Development of Single Crystal Fibers for Optical, Scintillation and Mechanical Applications

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Introduction

Crystals have fascinated mankind for thousands of years, were they snowflakes, minerals or jewels. For at least 50 years crystals have fascinated engineers as the key materials of modern electronics, optoelectronics and other technical fields of application. The formation of crystal in nature, like snowflakes and minerals, as well as the preparation of the crystals in laboratories and factories for technical applications is called Crystal Growth.

The growth of single crystals is both scientifically and technologically important, and the applications of such crystals today range from electronics to thermal management to synthetic gemstones. Single crystals reveal the fundamental properties of materials, especially properties with directional dependencies, which make crystals unique as compared to ceramics or glasses. These properties are often key to technological applications, as illustrated in the case of the semiconductor silicon. The electronic properties of silicon underlie the vast majority of electronic devices, and today silicon crystals are grown in sizes up to 30cm in diameter with carefully controlled purity.

A single crystal is defined by long-range atomic order extending over many atomic diameters, and having a repetitive structure. As a result, crystals have rigidity, fixed shape, and mechanical strength. In crystals, strong connection between the optical, electrical and mechanical responses with the crystal structure is often observed, and these features are used in many current technologies. Beyond utility, the beauty and mystery of crystals are continuing sources of fascination, and in many cases their growth remains a challenge.

There has been a continuing interest in the development of solid state materials for semiconductor industry, optical communications, medicine, electronic devices and industrial applications in general. Single crystals have played a major role in most
of these applications either in the form of bulk crystals (three dimensional), epitaxial thin films (two dimensional) or fiber crystals (nearly one dimensional).

Two major groups of growth methods are most often employed for single crystals, namely, growth from solution and growth from a melt.

The most frequently used and most important method of producing single crystals of a given material is by solidification of its own melt called ‘crystal growth from the melt‘ or just ‘melt growth‘. Its technical and economic importance is due to the fact that large single crystals (several kilograms up to 300kg) can be grown very efficiently and with a high yield at a relatively high growth rate (several millimeters per hour up to millimeters per minute). This growth rate is not limited by the transport of crystal species but only by the removal of the heat of crystallization. However, this rule holds only in principle because the temperature gradients in the growing crystal may not exceed certain values (depending on the material), since these gradients may cause crystal imperfections (by thermal stress). This requirement makes it necessary to design the thermal boundary conditions very carefully in the corresponding growth apparatus, which is strongly supported by the aid of computer modelling.

In the last decade single crystalline fibers became the subject of increasing interest, because of their remarkable characteristics. Due to large length-to-diameter ratio composed with perfect crystal structure and chemical homogeneity, the mechanical and physical properties approach theoretical values. In this work we are interested in growing single crystal fibers for Laser, optics, non-linear optics and Scintillation applications. Beside that, we are trying to develop new materials that have specific thermo-mechanical properties (in particular low loss angle) to be used as a suspension for the mirror in advanced gravitation waves detector in order to decrease the low thermal noise.

For these applications, it is important that fibers be produced in specific length, diameters and orientations.

In chapter I I will briefly review the principles of crystal growth techniques from the melt and the most famous methods to grow bulk and crystal fibers. I will also discuss why single crystal fibers became the subject of increasing interest. I will summarize the advantages and disadvantages of µ-PD method as preferable tool to grow single crystal fibers.
In chapter 2, I will briefly review the fundamentals of growth dynamics, in particular of the $\mu$-PD method. I will focus on the segregation and axial component distribution that play an important role in the growth by $\mu$-PD method.

In chapter 3, I will review the general theory of rare earth doped materials, their energy level and the energy transfer mechanisms.

In chapter 4, I will overview the different experimental setups we used to obtain the experimental data of this thesis. I will also show the main features of the crystals on which we performed our measurements.

In all the subsequent chapters I will show our growth and study on different crystals. Chapter 5 deals with LiNbO$_3$ single crystal, chapter 6 deals with LiF single crystal, chapter 7 deals with rare earth (RE$^{3+}$) doped Y$_3$Al$_5$O$_{12}$ (YAG) and Lu$_3$Al$_5$O$_{12}$ (LuAG) single crystals, chapter 8 deals with Ce$^{3+}$ doped YAlO$_3$ (YAP) single crystal for scintillation application and finally, chapter 9 deals with pure Si single crystal for Virgo project.

In all of these chapters I will show the growth process, the main problems encountered during the growth of these materials and the potentialities of the method. I will also show the structural measurements that we performed to check the structure, quality and homogeneity of the grown fiber. For the different RE$^{3+}$ doped hosts I will show the spectroscopic performance like absorption, fluorescence and decay time. Special attention to Ce$^{3+}$ doped YAP with scintillation performance is also shown.

Thermo-mechanical properties of grown Si fibers will be shown briefly at room temperature.

I should mention that, some of the measurements that I described in this thesis are performed in collaboration with other groups and universities. When necessary I will mention the group and/or the person that performed the measurement.
Chapter 1

Principles of Crystal Growth
Techniques from the Melt

1.1 Single Crystal Growth from the Melt

Two major groups of growth methods are most often employed for single crystals, namely, growth from solution and growth from a melt. Methods for growth from the melt have been named after those who invented them; e.g., Czochralski, Bridgman-Stockbarger, and Verneuil. All have in common the characteristics that a material of approximately the correct composition is melted congruently, i.e., the same crystalline phase is maintained before and after melting. The melt is then solidified in a carefully controlled fashion to cause the formation of a single crystal. In most crystal growth experiments, this solidification is accomplished using a well oriented seed material of the same crystal composition. Unfortunately, since most interesting materials have high melting temperatures (1500-2400°C), the melt techniques cannot always be useful because many materials decompose or vaporize at such high temperatures. Also, in some cases the melt may be viscous, so that a glass forms instead of a crystal.

In solution growth, the chemical components that form the crystal are dissolved in a liquid medium, or flux, and allowed to crystallize slowly as the temperature drops. According to the solubility of the crystal material, different solution growth techniques are employed, e.g., water solution growth at room temperature, flux growth and hydrothermal techniques. In this last case both high temperature and
pressure are needed. The growth from solution has many advantages, because it used for materials that:

(i) melt non congruently or
(ii) decompose before melting or
(iii) undergo a solid state phase transformation before melting or
(iv) have very high melting point.

Classification is based on the solvent type. The key requirement is a high purity solvent which is insoluble in the crystal.

Melt growth requires significant understanding of the material phase diagram, the cationic make-up of the desired crystal composition, and the high-temperature chemistry of the melt. A lot of work goes into developing these information before a crystal growth technique is selected. These information are often collected by mixing starting materials in the desired proportions, and sintering them both below and above the melting temperature. This very important and extensive work is necessary to develop the relevant growth information on a given crystal composition.

Growth from the melt requires some conditions:

1. The material must melt congruently (no change in composition during melting) e.g. Yttrium Iron garnet (YIG) is grown from solutions because it does not melt congruently.

2. The material must not decompose before melting. e.g. SiC is grown from vapor phase (sublimation-condensation) because it decomposes before melting.

3. The material must not undergo a solid state phase transformation between melting point and room temperature. e.g. SiO₂ is grown from solution (hydrothermal growth) because of a α − β quartz transition at 583°C.

Some advantages characterize growing from melt:

(a) Fast (~cm/hr); growth rate depends on heat transfer (not on mass transfer).
(b) Variety of techniques developed (e.g. crystal pulling and directional and zone solidification).

In the present work we are interested in growth from melt. In the following sections, some techniques of crystal growth from the melt are described.
1.1 Single Crystal Growth from the Melt

1.1.1 The Czochralski Technique

This method was originated by Czochralski in 1917 [2], although it is sometimes named after Kyropoulos, who worked on the technique in 1926. The growth technique and apparatus used are shown in Fig. (1.1).

The Czochralski (CZ) growth apparatus consists on a crucible which contains the charge materials in a protective environment, a heater capable of melting the charge, and a pulling rod positioned axially above the charge. The growth process begins by melting the charge material. A small seed crystal attached to the end of the pulling rod, is then lowered until it is dipped into the melt. The melt temperature is adjusted to form a small meniscus at the end of the seed while it is being rotated slowly. The rotation, which is typically around 10rpm, is necessary to reduce the effects of thermal asymmetry on the crystal and also to generate a desired effective solute redistribution coefficient by mixing the melt. In some cases, the crucible is also rotated to allow for a better melt homogeneity. The temperature is then kept constant and the seed is slowly lifted. Because of the surface tension between the

Figure 1.1: A schematic of a Czochralski growth unit
seed and the melt, a small amount of liquid rises with the seed and crystallizes with the same orientation as the seed. The main advantage of the Czochralski technique over others is the absence of a crystal container. This is particularly significant in the production of dislocation-free crystals because of the lack of stresses, which are normally generated by the mismatch in the thermal expansion coefficients of the container and the crystal. Another advantage of the technique is that the crystal diameter can be controlled, changing the melt temperature and the growth rate. This capability is used not only to produce crystals with large diameters, but also to obtain crystals with few or no dislocations. The latter is accomplished by first reducing the diameter, the procedure is called necking, so that most of the dislocations end at the necking site, followed by increasing the diameter to a desired size. The necking-down technique can also be used to select a particular crystal from a multicrystalline seed.

The criteria that must be fulfilled for successful pulling are:

(i) The crystal material should melt congruently, i.e., the composition should exhibit the same crystal structure before and after melting. If the crystal composition melts incongruently, it dissociates into two or more phases after melting, and growth becomes impractical.

(ii) The melting temperature should be attainable with the heaters available and should be well below the melting temperature of the crucible used for the growth.

(iii) It should be possible to establish a combination of pulling rate and thermal gradients where single crystal material can be formed. The principal advantage of pulling is that growth can be achieved on the seed under conditions of very good control. Good control results from the fact that the seed and grown crystal are visible during growth, and the crystal grower can use visual observation of the growth process to adjust the process to achieve crystal perfection. In addition, growth in any given direction is easily obtained when oriented seeds are employed.

1.1.2 The Bridgman-Stockbarger Technique

In the Bridgman growth technique, which is also called the unidirectional solidification method or vertical gradient freezing (VGF), the charge materials are loaded into a crucible, melted, and resolidified by the translation of a positive temperature gradient across the sample.
The gradient translation is accomplished by moving the crucible, as shown in Fig. (1.2), from the hot zone of the furnace towards the cold zone. Alternatively, the crucible can be kept stationary, and the furnace is allowed to translate across the sample. It is also possible to maintain both crucible and furnace stationary, and translate the gradient by reducing the furnace temperature. The latter technique, also referred to as the gradient freeze method, requires a multizone furnace in order to translate the temperature profile in a controlled and steady manner. The orientation of the crystal during Bridgman growth can be selected by using a seed crystal with the desired orientation at the cold end of the crucible. During the initial melting of the charge material, a small portion of the seed is also melted to allow for better adhesion between the seed and the melt. Another technique to produce single crystals with preferred orientation is to allow the growth to initiate in a narrowly confined region at the cold end of crucible. If the confined region is long enough, a single orientation could emerge from the region because of the preferential growth in certain directions. This technique is best suited for low melting temperature materials, and can be readily scaled up in size; fluorite crystals over 30 cm across are...
produced commercially (CaF$_2$, NaCl, AgCl, CaWO$_4$). Recently, this technique has also been employed for higher melting temperature ferroelectrics, such as tungsten bronze and perovskite with growth temperatures in the range 1300-1550°C.

### 1.1.3 The Verneuil Technique

This technique is particularly useful for high melting temperature materials, and has been widely used to grow, for example, synthetic gemstone crystals based on corundum (Al$_2$O$_3$).

If this material is pure, it is called white sapphire; if doped with chromium oxide, its color becomes red and is called ruby; if it exhibits other colors, it is termed sapphire again. This technique is also called flame fusion. In this process, single crystals have also been grown by the directional solidification procedure using a continuous feeding mechanism. As shown in Fig. 1.3, the flame is made to impinge on a pedestal, where a small pile of partly fused material quickly builds up. As the pile rises, it reaches into the hotter part of the flame, so that the tip becomes completely molten. The molten region increases in size and starts to solidify at the lower end. As more powder arrives, the solidified region broadens into a crystal with a molten cap on it.
At this point, lowering of the pedestal is begun and the crystal continues to grow in length only.

### 1.2 Why Single Crystal Fiber?

Interest in the growth of crystal fibers has been stimulated by their potential for use in a variety of fiber optics applications such as laser sources, electrooptic modulators, transmission line, remote sensors, etc. Single crystalline fibers have become the subject of intense study in recent years because of their remarkable characteristics. They have unique properties that have attracted some attention for applications in optical and electronic devices [1]. Usually, the word Fiber is used to indicate any materials in elongated form having a small diameter in the region from \(\mu\)m to mm, i.e. nearly one-dimensional. The term Fiber describes all types of materials that fit the definition, i.e. filaments, wires and whiskers. The scientific approach to the fiber growth process immediately brought to light its specific fundamental qualities too. Because of the very small crystal diameter only scarce values or even complete absence of dislocations were observed. Inoue and Komatsu[4] first showed this tendency in thin KCl rods and attributed this behavior to the drastically reduced thermo-mechanical stress. Moreover, in fibers the best conditions for the outgrowth of defects are fulfilled even if the glide directions are slightly tilted from the growth axis. Further, fibers grow usually by the diffusion controlled growth mode. The small melt zone and high growth rates produce an effective distribution coefficient near unity leading, as a result, to uniform axial component distribution. This fact makes also possible to study phase relations with incongruent melting behavior by using of a feeding melt reservoir with the same composition as the solid to be expected. Also we can apply the fiber growth method for fundamental investigations of the crystallization specifics of new multi-component materials. First the growth kinetics, composition stability and crystallinity can be tested in a low cost, material and time saving fiber pulling apparatus before the material is recommended (or rejected) for Czochralski bulk growth. Such approach is very effective for materials research, especially, in university and institute laboratories. Last, but not least, we can say that the growth of thin elongated crystals can result in new unusual properties, which may find wide application in fabrication of miniature or complex shaped devices thanks also to the ease of processing.
1.3 Methods for Single Crystal Fiber Growth

Basically, there are two ways to form single crystal fibers from the melt:
(i) the unidirectional solidification or micro zone melting in a capillary tube.
(ii) the containerless pulling of a filament from a melt meniscus. However, despite of a good diameter constancy, usually, case (i) is not used for fiber growth due to the limited heater length and the complicated fiber exposition after the growth. Nevertheless, Feigelson found few papers dealing with solidification experiments of low melting oxides and semiconductors in thin tubes. It is common practice to pull crystalline fibers from a free melt meniscus (case ii). One has to note, however, that it is not possible to grow crystals with very small diameters from a conventional Czochralski crucible, not only because of the acting convective and temperature oscillations in the melt affecting the meniscus demolition, but mainly due to the inherent capillary instability, typical for small ratios between crystal and crucible radius, as we will see in the next chapter.

Such crystal shapes, i.e. single crystal fibers, are possible to grow from melt, solution and vapor. For many applications like optical applications, it is important that fiber are produced in specific length, diameters and orientations. While there are wide varieties of techniques, which can be used to produce single crystal fiber, not all of them allow to control these parameters sufficiently to be useful. For this reason vapour and solution growth methods are generally undesirable.

There are several methods for growing crystal fibers, such as the edge-defined film fed growth (EFG), Laser heated pedestal growth (LHPG), etc. The choice of the method depends on the physical and chemical properties of the material to be grown. Clearly some methods or their adaptations are more versatile than others.

We can classify the melt growth fiber techniques in the following two main categories:
(1) micro floating zone methods, and
(2) pulling techniques from a shaper (i.e. die).

Whereas the methods of (1) vary by different principles of heating and heat focusing (laser beam, lamp, furnace) as well as floating directions (up-or downward) the variants of (2) differ by up-or downward pulling (drawing) from a non-wetting or wetting shaper. In the following these versions will be discussed briefly.
1.3 Methods for Single Crystal Fiber Growth

1.3.1 The Floating Zone Techniques

The functioning principle of diameter reduction of the growing crystal during the float-zone process is known from the first pedestal growth experiments of Poplawsky \[6\] who provided a focussed energy by an arc image furnace. On the basis of these experiences the laser heated pedestal growth (LHPG) method was developed first by Haggerty in 1972 \[5\]. This technique for crystal growth has been widely used since its first application to silicon in order to avoid container contamination. Fig.1.4 demonstrates the miniature pedestal growth of a single crystal fiber. A tightly focused \(\text{CO}_2\) laser, emitting 10.6 \(\mu\)m radiation is the heat source used to melt the refractory material. The source rod may be fabricated from a single crystal, polycrystalline, sintered or pressured powder material. A seed rod is used to determine the crystallographic orientation of the fiber to be grown. Growth proceeds by simultaneous upward (or downward) translation of the seed and source rods with the molten zone positioned between them. The laser focal spot, and consequently the zone height remains fixed during fiber growth. To achieve an axially symmetrical irradiance a reflaxicon as optical element was incorporated in the laser beam which consists of an inner cone surrounded by a larger coaxial one. The combination of
the reflaxicon with a parabolic mirror produces a minimum spot size of 30 µm. For the growth of oxide fibers, having a high absorption at 10.6 µm (the absorption coefficient of sapphire close to its melting point is 4000 cm$^{-1}$ [7], for example), it takes about 30 - 60 W to melt a rod of about 1 mm in diameter. Very high axial temperature gradients in the range of 100 K cm$^{-1}$ have been measured along the growth axis for oxide fibers [8][9]. The fiber-to-source rod diameter ratio is set by the mass balance to be the square root of the source rod-to-fiber translation rate [Eq.2.1]. Typical fiber growth rates range from 1 to 10 mm min$^{-1}$ with diameter reductions of approximately three. Such system can produce fibers 3 - 1700 µm in diameter and in length up to 20 cm. When the source rod is less than 100 mm, however, the power required to form and maintain the molten zone is so small that is difficult to maintain laser stability. Using an automated fiber-diameter control system diameter variations of less than 0.1 % have been achieved [11].

The float zone technique or LHPG technique have several advantages over other growth techniques, the most important being that the molten liquid does not come in contact with a container. The absence of the container also precludes stresses and defects caused by the thermal expansion coefficient mismatch between the crystal and container, as is the case for the Bridgman growth. Because of these advantages, the technique has been used for highly reactive materials, semiconductors, intermetallic and inorganic compounds, refractory materials, and oxides. Many heating methods have been used to form the molten zone. Examples include induction heating for silicon, optical heating for tellurium, electron beam heating for refractory metals, laser heating for $Al_2O_3$ and immersed heaters for $NaNO_3$.

Although the float zone technique seems to be superior to other growth techniques, it is only used in a small percentage of commercially produced crystals, owing to the difficulties in maintaining a stable molten zone. The size of the molten zone is limited because of the hydrostatic forces exerted by the column of the liquid held between the two solids. The maximum height of the liquid zone that can be supported by its own surface tension increases linearly with diameter for small diameters and approaches a limiting value for large diameters. The maximum allowable zone height has been calculated to be proportional to the square root of surface tension of the melt divided by its density and the gravitational acceleration. Another difficulty in growing large-diameter crystals is to melt through the entire cross-section and to maintain planar front at both melting and freezing interfaces. To overcome
these difficulties, a radio-frequency induction coil is used to constrict the liquid for growing large silicon single crystals. Another limitation of the float zone technique is the volatilization of the higher vapor pressure elements for growth of alloys or compound semiconductors such as GaAs and GaSb.

1.3.2 Pulling Techniques from a Die

(A)- Upward pulling from a meniscus shaper

- Edge defined Film-fed Growth (EFG)

Today, Edge defined Film-fed Growth (EFG) method with pulling upward direction is scarcely used for growing of fiber crystals. In the EFG technique, crystals are grown from a melt film formed on the top of a capillary die (Fig. 1.5). The melt rises to the crystallization front within the capillary channel. It is ideal for producing crystals with a small square cross-section. Sapphire crystals can be grown in an automated way with weight control [10].

Automated computer systems provide in situ crystal quality control as well as crystal shape control, which allow an increase in the output of high-quality crystals and the expansion of the areas of applications of sapphire crystals as
constructive and optical material. The technique of growing shaped sapphire crystals is well developed. Ribbons up to 150 mm in width, tubes up to 85 mm in diameter, fibers, rods of various cross-sections, rods with capillary channels, etc., have been grown by the EFG technique.

- **Micro-Czochralski (µ-Cz)**

Czochralski method could not be applied to the growth of single crystal fibers successfully because of thermal convection. The thermal convection is inevitable in heated liquid and causes a momentary temperature fluctuation in the crucible melt as well as a time lag in adjusting the temperature. In order to grow a crystal having a small diameter by Czochralski technique, the melt temperature in a small area comparable to the crystal diameter must be precisely controlled. Such a severe condition can not be achieved in Czochralski using a crucible melt because of thermal convection. In order to solve the above mentioned difficulties in the conventional Czochralski technique for the fiber growth, Ohnishi et. al. have contrived to miniaturize it so as to suppress the thermal convection in the melt. For this purpose, they employed a melt which wets the surface of a tiny heater, in place of a melt in a crucible, as shown in Fig. (1.6). The melt covering the heater surface is small in volume as
well as in thickness, which makes it effective in suppressing the thermal convection in the melt. In addition, the close contact between the melt and the heater improves the controllability of the melt temperature. At the same time a micro-protuberance made on the top surface of the heater brings additional advantages.

A seed crystal which is contacting the melt tends to be positioned at the top of this protuberance when the crystal is pulled. The melt covering the heater surface gathers around the protuberance because of the wetting action of the melt, which enhance local cooling through thermal emission from the melt surface contacting the protuberance and/or a local decrease in electrical resistivity around this point.

(B)- Pulling down from a meniscus shaper

When growing from a meniscus shaper, the fiber material must be not only stable on melting, but also non-reactive with the capillary tube material, and have a thermal expansion which will not lead to significant stress build-up or shrinkage. Recently, the micro pulling down (μ-PD) technique developed by Fukuda's laboratory in Japan [13] has shown promise in producing single crystal fiber with good diameter control and concentration homogeneity.

From many researches [13, 14] the following features of μ-PD were discovered:

- Because of high temperature gradient and small diameter of the fiber it is possible to use a very high growth speed without causing constitutional super-cooling, which leads to interface breakdown.
- Lower thermal distortion decreases the density of the dislocations or cracks.
- Melt convection is suppressed by the use of a narrow nozzle at the bottom of the crucible, due to the capillary effect. This allows growth from incongruent melt because the effective segregation coefficient is near unity, as we will discuss later.
- It is easy to control the crystal shape and composition.
- Crystals of both congruent and incongruent melting compounds can be grown.
- Fast, simple, inexpensive and valuable tool for surveying new materials. In Table [1.1], I summarized the advantages and disadvantages of μ-PD. Based on these characteristics, the fiber growth by μ-PD method is especially useful for fundamental research of the crystallization specifics of new multi-component materials. Basic
Table 1.1: Advantages and disadvantages of $\mu$-PD

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low segregation ($K \approx 1$)</td>
<td>Vibrations and seed shifting</td>
</tr>
<tr>
<td>High chemical uniformity and Melt Homogeneity</td>
<td>Low volume productivity (mass)</td>
</tr>
<tr>
<td>Crystal dimensions (Long length)</td>
<td>Weight control is not applicable</td>
</tr>
<tr>
<td>Low cost method for research</td>
<td>Currently only visual control</td>
</tr>
<tr>
<td>High growth rate (mm/min)</td>
<td>Crucible is necessary</td>
</tr>
<tr>
<td>Pre-sintering is not necessary</td>
<td>Melt zone stability (Gravity)</td>
</tr>
<tr>
<td>Crystal shaping and Continuous charge are possible</td>
<td>-</td>
</tr>
<tr>
<td>Easy crucible cleaning (Gravity)</td>
<td>-</td>
</tr>
</tbody>
</table>

crystallization parameters such as the growth kinetics and compositional homogeneity can be made clear before undertaking CZ bulk growth. The most important feature of $\mu$-PD method is the high temperature gradient in the vicinity of the solid-liquid interface, which brings high growth stability and homogeneous distribution of the dopant inside the crystal, and can lead to increased dopant incorporation and the formation of potentially interesting compounds. The high temperature gradient is useful in avoiding constitutional super-cooling that is usually a serious problem when the growth rate becomes very high. Therefore in a CZ technique the maximum growth rate that can be reached is only a few mm/h. On the contrary, $\mu$-PD crystals can be grown at over 600 mm/h, so it is possible to obtain good quality crystals in a short time. Basically the $\mu$-PD method involves downward pulling of a fiber crystal through a micro nozzle made at the bottom of the crucible as shown in Fig 1.7.

The method allows the growth of fiber-like samples with diameters in the range 0.15 mm to 5 mm at widely variable pulling rate. The melt is placed in crucibles made of materials stable at high temperatures, corresponding to the melting point of the target crystalline material. Platinum, Platinum/Rhodium, Iridium and Molybdenum are the most popular crucible materials used in $\mu$-PD systems. The crucibles are heated using a radio-frequency (RF) generator or a resistive heater. At the first stage the seed crystal fiber produced from previous experiment or cut from bulk crystal of the corresponding material is immersed into the crucible orifice (some times called the nozzle). Therefore the seed is pulled down, together with the grown fiber, using a precise pulling mechanism. Normally the surface forces do not allow
the melt to separate from the fiber material. Therefore the melt is passed through the nozzle made in the bottom of the crucible. Application of an after heater allows adjustment of the appropriate temperature gradient under the crucible and therefore regulation of the position of the solid-liquid interface in the vicinity of the crucible tip. The shape and location of the growth interface is one of the most important parameters determining the quality and uniformity of the resulting crystal. Therefore special attention is normally paid to monitor and detect the spatial distribution of the temperature gradient in the vicinity of the phase boundary. CCD camera and monitor are considered to be very good tools to view the solid-liquid interface and the meniscus region.
Chapter 2

Fundamentals of Growth
Dynamics of the $\mu$-PD Method

The quality of single crystals strongly depends on the growth conditions. The major imperfections encountered during growth can be summarized as follows:

(i) *Compositional inhomogeneities*, which may arise when the composition of the melt and crystal are different on a micro and macro scale. Micro-inhomogeneity, or microsegregation as it is commonly called, is caused by variations in the local growth rate and/or composition at the crystal-melt interface. Macrosegregation, on the other hand, relates to macroscopic inhomogeneities in the average concentration along the lateral or longitudinal direction of the crystal.

(ii) *Structural inhomogeneities*, which can be caused by periodic and/or random variations in the local growth rate and effective distribution coefficient at the interface. Structural defects found in crystals include lattice vacancies and their aggregates, interstitial or substitutional defects, anti-site defects in compound semiconductors, dislocations, arrays of dislocations forming lineage and sub-boundaries, twins, stacking faults, and inclusions.

(iii) *Nonstoichiometry*, which may occur in compound crystals such as GaAs or InP by the loss of volatile elements and deviation of the melt composition from the stoichiometric ratio. It should be noted that in some cases the compound single crystals may be intentionally grown in off-stoichiometric compositions such as arsenic-rich GaAs to impart specific electrical characteristics to the crystal.

(iv) *Contamination and impurity* pick-up from the crucible wall and/or interaction
of the melt with its surrounding environment. It should be noted that the interaction between the melt and the crucible may be caused by a third component, such as residual oxygen in the atmosphere, or gases adsorbed on the walls of the crystallization chamber or the initial charge.

Basic considerations, showing the characteristics of fiber growth were discussed firstly by Feigelson in 1986 [5]. He classified in i) conservation of mass, ii) conservation of energy, and iii) shape stability. Some considerations on dissociation of incongruent melts and crystal defects were added. I will proceed similarly, but I will supply the important phenomenon of segregation.

2.1 Conservation of Mass

The dimensional stability of a growing fiber from a shaped meniscus or pedestal requires that the zone length and volume is kept constant. Neglecting the density difference between melt and crystal the condition for steady-state growth of a fiber with constant diameter is:

$$R^2 v = R_{sh}^2 v_{sh}$$  \hspace{1cm} (2.1)

with $R$, $R_{sh}$ the radius of crystal and shaper (i.e. capillary), $v$, $v_{sh}$ the pulling rate and mean flow velocity in the capillary channel (i.e. push rate of the feed rod for LHPG), respectively. Velocity perturbation easily breaks the mass conservation condition yielding fluctuations of diameter.

2.2 Balance of Heat Transfer

At the crystallization front the heat-balance equation should be satisfied

$$\rho_s \Delta H_f v + K_L G_L = K_s G_s$$  \hspace{1cm} (2.2)

where $\rho_s$ is the density of the solid, $\Delta H_f$ the latent heat of fusion, $K_L$ and $K_s$ the thermal conductivities of the liquid and solid phases, respectively, $G_S$ the temperature gradient in the solid while $G_L$ the temperature gradient in liquid phases at the crystallization front (meniscus height). Numerous papers deal with the determination of the values $G_L$ and $G_S$ by measurements [14,15]. The very large axial temperature gradients, $G_S$, which increase with decreasing fiber diameter, as
2.2 Balance of Heat Transfer

Figure 2.1: Calibration Curve of measured temperature gradients $G_S$ and $G_L$ in LHPG LiNbO$_3$ fibers versus fiber diameter. After Ref. [9]

shown in Fig. (2.1), are responsible for the very high fiber pulling rates used [Eq(2.2)].

A characteristic length $Z = Z_d$ (decay length) along the fiber axis over which the temperature drops to the surrounding value was formulated by Korpela et al.[16] considering the coupled radiation-conduction heat transfer

$$Z_d = R[-\frac{1}{2}P_e + (\frac{1}{4}P_e^2 + 2B_i + 16\sigma_{St}n^2 T_s^3 K_pR^2/K)^{1/2}]^{-1}$$ (2.3)

where $R$ is the crystal radius, $P_e$ is Péclet number (= r c v R / k), r is reflectivity, c is specific heat, v is pulling velocity, k is thermal conductivity, $B_i$ is Biot number (= h R / k), h is convective heat transfer coefficient, $\sigma_{St}$ is Stefan-Boltzmann constant, n is index of refraction, $T_s$ is surrounding temperature and $K_p$ is Planck mean absorption coefficient. As it can be seen from Eq. (2.3), $Z_d$ increases as the Biot and Péclet numbers (i.e. fiber diameters) become smaller and the absorptive of the fiber lower. Thus, low absorptivity (oxides) prevents the cooling of the fiber by radiation. But it doesn’t mean that in materials with high absorbing power (semiconductors, metals) a smaller decay has to be expected. In this case the higher thermal conductivity k affects the value of $Z_d$ markedly. The authors showed that for very thin fibers neither the emissivity of the phase front, nor the reflectivity of the surface are of evident importance. Also from Eq. (2.3) the proportional influence of the pulling velocity v (i.e. cooling rate), involved in the Péclet number, can be determined.
2.3 Capillary Stability

Fig. (2.2) shows the principles of capillary shaping at different fiber growth methods. It can be seen that, a uniform cross section will be grown if the growth angle $\phi$ (the angle between the meniscus and the growth axis) is constant and equals $\phi_o$ (a material constant) which forms by the thermodynamic equilibrium condition at the three-phase interface line and, hence, does not depends on the growth parameters like pulling velocity, diameter or zone height. $\phi_o$ differs from zero and yields $11^\circ$ for Si ($<111>$ growth direction), $8^\circ$ for YAG ($<100>$ growth direction) [5] and $17^\circ$ for sapphire ($<0001>$ growth direction) [17]. Deviations of the actual growth angle $\phi$ from $\phi_o$ by perturbations of the meniscus height or radius lead to non-stationary variations of the fiber diameter in agreement with:

$$\frac{dR}{dt} = v \tan(\phi - \phi_o) \neq 0$$  \hspace{1cm} (2.4)

Note that Shimamura et al. [18] during pulling down growth of silicon fibers found that in this case a somewhat different growth angle $\phi$ of $9^\circ$ is required (instead of $\phi = \phi_o = 11^\circ$) to obtain steady state with constant fiber diameter, as shown in Fig. (2.3). They concluded that this effect is due to the gravity.
Kim et al. [19] studied the maximum stable zone length at float-zone growth of small diameter sapphire and silicon crystals (250 - 1500 \( \mu \text{m} \)) under the condition that the crystal radius equals the feed rod radius (\( R = R_0 \)). They showed that at such dimensions, where the Bond numbers \( B \) are much smaller than unity, the maximum stable zone length \( l_{\text{max}} \) and the zone stability are controlled primarily by the surface tension,

\[
B = \frac{\rho gd^2}{4\gamma} \ll 1 \quad (2.5)
\]

with \( \rho \) the density of the melt, \( g \) the gravity, \( d \) the diameter and \( \gamma \) the surface tension.

This result is in good agreement with the theory according to which \( l_{\text{max}} \) yields

\[
l_{\text{max}} = \pi d \quad (R = R_0) \quad (2.6)
\]

For the pedestal growth technique (LHPG)\[5\], where \( R < R_0 \), the theoretical capillary stability is kept until \( R > R_0 / 2 \).

In the practical case of fiber growth by LHPG even a slightly higher reduction ratio in the range from 1/2 to 1/3 can be used. A stable LHPG growth of oxides occurs
for zone length of

$$l_{\text{max}} = \frac{3}{2}(R + R_o)$$

(2.7)

Recently Young and Heminger [20] presented a model of the time-depending behaviour of a LHPG arrangement for a feed-to-crystal reduction ratio of 2 after which the change and distribution decay of the fiber diameter depend on the perturbation levels of the pulling rate, feed velocity and heating temperature as well as on coupled mechanisms very sensitively. They found that the material parameters, such as Peclet number, Stefan number and density ratio between solid and melt, play an important role in setting the response of the fiber radius too. Moreover, they supposed that the oscillatory Marangoni convection in the LHPG zone could set vibrating the growth angle, leading to diameter fluctuations of the growing fiber.

For the case of fiber drawing from a non-wetting die the maximal meniscus height $h_{\text{max}}$ can be determined as [21]:

$$h_{\text{max}} \approx R_{sh} = \frac{2\gamma}{P}$$

(2.8)

with P the mechanical pressure on the die (or hydrostatic pressure of the surrounded melt).

For the edge-defined growth from a wetting die, also applicable for the case of $\mu$-PD of Si from a graphite nozzle, the relationship between meniscus height and crystal radius is given by the equation [21]:

$$h_{\text{max}} = \cos \phi_o \left[ \cosh^{-1} \left( \frac{R_{sh}}{R \cos \phi_o} \right) - \cosh^{-1} \left( \frac{1}{\cos \phi_o} \right) \right]$$

(2.9)

($\mu$-PD and EFG condition) Schafer et al. [22] found a good agreement between Eq.(2.9) and experimental meniscus heights at the $\mu$-PD growth of $Si_{1-x}Ge_x$ fibers. Capillary stable crystals with constant diameter $d$ in the range $0.5d_{sh} < d < 0.7d_{sh}$ were grown without special diameter-control system.

### 2.4 Segregation and Axial Component Distribution

In general, the fiber growth techniques from the melt imply quite favorable conditions for axial homogeneous component distribution like high pulling rate, small solidifying volume and small melt zones. Additionally, the high axial temperature
2.4 Segregation and Axial Component Distribution

gradient and nearly undirected heat flow ensure the morphological stability of the growing interface.

Control of dopant and impurities in the grown crystal is important. The concentration of dopant different in crystal ($C_s$) than liquid ($C_o$, sometimes called $C_L$), the ratio between two concentrations is defined as segregation coefficient ($K_o$), where $K_o = C_s/C_o$. This causes segregation phenomena during melt growth. Normally $K$ in not unity so that either more constituent is incorporated ($K > 1$) or less constituent than in the growth melt is built into the crystal ($K < 1$). The case of $K = 1$ could be achieved, theoretically, in equilibrium or in quasi diffusionless growth, at very high solidification rates. These can not be applied in bulk crystal growth, but might be acceptable in certain cases of low dimensional growth. With $\mu$-PD method we can achieve $K = 1$ easily since it has high pulling rate and the fiber is nearly one dimensional.

As the growth proceeds, if $K$ is not strictly equal to unity, the concentration of the dopants in the melt changes, therefore $C_o$ tends to change. In particular $C_o$ decreases for $K > 1$, and $C_o$ increase for $K < 1$, so that the concentration $C_s$ in the solid along the fiber axis continuously changes. This causes an inherent concentration gradient in the crystal. The concentration of impurities in the solid after solidifying a fraction weight of ($g$) is given in terms of effective segregation coefficient $K_{eff}$ by the equation of Pfann \[^{23}\] for complete mixing:

$$\frac{C_s}{C_o} = K_{eff}(1-g)^{K_{eff}-1}$$  \hspace{1cm} (2.10)

During an actual freezing process the solute is rejected ($K_o < 1$) or preferentially absorbed ($K_o > 1$) by the propagating solid-liquid interface, forming an enriched or depleted solute boundary layer in front of it. The width, $\delta$, of this boundary layer is determined by the growth rate, $v$, and by the diffusive and convective species transport in the melt which is very often difficult to predict. A very popular model, commonly used in melt growth studies, was introduced by Burton, Prim, and Slichter (BPS) in 1953 \[^{23}\] for the steady state of segregation:

$$K_{eff} = \frac{K_o}{K_o + (1 - K_o) \exp(-v\delta/D)}$$  \hspace{1cm} (2.11)

where, $v$ is the growth velocity, $\delta$ is the thickness of the solute borderline and D is the Diffusion coefficient of the melt.
Figure 2.4: Mass Transfer at Solid-Liquid Interface and $K_{\text{eff}}$ for three growth situations according to Eq. (2.11)

It follows that $K_{\text{eff}}$ equals unity at high growth rates or/and motionless melts (i.e., high values of $\delta$). In such cases a high uniformity of the macroscopic distribution within the crystal can be reached. If the melt is stirred, however, the boundary layer is reduced by the melt flow ($\delta \to 0$) and $K_{\text{eff}}$ equals $K_o$. In this case the axial distribution of the solute is typically nonuniform. These extreme cases of axial solute distribution can be described by the equation of Pfann [23] for complete mixing.

In normal crystal growth, there is neither the case of high growth rate and $K_{\text{eff}} = 1$ nor we are near equilibrium and $K_{\text{eff}} = K_o$. Fig. (2.4) shows the situations at the crystal-liquid interface for the three cases of equilibrium, for the steady state normal crystal growth, and for fast diffusionless solidification. Also the concentrations in the solid and in the liquid with the diffusion boundary layers are shown. Equilibrium
can be achieved by complete mixing and/or with very low growth rates \((v \to 0)\). In this case \(K_{\text{eff}}\) approaches \(K_o\) \((K_{\text{eff}} \to K_o)\).

In the real crystal growth process the effective distribution coefficient \(K_{\text{eff}}\) lies between the equilibrium distribution coefficient \(K_o\) and 1 and is dependent on the diffusion boundary layer \(\delta\) and the growth rate \(v\).

In very fast solidification (diffusionless), \(K_{\text{eff}}\) approaches unity. In this case the starting material is completely molten and mixed. Thus, no special measures of homogenization are required if the composition is scaled exactly before the melting process. Further, the volume ratio of the bulk melt to growing single crystal fiber is very large compared to LHPG so that, the solute concentration change in the bulk melt is very small for a considerable length of the fiber. A quasi-diffusion controlled regime can be obtained if the capillary of the feeding nozzle is thin and long enough to satisfy the ratio \(v_{\text{cap}} \gg D/L_{\text{cap}}\) \((v_{\text{cap}} = \text{melt speed in the capillary} \approx \text{crystal pulling speed} v_{\text{cry}} = v, D = \text{diffusion coefficient of the given solvent in the melt}, L_{\text{cap}} = \text{capillary length})\), well-known from the double-crucible Czochralski method. The characteristics of axial distribution in fibers grown by the \(\mu\)-PD method are analyzed by Uda et al.\[24\] in detail. The solute diffusion boundary volume was differentiated into the molten zone (I) next to the interface and the capillary zone (II) leading to the bulk melt, as shown in Fig. (2.5). Solving the steady-state situation for both zones the distribution curves of Ge in the model system \(Si_{1-x}Ge_x\) in dependence on the crystal-to-capillarity diameter \(d_{\text{cry}}/d_{\text{cap}}\) and growth rates were obtained as
Figure 2.6: calculated curves of steady-state Ge distribution in zone I and II of Fig. 2.5(a) at various crystallization $v_{cry}$ rates for constant $d_{cry}/d_{cap} (= 1.6)$ and (b) various $d_{cry}/d_{cap}$ for constant $v_{cry} (= 5 \text{ cm/h})$

shown in Figs. (2.6 a and b).

As can be seen, there are deflections at the interface between zones I and II the degree of which depends on the growth speed and capillary diameter. The functions clearly show that at pulling rates $\geq 2 \text{ cm h}^{-1}$ the condition for a steady-state growth with effective segregation coefficient $K_{eff}=1$, i.e. high axial composition homogeneity, are fulfilled.
Chapter 3

Theoretical Background of Rare Earth doped Materials

Rare-earth doped materials have been extensively studied since the beginning of the last century because of their peculiar properties. The interest for the study of those ions is historically related to their rather surprising narrow absorption and emission bands. After the discovery of the laser action in the early 60s, rare-earth (RE$^{3+}$) doped solids have sparked great interest for many reasons. The complexities of compressed gases, circulating liquid dyes, etc. are eliminated by utilizing these materials. Currently there are large spectral gaps between existing laser sources. Laser dyes have helped to bridge these gaps but can be messy, short-lived, and difficult to find in the infrared (IR). By varying dopant, dopant concentration, co-dopants, and lattices, solid state materials are tunable in both a fine and coarse sense.

The most important features of rare earth ions in solids will be described in this chapter and we will introduce the theory of energy transfer in rare earth doped crystals. Then we will show the derivation of the effective cross-sections using the $\beta - \tau$ method.

All the results regarding the general features of rare earth ions and theory of the crystalline field are based on works [25]-[26].
3.1 Rare Earths

Rare earths are elements with atomical number $Z$ between 58 (cerium) and 71 (lutetium) that have very similar chemical properties. The interest for the study of the triple ionized ions of these elements goes back to the discovery of narrow absorption and emission bands, rather surprising if compared to the large bands arising from the doping with transition metals. Rare earth doped laser materials are generically composed of a large band gap ($E_g > 5$ eV) inert host crystal that is substitutionally doped with one (or more) kind of ions. A trivalent lanthanide has the electronic configuration of Xenon (1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$3d$^{10}$4s$^2$4p$^6$4d$^{10}$5s$^2$5p$^6$), plus two electrons in the 6s state, a partially filled 4f shell, and another electron is occasionally found in the 5d$^1$ state. These elements are chemically similar to Yttrium ([Xe]4d$^1$5s$^2$) and Lanthanum ([Xe]5d$^1$6s$^2$) and can substitutionally replace these elements in materials. The triply ionized state is dominant in crystals, although some can be found in the doubly ionized state (especially Eu, Sm, Yb) and seldom in the four-times ionized state (in particular Ce, Tb) under proper conditions.

3.2 Rare Earth Energy Levels

The triple ionized state occurs when the 6s$^2$ electrons and another one coming from the 5d or 4f shells form bonds with the neighboring fluorine or oxygen atoms. The remaining 4f electrons are shielded from the surrounding crystal environment by the filled 5s and 5p shells, that have a larger spatial extension with spherical symmetry; at the first order of perturbation theory the screening can be considered as their only effect. For this reason the rare earth ion energy levels are calculated taking into account only the interaction among the electrons in the 4f shell.

3.2.1 Free Ion Case

For the free ion case the system is usually described by a Hamiltonian operator that can be factorized in a part containing the angular dependence which holds information regarding the number of levels, their arrangement and the selection rules, the remaining part can be written as follows (neglecting the exchange-correlation
3.2 Rare Earth Energy Levels

terms):

\[ \mathcal{H} = T + V_{en} + V_{ee} + V_{so} = \]
\[ = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z e^2}{r_i} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \zeta(r_i) \mathbf{s}_i \cdot \mathbf{l}_i \]  
(3.1)

where \( e \) and \( m \) are the electron charge and mass respectively, \( \hbar \) is the reduced Plank constant, \( N \) is the total number of electrons in the incomplete shell, \( r_i \) is the radial coordinate of the \( i \)-th electron, \( r_{ij} \) is the relative position of the electron \( i \) respect to the electron \( j \), \( \mathbf{s}_i \) and \( \mathbf{l}_i \) are the spin and the orbital momentum for the \( i \)-th electron and \( \zeta \) is the spin-orbit interaction constant. The first three terms in Eq. (3.1) represents the kinetic energy (\( T \)), the electrostatic interaction between the electrons and the nucleus (\( V_{en} \)) and between each couple of electrons (\( V_{ee} \)) and the fourth term is the spin-orbit interaction (\( V_{so} \)).

It is also possible to introduce the so called central field approximation, described by the following hamiltonian operator:

\[ \mathcal{H}_{cf} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] \]  
(3.2)

with \( U \) representing the central field potential, that includes \( V_{en} \) and the spherical symmetric part of \( V_{ee} \). Such approximation assumes that each electron is moving independently in a potential of the form \( -U(r_i)/e \).

The corresponding Schrödinger equation reads \( \mathcal{H}_{cf} \Psi = E \Psi \). A solution can be of the type:

\[ \Psi = \prod_{i=1}^{N} \Psi^i \quad \text{with} \quad E = \sum_{i=1}^{N} E^i \]  
(3.3)

where \( \Psi^i \) and \( E^i \) the eigenfunction and eigenvalues of the one-electron problem. Being all the terms in Eq. (3.2) spherical symmetric, the degeneracy of the 4f electronic configuration (equal to \( \binom{2(2l+1)}{n} = \binom{14}{n} \)) can not be removed. The solution of the equation is the same as for the hydrogen atom (with the potential \( -U(r_i)/e \) instead of \( -e^2/r \)):

\[ \Psi(k_i = (r_i, \theta_i, \varphi_i)) = \frac{1}{r} R_{nl}(r_i) Y_{l}^{mi}(\theta_i, \varphi_i) \]  
(3.4)

where \( Y_{l}^{mi}(\theta_i, \varphi_i) \) are the spherical harmonic functions and \( R_{nl}(r_i) \) the radial functions. Due to the Pauli exclusion principle, the global eigenfunction must be anti-
symmetric, therefore it assumes the characteristic form:

$$\Psi(k_1k_2...k_N) = \frac{1}{\sqrt{N!}} \sum_{i=1}^{N!} (-1)^{P_i} \Psi(k_1)\Psi(k_2)...\Psi(k_N)$$  \hspace{1cm} (3.5)$$

where the sum extends to all the $N!$ permutation $P_i$ of the electronic coordinates, and $(-1)^{P_i}$ equals to ±1 for even or odd permutations, respectively. At this level the principal quantum number $n$, the orbital angular momentum $l$ and its component along the quantization axis $m_l$ are good quantum numbers.

It is clear that a single electron representation could not describe the structure of the rare earth energy levels; the problem is solved when the perturbation potential $V = H - H_{cf}$ is introduced. This potential splits the highly degenerated free ion states, and the energy levels can, in principle, be found calculating the matrix elements of $V$: unfortunately such an approach assumes a large amount of calculations and fails to solve the problem of labelling the energy levels.

### 3.2.2 Coupling Schemes

To solve the problem of labelling the energy levels a proper set of basic functions built from one-electron functions should be chosen in order to diagonalize the problem. The choice of the proper base depends on the order of magnitude of the terms that compose the perturbative potential. If $V_{ee} \gg V_{so}$ the most commonly used coupling scheme is the Russell-Saunders coupling (also known as $L - S$ coupling): in that scheme $V_{ee}$ is diagonal because the orbital angular momentum $L$ and the spin momentum $S$ are sum of the single electron orbital and intrinsic angular momentum $L = \sum_i l_i$ and $S = \sum_i s_i$ (obviously $J = L + S$); as suggested by the name, in the $L - S$ coupling $L$ and $S$ are good quantum numbers and are used to label the energy levels. This coupling is always efficient in describing most of the lanthanide ion ground states.

Optical line spectra of rare earth arise from transitions between levels of the $4f^N$ configuration. The positions of these levels arise from a combination of the Coulomb interaction between the electrons, the spin-orbit coupling and the crystalline electric field. The resultant splittings of the $4f^N$ configuration are shown schematically in Fig. 3.1. The electrostatic interaction yields terms $2S+1L$ with separations of the order of $10^4$ cm$^{-1}$. The spin-orbit interaction then splits these terms into $J$ states with typical splittings of $10^3$ cm$^{-1}$. Finally, the $J$ degeneracy of the free ion states
3.2 Rare Earth Energy Levels

Figure 3.1: Schematic diagram of the splitting of rare earth energy levels due to the electrostatic, spin-orbit and crystal field interactions

is partially or fully removed by the crystalline Stark field, yielding a Stark manifold usually extending over several hundred $cm^{-1}$.

The free ion states, obtained by diagonalizing the combined electrostatic and spin-orbit energy matrices, are linear combination of Russell-Saunders states of the form:

$$|f^N\gamma SLJ\rangle = \sum_{\gamma SL} C(\gamma SL) |f^N\gamma SLJ\rangle$$  \hspace{1cm} (3.6)

\(\gamma\) includes whatever other quantum numbers are required to specify the states.

3.2.3 Rare Earth Ions in the Crystal Field

Once the features of the free ion have been discussed, it is possible to introduce the effect of the crystalline field due to the environment that surrounds the ion when it is placed in a crystal as an impurity. The problem has been approached in two different ways: by means of the ligand field theory introduced by Ballhausen [27], and the crystal field theory introduced by Bethe [26].

In the first model the interaction between the rare earth ions and the surrounding environment is considered as predominant, therefore molecular orbitals with the
surrounding ions are created. Such a theory is more indicate to treat the electrons of the 3d valence-shell of the transition metals because they are not shielded from the crystalline field and will be not investigated in the present work.

For rare earth ions the crystal field reduces the \((2J + 1)\) fold degeneracy of free ion states in Eq. (3.6) and causes a small mixing of \(J\) states. Because of the shielding effects of the outer 5s and 5p shell electrons, the crystal field interaction with the inner 4f electrons is weak. The crystal field can thus be treated as a perturbation on the free ion states. The crystal field potential is expanded in a series of spherical harmonic terms of the form:

\[
V_{cf} = \sum_{q,k,i} B_{q}^{k} C_{q}^{k}(i)
\]

where the factors \(B_{q}^{k}\) are parameters describing the strength of the crystal components, \(C_{q}^{k}\) are tensor operator components which transform as corresponding spherical harmonics and the index \(i\) runs over the whole number of electrons of the central ion, making the approximation that it is simply generated by the superposition of the electrostatic potential of the other ions; the group theory and the punctual symmetry determine that \(k \leq 6\). In this model \(V_{cf}\) is regarded as a perturbation to the energy levels that removes partially or totally the degeneracy on the component of \(J\) along the quantization axis: the new sublevels are named Stark levels; in Fig. (3.1) we report the typical order of magnitude of energy level splitting inferred from absorption and emission spectra that are characterized by relatively narrow and well separated bands made up of several distinct absorption or emission peaks corresponding to the Stark sublevels.

The punctual symmetry of the crystal at the position of the ion is the main factor for the splitting of the energy levels and for the transition selection rules; for this reason the knowledge of the punctual group theory becomes fundamental to study the manifold of the rare earth ions [28]. The \(B_{q}^{k}\) parameters can not assume all the values but are limited by the fact that \(V_{cf}\) must be invariant under the operation of the punctual symmetry group. Kramer's theorem demonstrates that for an odd number of electrons, whatever the punctual symmetry, every Stark sublevel is at least two-fold degenerate due to the Hamiltonian symmetry for temporal inversions.

It is now clear why, even if the dipole transition between the various levels are parity forbidden because they belong to the same shell 4f, electronic transitions
3.2 Rare Earth Energy Levels

3.2 Rare Earth Energy Levels

Figure 3.2: Observed energy levels of the trivalent rare earths. (After G. H. Dieke, [29].)

The odd part of the crystalline field causes a little mixing of various sublevels with different quantum numbers $n$. Then the transitions are not strictly forbidden and rare earth ions reach excited states showing radiative transitions with very long decay times up to tens of ms: such a phenomenon suggested to adopt for the long living rare earth ions levels the name of metastable levels. A scheme of the energy levels for all triple-ionized ions is shown in Fig. (3.2).
3.3 Energy transfer mechanism in rare earth doped crystals

The energy transfer mechanisms in rare earth doped crystals occur among energy levels of the same ion or different ions. Relaxation studies are concerned with the appearance or absence of emission lines and their intensities. The decay of rare earth luminescence is principally a result of transitions between $J$ manifolds. Relaxation within a $J$ manifold is rapid because the level separations are generally within the range of phonon energies and hence one and two phonon processes are very probable as we will see in the next items. These relaxation processes can be divided into three main categories:

- radiative relaxation,
- non-radiative relaxation,
- cooperative mechanisms.

The simplified energy level diagram for a rare earth in Fig. 3.3 illustrates possible decay modes involving transitions between $J$ manifolds. Consider a photolumines-
3.3 Energy transfer mechanism in Rare Earth doped crystals

The absorption of optical radiation causing excitation from the ground state 0 to one or more of the upper levels 3, 4, 5. When the upper levels are closely spaced, relaxation occurs predominantly by a level-by-level non-radiative cascade to level 3 denoted by the wavy line transitions. If the energy gap between levels 3 to 2 is large, non-radiative decay by multiphonon emission is less probable and radiative transitions, from level 3 to terminal levels 2, 1, 0, denoted by straight lines, become important. Levels 2 and 1 subsequently relax to the ground state by multiphonon emission.

The lifetime of an excited multiplet \( a \) can be expressed as:

\[
\tau_a = \frac{1}{\sum_b W_{ab}^R + \sum_b W_{ab}^{NR}}
\]  

where the index \( b \) runs on the final states, \( W_{ab}^R \) is the radiative decay rate and \( W_{ab}^{NR} \) represents the rate for non-radiative decays and cooperative mechanism between ions.

It is worth noticing that the experimental measure of the decay-time has to be carefully performed, otherwise it can be affected by radiation trapping, a phenomenon consisting in radiative emission from one ion and immediate reabsorption of the emitted photon by another ion: as a consequence, the decay-time will be overestimated.

3.3.1 Radiative Relaxation

As suggested by the name of the process, a decay is radiative if there is emission of photons from an excited state that decays to another one. As it will be shown in Sec. 3.3.2, a fast thermal equilibrium \((10^{-12} - 10^{-13} \text{ sec})\) among the different Stark sublevels of a manifold permits to consider the initial manifold as a single level. The spontaneous emission rate between the starting level \( \Psi_i \) and the final one \( \Psi_f \) is expressed by the A Einstein coefficient:

\[
A_{if} = \frac{64\pi^4 \nu_i^3}{3hc^3 g_i} |\langle \Psi_f | P | \Psi_i \rangle|^2
\]

where \( \nu_{if} \) is the frequency of the transition, \( g_i \) is the degeneracy of the starting level and \( P \) represents the operator responsible for the transition.

All the transitions under investigation happen between electronic levels of the same configuration 4f: these decays would not be allowed in the electric dipole approxima-
tion due to the parity selection rule. The magnetic dipole and electric quadrupole transitions are allowed but their contributions to radiative decay are generally small or negligible and, therefore, can not be able to explain the intensity of the experimental spectra. The weak oscillator strengths and other experimental evidences suggest that the transitions happen because of induced dipoles produced by the influence of the crystal field, by means of its odd components that mix 4f states having different parity. Given appropriate eigenstates for the rare earth, the probabilities for magnetic dipole and electric quadrupole transitions can be calculated, similar calculations for electric dipole transitions are not possible. The reason for this are reviewed in [30] together with the Judd-Ofelt treatment which has been applied to interpret the optical intensities of rare earth ion. In summary, the Judd-Ofelt method provides a useful description of rare earth intensities and can be used to predict radiative decay probabilities. With this theory we can calculate the radiative life time $\tau_a^R$ and the fluorescence branching ratios $\beta_{ab}$ from a level $a$ defined by:

$$1/\tau_a^R = \sum W_{ab}$$

$$\beta_{ab} = W_{ab}/\sum W_{ab} = \tau_a^R W_{ab}$$

respectively, where the summation are over all terminal levels $b$.

### 3.3.2 Non-Radiative Relaxation

As explained in the previous sections phonons play a fundamental role in the processes that involve rare earth ions: their importance becomes even more striking in the case of non-radiative decays during which the excitation energy is released to the crystalline lattice as phonons.

In other words, non-radiative decays between $J$ states can occur by the simultaneous emission of several phonons sufficient to conserve the energy of the transition. The crystal field at the ion site is not static but undergoes oscillatory behavior due to the vibrations of the lattice or molecules groups. The lattice vibrations are quantized as phonons. When the lattice and the rare earth ions are treated as a coupled system, optical transitions are considered to occur between vibrational-electronic (vibronic) states.
A first evidence of non-radiative decay is the shortening of the decay-time of the excited levels as the energy gap between them decreases, till the extreme case in which the fluorescent signal is completely quenched if levels are close enough.

In the simplest model where the ion is considered as a point charge, it is possible to expand the crystal field Hamiltonian $\mathcal{H}_{cf}$ in a Taylor series around the equilibrium ion position as:

$$\mathcal{H}_{cf} = V_{cf} + \sum_i \frac{\partial V_{cf}}{\partial Q_i} Q_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 V_{cf}}{\partial Q_i \partial Q_j} Q_i Q_j + \ldots$$

(3.12)

where $V_{cf}$ is the static crystal field of Eq. (3.7) and $Q_i$ represents the $i$-th normal mode coordinate; experimental data allow us to adopt the approximation till temperatures of several hundreds °C. Since the cut-off of the phononic spectrum is of the order of hundreds of cm$^{-1}$ (the maximum is reached in oxide crystals with $\approx 1000$ cm$^{-1}$), non-radiative relaxation must involve many phonons.

Eq. (3.12), in principle, permits to calculate the multiphonon relaxation rate, but in fact it fails to make quantitative predictions and can only give the order of magnitude because of the uncertainties or lack of knowledge of the terms in Eq. (3.12). A different approach is the phenomenological one, and it is based on a single-frequency phonon model with weak electron-phonon coupling, i.e.:

$$\Delta E_{gap} = p_i \hbar \omega_i$$

(3.13)

where $p_i$ is the number of phonons necessary to bridge the energy gap $\Delta E_{gap}$ to the next-lowest level having frequency $\omega_i$, $\epsilon$ is a coupling constant that gives the phenomenological expression:

$$W = \frac{\Delta E_{gap}}{\hbar \omega_{max}} = C e^{-\alpha \Delta E_{gap}}.$$  

(3.14)

The values of $\alpha$ and $C$ are positive-definite constants depend on the crystalline host, being $C$ in the range $10^{12}$–$10^{13}$ s$^{-1}$, as previously stated.

### 3.3.3 Cooperative Mechanisms

The description of relaxation mechanisms in the previous section describes emission and absorption properties as single particle processes: such an approximation does not hold when the dopant concentration increases. As ions get spatially closer one
to another a coupling process could happen via exchange interactions in the case of wavefunction overlapping, via super-exchange interactions when intervening ions are involved or via electro-magnetic multipolar interactions. The rare earth ions can undergo an interesting and peculiar cooperative energy transfer mechanism, in which the excitation can be transferred from a donor ion to an acceptor one. Just because the decay-times are so long, the manifolds can act as energy sinks and permit different mechanisms of energy transfer that could not take place if the lifetime of the excitations were not long enough.

The basics of the theory for the energy transfer in rare earth doped crystals were pointed in the work of Förster [31] and Dexter [32].

The manner in which the interactions between two like or two unlike ions lead to energy transfer and relaxation is illustrated schematically in Fig. (3.4). An excited ion A decays form state (2) to (2′) while ion B, initially in its ground state, is excited to (1′). In the absence of any additional interactions, energy conservation impose the constraint of resonance; that is \((E_2 - E_{2'}) = (E_{1'} - E_1)\). As the ion-lattice coupling is considered, the processes can also be non-resonant and can require the creation or destruction of phonons. The different processes, whose schemes are depicted in Fig. (3.5), are:

- **Migration:**
  the transfer of the energy from an excited ion to another one. The previously
3.3 Energy transfer mechanism in Rare Earth doped crystals

Figure 3.5: Schemes representing the various energy transfer mechanisms.

• **Resonance transfer (migration) and non-resonance transfer**
  - An excited ion relaxes and transfers its energy to another one. This process can happen either between two ions of the same kind or not. Moreover, it can be a resonant transfer and a non-resonant one (i.e., a transfer involving one or more phonons).

• **Cross-relaxation**
  - In this process, an ion decays from an excited state to another one and transfers the energy to another ion, usually of the same kind. As a result, at the end of the process, two ions are excited and the sum of their energy is equal to the initial energy. This process can also involve phonons. In this case, the condition of the conservation of the energy is still fulfilled provided that one takes into account the phonon energy.

• **Up-Conversion**
  - This process happens when two excited ions, usually of the same kind, transfer their energy resulting in an ion which will acquire the sum of the energy of the
previous ones. Also in this case one or more phonons can be involved in the transfer.

- **Excited State Absorption (ESA):**
  it takes place when an excited ion absorbs the pump radiation thus reaching a higher level. Even if it is not an energy transfer process between ions inside the crystals, we report ESA for the sake of completeness.

### 3.4 Emission Cross Section by $\beta - \tau$ Method

This section will be dedicated to show the details of the method that had been used in this thesis to calculate the stimulated emission cross-section: the so-called $\beta - \tau$ method developed by Aull and Jenssen [33].

In gases the strength of a transition is usually measured in terms of dipole momenta: in the case of solids, the difficulty to decide the proper correction for the local field due to the polarization induced into the crystal, leads to the introduction of the concept of emission cross-section. The stimulated emission cross-section $\sigma(\nu)$ is defined as the intensity gain of a laser beam per unity of population inversion when no saturation effects are present or no ESA processes occur. It is clear that such a parameter is extremely useful to determine the possibility to achieve laser effect.

Entering the details of the method, some basic assumptions has to be done: first of all the energy spacing between the $J$ manifolds should be not too large, on the other hand we have to suppose that the population in every sublevel respects the Boltzmann statistics in the case of steady-state pump.

From the definition of $\sigma(\nu)$, it follows that the stimulated emission cross-section is proportional to the Einstein’s $B$ coefficient, that can be obtained studying the absorption and spontaneous emission processes. Calling $\sigma_{ji}$ and $\sigma_{ij}$ the cross-sections for spontaneous emission and absorption respectively for the $j \rightarrow i$ transition, we have:

\[
\sigma_{ji}(\nu) = \frac{g_i}{g_j} \sigma_{ij}(\nu) \quad (3.15)
\]

\[
\sigma_{ji}(\nu) = \frac{\lambda^2}{8\pi n^2} A_{ji} g_{ji}(\nu) \quad (3.16)
\]

where $g_i$ and $g_j$ are the degeneracies of the $i$ and $j$ manifolds, $A_{ji}$ is the spontaneous emission rate per unit time for the $j \rightarrow i$ transition, $g_{ji}(\nu)$ represents the normalized
3.4 Integral $\beta - \tau$ method

Line shape factor and $n$ is the refractive index of the crystalline host.

In the case of low pump, the fluorescence signal $I_{ji}$ will be given by:

$$I_{ji}(\nu)d\nu = G A_{ji}g_{ji}(\nu)\hbar\nu d\nu N_j$$  (3.17)

where $N_j$ is the population density of the level $j$ and $G$ is a calibration factor representing the fraction of the fluorescence which is collected by the optical detection apparatus corrected for the optical response of the system.

Using Eq. (3.16) and Eq. (3.17), is it possible to write:

$$I_{ji}(\nu)d\nu = G \frac{8\pi n^2}{c^2} (\nu)\hbar\nu^3 d\nu \sigma_{ji}(\nu) N_j.$$  (3.18)

The integral $\beta - \tau$ method permits to determine the emission cross-section from the measurement of the fluorescence spectra and the knowledge of the radiative lifetime of the manifold. In the case of pulsed pump, the temporal behaviour of the fluorescent signal should be exponential with a time constant $\tau_f$:

$$\frac{1}{\tau_f} = W^R + W^{NR} = \frac{1}{\tau_R} + W^{NR}$$  (3.19)

where $\tau_R$ is the radiative lifetime, $W^R$ represents the radiative relaxation rate and $W^{NR}$ the non-radiative one. A useful quantity is the radiative quantum efficiency $\eta_a$ of a manifold $a$, defined as:

$$\eta_a = \frac{\sum_b W^R_{ab}}{\sum_b W^R_{ab} + \sum_b W^{NR}_{ab}} = \tau_a \sum_b W^R_{ab}$$  (3.20)

that is equal to the ratio between emitted photons and excited ions. Using the definition of quantum efficiency, it is possible to write:

$$\frac{1}{\tau_R} = \sum_j f_j \sum_i A_{ji} = \frac{\eta}{\tau_f}$$  (3.21)

with $f_j$ representing the fraction of the population pumped in the sublevel $j$ calculated via the Boltzmann statistics.

If $\tau_R$ is known, $A_{ji}$ can be written as:

$$A_{ji} = \frac{\beta_{ji}}{f_j} \frac{1}{\tau_R}$$  (3.22)
where $\beta_{ji}$ is the branching ratio for the transition $j \rightarrow i$, i.e. the fraction of the total photon flux emitted from the upper level. Such a datum can be easily calculated from the experimental fluorescence spectra

$$\beta_{ji} = \frac{\int \frac{I_{ji}(\nu)}{h\nu} d\nu}{\sum_{k,l} \int \frac{I_{kl}(\nu)}{h\nu} d\nu} = \frac{\int \lambda I_{ji}(\lambda) d\lambda}{\sum_{k,l} \int \lambda I_{kl}(\lambda) d\lambda}. \quad (3.23)$$

In our approximation of steady-state pump, the total number of excited ions in the emitting multiplet $N_{tot}$ is linked to the population of the manifold $j$ through $N_j = f_j N_{tot}$. Summing over all the possible states and over all the frequencies both sides of Eq. (3.17) and dividing by $h\nu$, it is possible to use Eq. (3.21) to obtain:

$$\int \sum_{i,j} \frac{I_{ji}(\nu)}{h\nu} d\nu = \frac{G\eta N_{tot}}{\tau_f}. \quad (3.24)$$

Solving Eq. (3.24) for $GN_{tot}$ and replacing in Eq. (3.18) we find:

$$\sigma_{ji}(\nu) = \frac{\eta c^2}{\tau f f_j} \left( \int \frac{I(\nu)}{h\nu} d\nu \right) \frac{I_{ji}(\nu)}{8\pi n^2 h\nu^3}. \quad (3.25)$$

where $I(\nu) = \sum_{i,j} I_{ji}(\nu)$ is the total fluorescence, and the integral has to be performed on the entire fluorescent spectrum.

Considering the overlap with the other transitions $k \rightarrow l$ we must correct the stimulated emission cross-section as:

$$\sigma(\nu) = \sigma_{ji}(\nu) + \sum_{k,l} \frac{f_k}{f_l} \sigma_{kl}(\nu). \quad (3.26)$$

Replacing Eq. (3.25) in Eq. (3.26) and converting to wavelength we have:

$$\sigma(\lambda) = \frac{\eta \lambda^5}{\tau f f_j} \left( \int \lambda I(\lambda) d\lambda \right) \frac{I(\lambda)}{8\pi n^2 c}. \quad (3.27)$$

In Eq. (3.27) all the terms are known or can be calculated but $f_j$, and it has become normal practice to define an effective cross-section neglecting this factor. If the crystal has different crystallographic axes the formula has to be corrected in:

$$\sigma_p(\lambda) = \frac{\eta \lambda^5}{\tau f \frac{1}{3} \sum_s \left( \int \lambda I_s(\lambda) d\lambda \right) 8\pi n^2 c} I_p(\lambda) \quad (3.28)$$

where the sum has to be intended over the different polarizations and the index $p$ is a label for the orientation.
Chapter 4

Experimental Setup and
Crystals

In this chapter I will briefly describe the various experimental setup used to grow single crystal fibers and to obtain the results reported in this thesis. Before doing that I will briefly describe the main features of the different crystals involved in our structural and spectroscopic measurements.

4.1 Crystals

In the present work, we grew different single crystal fibers both fluorides (LiF), oxides (LiNbO$_3$, RE$^{3+}$ doped YAG, LuAG, YAP) and pure metal (Si) for non-linear optics, laser, scintillation applications and for low thermal noise suspension in advanced gravitational wave detectors (GW).

I grew these materials in two different academic institutions. In Physics Department of Pisa Univ., group of New Materials for Laser Application (NMLA) during my Ph.D. period (2003-2005), I grew LiF, LiNbO$_3$, rare earth (RE$^{3+}$) doped YAP and Si single crystal fibers.

During a scientific stage at the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku Univ., Japan, I grew RE$^{3+}$ doped YAG and LuAG single crystal fibers. Different measurements have been performed in different laboratories, the major part has been performed in Pisa, the others has been performed in Fukuda Lab in Japan, Padova Univ., INFN groups in Florence and Perugia.
When necessary the samples for the spectroscopic measurements were oriented by X-Ray Laue technique, cut and optically polished with alumina powder in order to investigate polarization-dependent optical properties.

### 4.1.1 LiF Crystal

The development of fluoride mono-crystal fibers is very interesting because these materials show a low phonon energy and a large transparent transmission window from UV to IR wavelength region. These two characteristics open the possibility to develop high efficiency laser devices for micro-optoelectronic and wave guides with low loss transmission. LiF crystal has cubic structure with $a = 4.026 \, \text{Å}$ and shows excellent transmittance in the UV region. It is used for windows, prisms, and lenses in the visible and infrared from 104 nm to 7000 nm. LiF crystal is sensitive to thermal shock and would be attacked by atmospheric moisture at 400°C. In addition irradiation produces color centers. LiF is softens at 600°C and is slightly plastic even at room temperature, that can be bent into radius plates. LiF has density equal to $2.64 \, \text{g/cm}^3$ and melting point around 850°C.

### 4.1.2 LiNbO$_3$ Crystal

LiNbO$_3$ is a technologically important and attractive material for its applications in optoelectronics and integrated optical devices. Doping with foreign ions modifies the optical properties of the matrix and makes the system useful for a wide variety of applications. A great variety of devices has been developed based upon this material having unique electro-optical, piezoelectric, ferroelectric and non-linear properties combined with good mechanical and chemical stability and wide transparency range. As an excellent nonlinear optical material, the crystal can be used to fabricate frequency doublers and optical parametric oscillators pumped at 1064 nm as well as quasi-phase matched devices. The LiNbO$_3$ structure has been determined by neutron and X-ray diffraction [34]. LiNbO$_3$ has a rhombohedral structure space group R3c and Point group 3m and is ferroelectric at all temperatures up to 1100°C, which is only slightly below the growth temperature of 1250°C. The structure consists of planar sheets of oxygen atoms in approximately hexagonal close packing with both Li and Nb occupying octahedral interstices. The octahedrons are irregular and the Nb containing octahedron shares a face with a vacant octahedron on one side and
4.1 Crystals

Figure 4.1: Hexagonal unit cell of LiNbO$_3$, (thin lines) which includes three rhombohedral cells (thick lines). The atoms which belong to a selected rhombohedral cell are painted dark.

with an Li-containing one on the other side. Both Li and Nb lie closer to one plane of oxygen atoms than the other.

The lattice parameters are $a = 5.148$ $c = 13.863$, and the density is 4.64 $g/cm^3$.

From the phase diagram of Li$_2$O and Nb$_2$O$_5$ system, LiNbO$_3$ crystal can be melted congruently with the composition of 48.6 mol% Li$_2$O at 1240°C. Almost all commercially available LiNbO$_3$ crystals are grown from the feed material with congruent melt composition.

4.1.3 RE$^{3+}$ doped YAG and LuAG Crystals

Y$_3$Al$_5$O$_{12}$ (YAG) is a cubic crystal belonging to the family of garnet-type structure $A_3B_2C_3O_{12}$ and has a large phonon energy close to 800 $cm^{-1}$.

YAG is the most widely used host for solid state lasers because it is chemically stable, durable, UV resistant. Furthermore it possesses a good thermal conductivity (14 $Wm^{-1}K^{-1}$), high damage threshold ($>500 MW/cm^2$) and high emission cross-sections. YAG bulk crystals are now commercially available with several doping ions such as Nd$^{3+}$ and Yb$^{3+}$. Yb:YAG shows great promise as a high power laser material. Several applications are being developed in the field of industrial lasers, such as metal cutting and welding. With high quality Yb:YAG now available, ad-
Figure 4.2: Scheme of the crystalline structure of Nd:YAG as a cubic type unit cell.

Figure 4.3: Scheme diagram of Laser transition at 1064 nm in Nd:YAG.
ditional fields and applications are being explored. Yb:YAG’s advantage is a wide pump band and an excellent emission cross section. It is ideal for diode pumping. The broad absorption band enables Yb:YAG to maintain uninterrupted pump efficiency across the typical thermal shift of diode output. High efficiency means that a relatively small dimension Yb:YAG laser crystal will produce high power output. Based on the YAG host crystal, Yb:YAG can be quickly integrated into the laser design process. This combination of properties enables straightforward elegant laser designs, and allows high powered lasers to be manufactured more easily. Laser designers can apply their depth of experience.

On the other hand, Nd:YAG is the active medium of a commercially available solid-state laser. Nd:YAG lasers may be operated in either pulsed mode or a continuous wave (CW) mode and produce a wavelength of 1064 nm as shown in Fig. (4.3).

Nd:YAG lasers have many and various applications because they are efficient even at room temperature because they are based on 4-level scheme and produce a good quality beam. The emission can be also doubled or tripled (or more) to obtain visible or UV laser radiation. The Nd:YAG lasers are used in: material processing such as drilling, spot welding, marking, pumping tunable visible light lasers, research applications such as Raman spectroscopy, remote sensing, mass spectrometry and military including range finders and target designators.

### 4.1.4 RE³⁺ doped YAP Crystals

There is a continuing effort to develop new scintillation materials characterized by high density and high light yield, and also fast response for applications. Yttrium aluminate (YAlO₃ or YAP) has a perovskite-type orthorhombic crystal structure with space group $D_{2h}^{16}$ (Pnma), unit-cell parameters of $a = 5.3265\ \text{Å}$, $b = 5.1777\ \text{Å}$, $c = 7.3690\ \text{Å}$ and density of $5.37\ \text{g/cm}^3$. A scheme of the YAP unit cell is reported in Fig. (4.4).

Yttrium aluminum perovskite activated by cerium is a fast, mechanically strong and chemically resistant scintillation material. YAP:Ce scintillators have very low energy secondary X-ray emissions which makes them desirable for imaging applications. YAP:Ce detectors are used for gamma and X-ray counting, electron microscopy, electron and X-ray imaging screens, and tomography systems. Cerium doped YAP crystal is a well-known scintillation material that possesses the properties of a high...
light output, as high as 40% that of NaI(Tl), a short decay time constant (25 ns), a moderate efficiency for $\gamma$ ray detection and high energy resolution (5.7% for 662 keV) [35]. These scintillation properties mean that Ce:YAP crystals have a variety of potential applications in the areas of high-energy physics, nuclear physics, medical imaging, astrophysics, etc. Therefore, the optical properties and scintillation mechanism of Ce:YAP have been extensively and systematically investigated. Mechanical properties of Ce:YAP are rugged and similar to those of garnet. It has high hardness, is mechanically and chemically stable, non-hygroscopic and is not soluble in inorganic acids and resistant to alkali. The mechanical properties allow the deposition of very thin layers of reflectors on the surfaces.

4.1.5 Si Crystal

Fig. 4.5 shows the arrangement of the silicon atoms in a unit cell, with the numbers indicating the height of the atom above the base of the cube as a fraction of the cell dimension. Silicon crystallizes in the same pattern as diamond, in a structure formed by "two interpenetrating face-centered cubic" primitive lattices. The lines between silicon atoms in the lattice illustration indicate nearest-neighbor bonds. The cell parameter for silicon is 0.543 nm.

Silicon shows thermo–mechanical properties that are extremely favorable to reduce thermal noise in the optic suspension of a Gravitational Wave (GW) interferometric detector. Silicon is expected to have large bulk tensile strength (about 7 GPa,
4.2 Fiber Crystal Growth Setup

With usual growth techniques, which are expensive, time-consuming and temperature limited, it is not an easy task to grow many samples with different contents of activator ions such as rare-earth or transition metal ions. In order to obtain high quality at low cost and large variety of host compositions and based on the description of $\mu$-PD in section (1.3.2B) and its Fig. (1.7), in the (NMLA) laboratory of the Physics Department of the University of Pisa we have set up two crystal growth furnaces that use the so-called micro pulling down technique ($\mu$-PD).

The $\mu$-PD method involves downward pulling of a crystal fiber through a micro nozzle placed at the bottom of the crucible as shown in Figs. (4.6, 4.7 and 4.8).

The method allows to grow crystals in shape of fibers, rods or ribbons with diame-
Figure 4.6: Schematic diagram for our $\mu$-PD growth apparatus In NMLA (Pisa, Italy)

Figure 4.7: Schematic diagram for our Hot-Zone part inside central body of Fig 4.6
4.2 Fiber Crystal Growth Setup

Figure 4.8: Photograph for our first $\mu$-PD growth apparatus

ters in the range 0.15 mm to 5 mm at widely variable pulling rates [13]. The shape of the crystal is depending on the crucible shape, in Fig (4.9) we can see different shapes for crucibles.

The melt is placed in crucibles made of materials stable at temperatures as high

Figure 4.9: Different shaped crucibles for shaped crystal growth by $\mu$-PD method in IMRAM (Japan).

as the melting point of the target crystalline material, usually we use Pt crucible for LiNbO$_3$ materials, Ir crucible for high melting materials like YAG and YAP and vitreous carbon or graphite crucibles for fluorides and Si materials. The dimensions
Figure 4.10: Design of Pt crucible and after heater for LiNbO$_3$ growth

Figure 4.11: Photograph of the shields surround the crucible in hot zone part.
4.2 Fiber Crystal Growth Setup

Table 4.1: characteristics of the shield materials

<table>
<thead>
<tr>
<th>characteristic</th>
<th>High Density Alumina</th>
<th>Zircoa (ZrO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.29</td>
<td>4.2</td>
</tr>
<tr>
<td>Thermal Conductivity 1000 °C (W/mK)</td>
<td>0.28</td>
<td>1.17</td>
</tr>
</tbody>
</table>

of the crucible used in our furnace are 27 mm in eight and 18 mm in diameter with various nozzle diameter depending on the fiber diameter that we want to grow, as shown in Fig. (4.10). The crucible is placed on an after heater and is heated using a radio- frequency (RF) generator with 20 kW maximum power and frequency variable between 50 and 75KHz depending on the material of the crucible. The inductor is about 80 mm long and 70 mm in diameter with 8 windings. The crucible should be shielded from surrounding by means of insulating shields, usually we use two cylindrical shields, Zircoa (ZrO₂) and high density and high-purity 99.7% alumina. The characteristics of these materials are shown in Table (4.1) and a photograph of the shields surrounding the crucible is shown in Fig. (4.11). The whole structure is placed in a vacuum chamber of about 0.06 m³ volume connected to a turbo molecular pump and a primary pump. The furnace can be evacuated with an ultimate pressure limited to 10⁻⁶ to 10⁻⁷ mbar and inert atmosphere is inserted, usually Ar gas with 5N purity, for crystals grown in Japan we used a flow of N₂ as inert atmosphere.

Few differences in Japanese µ-PD setup and in the growth process exist(see Fig (4.12) for their hot zone Part).

When necessary I will mention these differences during the discussion of the experimental procedures and the results in the following chapters.

- Cutting and Polishing
  Two precision cutters (one with a diamond wire and the other with a diamond disk) are used to cut the crystals with the desired orientation and dimension. The following step consists in polishing the sample surfaces using alumina and diamond powders of decreasing dimension; the optical quality of the obtained samples is tested observing the scattering of a visible light. The polishing procedure has to be carefully carried out in the case of laser samples since the quality of the surfaces is directly related to the behavior of the active medium.
4.3 Structural apparatus

We performed many tests to check different structural properties of our crystals. In particular, we performed X-ray measurement (Laue Method) to check the single crystal character of the fiber, powder X-ray diffraction to identify the generated phase of each fiber, Electron Probe Micro Analysis (EPMA) to analyze the distribution of the ion concentration inside the crystal and Secondary Ion Mass Spectroscopy technique (SIMS) for surface analysis of the crystals.

In the following sections I will describe the experimental setup for the various measurements.

4.3.1 X-Ray Diffraction, Laue Method

Many samples under investigation are not isotropic and, consequently, their spectroscopic features have to be studied as a function of the crystal orientation. This method allows to ascertain the single-crystal character of the samples, and to identify the direction of the crystal axes inside the sample. A schematic diagram for Laue
4.3 Structural apparatus

4.3.1 Laue X-Ray Diffraction Method

The X-ray source is a HT Generator PW1830/40 and a Copper tube PW2273/30 series by Philips. The X-rays emitted from a Berillium window scatter on the sample mounted on a precision goniometer (±0.1° in the x and y directions and ±2° along z). The Laue diffraction pattern is acquired in backreflection scheme by means of a photographic plate and no selection of the output rays wavelength is carried out. The image is then digitalized using a scanner and analyzed using a share ware software (Orient-express). With this analysis we tested the single-crystal characteristic of the samples and to identify the crystallographic axes orientation, we performed an X-ray Laue analysis on them.

4.3.2 Powder X-Ray Diffraction Method

To identify the generated phase of each fiber, I performed powder X-ray diffraction analysis (XRD) (at IMRAM, Tohoku Univ., Japan) in the 2θ range from 20° to 80° using the RIGAKU diffractometer. Measurements were performed in air and the X-ray source was Cu Kα, (1.54056 Å) the accelerating voltage was 40 KV, and the tube current was 40 mA. All X-ray experiments were carried out at room temperature.

4.3.3 Electron Probe Micro Analysis (EPMA)

The chemical composition was analyzed by electron microprobe analysis (EPMA) using the JEOL JXA-8621MX. The accelerating voltage was 20 KV and the prove
current was 0.05 µA. By this technique we can chemically analyze small selected areas of a solid sample, in which X-ray are ejected by a focused electron beam. A portion of these x-rays relates to the energy characteristic of the atom from which they originate. The energy of the x-ray emission is measured by the wave length dispersive spectrometer (WDS) and energy dispersive spectrometer (EDS) with the detectors positioned around the periphery of the microanalytical stage. Quantitative analysis is used to convert the x-ray intensity data measured on the fibers and the standard to chemical compositions.

By this technique we can analyze the distribution of the ions concentrations inside the crystal. The distribution of dopant cation in the crystal was measured along the growth axis using an electron probe 10 µm in diameter. We discussed the distribution and segregation coefficient in section 2.4 in details.

4.3.4 Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectrometry (SIMS) is a surface analysis technique in which energetic primary ions are used to bombard a surface. After impacting the surface, these primary ions generate positively and negatively charged secondary ions, which are subsequently mass-separated and detected. SIMS has the capability of analyzing the entire periodic table with isotopic discrimination and typical detection limits on the ppm level.

Dr. C. Sada from Padova Univ., Italy, performed SIMS measurements that were carried out by means of a mass spectrometer using a 10 KV Cs+ primary beam and by negative secondary ion detection (the sample potential was fixed at -4.5KV) with a final impact energy of 14.5 KeV. The SIMS spectra were carried out in ultra high vacuum conditions at different primary beam intensity (1-5nA) restraining over a nominally 125x125 µm² area. The measurements were performed in high mass resolution configuration to avoid mass interference artifacts. The charge build-up occurring in insulating samples during the in-depth profiling was compensated by an electron gun without any need to cover the surface with a metal film. The fiber was measured in different points through the lateral surface and at the end. The elemental identification was performed by checking the presence of each isotope.
4.3 Structural apparatus

4.3.5 Stress and Optical Quality Test

A qualification of the optical quality may assist to verify the phase/stoichiometry of the fiber crystal. Usually, the conoscopic observation of a cross section normal to the optic axis in a polarizing microscope is convenient to characterize the optical homogeneity [37]. Inhomogeneous birefringence will disturb the conoscopic figure. We put the fiber between two cross polarizer and observing the transmitted light by CCD camera before and after polarization. Two different experimental setup we used to do our measurements. Dr. Sada from Padova University used setup shown in Fig. (4.14). We setup a similar apparatus for this measurement that is shown in Fig. (4.15).

Figure 4.14: Experimental setup for stress measurement.(1) cw He-Ne laser.(632.8 nm, 20 mW), (2) mirror, (3) variable attenuator, (4) filter, (5) Lens (f=10), (6) linear polarizer, (7) Iris , (8) objective 5X, (9) Fiber sample, (10) XYZ linear translator, (11) fiber illumination, (12) mirror, (13) linear polarizer, (14) CCD

Figure 4.15: Our experimental setup for stress measurement in NMLA.
4.4 Spectroscopic apparatus

All spectroscopic measurements of the present work were carried out in the (NMLA) laboratory of the Physics Department of the University of Pisa. The following is a brief description of the different spectroscopic set-up.

4.4.1 Absorption Measurements

The measurement of the room temperature absorption coefficients have been performed by means of a spectrophotometer VARIAN CARY 500. Scan operating in the range 180 - 3200 nm, having a R928 photomultiplier as a detector in the UV-Vis region, and a cooled PbS photodiode for the NIR part of the spectrum.

4.4.2 Laser Sources

In order to excite the $Ce^{3+}$, $Yb^{3+}$ and $Nd^{3+}$ ions in the various matrices, we used different laser sources, depending on the rare earth involved and on the measurement we intended to perform.

- **Continuous Wave Titanium Sapphire**
  
  In our laboratories a X-folded 4-mirror Ti : $Al_2O_3$ cw laser pumped by a Coherent Innova Ar$^+$ laser is available. The Ti:Sapphire laser is tunable between 750 nm and 810 nm by means of a quartz plate inserted in one arm of the cavity. The maximum attainable output power is 400 mW.

- **Pulsed Titanium Sapphire**
  
  In the measurements requiring a short pulse duration we used a pulsed tunable Ti : $Al_2O_3$ (pulse duration $\approx$30 ns) laser pumped by the second harmonic of the 1.06 $\mu$m laser emission of a Q-switched Nd:YAG laser (Surelite I-10 by Continuum) with 10 Hz repetition rate. The pump wavelength could be varied between 750 nm and 980 nm by means of a Sapphire prism with a maximum energy available on the samples of 9.1 mJ without any attenuator.

- **Continuous-Wave Fiber-Coupled Diode Laser**
  
  When a longer wavelength was needed to excite the samples, we used a cw - fiber coupled semiconductor diode laser (Opto Power mod. H01-A001), this
4.4 Spectroscopic apparatus

Diode laser was mounted on a peltier in order to tune the output wavelength from about 967 nm up to 979 nm with a maximum power of 300 mW.

- **Excimer Laser**

Excimer laser refers to a rare-gas halide laser that emit powerful pulses of light whose wavelengths are mostly in the ultraviolet region of the spectrum. The word excimer is a combination of excited dimers, this comes from the fact that excimer lasers are made from a mixture of a rare-gas such as argon, krypton, and xenon; and a halide like fluorine, chlorine, and bromine. Most commercial excimer lasers produce pulses ranging from 3 to 35 nanoseconds in duration. Research lasers have produced pulses as short as 0.35 nanoseconds to as long as 100 nanoseconds. The output wavelength of most excimer lasers falls between 150 and 350 nanometers.

4.4.3 Setup for Steady-State Fluorescence Measurements

Room temperature fluorescence spectra were obtained by exciting the sample with cw Ti : Al₂O₃ laser (in case of Nd³⁺ ) or diode laser (in case of Yb³⁺ ) or Hg lamp (in case of Ce³⁺ ) each tuned to the maximum absorption of the samples under investigation. For the emission measurements the pump beam was focused onto the fiber with a 10 cm focal length lens. The fiber was mounted with the growth axis perpendicular to the pump beam. The fluorescence signal was detected perpendicularly to the pump laser direction to avoid pump spurious scattering. The luminescence was chopped and focused by a 7.5 mm focal length Infrasil lens on the input slit of a Jobin-Yvon monochromator with 25 cm focal length (a diagram is shown in Fig. 4.16).

The gratings used for the fluorescence measurements was either a 1200 gr/mm blazed at 0.5 µm, a 600 gr/mm blazed (as in case of Yb:YAG) at 1 µm or a 300 gr/mm grating blazed at 2 µm. The signal was detected by a liquid nitrogen cooled InSb detector for all the measurements, fed into pre-amplifiers, processed by a lock-in amplifier and stored on a PC. The acquired spectra were normalized for the optical response of the system.
Figure 4.16: Experimental Setup for Fluorescence Measurements with cw Ti:Sa laser

Figure 4.17: Experimental Setup for decay-time measurements with the pulsed Ti:Sa laser
4.4 Spectroscopic apparatus

4.4.4 Setup for Decay-time Measurements

Room temperature decay time curves were recorded with an apparatus similar to that described in the previous section, using the pulsed Ti:Sa (pumped by the 2nd harmonic of the 1.06 µm laser emission of a pulsed Nd:YAG laser or the Excimer laser). The samples were pumped near an edge and the fluorescence was collected from a thin section (≈1 mm) of the sample to observe a uniformly pumped volume and reduce radiation trapping effect; furthermore the power incident on the fibers was reduced by means of attenuators to suppress non-linear effects as much as possible. The signal from the detector (InSb photodiode or a photomultiplier with S1 cathode) was amplified, by fast amplifiers, and then processed by a Fluke digital oscilloscope, connected to a PC for storing purpose, a diagram is shown in Fig. (4.17).

In the case of fluorescence decay time measurements shorter than 1 ms, the sample was excited by the pulsed Ti:Sa laser. The response time of the system was 3 µs. When the decay time was longer than 2 ms, the pump source was the mechanically chopped Ti:Sa cw-laser: the rise-time, and hence the response time for the system was, in this conditions, 0.17 ms.
Chapter 5

Growth and Structural Properties of LiNbO$_3$ Single Crystal Fibers

The first crystal fiber we grew is LiNbO$_3$ (LN) because until now LN (and related compounds) is one of the most investigated oxide crystal materials thanks to its large nonlinear optical coefficients and high piezoelectrical performance which make it attractive for a wide range of application like in nonlinear optical devices, waveguides, surface acoustic wave devices or photorefractive data storage. It is also a promising laser crystal if doped by rare-earth ions. In each of the following sections I will discuss the measurements that we performed and their results.

5.1 Preliminary Procedures

Before getting start to grow, we clean the furnace by Isopropanol solution and we mounted the seed on its holder. The crucible is mounted on an after heater between the RF coil and cylindrical insulating shields are surrounding the crucible and finally the desired material is placed in crucible. Similar setting is shown in Fig. (4.11). For growth process, different from the one of LiNbO$_3$ growth, the furnace is evacuated with an ultimate pressure limited to $10^{-6}$ mbar and Ar gas with 5N purity as inert atmosphere is inserted. In case of LiNbO$_3$ neither evacuation has been done nor Ar
LiNbO$_3$ Single Crystal Fibers...

Table 5.1: Growth conditions of congruent LiNbO$_3$ fiber single crystals

<table>
<thead>
<tr>
<th>Starting melt Crucible</th>
<th>Congruent Composition ($Li_2O=48.6$ mol% and $Nb_2O_5=51.4$ mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Platinum with 0.5 mm nozzle</td>
</tr>
<tr>
<td>Heating method</td>
<td>RF Generator with RF coil</td>
</tr>
<tr>
<td>Seed orientation</td>
<td>$&lt;100&gt;$ LiNbO$_3$</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Air</td>
</tr>
<tr>
<td>Pulling rate</td>
<td>0.1 - 2 mm/min</td>
</tr>
<tr>
<td>Fiber length</td>
<td>15 - 300 mm</td>
</tr>
<tr>
<td>Fiber diameter</td>
<td>up to 1 mm</td>
</tr>
</tbody>
</table>

gas is inserted. Since LiNbO$_3$ needs excess of Oxygen during the growth, it is usually grown in air atmosphere. Beside that Pt crucible that used for LiNbO$_3$ growth does not oxidize in air at high temperature. This oxidation is happening if we grow in Ir crucible without evacuation and inert atmosphere.

The growth parameters of LiNbO$_3$ are summarized in Table (5.1). The starting materials were congruent LiNbO$_3$ ($[Li]/[Nb]=0.945$) powders of 99.9995% purity. The powder was then cold pressed into 2 mm thick, 10 mm diameter pellets, under 200MPa pressure. The raw materials were loaded in the crucible that was placed on a Zirconate pedestal in held by a vertical Alumina ceramic tube and was heated using an Radio Frequency (RF) generator. The calibrated orifice made in the crucible bottom was about 0.5 mm in diameter. The crucible temperature was controlled by the power of RF coil which was about 80 mm long and 70 mm diameter with 8 windings. Zircoa and Alumina materials were used as shields to surround the crucible to provide thermal insulation. The crystal was grown in Air and visual observation of the meniscus region, solid -liquid interface and the crystal growing was made by the CCD camera and monitor.

5.2 Seeding and Growth Procedure

As a first step, a $<100>$ oriented thin seed cut from CZ grown LN crystal was used as a seed. The achievement of good quality crystal fiber was found to require the controlled melting of the initial part of the original seed prior to initiation of the
5.2 Seeding and Growth Procedure

Figure 5.1: View of as-grown LiNbO₃ Fiber. The left arrow indicates the first part with regular diameter while the right arrow indicates the end part with irregularity in the fiber shape.

Figure 5.2: View of as-grown LiNbO₃ Fiber: (a) whole fiber, (b) the first part and (c) the end part

pulling process in order to eliminate part of the surface defect of the seed crystal that could propagate in the fiber to be grown. The controlled seed melting was performed by immersion of the seed into the crucible nozzle. Usually about 1mm of the seed crystal was melted just before starting the growth. The crystals were grown at pulling rate of 0.1 - 1.5 mm/min and were up to 1 mm in diameter and 15 - 300 mm in length. Growth of long crystal fibers is affected by vibrations which become especially intense at longer lengths. It was found that the amplitude of the crystal oscillations also depends on the fiber diameter[91]. Disconnection of the fiber growing from the molten zone was never observed. During the first growth operations we encouraged a fluctuation in fiber diameter and irregular shape especially at the end part of the fiber, as shown in Fig. (5.1).
could be because a poor temperature stabilization at the end of the growth process in the case of long fiber. We must supply more temperature during the growth process in order to compensate the temperature loss that happens in the crucible and in the hot zone when the fiber increases in length. The left arrow in Fig. (5.1) indicates the first part with regular fiber shape, while the right arrow indicates the end part with irregularity in the fiber shape. In the next growth operations we paid attention to this problem and we succeeded to grow fibers with good quality and regular shape. Fig. (5.2) shows a photograph of one of these as-grown LiNbO$_3$ fiber with regular shape. All fibers were transparent, and have uniform diameter, no visual cracks or defects are observed. We grew six LiNbO$_3$ single crystal fibers fibers with different lengths and diameters varying from 15 mm to 300 mm in length and up to 1 mm in diameter. After growth, as-grown crystals were cut into several test samples (10 mm long) perpendicular to the growth direction and polished surface sides using alumina and diamond powders. These several samples are used to perform different measurements as we will see in the following sections.

5.3 Laue X-Ray diffraction Measurement

Room temperature X-ray measurement was performed by X-ray diffractometer, Laue method. The accelerating voltage was 25 KV, and the tube current was 35 mA. Exposure time was 10 min.

According to Laue X-ray diffraction method, Fig. (5.3), all the X-ray reflections spots (black spots) are sharp and clear and the white circles of the numerical simulation match the experimental pattern. As a result, all grown crystal were single crystal and oriented in $<100>$ direction.

5.4 Absorption Measurement and Results

Room temperature absorption measurements were performed between 300 and 800 nm in UV-VIS region and between 2550 and 3200 in NIR region, with a resolution of 0.5 nm.

Absorption edge of LiNbO$_3$ is sensitive to the composition of the crystal. In a congruent LiNbO$_3$ crystal with the oxygen octahedron structure, the number of $Li^+$
ions is less than that of $Nb^{5+}$ (Li/Nb = 0.946). The Li-site vacancy model \[38\], the anti-site Nb ($Nb^{4+}_{Li}$) and Li vacancies appear because parts of $Nb^{5+}$ occupy Li sites.

The fundamental optical absorption edge is decided by the valence electron transition energy from the 2p orbits of $O^{2-}$ to the 4d orbits of $Nb^{5+}$. Hence, changes in the valence electronic state of $O^{2-}$ directly affects the position of the absorption edge and result from interactions of the positive and negative ions. For instance, an increase in the ability of a neighboring dopant ion to polarize an $O^{2-}$ ion decreases the valence electron transition energy and results in a shift of the absorption edge to longer wavelengths.

Absorption spectra for the fibers (Fig. 5.4) show that the absorption edge of LN was found to be nearly at 330 nm. This value shows a good agreement with similar results in literature \[39\], where the wavelength of the absorption edge shifts from 320 - 340 nm (congruent compositions) to 300 nm (stoichiometric compositions). Crystal growth of LiNbO$_3$ from the melt is commonly carried out in air atmosphere. Air always contains a certain degree of humidity from which $OH^-$ ions are incorporated into the lattice. Atmospheres rich in water give $OH^-$ concentrations one hundred times higher than in poorer atmospheres \[40\]. A very clear line due to the $OH^-$ ions absorption at 2870 nm is observed in the
as-grown crystals, which is the same value as in literature [41]. The observation of the $OH^−$ absorption band at 2870 nm can be used to analyze the location of dopant ions in LiNbO$_3$ lattice. It is known that $OH^−$ ions located at the $O^{2−}$ site generate $O^{1+}$ charge defect in the lattice [41]. Occupation of $Li^+$ sites by $X^{2+}$ or $X^{3+}$ ions also generates 1+ or 2+ positively charged defects, thus their incorporation should be in some way competitive for the generation of $OH^−$ ions. The location of $X^{2+}$ or $X^{3+}$ ions at $Nb^{5+}$ site generates a $3^−$ or $2^−$ negatively charged defects and should not retard the incorporation of $OH^−$ ions. Discussing this point in details by considering the following mechanism. Crystal growth from the melt is commonly carried out in air atmosphere. Air always contains a certain degree of humidity from which $OH^−$ ions are incorporated into the lattice. On the other hand, Uda and Tiller [42] in their study of the thermodynamic and kinetic behavior of LiNbO$_3$ melts, have shown that three dissociation reactions occur in the liquid:

$$2Li_{1−x}Nb_{1+x/5}O_3 \Leftrightarrow (1 − x)Li_2O + (1 + x/5)Nb_2O_5 \quad (5.1)$$

$$Li_2O \Leftrightarrow Li^+ + LiO^- \quad (5.2)$$

Figure 5.4: Absorption spectrum for LiNbO$_3$ in UV-Vis-NIR regions
5.5 Secondary Ion Mass Spectroscopy (SIMS) Measurement

\[ Nb_2O_5 \leftrightarrow Nb_2O_4^{2+} + O_2^- \quad (5.3) \]

leading to the presence of seven different species in the melt. So, we consider that the following oxidoreduction reactions occur at the melt-atmosphere interface:

\[ 2O_2^- \rightarrow O_2 + 4e^- \quad (5.4) \]

\[ 2H_2O + e^- \rightarrow H_2 + 2OH^- \quad (5.5) \]

the whole reaction being:

\[ 2O_2^- + 4H_2O \rightarrow 4OH^- + 2H_2 + O_2 \quad (5.6) \]

Finally, the \( OH^- \) ions produced according to reaction Eq. (5.6) would be incorporated in the lattice instead of \( O_2^- \).

5.5 Secondary Ion Mass Spectroscopy (SIMS) Measurement

Dr. C. Sada from Padova Univ., Italy, performed SIMS measurements by means of an IMS 4f mass spectrometer described in section (4.3.4). The fiber was measured in different points through the lateral surface, Fig. (5.5), and at the end, Fig. (5.6). The elemental identification was performed by checking the presence of each isotope. From the mass analysis carbon and hydrogen contamination were found both along the lateral surface and the end of the fiber. Other contaminants such as Ti, Al, K, Ca, Zr were detected in low concentrations but no quantification is possible by the SIMS technique, see Table (5.2). The compositional homogeneity is better than 5% along the fiber height. In the lateral surface the carbon and Zr contamination was found to be higher than that observed in the center of the end surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>H</th>
<th>C</th>
<th>F</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>K</th>
<th>Ca</th>
<th>Zr</th>
<th>Ti</th>
<th>Co</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contamination Level</td>
<td>H</td>
<td>H</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>L</td>
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Figure 5.5: SIMS Spectra of LN Single Crystal fiber through the lateral surface.

Figure 5.6: SIMS Spectra of LN Single Crystal fiber at the fiber end.
It is important to underline that some elements (such as Li) have a low yield as negative ions. The level of contamination (low, medium, high) therefore was derived by taking into account the weighting of the correspondent negative yield. For lithium, niobium and oxygen the SIMS yield is compatible with a congruent LiNbO$_3$ composition.

Some of contamination can come from the spattering of the surrounding shields, for example Zirconia and Alumina shields, others by air atmosphere. Some can also come from the impurities of the LiNbO$_3$ initial powder. It is well known that optical properties of pure LiNbO$_3$ crystals are sensitive to the presence of defects in the crystals [43]. Moreover, the electro-optic and non-linear optical properties [44] were shown to be strongly dependent on the concentration of these defects. It is important to have a good shield like high purity and compressed alumina to prevent any spattering from the shields and minimize the impurities and defects in the fiber.

5.6 Transmission Imaging and Optical Quality of LiNbO$_3$ Fiber

By means of the setup described in section (4.3.5) used by Dr. Sada from Padova University and shown in Fig. (4.14), the fiber was put between two cross polarizer and the transmitted light was observed by a CCD camera.

The photos are acquired in two configurations: Laser off and laser on. In the second case the photos are acquired in two polarization conditions: with the two polarizer axes parallel or crossed. The transmitted light is collected, focused by a 20X objective and then sent to the CCD camera. Two samples have been investigated: a long one and a small one.

5.6.1 Image with Laser off

Fig. (5.7) shows both short and long fibers in non-polarized direct illumination by a lamp when the laser was off.

In these two pictures, we observed some bright spots due to the scattering of diffused light. A crack is present near the top of the small fiber and reduces the area useful for the transmission of the light from the surface. We also observed some optical inhomogeneities in both samples.
Figure 5.7: Short (a) and long (b) LiNbO₃ fibers in direct illumination. The arrow indicates a crack. The oval evidences the presence of an optical inhomogeneity.

5.6.2 Image with Laser on

With this measurement it is possible to observe the local variation of refractive index that can not be determined with unpolarized light.

The intensity of the emitted light from the fiber can be expressed as follows:

\[ I_{\perp} = I_o \sin^2(2\psi) \sin^2(\Gamma/2) \] (5.7)

\[ I_{\parallel} = I_o - I_{\perp} \] (5.8)

for crossed or parallel polarizers, respectively.

\( I_o \) is the intensity of the incident light and \( \psi \) is the angle between the polarizer and the optical axis of the fiber, \( \Gamma \) is the phase difference between the ordinary and extraordinary wave. Difference of the intensity of the transmitted light in two different points of the fiber may be due to local variation of the refractive index (\( \Gamma \)), or a rotation of the crystal orientation (\( \psi \)).

As shown in Fig. (5.8) the regions that showed inhomogeneities with laser off, transmitted almost zero intensity in both samples for all polarization conditions. This indicates that these regions have high density of defects, which give rise to high loss because of scattering. In fact, if the regions have mechanical stress it would be possible to illuminate them in some polarization conditions. Some other regions are characterized by the existence of local variation birefringence, as we can observe from the comparison of two images with \( \psi = 45 \) and the polarizers perpendicular and
Figure 5.8: LiNbO$_3$ fibers in crossed Polarizers. Short (a) and long (c) LiNbO$_3$ fibers in complete extinction, while (b) and (d) represent short and long LiNbO$_3$ fibers, respectively, at $\psi = 45^\circ$.

Figure 5.9: LiNbO$_3$ fibers in parallel polarizers. (a) Short fiber, plane of polarization is horizontal regarding the image. (b) Long fiber at the same experimental conditions of figure (5.8).

parallel, as shown in Fig. (5.9). The measurements with different $\psi$ indicate the optical indication of the fibers have axes almost aligned with horizontal and vertical directions of the figures.
5.7 Conclusion

The $\mu$-PD method has shown to be a fast and effective technique for the preparation of such kind of single-crystalline fibers. Highly transparent and crack-free LiNbO$_3$ fibers with 300 mm in length and up to 1.2 mm in diameter were successfully grown by $\mu$-PD technique.

Improvements to obtain RE$^{3+}$ doped LiNbO$_3$ materials with high crystal perfection could drive the miniaturization of non linear systems.

Low second harmonic generation (SHG) efficiency and optical damage effect which exhibits in congruent melt grown LiNbO$_3$ certainly limits it’s applications in high power non-linear and Electro-Optic devices. For this purpose we will try to grow LiNbO$_3$ which has composition near stoichiometric similar to the Li-rich. Also doping the LiNbO$_3$ with RE$^{3+}$ or divalent ions like MgO, ZrO, ..etc, remarkably increases its optical properties like laser damage threshold and SHG efficiency.
Chapter 6

Growth and Structural Properties LiF Single Crystal Fibers

6.1 Introduction

The development of new shapes of the crystals opens interesting possibilities on different application fields, as optoelectronic, medical and mechanics. Moreover the actual request to develop devices of small size to be integrated in complex networks increases the interest in the development of mono-crystal fibers. Their final shape with a diameter between 0.2mm and 1mm, a length between 10 mm and 1000 mm is already in a form suitable for the applications. Many different oxide materials have been restated in this form for laser, non-linear and mechanical applications [13] and [45].

The development of fluoride mono-crystal fibers is very interesting because these materials show a low phonon energy and a large transparent transmission window from UV to IR wavelength region. These two characteristics open the possibility to develop high efficiency laser devices for micro-optoelectronic and waveguides with low loss transmission. Also since LiF crystals shows excellent transmittance in the UV region, it is used for windows, prisms, and lenses in the visible and infrared from 0.104 $\mu$m to 7 $\mu$m.

Some research groups have started to develop this type of mono-crystal fibers [46],
but their growth is very delicate because these materials are very sensitive to OH radical contamination. In fact a contamination of a few tens of ppm can compromise the optical characteristics of the samples. In this chapter we show high quality lithium fluoride (LiF) single crystal fibers grown by $\mu$-PD method. The dimension of fibers is 0.4 - 0.6 mm in diameter and up to 100 mm in length. We describe the experimental apparatus for the growth and analyze the sample structure and its spectroscopic characteristics.

### 6.2 Crystal Growth Process

In order to start the growth with high-purity material, we used LiF powder at 99.999% purity. A graphite crucible was heated by radio-frequency induction up to the melting temperature of LiF (nearly about 850°C). The crucible was designed as a cylinder with a conical bottom equipped with a nozzle of 0.5 mm in diameter.

The diameter of the crucible is 16 mm and its total height is 27 mm. To control the temperature gradient we mounted the crucible on a graphite pedestal which also served as after heater. This after heater was 20 mm height. During the growth the chamber was filled with pure Argon (99.999%) and the crystal fibers were pulled from the nozzle at pulling rates in the range of 0.1 to 0.5 mm/min. In these experimental conditions we have obtained fibers with lengths up to 100 mm. The first fiber grown started from Pt wire of 0.5 mm in diameter. After the first growth the first nearly oriented seed $<100>$ of LiF was obtained. Growth parameters are summarized in Table (6.1).

<table>
<thead>
<tr>
<th>Starting melt</th>
<th>LiF powder of 99.999% purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crucible</td>
<td>Graphite, conical shape with nozzle 0.5mm</td>
</tr>
<tr>
<td>Heating method</td>
<td>RF Generator with RF coil</td>
</tr>
<tr>
<td>Seed</td>
<td>Starting with Pt wire</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ar gas</td>
</tr>
<tr>
<td>Pulling rate</td>
<td>0.1-0.5 mm/min</td>
</tr>
<tr>
<td>Fiber length</td>
<td>up to 100 mm</td>
</tr>
<tr>
<td>Fiber diameter</td>
<td>0.4-0.6 mm</td>
</tr>
</tbody>
</table>

[47] and [49]
The grown LiF fibers were transparent, color-less, uniform in diameter and free of cracks along all their length, see Fig. (6.2).

Moreover LiF is slightly plastic and can be bent into radius plates that can be used specifically for monochromator plates. Thanks to plasticity feature of the material, we were able to bend the fibers and restore the straight condition without observing cracks inside the sample. Fig. (6.2) shows one example of this fiber. With a 0.5 mm diameter fiber we obtained a reversible fiber bending of 20 mm radius. This behaviour opens new interesting perspectives for applications.

We have obtained a fiber bending of 20 millimeter in radius without observing cracks inside the samples.

### 6.3 X-Ray Laue Simulation

To identify the crystal orientation of the fibers, X-ray diffraction analysis (Laue method) was performed at room temperature. The accelerating voltage was 25 KV, the tube current was 30 mA, and exposure time was 8 min.
We measured the crystal orientation and quality along the fiber length at various positions, at beginning, middle and the end of the fiber. An example of a Laue picture with the simulation superimposed is shown in Fig. 6.3. From this measurement we can say that the fibers are single crystal but the axis of the fiber was not oriented along any of the crystallographic axes of the lattice.

6.4 Powder X-Ray Diffraction Measurement

In order to verify the phase purity of the crystal fiber, a little section of the fiber has been hand milled in an agate mortar, the resulting powder has been put in a 0.4 mm Lindemann capillary and settled by ultra sonication. The powder diffraction pattern shown in Fig. 6.4 has been collected in the 2θ range 30-120° using a Bruker D8 advance diffractometer. The measurements has been performed at room temperature using a Cu source powered by 40 kV and 40 mA and equipped with a focusing primary Ge monochromator (λ = 1.540619 Å). The diffracted beam has been measured by means of a Braun PSD-50M linear position sensitive detector. The pattern of Fig. 6.4A is the result of a fitting process of the profile, calculated from the known structure of LiF [48], on the experimental one. The fitting has been obtained by refining the unit cell axis length, which converged to $a = 4.0312(2)$ Å. As it clearly appears, all peaks in the pattern are sharp and can be indexed on the
6.5 Absorption Measurement

Room temperature absorption measurement was performed between 190 and 2500 nm with a resolution of 0.1 nm and 1 nm in the visible and near-infrared regions, respectively.

Absorption spectra show that the absorption of LiF started to increase around 300 nm. Within the sensitivity of our apparatus absorption spectra did not show the presence of any contaminants as shown in Fig. (6.5).

6.6 Optical Quality of the Fiber

We inspected the optical quality of the fibers by means of the our setup described in section (4.3.5) and shown in Fig. (4.15). The fiber was put between two polarizers and the transmitted light was observed by CCD camera.

The illumination of the fiber was acquired in two different configurations: with parallel or crossed polarizer axes. Fig. (6.6) shows two pictures of the fiber when illuminated by the He-Ne laser. The first picture (Fig.6.6a) shows the transmitted light from the fiber when the two polarizers were parallel, while the second
Figure 6.5: LiF Absorption spectrum in NIR region

![Absorption spectrum of LiF](image)

Figure 6.6: Conoscopic interface patterns of a-axis single crystals grown from melt; (a) in parallel polarizer configuration, (b) in crossed polarizer configuration.

picture (Fig. 6.6b) shows fiber when the two polarizers were in crossed configuration and with a slight illumination from outside to evidence the contour of the fiber itself. As one can see in the first case the fiber shows an uniform illumination of the whole surface apart from a few dark spots due to imperfections of the polishing of the front surface or dust. On the contrary the fiber appears completely dark in the second picture as one might expect in crossed polarizer configuration if the material does not possess any intrinsic or spurious birefringence. These results demonstrate that the fiber does not alter the polarization of the light propagating through it, as expected from a cubic crystal with no stress regions inside.
6.7 Conclusion

In summary, the $\mu$-PD method has shown to be a fast and effective technique for the preparation of fluoride single-crystalline fibers. Highly transparent and homogeneous LiF fibers with 100 mm in length and up to 0.6 mm in diameter were successfully grown by the $\mu$-PD technique. We expect that the procedure developed for the preparation of LiF single-crystalline fibers is also appropriated for the growth of other fluoride fiber crystals. Improvements to obtain this class of materials with high crystal perfection could drive the miniaturization of fluoride laser systems. Moreover, $\mu$-PD can be an interesting and low cost technique to evaluate the growth possibilities of new fluoride materials.
Chapter 7

RE doped YAG and LuAG Single Crystal Fibers for Spectroscopic Applications

The development of solid-state lasers needs much effort in the synthesis of new luminescent single crystals and in the characterization of their optical properties. With usual growth techniques, which are expensive, time-consuming and temperature-limited, it is not an easy task to grow many samples with different contents of activator ions such as rare-earth or transition metal ions.

Rare earth doped oxide crystals are the most important class of solid-state gain media for the fabrication of miniature lasers. Yttrium aluminum garnet, $Y_3Al_5O_{12}$ (YAG) and Lutetium aluminum garnet, $Lu_3Al_5O_{12}$ (LuAG) are the most widely used laser materials due to their unusual combination of favorable chemical, optical, thermal, and mechanical properties. Although Nd$^{3+}$-doped YAG is the best known laser crystal, renewed interest in the development of Yb$^{3+}$-doped YAG in recent years is the result of the development of InGaAs diode lasers that emit around 980 nm, a radiation that is strongly absorbed by the Yb ion. Recently, room-temperature, high power diode-pumped lasers have been demonstrated using Yb:YAG active media. It has been proposed that Yb:YAG is a promising laser material which is an alternative to Nd:YAG in high-power systems.

Growth of un-doped, Nd and Yb-doped YAG and LuAG fiber crystals by $\mu$-PD technique is reported in this chapter. The fibers are considered to be attractive


Table 7.1: Growth parameters of RE$^{3+}$ doped YAG and LuAG single crystal fibers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting melt</td>
<td>$(M_{1-x}RE_x)<em>3Al_5O</em>{15}$, where $x=0$, 0.005, 0.01 and 0.02, $M=Y$ or Lu, $RE=Yb^{3+}$ or $Nd^{3+}$.</td>
</tr>
<tr>
<td>Crucible</td>
<td>Ir, conical shape with nozzle 0.7 mm</td>
</tr>
<tr>
<td>Heating method</td>
<td>RF Generator at a frequency of 20 KHz with RF coil</td>
</tr>
<tr>
<td>Seed orientation</td>
<td>$&lt;111&gt;$ YAG and $&lt;111&gt;$ LuAG</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>$N_2$ gas (gas flow 1.5 l/min)</td>
</tr>
<tr>
<td>Pulling rate</td>
<td>0.5 - 5 mm/min</td>
</tr>
<tr>
<td>Fiber length</td>
<td>up to 340 mm</td>
</tr>
<tr>
<td>Fiber diameter</td>
<td>0.5 - 1.5 mm</td>
</tr>
</tbody>
</table>

materials for the fabrication of miniature laser sources.

In each of the following sections I will discuss the measurements that we performed and their results.

7.1 Growth Process

During scientific stage at the Institute of multidisciplinary research for Advanced Materials (IMRAM), Tohoku Univ., Japan, I grew several rare earth doped $Y_3Al_5O_{12}$ and $Lu_3Al_5O_{12}$ fiber single crystals. Few differences in this growth process exist and I will mention them briefly in the following section.

7.1.1 Starting Materials

$Y_2O_3$, $Al_2O_3$, $Lu_2O_3$, $Nd_2O_3$ and $Yb_2O_3$ powders of 99.99% purity were used as starting materials without preliminary sintering. Powders were mixed in the stoichiometric ratio of $(Y_{1-x}RE_x)_3Al_5O_{15}$, where $x=0$, 0.005, 0.01 and 0.02, RE=$Yb^{3+}$ or $Nd^{3+}$.

Also for RE$^{3+}$ doped LuAG, powders were mixed in the stoichiometric ratio of $(Lu_{1-x}RE_x)_3Al_5O_{15}$ where $x=0$, 0.005, 0.01 and 0.02, RE=$Yb^{3+}$ or $Nd^{3+}$. Desired quantities of compounds were carefully weighted and mixed by grinding in Ethanol with an agate mortar and pestle for 15 to 20 min., and dried at 100°C during 3-5 hr. Ten different compositions were prepared by mixing the powders.
7.1.2 Hot Zone System and Growth Procedures

Mixed powders were loaded into the iridium crucible which was 38 mm in height and 16 mm in diameter. The crucible was placed on an Alumina pedestal in a vertical quartz tube and was heated inductively using RF generator at a frequency of 20 KHz. High density and high-purity 99.7% alumina ceramic was used to surround the crucible for the thermal insulation. Hot zone Japanese design are shown in Fig. (4.12). This heating system was specially designed for the fabrication of crystal fibers at high temperature (above 1800°C). The raw materials were melted in the Iridium crucible and allowed to pass through the micro-nozzle. The single crystal fiber was formed by attaching the seed crystal to the tip of the nozzle and melting its top part just before starting the growth, and then slowly pulled downward with a constant velocity. The crystals were grown in Nitrogen atmosphere (gas flow 1.5 l/min) to avoid oxidation of the crucible. Meniscus and growing crystal were observed with a CCD camera.

Temperature stabilization was obtained by controlling the power of the RF generator. The inductor was about 53 mm long and 70 mm diameter with 4 windings.

7.1.3 Growth Results

Two un-doped $<111>$ YAG and LuAG fibers of about 1.5 mm in diameter produced by the same technique were used as a seed. The crystals were grown at varying pulling-down rate form 0.05 to 5 mm/min. The fiber crystals were 0.5-1.5 mm in diameter and up to 340 mm in length.

The photographs of single crystals grown by the µ-PD are shown in Figs. (7.1 and 7.2). Transparent and crack-free crystals were obtained for these Yb$^{3+}$ and Nd$^{3+}$ concentrations. No visible inclusions are observed. As-grown crystals were slightly pale-blue colored. It may suggest the existence of a color center or even Yb$^{2+}$, because the crystals were grown in inert atmosphere and Yb$^{3+}$ can be easily reduced to Yb$^{2+}$. After annealing in air at 1400°C for 24 h, the color vanished.

After growth, as-grown fibers were cut to several test samples with different lengths perpendicular to the growth direction and both surface sides were polished using alumina and diamond powders. These several samples are used to perform the following different measurements. For powder X-ray measurements we grounded pieces of the samples to fine grain size.
Figure 7.1: The obtained crystals: (a) un-doped YAG, (b) 0.5% Yb:YAG, (c) 2.0% Yb:YAG and (d) 2.0% Yb:LuAG

Figure 7.2: The obtained crystals: (a) un-doped LuAG, (b) 0.5% Nd:LuAG, (c) 1.0% Nd:LuAG and (d) 0.5% Nd:YAG
7.2 Powder X-Ray Diffraction Measurements

To identify the generated phase of each fiber, powder X-ray diffraction analysis (XRD) was carried out in the $2\theta$ range from 10° to 80° using the RIGAKU diffractometer. Measurements were performed in air and the X-ray source was Cu $K\alpha$, the accelerating voltage was 40 KV, and the tube current was 30 mA. All X-ray experiments were carried out at room temperature.

Powder XRD patterns after growth process are shown in Fig. (7.3) for un-doped and Yb$^{3+}$ and Nd$^{3+}$ doped YAG, and in Fig. (7.4) for un-doped and Yb$^{3+}$ and Nd$^{3+}$ doped LuAG.

All peaks in each pattern are sharp and could be indexed. This means that single phase with garnet type structure was formed in all the concentration range and no impurity phases were observed. It is important to point out that 100% of the melt was usually solidified into the fibers and no shifting of melt composition resulting in second phase formation was detected during the growths. Therefore, the end parts of the crystals were single garnet phase materials of reasonable optical quality.

Lattice constants became systematically larger with Yb concentration in case of Yb doped LuAG. As the Yb concentration in LuAG increase, diffraction peaks shift...
Figure 7.4: Evolution of the powder X-ray diffraction as a function of the Yb and Nd concentrations in dodecahedral site of LuAG

to the left, constantly. This means that the lattice constant slightly increases as Yb increases. This tendency is reasonable. As the ionic radii of Yb$^{3+}$ is larger than that of Lu$^{3+}$, the lattice constant tends to increase linearly as the concentration of Yb$^{3+}$ increases.

On the other hand, the tendency was the opposite in the case of Yb:YAG. As the ionic radii of Yb$^{3+}$ is smaller than that of Y$^{3+}$, the lattice constant tends to decrease by the substitution in Y$^{3+}$ site linearly as the concentration of Yb$^{3+}$ increases. Both changes are in good agreement with Vegard’s law [50].

7.3 EPMA Measurements for RE doped YAG

Electron Probe Micro Analysis (EPMA) is used to analyze the distribution of the ion concentrations inside the crystal. We discussed the distribution and segregation coefficient in section (2.4) in details.

7.3.1 Segregation Coefficients of Yb and Nd doped YAG

Since the control of dopant and impurities in the grown crystal is important, rare earth doped YAG fibers were analyzed for the distribution of Yb$^{3+}$ and Nd$^{3+}$ ion
7.3 EPMA Measurements for RE doped YAG

Concentrations by EPMA using the JEOL JAX-8621MX. The compositions were measured along the growth axis using an electron probe 10 µm in diameter. Three pieces of 10 mm long each, are taken from the beginning, the middle and the end of the fiber respectively. The lateral surface of these three parts are polished. The EPMA composition analysis was performed with a step of 0.5 mm along the fiber length.

The results of these measurements are shown in Figs. (7.5 and 7.6). Each group of points on the graph represents the measurement on a piece of the fiber from three pieces that we taken to do the measurement.

Except for the starting point of the growth, which were affected by un-doped YAG seed, we did not detect any decrease or increase of Yb concentration along the growth axis. Taking into consideration the very small amount of Yb and Nd in the crystal and the corresponding accuracy of the measurements, we concluded that there was no tendency of a non-uniform axial distribution of the RE dopant. According to Eq. (2.10), we calculated the segregation coefficient of $Yb^{3+}$ and $Nd^{3+}$. In both cases it was found to be close to unity, in particular for $Yb^{3+}$ $K_{eff}(Yb^{3+}) \approx 1$, and for $Nd^{3+}$ $K_{eff}(Nd^{3+}) \approx 0.9$, which is a good result if we compare it with the typical value for CZ growth ($K_{eff}(Nd^{3+}) = 0.2$)\[5\]. The large oscillations in Yb concentration observed follow from the relatively low accuracy of the EPMA technique especially when the dopant concentration is very low with respect to all atoms forming the crystal.
7.4 Spectroscopic Measurements and their Analysis for Yb\(^{3+}\) doped YAG and LuAG

Room temperature absorption measurement was performed by means of the spectrophotometer described in (4.4.1). Absorption measurements of Yb\(^{3+}\) doped YAG and LuAG were performed between 200 and 3200 nm with a resolution of 0.5 nm down to 1050 nm and 1 nm further on.

On the other hand, the room temperature fluorescence spectra for Yb\(^{3+}\) doped crystals were measured by exciting the sample by a cw fiber-coupled semiconductor diode laser tuned to around 970 nm. The set up is described in section (4.4.3) in details.

7.4.1 Yb\(^{3+}\) Absorption and Emission Spectra

Absorption and fluorescence measurements were carried out at room temperature on optically polished samples of various lengths, 0.92 cm long for 0.5 % Yb:YAG, 0.85 cm long for 2% Yb:YAG and 0.76 cm long for 2% Yb:LuAG. The absorption spectra between 200 and 3000 nm of as-grown 2% Yb:YAG (as an example Yb\(^{3+}\) doped YAG and LuAG fibers) before and after annealing are shown in Fig. (7.7).

Two absorption bands located at wavelengths \(\approx 384\) and \(652\) nm, respectively. After annealing at 1450\(^\circ\)C in air for 24 h, the two absorption bands vanish. These two absorption bands degrade intrinsic absorption bands of Yb\(^{3+}\) in Yb:YAG. Since the
7.4 Spectroscopic Measurements and their Analysis for Yb$^{3+}$ doped YAG and LuAG

Figure 7.7: Room temperature absorption spectra of 2% Yb:YAG single crystal fiber before and after annealing.

crystals were grown in an inert atmosphere ($N_2$ gas), so it is possible for Yb$^{3+}$ to be reduced to Yb$^{2+}$, and 384 nm absorption band is attributed to the 4f-5d transition of Yb$^{2+}$ in the YAG host [51]. The experiments on Yb:YAG crystals with different annealing conditions verified that these two absorption band weakened or disappeared at the same time. As a result the F center perturbed by the rare-earth ion, Yb$^{2+}$ is responsible for the 652 nm absorption band. Therefore, after annealing, Yb$^{2+}$ → Yb$^{3+}$, the two absorption bands disappear.

The effects of Yb$^{2+}$ on Yb:YAG involved two aspects: one is that the charge needs to be compensated and the RE$^{3+}$-F color center is formed; The other aspect is the distortion of lattices due to the discrepancy between ion radius of Yb$^{2+}$ and Y$^{3+}$ in the octahedral structure, where $R$(Yb$^{2+}$) = 0.114, $R$(Yb$^{3+}$) = 0.0985 and $R$(Y$^{3+}$) = 0.106 nm. After annealing, the crystal changes from blue to colorless suggesting that the Yb$^{2+}$ and color center was eliminated.

The comparative result for the ytterbium absorption bands are reported in Figs. (7.8 and 7.9) and in Table (7.2). The arrows in each figures indicate the absorption transitions between Stark levels corresponding to Fig. (7.10).

The peak value of the $^2F_{7/2} → ^2F_{5/2}$ transition is $\alpha = 0.6 \text{ cm}^{-1}$ at 968.6 nm in 0.5% Yb:YAG, $\alpha = 2.3 \text{ cm}^{-1}$ at 968.3 nm in 2% Yb:YAG and $\alpha = 2.37 \text{ cm}^{-1}$ at
Figure 7.8: Room temperature absorption spectrum of the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition, the arrows indicate the absorption transitions between Stark levels corresponding to Fig. (7.10).

Figure 7.9: Room temperature absorption spectrum of the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition in 2% Yb:LuAG (solid line) in comparison with 2% Yb:YAG single crystal fiber.
7.4 Spectroscopic Measurements and their Analysis for Yb$^{3+}$ doped YAG and LuAG

Figure 7.10: Schematic energy levels diagram of Yb$^{3+}$ for absorption, ($^2F_{7/2} \rightarrow ^2F_{5/2}$ transition), and emission, ($^2F_{5/2} \rightarrow ^2F_{7/2}$ transition).

Table 7.2: Absorption coefficients of the zero phonon line (1→5) transition for the fibers under investigation

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Peak value (nm)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 % Yb:YAG</td>
<td>968.6</td>
<td>0.6</td>
</tr>
<tr>
<td>2 % Yb:YAG</td>
<td>968.3</td>
<td>2.3</td>
</tr>
<tr>
<td>2 % Yb:LuAG</td>
<td>967.7</td>
<td>2.37</td>
</tr>
</tbody>
</table>
967.7 nm in 2% Yb:LuAG.

From these values of absorption coefficients we can see that $\alpha_{0.5\%Yb:YAG} \approx \frac{1}{3} \alpha_{2\%Yb:YAG}$ and $\alpha_{2\%Yb:YAG} \approx \alpha_{2\%Yb:LuAG} \pm 0.07$ as expected.

Although the Yb ion has a simple electronic structure with only one excited state ($^2F_{5/2}$) above the ground state ($^2F_{7/2}$), the absorption spectra are rather complicated because they are composed by many different lines. In fact Yb ions replace Y in c-dodecahedral sites of $D_2$ local symmetry, as a consequence the degeneracy of the two multiplets is partially raised and a total of four Stark doublets are separated from the ground state and three from excited state are separated. Therefore a maximum of 12 lines are expected in the room temperature absorption and emission spectra. In our fibers, as we can see from Figs. (7.8 and 7.9) 11 absorption lines are observed for Yb$^{3+}$ doped YAG and LuAG single crystal fibers. The main absorption peaks are labeled with the arrows indicate the absorption transitions between Stark levels corresponding to Fig. (7.10).

Fig. (7.9) shows the absorption of 2% Yb:LuAG in comparison with 2% Yb:YAG. Both YAG and LuAG hosts have the same crystal garnet structure and both are doped with 2% Yb$^{3+}$, but the absorption spectra of both are different as expected. This is because Yb$^{3+}$ is substituted Y$^{3+}$ site in YAG and Lu$^{3+}$ site in LuAG. Since the ionic radius of Y$^{3+}$ and Lu$^{3+}$ are different, it is expected that the dopant will make a different distortion in the lattice depending on the ionic radius of the original ion.

Figs. (7.11, 7.12 and 7.13) show the emission spectra of the 0.5% Yb:YAG, 2% Yb:YAG and 2% Yb:LuAG fibers. The arrows in each figures are indicate the emission transitions between Stark levels corresponding to Fig. (7.10). Like in absorption, the emission spectra show a series of spectra lines corresponding to the transitions between the various stark sublevels corresponding to Fig. (7.10). The main difference with absorption is the different intensity of all the lines mainly due to the different Boltzmann population of the starting level. Moreover in the emission spectra the zero phonon line ($5\rightarrow1$) can not be observed because is covered by the pump laser scattering.
7.4 Spectroscopic Measurements and their Analysis for Yb$^{3+}$ doped YAG and LuAG

Figure 7.11: Room temperature fluorescence spectrum of the $^2F_{5/2} \rightarrow^2 F_{7/2}$ transitions in 0.5% Yb:YAG, the zero phonon line ($5\rightarrow 1$) can not be observed because is covered by the pump laser scattering. The arrows indicate the emission transitions between Stark levels corresponding to Fig. (7.10).

Figure 7.12: Room temperature fluorescence spectrum of the $^2F_{5/2} \rightarrow^2 F_{7/2}$ transitions in 2% Yb:YAG.
7.4.2 Yb$^{3+}$ Decay Time Measurements

To evaluate the quality of the samples in view of possible laser applications, it is necessary to measure the lifetime of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transitions. In fact, the presence of unwanted contaminations even at very low concentrations (ppm) can sometimes produce a quenching effect that shortens the lifetime of the emitting level.

For fluorescence lifetime measurements, the sample was excited by a pulsed tunable Ti:Sapphire laser (pumped by the 2nd harmonic of the 1.06 μm laser emission of a pulsed Nd:YAG laser) with 10 Hz repetition rate, 30 ns pulse width, a tunability range of 770-980 nm and 12 mJ of maximum pulse energy. We collected the signal from a short portion of the sample with a 1mm slit in front of the observed side of the fiber in order to detect a uniformly pumped volume and to reduce any undesired effect, such as radiation trapping, that can cause an uncorrected evaluation of the decay time; furthermore, the power incident on the fibers was reduced as much as possible by means of an attenuator (composed of two Brewster windows) to suppress non-linear effects. The signal from the detector (InSb) was sent, by fast amplifiers, to a digital oscilloscope connected to a computer. The response time of the system was ≈ 3 μs.

The decay curve of 0.5% Yb:YAG shows an exponential behavior, as shown in Figure 7.13: Room temperature fluorescence spectrum of the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transitions in 2% Yb:LuAG.
7.5 Spectroscopic Measurements and their Analysis for Nd$^{3+}$ doped YAG and LuAG

Fig. (7.14). Experimental lifetime values have been fitted to a unique exponential profile with an excellent agreement. Table (7.3) shows a summary of the result obtained for the life time measurements for 0.5% Yb:YAG, 2% Yb:YAG and 2% Lu:YAG. The data shows that as the Yb ion concentration increases in YAG and LuAG hosts, the lifetime becomes slightly longer. This can be because radiation trapping process. Our results are in good agreement with those obtained in bulk crystals. For example, the measured lifetime of Yb:YAG crystal is 1.08 ms [52].

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Decay Time (ms)</th>
<th>Error (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Yb:YAG</td>
<td>1.04</td>
<td>0.01</td>
</tr>
<tr>
<td>2% Yb:YAG</td>
<td>1.17</td>
<td>0.01</td>
</tr>
<tr>
<td>2% Yb:LuAG</td>
<td>1.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

7.5 Spectroscopic Measurements and their Analysis for Nd$^{3+}$ doped YAG and LuAG

As in case of Yb$^{3+}$ doped garnets, room temperature absorption spectra of Nd$^{3+}$ doped YAG and LuAG have been measured by means of the spectrophotometer.
Absorption measurements of Nd³⁺ doped YAG and LuAG were performed in two regions, between 250 to 900 nm with a resolution of 0.4 nm and between 1450 to 3000 nm with a resolution of 1 nm.

On the other hand, room temperature fluorescence spectra of Nd doped YAG and LuAG were obtained by exciting the sample by cw Ti : Al₂O₃ laser tuned to the maximum absorption of the samples under investigation, as described in section (4.4.3). The only difference is that the luminescence was chopped and focused by a 7.5 cm focal length Infrasil lens on the input slit of a monochromator (TRIAX320) with 25 cm focal length, as shown in Fig. (4.16). A suitable filter was put in front of the input slit of the monochromator to completely suppress any laser scattering from the samples.

For fluorescence lifetime measurements, the sample was excited (as in case of Yb doped crystals) by a pulsed tunable Ti:Sa laser (pumped by the 2nd harmonic of the 1.06 µm laser emission of a pulsed Nd:YAG laser) and the detection apparatus was similar to that described in section (4.4.3).

7.5.1 Nd³⁺ Absorption and Emission Spectra and their Analysis

As in the previous section of Yb³⁺ doped crystals, absorption measurements were carried out at room temperature on optically polished samples of various lengths, 0.96 cm long for 0.5 % Nd:YAG, 0.92 cm long for 1 % Nd:YAG, 1.43 cm long for 0.5 % Nd:LuAG and finally 0.85 cm long for 1 % Nd:LuAG.

Absorption bands between 300 to 900 nm and between 1450 to 2500 nm for Neodymium doped YAG are shown in Figs. (7.15 and 7.16) and those for doped LuAG are shown in Figs. (7.17 and 7.18). All the sharp bands shown are due to Nd³⁺ . The ground and first excited Stark levels of ⁴I₀/₂ (4f) ground multiplet of Nd:YAG are separated by ≈ 133 cm⁻¹ [53], and all transitions observed in the optical absorption spectra originate from the ground crystal field level ⁴I₀/₂. The peak values and the absorption coefficients of the transitions are shown in Table (7.4). For all samples we can see that the absorption around 800 nm is stronger and broader and higher Nd dopant concentrations, because of a more favorable segregation coefficient, can be reached, which is more interesting for diode pumping.

On the other hand, unexpected non linear dependence has been observed between
the concentration of the dopants and the absorption coefficients. This could be because the segregation of the Nd concentration is different from one along the fiber length. The Fluorescence spectrum of transitions between the various Stark sub-levels in Nd$^{3+}$ were measured by pumping the samples on the absorption peak of the 808 nm band which correspond to the $^4I_{9/2} \rightarrow ^4F_{5/2} + ^2H_{9/2}$ absorption. By means of integral $\beta - \tau$ method described in section (3.4) and decay time values described in the next section, we calculated the emission cross section of the obtained florescence.

Figs. (7.19 and 7.20) show the emission cross section spectra of the 0.5% Nd:YAG, 1% Nd:YAG, 0.5% Nd:LuAG and 1% Nd:LuAG fibers. The emission cross section spectra show a series of lines corresponding to the transitions from Stark components of manifold of the metastable $^4F_{3/2}$ state to the $^4I_J$ manifold after fast radiativeless decay occurs from the pumping level $^4F_{5/2}$ to the $^4F_{3/2}$. The $^4F_{5/2}$ level is identified as a second metastable state for Nd$^{3+}$ emission in YAG crystals. Nd$^{3+}$ ions substitute for Y$^{3+}$ ions in lattice sites having $D_2$ symmetry. As Nd$^{3+}$ ionic radius (0.112 nm) is larger than Y$^{3+}$ (0.106 nm), this substitution causes the formation of numerous micro-strains throughout the lattice [54] and limits the maximum concentration of Nd$^{3+}$ to a few percent in the garnet structure. Weak spectra appearing in the vicinity of strong emission or absorption lines from Nd$^{3+}$ ions in $D_2$ sites have
Figure 7.16: Room temperature absorption spectra of the Nd$^{3+}$ doped YAG between 1450 and 2500 nm.

Figure 7.17: Room temperature absorption spectra of the Nd$^{3+}$ doped LuAG between 300 and 900 nm.
7.5 Spectroscopic Measurements and their Analysis for Nd\(^{3+}\) doped YAG and LuAG

Figure 7.18: Room temperature absorption spectra of the Nd\(^{3+}\) doped LuAG between 1450 and 2500 nm.

Table 7.4: Absorption coefficients of different transition levels for the Nd\(^{3+}\) doped Garnet fibers under investigation

<table>
<thead>
<tr>
<th>Transition Level</th>
<th>(\lambda_{max}) (nm)</th>
<th>(\alpha (\text{cm}^{-1}))</th>
<th>(\alpha (\text{cm}^{-1}))</th>
<th>(\alpha (\text{cm}^{-1}))</th>
<th>(\alpha (\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(0.5% Nd:YAG)</td>
<td>(1% Nd:YAG)</td>
<td>(0.5% Nd:LuAG)</td>
<td>(1% Nd:LuAG)</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^2 D_{3/2} + ^2 D_{5/2})</td>
<td>354</td>
<td>0.439</td>
<td>1.440</td>
<td>0.394</td>
<td>0.951</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^2 G_{7/2})</td>
<td>531.2</td>
<td>0.399</td>
<td>1.302</td>
<td>0.295</td>
<td>0.466</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^2 G_{5/2})</td>
<td>588.8</td>
<td>0.802</td>
<td>2.204</td>
<td>0.497</td>
<td>0.858</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^4 F_{7/2} + ^4 S_{3/2})</td>
<td>748.4</td>
<td>0.827</td>
<td>2.800</td>
<td>0.530</td>
<td>0.976</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^4 F_{5/2} + ^2 H_{9/2})</td>
<td>808.4</td>
<td>0.953</td>
<td>3.197</td>
<td>0.582</td>
<td>1.070</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^4 F_{3/2})</td>
<td>868.7</td>
<td>0.306</td>
<td>1.030</td>
<td>0.183</td>
<td>0.338</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^4 I_{15/2})</td>
<td>1735</td>
<td>0.053</td>
<td>0.170</td>
<td>0.052</td>
<td>0.075</td>
</tr>
<tr>
<td>(^4 I_{9/2} \rightarrow ^4 I_{13/2})</td>
<td>2327</td>
<td>0.194</td>
<td>0.568</td>
<td>0.101</td>
<td>0.168</td>
</tr>
</tbody>
</table>
Figure 7.19: Emission cross section of 1% Nd:YAG from $^4F_{3/2}$ state to Stark components of manifold of the ground $^4I_J$ term.

Figure 7.20: Emission cross section of 1% Nd:LuAG form $^4F_{3/2}$ state to Stark components of manifold of the ground $^4I_J$ term.
7.5 Spectroscopic Measurements and their Analysis for Nd$^{3+}$ doped YAG and LuAG

Table 7.5: The emission cross section values for $^{4}F_{3/2} \rightarrow ^{4}I_{J}$ in the Nd$^{3+}$ doped Garnet fibers under investigation

<table>
<thead>
<tr>
<th>Transition Level</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\sigma_{em}$ ($10^{-20} \text{cm}^2$) (Nd:YAG)</th>
<th>$\sigma_{em}$ ($10^{-20} \text{cm}^2$) (Nd:LuAG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$</td>
<td>885.9</td>
<td>7.33</td>
<td>7.42</td>
</tr>
<tr>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$</td>
<td>1064.6</td>
<td>36.8</td>
<td>33.56</td>
</tr>
<tr>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{13/2}$</td>
<td>1338.6</td>
<td>40.9</td>
<td>38.84</td>
</tr>
</tbody>
</table>

been attributed in several cases as coming from Nd$^{3+}$ ions that experience a slightly different crystal field due to lattice strain and defects that arise during the growth process ([55] and [56]).

The emission in the range of 850 nm to 960 nm is attributed to the $^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$ transition, while in the range from 1050 to 1130 nm is attributed to the $^{4}F_{3/2} \rightarrow ^{4}I_{11/2}$ transition and in the range of 1300 to 1400 is attributed to the $^{4}F_{3/2} \rightarrow ^{4}I_{13/2}$ transition. The emission cross section values for these transitions are listed in Table (7.5) and are shown as a schematic diagram in Fig (7.21).

7.5.2 Nd$^{3+}$ Decay Time Measurements

As in the previous section of Yb$^{3+}$ decay time, to evaluate the quality of the samples in view of possibility laser applications, it is necessary to measure the lifetime of the $^{4}F_{3/2}$ manifold.

The sample was excited by a pulsed tunable Ti:Sa laser and the detection apparatus was similar to that described in sections (4.4.4 and 7.4.2).

The decay curves of Nd$^{3+}$ show an exponential behavior, as shown in Figs. (7.22 and 7.23). Experimental lifetime values have been fitted to a unique exponential profile with an excellent agreement. Table (7.6) shows a summary of the result obtained for the life time measurements for 0.5% Nd:YAG, 1% Nd:YAG, 0.5% Nd:LuAG and 1% Nd:LuAG.

The data shows that as the Nd ion concentration increases in YAG and LuAG hosts, the lifetime becomes slightly decrease. Our results are in good agreement with those obtained in bulk crystals. For example, the measured lifetime of Nd:YAG
Figure 7.21: Energy level structure of the trivalent neodymium ion (with wavelength numbers for Nd:YAG).

Table 7.6: Decay Time for the fibers under investigation

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Decay Time (µs)</th>
<th>Error (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% Nd:YAG</td>
<td>208</td>
<td>4.8</td>
</tr>
<tr>
<td>1% Nd:YAG</td>
<td>200</td>
<td>2</td>
</tr>
<tr>
<td>0.5% Nd:LuAG</td>
<td>199</td>
<td>3.8</td>
</tr>
<tr>
<td>1% Nd:LuAG</td>
<td>181</td>
<td>2.5</td>
</tr>
</tbody>
</table>

bulk crystal is 200 µs [57].
7.5 Spectroscopic Measurements and their Analysis for Nd$^{3+}$ doped YAG and LuAG

Figure 7.22: Room temperature decay time of the $^4F_{3/2}$ excited state in Nd:YAG

Figure 7.23: Room temperature decay time of the $^4F_{3/2}$ excited state in Nd:LuAG.
7.6 Conclusions

It has been demonstrated in this chapter that the micro-pulling-down technique is able to produce single crystalline samples characterized by uniform distributions of active dopants and optical quality comparable to that of bulk crystals present in literature. These features in combination with the relatively low costs of both production and mechanical processing nominate those samples as active media for the development of miniaturized solid state lasers.
Chapter 8
Spectroscopic and Scintillation Properties of Ce$^{3+}$ doped YAP Single Crystal Fibers

Introduction
At present, various scintillators such as Tl:NaI, Tl:CsI, BaF$_2$, etc. are used for many applications in the field of research, medicine and industry. New ones, for example CeF$_3$, Ce:YAG and others, are being investigated with good results [58]. It is a challenge to find a dense and fast radiation scintillator useful in high energy physics, astrophysics, medicine and other applications. Several studies ([59] and [60]) have shown that Ce:YAP is a good candidate as a $\gamma$-ray detector. Ce:YAP is an interesting scintillator which exhibits fast scintillation, high light yield and very good mechanical and chemical properties. It has a broad emission spectrum peaking at 370 nm and its scintillation decay time is 20 ns. The light output is about 40% that of Tl:NaI, twice that from BGO. Ce:YAP has the structure of Perovskite. Mechanical properties of Ce:YAP are similar to those of garnet. It has high hardness, is mechanically and chemically stable and is not soluble in inorganic acids and resistant to alkali. The mechanical properties allow the deposition of very thin layers of reflectors on the surfaces. The basic physical and chemical properties of Ce:YAP are presented in Table (8.1) and compared with those of other scintillator materials.

As it can be seen in Table (8.1), Ce:YAP shows some advantages in comparison to
other scintillators, in particular: relatively high density, high light yield and short decay time.
As in previous chapters, I will discuss the measurements that we performed and their results.

8.1 Growth Process

Usually, Ce:YAP single crystals are grown by the Czochralski method in a molybdenum crucible and in reducing atmosphere. The maximum concentration of Ce$^{3+}$ in a single crystal is limited by the segregation coefficient and growing conditions, and usually is about 0.6 mol%. The Ce$^{3+}$ activator ion is 1.18 Å in ionic radius, and has a $4f^1$ electron configuration. The size of the Ce$^{3+}$ ion suggests that the rare earth dopant would preferentially be replaced in the Y$^{3+}$ sites (1.06 Å), rather than the Al site (0.51 Å). But still the ionic radius of Ce$^{3+}$ is 12% larger than that of Y$^{3+}$, so it is difficult to incorporate a large amount of cerium into the lattice using the Czochralski method without constitutional supercooling effects and second-phase precipitations. Another major difficulty encountered during growth by the conventional Czochralski method and subsequent cutting of the crystals is a tendency to crack.

In this work, we have tried to use the $\mu$-PD method to grow single crystal fibers of
Table 8.2: Growth parameters of Ce$^{3+}$ doped YAP single crystal fibers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting melt</td>
<td>$(Y_{1-x}Ce_x)AlO_3$, $x=0$, 0.002, 0.005 and 0.007.</td>
</tr>
<tr>
<td>Crucible</td>
<td>Ir, conical shape with 0.5 mm or 2 mm diameter nozzle</td>
</tr>
<tr>
<td>Heating method</td>
<td>50 KHz RF Generator with RF coil</td>
</tr>
<tr>
<td>Seed orientation</td>
<td>$&lt;001&gt;$ Ce:YAP</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Ar gas (5N Purity)</td>
</tr>
<tr>
<td>Pulling rate</td>
<td>0.02 - 0.1 mm/min</td>
</tr>
<tr>
<td>Fiber length</td>
<td>10 mm to 150 mm</td>
</tr>
<tr>
<td>Fiber diameter</td>
<td>0.5 - 2.5 mm</td>
</tr>
</tbody>
</table>

high quality and transparency. With the $\mu$-PD technique we succeeded to incorporate a large amount of cerium (with respect to that of Czochralski method) into the lattice without constitutional supercooling effects and/or second phase precipitations. This is because of the relatively high growth rate and reasonable temperature gradient near the vicinity of solid liquid interface. The $\mu$-PD method can be characterized by the possibility to grow device size crystals without degradation in the quality or cracks, with low thermal strain compared to other growth methods. Moreover, it is easy to have a precise control of the temperature during the growth and to control the shape of the crystals as well.

During my Ph.D. work we succeeded in growing Ce doped YAlO$_3$ single crystal fibers with different lengths and diameters. We started growing 0.5 mm diameter fibers with length up to 150 mm. For scintillation applications, we were requested to provide shorter fibers (about 10 - 15 mm in length) but with much longer diameter ($\approx 2 - 2.5$ mm). The aim of this is to compare the scintillation performance of the $\mu$-PD grown crystal fibers with that of a similar size YAP pixel cut and polished from a Cz grown boule that is commercially available and usually used in $\gamma$-ray detectors for medical applications.

In order to reach this goal we modified the crucible nozzle to have a 2 mm diameter aperture and we succeeded in growing $\approx 2.5$ mm diameter fibers.
8.1.1 Starting Materials

$Y_2O_3$, $Al_2O_3$ and $Ce_2O_3$ high purity powders of 99.999% were used as starting materials. Ce:YAP, powders were mixed in the stoichiometric ratio of $(Y_{1-x}Ce_x)AlO_3$, where $x=0$, 0.002, 0.005 and 0.007.

Desired quantities of various compositions were carefully weighed and mixed by grinding in Ethanol with an agate mortar and pestle for 15 to 20 min., and dried at 100 °C for 3-5 hr. The powder was then cold pressed into 2 mm thick, 10 mm diameter pellets, under 200Mpa pressure. Preliminary sintering was performed by heating these disks in a furnace at 1450 °C for 24 hr.

The growth parameters are summarized in Table (8.2).

8.1.2 Hot Zone System and Growth Procedures

As in previous chapters, mixed powders were loaded into the iridium crucible that was placed on a Zircoa pedestal in a vertical high purity and high density Alumina ceramic tube. and it was inductively heated using RF generator. Compressed alumina and Zircoa tubes were used to surround the crucible for thermal insulation. Moreover, a vertical quartz tube was put for better thermal isolation. Our hot zone design is shown in Fig. (4.7). Fig. (8.1) shows a moment of fiber growth recorded by CCD camera, where the black cone at the top of the picture is the bottom part of the crucible, the white region is the meniscus (solid liquid interface) and the grown...
8.1 Growth Process

fiber is the vertical dark strip under the meniscus.

8.1.3 Growth Results

A Ce doped < 001 > oriented Ce:YAP parallelepiped of about 2 mm lateral size produced by the Czochralski technique was used as a seed. The crystals were grown at varying pulling rates from 0.02 to 0.1 mm/min. The crystal fibers were 0.5 - 2.5 mm in diameter and up to 150 mm in length. We observed that the quality of the fibers was dependent on the pulling rate and better quality fibers were obtained at slower pulling rates. The best fiber was grown at 0.05 mm/min. During the first growth attempts we observed a phase transformation to YAG at the end of the fiber growth. This is probably due to instability of the perovskite structure when the temperature exceeds the YAP growth temperature. In fact the two oxide crystals have similar melting points, YAG being only 100 °C higher. Moreover at the end of the growth process we increased the temperature to compensate the temperature loss during pulling down. Since our furnace works under voltage control we have not a direct temperature feedback, so sometimes the temperature exceeds the correct growth temperature and phase transformation to YAG phase can happens. Fig. (8.2) shows this phase transformation from YAP to YAG phase, that is characterized by yellow color.

After many attempts we had better sense in controlling the voltage to have the correct growth temperature throughout the whole growth process. Photographs of some of the single crystal fibers grown by the μ-PD are shown in Fig. (8.3). For these Ce³⁺ concentrations, the crystal were almost transparent, crack-free and moreover no garnet phase appeared. No visible inclusions are observed. After growth, as-grown fibers were cut to several test samples with different lengths perpendicular to the growth direction and polished on both surfaces using alumina and diamond powders if necessary. Several samples are used to perform the following different measurements.
8.2 Laue XRD Measurement

By means of Laue chamber described in section (4.3.1) we performed X-ray diffraction measurements to check the single crystalline character of the samples and also to identify the crystallographic axes direction. In case of Ce:YAP the accelerating voltage was 25 KV, and the tube current was 30 mA with 15 min exposure time. All X-ray experiments were carried out at room temperature.

An example of the Laue picture with the simulation superimposed is shown in Fig. (8.4). As we can see all the X-ray reflections spots are sharp and clear and the white circles of the numerical simulation match the experimental pattern almost perfectly. As a result, we can say that the fibers are single crystal and maintain the seed orientation throughout all their length.

8.3 Optical Quality and Twins in Ce$^{3+}$:YAP Fibers

By means of the conoscopic observation of a cross section normal to the optic axis in a polarizing microscope as described in section (4.3.5) we observed the optical quality of the fibers. Some of the fibers were characterized by twinning as shown in Fig. (8.5). This twinning in Ce:YAP crystal can be understood from interchange
8.3 Optical Quality and Twins in Ce$^{3+}$:YAP Fibers

Figure 8.4: Laue simulation for Ce doped YAP single crystal fiber

![Laue simulation for Ce doped YAP single crystal fiber](image)

Figure 8.5: Observation of twins in 0.2% Ce:YAP single crystal fiber. In (a) the two polarizers are parallel, in (b) and (c) are perpendicular

![Observation of twins in 0.2% Ce:YAP single crystal fiber](image)

between the nearly identical a (5.3265 Å) and b (5.1777 Å) lattice parameters [35], which means make the crystal twins easily. Because there are great differences between the thermal expansion coefficients along the three crystalline axes ($4.2 \times 10^{-6}$, $5.1 \times 10^{-6}$ and $11.7 \times 10^{-6}$ K$^{-1}$ for a, b and c respectively in YAP crystals [61]), thermal stresses during crystal cooling should also be responsible for the twins in Ce:YAP crystals. The twinning process is so likely that other authors [62] even reported that the twins could be produced in thin (0.2 mm) Ce doped LuAlO$_3$ crystal slices during polishing. Because of the isostructural property between Ce:YAP and Ce:LuAP crystals, one can infer that the mechanical stresses induced during cutting and polishing thin slices may also give rise to the twins in Ce:YAP crystals, twins can lead to optical inhomogeneity of crystals and also can make the crystal crack.
In order to prevent twinning in Ce:YAP single crystals, it is very important to adopt a small temperature gradient and a low cooling rate during crystal cooling.

The conoscopic figure of the fiber (Fig. 8.5) shows the existence of two different optically homogenous regions inside the fiber as a direct effect of twinning, which give origin to inhomogeneous birefringence. By putting the fiber between two parallel polarizer (Fig. 8.5a) it is possible to see the transmitted light from the whole fiber cross section but a dark line along a diameter indicates the presence of some inhomogeneities, while in Fig. (8.5b and c) we can see that the light is transmitted from one half of the fiber only, while the other appears opaque as a clear identification of two separate parts with different optical behaviour.

The key aspect to be noted while growing large RE$^{3+}$ doped YAP single crystals without twins and color centers is to avoid high thermal gradients during growth as well as a temperature shock due to disconnection of the crystal from the melt at the end of the growth process. The first issue can be fulfilled by the use of a longer after-heater to have a longer hot zone and therefore reduce thermal stress during the growth. The second issue is not so severe for fiber growth, anyway it is good practise to slowly decrease the crystal diameter towards the end of the crystal growth so that the thermal shock is minimized. Fig. (8.5) shows 0.5% Ce:YAP single crystal fiber in the two polarizers are perpendicular, no twins or stress are observed.
8.4 Spectroscopic Measurements: Results and Discussion

The trivalent rare-earth cerium ion (Ce$^{3+}$) with the electronic configuration $4f^1$ has $^2F_{7/2}$ and $^2F_{5/2}$ manifolds separated by about 2250 cm$^{-1}$ due to spin-orbit coupling. The $^2F_{5/2}$ ground manifold is occupied and the $^2F_{7/2}$ manifold is almost empty at room temperature because $kT \approx 200$ cm$^{-1}$. The first excited configuration is 5d at about 40000 to 50000 cm$^{-1}$ [63] and split by the crystal field in 2 to 5 components. Fig. (8.7) shows the simplified energy level scheme of the Ce$^{3+}$ ion. On the left hand side only the 4f level and 5d level are depicted without taking into account further interactions. On the right hand side the spin orbit (SO) coupling splits the 4f into two components, and the crystal field ($\Delta$) splits the 5d level into five crystal field components spanning all together some 15000 cm$^{-1}$.

Since the electron-lattice coupling of the 5d electrons is quite large, 4f $\leftrightarrow$ 5d transitions feature broad absorption and emission bands with large Stokes shifts between them. Weber [63] indicates that the ideal Perovskite structure of the YAlO$_3$ lattice is cubic with space group Pm3m. The cubic structure is slightly distorted when rare earth ions Ce$^{3+}$ enter the YAlO$_3$ lattice. The cerium ions Ce$^{3+}$ substitute for trivalent yttrium ions Y$^{3+}$ at $C_{1h}$ point site symmetry. The optical spectra of Ce$^{3+}$ doped in YAlO$_3$ crystals consist of f-f transitions in the infrared and f-d transitions in the ultraviolet.
Table 8.3: Absorption coefficients of the $^2P_{3/2} \rightarrow 5d$ transition for the fibers under investigation

<table>
<thead>
<tr>
<th>Fiber</th>
<th>thickness (mm)</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\lambda_{\text{peak}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% Ce:YAP</td>
<td>0.3</td>
<td>139.46</td>
<td>292</td>
</tr>
<tr>
<td>0.5% Ce:YAP</td>
<td>0.25</td>
<td>188.19</td>
<td>291</td>
</tr>
<tr>
<td>Pixel Ce:YAP</td>
<td>0.10</td>
<td>367.6</td>
<td>292</td>
</tr>
</tbody>
</table>

Figure 8.8: Ce:YAP Absorption spectrum in UV region.

8.4.1 Absorption of Ce$^{3+}$ :YAP

Room temperature absorption measurement was performed by means of the spectrophotometer described in section (4.4.1).

The measurement was performed between 200 and 400 nm with a resolution of 0.1 nm. The measurement is not polarized because the absorption band of Ce:YAP lie outside the transmission window of our polarizers. As 4f $\rightarrow$ 5d transitions are not parity forbidden, they have very high absorption (and emission) line strength cross sections. This leads to a very high absorption coefficient in the UV absorption region even for low doped samples. This fact, together with the small transversal dimension of our fibers, make the measurement quite difficult unless the sample is very thin. For this reason very thin optically polished slices of fibers are prepared for absorption measurements: 0.3 mm thick for 0.2 % Ce:YAP, 0.25 mm for 0.5 % Ce:YAP
and 0.21 mm for 0.7% Ce:YAP. Although the very small thickness (0.10 mm) of the most heavily doped sample we were not able to avoid saturation of the absorption. Moreover it was not possible to prepare a thinner sample without causing cracks or severe damage to the crystal. For this reason no quantitative results regarding the absorption coefficient or peak position are available for the 0.7% doping level.

The comparative results for the Ce$^{3+}$ bands are reported in Fig. (8.8) and in Table (8.3) together with the absorption background of the undoped YAP fiber that shown transparency in the region of interest.

As shown in Fig. (8.8), optical absorption bands for Ce$^{3+}$ in 0.2% Ce:YAP and 0.5% Ce:YAP are observed due to the electric dipole transitions from $^2F_{5/2}$ ground state to the first $5d^1$ excited state. The spectra show four peaks at 303 nm, 291 nm, 275 nm, and 238 nm. These values are identical and corresponds for those in the literatures [64].

According to the spectroscopic data, Weber [63] established the energy level diagram of 4f and 5d configurations of Ce$^{3+}$ in YAlO$_3$ at 300 K (Fig. 8.9).

The four peaks shown in Fig. (8.8) arise from Ce$^{3+}$. An additional weak peak at about 220 nm exists in energy level diagram for Ce$^{3+}$ doped YAlO$_3$ but is not evident in the absorption spectrum of 0.2% Ce:YAP and 0.5% Ce:YAP, but it is
clearly visible in the 0.7% Ce:YAP and in the pixel spectra. These five bands are all assigned to the 5d levels of Ce$^{3+}$.

### 8.4.2 Fluorescence of Ce$^{3+}$:YAP

Emission measurements were performed on an optically polished fiber for light polarized parallel ($\pi$) and perpendicular ($\sigma$) to the c crystallographic axis. The measurement was done between 310 and 460 nm. The two polarizations were selected using a UV Glan-Thompson polarizer. The emission measurements were performed between 310 and 460 nm by exciting the sample using a 100 W high-pressure mercury-lamp (HBO-100W) filtered by a 0.1 m Jobin-Yvon monochromator. With this setup we selected the 315 nm emission wavelength from the lamp that was focused on the crystal by means of a 7.5 cm focal length UV-grade silica lens. The emission was mechanically chopped and focused by a 10 cm UV-grade fused silica lens on the input slit of a computer-controlled 0.25 m monochromator and detected by a Hamamatsu R1464 photomultiplier. To avoid the spurious pump scattering, the signal was detected orthogonally to the direction of the exciting beam and processed by a lock-in amplifier. A UV Glan-Thompson polarizer selected the fluorescence polarization parallel ($\pi$) and perpendicular ($\sigma$) to the c optical axis. The overall resolution of the system was 3 nm. The optical response of the system was normalized for both polarizations by using a Deuterium lamp.

Fig. (8.10) shows the polarized emission cross-section spectra, evaluated by means of the so-called $\beta - \tau$ method [65], of the Ce$^{3+}$ in 0.5% Ce:YAP single crystal fiber together with the spectra of the Ce:YAP reference pixel for comparison purposes. These spectra arise from the transitions from the lowest crystal field components of 5d$^1$ excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground states and present two broad bands largely overlapping with a main peak of $6.61 \cdot 10^{-18}$ cm$^2$ located at 377 nm for the $\sigma$ polarization and a peak of $2.55 \cdot 10^{-18}$ cm$^2$ at 383 nm for the $\pi$ polarization. The emission spectra of the reference pixel do not differ from that of the fibers under study. The slight differences observed in the peak positions and in the line shape, may be ascribed to artifacts due to different re-absorption processes inside the two samples. Indeed, due to the very high line strength of the transition it is possible that some photons in the short wavelength part of the emission spectrum are re-absorbed before escaping the crystal. Since this probability depends on the doping
8.4 Spectroscopic Measurements: Results and Discussion

Figure 8.10: Polarized room temperature emission cross-sections of the 0.5% Ce:YAP (up) single crystal fiber, obtained from the emission spectra of 5d→4f, in comparison with Ce:YAP pixel (down).

concentration and on the geometry of the sample, different specimen may exhibit small differences in their spectra.

8.4.3 Decay time of Ce\(^{3+}\) :YAP

For the fluorescence lifetime measurements we excited the samples with a laser pulse at 263 nm and a duration of 5 ns full width half maximum (FWHM) by means of a fast phototube with 100 ps rise time and a 500 Gs/s sampling oscilloscope Tektronix TDS520 with a bandwidth of 500 MHz. We acquired the fluorescence decay in the spectral windows selected by using a 0.1 m Jobin-Yvon monochromator. For a determination of the lifetime, a single exponential fit was made on the tail of the decay but disregarding the first 15 ns after the rise of the fluorescence emission. In this way, we considered the evolution of the fluorescence emission in the absence of the excitation pulse. We performed the decay time measurement on our three fibers and in comparison with standard Ce:YAP crystal (pixel) grown by Czochralski method. The decay curves of Ce\(^{3+}\) show an exponential behavior, as shown in Fig. (8.11). Experimental lifetime values have been fitted to a unique exponential profile with
Figure 8.11: Room temperature decay time of the 5d excited state of Ce:YAP fibers in comparison with standard crystal.

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Decay Time (ns)</th>
<th>Error (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% Ce:YAP</td>
<td>21.9</td>
<td>0.5</td>
</tr>
<tr>
<td>0.5% Ce:YAP</td>
<td>22.5</td>
<td>0.8</td>
</tr>
<tr>
<td>0.7% Ce:YAP</td>
<td>22</td>
<td>0.6</td>
</tr>
<tr>
<td>Pixel Ce:YAP</td>
<td>23.5</td>
<td>1</td>
</tr>
</tbody>
</table>
an excellent agreement. Table (8.4) shows a summary of the result obtained for the life time measurements for 0.2% Ce:YAP, 0.5% Ce:YAP, 0.7% Ce:YAP and pixel Ce:YAP.

8.5 Scintillation Performance of Ce$^{3+}$ doped YAP Fibres

Scintillation performance has been performed by biophysics group in INFN, Pisa section. They performed the measurement, for medical and imaging applications, on our fiber and in comparison with standard crystal (pixel) grown by Czochralski method.

Introduction

Certain application-specific systems for Positron Emission Tomography (PET) require a spatial resolution below 2mm FWHM. The primary way to achieve such fine spatial resolution, whilst retaining a high stopping efficiency, is to use small, discrete scintillation pixels, formed into a 2D matrix. The relation of the pixel pitch to spatial resolution is seen in Eq. (8.1), where $\Gamma$ is the reconstructed image resolution (FWHM), $d$ the scintillation pixel width, $D$ the PET ring diameter, $R$ the effective positron range and $b$ is the pixel decoding process \[66\].

$$\Gamma = 1.25 \sqrt{\left(\frac{d}{2}\right)^2 + (0.0022D)^2 + R^2 + b^2}$$  \hspace{1cm} (8.1)

The scintillation material for the pixels is normally grown in a large boule which must then be cut to form the small individual pixels. Each pixel must then be polished, or at the very least, finely ground, before it is formed into a matrix. This cutting and polishing of a large number (several thousand) of small pixels (<2x2 mm$^2$) is very time consuming and therefore costly. It is hoped that this cost might be overcome by growing small diameter crystal fibres of scintillation material and forming them into a closed-packed array.

The objective of this project is therefore to investigate the possibility of growing YAP:Ce fibres of a doping and size that are well adapted to PET application. In order to test the performance of the samples a gamma-ray spectroscopy system has been employed.
8.5.1 Experimental Procedure

The scintillation light yields were measured under gamma-ray excitation ($^{22}$Na). The measurement setup was a very simple gamma-ray spectroscopy arrangement based upon a photomultiplier tube and multichannel analyzer, a schematic of which can be seen in Fig. (8.12). The photomultiplier used was the 12-stage XP2020 from Photonis, which is often employed for quantitative studies of scintillator light yield, for example [67] and [68]. The XP2020 has a gain of $3 \times 10^7$ at 2kV. The HV for the XP2020 is provided by a CAEN NIM module N126 whilst the PMT output signal is amplified and shaped by an Ortec 570 NIM module. This signal is then sent to a Tukan8k ADC and MCA PCI card for acquisition and display.

The various scintillators used in this test, including the fiber pieces, were first wrapped in PTFE (Teflon) tape on all sides, except the surface coupled to the PMT. The tape increases the light yield by providing a diffuse reflection of any light that escapes the crystal, such that it might reach the PMT. The scintillators were then coupled to the PMT entrance window with optical coupling grease of refractive index 1.46. We performed the measurement on our fibers and in comparison with standard crystal (pixel) grown by Czochralski method.

The photoelectron yield is defined as the number of photoelectrons ($N_{pe}$) created at the photocathode of the PMT. The relationship between this number and the
original number of photons per MeV ($\Psi$) is

$$N_{pe} = \Psi \cdot \varepsilon_{QE} \cdot E_\gamma \cdot \eta$$  \hspace{1cm} (8.2)

Where $E_\gamma$ is the gamma-ray energy in MeV, $\eta$ is the light collection efficiency and $\varepsilon_{QE}$ is the average quantum efficiency. In this paper we attempt to estimate the photoelectron yield of the YAP fiber samples in two ways;

- **By making a comparison with a calibrated scintillator.**
- **Using the single photoelectron electron peak of the XP2020 (Bertolaccini method [69]).**

### 8.5.2 Results of Comparative light yield

The spectra in Fig. (8.13) show the energy loss of gamma rays in a commercially produced 2x2x10 mm$^3$ Ce:YAP crystal, a 0.2% C:YAP fiber and a 0.5% Ce:YAP single crystal fibers. We repeated the measurements for all sample crystals under investigation in the same measurement conditions, several times each. Table 8.5 below shows a summary of the results, including the relative light outputs and the energy resolution at 511 keV (when the measurement is possible). Representative

![Figure 8.13: Spectrum of 0.2% Ce:YAP and 0.5% Ce:YAP in comparison with commercially produced 2x2x10 mm$^3$ Ce:YAP crystal.](image)
spectra for each of the fiber samples and the YAP pixel are shown in Fig. (8.13).
From this Table and Fig. (8.13) it can be seen that the two fiber samples have virtually the same light output. This is seen from the position of the Compton edge. However, the obvious observation is that the 0.5% sample has a much better energy resolution than the 0.2% sample because it has a clear photopeak visible. The fiber with 0.2% Ce doping has no visible photopeak, which is strange as, normally, the resolution depends upon the photon statistics which are virtually the same as for the 0.5% sample. Therefore, the degradation of the energy resolution must come from another source. This could be due to non-uniform doping of the Cerium, very high absorption or non-uniform light collection from surface or crystal imperfections, or fluorescence killer centers. Moreover the fiber samples have ~ 40% light output with respect to the Ce:YAP pixel.

8.5.3 Results of Absolute photoelectron yield

Two calibration methods were employed to estimate the absolute light yield; Firstly using a calibrated reference crystal and secondly via an absolute calibration of the photomultiplier using the Bertolaccini method [69].

Crystal calibration

A thin disc of BGO was used (Ø 10mm x 1mm) to provide an estimate of the \(N_{pe}\). BGO was chosen as it has a well defined light yield (\(\Psi\)) and has a high enough density and \(Z\) to stop a reasonable number of gammas and have a good photopeak. The flat surfaces were fine ground to reduce the contribution of the light trapped due to total internal reflection. This is particularly important for BGO as it has a high refractive index (\(n=2.15\)).

As with the other tests, multiple acquisitions were made to account for coupling differences, and average values of the 511 keV photopeak position, Compton edge and energy resolution recorded. Results are again shown in Table [8.5] Since BGO is our standard we will calculate the number of \(N_{pe}\) that we would expect theoretically for a 511 keV deposit using Eqn. [8.2]. We assume a light yield of 8200 ph/MeV and the average quantum efficiency of the XP2020 over the emission wavelengths of BGO is 15%. The LCE (\(\eta\) in Eqn. [8.2]) is more difficult to estimate. There are two articles in the literature that make reference to the \(\eta\) of BGO of very similar geometry; One
8.5 Scintillation Performance of Ce\textsuperscript{3+} doped YAP Fibres

article \[70\] states a \(\eta\) of 71\% for a geometry of 10 x 10 x 2 mm\(^3\) whilst the other \[67\] cites about 95\% for a geometry of 0 9mm x 1mm. We choose to use 95\% as the geometry is nearly identical to ours and the figure is based upon measured data as opposed to the former, which is based upon extrapolation from simulated data.

Employing Eq. 8.2 and the figures mentioned above, we arrive at a figure of 600 ± 90 photoelectrons. Using the measured average 511 keV photopeak position of 1391 ± 59 chn, this leads to a calibration of 2.3 ± 0.4 channels per photoelectron. Applying this to photopeak positions of the YAP fibers this gives 518 ± 149 and 549 ± 99 photoelectrons for the 0.5\% and 0.2\% Ce samples, respectively.

Table 8.5: Summary of the results from the measurements made with different scintillators. (R.L.O.= Relative Light output)

<table>
<thead>
<tr>
<th>Scintillator</th>
<th>Compton edge (chn)</th>
<th>Photopeak (chn)</th>
<th>FWHM (@511 keV)</th>
<th>R.L.O. (%) (scint. cal. method)</th>
<th>(N_{pe}) (PMT cal. method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce:YAP pixel</td>
<td>1875 ± 18</td>
<td>3022 ± 13</td>
<td>10.8 ± 0.2</td>
<td>100</td>
<td>1314 ± 228</td>
</tr>
<tr>
<td>0.5% Ce:YAP</td>
<td>712 ± 34</td>
<td>1191 ± 62</td>
<td>15.9 ± 1.4</td>
<td>39</td>
<td>518 ± 149</td>
</tr>
<tr>
<td>0.2% Ce:YAP (\d)</td>
<td>743 ± 15</td>
<td>-</td>
<td>-</td>
<td>41</td>
<td>549 ± 99</td>
</tr>
<tr>
<td>BGO</td>
<td>880 ± 10</td>
<td>1391 ± 59</td>
<td>14.8 ± 0.7</td>
<td>46</td>
<td>605 ± 109</td>
</tr>
</tbody>
</table>

PMT calibration

We observed the single photoelectron peak of the XP2020 at channel 145 ± 2.3 for an amplifier gain of 1000. Our measurements were made at a gain of 25, giving a calibration factor of 3.63 ± 0.07 channels per photoelectron at the measurement settings used. Applying this to the photopeak positions of the YAP fibers this gives 328 ± 18 and 347 ± 18 photoelectrons for the 0.5\% and 0.2\% Ce samples respectively. The photoelectron numbers using this calibration method are also summarized in Table 8.5.

\(\d\)Photopeak values extrapolated from Compton edge position.
8.5.4 Conclusion

For the first time we succeeded to grow Ce doped YAP single crystal fibers by $\mu$-PD method with different lengths and diameters. Absorption and emission spectra are in good agreement with literatures. The light yields from the fibers in comparison to a similar sized commercial YAP pixel were around 40% but similar to BGO crystal. Moreover the two tested samples were found to have very similar light yields, differing by 5% even though they had different doping levels. Strangely, despite the similar light yield, the 0.2% Cerium sample did not display a visible photopeak whilst the 0.5% sample did, thus implying poor energy resolution. These results are encouraging if one takes into account that the crystal features of our fibers are not completely optimized. In particular work is in progress in order to optimize the quality of the crystal fibers, the light collection efficiency, their size, and the Ce doping level.
Chapter 9

First Characterization of Silicon Fibres Produced by $\mu$-pulling Technique for Future Gravitational Wave Detectors

Introduction
The work described in this chapter has been carried out in the frame work of a collaboration with the VIRGO experiment and is based on our articles ([71]–[75]). The purpose of this collaboration is to study if Silicon (Si) fibers can be used as last stage suspension of the mirrors of a future gravitational waves (GW) interferometer. For this reason I will first introduce, briefly, VIRGO interferometer and why Si fibers could help in improving the suspension thermal noise.

9.1 VIRGO Interferometer
The VIRGO project is a collaboration between the French CNRS and the Italian INFN, located in the Pisa countryside (Italy). The detector consists of a 3 km-long suspended Michelson interferometer equipped with Fabry-Perot cavities in the arms and power recycling. A GW, propagating in the orthogonal direction with respect to the interferometer plane, will alternatively stretch one arm and shrink the other one, causing a mirror (acting as test mass) displacement $\delta L$ given approximately by
Figure 9.1: Global view of the SA. It is about 9 m tall and 1 ton heavy. The main components are indicated.

$\delta L \approx \frac{1}{2} h L$, where $L$ is the interferometer arm length and $h$ is the dimensionless amplitude of the wave. This perturbation induces a change in the interference pattern which is detected by measuring the intensity variation of the light leaving the interferometer output port.

The VIRGO detector has been conceived to reach a spectral strain sensitivity of $h \approx 10^{-23} \cdot 10^{-22} \text{ Hz}^{-1/2}$, in the frequency band starting from a few Hz to a few kHz (displacement sensitivity $\delta L \simeq 4 \times 10^{-18}, 10^{-19}, 6 \times 10^{-20} \text{ m}/\sqrt{\text{Hz}}$ at 10, 100, 1000 Hz, respectively) [76]. Various sources of noise limit this extremely high sensitivity. For example, the sensitivity between 5 and 500 Hz is limited by thermal noise: pendulum thermal noise below 100 Hz and mirror thermal noise above. The external noise sources (e.g. seismic) have been suppressed by the use of a specially design chain of different stages called super attenuator (SA). The development of the SA was pioneered by A. Giazotto et. al. in the late eighties at Pisa INFN laboratory [77]. The mechanical chain suspending the optical payload is based on a six-stage pendulum (Fig.9.1) suspended to a pre-isolator which is an inverted pen-
9.2 Thermal Noise in VIRGO Suspension System

In the design of advanced gravitational wave (GW) interferometric detectors, thermal noise represents the most serious sensitivity limitation in the frequency range from a few Hz to a few kHz. The thermal noise sources in an interferometric gravitational wave (GW) detector are mainly two: the suspension wires fluctuation which dominates the sensitivity curve up to 100 Hz, and the mirror internal vibration that expected to become the main noise source at larger frequencies, i.e., up to 1 or 2 kHz. Both the phenomena are described by the fluctuation-dissipation theorem \cite{79}.

The power spectral density of the thermal noise displacement of a suspended mirror is approximated by the following expression

\[ |X_p(\omega)|^2 \simeq \frac{4k_B T}{\omega^5} g \cdot \frac{1}{L_f^2} \sqrt{\frac{E g}{4\pi n m}} \cdot \left\{ \frac{\phi(\omega)}{C_s T_B} \right\} \]  

(9.1)

where \( L_f \) is the suspension fiber length, \( E \) is the Young’s modulus of the fiber material, \( n \) is the number of suspension fibres for each mirror of mass \( m \) (4 in case of VIRGO) and \( C_s \) is the percentage of tensile breaking stress \( T_B \) at which the fiber is loaded. The loss angle \( \phi(\omega) \) represents the sum of all the dissipative processes that occur in the material plus an effective loss angle for the losses associated with the connecting elements such as clamps, break off points or chemical bonded pieces. This loss angle \( \phi(\omega) \) that characterized the material is related to the quality factor of a mechanical pendulum suspended by \( n \) wires:

\[ Q = 2l \sqrt{\frac{M g}{n E I}} \frac{1}{\phi(\omega)} \]  

(9.2)

where \( l \) is the length of the pendulum wire, \( M \) is the suspended mass, \( E \) is the Young modulus, and \( I = \frac{4d^4}{64} \) is the moment of inertia of a wire cross section with diameter \( d \).

The thermo-elastic loss angle \( \phi_{th}(\omega) \) is given by:

\[ \phi_{th}(\omega) = \Delta \frac{\omega_T}{1 + (\omega_T)^2} \]  

(9.3)
where $\Delta$ is the amplitude of the thermo–elastic peak strength, related to the material Young’s modulus $E$, the specific heat per unit volume $c_v(T)$, the temperature $T$ and, mainly, to the thermal linear expansion coefficient ($\alpha$) through the formula \[80\]:

$$\Delta = \frac{E\alpha^2T}{c_v}.$$  \hspace{1cm} (9.4)

The frequency of the thermo–elastic peak is given by $f = 1/\tau$ where $\tau$ is the heat propagation characteristic time, related to the geometry of the fiber through its diameter $d_w$ and to the material properties through the thermal conductivity $k$.

In a cylindrical fiber \[80\]:

$$\tau = \frac{c_v d_w^2}{2.16 \cdot k}.$$ \hspace{1cm} (9.5)

The only crystalline material that seems promising to realize high performances suspensions is Silicon, thanks to its large thermal conductivity.

\section*{9.3 Silicon Thermo-Mechanical Properties}

This favorable characteristic of silicon fibers has already been suggested by VIRGO groups \[81,82\]. Silicon shows thermal and mechanical properties that are extremely favorable to reduce thermal noise in the optics suspension of a GW interferometric detector.

Silicon is expected to have large bulk tensile strength (about 7 GPa, dominated by surface effects that can decrease that value down to about 1 GPa \[83\]) and good intrinsic loss angle ($\phi_i(300K) \simeq 2.8 \times 10^{-8}$, $\phi_i(77K) \simeq 5 \times 10^{-9}$ and $\phi_i(4.2K) \simeq 6 \times 10^{-10}$). The behavior of the linear thermal expansion coefficient $\alpha$ and of the thermal conductivity $k$ is peculiar, as reported in Fig. \[9.2\] (all the thermo–mechanical properties of Silicon, reported in this paragraph are extracted from \[36\]).

The thermal expansion coefficient is expected to decrease with the temperature and to be zero at about 123 K, negative until 18 K and almost zero below 17 K. This means that the thermo-elastic dissipation will decrease quickly with the temperature (thanks to the dependence of both in $T$ and $\alpha(T)$) and it is expected to vanish at about 120-130 K.

The thermal conductivity $k(T)$ of silicon increases at low temperature pushing the thermo-elastic peak towards higher frequencies.

As an example, the thermo-elastic losses of different materials are compared in
9.3 Silicon Thermo-Mechanical Properties

Figure 9.2: Linear thermal expansion coefficient and thermal conductivity of silicon; the two temperatures (about 18 K and 123 K) where the thermal expansion coefficient vanishes, as well as the peak of the thermal conductivity at low temperature, are well evident.

Fig. (9.3). For instance, the advantage in using sapphire fibers is clearly nullified by the dominant thermo-elastic loss angle at low frequency. On the contrary, fused silica has an intrinsic loss angle below $10^{-7}-10^{-8}$ (depending on the type of fused silica) and, more notably, its thermo-elastic dissipation is apparently suppressed by a small thermal expansion coefficient. Fig. (9.3) suggests that another material could be chosen to realize low thermal-noise suspensions, namely crystalline silicon. In fact, silicon does have a large thermo-elastic peak, but it is located at very high frequencies. This is due to the high thermal conductivity of silicon. As a result, at low frequency, where the suspension thermal noise dominates, the thermo-elastic dissipation in silicon fibres could be even lower than in fused silica fibres. This effect, together with its low intrinsic loss angle, make silicon one of the most promising materials for low thermal-noise suspensions in GW detectors.

The main optics in present and future GW interferometric detectors are massive mirrors (more than 20 Kg in Virgo) that need very strong and safe suspension fibers. If the mirrors will be suspended by four fibers, the fiber diameter needed should be about 0.4-0.5 mm and, to keep the pendulum resonant frequency very low, the expected fiber length will be more than 30 - 40 cm. Similar Silicon fibers are not commercially available and for this reason we decided to develop the technology to
grow them in a dedicated research facility.

9.4 Si Growth

Silicon single crystals are grown by different methods, e.g. the floating zone (FZ), Czochralski (CZ) and micro pulling down technique ($\mu$-PD). The FZ technique is based on inductive heating of a poly-silicon rod by a high frequency coil, and the CZ method is the dominant growth process as it can create large diameter crystals up to 30cm and 300kg weight. The ($\mu$-PD) is different from these more traditional methods and is described in details in previous chapters.

The Cz growth process is easier and more stable than other techniques because Cz uses a seed crystal dipped into free-open surface melt and this prevent stress that can arrive from direct contact between the grown crystal and the crucible because of their different thermal expansion coefficients. For thermal stability during the growth the pulling rate is rather slow, of order mm/hour.

The principal difference of the Float Zone (FZ) process from Cz is that no crucible is
used and this reduces the impurity level in the crystal. For this reason the technique is practically suitable to grow materials with high resistivities and/or low oxygen content. But with this method it is difficult to scale up the crystal diameter due to stability of the liquid zone in a gravity environment; FZ wafers have greater microscopic resistivity variations than Cz. Moreover pre-preparation of starting material is needed to make it in shape of rod.

In case of $\mu$-PD method for Si crystal growth many parameters affect the growth of Si by $\mu$-PD method, for example, the low viscosity of the silicon melt causes a perturbation in meniscus height and hence instability in the fiber diameter. Unlike Cz growth, there is a direct contact between the seed-fiber and the crucible and this can produce stressed or contaminated crystal. Regularity of the diameter and stable growth depends on the meniscus stability. According to Fukuda’s work \cite{1}, stable growth requires larger meniscus diameter and height less than 0.20 - 0.25 mm if the pulling rate does not exceed 1.5 mm/min.

The $\mu$-PD technique is based on high temperature gradient in the vicinity of hot zone part. This high temperature gradient together with high thermal conductivity of the material can create strong instability that can even cause a partial freezing of the melt during the growth. For these reasons $\mu$-PD growth of Si present strong difficulties if compared to more traditional methods. Beside that, the high chemical reactivity of the Si make it difficult to find a suitable crucible to grow it without contamination and reaction with the crucible material.

In each of the following sub-sections we will describe how we tried to overcome the difficulties of growing Si.

\subsection*{9.4.1 Crucible}

Si material at its melting point has low viscosity, high surface tension and is highly reactive with most of other materials. Therefore only very few crucibles are suitable for growth. The crucible should be made from a material that must be stable at high temperatures, corresponding to the melting point of the target crystalline material. Silica and graphite (with high density $> 1.75 \text{g/cm}^3$) are commonly used for Si growth \cite{84}. In the case of graphite crucibles the silicon melt is always saturated with carbon leading by assistance of CO and SiO gases to the chemical formation of harmful SiC particles which affect the meniscus (solid liquid interface) temperature
and hence the growth stability and regularity of the diameter. In the worse case SiC is able to plug the nozzle channel and stop the growing process.

According to [85] there is strong reason to believe that all mechanisms for SiC precipitation during Si growth processing by $\mu$-PD should take place simultaneously:

1- The diffusion controlled growth of the continuous reaction forms SiC layer.

2- Carbon supersaturation of the local parts of silicon melt and resulting mass transport of SiC from hotter to colder parts of the crucible.

3- Carbon transport through ambient atmosphere in the form of CO.

Since Si is highly reactive, it reacts with the graphite crucible, the reaction does not stop and Si continue diffuse inside the graphite layers because graphite is a porous material, and this causes a damage of the crucible or even cracks along the crucible itself.

On the other hand, the problem of carbon contamination in Si crystal growth from a quartz crucible heated by graphite fixed the attention on the importance of CO as carbon transport agent. Many researchers [88, 89] and [90] suggested several reasons for the appearance of CO in the growth atmosphere. When the silica crucible is heated by graphite resistive heater, the reaction between the silica and the graphite retainer would be the main source of the CO. It could also originate from the polysilicon starting material, dissolved parts of the carbon crucible and out gassing of the graphite heater. In graphite hot zone, CO is mostly generated as a result of a reaction between the graphite components and oxygen. Each CO sources can be partially suppressed by some technological improvements.

When using graphite or silica crucibles, silicon melt is always saturated with carbon. Under these conditions CO acts as a transport agent of carbon as follows,

$$CO_{gas} + 2Si_{melt} = SiC_{solid} + SiO_{gas}$$ \hspace{1cm} (9.6)

This reaction occurs near the melt surface. SiO reacts with the hot graphite parts according to the following reaction,

$$SiO_{gas} + 2C_{solid} = SiC_{solid} + CO_{gas}$$ \hspace{1cm} (9.7)

Subsequently the new CO molecule return to reaction (9.6) and the reactions are repeated indefinitely. Another disadvantage of using silica crucible is its short lifespan. After only one growth, cracks appear in the crucible during the cooling and/or phase transformation of the silica material.
As an alternative to graphite, vitreous carbon is a good candidate crucible for growing Si. Vitreous carbon is a form of carbon with a highly disordered structure and glassy fracture pattern. The carbon atoms are arranged in planar layers with hexagonal symmetry. Unlike graphite, these layers are not arranged regularly over large areas. Bands of graphitic ordered and stacked layers build a polymeric structure. Instead of graphite, vitreous carbon is non-porous in the macro range, Si reacts with the first layers of the crucible wall and then the reaction stops and Si is not able to continue diffusing inside the carbon layers. For this reason we used a vitreous carbon crucible for growing Si. There are numerous voids between the graphite layers which have, comparable to glass, a diameter of 1 to 3 nm. As a consequence of the structural disorder, the material shows big differences if compared to graphite low density, low electrical and thermal conductivity and the isotropy of the material.

Figure 9.4: Two different Ar gas flow pattern in the μ-PD for Si growth.
One of the most interesting properties of vitreous carbon is the high temperature resistance in air up to 600°C and in vacuum or inert gas up to more than 3000°C. Another consequence of the disordered structure of glassy carbon is the inability to form intercalation compounds. This gives extremely high resistance to corrosion by acid and alkaline agents and melts. The only substances that can attack glassy carbon are oxygen at above 600°C and hot melts and acids with a powerful oxidizing action.

After many attempts of growing Si we believe that it is necessary to use flow of high purity Ar gas in the hot zone. In closed circular flow, Ar stream carries out the CO and SiO gases from the surface of the melt and keeps it clean. Boris, et. al. [85] made two different Ar gas flow pattern in the μ-PD as shown in Fig. (9.4). In Fig. (9.4b) the crucible was provided with lateral holes and a small gas permeable upper shield. The comparison of (a) and (b) types revealed a considerable difference in SiC precipitation. The amount of SiC in the bottom of crucible (a) was much greater. Also large amount of SiC particles was found near the melt surface. In crucible (b) the surface of the melt was free of SiC.

9.4.2 Temperature Gradient

As we mentioned before, μ-PD technique is based on high temperature gradient in the vicinity of hot zone part. This high temperature gradient together with the high thermal conductivity of the material can cause a partial or full freezing of Si during the growth and even stop it. For Si growth it is very important to have a smooth temperature gradient in and under the hot zone parts. Much work has been done to find the suitable temperature gradient. Adjusting the radio-frequency (RF) coil positions, after heater dimensions and insulating shields can lead to great change in the temperature gradient. The unstable behavior of the melt interface during several growth runs led us to think the temperature gradients in our furnace were too steep for the Si fiber although they proved to be suitable for other insulating materials. For this reason we decided to measure the temperature gradient experienced by the crystal during the growth process and try to make them smoother. We replaced the seed crystal with a W/Re thermocouple that was pulled under the empty crucible as if during a growth run. The alloy combination of our thermocouple was Tungsten (W) for positive lead
and Tungsten-26% Rhenium (W-26%Re) for negative lead. The thermocouple has a maximum useful temperature range from 0 to 2320 K. The experiment was repeated with different setup conditions by changing the design of the hot zone in order to identify the most suitable setup for Si growth.

■ First, a vitreous carbon crucible and 15 mm long after-heater made from the same material was used (Fig. 9.5).

We found that $\Delta T / \Delta L \approx 55$ K/mm which is a steep temperature gradient, typical temperature gradient curve is shown in Fig. (9.6).

High power supply was necessary to heat the crucible directly. Notably, greater power was necessary to obtain same temperature conditions when the crucible was used for the second time as compared with initial heating. This was probably because of chemical reaction between Si melt and the crucible that limited its lifetime.

■ In the second design, Fig. (9.7), a vitreous carbon crucible set together with 30 mm longer graphite after heater in order to check the effect of different AH materials and lengths on temperature gradient profile (Fig. 9.8).

■ In the third construction the vitreous carbon crucible was inserted inside a
graphite one with 30 mm long graphite AH and the ZrO$_2$ ceramic base was thinner (5 mm thick). It is clear from the two curves of Fig. (9.8), that the temperature gradient became smoother in a short distance until $\approx 15$ mm from the bottom of the crucible. An abrupt change in the temperature gradient ($\frac{\Delta T}{\Delta L} \approx 55$ K/mm) occurred between $\approx 15$ and $\approx 25$ mm distances. This region was still inside the graphite after heater, but outside of RF coil. This was probably the reason of steeper temperature gradient. The nearly identical curves of Fig. (9.8) mean that the long graphite after-heater with vitreous carbon crucible or vitreous carbon inside a graphite one is effective for smooth temperature distribution, but as mentioned, in a short distance until $\approx 15$ mm.

In last temperature gradient configuration (Fig. 9.9), an effective change has been done. With the vitreous carbon crucible inside a graphite holder mounted on 30 mm long graphite after heater with 5 mm thick ZrO$_2$ ceramic base, the RF coil was pushed down the ceramic base. Moreover, small graphite tube (30 mm in length and 13 mm in diameter) was set under the after-heater. As a result, the temperature gradient about 15 K/mm was established for a long distance in and under the hot
Figure 9.7: Hot Zone in $\mu$-PD technique with vitreous carbon crucible inside graphite holder and long after heater. The ceramic base becomes thinner.

zone. These conditions were applied in following growth runs resulting considerable improvement of the growth stability. The effect of these changes is shown in the Fig. 9.10.

### 9.4.3 Hot Zone Temperature Stability

Another serious problem we experienced during the growth is the temperature instability of hot zone. At the beginning the furnace was operated without any temperature sensor near the hot zone and the temperature stability was obtained through the control of the power delivered from the RF generator. This power was controlled through an external voltage (0 - 10 V) supplied by the computer. In this conditions the stability of the power supplied by the RF generator is $\approx 5\%$ as described by the company that produced the generator, given that the 380 V supplied by the national company for electricity is perfectly stable. This power stability proved to be enough for most of the insulating materials we grew previously but the melt instabilities led us to think that it is not enough for Si. Therefore, we inserted a W/Re thermocouple near the crucible to measure the temperature of the hot zone, as shown in Fig. 9.11. We observed, at constant voltage, there is a fluctuation
Figure 9.8: Temperature profile in $\mu$-PD technique corresponding to the design of Fig. (9.7); (—) curve represents the measurement with vitreous carbon crucible and long graphite after heater, while (■) represents the measurement with vitreous carbon crucible inside the graphite one with long graphite after heater.

in the temperature more than 3 K in the hot zone, as shown in Fig. (9.12). This is one of the reasons why we could not achieve a stable growth under constant voltage operation.

In order to have a better temperature stability, we decided to control the temperature directly. We modified the LabView software to read the temperature from a thermocouple placed near the hot zone outside the crucible and stabilize its value by controlling the voltage supplied by the computer. The stabilization was accomplished by a PID loop. With this setup we obtained a temperature stabilization as good as $\Delta T \approx 0.2$ K which is a great improvement if compared to 3 K (Fig. (9.13)).

9.4.4 Seeding and Growth Experimental Procedure

The starting material was Si pieces of 5-N purity. These pieces were inserted in a vitreous carbon crucible that was placed inside a graphite holder to be heated as shown in the temperature gradient analysis. Two types of vitreous carbon crucibles
were used: the first one is the conventional (µ-PD) crucible with a micro nozzle of about 0.3 or 0.5 mm in diameter at its bottom. This type of crucible is used to grow thin fibers (0.4 to 0.7 mm in diameter). Other type of crucibles have a nozzle of about 1 mm inner diameter with total bottom diameter of 2 or 3 mm for growth of rod shaped Si.

We grew Si single crystal fibers with different lengths and diameters. As a first step, a <100> oriented thin seed cut from Si disk was used as a seed. The achievement of growth of good quality fibers requires the controlled melting of the top part of the seed prior to initiation of the pulling process. This was performed by immersion of the seed into the crucible nozzle. Usually ≈ 1 mm of the seed crystal was melted just before starting the growth. But sometimes we could not succeed to melt the top part of the seed, may be because of impurities on the seed surface or oxide particles formed in previous growth processes.

In order to minimize the effect of any impurities we decided to perform two operations. the first one is to chemically etch the seed, removing the first Si layers. To
obtain an isotropic etching of the seed we use the so called HNA solution, a mixture of HF and nitric acid, diluted with water or acetic acid. A rather low etching velocity can be obtained using 75% HNO₃, 20% HF and 5% water for about 2 minutes. The second operation included heat treatment of the µ-PD chamber at temperature of about 1220 K during the evacuation process. At this stage, any gases or impurities adsorbed by various materials were removed from the chamber or minimized. Pre-melting of about 1 mm of the seed was also performed just after first contact seed and the meniscus. The crystals were grown at various pulling rate from 0.1 to 2 mm/min and were 0.4 - 3 mm in diameter (depending on the crucible used) and 40 - 310 mm in length. Disconnection of the fiber growing from the molten zone was not observed, but the growth process was not perfectly stable and some abrupt changes the meniscus and/or diameter happened probably due to instabilities of the RF generator or to reaction between silicon and the crucible. Also from time to time we noticed a partial freezing of the fiber at the crucible bottom. These events were more probable when we used a short after heater, rather than when we used a long one. Nevertheless most of the fibers have good shape quality.

Fig. (9.14) shows three different moments during the growth of the fiber that
recorded by CCD camera:
(a) before seeding, where the seed is below the bottom of the crucible,
(b) during seeding, and
(c) during stable growth.

From Fig. (9.14) we can see that the melt meniscus is clear and therefore we can control the growth process by varying the pulling rate and the RF power. Some typical Si crystal fibers grown with different diameters and lengths are shown in Fig. 9.15. In the case of thin fibers, the diameter control was difficult because of instability of temperature. Therefore some of the fibers were irregular in diameter (Fig. 9.16a); the diameter fluctuations were about 0.5 mm when average diameter was around 1 mm. With acquiring a better temperature control with the use of the thermocouple and growth of thicker fibers, the fiber shape was enhanced, as shown in Fig. 9.16b. This fiber has an average diameter of about 2.5 mm and fluctuations of the order of 0.3 mm. More than 30 Silicon fibers/rods have already been grown with different lengths up to 310 mm in length. But for most of them, the shape of the Si fibres produced is not perfectly cylindrical: the diameter varies along the
Figure 9.12: Instability of hot zone temperature under constant voltage.

Figure 9.13: Stability of hot zone temperature under variation of voltage.
9.5 Structural analysis and Characterization

X-ray diffraction analysis (Laue method) was carried out, using the setup described in section (4.3.1), to identify the crystal orientation of the fibers. Measurements were performed in air, the accelerating voltage was 25 KV, and the tube current was 35 mA. All X-ray experiments were carried out at room temperature. All the good quality parts of the fibers showed single crystalline character (Fig. 9.17), but we found that the orientation changes along the fiber length in every point (about every 10 to 20 mm) where the diameter is not stable. As a result the fibers are not single crystal along all their length, but are composed of several single-crystal parts. Incorporation of carbon particles into the Si lattice with following twisting and formation of re-oriented crystallite is considered as possible mechanisms explaining these transformations. The purity of crystal fiber was verified by powder X-ray diffraction. A short section of the fiber has been hand milled in an agate mortar, the resulting powder has been put in a 0.4 mm Lindemann capillary, settled by ultrasonication and the diffraction pattern has been collected in the 2θ range 30-120°.

Figure 9.14: Three different moments during the growth of the fiber.
Figure 9.15: As-grown Si Single Crystal Fibers with (a) 2.5 mm in diameter and 200 mm long, (b) 1.2 mm in diameter and 210 mm long, (c) and (d) 0.7 mm in diameter and 165 mm long.

Figure 9.16: View of as-grown Si Fiber. The right arrow of (a) indicates irregularity in diameter while the right arrow of (b) indicates the better fiber shape when acquiring a better temperature control.

The pattern of Fig. 9.18(a) is the result of a fitting process of the profile, calculated from the known cubic structure of Si [86], on the experimental one. The fitting has been obtained by refining the unit cell axis length, which converged to \( a = 5.4299 \) Å. As it clearly appears, all peaks in the pattern were sharp and could be indexed. Single phase with cubic type structure was formed in Si phase and no impurity phases were observed. It is pointed out that 100% of the melt was usually solidified into the fiber and no shifting of melt composition resulting in second phase formation was detected during the growth.
Figure 9.17: Laue simulation for Si

Figure 9.18: Measured (B) and calculated (A) powder X-ray diffraction patterns for Si. The pattern B has been obtained from a milled fibre using Cu–Kα radiation
Room temperature absorption measurement was performed by a Cary 500 spectrophotometer: between 1000 and 2600 nm in the near infra red region, with a resolution of 0.5 nm.

Absorption spectra show that the absorption edge of Si was found to be nearly at 1050 nm. These values show a good agreement with similar results in literature $[87]$. Within the sensitivity of our apparatus absorption spectra did not show the presence of any contaminants as shown in Fig. 9.19.

9.7 Measurements of Thermo-Mechanical Parameters of the Fibers

Two different experimental apparatuses have been setup to characterize the thermo-mechanical parameters of the fibers. in the INFN group of Florence/Urbino they performed the room temperature measurements and in the INFN group of Perugia they scanned the fiber dissipation down to low temperature.

A loss angle measurement realized on the produced fibers allows to reconstruct the thermo-elastic peak, from which it is possible to extract some thermal and
9.7 Measurements of Thermo-Mechanical Parameters of the Fibers

Figure 9.20: Measured loss angle of a 308 mm (289 mm free length) fiber with an average diameter of 746 µm. ∆ is the measured data, * is the prediction mechanical properties of these fibres. Loss angle measurements have been performed on two crystalline silicon fibres whose length were respectively 308 mm and 111.5 mm.

I will show only the loss angle result at room temperature for the first fiber of 308 mm in length before and after etching. More details about the experimental setup, procedures and complete results can be find in [72]-[74].

9.7.1 Results of Thermo–Elastic Measurement at Room Temperature

By means of the setup described in [72]-[74] the loss angle values for the Si fiber (308 mm long) are shown together with the model predictions in Fig. (9.20) (before etching). It is quite evident the presence of an excess loss in Fig. (9.20) for the fiber.

We suppose that this excess can be due to contaminations present on the fiber surface: after the production of the fiber, the external surface is in fact subject to oxidation and furthermore, during the growing process, it is possible the deposition
of some impurities on it. To verify this hypothesis we decided to submit the fiber to a chemical etch, removing the first Si layers. The etching process was performed without affecting the part of the fiber inside the clamp: in this way the diameter reduction can help in further reducing the clamp losses. To obtain an isotropic etch of the fiber we use the so called HNA solution, a mixture of HF and nitric acid, diluted with acetic acid. To keep the etching velocity at a low level we used a 75% HNO\textsubscript{3}, 15% HF and 10% CH\textsubscript{3}COOH solution.

In Fig. (9.21) the measured values of the loss angle for the same fiber after the etching process are shown. The diameter reduction shifts the position of the thermoelastic peak to higher frequencies and the excess loss is not present anymore, thus confirming the surface contamination hypothesis. A small excess is still found at low frequencies: this is probably due to clamp losses. In fact, if we slightly diminish the clamp pressure, the $\phi$ values increase at low frequency with the high frequency data remaining unaffected.
9.8 Conclusion

Second generation GW interferometric detectors will be room temperature and they will use some high performance material to realize the optics suspension. If this material will be crystalline Silicon, there is the possibility to foresee a further upgrade of the advanced detectors, working at low temperature and choosing as operative point the first temperature where the thermo–elastic effect vanishes in Silicon. Therefore the fibers produced with $\mu$-PD method, can be considered as promising materials for low thermal noise suspension for advanced gravitational wave detectors.

In this work the growth and the characterization of Si fibers grown by micro–pulling–down technique has been reported. XRD, and absorption measurements are reported. No contaminations were found within the sensitivity of our apparatus. Some main stability growth problems have been solved. Smooth temperature gradient are obtained for longer distance in and under the hot zone part by making an effective change in the hot zone. The temperature stabilization as good as $\Delta T \approx 0.2$ K can be established as compared with $\Delta T \approx 3$ K. Chemical etching and baking processes are effective tools to minimize the level of impurities. Searching and checking for a stable crucible, like SiC and special type of SiO$_2$ for growing Si and minimization the effect of impurities are the main challenge for Si single crystal fibers. Our work is a progress in this direction.

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Future Plan

The work about the growth with $\mu$-PD method will be further developed in order to improve the technique. In particular we are working to modify the hot zone and changing all insulating shields with non-pours materials.

Development of high quality single crystal fibers for different applications is our goal. In this way we will continue working to grow single crystal fibers for scintillation application, in particular we are trying to grow Ce:YAP fibers with higher doping level, and in the same time we are going to grow Yb:LuAG fibers for the same propose.

Since LiNbO$_3$ is a technologically important for a wide range of application like in nonlinear optical devices, waveguide, surface acoustic wave devices or photorefractive data storage, we are working to grow Er:LiNbO$_3$ single crystal fibers in collaboration with Padova and Rome Universities.

Si single crystal fibers for VIRGO project still remain our main challenge. Much work is needed to control the growth process to obtain regular diameter of the fiber and unique orientation. Searching and checking for a stable crucible, like SiC and special type of SiO$_2$ for growing Si and minimization the effect of impurities are the main challenge for Si single crystal fibers.

The laser performance is limited because the stress in our RE$^{3+}$:YAG and LuAg fibers. We are working to develop RE$^{3+}$ doped fibers for laser performance like Tm:YAP.
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