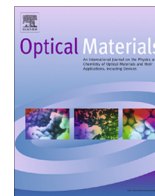




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# Effect of oxidation annealing on optical properties of YAG:Ce single crystals

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## ABSTRACT

YAG:Ce single crystals were annealed in air atmosphere at different temperatures. Their optical properties, such as optical absorption, cathodoluminescence spectra, cathodoluminescence decay and thermoluminescence were studied. Growth of UV absorption with increasing annealing temperature is explained by ionization of Ce<sup>3+</sup> ions during the oxidation annealing and consequent ligand-to-metal charge transfer to the Ce<sup>4+</sup> ions. Near-UV luminescence emission caused by presence of the antisite defects is undesirable for fast scintillation applications. After oxidation annealing, the emission related to the antisite defects is partially quenched due to the spectral overlap of the charge transfer absorption and the antisite defects emission. Together with suppression of electron traps due to the oxidation annealing, the described mechanism effectively decreases luminescence afterglow and improves YAG:Ce scintillation characteristics.

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## 1. Introduction

Cerium-doped yttrium aluminum garnet  $Y_{3-x}Ce_xAl_5O_{12}$  (YAG:Ce) is a material frequently used as yellow-green emitting scintillators [1–3], luminescent imaging screens [4–6], or as phosphors for white-light emitting LED sources [7–9]. The YAG:Ce crystal has been extensively studied over many decades since its first synthesis in 1967 [10]. In the late 70s, Robbins et al. shown that the various defects act as traps for electronic excitations and influence the energy transfer efficiency of the crystal [11,12]. It was shown in these reports that the cathodoluminescence (CL) spectrum consists of a trivalent cerium emission band peaked at 550 nm, and a broad near-UV band centered around 340 nm observed in both cerium-doped and undoped YAG crystals. Robbins et al. also noticed that the intensity of the near-UV band decreases when the crystal is annealed in pure oxygen atmosphere. This observation was later confirmed by Rotman and Warde in their absorption and photoluminescence studies of YAG annealed in oxidizing, or reduction atmospheres [13]. Rotman and Warde presented that although the near-UV band intensity decreases with the oxidizing annealing, the intensity of the absorption tail between 200 and 300 nm increases. This behavior was explained

by a model of two types of lattice defects (luminescent and nonluminescent one) related to the oxygen vacancies ( $V_O$ ).

The conclusion that the near-UV emission is caused solely by the  $V_O$  relaxation was supported mathematically [14,15], although Pujāts et al. had some critical remarks [16]. They suggested that the defect emission originates in the substitution defect of the yttrium ions in the site of aluminum ions called antisite defects (AD). Meanwhile, Kuznetsov et al. [17], Mürk et al. [18–20] and Kirm et al. [21] brought an evidence of formation of a metastable trapped excitations. The authors showed that the near-UV band is splitted into a high-energy band with the center around 4.9 eV related to the self-trapped excitons (STE), and into a low-energy band with the center around 4.2 eV connected with the self-trapped holes (STH) probably at oxygen ions. However, Zorenko et al. observed YAG crystals with different concentrations of the AD and suggested that the low-energy band has not STH origin, but is caused rather by recombination of free electrons with holes localized at the AD [22–24]. Other studies agreed that the near-UV emission is due to exciton localized around the AD [25–29].

Although the  $V_O$  influence on the emission spectra was rejected, their role was discussed in the case of absorption spectra. A few authors recently presented that the absorption tail of the YAG crystal between 200 and 300 nm is increased after annealing in the oxidizing atmosphere [30–33]. Varney et al. explained the increase of absorption by presence of  $V_O$  and Fe<sup>2+</sup> ions in the YAG:Ce crystal

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[33]. During the oxidation annealing, the divalent ions are ionized to  $\text{Fe}^{3+}$  by consequent trapping of electrons in the  $V_O$  centers. The created  $\text{Fe}^{3+}$  ions form absorbing states which increases absorption. Selim et al. [31] and Solodovnikov et al. [32] explained the UV absorption by the possible change of defect charge state after filling the  $V_O$  centers.

In this paper, we present a new explanation of the increase of the YAG:Ce UV absorption after oxidation annealing. We also clarify why some researchers incorrectly concluded that the near-UV emission results in the presence of the  $V_O$ . Our approach is much straightforward since it does not require any additional elements such as presence of impurity ions, or chemical changes due to the annealing. The theory presented herein is based on ionization of the  $\text{Ce}^{3+}$  ions during the oxidation annealing and consequent ligand-to-metal charge transfer to the  $\text{Ce}^{4+}$  ions. The theory is supported by our experimental data of optical absorption, cathodoluminescence spectra, cathodoluminescence decay and thermoluminescence. These measurements were carried out on series of YAG:Ce specimens annealed in air atmosphere at different temperatures.

## 2. Experimental

The YAG:Ce single crystal was grown using the Czochralski method in the (1 1 1) direction by the CRYTUR company. The nominal cerium concentration of crystals was 0.22 at.%. The crystal was cut to the disk shape perpendicular to the (1 1 1) direction with the diameter of 10 mm and the thickness of 0.5 mm. The specimens were optically polished. Four specimens (close-lying in the crystal) were chosen from each side of the boule (top and bottom) in order to obtain two series of similar specimens. These series were treated in the same way. One specimen from each series was left un-annealed and the three remaining were annealed in the air atmosphere for 12 h at following temperatures: 1200, 1350 and 1500 °C.

The specimens were examined by the optical absorption, cathodoluminescence (CL) and thermoluminescence (TL) measurements. The optical absorption was measured at room temperature in the wavelength range of 200–550 nm by the Varian Cary 5E spectrometer. The CL and TL measurements were carried out using a “home-built” apparatus [34]. This device creates a collimated electron beam of 10 keV energy which irradiates a specimen positioned in a thermostat. The thermostat can cool or heat the specimen in the range of 90–500 K. The e-beam can be deflected out of an aperture in order to create e-beam pulses with the frequency of 100 Hz and the duration of 10  $\mu\text{s}$ . The CL emission from the specimen side opposite the e-beam irradiation is collected by a light-guide and guided to the Horiba JY iHR 320 spectrometer. The spectrometer is equipped with the Horiba JY Synapse CCD camera for the spectral measurements, and with the ET-Enterprises 9113WB photomultiplier tube for the pulse-excited decay measurements in the UV region. The decay measurements of the broad cerium emission were carried out using the Tesla 65-PK-415 photomultiplier tube equipped with the band-pass optical filter transmitting the wavelength range of 470–800 nm. The same photomultiplier and optical filter was also used for the TL measurements. The TL measurements were carried out by cooling the specimen down to 90 K and by excitation using the e-beam. After the specimen excitation is stopped, the specimen was heated with the constant heating rate of 5 K/min and the TL emission was observed in the temperature range of 100–500 K.

## 3. Results

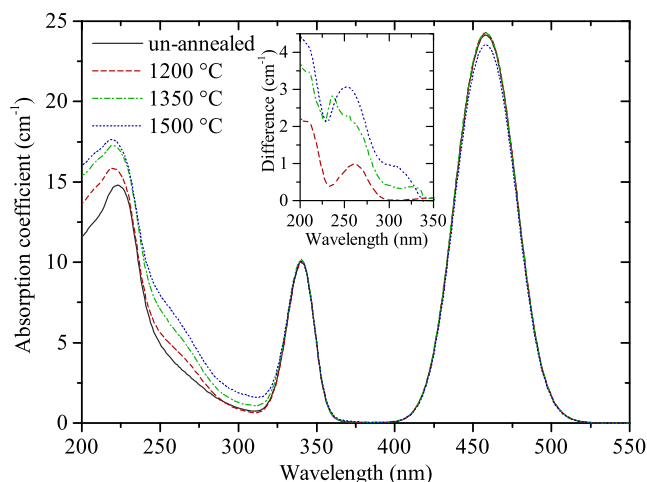
The measurement showed very similar results in both series of annealed specimens of YAG:Ce single crystals. There were only

small deviations within the series caused by slightly different cerium concentration, but the effect of annealing temperature was almost the same in both series, varying only in a few percent of magnitude. Therefore only the results from the first series of the specimens are shown here.

The annealed and un-annealed YAG:Ce single crystals were studied using optical absorption at room temperature, see Fig. 1. The absorption coefficient spectra show three major peaks at 226, 340 and 458 nm which are ascribed to the  $\text{Ce}^{3+} 4f \rightarrow 5d$  transition [35]. The intensity of the last two peaks does not vary considerably which is a sign of nearly same cerium concentration of individual samples. Below 330 nm, there is an absorption structure whose intensity significantly increases with increasing annealing temperature.

The cathodoluminescence (CL) spectra were measured at room temperature. They were corrected for the apparatus spectral transmittance and also for the detector spectral sensitivity. The spectra (see Fig. 2) exhibit a broad near-UV band which originates from the exciton recombination at the antisite defects. The dip at 340 nm is caused by  $4f-5d^2$  absorption of  $\text{Ce}^{3+}$  center. With increasing annealing temperature, the intensity of the near-UV band evenly decreases in the wavelength range of 200–330 nm and slightly increases in the range of 330–430 nm. In the CL spectra, there is also an emission band peaking around 550 nm which is ascribed to the trivalent cerium  $5d \rightarrow 4f$  transition. The integral intensity of this band is decreased by 11% after annealing and stays unchanged for different annealing temperatures. Slight difference of the CL intensity between the annealed specimens is visible around 560 nm. Such difference is caused only by the second diffraction order of the emission around 280 nm and has no physical meaning.

The CL decay curves (see Fig. 3) show a fast component after the end of the excitation pulse with the time constant of 80 ns. It is caused by the decay of promptly excited  $\text{Ce}^{3+}$  ions. There are also at least two weaker components with much longer decay time constants of 2,2  $\mu\text{s}$  and 47  $\mu\text{s}$ . The amplitude of these slow components decreases with increasing annealing temperature while their time characteristics remain unchanged. Similar decay time constants (but of different amplitudes) were found in CL decay of near-UV band (see inset of Fig. 3). In this case, the CL decay was measured using a monochromator transmitting wavelength range of 290–310 nm.



**Fig. 1.** Absorption coefficient spectra of YAG:Ce single crystals annealed in air atmosphere for 12 h at different temperatures. The inset graph shows the difference absorption spectrum (the absorption coefficient of the annealed crystals subtracted from the un-annealed one).

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