Modification of Er:YbAG film microstructure with a sintering agent

V Jakes¹, V Polák¹, K Rubešová¹, T Hlásek¹, D Mikolášová¹, L Nádherný¹, P Nekvindová¹ and J Oswald²
¹ University of Chemistry and Technology Prague, Department of Inorganic Chemistry, Technická 5, 166 28 Prague 6, Czech Republic
² Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10, 162 00 Prague 6, Czech Republic
Vit.Jakes@vscht.cz

Abstract. Thin films of erbium doped YbAG were prepared by spin-coating on fused silica substrates. The effect of two parameters on the microstructure of resulting films was observed: addition of a sintering agent (TEOS) to the solution deposited and crystallization under decreased atmosphere (100 mbar). All prepared samples were polycrystalline single phase YbAG. When comparing the reference (TEOS-free) samples crystallized in ambient pressure, the films with TEOS in a combination with decreased pressure during the crystallization had a smaller crystallite size and finer surface, as confirmed by AFM and Williamson–Hall analyses. A higher amount of TEOS caused cracking of the films though. All films containing TEOS were one-mode waveguides in the NIR region. This paper shows a way to modify microstructure of a waveguiding film via addition of a sintering agent without destroying the waveguiding ability.

1. Introduction
Garnets are widely used host materials for optical and optoelectrical applications thanks to their optical isotropy and transparency, non-toxicity, thermal and chemical stability and the possibility to tune their properties by a suitable substitution [1]. In optical applications such as lasers or active optical components, doping with rare earths (RE) cations is very often used. The luminescent properties of the RE cations can be affected by several factors, e. g. type of a host material, the concentration of the RE ions, particle size and surface morphology. Among the RE ions, Er³⁺ is one of the most often used as an optical activator. Depending on the excitation energy and Er³⁺ concentration, red [2], green [3] or infrared emission [4] of Er³⁺ can be achieved. The Er³⁺ ions have a low absorption cross-section; it is therefore desirable to use a sensitizing agent for its improvement. The photoluminescence of Er³⁺ for infrared emission is enhanced by Yb³⁺ ions as a co-dopant [5]. The Yb³⁺ cations are used as sensitizers because the energy of F⁵/₂ (Yb³⁺) level is close to the I⁷/₂ (Er³⁺) level. Thanks to a similar size of RE ions, the co-doping with both these ions into most of the host materials is very effective and used. Apart from garnets, other crystals with suitable optical properties are used as a host matrix, e. g. LiNbO₃ [6] or Y₂O₃ [7]. In YAG, all yttrium atoms can be substituted by ytterbium. When ytterbium is a part of a host matrix, every Er⁵⁺ ions have close neighbours for the...
energy transfer Yb$^{3+}$– Er$^{3+}$. This arrangement improves luminescent properties of Er$^{3+}$ ions and can be used, for example, in the amplification of an optical signal in the third telecommunication window (1530 nm) [8].

Garnets and RE-doped garnets for optical applications have been produced in the form of monocrystals, powder or thin film by a whole range of methods, such as pulsed laser deposition [9], sol–gel method [10] or solvothermally [11]. The sol–gel method has proven to be a very suitable method for the preparation of thin films and powders thanks to the solution stage of the process which enables a dopant to be homogeneously distributed in a final sample. This technique has also low demands on laboratory equipment and requires relatively common chemicals such as acetates, alkoxides or nitrates [12–14]. When preparing thin films, the solution of cations is deposited on a substrate which is afterwards subjected to thermal treatment to decompose organic compounds (e.g. chelating agents) and to crystallize the film. The microstructure of thin films can be modified by optimizing the technology parameters such as temperature and pressure used to decompose and crystallize the film or by the use of a sintering agent.

To obtain a dense ceramic material with a high transparency, it is necessary to use a sintering agent and sinter the sample in vacuum. This principle is applicable also at polycrystalline films preparation. In most garnet preparations, tetraethyl orthosilicate (TEOS) is used in a small concentration ≈ 0.5 wt% [15, 16] as a sintering agent. TEOS can affect the sintering mechanism by lowering the sintering temperature by about 100 °C [17].

In this paper, Er:YbAG solutions were prepared with acetic acid and polyvinylpyrrolidone (PVP) used as chelating agents. The use of PVP was described by our group in the preparation of thin films of lithium niobate [18] and YbAG [19]. Thin films were deposited by spin-coating on fused silica. The effect of pressure applied during the crystallization and the influence of TEOS addition were studied.

2. Experimental

Solution to be deposited

Three solutions were prepared to deposit (Yb$_{0.98}$Er$_{0.02}$)$_3$Al$_5$O$_{12}$ films with a different concentration of TEOS (0, 1, 10 wt%). Aluminium chloride, and ytterbium and erbium acetates (all supplied by Sigma–Aldrich, purity 99.9%) were used as a source of cations. The acetates were dehydrated at 200 °C prior the preparation.

AlCl$_3$ was dissolved in water to an approximate concentration of 5 g of Al$^{3+}$ per L; the exact concentration of Al$^{3+}$ was determined by gravimetry. To a measured volume of the Al$^{3+}$ aqueous solution, polyvinylpyrrolidone (Sigma–Aldrich, $M = 29,000$ g/mol) was added in a molar ratio of 1:4 (relative to moles of Er:YbAG). After its complete dissolution, acetylaceton (Sigma–Aldrich) and acetic acid (Penta) were added in a molar ratio of 1:2:16 (relative to moles of Er:YbAG). Finally, solid erbium and ytterbium acetates were added. The entire process was performed at room temperature with magnetic stirring. After a complete dissolution of the acetates, the concentration of the solution was adjusted to 0.10 mol/L (molar concentration refers to a total concentration of metals) by evaporation at 60 °C. In the final preparation step, the sintering agent TEOS (Sigma–Aldrich) was added in two different concentrations (1 and 10 wt% with respect to the resulting Er:YbAG) and the solution was stirred magnetically for 30 min.

Deposition

Thin films of Er:YbAG were spin-coated on amorphous fused silica substrates (supplied by Crytur). The rotation speed was 3000 RPM (10 seconds) with 30 rot/s$^2$ acceleration/deceleration rate. The solution was deposited onto the substrate at the point of reaching the maximum rotation speed; the volume deposited was 22.5 µL per cm$^2$ of the substrate area. The spin-coater WS-650SZ-6NPP/LITE (Laurell Technologies Corp.) with 650 controller unit was used for the deposition of the films.
After each deposition, the layer was dried at 700 °C for 10 min. After depositing 7 layers, the film was crystallized at 1000 °C in air at ambient pressure for 1 h. The deposition process described above was proved to produce films thick enough to waveguide [19].

In order to evaluate the effect of decreased pressure at high-temperature processing, decomposition and crystallization of the second set of samples was carried out in a decreased pressure of 100 mbar (while maintaining all the remaining deposition parameters unchanged). The labelling of the prepared samples is shown in Table 1.

### Table 1. Prepared samples of YbAG

| Sample name     | TEOS (wt%) | Pressure (mbar) |
|-----------------|------------|-----------------|
| YbAG–0–1000     | 0          | 1000            |
| YbAG–0–100      | 0          | 100             |
| YbAG–1–1000     | 1          | 1000            |
| YbAG–1–100      | 1          | 100             |
| YbAG–10–1000    | 10         | 1000            |
| YbAG–10–100     | 10         | 100             |

**Samples characterization**

The phase composition of the prepared films was determined by XRD analysis. Data were collected at room temperature with Bruker-AXS D2 Phaser powder diffractometer with parafocusing Bragg–Brentano geometry using CoKα radiation in a range of 18–53° 2θ with a step size of 0.014°. The phase analysis was performed in the HighScore Plus program using the PDF-4 database. For the purpose of calculating crystallite size and internal stress, the linearized WiJiamson–Hall equation [20] was used.

Roughness of the prepared films was measured by AFM analysis using the Ntegra Spectra (NT-MDT) device. The surface scanning was performed in the tapping mode. Cantilevers with a strain constant of 1.5 kNm$^{-1}$ equipped with a standard silicon tip with curvature radius lower than 10 nm was used for all measurements. The surface of the prepared films was observed using a scanning electron microscope VEGA 3 LMU (Tescan) with an EDS probe INCA 350 (Oxford Instruments) in a backscattered electron mode. The samples were coated with gold (2 nm) prior the analysis.

Waveguiding properties were measured by m-line mode spectroscopy with the Metricon Prism Coupler device. The measurement was performed using a prism with an effective range of refractive index values from 1.2 to 2.02 (for 633 nm wavelength) at the operating wavelengths of 633, 964, 1311 and 1552 nm in a TE polarization.

### 3. Results

As the XRD patterns in Figure 1. show, all samples were polycrystalline single phase YbAG with no secondary phases. The reflections were labelled according to the PDF-4 reference pattern No. 01-073-1369. The sample prepared at ambient pressure without the addition of TEOS (YbAG–0–1000) exhibited the lowest intensity. The measurements are presented only in a range of 2θ = (20–36)°. This range matches the range used in our earlier paper [19] for easy comparison.
Collected XRD data were used to calculate the crystallite size and internal stress of the prepared films using the Williamson–Hall equation (selected plots are shown in Figure 2); the results are summarized in Table 2. The crystallite size of all samples lies between approx. 50 nm and 120 nm. The TEOS-free samples (YbAG–0–1000 and YbAG–0–100) do not differ significantly in the crystallite size. However, the combined effect of TEOS addition and a lower pressure during the crystallization can be clearly seen – TEOS-containing samples showed lower crystallite size if crystallized at lower pressure. The internal stress values do not vary much; no conclusive relation between the internal stress on one side and the TEOS addition and/or lower pressure on the other side can be inferred.

**Figure 1.** XRD patterns of Er\(^{3+}\):YbAG samples in a range of 2\(\Theta\) = (20–36)°.

**Figure 2.** Williamson–Hall plots of selected samples.
Table 2. Values of crystallite size and internal stress, obtained from the Williamson–Hall plots.

| Sample      | Crystallite size (nm) | Internal stress (%) |
|-------------|-----------------------|---------------------|
| YbAG–10–100 | 49                    | 0.18                |
| YbAG–1–100  | 62                    | 0.27                |
| YbAG–0–100  | 98                    | 0.21                |
| YbAG–10–1000| 71                    | 0.23                |
| YbAG–1–1000 | 114                   | 0.27                |
| YbAG–0–1000 | 90                    | 0.25                |

The results of the Williamson–Hall analysis were further confirmed by AFM method. Figure 3 shows the AFM images of selected samples together with the values of their roughness $R_a$ and $R_q$ calculated from the AFM images for all samples. TEOS-free films showed only a small change in their respective roughness (YbAG–0–1000: $R_a = 6.30$ nm; YbAG–0–100: $R_a = 5.81$ nm) when the crystallization pressure had been decreased from 1000 bar to 100 bar (images not presented). When crystallized at ambient pressure, samples with the addition of TEOS showed increase in roughness. In contrast, the roughness of the samples with TEOS (both 1 and 10 %) decreased when a lower pressure was used during crystallization of the films. This decrease is more pronounced when higher amount of TEOS was added (to approx. 1/3 of the value at ambient pressure). These results are consistent with those obtained from the Williamson–Hall plot (Table 2).

![AFM images of selected Er:YbAG films with calculated values of roughness.](image)

Figure 3. AFM images of selected Er:YbAG films with calculated values of roughness.

The effect of TEOS addition and a lower pressure on the surface microstructure was further observed by SEM. Figure 4 shows surface images of the films. The surface of the TEOS-free films (YbAG–0–1000, YbAG–0–100) showed no visible cracks and visually these two films have similar structure. In contrast, samples with 1 % of TEOS (YbAG–1–1000, YbAG–1–100) are visibly different. The film prepared at atmospheric pressure contained cracks, while the film with identical composition, only prepared at lower pressure (100 mbar) exhibited a smooth surface with no visible defects. Samples with 10 % TEOS added (YbAG–10–1000, YbAG–10–100) showed visible cracks over the entire surface. When putting together the results from AFM and SEM analyses, we can conclude that the combined effects of a lower pressure at crystallization and addition of small amount...
of TEOS led to a film with smaller crystallite size and a crackless surface. However, when the amount of added TEOS exceeded a certain level, the surface microstructure started to exhibit cracks, in spite of maintaining small crystallite size. This fact may be due to quick evaporation of volatile products from the thermal decomposition of TEOS that caused the mechanical damage of the surface.

![Scanning electron micrographs the Er\textsuperscript{3+}:YbAG films.](image)

**Figure 4.** Scanning electron micrographs the Er\textsuperscript{3+}:YbAG films.

The Er doping level in samples presented here was established already in our earlier work where we found that 2% of the ytterbium sites being substituted by erbium resulted in major intensity of photoluminescence at ~1530 nm. To see how the addition of TEOS and a lower pressure at crystal-
lization affected the waveguiding properties of the films, we subjected them to the m-line mode spectroscopy. A representative of this measurement is shown in Figure 5, all results are summarized in Table 3. Except for the TEOS-free films, all the other films propagated 1 mode at higher wavelengths (1331 and 1552 nm). A TEOS-modified microstructure with a smaller crystallite size apparently enhanced the waveguiding ability of the films.

Table 3. Number of guided modes in dependence of the wavelength.

| Sample       | Wavelength (nm) |
|--------------|-----------------|
|              | 633  | 964  | 1311 | 1552 |
| YbAG–0–1000  | 0    | 0    | 0    | 0    |
| YbAG–0–100   | 0    | 0    | 0    | 0    |
| YbAG–1–1000  | 0    | 0    | 1    | 1    |
| YbAG–1–100   | 0    | 0    | 1    | 1    |
| YbAG–10–1000 | 0    | 0    | 1    | 1    |
| YbAG–10–100  | 0    | 0    | 1    | 1    |

4. Conclusion

Three solutions for the deposition of Er$^{3+}$:YbAG were prepared by a wet route method based on the water soluble polymer polyvinylpyrrolidone (PVP); the solutions contained different amount of TEOS (0, 1, 10 wt%). Er:YbAG thin films were spin-coated on fused silica substrates and the effect of TEOS and lowered pressure at crystallization (100 mbar) on the microstructure was studied.

All samples were polycrystalline single phase ytterbium aluminium garnet. Using the Williamson–Hall equation, the crystallite size was calculated to be approx. 20–120 nm in all samples.

The combination of TEOS addition and decreased pressure during crystallization of the films had a beneficial effect on the microstructure (smaller crystallite size and roughness, defects-free surface). A higher amount of TEOS, however, caused cracks in the films surface regardless the crystallization pressure.

Unlike the TEOS-free samples, all films with TEOS were one-mode waveguides. Together with our previous study, this paper shows a way to improve the microstructure of waveguiding films by the use of a sintering agent.

Acknowledgment

This work was financially supported from specific university research (MSMT) No. 20-SVV/2017 and by the GA CR, project No. P108/12/G108.
References

[1] Potdevin A, Chadeyron G, Briois V and Mahiou R 2011 Mater Chem Phys 130 500–6
[2] Xu C F, Yang Q B, Ren G Z and Liu Y X 2010 J. Alloy. Compd. 503 82–5
[3] Li Z P, Dong B, He Y Y, Cao B S and Feng Z Q 2012 J. Lumin. 132 1646–48
[4] Rubešová K, Hlásek T, Jakeš V, Matějka P, Oswald J and Holzhauser 2014 J. Sol-Gel Sci. Technol. 70 142–8
[5] Cantelar E and Cussó F 2003 J. Lumin. 102 525–31
[6] Shim J B, Yoshimoto N, Yoshizawa M and Yoon D H 2001 Cryst. Res. Technol. 36 1209–14
[7] Salhi R, Jimenez C, Deschanvres J L, Maalej R and Fourati M 2015 Chem. Vap. Deposition 21 26–32
[8] Kaczkan M, Borowska M, Malinowski M, Lukasiewicz T and Kolodziejak K 2009 Phys Status Solidi B 246 1677–85
[9] Diaz–Torres L A, De la Rosa E, Salas P, Angeles–Chavez C, Arenas L B and Nieto J 2005 Opt. Mater. 27 1217–20
[10] Hlásek T, Rubešová K, Jakeš V, Jankovský O and Oswald J 2014 J. Eur. Ceram. Soc. 34 3779–82
[11] Zhang X, Liu H, He W, Wang J, Li X and Boughton R I 2005 J. Cryst. Growth 275 e1913–17
[12] Fujioka K, Saiki T, Motokoshi S, Fujimoto Y, Fujita H and Nakatsuka M 2009 Ceram. Int. 35 2393–99
[13] Ramanujam P, Vaidyanathan B, Binner J, Anshuman A and Spacie C 2013 Ceram. Int. 40 4179–86
[14] Chen J, Huang X, Wang L and Zhang Q 2011 J Rare Earth 29 44–7
[15] Hostaša J, Matejíček J, Nait–Ali B, Smith D S, Pabst W and Esposito L 2014 J. Am. Ceram. Soc. 97 2602–06
[16] Chen X T, Lu T C, Wei N A, Lu Z W, Chen L J, Zhang Q H, Cheng G and Qi J Q 2015 J. Alloy. Compd. 653 552–60
[17] Kong L B, Huang Y Z, Que W X, Zhang T S, Li S, Zhang J, Dong Z L and Tang D Y 2015 Sintering and densification of transparent ceramics Transparent Ceramics (Topics in Mining, Metallurgy and Materials Engineering) ed. C P Bergmann (Cham: Springer International Publishing) chapter 7 pp 467–517
[18] Rubešová K, Mikolášová D, Hlásek T, Jakeš V, Nekvindová P, Bouša D and Oswald J 2016 J. Lumin. 176 260–65
[19] Hlásek T, Polák V, Rubešová K, Jakeš V, Nekvindová P, Jankovský O, Mikolášová D and Oswald J. 2016 J. Sol-Gel Sci. Technol. 80 531–37
[20] Williamson G K and Hall W H 1953 Acta Metall. 1 22–31