Luminescence and energy transfer in Lu$_3$Al$_5$O$_{12}$ scintillators co-doped with Ce$^{3+}$ and Pr$^{3+}$

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**Abstract**

Lu$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (LuAG:Ce) is a scintillator with a fast response time. The light yield is lower than theoretically expected and to increase the light yield co-doping with Pr$^{3+}$ is investigated. To better understand the energy flow to the Ce$^{3+}$ ion, first low temperature emission and excitation spectra of Pr$^{3+}$ doped LuAG were investigated, allowing the accurate determination of the zero-phonon lines for the 5$d$ states of Pr$^{3+}$ in LuAG and the temperature dependent energy transfer from the Self Trapped Exciton to Pr$^{3+}$. In addition VUV excitation and soft X-ray excited emission spectra of the co-doped LuAG:Ce,Pr were studied. The results show that energy transfer from Pr$^{3+}$ to Ce$^{3+}$ occurs but it is followed by back transfer to the 4$f$ states of Pr$^{3+}$.

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1. Introduction

Medical imaging continues to gain importance and the development of new scintillator materials for imaging techniques which rely on detection of ionizing radiation (X-rays and γ-rays), plays an important role in progress in this field [1]. Two important techniques are Computed Tomography (CT) and Positron Emission Tomography (PET) in which a scintillating material with a relatively fast response time and low afterglow is required [2,3]. A good scintillator is characterized by a high light yield (L.Y.), preferably larger than 50000 photons/MeV of excitation energy, a short decay time, preferably in the ns regime, and a small afterglow, preferably less than 10 ppm after 1 s [4–6]. Lu$_3$Al$_5$O$_{12}$:Ce is a good candidate. The life time of the Ce$^{3+}$ emission is short, ~55 ns [7]. However, the fast scintillation light yield for LuAG:Ce was found experimentally to be significantly lower, typically 12,500–15,000 photons/MeV [9,10]. A possible explanation is the inefficiency of energy transfer from the host lattice to Ce$^{3+}$ ions after high energy X-ray or γ-ray excitation. Competition by trapping of charge carriers by defects reduces the fast scintillation light output by Ce$^{3+}$ and results in a much slower light generation process by thermal release of the trapped charges [11,12]. Increasing the Ce$^{3+}$ concentration to enhance trapping of e–h pairs by Ce$^{3+}$ is not an option since concentration quenching by energy transfer between Ce-ions will reduce the light output [13].

To improve the fast scintillation light yield, a co-activator can be introduced which captures the e–h pairs more efficiently and subsequently transfers the excitation energy to the 5d state of Ce$^{3+}$. A good co-activator needs to fulfill at least the following criteria:

- the co-activator emission should show spectral overlap with Ce$^{3+}$ absorption;
- high concentration in the material and by this the trapping probability should be relatively high.

A potential candidate for co-activation is Pr$^{3+}$. Praseodymium has been chosen based on the analysis of the energy diagram presented in Fig. 1 which shows a Dieke diagram for Ce and Pr trivalent ions as well as the two lowest 4f-5d absorption and 5d-4f...
energy transfer between the ions.

Absorption and emission bands of both ions are included to show the possibilities for energy transfer from the host lattice to the 5d level of Pr$^{3+}$, the second annealing step was carried out under CO. Single phase formation in all samples was confirmed with the X-ray diffraction measurements recorded on Rigaku Miniflex II Equipment.

2.2. Characterization

Luminescence spectra were measured at the SUPERLUMI station (DESY, Hamburg) where the excitation source was synchrotron radiation from the storage ring DORIS III. The experimental setup was equipped with a 2 m McPherson primary monochromator with a highest possible resolution of ~1 Å and with an ARC Spectra Pro-308i emission monochromator equipped with a Hamamatsu R6358P photomultiplier [21]. The samples were mounted on the cold finger of a liquid He flow cryostat in which the sample temperature can be varied from 10 K to 300 K. The spectra were measured in three time windows: integrated, fast and slow, making it possible to distinguish between fast and slow emissions. The fast time window was recorded for a delay of 2 ns after the excitation pulse and a width of 14 ns. The slow time window monitored emission between 100 ns and 200 ns. The excitation spectra (65–335 nm) were corrected for the signal intensity distribution using the excitation spectrum of sodium salicylate. The emission spectra (180–700 nm) were not corrected for the instrumental response.

The RT excitation spectra in the range of 250–540 nm were monitored on the cold finger of a liquid He flow cryostat in which the sample temperature can be varied from 10 K to 300 K. The spectra were measured in three time windows: integrated, fast and slow, making it possible to distinguish between fast and slow emissions. The fast time window was recorded for a delay of 2 ns after the excitation pulse and a width of 14 ns. The slow time window monitored emission between 100 ns and 200 ns. The excitation spectra (65–335 nm) were corrected for the signal intensity distribution using the excitation spectrum of sodium salicylate. The emission spectra (180–700 nm) were not corrected for the instrumental response.

Soft X-ray excited emission measurements were recorded at room temperature (RT) using an Edinburgh Instruments FS920 spectrometer, equipped with a Deuterium DS-775 lamp, a TMS300 monochromator (Czerny-Turner optics) and a single photon counting Hamamatsu R928 photomultiplier. The spectra measured in the range of 150–340 nm were corrected for the lamp intensity and the throughput of the excitation monochromator using the excitation spectra of sodium salicylate as a reference. The RT excitation spectra in the range of 250–540 nm were monitored on the cold finger of a liquid He flow cryostat in which the sample temperature can be varied from 10 K to 300 K. The spectra were measured in three time windows: integrated, fast and slow, making it possible to distinguish between fast and slow emissions. The fast time window was recorded for a delay of 2 ns after the excitation pulse and a width of 14 ns. The slow time window monitored emission between 100 ns and 200 ns. The excitation spectra (65–335 nm) were corrected for the signal intensity distribution using the excitation spectrum of sodium salicylate. The emission spectra (180–700 nm) were not corrected for the instrumental response.

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Soft X-ray excited emission measurements were recorded at room temperature utilizing the white spectrum of a copper tube operated at 40 kV, with the energy in the maximum of the white band of about 28.7 keV.
3. Results and discussion

3.1. LuAG:Ce 0.1% and LuAG:Pr 0.1%

In the first section excitation and emission spectra for singly doped LuAG:Ce and LuAG:Pr with low activator concentrations are measured and analyzed aimed at gaining understanding of the location of 5d levels of the two ions and energy transfer from the host lattice to the 5d excited states of Ce$^{3+}$ and Pr$^{3+}$.

In Fig. 2 excitation spectra between 160 nm and 300 nm are shown for the 5d–4f emission in LuAG containing 0.1% of Ce$^{3+}$ or Pr$^{3+}$. The excitation is monitored at 550 nm emission wavelength for Ce$^{3+}$ and at 360 nm for Pr$^{3+}$ at 10 K. In each plot two curves are shown, one for the fast and one for the slow time window.

Fig. 2a shows a strong host lattice excitation band and a very weak band with a maximum at 225 nm. The origin of this band is possibly a high energy Ce$^{3+}$ 5d band but it can also be related to the host lattice. Two lower energy 5d bands of Ce$^{3+}$ have been studied in detail before and are situated around 340 nm and 445 nm [14]. The positions of these bands are included in Fig. 1.

For LuAG doped with 0.1% Pr$^{3+}$ excitation spectra of the 5d–4f emission are shown in Fig. 2b. A clear difference is observed between the spectra recorded in the fast and the slow time window. The well known allowed 4f–5d transitions of Pr$^{3+}$ with maxima at 286 nm and 241 nm dominate the spectrum in the fast time window. A third 5d band is observed around 175 nm, close to the onset of the host lattice absorption edge. The energy difference between the 175 nm band and the lowest 5d band around 286 nm is ~22000 cm$^{-1}$. This is similar to the energy difference between the 225 nm band observed for Ce$^{3+}$ and the lowest energy 5d band for Ce$^{3+}$ in LuAG, which supports the assignment of the 225 nm band in Fig. 2a to a high energy 5d state of Ce$^{3+}$; as the crystal field splitting is expected to be similar for Ce$^{3+}$ and Pr$^{3+}$ in the same host lattice. Excitation in the 5d bands is followed by fast 5d–4f emission. As a result, these 5d excitation bands are not observed in the slow time window. The weak band observed between 220 nm and 300 nm (Fig. 2b) in the slow time window is assigned to excitation of Self Trapped Exciton (STE) emission of the LuAG host lattice, the decay of which will be much slower [22,23]. The occurrence of this band proves STE-Pr$^{3+}$ energy transfer. For LuAG:Pr the host lattice absorption is clearly present with an onset around 175 nm. The host lattice excitation band is most prominent in the slow time window where excitation in the host lattice is followed by both STE and Pr$^{3+}$ emission for low dopant concentrations.

To investigate the energy level structure for Pr$^{3+}$ in LuAG in more detail, high resolution excitation and emission spectra were recorded at cryogenic temperatures. For low doping concentrations zero-phonon lines (ZPLs) and vibrational fine structure have been observed for Ce$^{3+}$ in LuAG [14] and the same is expected for Pr$^{3+}$. Fig. 3 shows the excitation spectrum for 320 nm 5d–4f emission and an emission spectrum recorded for 275 nm excitation. The ZPL of Pr$^{3+}$ in LuAG from this study is located at 294.15 nm (33996 cm$^{-1}$) and is shown in more detail in the inset. The ZPL of Ce$^{3+}$ in LuAG was found at 473.10 nm (21137 cm$^{-1}$) [14]. The spectra present a mirror structure over the ZPL but interestingly, the relative intensity of the ZPL is significantly weaker in the emission spectrum. A phonon progression is observed with the energy differences of 130 cm$^{-1}$ due to coupling to a 130 cm$^{-1}$ vibrational mode in LuAG, similar to the energy observed in the vibrational progression for Ce$^{3+}$ doped LuAG [14]. In YAG:Ce$^{3+}$ a higher energy vibrational mode (200 cm$^{-1}$) couples with the 4f–5d transitions, consistent with the lower mass of Y (88.90 u) compared to Lu (174.97 u) [13].

To study the efficiency and temperature dependence of energy transfer from the host lattice to the 5d states of Pr$^{3+}$ temperature dependent emission spectra were recorded for LuAG:Pr 0.1% under host lattice excitation at 160 nm. A low dopant concentration is required for these studies as high Pr$^{3+}$ concentrations (above 1%) no host lattice emission is observed down to 4 K. The emission spectra are shown in Fig. 4. The well known 5d–4f emission of Pr$^{3+}$ is present between 280 nm and 400 nm and is characterized by peak broadening as the temperature increases. The broad band emission between 210 nm and 285 nm is assigned to the STE and shows thermal quenching. The inset in Fig. 4 shows the variation of the total STE and 5d–4f emission intensities as a function of temperature. Between 100 K and 200 K the STE emission intensity decreases and is accompanied by an increase in Pr$^{3+}$ 5d–4f emission intensity. The variation can be explained by thermally activated exciton diffusion, resulting in almost complete energy transfer from the STE state to Pr$^{3+}$ 5d levels at elevated temperatures.

Fig. 2. Excitation spectra of (a) LuAG:Ce0.1%, monitoring the Ce$^{3+}$ emission at $\lambda_{em} = 550$ nm, and (b) LuAG:Pr0.1%, monitoring Pr$^{3+}$ emission at $\lambda_{em} = 360$ nm, recorded in fast and slow time window (see experimental) at 10 K.
Insight in the activation energy for exciton diffusion can be gained from the analysis of the inset a in Fig. 4.

The temperature dependence of the STE emission intensity can be fitted to:

\[
I(T) = \frac{I_0}{(1 + D \exp(-E_a/kT))}
\]

where \(I(T)\) is the intensity of the STE emission at temperature \(T\), \(I_0\) is the intensity at 10 K (or 0 K), \(D\) is a constant, \(E_a\) is the activation energy related to the process of exciton diffusion (eV) and \(k\) is the Boltzmann constant \((8.62 \times 10^{-5} \text{ eV/K})\). The intensity at 10 K was set to 1 \([13]\). The fit of the experimental data gives a value of 0.08 ± 0.005 eV for the activation energy (with \(D = 985\)). The temperature at which the STE intensity drops to 50% of its initial value \(T_{50\%}\) is ∼130 K.

To further characterize the STE emission, excitation spectra for 250 nm emission wavelength were recorded between 160 nm and 250 nm at different temperatures. The spectra are shown in Fig. 5. The spectra are characterized by a strong excitation band around 170 nm, corresponding to the band gap of LuAG. This observation confirms that the emission is related to the host lattice. The temperature dependent excitation spectra reveal a shift of the band gap excitation band to lower energies. The energies corresponding to the half the maximum intensity, indicated as horizontal dashed line, are plotted versus temperature in the inset. The temperature induced red shift of the band gap energy has been fitted to the Varshni equation that is commonly used to describe the temperature dependence of the band gap of a semiconductor \([24,25]\):

\[
E_g(T) = E_0 - \alpha T^2/(T + \beta)
\]

where \(E_0\) is the band gap at 0 K and \(\alpha\) and \(\beta\) are fit parameters. The fit of the data presented in the inset of Fig. 5 resulted in
\( a = 1.08 \pm 0.01 \text{ meV/K and } b = 402 \pm 80 \text{ K. The total shift between 4 K and 300 K is about } 1100 \text{ cm}^{-1}. \) It is interesting to note that the (empirical) Varshi model which is commonly used to describe the temperature dependence of the band gap of semiconductors [24] also can describe the temperature induced band gap shift in insulators.

It is important to note that the spectral position of the STE emission does not shift with temperature. As energy transfer to Pr\(^{3+}\) is very efficient (above 180 K) even for low Pr\(^{3+}\) concentrations (0.1%), an impurity as source of the 250 nm emission is excluded, in line with observations in Ref. [26].

Finally, the Stokes’ shift and electron–phonon coupling strength for the 5\(d\)–4\(f\) emission have been investigated. Fig. 6 shows the emission of LuAG doped with 0.1% Pr recorded at 4.5 K. For low doping concentrations and measurements at low temperatures the spectra are not distorted by re-absorption (which plays a role at higher concentrations), thermal broadening or inhomogeneous broadening (which is observed at higher dopant concentrations). From the peak positions and the relative intensities of ZPLs the Stokes’ shift and Huang–Rhys coupling parameter can be determined.

In Fig. 6 the low temperature emission spectrum for LuAG:Pr\(^{0.1\%}\) is shown. The spectra show emission bands corresponding to transitions from the lowest 5\(d\) state to different 4\(f\) states. In order to accurately determine peak maxima, the spectrum was fitted using four Gaussians, with maxima at 306 nm.
The simplest method to calculate the Stokes’ shift is the difference between excitation and emission maxima of the transition between $5d$ level to ground state. In this case a value of $2160 \text{ cm}^{-1}$ was established.

A second method involves calculation of twice the energy difference between the excitation maximum and the ZPL or the ZPL and the emission maximum. These calculations result in $1660 \text{ cm}^{-1}$ and $2670 \text{ cm}^{-1}$, respectively. We observe that the contributions to the Stokes’ shift are not equal in absorption and emission and that the largest part of the Stokes’ shift is found in the emission. This is consistent with the lower relative intensity of the ZPL in the emission spectrum in comparison with the ZPL in the excitation spectrum (see Fig. 3 and below). The intensity of the ZPL, relative to the corresponding absorption or emission band is to $\exp(-S)$ [27], $S$ being the Huang–Rhys parameter which the number of phonons involved in the transition for the maximum of the absorption or emission band. $S$ indicates the strength of the electron–phonon coupling. The contribution to the Stokes’ shift is $\hbar \Delta \omega$, $\hbar \omega$ being the frequency of the phonon involved in the optical transition. As phonon frequencies are similar in the ground- and excited state, a larger Stokes’ shift implies a larger value for $S$, i.e. a lower intensity of the ZPL.

From the relative intensities of the absorption and the emission bands and the corresponding ZPL we now estimate the contribution of ground- and excited state relaxation to the Stokes’ shift. We determine the values for $S$, from the relative intensities $\exp(-S)$ of the ZPL and the corresponding absorption or emission band (see above). From the observed relative intensity of 0.14% of the ZPL in the emission spectrum, a Huang–Rhys parameter of

![Excitation spectra for LuAG:Ce,Pr recorded at RT for (a) Pr$^{3+}$ emission at 360 nm, (b) Ce$^{3+}$ emission at 540 nm. The Pr-concentrations are indicated in the Figure. To understand the energy flow, excitation spectra of singly doped Pr$^{3+}$ or Ce$^{3+}$ LuAG are shown for comparison.](image1)

![Emission spectra of LuAG:Ce,Pr measured under soft X-ray excitation at 300 K. As normalization reference, LuAG:Ce$^{3+}$ was selected. Inset (a) depicts the decrease of the Ce$^{3+}$ emission intensity at 540 nm for increasing Pr$^{3+}$ content in co-doped samples, inset (b) shows magnification of the 250–450 nm range where 5d–4f emission of Pr$^{3+}$ is recorded.](image2)
3.2. LuAG:Pr,Ce

In order to investigate the efficiency of Pr\textsuperscript{3+}–Ce\textsuperscript{3+} energy transfer, co-doped samples of LuAG were synthesized and characterized. The samples prepared contain a fixed amount of Ce\textsuperscript{3+} (1\%) and increasing amounts of Pr\textsuperscript{3+} (0\%, 1\%, 3\%, 5\%, and 10\%). The higher dopant concentrations enhance the probability of energy transfer between the dopant ions, and of host lattice excitations to Pr\textsuperscript{3+}.

Fig. 7a presents the excitation spectra for Pr\textsuperscript{3+} emission at 360 nm. The Pr\textsuperscript{3+} 5d bands with maxima at 240 nm and 285 nm are clearly visible with intensities increasing with increasing Pr\textsuperscript{3+} content. Moreover, the band with a maximum just below the band gap is observed, close in position to the 180 nm band observed in the 4f–4f emission spectra for LuAG:Ce\textsuperscript{3+} (after subtraction of the Ce\textsuperscript{3+} emission band).

Energy transfer from Pr\textsuperscript{3+} to Ce\textsuperscript{3+} is evident from the analysis of the excitation spectra for the Ce\textsuperscript{3+} emission at 540 nm. Comparison of the excitation spectra for LuAG:Ce\textsuperscript{3+} and LuAG:Ce\textsuperscript{3+}Pr\textsuperscript{3+}(1–10\%) shows that Pr\textsuperscript{3+} 5d bands are present in the excitation spectrum of the Ce\textsuperscript{3+} emission, indicating energy transfer from Pr\textsuperscript{3+} to Ce\textsuperscript{3+}. These Pr\textsuperscript{3+} 5d bands increase in intensity with increasing Pr\textsuperscript{3+} concentration. This shows that Pr\textsuperscript{3+} acts as a sensitizer for Ce\textsuperscript{3+}.

To investigate the potential applicability of the co-doped materials as scintillating composition emission measurements were done under conditions that mimic the application. Therefore, soft X-rays were used as excitation radiation source. The X-ray excited emission recorded at 300 K is shown in Fig. 8. The Ce\textsuperscript{3+}-doped sample has the highest emission intensity with a maximum around 540 nm. A decrease of the intensity of the 5d band is observed upon co-doping with Pr\textsuperscript{3+}. The inset a in Fig. 8 shows the decrease in the Ce\textsuperscript{3+} emission intensity for increasing Pr-concentration. Inset b reveals that some Pr\textsuperscript{3+} 5d–4f emission remains between 300 nm and 400 nm giving evidence that the energy transfer from Pr\textsuperscript{3+} to Ce\textsuperscript{3+} is not complete for 1\% Ce\textsuperscript{3+}. The Pr\textsuperscript{3+} 5d–4f emission between 300 nm and 400 nm decreases when the Pr-concentration is raised from 1\% to 10\%. This can be explained by concentration quenching due to cross-relaxation between neighboring Pr\textsuperscript{3+} ions. Finally, also 4f–4f emission from Pr\textsuperscript{3+} appears with the strongest peak at 610 nm. The 4f–4f emission lines can be assigned to transitions originating from the 1D\textsubscript{2} level. The decrease of the Ce\textsuperscript{3+} emission around 540 nm and the observation of 4f–4f emission from the 1D\textsubscript{2} level can be explained by back transfer from the Ce\textsuperscript{3+} 5d level to the 1D\textsubscript{2} level of Pr\textsuperscript{3+}. Similar energy transfer from Ce\textsuperscript{3+} to Pr\textsuperscript{3+} has been reported for YAG co-doped with Ce\textsuperscript{3+} and Pr\textsuperscript{3+} [31].

To study the back transfer from the Ce\textsuperscript{3+} 5d levels to Pr\textsuperscript{3+} 4f levels in more detail emission spectra were recorded for LuAG:Pr\textsuperscript{1%} and LuAG:Ce\textsuperscript{1%}Pr\textsuperscript{1%} under soft X-ray excitation. The spectra are shown in Fig. 9. For LuAG:Pr\textsuperscript{1%} broad band 5d–4f emission as well as strong 4f–4f line emission are clearly visible. Both 4f–4f emission from the 3P\textsubscript{0} and 1D\textsubscript{2} level are present. For the co-doped sample the intensity of the Pr\textsuperscript{3+} 5d bands is reduced by more than 95\% while the Ce\textsuperscript{3+} 5d–4f emission is strongly enhanced, indicating very efficient Pr\textsuperscript{3+}–Ce\textsuperscript{3+} energy transfer. Analysis of 4f–4f Pr\textsuperscript{3+} emission spectra reveals an interesting difference. Inset a in Fig. 9 presents Pr\textsuperscript{3+} 4f–4f line emission in the spectral range from 590 nm to 635 nm in LuAG:Pr\textsuperscript{1%} while inset b shows the emission spectrum of LuAG:Ce\textsuperscript{1%}Pr\textsuperscript{1%} (after subtraction of the Ce\textsuperscript{3+} 5d–4f emission.
Clearly, the $^3P_0$ emission is absent in the co-doped sample. This indicates that from the $5d$ state of Ce$^{3+}$ back transfer to the $1D_2$ state of Pr$^{3+}$ dominates which is consistent with the larger spectral overlap of the Ce$^{3+}$ emission with the $1D_2$ excitation lines around 580–590 nm in comparison with the $^3P_0$ excitation lines between 450 nm and 490 nm. Note that part of the quenching of the $^3P_0$ emission from Pr$^{3+}$ can be explained by cross relaxation between Pr$^{3+}$ and Ce$^{3+}$. The $^3P_0$–$1D_2$ energy gap is $\sim$3500 cm$^{-1}$. Cross relaxation with the $^2F_{5/2}$–$^2F_{7/2}$ transition on a neighboring Ce$^{3+}$ ion has been shown to lead to quenching of the $^3P_0$ emission, leading to $1D_2$ emission [32]. In view of the energy mismatch for this cross-relaxation process (the $^2F_{5/2}$–$^2F_{7/2}$ gap is $\sim$2000 cm$^{-1}$) it is not expected that this process can account for the complete disappearance of the $^3P_0$ emission in a sample with only 1% of Ce$^{3+}$. Note that in Ref. [32] the quenching of the $^3P_0$ emission became effective only at elevated Ce-concentrations (above 10%). Inset c depicts the Pr(5$d$)–Ce(5$d$) energy transfer and Ce(5$d$)–Pr(1$D_2$) back transfer process.

Based on the energy level structure determined and information on the energy transfer processes from the excitation and emission spectra, a schematic diagram of the energy flow in LuAG:Ce,Pr is given in Fig. 10. It shows the Dieke diagram with the 5d levels of the dopants, the STE emission and the schematic of the energy transfer processes after host lattice excitation. The energy flow diagram presented can be used to understand processes occurring as a consequence of host lattice excitation which makes it relevant for the understanding of the material as scintillator. After high energy excitation, the STE is produced that is in resonance with Ce$^{3+}$ and Pr$^{3+}$ 5$d$ levels. Because Pr$^{3+}$ 5$d$ levels have a larger spectral overlap with the STE emission, energy transfer to Pr$^{3+}$ can be expected to be more efficient than to Ce$^{3+}$ for the same dopant concentration. Energy transfer from the STE to the Pr$^{3+}$ ions plays an important role for low Pr$^{3+}$ concentrations as at low temperatures we observe incomplete energy transfer from the STE to Pr$^{3+}$. At higher Pr$^{3+}$ concentrations the role of energy transfer via STE will be reduced as other mechanisms active in the scintillation process, e.g. direct hole trapping by Pr$^{3+}$ will become more efficient than STE formation. The strong spectral overlap of the Pr$^{3+}$ 5$d$ emission bands with the two lowest energy 5$d$ absorption bands of Ce$^{3+}$, energy transfer from Pr$^{3+}$ to Ce$^{3+}$ is efficient and almost complete for Ce$^{3+}$ concentrations as low 1%. The desired Ce$^{3+}$ emission is, however,
suppressed by the back transfer to Pr$^{3+}$ 4f levels, especially the $^1D_2$ level, from which the line emission occurs.

Further information on energy transfer processes in the co-doped material can be obtained from the analysis of luminescence decay curves. Fig. 11 shows luminescence decay curves for Pr$^{3+}$ 5d–4f emission (at 380 nm) for excitation into the lowest 5d level of Pr$^{3+}$ (at 270 nm) for different Pr-concentrations. LuAG doped with 1% Pr shows a single exponential decay with a time constant of approximately 19 ns, in agreement with the literature [23,33]. When 1% Ce$^{3+}$ is introduced there is a strong decrease in the decay time and the decay becomes non-exponential. The time in which the signal drops to 1/e of the initial intensity is 5.6 ns. The strong decrease in life time upon co-doping with 1% Ce$^{3+}$ is in agreement with the observed drop in intensity of the 5d–4f emission from Pr$^{3+}$ in the co-doped sample and confirms the efficient energy transfer from Pr$^{3+}$ to Ce$^{3+}$. Increasing the Pr-concentration also gives rise to a faster decay of the 5d–4f emission from Pr$^{3+}$. This can be explained by concentration quenching due to energy transfer between neighboring Pr$^{3+}$ ions. A variety of cross-relaxation processes can occur between Pr-neighbors [34,35]. The cross-relaxation is responsible for the overall decrease in emission intensity observed in Fig. 8. At higher Pr$^{3+}$ concentration energy transfer between Pr$^{3+}$ neighbors competes with energy transfer to Ce$^{3+}$ and causes the overall light yield to decrease.

To study the energy back transfer step from Ce$^{3+}$ to Pr$^{3+}$, also luminescence decay curves were recorded for the Ce$^{3+}$ 5d–4f emission under excitation into the 5d state of Ce$^{3+}$ for different Pr$^{3+}$ concentration (Fig. 12). In singly Ce-doped LuAG single exponential decay with a life time of 58 ns is observed, consistent with the values reported in the literature [7]. Upon adding Pr$^{3+}$ the decay becomes faster and non exponential due to energy transfer from Ce$^{3+}$ in the excited 5d state to neighboring Pr$^{3+}$ ions. The transfer efficiency for the back transfer process Ce → Pr is not as high as for the Pr → Ce energy transfer. The drop in decay time for 1% co-doping with Pr$^{3+}$ is from 58 ns to 29 ns. The lower efficiency is due to the forbidden character of the transition on the Pr-acceptor in case of Ce → Pr energy transfer. The oscillator strength of the $^3H_{4}–^1D_2$ transition on Pr$^{3+}$ is low and the energy transfer rate is proportional to the dipole strength of the transition on the acceptor. At higher Pr$^{3+}$ concentrations however the back transfer efficiency is high and the Ce$^{3+}$ 5d–4f emission is almost completely quenched for Pr$^{3+}$ concentrations of 5% and 10%.

4. Conclusions

The possibility to sensitize Ce$^{3+}$ emission by co-doping Pr$^{3+}$ in LuAG:Ce has been investigated, aimed at improving the light yield for scintillating applications. To gain insight in the energy transfer from the LuAG host to Pr$^{3+}$ and from Pr$^{3+}$ to Ce$^{3+}$, low temperature and high spectral resolution studies on LuAG doped with 0.1% Pr$^{3+}$ or Ce$^{3+}$ were performed. For the Pr 4f–5d transitions a ZPL is observed at 294.3 nm with phonon replicas at 130 cm$^{-1}$, both in excitation and emission. Interestingly, a stronger electron–phonon-coupling is observed in the excitation spectra. Under host lattice excitation STE emission is observed at low temperatures. Above 100 K the STE emission decreases and feeds Pr$^{3+}$ 5d–4f emission, indicating thermally activated diffusion of the STE towards Pr$^{3+}$ ions. Thermally activated dissociation of the STE can also explain the observations. From the onset of the STE emission band around 200 nm and the onset of the band gap absorption (<180 nm) an activation energy above 5000 cm$^{-1}$ is calculated which makes thermally activated STE dissociation not very probable in the 100–300 K range. The host lattice absorption edge shifts to longer wavelengths upon raising the temperature. The temperature dependent shift can be fitted to the Varshni model that is widely used to describe the temperature dependence of the band edge for semiconductors. In co-doped LuAG:Ce,Pr highly efficient energy transfer from the Pr$^{3+}$ to Ce$^{3+}$ is observed. For LuAG co-doped with 1% Pr$^{3+}$ and 1% Ce$^{3+}$ the energy transfer from the 5d states of Pr$^{3+}$ to the 5d state of Ce$^{3+}$ is already almost complete. The high Pr → Ce energy transfer efficiency is consistent with the favorable spectral overlap between the Pr$^{3+}$ 5d–4f emission and the Ce$^{3+}$ 4f–5d absorption bands and is also confirmed by luminescence decay measurements. In spite of the efficient Pr → Ce energy transfer, no increase in the light yield is observed for the scintillator material under soft X-ray excitation. Back transfer from the Ce$^{3+}$ 5d state to the intraconfigurational 4f$^2$ $^1D_2$ state of Pr$^{3+}$ reduces the light output which shows that co-doping with Pr$^{3+}$ is not a promising route to enhance the light yield of LuAG:Ce.

References
