Fluorescence quantum efficiency of Ti$^{3+}$:Al$_2$O$_3$ at cryogenic temperatures and excitation by laser diodes

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Abstract. In this work the temperature dependences of the fluorescence of a titanium-sapphire crystal excited by radiation with $\lambda$=507 nm, $\lambda$=454 nm and $\lambda$=405 nm are measured. The quantum efficiency of fluorescence is determined. It was found for the first time that the quantum efficiency of fluorescence exceeds 100% in the cryogenic temperature range when the crystal is excited by radiation with $\lambda$ = 454 nm. It is equal to (117 ± 5)% and (114 ± 5)% at $T$ = 77 K for crystals grown by the Czochralski method and by gradient of temperature one, respectively.

1. Introduction
It is known that at cryogenic temperatures the thermal conductivity of sapphire sharply increases and its spectroscopic characteristics change, which makes it possible to use high pump intensities and provide the highest output power of generation of titanium-sapphire lasers and amplifiers.

Measurements of the quantum efficiency (QE) of the titanium-sapphire (TiSa) crystal were carried out by various methods. For example, in [1], the internal QE was measured in the generation of a titanium-sapphire laser at room temperature (64%). When a TiSa laser was pumped at liquid nitrogen temperature by the blue lines of an argon-ion laser, the quantum efficiency of such laser was ~100% [2]. In [3], qualitative indications are given that at cryogenic temperatures and when a TiSa crystal is pumped at wavelengths of ~ 450 nm, the QE of fluorescence is greater than 100%. The authors of [4] performed measurements of the fluorescence quantum efficiency in a wide temperature range (150–550 K), when excited by a laser with a wavelength of 543 nm. As far as we know, at cryogenic temperatures there are no quantitative measurements of the quantum efficiency of fluorescence of a titanium-sapphire crystal irradiated with light radiation with a wavelength in the range of 400 - 500 nm.

The issue of quantum efficiency at cryogenic temperatures is very topical and is of scientific interest from the point of view of the processes occurring during excitation of a TiSa laser, as well as when choosing the optimal pump wavelength for TiSa lasers and amplifiers at low temperatures.

The aim of our work is to quantitatively measure the fluorescence quantum efficiency of Ti$^{3+}$:Al$_2$O$_3$ crystal at cryogenic temperatures and excitation by laser diodes at wavelengths 507 nm, 454 nm and 405 nm.

2. Experiment setup and methods
The experimental setup is shown in Figure 1. Linearly polarized radiation from a laser diodes (LD) with wavelengths of 507 nm, 454 nm and 405 nm is collimated by telescope (x0.3) to diameter of ~1 mm and directed in Ti$^{3+}$:Al$_2$O$_3$ crystal. The fluorescence from the crystal is collected by the lens (L) and recorded by the photodetector (FD). Unabsorbed radiation emerging from the crystal is reflected from an interference filter (F), (transmission 600-950 nm) to a photodetector (FD) to control the absorbed power.
The unsaturated gain $g_0$ under these excitation conditions was $10^{-5}$ cm$^{-1}$ (LD power ~30–100 mW), and the contribution of stimulated radiation was no more than 0.2 % of the fluorescence power incident on the photodiode.

Figure 1. Experimental setup. LD – laser diode, x0.3 – collimator, Cryo – cryostat F – interference filter, L – collected lens, PD – photodetectors, TiSa – titan-sapphire crystal.

The Ti$^{3+}$:Al$_2$O$_3$ crystalline rod grown by the Czochralski method with a diameter of 5 mm and a length of 10 mm with Brewster-cut and optically polished facets was placed in cryostat (Cryo) whose temperature could be changed from 77 K to 320 K. Fluorescence was excited by pumping from an appropriate laser diode into the π absorption band.

Figure 2 shows the plot of crystal absorption as a function of wavelength (points) and its approximation (yellow) with Gaussian curves (red).

To determine the quantum efficiency under pumping with radiation from 507 nm to 454 nm or 405 nm, the corresponding curve of the dependence of the fluorescence intensity as a function of temperature was recorded. The temperature dependence of the fluorescence at excitation at 454 nm and 405 nm was compared with the “reference” dependence obtained at excitation at 507 nm. The data obtained at 507 nm are normalized to the value of the fluorescence quantum efficiency (69.5%) at room temperature, measured by the calorimetric method in [5]. The output powers of the lasers are selected so that the same number of photons are absorbed in the Ti$^{3+}$:Al$_2$O$_3$ crystal (28 mW, 38 mW and 100 mW for 507 nm, 454 nm and 405 nm respectively).

Figure 2. Optical absorption spectra (points) and corresponding fitting results of Ti:Al$_2$O$_3$ crystal with Gaussian curves. Violet, blue and green lines – wavelength of laser diodes.
3. Results and Discussion

Figure 3 shows a plot of the dependence of the fluorescence intensity of titanium ions in sapphire under excitation by radiation with $\lambda = 507$ nm, 454 nm and 405 nm as function of temperature.

The fluorescence quantum efficiency of Ti$^{3+}$:Al$_2$O$_3$ crystal when pumped at 507 nm was $(97\pm5)$ %, and when pumped at 454 nm it was $(114\pm5)$ %. The quantum efficiency under pumping at 405 nm practically did not change with temperature and amounted to about 24% ± 5%. Similar measurements were carried out for a titanium-sapphire crystal grown by the temperature gradient method (TGT). The quantum efficiency at pumping at 507 nm and 454 nm was 95% and 114%, respectively. The quantum efficiency when pumped at 405 nm was 23%.

The reasons for the quantum efficiency of more than 100% can be associated with the presence in the Al$_2$O$_3$ matrix of complexes of Ti$^{3+}$-Ti$^{3+}$, 2Ti$^{3+}$-V$^+_0$+2e$^-$ ions, which form their own energy level schemes. It was noted in [6] that the Ti$^{3+}$-Ti$^{3+}$ complex participates in the formation of absorption spectra in the 400–450 nm region. In our opinion, this can lead to an increase in the quantum efficiency of luminescence by more than 100% by transferring excitation from the energy level of this pair to the energy levels of two Ti$^{3+}$ ions.
Figure 4. Simplified energy-level diagrams for isolated Ti$^{3+}$ and complex ions of Ti in sapphire (from Ref. [7]).

The theoretically calculations of such energy levels complexes Ti$^{3+}$-Ti$^{3+}$ and other complexes were theoretically performed in [7]. Figure 4 shows simplified level diagrams based on the results of this work (Figure 9b and Figure 10a). The red arrow points to the lowest inhabited level.

The transition wavelengths and energies are as follows (green stars in Figure 4):

- Ti$^{3+}$ - 448 nm (2.77 eV),
- Ti$^{3+}$ - Ti$^{3+}$ - 334 nm (3.71 eV), 373 nm (3.32 eV), 506 nm (2.45 eV), 961 nm (1.29 eV).

It is known that theoretical calculations of energies based on approximations like [7] give a large uncertainty (up to 40%) both when calculating the energy of the lower level and when calculating the distances between them; therefore, it is difficult to accurately identify the level, perhaps this is a transition from wavelength 334 or 373 nm.

Unfortunately, there are no published data on the calculations of the energy levels of the 2Ti$^{3+}$-V$_{O}$+2e$^-$ complex. In [8] the authors associate an absorption peak at about 400 nm with this complex.

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