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# Ce-doped $\text{LiYF}_4$ growth under $\text{CF}_4$ atmosphere

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## Abstract

Single crystals of Ce-doped  $\text{LiYF}_4$  have been grown by the Czochralski technique directly from raw materials under  $\text{CF}_4$  atmosphere. Optically clear single crystals were obtained without the previous conventional hydro-fluorination of the starting charge or the direct use of HF during the growth process. Optical characteristics were examined and compared with those of other rare-earth  $\text{LiYF}_4$ -doped crystals. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Since the 1970s, rare-earth-doped lithium yttrium fluoride crystals (YLF), have been well known as a laser active medium. In the early days, research on this crystal was driven by the demand for  $\text{Nd}^{3+}$ -doped crystals (for 1.06  $\mu\text{m}$  lasers), in particular because of some advantages of this host over Nd:YAG, such as, longer Nd fluorescence lifetime or smaller thermal lensing effect [1,2]. Interest has also centered upon YLF doped with  $\text{Ho}^{3+}$  ions and sensitized with  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions, known as  $\alpha\beta$ -YLF, as an eye-safe laser material emitting radiation at 2.06  $\mu\text{m}$  [3]. More re-

cently, the development of laser action in Ce : YLF [4,5] was reported. The broad 5d–4f vibronic emission bands of  $\text{Ce}^{3+}$ -doped fluoride crystals make these materials ideal for tunable solid-state lasers in the UV region.

Laser action in Ce : YLF was first demonstrated by Ehrlich [4], who observed a poor performance for this system resulting from the formation of transient and permanent color centers that absorb at the  $\text{Ce}^{3+}$  lasing transition. However, new studies by Okada et al. [6] showed that a large gain and wide tunability can be achieved with Ce : YLF crystals doped with low cerium concentrations and having sufficient optical quality.

The wide range of application of YLF crystals has resulted in several studies about their preparation, and the bulk growth of rare-earth-doped YLF is well developed at present. Reports about Bridgman–Stockbarger [7], Czochralski [8,9], and vertical gradient freezing (VGF) growth techniques [10]

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can be found in the literature. The successful growth of optically clear single crystals of YLF doped with rare earths depends not only on the growth process itself, but on the purity of the starting materials and the presence in the environment of oxygen-containing complexes. Common contaminants of fluorides are impurities derived from water and oxygen. The  $\text{OH}^-$  impurity posed a special problem, since water, the source of this impurity, is always present in the work environment. Its presence in large amounts results in degradation of the optical and mechanical properties of the crystals. The optical properties of fluoride crystals can be greatly affected by oxygen-related impurities by formation of defects as scattering centers, or more indirectly by the quenching of luminescence of a particular laser active impurity, as observed in  $\text{Ho}:\text{Er}:\text{YLF}$  laser crystals [11]. Oxygen contamination can originate from  $\text{OH}^-$  impurity [12]. Oxyfluorides and other oxygen contaminants can be formed from traces of oxygen not completely eliminated from the growth system, and from oxygen contaminants in the commercial chemicals. When such impurities are present, they can be accompanied by other impurity complexes like  $\text{Me}(\text{OH})_2$  complexes ( $\text{Me} = \text{Mg}, \text{Mn}$  or  $\text{Ti}$ ) [13].

Attempts to produce single crystals directly from the component fluorides under dry and oxygen-free inert gas atmospheres yielded crystals which were generally of poor quality. Usually, the preparation of fluorides follows one of the two approaches: previous purification of the components under HF and growth of the crystal in a controlled neutral atmosphere, or direct use of an HF reactive atmosphere during the growth process. The problem with using hydrogen fluoride atmospheres is that it demands expensive equipment, since HF is a highly corrosive gas and reacts easily at high temperatures with the metals, such as stainless steel, commonly used in growth chamber manufacture.

Earlier studies showed that HF reacts quickly with  $\text{M}(\text{OH}^-)$  or  $\text{MO}^{2-}$  compounds but has no action on water, while  $\text{CF}_4$  reacts more efficiently with water than with these compounds [14]. For this reason,  $\text{CF}_4$  is considered mainly useful as an HF complementary reactive agent. In this paper we report the growth of Ce-doped YLF under only

$\text{CF}_4$  atmosphere. We examined the optical characteristics of the obtained material and compared it to YLF doped with other rare earths. Variations of the host lattice parameter with dopant incorporation and the segregation coefficient are also discussed.

## 2. Experimental procedure

High purity commercial yttrium fluoride and lithium fluoride (99.999% grade) were used as starting materials. The crystals were grown in a vacuum-tight Czochralski system equipped with a graphite heater and automated diameter control by weight sensing of the crystal. After mixing in the appropriate compositions (52%  $\text{LiF}$ :48%  $\text{YF}_3$ ), the basic compounds and the dopant,  $\text{CeF}_3$  (99.9% Rare Metallic Co.) or  $\text{REF}_3$  ( $\text{RE} = \text{Nd}, \text{Er}, \text{Tm}, \text{Ho}, \text{Yb}, \text{Gd}, \text{Lu}$  99.9% Rare Metallic Co.) were melted in a platinum crucible in the Czochralski furnace under an atmosphere of  $\text{CF}_4$ . Prior to filling with gas and melting the charge, the growth chamber was evacuated to  $10^{-2}$  Pa. After melting, for complete purification of the charge, the temperature was kept constant for a period of 5–6 h. Crystals were grown at a pulling rate of  $1 \text{ mm h}^{-1}$  and rotation rate of 15 rpm. After growth they were cooled down to room temperature at a rate of  $30^\circ\text{C/h}$ .

The  $\text{Ce}^{3+}$  doping level in the grown crystals was measured, by the inductively coupled plasma technique. The determination of the lattice parameter of grown crystals were performed by X-ray powder diffraction.

Doped and pure YLF samples for spectroscopic measurements were cut perpendicular to the growth direction and polished manually. The IR spectrum was measured in an FTIR-8200PC spectrophotometer from Shimadzu.

## 3. Results and discussion

The initial melting of the compounds in the Czochralski furnace always resulted in the formation of a gray-black film on the melt surface. However, a clean and transparent melt was obtained if

the material was allowed to soak for 5–6 h under  $\text{CF}_4$  atmosphere prior to the growth. As already described by others [14],  $\text{CF}_4$  is useful as a secondary reactive atmosphere processing (RAP) agent to fast-acting HF, because it reacts with water (whereas HF does not) present in the environment according to the equation



The gray–black film formed on the melt surface after melting is due to the oxygen and carbon contamination of the raw materials. Oxyfluoride compounds have, in general, higher melting points than fluorides, and once they are formed they float on the melt surface. The source of carbon was not clearly identified.

The HF produced by reaction (1) is supposed to be the main agent in the elimination of this film by reacting with oxygen-derived impurities. Direct fluoride conversion by  $\text{CF}_4$  is also possible, but at the melt temperature of YLF, this conversion reaction is not as efficient as the HF one. As a result,  $\text{CF}_4$  atmosphere yields a double effect of purification by the removal of traces of water (Eq. (1)) and generation of a slightly HF atmosphere that reacts rapidly with  $\text{M}(\text{OH}^-)$  and  $(\text{MO}^{2-})$  complexes formed at the melt surface.

The carbon impurities cannot be completely eliminated by  $\text{CF}_4$  treatment. It is interesting to note that pure YLF crystals, after treatment, showed a very small amount of carbon impurities, as these generally stick to the crucible wall and do not disturb the growth process. The rare-earth-doped crystals, showed a larger amount of carbon on the melt surface after treatment. Usually, to grow these crystals it was necessary to clean the surface prior to the growth process.

Figs. 1 and 2 show a pure YLF crystal and Ce-doped YLF crystal grown after treatment under  $\text{CF}_4$ . The use of this fluorinating agent alone permitted the growth of transparent and scattering center-free single crystals, without previous conventional hydrofluorination or manipulation of high corrosive atmosphere (HF) during the growth procedure. An important advantage of the use of  $\text{CF}_4$  is that since only a small amount of HF is generated during the process as a product of reaction with trace water in the environment, problems

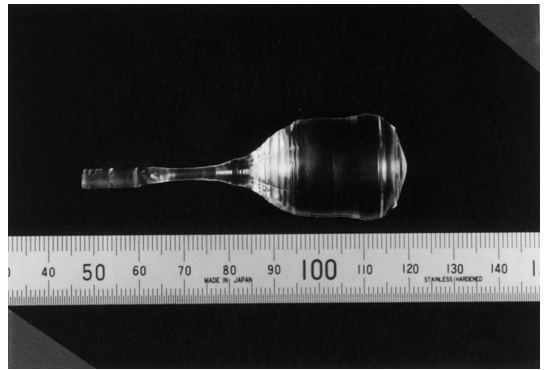


Fig. 1. Pure YLF crystal grown under  $\text{CF}_4$  atmosphere.



Fig. 2. Ce-doped YLF crystal grown under  $\text{CF}_4$  atmosphere.

in handling of residual HF and corrosion of the furnace are greatly minimized.

The distribution coefficient of  $\text{Ce}^{3+}$  ( $K_{\text{Ce}}$ ) in YLF was estimated as 0.26. To calculate ( $K_{\text{Ce}}$ ) we have considered the measured concentration ( $C_s$ ) (Table 1), in samples obtained from one crystal with initial dopant concentration ( $C_0$ ) of 0.5 mol%. The normal freezing equation:  $C_s = C_0 K(1 - g)^{K-1}$  was used to fit the experimental data considering the corresponding melt solidified fraction ( $g$ ) for each sample.

Lattice constants measured for one crystal are listed in Table 2. Lattice constants decreased with increased concentration of  $\text{Ce}^{3+}$ . The ionic radii of  $\text{Ce}^{3+}$  (1.01 Å) is larger than that of  $\text{Y}^{3+}$  (0.90) when the coordination number of  $\text{F}^-$  is 6 [15]. We suppose that the observed behavior is because of the

Table 1

Dopant concentration along a Ce-doped YLF crystal (Ce melt concentration: 0.5 mol%)

| Sample | Measured concentration<br>$C_s$ (mol%) |
|--------|--|
| #1     | 0.121                                  |
| #2     | 0.139                                  |
| #3     | 0.137                                  |
| #4     | 0.192                                  |

formation of some defect such as vacancies in the host lattice.

Fig. 3 shows the infrared spectrum of a 0.5 mol% Ce-doped YLF crystal. In fluorides, free  $\text{OH}^-$  radicals present bands in the region of 3800–3500  $\text{cm}^{-1}$ . There is no band corresponding to substitutional  $\text{OH}^-$  defects in this crystal, but we noted the presence of small bands in the range of 3250–2800  $\text{cm}^{-1}$ . The energy-level diagram for  $\text{Ce}^{3+}$  ions in host crystals [16], shows an energy level close to 3000  $\text{cm}^{-1}$ . The first hypothesis is that the observed bands can be associated to the dopant. However, similar bands in this wavelength interval were also observed in Er:OH-codoped YLF crystals [12] and were attributed to  $\text{O}_m\text{H}_n$  complexes and to  $\text{HCO}^-$  molecules. If  $\text{OH}^-$  ions are present during the growth process, they can dissociate, producing complexes absorbing in the wide spectral range from 4000 to 2400  $\text{cm}^{-1}$ . The  $\text{HCO}^-$  complex present sharp absorption bands at 2920 and 2850  $\text{cm}^{-1}$  and their production is attributed to carbon contamination.

If we suppose that traces of water vapor in our system are not completely eliminated by  $\text{CF}_4$  treatment, the formation of  $\text{O}_m\text{H}_n$  complexes can be expected. However, the origin of the carbon con-

tamination was not completely understood. It may be derived from the graphite of the resistive furnace, carbon present in the raw materials or from a secondary reaction involving  $\text{CF}_4$  gas.

To investigate the origin of these contaminations, we first grew a LiF crystal from the same raw material used for the growth of Ce:YLF crystals and under similar conditions pertaining to treatment of the system and atmosphere. As can be seen in Fig. 4, the LiF crystal showed very small absorption bands in the region of 2900  $\text{cm}^{-1}$ , indicating the presence of traces of  $\text{HCO}^-$ . However, there is no evidence of  $\text{O}_m\text{H}_n$  complexes or  $\text{OH}^-$  substitutional defects, which presents characteristic absorption band with maximum at 3720  $\text{cm}^{-1}$  in LiF crystals [12].

We have also grown a pure YLF crystal in an inductive furnace, instead of our resistive furnace, using a similar treatment in  $\text{CF}_4$  atmosphere, but because of system limitations the obtained vacuum prior to treatment was only 6 Pa. The infrared spectrum (Fig. 4) showed no contamination with carbon, but we observed a sharp absorption band at 3480  $\text{cm}^{-1}$ , probably because of  $\text{Me}(\text{OH})_2$  complexes. If the starting material is contaminated with free divalent ions ( $\text{Me}^{2+}$ ), IR active complexes can be formed in the presence of water.

The  $\text{CF}_4$  treatment was not completely effective in such cases. We suppose that the poor vacuum obtained in this system together with some furnace contamination, was the reason for the presence of such complexes. The inductive furnace was previously used for the growth of oxides crystals and even with vacuum treatment some spurious impurity could have eventually contaminated the fluoride raw material. Despite these problems no  $\text{O}_m\text{H}_n$  complexes or  $\text{COH}^-$  absorption bands were observed in a pure YLF crystal.

Table 2

Ce-doped YLF crystal lattice parameter measurements

| Sample              | #1             | #2             | #3             | #4             |
|---------------------|----------------|----------------|----------------|----------------|
| Solidified fraction | 1.0497         | 10.539         | 15.147         | 22.760         |
| <i>a</i> -axis      | 5.179 ± 0.002  | 5.175 ± 0.003  | 5.160 ± 0.002  | 5.151 ± 0.004  |
| <i>c</i> -axis      | 10.746 ± 0.005 | 10.747 ± 0.009 | 10.721 ± 0.007 | 10.706 ± 0.009 |

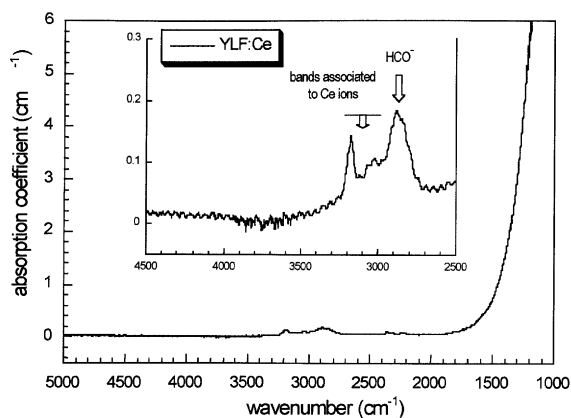


Fig. 3. Infrared absorption spectrum of a 10 mm Ce:YLF sample. The inserted figure presents the 4500–2500  $\text{cm}^{-1}$  region expanded, showing in detail the cerium derived bands (3250–3000  $\text{cm}^{-1}$ ) and the  $\text{HCO}^-$  characteristics bands (3000–2800  $\text{cm}^{-1}$ ).

We have compared the above results with other rare-earth-doped YLF crystals. Fig. 5 shows the absorption spectrum of a YLF crystal doped with 0.5 mol% of eight different rare-earth compounds (Ce, Nd, Gd, Ho, Er, Tm, Yb, Lu), grown in the same conditions as Ce:YLF, together with the

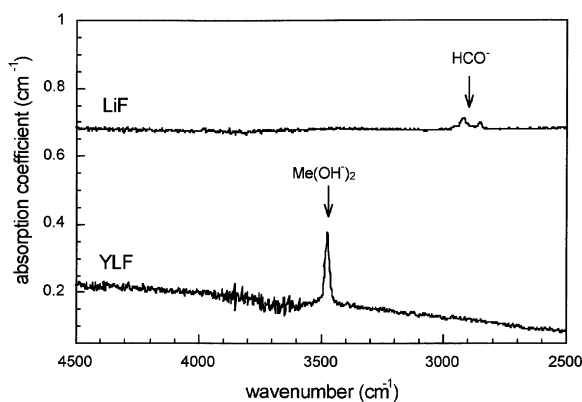


Fig. 4. Infrared absorption spectra of LiF and YLF crystals grown under  $\text{CF}_4$  atmosphere.

spectrum of a commercial Nd:YLF laser rod. It is interesting to note that, in both crystals, we observed only the characteristic Nd transitions in the region of 4000 and 2000  $\text{cm}^{-1}$ , and no  $\text{HCO}^-$ ,  $\text{OH}^-$  or  $\text{O}_m\text{H}_n$  complexes bands.

From the above experiments we concluded that the observed absorption bands close to 3000  $\text{cm}^{-1}$ , cannot be attributed to  $\text{O}_m\text{H}_n$  complexes formation in Ce:YLF crystals, since these complexes were

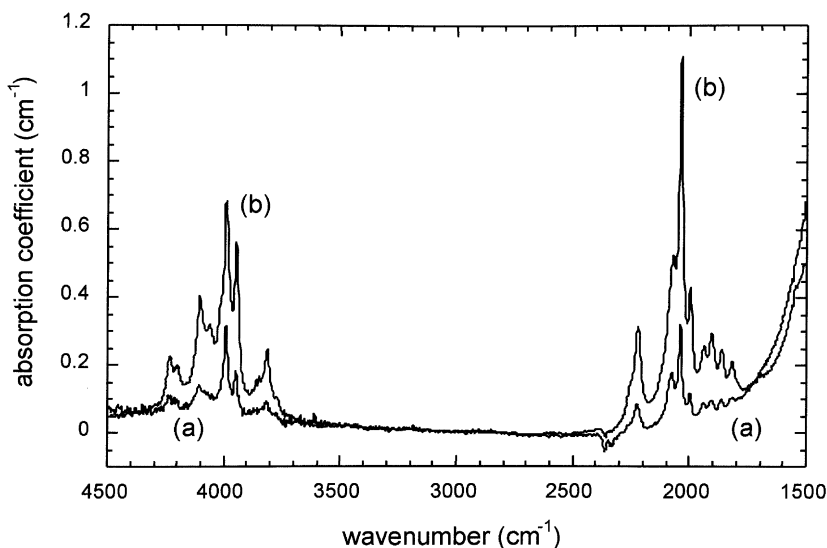


Fig. 5. Infrared absorption spectra of: (a) RE-doped YLF crystal (RE = Ce, Nd, Gd, Ho, Er, Tm, Yb, Lu); (b) commercial Nd:YLF laser rod. Both showing the characteristic  $\text{Nd}^{3+}$  ion transitions in YLF host, at the region of 4000 and 2000  $\text{cm}^{-1}$ .

not observed in pure YLF or multiple rare-earth-doped YLF grown under similar conditions. The presence of these bands is not related to an inefficiency of the  $\text{CF}_4$  treatment. It is also not possible to assume that carbon contamination originates exclusively in the resistive system, because  $\text{HCO}^-$  bands were not observed in multiple rare-earth-doped YLF, and were very weak in LiF crystals.

The observed infrared absorption bands in Ce-doped YLF, in the range of  $3250\text{--}3000\text{ cm}^{-1}$ , were probably derived from the  $\text{CeF}_3$  compound. Because of the presence of other rare earths, the cerium concentration in the multiple-doped crystal is too small compared to the single-doped crystals, and similar bands were not observed on the IR spectrum of RE-doped YLF.

#### 4. Summary

Ce:YLF single crystals were grown by the Czochralski technique, under  $\text{CF}_4$  atmosphere, directly from powdered raw materials. Infrared spectra showed small contamination with carbon, in the form of  $\text{HCO}^-$  molecules. The presence of this impurity was not completely understood, but it could not be attributed to inefficiency of  $\text{CF}_4$  as a fluorinating agent. In spite of the presence of these IR-bands, it is important to note that the detected amount of impurities indicates the presence of only traces of water contamination during the growth process, which is not enough to degrade the mechanical and optical quality of the samples. Optically clear crystals were obtained and no inclusion or scattering centers were observed in the grown single crystals. Moreover, for UV laser applications the detected complexes will probably not affect the laser performance.

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