1. Introduction

A laser emission in the yttrium-aluminium garnet doped with trivalent chromium, thulium and holmium ions (called CTH:YAG) is due to the quantum transition $5I_7 \rightarrow 5I_8$ in the Ho$^{3+}$ ion. Cr$^{3+}$ and Tm$^{3+}$ ions acts there as the sensitizers [1].

The laser emission from holmium ions has been observed in 1965 in Bell Laboratory [2,3]. Then it was proved that holmium atom cannot be excited directly by flash lamp, because it does not absorb in visible range (Fig. 1).

Erbium was applied as the sensitizer [4], but it happened that chromium was more efficient [5]. It results from two broad absorption bands existing in Cr$^{3+}$ ions in visible region. These bands overlap well the continuous emission spectrum of typical flash lamps. Transfer of excitation from Cr$^{3+}$ ions to the $3F^3$ state in Tm$^{3+}$ is possible due to the overlapping the Cr$^{3+}$ fluorescence band and $^3H_6 \rightarrow 3F_3$ absorption line of Tm$^{3+}$. Excited $3F_3$ state relaxes then to the $^3H_4$ one, and this is followed by cross-relaxation process from $^3H_4$ to $^3F_4$ state. Next, the excitation energy is diffused by Tm$^{3+}$ ions until it is trapped by Ho$^{3+}$ ions, exciting the ones to the $^5I_7$ state.

As the result of subsequent research the optimum concentrations of the dopants were found [6,7] and first solid-state laser based on CTH:YAG material was being operated. The following optimum values of the dopant concentrations were given [8,9]:

$$n(Cr) = 2.5 \cdot 10^{20} \text{ cm}^{-3}, \quad n(Tm) = 8 \cdot 10^{20} \text{ cm}^{-3}, \quad n(Ho) = 5 \cdot 10^{19} \text{ cm}^{-3}$$

In practice, such values of concentrations for thulium and holmium are accepted, but the chromium concentration is varied within the range $7.7 \cdot 10^{19} \div 2.3 \cdot 10^{20} \text{ cm}^{-3}$ [10].
2. Doping the crystal

The aim of this work was to achieve the following values of the dopant concentration in the CTH:YAG crystal:

Cr: 1% at, Tm: 5.7% at, Ho: 0.36% at

These values can be obtained in a crystal with the following stoichiometric equation:

\[(\text{Y}_{1-x-y-z} \text{Ho}_{x} \text{Tm}_{y} \text{Al}_{1-z-x-y-z} \text{Cr}_{z})_{2} \text{O}_{12}\]  \hspace{1cm} (1)

where \(x = 0.0036\), \(y = 0.057\) and \(z = 0.01\). The crystal with such a formula density \(\rho = 4.88 \text{ g/cm}^3\), lattice constant \(a = 12.01\) Å and formula weight equal to 609.38. The volume concentrations of dopants can be derived from these parameters, and it has been obtained:

\[n(\text{Cr}) = 2.3 \times 10^{26} \text{ cm}^{-3}, n(\text{Tm}) = 7.9 \times 10^{29} \text{ cm}^{-3}\]

\[n(\text{Ho}) = 5 \times 10^{19} \text{ cm}^{-3}\]

In manufacturing process the following oxides were used as raw materials (the purity of the oxide is given in parentheses):

\(\text{Y}_{2} \text{O}_{3} (5\%), \text{Al}_{2} \text{O}_{3} (4\%), \text{Tm}_{2} \text{O}_{3} (4\%), \text{Ho}_{2} \text{O}_{3} (3\%), \text{Cr}_{2} \text{O}_{3} (3\%)\).

These oxides were mixed together and then the synthesis reaction was carried out, accordingly to the stoichiometric equation:

\[1.5[(1-x-y-z) \text{Y}_{2} \text{O}_{3} + x \text{Al}_{2} \text{O}_{3} + y \text{Tm}_{2} \text{O}_{3} + z \text{Cr}_{2} \text{O}_{3}] = \text{Y}_{3-x-y-z} \text{Ho}_{x} \text{Tm}_{y} \text{Al}_{1-z-x-y-z} \text{Cr}_{z} \text{O}_{12}\]  \hspace{1cm} (2)

where \(x = 0.0036\), \(y = 0.0475\), \(z = 0.00417\), and formula weight is equal to 606.33.

The chemical composition of the melt in the crucible (Eq. 2) is not the same as the composition of the crystal being grown (Eq. 1). This is due to the fact that the values of distribution coefficients for some dopants are not equal to unity, i.e., \(k_{\text{Cr}} = 2.4\) [11], \(k_{\text{Ho}} = 1.0\), \(k_{\text{Tm}} = 1.2\).

The partition coefficients are given by Eqs. (1) and (2) together:

\[x = k_{\text{Ho}} x', y = k_{\text{Tm}} y', z = k_{\text{Cr}} z'\]  \hspace{1cm} (3)

These formulas define the relations between concentrations of dopants in the crystal and ones in the liquid phase. If the distribution coefficients are not equal to unity, then, as the crystal grows and volume of liquid in the crucible decreases, the concentrations of dopants in the crystal and in the liquid differs more and more. This is frequently observed phenomenon, leading to the creation of gradient of dopant concentrations within the crystal.

In many cases the value of this gradient can be minimized to such level that it has no further practical influence on the laser parameters. This is particularly important in the case of CTH:YAG crystals, because they are more sensitive to the absolute values of dopants concentrations and to quantitative relations between these values. An analysis of this problem seems to be necessary, but it is not described in the literature.

In normal freeze crystallization process, as in the case of Czochralski's method, the distribution of dopant concentration in the crystal is described by so called normal-freeze equation:

\[c = c_{0} (1 - g)^{k-1}\]  \hspace{1cm} (4)

where \(c_{0}\) is the dopant concentration in the crystal, \(c_{0}\) is the initial concentration of dopant in liquid phase, \(k\) is the distribution coefficient and \(g\) is the fraction of the crystallized melt.

If \(k = 1\) or \(g = 0\), then Eq. (4) becomes to the form \(c = c_{0}\), from which the Eqs. (3) are derived.

The values of the concentrations of chromium, thulium and holmium are given in Table 1 as a function of parameter \(g\) computed from Eq. (4). The values of parameter \(g\) correspond to the crystal mass under the range 0–30% of liquid phase mass. The concentrations are also given as plots in Fig. 1. One can note the linear character of the plots. The more the partition coefficient differs from unity, the greater are the concentration changes.

<table>
<thead>
<tr>
<th>(g)</th>
<th>(n(\text{Cr}) \times 10^{20} \text{ cm}^{-3})</th>
<th>(n(\text{Tm}) \times 10^{23} \text{ cm}^{-3})</th>
<th>(n(\text{Ho}) \times 10^{19} \text{ cm}^{-3})</th>
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3. Crystals and laser rods

The growth of single CTH:YAG crystals was carried out using Czochralski's method. The melting system was also the same as used in commonly applied garnet growth technology. The crucible was made of iridium and had the cylindrical shape. Its volume was equal to 84 cm³. The melt had chemical composition given by Eq. (2). The crucible was thermally isolated by zirconia (ZrO₂·HfO₂ granulate) and alumina ceramics, and the crystallization process was carried out in pure nitrogen atmosphere (2 ppm purity). The growing crystal was placed in iridium screen of cylindrical shape with longitudinal slots. Melting the substrates was done by RF field of frequency about 400 kHz.

The growth rate of the crystal was 1.8 mm/h with 30 rotations per minute. The following crystals were manufactured in such conditions:

- one crystal with diameter 18 mm (referred as G2), 70 mm length and 83 g mass (it means 28% of the total mass of substrates);
- one crystal with diameter 15 mm (referred as G3), 75 mm length and 70 g mass (i.e., 25% of total mass of the substrates).

Because mass distribution along the crystals is uniform, we can substitute the increase of mass by increase of crystal length. It can be found this way, that the change of parameter \(g\) from 0 to 0.28 corresponds to decrease of concentration of chromium from 2.3×10²⁵ to 1.45×10²⁵ cm⁻³, and thulium from 7.9×10²⁵ to 7.4×10²⁵ cm⁻³, along the entire length of crystal. Two laser rods were cut out from G2 crystal (they are referred as G21 and G22 in Table 1).

In the case of crystal G3 the same considerations give values of concentration varying along the crystal length within range 2.3×10²⁶–1.54×10²⁶ cm⁻³ for chromium, and 7.9×10²⁶–7.46×10²⁶ cm⁻³ for thulium. This crystal was used as the material for laser rods referred in Table 1 as G37 and G32.

Considering the data given in literature (see previous sections), we have found that variations of dopant concentrations in the crystals G2 and G3 are not too large. Hence, they should not influence the quality of laser rods made of these crystals.
4. Spectral characteristics

The optical quality of the manufactured single crystals was tested using the polariscope and the Mach-Zehnder interferometer. The crystals were also inspected with a 10 mW CW He-Ne laser beam. Optically homogeneous parts of the crystals were used to cut out samples with 15 mm diameter and 4.5 mm thickness. The transmission spectra of the samples were measured by means of spectrophotometers (Perkin-Elmer model LAMBDA 2 within 200-1100 nm range, and Beckman Instruments model ACTA MVII within 1.4-25 μm). The measured values of transmission were used to compute the absorption spectra a(λ). The multiple reflections of the laser beam within the sample were also taken into account.

The results of spectral investigations are presented in Fig. 2. The absorption of CTH:YAG crystal is given for 200 ÷ 2000 nm wavelength range. Short-wave cutoff edge of absorption in CTH:YAG crystal is observed at λ = 250 nm. For wavelengths greater than 6 μm the lattice absorption appears.

Fig. 2. Theoretical distribution of dopants along the length of CTH:YAG crystal

5. Laser characteristics

The manufactured laser rods were placed into the laser head equipped with cylindrical, silver-coated reflector. The reflector was made of fused silica doped with samarium. This provided conversion of the flash lamp radiation from ultraviolet range to longer wavelengths. Total length of the reflector was equal to 55 mm. The laser resonator used in the measurements had following parameters: geometrical length L = 20 cm, reflection coefficient of output mirror R = 68%, and radii of curvature of the both mirrors r = ∞ (plane surfaces).

The shape and the duration of pumping pulse were optimized to obtain maximum output energy of the laser. Discharge time of the condenser bank (with capacitance C = 210 μF) in power supply was measured on the level of 0.7 I max and was equal to 500 μs.

The energetic characteristics of the measured laser rods are shown in Fig. 3 (before annealing) and in Fig. 4 (after annealing process). The threshold values of pump energy E thr and differential efficiency of laser generation εthr are given in Table 2.

The energetic characteristics of the rods G31 and G32 were not varying during the measurements carried out before annealing. The rod G22 behaved in another way: after several minutes of operation in the resonator, its output energy has decreased from 300 to 170 mJ (at constant pump energy E thr = 270 J). It was also observed the deterioration of the spatial distribution of its output beam intensity. The energetic characteristics of G22 rod (shown in Fig. 3) were measured after this rod achieved its stable state and the efficiency has not decreased.

Annealing of laser rods essentially improves their laser features. This can be seen if the plots in Figs. 3 and 4 and data given in Table 2 are compared. It seems also that annealing eliminates the temporal decrease of laser efficiency. However, this conclusion should be confirmed in the future during measurements of long-term stability of the output energy.
In present work the laser head, the resonator geometry and the transmission of output mirror were not optimized. The length of flash lamp and lengths of laser rods were not matched as well.

6. Summary

The single CTH:YAG crystals manufactured by the authors have not significant optical nonhomogeneities out of the core area. However, the reasons of small laser efficiency have not been explained. Probably, this effect is caused by microscopic defects of the crystal structure, like stress, oxide vacancies or other point-like defects in the lattice. These defects disappear after annealing in temperature 1500°C and in oxidizing atmosphere.

Using raw materials of higher purity and adding oxygen presence during the crystallization process should eliminate the parasitic effects.

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References

12. Z. Frukacz — to be published