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Pr^{3+} as a sensitiser of red Eu^{3+} luminescence in $K_5Li_2GdF_{10}$:Pr^{3+}, Eu^{3+} upon VUV–UV excitation

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ABSTRACT

The intensity ratio of luminescence originating from the $^5D_0$ level to that originating from the $^5D_1$ level of Eu^{3+} in the $K_5Li_2GdF_{10}$:Pr, Eu system is found to be considerably greater upon the indirect excitation of 5d levels of Pr^{3+} or Gd^{3+} multiplets than in the case of direct excitation into Eu^{3+} levels. The generalized Yokota–Tanimoto model was used to explain the behaviour of decay curves of $^3P_0$ luminescence and to determine the kinetic micro-parameters: C_{DA} related to cross-relaxation, and D related to the energy migration probabilities. The Pr–Eu "critical radius" was calculated to be in the range 13.9–15.3 Å.

In fluorescent lamps, mercury vapours are used to transform the electric energy into visible emission of phosphor. The use of mercury electric discharge lamps is cheap and efficient; however, mercury vapours are poisonous. Schubert and Kim have discussed in Ref. [1] the future of solid-state light sources and have given after Ref. [2] the scale of the consumption of electricity used for lighting (11% in private homes, and 25% in commercial use, which gives overall 22%). Using solid-state lighting will offer the possibility to reduce this overall energy consumption at 22%, in half [1]. Most of popular phosphors have been still optimised for an excitation by mercury vaporous emission, therefore, it is necessary to find new phosphors which efficiently will convert mercury-free gases excitation into visible to minimise the total amount of mercury in the environment.

Auzel in 1966 have discovered the process that makes it possible to obtain more than one visible photon upon vacuum ultra violet (VUV) excitation with a photon [3]. This work was an inspiration for the Meijerink's group to look for new phosphors excited by noble gases in VUV region of spectrum. Their original work, especially, on Gd–Eu system in $LiGdF_4$ crystal have demonstrated that the excitation of the ^6G_J or higher energy 4f levels of Gd^{3+} brings about the emission of two visible photons originated from the $^5D_0$ multiplet of Eu^{3+} [4]. After excitation into the ^6G_J multiplets of Gd^{3+} at 202 nm, the first photon is created due to cross-relaxation process in the frame of Eu^{3+} $(^7F_1 \rightarrow {}^5D_0) \approx Gd^{3+}$ $(^6G_J \rightarrow {}^6P_J)$ transition. Then the second photon arises as a consequence of energy transfer from the ^6P_J levels of Gd^{3+} to Eu^{3+} multiplets and non-radiative cascade feeding of Eu^{3+} ^5D_J multiplets. Quantum efficiency of this process, called "downconversion" or "photon-cutting", should be theoretically of ~200%. The actual efficiency of conversion of VUV excitation to visible emission is considerably lower because of small spectral widths of absorption lines related to the $(^8S_{7/2} \rightarrow {}^6G_J)$ transitions of Gd^{3+} [5,6]. Recently, visible quantum cutting through "downconversion" has been discovered in green-emitting K_2GdF_5:Tb^{3+} phosphors [7].

During the earlier investigation of the $K_5Li_2GdF_{10}$ doped with Eu^{3+} (KLGF) system the "downconversion" processes discovered in Ref. [4] have been confirmed [8]. Although in the case of KLGF, the first photon is generated in radiative $^6G_J \rightarrow {}^6P_J$ transitions.

A different way to obtain two photons instead of one used for excitation of higher laying level was proposed theoretically by Dexter in 1957 [9]. According to his model it should be a possibility to obtain two visible photons, due to simultaneous, cooperative energy transfer process in materials heavy doped with activators.

This work reports results of our experiment with the KLGF polycrystalline sample containing both 10 at.% of Eu^{3+} and 10 at.% of Pr^{3+} ions. It will be demonstrated in the following that the system under study shows properties that have not been observed thus far although Pr + Eu systems have been under investigation in the past [10,11]. In YF_3:Pr^{3+}, Eu^{3+} [10] no energy transfer to Eu^{3+} from excited d levels of Pr^{3+} has been found and only quenching effects have been observed. Whereas, it has been demonstrated that in the GdF_3:Pr^{3+}, Eu^{3+} [11] such an energy transfer is accessible.

The crystal structure of the KLGF polycrystalline sample containing both 10 at.% of Eu^{3+} and 10 at.% of Pr^{3+} ions was the same

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as described in Ref. [12]. Room temperature experimental results are shown in Figs. 1–3. The experiments were carried out using setup of SUPERLUMI station at HASYLAB, DESY in Hamburg, Germany [13]. Fig. 1 presents excitation spectra (corrected on response of sodium salicilate) of Eu^{3+} luminescence, related to the ($^5D_0 \rightarrow {}^7F_2$) transition (monitored at 609 nm/16420 cm^{-1}) and to the ($^5D_1 \rightarrow {}^7F_2$) transition (monitored at 555 nm/18018 cm^{-1}). The latter spectrum is shown as inverted for better clarity of this figure. The Gd^{3+} multiplets ($^6P_{7/2}$, $^6P_{5/2}$, ^6I_J, ^6D_J and ^6G_J) and Eu^{3+} one ($^3P_0$, ^5I_J, ^5F_J and $^5K_6$) are marked for better readability. The intensity was calibrated for the ($^7F_J \rightarrow {}^3P_0$) Eu^{3+} transition response, according to Refs. [14–16]. The Pr^{3+} ($4f^2 \rightarrow 4f^15d^1$) excitation band appears in the range 238–192 nm (42000–52000 cm^{-1}). At longer wavelengths there are narrow lines related to transitions within $4f^N$ configuration of Gd^{3+} and Eu^{3+} ions. The significantly higher intensity of lines associated with sensitiser

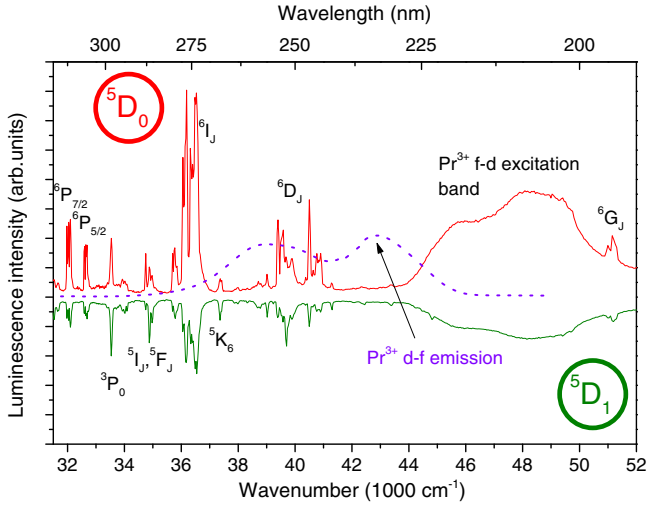

Fig. 1. The excitation spectra of luminescence in $K_5Li_2Gd_{0.8}Eu_{0.1}Pr_{0.1}F_{10}$ from the $^5D_0$ (red, in normal direction) and the $^5D_1$ (green, upside down). The spectra were recorded at 609 and 555 nm (both terminated at the $^7F_2$ state of Eu^{3+}). The f–d luminescence of Pr^{3+} in an analogue $K_5Li_2La_{0.9}Pr_{0.1}F_{10}$ crystal upon excitation at 170 nm is drawn with a violet, dotted line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

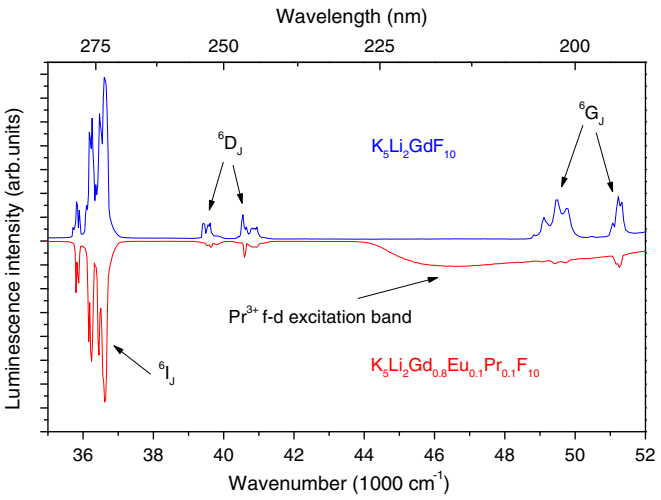

Fig. 2. The excitation spectra of luminescence from the $^6P_{7/2}$ of Gd^{3+} multiplet in $K_5Li_2GdF_{10}$ (blue, in normal direction) and in $K_5Li_2Gd_{0.8}Eu_{0.1}Pr_{0.1}F_{10}$ (red, upside down) recorded at 311 nm (32680 cm^{-1}). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

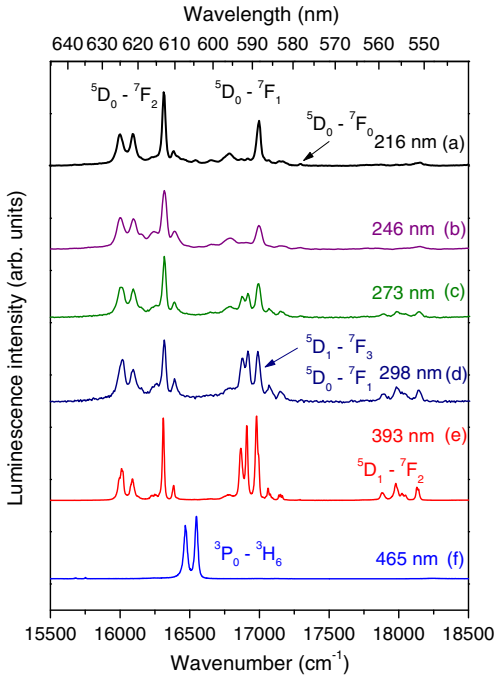

Fig. 3. The luminescence spectra of $K_5Li_2Gd_{0.8}Eu_{0.1}Pr_{0.1}F_{10}$ upon excitation at various wavelengths: 216, 246, 273, 298, 393 and 465 nm (46300, 40650, 36630, 33560, 25455 and 21500 cm^{-1}). One can see that upon excitation at 216 and 246 nm there is rather no luminescence from the $^5D_1$ state of Eu^{3+}.

(Pr^{3+} and Gd^{3+}) in the excitation spectrum of the $^5D_0$ luminescence was observed, whereas intensities of lines corresponding to direct Eu^{3+} excitation in these two spectra are similar. The spectral position of d–f emission band of $K_5Li_2La_{0.9}Pr_{0.1}F_{10}$ presented also in Fig. 1, implies that there is a crossing with the ^6D_J states of Gd^{3+}. Fig. 2 presents the excitation spectra of the $^6P_{7/2}$ Gd^{3+} multiplet in $K_5Li_2GdF_{10}$ and $K_5Li_2Gd_{0.8}Eu_{0.1}Pr_{0.1}F_{10}$. It can be seen that f–d excitation band of Pr^{3+} provides excitation of Gd^{3+} ions. Thus, the energy from excited Pr^{3+} ions can populate both the ^6D_J and the possibly ^6G_J states. The efficiency of the Pr^{3+}–Gd^{3+} energy transfer is quite high. The strong d–f emission, as well as, f–f emission coming from the $^3P_0$ state, observed in $K_5Li_2LaF_{10}$ (KLLF) crystal doped singly with Pr^{3+} [17], are almost completely quenched in KLGF:Pr^{3+} + Eu^{3+}. It can suggest that excited the Pr^{3+} ions very efficiently transfer the energy to Gd^{3+} ions. Such an efficient energy transfer has been observed in other system YF_3:Pr^{3+}, Gd^{3+} [18]. At low temperature emission spectra (not shown here) the Pr^{3+} f–f emission upon UV–VUV excitation was observed. It suggests that energy transfer from d levels of Pr^{3+} to Gd^{3+} states is thermally dependent.

The luminescence spectra recorded upon various excitations at room temperature are presented in Fig. 3. These data are in full agreement with those in Fig. 1. The excitation into the Pr^{3+} f–d band 216 nm (46300 cm^{-1}) and into the Gd^{3+} bands: the ^6D_J at 246 nm (40650 cm^{-1}), the ^6I_J at 273 nm (36630 cm^{-1}), or even the $^6P_{5/2}$, and $^6P_{7/2}$ at 306 and 311 nm (32680 and 32155 cm^{-1}), respectively, promotes emission from the $^5D_0$ state of Eu^{3+}, whereas the $^5D_1$ emission is hardly visible. At 273 nm (36630 cm^{-1}) both Gd^{3+} ^6I_J and the Eu^{3+} $^6K_6$ bands can be excited, therefore, the emission from the $^5D_1$ appears in the spectrum at ~555 nm (18020 cm^{-1}) and ~591 nm (16920 cm^{-1}). Upon excitation at 393 nm (33560 cm^{-1}) into the Eu^{3+} multiplet a typical emission originating in the $^5D_1$ and $^5D_0$ levels, bridged by multiphonon relaxation can be observed using setup that have been described in Ref. [19]. Upon direct excitation into Pr^{3+} at 465 nm (21505 cm^{-1}) no luminescence from Eu^{3+} ions was observed,

Table 1
The kinetic micro-parameters, C_{DA} and D related to the cross-relaxation and to the energy migration in $K_5Li_2Gd_{0.8}Pr_{0.1}Eu_{0.1}F_{10}$

Model	Concentration [at.%]	[ions/m^3]	Multiplet	S	R_0 [m^{-10}]	C_{DA} [m^S/s]	$\pm\Delta C_{DA}$ [m^S/s]	D [m^2/s]	$\pm\Delta D$ [m^2/s]	χ^2
Inokuti and Hirayama	10	3.4626×10^{26}	$^3P_0$	6	14.196	8.1855×10^{-50}	5.6587×10^{-52}	–	–	68.385
				8	14.934	2.4737×10^{-67}	2.5296×10^{-69}	–	–	57.025
				10	15.272	6.9010×10^{-85}	9.7559×10^{-87}	–	–	55.490
Yokota and Tanimoto	10	3.4626×10^{26}	$^3P_0$	6	13.947	7.3613×10^{-50}	5.3107×10^{-52}	1.1884×10^{-27}	7.1099×10^{-19}	72.267
				8	14.590	2.0537×10^{-67}	1.4339×10^{-70}	8.6540×10^{-29}	–	60.533
				10	15.139	6.3218×10^{-85}	3.8776×10^{-88}	4.5798×10^{-30}	–	55.776

The R_0 represents "critical radius". For description of parameters see Refs. [12,19].

which means that Pr^{3+} ions excited into ^3P_J states did not transfer the energy to the luminescent ^5D_J states of Eu^{3+}, which was shown in Fig. 2f.

It has been well ascertained that the "photon-cutting" process proceeding *via* cross-relaxation within the Gd^{3+}–Eu^{3+} pair is possible only upon excitation of the ^6G_J or higher energy multiplets of Gd^{3+} [4,20]. Liu et al. have emphasized it: "upon excitation in ^6I_J level with 273 nm, the quantum cutting never occurs because no cross-relaxation exists, so the $^5D_J \rightarrow {}^7F_J$ transitions emission of Eu^{3+} has a normal branching ratio between $^5D_0$ and $^5D_{1,2,3}$" [21]. Therefore, based on excitation and emission spectra shown in Figs. 1 and 3, an hypothesis was made that upon the UV–VUV excitation the energy of populated the $^6P_{7/2}$ long-lived multiplet of Gd^{3+} (lifetime ~ 10 ms) is branched into two channels: $Gd^{3+}/{}^6P_{7/2} \rightarrow {}^8S_{7/2} \approx Eu^{3+}/{}^7F_{0,1} \rightarrow {}^5D_2 + Pr^{3+}/{}^3H_4 \rightarrow {}^1G_4$. It is supposed that one channel populates the $^1G_4$ state of Pr^{3+} and the second cooperative relaxation channel populates the $^5D_2$ multiplet of Eu^{3+}. The $^1G_4$ state is situated at about 10 000 cm^{-1} whereas the $^5D_2$ one is situated at about 21 500 cm^{-1}. Unfortunately, the population of the $^1G_4$ multiplet was not confirmed due to SUPERLUMI station setup limitation. In such a case the condition of energy conservation law is fulfilled because the $^6P_{7/2}$ multiplet is situated at about 31 500 cm^{-1}. Such an explanation can account also for unusual quenching of the $^3P_0$ state of Pr^{3+} by the Ce^{3+} ions in the $K_5Li_2CeF_{10}$ (KLCF) matrix, that have been observed by Lempicki and McCollum [22].

In KLLF matrix singly doped with Eu^{3+} or Pr^{3+} ions at concentration of 10 at.% the decay curves have been found to be pure exponential with lifetimes: $^5D_0 = 12\,000$ μs, $^5D_1 = 2315$ μs and $^3P_0 = 10$ μs. The influence of Pr^{3+} ions on the ^5D_J lifetimes of the Eu^{3+} has been described in Ref. [19]. With the same method and parameters that have been described else in Ref. [12], the generalized Yokota–Tanimoto model [23] was used to explain the behaviour of decay curves of the $^3P_0$ luminescence due to the possible cross-relaxation process $(Pr/{}^3P_0 \rightarrow {}^1D_2 \approx Eu/{}^7F_{0,1} \rightarrow {}^7F_4)$ [24,25], and to determine the kinetic micro-parameters: C_{DA} related to cross-relaxation, and D related to the energy migration probabilities. The "critical radius" (R_0) for these interactions was calculated to be in the range of 13.9–15.3 Å. Results of calculation are given in Table 1. It was found that the quenching of the $^3P_0$ luminescence is quadrupole–quadrupole in nature. The energy migration probabilities were about 13 orders lower than typically have met in the literature and can be neglected [12]. The addition of Eu^{3+} to the KLGF crystal doped with Pr^{3+} changes the character of decay curve of $^3P_0$ to non-exponential time dependence. Therefore, it is impossible to calculate the real lifetime from the decay curve but only mean lifetime (τ_m) defined as [26]

$$\tau_m = \frac{\int_{t=0}^{\infty} tI(t)dt}{\int_{t=0}^{\infty} I(t)dt} \quad (1)$$

can be evaluated. The I is the intensity of luminescence and t represents time. The mean lifetime was found to be 5.55 μs, which means that addition of 10 at.% of Eu^{3+} ions quenches the $^3P_0$ luminescence about 1.8 times.

In summary, the data presented show that broad f–d band of lanthanides can be used as a sensitiser of Gd^{3+} excitation. Further, this excitation can be transferred to other ions that emit in the visible region of the spectrum. However, the concentration of the sensitiser should be controlled carefully because besides sensitiser properties the new ions, added to the system, can act also as luminescence quenchers. Fortunately, the f–d transitions are parity allowed, so their intensities are strong, which gives the possibility to keep the sensitiser concentration at low levels.

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