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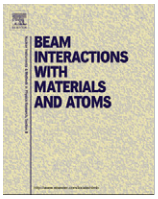

BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Optimization of decay kinetics of YAG:Ce single crystal scintillators for S(T)EM electron detectors

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ABSTRACT

To enhance the detective quantum efficiency (DQE) of scintillation electron detectors for scanning electron microscopes or scanning transmission electron microscopes (S(T)EM), the cathodoluminescence (CL) decay kinetics of YAG:Ce single crystal scintillators is studied in this paper. Some possibilities for reductions of decay time and afterglow of the mentioned scintillators are presented. The pulse mode utilizing a blanking system and 10 keV electrons for the excitation and a sampling oscilloscope for the CL detection were used for the measurement of decay characteristics. The CL decay characteristics of YAG:Ce single crystals of different Ce concentrations, pulled by the Czochralski method and cleaned and annealed under specific conditions, were measured in dependence on excitation pulse duration and on the specimen temperature. To interpret the presented results, a kinetic model of cathodoluminescence of the YAG:Ce single crystals was created. The effects of quenching impurities and of defect centers in YAG:Ce were specified.

1. Introduction

The process of optimization of a scintillation electron detector for S(T)EM offers many options, such as the optimization of electron collection, electron–photon conversion, photon collection, as well as of photon–electron conversion [1]. In addition to the electron–photon conversion efficiency [2] and to the photon transport efficiency [3], kinetics of a scintillator is also of great importance in an Everhart–Thornley scintillation detection system [4]. This is because the scintillator strongly influences the detective quantum efficiency (DQE) [5], which is the most important criterion for the quality of the whole detector. As for the DQE, the scintillator is a problematic part of any scintillation detector for S(T)EM. The reason lies in its decay time and especially in its afterglow, which deteriorate the ability to transfer image contrast. In other words, the slow scintillator causes a bad modulation transfer function (MTF) for the whole detector. If a series of alternating white and black points is transferred using such a scintillator, the image is somewhat degraded at the typical S(T)EM spatial frequency. To enhance the MTF of the scintillation detector, the cathodoluminescence (CL) decay kinetics of YAG:Ce single crystal scintillators was studied and some of the possibilities for decay time and afterglow of YAG:Ce single crystal scintillators reductions are presented in this paper.

2. Experimental

The kinetic properties of many single crystal scintillators were measured at our laboratory [2]. Of these, single crystals of cerium-activated yttrium aluminum garnet (YAG:Ce – $Y_3Al_5O_{12}$:Ce^{3+}), cerium-activated yttrium aluminum perovskite (YAP:Ce – $YAlO_3$:Ce^{3+}), and cerium-activated yttrium silicate (YS:Ce – Y_2SiO_5:Ce^{3+}, which chemically corresponds to the powder phosphor P47) were chosen as the most interesting ones for S(T)EM electron detector applications. The most used of these mentioned scintillators are the YAG:Ce single crystals. In comparison with the powder ones (often referred as P46), the YAG:Ce single crystals show higher efficiency and lower afterglow both for excitation energies of 10 keV typical in SEM [6] and for excitation energies of 0.1–1 MeV typical in STEM [7]. So the YAG:Ce single crystal scintillators have been chosen for the study of kinetic properties. The investigated single crystals were pulled by the Czochralski method using molybdenum crucibles, resistance heating and a 98% Ar + 2% H_2 protective atmosphere in the company Crytur. The initial material contained less than 10^{-4} wt.% impurities [8].

The as-grown single crystals were cut and ground into the form of disks $\varnothing 10 \times 0.5$ mm. The surface intended for the output of photons was matted so that the relief roughness was approximately 0.2 μm. The surface intended for the input of electrons was polished. All specimens were cleaned in organic solvents. Some specimens were additionally cleaned by boiling them in

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acids. Some specimens were annealed in oxidizing and reducing atmospheres, O_2 and H_2, respectively, at a temperature of 1500–1700 °C. For all specimens, the side intended for the input of electrons was coated with a thin aluminum film (50 nm) to prevent the charging of the surface on the one hand, and to increase the light signal collection efficiency [9,10] on the other hand.

CL properties were measured using the equipment built in our laboratory. The device was designed not only for phosphor studies, but also for characterizations of weak light-emitting solids, especially for the study of the polymer degradation [11]. The block scheme of the equipment is shown in Fig. 1. The excitation unit was formed by an adapted electron microscope with an electrostatic deflection system and a blanking diaphragm placed above the Faraday cage as presented in Fig. 2. In the pulse mode, the excitation electron beam can be deflected outside the blanking diaphragm, so that for 10 keV electrons, the rise and decay times of the excitation pulse were the same, approximately 5 ns. The pulse mode was intended for the determination of kinetic properties, but it can also be used with advantage for the measurement of emission spectra. The CL efficiency was measured in the continuous mode. The investigated single crystal specimen was positioned at the face of the light guide (inside the Faraday cage), and the signal was guided directly toward the entrance window of the PMT, when spectrally non-decomposed CL properties (integral efficiency and decay characteristics) were measured. When spectrally decomposed CL properties were measured, the signal was guided toward the entrance slit of the mirror monochromator. During the measurement of decay characteristics, the PMT output was connected to the sampling oscilloscope. The individual instruments were connected to the general purpose interface bus (GPIB, IEEE-488), and the measuring apparatus was controlled by a personal computer which also processed the obtained data. The data measuring and processing software (which contains correction algorithms) was written in Turbo Pascal and Basic.

3. Results and discussion

Some typical CL decay characteristics of single crystals for SEM, measured in our laboratory, are shown in Fig. 3. The best solution for application in a S(T)EM scintillation detector would be YS:Ce and YAP:Ce single crystals having reasonable CL efficiency and the decay time of 34 and 38 ns, respectively. Nevertheless, from the crystals shown in Fig. 3, the YAG:Ce is the cheapest one and so its usage is widespread. However, its decay time is often longer than 100 ns, and moreover, its decay characteristic is multi-exponential with the afterglow of 2% at 5 μs after the end of excitation. In a quest to find a kinetic model of CL in YAG:Ce single crystals and, subsequently, to understand and improve the decay characteristics of the crystals mentioned, a set of measurements for decay characteristics for different YAG:Ce growth and treatment at different measurement conditions were done. The CL decays were measured in dependence on excitation pulse duration, in dependence on crystal temperature, in dependence on activator concentration, and in dependence on crystal treatment.

The influence of the excitation pulse duration on the CL decay of YAG:Ce single crystal scintillators is shown in Fig. 4. It can be seen from Fig. 4 that the short-term decay component (decay time) of YAG:Ce crystals depends only negligibly on the duration of excitation. On the contrary, the long-term component of the decay characteristic depends strongly on the duration of excitation. Therefore, at a very short excitation, the afterglows of YAG:Ce are one order smaller compared to a long excitation.

It is evident, after a decomposition of the decay characteristics from Fig. 4, that not only emission from the activator is present in the CL recombination processes in YAG:Ce single crystals. Using the correction for the decay constant of the measuring device, for YAG:Ce, the fastest decay constant is at whichever duration of excitation about 60 ns. This corresponds to the single-exponential decay at the photoluminescence measurement [12]. Therefore, the

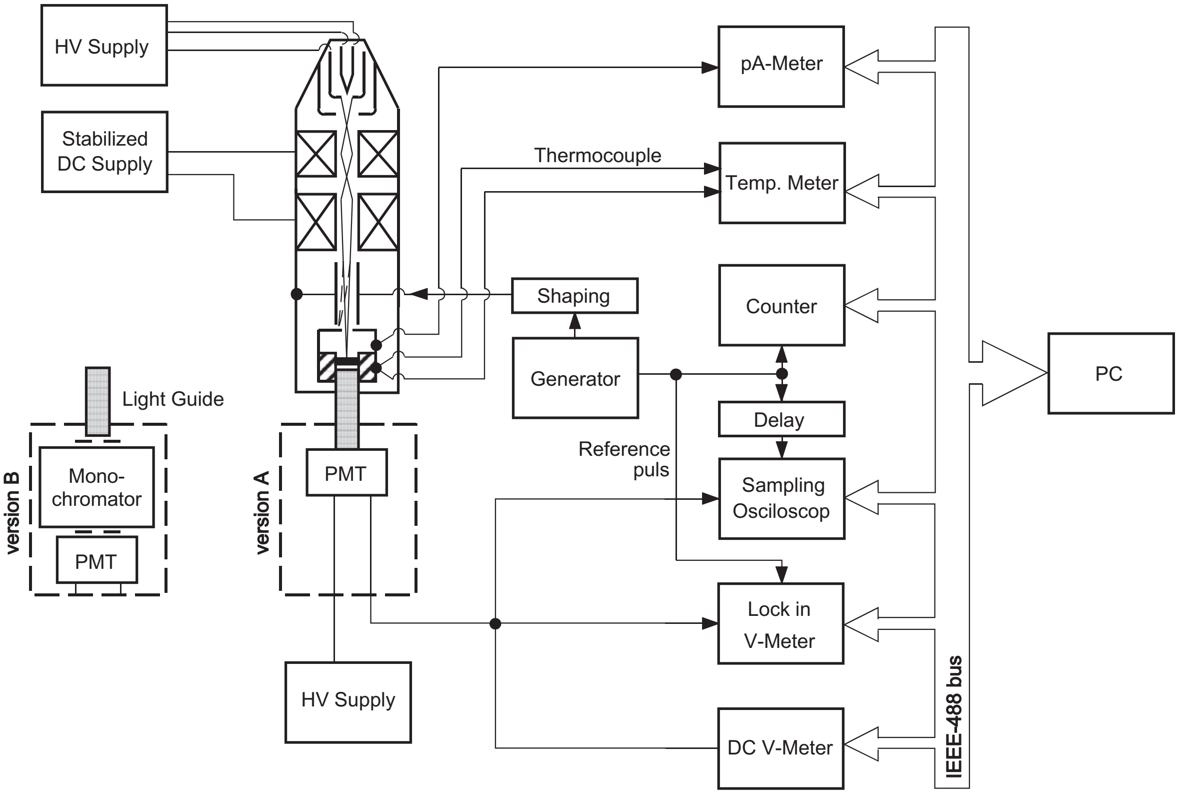

Fig. 1. Equipment used for CL property measurements.

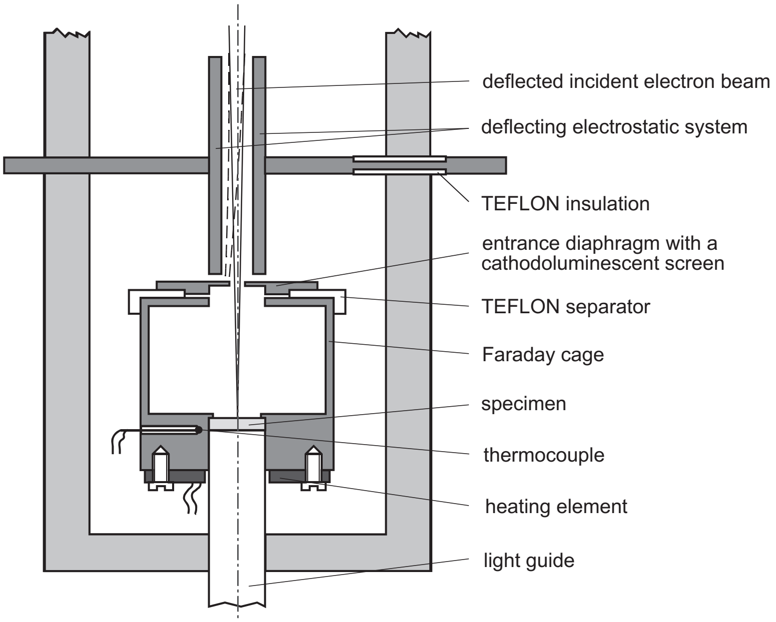

Fig. 2. Specimen chamber arrangement with the blanking system. The specimen was positioned at the face of the light guide and the signal was guided toward the detection unit.

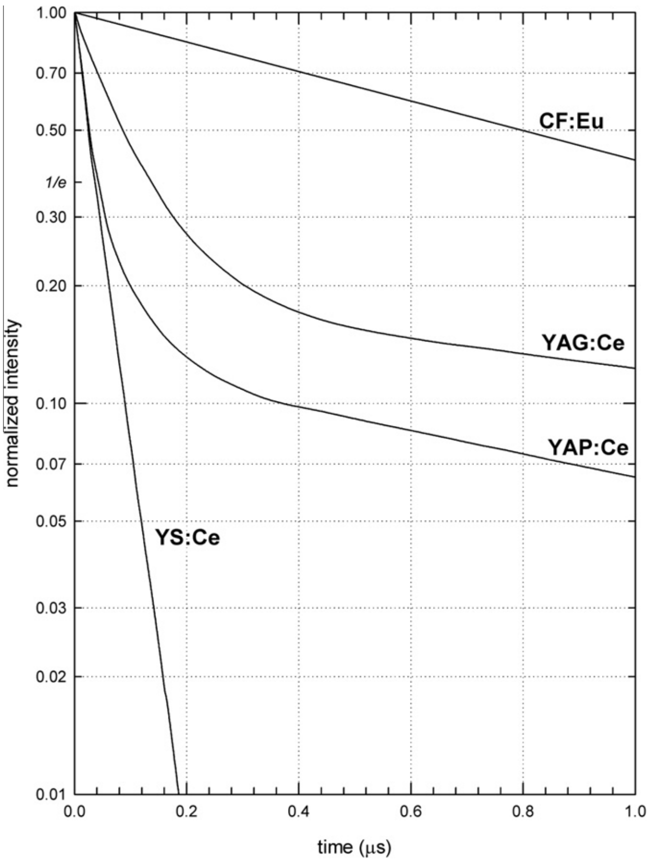

Fig. 3. Decay characteristics of single crystal scintillators for SEM. Excitation pulse duration 10 μs.

fastest decay constant of the multi-exponential decay characteristic can be ascribed to the emission from the activator. The other decay constants can be ascribed to both radiative and nonradiative transitions originating from unwanted defect and impurity centers. The existence of defect centers in YAG:Ce crystals, and their influence on CL kinetics, were supported by the decay measurement of YAG:Ce at different temperatures in Fig. 5. As is seen, the thermalization of defect centers improves the kinetics of YAG:Ce.

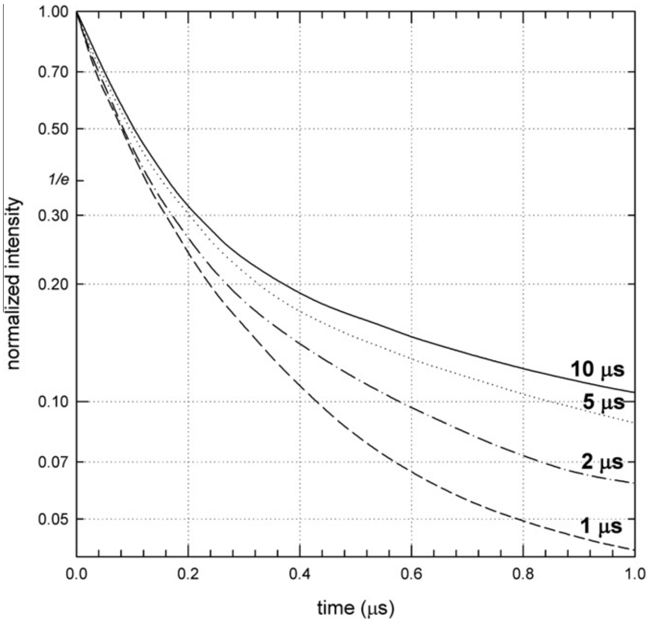

Fig. 4. Influence of the excitation pulse width on the cathodoluminescence decay of YAG:Ce single crystal scintillators.

If the defect and impurity centers in YAG:Ce are responsible for its multi-exponential decay characteristics, a measurement of the activator (Ce) concentration dependences can help to find the possibilities of the decay time reduction of these single crystals. So, the YAG:Ce single crystals were grown using different stoichiometry, and YAG:Ce specimens having the Ce concentration of 0.0013, 0.029, 0.13 and 0.32 mol.% were obtained. Their decay characteristics are shown in Fig. 6. It is obvious from these measurements that YAG:Ce single crystals containing the highest Ce concentration are

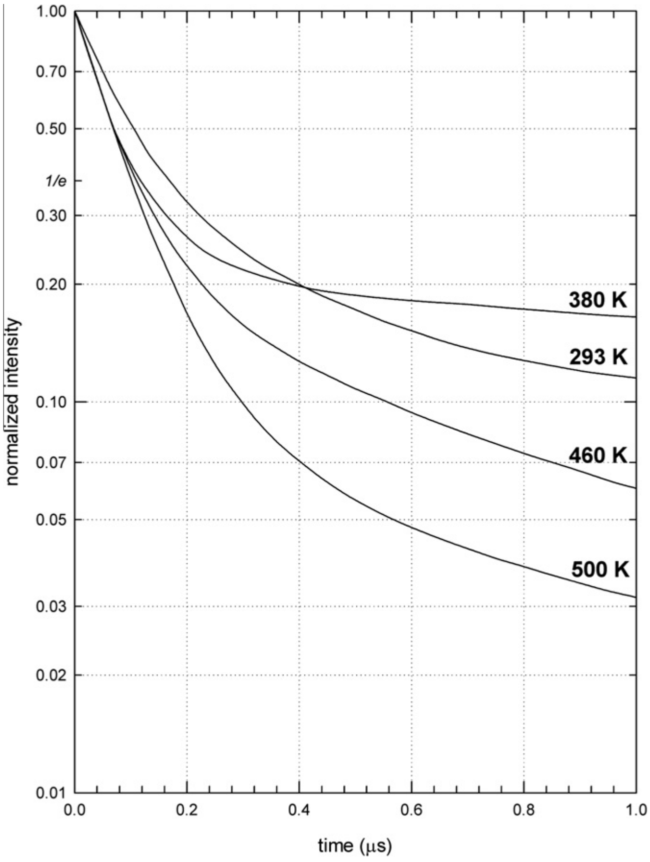

Fig. 5. Influence of the specimen temperature on the cathodoluminescence decay of YAG:Ce single crystal scintillators.

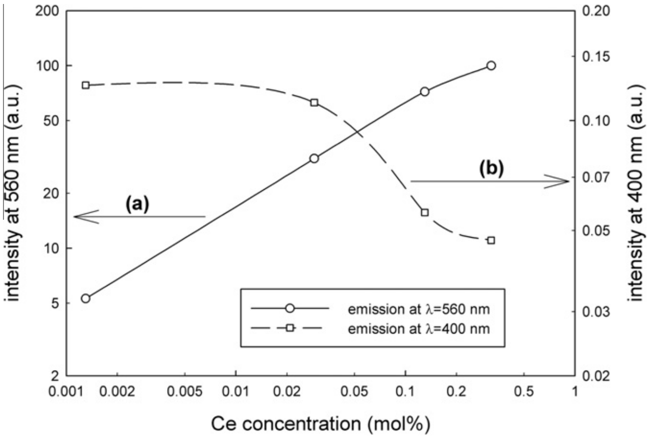

Fig. 7. Influence of Ce concentration in YAG:Ce single crystal on the (a) characteristic CL emission from the activator (560 nm), and (b) CL emission from the defects or the impurities at (360 nm) related to the maximum of the characteristic emission.

the fastest ones. As demonstrated in Fig. 7, no concentration quenching of cathodoluminescent emission was recorded for these single crystals. Unfortunately, it is a great technological problem to grow YAG:Ce single crystals resulting in an activator concentration higher than 0.3 mol.%. If one succeeded in growing such single crystals, then cathodoluminescent responses might approach very fast decays because of the higher probability of direct activator excitation.

The decay time reduction utilizing the activator concentration optimization is interesting particularly for producers of single crystals. However, there still exists another simple possibility for decay time reduction of YAG:Ce single crystal scintillators, which is interesting also for producers and/or operators of electron microscopes. As another approach to the YAG:Ce single crystal decay time reduction, scintillator surface treatment effect was studied in our laboratory. After cutting, polishing and cleaning in ethyl alcohol, the YAG:Ce scintillator disks were boiled in different solutions and fired in oxidizing (O_2) and/or reducing (H_2) atmospheres. It is obvious from Table 1 and from Fig. 8 that YAG:Ce single crystals, whose surfaces have been treated under different conditions, show different decay characteristics. Although the specimens boiled in aqua-regia possess high cathodoluminescent efficiency, they have quite poor decay time. Similarly, the YAG:Ce scintillators fired in a reducing atmosphere show better efficiency, but it is impossible to use them at TV rates at the same time. It can be summarized that the YAG:Ce scintillators cleaned in ethyl alcohol and fired in oxidizing atmosphere have the shortest decay time. Unfortunately, this favorable effect is accompanied by some decrease in cathodoluminescent efficiency.

Both the Ce activator concentration and treatment of the YAG:Ce single crystals have a relatively strong influence on the kinetics of cathodoluminescence, which is probably due to the

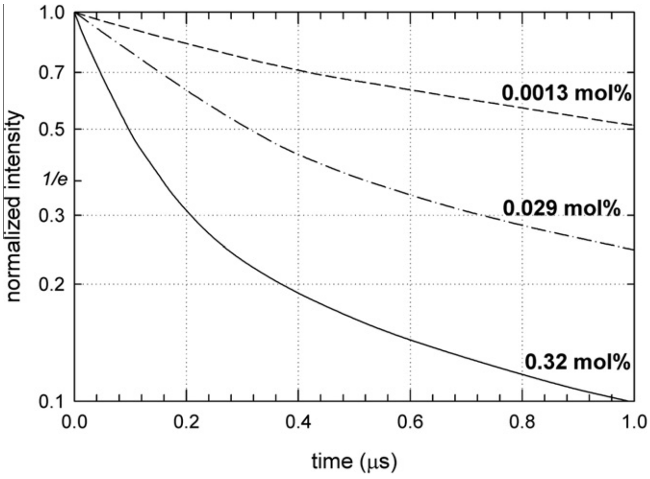

Fig. 6. Cathodoluminescence decay characteristics of YAG:Ce single crystals with different Ce concentrations.

Table 1
Cathodoluminescence properties of YAG:Ce single crystals with different treatment conditions.

Treatment[a]	Relative intensity (560 nm)[b]	Relative intensity (400 nm)[c]	Decay time[d] (ns)	Afterglow[e] (%)
No treatment (as grown)	1.00	0.0086	212	0.123
HNO_3 + 3HCl boiled; H_2 fired	1.07	0.0109	196	0.115
H_2 fired	1.10	0.0114	224	0.151
HNO_3 + 3HCl boiled; O_2 fired	0.80	0.0064	375	0.250
O_2 fired	0.59	0.0030	135	0.069

[a] Additional treatment of "as grown" YAG:Ce single crystal.

[b] Intensity of the characteristic emission ($X = 560$ nm) related to the characteristic emission of the not treated single crystal.

[c] Intensity of the defect emission ($X = 400$ nm) related to the characteristic emission of the not treated single crystal.

[d] Time measured at the relative spectrally unresolved intensity of 1/e (e–base of the natural logarithm).

[e] Spectrally unresolved intensity measured 1 [j,s after the end of excitation.

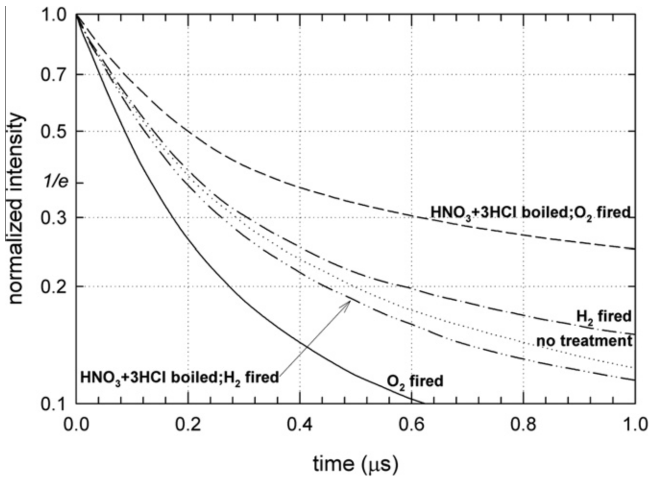

Fig. 8. Cathodoluminescence decay characteristics of YAG:Ce single crystals with different treatment conditions.

presence of impurities and defects in the crystal lattice. Decomposition of the decay curves results to a four-component equation

$$I = \sum_{i=1}^{4} A_i e^{-\frac{t}{\tau_i}}$$

where I is the CL intensity at the time t after the end of the excitation. The existence of multiple relaxation components supports the idea that in addition to the presence of Ce activator centers, which can be attributed to the shortest time constant $\tau_1 = 60$ ns, several kinds of impurity or defect centers are present. For example, the largest analyzed decay constant $\tau_4 = 3.5$ μs corresponds to the decay time of YAG:Nd, so the presence of Nd impurities can be presumed. Other time constants are not yet unambiguously assigned, but due to earlier experiments [13,14], one can expect the presence of Fe, Pt, Ir and Mo. Fe and Pt are known as significant quenching impurities. On the contrary, it was published in the papers just mentioned that Mo significantly contributes to the radiative emission from the activator. Increasing concentration of both Mo and Ce contributes to the CL efficiency, however, higher concentration of the Ce also significantly contributes to the reduction of the decay time of YAG:Ce, which has not been observed for Mo so far.

To interpret the presented results and previous measurements of dependences of the CL intensities and CL decays of the spectral peaks on the activator concentration [2], a schematic kinetic model of radiative and nonradiative transitions at the CL in the YAG:Ce single crystals was created in Fig. 9. In the kinetic model, g represents the exciton generation rate; e_D is the thermalization rate from the defect centers; c_D, c_I, and c_A are the capture rates to the defect, impurity and activator centers, respectively; s, s_D, and s_I are the nonradiative rates from the lattice states, defects and impurities, respectively; w_{IA} is the transfer rate from the impurity to the activator centers, and f_D, f_I, and f_A are the radiative (emission) rates from the defect, impurity and activator centers, respectively.

It is good to remember that from the macroscopic point of view, cathodoluminescence is a surface phenomenon. Therefore, cleaning and particularly annealing can significantly affect the formation of defects and impurities in the active surface layer. Since the treatment in oxidizing atmosphere significantly reduces both the CL decay time and the CL efficiency, this process is likely to increase the nonradiative rates s_D from defects or s_I from impurities. This inevitably decreases the radiative rate f_D from defects or f_I from impurities, or the thermalization rate e_D from the defects as well as the transfer rate w_{IA} from the impurity to the activator centers. This is consistent with earlier studies of absorption spectra [13] exhibiting increased optical absorption in the spectral range of up to 400 nm after oxidizing treatment, which is explained by the presence of Fe or other impurities. The above mentioned reduction of the radiative rate f_D from defects or f_I from impurities after the treatment in oxidizing atmosphere is experimentally supported in Table 1.

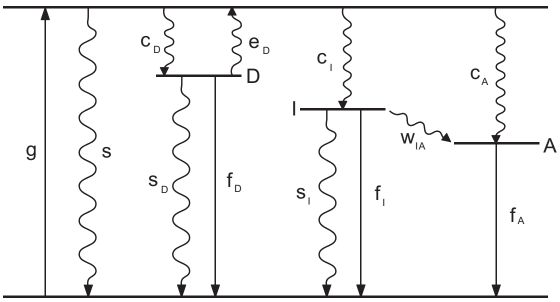

Fig. 9. The kinetic model of the cathodoluminescence of YAG:Ce. g represents the exciton generation rate; e_D is the thermalization rate from the defect centers; c_D, c_I, and c_A are the capture rates to the defect, impurity and activator centers, respectively; s, s_D, and s_I are the nonradiative rates from the lattice states, defects and impurities, respectively; w_{IA} is the transfer rate from the impurity to the activator centers, and f_D, f_I, and f_A are the radiative (emission) rates from the defect, impurity and activator centers, respectively.

On the other side, treatment of YAG:Ce in reducing atmosphere suppresses absorption in the near UV spectral region mentioned [13] and it increases the radiative rates f_D from defects or f_I from impurities at the same time, as is evident from the measurements of the CL intensity of defect emission ($\lambda = 400$ nm) in Table 1. Since similar effects were observed with an increased concentration of Mo ions [14], it can be assumed that annealing in reducing atmosphere contributes to the formation of Mo impurity ions, which is consistent with the results presented as well as with the previous study [13].

4. Conclusions

After interpretation of the activator concentration dependence, the crystal treatment dependence, as well as temperature and excitation duration dependence, in accordance with other results presented in previous papers [2,13–19], some conclusions can be made for the CL kinetics of YAG:Ce single crystals.

Excitation by an electron beam results in electron–hole generation (probably exciton). Fe, Pt and Ir are quenching impurities, and nonradiative recombination is possible from them. They do not participate in energy transfer. Nd, Mo and defect centers participate in an energy transfer. Excitons can be captured in the above mentioned centers and in the activator. Energy carriers from the defect centers can be thermalized back to the lattice states or they can be utilized by radiative and nonradiative transitions. Thermalization from impurities does not exist. Radiative and nonradiative transitions are realized from impurities, and the direct energy transport is realized from impurities to the activator. Energy captured in the activator cannot be thermalized. Transfers from Ce^{3+} ions are mostly radiative. Probability of a nonradiative transfer is low. From a practical point of view, YAG:Ce scintillators cleaned in ethyl alcohol and fired in an oxidizing atmosphere possess the best decay characteristics.

The results presented can be utilized not only in the design and construction of an imaging unit in S(T)EM [5], but also for other instruments, where low-noise scintillation detectors are applied [20]. Owing to the extraordinarily high resistance of YAG:Ce, the investigated single crystal scintillators can be also used for the detection of heavy particles [21].

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