1.1 INTRODUCTION

Crystals are solids in their most ordered form. The ideal crystal is an infinite lattice of atoms arranged in patterns which repeat in all three dimensions with repeated distances (lattice spacings). Real crystals are finite and contain defects but nevertheless have long-range order, and it is this order (or in some cases more appropriately the lack of order) which gives crystals their unique properties (Brice 1986).

Crystal Growth is a process which involves the ordering of atoms into a crystalline lattice from a liquid/melt, vapour or solid phase. Of these processes, the growth from liquid phase has been widely employed. Nearly 85% of the crystals are grown from liquid/melt. Czochralski technique, Bridgman-Stockbarger technique, Kyropoulos technique, Zone melting technique and Verneuil technique are some of the techniques being adopted to grow crystals from the melt. Of these techniques, Czochralski (CZ) technique (named after the Polish Scientist Jan Czochralski who discovered the technique) most widely known as crystal pulling technique has evolved as a most important technique to grow tons and tons of crystals of semiconductor and oxide every year.

Czochralski technique developed in 1916 was initially used to measure the crystallization rates of metals. The method was developed as the result of accident and through Czochralski's careful observations. When he was writing notes on a crystallization
study, lost in thoughts, instead of dipping his pen in the inkpot, he dipped it in the crucible containing molten tin and withdrew it quickly. He observed then a thin thread of solidified metal hanging at the tip of the nib. The nib slot, in which crystallization was initiated, was replaced by a special narrow capillary and in some cases by a seed of the growing crystal. Czochralski checked later that the crystallized wire was a single crystal. The discovery was published (Czochralski 1918) with the diagram of the apparatus shown in Figure 1.1. The increasing demand for the electronic materials in 1950 led the Americans G.K. Teal and J.B. Little from Bell Telephone Laboratories to rediscover and widely apply this growth method, giving it world-wide fame as the Czochralski technique for growing large single crystals on an industrial scale. At present, no other crystal growth technique can compete with the Czochralski technique. Many variations of this technique exist throughout the literature, however the basic process remains the same as schematically shown in the Figure 1.2.

1.2 THE TECHNIQUE

The material to be "grown" is placed in a suitable container or crucible. The crucible is then heated either by resistance or induction heating methods until the charge is melted. The temperature of the molten charge is then adjusted so that the centre of the liquid is at its freezing point. A seed crystal is dipped into the liquid and the crystal growth or "pulling" process begins by slowly withdrawing the seed. With proper temperature control of the liquid, crystallization on the seed crystal can be started as the seed is withdrawn from the liquid. Further adjustments of the liquid temperature during the pulling process provide control of the diameter. When the desired crystal length is reached, the crystal is quickly raised from the liquid surface or the liquid temperature is slowly increased to reduce the diameter. When the crystal is free from the liquid, the temperature is lowered to room temperature and the crystal is withdrawn from the growth apparatus.
Figure 1.1 Original apparatus developed by Czochralski
Figure 1.2 Schematic representation of the CZ crystal growth process
1.3 MATERIALS REQUIREMENTS

The material to be crystallized must fulfill the following essential requirements

(i) It should melt congruently, i.e. it should not decompose upon or before melting
(ii) The material should possess relatively low vapour pressure
(iii) It should not have any first order solid-solid phase transitions or reconstructive phase transitions
(iv) There should not be any reaction between the container and the material at and above the melting point.

Although a variety of materials including, semiconductors, oxides, halides, etc. can be crystallized by Czochralski technique, there are certain distinct complexities involved in the growth of oxide crystals which do not occur or which are uncommon in the growth of other materials.

1.4 COMPLEXITIES ASSOCIATED WITH THE OXIDE CRYSTAL GROWTH

Successful growth of oxide crystals using Czochralski geometry depends upon
1. a detailed understanding of the material system and the phase relationships in the region of interest, 2. the interaction of the heating system with the molten oxide-crucible system, 3. the role of fluid dynamics in establishing the thermal environment and fluid flow patterns of the liquid, and 4. the limitations imposed on the growth process by CZ geometry (Brandle 1985).

The dominant problems associated with the high temperatures involved in oxide single crystal growth are how to heat the material to its melting point, how to contain the melt and what sort of ambient atmosphere to employ. In oxide Czochralski growth, the most common practice is to use high frequency heating in conjunction with a crucible susceptor. The geometry of heat shielding assembly to contain the heat and achievement of
the required temperature gradient are quite tricky. Unlike semiconductor growth, the crucible remains stationary during growth, therefore the effect of liquid level drop on the actual growth rate of the crystal must be considered. The crystal/crucible diameter and the crucible height/diameter ratios are also crucial parameters to avoid thermal oscillations in the melt and growth fluctuations.

The growth of oxide crystals, with few exceptions, usually involved the growth from multi-component systems, i.e. molten liquids containing two or more simple oxides. Thus, there is an additional variable which can influence the quality of the crystal and its properties, that of stoichiometry. Many oxide crystals are solid solutions and as such exhibit all of the problems associated with solid solution growth, such as variation of dopant concentration both radially and lengthwise, growth striations, interface breakdown, and second phase formation. For many of the more complex oxides, the congruent melting composition is not the stoichiometric one for example LiNbO₃ and LiTaO₃ (Miyazawa and Iwasaki 1971). The loss of one of the constituent oxides can result in a serious shift in the melt composition during growth. Examples are Bi₂TeO₅ (Kumaragurubaran et al 1999; 2000a) and PbMoO₄ (Zeng et al 1994).

The growth atmosphere also plays an important role in the growth of oxide crystals. For many oxides, such as Sapphire, Gadolinium Gallium Garnet (GGG) and Yttrium Aluminum Garnet (YAG), the melting point is sufficiently high and hence platinum crucibles cannot be used to contain the melt. For these materials, the only choice is iridium which requires a less oxidizing atmosphere than platinum. A compromise must then be achieved between iridium oxidation and melt stability. For example, growth of (GGG) in neutral atmosphere (N₂) results in the formation of a second phase in the liquid (Brandle et al 1972). An addition of 2% O₂ to the atmosphere results in the elimination of this second phase and aids in the growth of high-quality crystals. Even for the more stable oxides such as sapphire and YAG the addition of O₂ in the parts per million range can have a dramatic effect on the crystal quality and melt rheology (Brandle 1985). For many low melting oxide crystals, where usage of platinum crucible is possible, the percentage of oxygen content in
the growth atmosphere can have a dramatic effect on the optical quality and colour of the resulting crystal. Hence, the oxide crystals are generally annealed in an oxygen atmosphere after the growth process to bleach the colouration and improve the transparency.

The melt dynamics in the crucible has an enormous influence on the quality of the resulting crystal. The liquid flow in the crucible, to be discussed in the next section, will establish the shape of the growth interface, the degree of growth striations, the thermal profile in the liquid and the radial dopant uniformity. Unlike semiconductors, the oxides have very high viscosity, density and low thermal diffusivity. Because of this, the problems like bubbles incorporation into the crystal, constitutional supercooling, interface instability etc. arise which are detrimental to the crystal quality. The main flows in the Czochralski environment are discussed below.

1.4.1 Fluid flows in the melt

The three main sources of flow are 1. buoyancy-driven convection caused by solute and temperature dependence of the density, 2. surface-tension gradients along melt / fluid menisci and 3. forced convection introduced by the motion of solid surfaces such as crucible and crystal rotation. Figure 1.3a represents all these flows and the regions in which they are effective in the CZ geometry. As far as the Czochralski growth of oxides is concerned, the flow due to surface-tension gradients is less effective and is generally ignored in the ground experiments. On the other hand, it is more effective and plays a dominant role when the experiment is conducted in reduced gravity (microgravity) where the convective flow is less dominant due to low value of the gravity. Also, the rotation of crucible is uncommon in oxide crystal growth, and therefore the flow due to crucible rotation does not come into picture. Hence, the two major flows that influence the growth are the natural convective flow and the forced convective flow due to crystal rotation.
Figure 1.3 (a) Various flows associated in the CZ crystal growth process
(b) Convex interface resulting from natural convective flow
(c) Concave interface resulting from forced convective flow
1.4.1.1 Natural convective flow

In Czochralski arrangement, the crucible is heated from sideways and the fluid adjacent to the crucible wall will have higher temperature and therefore low density. Thus the hot layer of liquid adjacent to the vertical crucible wall rises entraining fluid which, in the absence of crystal and crucible rotation, is carried around in a toroidal motion giving rise to a single doughnut circulation. The fluid descends beneath the axis of the crystal (Battaro and Zebib 1989). Since the driving force for this fluid motion is the temperature gradient prevailing in the melt, it is called natural convective flow or free convective flow. This type of flow is also called as buoyancy-driven convective flow. Since the flow is from the wall to the centre, in the real growth experiments, it results in the convex shape of the crystal-melt interface toward the melt as illustrated in Figure 1.3b.

The magnitude of this flow is expressed by a dimensionless number called Grashof number, defined as the ratio between the buoyancy force to the viscous force and mathematically expressed as

$$G_r = \frac{g \beta \Delta T D^3}{\nu^2}$$

where, $g$ is the acceleration due to gravity, $\beta$ is the bulk expansion coefficient, $D$ is the diameter of the crucible, $\nu$ is the kinematic viscosity and $\Delta T$ is the temperature gradient between the crucible and crystal.

1.4.1.2 Forced convective flow due to crystal rotation

The rotating crystal in contact with the melt acts like a centrifugal fan, drawing in fluid axially imparting angular momentum to it within the thin layer adjacent to the crystal and expelling it tangentially. The flow direction in this case is just opposite to the case of free convective flow. Since the flow is imparted into the fluid due to the crystal rotation it is called forced convection. The convection becomes stronger, when the crystal rotation rate is high. At higher rotation rates, the forced convection is stronger and a stream of hot
liquid strikes the centre of the interface melting it and thus making the shape of the interface concave which is schematically shown in Figure 1.3c. The magnitude of the forced convection is expressed by the Reynolds number and is the ratio between the convective momentum transport and diffusive momentum transport i.e.

\[ R_e = \frac{\omega d^2}{\nu} \]

where, \( \omega \) is the crystal rotation rate employed, \( \nu \) is the kinematic viscosity and \( d \) is the diameter of the crystal.

In the absence of crystal rotation, only the natural convection is predominant and the interface shape is convex with respect to the melt. When the crystal is rotated, the forced convection becomes effective and dominant at higher rotation rates and the interface shape is concave with respect to the melt. When the magnitude of these two forces are perfectly matched, a flat interface is achieved. In real crystal growth experiments, achieving a flat interface throughout the crystal growth process is generally preferred and is tricky and difficult.

It is obvious from the expressions for forced convection and free convection that these flows mainly depend on the viscosity of the melt. Hence viscosity of the melt plays a key role in the growth of crystals. The high viscous oxide melt has very low growth rates hence the pulling rates generally employed are of the order of 0.5 - 3 mm/h (at times less than 0.5 mm/h). This range is very much lower than the pulling rates generally employed for the growth of semiconductor materials which are less viscous in nature.

In addition to the above material parameters that need to be considered before growth, there are certain unique design considerations of the instrument, which need to be addressed, for the growth of oxide crystals. As discussed earlier, except a few, all the oxide materials, in general, have higher melting points. Hence, the design of any oxide crystal growth system must have a heating system capable of melting the oxide charge in preferred atmospheres and a precise mechanism for seed rotation and pull (of the order of less than
1 mm/h). The details of construction of oxide crystal growth facility, which is used in the present study, are discussed in the next section.

1.5 DEVELOPMENT OF CRYSTAL GROWTH FACILITY

Good crystals are grown in good equipment in a selective good environment. The design of good equipment needs consideration for creating and controlling the environment in which a crystal with desired properties can grow. Specifications of environment require specifications of temperature, atmosphere, container materials, parameters which control growth velocities, and growth instabilities. Hence the essential parts of an oxide crystal growth system are

(i) a good heat source with provisions for the control and manipulation of parameters of the power that is supplied to melt the charge
(ii) an insulating arrangement to contain the heat radiation
(iii) an accurate mechanism for rotation and pulling of the crystal
(iv) a provision to conduct the experiment in a preferred atmosphere

The whole system must rest on a vibration free platform to isolate the system from external vibrations that may disturb the interface stability during growth. An automatic diameter control unit, mass flow controller to control the gas flow, a charge coupled device camera with closed loop television monitoring systems are some of the optional parts. The essential parts of the crystal growth system are discussed below.

1.5.1 Heat sources

Although various methods of heating with different kinds of power sources have been developed for commercial practice, only two common heating sources are being used for the growth of oxide crystals. They are resistance heating and induction heating methods.
1.5.1.1 Resistance heating furnace

Resistance heated furnaces are usually limited to the lower temperature ranges and can have one of several types of elements which are listed in the Table 1.1. The main design parameters of this type of furnace elements are resistivity, temperature coefficient of resistivity, current carrying capacity, maximum and operating surface temperatures and surface emissivity, and the operating atmospheric conditions for a long life. Because of temperature and ambient gas limitations, resistance heating usually finds use in the growth of low melting oxides like LiNbO₃, TeO₂, Bi₁₂(Si,Ge)O₂₀, Pb(W,Mo)O₄ and Bi₂TeO₅. Higher temperature requires either special elements such as platinum-rhodium alloys or a hard vacuum operation to protect refractory metal elements from oxidation. The advantage of resistance heated furnaces over other types is greater electrical efficiency and therefore reduced operation costs. Moreover the power input into the furnace, and therefore the temperature control of the furnace, can be easily accomplished without the need for elaborate control equipment.

Table 1.1

<table>
<thead>
<tr>
<th>No.</th>
<th>Material</th>
<th>Useful Temperature (°C)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kanthal A-1</td>
<td>≤ 1200</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>(22% Cr, 5.5% Al, 72.5% Co+Fe)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nichrome</td>
<td>≤ 1200</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>(80% Ni, 20% Cr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Kanthal super</td>
<td>≤ 1500</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>(MoSi₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Globar</td>
<td>≤ 1500</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>(SiC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Pt50%-Rh</td>
<td>≤ 1800</td>
<td>Air</td>
</tr>
<tr>
<td>6</td>
<td>Molybdenum</td>
<td>≤ 2400</td>
<td>Vacuum, neutral, or reducing</td>
</tr>
<tr>
<td>7</td>
<td>Carbon</td>
<td>≤ 3000</td>
<td>Neutral, reducing</td>
</tr>
<tr>
<td>8</td>
<td>Tungsten</td>
<td>≤ 3000</td>
<td>Vacuum, neutral, or reducing</td>
</tr>
</tbody>
</table>
Unlike direct Joule heating phenomenon which finds application in molten zone crystal growth process, the indirect electrical heating furnaces are widely used in Czochralski pulling process of growing crystals. In most designs the windings of a suitable metal or wire or a ribbon are incorporated either on the exterior surface, of the refractory shape, such as a muffle or a tube, or in contact with the interior surface of the refractory. To avoid short-circuiting of the turns of the windings at an operating temperature each turn is placed in a groove or a slot on the refractory. Alternatively, each turn is separated by protrusions or "pips" on the refractory surface and/or embedding the windings in a refractory cement. Care must be exercised to ensure that the windings are not subjected to undue mechanical strains as often the metallic heating elements become brittle on continuous usage, due to oxidation and/or recrystallization.

In the present investigation, an indirect type of furnace construction was made to grow the crystal at various temperature gradients (10 - 30°C/cm). The sketch of the furnace configuration is illustrated in the Figure 1.4a. A-1 kanthal wire of SWG 18 was used as heating element. Before the process of winding, the wire was heated to red hot to remove any bend in the wire and also to make the wire flexible to wind. The wire was wound over an alumina tube of 30 cm length, inner diameter of 6 cm and wall thickness of 3.5 mm. The windings were made in such a way that the space between the windings gradually becomes narrow at the ends of the tube compared to the space at centre of the tube to compensate the heat losses at the ends of the tube to a certain extent. The windings were insulated by applying a paste of corundum cement and silica gel mixture and fired at 600°C. The tube is then packed inside a stainless steel container using zirconia grade fibre blanket of density 128 kg/m³. The ceramic wool serves two purposes; it acts as a heat shield and aids in the vertical positioning of the tube. Bubble alumina bricks were cut in the form of discs of 5.5 cm diameter and 1 cm thick and arranged inside the muffle to place the crucible inside the tube. The crucible can be placed at a desired height inside the furnace by just adding or removing the bricks. At the center of each brick, a hole of 0.7 cm diameter was made so that the thermocouple can be placed just beneath the crucible bottom. The required temperature gradient was achieved either by altering the position of the crucible or by
Figure 1.4a Sketch of the resistive heated furnace

Figure 1.4b Temperature profile at 960°C
altering the space between the windings. The temperature profile of the furnace at 960°C is shown in figure 1.4b.

1.5.1.2 Induction heating furnace

The second type of heating source is high frequency induction heating. This type of heating method is of major importance in oxide crystal growth process because it can achieve, easily, a large range of temperature with a reasonably high efficiency of energy transfer and is capable of operating in a variety of process ambients and can, in principle, make the crystal growth process free of contamination. It is also versatile for direct and indirect heating (Shah 1980).

Heating of a material by induction method relies on the induction of eddy currents (Foucault currents) into the material. The induction of eddy currents mostly occurs in conducting medium by an electromagnetic field of high frequency current carrying coil. The density and distribution of eddy currents depend on the frequency, conductivity of the material and distance between the conductor and the coil. At higher frequencies, the impedance at the centre of the conductor is high due to higher flux density. Thus the current density in the central core is negligible and most of the current flows in a thin layer at the periphery of the conductor. The strength of the current decreases exponentially inside the conducting media. The same is mathematically expressed as

\[ I(r) = I_0 \exp\left(-\frac{r}{\delta}\right) \]

where \( I(r) \) is the current density at the depth \( r \) below the surface of the conductor, \( I_0 \) is the current density at the surface, and \( \delta \) is a parameter called skin depth and is defined as depth inside the conductor at which the current value diminishes by \( 1/e \) (37%) of the surface value. The same can be calculated from the expression

\[ \delta = \frac{1}{2\pi} \left( \frac{\rho_r x10^1}{\nu \mu} \right)^{1/2} \]

where, \( \rho_r \) is the resistivity of the conductor, \( \mu \) is the relative permeability of the material and \( \nu \) is the frequency. It is obvious from the above expression that the skin depth and
frequency are inversely proportional to each other. Hence low frequency operation will lead to much penetration of the current in the conductor. At higher frequencies, the current flow will be more limited to the surface of the conductor.

The choice of the frequency of the generator for crystal growth process depends upon the degree of penetration required and the efficiency of the power transfer. The medium frequency operation (10 - 100 kHz) offers a great depth of penetration and thus larger volume in which heat is generated. Also at high frequencies the power losses via lead connections, etc. is a very serious matter of concern. A proper impedance matching is required between the coil and the load for an efficient power coupling. The resistance of the coil at resonance is given by

\[ R_{(r)} = \frac{530Q}{Cv_0} \]

where \( v_0 \) is the resonant frequency and is expressed as

\[ v_0 = \frac{1}{2\pi\sqrt{LC}} \]

Here \( Q \) is the quality factor which is the ratio of the reactance to resistance of the circuit, \( C \) is the circuit capacitance and \( L \) is the inductance in the tuned resonant circuit.

Now-a-days medium frequency solid state generators are available which are more accurate and versatile compared to the conventional tube generators. In the present investigation, the induction heating unit which was designed is an all solid state 40 kW dual frequency system; the system can operate either at 25 kHz or at 10 kHz depending upon the requirement (quantity of the charge and the physiochemical nature of the material to be melted). The unit is basically a current source inverter and the essential parts of the unit are the power supply, tank circuit (tank capacitors and work coil in parallel combination), cooling tower and heat exchanger. The power supply is integrated with an array of tank capacitors with taps. The capacitor values can be altered just by tightening the nuts so that a variety of capacitance values can be chosen for load tuning either by series or parallel combinations of capacitors. The work coil was made from 0.25" electrode grade copper
tube. Two separate coils with different number turns were fabricated. The number of turns in one coil was made to three and in the other coil it was five to induce current in a crucible of 5 cm in diameter and 5 cm in height. The turns in the coil were insulated by fibreglass tape wound on the surface of the tube. The coils are shown in Figure 1.5.

The capacitors and the work coil are cooled by deionized water during operation. The specifications of the water used were: pH approximately 7.25, the solid contents less than 200 ppm and the resistivity more than 2,500 ohm-cm at 25°C. The hot deionized water from the coil was cooled by raw water through a heat exchanger. This water-to-water heat exchanger is satisfactory where adequate cooling of raw water is available. In this case, the raw water was made to fall as a stream, through a corrugated mesh, was cooled by a fan. Two motors of 5 hp power each were used to pump the raw as well as the deionized water for circulation. The connections to the heat exchangers and to the cooling tower were made from non-ferrous pipes. The water pressure and temperature both at the inlet and outlet were monitored continuously.

In the power supply, the principal sections are power section, control section and display section

1.5.1.2a Power section

The basic components in the power section are
(i) Circuit breaker - turning off the breaker removes all high voltage from the system
(ii) Input main transformer - is a three-phase auto transformer which reduces the 415 V input voltage to 330 V and the lower voltage taps provided may also be chosen if needed.
(iii) Rectifier - to convert the input AC to DC voltage
(iv) DC reactor - is fundamentally a choke and it acts as a constant current source
(v) Inverter assembly - whose output is connected to tank circuit
Figure 1.5 Heating coils
In addition, many line fuses are provided as back-up protection against any kind of control circuit failure. The basic block diagram of the power supply is illustrated in the Figure 1.6.

1.5.1.2b Operating principle

The power supply is a commonly used current source inverter. The three-phase AC input voltage is converted to a single-phase DC voltage using six phase angle fired silicon controlled rectifiers. A reactor (inductor) in the DC circuit enables it to produce a filtered current into the inverter. This constant current is fed into the parallel tuned tank circuit from either direction to produce a sinusoidal voltage across it. This voltage produces a square wave of current in the work coil resulting in induction heating of the part within the work coil. As the charge inside coil heats, the control circuit tracks the resonant frequency of the circuit. Power regulation is achieved by varying the DC voltage input to the inverter. For a given load, the DC current, inverter output voltage and the output power are directly dependent upon the DC voltage. The specialty of the unit is the incorporation of Integrated Gate Bipolar junction Transistor (IGBT) which has very fast switching action compared to the conventional valves and high power transistors.

1.5.1.2c Control section

The control section consists of various safety and regulating devices in the form of boards named after their operation.

(i) Feedback board: This receives voltage and current signals and adjusts the output to changing load conditions.

(ii) Main control board: Controlling of the output frequency, all limits, all electronic trip settings, calibration of control meter and associated logic circuitry are looked after by this board.
Figure 1.6 Block diagram of power supply
(iii) Gate Driver / Trigger Board: There are four gate driver circuit boards and one gate trigger circuit board associated with the unit. The driver boards interface the main control board with each of four inverter IGBTs and the trigger board interfaces the main control board with the rectifier (Silicon Controlled Rectifiers).

(iv) Relay board. The relays on its function will isolate the control, the interlocks, water trips, start / reset / stop functions, local / remote functions and manual / auto control.

In addition, the temperature trip will occur when the deionized water temperature in the inlet and outlet exceeds more than 42°C and 65°C respectively and when the pressure is more than 30 PSI at the inlet, the water pressure trip will be enabled.

1.5.1.2d Display section

All the control boards are connected to a diagnostic display of LED which indicate the sequence of operation and failure in any of the operations like high frequency trip, low frequency trip, inverter trip, high value of current across IGBT, water trip due to high or low values, temperature trip, etc. for easy identification of the problem that has occurred. Also there are three analog meters for the indication of the resonance frequency and power and voltage that are being delivered. All the meters are 0-160% deflections and can be calibrated to the required rated power and frequency.

1.5.1.3 Installation of heating unit and interfacing with UPS

The Uninterruptible Power Supply (UPS) is a solid state 60 kVA system which can back-up for about 30 minutes at full rated power. The back up was provided by a series connection of 64 Sealed Maintenance Free (SMF) 12V batteries.

While interfacing the power line to the heating system and installation, the following points were considered.
(i) **Distance from the UPS:** The incoming power line length was kept to a minimum since there is an economic and power advantage. In general there will be less line drop if the 50/60 Hz lines are within a 200 ft. run per phase. However, large kVA sources (i.e. 10X requirement) at short distances to the supply will present a low source impedance to the supply causing an increase in surge current

(ii) **Distance from the load:** The distance between the load and power supply was made as short as possible to minimize the power loss through the leads. Long distance will increase inductance and cause power loss

While interfacing with the UPS, the three-phase output from the UPS was properly phased to the input of the heating unit. To assist in determining proper phasing, a phase sensing circuit incorporated on the feedback board was used. The connections from the UPS were made by 100 A cable through an isolator in such a way that the power loss in the line and the noise reflected are minimized.

### 1.5.1.4 Interfacing of the heating unit with power controller

Although the power delivered can be controlled by an in-built potentiometer available in the unit to an accuracy of ± 0.1% of the power, in real growth experiments, such a manual control is not advisable. As most of the oxide crystals are anisotropic in nature having very high melting temperature, they cannot accommodate such a varying thermal environment and will crack. Hence it is essential to have power controller which controls the power in a preferred rate. The controller which was integrated with the system was from Eurotherm U.K. (Model 902) which can take the input in the form of voltage ranging from -10 to + 100 mV or -1 to 10 V and current 0 - 20 mA or 4 - 20 mA. The sampling period of the controller is 125 milliseconds and linearity error and calibration error are respectively better than ± 0.1% and ± 0.25% of input span. Easy operation, flexibility, accuracy and adaptability are the feature of this instrument. A feedback line from the tank circuit was fed as input to the controller and accordingly the power delivered to the work coil is controlled to an accuracy of ± 0.01% of power in a preferred...
heating/cooling cycle. However, the control accuracy and hence the temperature stability largely depends on the heat shielding arrangement that is being employed.

### 1.5.2 Insulation arrangement

In the Czochralski growth of oxide crystals employing induction heating method, the refractory insulation arrangement deserves a careful attention to achieve the required temperature gradient and also to minimize heat loss and thus low power consumption. A variety of materials with tailored properties are available commercially. Beryllia (BeO), Magnesia (MgO), Zirconia (ZrO₂), Thoria (ThO₂) and Alumina (Al₂O₃) are, to mention a few. The selection of these materials for crystal growth applications, mainly depends on the operating temperature, casting of these material to the required size and shape and cost. The thermal conductivity, linear expansion coefficient, thermal shock resistance and chemical inertness to its environments are also considered prior to the application. For commercial and laboratory research, insulation parts fabricated from alumina and/or zirconia based refractories are widely used for the growth of oxide crystals. The refractory parts made from magnesia are also seldom used due to its low cost.

The sketch of the insulation assembly designed is illustrated in Figure 1.7. The crucible is placed on top of discs arranged one over the other. Surrounding the crucible is the refractories segments arranged such that three such pieces combination forms a circular ring. Many such rings can be added one over the other till the required height is reached. Similarly the crucible position can also be altered. The zirconia based felt lining is provided inside as well as outside the rings arrangement. The gap between the crucible and the felt is filled with zirconia based single crystal grogs of particle sizes varying approximately from 0.6 to 2.35 mm. The crucible mouth is covered by a disc (two D shaped discs) with a big hole at the centre to facilitate the seed rod movement. Upon the discs, an after heater tube with a split and a hole of 1.5 x 1 sq. cm is provided to monitor the growth process. A metal (Pt or Ir) lining may be given inside the tube to grow the crystal under low temperature gradients. Another disc with hole at the centre covers the top of cylinder. The entire
Figure 1.7 Sketch of the insulation assembly configuration
arrangement is enclosed in a quartz / alumina tube. The samples of the zirconia blocks, felt, grogs are shown in Figure 1.8.

The zirconia based discs, ring segments and the tube were made from zirconia sintered and hot pressed and stabilized with 8 wt % of Y$_2$O$_3$ and contained less than 2% of HfO$_2$. The zirconia single crystal grogs produced by skull melting technique possessing monoclinic structure were used since they can withstand temperatures up to 2400°C. The filling up of the gap between the crucible and the ring arrangement is crucial because the irregular shaped grogs give a good packing and thereby a good uniform insulation (like low dense bulk insulation). Also these grogs can accommodate any dimensional variation due to thermal expansion of crucible or the refractory arrangement and hence protect the insulation assembly from cracking. To reduce the damage due to the thermal stress and thermal expansion coefficient the after heater tube is provided with a split. The same is the reason for the arrangement of rings (which are formed by three segments instead of one single ring). The temperature profile for various configurations of insulation assembly and crucible position with respect to the coil position has been studied by Brandle (1980).

1.5.3 Crucible material selection

The selection of the crucible material is based upon 1. compatibility with melt 2. melting point of the crucible material versus that of the compound to be grown, 3. type of heating, 4. chemical stability and 5. mechanical properties (Brandle 1980).

In the growth of oxide crystals, which generally possess higher melting temperature, crucible made from refractory metals or the noble metals are used. Some of the more commonly used materials are listed in Table 1.2 along with their useful range. The use of platinum, iridium, or in some special cases tungsten or molybdenum, provides the most reasonable compromise between chemical stability, ease of fabrication, and mechanical strength. Of the materials listed in Table 1.2, platinum is the only one that has to be operated far below its melting point because of large changes in its resistivity with
Figure 1.8 Samples of Zirconia (a) felt, (b) block and (c) grogs
temperature as one approaches its melting point. This causes localized "hot spots" to develop in the crucible wall that can result in crucible failure. The same localized "hot spots" may occur if the dimensions and surface finishing of the crucible are not uniform. The aspect ratio (height to diameter) of the crucible is normally maintained to be unity. The effect of crucible dimension on the convection has been examined by Carruthers (1976).

Table 1.2
Some of the commonly used crucible materials and maximum operating temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Maximum operating temperature (°C)</th>
<th>Melting point (°C)</th>
<th>Heating method</th>
<th>Permitted atmospheres</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>1400</td>
<td>1773</td>
<td>Resistance and High frequency</td>
<td>Oxidizing, Neutral</td>
</tr>
<tr>
<td>Iridium</td>
<td>2150</td>
<td>2452</td>
<td>Resistance and High frequency</td>
<td>Reducing, Neutral</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2300</td>
<td>2620</td>
<td>Resistance and High frequency</td>
<td>Reducing, Neutral</td>
</tr>
<tr>
<td>Tungsten</td>
<td>2800</td>
<td>3370</td>
<td>Resistance and High frequency</td>
<td>Reducing, Neutral</td>
</tr>
<tr>
<td>Graphite</td>
<td>3000</td>
<td>-</td>
<td>Resistance and High frequency</td>
<td>Reducing, Neutral</td>
</tr>
<tr>
<td>Silica</td>
<td>1550</td>
<td>1700</td>
<td>Resistance</td>
<td>Neutral</td>
</tr>
<tr>
<td>Alumina</td>
<td>1800</td>
<td>2050</td>
<td>Resistance</td>
<td>Oxidizing, Neutral</td>
</tr>
</tbody>
</table>

In the present investigation the platinum crucibles were used to contain the charge and the same crucible was cleaned and reused repeatedly.

Once the provision to melt the charge is developed, it is necessary to have an accurate mechanical and electronic arrangement to rotate and translate the seed to grow the crystal, the details of which are described below.
1.5.4 Rotation and translation assembly

The arrangement for simultaneous translation and rotation of seed is the heart of the crystal growth system, the operation of which should be very much precise to get crystals of very high quality. It requires two motors for each movement involved in this process. The control of such units must allow the movements as low as possible (of the order of few mm/h) to as high as it can (of the order of few hundred mm/h).

The instrument that was used for this study is shown in Figure 1.9. The arrangement has three cylindrical guide rods stem vertically on a base plate with 120° separation between them. There is another wedge shaped guide rod and a hardened and precision-ground linear slide assembly in which the translation head is mounted. Translation is achieved by a 5-phase micro-stepper motor, with 10,000 steps per revolution, located at the top of the guide rods. The motor drives a 2.5 mm pitch recirculating ball lead screw via a toothed belt and pulleys to give a single step increment of 0.25 μm on the pullshaft (seed rod) and a maximum total traverse of 280 mm. Rotation is achieved by a second identical stepper motor which is connected to the shaft by a flexible coupling to minimize the vibrations being transferred from the motor to the pull shaft.

The pull shaft is made of stainless steel, which may be water-cooled, whose lower end is located in a long, precision-machined phosphor-bronze bearing fitted with two vacuum lip seals. This bearing and seal assembly is secured to the base plate by a knurled screw ring. The shaft is coated with titanium nitride to provide a low friction, hard bearing surface. The upper end of the shaft passes through a water manifold and is coupled to the rotation motor.

Both rotation and translation modes are achieved using fully integrated, microprocessor controlled microstepper drive units which are designed for powering 5-phase, 10,000 steps per revolution, micro stepper motors. The motor amplifier is driven by control electronics, which produce the required pulse train and direction signals, derived
Figure 1.9 Rotation and Translation assembly
from a precision quartz oscillator. Using this, the rotation rate can be varied between 0.01 and 99.99 rpm and the translation between 0.01 and 9999 mm/h.

The system is provided with two translation limit switches, operated by user adjustable stop rings on one of the support pillars. 'Soft' limit switches are also available which limit the traverse within a particular position. The operation of the units is by simple menu-driven commands, viewed through liquid crystal display (LCD), operated by front panel push buttons located in the microprocessor drives.

### 1.5.4.1 Seed rod assembly

The seed rod assembly also needs due consideration since it also determines the quality of the crystal. Any eccentricity in the seed rotation will result in the thermal imbalance and result in growth problems like twisting, twinning and misorientation of the crystal etc. The seed rod assembly fabricated and used in this study is shown in Figure 1.10. The pull shaft is attached to a stainless steel tube through a male thread and a side screw. The stainless steel tube has three screws located at top with 120° separation between them. Similarly three more screws are provided in the bottom of the tube. The diameter of the stainless steel tube was such that it can accept one end of long alumina tube freely. The other end of the alumina tube has a noble metal tube (Pt or Ir) fitted rigidly by Pt or Ir pin through a groove available in the alumina tube. The other end of the metal tube is attached with the seed in a similar fashion by groove made on the seed. The attachment of seed to the alumina tube through a metal tube is more critical in oxide crystal growth, especially during seeding. Since the oxide crystals have very low conductivity, the conduction through the seed is normally low. The metal tube acts as a sink and removes the heat from the seed and thereby increasing the conduction through the seed rod and hence the crystal growth. In the absence of metal tube a metal foil can be wound around the seed and then attached to the alumina tube. The three screws at the top of stainless steel tube can rigidly hold the alumina tube. The three screws located at the lower end of the tube can be adjusted.
Figure 1.10 Sketch of seed rod assembly
to correct any eccentricity in rotation and hence better thermal and mechanical symmetry of the system.

The crystal growth assembly requires some rigid and sturdy arrangement on which it can be fitted vertically and also to perform the growth under preferred atmosphere. Therefore a crystal growth chamber with provisions for heating coil feed through, evacuation, gas purging, water circulation and viewing is essential.

1.5.5 Crystal growth chamber and stand

Since the crystal growth is to be carried out in an electrical, chemical and thermal environment, the points that matter in the selection of material by which the chamber is to be made are non-corrosiveness, non-magnetic (as the high current through the coil should not induce any stray heating in the material), heat conduction, mechanical strength and fabrication cost.

In view of these factors, stainless steel SS 316 grade appears to be a good candidate. The design of the chamber depends on the parameters like pressure to which it should withstand and the vacuum level needed etc.

In this investigation, a double walled chamber of 80 cm height and 45 x 45 cm² cross-section was made from SS 316 grade. The chamber has a hinged door with view port. The view port has two pyrex glass plates held parallel and attached to the door. The view angle of the port was designed using Computer Aided Design (CAD) diagram, in such way that it is possible to view the growth process through a 1.5 x 1 cm² hole in the refractory arrangement. With this aid, it is possible to view the process during seeding, where the melt level in the crucible is near the crucible edge, as well as during the snatch of the crystal from the melt from lower melt levels in the crucible. The chamber, door and the view port are separately water-cooled. A gas purging facility has been made in the view port to avoid deposition of vapour in the view glass.
The topside of the chamber was fitted to the digital pulling head assembly through a flange. The flange was machined in such a way that it fits exactly with the base plate of the pulling head assembly to have better vacuum conditions. On one side of the chamber at right angles to the door side, a provision for coil lead feed through was made. The coil leads are insulated from the chamber through a fibre glass plate. On the opposite side, an opening was made and is connected to the evacuating system. At the bottom of the chamber an opening was kept which can be used for crucible weighing mechanism. The water circulation is made to flow from the top to the bottom of the chamber. Similarly provisions for gas purging inlet and outlet were made.

The entire chamber with digital pulling head was rested on a rigid mild steel stand. The stand was fabricated from 2" square tube. A support was given to one side of the chamber to give more rigidity in addition to its own inertia. The stand has four leveling screws and antivibration pads through which it rests on the vibration free platform. The civil construction of vibration free platform is described below.

The ground of area 5 x 5 sq. ft and 3 ft depth was dug. The anti-vibration pads used were made from neoprene and cork of one sq. ft and 2" thickness. The neoprene pads were packed in the base and cork pads were packed along the sides. A concrete mixture was filled in the space for about 15" height and again the shock absorbers were arranged and the concrete mixture was filled up to normal ground level.

The complete oxide crystal growth system, resting on the vibration free platform, interfaced with induction heating unit is shown in the Figure 1.11a. The same chamber can also be used to grow crystals using resistive heated furnace also. The resistive heated furnace inside the chamber, connected to temperature controller is shown in Figure 1.11b.

Having developed the oxide crystal growth system, the present thesis is aimed to the growth and characterization of technologically important crystals of 1. Paratellurite (TeO₂)
Figure 1.11 Oxide crystal growth system in (a) induction heating and (b) resistive heating modes.
which is extensively used as modulator and deflectors for laser light, tunable filters and in signal processing by making use of the interaction of acoustic and optical waves (acousto-optic phenomenon) in the crystal and 2. Bismuth tellurite (Bi$_2$TeO$_3$) and Bismuth silicon oxide and Bismuth germanium oxide Bi$_{12}$(Si,Ge)O$_{20}$ which are widely applied as storage media by exploiting the phenomenon of photon induced refractive index variation (photorefractive effect).

In addition to the growth and basic characterization studies, the modification of properties of the crystal by ion implantation and doping is also studied and the results are discussed. The thesis concludes with the summary of the work and suggestions for future research plan.