

1 Introduction

In the beginning of the 20th century, several scientists investigated the nature of light and matter as well as the interaction between these two fundamental components. With the help of the quantum theory several aspects in this field could be explained in a sufficient way. Based on this theory Einstein predicted the realization of lasers¹ in 1916 [Ein16]. However, it was more than 40 years later when Maiman demonstrated laser oscillation for the first time [Mai60]. He used a flashlamp as pump source for a ruby ($\text{Cr}^{3+}:\text{Al}_2\text{O}_3$) laser rod. Soon afterwards, other transition metal ions as well as rare earth ions were investigated with respect to their laser performance. While the transition metal ions offer a wide laser tunability range of several hundreds of nanometers, the optical transitions of rare earth ions feature spectrally narrow optical transitions. With the development of laser diodes (LDs) of suitable wavelength, highly efficient and compact diode-pumped solid-state lasers (DPSSLs) could be realized.

The trivalent praseodymium ion (Pr^{3+}) offers several transitions in the visible spectral range from blue to near IR. Thus, with Pr^{3+} -lasers operated at visible transitions, it is easy to achieve UV radiation only by a single step of second harmonic generation (SHG), making these lasers interesting for several biotechnological and medical applications. The fundamental radiation in the visible spectral range is interesting for display applications, too. While the first Pr^{3+} -based laser was a flashlamp pumped $\text{Pr}^{3+}:\text{CaWO}_4$ under cryogenic temperatures [Yar62], Pr^{3+} -lasers to date oscillate at ambient temperatures and the flashlamps are substituted by laser systems. Direct pumping of Pr^{3+} -lasers operating at room temperature was realized with Ar-ion lasers or the radiation obtained by intracavity SHG of a $\text{Nd}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ laser operated at the ground state transition [San94b, Heu99]. These pumping systems did not match the absorption lines of Pr^{3+} well and thus resulted in moderate efficiencies. Furthermore, the pump sources were bulky or complex. Suitable laser diodes based on GaN emitting in the blue spectral region are commercially available since about 2003. Just one year later, a GaN-LD-pumped Pr^{3+} -laser was realized for the first time by our group [Ric04b]. These laser diodes enable quite cheap and compact laser set-ups as well as improved efficiencies. A second option for even higher efficiencies are frequency doubled optically pumped semiconductor lasers (OPSLs) operating at suitable wavelengths.

This work deals with the fabrication, spectroscopic investigations and laser performance of Pr^{3+} -doped fluoride single crystals. The first chapter deals with the crystal growth process by the method of Czochralski. Besides the discussion of the challenges of crystal growing, detailed physical properties of the fluoride materials will be given herein. The

¹LASER: light amplification by stimulated emission of radiation

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next chapter focuses on the spectroscopic investigations performed both at room temperature and cryogenic temperatures of 10 K. Different mechanisms regarding microscopic energy transfer between adjacent Pr^{3+} -ions will be discussed and evaluated. The last chapter contains the results of the performed laser experiments. The Pr^{3+} -laser performance under OPSL-pumping and GaN-LD pumping will be presented both in continuous wave and Q-switch mode. Furthermore, the experiments and results from intracavity second harmonic generation will be discussed. To conclude, a summary and an outlook will be given.

2 Crystal Growth

This chapter focuses on the crystal growth of Pr^{3+} -doped fluoride single crystals. In Section 2.1 the growth process and the Czochralski growth setup used in this work is described while structural and optical properties of the crystalline materials will be presented in Section 2.2. Afterwards, some challenges which occurred during the crystal growth process will be highlighted and possible solutions will be discussed in Section 2.3. Finally, a summary will be given in Section 2.4. Further details of the Czochralski growth process can be found in the book by Wilke and Bohm [Wil88].

2.1 The Crystal Growth Procedure

Weighting and Prefluorination

In the beginning of the crystal growth procedure, the raw materials, usually 4N or 5N fluoride powders, are weighted according to the stoichiometry of the crystalline material and subsequently mixed in ambient atmosphere. This mixture is treated by a pre-fluorination process.

Using prefluorinated materials has several advantages. First of all, the amount of oxygen impurities is reduced significantly. Secondly, the mixed powders have already reacted and exhibit a polycrystalline structure of the desired material. Thus improved handling conditions are achieved in this way, because the desired structures are generally not hygroscopic in contrast to some of the starting materials like potassium fluoride (KF). And at last, the surface-to-volume ratio is reduced leading to a smaller amount of contaminations during the following steps. Thus, an increased crystal quality can be expected.

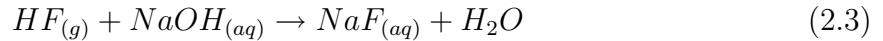
The pre-fluorination process takes place in a set-up consisting of two connected furnaces. A bowl made of glassy carbon and filled with the mixed powders is placed in the main furnace, while the auxiliary furnace contains a crucible filled with 12 g of potassium hydrogen fluoride (KHF_2). The main furnace is evacuated to $5 \cdot 10^{-2}$ mbar and subsequently filled with a 5N nitrogen atmosphere. Finally a constant gas flow of N_2 of 6 l/h is set. This gas flows from the inlet through the auxiliary furnace, the main furnace and through an aqueous solution of sodium hydroxide. Then, the main furnace is heated up to the melting point of the desired crystalline material and the auxiliary furnace slightly below the decomposition temperature of KHF_2 of about 400°C . When the main furnace temperature reaches the melting point, the auxiliary furnace is heated up slightly above 430°C . Now, KHF_2 decomposes according to



and HF gas is produced. The gas is transported by the nitrogen gas flow into the main furnace and reacts with any metal oxide (M_2O , MO , M_2O_3) compounds within the melt forming the corresponding fluoride compounds and water, that is for example:



In an aqueous solution of sodium hydroxide the excess HF molecules are neutralized as follows:



After 4 hours the prefluorination process is terminated, both furnaces are cooled down to ambient temperatures and the prefluorinated materials are removed from the furnace.

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After the pre-fluorination process, the crystal growth process can be started. Figure 2.1 shows the setup used for growing fluoride single crystals by the Czochralski method. It consists of a conical crucible with 35 mm outer diameter and 38 mm in height, placed in a larger crucible (49 mm in height, 50 mm in diameter), which is filled with 2-mm diameter pellets for thermal insulation. The crucibles and the pellets are made of glassy carbon. This crucible system is mounted on a carbon-made pedestal. A carbon heat shield placed on top of the inner crucible completes the growth setup. The RF-coil surrounding the crucibles provides the power for heating the outer and inner crucible as well as the materials in the inner crucible. Due to the weak electric conductivity of carbon ($\sigma_C = 1.28 \times 10^5 \text{ S/m}$, [ECTI]) the skin depth is $\delta \approx 3.8 \text{ mm}$ and the RF field is not significantly reduced by the 1.85 mm thick walls of the outer crucible. The remaining RF power is coupled into the inner crucible and heats the materials inside. A nickel wire is used as seed.

Prior to each growth run, the furnace with the prepared growth setup is evacuated to $6 \cdot 10^{-2} \text{ mbar}$ and filled twice with 5N argon gas slightly above standard atmospheric pressure. This procedure results in an oxygen partial pressure below 10^{-2} mbar . During the crystal growth run, the prepared Argon atmosphere slightly above standard atmospheric pressure remains in the chamber. In the next step, the fluoride materials are heated to the melting point. Then, the seed wire is lowered close to the melt surface to adjust the temperature of the wire. After 20 minutes, the wire, rotating with 9 rpm, is dipped into the melt to initiate the process of crystallization. In case of crystallization, the rotating wire is pulled up with a pulling speed of 0.85 mm/h. The amount of crystallizing material is controlled by manually adjusting the melt temperature. Carbon contaminations on the melt surface induce a locally distorted temperature profile. Because of these conditions,

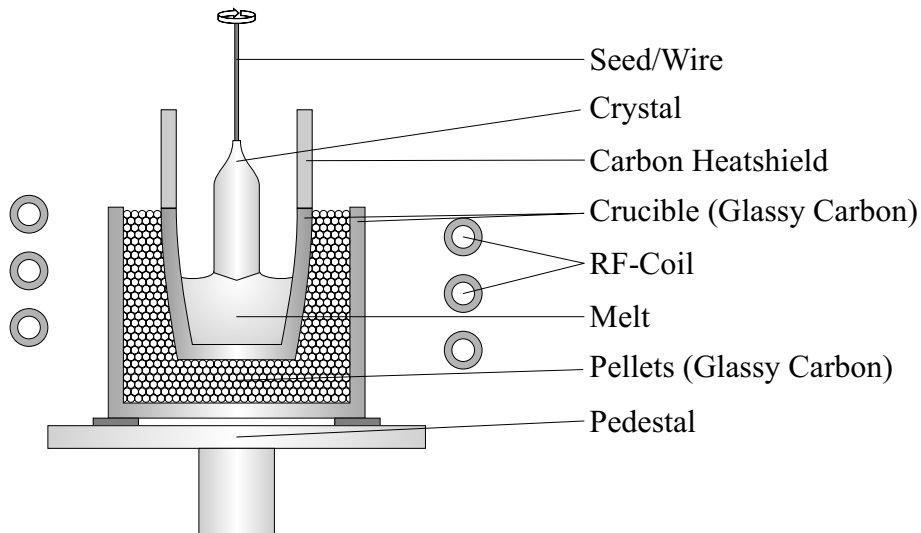


Figure 2.1: Schematic set-up of the Czochralski growth apparatus (modified from [Hen01])

the first part of the grown crystal is polycrystalline and features a large diameter. By increasing the melt temperature, the diameter is reduced until grain selection leads to single crystalline growth. Now the melt temperature is reduced again to increase the diameter, resulting in a bottleneck-shaped structure. When the desired diameter is reached, the thermal conditions are carefully adjusted to obtain a constant diameter of the crystal. After growing a certain amount of material, the growth procedure is stopped by removing the grown crystal from the melt. To reduce thermal stress in the grown crystal, the temperature is reduced slowly. After 4 hours ambient temperature is reached and the growth chamber is evacuated to $6 \cdot 10^{-2}$ mbar and refilled with argon gas once again so that all fluoride compounds existing in the gas phase are removed.

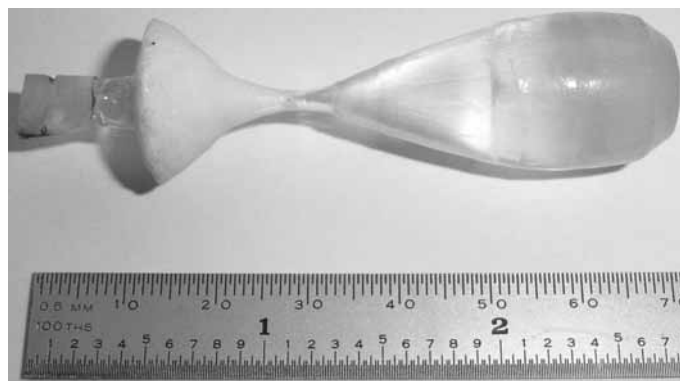


Figure 2.2: As-grown $\text{Pr}(0.45\text{at.\%})\text{:LiLuF}_4$ -crystal boule

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	LiYF ₄	LiLuF ₄	BaY ₂ F ₈	KY ₃ F ₁₀
Growth location	Hamburg	Hamburg (Pisa)	Pisa	Hamburg (Pisa)
Initial melt composition (mol%)	LiF-YF ₃ 53%-47%	LiF-LuF ₃ 50%-50%	BaF ₂ -YF ₃ 33%-67%	KF-YF ₃ 25%-75%
Melting point T_m (°C)	830	850	960	1030
Melt specification	incongruent	congruent	congruent	congruent
Rotation speed (rpm)	9	9 (5)	5	10 (5)
Pulling speed (mm/h)	0.85	0.85 (1)	0.5	0.85 (1.00)

Table 2.1: Material and growth parameters applied for growing of fluoride crystals by the Czochralski method ([Tho61, Sob82, Har83, Cha93])

Figure 2.2 shows a photograph of a grown $\text{Pr}^{3+}(0.45\text{at.}\%):\text{LiLuF}_4$ single crystal. The shape results from the procedure described above.

Table 2.1 shows the melt and growth parameters used for the different growth runs as well as their thermal properties. The BaY_2F_8 crystals were provided by the University of Pisa. Both KY_3F_{10} - and LiLuF_4 -single crystals were grown in Hamburg as well as in Pisa.