

Rare-earth doped fluoride thin films grown by pulsed laser deposition as possible new optical active materials

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The influence of the LiYF₄ substrates temperature on the pulsed laser deposition growth of Nd³⁺ doped LiYF₄ films is investigated with spectroscopic techniques and scanning electro microscopy analysis. The preliminary results of the first Tm³⁺ doped LiYF₄ film realized with the same procedure are also reported.

1 Introduction

Fluorides crystals doped with rare earth (RE) ions have been studied for decades to realize efficient laser sources in the IR. The production of crystalline RE doped fluorides in film shape would enhance the excellent optical properties of these materials. The goal of this research is the pulsed laser deposition (PLD) of crystalline RE-doped fluorides thin films for their possible applications in the field of photonic devices. The experimental apparatus was described in detail in [1]. The depositions were performed in a UHV chamber filled with 1 Pa of He controlled atmosphere by ablating LiYF₄ (YLF) mono-crystal targets doped either with Nd³⁺ or with Tm³⁺ ions (1.5% and 4% atomic concentration respectively) with 10 Hz repetition rate, 355 nm laser pulses. Some preliminary experiments on the expansion dynamic of the plume produced in the pulsed laser ablation of YLF mono-crystals, proved that the use of a controlled atmosphere of He in the deposition chamber was essential to slow down the Li atoms and to favour its stickiness to the substrate [1]. The ablation took place for 20 minutes with 10 J/cm² laser fluency for all the depositions. The temperature of the YLF substrates was either 350°C followed by post-annealing at 650°C for 36 hours or 650°C without any post annealing. In the effort to reduce the effects of the high fluoride crystals thermal shock sensitivity, the substrates temperature during their heating/cooling cycles were increased/decreased linearly with 1°C/min rate. The presence of the rare earth ions in the film was checked by comparing the film fluorescence spectrum profile following laser excitation at 355 nm with the corresponding one from the target taken in similar experimental conditions. The Nd³⁺ doped fluoride films optical characteristics were investigated by analyzing the fluorescence profiles spectra, either unpolarized or polarized with E|| or E⊥ to the c-axis of the YLF substrate, corresponding to the Nd³⁺ ⁴F_{3/2} → ⁴I_{9/2} and ⁴F_{3/2} → ⁴I_{11/2} manifolds transitions (900 nm and 1050 nm ranges respectively) following the diode laser excitation of the Nd³⁺ ⁴I_{9/2} → ⁴F_{5/2} + ⁴H_{9/2} fundamental

transition at 806.6 nm and by comparing them with the corresponding ones recorded from the targets, unpolarized or polarized with E|| or E⊥ to its c-axis, in the same experimental conditions. In the same way the Tm³⁺ doped fluoride films optical characteristics were analyzed by comparing the fluorescence profiles corresponding to the Tm³⁺ ³F₄ → ³H₆ and ³H₄ → ³F₄ manifolds transitions (1.8 μm and 1.45 μm ranges respectively) following diode laser excitation of Tm³⁺ ³H₆ → ³H₄ manifolds transition at 792.0 nm with the corresponding ones recorded from the targets in the same experimental conditions. The lifetimes of the Nd³⁺ ⁴F_{3/2} manifold and of the Tm³⁺ ³F₄ manifold in the corresponding films were also measured and compared with those obtained in the correspondent targets in the same experimental conditions. The quality of the films surfaces was checked with a scanning electron microscope (SEM)

2 Results

According to the indication reported in the literature, high optical quality thin films should be deposited by keeping the substrate temperature slightly lower than half of its melting point [2]. For this reason in the first deposition, performed by ablating the Nd³⁺ doped YLF (Nd³⁺:YLF) mono-crystal, the substrate temperature was set at 350°C. After checking the presence of the dopant ion in the deposition, the film undergo the optical characterization. The pretty good superposition, both in the 900 nm and in the 1050 nm regions, of the LIF spectra taken from different point of the film surface indicated the presence of an homogeneous deposition. At the same time the good overlap in both the two regions between the LIF spectra taken from the target and the corresponding ones taken from any point of the film surface, which showed the presence of well resolved lines on a small pedestal, confirmed that the deposition was a crystalline Nd³⁺:YLF film. The comparison between the polarized film fluorescence spectra in the regions mentioned above and the corresponding target ones gave indication that no orientation

was transferred from the substrate to the film. The time resolved $\text{Nd}^{3+} \ ^4\text{F}_{3/2}$ fluorescence recorded at several points of the film surface always manifested a single exponential decay. The $^4\text{F}_{3/2}$ manifold lifetime measured in the film varied randomly from point to point on the film surface within 4% around the mean value $432 \ \mu\text{s}$ which is lower than the one measured in the target ($464 \pm 2 \ \mu\text{s}$) testifying that in the film the Nd^{3+} ion concentration was, on an average, slightly higher than in the bulk as a higher Nd^{3+} ion concentration corresponds to a lower $^4\text{F}_{3/2}$ manifold lifetime and vice versa [1]. A SEM photo of such Nd^{3+} :YLF film is shown in Fig. 1a. The evidence of splashed materials on the deposition is an indication of a low quality film.

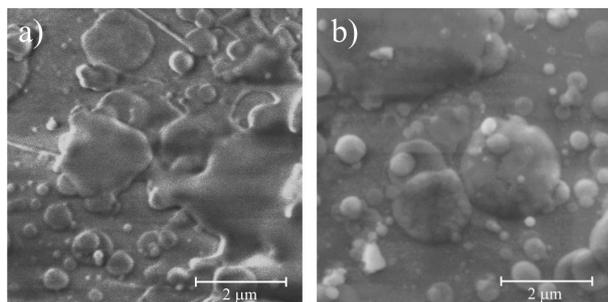


Fig. 1 SEM picture of the Nd^{3+} doped YLF film deposited in the presence of 1 Pa of He on: a) an YLF substrate kept at $350 \text{ }^\circ\text{C}$, b) an YLF substrate kept at $650 \text{ }^\circ\text{C}$ [1].

The film was post-annealed in the effort to enhance its quality but the results obtained were not promising as a deterioration of the film optical properties and of its surface quality was observed. On the contrary the film deposited at $650 \text{ }^\circ\text{C}$ without any post-annealing resulted with a good surface morphology with few microns size particulates not affected by splashing scattered on a core uniform background. Fig. 1b, already reported in [1], show the SEM picture of such film surface. The optical analysis showed an homogeneous crystalline Nd^{3+} :YLF film already suitable for its use as active medium in $1 \ \mu\text{m}$ range with a large degree of order and with some features attributed to a substantial transfer of the YLF substrate orientation to the film. Also the Nd^{3+} ion target concentration was transferred from the target to the film as testified by the same Nd^{3+} ion $^4\text{F}_{3/2}$ manifold lifetime measured in the film and in the target. On the basis of these results the first Tm^{3+} doped fluoride film, deposited by ablating the Tm^{3+} doped YLF (Tm^{3+} :YLF) mono-crystal, was grown by using an YLF mono-crystal substrate kept at $650 \text{ }^\circ\text{C}$ in presence of 1 Pa of He in the chamber. After the preliminary analysis to check the presence of the Tm^{3+} dopant ions, the deposition was characterized by comparing the Tm^{3+} :YLF target unpolarized, normalized fluorescence spectra in the $1.8 \ \mu\text{m}$ and $1.45 \ \mu\text{m}$ ranges with those of the film taken from different points of its surface in the same experimental conditions. The result, plotted in Fig. 2 for any of such points,

showed a good matching between the target and the film spectral profiles indicating a crystalline Tm^{3+} :YLF growth.

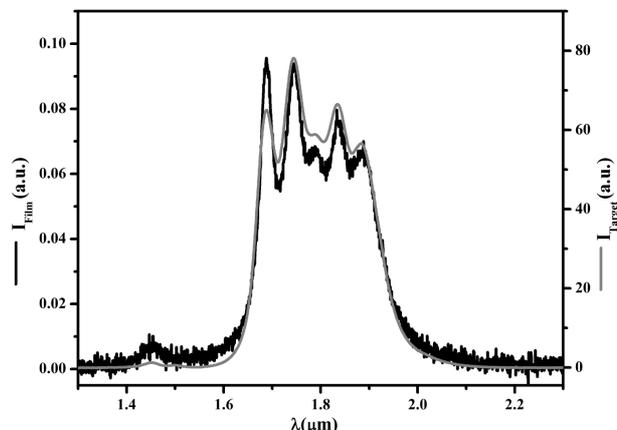


Fig. 2 Portion of the LIF spectrum following 792.0 nm diode laser excitation recorded from the Tm^{3+} doped YLF film (black line, left scale) and from the target (grey line, right scale).

Besides the Tm^{3+} ion $^3\text{F}_4$ lifetime measured in the film at different points ($14 \pm 2 \text{ ms}$) was the same, within the errors, of that measured in the target ($15.5 \pm 0.5 \text{ ms}$). To estimate the Tm^{3+} ion concentration in the film the ratio between the $\text{Tm}^{3+} \ ^3\text{F}_4 \rightarrow ^3\text{H}_6$ and $^3\text{H}_4 \rightarrow ^3\text{F}_4$ manifolds intensities was measured and compared to the values reported in [3] where the intensities of these two manifolds transitions are analyzed versus the dopant ion concentration in bulk YLF crystals. According to this analysis the Tm^{3+} ion concentration in the film could be located between 2% and 3%. This means that the target concentration was not transferred to the film.

3 Conclusions

A Nd^{3+} :YLF film with remarkable optical and morphological properties was deposited on an YLF substrate kept at $650 \text{ }^\circ\text{C}$ by ablating a Nd^{3+} :YLF mono-crystal with 10 J/cm^2 laser pulses in the presence of 1 Pa of He. The first Tm^{3+} :YLF crystalline film deposition on YLF substrate was accomplished.

References

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