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UNDERSTANDING AND CONTROLLING THE RESPONSE TIME OF THE LUMINESCENCE SIGNAL FORM SCINTILLATOR CRYSTALS IS DISCUSSED. FOR THE NEXT GENERATION OF PET-SCANNERS A FASTER RESPONSE IS CRUCIAL: A BUILD-UP TIME BELOW 1 NS AND A DECAY TIME BELOW 20 NS ARE NEEDED. HERE THE FOCUS IS ON THE BUILD-UP TIME (OR RISE TIME). SYSTEMATIC STUDIES ON THIS ASPECT ARE SCARCE. HERE WE REPORT ON A NUMBER OF MODEL SYSTEMS AND SHOW THAT THE BUILD-UP TIME DEPENDS ON THE CONCENTRATION OF THE LUMINESCENT DOPANT ION (OR ACTIVATOR), TEMPERATURE, HOST LATTICE, EXCITATION WAVELENGHT AND SYNTHESIS CONDITIONS. A FAST RISE TIME, CLOSE TO THE DETECTION LIMIT OF ~100 PS, IS ACHIEVED FOR RELATIVELY HIGH DOPANT CONCENTRATIONS (>1%) IN YPO_4:ND AND YAG:PR. FOR THE PRESENT APPLICATION, THIS FAST RESPONSE IS WELL WITHIN THE REQUIRED LIMIT (FASTER THAN 1 NS). SLOWER KINETICS ARE OBSERVED FOR GD_2SIO_5:CE AND IS DUE TO A SLOW INTERMEDIATE STEP INVOLVING ENERGY MIGRATION OVER THE GD-SUBLATTICE. BASED ON THIS OBSERVATION, GD-HOST LATTICE ARE EXCLUDED AS CANDIDATES FOR FAST RESPONSE SCINTILLATOR CRYSTALS.THE VARIATION OF THE BUILD-UP TIME WITH DIFFERENT PARAMETERS (TEMPERATURE, EXCITATION WAVELENGTH, ACTIVATOR CONCENTRATION) IS DESCRIBED QUALITATIVELY USING A MODEL IN WHICH THE ROLE OF DEFECT (TRAPPING) STATES PLAYS A CRUCIAL ROLE. TRAPPING OF FREE CHARGE CARRIERS (ELECTRONS AND/OR HOLES) IN SHALLOW TRAPS CAUSES A SLOW FEEDING OF LUMINESCENCE FROM THE ACTIVATORS BY SLOW, THERMALLY ACTIVATED RELEASE OF THE CHARGE CARRIERS FROM THE TRAPS. THIS PROCESS INFLUENCES BOTH THE RISE TIME AND THE DECAY TIME (AFTERGLOW) OF THE EMISSION. BASED ON THE PRESENT INVESTIGATIONS IT IS POSSIBLE TO UNDERSTAND AND IMPROVE THE TIME RESPONSE TO MEET THE CRITERIA SET WITHIN THIS PROJECT. THE INFORMATION WILL SERVE AS INPUT FOR WP 2 AND WP 3. THE OPTIMUM CONCENTRATION OF ACTIVATOR IONS IS 1-3%. IN THE SYNTHESIS AND SINTERING PROCEDURE DEFECT FORMATION SHOULD BE AVOIDED. IF, AFTER SINTERING OF A TRANSPARENT MATERIAL IN WP3, THE RESPONSE TIME (BUILD-UP AND AFTERGLOW) IS SLOWER THAN FOR THE STARTING MATERIAL THIS WILL PROBABLY BE RELATED TO A HIGHER DEFECT (TRAP) CONCENTRATION THAT CAN BE REDUCED BY (BETTER) ANNEALING PROCEDURES. 2. INTRODUCTION **4**

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1. Executive summary

Understanding and controlling the response time of the luminescence signal form scintillator crystals is discussed. For the next generation of PET-scanners a faster response is crucial: a build-up time below 1 ns and a decay time below 20 ns are needed. Here the focus is on the build-up time (or rise time). Systematic studies on this aspect are scarce. Here we report on a number of model systems and show that the build-up time depends on the concentration of the luminescent dopant ion (or activator), temperature, host lattice, excitation wavelenght and synthesis conditions. A fast rise time, close to the detection limit of ~100 ps, is achieved for relatively high dopant concentrations (>1%) in YPO_4:Nd and YAG:Pr. For the present application, this fast response is well within the required limit (faster than 1 ns). Slower kinetics are observed for Gd_2SiO_5:Ce and is due to a slow intermediate step involving energy migration over the Gd-sublattice. Based on this observation, Gd-host lattice are excluded as candidates for fast response scintillator crystals.The variation of the build-up time with different parameters (temperature, excitation wavelength, activator concentration) is described qualitatively using a model in which the role of defect (trapping) states plays a crucial role. Trapping of free charge carriers (electrons and/or holes) in shallow traps causes a slow feeding of luminescence from the activators by slow, thermally activated release of the charge carriers from the traps. This process influences both the rise time and the decay time (afterglow) of the emission. Based on the present investigations it is possible to understand and improve the time response to meet the criteria set within this project. The information will serve as input for WP 2 and WP 3. The optimum concentration of activator ions is 1-3%. In the synthesis and sintering procedure defect formation should be avoided. If, after sintering of a transparent material in WP3, the response time (build-up and afterglow) is slower than for the starting material this will probably be related to a higher defect (trap) concentration that can be reduced by (better) annealing procedures.

2. Introduction

An important topic within the STRING project is the identification of fast scintillator materials for application in PET scanners. Suitable materials have to meet a number of criteria:

- high density (>5 g/cm^3)
- high efficiency (>25 000 photons/MeV)
- short emission decay time (<20 ns)
- fast rise time (<1 ns)
- no afterglow
- obtainable as transparent ceramic by sintering (cubic crystal structure)
- stable under high energy radiation

In this report we focus on understanding and controlling the response time of the emission and in particular on the rise time. A short rise time is in particular important for time-of-flight PET where the difference in time of detecting of the first photon emitted by two scintillator crystals positioned at 180^o angles gives important spatial information on the location of the positron emitter. In the literature information on the rise time of the scintillator response is scarce and little is known on the factors influencing the rise time of the luminescence intensity upon high energy excitation. The main reason for this is the fact that the time response is very fast (ns or sub-ns) and detection of rise times in this time regime requires both very short (ps) high energy excitation pulses and fast (sub-ns) detection of the UV emission. The SUPERLUMI beamline of the DESY synchrotron in Hamburg does have excellent time resolution for this type of measurements and rise times down to ~100 ps can be measured. In this report we present results on systematic studies of the rise time in a selection of model systems, viz. (Y,Gd)Si_2O_5:Ce, YPO_4:Nd and YAG:Pr. The results and interpretation have been obtained in a close cooperation between Philips Aachen (Cees Ronda), University of Tartu (Vladimir Babin) and the Utrecht University (Konstantin Ivanovskikh, Aleksander Zych, Janne Niittykoski and Andries Meijerink). The rise time of the scintillator emission is measured as a function of a large number variables viz. excitation wavelength, activator concentration, temperature and synthesis conditions. The results show that the desired sub-ns build-up time can be easily obtained by choosing a sufficiently large activator concentration (typically above 1%) and optimizing the synthesis conditions to minimize the concentration of defects which slow down the response (both rise and decay time) by trapping of the created free charge carriers. Based on the measurements a general model is presented to explain the time response of scintillator crystals.

3. Model Systems

3.1 YAG:Pr

To study the build-up time of the emission intensity upon high energy excitation in YAG:Pr several samples were studied with Pr-concentrations varying between 0.1 and 3%. The emission spectra of YAG:Pr (Fig. 1) show two broad bands at *ca.* 320 and 390 nm. These bands are due to the $4f^15d^1 \rightarrow 4f^2$ transitions of the Pr^{3+} ion. In addition, sharp ff-emission lines were observed at longer wavelengths. These lines are due to the transitions from the excited $^3P_0$ and $^1D_2$ levels to the $^3H_{4\text{-}6}$ and $^2F_2$ ground levels of Pr^{3+}. The intensity of the fd-bands was slightly increased, but the shape of the spectra remained the same, with the increasing Pr^{3+} concentration reaching maximum with the 1 mol-% concentration. The ff-lines were quenched with higher Pr-concentrations due to cross-relaxation.

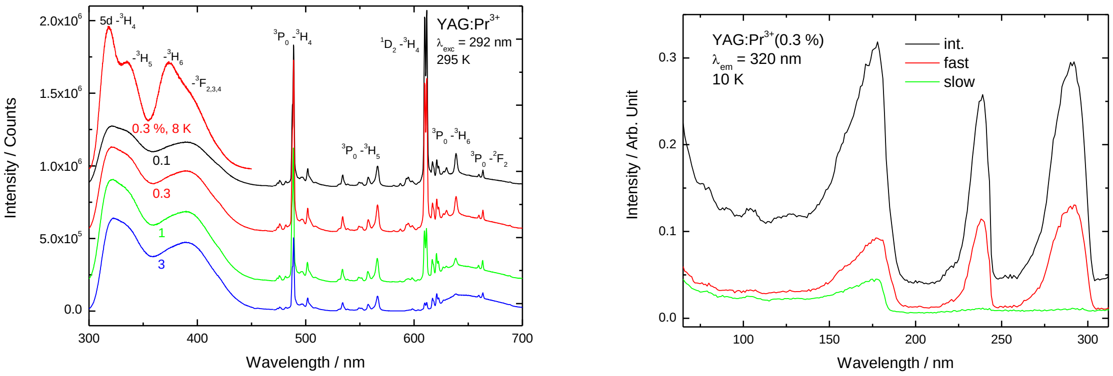

Figure 1 – Emission (left) and excitation (right) spectra of YAG:Pr.

The broad band at 293 nm was observed in the UV excitation spectra of $YAG{:}Pr^{3+}$. This band is due to the lowest $4f^2\ (^3H_4) \rightarrow 4f^15d^1$ transition of the Pr^{3+} ion. Two broad bands peaking at *ca.* 238 and 290 nm are observed in the synchrotron radiation excitation spectra. These bands are due to the $4f^2\ (^3H_4) \rightarrow 4f^15d^1$ transitions of the Pr^{3+} ion. The absorption band peaking at *ca.* 175 nm is due to the YAG host. This band continued down to *ca.* 150 nm. The intensity started to increase again at *ca.* 100 nm. The excitation spectrum in the slow window was different showing only the host band absorption due to the slower decay with the host excitation. The presence of the host lattice excitation band in the slow window shows that there is some delayed excitation of the fd luminescence after host lattice excitation.

Exponential decay was observed for the fd-emission of Pr^{3+} in YAG (Fig. 2) under direct fd-(240 nm) and host band (160 nm) excitations. With the 100 nm excitation, the decay curves were not fully exponential. The life- and risetimes were obtained by fitting with the first order exponential decays for the build-up and decay processes. In some cases, only a part of the decay curve was used for the fits. The radiative lifetime of Pr^{3+} is about 21 ns. With the direct fd-excitation, the risetime was not observed. A clear influence was observed for the Pr-concentration and the excitation wavelength on the emission kinetics. In general, both the life- and risetimes were longer with the higher excitation energy and on the other hand, faster with the higher Pr-concentration. When the Pr^{3+}-ion is excited via the host, the expected effect is delaying of the rise- and lifetimes. The effect of the excitation energy might be due to the increasing number of pathways for the energy transfer from the host to Pr^{3+}. The decrease of the risetime as a function of the Pr-concentration is due to the increase of the efficiency for the energy transfer from the host. On the other hand, the decrease of the lifetime is due to the concentration quenching. It is interesting to notice that the effect of the concentration is more pronounced with the 100 and 160 nm excitation *i.e.* the lifetime is decreased more rapidly compared the 240 nm excitation. This can be due to the increasing amount of the non-radiative relaxation paths for the host excitation, since with the 100 and 160 nm excitation in addition to Pr^{3+}-Pr^{3+}-interactions there are also host-Pr^{3+}-interactions.

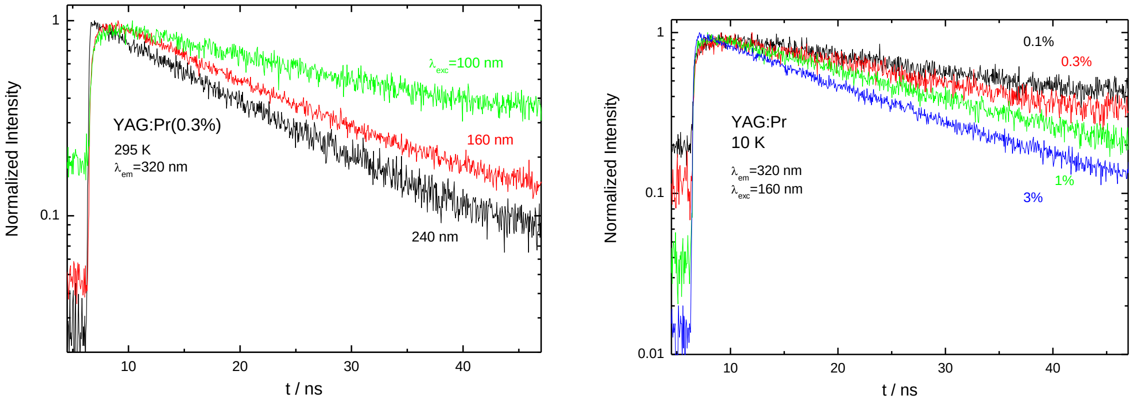

Figure 2 - Typical decay curves of YAG:Pr^{3+} as function of excitation wavelength (left) and Pr-concentration (right).

The effect of temperature on the life- and risetimes was not as clear as that of the Pr-concentration. With the direct fd-excitation, the lifetime was almost constant from 10 to 100 K, but decreased thereafter rapidly. The decrease of the lifetime is due to the increasing probability for the non-radiative relaxation to 4f-levels and/or a photoionization. With the 100 and 160 nm excitation, the lifetime is in generally decreased and the risetime increased with increasing temperature, but not with a systematic manner (see Fig. 3). Longer rise- and lifetimes are due to processes that delay the energy transfer from the host to traps and Pr^{3+}. In YAG:Pr^{3+}, at least five traps have been found at the temperature range of 50-250 K by thermoluminescence that explains the complicated temperature dependence. The defects behind the traps should be studied more detailed in order to understand better the luminescence build-up and relaxation processes.

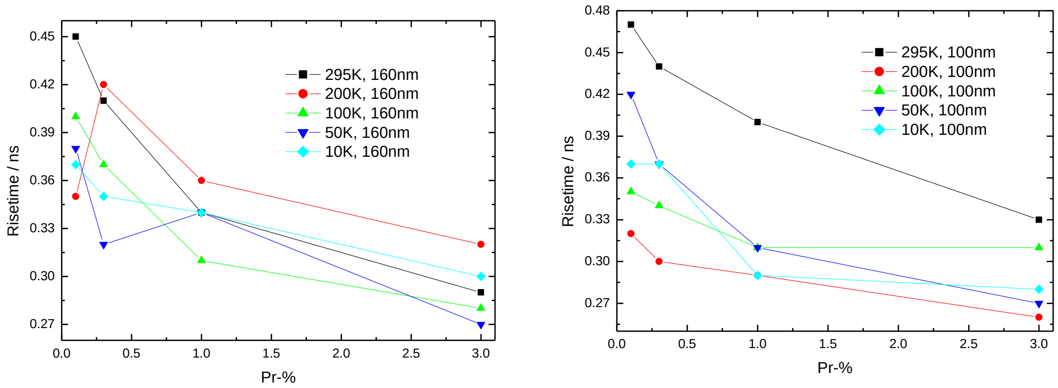

Figure 3 – Rise time of the d-f emission intensity as a function of temperature for two (supra bandgap) excitation wavelengths (160 and 100 nm).

3.2 YPO_4:Nd

A systematic study has also been performed on the performance of YPO_4:Nd, again with the goal to understand the influence of dopant concentration, host lattice luminescence, temperature and synthesis method (single crystal vs. crystalline powder) and excitation wavelength on the luminescence and the time response of the f-d emission. Temperature dependent measurements were done on 10 different samples, varying in composition (no dopant, and 0.05 – 10 % Nd). In Fig. 4 the excitation and emission spectra of YPO_4:Nd are shown.

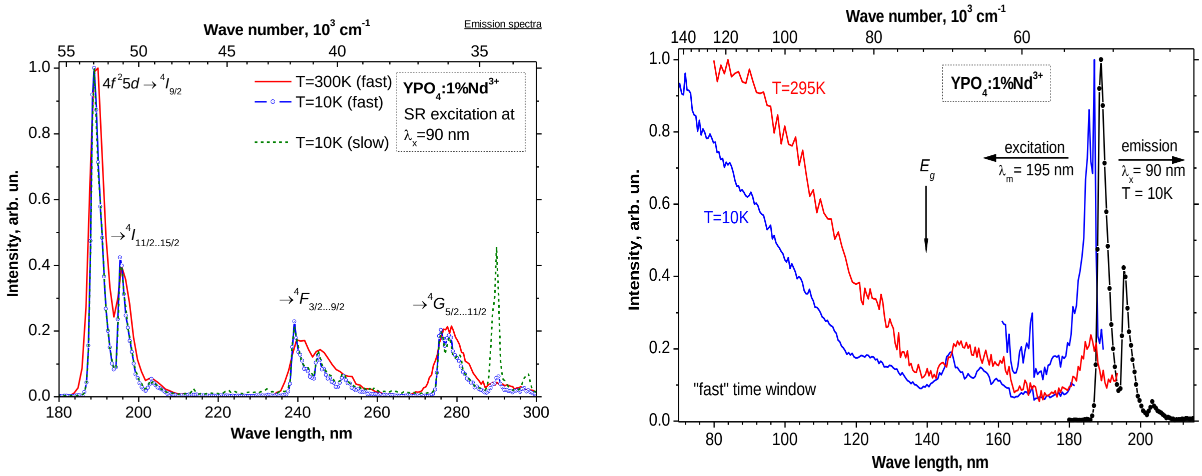

Figure 4 – Emission (left) and excitation (right) spectra of YPO$_4$:Nd1% at 10 K and at 300 K.

In the Fig. 5 examples are shown of the luminescence decay curves. For YPO$_4$ with 1% of Nd^{3+}. The luminescence life time of the Nd-emission is short (8-9 ns). A build-up is observed in the emission intensity at a time scale of 100-300 ps, which is temperature dependent. The variation of the build-up time as a function of temperature is not regular. At 8 K the build-up time is relatively long and clearly observed. Upon raising the temperature, the build-up time becomes faster (at 100 K) but then increases again to be slower at 200 K. Between 200 and 300 K the build-up time becomes faster again. The 300 K build-up is around 300 ps, fast enough for application in the present PET-scanner concept.

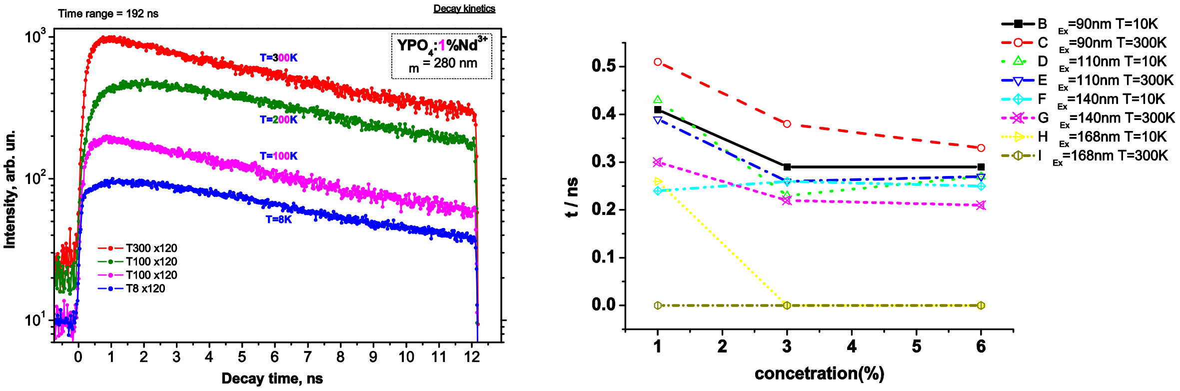

Figure 5 - Temperature dependent luminescence decay curves for the Nd-emission in YPO$_4$ (left) and risetimes determined for the d-f emission from Nd for different excitation wavelengths and concentrations at 10 K and at 300 K.

To study the influence of the Nd-concentration on the rise time of the luminescence, decay curves were recorded for the Nd-emission upon excitation over the bandgap for various concentrations. In general, a longer build-up is observed for lower Nd-concentrations. Especially at the lowest concentrations, 0.1 or 0.3 % of Nd, a build-up is visible.

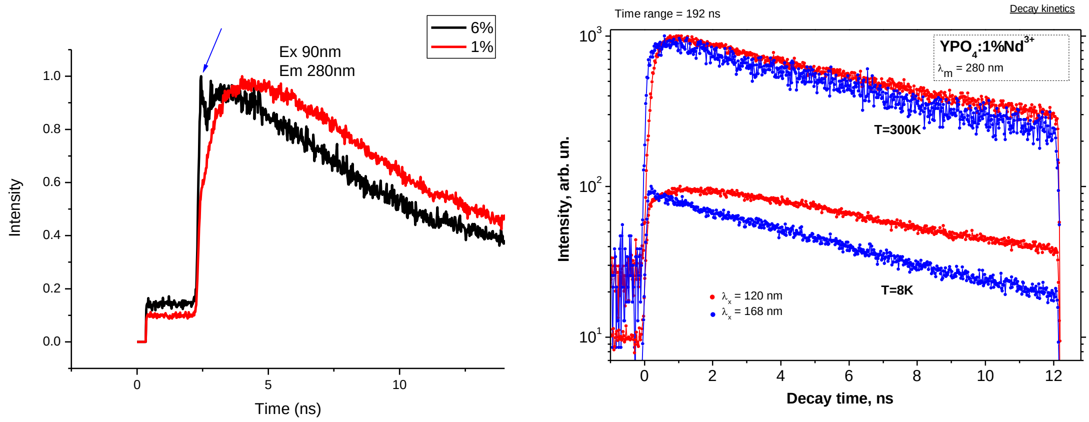

Figure 6 – Concentration dependence (left) and excitation wavelength dependence (right) of the luminescence decay for $YPO_4:Nd^{3+}$.

Finally, higher energy excitation (soft x-rays) were also used to study the time response and energy dependence of the luminescence output upon excitation far over the bandgap. Typical spectra are shown below and show a sub-ns rise time.

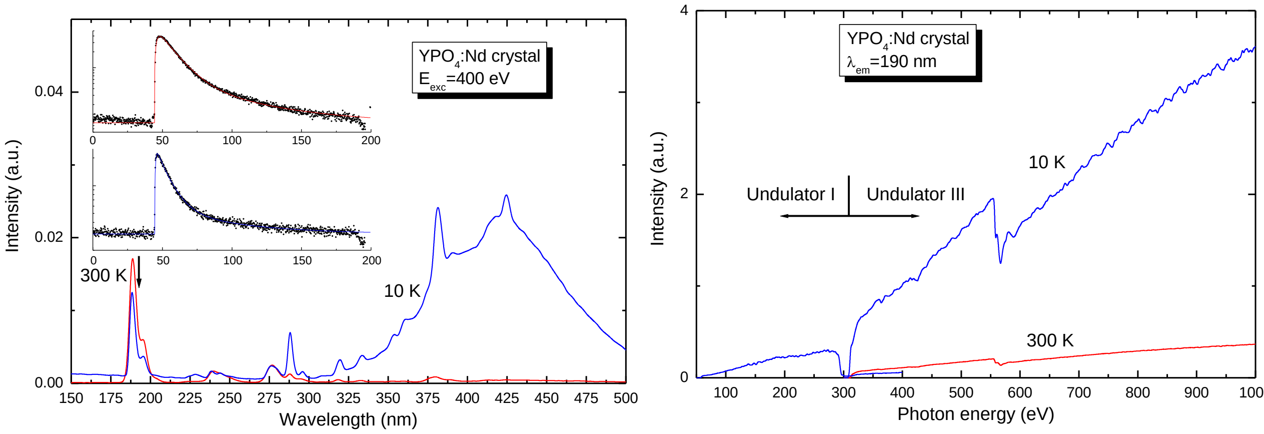

Figure 7 – Emission spectra and luminescence decay curves from YPO_4:Nd upon high energy (400 eV) excitation at 8 K and at 300 K (left. Soft x-ray excitation spectrum of the Nd emission in the range between 100 and 1000 eV at 8 K and 300 K.

The analysis of the results shows that for the YPO_4:Nd system at low dopant concentrations a build-up is observed in the Nd f-d emission. At higher dopant concentration (>1%) and at 300 K there is a fast build-up (<0.5 ns) and the decay time is fast (~8-9 ns) in line with the requirements.

3.3 $(Y,Gd)_2SiO_5$:Ce

A final system that is actively investigated involves Y_2SiO_5:Ce and Gd_2SiO_5:Ce. This material is at present applied in commercial PET-scanners. Again, the dependence on dopant concentration, temperature, excitation wavelength and host lattice has been studied. Some interesting observations are: in the Gd-system a slow feeding of the fd-emission from Ce is observed. This is assigned to slow energy transfer via the Gd-sublattice. The contribution of the slow component is dependent on the excitation wavelength, indicating that the route via the Gd-sublattice is partly bypassed by direct transfer from the host lattice for high energy excitation. The temperature dependence shows that the feeding is faster at higher temperatures due to faster energy migration over the Gd-sublattice. The Y-silicate show a faster response, confirming the model presented above. The slower response and the less efficient energy transfer from the HL to the Ce^{3+} ions, make the YSO and GSO doped with Ce less attractive for the present application where a fast response is crucial.

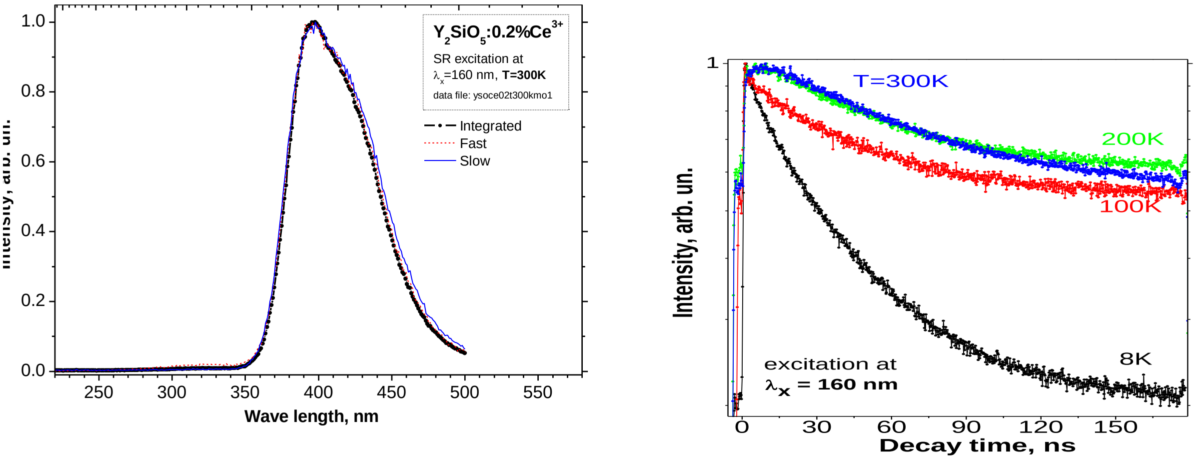

Figure 8 – Emission spectra (left) and luminescence decay curves (right) for $Y_2SiO_5:Ce^{3+}$ 0.2%.

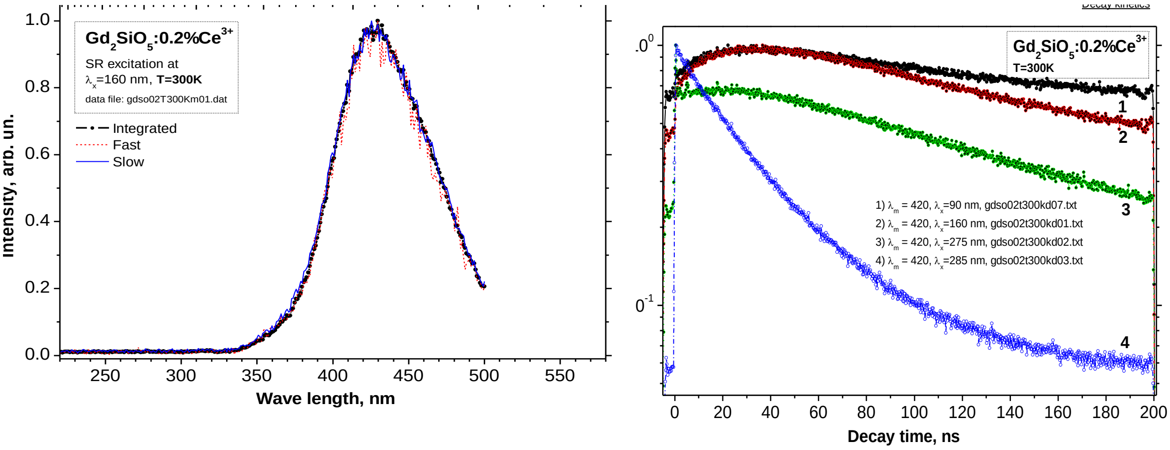

Figure 9 - Emission spectra (left) and luminescence decay curves (right) for $Gd_2SiO_5:Ce^{3+}$ 0.2% at 300 K.

The relatively slow time response (~10 ns both in build-up and afterglow) for the Ce-doped silicates makes these materials less attractive for application in PET-scanners. The slow time response for the Gd-compounds is well understood and is due to feeding of the activator emission through energy migration over the Gd-sublattice. This observations shows that concentrated Gd-systems are not promising for fast scintillators. The origin of the relatively slow response of the Y-silicate compositions is not as clear. It may be related to the relatively high concentration of defects in the silicate. For higher Ce-concentrations (1 and 3%) the response time is faster but still >1 ns at 300K. This makes these materials less promising for application.

3.4 Model

Based on the results obtained in this work, a model is proposed for the luminescence processes in scintillator crystals (Fig. 10), using Pr^{3+} as example for the activator ion. The simplified model consists of the following processes: (1) Host excitation by VUV radiation producing free electron (e) and hole (h) to conduction and valence bands, respectively. (2) e-h recombination (exciton). (3) Energy transfer to Pr^{3+}. (4) Excitation of Pr^{3+} from $^3H_4$ ground level to 5d-levels. (5) Non-radiative relaxation to the lowest 5d-level. (6) fd-emission of Pr^{3+}. (7) Electron trapping from Pr^{3+}

or thermally stimulated electron transfer from trap to Pr^{3+} via conduction band. (8) Electron trapping from Pr^{3+} or electron transfer from trap to Pr^{3+} by tunneling. (9) Electron migration through conduction band to trap or thermally stimulated electron transfer from trap to conduction band. (10) Hole migration through valence band to trap. (11) e-h recombination.

At least five different Pr^{3+} emission schemes can be considered: (I) Simple fd-emission 4→5→6. (II) Trap perturbed fd-emission 4→7(or 8)→5→6. (III) Host excited fd-emission 1→2→3→4→5→6. (IV) Host excited trap perturbed fd-emission via spontaneous e-h recombination 1→9,10→11→3→4→5→6. (V) Host excited trap perturbed fd-emission via thermally stimulated e-h recombination 1→9,10→2→3→4→5→6.

The direct (fd) excitation produces naturally type (I) emission. Type (II) emission is probably a minor process, since the decay curves under 240 nm are single exponential. The 100 nm and 160 nm excitation can produce type (II), (III), (IV) or (V) emission. The emission schemes (II) and (V) contain thermally stimulated processes which make them more complicated. They are strongly affected by temperature and both the build-up and decay processes might be modified. In addition, different traps can be active in different temperatures. The schemes (III) and (IV) do not contain thermally stimulated processes and they mainly affect the build-up process, because the energy transfer processes (1-3 and 11) can be considered to be fast. However, the temperature might affect the probability and rate of these energy transfer processes. The schemes might also compete with each others and occur even simultaneously, *e.g.* (III)-(V) all together or two of them.

As mentioned above, the schemes (II) and (V) are strongly temperature dependent, since they contain traps. The lifetime of a trap depends on the trap depth (E_{trap}) and the present temperature. Three different correlations between the trap depth and the present temperature can be considered: (A) $kT \ll E_{trap}$ (i.e. temperature is too low to untrap electron/hole). In this case, no 7 or 9/10 occur, but 8 might occur since tunneling is not necessarily temperature dependent process. fd-emission is fast. Build-up process might be observed if the schemes (III) or (IV) occur simultaneously. (B) $kT \leq E_{trap}$ (temperature is slightly enough to untrap electrons/holes). In this case, 7 or 9/10 occur. fd-emission is slow. Decay curves might be non-exponential. Build-up process is not probably affected, since processes 7 and 9/10 can be too slow (i.e. continuous feeding). Build-up process might be, however, observed if the schemes (III) or (IV) occur simultaneously. (C) $kT > E_{trap}$ (temperature more than enough to untrap electrons/holes). In this case, 7 or 9/10 occur, decay long but not as long as B, build-up long (longer than A and B) since 7 or 9/10 fast (occurs right away). If there is more than one trap, the situation is even more complicated. That is often the case as can be seen in the thermoluminescence glow curves in the temperature range of 4-350 K. The presence of multiple peaks indicates that there is large variety of traps with different trap depths that are responsible for a delayed luminescence in different temperature and time regimes.

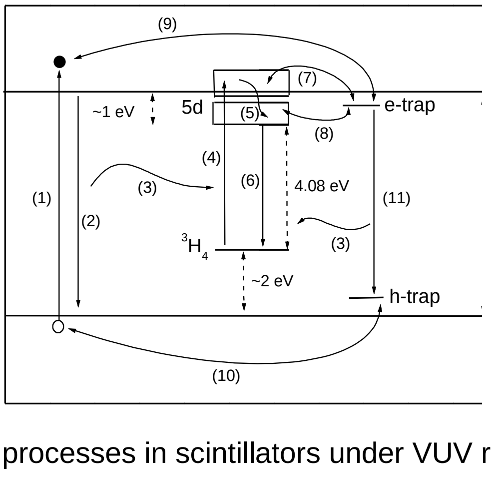

Figure 10 - Model of luminescence processes in scintillators under VUV radiation excitation.