Spectral-kinetic studies of SrAlF$_5$ doped by trivalent rare-earth ions

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ABSTRACT

Photochemical properties of Ce^{3+}:SrAlF$_5$ and Ce^{3+},Yb^{3+}:SrAlF$_5$ single crystals together with spectroscopic and kinetic characteristics of several optically nonequivalent impurity centers and energy transfer between them are described. It is shown that co-activation by Yb^{3+} ions effectively suppresses color centers in Ce,Yb:SAF crystals. It was found out that in Ce,Yb:SAF crystals Yb ions exist simultaneously in 2+ and 3+ valent state. Three types of optically nonequivalent luminescent centers corresponding to the doublets in luminescence spectrum centered at 290, 305 and 370 nm (Ce^{I}, Ce^{II}, Ce^{III}, respectively) have been observed. Analysis of luminescence spectra and decays leads to the conclusion that there is no energy transfer between either cerium centers or from Ce^{3+} to Yb^{2+} apart from the Ce^{III} center which luminescence is slightly quenched by Yb^{2+}.

1. Introduction

Searching for and investigating new perspective active media for UV tunable solid state lasers is an urgent task, because modern technology requires as short wavelength of laser emission as possible [1]. SrAlF$_5$ (SAF) crystals doped by rare-earth (RE) ions, especially Ce^{3+} [2], is a very promising laser material for the UV/VUV spectral ranges due to broad band-gap (12.3 eV [3,4]) and chemical composition similar to the most effective UV laser active media LiCaAlF$_6$ and LiSrAlF$_6$. SAF crystals doped by iron-group ions are known as rather effective IR laser material [7]. It could also be doped by of RE^{3+} ions and despite their rather low segregation coefficient it is still enough for practical applications in quantum electronics devices based on interconfigurational transitions of active ions.

Because of Goldschmidt's rule trivalent RE^{3+} ions dominantly substitute for divalent strontium lattice cations which in this crystal exist in four nonequivalent positions [8]. Besides charge compensation is required. Thus several optically nonequivalent RE^{3+} centers formation are expected. Presence of the few types of optically nonequivalent active centers in one medium especially if the energy exchange between them is ineffective will inevitably lead to the dissipation of excitation energy and puts into question the use of this material for laser applications [9].

In literature there are a lot of contradictory assignments of the SrAlF$_5$ crystalline space group [5,6]. According to the most common viewpoint this crystal belongs to the noncentrosymmetric space group $I4$ and there are a lot of studies in favor of

ferroelectric effect existence in this material [5]. In such case active medium with controllable spectral properties is the one of interest. But on the other hand more recent theoretical and experimental studies report centrosymmetric space group $I4_1/a$ for SrAlF$_5$ which eliminates any ferroelectric behavior [6]. Therefore optical and spectroscopic properties studies of this crystal still remain an urgent task.

Another problem in the way of the search for the new materials for UV laser applications is that the most fluoride crystal hosts are subjected to the strong coloration under pumping condition (for example, [10]).To level this effect coactivation with Yb^{3+} ions has been successfully applied before [10]. The disadvantage of such approach are that: (a) doping by RE^{3+} ions generally leads to the formation of crystal lattice defects serving as the nuclei for color centers formation; and (b) Ce^{3+} ions 5d–4f luminescence could be significantly quenched by ytterbium ions, thus optimization of activator ions concentrations should be performed.

This paper reports on spectral, kinetic and photochemical properties of Ce:SAF and Ce,Yb:SAF single crystals of several optically nonequivalent RE impurity centers and energy transfer between them.

2. Experimental details

The tetragonal Ce:SAF and Ce,Yb:SAF crystals with doping concentration ~0.5 at% in the melt were grown in Ar-atmosphere in carbon crucibles using Bridgman–Stockbarger technique. The melt contained a slight excess of AlF$_3$ above the stoichiometric composition. High-purity chemicals (> 99.99%) of commercially available SrF$_2$, AlF$_3$, CeF$_3$, and YbF$_3$ powders were

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utilized. Polished disk-shaped samples of 1.2 mm thickness and 7 mm in diameter with optical axis in disk plane were prepared.

Absorption and luminescence spectra were registered by CCD spectrometer Stellarnet EPP2000-HR with detector integration time more than 1 ms and deuterium and halogen lamp as light sources. Luminescence spectra were studied using site-selective laser spectroscopy technique. As a pumping source the 4th harmonic radiation of YAG:Nd laser (266 nm) and its stimulated Raman scattering component emission (217, 238, 300 nm) from H_2 Raman-cell were used. Laser radiation pulse duration did not exceed 7 ns. These wavelength conform well to the 4f–5d absorption bands of Ce^{3+} ions in SAF crystals and absorption band belonging to Yb^{2+} ions in Yb:SAF [8]. Luminescence decays were registered by photomultiplier tube FEU-87 with a rise time about 6 ns and digital oscilloscope Aktakom AOC-2282.

3. Results and discussion

Polarized absorption spectra of both Ce:SAF and Ce,Yb:SAF crystals registered at 77 K are shown on Fig. 1. Generally absorption spectra of Ce:SAF contain several broad bands localized at about 232, 244, 249, 265, 307 nm, but due to several nonequivalent Ce^{3+} centers formation it's impossible to assign these bands to specific transitions. One observes though that in the view of obtaining laser action Ce:SAF and Ce,Yb:SAF are suitable for such pumping sources as Nd:YAG ($\omega_4=266$ nm) and KrF ($\omega=248$ nm) as indicated on Fig. 1b.

Fig. 2 shows transmission of Ce:SAF and Ce,Yb:SAF crystals during irradiation of the samples by high-energy (~ 0.8 J/cm^2) emission of Nd:YAG laser's 4th harmonic (266 nm). It demonstrates effective suppression of color centers absorption in Ce:SAF
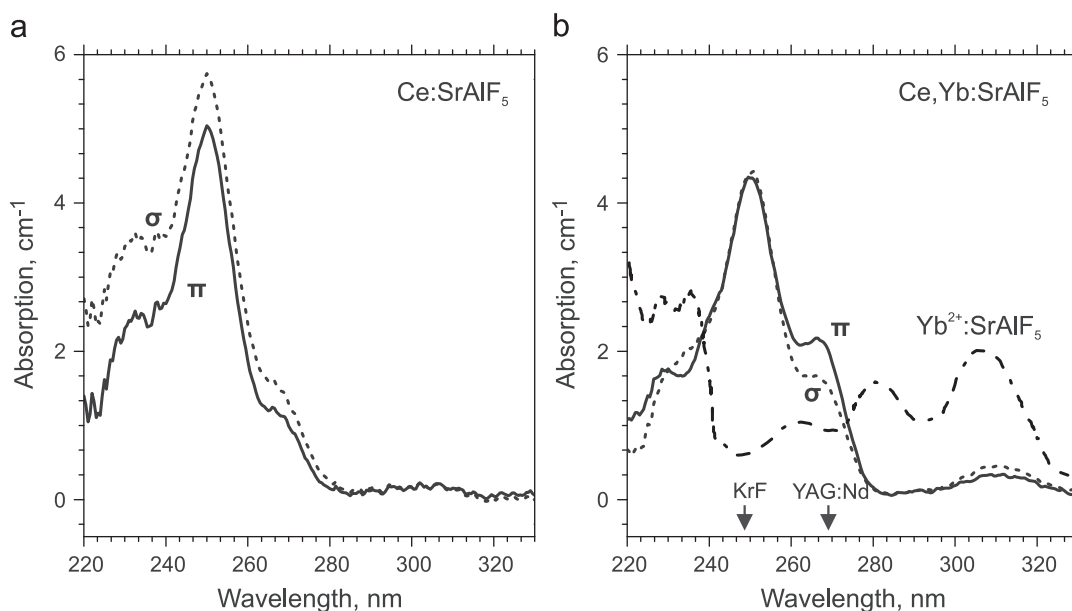
Fig. 1. Polarized absorption spectra of Ce^{3+}:SrAlF$_5$ (a) and Ce^{3+},Yb^{3+}:SrAlF$_5$ (b); π-polarized absorption spectrum (solid) and σ-polarized absorption spectrum (dashed). Non-polarized absorption spectrum of Yb^{2+}:SrAlF$_5$ crystal (dot-dashed curve) is given from [8]. The arrows show suitable pumping source wavelengths: YAG:Nd ($\lambda_4=266$ nm) and KrF ($\lambda=248$ nm).
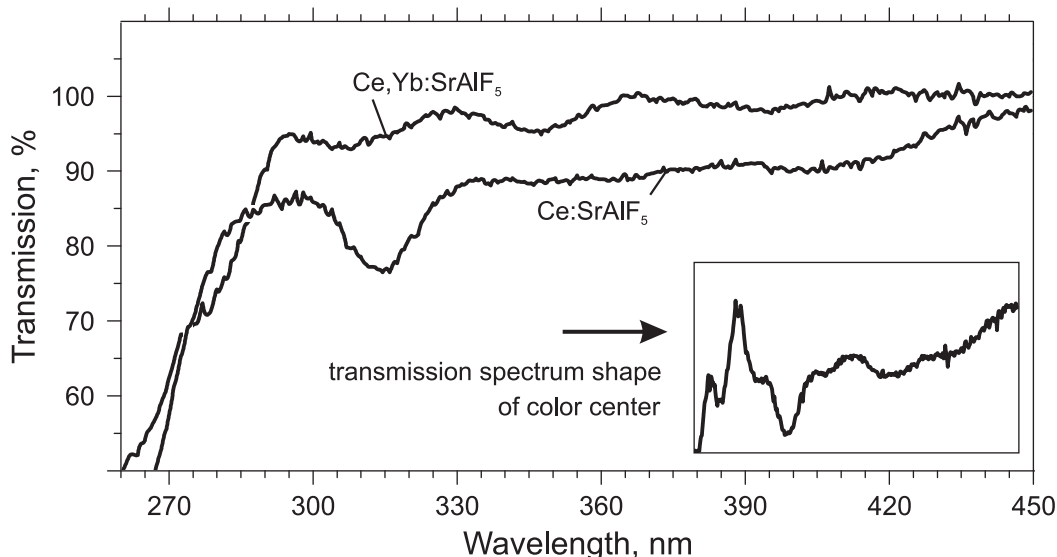
Fig. 2. π-polarized transmission of Ce^{3+}:SrAlF$_5$ (T$_{Ce}$) and Ce^{3+},Yb^{3+}:SrAlF$_5$ (T$_{Ce,Yb}$) crystals under irradiation of the samples by the 4th harmonic of Nd:YAG laser emission (266 nm) with a flux~ 0.8 J/cm^2 at the room temperature. (Inset) suggested transmission (in the same scale) spectrum shape of color centers suppressed due to Yb^{3+} ions co-doping is shown (taken as the ratio T$_{Ce}$/ T$_{Ce,Yb}$).

crystals co-doped by Yb^{3+} ions in comparison with one doped solely by Ce^{3+}. On the inset to the Fig. 2 suggested transmission spectrum shape of color centers suppressed due to Yb^{3+} ions co-doping is shown. Currently the nature of these photoinduced color centers in Ce:SAF crystals is under investigation by ESR method.

Fig. 3 shows π-polarized luminescence spectra of Ce:SAF and Ce,Yb:SAF crystals at $T=300$ and $T=77$ K under the excitation at different wavelengths (217, 238, 266, 300 nm). Luminescence bands in the range 250–400 nm belongs to 5d–4f transitions of Ce^{3+} ions while a broad band near 500 nm corresponds to the emission of color centers [11]. σ-polarized luminescence spectra are not presented here because they did not show any significant differences in shape in comparison with the π-polarized ones in terms of our analysis.

As it can be seen from Fig. 3c luminescence spectrum of each non-equivalent Ce^{3+} impurity centers in Ce:SAF crystal consists of two overlapping bands typical for radiative $5d \rightarrow {}^2F_{5/2}, {}^2F_{7/2}$ transition of Ce^{3+} ions. Excitation by laser radiation at different wavelengths enabled us to single out 3 different types of Ce^{3+}

luminescent centers marked as Ce^I (with a doublet peaked at about 290 nm), Ce^{II} (~ 305 nm), and Ce^{III} (~ 370 nm). These centers and their luminescence bands are in agreement with [9] where 3 different optical Ce^{3+} centers have been observed as well.

Wide bandwidth and overlapping of the 5d–4f luminescence and absorption bands typically lead to the energy exchange between impurity centers. However the fact that the shape and position of the observed Ce^{3+} luminescence bands differ for each pumping wavelength and that these bands belonging to different Ce^{3+} centers can be registered by CCD spectrometer separately under selective excitation apparently indicates that while different cerium centers are excited there is no energy transfer between them even at the room temperature (see Fig. 3a).

Situation changes if co-dopant Yb^{3+} ions were supplemented into the crystal. Broad band with the peak at about 500 nm disappears, which supports our guess about the color centers origin of this luminescence band. Moreover, the intense band centered at 405 nm appears which is shifted towards longer wavelengths compared to the much less intense doublet
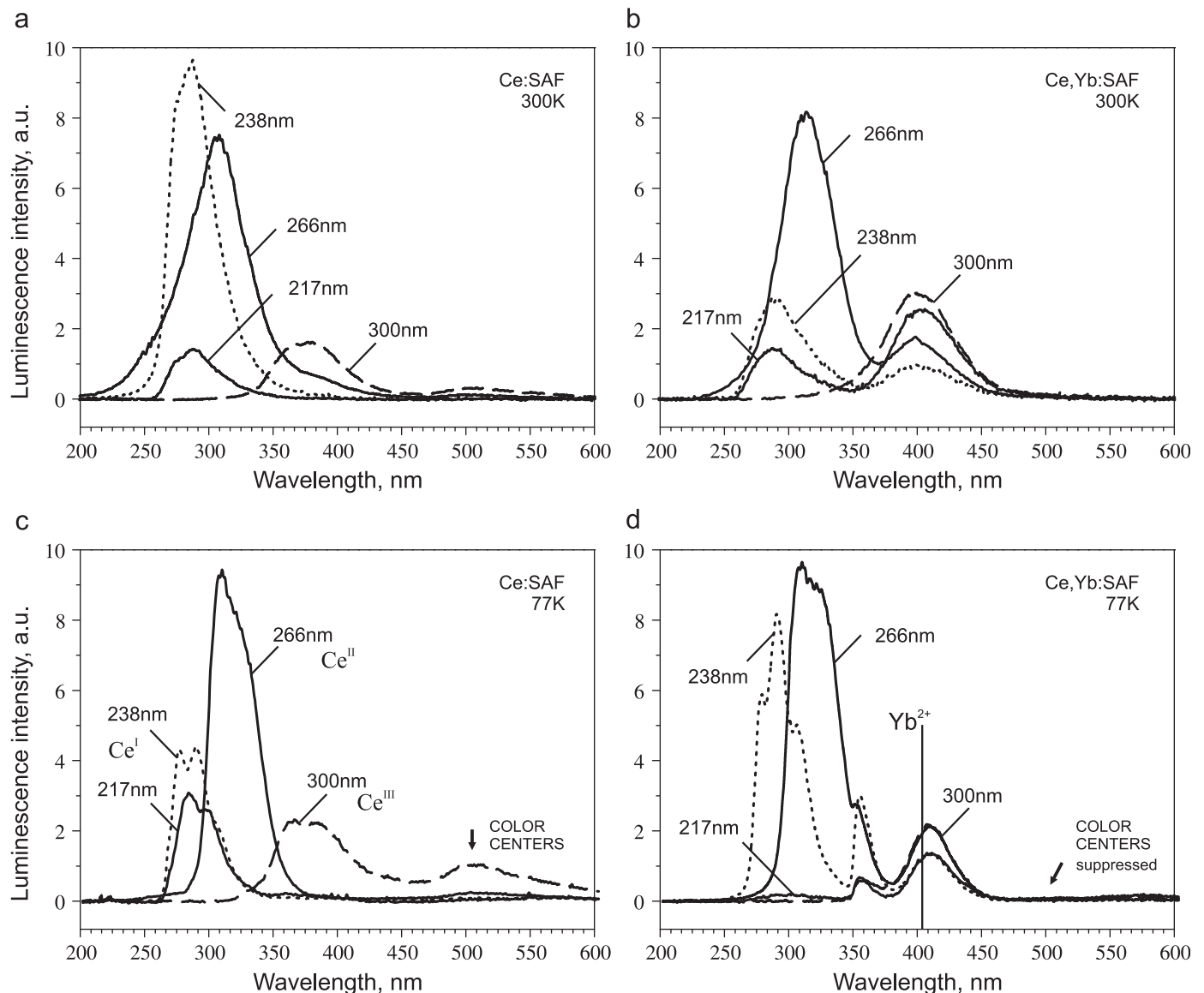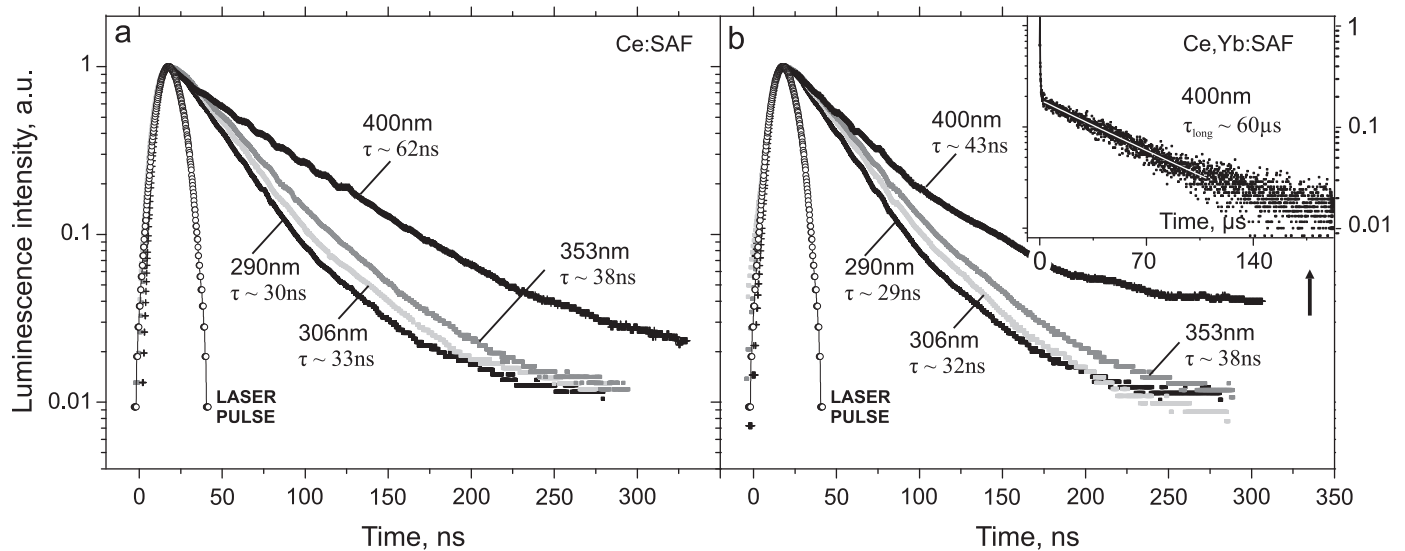

Fig. 3. π-polarized luminescence spectra of Ce^{3+}:SrAlF$_5$ (a) and (c) and Ce^{3+},Yb^{3+}:SrAlF$_5$ (b) and (d) crystals under excitation at $\lambda_{ext}=217$, 238, 366 and 300 nm at $T=300$ K (a) and (b) and $T=77$ K (c) and (d). Vertical line indicates the position of the center of Yb$^+$ luminescence band in SAF [8]. Bands assigned to different non-equivalent Ce^{3+} impurity centers are, respectively marked as Ce^I, Ce^{II} and Ce^{III}.

Fig. 4. Luminescence decays of Ce^{3+}:$SrAlF_5$ (a) and Ce^{3+},Yb^{3+}:$SrAlF_5$ (b) crystals registered for the luminescence peak of the each type of Ce^{3+} emitting centers (at 290, 306, 353 and 400 nm) and exited by laser pulses at 266 nm; $T = 300$ K. On the inset slow component of Ce^{3+},Yb^{3+}:$SrAlF_5$ crystal decay is shown. Laser pulse profile is shown as well.

belonging to Ce^{III} center. This band seems to be corresponding to the luminescence of Yb^{2+} ions [8]. Yb^{2+} ions may appear in the crystal either during growth process [8] or as a result of recombination processes when Yb^{3+} acts as a trap for free carriers resulting in change of its valence ($Yb^{3+} \rightarrow Yb^{2+}$) [12]. Nevertheless, Yb^{2+} ions exist in investigated Ce,Yb:SAF crystal simultaneously with Yb^{3+} ions. It is confirmed by the fact that luminescence of Yb^{3+} has been observed as well in IR spectral range (950–1000 nm) which is the subject of the separate investigation.

In contrast to Ce:SAF crystal luminescence spectral shape of Ce^{3+} ions in the crystal co-doped with Yb^{3+} ions seems to indicate that some energy transfer between centers takes place (see Fig. 3c and 3d). But in fact apparent spectra distortions could be either due to the energy transfer between Ce^{3+} centers initiated by Yb^{3+} co-doping or the evidence of Ce^{3+} luminescence reabsorption by Yb^{2+} ions. In order to clarify this issue Ce:SAF and Ce,Yb:SAF emission decays were investigated.

The decays of luminescence of Ce:SAF and Ce,Yb:SAF crystals registered for the luminescence peak of the each type of Ce^{3+} emitting center (at 290, 306, 353 and 400 nm) and exited by laser pulses at 266 nm wavelength at the room temperature are shown on Fig. 4. Decay curves qualitatively could be divided into 2 parts, intercenter luminescence (exponential decay) and recombination glow (non-exponential decay) [13]. Here only the intercenter parts of the Ce^{3+} ions fluorescence decays were analyzed.

These decays could be well fitted by exponential function with deviation ~ 7%. In Ce:SAF sample the decay times are slightly different for the each type of cerium centers which can be associated with the peculiarity of their symmetry. There are no significant differences between corresponding lifetimes in Ce,Yb:SAF and Ce:SAF samples for registration at 290, 306, 353 nm which implicates the absence of any energy transfer either between cerium centers or from Ce^{3+} to Yb^{2+} ions.

For the fluorescence decay measured at 400 nm however much longer exponential component appears for Ce,Yb:SAF crystal in addition to the fast Ce^{3+} kinetic with a lifetime about 60 μs (see Fig. 4, inset). It may be suggested that this long component belongs to Yb^{2+} ions, which is in agreement with the lifetimes reported for Yb^{2+}:SAF crystal in [8]. At the same time Ce^{III} fluorescence decay becomes slightly shorter compared to Yb-undoped sample (43 ns and 62 ns, respectively) which implies that Ce^{III} luminescence is partially quenched by Yb^{2+} ions.

4. Conclusion

Thereby, spectral-kinetic properties investigation of $SrAlF_5$:Ce^{3+} and $SrAlF_5$:Ce^{3+},Yb^{3+} crystals was performed and luminescence spectra of 3 optically nonequivalent types of Ce^{3+} centers have been observed. Each center (marked as Ce^{II}, Ce^{I}, Ce^{III}) corresponds to a 5d–4f luminescence doublet centered at 290, 305 and 370 nm, respectively. It is shown that color centers luminescence with a maximum at about 500 nm occurs in Ce:SAF crystal under UV excitation and is efficiently suppressed due to the co-activation by Yb^{3+} ions in Ce,Yb:SAF crystal. It was found out that in Ce,Yb:SAF crystals Yb^{3+} and Yb^{2+} ions could simultaneously exist. Analysis of luminescence spectra and decays leads to the conclusion that there is no energy transfer between either cerium centers or from Ce^{3+} to Yb^{2+} apart from the Ce^{III} center which luminescence is slightly quenched by Yb^{2+}. Therefore, Ce:SAF crystal co-doping with Yb^{3+} ions leads to the sufficient suppression of color centers in this material while leaving its spectral and kinetic properties associated with Ce^{3+} 4f–5d interconfigurational transitions unchanged. The latter positively distinguishes Ce,Yb:SAF active medium amongst the other promising fluoride host materials, doped by Ce^{3+} and co-doped by Yb^{3+} ions (for example Ce:$LiREF_4$ [14,15]).

Thus Ce,Yb:SAF crystal is a perspective material for UV quantum electronics devices suitable for pumping by available laser sources, such as YAG:Nd ($\lambda_4 = 266$ nm) and KrF ($\lambda = 248$ nm). Laser test are in progress.

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