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Optical *in situ* Study of Reduction/Oxidation Processes in Cr,Mg:YAG Epitaxial Film

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The changes of the optical absorption spectra of Cr,Mg:YAG epitaxial film caused by high-temperature redox treatment are investigated by means of *in situ* spectroscopy. The spectra were registered in the visible and near-IR spectral regions at temperatures up to 1100 K. The kinetics of optical absorption changing were obtained in the temperature range from 936 K to 1091 K and were described by mathematical model connecting the chromium recharging process with oxygen vacancies diffusion. The parameters of the model were determined from the approximations of the experimental kinetics.

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1. Introduction

The yttrium-aluminium garnet containing the tetravalent chromium ions is used for passive Q-switching of Nd^{3+}:$Y_3Al_5O_{12}$ (Nd:YAG) laser and as a generating medium of the tunable near-IR lasers [1–8]. Usually, the single crystals of Cr:YAG are used for these applications. However, as it is shown in [9–11], the Cr:YAG films obtained by liquid-phase epitaxy are also the perspective medium for passive Q-switching. The required properties of the films, particularly, the concentration of phototropic centers — tetrahedrally coordinated Cr^{4+} ions can be ensured by the thermal-chemical treatment in the appropriate atmosphere. The influence of high-temperature annealing on the optical properties of epitaxial Cr,Mg:YAG films was studied in Ref. [12]. However, these investigations were carried out *ex situ*, i.e., all changes of the optical properties were registered after the treatment. It may cause the differences between the observed effects and the real physical processes in the film during annealing. Such an uncertainty can be avoided by the investigations in *in situ* regime. On the other hand, the *in situ* investigations of Cr^{4+} ions recharging in single Cr:YAG crystals were carried out by the authors in Ref. [13]. The similar studies for Cr:YAG epitaxial films allow to reveal the peculiarities of the recharging processes in the films and the single crystals caused by different methods of obtaining of these materials.

2. Experimental details

The Cr,Mg:YAG films were obtained at the Scientific Research Company “Carat” by liquid-phase epitaxy (LPE) from the solution-melt of PbO–B_2O_3. The films were deposited on both sides of Nd:YAG substrate in the [111] direction. The rate of the growth was equal to 1.24 μm/min. The width of the film on the each side of the substrate was equal to 37 μm, the total width of the structure was 743 ± 3 μm. The samples for experiments were cut from the epitaxial film and have got the transversal dimensions about 5 mm.

The experiments have been performed using a specially designed high-temperature furnace placed in a Perkin–Elmer Lambda 900 spectrophotometer, see Ref. [14] for details. The maximal temperature of annealing in our experiments was 1091 K. The heating and cooling rates were equal to 5 K/min. The experimental setup 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 measured the 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. The optical spectra were registered after high-temperature annealing in reducing (5%H_2 +95%Ar) and oxidizing (pure O_2) atmospheres. The spectral region investigated in our experiments ranged from 200 nm to 2000 nm. The kinetic curves of the absorbance were registered at 450 nm. The absorption spectra obtained at high temperatures

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(> 800 K) were additionally corrected to avoid the influence of the heat radiation from the furnace on the optical spectra measurement.

3. Experimental results

The sequence of the spectra obtained during heating of the as-grown film in O_2 to the temperature of annealing (1091 K) after reduction and oxidation treatment, and during cooling in H_2/Ar to the room temperature is shown in Fig. 1.

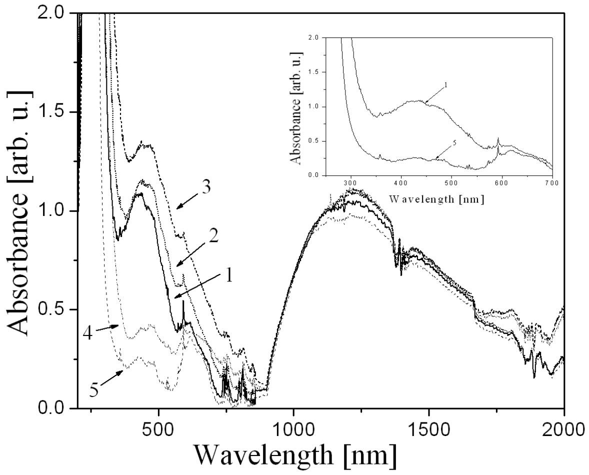

Fig. 1. The absorbance of Cr,Mg:YAG epitaxial film at 423 K (1), 1061 K (2), oxidized (3) and reduced at 1091 K (4) and after cooling in H_2/Ar to room temperature (5). In the inset the absorbance spectra of the oxidized (1) and reduced (5) film in the visible region are shown.

At low temperatures two absorption bands (460 nm and 630 nm, see inset in Fig. 1) are observed in the visible region of the spectra of the reduced film. Both of them are caused by transitions between levels of the octahedrally coordinated Cr^{3+} ions. The considerable absorption bands are also observed in the UV and near-IR regions. The UV band is caused by absorption of Pb^{2+} impurity that enters the crystal from the solution-melt PbO–B_2O_3 [15, 16], whereas the near-IR one — by intra-center transitions of Cr^{4+}(tetra) ions [17–20]. After oxidation the additional absorption is observed near 275 nm, 480 nm and 630 nm at room temperature (see inset in Fig. 1). Two first bands are caused by intra-center transitions of Cr^{4+}(octa) whereas the last one is the result of superposition of the absorption caused by intra-center transitions of Cr^{4+}(tetra) [20, 21] and tail of the absorption band centered at 630 nm. Oxidizing annealing leads also to small increase of the absorption in the near-IR region. This corresponds to the results obtained in [13] for the thermal-chemical treatment of Cr,Mg:YAG single crystals, where the changes in the near-IR are also insignificant at the temperatures lower than $\approx$ 1100 K. Thus, the formation/removing of the tetrahedrally coordinated Cr^{4+} ions practically does not take place during redox treatment of Cr,Mg:YAG film at $T < 1100$ K.

The sharp peaks observed in the spectra for both the reduced and oxidized films are caused by absorption of Nd^{3+} ions in the substrate.

The kinetics of absorbance changes were registered at $\lambda = 450$ nm, which corresponds to the maximum of the Cr^{4+}(octa) absorption band (Fig. 2). As it is seen in figure, the equilibrium state is achieved faster during oxidation than during reduction. The peculiarity of the oxidation kinetics in comparison with the ones obtained for Cr,Mg:YAG single crystal is the absence of the non-monotony observed for single crystal at temperatures lower than 1300 K [13]. In [13] this non-monotony is connected with formation of the defects absorbing in visible and near-IR regions. The absence of such defects in Cr,Mg:YAG film is probably caused by higher structural perfection of the films obtained by LPE in comparison with single crystals [16].

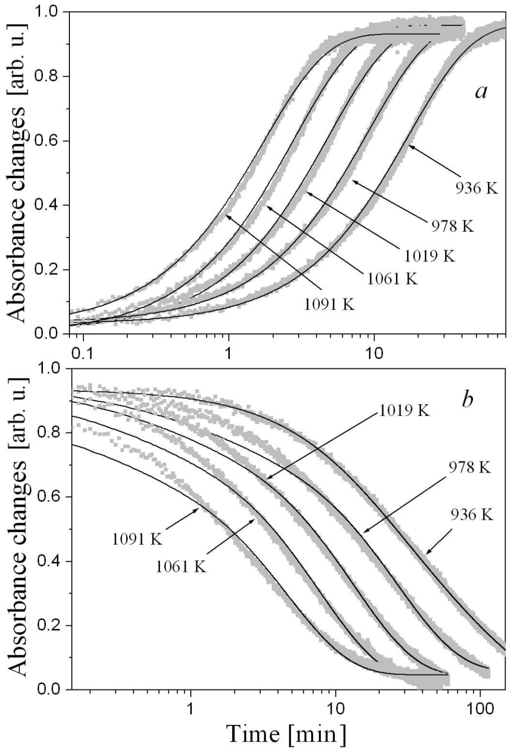

Fig. 2. Kinetics of the absorbance change at 450 nm (grey points) during oxidation (a) and reduction (b) and their approximations by diffusion model (black lines).

For the estimation of the reproducibility of kinetics, changes of absorbance during reduction at 1091 K were registered during two consecutive annealings in H_2/Ar separated by oxidation annealing. The obtained kinetics are close to each other (Fig. 3), only at the short times the difference between them is noticeable (see inset in Fig. 3), that is obviously caused by some difference in the initial conditions. This result confirms that the reproducibility of our experiments is high enough and no considerable irreversible changes take place during annealing.

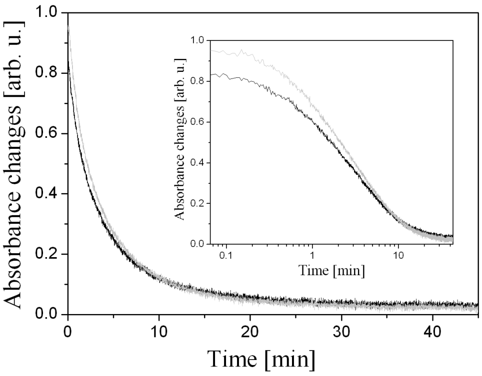

Fig. 3. Two different kinetics of absorbance changes caused by reduction at 1091 K. In the inset the same kinetics are shown in the logarithmic scale.

4. Approximation of the kinetics of Cr,Mg:YAG film redox treatment by diffusion model

The approximation of the experimental kinetics is based on the assumptions of the vacancy out-diffusion during oxidation and in-diffusion during reduction that leads to recharging of chromium ions, Cr^{3+}(octa) $\leftrightarrow$ Cr^{4+}(octa) [22, 23]. Under the assumptions that the rate of Cr^{4+}(octa) concentration n changing is proportional (with the opposite sign) to the rate of vacancies concentration n_V changing,

$$\frac{\partial n}{\partial t} = -\eta \frac{\partial n_V}{\partial t}, \tag{1}$$

and the vacancy diffusion is described by one-dimensional diffusion equation with third type boundary conditions (see [13, 24] for details), the absorbance change during annealing can be described as

$$\Delta A(t) = 2\frac{\sigma}{\ln 10}\left(\int_0^{d_f} n(t,x)dx - N_0 d_f\right) = \Delta A_\infty \left\{1 - \frac{1}{d_f}\sum_{k=0}^{\infty}\frac{4h^2}{d_f\left(h^2+\lambda_k^2\right)+2h}\frac{1}{\lambda_k^2} \times \left[1+\frac{\lambda_k}{h}\sin(\lambda_k d_f) - \cos(\lambda_k d_f)\right]\exp(-D\lambda_k^2 t)\right\}. \tag{2}$$

Here d_f is the thickness of the film, N_0 is the initial concentration of absorption Cr^{4+}(octa) centers, σ is their absorption cross-section, $\Delta A_\infty = 2\frac{\sigma}{\ln 10}\varepsilon(N_{V0} - N_{V\infty})d_f$ is the change of absorbance achieved at $t \to \infty$, N_{V_0} and N_{V_∞} are the initial and final concentrations of vacancies (obviously, $N_{V_0} \gg N_{V_\infty}$ for the oxidation process and $N_{V_0} \ll N_{V_\infty}$ for the reduction one), D is the vacancy diffusion coefficient, $h = R/D$ (R is the coefficient of the mass-transfer of diffusant (oxygen) from/to the surface), λ_k are the eigenvalues of the Sturm–Liouville problem, determined from equation [25]:

$$\mathrm{tg}\,(\lambda_k d) = \frac{2h\lambda_k}{\lambda_k^2 + h^2}, \tag{3}$$

where d is the width of the structure, $d = d_s + 2d_f$ (d_s is the width of the substrate).

The experimental redox kinetics are fitted by expression (2) with fitting parameters: D, $h_d = hd$, ΔA_∞. The fitting accuracy is estimated by χ^2 criterion and the accuracy of the fitting parameters determination — by standard error [13, 26].

The results of approximation are shown in Fig. 2. The obtained values of the fitting parameters, the corresponding standard errors and χ^2 criteria are indicated in Table. As it is seen from Fig. 2, the approximation of the experimental kinetics by the diffusion model is satisfactory. However, the diffusion coefficients D and parameters h_d are determined correctly only for the case of reduction, whereas for the oxidation the standard errors of these fitting parameters are too high.

The temperature dependences of the vacancy diffusion coefficient D and the coefficient of mass-transfer $R = Dh_d/d$ obtained from the approximation of the reduction kinetics are shown in Fig. 4 in an Arrhenius plot. Both dependences can be approximated by straight lines. Fitting of different reduction kinetics registered at 1091 K give the essentially different values of the diffusion coefficients: 7.90×10^{-6} cm^2/s and 1.47×10^{-5} cm^2/s. First of them corresponds to the more precise approximation (with $\chi^2 = 1.62 \times 10^{-4}$) and noticeably better agree with the straight line approximation in an Arrhenius plot (see Fig. 4). At the same time the difference between the mass-transfer coefficients for these kinetics is insignificant and lies in the error limits (Table).

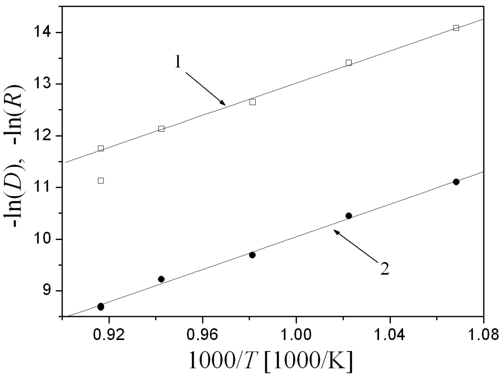

Fig. 4. Fit of the dependences of the diffusion (1) and the mass-transfer (2) coefficients on temperature in an Arrhenius plot.

As it is seen in Fig. 4, the temperature dependences of diffusion and mass-transfer coefficients are practically parallel in the Arrhenius plot. The activation energies of these processes are equal to 1.34 ± 0.04 eV for diffusion and 1.36 ± 0.05 eV for mass-transfer, i.e., coincide in limits of the statistical error. In other words, the energy required for the oxygen ion transfer from the regular position of the crystal lattice to the saddle (interstitial) point coincides with the energy required for its transfer from the near-surface layer to the environment.

The obtained value of the activation energy of diffusion in Cr,Mg:YAG film is essentially (≈ 1.5 times) lower than the one of Cr,Mg:YAG single crystal, that is equal to 1.95 ± 0.19 eV [13] (for comparison, the activation energy of diffusion for Cr,Ca:YAG single crystal is about 1.7 eV [20]).

TABLE

The values of fitting parameters and the precision of approximation*.

Fitting parameters	Temperature				
	936 K	978 K	1019 K	1061 K	1091 K
			Oxidation		
D [cm^2/s]	–	–	–	–	–
hd	–	–	–	–	–
ΔA_∞	0.9285 ± 0.0003	0.9370 ± 0.0004	0.9516 ± 0.0003	0.9579 ± 0.0002	0.9101 ± 0.0002
χ^2	1.58×10^{-4}	1.90×10^{-4}	2.24×10^{-4}	1.60×10^{-4}	1.46×10^{-4}
			Reduction		
D [cm^2/s]	$(7.67 \pm 0.06) \times 10^{-7}$	$(1.505 \pm 0.014) \times 10^{-6}$	$(3.21 \pm 0.03) \times 10^{-6}$	$(5.40 \pm 0.06) \times 10^{-6}$	$(7.90 \pm 0.11) \times 10^{-6}$ $(1.47 \pm 0.03) \times 10^{-5}$
hd	$1.46575 \pm 5 \times 10^{-5}$	$1.43160 \pm 6 \times 10^{-5}$	$1.31547 \pm 6 \times 10^{-6}$	$1.35816 \pm 8 \times 10^{-5}$	$1.60119 \pm 1.1 \times 10^{-4}$ $0.84457 \pm 1.6 \times 10^{-4}$
R [cm/s]	$(1.513 \pm 0.013) \times 10^{-5}$	$(2.90 \pm 0.03) \times 10^{-5}$	$(6.18 \pm 0.06) \times 10^{-5}$	$(9.87 \pm 0.12) \times 10^{-5}$	$(1.70 \pm 0.02) \times 10^{-4}$ $(1.67 \pm 0.03) \times 10^{-4}$
ΔA_∞	0.8925 ± 0.0005	0.9004 ± 0.0005	0.9240 ± 0.0005	0.9232 ± 0.0004	0.8414 ± 0.0002 0.9209 ± 0.0003
χ^2	1.88×10^{-4}	1.84×10^{-4}	1.65×10^{-4}	1.64×10^{-4}	1.62×10^{-4} 2.09×10^{-4}

*For reduction at 1091 K the results of approximation are indicated for both kinetics shown in Fig. 3.

Correspondingly, the diffusion coefficients for Cr,Mg:YAG film are more than in one order higher than the ones of single crystal. The analogous difference takes place also for the coefficients of mass-transfer. Thus, the transport processes in Cr,Mg:YAG epitaxial films are significantly faster than the ones in Cr,Mg:YAG single crystals. This result is in some contradiction with the observation of the non-monotony on the kinetics obtained for Cr,Mg:YAG single crystal [13]. Indeed, this non-monotony is obviously caused by the presence of some defects in the single crystal. On the other hand, the transport processes are faster in the crystals with higher amount of defects, so one may expect that the diffusion in single crystals should be faster than in the films. In principle, such a discrepancy can be explained if we suppose that the diffusant (vacancies) forms some short-lived complexes with other defects in the single crystal that decelerate the vacancy migration. However, the additional investigations are necessary to reveal the real reasons of this contradiction.

5. Conclusions

The optical absorption spectra of Cr,Mg:YAG epitaxial film were studied at *in situ* conditions during high-temperature annealing in oxidizing and reducing atmospheres. The spectra were measured in the spectral range from 200 nm to 2000 nm at temperatures up to 1100 K. The kinetics of optical absorption changes were registered at the wavelength of 450 nm that corresponds to the center of the absorption band caused by Cr^{4+} ions in the octahedral sites.

The oxidation leads to recharging of chromium ions $Cr^{3+}(\mathrm{octa}) \rightarrow Cr^{4+}(\mathrm{octa})$, whereas the reduction causes the backward process as well as in the single Cr,Mg:YAG crystal. On that the migration of Cr^{4+} ions from the octahedral sites to the tetrahedral ones is negligible for the temperatures up to 1100 K. The main peculiarity of the oxidation kinetics of Cr,Mg:YAG epitaxial films, in comparison with the ones of the single crystals is the absence of non-monotony that is specific for the single crystal. It seems probable that this difference is caused by the higher structural perfection of the films obtained by liquid-phase epitaxy, that inhibits the formation of defects typical for single crystals.

The experimental redox kinetics are successfully described by the mathematical model that takes into account the out-diffusion of oxygen vacancies during oxidation and their in-diffusion during reduction. The vacancy diffusion coefficient obtained from the fitting of reduction kinetics increases from $(7.67 \pm 0.06) \times 10^{-7}$ cm^2/s at 936 K to $(7.90 \pm 0.11) \times 10^{-6}$ cm^2/s at 1091 K. Simultaneously, the mass-transfer coefficient of the oxygen transport from the crystal surface to surroundings increases from $(1.513 \pm 0.013) \times 10^{-5}$ cm/s to $(1.70 \pm 0.02) \times 10^{-4}$ cm/s. The activation energies of the diffusion and mass-transfer processes, obtained from their temperature dependences, are correspondingly equal to 1.34 ± 0.04 eV and 1.36 ± 0.05 eV.

The comparison between the values of the diffusion and mass-transfer coefficients obtained for the Cr,Mg:YAG film and for the single crystal at close temperatures shows that transport processes in the epitaxial films are essentially faster than the ones in single crystals.

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