Compositional tuning of yttrium iron garnet film properties by multi-beam pulsed laser deposition

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Abstract

We report an investigation of the effects of variation of composition on the properties of yttrium iron garnet films grown on yttrium aluminium garnet substrates by multi-beam pulsed laser deposition. The ferromagnetic resonance linewidth is used as a quality factor: a significant variation is noticed from changing composition, with an experimentally observed optimum at Y₃.₅Fe₄.₅O₁₂.

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1. Introduction

Yttrium iron garnet (Y₃Fe₅O₁₂), often abbreviated as YIG, is a cubic crystal featuring ferromagnetic and magneto-optic properties, which can be used in different application fields, ranging from optical communications, where Faraday and Kerr effects in YIG can be exploited for optical isolators and rotators [1], to microwave, where phase shifters, circulators and filters can be made thanks to the magnetic properties and the narrow ferromagnetic resonance (FMR) linewidth of YIG at GHz frequencies [2].

YIG and magneto-optic garnet films can be grown by several deposition techniques, such as liquid phase epitaxy (LPE) [3], sputtering [4] and pulsed laser deposition (PLD). Although LPE allows the growth of very high-quality YIG layers, PLD has proven to be a relatively cheap, fast and versatile deposition method for several crystals, including garnets [5]: moreover it is possible to grow thermodynamically unstable materials, such as Bi:YIG and BiFeO₃ (Bismuth Iron Garnet, Bi₃Fe₅O₁₂), which cannot be grown by LPE [6].

PLD-grown YIG films on GGG (Gadolinium Gallium Garnet, Gd₃Ga₅O₁₂) substrates with an FMR linewidth comparable to that of LPE-deposited YIG films on GGG [7] have recently been reported in [8]. More recently we have reported optimised PLD of YIG on YAG (Y₃Al₅O₁₂) substrates, which are cheaper than GGG and seem to induce better magnetic properties in the overgrown YIG layers [9]. However, single-beam PLD from a stoichiometric target usually leads to films that are iron (Fe) deficient, as previously reported in the literature [8] and confirmed in our experiments [9]. For this reason we have studied the composition and the effects of stoichiometric variation on the resultant properties of PLD-grown YIG films, whose yttrium (Y) and Fe concentration is varied by co-ablation of two separate targets of polycrystalline YIG with either an yttria (Y₂O₃) or an iron oxide (Fe₂O₃) target.

2. Experimental techniques

2.1. Fabrication

All YIG films were grown on 10 × 10 mm² × 1 mm-thick (100)-oriented YAG substrates in our multi-beam, multi-target (‘multi-PLD’ from now on) deposition chamber, described in detail in [10]. Up to three targets can be ablated with a KrF excimer laser, a Coherent COMPexPro 102F operating at λ = 248 nm (20 ns pulse duration), and two frequency-quadrupled Nd:YAG lasers, Continuum Surelite II-10 operating at λ = 266 nm (~5 ns pulse duration) with a fixed pulse repetition rate of 10 Hz. A Synrad J48-2W carbon dioxide (CO₂) laser operating at 10.6 μm (max. output power: 40 W) was used to heat the substrate during the deposition: the laser beam was raster-scanned on the back-side of the substrate, as described in [10]. The substrates were continuously rotated during the depositions to improve thickness uniformity. The targets were rotated and tilted continuously, in order to improve film homogeneity and ensure a uniform usage of the target surface. The targets used were a polycrystalline YIG target and sintered Y₂O₃ and Fe₂O₃ targets. The vacuum chamber was pumped down to a base...
pressure at least two orders of magnitude lower than the deposition value (i.e. $p_{\text{base}} < 0.068 \text{ Pa}$), then filled with $\text{O}_2$.

The substrate temperature was set to the maximum value possible with this system, i.e. $T \approx 1150 \text{ K}$, which is ~100 K lower than the optimum value we found for YIG growth on YAG (~1250 K) in our single-beam single-target PLD system. The duration of each deposition was set at ~72,000 laser pulses, unless otherwise stated.

Before starting the multi-PLD experiments, preliminary YIG depositions were performed in the multi-PLD chamber, in order to fine-tune the growth conditions of pure YIG and compare ablation of the YIG targets were performed in the multi-PLD chamber, in order to set at ~72,000 laser pulses, unless otherwise stated.

### 2.2. Characterisation

The thickness of the YIG films was measured by a stylus profiler (KLA-Tencor P-16). Surface morphology was determined by optical microscopy and scanning electron microscope (Zeiss EVO 50), normally operated in variable pressure mode, with a 100 μm aperture, a voltage of 20 kV and a probe current of 2 nA. The composition was checked by energy-dispersive X-ray spectroscopy or EDX (Oxford Instruments INCA PentaFETx3), with a cobalt stub used for energy calibration before measurements and the stoichiometric YIG target and blank YAG substrates used for reference; oxygen concentration was assumed constant (i.e. $\text{O}_2$) then filled with $\text{O}_2$.

Transmission spectra were taken with the Varian Cary 500 Scan spectrophotometer. The broadband FMR spectroscopy was performed as described in [9,11], using a vector network analyser (HP E5071C) FMR technique (VNA-FMR), which allows FMR in the frequency range of 300 kHz to 20 GHz: the FMR linewidth of YIG films was measured with an accuracy of the order of 0.1 mT. The measurements were performed at a fixed excitation frequency of 6 GHz to ensure saturation of the sample within the applied field range available. DC magnetic fields of up to 0.6 T were available. For the characterisation of each film the applied magnetic field is swept while monitoring the scattering matrix parameter $S_{21}$ (microwave absorption). This method reveals sub–mT features or ‘satellites’ of the main FMR mode. These modes can have several origins, such as (i) an increase in the intrinsic linewidth of the film by a process known as inhomogeneous broadening, as VNA-FMR excites only a very narrow frequency in time, and (ii) spin-waves and unresolved magnetostatic (dipolar) modes [12,13]. These arise from the geometry of the $h_{\text{RF}}$ (microwave excitation field) with respect to the applied magnetic field $H$ [14]. Both of these would contribute to obscuring the true intrinsic linewidth measurement for the film.

### 3. Results and discussion

#### 3.1. Comparison of YIG ablation with different lasers

In this section we compare the ablation of a polycrystalline YIG target with two different lasers: a KrF excimer laser ($\lambda = 248 \text{ nm}$) and a frequency-quadrupled Nd:YAG laser ($\lambda = 266 \text{ nm}$). We also discuss the optimisation of YIG growth in the multi-PLD chamber.

#### 3.1.1. Ablation of YIG with the KrF laser

First of all, a deposition test (sample E1) was performed under the same conditions as Y20, the best YIG film grown on YAG in our single-beam single-target (“single-PLD”) system [9], except for substrate temperature ($T \approx 1150 \text{ K}$), which is limited by the heating method in our multi-PLD system: KrF laser fluence was set at $f_{\text{KrF}} \approx 3 \text{ cm}^2/\text{J}$, pulse repetition rate at $r_{\text{RF}} \approx 20 \text{ Hz}$, oxygen pressure at $P_{\text{O}_2} \approx 1 \text{ Pa}$ and target-substrate distance $d \approx 6 \text{ cm}$. As shown in Table 2, there are only two big differences between Y20 and E1: film thickness and the FMR linewidth ($\Delta H$). The lower film thickness in E1, compared to Y20, is due to the continuous tilting of the targets during their ablation and to the target configuration in the multi-PLD chamber, where the three target holders are symmetrically off-axis with respect to the substrate, thus causing a lower deposition rate, compared to film growth in the single-PLD system with the on-axis configuration. The FMR linewidth is almost twice the value of Y20, most likely because of the lower substrate temperature: in fact, the FMR linewidth of E1 is roughly the same as that of Y11 ($\Delta H \approx 2.9 \text{ mT}$), grown under similar conditions ($T \approx 1150 \text{ K}$, $d = 6 \text{ cm}$, $P_{\text{O}_2} \approx 3.3 \text{ Pa}$) [9].

### Table 1

Summary table of targets and lasers used, as described in each section of this paper.

<table>
<thead>
<tr>
<th>Section</th>
<th>Targets</th>
<th>YIG</th>
<th>Fe$_2$O$_3$</th>
<th>Y$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.1</td>
<td>KrF</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Nd:YAG</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Nd:YAG</td>
<td>KrF</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.2.2</td>
<td>KrF</td>
<td>Nd:YAG</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>3.3</td>
<td>Nd:YAG</td>
<td>–</td>
<td>KrF</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 2

Deposition conditions and results of samples E1–E4. Sample Y20 is shown as a reference. “Conc.” stands for concentration.

<table>
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<tr>
<th></th>
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<th></th>
<th></th>
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<td>6</td>
<td>2.4</td>
<td>3.55</td>
<td>4.45</td>
<td>1.25</td>
<td>1.8</td>
<td>Yellow</td>
</tr>
<tr>
<td>E1</td>
<td>1</td>
<td>6</td>
<td>1.4</td>
<td>3.54</td>
<td>4.46</td>
<td>1.26</td>
<td>3.0</td>
<td>Yellow</td>
</tr>
<tr>
<td>E2</td>
<td>1</td>
<td>4</td>
<td>3.3</td>
<td>3.36</td>
<td>4.64</td>
<td>1.38</td>
<td>7.2</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>E3</td>
<td>3.4</td>
<td>4</td>
<td>2.5</td>
<td>3.52</td>
<td>4.48</td>
<td>1.27</td>
<td>3.9</td>
<td>Yellow</td>
</tr>
<tr>
<td>E4</td>
<td>6.8</td>
<td>4</td>
<td>2</td>
<td>3.47</td>
<td>4.53</td>
<td>1.31</td>
<td>6.6</td>
<td>Yellow</td>
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Table 3
Deposition conditions and results of samples N1–N4. Sample Y20 is shown as a reference.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
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</thead>
<tbody>
<tr>
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<td>1</td>
<td>6</td>
<td>2.4</td>
<td>3.55</td>
<td>4.45</td>
<td>1.25</td>
<td>1.8</td>
<td>Yellow</td>
</tr>
<tr>
<td>N1</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>3.46</td>
<td>4.54</td>
<td>1.31</td>
<td>4.3</td>
<td>Yellow</td>
</tr>
<tr>
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<td>4.67</td>
<td>1.4</td>
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</tr>
<tr>
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<td>4</td>
<td>2</td>
<td>3.37</td>
<td>4.63</td>
<td>1.37</td>
<td>4.7</td>
<td>Yellow</td>
</tr>
<tr>
<td>N4</td>
<td>6.8</td>
<td>4</td>
<td>1.2</td>
<td>3.38</td>
<td>4.62</td>
<td>1.37</td>
<td>5.1</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

Table 3. XRD analysis confirmed crystallinity and epitaxial growth of all YIG films.

Sample N1 was deposited under the same conditions as Y20 and E1, i.e. at T ≈ 1150 K, P_{O_2} ≈ 1 Pa and d ≈ 6 cm, but it has a broader FMR linewidth (ΔH = 4.3 mT) than Y20 (by a factor of ~2.4) and E1 (by a factor of ~1.4). Film thickness is just ~1 µm.

Reducing the target–substrate distance from 6 cm to 4 cm without compensation of oxygen pressure (N2) allows a doubling of the growth rate, but it also causes a dramatic increase in the FMR linewidth: ΔH = 13.25 mT, which can be explained as originating from a worsening of crystal quality, according to the dark yellow colour and the transmission spectrum (see Fig. 2).

The sample (N3) grown with the same growth dynamics as Y20 and N1, i.e. at P_{O_2} ≈ 3.4 Pa and d ≈ 4 cm, features a similar thickness, but a narrower FMR linewidth (ΔH = 4.7 mT) than N2. When doubling the oxygen pressure (P_{O_2} ≈ 6.8 Pa), the growth rate is almost halved and no improvement in the FMR linewidth is observed (ΔH = 5.1 mT from N4). In any case we observe a broader FMR linewidth in this batch of YIG films, compared to the batch “E”.

3.2. Multi-PLD of YIG + FeO_{3}

In this section we discuss the results achieved by multi-PLD of YIG and FeO_{3}. In the first sub-section we show the results obtained from ablating the YIG target with the frequency-quadrupled Nd:YAG laser and the FeO_{3} target with the KrF laser; in the second paragraph the results attained with the reversed laser set-up are presented.

3.2.1. Ablation of YIG with the Nd:YAG laser

The depositions with the frequency-quadrupled Nd:YAG laser were performed with the following laser settings: fluence on the target set at F_{Nd:YAG} ≈ 1.3 J/cm², and pulse repetition frequency fixed at f_{Nd:YAG} ≈ 10 Hz. Again we studied the effect of changes in target–substrate distance and oxygen pressure on film properties, which are summarised in Table 4.

Table 4
Deposition conditions and results of samples YF1–YF5. Samples Y20 and N3 are shown as reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>F_{Nd:YAG} [J/cm²]</th>
<th>r [cm]</th>
<th>t [µm]</th>
<th>Y conc. [formula number]</th>
<th>Fe conc. [formula number]</th>
<th>Fe/Y</th>
<th>ΔH [mT]</th>
<th>Sample colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y20</td>
<td>–</td>
<td>0</td>
<td>2.4</td>
<td>3.55</td>
<td>4.45</td>
<td>1.25</td>
<td>1.8</td>
<td>Yellow</td>
</tr>
<tr>
<td>N3</td>
<td>–</td>
<td>0</td>
<td>2</td>
<td>3.37</td>
<td>4.63</td>
<td>1.37</td>
<td>4.7</td>
<td>Yellow</td>
</tr>
<tr>
<td>YF1</td>
<td>2.4</td>
<td>0.1</td>
<td>2</td>
<td>2.92</td>
<td>5.08</td>
<td>1.74</td>
<td>30.4</td>
<td>Dark red</td>
</tr>
<tr>
<td>YF2</td>
<td>1.3</td>
<td>0.1</td>
<td>1.4</td>
<td>3.11</td>
<td>4.89</td>
<td>1.58</td>
<td>17.2</td>
<td>Orange</td>
</tr>
<tr>
<td>YF3</td>
<td>1.3</td>
<td>0.2</td>
<td>1.8</td>
<td>3.02</td>
<td>4.98</td>
<td>1.65</td>
<td>21.1</td>
<td>Light red</td>
</tr>
<tr>
<td>YF4</td>
<td>1.3</td>
<td>0.3</td>
<td>1.7</td>
<td>2.93</td>
<td>5.07</td>
<td>1.73</td>
<td>24.0</td>
<td>Dark red</td>
</tr>
<tr>
<td>YF5</td>
<td>1.3</td>
<td>0.4</td>
<td>1.7</td>
<td>2.92</td>
<td>5.08</td>
<td>1.74</td>
<td>29.8</td>
<td>Dark red</td>
</tr>
</tbody>
</table>
All the films of this batch have a darker colour than YIG films grown by ablating only the YIG target and show a non-uniform and hazy surface, with a more opaque region in the centre, which appears to have higher particulate density than the rest of the film surface from inspection by optical microscopy and stylus profilometry: the high surface roughness did not allow the correct measurement of transmission spectra, due to undesirable surface light scattering. XRD analysis confirmed crystallinity and epitaxy of all YIG films.

Table 4 shows that Fe deficiency was compensated from the first attempt: YF1 is actually Fe-overstoichiometric; however, the film has a very broad FMR linewidth ($\Delta H \approx 30.4$ mT), a dark reddish colour and a rough surface, featuring a high particulate density region in the centre, similar to an Fe$_2$O$_3$ tester film (1.5 $\mu$m thick) grown on a c-cut sapphire ($\alpha$-Al$_2$O$_3$) substrate, which suggests that the problem lies in the ablation of the Fe$_2$O$_3$ target with the excimer laser. The KrF laser fluence on the Fe$_2$O$_3$ target was therefore reduced, in the hope that this would produce better-quality films.

Lower excimer laser fluence ($F_{KrF}$) means lower deposition rate from the Fe$_2$O$_3$ target, thus lower Fe in the YIG films: in fact, overstoichiometry was reached at $F_{KrF} = 3$ Hz (YF4) and $F_{KrF} = 4$ Hz (YF5) instead of $F_{KrF} = 1$ Hz as in YF1, but the film quality worsened as the KrF laser repetition frequency was increased, as seen in Fig. 3: films became less reflective, more opaque, redder and rougher — film colour, particulate density and surface roughness seem to be related to concentration of Fe. However, XRD analysis confirmed crystallinity and epitaxial growth of all YIG films, as shown in Fig. 4. From analysis of XRD patterns we observed a small shift of the YIG (400) peak towards higher angles (see Fig. 5), which suggests a reduction of the lattice constant ($a = 12.376$ Å) with increasing Fe concentration, as expected from theory: the larger lattice constant in Fe-deficient YIG films is due to the high concentration of yttrium that has a large ionic radius; so, the increase of Fe and the decrease of Y in YIG tructure by ablating only the YIG target and show a non-uniform and hazy surface, with a more opaque region in the centre, which appears to have higher particulate density than the rest of the film surface from inspection by optical microscopy and stylus profilometry: the high surface roughness did not allow the correct measurement of transmission spectra, due to undesirable surface light scattering. XRD analysis confirmed crystallinity and epitaxy of all YIG films.

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Fig. 6 shows the variation of the FMR linewidth with Fe concentration, which increases with increasing KrF laser repetition frequency ($F_{KrF}$ or target ablation ratio $r$) (see Table 4). The increase of the FMR linewidth with increasing Fe concentration in the YIG films agrees with previous findings in our single-PLD-grown films (N1–N4, but also E1–E4) and with the results in YIG films grown by single-PLD from an Fe-overstoichiometric YIG target reported in [8].

Considering that a variation in target-substrate distance or in oxygen pressure causes a significant change in deposition rate and in the FMR linewidth in pure YIG films (see samples N1–N4), the only option available to improve film quality was changing the laser set-up (i.e. actually swapping target positions) and therefore ablating the Fe$_2$O$_3$ target with the Nd:YAG laser and the YIG target with the KrF laser (although this required higher fluence and use of the excimer at maximum output energy), as discussed in the next paragraph.

3.2.2. Ablation of YIG with the KrF laser and Fe$_2$O$_3$ with the Nd:YAG laser

The batch of YIG samples whose growth conditions and properties are summarised in Table 5 was deposited by multi-PLD, ablating the YIG target with the KrF laser ($F_{KrF} \approx 2.8$ J/cm$^2$ and $F_{KrF} = 20$ Hz, except for YF1, deposited with $F_{KrF} = 16$ Hz) and the Fe$_2$O$_3$ target with the Nd:YAG laser, whose fluence was set to $F_{Nd:YAG} = 1.3$ J/cm$^2$, whereas pulses were gated with a shutter with different open and close times, in order to grow YIG films with different Fe concentrations. The other conditions were the same as before (see Section 3.2.1). Deposition duration was 72,000 excimer laser pulses for all samples.

We now define the inverse target ablation ratio, $ir$, in Table 5 as the ratio of the number of Nd:YAG laser pulses per second on the Fe$_2$O$_3$ target over the number of excimer laser pulses per second (set to $F_{KrF} = 20$ Hz in all cases, except for YF1, grown at $F_{KrF} = 16$ Hz) on the YIG target: $ir = F_{Nd:YAG}/F_{KrF}$. With this definition we avoid an infinite target ablation ratio $r$ for $F_{Nd:YAG} = 0$ Hz, according to the previous definition in Section 3.2.1, and we can compare this batch of samples (YF) with the previous one (YF), by referring to the ratio of the number of laser pulses per second on the Fe$_2$O$_3$ target over the number of laser pulses per second on the YIG target.

As shown in Fig. 7, the films of this batch have a progressively darker colour with increasing inverse target ablation ratio, but they show a smoother and more uniform film surface than the “YF” batch. Also the Fe$_2$O$_3$ tester (1.5 $\mu$m thick) grown on a c-cut sapphire substrate with the Nd:YAG laser compares better (more uniform and smoother) than the one grown ablating the Fe$_2$O$_3$ target with the KrF laser, suggesting that the problem lies in the ablation of the Fe$_2$O$_3$ target with the excimer laser, which probably causes the formation of a more energetic plume.
than in the Fe concentration is more uniform across the observed in single-PLD experiments; also, EDX analysis showed that YIG ablation by excimer laser produces better quality in YF1, with an Fe concentration of 5.08 formula units, suggesting that in YFi5, with an Fe concentration of 5.11 formula units, versus 30.4 mT ples is not as strong as in the previous batch: the largest value is 16 mTFig. 8). However the broadening of the FMR linewidth in this set of sam-

colour becomes darker, opacity increases, re

The accuracy of FMR linewidth measurements is ~0.1 mT. The number in parentheses is the inverse target ablation ratio E3. Error bars show the accuracy of EDX compositional analysis for Fe concentration: ±0.04 formula numbers. In this section we discuss the results achieved by multi-PLD of YIG and Y2O3. All the experiments were performed at ‘standard deposition conditions’ by ablating the YIG target with the Nd:YAG laser (\( f_{\text{Nd:YAG}} \approx 1.3 \, \text{J/cm}^2 \) and \( f_{\text{Nd:YAG}} = 10 \, \text{Hz} \)) and the Y2O3 target with the KrF laser, whose fluence was set to \( f_{\text{KrF}} \approx 1.3 \, \text{J/cm}^2 \) and pulse repetition frequency was changed in the range \( f_{\text{KrF}} = (1–4) \, \text{Hz} \), in order to grow YIG films with different Y concentrations. Deposition duration was ~72,000 Nd:YAG laser pulses (i.e. 2 h) for all samples.

Fig. 7. Samples YFi1–YFi5 compared to sample E3. ir is the target ablation ratio.

Table 5 shows that Fe deficiency was almost compensated in YFi3, whereas samples YFi4 and YFi5 are Fe-overstoichiometric. As in the multi-PLD batch with swapped laser configuration (YFi1–YFi5), the film colour becomes darker, opacity increases, reflectivity decreases and the FMR linewidth broadens with increasing Fe concentration (see Fig. 8). However the broadening of the FMR linewidth in this set of samples is not as strong as in the previous batch: the largest value is 16 mT in YFi5, with an Fe concentration of 5.11 formula units, versus 30.4 mT in YFi1, with an Fe concentration of 5.08 formula units, suggesting that YIG ablation by excimer laser produces better quality films, as already observed in single-PLD experiments; also, EDX analysis showed that Fe concentration is more uniform across the film surface in this batch than in the “YF” batch.

Ablation of Fe2O3 by the Nd:YAG laser produces better quality films: in fact, the Fe2O3 tester film grown on sapphire with the Nd:YAG laser is smoother and more uniform than the one grown with the KrF laser, which instead featured a large hazy area and a dark and opaque region in its centre, with a higher density of particulates. This is reflected in multi-PLD-grown YIG films using the same laser set-up, as observed above, suggesting that optimum ablation of both targets is crucial for deposition of high-quality YIG films with a higher Fe concentration.

Optical transmission spectra are shown in Fig. 9, where it is clear how optical transmission in the near infrared and visible decreases with increasing Fe concentration in the YIG films. The darkening of film colour and the increase of opacity agree with the trend of optical transmission with Fe concentration. A shift towards longer wavelengths (red-shift) with increasing Fe concentration can be noticed too, which agrees with the transmission spectra of our Fe2O3 testers, featuring an absorption edge at ~600 nm (typically between ~550 nm and ~450 nm for our YIG films grown by single-PLD).

Fig. 10 shows XRD patterns of samples YFi1–YFi5: except for YFi1, whose YIG (400) peak is at 28.87°, all YIG (400) peaks are aligned at ~28.89°–28.90°, diffraction angle of stoichiometric bulk YIG for (400) orientation, meaning that all samples have the same lattice constant of bulk YIG (\( \alpha = 12.576 \, \text{Å} \)).

3.3. Multi-PLD of YIG + Y2O3

In this section we discuss the results achieved by multi-PLD of YIG and Y2O3. All the experiments were performed at ‘standard deposition conditions’ by ablating the YIG target with the Nd:YAG laser (\( f_{\text{Nd:YAG}} \approx 1.3 \, \text{J/cm}^2 \) and \( f_{\text{Nd:YAG}} = 10 \, \text{Hz} \)) and the Y2O3 target with the KrF laser, whose fluence was set to \( f_{\text{KrF}} \approx 1.3 \, \text{J/cm}^2 \) and pulse repetition frequency was changed in the range \( f_{\text{KrF}} = (1–4) \, \text{Hz} \), in order to grow YIG films with different Y concentrations. Deposition duration was ~72,000 Nd:YAG laser pulses (i.e. 2 h) for all samples.

Fig. 9. Optical transmission spectra of YFi1–YFi5 and E3. Ripples are etalon fringes [15]. The number in parentheses is the inverse target ablation ratio ir.

Fig. 10. XRD patterns of samples YFi1–YFi5. Most diffraction peaks appear as double, due to Cu-Kα2 radiation being present in the diffractometer.

Fig. 11. Samples YY1–YY4 compared to sample N3. ir is the target ablation ratio. Samples YY2–YY4 appear more opaque due to the rougher surface of the back side of the substrates (which were polished only on one side).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ir</th>
<th>t [μm]</th>
<th>Y concentration [formula number]</th>
<th>Fe concentration [formula number]</th>
<th>Fe/Y</th>
<th>ΔH [mT]</th>
<th>Sample colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y20</td>
<td>0</td>
<td>2.4</td>
<td>3.55</td>
<td>4.45</td>
<td>1.25</td>
<td>1.8</td>
<td>Yellow</td>
</tr>
<tr>
<td>E3</td>
<td>0</td>
<td>2.5</td>
<td>3.52</td>
<td>4.48</td>
<td>1.27</td>
<td>3.9</td>
<td>Yellow</td>
</tr>
<tr>
<td>YFi1</td>
<td>0.05</td>
<td>2.2</td>
<td>3.40</td>
<td>4.60</td>
<td>1.35</td>
<td>6.0</td>
<td>Yellow</td>
</tr>
<tr>
<td>YFi2</td>
<td>0.1</td>
<td>3</td>
<td>3.22</td>
<td>4.78</td>
<td>1.48</td>
<td>6.5</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>YFi3</td>
<td>0.125</td>
<td>3</td>
<td>3.03</td>
<td>4.97</td>
<td>1.64</td>
<td>9.2</td>
<td>Brownish/dark yellow</td>
</tr>
<tr>
<td>YFi4</td>
<td>0.15</td>
<td>4</td>
<td>2.88</td>
<td>5.12</td>
<td>1.78</td>
<td>8.7</td>
<td>Light brown</td>
</tr>
<tr>
<td>YFi5</td>
<td>0.2</td>
<td>3.5</td>
<td>2.80</td>
<td>5.11</td>
<td>1.77</td>
<td>16.0</td>
<td>Brown</td>
</tr>
</tbody>
</table>
Thickniess measurements of YY2–YY4 were not conclusive, due to the high curvature of the YAG substrates used; however, from growth
time, it is expected to be ~(1.7–2) μm.

XRD analysis showed that only YY1 and YY2 are epitaxial crystalline
YIG films, as their diffraction patterns feature YIG (400) and YIG (800)
peaks, which are missing in the XRD patterns of YY3 and YY4, where
only YAG (400) and (800) peaks due to the substrate appear. YY3 and
YY4 differ from YY1 and YY2 also in terms of

**Table 6** shows an obvious increase in Y concentration, a decrease in
Fe concentration and an increase of the FMR linewidth with increasing
target ablation ratio r from 0 to 0.4, i.e. with increasing KrF laser repeti-
tion rate \(f_{KrF}\) from 0 Hz to 4 Hz; actually, FMR absorption disappears in
YIG films grown with \(r \geq 0.3\), i.e. \(f_{KrF} \geq 3\) Hz. From the results of Fe-
doping experiments, a decrease of the FMR linewidth with decreasing
Fe concentration (or increasing Y concentration) was expected. The op-
posite trend observed may be due to either the dilution of ferromagnetic
Fe ions in Y-rich films or the lattice distortion, whereas the lack of FMR
absorption in YY3 and YY4 is likely due to the fact that the films are not
crystalline.

**Table 6** shows the variation of composition of YIG films (N3 + YY1–
YY4) with target ablation ratio. It can be noticed that Y-doping in these
samples is heavier than Fe-doping in previous experiments: this is be-
cause less material is lost or the KrF laser ablates more material from
the \(Y_2O_3\) target than from the \(Fe_2O_3\), despite using the same KrF laser
fluence as in the “Y” batch \((F = 1.3\,J/cm^2)\). In fact, under the same con-
ditions the \(Y_2O_3\) growth rate is ~0.025 nm/pulse \((-1.8\,μm/h)\) versus
~0.0083 nm/pulse \((-0.6\,μm/h)\) for the \(Fe_2O_3\) growth rate. Also, during
the deposition of YY1–YY4 the YIG growth rate was probably lower
than before (N3), due to a decrease in Nd:YAG laser fluence, thus mak-
ing these YIG films even more Y-doped.

**Fig. 12** shows the XRD patterns of N3, YY1 and YY2: a large shift to-
wards lower angles can be noticed for the YIG (400) peaks, whose positions
are plotted versus Y concentration in **Fig. 13**. The higher the Y
concentration, the lower the YIG (400) peak position, which means a
larger lattice constant, which agrees with the expected theoretical
trend: Y has a larger ionic radius, so the higher the Y concentration in
larger lattice constant, which agrees with the expected theoretical
concentration, the lower the YIG (400) peak position, which means a

**Fig. 12** shows the XRD patterns of samples YY1–YY4. All diffraction peaks appear as double,
due to Cu-Kα2 radiation being present in the diffractometer.

**Fig. 13** shows the XRD patterns of samples YY1–YY4: a large shift to-
wards lower angles can be noticed for the YIG (400) peaks, whose positions are plotted versus Y concentration. Error bars show the
accuracy of EIDX compositional analysis for Y concentration: ±0.04 formula numbers. The accuracy of XRD measurements is ~0.01°. The number in parentheses is the target ablation ratio \(r\).

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**4. Conclusions**

Multi-beam, multi-target PLD allows the compositional tuning of
materials for tailoring their properties. In this paper we have studied the
systematic variation of crystallinity, and optical and magnetic prop-
erties of YIG films as a function of composition: this was achieved by si-
multaneous ablation of a polycrystalline YIG target and an \(Fe_2O_3\) target,
for compensation of Fe-deficiency in YIG films, or a Y₂O₃ target, in order to study the change of YIG properties with increasing Y concentration.

We showed that growth dynamics are important for deposition of high-quality YIG films, as well as the choice of lasers for the ablation of the targets. The KrF excimer laser (248 nm) ablates YIG better than the frequency-quadrupled laser (266 nm), as demonstrated in both single-PLD and multi-PLD experiments: an FMR linewidth of 3.9 mT was achieved in the YIG film (E3) grown with the KrF laser, compared to the 4.7 mT measured from N3, grown with the Nd:YAG laser. In multi-PLD runs we also observed that ablation of Fe₂O₃ with the Nd: YAG laser produces smoother and more uniform YIG films, with narrower FMR linewidth than YIG samples grown ablating the Fe₂O₃ target with the KrF laser. However, in both cases, the compensation of Fe-deficiency did not improve ferromagnetic properties of YIG, but actually FMR linewidth broadened with increasing Fe concentration; also surface roughness and optical transmission worsened with increasing Fe concentration. An increase in Y concentration was thought to improve ferromagnetic properties of YIG, however FMR linewidth broadened also with increasing Y concentration until FMR disappears completely when the film becomes amorphous. The narrowest FMR linewidth is observed for YIG films with an off-stoichiometric composition, close to Y₁₋ₓFeₓSc₂O₁₂.

Although the best results were achieved by single-PLD of YIG with the excimer laser, multi-PLD was proven to be a viable technique to tailor thin film properties by changing the material composition: for YIG and magneto-optic garnets in particular, multi-PLD can be used to tune FMR linewidth of the material for application in microwave communications (phase shifters, circulators and magneto-static wave filters) or to vary the Faraday rotation for applications in optical communications (rotators and isolators).

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References