Invited Article

(INVITED) On the mechanism leading to afterglow in Gd$_2$O$_2$S:Pr

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ABSTRACT

The performance of scintillator materials and phosphors for x-ray imaging is adversely affected by afterglow, giving rise to ghost images and thus compromising image quality. Here, the afterglow of the well-known computed tomography (CT) phosphor Gd$_2$O$_2$S:Pr is investigated with time-delayed afterglow spectroscopy. It is shown that these afterglow spectra mainly show Eu$^{3+}$ emission. This points to a mechanism, during excitation across the bandgap, in which holes are captured by Pr$^{4+}$ ions, resulting in Pr$^{4+}$ and electrons are captured by Eu$^{3+}$ ions, creating Eu$^{3+}$. Afterglow is due to thermal excitation of electrons from the valence band to Pr$^{4+}$ ions (detrapping of holes from Pr$^{4+}$), restoring Pr$^{3+}$ ions. Capture of the resulting holes in the valence band by Eu$^{3+}$ ions leads to excited Eu$^{3+}$ ions that generate Eu$^{3+}$ emission thus causing the undesired afterglow. Time delayed Eu$^{3+}$ afterglow spectra are observed already for very low Eu$^{3+}$ concentrations (<10 ppm). These observations provide insight in the dominant afterglow mechanism in Gd$_2$O$_2$S:Pr$^{3+}$ phosphors and allow to optimize the performance and improve the CT image quality by selection of starting materials with the lowest possible Eu$^{3+}$ contamination levels to effectively reduce afterglow without loss of light yield.

1. Introduction

Computed Tomography (CT) is an important medical imaging modality [1]. In a CT examination, the attenuation of X-rays by the body of the patient is measured while the X-ray source and detector combination is rotating around the patient. The imaging procedure should take place in a very short time, as patient movements will reduce the image quality [1,2]. The rotation speed that can be applied is however limited by the decay time of the emitting ion in the CT phosphor and by afterglow. One speaks of afterglow when the time dependent intensity drop is slower than expected based on the decay time of the emitting ion.

Typically, the ceramic or single crystalline scintillators have a thickness in the order of a few mm. The scintillator elements are structured, using reflective layers, to optimize the light impinging on the photodiodes (Fig. 1). The size of the small elements in the scintillator ceramics is adjusted to the size of the photodiodes capturing the visible light emitted by the ceramic scintillator. In CT a number of different scintillating materials (that convert the energy of the impinging X-rays into visible light) are used, some of these are GdWO$_4$, (Y,Gd)$_2$O$_2$:Eu, garnet materials doped with Ce$^{3+}$ (e.g. (Y, Tb, Lu)$_3$Al$_5$(O$_{12}$:Ce) and also Gd$_2$O$_2$:Pr$^{3+}$ [3,4]). GdWO$_4$ is a self-activated material, used as single crystalline material while the other three materials rely on emission from an activator and are used in ceramic form. In Table 1 some of the performance parameters of these CT phosphors are summarized. Both (Y,Gd)$_2$O$_2$:Eu and the garnet materials can be processed to transparency as the host material possesses cubic symmetry. Gd$_2$O$_2$S crystallizes in hexagonal symmetry and consequently only translucent material can be obtained. Advantages of Gd$_2$O$_2$S:Pr are the high stopping power of the host lattice (due to its high density: 7.34 g/cm$^3$) and the relatively high light yield (40000 photons/MeV excitation energy). Disadvantage is the relatively long afterglow. The afterglow in Gd$_2$O$_2$S:Pr$^{3+}$ has been extensively investigated but so far the origin remains elusive. Several studies have shown that the afterglow of Gd$_2$O$_2$S:Pr can be reduced by co-doping with minute amounts of Ce$^{3+}$ or F$^-$ ions, however at the cost of some light yield [3-7].

To improve the image quality that can be realized in CT-scanners, reducing afterglow of the Gd$_2$O$_2$:Pr$^{3+}$ phosphor is essential. Here we investigate the origin of afterglow and in the course of the investigations, it became clear that subtle differences in trace levels of impurities are important in the mechanism leading to afterglow as significant changes in afterglow were found in scintillating ceramics produced from different starting materials. In this paper, we will focus on the spectroscopic characterization of Gd$_2$O$_2$:Pr powders and will demonstrate that especially Eu$^{3+}$ impurities already at ppm levels give...
rise to an increased afterglow that can be mitigated by selection of ultrapure starting materials with low Eu$^{3+}$ levels.

2. Experimental

To investigate the origin of afterglow, high resolution emission spectra of Gd$_2$O$_2$S:Pr$^{3+}$ microcrystalline powders were recorded using an Edinburgh FLS 920 spectrophotofluorometer, allowing for excitation over a wide wavelength range including 250 nm (4.85 eV, above the band gap of Gd$_2$O$_2$S which is 4.6 eV). Time-resolved emission spectra were recorded under pulsed (10 Hz, 10 ns pulse width) excitation over the bandgap with the fourth harmonic of a Spectra Physics Nd:YAG laser (266 nm). Emission spectra overlapping in time with the excitation pulse (direct emission) as well as emission spectra starting ~10 ms after the pulse (afterglow emission) were measured. The emission was collected with an optical fiber coupled to an Acton Research 0.25 m monochromator with a liquid nitrogen cooled Princeton Instruments CCD camera. By using a 150 lines/mm grating a wide spectral range could be detected. Typical integration times of 50 ms were selected to capture the afterglow emission spectrum within the time window of 100 ms in between excitation pulses.

3. Results and discussion

The emission spectra of Pr$^{3+}$ in Gd$_2$O$_2$S are well known [8–10]. In Fig. 2 the emission spectrum of Gd$_2$O$_2$S:Pr$^{3+}$ is shown for a typical material that is not intentionally doped with Eu$^{3+}$ but does contain some Eu$^{3+}$ impurities. Note that Eu$^{3+}$ is a common impurity in Gd$_2$O$_2$S or other Gd-containing starting materials as neighboring lanthanides are the most abundant impurities based on the purification methods of lanthanides relying on differences in ionic radius. As Gd and Eu (element numbers 64 and 63) have similar ionic radii, relatively higher impurity levels of Eu (and also the other neighbor Tb, element 65) can be expected in Gd$_2$O$_3$ than in, for example, Lu$_2$O$_3$. The emission spectrum of Gd$_2$O$_2$S:Pr$^{3+}$ shows the characteristic strongest Pr$^{3+}$ emission lines around 510 nm, weaker lines between 520 and 660 nm and stronger lines around 670 nm. The stronger emission lines correspond to $^{3}P_0$–$^3H_4$ emission (~510 nm) and $^{1}P_0$–$^3F_2$ emission (~670 nm). Weak emission lines that are observed under 250 nm (supra bandgap) excitation but not under ~450 nm direct excitation in the $^3P_1$ levels of Pr$^{3+}$ are marked with blue arrows in Fig. 2. These weak lines are assigned to Eu$^{3+}$ emission originating from the $^5D_2$ level (around 470 nm), $^5D_1$ level (around 530 nm) and $^5D_0$ level (around 585 and 620 nm).

To confirm that these weak emission lines originate from Eu$^{3+}$ impurities, Gd$_2$O$_2$S:Pr$^{3+}$ was synthesized with an additional 10 ppm Eu$^{3+}$ (relative to Gd$^{3+}$), now intentionally added. The emission spectrum for this material under 250 nm excitation is shown in Fig. 3. One can clearly observe that the lines assigned to Eu$^{3+}$ emission from the various $^5D_j$ levels are much more intense, confirming the assignment to Eu$^{3+}$ emission and indicating very efficient energy transfer of the charge carriers/excitions created upon 250 nm excitation towards Eu$^{3+}$ ions. Note that the Pr$^{3+}$ concentration is significantly (100x) higher than the Eu$^{3+}$ concentration with 0.1 mol% or 1000 mol ppm of Pr$^{3+}$ vs. 10 ppm of Eu$^{3+}$. The relative intensity of the Pr$^{3+}$ emission is less than 100x higher indicating that charge carriers or excitons created upon excitation over the bandgap are more efficiently captured by Eu$^{3+}$. The comparison also reveals that in the unintentionally doped material, the Eu$^{3+}$ concentration is very small, significantly below 10 ppm and can be estimated to be around 2 ppm based on the approximately five times

![Fig. 1.](image1.jpg) **Fig. 1.** Gd$_2$O$_2$S:Pr ceramic scintillator layer, with reflective layers. In the CT scanner the small squares are each connected with a light detector, monitoring the emission intensity from x-rays converted into light by the Gd$_2$O$_2$S:Pr$^{3+}$ phosphor.

![Fig. 2.](image2.jpg) **Fig. 2.** Emission spectrum of Gd$_2$O$_2$S:Pr, without intentional doping with Eu$^{3+}$, excited with UV radiation at 250 nm at 300 K. The arrows indicate Eu$^{3+}$ emission lines.

![Fig. 3.](image3.jpg) **Fig. 3.** Emission spectrum of Gd$_2$O$_2$S:Pr intentionally doped with Eu$^{3+}$ (10 ppm), excited with UV radiation of 250 nm at 300 K. The arrows indicate Eu$^{3+}$ emission lines.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>$i_{max}$ (nm)</th>
<th>Light yield (photons/MeV)</th>
<th>Decay time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdWO$_4$</td>
<td>7.90</td>
<td>480</td>
<td>28000</td>
<td>10, 5000</td>
</tr>
<tr>
<td>(Y,Gd)O$_2$:Eu</td>
<td>5.91</td>
<td>611</td>
<td>19000</td>
<td>$\sim 10^8$</td>
</tr>
<tr>
<td>Gd$_2$O$_2$:Pr</td>
<td>7.34</td>
<td>510</td>
<td>40000</td>
<td>3000</td>
</tr>
<tr>
<td>(Y,Tb)</td>
<td>6.0</td>
<td>580</td>
<td>30000</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 1 Overview of performance parameters of a selection of commercially relevant scintillator materials for application in CT.
lower relative intensity of the Eu$^{3+}$ emission. Note the occurrence of Eu$^{3+}$ emission lines not only from the $^5$D$_0$ but also from the $^5$D$_1$ and $^5$D$_2$ levels. Eu$^{3+}$ emission originating from higher excited $^5$D$_2$ levels is observed only when Eu$^{3+}$ concentrations are very low and in hosts with low phonon frequencies as cross-relaxation (for higher Eu-concentrations) and multi-phonon relaxation (for higher phonon energies) are known to quench emission from the higher energy $^5$D$_2$ and $^5$D$_1$ levels.

To investigate the origin of afterglow, Gd$_2$O$_2$S:Pr powder that is used in scintillating ceramics was excited with UV radiation of 266 nm that resulted from a pulsed and frequency quadrupled Nd:YAG laser. The photon energy (4.7 eV) is larger than the band gap of Gd$_2$O$_2$S (4.6 eV), so excitation takes place across the band gap, in this way mimicking X-ray excitation in the creation of free charge carriers. The time integrated emission spectrum was recorded for emission overlapping with the excitation pulse and also starting ~10 ms after the laser pulse and are shown in Figs. 4 and 5, respectively.

The time integrated spectrum with accumulation in a time window including the excitation pulse shows well-known Pr$^{3+}$ emission lines. The time integrated spectrum with the energy levels is given in Fig. 6. To validate the model proposed for the afterglow, the energies in this diagram are known to quench emission from the higher energy levels. Eu$^{3+}$ emission lines not only from the $^5$D$_0$ but also from the $^5$D$_1$ and $^5$D$_2$ levels. Eu$^{3+}$ emission originating from higher excited $^5$D$_2$ levels is observed only when Eu$^{3+}$ concentrations are very low and in hosts with low phonon frequencies as cross-relaxation (for higher Eu-concentrations) and multi-phonon relaxation (for higher phonon energies) are known to quench emission from the higher energy $^5$D$_2$ and $^5$D$_1$ levels.

The corresponding energy level diagram is given in Fig. 6. To validate the model proposed for the afterglow, the energies in this diagram have been taken from Refs. [11,12]. The thermal detrapping energy for a hole trapped by Pr$^{4+}$ is ~0.4 eV which is consistent with slow thermal release of holes from Pr$^{4+}$ to the valence band at room temperature.

Recombination of the valence band hole with Eu$^{2+}$ produces Eu$^{3+}$ in the excited $^5$D$_1$ states and the characteristic Eu$^{3+}$ afterglow emission. Note also that the thermal trap depth of the electron trapped on Eu$^{3+}$ in this band diagram is larger and thus Eu$^{2+}$ is relatively stable, making it the recombination center which is consistent with the observation of Eu$^{3+}$ emission afterglow. It is also interesting to note that a similar charge transfer mechanism is operative in the ion couple Ce$^{3+}$ - Eu$^{3+}$, in which it leads to strong luminescence quenching as has been reported by Blasse [13].

The location of the energy levels in Fig. 6 can also explain the role of Ce$^{3+}$ in reducing afterglow. As the ionization energy level of Ce$^{3+}$ is located near the middle of the energy gap. In this manner Ce$^{3+}$ competes with hole trapping by Pr$^{3+}$ but does not release holes at room temperature. Recombination of a conduction band electron with Ce$^{3+}$ results in Ce$^{3+}$ in the excited 5d state, which is known to be non-luminescent in Gd$_2$O$_2$S. This mechanism explains the reduced afterglow and also the reduced light yield since Ce$^{3+}$ does not emit in Gd$_2$O$_2$S resulting in some light loss [12]. For this reason, the Ce$^{3+}$ concentration should be as low as possible, and the optimum concentration in turn, is determined by the Eu$^{3+}$ concentration in Gd$_2$O$_2$S (see also [14]) and the content of cerium is to be chosen such that it is in excess of the content of europium with a ratio of Eu to Ce of 1:10 to 1:150.

4. Conclusions

The afterglow mechanism operative in Gd$_2$O$_2$S:Pr scintillators is investigated. It is shown that Eu$^{3+}$ ions, present in trace amounts, play a
major role. Upon excitation across the bandgap (by x-rays or UV radiation) free charge carrier trapping causes Pr$^{3+}$ to be oxidized to Pr$^{4+}$ and Eu$^{3+}$ to be reduced to Eu$^{2+}$. Thermal excitation at room temperature releases the hole trapped by Pr$^{4+}$ and the resulting valence band hole is captured by Eu$^{2+}$, rendering excited Eu$^{3+}$ and leading to Eu$^{3+}$ afterglow. The present findings are consistent with earlier observations that afterglow can be reduced by addition of small amounts of Ce$^{3+}$ (albeit at the expense of light yield). More importantly, it shows how reduction of afterglow without loss of light yield can be achieved by using ultrapure (low Eu$^{3+}$ contamination levels) starting materials in the scintillator production process. This can help in improving the quality of images in computed tomography with Gd$_2$O$_2$:Pr$^{3+}$ scintillators.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References