

Spectral properties of Er-doped yttrium aluminum garnet crystals grown by modified horizontal directional crystallization method

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For the first time Er³⁺-doped yttrium aluminum garnet single crystals were grown by modified horizontal directional crystallization method in the reducing atmosphere Ar+(CO, H₂). The absorption and photoluminescence spectra of the grown crystals were measured. The absorption spectra consisted of the bands corresponding to the optical transitions between the ground and the excited states of Er³⁺ ions and the bands caused by intrinsic defects and the impurity ions Ti³⁺. Post-growth annealing in an oxidizing atmosphere reduced or eliminated these absorption bands. The IR photoluminescence spectra consisted of several emission peaks in 1450–1700 nm region. The up-conversion photoluminescence lines in the UV region at 382 nm excitation were detected. A model is proposed in which the absorption by the excited state is considered to be the main up-conversion mechanism.

Keywords: Er-doped yttrium aluminum garnet, modified horizontal directional crystallization method, reducing atmosphere, optical absorption, photoluminescence.

Методом модифікованої горизонтальної направленої кристалізації в восстановительной атмосфере Ar+(CO, H₂) впервые выращены монокристаллы иттрий-алюминиевого граната, легированные Er³⁺. Измерены спектры оптического поглощения и фотолюминесценции выращенных кристаллов. Спектры поглощения состоят из линий, соответствующих оптическим переходам между основным и возбужденным состояниями ионов Er³⁺ и полос, связанных с F-центрами и примесными ионами Ti³⁺. Пост-ростовой отжиг в окислительной атмосфере уменьшает или устраняет эти полосы поглощения. Спектры ИК фотолюминесценции состоят из нескольких пиков излучения в области 1450–1700 нм. При возбуждении 382 нм зафиксированы линии ап-конверсионной люминесценции в УФ области. Предложена модель, в которой основным ап-конверсионным механизмом является поглощение из возбужденного состояния.

Спектральні властивості кристалів Ер-легованого ітрій-алюмінієвого гранату, вирощених методом горизонтальної спрямованої кристалізації. *С.В. Ніжанковський, А.А.Козловський, Н.О.Коваленко, С.І.Кривонозов, Ю.В.Сірик.*

Методом модифікованої горизонтальної спрямованої кристалізації у відновній атмосфері Ar+(CO, H₂) вперше вирощено монокристали ітрій-алюмінієвого гранату, леговані Er³⁺. Виміряно спектри оптичного поглинання та фотолюмінесценції вирощених кристалів. Спектри поглинання складаються з ліній, які відповідають оптичним переходам між основним і збудженим станами іонів Ер³⁺ і смуг, пов'язаних з F-центрами і домішковими іонами Ті³⁺. Відпал після вирощування в окислювальній атмосфері зменшує або усуває ці смуги поглинання. Спектри ІЧ фотолюмінесценції складаються з декількох піків випромінювання в області 1450–1700 нм. При збудженні 382 нм зафіксовано лінії ап-конверсійної люмінесценції в УФ області. Запропоновано модель, в якій основним ап-конверсійним механізмом є поглинання зі збудженого стану.

1. Introduction

Interest in laser devices emitting in the spectral range 1.5–1.7 μm is due to a number of factors. First of all, such a radiation is considered relatively safe for the human visual system. The optical absorption in this spectral range by liquid water of the eye's transparent tissues is significant, so the damaging effect of laser light on the retina is minimized. In addition, the Earth's atmosphere is almost transparent for this spectral region, thus the 1.5 μm radiation extends through the atmosphere practically no distortions and losses. These features provide applications of 1.5–1.7 μm lasers in the systems of laser location, aerial navigation, remote sensing and ranging [1]. Lasers operating in the eye-safe range, are also useful for detection of methane CH_4 , which optical absorption band is 1645 nm [2]. Methane is a strong greenhouse gas 25 times more powerful per unit mass in warming the climate than CO_2 . In addition, this wavelength range corresponds to high sensitivity of photodetectors (InGaAs photodiodes).

Er^{3+} -doped host materials are traditionally used as laser media for generation of 1.5–1.7 μm radiation. In recent years, there has been a growing interest in the laser operation of Er^{3+} :YAG single crystals due to considerable progress in laser-pumping technology [3–7]. The absorption lines of Er:YAG crystal are 1532 nm and 1470 nm, that allows direct pumping. Resonant pumping sources are Er:Yb fiber lasers emitting at 1532 nm [8] or laser diodes emitting at 1470 nm and 1532 nm [9]. The main advantage of Er:YAG resonant pumping is a low quantum defect [10]. Moreover, YAG has a number of additional advantages as a host matrix for laser applications, including high thermal conductivity, chemical inertness, mechanical strength and thermal re-

sistance. To obtain the laser generation 1.5–1.7 μm , Er:YAG crystals with low Er concentration (0.1–1 at.%) are required [11, 12]. Earlier it was reported about growth of Er:YAG single crystals by the Czochralski method [13, 14], laser-heated pedestal growth technique [15] from iridium crucible in an oxidizing atmosphere.

In this paper we report the production and characterization of spectroscopic properties of Er:YAG single crystals grown for the first time by the modified horizontal directional crystallization (MHDC) method [16] in reducing carbon-containing environment with using molybdenum crucible.

2. Experimental

The main disadvantage of the growth of yttrium-aluminum garnet crystal by traditional HDC method in vacuum is a significant burning of the constructional materials (Mo, W) of the furnace. In this connection, the crystallization processes in molybdenum crucibles by MHDC were carried out in weakly reducing atmosphere $\text{Ar}+(\text{CO}, \text{H}_2)$ at a pressure of 0.1 MPa. The crystallization rate was 2–2.5 mm/h. The temperature gradient at the crystallization front was 10–30 K/cm depending on the stage of the growth and the degree of overheating of the melt.

The dimensions of Er^{3+} :YAG (0.5 at % Er^{3+}) crystals were up to 70×150×15 mm³. To investigate the influence of the growth conditions on the optical properties of the crystals, annealing of the grown crystals was carried out in vacuum and in the air. For comparative analysis of the optical characteristics, Er-doped YAG crystals were also grown by Czochralski method from iridium crucible.

The optical absorption spectra of the crystals were measured at room temperature by means of a UV-Vis spectrometer (Optizen 3220, double beam) with a step of 1 nm.

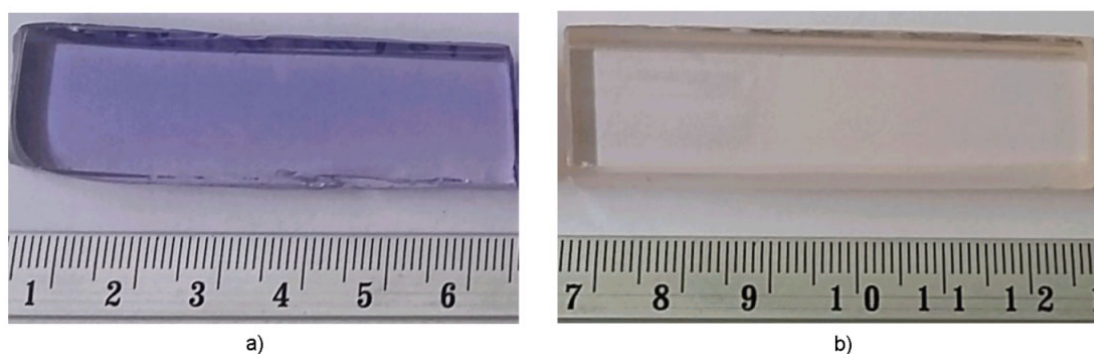


Fig. 1. Grown Er:YAG single crystal before (a) and after (b) annealing.

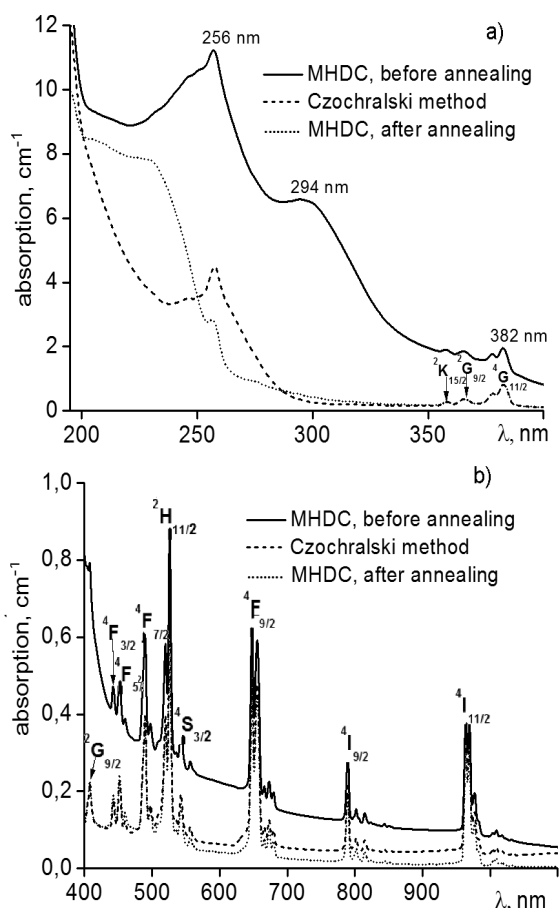


Fig. 2. Optical absorption spectra of $\text{Er}^{3+}:\text{YAG}$ single crystals grown by the MHDC and the Czochralski method in the near- and middle-UV spectral ranges (a) and in the visible and near-IR spectral ranges (b).

3. Results and discussion

The grown $\text{Er}^{3+}:\text{YAG}$ crystals were blue-violet (Fig. 1a). After the annealing conducted in an oxidizing atmosphere at temperatures of 1100–1200°C for 24 h, the crystals became slightly pink (Fig. 1b).

The sharp absorption bands in $400 \text{ nm} < \lambda < 1100 \text{ nm}$ spectral region correspond to the optical transitions of erbium ions from the ground state ${}^4I_{15/2}$ to different excited energy levels. Based on the literature data [17–21], nine absorption bands in this spectral region for grown crystals were identified and marked in Fig. 2b.

Besides the absorption lines of Er^{3+} , there are observed intense bands peaked in UV spectral region and broad absorption band at 550–600 nm. The intense absorption maxima in UV spectral region were recorded at 256 nm, 294 nm and 382 nm. After annealing in an oxidizing environment the peak at 256 nm decreased, and the

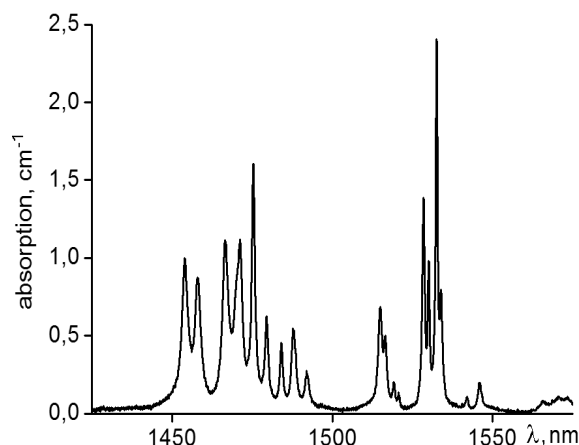


Fig. 3. Absorption spectrum of $\text{Er}^{3+}:\text{YAG}$ single crystals grown by MHDC in the spectral range corresponding to optical transition ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$.

peak at 294 nm disappeared completely. This testifies to a possible connection of these peaks with the F -centers. The intensity of absorption at 382 nm after oxidative annealing also decreased significantly. The spectral position of this peak coincides with optical transition ${}^4I_{15/2} \rightarrow {}^4G_{11/2}$ of Er^{3+} . Therefore, the intensive optical absorption at 382 nm is due to both the corresponding optical transition of Er^{3+} ions and the absorption by intrinsic point defects such as the oxygen vacancies.

The broad absorption band at 550–600 nm also vanished entirely after annealing. The appearance of this absorption band in the unannealed crystal is associated with the presence of a small ($\approx 10^{-3}$ wt.%) amount of Ti^{3+} impurity. The content of the impurities was determined by means of the method of inductively coupled plasma-atomic emission spectrometry using a spectrometer ICAP 6300 Duo (Thermo Scientific, USA). It is known that Ti^{3+} ions are characterized by optical absorption in the 550–600 nm band. Annealing in an oxidizing atmosphere leads to a change of the charge state of titanium ions $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$. Tetravalent titanium has the electron configurations $3d^0$. Due to empty $3d$ -levels, there are no electron transitions amongst d -orbitals of Ti^{4+} . This explains decoloration of the crystal after annealing.

Thus, annealing improves the optical properties; in particular, the optical absorption by the matrix of yttrium-aluminum garnet decreases, and the absorption bands caused by intrinsic point defects such as the oxygen vacancies decrease or completely disappear. After annealing, optical properties

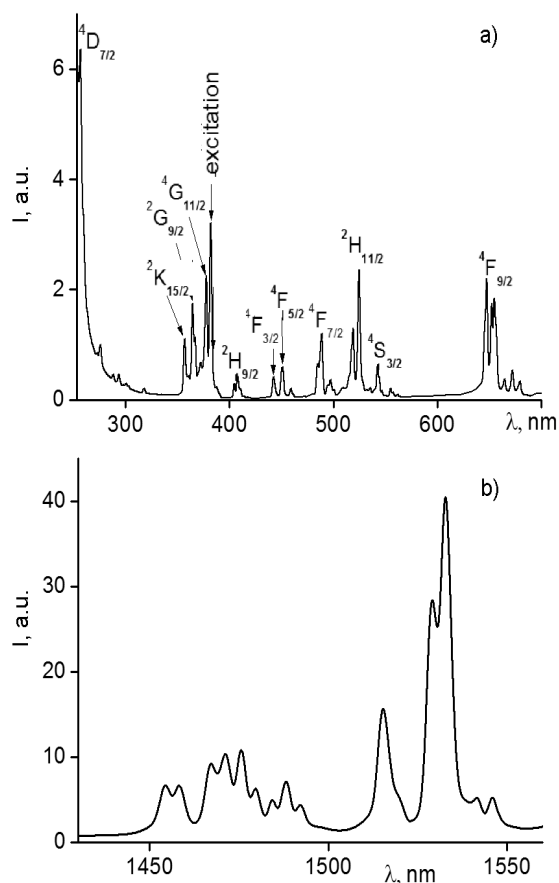


Fig. 4. Er^{3+} :YAG emission spectra in: (a) visible and near-UV ranges, (b) IR band.

of Er^{3+} :YAG crystals grown by HDC are equivalent to the properties of crystals obtained by the Czochralski method using iridium crucibles (Fig. 2).

Fig. 3 shows the IR absorption spectra of the grown crystals in the range corresponding to the optical transitions between $^4I_{13/2}$ and $^4I_{15/2}$ multiplets of Er^{3+} where generation is formed. A characteristic property of this spectral region is the presence of several spectral bands that form two groups located in the range below and above 1.5 μm and separated by a spectral interval with a width of about 25 nm. The width of each of the bands is approximately 1 nm. Such features of the absorption spectrum in this range are the result of the splitting of the $^4I_{15/2}$ and $^4I_{13/2}$ multiplets of Er^{3+} ions into several Stark components, which form two groups of closely spaced bands separated by a wider energy interval [17, 22]. Among the spectral bands of this range there are the most intense bands with $\lambda = 1470$ nm and $\lambda = 1532$ nm, which may be used for resonant pumping. These peculiarities of the absorption spectra of the grown single crys-

tals are similar to those of the absorption spectra of Er^{3+} :YAG (0,5 at. % Er^{3+}) crystals grown by the Czochralski method [7].

The photoluminescence spectra are shown in Fig. 4. The spectrum in range 250–700 nm was obtained under optical excitation by LED with emission wavelength $\lambda_{max} = 382$ nm and half-width of excitation band $\Delta\lambda = 30$ nm. The emission spectrum of the transition $^4I_{13/2} \rightarrow ^4I_{15/2}$ was recorded under the excitation at $\lambda_{max} = 524$ nm of LED with $\Delta\lambda = 10$ nm.

The main peaks of the luminescence spectrum in 400–700 nm range correspond to the optical transitions of erbium ions identified from the absorption spectrum (Fig. 4a). In the spectral region for $\lambda < \lambda_{ex}$, several up-conversion emission bands were observed (at 378 nm, 366 nm, 357 nm and 256 nm). Thermal excitation of higher quantum states can not exceed a value of the order of kT [23]. At room temperature $kT \approx 250$ cm^{-1} . The energy difference Δ between the Stark levels of $^4G_{11/2}$ state is $\Delta E = E_{378 \text{ nm}} - E_{382 \text{ nm}} \approx 270$ cm^{-1} . The comparable values ΔE and kT shows that the 378 nm band may be due to the anti-Stokes processes.

To explain the origin of luminescence bands with $\lambda < \lambda_{ex}$, it is necessary to consider possible up-conversion processes in the system Er^{3+} :YAG. Fig. 5 presents energy levels diagram of Er^{3+} ions and a simplified mechanism of ultraviolet up-conversion luminescence in Er^{3+} :YAG crystals. The main step of the up-conversion process is excited state absorption (ESA). The excitation emission at 382 nm with the photon energy corresponding to the multiplet $^4G_{11/2}$ ($E \sim 26200$ cm^{-1}) is absorbed by the excited state $^4I_{9/2}$ ($E \sim 12700$ cm^{-1}). As a result, the energy of Er^{3+} ions is increased to the higher $^4D_{7/2}$ level ($E \sim 39000$ cm^{-1}). Then some ions at $^4D_{7/2}$ level relax non-radiatively to the lower energy states $^2K_{15/2}$ and $^2G_{9/2}$. When Er^{3+} ions at the multiplets $^2K_{15/2}$ and $^2G_{9/2}$ transfer into the ground state $^4I_{15/2}$, they produce 357 nm and 366 nm UV emissions, respectively.

It should be noted that in comparison with other UV luminescence bands, the emission band around 256 nm has the largest width. The broadening of this band is obviously due to intrinsic point defects. Thus, UV emission 256 nm can be explained by the following steps: the process of energy transfer (ET) from the excited states $^4D_{7/2}$ of some Er^{3+} ions to the energy level of the defect centers followed by relaxation with emission with wavelength 256 nm (Fig. 5).

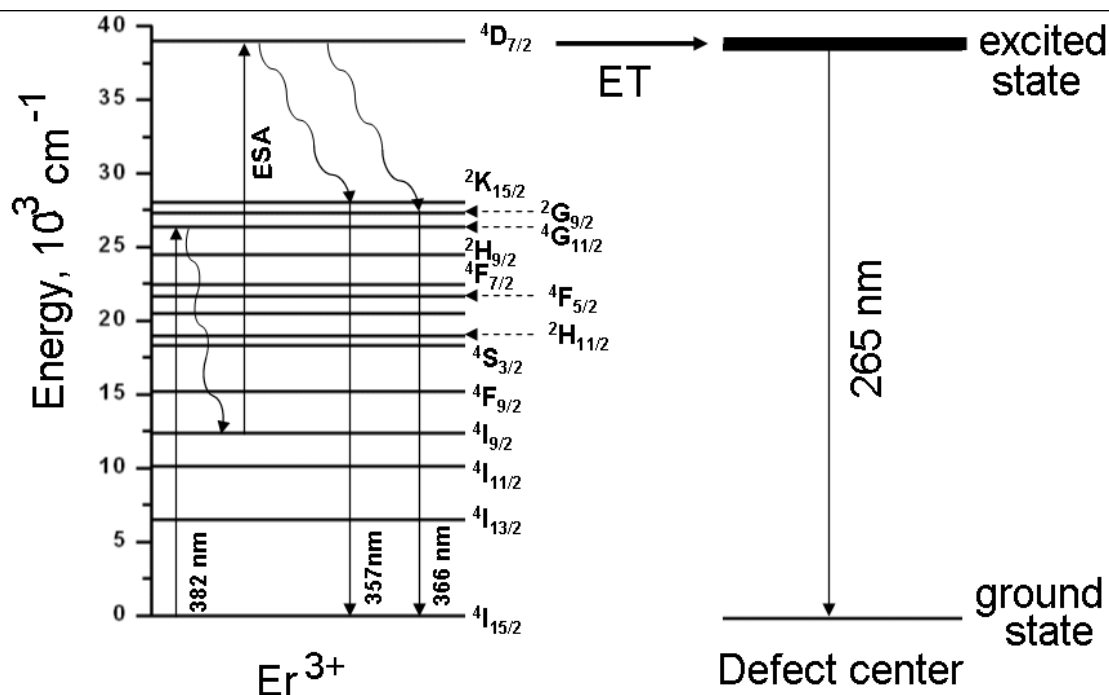


Fig. 5. Energy level diagram and up-conversion processes excited at 382 nm in Er^{3+} :YAG crystal.

The luminescence spectrum of the optical transition of Er^{3+} :YAG had characteristic features similar to the absorption spectrum in the same spectral range (Fig. 4b). There were also two groups of narrow emission peaks separated by a wider energy interval. The peaks from a group with a longer wavelength were more intense. The bands at 1470 nm and 1532 nm were the most intense in each of these groups.

4. Conclusions

For the first time, Er^{3+} :YAG (0,5 at % Er^{3+}) single crystals were successfully grown by the modified method of horizontal directional crystallization in reducing atmosphere $\text{Ar}+(\text{CO}, \text{H}_2)$. Optical spectroscopic measurements showed that the main spectral bands corresponded to the optical transitions between the ground and excited states of Er^{3+} ions incorporated into the YAG crystal lattice. In the absorption spectra there were also the bands in UV region attributed to F -centers, which reduced or disappeared completely after annealing in oxidizing atmosphere. The infrared photoluminescence spectra presented several emission peaks in 1450–1700 nm ranges, caused by the transition $4I_{13/2} \rightarrow 4I_{15/2}$. Up-conversion photoluminescence was detected in UV spectral range and was explained by excited state absorption.

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