

## THE INFLUENCE OF THE THERMO-CHEMICAL TREATMENT ON THE OPTICAL PROPERTIES OF YAG:Cr,Mg AND GGG:Cr,Mg EPITAXIAL FILMS

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The optical absorption spectra of YAG:Cr,Mg and GGG:Cr,Mg films are studied at *in-situ* conditions during high-temperature annealing in oxidizing and reducing atmospheres. The absorption spectra were measured in the range from 250 to 1500 nm at temperatures up to 1190 °C and the kinetics of absorption changes are registered at the wavelength of 450 nm. As it is shown, the oxidation of YAG:Cr,Mg films grown at low growth rates leads to increasing of the absorption in the visible region that caused by recharging of chromium ions, whereas the reduction of YAG:Cr,Mg films leads to the backward process. On the contrary, the reduction of GGG:Cr,Mg films increases their absorption, at that the kinetics of reduction has got the complicate, non-monotonous character. At sufficiently low temperatures (~ 800 °C) the oxidation leads to the opposite changes of the spectra of GGG:Cr,Mg films, however, at higher temperatures the changes of gas environment do not cause the noticeable changes of the spectra and the absorption remains at the sufficiently high level. The YAG:Cr,Mg film grown at higher growth rate demonstrates the behavior analogous to the one of GGG:Cr,Mg.

**Key words:** optical in-situ spectroscopy; oxidation and reduction kinetics; oxygen defects; yttrium-aluminium garnet; gadolinium-gallium garnet.

### Introduction

The epitaxial crystalline films of yttrium-aluminium  $Y_3Al_5O_{12}$  (YAG) and gadolinium-gallium  $Gd_3Ga_5O_{12}$  (GGG) garnets, doped by chromium and magnesium or calcium can be effectively used as saturable absorbers for Q-switched microchip lasers. In comparison with the bulk crystals, the crystalline films obtained by liquid phase epitaxy (LPE) technique characterized by higher structural perfection, higher achievable concentration of the phototropic centers, possibility of batch processing [1–2]. Besides, GGG:Cr,Mg(Ca) films synthesized on GGG substrates are perspective materials because of well developed method of the growth of high-dimensioned GGG single crystals with low concentration of defects [3]. The required properties of the films, particularly, the concentration of the phototropic centers, i.e. the tetrahedrally coordinated  $Cr^{4+}$  ions are ensured by after-growth annealing in the appropriate atmosphere. The investigations of the influence of high-temperature annealing on the properties of YAG:Cr,Mg and GGG:Cr,Mg films are carried out in [2, 4–6]. Particularly, it is shown that the annealing in air at temperature of 1400°C leads to opposite changes of the absorption spectra of YAG:Cr,Mg and GGG:Cr,Mg [5]. However, most of these investigations are carried out *ex-situ*, i. e. all changes are registered after finishing of the thermo-chemical treatment. It may cause the differences between the observed effects and the real physical processes in the investigated sample during annealing. The one exception is Ref. [6] where the changes of the optical absorption of YAG:Cr,Mg film are measured during annealing (*in-situ*). However, the investigations of [6] were carried out only for one film that does not allow determining connections between the growth conditions and the peculiarities of the processes taking place during annealing. Continuing the investigations of [6], in the present work we study the processes of high-temperature treatment of a number

of YAG:Cr,Mg and GGG:Cr,Mg films in oxidizing and reducing atmospheres by *in-situ* technique. The obtained results form the basis of the comparative analysis of reduction/oxidation processes in different garnet films obtained at different growth conditions.

### Experimental details

YAG:Cr,Mg and GGG:Cr,Mg films were obtained at the Scientific Research Company 'Carat' by liquid-phase epitaxy (LPE) from the supercooled solution-melt of the garnet-formative components in PbO-B<sub>2</sub>O<sub>3</sub> solvent. The films were deposited on YAG:Nd and GGG substrates in the [100] and [111] directions respectively. The parameters of the films are indicated in Table 1. As it is seen from the Table, the growth rates of the majority of YAG:Cr,Mg films are in one order lower than the growth rates of GGG:Cr,Mg ones. Only one YAG:Cr,Mg film (Y<sub>4</sub>) was grown with higher rate equal to 0.704 μm/min. All films with exception of Y<sub>3</sub> were double-sided.

**Table 1.** Parameters of YAG:Cr,Mg and GGG:Cr,Mg epitaxial films

Parameter	YAG:Cr,Mg				GGG:Cr,Mg		
	Y1	Y2	Y3	Y4	G1	G2	G3
Thickness, μm	100	60.38	104.94	42.22	28.83	82.5	104.3
Growth rate, μm/min.	0.158	0.109	0.126	0.704	1.44	1.1	1.16
Temperature of growth, °C	1028	1036	1017	1011	1052	1009	1072
[Cr <sub>2</sub> O <sub>3</sub> ]/[Al(Ga) <sub>2</sub> O <sub>3</sub> ]	2.66	2.6	3.8	2.4	0.56	0.84	0.85
[Cr <sub>2</sub> O <sub>3</sub> ]/[MgO]	5.56	5.56	5.56	5.55	5.2	8.9	11

The optical *in-situ* experiments have been performed at the laboratory of the Technical University of Braunschweig using a specially designed high-temperature furnace placed in a Perkin-Elmer Lambda 900 spectrophotometer, see Refs. [7] for details. All consecutive spectra and kinetics are obtained on the same samples that were cut from 'substrate + film' structures. The experimental set-up ensures fast (~1 min.) replacement of gas atmospheres in the furnace and the registration of the subsequent reduction/oxidation kinetics at a certain wavelength. We registered the spectra of absorbance  $A = \log(I_0/I)$ , where  $I_0$  and  $I$  are intensities of incoming and transmitted light respectively, and kinetic curves of the absorbance changes after sudden changing of the gas atmosphere from reducing (5% H<sub>2</sub> + 95% Ar) to oxidizing (pure O<sub>2</sub>) one and vice versa. The absorption spectra were measured in the range from 250 to 1500 nm at temperatures up to 1200 °C. The kinetics of absorption changes are registered at the wavelength of 450 nm that is approximately corresponds to the center of the absorption band caused by Cr<sup>4+</sup> in the octahedral sites. As well as in [7], the absorption spectra obtained at sufficiently high temperatures (>400 °C) are additionally corrected to avoid the influence of the heat radiation from the furnace on the optical spectra measurement.

## 2. Results and discussion

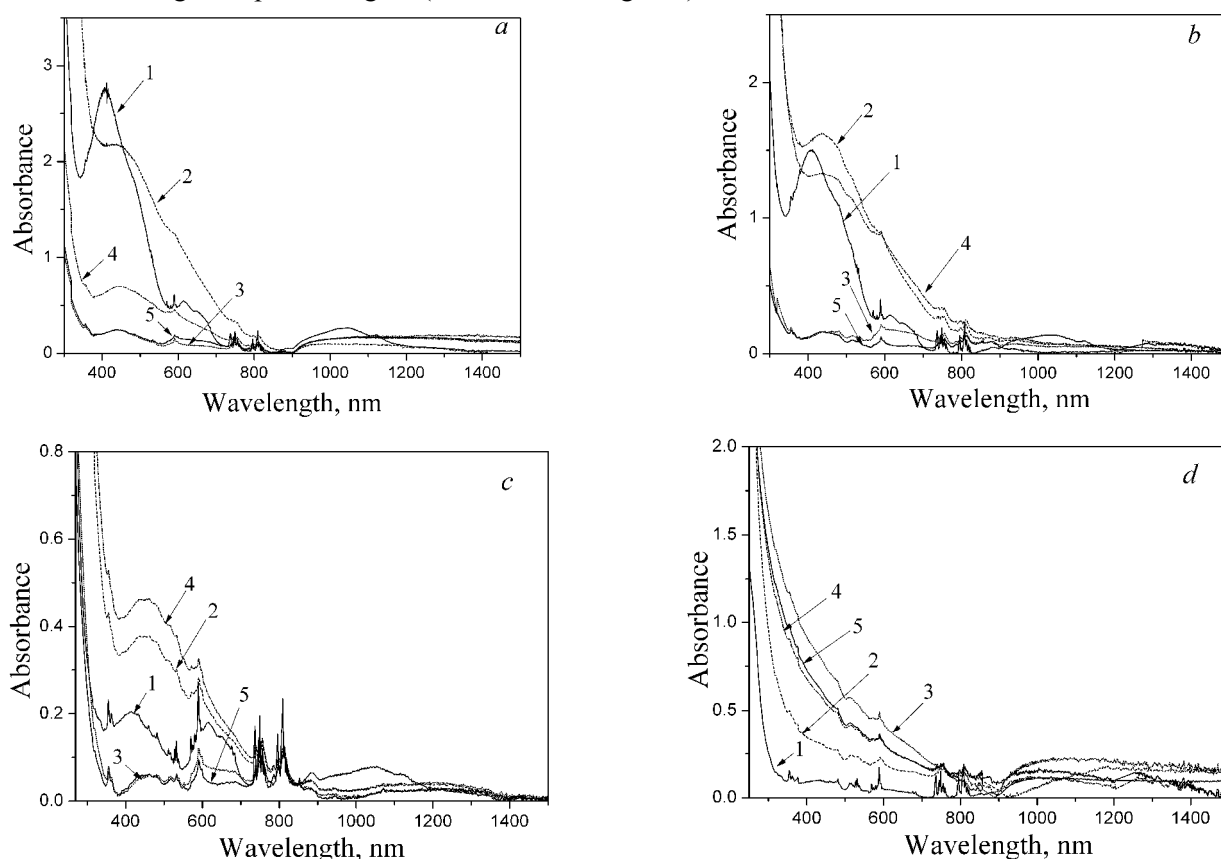
The sequences of the spectra obtained during reduction and oxidation treatment and the kinetics of absorbance changes of YAG:Cr,Mg films are shown in Fig. 1, *a-d* and 2–5 respectively.

The structure of the spectra registered before treatment is the typical for the Cr,Mg(Ca) – doped garnets [8]. The absorption bands at the wavelength lower than 600 nm are identified as caused by transitions between levels of Cr<sup>4+</sup>(octa) ions, whereas the bands located at 600–700 nm and near 1000 nm – by transitions between levels of Cr<sup>4+</sup>(tetra) [9]. Note that the tail of the Cr<sup>4+</sup>(octa) absorption band placed near 450 nm is imposed upon the absorption of Cr<sup>4+</sup>(tetra) at 600–700 nm (especially at high temperatures) so it is difficult to unambiguously connect the changes of the absorption in this region with changes of concentration of Cr<sup>4+</sup>(octa) or Cr<sup>4+</sup>(tetra). The bands near 432 and 600 nm observed in the reduced

YAG:Cr,Mg(Ca) crystals and films are caused by absorption of  $\text{Cr}^{3+}(\text{octa})$ . In the oxidized samples these bands are also present, however they are masked by strong absorption of  $\text{Cr}^{4+}$  ions. The sharp peaks observed in the spectra both of the reduced and oxidized films at 580, 750, 808 nm are caused by the absorption of  $\text{Nd}^{3+}$  ions in the substrate [10].

As it is seen from Fig. 1, *a-c* and 2–4, the YAG:Cr,Mg films obtained at low growth rates (0.11–0.16  $\mu\text{m}/\text{min.}$ ) demonstrates the same behaviour during annealing: the oxidation leads to increasing and the reduction – to decreasing of the absorption in the visible region. Obviously, these changes are caused by recharging of chromium ions at the octahedral sites,  $\text{Cr}^{3+}(\text{octa}) \leftrightarrow \text{Cr}^{4+}(\text{octa})$  as well as in the case of YAG:Cr,Mg or YAG:Cr,Ca bulk crystals [9, 11]. At the same time, no changes are observed in the near IR region (900 – 1500 nm) during annealing of  $Y_2 - Y_3$  films, whereas for  $Y_1$  these changes take place only during the first cycle of annealing at 960°C. At that the reduction leads to some increasing of the absorption in near-IR region of this film (Fig. 1) that is in contradiction with the changes observed in the bulk crystals of YAG:Cr,Mg(Ca).

The film  $Y_4$  grown with higher rate (0.704  $\mu\text{m}/\text{min.}$ ) shows the behaviour essentially differ from the one of  $Y_1 - Y_3$  films: in the first cycle of annealing at the temperature of 1190°C the reduction leads to increasing of the absorption in visible and near IR region whereas the oxidation causes its decreasing. In the second cycle of annealing at the temperature of 1090°C no essential changes of the absorption are observed in whole investigated spectral region (curves 4–5 in Fig. 1, *d*).

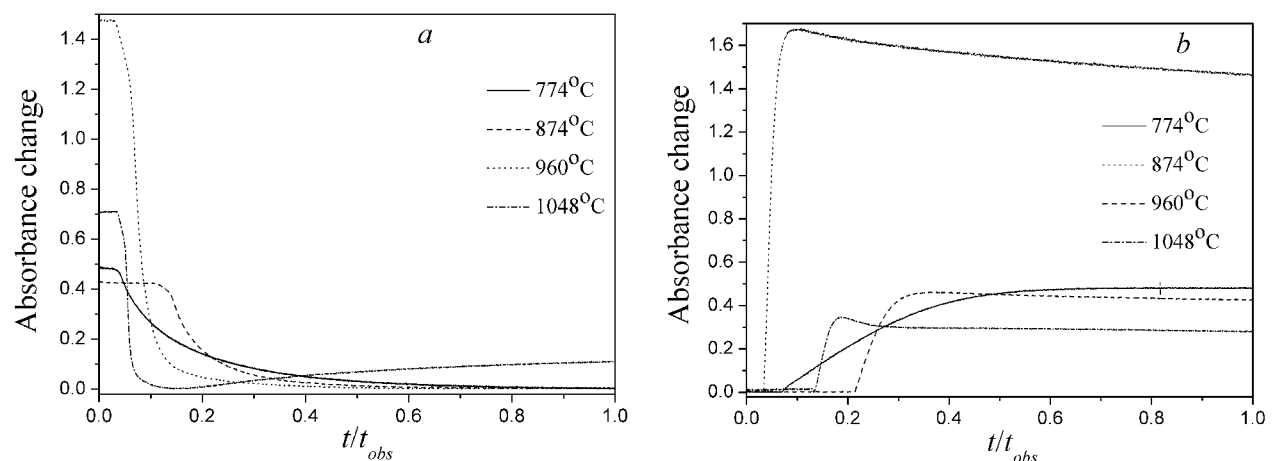


**Fig. 1.** The absorption spectra of YAG:Cr,Mg epitaxial films: fig. a –  $Y_1$  film, 1 – room temperature, 2, 3 – after oxidation and reduction at 960 °C, 4, 5 – after oxidation and reduction at 874 °C; fig. b –  $Y_2$  film, 1 – room temperature, 2, 3 – after oxidation and reduction at 862 °C, 4, 5 – after oxidation and reduction at 1100 °C; fig. c –  $Y_3$  film, 1 – room temperature, 2, 3 – after oxidation and reduction at 875 °C, 4, 5 – after oxidation and reduction at 973 °C; fig. d –  $Y_4$  film, 1 – room temperature, 2, 3 – after oxidation and reduction at 1190 °C, 4, 5 – after oxidation and reduction at 1090 °C

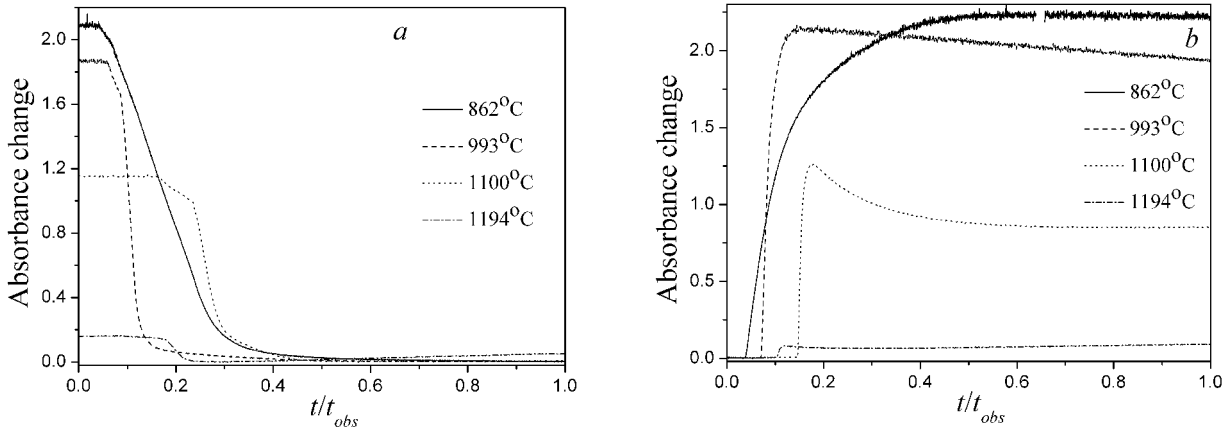
As it is seen from Figs. 2 – 5, the main changes of the optical absorption for all films occur during units – tens of minutes, i.e. essentially faster than the ones for the case of YAG:Cr,Mg bulk crystal [11]. Obviously, it is caused by lower thickness of the films in comparison with the one of YAG:Cr,Mg samples ( $\sim 1$  mm) used in the experiments of Ref. [11].

The distinctive peculiarity of the kinetics of YAG:Cr,Mg during reducing annealing is the presence of non-monotonies observed usually at higher temperatures. Particularly, the non-monotonies are noticeable on the kinetics for  $Y_1 - Y_2$  films at the temperatures of 1048 °C and 1194 °C, respectively (Fig. 2, a, 3, a). At lower temperatures the reduction kinetics for these films are monotonous. Also some slowness of the first stage of annealing process is clearly visible on the kinetics of reduction (especially for  $Y_3$ , Fig. 4, a). The kinetics of reduction of  $Y_4$  film is essentially non-monotone (Fig. 5, a). During first stage of annealing the optical absorption decreases as it can be expected in Cr-doped garnets due to recharging of chromium ions,  $Cr^{4+} \rightarrow Cr^{3+}$ . However, at the second stage the optical absorption strongly increases. Because the temperature of annealing in this case is sufficiently high (1190 °C) one may propose that for  $Y_4$  the same but more strongly pronounced non-monotonies as for  $Y_1 - Y_2$  are observed. In turn, it allows to suppose that the processes causing the increase of absorption of  $Y_4$  film during reduction also take place for the other YAG:Cr,Mg films, however, in the film grown with higher rate they are more considerable. Such peculiarities did not observed for YAG:Cr,Mg bulk crystal during reduction [11].

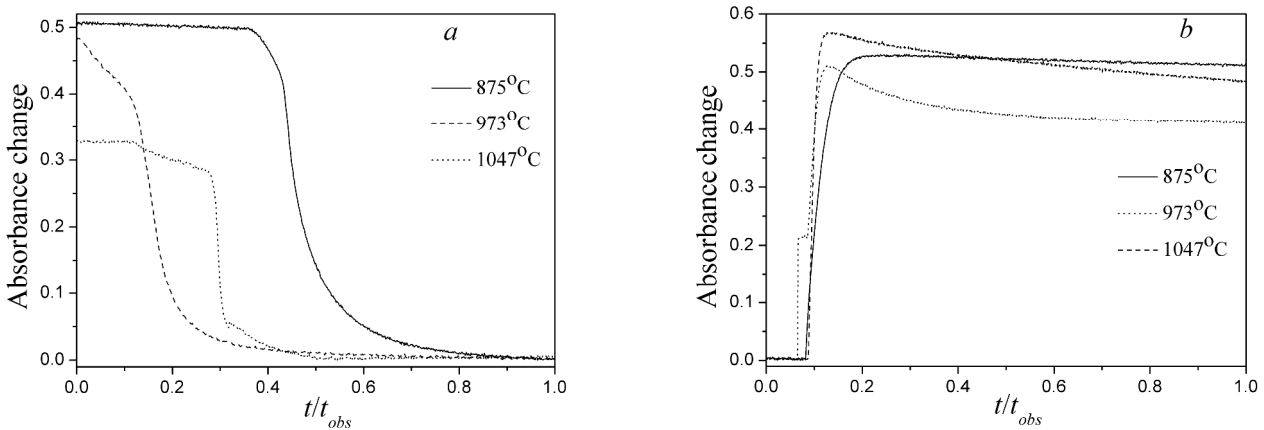
The non-monotonies are also observed on the oxidation kinetics of  $Y_1$  film (Fig. 2, b) at the temperature of 874°C and higher and on the one of of  $Y_2$  film at the temperature of 993°C and higher (Fig. 3, b). All oxidation kinetics of  $Y_3$  are non-monotonous (Fig. 4, b). The oxidation kinetics of  $Y_4$  film registered at 1190°C is monotonous, at that the observed changes of the optical absorption are in order lower than the ones for the case of  $Y_1 - Y_3$  films (Fig. 5, b). The analogous non-monotonies are observed during oxidation of YAG:Cr,Mg bulk crystal [11], so they can not be cause by the differences between film and bulk media. However, in the case of the bulk crystal they are observed only at the temperatures lower than 1000°C whereas in the case of the films (at least  $Y_1 - Y_2$ ) there is the bottom temperature limit of the non-monotonies appearance. It should be mentioned, that in Ref. [6] no non-monotonies or slowness are observed during redox treatment of YAG:Cr,Mg film. Obviously, it is caused by not high enough temperatures of annealing used in the investigations of [6] – up to 818 °C only.



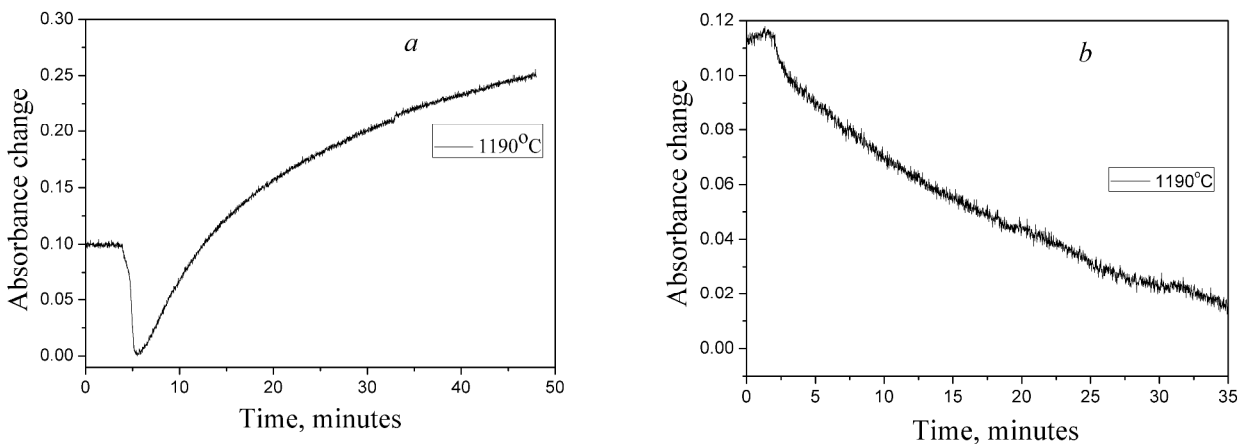
**Fig. 2.** The kinetics of the absorbance changes of  $Y_1$  film during reducing (a) and oxidizing (b) annealing at different temperatures. For a better visualization, the time is normalized for each curve to the full time of observation  $t_{obs}$ ; figure a:  $t_{obs} = 65.8$  min. at 774 °C, 29 min. at 874 °C, 28.4 min. at 960 °C, 49.7 min. at 1048 °C; figure b:  $t_{obs} = 29.9$  min. at 774 °C, 30.3 min. at 874 °C, 61.5 min. at 960 °C, 47.5 min. at 1048 °C



**Fig. 3.** The kinetics of the absorbance changes of  $Y_2$  film during reducing (a) and oxidizing (b) annealing at different temperatures. For a better visualization, the time is normalized for each curve to the full time of observation  $t_{obs}$ ; figure a:  $t_{obs} = 32.5$  min. at  $862^\circ\text{C}$ ,  $31.4$  min. at  $993^\circ\text{C}$ ,  $11.6$  min. at  $1100^\circ\text{C}$ ,  $9.1$  min. at  $1194^\circ\text{C}$ ; figure b:  $t_{obs} = 31.3$  min. at  $862^\circ\text{C}$ ,  $27.3$  min. at  $993^\circ\text{C}$ ,  $17.9$  min. at  $1100^\circ\text{C}$ ,  $17.5$  min. at  $1194^\circ\text{C}$



**Fig. 4.** The kinetics of the absorbance changes of  $Y_3$  film during reducing (a) and oxidizing (b) annealing at different temperatures. For a better visualization, the time is normalized for each curve to the full time of observation  $t_{obs}$ ; figure a:  $t_{obs} = 13.5$  min. at  $875^\circ\text{C}$ ,  $8.5$  min. at  $973^\circ\text{C}$ ,  $16.9$  min. at  $1047^\circ\text{C}$ ; figure b:  $t_{obs} = 13$  min. at  $875^\circ\text{C}$ ,  $25$  min. at  $973^\circ\text{C}$ ,  $20.2$  min. at  $1047^\circ\text{C}$



**Fig. 5.** The kinetics of the absorbance changes of  $Y_4$  film during reducing (a) and oxidizing (b) annealing at  $1190^\circ\text{C}$

One more peculiarity of the investigated films is considerable decreasing of the difference between levels of absorbance at the wavelength of 450 nm achieved by reduction and oxidation at high enough temperatures (Fig. 2–3, 5). This decreasing is irreversible – the redox treatment at lower temperatures can not essentially change the absorption of the film. Particularly, because of this feature, only one redox kinetics was registered for  $Y_4$  film. The film annealed at such conditions became slightly darker but not lose the transparency. This fixing of the optical absorption did not observed for YAG:Cr,Mg bulk crystal [11] although the temperature of annealing in [11] reaches the value of 1185 °C.

The sequences of the spectra obtained during reduction and oxidation treatment and the kinetics of absorbance changes of GGG:Cr,Mg films are shown in Fig. 6, *a–c* and 7–9 respectively.

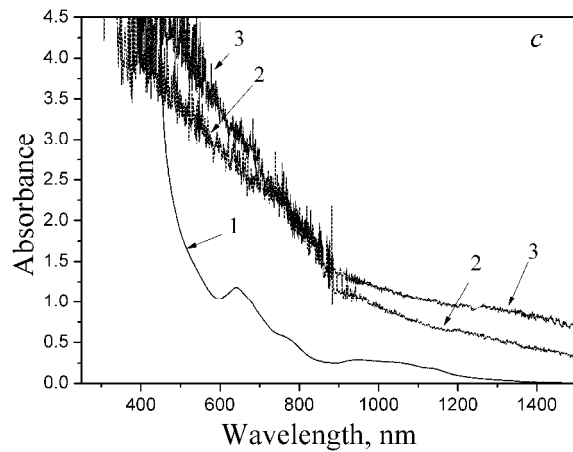
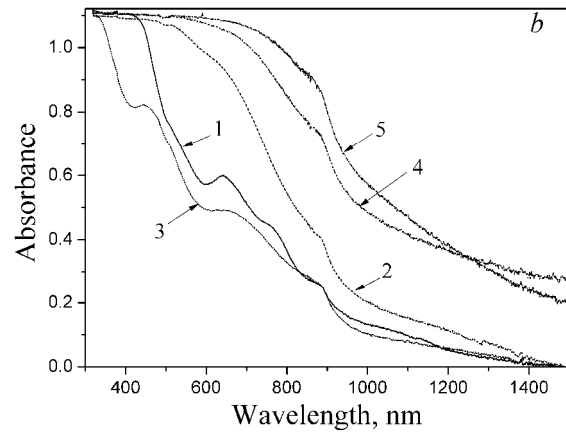
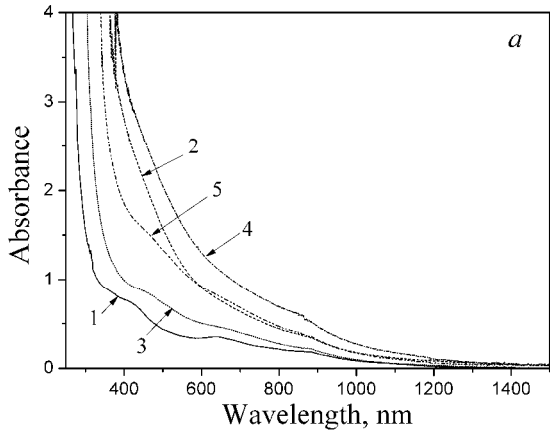
As it is seen from Fig. 6, the absorption bands observed in the initial (room temperature) spectra of GGG:Cr,Mg films are generally the same as in the spectra of YAG:Cr,Mg but slightly less pronounced.

For the  $G_1$  film the essential changes of absorbance are observed only in the visible region (Fig. 6, *a*), at that, similarly to the case of  $Y_4$ , the reduction leads to increasing and the oxidation – to decreasing of the optical absorption. As it is seen from Fig. 7, the redox kinetics for this film are monotonous with exception of the slight initial splash of the absorbance during reduction (Fig. 7, *a*). The similarity between the changes of the spectra of  $G_1$  and  $Y_4$  films during redox treatment can be connected with their higher growth rates in comparison with the ones of  $Y_1 – Y_3$  (Table 1). Thus, the differences in behaviour of  $G_1$ ,  $Y_4$  films, on the one hand, and  $Y_1 – Y_3$ , on the other hand, looks as caused firstly by the growth conditions and not by the difference in the compositions of the films.

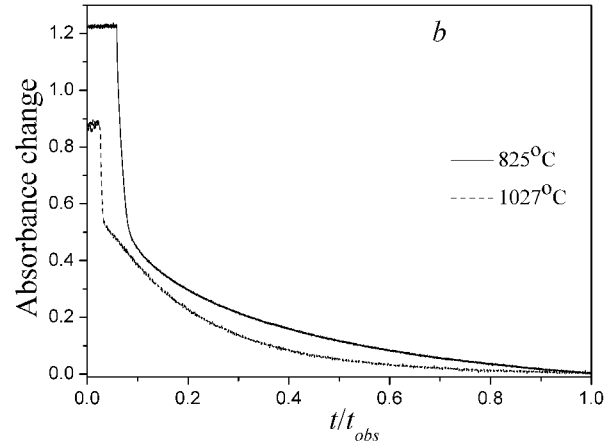
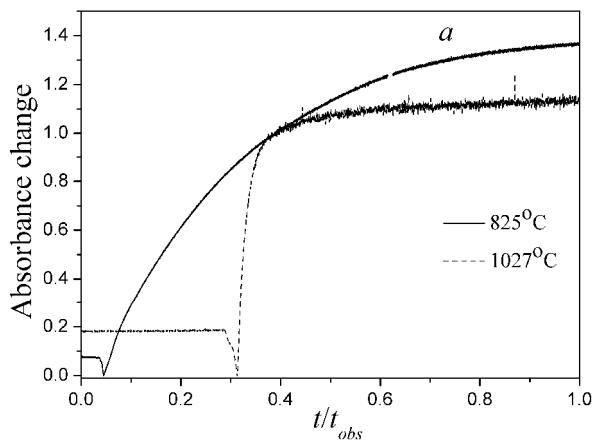
The film  $G_2$  (Fig. 6, *b*) demonstrates more complicated behaviour during redox treatment than  $G_1$ : the oxidation at 834 °C leads to increasing of the optical absorption in the visible and near IR region and the reduction – to its initial decreasing (curve 3 in Fig. 6, *b*). However, further reduction causes increasing of the absorption in the visible region approximately to the same level as achieved after oxidation (Fig. 8, *a* and, especially, insert in Fig. 8, *b*). At that (see insert in Fig. 8, *b*) the „depth” of the minimum on the kinetics of second reducing annealing is lower than the one for the first annealing in  $H_2/Ar$ . Probably, the consecutive annealing in  $H_2/Ar$  and  $O_2$  leads to the mentioned above fixation of the absorbance level. Oxidizing annealing of  $G_2$  film at 1030 °C leads to decreasing of the absorption at 600 – 1250 nm in comparison with the one of reduced film and its increasing at  $\lambda > 1250$  nm (Fig. 6, *b*). At the same time the absorption at the wavelengths lower than 600 nm remains practically fixed.

The optical absorption of  $G_3$  film, similarly to the one of  $G_2$ , essentially increases after annealing at temperatures about 1000 °C or higher (Fig. 6, *c*), at that the oxidation leads to some increasing of the absorption in the visible and near-IR regions. The changes of the absorbance near 450 nm during redox treatment at 1174 °C are insignificant (Fig. 9, *a–b*) that is obviously caused by the effect of high-temperature fixation of the absorption.

Thus the processes taking place in the epitaxial films of yttrium–aluminium and gadolinium–gallium garnets doped by Cr and Mg are essentially more complex than the ones in the YAG:Cr,Mg(Ca) bulk crystals. The common peculiarity of annealing of the bulk crystal and the epitaxial films are the non-monotony of the oxidation process, that becomes apparent for some investigated YAG:Cr,Mg films. The non-monotones of reduction process are observed on some kinetics both for YAG:Cr,Mg and GGG:Cr,Mg films but not for the bulk crystal. Also both for YAG:Cr,Mg and GGG:Cr,Mg films but not for the bulk crystal the effect of high-temperature fixation of the absorption is observed.



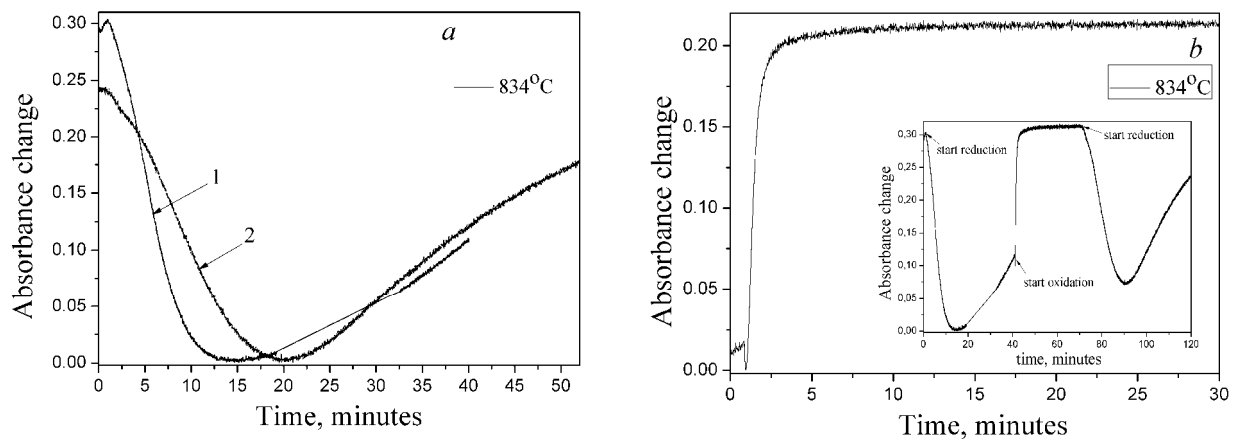
**Fig. 6.** The absorption spectra of (GGG:Cr,Mg): fig. a – G<sub>1</sub> film, 1 – room temperature, 2, 3 – after reduction and oxidation at 825 °C, 4, 5 – after reduction and oxidation at 1027 °C; fig. b – G<sub>2</sub> film, 1 – room temperature, 2, 3 – after oxidation and reduction at 834 °C, 4, 5 – after oxidation and reduction at 1030 °C; fig. c – G<sub>3</sub> film, 1 – room temperature, 2 – after reduction at 1174 °C, 3 – after oxidation at 1067 °C



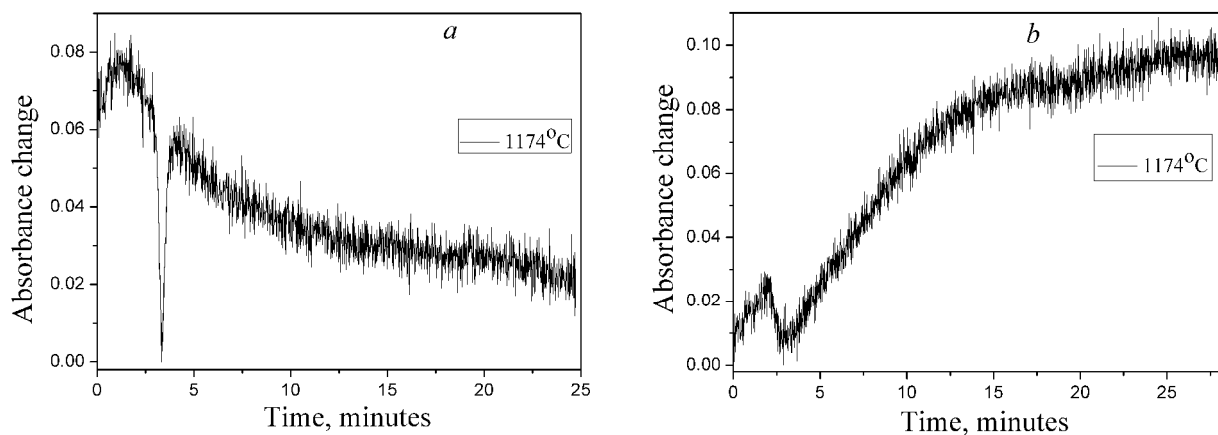
**Fig. 7.** The kinetics of the absorbance changes of G<sub>1</sub> film during reducing (a) and oxidizing (b) annealing at different temperatures. For a better visualization, the time is normalized for each curve to the full time of observation  $t_{obs}$ ; figure a:  $t_{obs} = 146.4$  min. at 825 °C, 46.9 min. at 1027 °C; figure b:  $t_{obs} = 46.9$  min. at 825 °C, 36 min. at 1027 °C

At the same time the essential difference in the behavior of YAG:Cr,Mg and GGG:Cr,Mg films takes place. Firstly, annealing of G<sub>2</sub> and G<sub>3</sub> films of GGG:Cr,Mg leads to considerable increasing of the optical absorption in the near IR region. For YAG:Cr,Mg films such changes are not observed (for Y<sub>2</sub>, Y<sub>3</sub>) or they are not so essential (for Y<sub>1</sub>, Y<sub>4</sub>). Secondly, the oxidation of Y<sub>1</sub> – Y<sub>3</sub> films (YAG:Cr,Mg) leads to increasing and the reduction – to decreasing of the absorbance in the absorption region of Cr<sup>4+</sup>(octa) ions (near 450 nm), whereas for the GGG:Cr,Mg films the more complex picture takes place: for G<sub>1</sub> the absorbance

decreases during the oxidation and increase during reduction, for  $G_2$  and  $G_3$  the fixation of the absorption near 450 nm is observed. The changes of the spectra of  $Y_4$  film in the visible region are generally the same as for  $G_1$  one: the optical absorption increases during reduction and decreases during oxidation. In the case of GGG:Cr,Mg one may suppose that the thermo-chemical destroying of the films takes place during annealing in hydrogen-containing atmosphere. However, it is not typical for YAG crystals under annealing at such temperatures, so, probably, the other process is responsible for the fixation of the absorption. Thirdly, the kinetics of oxidation of GGG:Cr,Mg films remain monotonous at all temperatures, whereas for  $Y_1 - Y_3$  films the high-temperature kinetics contain the non-monotonous. Also the redox processes of GGG:Cr,Mg films are noticeably slower than the ones of YAG:Cr,Mg: the typical durations of these processes are equal to 15–100 minutes for GGG:Cr,Mg in the temperature range from 830 to 1200 °C.



**Fig. 8.** The kinetics of the absorbance changes of  $G_2$  film during reducing (a) and oxidizing (b) annealing at 834°C. In Fig. a two consecutive kinetics (1 and 2) of reduction are shown. In the insert in Fig. b the sequence of the kinetics registered during the cycle  $O_2 \rightarrow H_2/Ar \rightarrow O_2 \rightarrow H_2/Ar$  is shown



**Fig. 9.** The kinetics of the absorbance changes of  $G_3$  film during reducing (a) and oxidizing (b) annealing at 1174°C

In general, one may conclude that the processes taking place in the investigated films during redox treatment are similar but significantly differ in their intensities: the dominating process caused the coloration or bleaching of the film is determined by its growth rate, composition and temperature of annealing. Because of essential variety of these processes it is difficult to propose the unified model that explains all mentioned



above peculiarities. The construction of such a model will become possible after realization of the combined spectroscopic, luminescence and ESR studies intended in future.

### Conclusions

Our investigation leads to the following conclusions:

- 1) the treatment of YAG:Cr,Mg and GGG:Cr,Mg films in reducing (5% H<sub>2</sub>+95% Ar) and oxidizing (O<sub>2</sub>) atmospheres reveals that the processes taking place in the films during annealing have got the more complex character than the ones in YAG:Cr,Mg bulk crystal;
- 2) the oxidation of YAG:Cr,Mg films synthesized with low growth rates leads to increasing and the reduction – to decreasing of the absorption near 450 nm, whereas for at least one GGG:Cr,Mg film and the YAG:Cr,Mg film synthesized with higher growth rate the opposite processes take place;
- 3) during high-temperature annealing of some GGG:Cr,Mg films the essential increase of the absorption in the near-IR spectral region is observed, whereas for YAG:Cr,Mg films such an effect is not observed;
- 4) for some YAG:Cr,Mg and GGG:Cr,Mg films the effect of high-temperature fixation takes place. It consists in invariability of the absorption in the certain spectral region after redox treatment;
- 5) the oxidation kinetics of GGG:Cr,Mg films remain monotoneous at all temperatures of annealing, whereas the oxidation kinetics of YAG:Cr,Mg films obtained with low growth rates become non-monotoneous at high temperatures;
- 6) the reduction kinetics of the majority of investigated YAG:Cr,Mg and GGG:Cr,Mg films have got the non-monotones that did not observed for YAG:Cr,Mg bulk crystal;
- 7) the durations of redox processes in GGG:Cr,Mg films are noticeably slower than the ones in YAG:Cr,Mg films at the close temperatures.

So the character of processes observed during annealing of the films is not determined by their compositions, growth rates or temperature only. Obviously, the complex interaction of these factors determines the type of dominating process taking place during redox treatment.

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- [1] Izhnin I.I., Vakiv N.M., Izhnin A.I., Syvorotka I.M., Ubizskii S.B., Passively Q-switched microchip lasers based on Nd:YAG/Cr<sup>4+</sup>:YAG epitaxial structures // *Techn. and Des. in El. App.* 6 (2005) 30-32, in Russian.
- [2] Zakharko Ya.M., Luchechko A.P., Syvorotka I.M., Syvorotka I.I., Ubizskii S.B., Melnyk S.S., Transformation of valence states and luminescence of chromium ions in the YAG:Cr,Mg and GGG:Cr,Mg single crystalline films // *Phys. Stat. Sol. (c)*, 2 (2005) 551-554.
- [3] Brandle C.D., Growth of 3'' diameter Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> crystals // *J. Appl. Phys.* 49 (1978) 1855–1858.
- [4] Ubizskii S.B., Melnyk S.S., Padyak B.V., Matkovskii A.O., Jankowska–Frydel A., Frukacz Z., Chromium recharging processes in the Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> single crystal under the reducing and oxidizing annealing influence // *Proceedings of SPIE* 4412 (2001) 63-68.
- [5] Melnyk S.S., Liquid phase epitaxy of layers YAG:Cr<sup>4+</sup>, GGG:Cr<sup>4+</sup> and YAG:Yb<sup>3+</sup> for microchip and disc lasers / *Dissertation*, Lviv Polytechnic National University, Lviv, 2006, in Ukrainian.
- [6] Buryy O., Ubizskii S., Syvorotka I.I., Becker K.-D., Optical in situ study of reduction/oxidation processes in Cr,Mg:YAG epitaxial film // *Acta Phys. Pol.(a)* 117 (2010) 184-188.
- [7] Sugak D., Zhydachevskii Ya., Sugak Yu., Buryy O., Ubizskii S., Solskii I., Shrader M., Becker K.-D., In-situ investigation of optical absorption changes in LiNbO<sub>3</sub> during reducing/oxidizing high-temperature treatments, // *J. Phys.: Condens. Matter.* 19 (2007) 086211 – 12 pages.
- [8] Garmash V.M., Jitniuk V.A., Ochrimchuk A.G., Shestakov A.V., The spectral properties of rare-earth garnets doped by chromium and magnesium // *Proceedings of USSR Academy of Sciences. Inorganic materials* 26 (1990) 1700-1705, in Russian.

- [9] Feldman R., Shimony Y., Burshtein Z., Passive Q-switching in Nd:YAG/Cr<sup>4+</sup>:YAG monolithic microchip laser // Opt. Mat. 24 (2003) 333-344.
- [10] Zverev G.M., Goliaev Yu.D., Shalaev E.A., Shokin A.A., Lasers on the yttrium-aluminium garnet with neodymium / "Radio i sviaz", Moskow, 1985, in Russian.
- [11] Ubizskii S., Buryy O., Börger A., Becker K.-D., Investigation of the chromium ions recharging kinetics in Cr,Mg:YAG crystal during high-temperature annealing // Phys. Stat. Sol.(a) 206 (2009) 550-561.

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## ВПЛИВ ТЕРМОХІМІЧНОЇ ОБРОБКИ НА ОПТИЧНІ ВЛАСТИВОСТІ ЕПТАКСІЙНИХ ПЛІВОК YAG:Cr,Mg ТА GGG:Cr,Mg

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Спектри оптичного поглинання плівок YAG:Cr,Mg та GGG:Cr,Mg досліджувалися в режимі *in-situ* при високотемпературних відпалах в окисній та відновній атмосферах. Спектри поглинання вимірювалися в інтервалі від 250 до 1500 нм за температур до 1190°C, кінетичні криві зміни оптичної густини реєструвалися на довжині хвилі 450 нм. Показано, що окислення плівок YAG:Cr,Mg, вирощених за нижчих швидкостей, веде до зростання оптичної густини у видимій області, що обумовлено поглинанням іонами хрому, тоді як відновлення плівок YAG:Cr,Mg веде до протилежного процесу. Навпаки, відновлення плівок GGG:Cr,Mg веде до зростання поглинання в цій області, при цьому кінетична крива зміни оптичної густини має складний, немонотонний характер. За істотно нижчих температур (~ 800°C) окислення веде до протилежних змін у спектрах поглинання плівок GGG:Cr,Mg, проте при вищих температурах зміна атмосфери відпалу не веде до помітних змін спектра і поглинання фіксується на достатньо високому рівні. Плівка YAG:Cr,Mg, синтезована при більшій швидкості, демонструє при відпалах поведінку, аналогічну до поведінки плівок GGG:Cr,Mg.

**Ключові слова:** оптична *in-situ* спектроскопія; кінетика окислення та відновлення; кисневі дефекти; ітрій-алюмінієвий гранат; гадоліній-галієвий гранат.