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Liquid Phase Epitaxy growth, structure and spectroscopy of highly-doped 20 at.% Yb³⁺:LiYF₄ thin films

Gurvan Brasse^a, Pavel Loiko^a, Clara Grygiel^a, Abdelmjid Benayad^a,
Franck Lemarie^a, Viktor Zakharov^b, Andrey Veniaminov^b, Jean-Louis
Doualan^a, Alain Braud^a, and Patrice Camy^{a,*}

^a*Centre de recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252
CEA-CNRS-ENSICAEN, Université de Caen Normandie, 6 Boulevard du Maréchal Juin,
14050 Caen Cedex 4, France*

^b*ITMO University, 49 Kronverkskiy Pr., 197101 St. Petersburg, Russia*

*Corresponding author, e-mail: patrice.camy@ensicaen.fr

Abstract. Highly doped (20 at.%) Yb³⁺:LiYF₄ single-crystalline thin films are grown on (001)-oriented bulk undoped LiYF₄ substrates by Liquid Phase Epitaxy using lithium fluoride (LiF) as a solvent. The growth temperature lies around 741 °C (0.5–1 °C supercooling) and the growth rate is 1.8-2.6 μm/min. The single-crystalline nature of the films is confirmed by X-ray diffraction and polarized Raman spectroscopy. The film morphology is studied and discussed. The polarized spectroscopic properties of Yb³⁺ ions are reported, indicating a stimulated-emission cross-section of 0.88×10⁻²⁰ cm² at 993.9 nm in π-polarization and a radiation trapping free lifetime of the ²F_{5/2} state of 2.00 ms indicating weak concentration-quenching. The crystal-field splitting of Yb³⁺ multiplets is resolved at 12 K. Highly-doped Yb³⁺:LiYF₄ / LiYF₄ homoepitaxies are promising for waveguide and thin-disk lasers at ~1 μm.

Keywords: Liquid phase epitaxy; lithium yttrium fluoride; thin films; ytterbium ions; luminescence.

1. Introduction

Lithium (rare earth) fluoride crystals with a general chemical formula of LiLnF_4 (where $\text{Ln} = \text{Gd}, \text{Y}$ or Lu is the host-forming cation) doped with trivalent laser-active rare-earth ions (RE^{3+}) are known for efficient laser emission in the near-infrared [1]. The LiLnF_4 crystals belong to the tetragonal crystal class (sp. gr. $I4_1/a$) and they have a scheelite-type ordered structure [2].

As host matrices, these crystals possess several advantages. First, they provide good thermo-mechanical properties such as high thermal conductivity (e.g., for $\text{Yb}:\text{LiYF}_4$, $\kappa_a = 4.1$ W/mK and $\kappa_c = 5.2$ W/mK [3]), weak anisotropy of thermal expansion and negative thermo-optic coefficients dn/dT leading to weak negative thermal lensing [4]. Second, they have attractive optical properties such as broad transparency range, low refractive indices and natural birefringence eliminating the depolarization losses (e.g., for LiYF_4 , $n_o = 1.449$ and $n_e = 1.471$ at $\sim 1 \mu\text{m}$ [5]). Third, the low maximum phonon energies ($h\nu_{\text{ph}} = 446 \text{ cm}^{-1}$ for LiYF_4) [6] reduce the probability of non-radiative (NR) relaxation for the excited-states of the RE^{3+} ions [7]. Finally, for the RE^{3+} doping, the LiLnF_4 crystals offer a single substitutional rare-earth site and high available doping levels [1,8]. The Czochralski growth of bulk LiLnF_4 crystals is also well developed [9].

The early studies focused mainly on Nd^{3+} doping of LiYF_4 crystals [10]. Ytterbium (Yb^{3+}) ions, as compared to the Nd^{3+} ones, have greater potential for laser emission at $\sim 1 \mu\text{m}$. Yb^{3+} (electronic configuration: $[\text{Xe}]4f^{13}$) has a simple energy-level scheme eliminating unwanted energy-loss processes such as excited-state absorption or energy-transfer upconversion. The in-band pumping scheme results in high pump Stokes efficiency and reduced heat loading. The Yb^{3+} ions can be easily pumped by commercial InGaAs laser diodes emitting at $\sim 0.96 \mu\text{m}$ [11].

Diode-pumped bulk $\text{Yb}:\text{LiYF}_4$ [11,12] and $\text{Yb}:\text{LiLuF}_4$ [13] lasers were reported. The possibility of laser operation with heavily Yb^{3+} doped crystals was demonstrated: a room-temperature 30 at.% Yb^{3+} -doped LiYF_4 laser generated a maximum peak power of 4.0 W at 1059 nm with a slope efficiency of 62.8% [8]. Mode-locking of $\text{Yb}:\text{LiLnF}_4$ oscillators was also realized [14-16]. Pirzio *et al.* reported on a SESAM mode-locked $\text{Yb}:\text{LiYF}_4$ laser delivering 87 fs pulses at ~ 1052 nm at a repetition rate of 100 MHz [16]. A great improvement of the diode-pumped laser performance was achieved under cryogenic temperatures [17]. Zapata *et al.* demonstrated a cryogenically cooled (80 K) diode-pumped $\text{Yb}:\text{LiYF}_4$ laser delivering an output power of 224 W at 995 nm with a slope efficiency of 68% and extremely low quantum defect [17]. These crystals were also considered for radiation cooling [18].

Besides bulk laser applications, the LiYF_4 crystals are well suited for fabrication of RE^{3+} -doped single-crystalline thin films by Liquid Phase Epitaxy (LPE) [19]. Such active structures are of interest for waveguide lasers [20]. The growth, spectroscopy and efficient waveguide laser operation of LiYF_4 -based epitaxies doped with Pr^{3+} [21], Yb^{3+} [22], Tm^{3+} [23], Ho^{3+} [24] and Nd^{3+} [25] ions were reported. In particular, a 4 at.% Yb, 5 at.% Gd: LiYF_4 / LiYF_4 LPE-based waveguide laser generated 2.8 W at 1020 nm with a slope efficiency of 43% [22]. Note that the Gd^{3+} ions were added for the enhancement of the refractive index contrast between the substrate and the film. RE^{3+} -doped LiYF_4 thin films were also fabricated by Pulsed Laser Deposition (PLD) [26-27] and Matrix-Assisted Pulsed Laser Evaporation (MAPLE) [28].

Another possible application of LPE-grown crystalline thin films is their use in thin-disk lasers instead of the traditional technology which requires handling with thin (few hundreds of μm) laser elements. This would require either high transition cross-sections for the RE^{3+} ions or high RE^{3+} doping levels. The latter condition can be easily satisfied in Yb^{3+} -doped LiYF_4 . So far, efficient thin-disk lasers based on epitaxies doped with Yb^{3+} [30], Tm^{3+} [31] and Ho^{3+} [32] ions were reported. Very recently, we achieved laser operation in highly Tm^{3+} -doped (20 at.%) LiYF_4 thin films [33].

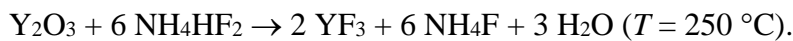
In the present work, we report for the first time on the LPE growth, structural and morphological characterization and detailed optical spectroscopy of highly-doped (20 at.%) single-crystalline $\text{LiY}_{1-x}\text{Yb}_x\text{F}_4$ thin films on oriented bulk LiYF_4 substrates intended for the potential use in waveguide and thin-disk lasers.

2. Elaboration of single-crystalline films

LPE is very suitable for the growth of thick single-crystalline films onto bulk substrates of the same nature (this process is called homoepitaxy). It allows the growth of high optical grade epitaxial layers with a thickness lying between few μm and few hundreds of μm . In the present work, the experimental process to get such layers consisted of the following steps: (i) the growth of undoped LiYF_4 crystals by the Czochralski (Cz) method, (ii) the orientation of the crystals and fabrication of the required oriented substrates for the epitaxial growth, (iii) the epitaxial growth of Yb^{3+} -doped LiYF_4 films onto the oriented substrates and (iv) preparation / shaping / polishing of the epitaxy to achieve the required dimensions and optical quality regarding the potential laser application.

2.1. Cz growth of undoped LiYF_4 single-crystals

High optical quality undoped LiYF_4 single crystals were grown by the Cz method. As raw materials, we used LiF (Alfa-Aesar, optical grade 99.5%) and Y_2O_3 (Alfa Aesar, 4N-REO) following the molar ratio of 52% LiF - 48% YF_3 , according to the related phase diagram of the LiF - YF_3 binary system [34], Fig. 1. The oxide precursor Y_2O_3 was fluorinated using a large excess of ammonium hydrogen bifluoride (NH_4HF_2) solution under heating at 250 °C, following the chemical equation:



The dry cake obtained in this way needs to be annealed at 650 °C under a controlled argon atmosphere to remove the residual NH_4F and moisture. After synthesizing the required fluoride precursor YF_3 , the Cz growth of bulk LiYF_4 was performed under an oxygen-free Ar atmosphere using a [001]-oriented seed of undoped LiYF_4 . The pulling rate was fixed at 1 mm/h. An example photograph of a LiYF_4 boule is shown in Fig. 2(a).

The substrates were oriented along the (001) crystallographic plane because of the following reasons: (i) the growth direction of undoped LiYF_4 crystal was along the [001] axis and, consequently, it was easier to prepare the substrates with better uniformity and optical

quality in the orthogonal plane; (ii) due to isotropic thermo-mechanical properties of LiYF₄ in the *a-b* plane, it is easier to perform LPE.

Typically, substrates with transverse dimensions of 30×11 mm² and a thickness of 3.0 mm were used for the LPE process, so that bulk crystals grown by the Cz technique were around 60 mm in height and 30–40 mm in diameter. The substrates were finely polished on both faces and a special attention was paid concerning their flatness (measure to be $\lambda/8$) and roughness of the polished surfaces (measured to be in the range of few nm).

2.2. Epitaxial growth of Yb:LiYF₄ single-crystalline layers

The schematic of the LPE setup is described in detail in [20,35]. It can be divided into two main areas: the upper and bottom zones which are isolated from each other by an electro-valve. The upper area is an exchange airlock that allows for changing the samples, substrates and stirrer, while keeping the furnace in the proper temperature regime without contaminating the melt in the crucible located in the growth chamber. The glassy carbon crucible containing raw materials is installed in one-end-sealed silica tube which constitutes the growth chamber and is located in the heating zone of a tubular furnace where the thermal gradient is the lowest. The furnace has a dual heating zone that ensures a homogeneous temperature field through the whole height of the melt in the crucible and the temperature is controlled with a precision of 0.1 °C. The growth of fluoride crystalline materials requires oxygen-free atmosphere of high purity.

In the case of Yb:LiYF₄ growth, the reagents are LiF (Alfa-Aesar, 99.5%), Y₂O₃ and Yb₂O₃ (both Alfa Aesar, 4N-REO). The rare-earth oxides Ln₂O₃ (Ln = Y, Yb) are fluorinated according to the procedure described in Section 2.1 yielding LnF₃ (Ln = Y, Yb) fluorides. The raw materials that compose the molten bath used for the LPE growth are taken according to the molar ratio 27% (YF₃ + YbF₃) - 73% LiF, in the manner to work at lower temperatures and to anticipate the vaporization of the LiF solvent, which will move the equilibrium on the phase diagram. The Yb³⁺ doping level is set to 20 at.% with respect to Y³⁺, according to the formula LiY_{0.80}Yb_{0.20}F₄.

The fluorinated raw materials are introduced in the LPE growth chamber to be degassed under heating and then they are superheated to ensure good homogenization of the molten bath. An additional mechanical stirring of the LiF – YF₃ – YbF₃ mixture is also done.

A part of the phase diagram of the LiF–YF₃ binary system relevant for the LPE growth experiment is shown in Fig. 3. Our own studies confirm incongruent melting of LiYF₄ with a peritectic molar composition about 49% YF₃ – 51% LiF, in agreement with [19,34]. For the selected bath composition, 27% (YF₃ + YbF₃) - 73% LiF, the liquidus temperature was determined to be ~744 °C with an uncertainty of about 3-4 °C. This value agrees better with the phase diagram constructed by Thoma et al. [34]; the liquidus temperatures determined by Rogin *et al.* [19] seem overestimated. The apparent onset of crystallization (by visual observation) was approximately at 741.5 °C. The transition from dissolution to growth upon cooling was not very sharp (within a temperature range of about 1-1.5 °C).

After homogenizing of the bath, the temperature was slowly decreased just over the apparent onset of crystallization in a supersaturation regime and stabilized. After installing the

substrate in the exchange airlock, the epitaxial growth process began by dipping the substrate into the molten bath. The growth temperature was set in the range of 741–740.5 °C (i.e., the apparent supercooling was 0.5–1.0 °C). The substrate was rotated at a speed of 10 rev/min in the molten bath. The dipping duration varied between 20 min and 3 hours depending on the desired layer thickness, as well as on the particular temperature and viscosity of the bath. The mean growth rate estimated at a fixed dipping duration of 30 min amounted to 1.8 ± 0.5 $\mu\text{m}/\text{min}$ and 2.6 ± 0.5 $\mu\text{m}/\text{min}$ for 0.5 °C and 1 °C supercooling, respectively. This value accounts only for the uniform thickness of the Yb:LiYF₄ layer, i.e., when excluding the features of its bumpy surface and polycrystalline solvent residuals (see Section 4.1).

The obtained growth rates at a given supersaturation reasonably agree with the previous work of Rogin *et al.* where the bath composition of 40% (YF₃ + REYF₃) – 60% LiF was studied (i.e., located closer to the peritectic one). Thus, we can conclude that the growth mechanism of the layer is relying on attachment of new building units anywhere at the layer edge (in contrast to the regime of small supercoolings when this can happen only at kink positions). This growth mechanism provides higher growth rates which change almost linearly with increasing the apparent supercooling.

In our work, for obtaining high optical quality Yb:LiYF₄ layers, a relatively narrow range of growth temperatures (and, accordingly, apparent supercoolings) was used. Further increase of the supercooling to 3 – 5 °C resulted in higher growth rates albeit with lower control of the layer uniformity, thickness and formation of macroscopic defects (cracks) and appearance of polycrystalline material (a mixture of Yb:LiYF₄ and LiF).

After removing the substrate from the molten bath, a smooth cooling ramp is applied to avoid crack formation in the grown layer [36]. A photograph of the as-grown Yb:LiYF₄ / LiYF₄ epitaxy is shown in Fig. 2(b). Approximately 2/3 of the substrate contain the grown film which is separated from the non-dipped part of the substrate by the growth meniscus. The film is transparent, but its surface is covered by a white-colored residual crystallized solvent (LiF). It is easily removed by the top polishing of the layer.

3. Experimental

The surface morphology of the as-grown films was studied employing a confocal and interferometric optical microscope (Sensofar, S-neox) equipped with a blue light-emitting diode (LED, $\lambda = 405$ nm) in the reflection mode. The surface roughness was studied in the confocal mode.

The polished end-facet of the epitaxy was studied using a confocal laser microscope (LSM 710, Carl Zeiss) equipped with a polarizer (P), an analyzer (A), and a blue GaN laser ($\lambda = 405$ nm) in transmission mode. Two microscope objectives were used (one: 20 \times , N.A. = 0.75 and another: 50 \times , N.A. = 0.95).

The structure of the films was studied by single-crystal X-ray diffraction (XRD) using a Bruker AXS D8 Discover diffractometer with a four-circle goniometer, a line focus Cu X-ray source equipped with a Goebel mirror and a Ge (220) double-bounce monochromator providing a parallel and monochromatic (Cu K α 1, $\lambda = 0.15406$ nm) incident X-ray beam. A Ge (220) crystal analyzer was used to further limit the scintillator detector acceptance. Symmetric 2θ

scans and reciprocal space maps (RSM) obtained by taking a series of 2θ - ω patterns ($\pm 0.5^\circ$ around the reference) at successive ω values ($\omega = \theta \pm \Delta$; $\pm 0.5^\circ$ around the reference) were recorded. For the RSM representation, the DxTools viewer [37] was used.

The composition of the films was studied by Energy Dispersive X-ray (EDX) spectroscopy using a scanning electron microscope (SEM, Jeol 6400). It was equipped with a tungsten filament thermoelectronic gun and a 10 mm² X-microanalysis diode (Oxford-instrument).

The polarized Raman spectra were measured with a Renishaw inVia confocal Raman microscope equipped with a half-wave ($\lambda/2$) plate and a polarizer (P) using a Leica x50 objective (N.A. = 0.75). The excitation wavelength λ_{exc} was 488 nm (Ar⁺ laser line).

First, the spectroscopic studies were performed at room temperature (RT, 293 K). The absorption spectra were measured using a spectrophotometer (Lambda 1050, Perkin Elmer) and a Glan-Taylor polarizer. The luminescence spectra were measured using an optical spectrum analyzer (OSA, Ando AQ6315-E) and a Glan-Taylor polarizer. As an excitation source, we used a CW Ti:Sapphire laser tuned to ~ 0.93 μm . The spectral resolution was 0.5 nm. The luminescence decay was studied using a 1/4 m monochromator (Oriel 77200) and an InGaAs detector. The luminescence was excited by the output of a ns optical parametric oscillator (Horizon, Continuum) tuned to ~ 0.96 μm . The luminescence decay curve was fitted with a single-exponential law, $I_{lum}(t) = I_0 \exp(-t/\tau_{lum})$.

For low-temperature (LT, 12 K) absorption and luminescence studies, the sample was mounted on an APD DE-202 closed-cycle cryo-cooler equipped with an APD HC 2 Helium vacuum cryo-compressor and a Laceshore 330 temperature controller. A silver paint was used for better thermal contact between the sample and the cryo-cooler. The LT absorption spectrum was measured using a 20 W halogen lamp with a spectrally-calibrated emission and the OSA. The LT luminescence spectrum was measured using the same OSA. The spectra resolution was 0.2 nm.

4. Results and discussion

4.1. Surface morphology

The morphology of the top surface of the as-grown Yb:LiYF₄ film was first studied using a confocal optical microscope in the reflection-mode, Fig. 4. This study revealed the presence of two contributions to the surface topography. First, these are “hills” with a transverse size of few tens of μm and a height of few μm separated by “valleys” both belonging to the Yb:LiYF₄ film. On top of the “hills”, dendritic polycrystalline crystalline structures due to the solvent residuals (LiF) can be observed while the film “valleys” are clean from the solvent. No surface cracks are observed in the Yb:LiYF₄ film. Such a morphology is typical for LPE-grown fluoride thin-films [33,35]. The bumpy surface of the layer is attributed to two main reasons. First, upon extraction from the solution, a thin liquid film (about few μm) cannot be completely removed. Upon cooling, this film crystallizes leading to an additional increase of the layer thickness and a precipitation of the excess of LiF at the surface forming the dendritic structures. Second, a tendency to follow such a morphology can be assigned to higher viscosity of the flux at lower growth temperatures determined by the selected composition of the solution. Moving the bath

composition closer to the peritectic point is expected to reduce the flux viscosity potentially improving the surface smoothness of the epitaxial layer.

It is known that the excess of the melt can be removed from the layer surface by fast spinning in the horizontal dipping geometry of LPE. It was used for the fabrication of fluoride (Yb:CaF₂) epitaxial layers [38]. However, vertical dipping keeping a small part of the substrate clean is useful for further polishing of the epitaxy when this part is used as a plane reference. It also prevents the Pt holder from being covered by crystallized solvent (otherwise, it may be difficult to remove the epitaxy without fracturing it).

The surface roughness of the film was further examined, Fig. 5. This plot clearly reveals the presence of “hills” and “valleys”, as well as sharp solvent residuals. The root mean square (r.m.s.) surface roughness is about 0.7 μm. For comparison, the thickness of the films used in this study lies in the range of 40–100 μm. Note that the surface roughness of the laser-grade-polished LiYF₄ substrates is in the nanometer range.

The substrate / layer interface was further studied by observing the polished end-facet of the epitaxy using a confocal laser microscope in transmission mode (such mode allowed us to avoid the effect of the surface imperfections), Fig. 6. A clean and straight interface is observed. No cracks in the film propagating along its growth direction are visible, see Fig. 6(a). The light intensity for the layer is slightly different owing to the refractive index variation due to the Yb³⁺ doping. For the substrate / layer interface observed with crossed polarizers (P || [001], A || [100]), Fig. 6(b), only a weak stress field in the substrate is visible, which means a weak lattice mismatch for the films.

The “hilly” surface morphology of the as-grown epitaxial films does not present a serious limitation for their applications. Typically, the as-grown epitaxies are subjected to top surface polishing to ensure a uniform layer thickness, as well as to control the latter in a precise way. The final (post-polishing) thickness of the layer, as well as the refractive index contrast with respect to the substrate determine the mode guiding properties of the epitaxy (e.g., single-transverse-mode operation). Moreover, the top polishing eliminates the unwanted surface roughness and reduces the propagation losses in the layer. Another approach to produce a relatively smooth surface of the RE³⁺-doped (active) layer is its overgrowth by an undoped cladding layer: during the thermal equilibrium step before the overgrowth, the rough layer surface will be liquified leading to a smooth layer / cladding interface [19]. In this case, the surface state of the cladding is not very critical. For waveguide applications, two opposite side facets of the epitaxy should be polished as well.

The processing of epitaxies intended for the use in thin-disk elements is similar, i.e., it involves laser-grade polishing of the layer surface and the opposite substrate face [32]. Later on, both surfaces are subjected to dielectric coatings and the substrate is soldered to a heat sink. Note that for thin-disk laser applications, the epitaxies do not need to exhibit a refractive index contrast. The fabrication of thin-disk elements based on the LPE technology can be referred as a “bottom-up” approach. The more widespread one (a “top-down” approach) is the fabrication of thin crystal plates from bulk crystals by mechanical processing. It enables fabrication of plates with a thickness ranging between few tens and few hundreds of μm (depending on the mechanical properties of the material). The “top-down” approach is simpler from the

technological point of view; however, such thin crystal plates suffer from internal stresses and surface bulging both affecting their laser performance. However, LPE-based thin-disk laser elements have not been commercialized so far.

The fabrication of planar waveguides by direct optical bonding of thinned crystal plates prepared from bulk crystals is also known [39]. Mackenzie *et al.* developed single- and double-cladding planar waveguide structures produced by direct bonding of undoped and RE³⁺-doped Y₃Al₅O₁₂ and sapphire (α -Al₂O₃) crystal plates [40]. Such systems appear promising for power scaling at the expense of tolerated spatial beam quality. However, a direct application of this approach to fluorides will face a problem of lower hardness of the latter (as compared to oxides mentioned above). Handling with LiYF₄ crystal plates with a thickness below 100 μm is very complicated and from this point of view, LPE is more reliable and reproducible.

4.2. Structural study

The phase purity and the structure of the grown films were confirmed by X-ray diffraction (XRD), Fig. 7(a). In the measured XRD pattern of the film, only the reflections assigned to the tetragonal LiYF₄ phase (cf. Fig. 7(b) showing the diffraction peaks according to the Inorganic Crystal Structure Database (ICSD) card No. 81-2254 [41]) are observed. The 20 at.% Yb:LiYF₄ film has a tetragonal structure (sp. gr. C_{6h} - I4₁/a, No. 88, centrosymmetric point group 4/m). The films are isostructural to undoped LiYF₄ which presents a scheelite (CaWO₄) type structure. The orientation of the film well follows that of the bulk undoped LiYF₄ substrate, namely, along the [001] axis. Indeed, in the XRD pattern, there are only two intense reflections both corresponding to the (00*l*) Miller's indices, namely (004) at $2\theta \approx 33.4^\circ$ and (008) at $2\theta \approx 70.2^\circ$. By plotting the measured XRD pattern in a semi-log scale, we make it possible to observe weak parasitic reflections coming from slight mosaicity of the film among which, the peak at $2\theta \approx 38.3^\circ$ can be unambiguously assigned as (202). However, their intensity is by 3 orders of magnitude weaker than that for the (00*l*) reflections.

Prior to further discussion, we describe shortly the structure of Yb:LiYF₄. For undoped LiYF₄, the lattice constants are $a = 5.164(1) \text{ \AA}$ and $c = 10.741(2) \text{ \AA}$ (the number of the formula units in the unit-cell: $Z = 4$), so that the volume of the unit-cell V is $286.5(1) \text{ \AA}^3$ and the theoretical density $\rho_{\text{calc}} = 3.99 \text{ g/cm}^3$ [2]. The Li⁺ ion has four and the Y³⁺ ion has eight nearest-neighbor F⁻ ions. The two Y–F distances are 2.244 \AA and 2.297 \AA [2]. The symmetry of the Y³⁺ site in the slightly distorted dodecahedron [YF₈] is S₄ (a slight distortion of D_{2d} for scheelite crystals) [2,41]. The [LiF₄] tetrahedra are corner-sharing with the edge-sharing [YF₈] dodecahedrons.

When doped with Yb³⁺ ions, the latter are expected to replace the Y³⁺ ones in the S₄ symmetry sites. This process is favored by the closeness of ionic radii of these cations ($R_{\text{Yb}} = 1.12 \text{ \AA}$ and $R_{\text{Y}} = 1.16 \text{ \AA}$ for the VIII-fold fluorine coordination [42]). Note that the isostructural stoichiometric compound, LiYbF₄, exists [43]. Its lattice constants are $a = 5.133 \text{ \AA}$ and $c = 10.587 \text{ \AA}$ [43].

A close look on the (008) reflection, Fig. 7(c), reveals a split peak structure, with the narrower component at smaller 2θ angles (related to the substrate) and the broader one at higher

2θ (corresponding to the film). This reflects the decrease of the lattice constants of the film due to the difference in ionic radii of Y^{3+} and Yb^{3+} .

To determine the lattice constants of the film, we used the following equation for tetragonal crystals:

$$\sin^2 \theta = \frac{\lambda^2}{4} \left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right), \quad (1)$$

where θ is the diffraction angle, (hkl) are the Miller's indices of the reflection, and $\lambda = 0.15406$ nm is the wavelength of X-rays. We analyzed the (134), (202), (004) and (008) reflections which were unambiguously assigned. The resulted values are $a = 5.157 \text{ \AA}$ and $c = 10.714 \text{ \AA}$. They are smaller than those for the undoped crystal, as expected. The lattice mismatch $\Delta a/a_{\text{subst}} = -0.14\%$ and $\Delta c/c_{\text{subst}} = -0.25\%$. The compositions $LiYF_4 - LiYbF_4$ form an isostructural series of solid solutions $LiY_{1-x}Yb_xF_4$, so that a linear evolution of the lattice constants is expected yielding to the following calculated values: $a_{\text{calc}} = 5.158 \text{ \AA}$ and $c_{\text{calc}} = 10.710 \text{ \AA}$, which are in good agreement with the experimental observations.

The reciprocal space mapping (RSM) of the (103) node for the Yb:LiYF₄ layer is shown in Fig. 8(a) and it leads to the corresponding rocking curve, Fig. 8(b). The (103) direction is not perpendicular to the surface of the substrate. By this way, it takes into account the strain induced by the substrate on the lattice parameter a in the plane of the epitaxial layer. The full width at half maximum (FWHM) of the rocking curve is 0.113° , which reflects very low mosaicity of the crystalline film. In other words, there is a weak local disorientation of crystalline planes regarding the normal to the surface.

A typical EDX spectrum of the raw surface of the Yb:LiYF₄ film is shown in Fig. 9. The EDX clearly confirms the presence of Yb^{3+} ions in the film, together with the host-forming elements (Y, F). Note that light Li atoms cannot be detected by EDX. A weak signal from O originate from the post-growth hydroxyl and oxygen absorption on the residual solvent, while the Si traces can be explained either by possible weak contamination coming from the LPE silica tube constituting the growth chamber or by a Si pollution of the SEM chamber which is also used for analyzing Si wafers. The traces of C are referred to organic contamination of the sample, especially by the use of acetone for cleaning the sample.

The actual concentration of Yb^{3+} ions in the layer with respect to Y^{3+} was determined by EDX to be 19.6 ± 1 at.% ($N_{Yb} = 27.0 \times 10^{20} \text{ cm}^{-3}$), corresponding to a segregation coefficient $K_{Yb} = N_{\text{layer}}/N_{\text{solution}} = 0.98 \pm 0.05$, in agreement with our previous studies [22,23]. Close to unity value of K_{Yb} is determined by the small difference of ionic radii of Y^{3+} and Yb^{3+} cations. The layers exhibited a relatively uniform distribution of Yb^{3+} ions, with a variation of ~ 2 at.% along the dipping (vertical) direction.

4.3. Raman spectra

The polarized Raman spectra were measured using a polished end-facet of the epitaxy in the $a(ij)a$ configuration (where both $i, j = \pi$ or σ), according to the Porto's notations [44]. The studies were performed for both the bulk $LiYF_4$ substrate and the Yb:LiYF₄ thin-film. The results are shown in Fig. 10.

LiYF₄ crystallizes in the scheelite structure. The scheelite primitive cell containing two LiYF₄ formula units has 36 degrees of freedom. At the center of the Brillouin zone Γ ($\mathbf{k} = 0$), these vibrational modes are distributed over the irreducible representations of C_{4h} as follows: 3A_g + 5B_g + 5E_g + 5A_u + 3B_u + 5E_u [6]. One A_u and one E_u modes correspond to rigid translations of the whole crystal, and other A_u and E_u modes are IR-active. The *gerade* (g) modes (5B_g + 5E_g) are Raman-active and the remaining modes (B_u) are silent.

In the Raman spectra of the substrate, Fig. 10(a), the most intense mode at 262 cm⁻¹ is assigned as A_g. The highest energy vibrations are observed at 424 (B_g) and 443 (E_g) cm⁻¹. These two are related to the Li motions. In LiYF₄, the internal binding of the [LiF₄]⁻ tetrahedra does not differ too much from other ionic forces in the crystal, so it is difficult to assign the internal and external vibrations [6,45].

For the **layer**, the polarized Raman properties are well preserved, Fig. 10(b). There are only minor shifts in the peak positions of the bands (within 1 cm⁻¹). This is in agreement with the Raman observations for stoichiometric LiYbF₄ [43,45]. The differences are revealed by examining the intense bands at 262 and 424 cm⁻¹. For both bands, the peak Raman intensity for the film decreases and the bands are broadened. Indeed, the FWHM of the 424 cm⁻¹ band increases from 11.3 cm⁻¹ (substrate) to 13.0 cm⁻¹ (film). Thus, we conclude that the anisotropic crystal structure of LiYF₄ is well preserved for the film, however, a certain reduction of its crystallinity with respect to the substrate is expected.

4.4. Optical spectroscopy

Tetragonal LiYF₄ crystals are optically uniaxial (the optical axis is parallel to the crystallographic *c*-axis) [5]. Thus, there exist two principal light polarizations, denoted as π ($\mathbf{E} \parallel \mathbf{c}$) and σ ($\mathbf{E} \perp \mathbf{c}$) with the corresponding refractive indices n_e and n_o . As $n_e > n_o$, this crystal is positive uniaxial.

For comparison, we studied a 10 at.% Yb:LiYF₄ bulk crystal.

The stimulated-emission (SE) cross-sections, σ_{SE} , were determined from the measured RT luminescence spectra calibrated for the spectral response of the set-up $W'_i(\lambda)$ using the Füchtbauer–Ladenburg (F-L) equation [46]:

$$\sigma_{SE}^i(\lambda) = \frac{\lambda^5}{8\pi \langle n \rangle^2 \tau_{rad} c} \frac{1}{3} \frac{W'_i(\lambda)}{\sum_{j=2\sigma, \pi} \int \lambda W'_j(\lambda) d\lambda}, \quad (2)$$

where, λ is the light wavelength, $\langle n \rangle$ is the mean refractive index at the emission wavelength $\langle \lambda_{lum} \rangle$, c is the speed of light, τ_{rad} is the radiative lifetime of the emitting state ²F_{5/2} and $i = \pi$ or σ is the light polarization. The polarization-averaging is performed as $1/3(2\sigma + \pi)$.

The results are shown in Fig. 11(a). For the LPE-grown film, the maximum σ_{SE} is 0.88×10^{-20} cm² at 993.9 nm in π -polarization. Another intense emission peak is observed at 1018.8 nm. These two peaks are assigned to the 0' \rightarrow 1, 2 and 0' \rightarrow 3 transitions, respectively (here, $s = 0 \dots 3$ and $p' = 0' \dots 2'$ indices number the Stark sub-levels of the ground-state and the excited-state, respectively, as each ^{2S+1}L_J multiplet is split into a total of $2J + 1$ sub-levels [47]). The total emission bandwidth (FWHM) $\Delta\lambda_{lum}$ is 41.2 nm (if analyzing the peaks separately, it

is ~ 18 nm for the most intense one). For σ -polarization, the SE cross-sections are lower, namely $\sigma_{SE} = 0.42 \times 10^{-20}$ cm² at 1018.1 nm.

The SE cross-sections for the film slightly differ from those for the highly-doped bulk crystal, Fig. 11(a). In particular, the emission band for the film is broadened, as expressed by larger $\Delta\lambda_{lum}$ value (compare with $\Delta\lambda_{lum} = 37.8$ nm for π -polarized light for the bulk crystal); the peak σ_{SE} value for the film is also slightly reduced. The broadening of the emission band is confirmed by calculation of the polarization-averaged integrated σ_{SE} value which is almost the same for both the bulk crystal and the layer. The reduction in intensity and broadening of the emission spectra for the films is in line with the results of Raman spectroscopy.

Previously for heavily doped (30 at.%) Yb:LiYF₄ single-crystals, Vannini *et al.* reported $\sigma_{SE} = 0.83$ (π) and 0.34 (σ) [10^{-20} cm²] at ~ 1018 nm as calculated by the F-L method [8] which agrees with our observations.

The RT absorption spectrum for the epitaxy was measured for light propagating orthogonal to the polished top-surface (i.e., along the *c*-axis). Thus, only the σ -polarization was available. The absorption cross-sections were calculated from the measured absorption coefficient, $\sigma_{abs} = \alpha_{abs}/N_{Yb}$, where $N_{Yb} = 2.75 \times 10^{21}$ cm⁻³ is the Yb³⁺ ion density. For another polarization (π), the absorption cross-sections were calculated using the corresponding σ_{SE} spectrum with the reciprocity method (RM) [48]:

$$\sigma_{SE}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_1}{Z_2} \exp\left(-\frac{hc/\lambda - E_{ZPL}}{kT}\right), \quad (3a)$$

$$Z_m = \sum_k g_k^m \exp(-E_k^m/kT). \quad (3b)$$

Here, h is the Planck constant, hc/λ is the photon energy (in cm⁻¹), k is the Boltzmann constant, T is the crystal temperature (RT), E_{ZPL} is the energy difference between the lowest lying Stark sub-levels of the two multiplets (the so-called zero-phonon line (ZPL), $0 \rightarrow 0'$), Z_m are the partition functions of the lower ($m = 1$) and upper ($m = 2$) Yb³⁺ multiplets, g_k^m is the degeneracy of the sub-level with the number k and the energy E_k^m measured from the lowest sub-level of each multiplet. Such a calculation could suffer from reabsorption losses affecting the measured luminescence spectra. However, this effect is greatly reduced in the studied films with a thickness of few tens of μ m.

The σ_{abs} spectra are shown in Fig. 11(b). For the Yb:LiYF₄ layers, the maximum $\sigma_{abs} = 0.67 \times 10^{-20}$ cm² at 959.7 nm in π -polarization and the FWHM of the absorption peak is 19.3 nm. For σ -polarization, the absorption cross-section at the same wavelength is lower ($\sigma_{abs} = 0.48 \times 10^{-20}$ cm²). This absorption line is due to the $0 \rightarrow 1'$ transition. As compared to those for the single-crystal, the absorption spectra experience a broadening which is especially evident for π -polarization.

The crystal-field splitting for Yb³⁺ multiplets in Yb:LiYF₄ epitaxial films was determined from LT absorption and emission spectra, Fig. 12. The spectra were interpreted accounting for the Raman spectra in order to exclude the vibronic sidebands (marked in Fig. 12 by " $h\nu$ "). The assignment of electronic transitions (between the Stark sub-levels) is according to [47,49]. The following set of Stark sub-levels was obtained: ${}^2F_{7/2} = (0, 216, 245, 482)$ cm⁻¹ and ${}^2F_{5/2} = (10295, 10420, 10554)$ cm⁻¹, cf. Fig. 13, yielding the partition functions $Z_1 = 1.820$ and $Z_2 =$

1.739 and the ratio $Z_1/Z_2 = 0.955$ (at room temperature). The determined Stark splitting is similar to that reported previously for bulk low-doped 0.5 at.% Yb:LiYF₄ crystal, namely ${}^2F_{7/2} = (0, 218, 248, 485) \text{ cm}^{-1}$ and ${}^2F_{5/2} = (10293, 10416, 10554) \text{ cm}^{-1}$ [47].

For Yb³⁺ ions, the luminescence at $\sim 1 \mu\text{m}$ spectrally overlaps with the absorption due to the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Thus, with increasing the Yb³⁺ doping level, the luminescence lifetime τ_{lum} measured for bulk samples can be elongated due to reabsorption (also called the radiation trapping effect). To avoid it, several approaches were proposed, such as the pinhole method [50] and the powder suspension method [51]. The first one is non-destructive and thus it was selected in the present work.

Other possible effects which may influence τ_{lum} are the concentration-quenching and the energy-migration to impurities both leading to the shortening of the lifetime. Note that for Yb³⁺ ions in LiYF₄, the non-radiative relaxation from the emitting state (${}^2F_{5/2}$) is negligible.

The RT luminescence decay curve for the 20 at.% Yb:LiYF₄ epitaxy is shown in Fig. 14(a), as measured using the smallest pinhole diameter d . It is clearly single-exponential in agreement with a single site for Yb³⁺ ions (symmetry: S₄, C.N. = VIII). The extrapolation of the linear fit of the dependence of τ_{lum} on d , Fig. 14(b), to the limit of $d \rightarrow 0$ gives an estimation for the radiation-trapping free lifetime $\tau_0 = 2.00 \pm 0.05 \text{ ms}$.

For comparison, we also studied two bulk Yb:LiYF₄ crystals doped with 2 at.% and 10 at.% Yb. The corresponding decay curves are shown in Fig. 14(a). For the crystal with 2 at.% Yb, $\tau_0 = 2.26 \text{ ms}$. Its only slightly decreased for the crystal with 10 at.% Yb (2.24 ms). Thus, the concentration-quenching owing to the energy migration for this range of doping concentrations is relatively weak. From this considerations, one can assume that $\tau_0 \approx \tau_{\text{rad}}$. The slightly lower τ_0 for the film than that for the single-crystal may originate from the varied crystal-field both due to the form of the material (thin crystalline film) and high Yb³⁺ doping.

Previously, De Loach *et al.* determined the luminescence lifetime for Yb:LiYF₄ crystals with a low doping concentration (the so-called intrinsic one) as $\tau_{\text{lum},0} = 2.16 \text{ ms}$ [52]; the authors also estimated the radiative lifetime by means of the RM as $\tau_{\text{rad}} = 2.27 \text{ ms}$. Yasukevich *et al.* evaluated $\tau_{\text{lum},0}$ for the isostructural Yb:LiLuF₄ crystal by the powder suspension method to be 1.94 ms [53]. Our work agrees well with these results.

5. Conclusions

Liquid Phase Epitaxy is a suitable method for the growth of highly-doped (20 at.% Yb, in the present work) Yb³⁺:LiYF₄ single-crystalline thin-films on undoped LiYF₄ substrates. In the present work, the maximum film thickness of 215 μm was reached; it can be varied by changing the dipping duration and the growth temperature. The grown films show a proper orientation, high crystallinity and low mosaicity, a uniform thickness over the substrate with the lack of cracks and well-preserved anisotropic emission properties of Yb³⁺ ions. A slight broadening of the emission spectrum of the Yb³⁺:LiYF₄ thin films (more evident for the π -polarization) is detected as compared to the corresponding single-crystals which may be favorable for laser applications, especially for mode-locked lasers. A weak concentration-quenching is observed as confirmed by the radiation trapping free upper laser level lifetime, $\sim 2.0 \text{ ms}$, indicating weak unwanted energy-transfer to impurities.

The developed epitaxies are attractive for thin-disk laser applications. For a 100 μm -thick film, the estimated small-signal single-bounce (double-pass) pump absorption at 960 nm is $\sim 23\%$. This parameter can be further increased by growing films with even higher doping levels (30–50 at.% Yb); however, this may be accompanied by stronger effect of energy-migration on the upper laser level lifetime. Still, the lattice mismatch for such Yb^{3+} doping levels is expected to be low. Another alternative is the use of (100) oriented LiYF_4 substrates. This will allow one to access another light polarization (π) corresponding to higher transition cross-sections both in absorption and emission. However, a possible challenge here is the anisotropy of the thermal conductivity and thermal expansion in the film plane.

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Figure 1. Phase diagram of the LiF – YF₃ binary system (after [34]), *red solid line* marks LiYF₄ solid phase, *blue dashed line* indicates the composition selected for the LPE growth.

Figure 2. (a) Photograph of an as-grown undoped LiYF₄ boule used for preparing the substrates for LPE. The growth direction is along the [001] axis; (b) Photograph of the Yb:LiYF₄ / LiYF₄ epitaxy directly after the LPE growth process. The substrate is oriented along the (001) plane.

Figure 3. A fragment of the phase diagram of the LiF – YF₃ binary system relevant for the LPE growth experiments, after Thoma *et al.* [34] and Rogin *et al.* [19]. *Red squares* – liquidus temperatures, *red circles* – apparent onset of crystallization (both after [19]), *blue square* – liquidus temperature, *blue asterisk* – growth temperature (both - this work). *Blue dashed line* – the selected bath composition.

Figure 4. Observation of the raw surface of a LPE-grown Yb:LiYF₄ film (top view) using a confocal optical microscope. Reflection mode, bright field, the objective magnification is 20×, $\lambda = 405$ nm.

Figure 5. Surface roughness plot of the raw surface of a LPE-grown Yb:LiYF₄ film, obtained using a confocal optical microscope. *Black lines* indicate the range of root mean square (r.m.s.) deviation, *inset* - the corresponding topography map, *while line* – the analyzed direction. Reflection mode, $\lambda = 405$ nm.

Figure 6. Confocal microscope images of the polished end-facet of the Yb:LiYF₄ / LiYF₄ epitaxy: (a) polarized light, P || [001], (b) a close look on the substrate / layer interface in crossed polarizers (P || [001], A || [100]). Transmission mode, the objective is (a) 20×, N.A. = 0.75, (b) 50×, N.A. = 0.95, $\lambda = 405$ nm.

Figure 7. Single-crystal X-ray diffraction (XRD) study of the 20 at.% Yb:LiYF₄ / LiYF₄ epitaxy: (a) single-crystal XRD pattern of the film; (b) theoretical XRD pattern of LiYF₄ (ICSD card No. 81-2254); (c) a close look on the (008) reflection. *Numbers* indicate the Miller's indices, (*hkl*).

Figure 8. (a) Reciprocal space mapping of the (103) node for the Yb:LiYF₄ layer; (b) the rocking curve of this node.

Figure 9. Typical EDX spectrum of the 20 at.% Yb:LiYF₄ film grown by the LPE method (top raw surface).

Figure 10. Polarized Raman spectra of the undoped LiYF₄ substrate and the LPE-grown 20 at.% Yb:LiYF₄ layer in the $a(ij)a$, $i, j = \pi, \sigma$, configuration (Porto's notations), *numbers* indicate Raman frequencies in cm⁻¹, FWHM – full width at half maximum, $\lambda_{\text{exc}} = 488$ nm.

Figure 11. (a) Stimulated-emission (SE), σ_{SE} , and (b) absorption, σ_{abs} , cross-section spectra for the ${}^2F_{5/2} \leftrightarrow {}^2F_{7/2}$ Yb³⁺ transition in 20 at.% Yb:LiYF₄ LPE-grown layer in π and σ polarizations; the spectra for the bulk 10 at.% Yb:LiYF₄ crystal are given for comparison. σ_{SE} : calculation using Eq. (2), the F-L formula.

Figure 12. Low-temperature (LT, 12 K) absorption and luminescence spectra for the 20 at.% Yb:LiYF₄ LPE-grown layer in σ polarization, $\lambda_{\text{exc}} = 933$ nm. “+” mark the electronic transitions, “ $h\nu$ ” – the vibronic sidebands. The spectral resolution is 0.2 nm.

Figure 13. Crystal-field splitting of Yb³⁺ multiplets in highly-doped (20 at.%) Yb:LiYF₄ epitaxial films, the *arrows* indicate the electronic transitions in absorption and emission at 12 K.

Figure 14. (a) Luminescence decay curve for the 20 at.% Yb:LiYF₄ LPE-grown film (a semi-log plot): *black curve* – experimental data, *green line* – single-exponential fit, the data for 2 at.% Yb and 10 at.% Yb:LiYF₄ bulk crystals are given for comparison, all the curves are measured using the smallest pinhole; (b) evaluation of the radiation trapping-free lifetime τ_0 for the epitaxy by the pinhole method. $\lambda_{\text{exc}} = 960$ nm, $\lambda_{\text{lum}} = 1030$ nm.

