Lasers Crystals: Synthesis, Growth and Characterization

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Abstract

Since 1980 a successful program to the development of solid state laser has been maintained at IPEN including coordinated activity between different areas, such as crystal growth, laser spectroscopy and laser engineering. In this paper we review, in particular, the research done in the crystal growth laboratory, for the development of synthesis, purification, growth and characterization of single crystals for laser applications.

Introduction

The growth of single crystals has been developed over the years to meet needs for basic research and applications in the condensed matter physics. The materials science program started at IPEN during the seventies included the growth of alkali halides crystals to the study of radiation induced defects. In the beginning of our program, the need of synthetic crystals was due to the demand of radiation solid state dosimeters like TDL-LiF. In solid state research alkali halides single crystals had played a major role. Because of their mainly ionic binding type, their high structural symmetry and their wide band gap, they became model-systems for basic experimental and theoretical investigations in insulators. The first open air growth runs of alkali halide crystals at IPEN has been developed in a Czochralski home made system composed of a crucible inside a tubular resistive furnace. At high temperatures alkali halides form oxides, hydroxides and carbonates due to the reaction with oxygen, carbon dioxide and moisture in air; therefore an inert or reducing atmosphere is necessary to keep the purity if the salts are molten. Because of that, the above system was early substituted by two Czochralski resistive systems composed by a cold-wall growth chamber that permitted vacuum and gas handling. With those apparatus it was possible to obtain 40x50 mm, LiF, KCL, NaCl and KBr single crystals manually pulled.

The optical spectroscopic properties of these materials were subject of basic investigations, concomitantly with the advance of color centers as useful laser sources in these crystals [1]. The combined effect of having the crystal growth facilities and the spectroscopic tools led to the first color center lasers in our laboratories [2]. Since then, the association between the crystal growth group and the laser group at IPEN were maintained resulting in a very profitable 14 year scientific program that includes basic research and technology to the development of solid state lasers. The materials already studied in this collaboration program included alkali halides (LiF, KCl, KBr, NaI), rare earth chlorides ($PrCl_3$, $SmCl_3$), ternary fluorides ($LiYF_4$, $BaLiF_3$), and phosphates (KH_2PO_4 - KDP), obtained by the growth from the melt (using standard methods like Bridgman, Czochralski and Zone melting techniques) and by the solution growth (method from aqueous solution) [3,4].

In addition to the research of crystal's synthesis, the major equipment for crystal growth experiments was also constructed at our laboratories and has been continuously refined to enhance their applicability for specific materials. The two Czochralski systems initially constructed, have today automatically pulling systems and programmable temperature controls with 0.01 % precision (both constructed at IPEN), providing operation under highly purified static atmospheres (low pressures).

Besides these growth furnaces we constructed two Bridgman systems (a dynamic and a static one), two zone melting apparatus for fluorides and chlorides runs, and set up a complete laboratory for handling reactive fluorides. Laboratory manipulation of gaseous HF requires rigorous safety procedures. Moreover, most fluorides are moisture sensitive (which requires dry environments), some of them being very corrosives (all experiments must be carried out under perfectly ventilated hoods).

In this paper we will review the research done in the crystal growth laboratory at IPEN, for the development of synthesis, purification, growth and characterization of single crystals for optical applications.

Materials Preparation

Over the years, highly purified materials have been required for meaningful investigations of intrinsic properties and of extrinsic effects caused by defined dopants in low concentrations, as well as for technological applications in optical components. To improve the purity of the materials utilized at Czochralski and Bridgman crystal growth, we began to study methods for the fluoride and chloride purification. This work included the utilization of reactive atmosphere treatments, synthesis process and zone melting technique [5, 6, 7]. The study and development of these purification process were essential to achieve the quality needed in crystals for laser applications.

a) synthesis and reactive atmosphere processing

The successful operation of a material as an optical component is dependent on a number of factors directly related to the crystal preparation, but the most important one is the initial use of high purity chemicals. The choice of commercial high purity chemicals do not assure the purity of the final crystal. Manipulation of the products without the correct procedure can introduce spurious contamination, mainly in the case of more complex compounds as $LiYF_4$ or $LiCaAlF_6$ used as laser matrix hosts (these materials need to be previously synthesized before the crystal growth process), and for hydrated materials, which need to be dried in protective atmospheres to avoid contamination derived from water.

In the early work of preparation of alkali halides to use as windows for high power lasers, the OH^- impurity posed a special problem. The H_2O, source of the this impurity, is always present in the work environment and the OH^- characteristic infrared absorption changed the optical properties of the window crystals. To solve this problem it was applied the concepts of reactive atmosphere processing (RAP) [8]. In the growth of fluorides or chlorides, the RAP decomposes anions, i.e., OH^-, NH_2^-, NO_2^-, NO_3^-, CO_3^{--}, etc., and quantitatively substitutes the halide. The heterogeneous reaction (hydrolysis) in crystal growth can be described by:

$$X^-(s) + HOH(g) \leftrightarrow OH^-(s) + HX(g) \qquad (1)$$

where X^- represents a halide (Cl^-, F^-), (s) a condensed phase (crystal and/or melt), and (g) the gas phase. The reactive atmosphere (HX) drive the equilibrium of equation (1) to the left, preventing the OH^- formation.

We used the RAP to the growth of spectroscopic samples of $PrCl_3$. The hydrated chloride, $PrCl_3.7H_2O$, (first prepared from dissolution of the oxide Pr_6O_{11} in hydrochloric acid) was carefully dried with a protective atmosphere of anhydrous HCl and Ar. The consecutive growth process by zone melting technique was also realized under an anhydrous HCl and Ar moisture flow [5]. The same procedure was applied to the pre-purification of KCl used in the growth of KCL:Tl samples [6] and to the preparation of compounds such as $LiYF_4$, $BaLiF_3$ [7] and $LiMAlF_6$, which are obtained by the fusion of the basic compounds (LiF, YF_3, BaF_2, AlF_3, etc.) under an anhydrous HF and Ar moisture flow.

Although it is possible today to find commercially a great variety of basic compounds with relative high purity, we normally synthesize the basic compounds (fluorides and chlorides) used in our laboratory. A standard method of fluoride (chloride) preparation is its synthesis in hydrofluoric acid (hydrochloric acid) solutions. In this process the compounds are mixed in stoichiometric quantities in platinum or Teflon vessel with aqueous solution of HF (HCl). After that, the product is dried under a stream of gaseous HF (HCl).

In general, for fluoride preparation, it is preferable do to this operation under strictly anhydrous conditions, obtained by the use of gas-solid reaction synthesis methods. The most common technique is the use of streaming gaseous HF over metals, halides, or oxides heated under appropriated temperatures [9]. Figure 1 shows the apparatus constructed in our laboratory to carry out fluorinations by gaseous hydrofluoridric acid at atmospheric-pressure. The oxide or carbonate is placed in a platinum or vitreous carbon crucible and introduced into a reaction chamber under a mixed flow of gaseous HF and Argon previously dried and freed of oxygen.

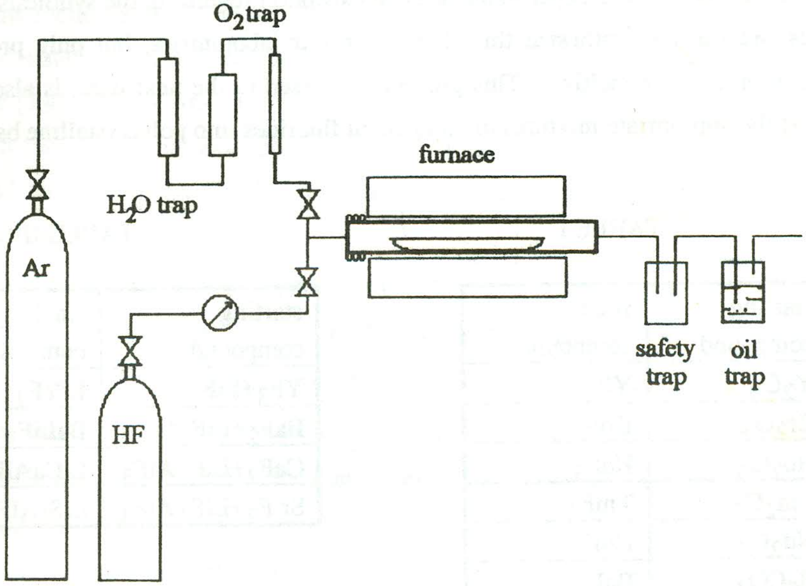

Figure1. Hydrofluorination system

The reaction chamber is made in platinum and monel, and the tubing which transport the gas mixture in/out this chamber is made of copper (at low temperatures copper resists reasonably to HF). Table I shows the fluorinations already obtained with this system. Considering the synthesis of AlF_3, as an example, the conversion reaction can be described by the following equation:

$$Al_2O_3 \quad + \quad 6\,HF \quad \overset{\Delta T}{\rightarrow} \quad 2\,AlF_3 \quad + \quad 3\,H_2O \qquad (2)$$

The final compounds - $LiYF_4$, $BaLiF_3$ or $LiMAlF_6$ - are obtained in the same system, as already mentioned, by the fusion in controlled conditions of two or more previously synthesized fluorides with Lithium fluoride (Table II). It's important to note that the LiF used in our experiments it is an exception regarding the synthesis process, that is, we do not synthesize this fluoride in our laboratories, but only provide its purification by zone melting. This process, discussed in the next item, is also used to convert the appropriate mixtures of component fluorides into polycrystalline bars of the

TABLE I

starting compound	final compound
Y_2O_3	YF_3
Er_2O_3	ErF_3
Ho_2O_3	HoF_3
Tm_2O_3	TmF_3
Nd_2O_3	NdF_3
$BaCO_3$	BaF_2
$CaCO_3$	CaF_2
$SrCO_3$	SrF_2
Al_2O_3	AlF_3

TABLE II

starting compound	final compound
YF_3+LiF	$LiYF_4$
BaF_2+LiF	$BaLiF_3$
CaF_2+LiF+AlF_3	$LiCaAlF_6$
Sr F_2+LiF+AlF_3	$LiSrAlF_6$

required compound. It's already known that single crystals produced directly from the component materials result, in general, in crystals with poor quality. Several factors could contribute to this effect including impurity in one or more components, deviation from stoichiometry and contamination during preparation. Moreover, the zone refining procedure also purifies the final compound to be finally used to the crystal growth.

b) zone melting

There are several process of materials purification but zone melting has probably became the most widely used technique by the crystal growth laboratories. In this process the material is, in general, contained in a boat placed horizontally in a controlled atmosphere reaction chamber. The temperature gradient is arranged so that a narrow molten zone is produced. The molten zone is established at one end of the charged material and is slowly advanced by moving either the container ("boat") or the furnace [3,4]. The purification is obtained considering the impurity segregation effect between the liquid and solid phases moving along the solid-liquid interface. By the repeated passage of the zone, the initial (or final) segment of the crystal becomes progressively purer.

Figure 2 shows the apparatus constructed at IPEN for the zone refining of fluorides. An automatic electro-mechanical system controls the globar furnace movement though the reaction chamber. The material is placed in a platinum or vitreous carbon crucible introduced into a reaction chamber where a mixture of gaseous HF and Ar previously dried and freed of oxygen flows. The moving zone rate and passes number are determined by the materials characteristics and the desirable degree of purification. For the Chloride purification the platinum chamber is substituted by a quartz tube and the reactive atmosphere by a mixed flow of HCl and Ar.

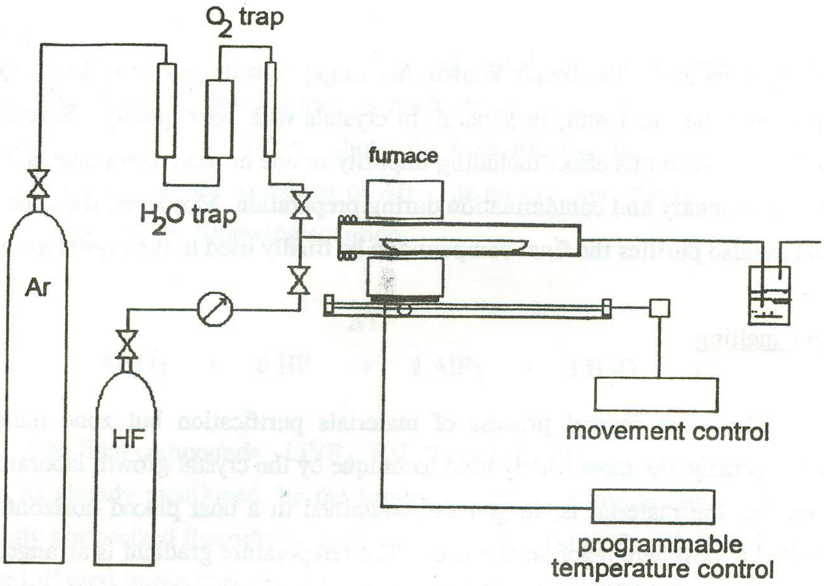

Figure 2. Zone melting system

Crystal Growth

a) Bridgman-Stockbarger Method

This method is based on the slow solidification of a melt. In essence, the Bridgman-Stockbarger technique produces nucleation on a single solid-liquid interface by carrying on the crystallization in a temperature gradient. The material to be crystallized is contained in a cylindrical crucible with a conical tip which is lowered through a temperature gradient [3,4]. It is also possible to keep the crucible and furnace stationary and use controlled temperature lowering. The latter procedure is also know as stationary or static Bridgman technique.

For the growth of alkali halide crystals we constructed a Bridgman apparatus. It was composed by two commercial Marshall furnaces and a stainless steel growth chamber for the growth under inert gas flow. This system provided the growth of large NaCl crystals (50x60 mm) useful for the preparation of optical windows. Later it was also used to the growth of NaI:Tl crystals for gamma radiation detector's application.

More recently, it was constructed a Stationary Bridgman System [6], where it's possible to obtain small crystals (typically 15 x 35 mm) for preparation of spectroscopic study samples. The apparatus is basically formed by a furnace, designed to produce an appropriate temperature gradient, and a programmable temperature controller. In the growth of KCl:Tl crystals, for example, the gradient in the solidification region is ≈ 30°C/cm and the cooling rate was 5°C/h. Because of the high vapor pressure of the dopant we used sealed quartz crucibles. The Tl concentration in the obtained samples ranged from 0.5 to 1.2 mole%. This system is being changed to make possible the growth under fluorinating atmospheres. An adjustment of the thermal environment of the system is being done to compensate the introduction of a reaction chamber, constructed in nickel and monel, which will permit growth, with vitreous carbon crucibles, under low pressures of HF. The reactive atmosphere will be obtained by the use of NH_4HF_2. The Ammonium difluoride at high temperatures dissociates into NH_3 and HF, providing a reactive atmosphere during the material melting. The advantage in the utilization of the difluoride instead of gaseous HF is that the first one is handled more easily because it can be manipulated without problems at room temperature. However, the NH_3 elimination requires a hard clean treatment of the system after each growth run, because this compound usually adheres to the chamber wall. Growth runs of $LiMAlF_6$ will be performed in this system.

b) Czochralski Method

This method is especially versatile and is used to the growth of different types of materials (oxides, semiconductors, fluorides). The material contained in a suitable crucible is heated until its charge is melted. The thermal environment is adjusted so the equilibrium between liquid and solid is approached on the surface of the melt. A seed crystal is placed in contact with the melt and by controlling the melting temperature the solidification process starts. When the seed is pulled from the melt with a rate not exceeding the crystallization rate, a cylindrical crystal known as a "boule" is obtained [3,4]. Although simple in principle, the pulling method is complex in detail. The success in pulling crystals using Czochralski technique depends on the right combination of numerous variables, such as: pulling rate, rotation rate, thermal geometry, mass flow, heat flow and melt size.

Over the years the Czochralski technique has been mostly used for congruently melting compounds, however if a crystal melts incongruently, it may be possible to grow it from a melt of such a composition that the crystal is the stable phase. Both laser's crystals: $LiYF_4$ and $BaLiF_3$, grown in our laboratories, present incongruent melting. Their growths require a melt containing an excess of LiF to avoid the precipitation of YF_3 and BaF_2, respectively, and this excess of LiF must be maintained throughout the growth period. We operate without an automatic diameter control, but considering the phase diagram of the system LiF-BaF_2 (or LiF-YF_3) and the thermal conditions and dimensions of our Czochralski furnace, we have determined a non-linear program of temperature that assure the growth of cylindrical and homogeneous $BaLiF_3$ (or $LiYF_4$). Both crystals are grown with pulling rate of 1 mm/h; the rotation rate depends on the crucible size used for each experiment (the heat flow is dependent on the crucible size). The crucible diameter can be chosen among 30, 40, 50 or 60 mm. Single crystals of $LiYF_4$:Nd and $LiYF_4$:Er:Tm:Ho are usually grown in the laboratory for the laser rod production as boules of 30 x 90 mm. Small samples are also grown for spectroscopic studies. $BaLiF_3$ single crystals doped with Ni, Co and Pb are grown, with dimensions of 20 x 50mm, for the realization of spectroscopic studies and laser tests.

c) Aqueous Solution Growth

The growth of crystals from solution is probably the oldest method of crystal growth. In aqueous-solution growth, as in all solution growth, the object is to supersaturate the solution without causing spontaneous nucleation and to make the supersaturation and hence the rate as high as is proportionate with controlled growth on a seed of material of the requisite perfection [3].

KDP crystals were obtained in our laboratory by the traditional growth method from aqueous solution at low temperature (42°C) and by the method of crystallization from boiling aqueous solution [10]. Boiling causes important changes in growth mechanisms by promoting the process of fixing of particles at the crystalline surface. The effect results in an up to 10-fold increase in growth velocity compared to the low temperature growth. Even so, there is no loss of crystal quality, shown by analysis of defects and crystal structure, and in the efficiency of frequency doubling of the Nd:YAG laser radiation. However, the boiling method shows some disadvantages such as the cooling of crystals after growth. Some crystals cracked during cooling from boiling temperature (100°C) to room temperature.

Characterization and Growth Parameters

The characterization of the materials obtained in the synthesis and purification process in our laboratory are usually done by atomic emission spectrography and x-ray diffraction. The chemical analysis determines the purity grade and the X-ray diffraction shows what phases were obtained. Recently we began to study the utilization of thermal analysis - differential thermal analysis (DTA) and thermo-gravimetric analysis (TG) - for characterization of the fluorides synthesized for the growth of $BaLiF_3$ and $LiMAlF_6$ (M=Ca, Sr) single crystals. These techniques provide several information regarding the phase transitions, dehydration and/or dissociation reactions, melting behavior because of dopant introduction or presence of spurious impurities; being excellent complementary characterization methods to the two techniques already used.

Assuming that high purity materials were synthesized, the optical and crystalline quality of the desired laser material will depend basically on the growth parameters, such as growth rate, crystallographic orientation, interface shape and dopant distribution. The determination of the influence of these parameters in the final quality of the crystal always involve extensive experience of the crystal grower, that is, the realization of several experiments in different conditions followed by characterizations with different techniques.

The first analysis of any crystal is a qualitative visual observation. The presence of macroscopic defects and/or scattering centers immediately compromise their use for optical applications. In the case of fluorides like $BaLiF_3$ and $LiYF_4$, visual observations can even been made during the crystal growth process: the melt must be clear and the solidified part transparent. If the crystalline material is not transparent this indicates that two or more phases are crystallizing simultaneously.

The optical quality is not only affected by scattering sites but also by strain and refractive index variations. These defects can be identified by interferometry analysis. In the pure $BaLiF_3$ growth study, for example, we observed that the interferograms of the first crystals obtained showed a poor optical quality with large stressed areas [7,11]. In melts of moderate thermal conductivity (oxides and fluorides), heat transport is mainly by convection. Experimentally, we observed in the growth of $BaLiF_3$ single crystals that temperature distribution in the liquid was considerably influenced by convective flow in the crucible. The solid-liquid interface shape changed from convex to concave with the variation of the applied rotation rate. The characterization by interferometry of samples grown with difference rotation rates showed that only a flat interface allowed the growth of relatively stress-free crystals.

Crystallographic orientation is another important parameter to minimize crystals misorientatition, lowering dislocation densities and reducing optical scattering centers. Rocking curves obtained with neutron diffraction showed to be a powerful tool to study the influence of the interface shape and of the crystallographic orientation in quality of Czochralski $BaLiF_3$ crystals [12]. When a convex or a concave interface of growth is formed, we note a quite large number of mosaic domains with a large dispersion between them. In a few words, the crystal exhibits a poor crystalline quality. Inverse results are observed for flat and semiflat interfaces of growth. In this case, we note a decrease in the number and dispersion of the mosaic domains, that is, the crystals have an improved crystalline quality (figure 3).

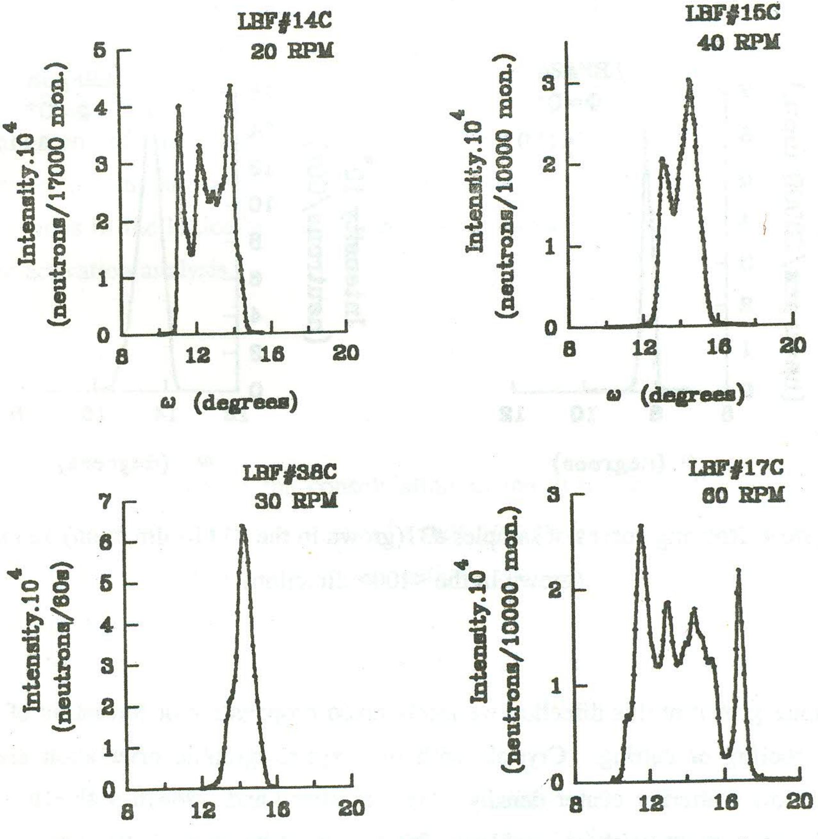

Figure 3. Rocking curves of samples grown with different rotation rates and consequently different interface shapes (#14C - convex, #15C - semiflat, #38C - flat, #17C - concave)[12].

Rocking curves for <111> oriented crystals show mosaic widths about two times greater than those of <100> oriented crystals (figure 4). However, it is important to note that this result does not mean that <111> oriented crystals have a poor crystalline quality but only that they are not as good as the crystals grown in the <100> direction. Growth with <111> seed crystals was possible at high or low rotation rates.

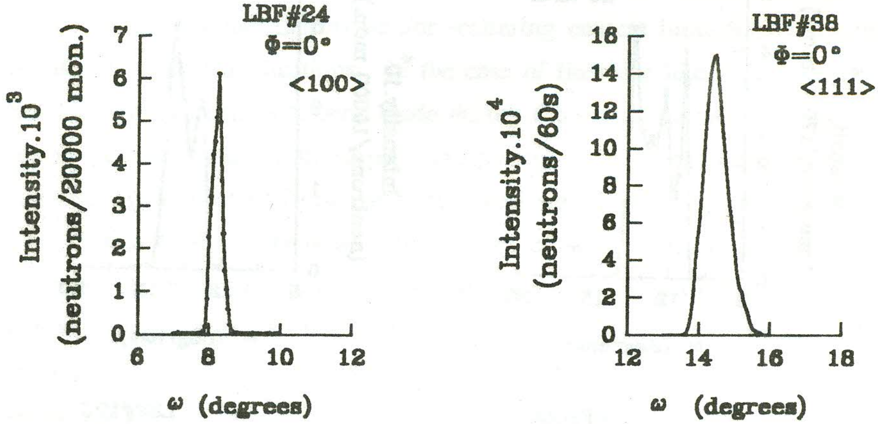

Figure 4. Rocking curves of samples #31(grown in the <111> direction) and #24 (grown in the <100> direction).

In samples grown in this direction we rarely noted propagation or formation of cracks during cooling or cutting. Crystals with this crystallographic orientation show, in general, low scattering center density. On the other hand, growth with <100> seed crystals takes place without problems for low rotation rates (≈10 rpm - convex interface). However, at higher rotation rates (≈ 30rpm - flat interface) we noted very often the occurrence of cracking during cooling or just after the furnace opening. In general, these crystals presented a great segregation in their central region. This means that, although the study of mosaicity shows the <100> as being a good growth direction, for optical applications the best conditions for the growth of $BaLiF_3$ single crystals are seeds at <111> as growth direction and a rotation rate which leads to a flat or semiflat interface shape. These conditions lead to crystals with good optical and crystalline quality.

Another method of crystals characterization is by IR and UV-VIS absorption spectroscopy. It permits to check the presence of spurious impurity absorption bands, such due to OH^- absorption, and in the case of doped crystals, to estimate the dopant concentration in the crystal. The dopant distribution in a crystal is dependent on the distribution or segregation coefficient (K)[3,4]. This coefficient, is obtained by the determination of the doping concentration in crystals grown with different concentrations. In our case, the crystals are examined for the introduction of the impurity ions in the lattice by x-ray fluorescence, atomic emission spectrography and neutron activation analysis.

Conclusion

This paper showed the consolidation in our Institute of the techniques of synthesis, growth and characterization of single crystals for laser applications. From this facility laser crystals with good optical quality were provided to several laboratories including our own.

These crystals provided a great range of utilization due to their application in color center lasers, surface lasers and a wide range of power lasers CW or pulsed. Crystal laser hosts for rare earths such as Nd, Ho and Er were grown for several applications in medicine or industry. Crystals obtained in our laboratories were also employed in frequency doubling, pulse shaping and Q-Switching devices after an extensive investigations of their physical properties, the main purpose of our basic research.

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