PLD-grown Yb-doped Sesquioxide Films on Sapphire and Quartz Substrates

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Abstract. This paper focuses on the fabrication and characterization of crystalline Yb-doped sesquioxide films (Yb$_2$O$_3$, Yb:Lu$_2$O$_3$, Yb:Sc$_2$O$_3$) grown by pulsed laser deposition on single crystal sapphire (α-Al$_2$O$_3$) and quartz (α-SiO$_2$) substrates as well as on lutetia (Lu$_2$O$_3$) and scandia (Sc$_2$O$_3$) substrates. Such ytterbium doped active films can be promising for use in a thin-disk laser setup. X-Ray diffraction measurements show that the films grow highly textured along <111> direction. The ω-scan (rocking curve) shows deviation of the crystallite orientation ~4° in case of Lu$_2$O$_3$ and Yb$_2$O$_3$ films and <1° for Sc$_2$O$_3$ films. Yb$_2$O$_3$ films reveal no luminescence at room temperature and the well known Yb$^{3+}$ emission in the 975-980 nm region (zero-phonon line) can only be observed at temperatures below 20 K. A similar effect is observed in a bulk Yb$_2$O$_3$ crystal. Ytterbium emission and excitation spectra measured at room temperature for Yb(5%):Lu$_2$O$_3$ and Yb(4%):Sc$_2$O$_3$ films resemble those of the bulk crystal very closely. Luminescence decay lifetimes are also comparable to those measured in a bulk crystal. This indicates a high quantum efficiency of the Yb$^{3+}$-emission and allows application of such films as active media for thin disk lasers.

1. Introduction
After the invention of the thin-disk laser set-up [1], Yb-doped oxide materials have attracted increasing attention. This set-up is especially suitable for high power lasers, as it reduces the influence of the thermal effects on the lasing characteristics. Yb-doped materials in comparison with, for example, widely used Nd-doped materials allow to decrease the heat dissipation due to a very small quantum defect, so even further reducing thermally induced problems. The very simple level structure of the Yb$^{3+}$-ion also eliminates the possibility of the depopulation of the upper laser level due to cross-relaxation and up-conversion processes. This is an important advantage at high concentration levels and pump rates used in the thin-disk laser. Using this set-up, for example, a mode-locked Yb:YAG thin-disk laser has been used recently to demonstrate a multi-watt RGB laser source [2]. Apart from the classical laser host material YAG, the sesquioxides Sc$_2$O$_3$, Y$_2$O$_3$, and Lu$_2$O$_3$ are very promising host materials for high-power laser applications [3], mainly due to their high thermal conductivity and high absorption and emission cross-sections of trivalent rare-earth ions in these materials. Effective mode-locked laser operation has been also demonstrated recently using Yb:Sc$_2$O$_3$ [4] and Yb:Lu$_2$O$_3$ [5] single crystals.

In order to improve the heat flow in any thin-disk laser, even thinner crystal disks with higher dopant concentrations are required. Nowadays the active crystal can be as thin as 100 µm. Hence some
difficulties may arise during fabrication and handling of such thin crystals as well as during bonding them onto a heat sink or an undoped substrate. A good alternative could be deposition of active material directly on an undoped substrate. Following this route, Ubizskii et al. produced highly Yb-doped epitaxial YAG films by liquid-phase epitaxy which subsequently showed continuous-wave laser action in a thin-disk set-up [6].

In this paper we present the results on growth and characterization of highly Yb-doped sesquioxide films produced by pulsed laser deposition (PLD). We believe that the PLD technique is a promising method for the production of highly Yb-doped films, as the nature of the process eliminates the possibility that the grown films can be contaminated by impurities from the flux (like in case of liquid-phase epitaxy) or from the crucible material (in case of bulk crystal growth). During the PLD process the material is transferred directly from a target onto a substrate in vacuum or in a suitable atmosphere. Due to high energy migration rates at high Yb densities even low concentrations of impurities can lead to significant quenching of the ytterbium luminescence [7].

2. Film Fabrication
The pulsed laser deposition (PLD) technique has been used to deposit sesquioxide films. A KrF excimer laser operating at 248 nm, a repetition rate of 31 Hz and with pulse duration of 25 ns was used. The laser beam was focused onto a ceramic target to achieve radiation densities of 2.7-4 J/cm². The target was produced by pressing and sintering (at 1600°C) of the source materials in form of powders mixed in the desired stoichiometry. The background atmosphere during the process was oxygen at 1 Pa. During the deposition the substrates were heated up to 700°C. The target to substrate distance was 9 cm. The Yb₂O₃ films were deposited on (0001)-oriented single-crystal sapphire (α-Al₂O₃) and quartz (α-SiO₂) substrates with the thicknesses ranging from 20 nm to 500 nm. The Yb:Lu₂O₃ and Yb:Sc₂O₃ films were deposited also on (0001)-oriented α-Al₂O₃ substrates and homoepitaxially on (111)-oriented single-crystal Lu₂O₃ and Sc₂O₃ substrates, respectively. The film thicknesses were in the range of 3.5-4 µm in this case. The intensity oscillation of a red laser diode beam reflected from the substrate surface was used to control the film thickness during the deposition.

3. Characterization of Yb₂O₃ Films
First Yb₂O₃ films have been produced, as this would result in the thinnest possible active medium design for thin-disk laser. Crystalline quality of the deposited film influences the spectroscopic properties of the film. Hence, the structure of the films was investigated by X-Ray diffractometry (XRD), which revealed that the films are highly textured along the <111>-direction. The {111}-reflex is getting stronger with the thickness of the films, but no evidence of other orientations was observed either on early stages of the growth or later. Figure 1 shows the diffraction patterns for the films deposited on sapphire substrates; the same picture is observed in the case of quartz substrates.

![Figure 1. X-Ray diffraction patterns of 20, 100 and 500 nm thick Yb₂O₃ films deposited on α-Al₂O₃ substrates.](image1)

![Figure 2. Luminescence spectrum of a 500 nm thick Yb₂O₃ PLD-film on a quartz substrate (λₑₓ=220 nm, T=9 K).](image2)
Table 1. X-Ray diffraction measurements results.

| Sample                      | \{222\}-reflex width (deg) | Crystallite size (nm) | \(\Omega\)-scan width (deg) |
|-----------------------------|-----------------------------|-----------------------|-----------------------------|
| Lu₂O₃ bulk crystal          | 0.11                        | -                     | 0.12                        |
| Yb:Lu₂O₃ film on \(\alpha\)-Al₂O₃ | 0.37                        | 26                    | 3.52                        |
| Yb:Lu₂O₃ film on Lu₂O₃      | 0.13                        | 122                   | 0.50                        |
| Sc₂O₃ bulk crystal          | 0.10                        | -                     | 0.11                        |
| Yb:Sc₂O₃ film on \(\alpha\)-Al₂O₃ | 0.16                        | 77                    | 0.83                        |
| Yb:Sc₂O₃ film on Sc₂O₃      | 0.14                        | 97                    | 0.12                        |

Emission spectra under 220 nm excitation show the well-known Yb\(^{3+}\) emission in the 975 nm-990 nm spectral region (zero-phonon line) at temperatures below 20 K (see Figure 2.). Above 20K the intensity of the Yb\(^{3+}\) emission decreases rapidly. A similar effect is observed in a Yb₂O₃ bulk crystal that was used as a reference. This is caused by very fast energy migration at high ytterbium concentrations, which ends up at an impurity or a defect resulting in a nonradiative deexcitation. It is believed that impurities in the ppm range already present in the source materials cause this strong quenching behavior. Therefore films with lower Yb-concentrations have been produced in order to reduce the energy migration rate.

4. Characterization of Yb:Lu₂O₃ and Yb:Sc₂O₃ Films

Lutetia, scandia, and ytterbia have the same cubic C-type bixbyite crystal structure with the lattice constants 10.39Å, 9.85Å, and 10.43Å, respectively. Thus lutetia can be doped with any concentration of ytterbium without distorting the crystal structure. Since the lutetium- and ytterbium-ions have a similar mass, the intrinsically high thermal conductivity of lutetia does not degrade at high doping levels. This can be beneficial, especially in the case of high power laser applications. Due to the difference in lattice constants, scandia may have some limits in accepting Yb-ions without distorting the crystal structure. However scandia is still an interesting host, since Yb\(^{3+}\)-dopant has the highest emission and absorption cross-sections in comparison with the other sesquioxides or with the garnets.

4.1. X-Ray Diffraction

The Yb:Lu₂O₃ and Yb:Sc₂O₃ films as well as the Yb₂O₃ films grow highly textured in <111>-orientation. Using the Scherrer equation, the crystallite size was estimated through the width of the diffraction peaks (see table 1). The measurements have been carried out using an X-Ray diffractometer with Bragg-Brentano geometry and Cu-K\(\alpha\)₁ radiation. The resolution was 0.018°. An \(\omega\)-scan (rocking curve) has been performed to determine the deviation in the crystallite orientation.

4.2. Emission and Excitation Spectroscopy

Both, emission and excitation spectra of Yb\(^{3+}\) in the lutetia and scandia films resemble closely the spectra of the corresponding bulk crystals (see figure 3). These spectra were measured using a Ti:Sapphire laser as an excitation source. The peak emission cross-sections of Yb\(^{3+}\) (calculated using Füchtbauer-Ladenburg equation) appear to be somewhat smaller in the PLD-films in comparison with the bulk crystals.

Table 2. Room temperature fluorescence lifetimes of the \(^2\)F₅/₂ multiplet of Yb\(^{3+}\).

| Host                      | Yb-density \((10^{21} \text{ cm}^3)\) | \(\tau\) (µs) |
|---------------------------|--------------------------------------|--------------|
| Lu₂O₃ film on \(\alpha\)-Al₂O₃ | 1.43 (5%)                            | 550          |
| Lu₂O₃ film on Lu₂O₃       | 1.43 (5%)                            | 420          |
| Sc₂O₃ film on \(\alpha\)-Al₂O₃ | 1.34 (4%)                            | 500          |
| Sc₂O₃ film on Sc₂O₃      | 1.34 (4%)                            | 573          |
| Lu₂O₃ crystal            | 0.13 (0.46%) / 2.81 (10%)            | 820 / 530 [8]|
| Sc₂O₃ crystal            | 0.1 (0.3%) / 3.36 (10%)              | 730 / 776 [8]|
The fluorescence decay lifetimes of the $^2F_{5/2}$ multiplet of Yb$^{3+}$-ion have been measured at room temperature using pulsed laser excitation ($\lambda_{\text{ex}}=940-950\,\text{nm}$, $\lambda_{\text{em}}=977-978\,\text{nm}$). The results are presented in table 2. It can be seen that lifetimes are only slightly reduced compared with the bulk crystals. This indicates the high quantum efficiency of the Yb$^{3+}$ emission in the grown films.

5. Conclusions
Ytterbia as well as Yb-doped lutetia and scandia films have been produced by pulsed laser deposition. All films were grown highly textured in $\{111\}$-direction. The ytterbia films show no luminescence at room temperature. The lutetia and scandia films doped with ytterbium on the contrary reveal spectroscopic properties close to the corresponding bulk crystal. This enables application of such films as active medium in a thin disk laser.

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References
[1] Giesen A, Hügel H, Voss A, Wittig K, Brauch U and Opower H 1994 Appl. Phys. B 58 365
[2] Brunner F, Innerhofer E, Marchese S V, Südmeier T, Paschotta R, Usami T, Ito H, Kurimura S, Kitamura K, Arisholm G and Keller U 2004 Opt. Lett. 29 1921
[3] Petermann K, Fornasiero L, Mix E and Peters V 2002 Opt. Mater. 19 67-71
[4] Klopp P, Petrov V, Grieben U, Petermann K, Peters V and Erbert G 2004 Opt. Lett. 29 391-3
[5] Grieben U, Petrov V, Petermann K and Peters V 2004 Opt. Express 12 3125-30
[6] Ubizskii S B, Matkovskii A O, Melnyk S S, Syvorotka I M, Müller V, Peters V, Petermann K, Beyerl A and Giesen A 2004 Phys. Status Solidi A 201 791-7
[7] Petermann K, Fagundes-Peters D, Johannsen J, Mond M, Peters V, Romero J J, Kutovoi S, Speiser J and Giesen A 2005 J. Cryst. Growth 275 135-40
[8] Peters V 2001 Growth and Spectroscopy of Ytterbium-Doped Sesquioxides (PhD Thesis) (University of Hamburg, Hamburg, Germany)