Topography", Yoo, K.C., *Materials Letters*, **3**, 368 (1985).

"Effects of Non-equilibrium Solidification on the Material Properties of Brick Silicon for Photovoltaics", Regnault, W.F, Yoo, K.C., Soltani, P.K. and Johnson, S.M., Proceedings of Research Forum on "High Speed Growth and Characterization of Crystals for Solar Cells", July, 1983.

**PRESIDENT:**

**DR. WARREN RUDERMAN**

**EDUCATION:**

Ph.D., Chemical Physics, Columbia University, 1949

**EMPLOYMENT:**

1973-Present *President, Chairman and Founder, INRAD, Inc.*  
1956 - 1973 *President, Director and Founder, Isomet Corp.*  
1953 - 1957 *Consultant, Columbia Univ., Gov. Contracting Division, Atomic Energy Project*  
1952 & 1953 *Guest Physicist (Summer), Brookhaven National Laboratory*  
1949 - 1953 *Lecturer in Chemistry and Research Associate, Columbia University*  
1946 - 1948 *Teaching Fellow, Columbia University*  
1940 - 1946 *Research Chemist, St. Regis Paper Co., Panelyte Division*

**TECHNOLOGICAL ACHIEVEMENTS:**

- First commercial production in the U.S. of trans-stilbene and p-terphenyl scintillation crystals.
- Growth and fabrication of first 4-level laser host crystal,  $\text{CaF}_2:\text{Sm}^{2+}$ , for Dr. Peter Sorokin (IBM).
- Development and first commercial production in the U.S. of KAP and RAP X-ray monochromator crystals (sponsored by Naval Research Laboratory and Wright-Patterson Aeronautical Systems Div., Materials Lab).
- First commercial production in the U.S. of highly deuterated KDP crystals and Pockels cells incorporating these crystals.
- First commercial production in the U.S. of single crystals of lithium niobate, lithium tantalate, tellurium dioxide, lead molybdate and bismuth germanium oxide ( $\text{B}_{12}\text{GeO}_{20}$ ).
- Development and manufacture of organic X-ray monochromator crystals with long 2d spacings (30 to 100 Å) for the Orbiting Solar Observatory (sponsored by NASA/Goddard).
- Development of a manufacturing process for high quality CD\*A crystals (sponsored by Wright-Patterson Aeronautical Systems Division, Avionics Laboratory).
- First development and manufacture in the U.S. of acousto-optic modulators, deflectors, and tunable filters.
- First successful manufacture of large KDP crystals (~25 cm) for use in fusion lasers for harmonic generation.

**PUBLICATIONS:**

Dr. Ruderman holds a dozen patents and has published several scientific papers. A selected list is presented.

"Photochlorination of n-Alkanes Absorbed on Pentasil Zeolites", Turro, N.J., Fehlner, J.R., Hessler, D.P., Welsh, K.M., Ruderman, W., Firnberg, D. and Braun, A.M., *J. Am. Chem. Soc.*, **53**, 3731 (1988)

"Extending the Wavelength Range of Fundamental Laser Sources", Ruderman, W., *Biophys. J.*, **24**, 73 (1978)

"Generation of Tunable Radiation Below 2000 Å by Phase Match Sum - Frequency Mixing in  $\text{KB}_5\text{O}_{8,2}\text{D}_2\text{O}$ ", Paisner, J.A., Spaeth, M.L., Gerstenberger, D.C. and Ruderman, W., *Appl. Phys. Letters*, **32**, 476 (1978)

"New Synthesis Methods for CD\* A Growth", Ruderman, W., AFAL-TR-77-233 (Dec. 1977)

"Analyzer Crystals for X-Ray Spectroscopy in the Region 25-100 Å", Ruderman, W., *Appl. Phys. Lett.*, **1**, 17 (1965)

"Development of Laser Crystals", Ruderman, W., ASD-TDR-63-362 (June 1963)

"A Comparison of the Energy Output of Various Solid State Laser Materials" *Lasers & Appl.* (Ohio State Univ. Press)

"Regeneration of Oxygen from Carbon Dioxide in Closed Ecological Systems" WADD Technical Report 60-574, August 1960

"New Horizons for Stable Isotopes" *Proc. of 2nd U.N. Int. Conf. on the Peaceful Uses of Atomic Energy*, **20**, 1958

"Neutron Reflecting Mirrors for Determining Coherent Scattering Cross Sections" *Rev. Sci. Instr.*, **27**, 620 (1956)

"A Neutron Diffraction Study of Vitreous Silica", *Phys. Rev.*, **317**, 7744 (1954)

"Neutron Resonances of Tellurium" *Phys. Rev.* **83**, 660 (1951)

"Photographic Methods of Measuring Slow Neutron Intensities" *Rev. Sci. Instr.* **214**, 232 (1950)

"A New Method for Determining the Relative Phase with which Slow Neutrons are Scattered by Nuclei" *Phys. Rev.*, **77**, 575 (1950)

## 8. REPORT OF INVENTIONS

No inventions were made during the performance of this work.

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