Controlling of the charge states in laser crystals

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Abstract. A basic spectroscopy (i.e. luminescence, excitation, absorption and emission kinetic measurements), excited states absorption measurements and additional absorption measurements after gamma, electron and proton irradiations of the YAG crystals activated by cerium and magnesium are presented. The excited state absorption spectrum of the YAG: Ce, Mg appears to be broader and shifted to the shorter wavelengths with respect to that of the YAG: Ce crystal. UV influence on ESR lines is discussed. It seems that UV irradiation changes Ce ions valency and especially Ce^{3+} concentration.

Keywords: charge states, irradiation, luminescence, emission kinetics

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1. Introduction

In the past decade, the renewal in the search of new optical materials covering the widest spectrum from ultraviolet to infrared has been very strong and the demand of various applications in many areas is increased. Investigations of laser

materials can be performed in a classic manner, looking for new materials, and/or new dopants and emission wavelengths or, using non-classic methods for known materials. The both ways are of the same importance.

The first question was: can we use existing point defects in well known crystals to prove their optical properties? Our investigations indicated that this is really possible.

1. We can induce color centers, e.g. in YAG: Er crystal and, due to energy transfer to excited laser state increase its inversion population and in a consequence slope efficiency of the optical output [1],

2. We can also change the effective content of the active dopant as, for example, in the case of YAG: Ce^{3+}, YAG: Pr^{3+}, $LiNbO_3$: Cr^{3+}, $LiNbO_3$: Fe^{3+} and $LiNbO_3$: Dy^{3+} crystals [2-6],

3. We can change effective content of sensitizing dopant, as in the case of Cr^{3+} in Cr, Tm, Ho: YAG [7],

4. We can shift short-wave absorption edge, as in the case of rare-earth doped $SrLaGa_3O_7$ and $BaLaGa_3O_7$ crystals [8-9],

5. We can shift fundamental absorption edge, as in the case of Ce doped $Y_3Al_5O_{12}$ crystal, using codoping with Mg [10],

applying also irradiation and/or annealing treatments.

The main goal of this paper is to present answers on the second question: Is it possible to shift the excited state absorption (ESA) spectrum with the use of codoping and/or irradiation methods, may be out of the luminescence range?

2. Experimental

2.1. Spectroscopic studies

From single crystals obtained in Institute of Electronic Materials Technology, the following parallel plates of 1 mm thick were cut-out and polished both sides: pure YAG, YAG: Ce (0.1 at. % Ce) (S1), YAG: Ce (0.2 at. % Ce) (S2), YAG: Ce, Mg (0.2 at. % Ce + 0.1 at. % Mg) (S3), YAG: Ce (0.05 at. %) (S4) and YAG: Mg (6 at. %). Also cubes 7*7*7 mm were cutted and polished for ESA measurements. The optical transmission was measured before and after the thermal or radiation treatment: in UV-VIS region by means of a LAMBDA-2 Perkin-Elmer spectrophotometer and in IR region by a FTIR-1725 spectrophotometer. After measurement of the transmission, the additional absorption (ΔK factor) was calculated according to the formula:

$$\Delta K(\lambda) = 1/d \ \ln(T_1/T_2) \tag{1}$$

where K is the absorption, ΔK is additional absorption, λ is the wavelength, d is the sample thickness, T_1 and T_2 are the sample transmissions before and after the treatment, respectively.

The fluorescence spectra were recorded by means of a spectrofluorimeter LS-5B of Perkin-Elmer. The excitation spectra were measured at the SUPERLUMI station at HASYLAB, Hamburg, Germany where the VUV range synchrotron radiation was used to excite the samples. Details of this setup can be found in Ref. [11].

Radioluminescence spectrum at 300K was measured in the range 200-850 nm using excitation with X-rays (DRON, 35 kV / 25 mA) and Spectrograph: ARC SpectraPro-500i (Hol-UV 1200 gr/mm grating, 0.5 mm slits), PMT: Hamamatsu R928 (1000 V).

For luminescence kinetic analysis we have excited our crystals using YAG: Nd - dye lasers system working in mode-locking mode and providing few tens picoseconds duration laser pulses of the wavelength of 290 nm.

The excited state absorption (ESA) spectrum was detected with a setup consisting of an RD-EXC-150/25 XeCl excimer laser (excitation source) working at 308 nm, a Hamamatsu xenon pulse lamp as the probe beam and the OMA system (Fiber Microspectrometer S-1000, Ocean Optics.

The dimensions of samples for ESR investigation were the following 3.5x3.5x2 mm. They were investigated in Bruker ESP300 ESR spectrometer (X-band). The spectrometer was equipped with helium flow cryostat type ESR900 Oxford Instruments. The ESR investigations were performed in the temperature range from 10 to 300 K and microwave power from 0.002 to 200 mW for "as grown" crystals and irradiated by -quanta with a dose of 10^5 Gy and UV with the use of mercury lamp.

2.2. Irradiation conditions

Crystals were irradiated: by gamma quanta, immediately after the growth was accomplished (as grown), at both room and liquid nitrogen temperatures; by protons, after annealing at 1400° C and by electrons after annealing at 800° C.

The gamma source of a ^{60}Co with a strength of 1.5 Gy/s was used. Samples were irradiated with gamma doses up to 10^6 Gy.

For proton irradiation the beam from a C-30 cyclotron of the Sołtan Institute of Nuclear Studies in Świerk was used. Proton energy was about 26 MeV, and the beam current at the sample was about 0.2 mA. The proton fluency were varied from 10^{13} to 10^{16} cm^{-2}.

For electron irradiation the electron beam from Van de Graaf accelerator was used. The electron energy was 1 MeV and electron fluency was 10^{16} cm^{-2}.

3. Results and discussion

Irradiation, due to recharging processes, such as ionization and recombination, changes equilibrium balance between different kinds of active ions (ions with different valency), e.g., V (2+, 3+, 4+ and 5+), Cr (2+, 3+ and 4+), Ce (3+ and 4+), Fe (2+ and 3+), Cu (2+ and 1+) and Pr (3+ and 4+) inside a given lattice. Here we present an example of the above trends: YAG: Ce crystal codoped with Mg.
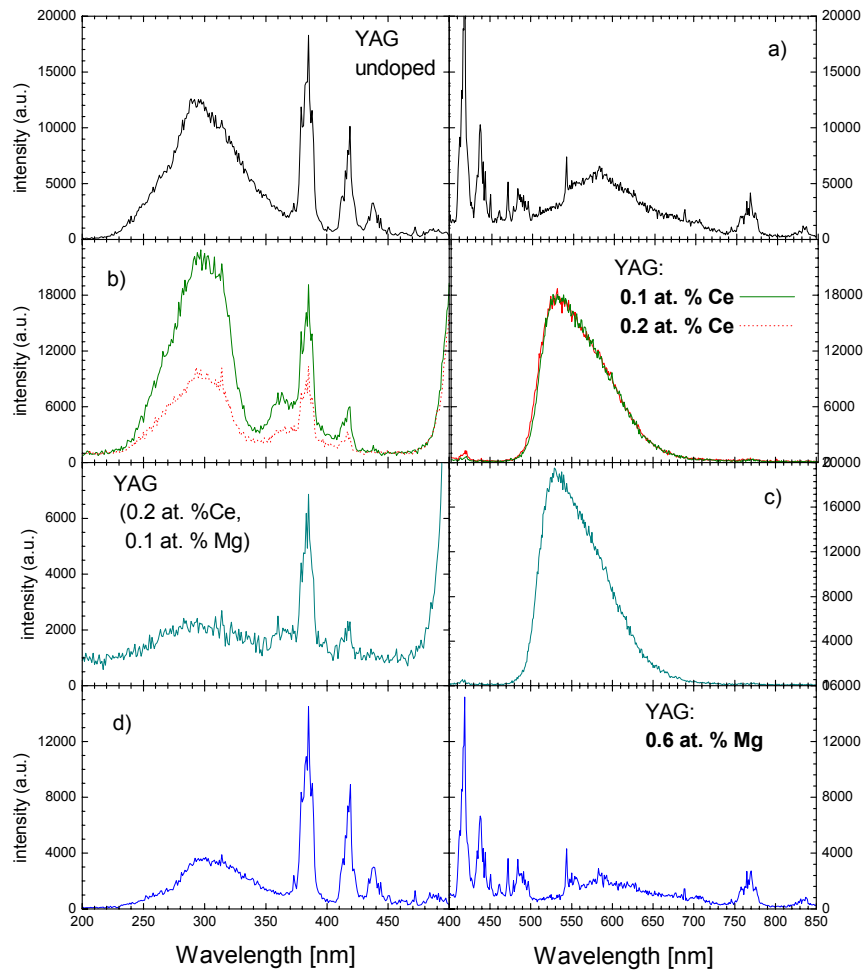

Fig. 1. Radioluminescence of pure YAG (a), YAG: Ce (0.1at.% and 0.2at.%) (b), YAG: Ce, Mg (0.2 at. % Ce, 0.1 at. % Mg) (c) and YAG: Mg (6at.%) (d) single crystals in the ranges 200-500 nm and 400-850 nm

This material is still very interesting as a possible scintillator or X-ray phosphor. Hamilton [12] and Miniscalco [13] have shown that the laser action in YAG: Ce crystal is impossible because ESA in this crystal quenches the stimulated emission and prevents the build-up of any optical gain.

What changes among optical properties of YAG: Ce crystal after its codoping with Mg^{2+}? Fundamental absorption edge of Ce^{3+} and Mg^{2+} doped YAG crystal is shifted with respect to YAG: Ce towards longer wavelengths by about 100 nm [10, 14], what leads to decrease of band gap width. Broad emission band arises in the range of 450-700 nm with any Mg emission (see Fig. 1). In Fig. 1, for comparison, there are shown radioluminescence spectra of pure YAG and YAG doped with only Mg.
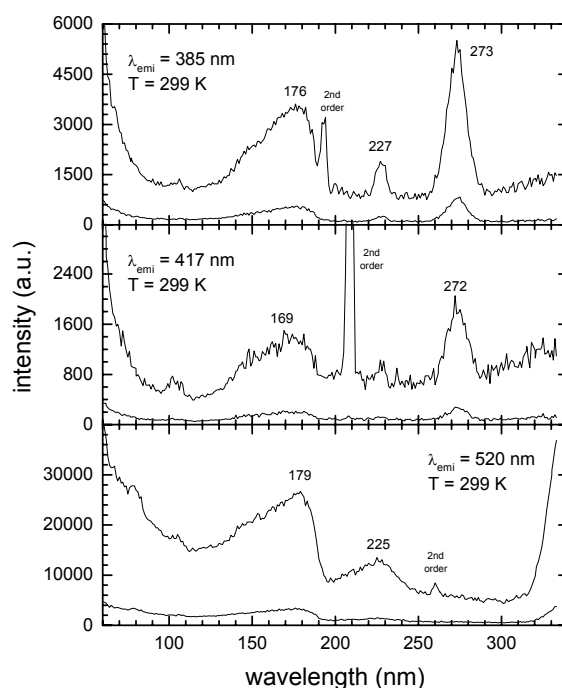

Fig. 2. 299 K excitation spectra of YAG: Ce (0.2 at. % Ce, 0.1 at. % Mg) for λ_{emi}=385, 417 and 520 nm, corrected for the setup characteristics. Resolution 0.3 nm

It seems that strong lines in blue, red and also green parts of the above spectra are coming from the small content (non-controlled impurity coming from starting materials) of Tb^{3+} ions (<1ppm). This conclusion confirm stronger blue than green fluorescence, which is seen in Fig. 1. Moreover weak emission lines are seen (e.g. at about 360 nm), characteristic for transitions from higher d level of Ce ion into f one (not only from lowest d level - broad band) or coming from other non-

controlled impurities. In Fig. 2 it is seen, that in absorption spectrum of YAG: Ce, Mg crystal the band exist, centered at about 325 nm, which can excite 360 nm emission band.

The Mg influence is seen only in the curves of the rise lifetime [15]. It is possible that this effect is related to the very fast capturing of the free holes by negatively charged Mg ions. It was stated that Mg^{2+} ions shorten the Ce^{3+} luminescence increasing time by shortening the lifetime of the thermalised holes.
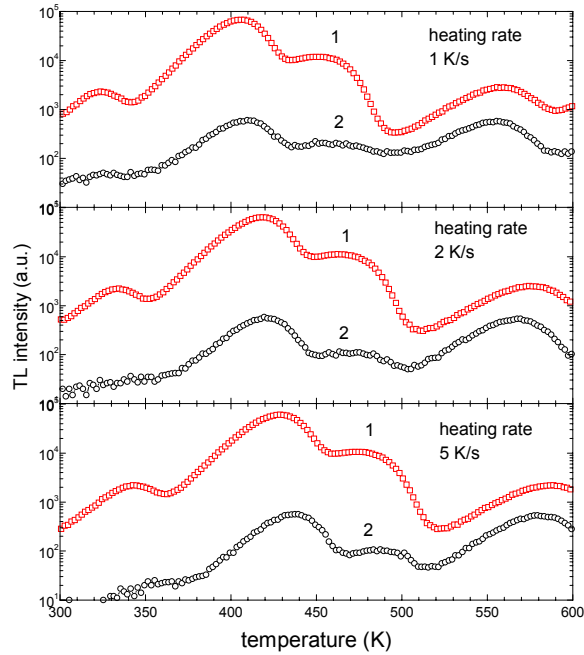

Fig. 3. Comparison of glow curves at temperatures from 300 to 600 K obtained for YAG: Ce (1) and YAG: Ce, Mg (2) single crystals and different values of heating rates (1-5 K/s)

The effect of hole capturing by Mg is observed also by monitoring of Ce^{3+} thermoluminescence, which is much weaker in the case of samples codoped with magnesium. As is seen in Fig. 3, the thermoluminescence intensity drops about 100 times when we deal with YAG: Ce, Mg in comparison with YAG: Ce crystal. Moreover, one can easily distinguish four thermoluminescence peaks at about 330, 410, 460 and 550 K. The peaks may be associated with four different electron traps occurring in the crystals. The glow curve of YAG: Ce, Mg can be well represented by the same sets of trap parameters as glow curve of YAG: Ce, what means that the Mg-codoping does not influence the trap distribution in the YAG: Ce lattice [16].
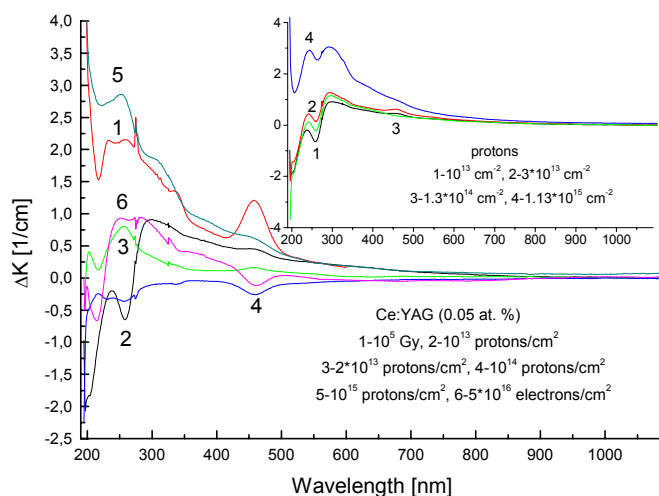
Fig.4. Additional absorption for YAG: Ce crystal (intentional doping 0.05 at. %) after different kinds of ionizing radiation: Fig. 3a: (1)-γ-rays, (2-6) protons for relative subsequent doses and, (7) electrons, and Fig. 3b: protons - absolute doses

Here magnesium competes with cerium for the holes. When, during the thermoluminescence measurement, we excite the crystal with beta radiation and create electron-hole pairs, the holes are immediately captured by the Mg, then there is lower number of the holes on cerium, making the thermoluminescence intensity much smaller.

After γ-irradiation of the YAG: Ce crystal additional absorption bands are observed in UV-VIS part of the absorption spectrum, which indicate also changes in valency and content of Ce^{3+} ions (Fig. 4). These bands vanish when crystals are heated at $400^{o}C$ for 3h and stay larger and larger when crystal is irradiated at lower temperatures. For small concentrations of cerium ions (~0,01at.%) increase in luminescence (~100%) while for greater ones (>0,1at.%) only small increase was observed after gamma irradiation with a dose of 10^6 Gy [17]. This increase was due to the growth of Ce^{3+} ions concentration after γ-irradiation (~50%), which was connected with the $Ce^{4+} \rightarrow Ce^{3+}$ recharging reaction. For highly doped YAG: Ce crystals (0,1at%, 0,2at.%) also the increase but much smaller (4%) for Mg codoped YAG: Ce crystals (0,1at.%) was only observed. In the case of Mg codoped highly Ce doped YAG crystals additional absorption is positive in the ranges of Ce^{3+} transitions (bands centered at 338 and 458 nm), what means reaction of the type $Ce^{4+} \xrightarrow{\gamma} Ce^{3+}$. So, Mg codoped high Ce doped YAG crystal behaves as low doped YAG: Ce crystal, that is, exhibits the presence of Ce^{4+} ions [2].

Different kinds of ionizing radiation in different ways influence the properties of YAG: Ce crystals (compare curves 1 - gamma, 2 - protons and 6 - electrons in Fig. 4a). Critical dose arises for proton irradiation (10^{14} protons/cm^2 - see curve 4 in Fig. 4a or curve 3 in Fig. 4b), below which recharging processes dominate and above which Frenkel defects are clearly seen (see curves 4 and 5 in Fig. 4b - quantitative rise in additional absorption).

In Fig. 5 changes in a luminescence of YAG: Ce, Mg crystal are seen after γ-irradiation with a dose of 10^6 Gy. It is seen that concentration of Ce^{3+} ions increases after γ-irradiation, what lead to increase of luminescence.
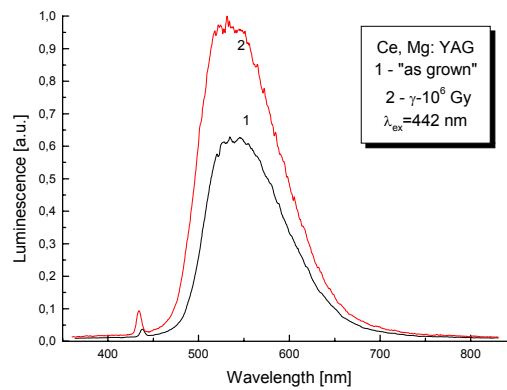

Fig. 5. Change in a luminescence of YAG: Ce, Mg crystal after γ-irradiation with a dose of 10^6 Gy

Very interesting results we have obtained for ESR lines measured before and after UV irradiation. Fig. 6 presents changes in ESR lines intensity after UV- irradiation from mercury lamp.

ESR measurements were performed for P=0.2 mW and temperature range about 15 K. As is seen in Fig. 6c and d, the two investigated crystals had different values of maximal ESR intensity temperature, 16.5 K and 15 K. To obtain correct results it was necessary to perform the investigations with stable conditions for temperature dependence of ESR intensity. In the first case (YAG: Ce), increase in ESR intensity equal to 58% was observed, while in the second one (YAG: Ce, Mg), also increase but equal to 85% was stated. It means that in the YAG: Ce, Mg crystal greater number of Ce^{4+} ions exists than in YAG: Ce one, giving more Ce^{3+} ions after UV-irradiation.

The main question of the paper is: Is it possible to shift the ESA spectrum out of the luminescence range? We have tried to give the answer on this question by codoping the YAG: Ce crystal with magnesium. We have found, that YAG: Ce, Mg crystals reveal quite different ESA spectrum, shifted towards the shorter
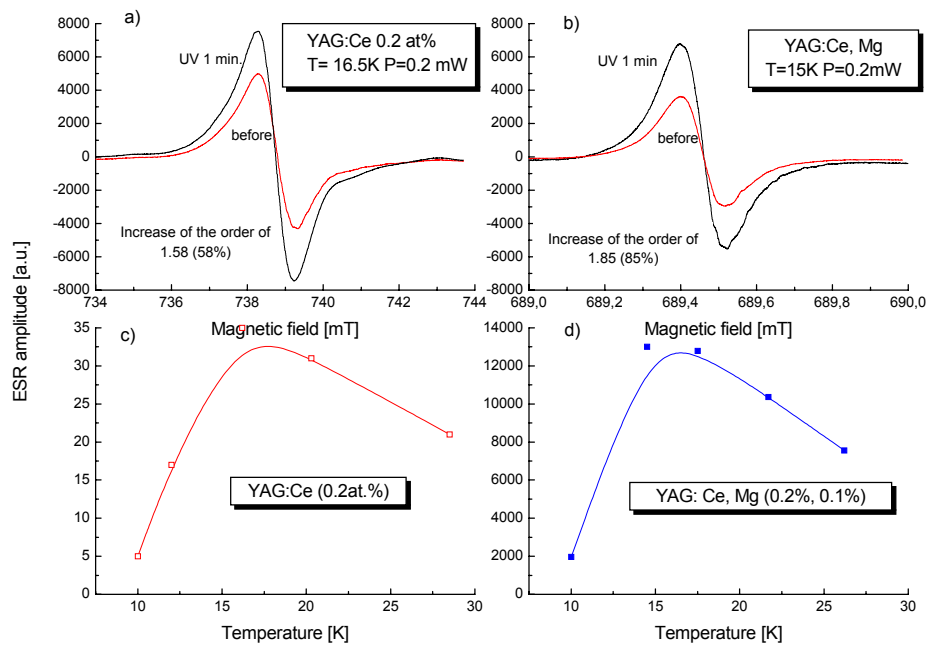
Fig. 6. Changes in ESR intensity of YAG: Ce (a) and YAG: Ce, Mg (b) single crystals after UV-irradiation from mercury lamp
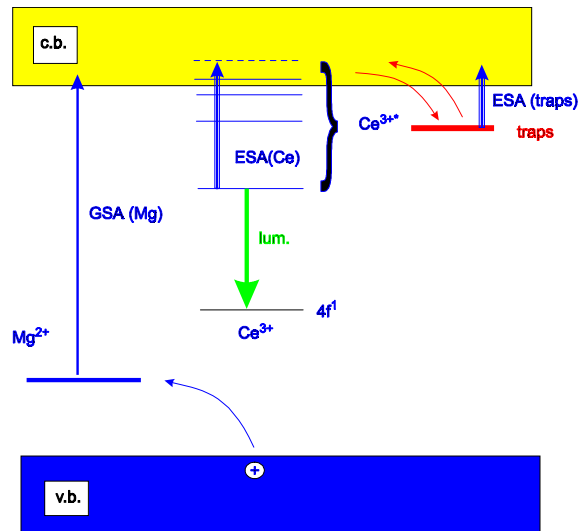

Fig. 7. ESA scheme for Mg codoped Ce: YAG crystal

wavelengths. Exciting energy for ESA experiment (λ=308 nm) was, however, of the order of photo-ionization energy, though not all of conclusions are valid (especially about direction of the shifting of ESA spectrum).

The model of the above shifting is following: magnesium substituting yttrium forms a very efficient acceptor state (Fig. 7). With the UV excitation Mg provides excessive electrons into the conduction band, and then the thermoluminescence traps are filled. We believe, that the observed modified ESA spectrum is due to the transitions from traps to the conduction band. So, the spectrum contains contributions from the Ce^{3+} as well as from the following three-step process: 1) an electron transition from the filled acceptor-like Mg state to the conduction band, 2) capturing of the electron by a thermoluminescence trap, 3) the ESA transition from the filled trap level to the conduction band.

4. Conclusions

— Mg^{2+} codoped high Ce doped YAG crystal behaves as low doped Ce: YAG crystal, that is, it exhibits the presence of Ce^{4+} ions,
— Ionizing radiation can only change effective concentration of Ce^{3+} ions (all types of irradiations) or introduce to the crystal Frenkel pairs (electrons and protons),
— It is possible to shift the ESA spectrum of YAG: Ce crystals with the use of codoping with Mg but direction of this shifting demand more investigations,
— the ESR effect appears otherwise similar to the ESA increase under the excimer   laser irradiation and has, most likely, the same mechanism; the transfer of electrons from the low lying defect levels to the conduction band and then to Ce^{3+} ions,
— Mg ion acts like efficient acceptor and there is a competition between Mg and Ce in capturing of free holes,
— When the negative (with respect to the lattice) Mg^{2+} ions are incorporated, they shorten the Ce^{3+} luminescence increasing time by shortening the lifetime of the thermalised holes (luminescence increasing life time was: 78ns for YAG: Ce and 69 ns for YAG: Ce, Mg crystals),
— Mg may absorb electrons lowering optical density of the crystal,
— Mg may change laser properties of the crystal.

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Kontrolowanie stanów ładunkowych domieszek aktywnych w kryształach laserowych

Streszczenie: Przedstawiono wyniki podstawowych badań spektroskopowych (luminescencja, wzbudzenie, absorpcja i kinetyka emisji), pomiarów ESA oraz wartości dodatkowej absorpcji po naświetleniach kryształów YAG domieszkowanych cerem i magnezem elektronami, protonami i kwantami gamma. Widmo ESA kryształu YAG: Ce, Mg wydaje się być poszerzone i przesunięte w stronę fal krótszych względem odpowiedniego widma dla kryształu YAG: Ce. Po naświetleniu obu kryształów światłem UV z lampy rtęciowej, obserwuje się wzrost intensywności linii ESR, odpowiednio o 85% i 58%.

Słowa kluczowe: kryształy YAG, krystalografia, badania spektroskopowe

Kontrol% sostoqnij zarqda w lazernyh kristallah

   Rez@me. Predstawleny rezultaty bazisnyh spektroskopi$eskih issledowanij (luminescenciq, wozbuvdenie, absorpciq i !misionnaq kinetika), izmerenij ESA, a takve absorpcii posle osweⓈenii kristallow YAG: Ce, Mg i YAG: Ce !lektronami, protonami i gamma kwantami.