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Investigation of the photoionization of Ce^{3+} ions in YAG crystal by microwave resonant technique

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Kinetic and spectral characteristics of the complex dielectric constant of Ce:YAG crystal under laser irradiation in 250–275 nm spectral range are investigated. The lifetimes of free charge carrier and charge carriers, localized at the lattice defects (color centers), are estimated. It was established that photoconductivity signal of the sample is essentially caused by one-photon ionization processes from the $^2F_{5/2}$ ground state of Ce^{3+} ions.

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1. Introduction. A microwave resonant technique based on the measurements of the cavity resonator parameters variations after the investigated material was put inside is the powerful instrument for research of the dielectric properties of semiconductors, insulators, liquids and even gases [1–3]. It allows not only to determine absolute values of the complex dielectric constant of the matter, but to investigate the photoconductivity and photodielectric effects as well [4]. This technique as compared with the conventional method utilizing blocking electrodes has a number of advantages. Firstly, the use of the cavity resonator leads to a better shielding from the external interferences, which in turn enables the investigation of extra small variations of the dielectric properties of the matter. Secondly, the abandonment of metal blocking electrodes prevents the distortion of the investigated materialś energy bands and mutual displacement of the Fermi level and energy levels of the impurity ions in the investigated material in the vicinity of metal-dielectric contact, which could appreciably influence the result of photoconductivity measurements [5]. It also allows to eliminate stray wire inductances and interelectrode capacitances of the measuring cell. Finally, the transient time of electromagnetic field in the cavity resonator is small enough to provide subnanosecond temporal resolution (which is impossible via conventional method) and, therefore, makes it possible to investigate the kinetics of the fast processes associated with the photoinduced charge carriers.

The potential of microwave resonant technique is illustrated by the progress of investigations of the electrophysical parameters of semiconductors, such as: surface recombination rate, mobility and lifetime of the free charge carrier [6–9]. The authors of [10] were the first to apply microwave resonant technique to study rare earth photoionization threshold investigations in dielectric crystals. The study of the impurity photoionization is especially important for the solid-state materials used in quantum electronics that operate on the interconfigurational transitions of the impurity ions. This is due to the fact that the majority of activated materials experience degradation of optical properties under UV excitation. The study [11] showed that one- or multiphoton impurity ionization (depending on the impurity ion and crystalline matrix) is the main reason of such degradation. Impurity photoionization leads to the generation of free charge carriers (electrons and holes) in the appropriate energy bands of the crystal, that could be captured by lattice defects (color center formation). So impurity photoionization significantly changes optical and electro-physical properties of the crystal undergoing intense irradiation. In particular, these processes limit spectral and energy characteristic of laser media operating on the $5d$–$4f$ interconfigurational transitions of trivalent rare earth ions, and may even prevent any lasing. Therefore, the study of photoionization spectra is important both for the choice of pumping source for the solid-state active media and for the creation of crystalline scintillators with predefined properties. In addition the study of impurity photoionization will enable to determine the positions of the energy states of the impurity centers relative to the bands of the host.

2. Concept of the microwave resonant technique. The microwave resonant technique permits the research of the change of the complex dielectric constant of the matter undergoing different external influ-

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ences (optical irradiation in particular). Variations of the imaginary and real parts of the complex dielectric constant of the medium are caused by photoconductivity and photodielectric effects, respectively.

In activated crystals the photoconductivity is mainly contributed by the free charge carriers generated as a result of the impurity photoionization. As opposed to the photoconductivity, photodielectric effect is caused by the change of dielectric polarization of the crystal under external influence. Here the electrons and holes, localized at the impurity ions or the electron traps, play the key role.

In general, the change of dielectric properties of the sample, which is placed inside the cavity resonator in the maximum of the electric field, under optical irradiation will lead to a shift of the resonance frequency and change of the cavity Q factor. The relationships between dielectric parameters of the crystal and these characteristics of resonator can be obtained by means of Maxwell equations [12, 13]:

$$\frac{\delta f}{f_0} = -\delta\epsilon' \frac{\int_v EE^* dv}{2\int_V EE^* dV},$$

$$\frac{1}{Q_l} - \frac{1}{Q_{l0}} = \delta\epsilon'' \frac{\int_v EE^* dv}{\int_V EE^* dV},$$

where f_0 – is the resonance frequency of the cavity in the absence of irradiation; δf – the variation of resonance frequency under optical irradiation of the sample; Q_{l0}, Q_l – are the loaded quality factor of the cavity before and under irradiation, respectively; $\delta\epsilon'$, $\delta\epsilon''$ – the variation of real and imaginary parts of complex dielectric constant of the crystal under optical irradiation, respectively; v, V – the volumes of the dielectric crystal and cavity resonator, respectively; E – is the electric field intensity. It should be noted that these relationships are only valid if the field distortions in resonator produced by the sample and its irradiation are small.

3. Material. In this work YAG crystal doped with Ce^{3+} ions has been studied. Its photoionization spectrum has already been obtained before by means of conventional photoconductivity measurements with blocking electrodes [14]. The crystal Ce^{3+}:$Y_3Al_5O_{12}$ (c = 1 at.%) was grown in A.V. Shubnikov Institute of Crystallography of the Russian Academy of Sciences (IC RAS) by means of the Czochralski technique. The sample was polished and shaped as a parallelepiped with the size of $1.5 \times 1.5 \times 0.5\,\mathrm{mm}^3$.

4. Experimental. The technical realization of microwave resonant technique is similar to the electron spin resonance technique. Schematic diagram of the microwave part of the experimental set-up is shown on Fig. 1.

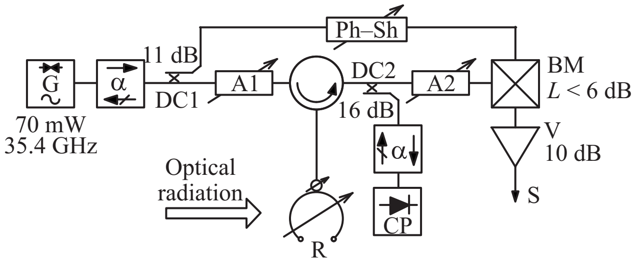

Fig. 1. Schematic diagram of the microwave part of experimental set-up: G – Gunn diode; α – ferrite isolator; DC1 and DC2 – directional couplers; A1 and A2 – attenuators; C – circulator; R – tunable rectangular resonator; CP – microwave detector; Ph-Sh – phase-shifter; BM – balanced mixer; V – broad-band amplifier; S – signal detected by digital oscilloscope

The principal of the setup operation is as follows. The microwave power is supplied by the generator (G) and via directional coupler (DC1) enters the signal and the reference channels of the setup. In the signal channel it passes through adjustable attenuator (A1) and circulator (C) to the tunable rectangular resonator. At first, the sample is placed in the maximum of the electric field in the resonator, and then adjusting the volume of the resonator it is tuned on the operating frequency of Gunn diode. The tuning of the resonator is performed by means of microwave detector (CP), which monitors the portion of microwave power reflected from the resonator. Later when the sample is irradiated by the pulsed laser light, the variation of dielectric properties of the sample leads to the shift of the resonance frequency and change of the cavity Q factor (see section 2). This in turn causes the change of the microwave power reflected from the resonator, and that change is registered.

The use of the phase-shifter, located in the reference channel, and the balanced mixer makes it possible to separately register the variation of either real or imaginary parts of complex dielectric constant (hereinafter photodielectric and photoconductivity signals, respectively) of the sample undergoing laser irradiation [15]. Therefore, certain phase relations between the propagating electromagnetic waves in signal and reference channels should be performed. Notably, photoconductivity measurements will require the phase difference to be equal 0, whereas for the investigation of photodielectric effect the phase difference should be equal $\pi/2$. For any other values of the phase difference the output signal from the balanced mixer will present the mixture of the both signals.

The resonatorś unloaded quality factor Q_u is 800 and time constant τ is about 2 ns and it operates in the TE_{102} mode. The microwave power of Gunn diode

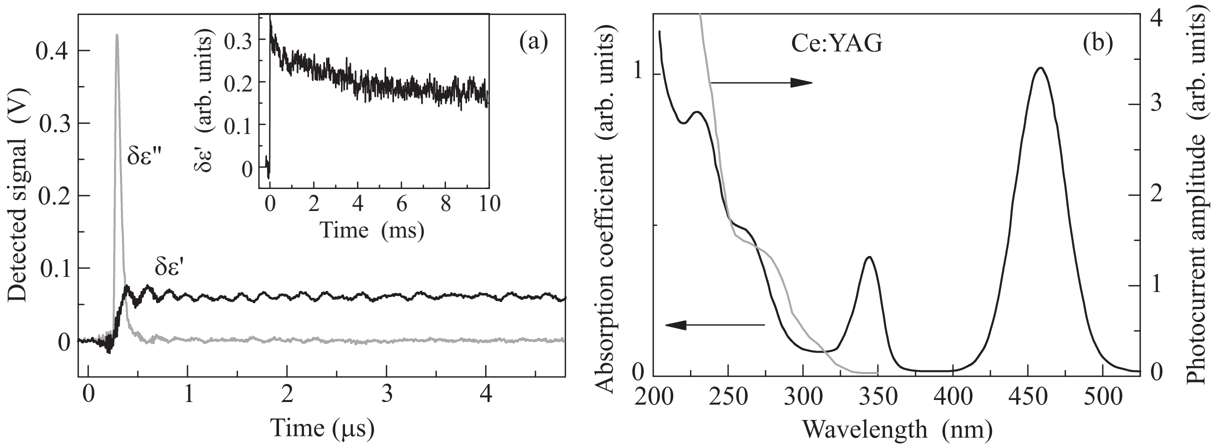

Fig. 2. (a) – Time decays of the real and imaginary parts of complex dielectric constant of YAG:Ce crystal excited by radiation at 250 nm and $T = 300$ K. (b) – The absorption spectrum and spectrum of photoconductivity for Ce:YAG crystal at $T = 300$ K obtained in [14]

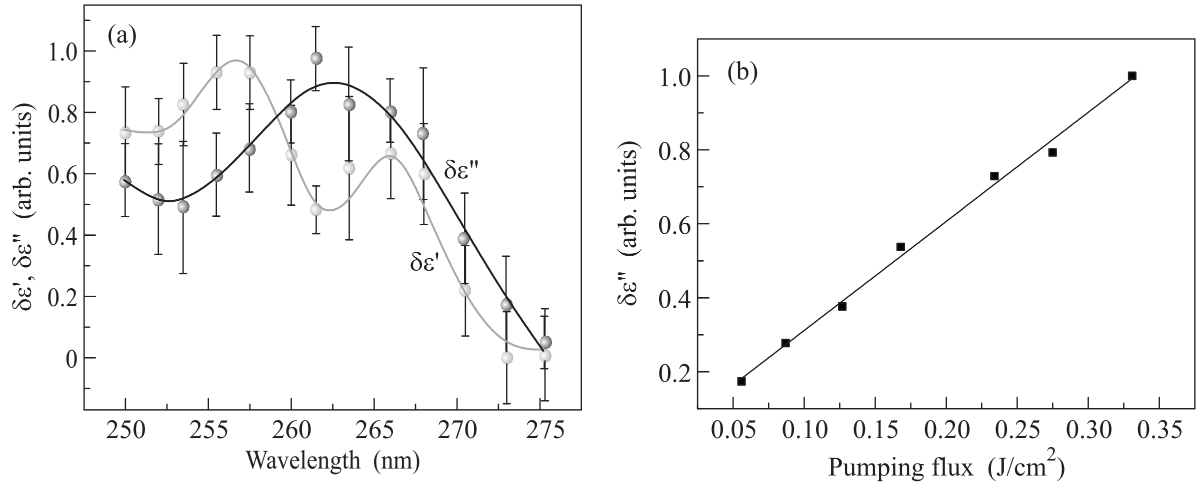

Fig. 3. (a) – Spectral dependences of photoconductivity and photodielectric signals; (b) – Photoconductivity signal as a function of energy density of excitation radiation at 260 nm ($T = 300$ K)

is 70 mW and its operating frequency is 35.4 GHz. The sample was excited by radiation of the third harmonic of tunable Al_2O_3: Ti laser. Pulse duration and pulse-repetition frequency of the exciting radiation were 15 ns and 10 Hz, respectively. The optical radiation of laser was focused on the crystal to a spot 1.5 mm in diameter. The registration of the signal was carried out by means of 10-bits digital oscilloscope Bordo-423 with 200 MHz bandwidth in equivalent sampling mode with sampling frequency 5 GHz. All the experiments were performed at the room temperature.

5. Experimental results and analysis. Typical registered signal, corresponding to the change of the real and imaginary parts of complex dielectric constant of the investigated crystal under irradiation at 250 nm, are shown in Fig. 2a.

The decay time of photoconductivity signal $\delta\epsilon''(t)$, which characterizes the average free charge carriers lifetime in Ce:YAG crystal appeared to be 47 ± 1 ns. The photodielectric signal $\delta\epsilon'(t)$ is characterized by the decay time $\tau = (45 \pm 5) \cdot 10^{-4}$ s with a build-up time of the order of hundred nanoseconds. As already noted (see section 2) the photodielectric effect is caused by the change of the concentration of charge carriers, localized at the impurity ions or the electron traps. However, there are reasons to suppose that the observable photodielectric signal is not associated with the interconfigurational transitions of the impurity ions. Firstly, the build-up time of photodielectric signal roughly matches the decay time of photoconductivity signal and photodielectric signal decay time is considerably exceeds the average lifetime of the excited 5d-state of Ce^{3+}

ions [16]. Secondly, when the sample was excited in the spectral range 340–350 nm, which corresponds to the second Ce^{3+} $4f$–$5d$ absorption band in YAG crystal (shown in Fig. 2b), the photodielectric signal was not observed.

Spectra of photoconductivity and photodielectric signals in Ce:YAG crystal in the range of 250–275 nm are shown in the Fig. 3a. The photoconductivity spectrum which in fact represents photoionization spectrum of Ce^{3+} ions reveals the band with the maximum at about 265 nm. It is in a good agreement with the ground-state photoconductivity spectrum (see Fig. 2b) registered by means of the conventional method with blocking electrodes [14]. The authors of [14] have also determined the threshold of Ce ions photoionization around 3.8 eV (326 nm) and concluded that the excitation in the UV absorption band peaking around 3.65 eV (340 nm) does not lead to photoconductivity. It is confirmed by our findings that the photoconductivity signal excited by radiation in 340–350 nm spectral range was not observed.

For the correct interpretation of the impurity photoionization spectrum (shown in Fig. 3a) it should be mentioned that for YAG crystal with band-gap energy about 6.2 eV [17] the one-photon ionization process and the two-photon ionization through $5d$-state of Ce ions are possible in 240–295 nm spectral range. However, linear dependence of the photoconductivity signal on the energy density of excitation radiation at 260 nm (shown in Fig. 3b) suggests that the photoionization spectrum observed here is essentially caused by one-photon ionization process originating from the $^2F_{5/2}$ ground state of Ce^{3+} ions.

Spectral dependence of the photodielectric signal, according to the foregoing arguments, apparently reproduces the absorption spectrum of the long-lived color centers with an average lifetime of five milliseconds. However, since no information on the lifetimes or spectra of color centers in Ce:YAG in 250–275 nm spectral domain were found in literature, these findings require further studies.

6. Summary. The kinetic and spectral variations of the complex dielectric constant in Ce:YAG crystal induced by the pulsed laser radiation in 250–275 spectral range are investigated by means of the microwave resonant technique. The lifetimes of free and color centers bounded charge carriers are estimated. The photoionization spectrum of Ce^{3+} ions in the investigated crystal is determined that is in a good agreement with the one registered by means of conventional photoconductivity technique. It was confirmed that main contribution to the photoconductivity signal is made by one-photon ionization process from the $^2F_{5/2}$ ground state of Ce^{3+} ions. The new results of the color center absorption spectrum investigation in Ce:YAG crystal are determined.

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