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13. ABSTRACT *(Maximum 200 words)*

A Double Crucible Liquid Encapsulated Czochralski (DCLEC) process was developed for the growth of single crystals of $In_xGa_{1-x}As$. The conditions for the flow of non-wetting liquids through capillaries were determined and applied to Hot Pressed Boron Nitride crucibles to achieve stable flow of InGaAs melts, wothout back-diffusion of In, and without interference from the boric oxide encapsulant. The problem of mixing int the inner crucible was solved by the use of super-cooled melts to obtain fine grained, uniform composition pre-cast charges. Growth of $In_xGa_{1-x}As$ with x values up to 0.035 was achieved. This material was semi-insulating.

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BULK GROWTH OF $In_xGa_{1-x}As$

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FOREWORD

This program was begun in July 1992 with a Phase 1 SBIR program, funded by BMDO and administered by the Army Research Office, technical monitor Dr. M. Littlejohn.
The objective was to develop a process for the growth of single crystals of $In_xGa_{1-x}As$ of uniform composition, with x equal to any desired value up to 0.11.
Phase 1 ran from July to December 1992 and Phase 2 from September 1993 to December 1994.
The Phase 2 proposal included participation by the team:-

Ware Technical Services(prime contractor)...crystal growth
Arizona State University,characterization and device studies
Litton Airtron, wafer cutting and polishing
Epitronics Corporation, epitaxial growth.

The funding requested for a two year program was $750,000. BMDO awarded $250,000 for one year, with a commitment to match any non SBIR funding up to $500,000. In view of the limited funding, it was decided to concentrate initial efforts on the crystal growth program, whilst attempts were made to raise additional funds. In spite of considerable industrial interest in these materials, including offers to buy significant quantities of the wafers when available, it was not possible to obtain the necessary funding.
Thus, although much progress was made in solving the problems in this difficult materials system, the work was stopped in December 1994.

CONTENTS

1. The Opportunity and the Problem

1.1. Potential Applications and advantages of InGaAs

At present. III-V compound semiconductor substrates are of binary composition. All III-V devices that contain ternary or quaternary materials, such as heterojunction bipolar transistors(HBTs) and high electron mobility transistors (HEMTs), are fabricated with epitaxial layers grown on binary substrates. In other words, the "bandgap engineering" which has become the hallmark of compound semiconductor research and development is carried out only with epitaxial materials, not substrates. For the most part, this has not been a serious drawback because of the great advances in epitaxial technology, permitting both lattice matched and strained-layer epitaxial growth for a vast array of device structures.

As a case in point, consider the HEMT. The conventional structure of this device includes an undoped GaAs channel layer and an n-type $Al_{1-x}Ga_xAs$ layer to provide carriers for the channel. This device has in general very impressive low noise, high speed performance. Recently, the use of pseudomorphic (strained, but coherent) $In_xGa_{1-x}As$ channel layers has resulted in dramatic improvements in the high frequency,noise,and power performance of HEMT structures[1-4]. The conduction band offset of the $Al_{1-x}Ga_xAs/In_xGa_{1-x}As$ heterojunction is larger than that for $Al_{1-x}Ga_xAs/GaAs$, so higher sheet carrier densities can be achieved. With higher carrier densities, there is enhanced current drive capability and speed. Furthermore, the higher conduction band offset permits the use of lower Al content which reduces problems in cryogenic operation caused by DX centers[5,6].

Curiously enough, the high performance of the pseudomorphic HEMTs occurs in spite of the strain in the $In_xGa_{1-x}As$ layer. Because unstrained InxGa1-xAs shows very high mobility, it is often assumed that strained $In_xGa_{1-x}As$ must also have superior transport properties. In fact, it has been demonstrated both theoretically and experimentally that strained InxGa1-xAs has inferior transport properties[7,8]. It would therefore be very advantageous to reduce or eliminate the strain in the $In_xGa_{1-x}As$ layer, a task of fundamental difficulty when the film is grown epitaxially on the binary GaAs substrate. Although the growth of a very thick graded $In_xGa_{1-x}As$ to act effectively as a ternary substrate(a relaxed buffer layer) is one possible approach, this is most difficult in practice[9]. Alternatively, $In_xGa_{1-x}As$ can be grown on InP substrates, but only at one particular indium fraction which is not well suited for HEMT operation.

A better approach would be to start with a low defect $In_xGa_{1-x}As$ ternary substrate. The $In_xGa_{1-x}As$ channel layer could then be lattice matched and unstrained, or grown with a higher indium content, (to form a channel with even higher mobility) with significantly reduced strain penalty. The use of bulk $In_xGa_{1-x}As$ substrates would extend bandgap engineering in another direction - substrate engineering - and could lead to a whole class of electronic and optoelectronic devices, in addition to the enhanced HEMTs described here.

After the program a further possible application was identified. An $In_{0.06}Ga_{0.94}As$ substrate would provide a lattice match for a direct gap alloy of InAlP with an energy gap of 2.2 eV giving the possibility of very efficient green LEDs.

1.2. Problems involved in obtaining high quality $In_xGa_{1-x}As$.

The difficulties encountered in the melt growth of ternary III-V compounds by the LEC process can be understood by considering the pseudo-binary phase diagram for InAs-GaAs, Figure 1. Although solid solutions exist over the full range of composition, the wide separation of solidus and liquidus gives rise to severe problems of composition control. For example, the solid in equilibrium with liquid of composition A has a much higher gallium content, corresponding to position B.
Attempts to grow a crystal from a melt at A would yield a solid whose composition starts at B, and then follows the solidus thus showing an increase in indium content along the length of the crystal..

Czochralski growth is a form of "normal freezing" and the distribution of impurities during freezing is given by

$$Cs = kCo(1-g)k-1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where Cs is the solute concentration in the solid, Co is the initial concentration in the melt, k is the equilibrium distribution coefficient and g is the fraction of melt solidified.
Curves corresponding to a range of distribution coefficients are shown in Figure 2. This represents the situation of complete mixing in the melt. Where segregation is taking place there will be a boundary layer in front of the interface, with either a depleted or an enhanced concentration of solute depending on whether k is greater or less than one. In this case k should be replaced by the effective distribution coefficient keff where

$$keff = k/[k +(1-k)\exp(-vd/D_L)] \ldots\ldots\ldots(2)$$

and D_L is the diffusion coefficient of the solute in the melt, d is the solute boundary width, and v is the growth rate.

In the case of InAs/GaAs at the GaAs side of the phase diagram, In can be considered as an impurity. Its distribution coefficient varies with melt composition. At low indium concentrations k_{eff} has been reported to be 0.13[10]. Bonner's results suggest values of 0.13 and 0.22 at melt compositions of 17mol% and 25mol% InAs respectively[11]. We would therefore expect the In concentration in the crystal to increase along a curve falling between those for k =0.1 and k = 0.5 in Figure 2. Thus in the case of normal freezing, a composition gradient along the crystal is inevitable and only a short length of the crystal will possess the desired In:Ga ratio. Bonner has pioneered the growth of ternary compounds by the LEC process[11,12] and, in particular, has grown $In_xGa_{1-x}As$ over the composition range $0.02<x<0.12$. Bonner used a more-or-less standard LEC process with the result that, as expected from the above discussion, his crystals showed marked composition variations from seed to tail, or rather from seed to the point at which they become polycrystalline, probably due to constitutional supercooling (see below and Figure 6) This effect is clearly illustrated in Figure 3, showing the axial variation in Indium content for several of Bonner's crystals.

Since the indium content of the crystal is much lower than that of the melt in equilibrium with it, the effect of growing a crystal is to deplete the melt of GaAs. Nakajima, Kusunoki and Takenaka[13] have taken an approach in which polycrystalline GaAs is fed into an InGaAs melt to maintain a constant composition. The crystals are then grown at constant temperature. In one publication they describe a process in which a rod of GaAs is fed into an InGaAs melt, close to the crucible wall, in a conventional LEC set-up. Small crystals (4mm long) of composition $In_{0.14}Ga_{0.86}As$ were grown from melts of composition $In_{0.36}Ga_{0.64}As$. The same authors also describe the use of a double crucible system[14], with two chambers connected by a slit. The crystal is pulled from one chamber and GaAs fed into the other. The added solute is then supposed to diffuse to the crystal through the slit. This time the melt composition was $In_{0.386}Ga_{0.614}As$ and the crystals $In_{0.055}Ga_{0.945}As$. However the same crystal composition was obtained even when no GaAs was added. This fact, and the widely different crystal compositions for similar melts, suggest that the proposed mechanism was not working. In view of our experience with the flow of GaAs through holes(see Section 1.4.3."Melt flow in capillaries") it seems likely that flow was inhibited by surface tension forces,

The use of a double crucible does however offer the possibility of growing uniform crystals if approached somewhat differently and this is outlined in the next section.

1.3.Approach taken in this programme

Consider the process known as"zone melting"[15] in which a narrow molten zone is passed along a solid rod. The corresponding equation for this form of growth is

$$C_s/C_o = 1-(1-k_{eff})\exp(-k_{eff}x)..........(3)$$

where $x = vt/l$, the distance growm in zone lengths. This situation is shown schematically in Figure 4 for single pass zone melting, in which the length of the molten zone is very small compared with the length of the rod. Figure 5 shows solute distribution for several values of the distribution coefficient in the case where the zone length is one tenth of the total.Note the difference in shape of these curves compared to those for normal freezing.
Reverting to Figure 4, the explanation for the shape of the curve is as follows. In the first, curved, region the first- to-freeze material has the composition kC_o, lower than that of the main charge.Hence, as the zone moves the solute concentration builds up until it reaches a value equal to C_o/k. From this point on, the concentration of solute

in the material freezing out is equal to that of the material melting in and the composition remains constant at Co. Both these regions are described by equation (3). The final region consists of the normal freezing of the last zone, and is described by equation (1).
If the composition of the first zone is set at C_o/k, then the composition of the grown crystal will be Co throughout the first two regions.

For Czochralski growth, a situation corresponding to zone melting can be obtained by use of a double crucible, as illustrated schematically in Figure 7.The contents of the inner crucible correspond to the molten zone and those of the main crucible to the unmelted section of the rod. The two crucibles are connected by a small hole. For efficient zone melting, this hole must be such that back diffusion of solute is negligible.
In a similar way to zone melting, this arrangement can operate in two ways. In the first the composition of the melt is the same in both inner and outer crucible. The composition of the crystal will then follow a curve from Figure 5. If the inner crucible is preloaded with a melt of composition C_o/k, then the resulting crystal should be uniform except for the last section to freeze. The crystal can be terminated before this section is reached in order to avoid the stresses accompanying compositional changes.
Similarly to avoid stresses at the seed end of the crystal it is important to use seeds of the desired composition. Such seeds are not readily available, and hence must be prepared in a stepwise manner. For instance, Nakajima [16] used a 'compositionally graded' seed with $0.05<x<0.08$. This composition could be grown onto pure GaAs, and could then in turn be used as seeds with higher In content. It was decided to approach the desired composition in several steps to minimise the stress which otherwise results and can cause cracking[16].Bonner points out that it is advisable to use seeds of slightly higher gallium content than the melt to avoid uncontrollable melting of the seed[11].

The approach chosen was,therefore, to mount a small crucible within the main LEC crucible, connected to it by a small hole.The melt level in both crucibles would be maintained constant by raising the outer crucible during growth.

The main difficulty expected in this work was constitutional supercooling, leading to the breakdown of crystal structure. This condition occurs when the rejection of solute by the growing crystal causes a reduction in freezing point in the melt adjacent to the interface.There will be a gradient in the freezing point from the crystal into the bulk of the melt. Depending on the temperature gradient in the melt, this region can become supercooled and hence unstable. In Figure 6, the temperature gradient 2 will cause instability, leading initially to cellular growth and then to structural breakdown. The condition governing the occurrence of constitutional supercooling is given by

$$G_L > mvC_o(1-k)/D_Lk \ldots\ldots\ldots\ldots\ldots(4)$$

where G_L is the temperature gradient in the melt adjacent to the interface, and m is the slope of the liquidus. From this equation it can be seen that the onset of constitutional supercooling can be delayed by maximising the temperature gradient in the melt and reducing the growth rate. Reducing the boundary thickness would also help.To these ends Nakajima[14]et al. grew at 1.5mm/hr. and rotated the crystal at 40 rpm.

We decided to combine the double crucible with the Spectrum Technology Inc. proprietary crystal growth technique known as the GAMMA process. This method has been shown greatly to increase single crystal yield in the CI 358 LEC crystal puller, the machine used in this program.

In the GAMMA process the thermal environment is modified to:-

(1) reduce heat flux from the crystal to the boric oxide encapsulant, improving the interface shape.

(2) stabilise the temperature gradients in the melt close to the growing crystal, and make them truly circular. This makes diameter control easier.

(3) control the radiative coupling between crystal and crucible wall.

(4) Prevent the cooling fin effect of the crucible wall as it emerges above the heater insulation. Without this modification the 'cooling fin' effect causes major perturbations in melt convection leading to polycrystalline growth.

(5) reduce and control the carbon content in the crystal, improving electrical properties.

1.4. Practical Problems in Double Crucible LEC (DCLEC).

Whilst simple in theory, DCLEC has a number of practical difficulties. Most of the efforts at Ware Technical Services were devoted to the solution of these problems to develop a practical and reliable double crucible system.. Some of these difficulties apply to any double crucible system; some are specific to DCLEC.

1.4.1. Melt Level Control

In the combined GAMMA-DCLEC process the inner crucible is fixed relative to the heater and insulation package, The melt level is adjusted by controlling the vertical position of the outer crucible.

1.4.2. Material Choice

The material of the inner crucible must meet the usual criteria for crystal growth. It must maintain its strength and chemical stability at the operating temperatures. It must not react with the melt or with the encapsulant, nor dope the crystal by contamination with electrically active impurities. in addition it must meet other criteria which determine the melt flow in the capillary connecting the inner and outer crucibles.
Pyrolytic boron nitride has long been established as the most suitable material for the growth of gallium arsenide and this was chosen for

the inner crucible in Phase 1. Due to limitations on size and ease of machining, we changed to hot pressed boron nitride in Phase 2.

1.4.3. Melt Flow Though Capillaries.

To obtain uniform crystal composition we are faced with two conflicting requirements. The capillary diameter should be as large as possible to permit melt flow, and as small as possible to prevent back diffusion of indium.
Since the InGaAs melt does not wet the boron nitride, there is a resistance to flow through holes arising from surface tension at the entrance and exit points.

For a hole of radius r, the surface tension force resisting flow is 2 ro ,

For the situation in which there is GaAs on one side of the hole and boric oxide on the other, the hydrostatic pressure across the hole is

$$r^2h(d_{GaAs}-d_{oxide})$$

For flow through the hole, the hydrostatic pressure across the hole must exceed the surface tension force i.e.

$$r^2h(d_{GaAs}-d_{oxide}) > 2\ ro \ldots\ldots\ldots\ldots(5)$$

where r = radius of the hole
h = depth of centre of hole below melt surface.
o = surface tension of liquid GaAs = 442 $dynes.cm^{-1}$
d_{GaAs} = density of liquid GaAs = 5.71 $g.cm^{-3}$
d_{oxide} = density of liquid boric oxide = 1.54 $g.cm^{-3}$

This reduces to

$$rh > 0.21 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

This relationship was experimentally confirmed in Phase 1.

The theory of double crucible action outlined above assumes no back diffusion of indium from the inner to the outer crucible. For back diffusion to be negligeable, the requirement is that

$$vl>>>D$$

where v is the linear velocity of the melt through the capillary, and D the diffusion coefficient of In in InGaAs.
Diffusion coefficients in III-V melts are typically in the 10^4-10^5 cm^2sec^{-1} range. A vastly different value of D = 0.034 for In in GaAs was reported by Matsumoto et al (17). This value is suspect, since it leads to the unlikely figure of 7cm for the diffusion boundary layer between a growing crystal and the melt.

Okada et al.(18) investigated the use of boron nitride double crucibles for the growth of InGaAs (presumably hot pressed BN, although this not explicitly stated). They found that the InGaAs melts would not flow through 3mm diameter holes. Flow occurred through 5mm diameter holes, but then back diffusion prevented the growth of uniform crystals. They concluded that boron nitride is unsuitable as a material for this purpose. They came to the same conclusion regarding pyrolytic boron nitride, carbon and aluminium nitride.

The behaviour of their system is easily understood by considering the rh and vl values.

Table 1. Okada crucible characteristics

Capillary Diameter	Capillary Length	rh	vl
0.3cm	1.0cm	0.15	0.010
0.5cm	1.0cm	0.25	0.0034

It can be seen that the rh value for the 3mm hole is less than the critical value of $0.21cm^2$, so flow would not be expected. Similarly the low value of vl for the 5mm hole would be expected to lead to back diffusion.

1.4.4.Problems specific to DCLEC

In the early stages of Phase 2, using crucibles of Type II, Figure 8 we experienced the following difficulty. Introduction of the melt into the inner crucible proceeded smoothly, once tne critical value of rh was exceeded. However, during the early stages of growth, flow through the capillary was cut off, as evidenced by a contact device. As a result growth was restricted to that material in the inner crucible. By the use of a suitable bench model simulation, we were able to demonstrate that the cut off was due to the blockage of tha capillary exit by the boric oxide drawn down by capillary action between the melt and the crucible wall. A study of the wetting of HPBN by molten boric oxide enabled us to develop a combination of surface treatment and geometry which prevented this effect, and allowed unrestricted flow through the capillary.

1.4.5.Initial melt composition and mixing in the inner crucible

In the ideal situation, the equipment is set up with a charge in the outer crucible of composition equal to that desired in the crystal($C_S=C_O$), and the inner crucible charge of composition C_O/k_{eff}. The inner charge has a much lower melting point than the outer, so there is a danger that it will run out before the surfaces are levelled.

Four approaches to this problem were investigated.

(1) Pure InAs was preloaded into the inner crucible. The melt entry hole was above the surface of the molten InAs. With the hole in this position, h was small and r had to be increased to obtain flow, to a point at which back diffusion occurred. Also the InAs, which is denser than the GaAs did not mix with the rest of the charge.

(2) The composition in the inner crucible was adjusted to the desired value by introducing an InAs disc attached to the seed crystal. This method worked reasonably well, but there were still mixing problems. Also controlling the rate of melting of the InAs to keep the liquid surfaces level was difficult.

(3) Precast Charges

This approach is based on observations made over many years experience with III-V and II-VI melts. These melts, when encapsulated with boric oxide, can sustain surprisingly high levels of supercooling. For instance, we have measured 250°C of supercooling in GaP melts, and values in the range 140-230°C for GaAs, InP, and CdTe. Presumably the reason for this behaviour is that the melts are completely surrounded by liquid B_2O_3, so that there is no solid contact to act as a nucleation centre. When freezing does occur it is very rapid, and a disc of very fine grained unifore polycrystalline material is obtained. This process is illustrated in Figures 9 & 10.

Figure 9a is an electron micrograph of a residual melt of overall composition 41.5 mol% InAs. it can be seen that as it froze two phases separated. Figure 10 shows the composition of this material as determine by X-ray powder diffraction. It can be seen clearly that the composition of the two phases are 50.6 mol% and 6.9 mol% InAs. The structure of a pre-cast charge of 52.5 mol% is shown in Figure 9b, revealing its very fine grained structure. Similar pictures can be obtained from anywhere in the cast ingot. The results of X-ray powder diffraction of this material in Figure 10 shows that no clear composition peaks were obtained.

In the final process, the inner crucible charges were precast in this form, thus overcoming the initial mixing problem.

(4) Crucible shutter

Because of the nature of the puller geometry, the oxide and charge in the outer crucible must be melted before the crucible can be raised so that the melt surrounds the inner crucible. During this time there is a danger that the inner charge, which has a lower melting point (see Table 2), will melt and run out.
To prevent this the inner crucible is fitted with a shutter which can be opened at operating temperatures to connect the inner and outer melts, once both charges are melted and levels aligned.

1.4.6.Evolution of crucible design

1.4.6.Evolution of crucible design

1.4.6.1.Criteria

Given the properties of stability and chemical inertness mentioned above, the crucible should be wetted by boric oxide , but not by the melt (to reduce contamination).

It should have a low thermal conductivity perpendicular to the crucible wall to permit steep temperature gradients.
Table 2 illustrates the temperature drops necessary between inner and outer melts for a number of compositions (taken fron the pseudo-binary phase diagram)

Table 2
Data extracted from the InAs/GaAs pseudo-binary phase diagram

Composition mol%		Liquidus Temperatures °C		
Liquidus	Solidus	TL1	TL2	T
5	0.5 appr.	1230	1242	12
10	2.2	1222	1234	17
20	3.3	1205	1236	31
31.5	5.0	1176	1233	57
40	5.6	1161	1231	70
41.2	6.0	1159	1230	71
51.5	8.0	1128	1227	99
59.5	10.0	1121	1226	105

TL1 and TL2 are liquidus temperatures corresponding to the compositions on the left. T is the minimum temperature difference which must be maintained between the inner and outer crucibles in a double crucible system.

For example to grow a crystal of composition $In_{0.06}Ga_{0.94}As$, the outer crucible will contain a melt of 6 mol% InAs, the inner 41.2 mol% InAs and the temperature drop must be at least 71°C.

1.4.6.2.Crucible design

In many ways pyrolytic boron nitride is an ideal material for the inner crucible since it meets the requirements of stability and inertness, and has a relatively low thermal conductivity perpendicular to the crucible. However it is limited in thickness to about 1mm and hence it is difficult to get high values of vl to prevent back diffusion. Hot pressed boron nitride has a higher thermal conductivity, but is readily available in large blocks and cylinders and can easily be machined.

To evaluate the crucible's ability to establish steep thermal gradients we use the thermal resistance = t/k, where k is the thermal conductivity and t the wall thickness.
Schematic cross sections of three types of crucible are shown in Figure 8, together with values of t/k and vl.

The simple PBN crucible used in Phase 1 served to demonstrate the principle of the technique, but due to the low value of vl, back diffusion of indium prevented the growth of material of uniform composition. In addition the InAs melt tended to stay at the bottom of the crucible and not mix with the rest of the charge. This was shown by the recovery of buttons of almost pure InAs from the crucible at the end of the run.

The Phase 2/Type 1 crucible made of hot pressed BN(Advanced Ceramics Corp. Grade HBC) has a 4mm diameter by 5 cm long capillary to increase vl. Due to the higher conductivity of HPBN compared with PBN, the t/k value is lower. We found that the limiting compositions which could be used with this crucible was 31 mol% inner/ 5 mol% outer which should , of course yield 5 mol% crystals. When we attempted to grow 6 mol% crystals from a 41.5 mol% inner charge, the material in the outer crucible froze before the temperature in the inner crucible was low enough for seed on. We were unable to sustain the necessary 71^{o}C temperature difference.
Since the lowest composition of interest to device manufacturers was 6 mol%, it was important to design a crucible with higher t/k.

The phase 2/Type 2 crucible in use at the termination of the work showed several important advances.

(1) Both vl and t/k were significantly larger
(2) The shape enabled us to pull a higher proportion of the charge,
(3) It is fitted with a shutter mechanism

Initial runs, carried out with this crucible before funds ran out, indicated that with experience its use would have enabled us to grow crystals in the 6-11 mol% range which is currently of most interest.

2. Growth Results

2.1.Phase 1

Nine crystals were grown in Phase 1. A full account of this work is given in the Phase 2 proposal. The main achievements of this stage were as follows:-

(1) A durable double crucible system was constructed, well able to survive protracted growth runs of over 100 hours.
(2) Double crucible action had been demonstrated although uniformity was poor due to back diffusion.
(3) Crystals with single regions of 40-50 mm diameter, lengthds greater than 12 cm, and weights greater than 500 gm were grown. The maximum InAs content was 1.8 mol%.

2.2. Phase 2

2.2.1.Normal freezing

In order to obtain seeds for use in the DCLEC process some crystals were grown by normal freezing. For this we used the Spectrum Technology GAMMA process. This process, described in the Appendix to the Phase 2 proposal, was developed to improve the yield and uniformity of semi-insulating GaAs. For example, Crystal # SBIR 2-5 was grown from a charge of 6 mol% InAs and yielded a completely single crystal of 53-58 mm diameter, weighing 1.92 kg. The composition of this crystal is illustrated in Figure 2-5, Fitting the normal freezing equation to this data yielded a value of k_{eff} between 0.14 and 0.176, which compares well with the value of 0.18 obtained for k_o from the phase diagram. This crystal was annealed and cut into seeds.

2.2.2.Growth from Type 1 crucible

This crucible was designed to reduce back diffusion. The vl value was 70 times greater than that of the Phase 1 crucible (Figure 8). The use of hot pressed boron nitride made it possible to machine the capillary, which was 3mm diameter by 50 mm long.

The reduction in the value of t/k was due to the higher thermal conductivity of HPBN vs PBN (0.034 vs 0.007 cal. $cm^{-1}sec^{-1}$.
Initial runs in this crucible suffered from the problem of cut off, as mentioned before. The cause was identified as accumulation of boric oxide in the exit of the capillary. This was cured by a combination of surface treatment of the HPBN and modifications to the geometry. With these changes it was found possible to pull almost all the charge(1900 gm from 2300 gm).
However, the ratio of the diameters of the inner and outer crucibles, 70 :140, meant that only about 850 gm could be pulled before the inner crucible 'bottomed'. After this the composition varied as the liquid level fell.

The composition in the inner crucible was set up as follows. After the charge was melted, the outer crucible was raised until melt flowed in through the capillary. Then a disc of InAs attached to the seed crystal was lowered into the melt, to give the desired InAs content. Growth was then started. Uniform crystals were not obtained, as shown , for example, by Runs SBIR 2-9, 2-11 in Table 3. Analysis of the data showed that the cause was not back diffusion, but more likely poor mixing between the original melt and the added InAs. There is probably very little convective mixing in the inner crucible, as the melt is shallow (1.5cm) and the temperature gradients low.
Attempts were made to stir the melt with GaAs paddles attached to the seed, but these were only partially successful.

2.2.3.Growth from Type II crucible

Simultaneously with the introduction of the Type II crucible we solved the mixing problem with the introduction of the pre-cast charges, as described in Section 1.4.5.

The final procedure was as follows :-

The pre-cast charge was loaded into the inner crucible, which was then placed in position in the puller, suspended above the main charge. When the boric oxide in the outer crucible was liquid, the outer crucible was raised, and when the charge was fully molten, the outer crucible was brought up so that the melt levels in both crucibles were aligned.
In Runs 2-15, 2-16, and 2-18, it was assumed the temperature gradients in the system would allow the outer crucible to be moved into position before the inner charge melted. However, the composition results given in Table 3 suggest that some of the inner charge melted and ran out and was then replaced by 5 or 6 mol% material. It also seems likely that when the melt flows in, some stratification occurs, with the less dense material from the outer crucible rising to the top.

To avoid loss of melt from the inner crucible, it was fitted with a 'shutter'. This shutter separates the inner and outer crucibles and is kept closed until both charges are fully molten and the liquid levels are aligned. The shutter is then opened and growth proceeds. Initial trials of this system were in progress when the work was terminated.

3.Achievements in Phase 2

Established the GAMMA-DCLEC process, including:-

(1) Determining conditions for the flow of non-wetting liquids through capillaries, and applying this to HPBN crucibles to achieve stable flow of InGaAs melts without interference from boric oxide encapsulants.
(2) Use of supercooled melts to obtain fine grained, uniform composition pre-cast charges.
(3)Development of crucible 'shutter' which operates at high temperatures.
(40 Growth of $In_xGa_{1-x}As$ with x values up to 0.035.

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Ron Puechner - graduate student
Mark Morris - graduate student.

Mark Morris obtained his Master's degree based on the work he carried out on this project.

6.Report of Inventions

(1) Method of controlling wetting and flow of boric oxide in contact with boron nitride.

(2) Design of inner crucible for Double Crucible Liquid Encapsulated Czochralski, incorporating a high temperature shutter.

7.List of Figures and Tables.

7.1.Figures.

7.2.Tables,

Table 3 Composition (InAs mole%) obtained from powder diffraction x-ray data.

Fraction pulled	SBIR 2-9	SBIR 2-11	SBIR 2-15	SBIR 2-16	SBIR 2-18
0.001	3.6	2.05	1.3	1.0	1.6
0.002				1.1	
0.01	3.9				
0.02		2.5	1.4		
0.05	2.0	2.15		1.2	
0.10		2.45			
0.12			1.6		
0.14				1.9	
0.16		3.3			
0.19			2.0		
0.23	2.2	3.4			
0.26				2.1	
0.29		3.5			
0.41				3.1	
0.46			2.2		3.4

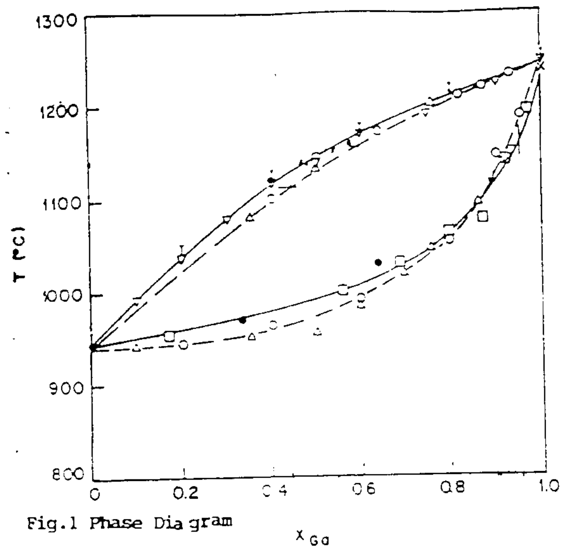


Fig.1 Phase Diagram

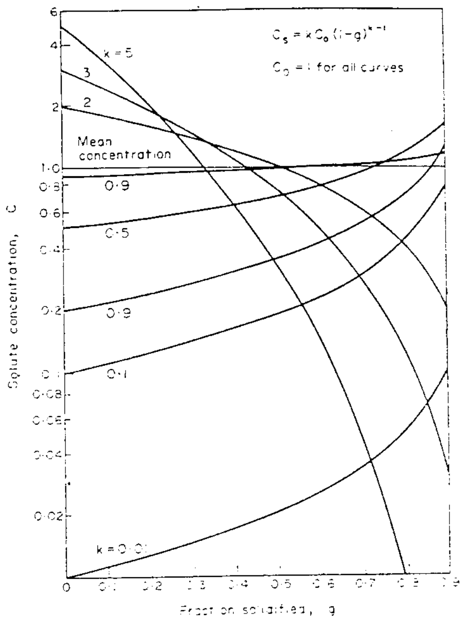


Figure 2 Normal Freezing

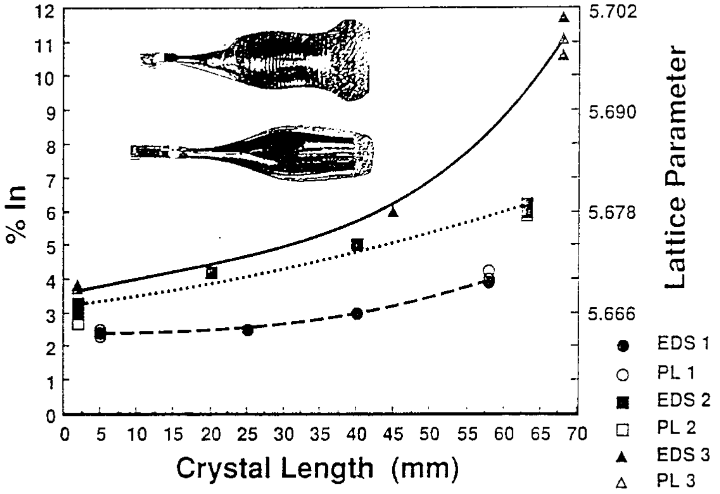


Figure 3 Indium Concentration vs Length (Bonner)

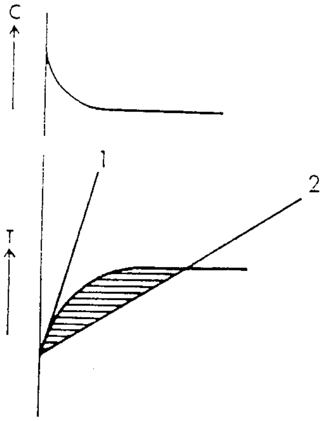


Fig.6 (top) Solute distribution in the melt for a solute with $k < 1$. (bottom) Possible actual temperature gradients in the melt: lines 1 and 2. Shaded area is a zone of constitutional supercooling which is present for the temperature distribution labelled 2.

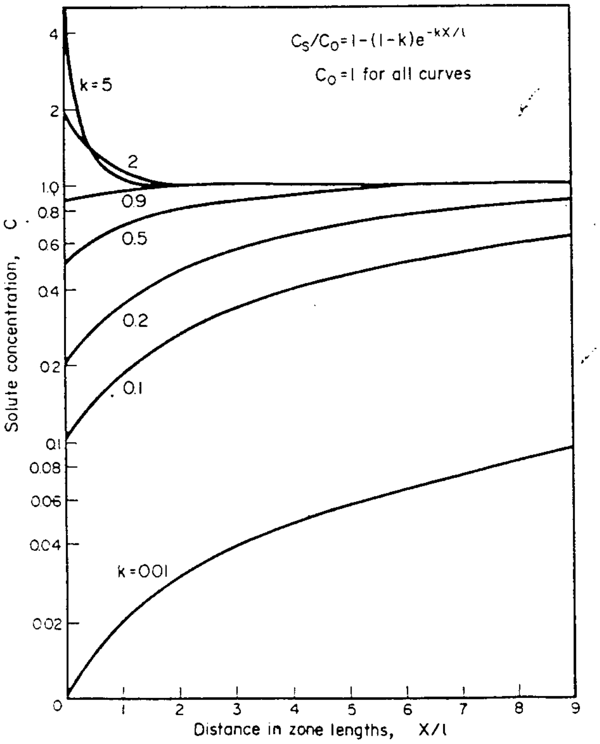


Figure 5

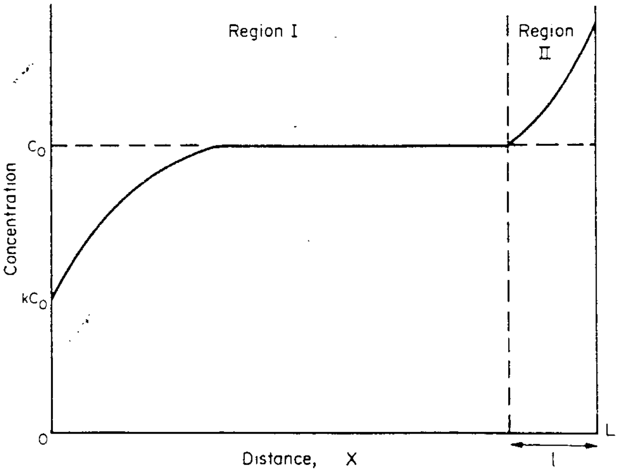


Figure 4

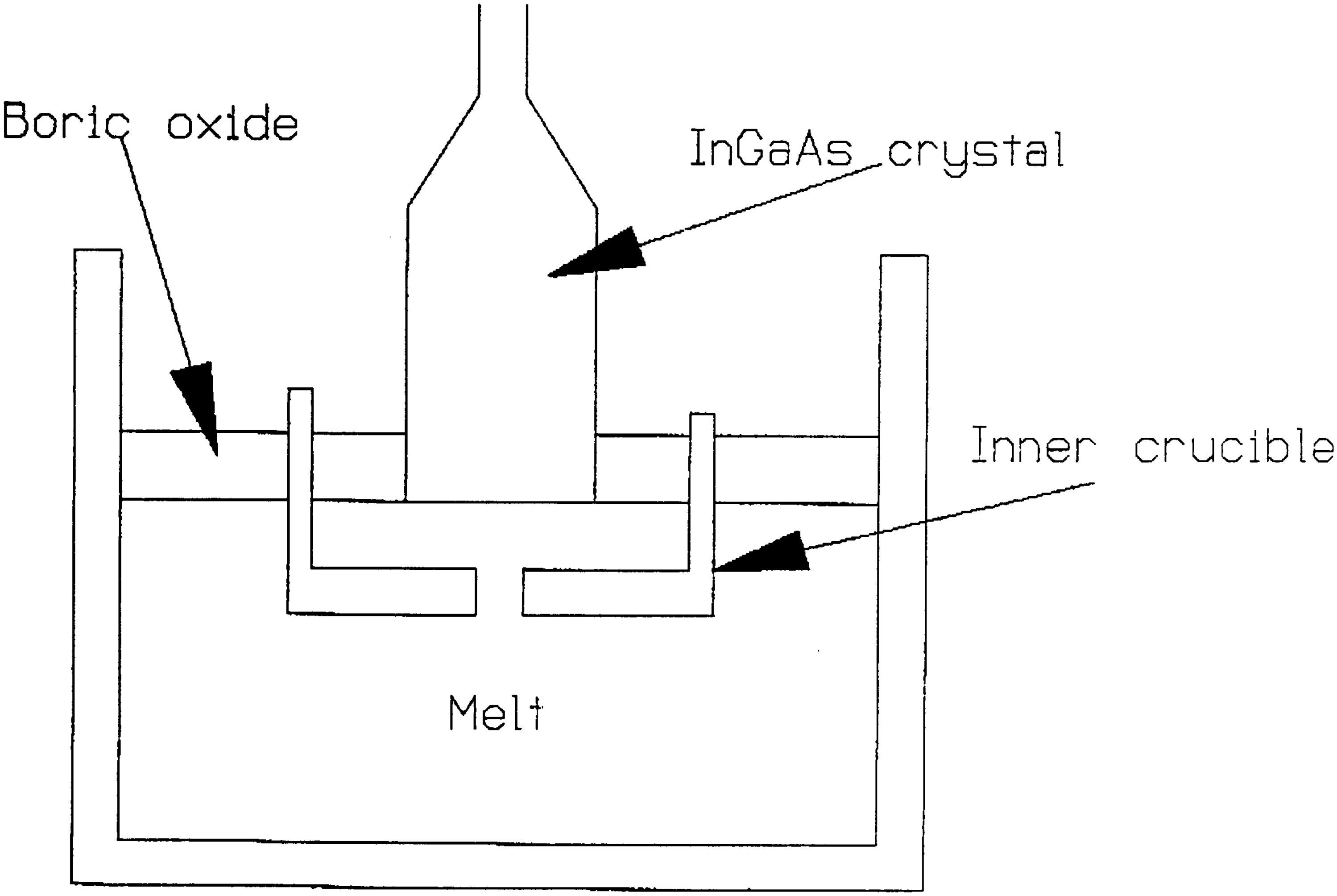
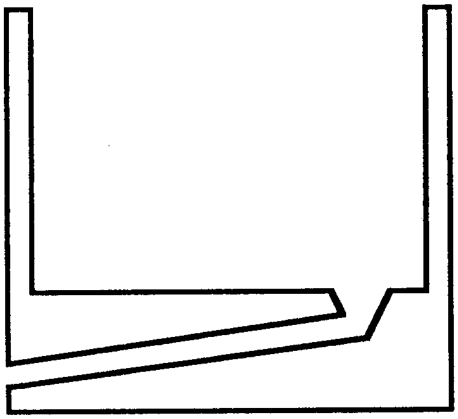
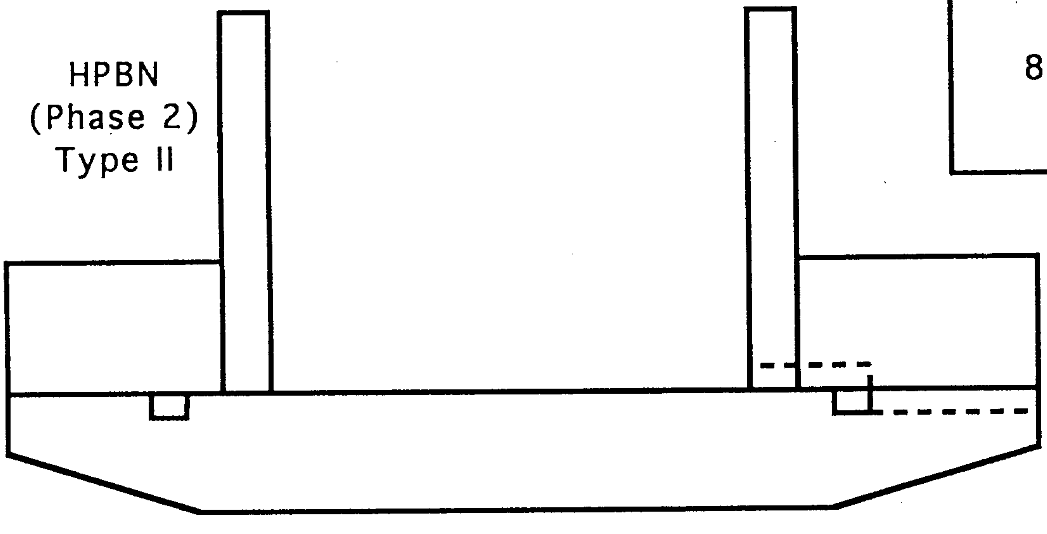


Figure 7 Double Crucible-schematic

Fig. 8 Cross sections of inner crucibles





	t/k $cm^2\ sec\ ^oC\ cal^{-1}$	vl $cm^2\ sec^{-1}$
PBN (Phase 1)	14	0.00007
HPBN (Phase 2) Type I	7.5	0.005
HPBN (Phase 2) Type II	81	0.25

Figure 9a Electron micrograph of residual melt.

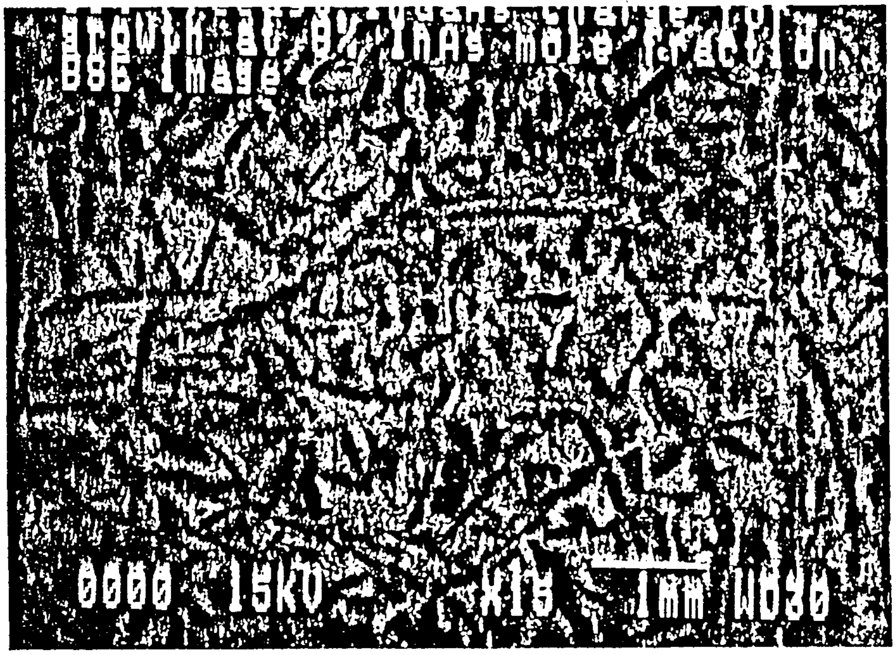
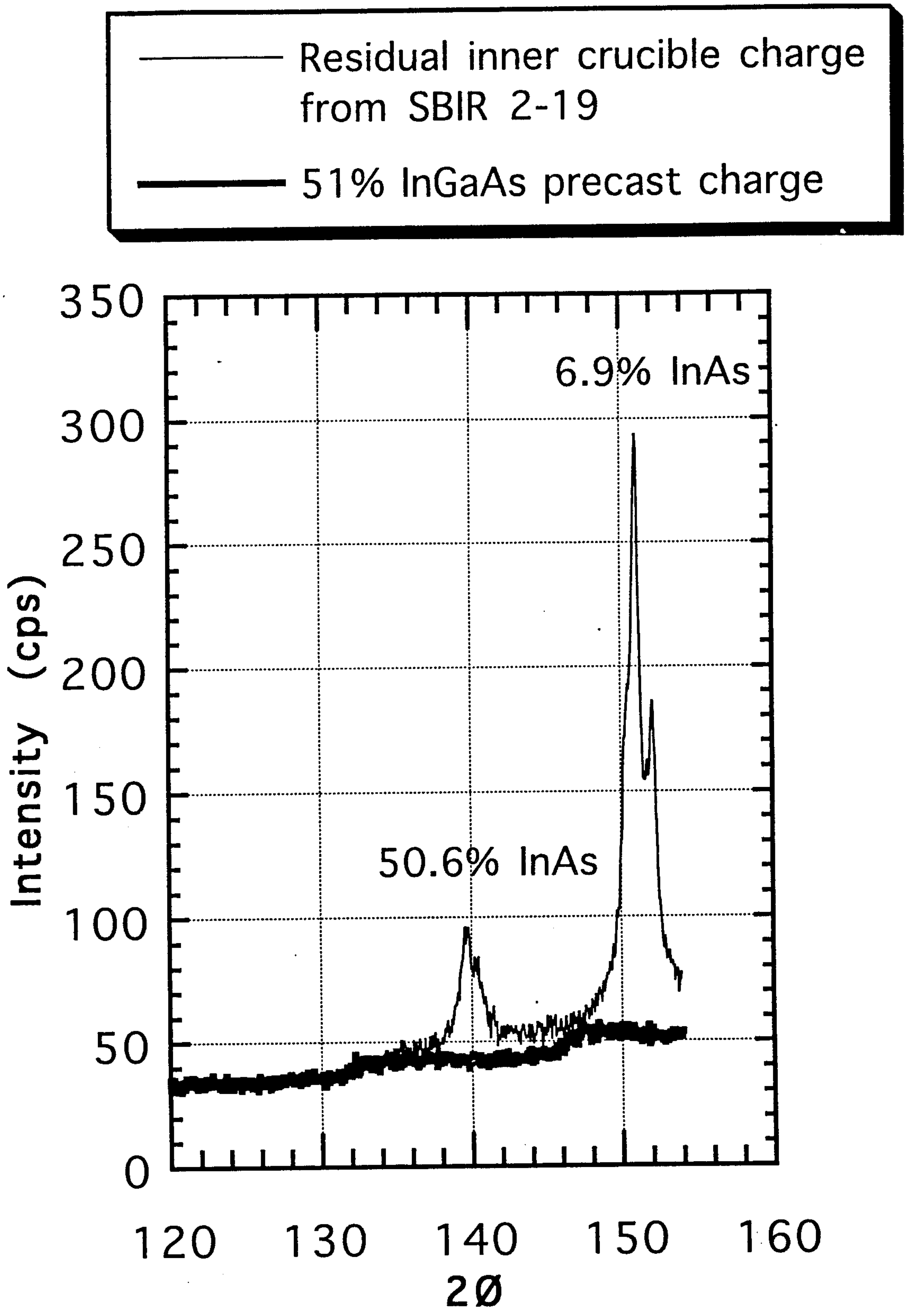


Figure 9b Electron micrograph of precast charge.

Figure 10 Powder Diffraction X-ray Spectra



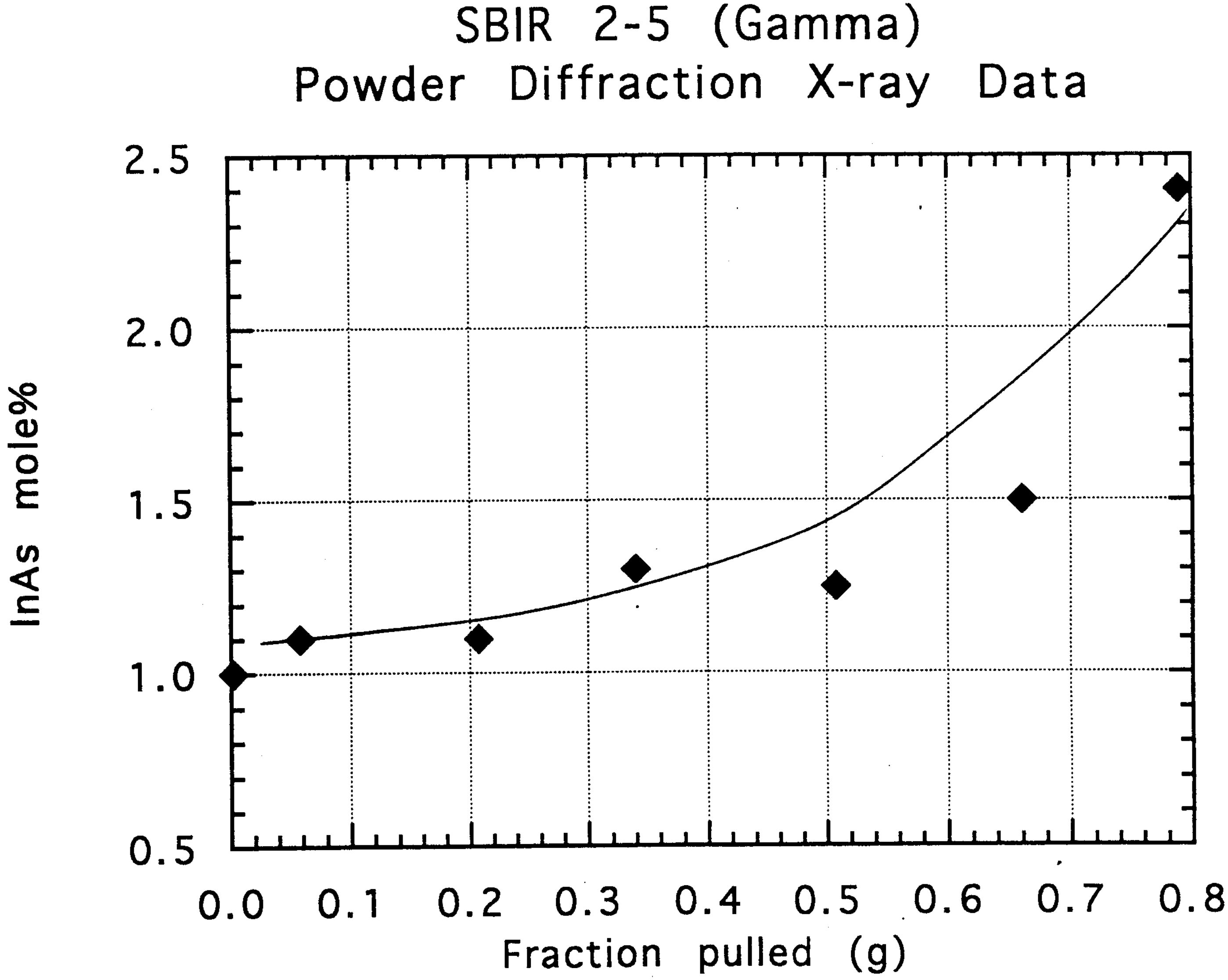

SBIR 2-5 (Gamma)
Powder Diffraction X-ray Data
InAs mole%
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Fraction pulled (g)

FIGURE 11