Zone melting growth of LiSrAlF$_6$:Cr crystals for diode laser pumping

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Abstract

In this work we demonstrate the growth and the laser operation of high-quality Cr:LiSAF crystals by zone melting method. CrF$_3$ dehydration and oxidation were carefully studied to optimize Cr incorporation in the LiSAF host. The obtained crystals have presented low losses and high laser gain, characteristics that are very suitable for diode-pumped laser operation. We studied the thermal behavior of these crystals during laser action and compared their CW performance with that of a commercial highly doped Czochralski-grown crystal. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Cr^{3+}-doped LiSrAlF$_6$ (Cr:LiSAF) single crystals have been reported since 1989 and they soon became recognized as an efficient laser-active material for many purposes, such as ultrashort pulse generation, laser amplification, Q-switching and microchip lasers [1–6]. Moreover, they have great advantages for generation of ultrashort pulses in the near infrared, and can be efficiently diode pumped.

Optical properties of laser hosts are very important in determining laser performance. Even small crystals, as those required by diode-pumped systems (at the most 10 mm long samples), must exhibit good quality. Up to now, the best results for laser operation of Cr:LiSAF samples were obtained with crystals grown by the Czochralski technique [7]. However, small samples can be grown by different methods. The growth of high-optical quality fluoride crystals is affected by the growth procedure, the degree of purity and, in some cases, the initial composition of the material used for the growth. Detailed studies of the synthesis processes and influence of the degree of

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purity, and dopant incorporation in Cr:LiSAF crystals were previously reported [8]. In this work, we demonstrate the growth of high-quality Cr:LiSAF crystals with Cr^{3+} concentration ranging from 4 to 6.5 mol%, by the zone melting method, for gain media for diode laser pumping.

2. Experimental procedure

The starting fluorides AlF_3 and CrF_3 were obtained by dehydration under HF atmosphere, from $AlF_3 \cdot 4H_2O$ (99.99%) and $CrF_3 \cdot 4H_2O$ (97%). Both dehydrations were carefully carried out in order to prevent oxide and hydroxyfluoride contamination (item 3). LiF (99.95%) was previously purified by the method of zone melting under a dynamic atmosphere of HF and SrF_2 used was a commercial material (99.99%). The Cr:LiSAF compound was obtained by melting components under HF flow, in vitreous carbon crucibles, with an initial concentration of 7 mol% of Chromium. Synthesis was performed with stoichiometric mixtures ($LiF:SrF_2:AlF_3$) and with compositions with excess of one of the components (AlF_3 and/or LiF) to compensate eventual evaporation losses. Zone melting experiments with 1–2 thermal cycles were accomplished using a zone speed rate of 4 mm/h.

The diffraction experiments were performed in a Rigaku Difractometer, model RINT-2000 using Cu-Kα radiation; Cr^{3+} concentration in the zone melted ingots was determined by X-ray fluorescence using a WD-XRF RIX 3000 Rigaku system.

3. Cr:LiSAF preparation

3.1. CrF$_3$ synthesis

The incorporation of the chromium dopant in the LiSAF host is usually lower than the melt concentration. However, several works have shown that the chromium concentration, in the solid phase, is constant along the growth axis [8,9], that is, the segregation coefficient is close to unit. A possible explanation considered by Klimm et al. [10] stated that partial hydrolysis of CrF_3 with

traces of moisture being present in the growth atmosphere and in the starting material was responsible for the reduced incorporation of Cr^{3+} within the crystals.

Chromium fluoride (CrF_3), as most of the fluoride materials, is sensitive to water and oxygen. As known from the literature, it is a very hygroscopic material and its reaction with water yields chromium-oxide [10,11]:

$$2CrF_3 + 3H_2O \rightarrow Cr_2O_3 + 6HF. \tag{1}$$
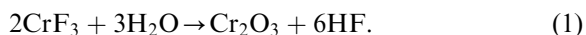
When heated in closed systems it melts close to 1100°C, but in open systems it begins to decompose at 600°C [12]. Wanklyn [13] mentioned that crystal growth from the melt of such material is not possible as decomposition occurs at 600°C following the equation:

$$3CrF_3 \rightarrow 2CrF_2 + CrF_5. \tag{2}$$

Santo et al. [8], studying the dehydration of $CrF_3 \cdot H_2O$ by thermal analysis, observed main dehydration at 192°C and simultaneous events from 300°C to 600°C (elimination of last water molecule, oxidation and decomposition). Oxidation is observed at onset temperature of 560°C during decomposition of CrF_3, and it may happen due to the reaction with one of the reaction products of Eq. [2].

Anhydrous CrF_3 can be obtained by HF reaction with $Cr°$, Cr_2O_3 and from dehydration of $CrF_3 \cdot H_2O$. Fergusson [14] suggested that the reaction of Cr (III) compounds with fluoride acid in anhydrous conditions and high temperatures results in CrF_3; however, the reaction of $Cr°$ with HF requires a prolonged treatment and the reaction rarely is complete. Metal chromium (powder, 2 μm) was heated in a stream of HF during 2 h, at 890°C, using a carbon crucible. In fact, the mass balance of the reaction and X-ray diffraction analysis showed only partial formation of CrF_3 in agreement with Fergusson's review.

The hidrofluorination by gaseous HF of Cr_2O_3 is an alternative method to CrF_3 synthesis [12]. Considering that the oxidation reaction (Eq. [1]) occurs between 400°C and 600°C, we heated Cr_2O_3 (99.997%) slowly from 300°C to 800°C in a HF flow. After 6 h we observed the formation of a bright-green product on the surface of the initial

material showing that reaction happened only on the surface. The process can be considered efficient only for very small amounts of material.

Anhydrous CrF_3 can also be obtained from $CrF_3 \cdot H_2O$ by dehydration under protective atmosphere. However, the process must be carefully carried out in order to prevent oxide and oxyfluorides contamination. In our first experiments dehydration of $CrF_3 \cdot H_2O$ was performed by slowly heating, under Argon flow, up to 400°C; after that the HF gas was introduced and the temperature was raised to 600°C and kept stable for several hours. We identify this synthesis process as *Procedure A*. The obtained material was a mixture of two different color phases: a bright-green and a dark-green one. X-ray diffraction showed the presence of Cr_2O_3 on dark-green phase.

Following Amiel [11], the oxidation reaction occurs in the range of 400–600°C and is reversible. The experiment of dehydration of $CrF_3 \cdot H_2O$ was repeated by heating the material under HF (slowly enough to prevent hydrolysis of chromium fluoride with water eliminated on the process) up to 750°C. In addition, this temperature was kept constant for several hours to convert possible oxides produced during dehydration reaction. This process was identified as *Procedure B*. The final material presented one single phase of bright-green color. X-ray diffraction of the dehydrated material showed only CrF_3 phase.

3.2. Synthesis and zone melting of Cr:LiSAF

In the first experiments Cr:LiSAF was synthesized in stoichiometric mixtures ($LiF:SrF_2:AlF_3$). The CrF_3 obtained by *Procedure A* was used as dopant. The initial compound mixture was previously treated under Ar flow to eliminate moisture contamination. A gas mixture of HF and Ar was then introduced and temperature was elevated up to the melting point. The ingots synthesized under such conditions showed always a dark-green region at the bottom of the crucible boat. Fig. 1 shows a lateral cut view of the synthesized ingot where the dark-green region can be clearly observed. The dark phase was identified by X-ray diffraction as a mixture of

Fig. 1. Polycrystalline Cr:LiSAF (*Procedure A*) showing the dark-green phase at the bottom of the ingot resulting from CrF_3 oxidation.
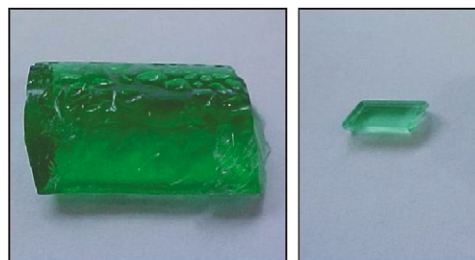

Fig. 2. Selected single crystalline part of the Cr:LiSAF ingot obtained by the zone melting process and one of the Brewster-cut slab for CW diode-pumped laser operation prepared from it.

Cr_2O_3 and CrF_3. This region was mechanically separated from the bright-green part of the ingot. A zone melting experiment was performed with the dark material placed at the end of the crucible boat. After two cycles we observed a larger segregation of the dark phase to the end of the boat. The initial part of the ingot showed crystalline Cr:LiSAF. The Cr concentration in these ingots was measured by X-ray fluorescence resulting at the initial part (crystalline region) equal to 4 mol% and at the end (dark region) 14 mol%, in

accord with Cr segregation, as oxide phase, to the end of the ingot.

In a new experience, Cr:LiSAF was synthesized using CrF_3 prepared by *Procedure B*. The compound was also previously treated under Ar flow to eliminate moisture contamination. However, HF + Ar gas mixture was introduced at the temperature where oxidation reaction starts ($400^\circ C$); the temperature was slowly raised to the melting point. The ingots synthesized under such conditions presented only a superficial dark region at the bottom of the crucible boat. Zone melting of this material confirmed the segregation of the chromium oxide phase, to the end of the ingot, without any previous mechanical selection of different phases. The measured Cr^{3+} concentration along the ingot remained approximately constant (6.5 mol%) except for the sample corresponding to the final part of the ingot where Cr concentration rises up to 8 mol%. This value can be explained by the presence of the Cr_2O_3 phase as pointed out by X-ray diffraction. The initial part of the ingot showed crystalline Cr:LiSAF. Fig. 2 shows in detail a selected crystalline part of the Cr:LiSAF zone melted ingot and one sample prepared from it.

4. Laser performance

Brewster-cut (for π polarization) slabs for CW diode-pumped laser operations were prepared from selected regions of the first zone melted ingots obtained. The final dimensions of those active media were $2 \times 3 \times 4.5 \, \text{mm}^3$ with 4 mol % of Cr^{3+} concentration. The laser operation was performed by using a standard X-fold astigmatic-compensated resonator, and the gain medium was positioned between two mirrors (M_1 and M_2) with radius of curvature 100 mm, as shown in Fig. 3. The mirrors M_3 and M_4 are plane. With the exception of mirror M_3, all the mirrors are highly reflective at the laser emission wavelength of 850 nm. The Cr:LiSAF crystal was pumped by two diode lasers (Coherent S-67-350C-50 T) s/n 13084 emitting at $\lambda = 672 \, \text{nm}$ and s/n 11279 emitting at $\lambda = 679 \, \text{nm}$. Due to the losses introduced by the diode beam shaping optics, the total pump power is 420 mW at the gain medium. We compared the laser performances of crystals grown by the zone melting method with a commercial, highly doped (6 mol%) Czochralski-grown Cr:Li-SAF crystal (VLOC) of dimensions $2 \times 2 \times 3 \, \text{mm}^3$ in order to evaluate the quality of the first as a laser medium. The temperature of the crystals was stabilized at $14^\circ C$ by a Peltier thermoelectric cooler. Fig. 4 shows the measurement of the output power for both cases as function of the output reflectivity. By fitting the experimental data with the expression for the output power from the oscillator model—$P_{OUT} = K(1 - R)[\Gamma/(L - \ln(R)) - 1]$—we determined the double-pass small-signal gain Γ, the cavity losses L, and $K = AI_s/2$, where A is the beam area at the active medium, I_s the emission saturation intensity and R is the output mirror reflectivity. For both crystals, all the experimental setup parameters such as the pump power, pump beam geometry and all mirror reflectivities were kept unchanged.

As can be seen from Fig. 4, the passive losses of the zone melting Cr:LiSAF laser (2.1%) are just slightly higher than those of the Czochralski
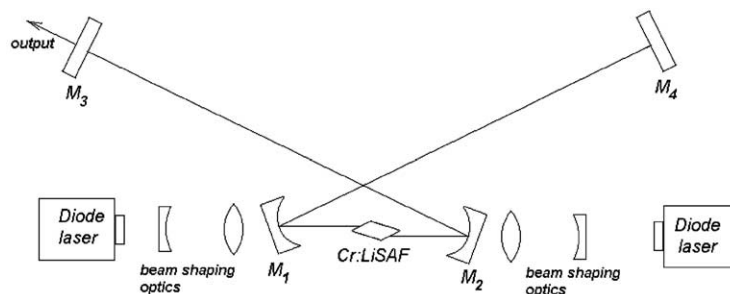

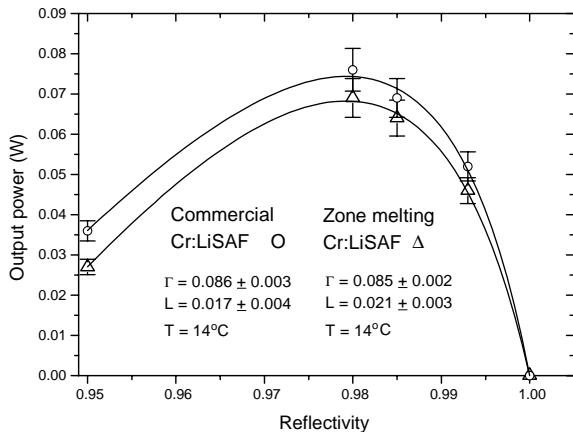Fig. 3. Diode-pumped Cr:LiSAF laser setup.

Fig. 4. Output power as a function of the output mirror reflectivity for the zone melting Cr:LiSAF laser (triangles) and for the commercial Czochralski laser (circles).
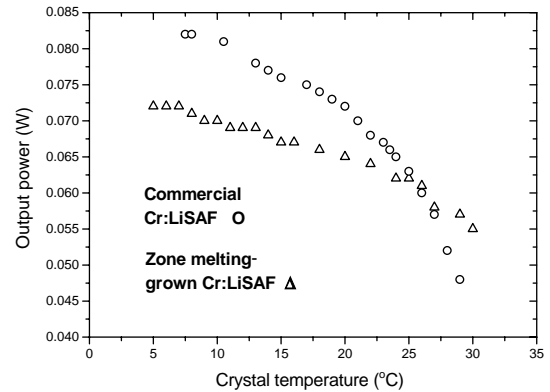

Fig. 5. Output power as a function of the gain medium temperature for the zone melting Cr:LiSAF laser (triangles) and for the commercial Czochralski laser (circles).

Cr:LiSAF laser (1.7%). Since the zone melting crystal is 50% longer than the Czochralski one, this result shows that the zone melting growth technique can provide laser crystals with high Cr^{3+} concentration and excellent optical quality, even for laser systems with typically very low gain, such as diode-pumped Cr:colquiriite lasers. The lower output power of the zone melting Cr:LiSAF laser can be mainly attributed to the lower Cr^{3+} concentration of the crystal. Experiments to compare the laser performances of highly doped crystals (6.5 mol%) grown by the zone melting method with the commercial Czochralski-grown Cr:LiSAF are in progress.

We measured the laser output power in function of the crystal temperature in order to investigate how the Cr^{3+} concentration affects the laser output power for different temperatures. For crystals with higher concentrations, more pump power is absorbed and therefore, more heat is generated inside the gain medium. It is well known that the upper-state lifetime of Cr:LiSAF and consequently the output power are severely reduced at higher temperatures [4,15]. The results for the Cr:LiSAF-zone melting and -Czochralski lasers are shown in Fig. 5. In fact, as the crystal temperature decreases, the output power of the Czochralski Cr:LiSAF laser becomes significantly higher than that of the zone melting Cr:LiSAF

laser, and this is clearly due to the higher Cr^{3+} concentration of the Czochralski crystal. However, CW laser operation on a long term with temperatures below 14°C is not recommended, since such temperatures may lead to water condensation on the laser crystal or on the thermoelectric cooler.

5. Conclusion

One of the main problems in the preparation of Cr-doped LiSAF crystals is the chromium oxidation during growth process. In this work, we showed that an attentive synthesis under HF atmosphere and purification and growth by zone melting eliminate the dark-green particles that usually affect the crystalline quality of such crystals. The CrF_3 oxidation is a reversible process and can be controlled by appropriate thermal treatment. Despite the size of the sample obtained by zone melting is limited relative to Czochralski boules, zone melting technique under HF flow can provide Cr:LiSAF crystals with high optical quality and excellent laser performance.

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