

Optical and laser properties of Ti-sapphire grown by different methods in reducing medium

*E.V.Kryvonosov, S.V.Nizhankovskiy, L.A.Lytvynov, A.A.Bui**

Institute for Single Crystals, "STC Institute for Single Crystals" National of Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
*"SOLAR TII, Ltd", 58 Nezavisimosti Ave., 220005 Minsk, Belarus

Received January 19, 2012

Optical and laser properties of Ti-sapphire grown in reducing gaseous medium are studied. It is shown that HDSM-crystals have satisfactory functional characteristic and can be used for the making of wide-aperture laser elements with wide diameter of 25–50 mm. Minimum distortion of the wave front (0.1λ) and FOM-factor of 200–250 are characteristic of the elements with the ends oriented parallel to the crystallization front of the initial crystal annealed in reductive medium with the reduction potential ε ≈ −180...−230 kJ/mol.

Исследованы оптические и лазерные свойства Ti-сапфира, выращенного в восстановительной газовой среде. Показано, что ГНК-кристаллы имеют достаточно высокие функциональные характеристики и могут использоваться для изготовления широко-апертурных лазерных элементов диаметром 25–50 мм. Минимальным искажением волнового фронта (0,1λ) и значением FOM-фактора 200–250 характеризуются элементы с торцами, ориентированными параллельно фронту кристаллизации исходного кристалла, прошедшие термообработку в среде с восстановительным потенциалом ε ≈ −180...−230 кДж/моль.

1. Introduction

Modern high-power tunable laser systems use wide-aperture active laser elements made from Ti-sapphire grown by Chochlralski and HEM methods [1, 2]. An alternative for these technologies is horizontal directed solidification (HDSM) which potentialities are considerably widened by the use of reducing gaseous media in the growth procedure [3]. The present paper is devoted to comparative analysis of different methods for the obtaining Ti-sapphire crystals for laser application.

2. Experimental

The crystals with the content of titanium C_{Ti} = 0.05–0.2 wt % were grown by HDSM and Czochlralski method in reducing medium under the pressure of argon P_{Ar} = 0.1...0.12 MPa, the crystallization rate was 1.0–1.5 mm/h [4, 5]. As a raw material there was used breakage of sapphire crystals grown by Verneuil method and HDSM. Titanium was introduced into the starting material in the form of high-purity TiO_2 powder.

The concentration of titanium in the grown crystals was controlled using KSVU-2 spectrophotometer by the intensity of the optical absorption band at 495 nm. The optical homogeneity of the crystals was studied on IKD-101 and ZYGO Mark-III interferometers, the laser characteristics were determined by means of special optical and laser test benches.

Due to evaporation of titanium from the melt its maximum content in the crystal is defined by the pressure of gaseous growth

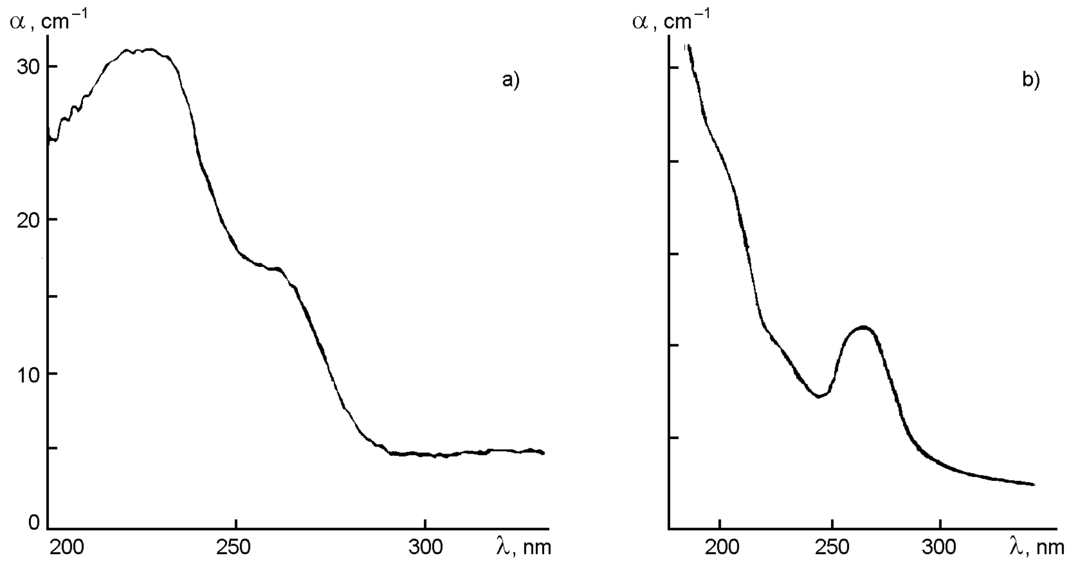

Fig. 1. UV-absorption of Ti-sapphire grown in carbon-containing gaseous medium by HDSM (a) and Chochralski (b) method.

Table 1. Content and distribution of Ti in Ti-sapphire crystals grown under different conditions

Method	Pressure medium for growing	The concentration of titanium (C_{Ti}), wt %	
		Beginning of the crystal (L=30 mm)*	End of the crystal (L= 150 mm)*
Kyropoulos	$1\cdot10^{-2}$ (vacuum)	0.02	0.025
HDSM	10 (CO, H_2)	0.07	0.03
HDSM	$1.2\cdot10^5$ (Ar)	0.08	0.15
Cz	$1.4\cdot10^5$ (Ar)	0.022	0.35

* *L* is the distance from the seed crystal

medium. In particular, the use of Kyropoulos method at the residual growth medium pressure $P \approx 10^{-2}$ Pa makes it possible to obtain the crystals with titanium content $C_{Ti} \le 0.03$ wt %. Thereat, the level of titanium evaporation depends, first of all, on the melt overheating and the crystallization rate. Growth of the crystals with higher concentrations of titanium requires a pressure not lower than 0.1 MPa (Table 1).

One of the main difficulties in producing of laser Ti-sapphire crystals is the necessity to prevent the formation of light scattering centers which arise due to high content of gas in the melt and the capture of gas bubbles by the growing crystal. In Chochralski method rejection of gas bubbles by the crystallization front is facilitated by ultrasonic treatment of the melt [6]. In HDSM this can be achieved owing to the angle between the crystallization direction and the crystallization front, large free surface of the melt and sufficiently high temperature gradient at the crystallization front.

3. Results and discussion

As found in [7] Ti-sapphire crystals grown by HDSM (HDSM-crystals) have no submicron pores typical of the crystals obtained by Czochralski method (Cz-crystals) in carbon-containing medium. Thereat, such crystals may contain gas bubbles and 5–20 μm micropores located in the ingot nose and near the walls of the crucible.

Optical absorption spectrum of HDSM-crystals has a band in the UV-range at 190–250 nm (Fig. 1) which is absent in the spectrum of Cz-crystals [4]. Such a band corresponds to the electron transitions of Ti^{4+} ions [8]. It points to the presence of Ti^{4+} ions in the crystal lattice, obviously connected with some uncontrolled bivalent impurity in the crystal.

In HDSM the reduction potential of the crystallization medium is not sufficient for the transition $Ti^{4+} \to Ti^{3+}$ of all titanium ions. Therefore, the crystals were annealed at a residual pressure of the gaseous atmosphere of 10...15 Pa, with the reduction chemical potential $\varepsilon \approx -230$ kJ/mol [9]. After annealing the absorption band characteristic of Ti^{4+} ions disappeared, and there emerged the bands with absorption maxima at 206, 225 and 268 nm typical of F-, F^+-

Table 2. FOM-factor of Ti-sapphire sample (HDSM)

Crystal	λ_{532}, mJ		λ_{800}, mJ		$\alpha_{532}\cdot l$	$\alpha_{500}\cdot l$	$\alpha_{800}\cdot l$	FOM
	I_0	I_1	I_0	I_1				
Before annealing	90.0	1.8	9.9	8.0	3.912	5.063	0.049	103
After annealing	96.0	1.09	10.8	8.99	4.324	5.578	0.025	223

I_0, I_1 is the intensity of the incident radiation and of the radiation transmitted through the crystal, respectively, α_λ is the coefficient of optical absorption of the crystal at the wavelength λ, l = 16 mm is the thickness of Ti-sapphire sample

centers and activator-vacancy complexes [Ti^{3+}–(V_O+$2e^-$)], respectively, in Cz-crystals [4, 8].

The most significant optical characteristic of Ti-sapphire is FOM-factor, i.e. a ratio of the optical absorption at the pumping wavelength (500 nm) to the optical absorption at the generation wavelength (800 nm). In HDSM-crystals optical loss at 800 nm is related to the presence of the complexes [Ti^{3+}–Ti^{4+}] which define their FOM-factor of the order of 100. At the same time for Cz-crystals the corresponding value is 200–250. Additional high-temperature annealing of the ingots of laser elements made from Cz-crystals in a medium with the reduction chemical potential $\varepsilon \approx -180...-230$ kJ/mol raises the FOM-factor (Table 2) up to 200–250 due to destruction of the complexes [Ti^{3+}–Ti^{4+}]. Moreover, it improves the optical homogeneity of the articles by reducing bulk residual elastic stresses in them [9–11].

The generation parameters and application of the crystal (in picosecond or femptosecond lasers) are defined by distortion of the wave front of the laser radiation. In general case this value must not be higher than $\lambda/4$, but for the laser elements which work at considerable radiation energy densities it must not exceed $\lambda/6$. For large-diameter laser elements made from Cz-crystals obtaining of such optical characteristics is problematic. This is caused by the curvature of the crystallization front.

Promising for the making of wide-aperture laser elements is HDSM, because in this case the crystallization front curvature does not change sharply. The main factors influencing the optical homogeneity of the crystals grown by this technique are the character of titanium distribution along the crystal and the block structure of the crystal matrix. Such crystals are distinguished by the presence of impurity striation along the growth direction which make it possible to establish the shape of the crystallization front and its orientation with respect to the ingot base (Fig. 2a). Inclination angle of this streation, this width, repetition frequency and contrast depend on the technological growth conditions and on the content of titanium in the melt. As a rule, the period of striation diminishes with the rise of titanium concentration. Under unfavorable thermal growth conditions some crystals may acquire a block structure where disorientation of the interblock boundaries is up to a few tens of angular minutes. This structure is observed in polarized light (Fig. 2b).

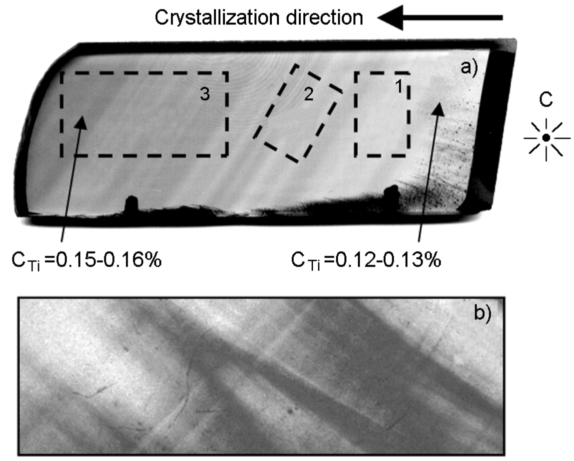

Fig. 2. Impurity macro-striation of HDSM-crystal (a) and its block structure in crossed polaroid light (b): *1*, *2*, *3* — variants of pattern cutting of HDSM crystal into ingots of laser elements; *C* — direction of [0001] crystallographic axis.

The presence of the striation may be caused by instrumental and physical factors. The former of them includes nonuniformity of the motion of the pulling mechanism and variations of the heater power. As a rule, they give rise to macro-striation with relatively large period and width ($\geq$ 1 mm). The latter factors are bound up with certain effects in the melt arising at the crystallization front. They are: concentration overcooling or change of the effective coefficient of titanium distribution due to convective instability of the melt and temperature fluctuations.

For Chochralski and HDSM Ti^{3+} distribution along the crystal is characterized by monotonic rise of concentration at the end of the crystallization process (Fig. 3). This is defined by a low effective coefficient of titanium distribution in sapphire. For Ti-sapphire grown in argon atmosphere (0.1 MPa) the coefficient of Ti^{3+} distribution is $k \approx 0.12-0.15$ [5]. Depending on the initial content of titanium in the melt the concentration of titanium in the HDSM-crystals may increase in the process of crystallization by 1.5–2 times. Thereat, in the crystal cross-section the titanium distribution non-uniformity is essentially lower and does not exceed 5 %. The nonuniformity of titanium distribution along the length of Cz-crystals is somewhat less in comparison with the one in HDSM-crystals due to a large starting melt volume and it depends on the ratio of the crystal and crucible diameters. Similar distribution of the activator is observed at the growth of the HEM-crystals [12].

The optical homogeneity of Ti-sapphire laser elements was examined using Solar TII test benches (Belarus). There were obtained shadow pictures from ∅25×15 mm elements while transmitting YAG:Nd laser radiation through them. The pictures for HDSM-crystals contain the bands caused by impurity macro-striation which are typical for nonuniform distribution of optical absorption over the aperture of the elements. This may give rise to distortions of the wave front of the transmitted radiation. Cz-crystals do not have impurity striation, and no bands are observed in their shadow pictures.

Titanium nonuniform distribution in the laser element results in formation of optical lens or wedge, as well as in local distortion of the optical refractive index. In this connection, while cutting the crystals into ingots one must take into account the peculiarities of growth method and the shape of the crystallization front. An influence of pattern cutting on the optical quality of the laser elements was studied on the elements cut out of the crystals grown by both of the considered methods.

In the case of Cz-crystals the ingots are cut out along the geometric axis of the boule that allows to diminish the influence of the crystallization front curvature on the radial nonuniformity of titanium distribution in the laser element. Due to the stria-

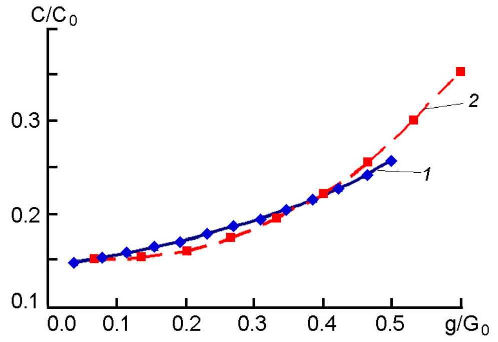

Fig. 3. Change of titanium content in Cz(*1*)- and HDSM(2)-crystals of Ti-sapphire in the process of crystallization: C_0 — initial titanium content in the melt; C — titanium content in the crystal; G_0 — initial weight of the raw material; g — weight of the growing crystal.

tion, at the longitudinal cutting of HDSM-crystals (Fig. 2a — 1) the end of the element contains regions with different titanium concentration. Nonuniformity of the distribution of titanium is also observed over the diameter of the element and along its length. This may give rise to nonuniform distribution of the radiation energy over the cross-section of the active element and to the effect of "strips" on the shadow pictures.

The interference pattern of the ingot cut out from HDSM-crystal along crystallization direction shows a faint distortion of the interference bands that testifies to local inhomogeneity of the refractive index of the crystal (Fig. 4a). This may be connected with the impurity macrostriation over the ingot aperture, or with the presence of interblock boundary in the crystal which also defines the wave front distortion with $PV = 0.362\lambda$.

The interference pattern of the ingot cut out from the crystal at an angle with the crystallization direction (Fig. 2a — 2) does not show disturbances of the optical homogeneity caused by structure defects (Fig. 4b). The wave front chart shows the maximum distortion $PV = 0.103\lambda$. This is caused by an optical wedge arising due to nonparallelism of the ingot ends and monotonous nonuniformity of the radial distribution of titanium. The wave front chart also shows small distortions with amplitude of about 0.015λ. The nature of such distortions seems to be connected with fine structure imperfections in the crystalline lattice, as well as with nonuniform distribution of

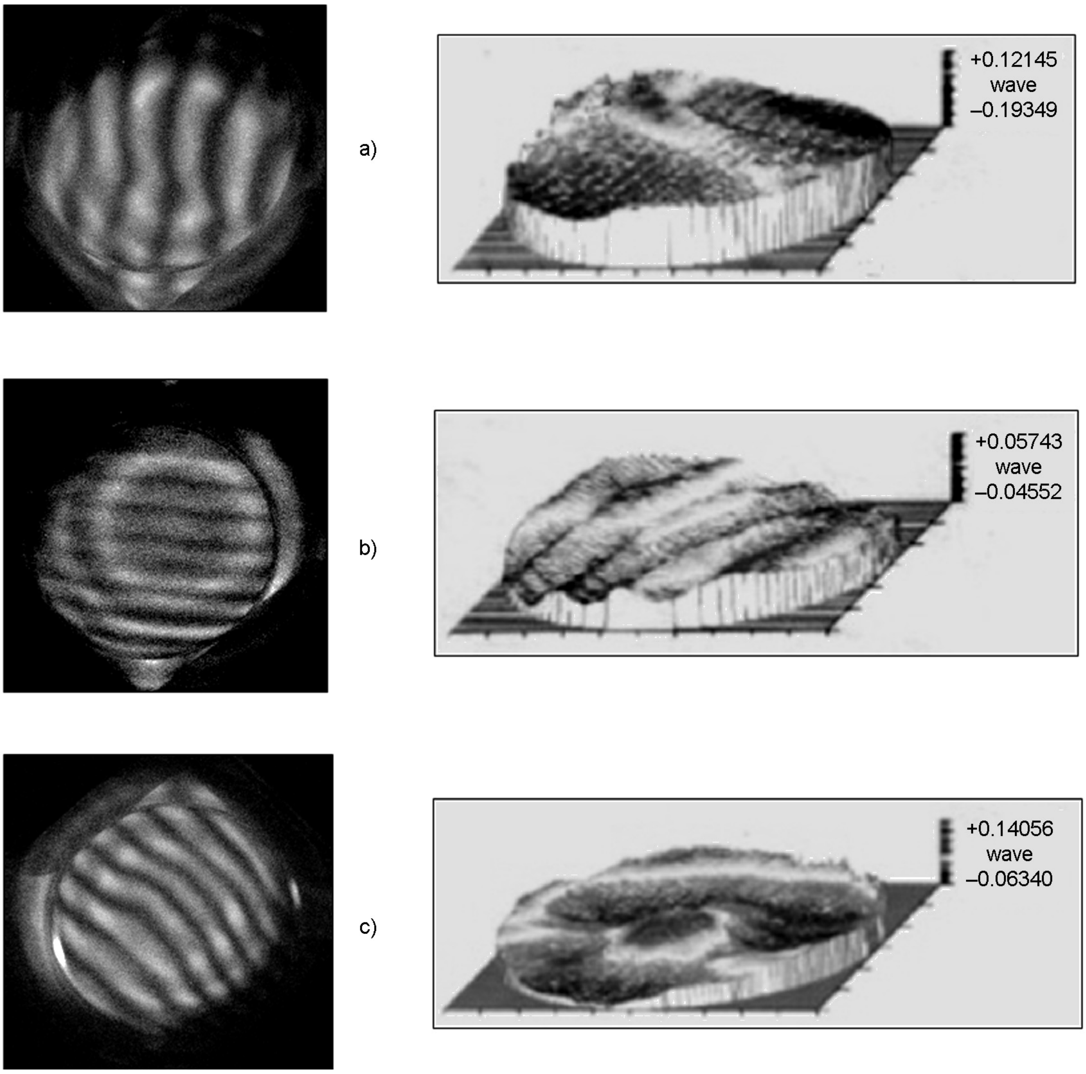

Fig. 4. Interference pattern and wave front chart of (∅25×15 mm^2) laser elements from Ti-sapphire grown by HDSM (a, b) and Cz (c) methods. The ingots are cut out along (a, c) and at an angle with the crystallization direction (b).

elastic stresses in surface-adjacent layers near the ends of the elements. Such stresses are formed in the process of finishing mechanical treatment which is not followed by annealing.

In the central part of Cz-ingot the total wave front distortion $PV = 0.212\lambda$ is bound up with monotonous radial nonuniformity of the distribution of titanium caused by convex crystallization front (Fig. 4c). Therefore, the crystallization front curvature is the main factor which defines the optical homogeneity of the considered crystals.

The influence of the optical homogeneity of Ti-sapphire grown by HDSM on its laser generation was studied in the process of its work in 100 TW Altechna amplifier. A laser element with the dimensions 50×50×25 mm^3 cut out perpendicularly to the crystallization direction (Fig. 2a,3) was tested in a vacuum cryostat under the residual pressure $1\cdot10^{-4}$ Pa at temperature not higher than 150°C. The element was pumped by a 400 mJ laser ray with a diameter of 30 mm, a spectral width of 50 nm and a radiation maximum at 800 nm.

The crystal structure quality is defined by the character of the distribution of intensity of laser radiation transmitted though Ti-sapphire. A ray transmitted through Ti-sapphire element without amplification acquires periodic streaky structure of the energy distribution over the cross-section with a period of about 4 mm (Fig. 5). This is caused by the presence of interblock boundaries with a low disorientation angle

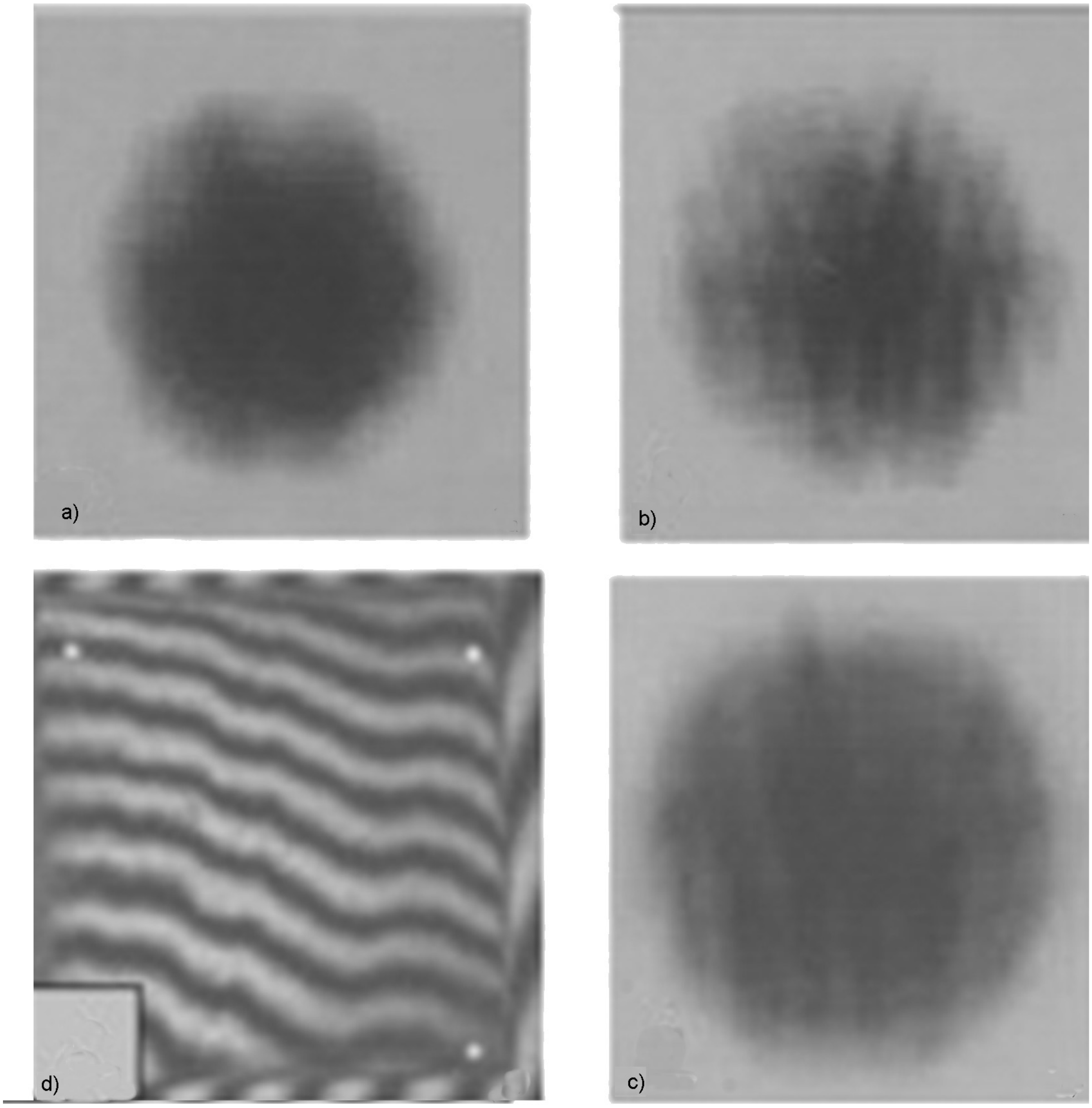

Fig. 5. Interference pattern of 50×50×25 mm active element from Ti-sapphire and energy structure of amplifier laser ray on this crystal: a — input ray (E = 510 mJ); b — output ray (E = 425 mJ) in passive regime; c — amplifier output ray (E = 2.2 J) in active regime; d — interference pattern of the laser element.

that is confirmed by the interference pattern of the laser element. Such a structure of the distribution of radiation intensities is also characteristic of the ray transmitted through Ti-sapphire element in the working regime.

In terms of amplification coefficient HDSM-crystal compares favorably with the HEM-crystal grown by Crystal Systems. However, nonuniform distribution of radiation energy over the laser ray cross-section at high energy loads in the process of generation may be a decisive factor which defines the working characteristics of the material. Optimization of the crystallization conditions and pattern cutting make it possible to minimize the block structure of the crystal and nonuniformity of the distribution of the activator in the laser elements.

4. Conclusions

Thus, the crystals of Ti-sapphire obtained by different methods under reducing conditions have optical and structural peculiarities and demonstrate rather high and comparable functional characteristics. There is shown the possibility to use Ti-sapphire crystals grown by HDSM in reducing medium for the making of wide-aperture laser elements with a diameter of 20–50 mm. The minimum wave front distortion (0.1λ) and FOM-factor of 200–250 are characteristic for the elements with the ends oriented in parallel to the crystallization front of the initial crystal after their thermal treatment in medium with the reduction potential $\varepsilon \approx -180...-230$ kJ/mol. The main problem to be solved for the development of the technology of HDSM for the growth of Ti-sapphire laser crystals is optimization and increase of the stability of the growth conditions.

References

1. Je Stone-Sundberg, in: Materials of First Workshop on Technological Bottlenecks in Compact High Intensity Short Pulse Lasers, Paris, France, April 1–4 (2003).
2. D.B.Joyce, F.Schmid, *J.Cryst. Growth*, **312**, 1138 (2010).
3. A.Ya.Dan'ko, S.V.Nizhankovsky, V.N.Kanischev et al., *Functional Materials*, **13**, 426 (2006).
4. E.V.Krivonosov, L.A.Litvinov, *Functional Materials*, **3**, 77 (1996).
5. S.V.Nizhankovskiy, A.Ya.Dan'ko, E.V.Krivonosov, V.M.Puzikov, *Inorgan. Mater.*, **46**, 35 (2010).
6. S.D.Vishnevsky, E.V.Kryvonosov, L.A.Lytvynov, *Inorganic Materials*, **45**, 1009 (2009).
7. S.D.Vishnevsky, E.V.Kryvonosov, L.A.Lytvynov, *Crystallography*, **53**, 156 (2008).
8. V.S.Konevsky, E.V.Kryvonosov, L.A.Lytvynov, M.I.Shakhnovich, *J.Appl. Spectroscopy*, **50**, 651 (1989).
9. S.D.Vyshnevskiy, E.V.Kryvonosov, L.A.Lytvynov, *Functional Materials*, **10**, 238 (2003).
10. V.S.Konevsky, E.V.Kryvonosov, L.A.Lytvynov, *Inorgan. Mater.*, **25**, 1486 (1989).
11. Ulraine Patent 53469 (2002).
12. J.Dong, P.Deng, *J.Cryst. Growth*, **261**, 514 (2004).

Оптичні і лазерні властивості Ti-сапфіру, що вирощений у відновному середовищі

Є.В. Кривоносов, С.В. Ніжанковський, Л.А. Литвинов, А.А.Буй

Досліджено оптичні і лазерні властивості Ti-сапфіру, що вирощений у відновному газовому середовищі. Показано, що ГСК-кристали мають достатньо високі функціональні характеристики і можуть використовуватися для виготовлення широкоапертурних лазерних елементів діаметром 25–50 мм. Мінімальним спотворенням хвильового фронту (0,1λ) і значенням FOM-чинника 200–250 характеризуються елементи з торцями орієнтованими паралельно фронту кристалізації початкового кристала, що пройшли термообробку у середовищі з відновним потенціалом $\varepsilon \approx -180...-230$ кДж/мол.