Growth of oxide laser crystals

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Abstract

Optically pumped solid state lasers are frequently single crystals of inorganic oxides containing active elements. While, most of these crystals are simple inorganic oxides or binary mixtures of two oxides by adding active ions and activators, sometimes in significant quantities, these system become more complex. Resulting mixtures of four sometimes five oxides display more complicated properties than are those of simple oxides. Examples of such systems are CTH:YAG (Chromium, Thulium, Holmium Garnet), and CTE:YAG (Chromium, Thulium, Erbium Garnet). The need for very high optical quality crystal in laser applications made the manufacture (crystal growth and fabrication) one of the most demanding manufacturing processes.

A description of the growth of research and development type crystals, as well as scaling the process to industrial level is described. The best understood and most practiced technique in commercial crystal growth is described along with its advantages and limitations. The effects of composition and properties of individual crystals on process variables, growth parameters, and thermal designs are described. The crystal quality enhancement and control by recognizing, understanding, and minimizing or elimination of crystal defects are described. Emphasis is given to material properties that play a role in the selection of growth parameters for individual host systems such as garnet-based or corundum-based laser crystals.

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1. Introduction

Crystals manufacturing “Crystal Growth” has been connected with optics and lasers since the very beginning of development of quantum amplifiers of light. It is very well known, that the first operational laser was built using a synthetic ruby crystal. Synthetic is a key word. In order to progress in optical science it is imperative that the materials used, are of uniform reproducible quality, and their supply is stable. In order to secure stable sources of high quality optical crystals for research, and commercialization, it was necessary to abandon natural sources, and turn to man-made crystals. There already existed the production of synthetic sapphires and rubies at the beginning of the 20th century [1] whose objective was strictly jewelry trade. The first crystal growth for industrial purposes was motivated by a need to produce jewel bearings in large amounts for aviation instrumentation in early 1940s, under the looming shadow of the impending world war. The first technology utilized was the flame fusion developed manufacturing synthetic jewelry crystals. However, developments in optical physics, and lasers, soon demanded improvements in crystal quality. The flame grown crystals were highly strained, and had numerous other problems. The need for better crystals led at first to improvements of the flame fusion technology, and then to a search for alternative crystal growth methods. The one which became the most successful was the technique already used for the growth of semiconductor grade of silicon, germanium. This technique is referred to as Czochralski Growth. The term appeared first in the Buckley’s book in 1951 [2]. The apparatus Prof. Czochralski used to study crystallization of metals would hardly be recognized today, as a device for growing crystals. It was Teal and Little [3], who added a
crystal seed, seed rotation, and control of crystal shape by the use of changes in the melt temperature. By these changes, means to reproducibly manufacture single crystals had been created. The popularity of the method is derived from its relatively rapid growth, reproducibility, and freedom in controlling numerous growth parameters. The success of pulling technique in manufacture of semiconductors was not lost on crystal growers working in optics. Union Carbide’s East Chicago Laboratory Originally charged with the growth (flame fusion) of corundum for instrument bearings applications, initiated crystal growth of ruby for lasers. For a period of time the flame fusion and pulling method were used concurrently. The work in flame fusion focused on improvements, while the work in pulling revolved around innovation. Stunning improvements in the quality of the “pulled” ruby, achieved in 1964, could not be matched by flame fusion, and pulling was adopted as a principle method for laser crystal manufacture. The major contributions by the East Chicago, and later Speedway Laboratories were the addition of radio frequency heating, and iridium as a crucible material. These contributions made the pulling method applicable for growth of materials with high melting points. The technology was quickly adopted by Bell Telephone Laboratories in New Jersey, which at that time were deeply involved in laser physics and laser materials research (Fig. 1).

Since then the demand on crystals optical quality for applications as active laser sources made the growth of single crystals one of the most demanding manufacturing technologies. The field of crystal growth has merged various aspects of physics, chemistry thermodynamics, and transport phenomena with aspects from engineering.

2. The pulling method concept

The method is relatively simple; the constituents of the crystal are melted. After that, the liquid phase is converted back to a solid by removing the heat of fusion. Matching the rates of heat removal with a mass transfer allows controlling the crystal growth rate. Simply the process control is accomplished by balancing the input power with the amount of heat needed to facilitate the change of the liquid to solid at a desired rate. The temperature at the point of solidification only follows the crystallization temperature determined by the composition. Seed crystal is inserted into the melt, and equilibrated, so that no melting or growth takes place. When the heat is removed a quantity of solid forms on the seed corresponding to the amount of heat is removed. The solid deposited on the seed is a single crystal and replicates the crystalline structure and orientation of the seed. In the Czochralski method the crystal is pulled out of the melt at a speed corresponding to the growth rate. The crystallization of each successive portion of the melt proceeds only on the crystal immersed in the melt, and only between the container (crucible) wall and the crystal/melt interface when there is a temperature gradient which produces free convective flow of liquid.

3. Important process parameters

It appears that a successful crystal growth relies on experimental intuition; however, the underlying science of crystal growth is based on strong foundations. These foundations had been developing over a period of more than 50 years prompted by the characteristics of the process which include:

- Dynamic instabilities, turbulent fluid convection, and temperature fluctuations.
- A need for precise weight control.
- The growth is taking place in the proximity of the melt surface at the thermodynamic “triple point”.
- The growing crystal is affected by:
  - The surface hydro-static and surface tension forces shaping the meniscus on the melt surface in contact with the growing crystal.
  - The shape of liquid/solid interface which is rarely flat. The exact curvature of the interface is determined by fluid flow in the crucible.
- Temperature gradients influence the crystal perfection by affecting the fluid dynamics, and kinetics of a growing crystal.
- The dynamic heat flow created by the rotation and/or of the crucible increases the thermal symmetry of the system, and decreases temperature fluctuations.
- Growth rate is also a variable which plays a large role in a growth of doped and mixed crystals.

Today a process with so many variables would not be considered practical, and would not even be attempted. But over 50 years of practice, the absence of a better technique, demand for crystals, and research led to a development of an extensive theoretical treatment which includes analysis of fluid dynamics and heat transfer [4–15]. Recently computers brought to life theoretical modeling of crystal growth processes [16–18], which has proved to be an extremely helpful tool. A working knowledge of process control basics and electronics are also very useful.
3.1. Fluid dynamics

The fluid dynamics issues are closely related to heat transfer, but are by established customs, usually treated separately. The problem may be characterized as balancing the natural fluid flow in the crucible arising from thermal geometry (temperature gradients) with a “forced convection,” which is a result of crystal and/or crucible rotations. The natural convection is usually characterized by Grashof number $Gr$, of buoyancy force to viscous force, and is a function of gravity acceleration, volumetric thermal expansion coefficient, radial thermal gradient, and a kinematic viscosity of the melt. The forced convection is characterized by the Reynolds number $Re$, which is a ratio of external force to viscous force. It is a function of characteristic velocity arising from rotation speed, crystal diameter, and viscosity of the melt.

At a critical rotation rate, forces of natural and forced convections opposing each other become equal, and crystal interface becomes flat. The fluid convection issues are further complicated by a need to account for the behavior of the melt where it comes in contact with the gaseous phase. Surface tension driven Maragoni flows due to both thermal gradients and component evaporation are very important, and markedly affect the heat and mass transfer. Maragoni flows are described by $Ma$ which is a ratio of surface tension, viscosity, and crucible radius.

3.2. Heat transfer

The only variable to control the heat transfer at crystal growers disposal is usually a furnace redesign accomplished by adding or removing insulation, and various types of passive or active after-heaters.

3.3. Crystal growth equipment

The crystal growth system consists of

- Furnace containing crucible with the molten charge.
- Heat supply.
- Pulling device.
- Process control system.
- Ambient gas enclosure and gas delivery system.

The growth furnace is usually constructed from stabilized zirconia ceramic parts. Because the growth and diameter control depend on the radial temperature gradient in the liquid, and the heat dissipation and convection on the vertical gradient, some flexibility for adjustments must be built into the design. For smaller systems, these adjustments can be made by varying insulation materials and ceramic parts sizes. In the case of large systems, the radial gradients may decrease significantly, and therefore the need for very precise control increases dramatically. It is also essential to control environmental variables affecting the growth stations. These variables include room temperature, quality of electrical power, cooling water flow and temperature, and vibrations.

3.3.1. Power supplies

Noble metal crucibles are used in high temperature oxide growth (normally iridium or platinum) and are heated by coupling to the energy from radio frequency generators operating in frequency ranges varying from 10 to 400 kHz. Most of the newer solid state RF generators operate in 10-30 kHz range; the lower frequencies are being preferred because they produce lower voltages on coupling coils as well as much more uniform heating.

3.3.2. The pulling device

This consists of rotating shaft which may be vertically lifted at controlled velocities. The shaft facilitates the means for rotating the seed, immersing it into the melt, and withdrawing the growing crystal. Because the diameter control is usually accomplished by controlling the crystal weight, a load cell is incorporated into the device. Therefore extreme care must taken to eliminate any vibration generated by the device movements.

3.3.3. Process controllers

These devices are used to control the weight of the growing crystal. As the crystal is pulled from the melt, the load cell detects any deviations from the programmed value and signal is sent to the power supply to adjust the input power, and correct the rate of heat transfer. There is a wide selection of analog and digital devices for this task today. However, they must very carefully evaluated for their operational stability, sensitivity to external influences (temperature, signal interference’s etc.), and ease of operation. Digital devices are generally more flexible in accepting complex control algorithms.

3.3.4. Gas delivery systems

Because is necessary to protect crucibles at high temperature and/or to control the melt volatility, the growth is carried out under protective atmospheres. Such atmospheres usually contain an inert gas, or an inert gas with small additions of oxygen to control the dopant oxidation states or the volatility of the melted material.

3.4. Growth of laser crystals

When growing crystals for laser applications the growth is further complicated by additions of dopants and activators into the materials. This often changes the high temperature behavior of the melts. Properties such as melting temperatures, viscosity, surface tension, heat absorption and often difficulties in forming solid solutions in the growing crystal result. The melt composition is frequently different than composition of the crystal. This difference is usually characterized by a distribution coefficient “$k$” which is the ratio of concentration of dopant in the crystal to the concentration of dopant in the melt. If $k$ is less than
one, the crystal grows with a lower concentration than is in the melt and vice versa if \( k \) is greater than one, the crystal grows with higher concentration. So the concentration in the melt is continuously changing, in the first case it is increasing, and in the second case the melt is being depleted. However slow and gradual this change may be, it effects the growth, and may limit the size of the grown crystal. Examples of \( "k" \) larger than unity is the incorporation of chromium into YAG, and an example of low \( "k" \) is the incorporation of neodymium into Nd:YAG. The distribution coefficient is not really a constant. In reality it stays constant only if other parameters (rotation rate, crystal diameter, the ambient atmosphere) remain constant. For example, changes in oxygen concentration in the ambient atmosphere over growing ruby can lead to a change in the distribution coefficient for chromium from 0.4 to 1.6, and in case of Cr:YAG the distribution coefficient can be manipulated from \( k = 1.5 \) to \( k = 3 \) with a relatively small change in oxygen partial pressure.

3.5. Growth of ruby crystals

Ruby i.e. the chromium-doped corundum is the oldest or “original” solid state laser crystal. The ruby crystal growth underwent the transition from flame fusion growth to Czochralski some 39 years ago. Ruby crystals can be reliably grown as very large boules, 3–3.500 diameter 10–12’’ long, while maintaining very close chromium concentration tolerances. The preferred orientation is 60° off the c-axis. The early complication known as the “orange” ruby, due to a presence of divalent ions in the melt, is now well understood, and eliminated by a proper choice of raw materials.

3.6. Growth of Yttrium Aluminum Garnet, YAG

YAG is a host crystal for several laser materials such as CTH:YAG, Er:YAG, Yb:YAG, CTE:YAG, Nd:YAG. The crystal growth of “white” (un-doped) YAG from the whole YAG family is the easiest to be carried out. Sophisticated raw material selection and handling are critical in the elimination of impurities from laser crystals. The most damaging impurities are the ions in any oxidation state different than 3+. If such impurities enter the YAG lattice, they are the source of color centers either transient or permanent. Also an effect of the ambient atmosphere on the crystal’s oxygen stoichiometry may be pronounced. For example the Yb:YAG is sensitive to ambient atmosphere composition. Ytterbium has a tendency to be reduced to divalent, and coloration as well as color centers may result in the crystal if the growth is carried out under an oxygen poor ambient atmosphere. Raw material purity with respect to rare earth impurities plays an important role in the performance of Erbium doped YAG. The “heavy” rare-earth (Ho, Dy) have a negative effect on the performance of Er:YAG. In YAG, crystals containing chromium as an activator, the critical impurities are divalent elements.

The presence of divalent ions in YAG lattice forces the chromium to assume the four-valent state for charge compensation. This removes a part of the activators, creating transition color centers, and causing optical loses (Fig. 2).

3.7. The growth of Nd:YAG

The ease of growth of un-doped YAG is in sharp contrast with difficulties encountered in the growth of YAG doped with neodymium. The distribution coefficient for neodymium in YAG is only about \( k = 0.16 \). Large concentrations of Nd must be used in the melts, and the melt changes composition during the growth. This means very slow growth rates, on the order of 0.5 mm/h or lower. The common crystal growth orientation is the \( \{111\} \) resulting in a triangular symmetry in facets forming the external shape of the crystal.

Even more important is the internal stresses created by a different rate of orientation dependant incorporation of the dopant. The faceting may be to some extent controlled by temperature gradients and rotation rates. Attempts to grow “flat interface” YAG have rarely been successful (Fig. 3).

3.8. Growth titanium doped sapphire

Ti-sapphire is produced by two techniques; Heat exchange method also known as HEM, and by the pulling technique. In the pulling technique the aluminum oxide charge containing the desired quantity of dopant, titanium oxide, is melted in an iridium crucible by means of RF heating under an atmosphere of a pure nitrogen or argon.
Charge preparation must take into account a very low distribution coefficient $k = 0.1$ under a majority of growth conditions. The pulling rates are slow in the vicinity of 0.25 mm/h. The Czochralski pulled Ti:sapphire must always be subjected to post-growth annealing [19] to eliminate the effect of an incorporation of four-valent titanium ions formed during the process, and incorporated in the crystal. The four-valent titanium ion is a defect causing impurity and therefore increases in optical loss may be expected with increases in titanium concentration. Jones et al. [20] describe a reversible oxydo-reduction process involving titanium sapphire. This process became bases for the post-growth treatment of Ti:sapphire which allows to the optical quality of the pulled crystals to a laser quality requirement.

4. Conclusion

The Czochralski or pulling method is still the most widely used crystal growth technique used to manufacture oxide laser crystals. The advent of computer modeling will undoubtedly lead to further improvements. However, an understanding of the technology must include an awareness of its limitations. As the laser applications expand, crystals will not be only source of laser elements for all applications. Glass, semiconductor, and fiber laser sources will play an expanding role in the future. The applications for crystals will be focused on their use in high power lasers with high beam coherence. Such a trend will further increase demand on crystal sizes, and perfection. But a scale-up in the method is not unlimited, because, in order to maintain the necessary thermal gradients, while increasing physical dimensions, limits will be reached given by properties of used materials. For example, melting temperature of crucible materials is a limitation.

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