CHAPTER 1

INTRODUCTION TO 1222 TYPE HIGH TEMPERATURE SUPERCONDUCTORS AND FLUX GROWTH

1.1 INTRODUCTION

The discovery of superconductivity at high temperature (T_c) that exceeds 90 K in RBA_2Cu_3O_7-δ (RBCO), (Bednorz and Müller 1986, Wu et al 1987) has led worldwide efforts to find novel superconductors and their superconducting mechanism. This was followed by the achievement of high temperature superconductivity in Bi-Sr-Ca-Cu-O (BSCCO) (Maeda et al 1988), Tl-Ba-Ca-Cu-O (TBCCO) (Sheng and Hermann 1988) and Hg-Ba-Ca-Cu-O (HBCCO) (Putilin et al 1993). Figure 1.1 shows the year wise increase in T_c in various superconducting materials. One of the main reasons for the rapid development in this area of research has been the simplicity of the preparation conditions of these new fascinating materials. Therefore, a large number of new superconductors and other hitherto unknown materials have been synthesized. Although considerable amounts of experimental data have been reported, many controversial puzzles involved in the phenomenon of high T_c superconductivity are still unclear. Hence it is necessary to accumulate more data from a variety of angles on various cuprate superconductors in order to understand the mechanism and for the advancement towards room temperature superconductors.
Figure 1.1 Milestones in superconductivity research as $T_c$ Vs year
1.1.1 High \( T_c \) superconductors

High temperature superconductivity in oxide compounds is based on Cu-O or Bi-O complexes. Although recent discovery shows the existence of high \( T_c \) superconductivity in MgB\(_2\) and other non-copper compounds, in general no high \( T_c \) superconductors was found without these two complexes as seen from Figure 1.1. In order to study the relation between the crystallographic structure of the high-\( T_c \) superconductors and their physical properties like \( T_c \), \( H_{c2} \), etc, knowledge of the crystallographic structures is indispensable. All high-\( T_c \) superconductors based on copper, have a crystallographic structure, which consists of perovskite-like blocks. These blocks are arranged in such a way that CuO\(_2\) planes are formed. Although no definite theoretical model on high-\( T_c \) superconductivity is available, it is generally accepted that the superconductivity is related to these CuO\(_2\) planes because this feature is common to all crystal structures of Cu-based high-\( T_c \) compounds. It is assumed that other elements are essential to stabilize the crystal structure and to create necessary conditions for superconductivity. It is known at present that the high-\( T_c \) superconductivity is observed only when these Cu-O planes are doped with an appropriate density of positive (hole-like) or negative (electron-like) charge carriers. Hence, high-\( T_c \) superconductors are doped by holes or electrons, which are the charge carriers for electrical current. In copper based high-\( T_c \) superconductors, these holes or electrons move to the CuO\(_2\) plane. The superconducting materials discovered so far consist of perovskite-like blocks either with Cu-O or Bi-O complexes.
1.1.1.1 New type of high $T_c$ superconductors

The primary challenge for the superconductivity researchers is to find materials with higher superconducting transition temperatures in order to achieve room temperature superconductivity. Another important effort is to look for the non-copper oxide materials with higher $T_c$. Although there are several papers, which reports on non-copper superconductors, still systematic studies are required for clear understanding of the existence of superconductivity in these materials. Hence, the search for novel materials with higher $T_c$ and understanding of their superconducting mechanism are very essential. In general, an important feature in the structure of superconducting cuprates is that they all contain at least one layer of 4 to 6 co-coordinated CuO in two-dimensional (2-d) planes within the unit cells. It is thought that any compound which contains a CuO plane and an appropriate density of carriers might become a superconductor (Whangbo and Torardi 1990). It is well established that the Cu-O planes in the structure play a dominant role in the superconductivity properties. Thus, compounds with 2-d CuO planes is a major concern in the search for new types of high $T_c$ superconductors with different layered cuprates. At the same time, efforts should be focussed on the remaining class of compounds of non-superconducting structures with CuO$_2$ layers. Hence, a study on the structure of existing non-superconductors with respect to the known superconductors may give rise to new and novel compounds.

In view of this, a great deal of effort has been devoted to explore new type of superconductors. It has been suggested that with different combinations of the block layers and CuO planes one can design new structure types of layered cuprates (Tokura and Arima 1990). The block layers can be further classified into two different types (Li Rukang et al 1992a); connecting layer, which
connects CuO planes by joining common apical oxygen atoms and separating layer which separates CuO planes between the sides without apical atoms. Therefore, by these three different combinations of connecting, separating layers and CuO planes, one may reconstruct all the known cuprate superconductors as well as some non-superconducting layered cuprates. Since the variation of CuO planes is limited to square planar CuO$_4$, pyramidal CuO$_5$ and octahedral CuO$_6$, a search for new types of connecting and separating layers for CuO planes is essential to explore new high $T_c$ superconductors. These three types of stackings can be observed as perovskite-like, rock salt-like and fluorite-like. The perovskite structure consists of an alternating stacking of an AO layer with a BO$_2$ layer. The rock salt structure consists of a stacking of AO and BO layers and the fluorite structure is a stacking of A and O$_2$ layers. Based on this idea, as oxides are very easy to synthesize, a series of layered oxide compounds composed of different connecting layers have been successfully synthesized. These materials all crystallize in the so-called 1222, 1212, 2222 and other type structures of novel superconductors (Li Rukang et al 1992a).

1.2 1212 AND 1222 TYPE CUPRATE MATERIALS

From this perspective, the recent discoveries of high $T_c$ superconductors such as 1212 and 1222 perovskite type structural materials of MSr$_2$LnCu$_2$O$_8$ (M-1212) and MSr$_2$(Ln$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10-δ}$ (M-1222) (M = Ta, Nb, Ti, Ru and Ln = Sm, Eu, Gd) (Li Rukang et al 1991a,b, Cava et al 1992a, Goodwin et al 1992, Helebrand et al 1994, Bauernfeind et al 1995a,b, Vybornov et al 1995, Kopnin et al 1996 and Awana et al 1996) are attractive in the context of current research on superconductivity. These materials have crystal structures very similar to that of RBCO and also each one possesses
some peculiar properties, which are unsolved yet. Nomenclature of these compounds simply follows the popular notation generally used for the existing high $T_c$ cuprates. Although, superconducting MSr$_2$(Ln$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10.5}$ has not been studied as extensively as MSr$_2$LnCu$_2$O$_8$, it is apparent that their unusual properties are more important and refined preparation techniques may improve the superconducting property of these compounds. Hence, much attention has been focused on MSr$_2$(Ln$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10.5}$ (M-1222), which has phase resemblance with RBCO.

The first superconductor containing fluorite type block layers (Nd, Sr)(Nd, Ce)CuO$_4$ ($T^*$-214 phase) was discovered by Akimitsu et al (1988). After this discovery, superconductors with fluorite-type block layers, such as (Nd, Ce)$_2$CuO$_4$ (T -214 phase) (Tokura et al 1989a), (Ln, Ce)$_2$(Ba, Ln)$_2$Cu$_3$O$_{10}$ (223 or Cu-1222 phase, Ln = rare-earth elements) (Sawa et al 1989 and Ichinose et al 1989), Bi$_2$Sr$_2$(Ln, Ce)$_2$Cu$_2$O$_y$ (2222 phase) (Tokura et al 1989b, Arima et al 1990) and TlBa$_2$(Eu, Ce)$_2$Cu$_2$O$_y$ (1222 phase) (Martin et al 1989) were reported. Following this, a variety of new layered cuprates with 1222 type structure has been reported, such as TlBa$_2$(Eu, Ce)$_2$Cu$_2$O$_y$ (Liu et al 1992) and Msr$_2$(Ln, Ce)$_2$Cu$_2$O$_y$ { M = [Tl, Pb,Cu] (Maeda et al 1991, Vijayaraghavan et al 1993 and Sakai et al 1993), [Bi, Cu] (Schilling et al 1992), [Nb, Ta, Ti, Ru, Al, Ga and Co] (Li Rukang et al 1991a and 1992a, Cava et al 1992a,b, Goodwin et al 1992, Bauernfeind et al 1995a,b and Kaibin et al 1996)}. Recently, Hg based 1222 cuprates have also been reported (Maignan et al 1995, Tang et al 1995, Kandyel et al 2000a). The structure of these 1222 type cuprate oxides is stabilized by substituting an Ln$_2$O$_2$ fluorite block for the single oxygen-vacant layer between two CuO$_2$ layers of the 123 structure.
Hole carrier concentration in these compounds depends on the Ce\textsuperscript{4+} content in the fluorite-type layers and the oxygen content in the charge reservoir, MO-layer. Hole doping is, however, very difficult and most of M-1222 superconductors have been obtained either by annealing under high oxygen pressure or by refined preparation methods (Kandyel et al 2000b). However, superconductivity is observed only for a narrow range of oxygen pressure, synthesis temperature, annealing time and cooling rate, including the need for striking a delicate balance among solid solubility, cation ordering and oxygen content. It is noteworthy that the T\textsubscript{c} of 1222 superconductors reported previously are below 50K. However, optimization of synthesis and annealing conditions has not been performed for almost all 1222 superconductors and further studies are needed to determine the highest T\textsubscript{c} value for this type of compounds.

1.3 STRUCTURE OF 1212 AND 1222 TYPE CUPRATES

The structures of high T\textsubscript{c} cuprate superconductors may be described as a stacking of blocks containing conducting CuO\textsubscript{2} layers alternating with insulating charge reservoir blocks. The immediate consequences are strongly anisotropic electronic properties. In LnBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} (Ln = Y and most of the trivalent lanthanides), the intrinsic electronic properties are much closer to three-dimensional behaviour than in other high T\textsubscript{c} cuprates, since the charge reservoir contains metallic chains formed by CuO\textsubscript{4} squares that couple the CuO\textsubscript{2} layers along the c-axis.

The layered cuprates MSr\textsubscript{2}LnCu\textsubscript{2}O\textsubscript{8} (M-1212) and MSr\textsubscript{2}(Ln\textsubscript{1-x}Ce\textsubscript{x})\textsubscript{2}Cu\textsubscript{2}O\textsubscript{10}\textsubbox{6} (M-1222) (M = Ta, Nb, Ti, Ru and Ln = Sm, Eu, Gd) were discovered in an attempt to introduce different conducting metal-oxide layers in the charge reservoir.
reservoir block. The structures of 1212 and 1222 type cuprates shown in
Figures 1.2a and 1.2b are closely related to that of “123-cuprates” of the
RBa$_2$Cu$_3$O$_{7.8}$ or CuBa$_2$RCu$_2$O$_{7.8}$ (Cu-1212) type (Figure 1.2c) with M replacing
Cu in the charge reservoir layer and CuO$_{1.8}$ chain replaced by a MO$_2.5$ sheet.
The primary features of these structures are CuO$_2$ square-planar substructures
which are universal to all high $T_c$ cuprate structures and are widely believed to
be responsible for the unusual transport properties and high $T_c$ values.

Crystalline structure of M-1212 can be described as a triple perovskite
cell similar to that of RBa$_2$Cu$_3$O$_7$ (Cu-1212) (Figure 1.2c), where Y and Ba are
substituted by M and Sr respectively, and the CuO$_2$ planes are separated from
one another by MO$_6$ octahedral planes instead of Cu-O chains (Figure 1.2b).
The structure of MSr$_2$LnCu$_2$O$_8$ (M-1212) consists of a layer sequence RE-
CuO$_2$-SrO-MO$_2$-SrO-CuO$_2$ having a perovskite-like structure (Zandbergen et al
1992a). It is an $m = 1$, $r = 2$, $n = 2$ member of “category-A” cuprates,
$M_{m}A_{n}Q_{n-1}Cu_{m}O_{m-2+2n-8}$ or $M-mr(n-1)n$, i.e. M-1212. According to this general
categorization scheme, the standard CuBa$_2$RCu$_2$O$_{7.8}$ phase is referred to as

The tetragonal M-1222 structure is evolved from the RBCO structure
by inserting a fluorite type $R_{1.5}Ce_{0.5}O_2$ layer instead of the R layer in RBCO
(Cu-1212), thus shifting alternate perovskite blocks by $(a+b)/2$, while strontium
atoms are substituted in for barium atoms. In general, the M-1222 ($M = Ta,$
Nb, Ti, Ru, etc ) compounds crystallize in tetragonal structure with the space
group I$4/m$m$m$, whereas an orthorhombic structure was formed for $M = Ga$
with space group Fmmm (Felner et al 1995 and 1997a). The $M$ ions reside in
the Cu(1) site and only one distinct Cu site [corresponding to Cu(2) in RBCO]
exists with five fold pyramidal coordination. These CuO$_2$ layers are separated
Figure 1.2 Unit cells of (a) MSr$_2$(Ln$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10.8}$ (b) MSr$_2$LnCu$_2$O$_8$ and (c) LnBa$_2$Cu$_3$O$_{7-δ}$ high $T_c$ cuprate structures. Both the rare earth-nearest neighbour oxygen and intra-Cu$_2$O$_2$ planar copper-oxygen bonds are highlighted for the MSr$_2$(Ln$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10.8}$
on one side by $\text{MO}_6$, which replaces the Cu-O chains, and on the other side by fluorite-structure $\text{R}_{1.5}\text{Ce}_{0.5}\text{O}_2$ layers (Figure 1.2a). The structure of $\text{MSr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10-\delta}$ (M-1222) consists of a block of layers $\text{CuO}_2$-$\text{SrO}$-$\text{MO}_2$-$\text{SrO}$-$\text{CuO}_2$ having a perovskite-like structure sandwiched with a $(\text{RE}_x \text{Ce})$-$\text{O}_2$-$(\text{RE}_x \text{Ce})$ block, which has a fluorite-like stacking (Zandbergen et al 1992b,c). Actually, this is very similar to SrO-MO$_2$-SrO trilayer of the $\text{MSr}_2\text{LnCu}_2\text{O}_8$ and the BaO-CuO-BaO trilayer of the RBA$_2$Cu$_3$O$_7$ (RBCO). It is an $m = 1$, $k = 1$, $s = 2$ member of “category-B” cuprates, $\text{M}_m\text{A}_{3k}\text{Ba}_x\text{Cu}_{1+s}\text{O}_{m+4k+2s-\delta}$ or $\text{M}-\text{m}(2k)s(1+k)$, i.e. M-1222 (Awana et al 2003). The hole doping of Cu-O planes, which yields the metallic and superconducting behaviour, can be optimized by varying the R/Ce concentration ratio or by oxygen doping. The M-1222 compounds are superconducting with $T_c \sim 20$-$50$ K.

The efforts for improved synthesis procedure may lead to the discovery of new superconducting systems. Also a thorough study of the known superconducting materials, their structure and characteristics may give an idea of designing new materials with higher $T_c$ values.

1.4 AIM AND SUBJECT OF THE WORK

Although many studies have been done on $\text{MSr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10-\delta}$ (M-1222) polycrystalline samples, the influence of impurities on superconductivity, magnetism and other properties has been viewed differently by different groups (Li Rukang et al 1991a,b, Cava et al 1992a, Blackstead et al 1997 and Felner et al 1997b). It has been realized that the synthesis method plays a very important role on the superconducting properties of M-1222 compounds. Characterization of single crystal specimens is necessary in order to reveal the intrinsic properties of M-1222 compounds. However, in order to
understand the nature of this exciting class of materials, reliable measurements of transport and magnetic properties are necessary, which allow one to further explore the complex and puzzling electronic and magnetic properties. Single crystals of M-1222 type compounds are mandatory for two basic reasons. The first one is true for any class of material, that is high quality single crystals restrict the grain boundary effects. The second one is that M-1222 possesses a highly anisotropic structure, and this obviously implies that the physical properties should be anisotropic (Mele et al 2003a).

Nevertheless, it is well known that growth of single crystals of oxide perovskites is difficult and requires a careful control of the growth conditions. M-1222 compounds are relatively new and to focalize the best growth method to obtain single crystals is possible only upon sincere efforts. Among the single phase compounds formed with trivalent cations such as Ln = Sm, Eu, Gd, purity of 1222 phase increases for Eu and Gd. The substitution of smaller or larger trivalent ions of Ln into M-1222 compounds resulted in the formation of impurity phases (Bauernfeind et al 1995b and Shannon 1976). So far only a few reports describe the growth and characterization of monocrytalline Nb-1222 with Sm in this M-1222 series of high Tc superconductors (Samata et al 1998). With this motivation, single crystals growth and characterization studies of some selected compounds of MSr2(Ln1-xCex)2Cu2O10-y (M = Nb, Ti, Ru and Ln = Eu, Gd) high Tc superconductors have been investigated.

Growth of single crystals of M-1222 is a challenging task owing to the non-availability of prescribed phase diagram, incongruent nature, inevitable formation of 2222 and 1212 phases and decomposition into a mixture of R2O3, CeO2, Sr3MO5.5 and CuO2 above 1120°C (Samata et al 1998). Therefore, M-1222 crystals cannot be grown by the melt process and the flux method
appears to be only promising method to grow these crystals. In the present investigation, flux technique is adopted to grow single crystals of various M-1222 type high $T_c$ superconductors.

A particular interest for the investigation of Sr$_2$GdRuO$_6$ arises from the fact that this compound is involved in the preparation of RuSr$_2$GdCu$_2$O$_8$ (Ru-1212) and RuSr$_2$Gd$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (Ru-1222) superconductors. Using Sr-2116 as one of the precursors along with $\frac{1}{2}$CeO$_2$, $\frac{1}{4}$Gd$_2$O$_3$ and CuO, high purity Ru-1212 and Ru-1222 can be synthesized. This preparation route is essential to avoid the appearance of perovskite impurities in Ru-1212 and Ru-1222 samples (Bauernfeind 1998) and has been widely adopted. It appears that the presence of pentavalent ruthenium in Sr$_2$GdRuO$_6$ effectively inhibits the formation of impurities (with tetravalent ruthenium) under oxidizing conditions. Braun et al (2002) proposed that the reaction path of Sr-2116 and CuO most likely follows the straight line in the phase diagram involving pseudo-binary equilibria and thus giving no room for the appearance of other phases. Hence, a systematic study on the synthesis aspects of Sr$_2$GdRuO$_6$ (Sr-2116) has been performed.

1.5 PREPARATION OF HIGH $T_c$ SUPERCONDUCTORS

1.5.1 Single crystal growth

Growth from high temperature solution (flux) is highly suitable for the crystal growth of high $T_c$ superconductors. Crystal growth processes from the flux are phase transformations, which are driven by differences in chemical potential between crystallizing and nutrient phase (Carruthers et al 1977). It is crucial during the crystal growth procedure to control the way of solidification under virtually equilibrium conditions. Phase diagrams play a vital role in optimizing the crystal growth conditions.
Since the discovery of high T<sub>c</sub> superconductivity in the La-Ba-Cu-O system, a large number of investigations have been performed on polycrystalline ceramic samples of high T<sub>c</sub> superconductors, which consist of sintered micrometer sized crystallites. These samples are quite easy to prepare by a solid-state reaction and knowledge of their phase diagrams are not mandatory. For powder X-ray diffraction measurements, samples in polycrystalline form are useful but other definite physical property studies are often difficult due to the polycrystalline nature. To understand the intrinsic physical properties of the high T<sub>c</sub> superconductivity, not only from fundamental aspects but also from the application point of view, it is important to study well-defined high quality single crystals. Not only the quality but also the size of the single crystals is an important factor for performing physical property measurements. However, it is still rather difficult to grow larger size crystals of high T<sub>c</sub> superconductors. Non-availability of prescribed phase diagrams for all the existing high T<sub>c</sub> superconductors makes crystal growth experiments more difficult. Generally these materials melt incongruently. The high reactivity with the container, the large evaporation and the poor stability are the major difficulties encountered during the single crystal growth of high T<sub>c</sub> superconductors.

### 1.5.2 Congruently and incongruently melting compounds

According to the melting behaviour, the materials are divided into two main categories such as congruent and incongruent melting materials. A congruently melting solid material can exist in equilibrium with the liquid phase in the same composition at the melting temperature. The compound A<sub>2</sub>B in Figure 1.3 is a congruently melting compound. Examples of congruently melting compounds are La<sub>2</sub>NiO<sub>4</sub> and Cu<sub>2</sub>O. These materials can directly be grown from the melt.
Figure 1.3 Congruent and incongruent melting compounds, $A_2B$ melts congruently and $AB_2$ melts incongruently
An incongruent melting compound decomposes upon heating at the peritectic temperature $T_p$ into a solid and liquid of different composition. The compound with the composition $AB_2$ in Figure 1.3 starts decomposing at the peritectic temperature and forms a liquid with composition $X_p$ and a solid with composition B. High $T_c$ superconductors are generally incongruently melting compounds, which decompose via the peritectic route. These compounds can be obtained by a peritectic reaction of a solid and liquid of different composition.

The time and temperature dependence of the peritectic reaction is now considered. The materials transfer density during this reaction is, according to Fick's law, proportional to the diffusion coefficient and concentration gradient of the reactants and inversely proportional to the thickness of the reacted product between the solid and the liquid. For this reason, the smaller size grains are completely reacted at a faster rate. The size of these grains depends on the heat treatment of the partially melted material before the peritectic reaction occurs. The temperature dependence of the reaction is mostly determined by the temperature dependence of the rate of diffusion coefficient $D$ of the reactants, which follows the Arrhenius equation, (Kingery 1960)

$$D = D_0 \exp(-Q/RT)$$

(1.1)

where

- $R =$ universal gas constant \([J/mole K]\)
- $T =$ absolute temperature \([K]\)
- $Q =$ experimental activation energy \([J/mole]\)
- $D_0 =$ constant

Thus a high peritectic temperature is favourable for a fast reaction speed. In general, the peritectic reaction is very slow because the diffusion is
small. Thus growing a crystal of a peritectic compound directly from a stoichiometric composition is difficult.

1.5.3 Solid State reaction method

The solid-state reaction method is used for the preparation of polycrystalline ceramic material, below the melting temperature. In this thesis work, solid-state reaction method has been used to prepare starting materials for the self-flux method. Since the properties of the starting materials influence the final results of these experiments, some basic information concerning this method is given below.

The theoretical density of a high $T_c$ superconducting compound cannot achieved by the solid-state reaction method. By using this method, only micrometer-sized crystals can be obtained in a rather simple way. In the case of high $T_c$ superconductors the starting materials like oxides and carbonates are thoroughly mixed in the stoichiometric ratio. With intermediate grinding and pressing into pellets, the compound is formed by a solid-state reaction at a temperature below the peritectic temperature. Reactions between solids, in order to form a new phase, involve a diffusion process. The driving force of this reaction is the concentration gradient. Diffusion is the limiting factor in the solid-state reaction. The temperature and time dependence of the reaction is the same as discussed above for the peritectic reaction (Kingery 1960). The reaction must take place at a temperature as close as possible to the peritectic temperature in order to improve the diffusion rate (equation 1.1). Small sized starting material is essential to complete the reaction faster. A second advantage of starting material with small particle size is that a higher density can be obtained by pressing, which improves the contact between particles. During the reaction shrinkage takes place if the formed phase is denser than the starting material. Sometimes, voids are created inside the polycrystalline material,
which disturbs the diffusion and consequently the reaction. Intermediate grinding and pressing improve the quality of the product, because diffusion boundaries between starting materials and voids are removed. The pellets are finally sintered just below the peritectic temperature in order to avoid partial melting of the product.

1.6 FLUX GROWTH

Flux growth is the term most commonly used to describe the growth of single crystals of a wide range of materials from molten salt solvents (flux) at high temperature. Growth from flux is obtained by decreasing the temperature of a supersaturated solution. A high temperature solvent is referred to as a flux because it permits growth to proceed at temperatures well below the very high melting point of the solute phase. If the material melts incongruently, i.e., decomposes before melting, or exhibits a phase transition below the melting point, one has indeed to look for growth temperatures lower than these phase transitions. This reduction in temperature is probably the principal advantage of flux growth over growth from the pure melt, and the flux method is normally preferred when

1) the material melts incongruently or exhibits, at some lower temperature, a phase change, which leads to severe stress or fracture
2) materials which are volatile at the melting point
3) the material is non-stoichiometric at its melting point due to a high vapour pressure of one or more constituents.
4) crystals relatively free from thermal strain are required
Thermal strain is minimized in this technique owing to relatively low temperature, small thermal gradient applied and the free growth into a liquid, allowing the formation of growth facets.

1.6.1 Choice of a flux

The number of possible fluxes is vast and detailed principles, which may be used in the selection of the optimum solvent for the growth of a given material, have not yet been established. The problem of selection is aggravated by the scarcity of data on phase diagrams and on such important parameters as the viscosity and vapour pressure of fluxes.

The main requirement of the flux material is that the solvent should dissolve the solute to an appreciable amount and a practical minimum is usually considered to be about 1%. The solvent must not react with the solute to form new solid compounds because the crystal phase required should be the only stable phase in the crystallization temperature range. Furthermore the range of solid solutions between solute and solvent should be as small as possible to avoid elements, which are incorporated into the growing crystal. This is nothing but, the ionic radii of cations of the flux and of the compound should differ and also the charge of the flux and of the compound should differ. The first one is more important than the second. At the same time, the solubility change with temperature should have an appreciable level to increase the yield of crystals by any regular technique used to obtain supersaturation, mostly by slow cooling. A low viscosity of the solution is desirable to achieve better homogenization and fast stable growth. An ideal solvent should supply both a low melting point and low growth temperatures to prevent destructive phase transitions and a high concentration of equilibrium defects. This is the most important point in the case of growth of incongruently melting compounds. The lower temperature is
also more beneficial with respect to furnace and crucible requirements. The crucible material is also primarily important, because high reactivity with the container material as well as high tendency of the solvent to creep out of the crucible can change the solution composition and melting point during the growth process. Obviously, for an ideal solvent easy separation of the grown crystals, low cost and low toxicity are required. The solvent which successfully fulfills all these ideal properties are very rare and experimental compromise is always necessary. One of them is using a eutectic mixture composed of compounds present in the crystallizing system and compatible with the required crystallizing phase. A eutectic composition is the most suitable choice provided the required material crystallizes as the stable solid phase. This is called self-flux growth.

In general, crystal growth from flux is commonly preferable when small crystals are needed for basic investigations and measurements of physical properties although this method cannot supply the large size single crystals of high $T_c$ superconductors desired for industrial and many other practical applications.

1.7 SELF-FLUX METHOD

Bigger size single crystals of high $T_c$ superconducting compounds can be grown by the self-flux method. Crystals are grown without undergoing a peritectic reaction. The driving force of the crystal growth is the cooling. In this case the off-stoichiometric composition $X_f$ with $X_f$ between $X_e$ and $X_p$ is melted and subsequently slowly cooled down as shown in Figure 1.4. By using this method the crystals precipitate in the melt. In this case, the primary crystallization field is determined by the composition range between $X_p$ and $X_e$ and the temperature range between $T_p$ and $T_e$, (Figure 1.4). High purity starting
Figure 1.4  Principle of self flux crystal growth
materials are necessary to avoid heterogeneous nucleation. However, at the crucible wall heterogeneous nucleation takes place. If the liquidus line is passed, the peritectically melting compound $X_i$ precipitates following the lever rule (Rosenberger 1979),

$$\frac{n(X_i)}{n(X_i)} = \frac{ds}{dl} \quad (1.2)$$

where,

- $n(X_i), n(X_f)$ = the number of moles of the solid and liquid with composition $X_i$ and $X_f$ respectively
- $d_i, d_s$ = distances between $X_i$ and $X_f$ and $X_f$ and $X_i$ respectively shown in the phase diagram

Due to the cooling, the composition $X_i$ of the liquid changes and the size of the crystals depends very much on the phase diagram. A phase diagram or at least a portion of a phase diagram pertinent to the temperature range used for crystallization is desirable but rarely available. This technique has been adopted to grow single crystals of M-1222 type compounds with various substitutions in this thesis work.

1.8 FACTORS INFLUENCING GROWTH OF HIGH $T_C$ OXIDE SUPERCONDUCTORS

1.8.1 Influence of starting compositions

The different starting compositions used for crystal growth of high $T_c$ superconductors have been reported to influence some factors such as superconducting properties, morphology of the crystals, crucible corrosion, and viscosity of the flux. In the case of YBCO, Licci et al (1991) studied corrosion of $\text{Al}_2\text{O}_3$ crucibles for various $\text{BaO}/\text{CuO}$ ratios in the solvent and observed a
minimum aluminium content in flux with BaO/CuO ratio of 28/72, i.e., close to the eutectic composition and the aluminium content decreased with increasing barium content in the starting composition. The starting composition also influences the superconducting transition temperature, size and shape of the grown crystal (Schneemeyer et al 1987).

1.8.2 Influence of the crucible material

The lack of an inert crucible material is a factor that has made crystal growth of oxide superconductors complicated. The superconducting transition decreases due to substitution of elements from the crucible material into grown crystals. The dissolution of the crucible material into the solvent from which the crystals are grown complicates the phase relations required for crystal growth. Instead of a four-component system, the phase relations have to be described within a five-component system. In YBCO case, the ability of YO\textsubscript{1.5}-CuO-BaO melt to creep along the crucible material might change the composition of the melt especially in the case of partial melting. Use of porous crucible materials, where the melt is sucked into the crucible due to capillary forces, might result in a similar effect on the composition of the material left in the crucible. The creep ability was utilized for growth of high quality YBCO crystals from gold crucibles. Twin free YBCO crystals have also been grown by taking the advantage of the creeping phenomena (Jayavel et al 1994).

Since alumina crucibles are the most frequently used crucible material for growth of high T\textsubscript{c} oxide superconductors, the effect of contamination from this crucible material has been studied widely. The influence of contamination from crucibles reduces the melting point and wetting of melts due to dissolution of aluminium in the flux (Wolf et al 1989, Scheel et al 1989). Actually alumina
was strongly wetted by melt and the melt could creep out of the crucible, mainly at temperatures exceeding 1000°C. Wolf et al (1989), reported that dense Al₂O₃ crucibles were not wetted by these melts and the melt did not creep on the walls of the crucible. Differences in temperature range might be an explanation for this discrepancy in the results.

1.8.3 Influence of the growth temperature and the cooling rate

The growth rate depends on the cooling rate if crystals are grown by slow cooling method. However, the steepness of the liquidus surface given by the lever rule, the actual composition and temperature range will also influence the growth rate. Slow cooling has been mostly adopted to achieve supersaturation for the growth of high Tc oxide superconductors while using excess fluxes. Scheel (1989) reported the influence of the cooling rate on the morphology of YBCO crystals and also they found that the thickness of the YBCO crystals depends on the cooling rate. Thick, rather isometric crystals were grown from cooling rates below 1 °C/h, while thin crystals typically in the range 0.05-0.2mm were grown from cooling rates between 2 and 5 °C/h. These results were confirmed by Wolf et al (1989) and also observed in the present work.

1.8.4 Influence of viscosity on crystal growth

The rate of crystal growth from solutions will be determined either by volume diffusion of solute to the crystal surface or by the kinetics of the integration of the solute on the crystal surface. According to Elwell and Scheel (1975), volume diffusion will most probably be the rate-determining step for growth from unstirred solutions. The viscosity becomes an important factor for crystal growth when volume diffusion is the rate-determining step as the
viscosity of the melt influences the diffusion of the growth units. An ideal solvent should according to Elwell and Scheel (1975) have a viscosity between 1 and 10 cp. The maximum practical viscosity for a solvent used for crystal growth should be 5-10 cp.

The viscosity of the melts is also influenced by the dissolution of the different crucible materials. Dissolution of aluminium oxide is known to decrease the viscosity of the flux (Wolf et al 1989). The difference in viscosity can be ascribed to dissolution of zirconium in the flux and the dissolution leads to a higher viscosity of the melts than the dissolution of aluminium.

1.9 SLOW COOLING

In this method, reducing the solubility of the solute by decreasing temperature induces the nucleation and crystal growth process. The essential requirement for crystal growth from fluxed melts is the creation of supersaturation. There are three most prominent methods by which supersaturation can be achieved for crystal growth. This means supersaturation and supercooling are defined by the phase diagram. Figure 1.5 shows schematically a pseudo-binary system of flux and solute and the three main ways for crystal growth.

1) crystal growth by slow cooling (SC) when the temperature is decreased from A to B and growth occurs along the arrow to C at varying growth temperature $T_g$.

2) crystal growth by flux evaporation (Evap) when the solvent or a part of it is evaporating with an increase in solute concentration from A to D. $T_g$ is a constant.
Figure 1.5 Means of achieving crystallization from fluxed melts: ABC, slow cooling; AD, evaporation; EF, temperature gradient transport.
3) crystal growth by vertical temperature gradient transport (VTGT) when the crystal grows in a cooler region F and the crystallized material is replaced at a hotter region E generally from a polycrystalline nutrient.

When the flux has a high vapour pressure and a part of it evaporates during slow cooling a combination of all the three possibilities is applied.

There is no general rule prevailing for the selection of any one of the above methods to a material to be crystallized. The growth of crystals is mainly influenced by three factors, (i) the experimental arrangement and (ii) the property of the melt solution, and (iii) the required quality – size, purity, homogeneity – of the crystals.

1.9.1 Crystal growth by slow cooling

In general, for the most cases slow cooling method is adopted for crystal growth. In this method, the components of the material to be grown and the appropriate solvent are taken in a suitable crucible. The temperature of the furnace is raised to a value slightly above the saturation point for a sufficient time to ensure complete homogenization in dissolution of solute. This is important since any undissolved solute particles will act as nucleation centers when crystallization starts. If the density of the solvent is very different from that of the solute, it is desirable to heat the crucible in a high temperature gradient to promote convective mixing. The solution is then cooled at a low rate $dT/dt$ through a temperature range, where the desired crystal is known to precipitate. The supersaturation will depend on the values of the temperature coefficient of solubility ($dS/dT$) in the chosen temperature interval. During cooling, the temperature gradient must be in the opposite direction so that growth occurs on or near the base of the crucible. As the melt is cooled through
the metastable region, many crystallites will nucleate and the result of the experiment will normally be many tiny crystals.

Usually the cooling rate \((dT/dt)\) is adjusted so that \(dS/dt\) is in the range of 0.02 to 0.20 wt % per hour. For most values of \(dS/dT\), this results in \(dT/dt\) to be in the range of 1 to 5°C per hour. Crystals usually nucleate first at the coolest point of the crucible. It is preferable that nucleation be confined to a few initial sites. Once initial nucleation takes place \(dS/dt\) will be low enough so that no further nucleation occurs. Hence the initial sites only sinks for subsequent growth, and the crystals obtained will be of maximum size. Thus the smaller the \(dT/dt\) the larger the crystals obtained, but a lower limit of \(dT/dt\) is usually set either by accuracy of temperature control or by the time available. Once the temperature range of growth is traversed, the crucible may be cooled rapidly to room temperature. The crystals are found on the surface of the solidified charge and also on the walls of the crucible. The grown crystals are carefully removed by hand sorting.

In general, slow cooling will produce several crystals even if a small region of the crucible is cooled in an attempt to restrict the area over which nucleation occurs. Even when effective means of precise localization of nucleation are not available, selection of relatively few nuclei for further growth may be achieved by cyclic temperature variations in the early stages of the growth experiment. The principle is illustrated in Figure 1.6, in which \(T_L\) denotes the liquidus temperature and \(T_c\) the limit of the metastable region. When these temperatures are known to be better than \(\pm10^\circ C\), the procedure indicated by the full curve may be used. After holding the temperature about 50°C above the liquidus for at least 12 h, the melt is cooled rapidly to B, and then cooled at about 1-2°C/h to a point C, well below the metastable limit. The
Figure 1.6  Temperature programmes for minimization of nucleation
temperature is then raised to D, about 5°C below $T_L$, and held at this temperature for several hours so that the smaller crystals, formed during cooling, will dissolve. Programmed cooling then begins at E and growth will occur on the small number of nuclei remaining, provided that the solution remains sufficiently homogeneous so that further nucleation is avoided.

When precise data are not available, $T_L$ may be estimated by trial experiments and the alternative procedure, shown as the dotted line, may be used. After cooling to C, the cycle of heating to F, slow cooling to $C'$, heating to $F'$, etc is continued until the upper point (G) is well below the liquidus, after which the programmed cooling may be commenced. There is other alternative way for the use of an oscillatory curve for the whole period of growth. But this procedure is not advisable since the rate of growth during the cooling half-cycles will be well above the stable limit unless a period of several months is taken for the experiment.

1.10 GROWTH MECHANISM

When crystal growth occurs in a fluxed melt, which does not contain seed crystals, the following stages of growth may be identified: Nucleation, dendritic growth, layer growth nucleated at corners or edges of a crystal face, and layer or spiral growth originating at screw dislocations.

1.10.1 Nucleation of crystals

Crystallization can be regarded as a two-stage process-nucleation and growth. Nucleation is the initiation of the crystal growth, and plays an important role in crystal growth processes. Nucleation is the formation of a stable, critical-sized molecular aggregate called a "nucleus". Nucleation, which
is induced by crystals of the same compound, i.e., seeds, is called secondary nucleation (Pamplin 1975). Nucleation without those seeds is called primary nucleation, which can easily be separable into two major types called "homogeneous nucleation" or "three-dimensional nucleation" and "heterogeneous" or "two-dimensional nucleation".

Homogeneous nucleation is an intrinsic spontaneous nucleation, which is possible only if very pure starting materials are used. In this case a supercooled melt suddenly shows crystallization. The nucleation barrier is caused by the fact that small clusters of atoms are unstable compared with larger clusters (Pamplin 1975). In a supercooled melt small clusters break up, due to the thermal energy, before other atoms are added. This type of nucleation requires a critical supersaturation (undercooling) whereby the size of the crystal nucleus exceeds the minimum size on which crystal growth can take place. This is simply the nucleus size and solute supersaturation at which more material adheres to the nucleus than is dissolved by the solution. The size range should hold for most flux systems as well, since they appear to be ionic in character. The critical supersaturation ratios (supersaturation divided by solubility) have been estimated to be between 2 and 1000 depending on the material and purity.

Heterogeneous (two-dimensional) nucleation, which occurs at higher temperatures than homogeneous nucleation, is initiated through crucible walls, foreign phases or impurities and requires smaller supersaturations to be effective. Heterogeneous nucleation can be employed to generate any number of nuclei desired in the experiment and effectiveness of foreign particles relative to size, shape, lattice mismatch, etc., acting as the nuclei.
The nucleation in flux growth is normally of heterogeneous nature since it tends to occur at undissolved particles or on the surface of the container. This requires a smaller degree of supersaturation at higher temperatures than homogeneous nucleation, which often takes place in industrial bulk crystallization. Perhaps the first indication of this is the fact that the number of crystals grown varies over a relatively small range, regardless of the size of the crucible or process used. Another indication that the mechanism is heterogeneous is that crystal sizes are rarely similar, rather range over an order of magnitude (indicating different nucleation times). If the crystals were homogeneously nucleated, one would expect them to be approximately the same size, since supersaturation would decrease upon initial crystal nucleation and would not nucleate new crystals by subsequently exceeding the low supersaturation required for continued growth. Of all the parameters that can easily change the numbers of crystals nucleated, only impurities, thermal and supersaturation effects and solubility effects are generally found in flux growth.

In general, the number of growth sites on the container is not large, under favorable conditions, because the supersaturation $S_n$ necessary to cause nucleation on the container surface is higher than the supersaturation $S_g$ required for growth on the crystal faces. Under unfavorable conditions, when the ratio $S_n/S_g$ is near unity, many nuclei inevitably form. The number of nuclei depends also on the amount of mixing that takes place. This governs the degree to which supersaturation can develop high values locally and so nucleate more crystals.

If any solute particles remain undissolved, an excessive degree of nucleation is likely to result. It is also possible that impurities may act as nucleation centers and thus it is usually rewarding to keep the melt at a
temperature well above the liquidus for a “soak” period of 2 to 25h. For most materials, fewer crystals nucleate if the soak temperature exceeds that at which solution is evidently complete by about 50°C, provided that the flux is non-volatile.

1.10.2 Dendritic growth

The heterogeneous nucleation in flux growth requires only a low supersaturation for effective nucleation and growth. Since nucleation occurs at relatively high supersaturation values, the initial growth is rapid and exhibits a dendritic character with tree-like or branched non-faceted crystal formations spreading along the fast growth directions. Originally, a dendrite is thought to be the result of growth at a protrusion on the crystal surface. It is felt that the protrusion would be in a position to collect more material and hence grow more rapidly than the rest of the crystal surfaces. The dendritic arms may reach a length of one cm, or even more, since the arms tend to spread into regions of increasing supersaturation.

1.10.3 Layer growth

This is a type of crystal growth in which the crystal grows by propagation of distinct layer across the crystal face, either as a continuous layer with a permanent step or by a process requiring a new layer to nucleate each time a propagating layer is completed. Layer growth gives rise to flat crystal surfaces. There are two types of layer growth; one type requires nucleation of a new step and the other type is associated with screw dislocations. Either or both of these processes are normally involved in the growth of crystals from solution.
1.10.3.1 Layer growth by two dimensional nucleation of new steps

In this mechanism of growth, the atomistic consideration rather than thermodynamics is considered. A crystal can be pictured as bound by close-packed planes of atoms or molecules in the form of hypothetical cubes stacked face to face. Each cube is attracted equally by its six nearest neighbours. The structure of a low index face is depicted as a flat surface, which may be partially covered by another layer. If the crystal is in stable equilibrium with the solution, then the number of "kinks" or sites for attachment of new molecules will remain constant, with material arriving at and leaving the face at equal rates. If more material arrives at the face than departs, the step advances across the face and eventually fills the layer. For crystal growth to continue, a new step must be generated.

This type of growth is observed in the growth of a number of compounds from flux systems. In particular, nucleation of new layers is found to occur as an intermediate growth stage (between dendritic growth and growth by a screw dislocation process). The curvatures of the steps reflect higher concentrations of solute near the corners and edges of the steps indicating that diffusion plays an important role in the process. If step nucleation at the corners and edges proceeds faster than the steps can propagate across the crystal face during this stage, growth proceeds laterally between the edges and traps solvent as sheets parallel to the face. Growth of this type is indicative of rapid growth associated with high supersaturations and can be avoided by reduction in supersaturation.

If a crystal with a stepped interface is in contact with a supersaturated solution, the process of crystal growth requires some mechanism by which atoms will be integrated into the crystal more readily than on the remaining
surface. The mechanism required for the growth are (i) transport of solute from the bulk solution by diffusion, convection or forced flow, (ii) volume diffusion through a boundary layer, (iii) adsorption onto the crystal surface, (iv) surface diffusion to a step, (v) attachment at a step, (vi) diffusion along the step, and (vii) integration into the crystal a “kink” in the step. Stages (iii), (v) and (vii) may each involve partial desolvation. The above stages during the process of growth are schematically shown in Figure 1.7. For simplicity, solvation is indicated by a cluster of six (unshaded) solvent particles around the (shaded) solute particle.

1.10.3.2 Layer growth at a screw dislocation

After nucleation and initial growth, if the rate of cooling is sufficiently slow, the supersaturation decreases to a level at which growth takes place mainly spiral growth at screw dislocation (Sungawa 1987). Thus, spiral growth or growth generated by a screw dislocation is the type of growth that normally takes place on crystals grown under conditions of low supersaturation. It has been estimated that crystals grow by this mechanism at supersaturation of less than 1%, while normal two-dimensional layer growth requires supersaturations of 25-50%. This is an important growth process, for the material grown by this mechanism is generally of very high quality with respect to the normal defects found in crystals.

Again, as with two-dimensional, the crystal is assumed to be bound by close-packed planes of atoms or molecules added to the step surface. The step rapidly winds around itself, with its length becoming longer as each row is added. This process continues until a growth spiral results. The spacing between parallel portions of the step is governed by the supersaturation of the system and surface diffusion processes. High supersaturations with
Figure 1.7  Stages in the process of growth on a habit face
low surface diffusion rates favor close spacings, while low supersaturations with low surface diffusion rates favor widely spaced steps. In this case the crystal surface becomes a spiral ramp comprised of one lattice layer interrupted by one continuous step. The presence of this step allows the crystal to grow continuously at low supersaturations, since nucleation processes are not required for continued growth. While crystal growth by this process requires only one such defect and its associated growth spiral, each crystal face generally has several defects.

Step shapes other than those related to single spirals are regularly found on crystals. More complex step systems evolve when more than two dislocations are present. In general, growth spirals have been observed on a number of different crystals grown from flux systems and growth by this mechanism is believed to be the final stage of growth for crystals grown under conditions of low supersaturation. In solution growth, most techniques eventually yield the low relative supersaturations where this is the only operative growth mechanism.

The spiral may either be smoothly curved or modified by difference in growth rates in the planes of growth. Rounded spirals result from fast growth of crystals that exhibit growth rates that are nearly isotropic in the growth plane. In general, the flat sections of the spiral correspond to close-packed planes and are parallel to faces adjacent to the face on which the spiral is growing.

Another type of surface feature, other than the growth spiral is observed on crystals grown by this mechanism. These are termed as "vicinal faces" and are a direct result of the growth spiral. A vicinal face is a crystal face that nearly parallels a crystallographic plane. A vicinal face has no
relationship with the crystallographic planes of the crystal other than the fact that it always deviates from a crystallographic plane by some fraction of a degree to 1 or 2 degrees. It is separated from the low index crystal face by the steps that represent the growth of the crystal. The angle it makes with the crystallographic plane depends on step density and step height.

1.10.3.3 Growth hillocks

The continuation of relatively stable growth will eventually lead to the appearance of habit faces, which are the slowest-growing faces of the crystal. At relatively high values of supersaturation, growth on the habit faces occurs by a spreading of layers from corners or edges of the crystal, where the supersaturation is higher than at the face centers. At lower supersaturations the dominant surface features are growth hillocks, which are presumed to originate at screw dislocations. In the most stable mode of growth of larger crystals, the centre normally dominates the growth of the entire face. The observation of hillocks and spirals is strong evidence for the Frank screw dislocation mechanism.

1.10.3.4 Hopper growth

As growth proceeds, the supersaturation falls because of depletion of solute and the crystal takes on a terraced structure as more stable growth occurs on the dendrite arms. If growth is terminated at this stage, the crystal is said to exhibit a hopper morphology.

Hopper growth is a type of crystal growth that yields “hopper-shaped” faces on the crystals. It appears to be an intermediate stage between dendritic growth and subsequent two-dimensional growth resulting in flat faces. For this
reason, one would expect hoppers to be formed in the course of most flux growth experiments, since growth from a dendrite to a crystal with flat faces is a common occurrence in such systems. Hopper formation represents high growth rates and the initial formation of faces on the crystals. Generally, the arms of the dendrite form small incipient faces that begin to fill in as the growth proceeds. If the filling rate is sufficiently slow, stepped terraces parallel to low index planes are formed and if the growth continues, uninterrupted flat faces will form on the crystal. This yields a crystal with trapped inclusions. This type of hopper growth and subsequent fill-in occur on the faces of the crystal, which are in contact with the melt at all times. Another type of hopper formation process common in flux growth is the case in which one surface is not in contact with the melt. In this case, the crystal floats on the melt surface and the crystal “face” which is not in contact with the melt become hopper-shaped. This situation occurs in systems where the crystal has a somewhat higher density than the melt and is held on the surface by surface tension. As the crystal mass becomes larger, it tends to pull the melt surface down and allows the new layers to grow above the original surface. This type of hopper, resulting from growth on the surface, is difficult to eliminate; however, since the other type is related to dendritic growth, it can be avoided in general by employing the same procedures used to eliminate dendritic growth.

1.11 PRACTICAL ASPECTS

1.11.1 Crystal growth system

Growth of crystals from high temperature solution requires very accurate crystal growth system and substantial volumes to be heated for protracted periods of time. The furnace in the present investigation was fabricated by following these considerations and in essence, it is a vertically
oriented, resistive heated furnace. The schematic diagram of typical furnace employed in the present work is shown in Figure 1.8. The required dimensions of recrystallized alumina tubes were used.

To provide resistive heating A1 kanthal wire of SWG 20 was used. Initially, the kanthal wire was softened by preheating. This process makes the wire more flexible for effective winding. The kanthal wire was then wound round the outer surface of the mullite tube by maintaining an equi-distance of 2 mm between adjacent windings. In order to avoid short circuit between adjacent turns of windings, corundum powder mixed with sodium metasilicate was applied over the windings and allowed to dry for a few hours. This prevents short circuit between the turns which generally expand upon heating. The mullite tube was then placed in an aluminium container and packed with zirconia grade ceramic fibre blanket of density 128 kg/m$^3$ and of thickness 2.5cm. The maximum operating temperature of the blanket is around 1440$^\circ$C. This blanket is made into circular cross-section and inserted into the aluminium container for providing effective insulation to the mullite tube.

In order to prevent loss of heat, the bottom of the furnace was covered with ceramic brick leaving a small hole to adjust the crucible support. This provision allows vertical movement of the crucible to a position where the spatial temperature distribution inside the crucible is optimal.

1.11.2 Temperature sensors

Temperature of the growth system can be detected by resistance thermometers, thermocouples and pyrometers. Thermocouples are often used depending on the temperature requirements and also any type of thermocouple can be configured to the Eurotherm temperature controller. The thermocouples
Figure 1.8 The schematic diagram of typical furnace employed in the present work
used were Ni:Cr-Ni:Al (K type) of SWG 22. Since the furnace would be operated around 1100 – 1200 °C, K type is preferred rather than Pt-Pt/Rh since it gives higher millivolt signals and more sensitivity. However, an important disadvantage of using the K type thermocouple is that they have to be replaced quite often while the R and S type thermocouples have a longer life. In general, both K and R type thermocouples were used in the present work.

1.11.3 Temperature controllers / programmers

The importance of temperature accuracy in flux growth must be emphasized and use of best possible controller is essential to regulate the temperature of the furnace. In most cases, thyristorised proportional band integral differential (PID) temperature controllers are used for accurate controlling. In the present study a Eurotherm temperature programmer controller of accuracy ± 0.1°C and a very slow cooling rate, has been used. The furnace was powered by phase angle fired thyristor (model 461) and the temperature was regulated with the precise Eurotherm controllers (902P and 818P). It has several salient features such as (i) control accuracy as high as ± 0.1°C, (ii) self tuning of the PID parameters to make it fast adaptable to any kind of furnace and (iii) adaptive tuning facility to monitor load changes if any, and to instantaneously change the PID parameters accordingly. Moreover, easy configurability of different input, output and control parameters make it a versatile instrument. SHIMADEN (FP21 model) temperature programmer controller has also been used.

1.11.4 Crucibles

Some of the basic requirements needed for the crucible to be used for the flux growth are, resistant to corrosion by the solvent, solute and the
atmosphere at the growth temperature, high mechanical strength, good thermal 
shock resistance, ease of shaping and of cleaning, reasonably long life time and 
low price. However, no crucible material is found to be completely suitable for 
growth of high $T_c$ oxide superconductors. Erb et al (1996) have reported that the 
use of BaZrO$_3$ crucible resulted in good quality crystals with very little or no 
contamination. But in most cases recrystallised alumina crucibles were used 
and in the present case Al$_2$O$_3$ crucibles have also been used. Though the 
crystals were found to be contaminated due to the reaction with the crucible, the 
crystals from the center portion and those found in the cavities were free from 
contamination.

1.11.5 Separation of the grown crystals

As the crystallization from the high temperature solution terminates 
with the flux at a temperature above the eutectic point, the grown crystals are 
separated from the solution either by pouring the remaining fluxes from the 
crystals or by dissolving the solidified flux in an appropriate solvent. The 
former case includes decanting of flux through a hot sieve, by tilting or rotating 
the crucible or by sucking the flux at high temperatures. Although, the latter 
procedure produces no harmful effect to the crystal, there is a limitation in 
finding the suitable solvent for the desired flux materials. When a suitable 
leaching agent is not available to selectively dissolve the flux for the 
superconducting materials, the crucible is broken to recover the crystals.

1.12 SUMMARY AND SCOPE OF THE PRESENT WORK

An introduction to high $T_c$ superconductors have been given with 
special emphasis on 1222 type materials. The principle of flux technique and 
aim of the present work is presented in detail.
In view of the scientific and academic interest on 1222 type high $T_c$ superconductors and their increasing demand, the present investigation is aimed at:

i) growing some selective single crystals of 1222 type high $T_c$ superconductors and

ii) studying their characteristics

The study concerned with four 1222 type high $T_c$ superconductors namely NbEu$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O$_{10.5}$, NbGd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O$_{10.5}$, TiEu$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O$_{10.5}$, RuGd$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$O$_{10.5}$ and also synthesis aspects of Sr$_2$GdRuO$_6$ (Sr-2116).