Photoconductivity of SrAlF$_5$ crystals doped with Ce^{3+} ions

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Abstract. Temporal behaviour of the complex permittivity of Ce:SrAlF$_5$ and Ce,Yb:SrAlF$_5$ crystals under laser irradiation in 240–280 nm spectral range was investigated by a microwave resonance technique. The photoconductivity spectrum of these crystals was detected. It was established that photoconductivity signal of the samples in 240-280 nm spectral range is caused by two processes: excited-state absorption of Ce^{3+} ions and photoionization of color centers.

1. Introduction
Until recently Ce-doped SrAlF$_5$ (SAF) crystal was considered as a promising active medium for UV lasers [1]. However stable laser action in this crystal has not been obtained till now. This is due to the fact that high energy UV radiation initiates the nonlinear photostimulated processes. Photostimulated processes caused by the impurity photoionization deteriorate spectral and energy characteristics of the vast majority of UV solid-state active media [2], and for Ce-doped SAF crystal these processes completely prevent any lasing. Therefore the study of impurity photoionization processes in activated crystals is an important task, since it allows us to determine the necessary conditions for lessening the harmful influence of nonlinear photodynamic processes. In addition it enables us to determine the positions of the energy states of the impurity centres in relation to the bands of the host.

It is known that one of the way to improve laser efficiency of Ce^{3+} doped fluoride crystals is the co-doping of the host crystal by ytterbium ions. In some Ce-doped fluoride crystals (for example Ce^{3+}:LiYF$_4$ and Ce^{3+}:LiLuF$_4$ crystals) the additional activation by Yb^{3+} ions engages a supplementary recombination channel for free carries and decreases the concentration of color centers [3]. The aim of this study is to detect photoconductivity spectrum of Ce:SAF and Ce,Yb:SAF crystals and to investigate the influence of ytterbium ions on the nonlinear photostimulated processes.

As the photostimulated processes significantly change complex permittivity of matter ($\varepsilon = \varepsilon_1 - j\varepsilon_2$) [4], dielectric spectroscopy measurements have been applied to achieve our aim. For instance, the variation of imaginary part of the permittivity of crystal $\delta\varepsilon_2$ can be caused by the appearance of free charge carriers generated as a result of one- or multi-photon impurity ionization, in other words, by photoconductivity effect. On the other hand, the variation of real part of the permittivity $\delta\varepsilon_1$ is associated with photodielectric effect. As opposed to the photoconductivity, photodielectric effect is caused by a change of dielectric polarization of the crystal under external electromagnetic action. Here electrons and holes, localized at impurity ions or traps, play the key role.

2. Materials
In this work Ce:SAF and Ce,Yb:SAF fluorite single crystals grown by means of the Bridgman technique have been studied. The concentrations of impurity ions (cerium and ytterbium ions) were

0.5 at% in the melt. It has been obtained earlier that during growth process ytterbium ions incorporate into the crystal host in trivalent and divalent states and the absorption bands of corresponding Yb^{2+} ions are overlapped with the absorption bands of Ce^{3+} ions in UV spectral region [5]. All crystalline samples were polished and shaped as parallelepipeds with the size of $1.5 \times 1.5 \times 1$ mm. The size of the samples is limited to the experimental technique used in this work.

3. Experimental technique

Microwave resonant technique is one of the most informative methods of dielectric spectroscopy for studying the characteristics of photostimulated processes in rare-earth doped crystals [6]. This technique allows study of the change of both parts of the complex permittivity of matter undergoing different external influences (optical irradiation particularly) and registration photoconductivity and photodielectric effect separately. The microwave technique as compared with the conventional photoconductivity measurements with blocking electrodes has a number of advantages. Firstly, photoconductivity measurements in the microwave cavity are a contactless. When excluding the metal blocking electrodes we prevent the sample from distortion of 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 impact on research results. Secondly, the transient time of electromagnetic field in the cavity resonator is small enough to provide nanosecond temporal resolution (which is impossible via conventional method) and, therefore, it enables us to investigate rapid dynamics of the photostimulated processes.

The microwave part of experimental set-up is shown in figure 1 and has the signal and reference channels. The microwave source was a Gunn diode generator (G) that has the operating frequency of 35.4 GHz and the microwave power of about 70 mW. In the signal channel the microwave power passes through circulator (C) to the tunable rectangular resonator (R) where sample is placed in the antinode of the electric field. At first, the resonator is tuned on the operating frequency of Gunn diode by adjusting the volume. Then the sample is irradiated by the pulsed laser radiation that leads to the change of its permittivity. This in turn causes the change of microwave power reflected from the resonator and resulting change is registered by means of a quadrature balanced mixer (QBM). The mixer combines two balanced mixers that were operated at 90 degree phase shift. The use of quadrature balanced mixer and phase-shifter (Ph-Sh), located in the reference channel, allows us to register the variation of real and imaginary parts of the complex permittivity of sample separately. Detailed description of experimental set-up used in this work is given in [7, 8].
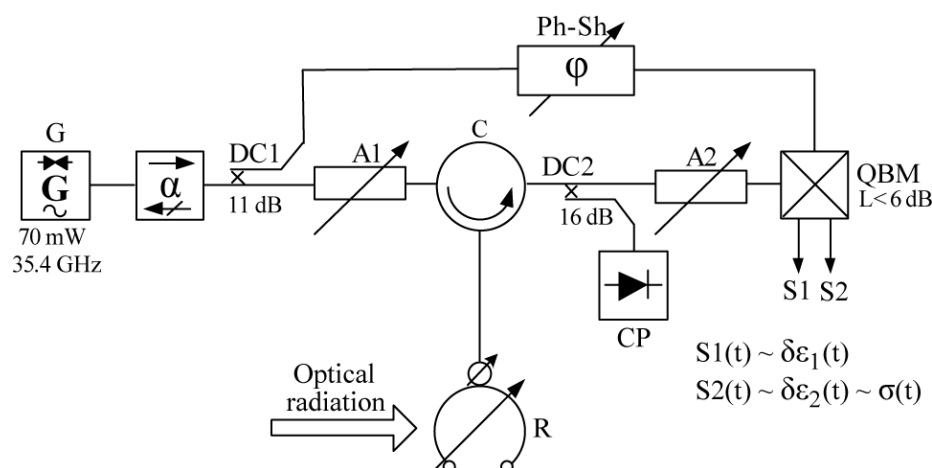

Figure 1. Schematic diagram of the microwave part of experimental set-up: G – Gunn diode; α – ferrite isolator; DC1 and DC2 – directional couplers; A1 and A2 – attenuators; C – circulator; R – tunable rectangular resonator; CP – microwave detector; Ph-Sh – phase-shifter; QBM – quadrature balanced mixer; S1 and S2 – photodielectric and photoconductivity signals, respectively.
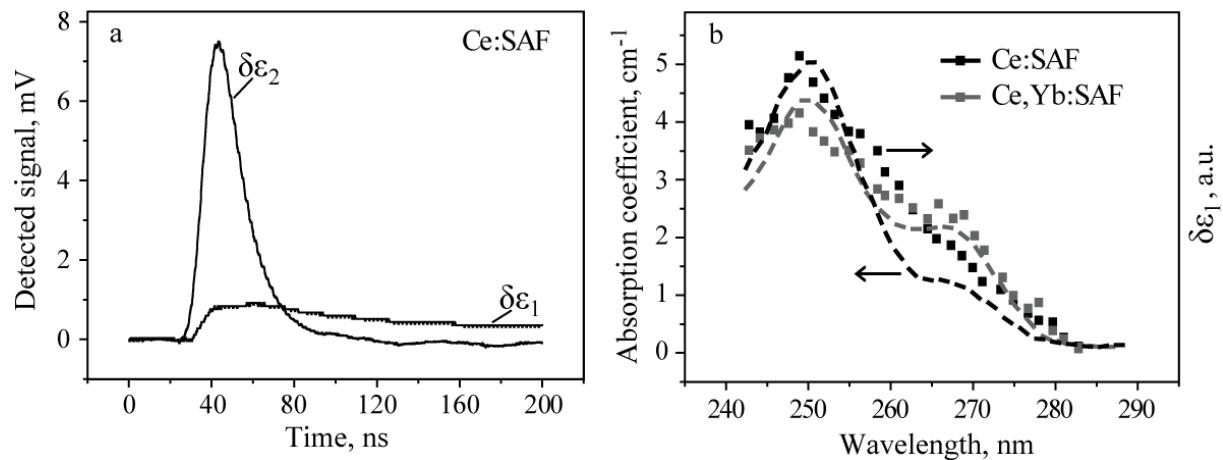
Figure 2. (a) Temporal behavior of real $\delta\varepsilon_1(t)$ and imaginary $\delta\varepsilon_2(t)$ parts of complex permittivity of Ce:SAF crystal excited by radiation at 266 nm; (b) absorption spectra (dashed line) [5] and spectral dependences of photodielectric signal $\delta\varepsilon_1(\lambda)$ (dots) for the Ce:SAF (black line) and Ce,Yb:SAF (grey line) crystals.

It should be noted that the transient time of electromagnetic field decay in the microwave cavity is about 2 ns. Taking into account 250 MHz-bandwidth of the microwave mixer and 200MHz bandwidth of the digital oscilloscope, which was used for a signal registration, the time constant of the measuring system enabled us to investigate transient responses of the dielectric permittivity of the crystals with about 5 ns temporal resolution.

The studied crystals were excited by radiation of the third harmonic of tunable Al_2O_3:Ti laser in spectral range from 240 to 280 nm. This spectral range corresponds to the 4f–5d transitions of the Ce^{3+} ions. Pulse duration and pulse repetition rate of the excitation radiation were less than 10 ns and 10 Hz, respectively. All experiments were performed at room temperature.

4. Experimental results and discussion

Timing performances of registered signal, corresponding to the variations of real and imaginary parts of the complex permittivity of sample, do not depend on sample and excitation wavelength. The temporal behaviour of the complex permittivity of Ce:SAF crystal is shown in figure 2a. The photoconductivity signal pulse form $\delta\varepsilon_2(t)$ for the studied crystals is characterized by the decay time of about 7 ns and almost coincides with one of the excitation pulse. That indicates the average lifetime of free charge carriers is less than 7 ns. The decay time of photodielectric signal $\delta\varepsilon_1(t)$, which characterizes the recovery time of dielectric polarization of crystal after pulse irradiation, appeared to be about 100 ns.

Normalized dependences of the amplitude of photodielectric signal versus excitation wavelength $\delta\varepsilon_1(\lambda)$ are shown in figure 2b. As it can be seen from figure 2b, the obtained spectra of photodielectric effect are similar to the ground state absorption spectra of Ce^{3+} ions. This means that interconfigurational 5d-4f transitions of the rare-earth ions significantly change dielectric polarization of crystal. Distinction between the lifetime of the excited 5d-state of Ce^{3+} ions, which is about 30 ns [9], and the decay time of photodielectric signal can be explained by the fact that the dielectric polarization of crystal cannot be changed instantaneously in response to an applied electromagnetic field.

Spectral dependence of the imaginary part of dielectric constant of the samples $\delta\varepsilon_2(\lambda)$ is shown in figure 3a. The photoconductivity spectrum of Ce:SAF crystal revealed a band with a maximum at 260 nm wavelength, which is absent for double-doped Ce,Yb:SAF crystal. Linear dependence of the photoconductivity signal for Ce:SAF crystal on the energy density of excitation radiation at 260 nm wavelength suggests that this band is essentially caused by one-photon ionization process.
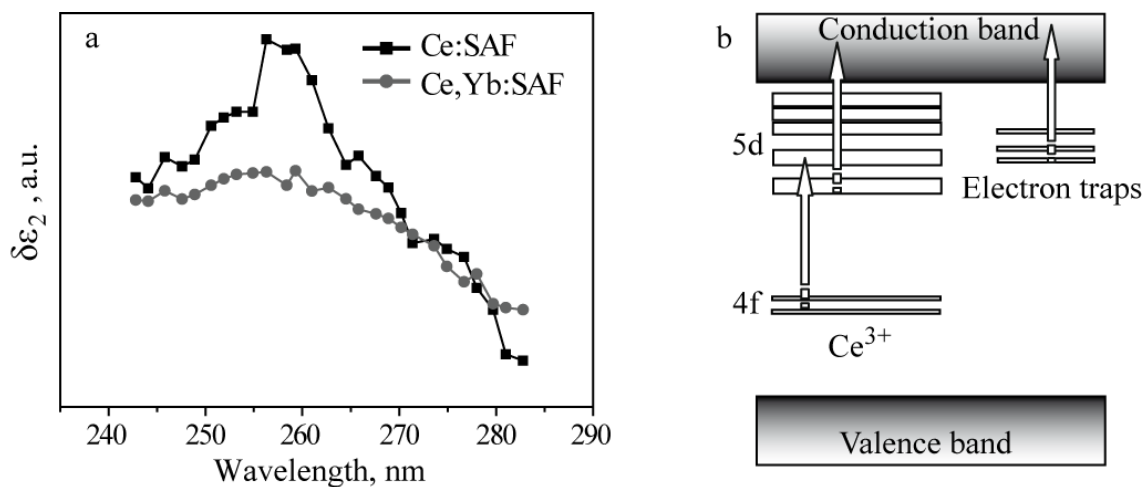
Figure 3. (a) Spectral dependences of photoconductivity signal $\delta\varepsilon_2(\lambda)$ for the Ce:SAF (black line) and Ce,Yb:SAF (grey line) crystals; (b) Interpretation of photoconductivity spectrum in 240-280 nm spectral range for Ce:SAF and Ce,Yb:SAF crystals.

As photoionization of Ce^{3+} ions in SAF crystal at the wavelength of 260 nm cannot be the result of one-photon absorption, the only possible interpretation of this 260 nm-band is photoionization of color centers. This confirms the fact that the additional activation by Yb^{3+} ions lowers the concentration of color centers. Therefore we can interpret the obtained photoconductivity spectrum of Ce:SAF and Ce,Yb:SAF crystals in 240-280 nm spectral range as superposition of two processes: excited-state absorption of Ce^{3+} ions and photoionization of color centers (figure 3b).

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