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# Crystal growth of $Cr^{3+}$:$LiCaAlF_6$ by Bridgman technique

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**Abstract**

In this paper, the crystal growth technique of the tunable laser material, $Cr^{3+}$:$LiCaAlF_6$, by the Bridgman method is discussed. High-quality single crystals with dimensions of up to 10 × 120 mm and 20 × 60 mm have been grown. Flashlamp-pumped operation of a Cr:LiCAF laser rod [illegible] provided an electrical slope efficiency of 1.07%.

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## 1. Introduction

In recent years several varieties of tunable solid-state laser crystals have developed rapidly, with practical applications in defence, medical and environmental science. The most promising crystals are Ti:sapphire, alexandrite, Cr:LiSAF, Cr:LiCAF, Co:$MgF_2$ and forsterite. Their tuning ranges are listed in Table 1.

As a tunable laser material, Cr-doped colquiriite ($Cr^{3+}$:$LiCaAlF_6$ → Cr:LiCAF) was discovered at the Lawrence Livermore National Laboratory (LLNL) [1]. It has a wide tunable range, long lifetime, wide wavelength of absorption, and a high quantum efficiency. It can be doped to very high levels without luminescence quenching and is suitable for being pumped by laser diode or flashlamp. It also has good thermal and mechanical properties. All these excellent properties [2] make Cr:LiCAF a very promising tunable laser crystal with commercial potential.

The first crystals were grown at LLNL [3] by horizontal zone melting from purified binary component fluorides. Kway et al. reported [4] that better quality is attainable by Czochralski growth of the congruently melting composition. Large crystals have also been grown by the gradient freeze method [5]. Bolt and Uhrin reported [6] top-seeded solution growth in an HF atmosphere. In this paper, we report our investigations on the crystal growth by the Bridgman method.

Table 1
Tunable wavelength covered for tunable solid-state laser

| Crystals | Tuning range (nm) |
|---|---|
| Alexandrite | [illegible] |
| Co:$MgF_2$ | 1550–2500 |
| Cr:LiCAF | 720–840 |
| Cr:LiSAF | 760–1010 |
| Forsterite | 1167–1345 |
| Ti:sapphire | 670–1100 |

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## 2. Experimental procedure

### 2.1. Furnace construction

In order to obtain the optimum growth conditions, we designed a multi-zone vertical Bridgman furnace (see Fig. 1). The furnace consisted of six independent segments. Three heater zones are controlled independently by Shimaden FP21 programmable controllers. Pt/Pt–Rh thermocouples are used for the control and measurement of temperature. The temperature profile can be adjusted readily and the small size of furnace permits more rapid attainment. A temperature profile found beneficial to crystal growth is shown in Fig. 2.

The crucible materials we use are graphite or platinum. The ampoule shape is shown in Fig. 1 and the narrow part is for a seed crystal.

### 2.2. Crystal growth

We used hydrofluorination [7] to get rid of hydrated and adhesive water from the binary fluorides, especially $AlF_3$ and $CaF_2$.

LiCAF is a trigonal crystal ($P\bar{3}1c$). The emission cross section for the electric field polarized parallel to the *c*-axis is about 50% larger than for perpendicular polarization in Cr:LiCAF [3], and it was found to exhibit fast growth in the direction perpendicular to the *c*-axis [7]. For these reasons, seed crystals of [10$\bar{1}$0] orientation were normally chosen. Seeding was gauged by standard thermocouples located outside the ampoule.

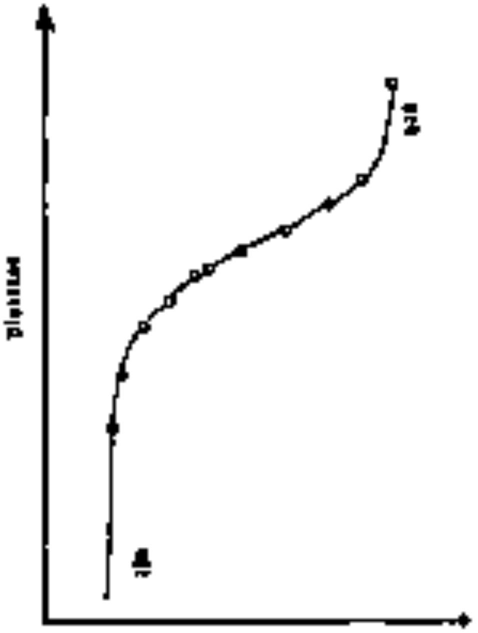

Fig. 2. Temperature profile.

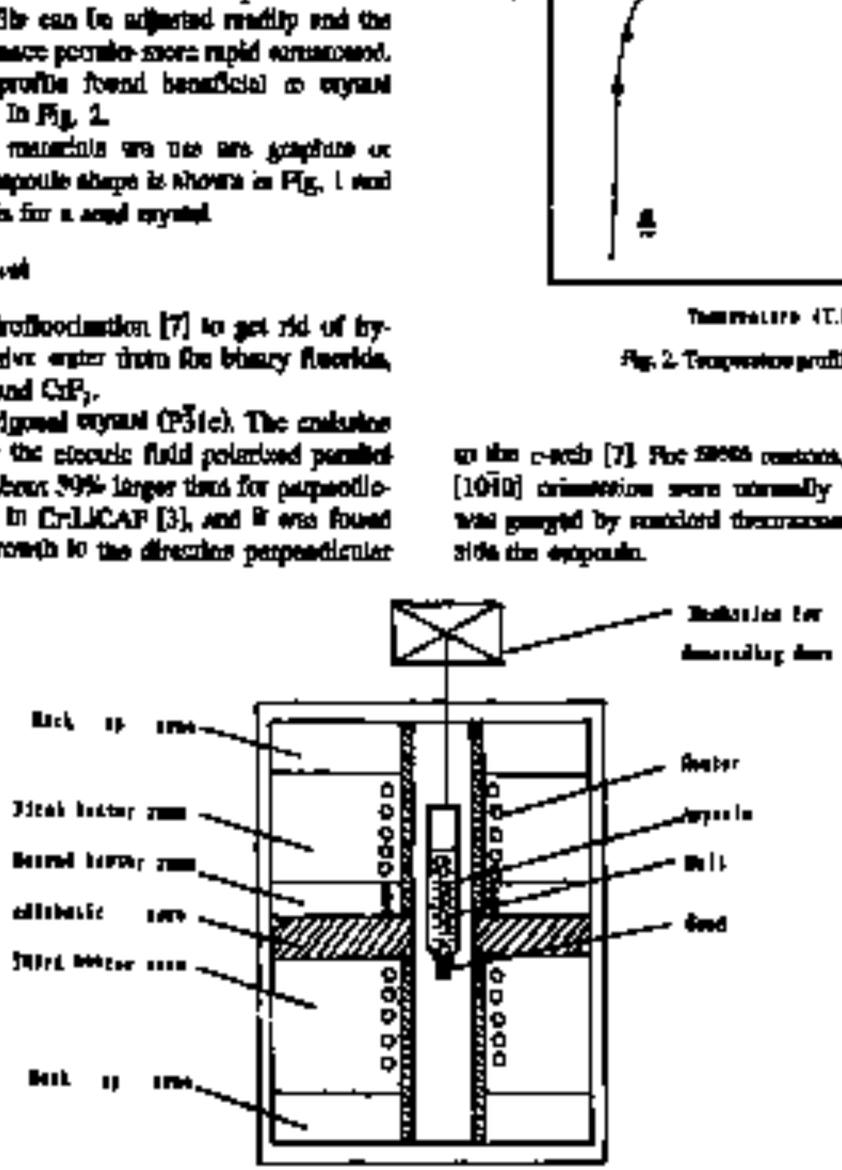

Fig. 1. Schematic diagram of the Bridgman furnace for growth of Cr:LiCAF.

Fig. 3. Crystals grown by the Bridgman method.

Cr:LiCAF crystals have been grown in axial temperature gradients between 10 and 40°C/cm, and at rates between 1 and 3 mm/h. The lower growth rates correspond to the smaller temperature gradients. The melt/crystal junction is set up at the zone with the largest gradient. The melt/crystal interface shape is controlled to be slightly convex, which aids the escape of bubbles and the exclusion of impurities.

To exclude water and oxygen in the growth environment, two methods have been used. We placed a platinum liner tube in the furnace through which a $N_2$–HF gas flowed during the growth and cooling of the crystals. The alternative is to seal the ampoule.

### 2.3. *Flashlamp-pumping experimental arrangement*

The laser rod used in this work was grown by the Bridgman method with a $Cr^{3+}$ doping of 3 mol%. The boule was ground into a 6 mm diameter × 53 mm laser rod along the c-axis. The end faces were polished to λ/10 flatness and not antireflectively coated. The laser rod was mounted in an elliptical pump chamber through which cooling deionized water was circulated, and excited with two 76 mm long, 6 mm bore xenon flashlamps. In this work the pump pulse duration was 200 μs and the capacitor was 100 μF. The stable optical resonator was 40 cm long and consisted of a flat output mirror and a high-reflectivity concave mirror with a 5 m radius of curvature.

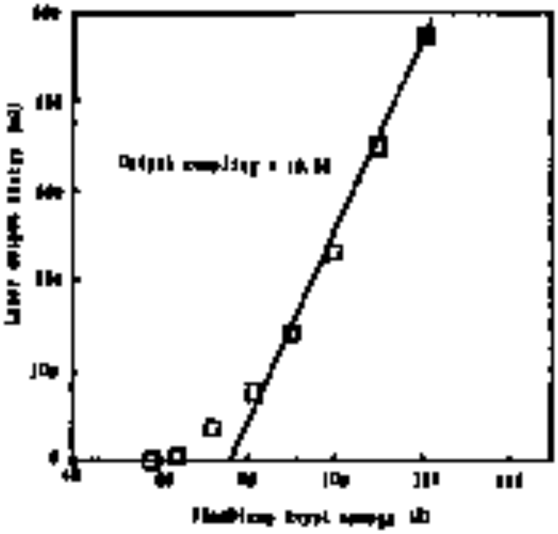

Fig. 4. Flashlamp-pumped performance data for Cr:LiCAF.

## 3. Results and discussion

Some of our crystal boules are shown in Fig. 3. The crystals are glittering and transparent, and their color changes from light green into bluish green when $Cr^{3+}$ doping density increases. Up to 10 mm diameter × 120 mm and 20 mm diameter × 80 mm intact, high-quality crystals have been grown without macroscopic defects.

During our growth runs, there was sometimes an opaque zone at the crystal end, especially the first growth from raw materials. Composition and impurities were analysed by chemical analysis and X-ray photoelectron spectroscopy [8]. The results showed that the composition of the opaque zone had deviated

Table 2
Semi-quantitative spectral analysis (wt%)

| | K | Fe | Ti | Pb | Ga | Mg | Mn |
|---|---|---|---|---|---|---|---|
| Crystal | 0.003 | < 0.01 | | < 0.01 | | < 0.001 | 0.001 |
| Opaque | 0.005 | 0.1 | < 0.001 | ~ 0.01 | 0.001 | 0.001 | ≤ 0.1 |

Table 3
Comparison of flashlamp-pumped results between LLNL and BJRC

| Lab | Laser rod | | | | Chamber | Output coupling | Slope efficiency |
|---|---|---|---|---|---|---|---|
| | Size | End | $C_{Cr}$ (mol%) | Growth | | | |
| LLNL | 6.35 × 89 | Coated | 1.5 | CZ | Coated | 18.6% | 1.64% |
| BJRC | 6.00 × 59 | Chamfered | 3 | BG | Uncoated | 16.3% | 1.07% |

from the formula $LiCaAl_{(1-x)}Cr_xF_6$. Table 2 shows the results of semi-quantitative spectral analysis of the crystal matrix and the opaque layer. It was found that the impurity content of the opaque zone was higher than that of the crystal itself.

The impurity content of the crystal, given in Table 2, is very low and shows that the melt has a powerful ability to exclude impurities. To obtain high crystal quality, crystals were first fast-grown from the stoichiometric starting melt composition by zone melting, then grown without the opaque end by the Bridgman method.

The data obtained for Cr:LiCAF flashlamp pumping is shown in Fig. 4. The output coupling utilized is 16.3%. Output energy of 472 mJ was obtained against the electrical input energy of 121 J. Slope efficiency of 1.07% and a tuning range of 722–836 nm have been obtained.

The aim of this work is primarily to establish the potential performance level of Cr:LiCAF. A better result may be attained by coating the laser rod and the pump chamber, changing the output coupling, decreasing the scattering loss of crystal, utilizing a standard-length rod and optimizing the pump conditions. This work is in progress.

## 4. Conclusions

We have compared the flashlamp-pumped performance reported by LLNL in 1990 with our results, which are shown in Table 3. From this comparison it can be concluded that large size and high-quality Cr:LiCAF laser rods can be grown by the Bridgman method.

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