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# Influence of neutral environment in the growth of Cr-doped LiCAF/LiSAF crystals: X-ray powder diffraction and EPR analysis

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## Abstract

Cr-doped LiCaAlF<sub>6</sub> (LiCAF) and LiSrAlF<sub>6</sub> (LiSAF) were synthesized and single crystals were grown under an Ar atmosphere. The composition of the synthesis, the melt residues and the crystals grown were analysed by X-ray powder diffraction. Ar flow influence in the growth was studied in order to improve crystals quality and growing efficiency. Electron paramagnetic resonance (EPR) measurements were carried out to investigate the incorporation of Cr into the LiSrAlF<sub>6</sub> matrix, as well as to propose a model for the Cr defect produced. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The laser materials Cr:LiSrAlF<sub>6</sub> and Cr:LiCaAlF<sub>6</sub> (Cr:LiSAF and Cr:LiCAF) exhibit a combination of laser and optical properties which make them unique among advanced solid-state laser materials. Lasing in Cr:LiSAF was first reported by Payne et al. [1] in 1989 using Kr-ion laser pumping. Since then several researchers and a growing number of laser companies have exploited the features of these colquiriites materials to produce new types of lasers.

LiCAF was first obtained by Viebahn, who also resolved the crystalline structure [2]. Both laser

materials can be pumped by diode laser and conventional flashlamps [3].

There arise some problems during the growth of colquiriite crystals. As it has been found before [4], fluctuations of mass signal because of the creeping melt on crucible walls leads to fluctuations at the diameter control system. Moreover, additional problems not reported before, such as those related to growth duration, should be taken into account.

The hydrolysis of the fluorides at high temperature [4] forces to maintain a neutral atmosphere during colquiriite synthesis and single crystal growth. Since then several different atmospheres have been used. So, Klimm et al. [4] try to avoid this hydrolysis rising in the growth chamber with 5N nitrogen. Shimamura's group started their experiments with an Ar atmosphere preceded by a

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vacuum process [5], but later they used a  $\text{CF}_4$  atmosphere [6].

On the other hand, the incorporation of Cr in the colquiriite matrix has been supposed until now as  $\text{Cr}^{3+}$  in the  $\text{Al}^{3+}$  sites. Rupp et al. [7] proposed this model of the Cr defect based on EXAFS studies. In order to confirm the valence state of Cr as well as its location in the matrix, the EPR technique should be very helpful.

The main research objective of these investigations is to find a easier way of growing LiSAF/LiCAF, avoiding the use of corrosive gases to ensure a neutral atmosphere in the growth chamber.

In this work, we present the results and conclusions of X-ray powder diffraction and EPR investigations on Cr:LiCAF, LiSAF single crystals grown under Ar flow by the Czochralski (CZ) technique. A new neutral atmosphere device is proposed to improve single crystals quality. The influence of neutral environment in the grown crystal composition and in the crystal growth is analysed. The stoichiometry of the starting materials, the experience duration, the purity of the inert flow used and the dopant concentration have been taken into account.

## 2. Experimental procedure

During our investigations three series of growths were carried out. The first one was focused on the growth of pure and Cr-doped LiCAF, the second one introduced the growth of different Cr concentrations (2.5; 5 and 10 at%) for Cr:LiSAF single crystals, and the last one was devoted to the growth of 10 at% Cr-doped LiSAF single crystals with one or two Ar entrances.

LiCAF and LiSAF single crystals were prepared from mixtures of the constituents LiF,  $\text{CaF}_2$  (or  $\text{SrF}_2$  respectively),  $\text{AlF}_3$  and  $\text{CrF}_3$  with purity always  $> 99.99\%$ . The first procedure consists of the syntherization of the colquiriite. This is necessary since pulling the crystal from a stoichiometric melt of the initial fluorides does not produce the complete reaction of the fluorides before the single crystal is grown. All syntheses were carried out in a tubular SiC furnace at  $950^\circ\text{C}$ .

The mixture was kept in a closed Pt container at 2 atm of controlled Ar atmosphere.

The Czochralski (CZ) method with resistance heating and automated diameter control by crystal weighting was used to grow single crystals. A rotation frequency of 10–20 rpm and a pulling rate of 0.33 mm/h were employed.

A special device was performed in order to allow the free and continuous flow of Argon in the growth chamber. Fig. 1 depicts the growing mechanism with two Ar entries, one near the melt and the other at the bottom of the resistance.

X-ray powder diffraction (XRPD) data were collected on a SIEMENS D5000 Diffractometer using  $\text{Cu K}_\alpha$  radiation and a Ni filter, with a step interval of  $0.02^\circ$  in the  $2\theta$  region from  $15^\circ$  to  $90^\circ$  or  $120^\circ$ . The analysed materials were initial fluorides mixtures, synthesized materials, pulverized single crystals, melt residues and evaporated products.

EPR spectra of Cr: LiSAF samples, with Cr concentration of 10 at%, were obtained by means of a BRUKER ESP 300E spectrometer working in the X band.

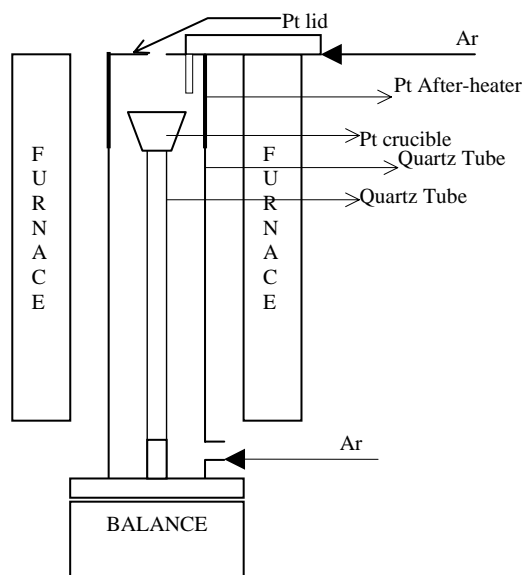


Fig. 1. Schematic view of the experimental device with two Ar entrances: Two quartz tubes, with an upper and a lower Ar entrances are adjusted on a CZ crystal growth system with diameter control. A Pt crucible, after heater, seeding bar and Ar entrances are used to avoid the chemical attack by the fluorides.

### 3. Results and discussion

At LiCAF and LiSAF melting points (800°C and 760°C, respectively) LiF, AlF<sub>3</sub> and CrF<sub>3</sub> get volatile [8]. The evaporation losses of these compounds produce changes in melt stoichiometry and also have an influence in colquiriite synthesis. Fig. 2 shows X-ray diffraction patterns of both the syntheses of a stoichiometric fluoride mixture and a mixture with an excess (10%) of LiF and AlF<sub>3</sub>. In the second experiment, new LiCAF peaks appear, while some CaF<sub>2</sub> and AlF<sub>3</sub> diffraction peaks have disappeared. Therefore, the addition of this excess improves synthesis efficiency. It also produces an improvement in melt stoichiometry during crystal growth. In Fig. 3, the X-ray diffractions patterns from melt residues of the experiments in Fig. 2 are compared. There are less CaF<sub>2</sub> peaks in the case with an excess of fluorides, which indicates the best melt composition.

The CrF<sub>3</sub> concentration in the charges does not modify synthesis conditions, growth conditions or crystal quality in the range under study.

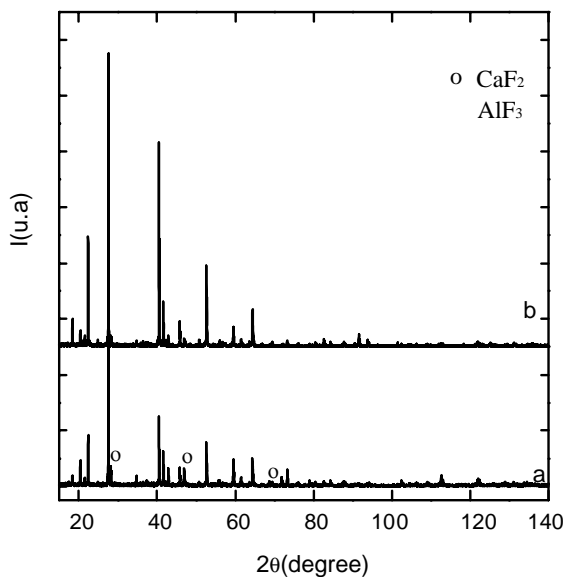


Fig. 2. X-ray powder diffraction patterns of two LiCAF syntheses obtained from different starting mixtures: (a) a stoichiometric fluoride mixture and (b) a mixture with an excess of 10% LiF and 10% AlF<sub>3</sub>. The peaks without signal are LiCAF peaks.

Regarding the growth duration, there is a new problem due to colquiriite decomposition. Fig. 4 shows the XRPD pattern of an LiCAF melt maintained at melting point for five days. Traces

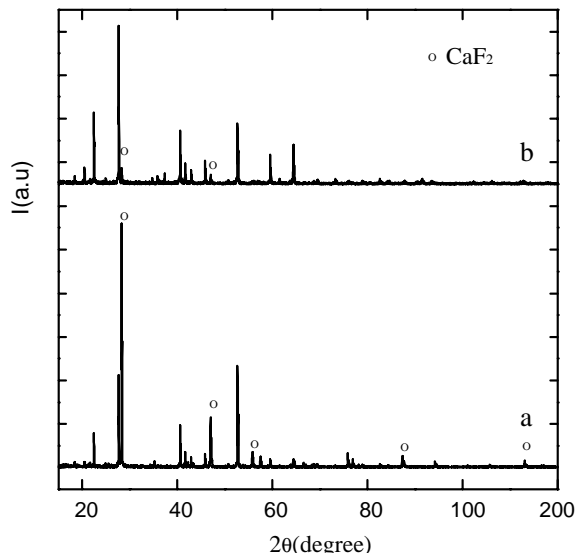


Fig. 3. X-ray powder diffraction patterns of melt residues of two LiCAF growths corresponding to the cases of Fig. 2: (a) a stoichiometric synthesis and (b) a mixture with a 10% excess of LiF and AlF<sub>3</sub>.

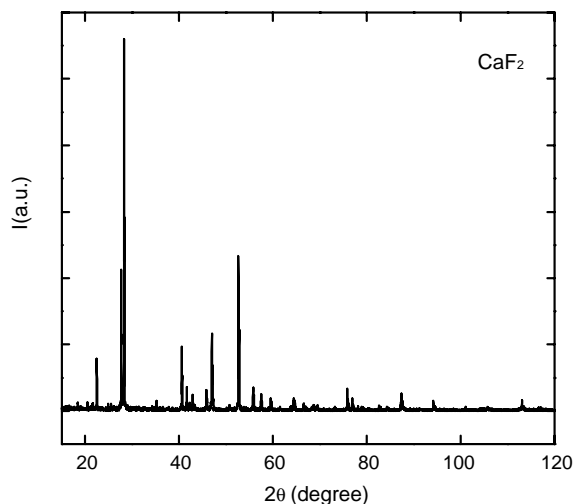


Fig. 4. X-ray powder diffraction patterns of melt residues maintained during 5 days at LiCAF melt point.

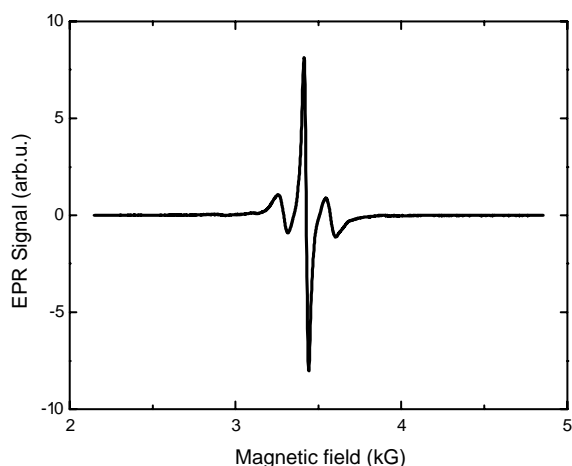


Fig. 5. EPR spectrum of Cr-doped LiSAF single crystals measured at room temperature.

of  $\text{CaF}_2$  appeared, which show that maintaining the melt at this temperature can result in the disappearance of LiCAF in XRPD analysis.

The use of only one Ar entrance at the bottom of the growth chamber did not ensure the neutral atmosphere in all growths, leading to some white polycrystalline crystals. The incorporation of the upper Ar entrance did not disturb the growth conditions or melt stability. At the same temperature, pulling and rotating conditions, there was an improvement in the number of successful growths as well as in the single crystals' quality.

EPR spectra of Cr:LiSAF samples have been recorded at room temperature. Fig. 5 shows a typical spectrum for an arbitrary orientation of the magnetic field with respect to the crystal axes. It should be pointed out that the lines in the spectra do not appreciably change their resonance positions as the magnetic field orientation is changed in various planes of the crystal. The intense peak in Fig. 5 has an isotropic  $g$  value of  $1.970 \pm 0.002$ , which is typical of  $\text{Cr}^{3+}$  in different matrices [9]. Moreover, the fact that the spectra are observed at room temperature indicates that they are due to  $\text{Cr}^{3+}$  ions in octahedral coordination. Therefore, we ascribe the intense peak in Fig. 5 to the  $|\frac{1}{2}\rangle \rightarrow |-\frac{1}{2}\rangle$  allowed transition of this ion (electronic spin  $S = \frac{1}{2}$ ), whereas the smaller and symmetrically

arranged peaks can be understood as the  $|\pm\frac{3}{2}\rangle \rightarrow |\pm\frac{1}{2}\rangle$  allowed transitions. The isotropic  $g$  value and the close line position for the three transitions indicate that  $\text{Cr}^{3+}$  is located at a site of high symmetry in the LiSAF matrix. Taking into account the degree of distortion of the fluorine octahedra around the cationic sites [7], we exclude the  $\text{Li}^+$  site as that occupied by  $\text{Cr}^{3+}$ , since it is the most distorted one. Moreover, attending to charge difference and ionic radii agreement, we can conclude that  $\text{Cr}^{3+}$  ions substitute for  $\text{Al}^{3+}$ . It must be noted that an analogous conclusion was reached by Rupp et al. [7] for Cr:LiCAF crystals studied by means of the EXAFS technique.

#### 4. Conclusions

A 10% excess of LiF and  $\text{AlF}_3$  in the initial mixture preserves the stoichiometry of the melt and, consequently, single crystals' quality is improved. Moreover, this does not perturb dopant incorporation into single crystals.

The addition of two Ar focuses increases neutrality of growth atmosphere without modifying the growth conditions and increasing its efficiency.

The EPR study confirms the incorporation of Cr in the LiSAF matrix as  $\text{Cr}^{3+}$  ions substituting for  $\text{Al}^{3+}$ , in agreement with other works for LiCAF.

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