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LiCaAlF$_6$ and LiSrAlF$_6$: tunable solid state laser host materials

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Abstract

Tunable all-solid-state lasers find more and more applications in different fields. Chromium-doped ternary colquiriites, LiCaAlF$_6$ (LiCAF) and LiSrAlF$_6$ (LiSAF), show a tunable laser activity in the region of 720–840 nm and 780–1010 nm, respectively. Other interesting properties enable them to be used as scintillators and window materials. Single crystals of LiCAF and LiSAF have been grown by various methods, including the Czochralski, Bridgeman, zone melting and top-seeded solution growth techniques. Vertical gradient freezing (VGF) is proposed for producing high optical quality crystals.
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1. Introduction

Due to a certain range of emission wavelengths, tunable solid-state lasers have opened a wide field for scientific and real-world applications: In medicine and life science, fiber optic catheters allow in situ and on-site diagnostic investigations [1]. In telecommunication, tunable lasers are used to characterize the transmission,

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reflection and further optical characteristics of networks [2]. Furthermore, remote sensing and environmental monitoring with the LIDAR-technology [3] is a promising field of application [4].

First tunable lasers were systems using organic dye molecules in solutions [5]. Although these lasers are still operated today, this technology is e.g. not suited to build up small-sized integrated optical systems. One of the first tunable solid-state gain media was the alexandrite host ($BeAl_2O_4$) doped by Cr^{3+}, providing an emission range of 701–818 nm [6]. However, today's most frequently applied tunable solid-state laser is Ti-sapphire (α-Al_2O_3) offering emission between 670 and 1100 nm, where the maximum intensity is obtained at about 800 nm. In Ti^{3+} the wide bands are due to a vibronical broadening of the $^2T_2 \rightarrow {}^2E$ absorption [7]. Although a Ti-sapphire system shows many advantages, pumping with e.g. flash lamps is not efficient because of a relatively short lifetime of $\sim$3 μs of the upper laser level. Therefore, pumping is commonly performed by a frequency doubled Nd:YAG (Nd^{3+}:$Al_3Y_5O_{12}$) laser. Again, in this configuration systems become rather large and are not preferably suited for integration.

A laser media family which gives a similar tuning range as Ti-sapphire including the possibility for diode pumping are Cr^{3+}-doped ternary colquiriites, e.g. $LiCaAlF_6$ (LiCAF) and $LiSrAlF_6$ (LiSAF) [8,9]. Colquiriite is derived from the name of a tin deposit in Bolivia, where such a mineral was found originally [10].

Along this short review we report on basics and on progress in the crystal growth of LiCAF and LiSAF. Ongoing research in this field is performed in our laboratory.

2. Crystal structure and synthesis of LiCAF and LiSAF

$LiCaAlF_6$ and $LiSrAlF_6$ are isomorphous and crystallize in a trigonale structure with the space group $P\bar{3}1c$ ($\bar{3}m$). This structure is found a member of ternary fluorides of the $LiM(II)M(III)F_6$ type [11,12]. Here (Fig. 1), $[Ca(Sr)F_6]^{4-}$ groups are isolated but connected via the corners of $[LiF_6]^{5-}$ or $[AlF_6]^{3-}$ octahedrons. $[LiF_6]^{5-}$ and $[AlF_6]^{3-}$ units are connected via edges. Because of a similar ionic radius (CN: 6), Cr^{3+} can replace the Al^{3+} site [13]. Crystals of the composition $LiSr_xCa_{1-x}AlF_6$ were also reported [14].

Given the point group $\bar{3}m$, LiCAF and LiSAF are optically uniaxial crystals. A major problem for the growth of bulk crystals is the anisotropic thermal expansion coefficient: Both materials show a higher thermal expansion in the lateral than in the axial direction (Table 1). In the case of LiSAF the axial value is even negative. This leads to the conclusion that growing LiSAF in crucibles by e.g. the vertical gradient freezing (VGF) method is preferably done along the *c* direction.

The ternary phase diagram LiF–CaF$_2$–AlF$_3$ is not yet sufficiently investigated, also it is not clear, whether LiCAF is melting congruently or not. Incongruent melting was reported assuming a deficiency of CaF_2 [25]. Contrary, LiSAF showed congruent melting. However, there are other reports claiming that both, LiSAF and LiCAF are congruently melting [22], even though there are some remaining questions [26].
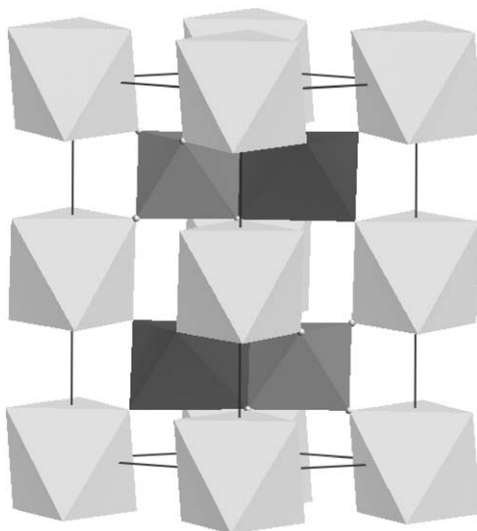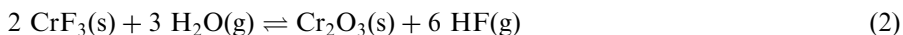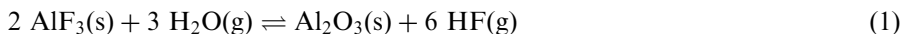
Fig. 1. Crystal structure of LiCAF showing the $[CaF_6]^{4-}$ (gray), $[LiF_6]^{5-}$ (white) and $[AlF_6]^{3-}$ (black) octahedrons [11].

In Fig. 2, a reconstructed phase diagram is shown, taking into account known experimental work on different sub-systems. Besides LiCa(Sr)AlF$_6$, there are two known compounds in the CaF$_2$–AlF$_3$ system, CaAlF$_5$ and Ca$_2$AlF$_5$ [27] and one (Li$_3$AlF$_6$) in the LiF–AlF$_3$ system [28]. LiAlF$_4$ is reported to by only existent in the gas phase [29]. The ternary system LiF–Li$_3$AlF$_6$–CaF$_2$ was investigated experimentally [30–32] and as well as by theoretical means [33].

The commonly used starting materials for growing LiCAF and LiSAF show an affinity towards water, especially AlF$_3$. The most frequent doping material CrF$_3$ is similarly air and moisture sensitive. On heating only a part of the moisture evaporates and remaining water can lead to hydrolysis:

$$2\ AlF_3(s) + 3\ H_2O(g) \rightleftharpoons Al_2O_3(s) + 6\ HF(g) \tag{1}$$

$$2\ CrF_3(s) + 3\ H_2O(g) \rightleftharpoons Cr_2O_3(s) + 6\ HF(g) \tag{2}$$

For the temperature range of crystal growth (800 °C) it was shown [24], that for atmospheric conditions the hydrolysis of CrF$_3$ is nearly complete. The resulting oxyfluoride inclusions lead to scattering centers, which are not compatible with optical use.

Usually precursors are purified via sublimation or hot hydrofluorination. In our laboratory we have developed a combined procedure towards high purity starting materials: In a first step the materials are synthesized in an aqueous medium, using a so-called wet-chemical approach. Afterwards the dried products are treated with gaseous HF at 600 °C.

This was approved first for the preparation of LiYF$_4$ [34] and is now being applied for LiCAF and LiSAF by a two step reaction, starting from chlorides, using NH$_4$F

Table 1
Properties of LiSAF and LiCAF

	LiCAF	LiSAF	Refs.
Laser characteristics			
Tuning range (nm)			
Cr^{3+}	720–840	780–1010	[15,16]
Ce^{3+}	280–316	280–316	[17]
Peak lasing wavelength (nm)			
Cr^{3+}	780	825	[15,16]
Ce^{3+}	290	290	[17]
Pump wavelength (nm)			
Cr^{3+}	670		[16]
Ce^{3+}	266 (4ω–Nd:YAG)		[18]
Exited state lifetime (µs) (300 K)			
Cr^{3+}	170	67	[19,20]
Crystallographic and physical data			
Space group lattice constants	$P\bar{3}1c$	$P\bar{3}1c$	[11,12]
a (Å)	4.996	5.071	[11,12]
c (Å)	9.636	10.189	[11,12]
Density (g/cm^3)	2.983	3.45	[21]
Melting point (K)	1083	1063	[22]
Thermal conductivity			
κ_{11} (WK^{-1}m^{-1})	4.58	—	[23]
κ_{22} (WK^{-1}m^{-1})	5.14	3.09	[23]
Thermal expansion			
α_{11} (10^{-6} K^{-1})	22.0	18.8	[24]
α_{33} (10^{-6} K^{-1})	3.6	−10	[24]
Fracture toughness			
K_{IC} (M Pa m)	0.18–0.37	0.40	[23]
Refraction indices			
ε	1.3852	1.384	[21]
ω	1.3882	1.380	[21]

as fluoride source:

$$3\ LiCl(aq) + AlCl_3(aq) + 6\ NH_4F(aq) \rightarrow Li_3AlF_6(s) + 6\ NH_4Cl(aq) \qquad (3)$$
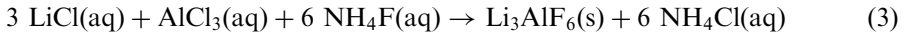
In a second step, LiAlF$_6$ is suspended in an aqueous solution of MCl$_2$ (M = Ca,Sr) and heated in an ultrasonic bath.

$$Li_3AlF_6(s) + MCl_2(aq) \rightarrow LiMAlF_6(s) + LiCl(aq) \quad M = Ca, Sr \qquad (4)$$
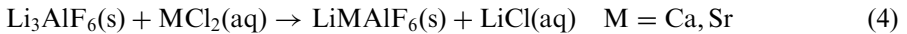
A setup as shown in Fig. 3 is suitable for a hot hydrofluorination. As a source for the hydrogenfluoride, KHF$_2$ is heated to lose HF(g) [35]. To avoid a shift of the melting temperature as the fraction of KF increases, an excess of KF is added, making the vapor pressure only a function of the temperature. The HF is carried from the auxiliary furnace by a nitrogen stream into the horizontal main reaction furnace, where it passes over the charge placed in vitreous carbon boats. The water, which is contained in the initial charge, evaporates upon heating and the hydrogen
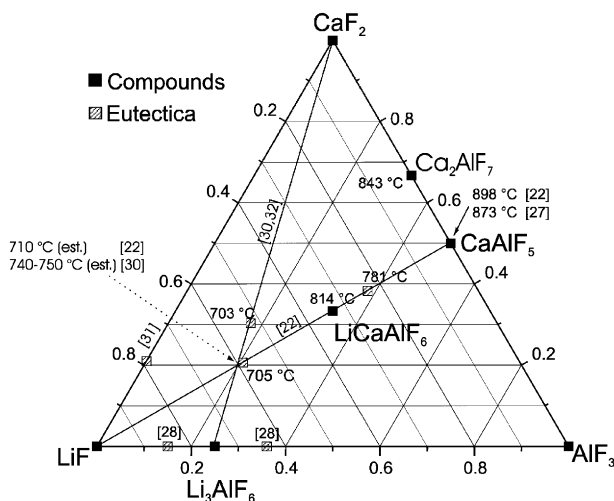
Fig. 2. Phase diagram of the ternary system $LiF–AlF_3–CaF_2$, constructed from cited work.
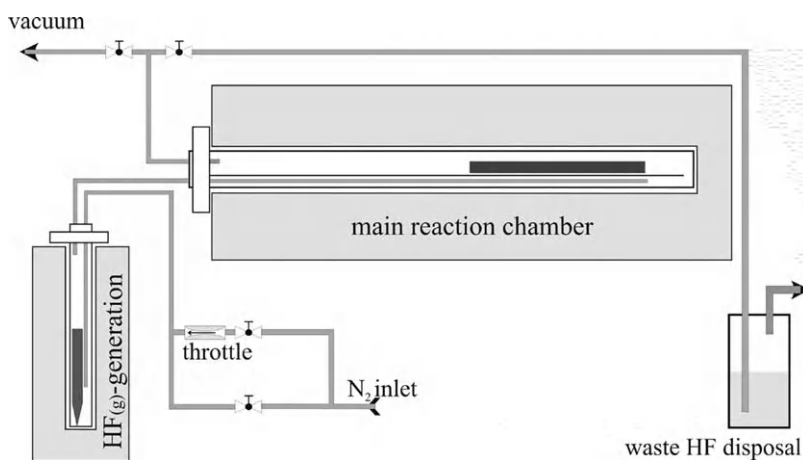

Fig. 3. Setup for the hot hydrofluorination. In the small vertical furnace HF is produced, whereas the reactions are performed in the horizontal main furnace [34].

fluoride converts the residual anionic impurities into fluorides. The leaving gas is carried through an aqueous solution of NaOH to remove remaining hydroflouride.

3. Crystal growth of LiCAF and LiSAF

In recent years, many attempts were made to obtain optical quality crystals of LiCAF and LiSAF. Preferably, the Czochralski pulling technique [23–24,36,39] was applied. Other efforts have used the Bridgman [40], the zone melting [41] or the top-

seeded solution growth method [42]. An overview on the conditions of growth by different approaches is given in Table 2.

Crystals with a diameter up to 18 mm have been grown quite easily by Czochalski pulling. Higher diameters were more difficult to obtain, because the already mentioned thermal expansion anisotropy, as this effect may lead to a cracking of crystals [24]. Nevertheless, crystals up to a diameter of 3 in have been already achieved, this by carefully controlling the pulling rate, rotation and by application of a slow rate of cooling down to room temperature. In the Czochralski growth the quality of the crystals was found to depend on diameter fluctuations. Therefore, considerable efforts had to be spent to control the diameter by means of a weight feedback system [43,44].

In this respect, the use of the *vertical gradient freeze technique* (VGF) would allow a more simple approach for the growth of LiSAF and LiCAF:

Here, starting materials are melted in a vertical (for example glassy carbon) and closed crucible. After a couple of hours set to homogenize the melt, the temperature is reduced slowly by less than $1 \, \text{K/h}$. Due to the temperature slope in the oven the melt starts to crystallize at the bottom of the crucible, where a seed may be placed. The growth front is moving upwards as the melt is slowly being cooled down.

A main concern for successfully growing crystals by the VGF method is to achieve a constant lowering of the temperature without major fluctuations. For this, a setup may use a controller, allowing the input of two thermocouples: One to control the temperature of the heating element, a second for observing the temperature below

Table 2
Overview on recent work in crystal growth of LiSAF and LiCAF

	Method	Diameter/size (mm)	Dopant/concentration	Atmosphere	Refs.
LiSAF	Czochralski	18	Ce^{3+}	CF_4	[36]
		18			[24]
		15	Ce^{3+}		
			2 mol%		[39]
		30			[23]
	Zone melting		Cr^{3+}		
			4–6.5 mol%		[41]
LICAF	Czochalski	76	—	CF_4	[37]
		18		CF_4	[36]
		20			[38]
		15	Ce^{3+}		
			2 mol%		[39]
		18		N_2	[24]
		30		N_2	[23]
	Top-seeded solution growth	18	Cr^{3+}	HF	[42]
	Bridgeman	10*120			
		20*80	Cr^{3+}		[40]

the crucible. To achieve a high temperature stability, a cascade control loop can be installed. In our setup, the secondary control loop could reduce fluctuations down to about 0.1 K (Fig. 4.)

Bulk crystals of pure $LiYF_4$ and doped (Er^{3+}, Nd^{3+}) were grown successfully by the VGF approach [34], as described here.

The VGF technique combined with a wet chemical synthesis of starting materials is now being adopted to the growth of bulk LiSAF and LiCAF crystals. Preliminary results show that optical quality crystals can be obtained. Samples of the first attempts were grown upon spontaneous nucleation and showed cracks. However, these crystals are now being used to prepare seeds for further growth.

4. Some details on LiCAF and LiSAF lasers and other optical applications

At the end of the 1980s, Payne et al. first examined the laser performance of chromium doped LiCAF [15] und LiSAF [45]. Trivalent chromium is a long known activator ion, as lasing was realized first for $Cr^{3+}:Al_2O_3$ [46] (ruby laser). In the colquiriites the laser oscillation is based (similar to alexandrite) on the vibronically broadened $^4T_2 \rightarrow ^4A_2$ transition [47]. In case of LiCAF the peak lasing wavelength is at 780 nm with a tuning range from 720 to 840 nm [15]. LiSAF has an even wider tuning range, covering 780–1010 nm. Here, the peak lasing wavelength is at 825 nm [16]. A broad absorption band around 670 nm allows pumping by laser diodes. Although the first results on laser activity were achieved with Kr laser pumping [16],
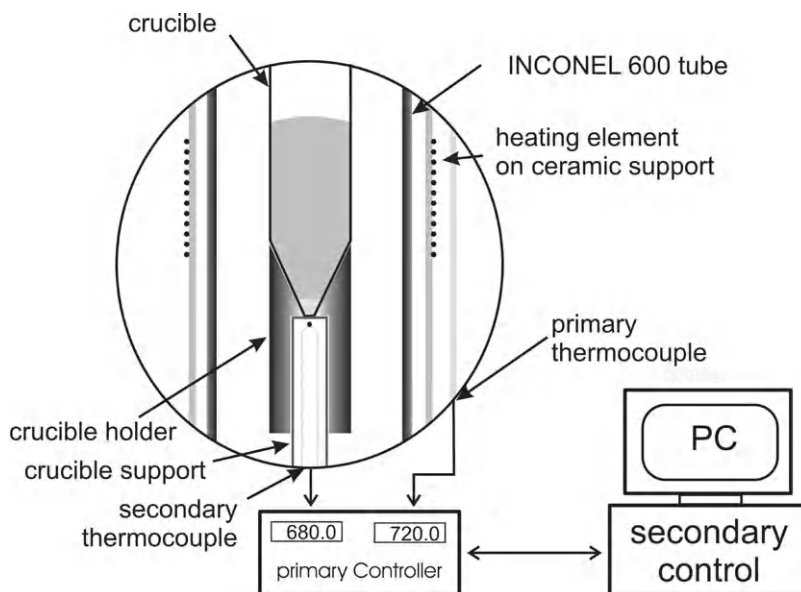

Fig. 4. Temperature controlling system used for the growth of bulk crystals by the vertical gradient freeze method [34].

the widest tuning range can be obtained by flash lamp activation [48]. Diode pumping was first reported to be limited to a range of 100 nm [49], but improving the spectral resolution of the coupling cavity, finally a tuning rang of 148 nm was achieved [50]. In the case of Cr:LiCAF, a slope efficiency of 67% was reached [15]. For LiSAF, at first, a rather low slope efficiency of 36% was reported [16]. However, recently a high power Cr:LiSAF laser with an output power of 0.55 W and a slope efficiency of 51% could be demonstrated, this by using a doping level of only 1.5% (for reducing thermal quenching) [51].

In the colquiriites the excited state life time is rather long: 67 µs for LiSAF and 170 µs for LiCAF [19,20] at room temperature. These values (especially for LiSAF) are strongly temperature dependent. The lifetime decreases with the temperature, being half already at 69 °C (Cr:LiSAF). Cr:LiCAF shows improved properties with the halfvalue at 528 K [52], showing no significant loss up to 400 K [53].

Intracavity frequency doubling techniques, using $KNbO_3$ [54] and LiB_3O_5 [55] for the generation of the second harmonic, allowed to set up tunable blue laser light sources.

Besides the tunablity of Cr:LiSAF and Cr:LiCAF lasers, it was also demonstrated that it is possible to build femtosecond lasers. The availability of this type of lasers, offering high output power during a short time, opened a wide field of new applications for the analysis of fast processes (e.g. chemical reactions) and in production techniques [56]. Pulses in the 10 fs regime could be realized using mode-locked setups either for LiSAF [57] or LiCAF [58,59]. With $KNbO_3$ for frequency doubling, a portable Cr:LiSAF setup, emitting blue light pulses in the femtosecond regime (~540 fs) was demonstrated recently [60].

Cr^{3+}:colquiriite dioded pumped laser gain media are nowadays commercially available solid state lasers: *Mellesgriot* [61] offers frequency doubled Cr:LiSAF at fixed wavelengths of 430 and 442 nm, e.g. as a replacement for helium–cadmium lasers. *High-Q-Lasers* [62] has offered a femtosecond Cr:LiSAF laser, but as the pumping diodes have not yet shown the requested reliability, the availability of a small sized frequency doubled Nd:YAG laser source for pumping has replaced LiSAF by a Ti:sapphire system of similar size. Most recently, a commercial tunable CW Cr:LiSAF-laser was presented by *Rainbow Photonics* [63], a spin-off of the Nonlinear Optics Laboratory at the Swiss Federal Institute of Technology (ETH), delivering a power of 100 mW over a tuning range of 820–970 nm.

Not only chromium-doped crystals showed laser performance: Cerium(III)-doped LiCAF is an active medium for tunable solid state lasers in the UV region [17], representing a new opportunity for solid state lasers [18]. Laser activity of Ce^{3+}-doped material is based on the 5d→4f transition. In the case of LiSAF and LiCAF, the transitions are broadened showing therefore tunablity in the range of 280–316 nm [64]. Pumping is achieved by the forth harmonic of a Nd-YAG laser [18].

The tuning range make Ce:LiSAF or Ce:LiCAF interesting materials for LIDAR applications in atmospheric remote sensing [65]. Important pollutants like O_3 and SO_2 exhibit absorptions bands in their tuning range [66,67]. Similarly, Cr:LiSAF was proposed for LIDAR applications [68].

In recent years, scientist have opened further fields for an application for LiSAF and LiCAF, making them interesting materials in optics: Cerium-doped LiCAF does not only show lasing properties, it can also be used as a scintillator material [69,70]. Furthermore, the utilization of LiCAF as a windows material for the 157 nm photolithography, representing the next step on the roadmap for semiconductors [71], has gained interest. Problems with radiation damage, which are typical for many fluoride crystals, could be solved by co-doping with tivalent rare earth ions [72,73] or Mg^{2+}/Ba^{2+} [74,75].

5. Conclusions

In essence, both LiCAF and LiSAF are interesting optical materials in respect to many existing or oncoming optical applications. The more important are therefore all aspects of synthesis and crystal growth including waveguide formation. In case of LiSAF and LiCAF, there is just little work reported up to now [76,77]: First waveguides were obtained by ion beam implantation. An alternative technique would be liquid-phase epitaxy in combination with chemical wet etching. This was successfully elaborated in our laboratory in case of $LiYF_4$ [78–80], allowing to demonstrate the first 1-D waveguide for a fluoride laser material [81].

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