Propositions belonging to the thesis
Luminescence and scintillation of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
Hans van 't Spijker

1. Without direct identification of the charge and energy carriers that are involved in energy transfer to the luminescence centre in a scintillator material, many explanations of the scintillation process are restricted to a sophisticated level of reading tealeaves.

2. For a better understanding of the energy transfer in a scintillator it is commendatory to perform a systematic study. Suitable materials are for example the elpasolites Cs$_2$NaMX$_6$:Ce$^{3+}$ (M=La,Gd,Lu, X=F,Cl,Br).

(summary and conclusions)

3. For a good judgement of the accuracy and reliability of a measurement result, a detailed description of the employed measurement set-up is necessary. Such a description is not common practice in publications on scintillator research.

(chapter 8 of this thesis)

4. From the carbon isotope-ratio analysis performed on tooth enamel of the Australopithecus africanus it can not univocally be deduced that this hominid was a carnivore$^{[1]}$. The remark of an enthusiastic colleague researcher: “This [direct analysis] is what we want to see”$^{[2]}$ can therefore also be explained in another way than was meant.


5. The IRI (Interfaculty Reactor Institute) contains a nice example of the status of scientific research: The director is being housed in a 10 years-old shed.

6. The volume of certain types of energy production is partly a consequence of mankind’s laziness, comparable with e.g. unnecessary use of cars.

7. We, inhabitants of the Netherlands, are the happiest people in the world: we have a decent and politically correct opinion, we are -of course- tolerant and export our famous “poldermodel”.

8. Nowadays opinions are more and more quickly put in the sale.

9. Now the euro is introduced, it is also advisable to adopt a new language, the babyleuropean.

10. The disability to discriminate between twin brothers (and sisters) expresses lack of interest.
Stellingen behorende bij het proefschrift
Luminescentie en scintillatie van Ce$^{3+}$ gedoteerde anorganische materialen voor gammastralingsdetectie
Hans van 't Spijker

1. Zonder directe identificatie van de ladings- en energiedragers, die verantwoordelijk zijn voor energieoverdracht naar het luminescentiecentrum in een scintillator, hebben veel verklaringen van het scintillatieproces het niveau van veredeld koffiedik kijken.

2. Voor een beter begrip van de energieoverdracht in een scintillator is het raadzaam om een systematische studie uit te voeren. Hiervoor geschikte materialen zijn bijvoorbeeld de elpasolieten Cs$_2$NaMX$_6$:Ce$^{3+}$ (M=La,Gd,Lu, X=F,Cl,Br).

samenvatting en conclusies

3. Voor een goede beoordeling van de betrouwbaarheid en nauwkeurigheid van een bepaald meetresultaat is een gedetailleerde omschrijving van de gebruikte meetopstelling noodzakelijk. Zo'n omschrijving komt in het algemeen niet voor in publicaties over resultaten van scintillatoronderzoek.

hoofdstuk 8 van dit proefschrift

4. Uit de analyse van de verhouding van koolstofisotopen in tandglazuur van de Australopithecus africanus kan niet eenduidig worden vastgesteld dat deze hominide een vleeseter was [1]. De uitspraak van een enthousiaste collega-onderzoeker: "Dit [directe analyseresultaat] is wat we willen zien" [2] kan dan ook anders worden uitgelegd dan werd bedoeld.


5. Het IRI (interfacultair reactor instituut) bevat een mooie illustratie van de huidige status van wetenschappelijk onderzoek: de directeur huist in een tijdelijke barak, die inmiddels al 10 jaar oud is.

6. De omvang van bepaalde vormen van energieproductie is ten dele een gevolg van gemakzucht van de mens, te vergelijken met bijvoorbeeld onnodig autogebouw.

7. Wij, Nederlanders, zijn de gelukskigste mensen op deze aardbol: wij zijn politiek correct, wij hebben een fatsoenlijke mening, we zijn -vanzelfsprekend- tolerant, en exporteren ons fameuze poldermodel.

8. Opvattingen worden tegenwoordig steeds sneller in de uitverkoop gedaan.

9. Nu de euro is ingevoerd, is het ook raadzaam om een nieuwe taal, het babyleuropees, te introduceren.

10. Het niet kunnen onderscheiden van tweelingbroers (en -zussen) geeft blijk van desinteresse.
Luminescence and scintillation of
Ce\textsuperscript{3+} doped inorganic materials
for gamma-ray detection

Luminescentie en scintillatie van
Ce\textsuperscript{3+} gedoteerde anorganische materialen
voor gammastralingsdetectie
The research described in this thesis was performed at the Radiation Technology Group of the Interfaculty Reactor Institute, Delft University of Technology, Mekelweg 15, 2629 JB Delft.

This research was financially supported by the Dutch Technology Foundation (STW)
Luminescence and scintillation of 
$\text{Ce}^{3+}$ doped inorganic materials 
for gamma-ray detection

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aan de Technische Universiteit Delft 
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in het openbaar te verdedigen ten overstaan van een commissie, 
door het College voor Promoties aangewezen,

op maandag 15 maart 1999 te 10.30 uur

door
Johannes Christiaan VAN 'T SPIJKER

elektrotechnisch ingenieur
geboren te Zwolle
Dit proefschrift is goedgekeurd door de promotor:
Prof. dr. ir. C.W.E. van Eijk

Samenstelling Promotiecommissie

Rector Magnificus, voorzitter
Prof. dr. ir. C.W.E. van Eijk, Technische Universiteit Delft, promoter
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Als ik Uw hemel aanzie, het werk Uwer vingeren, de maan en de sterren, die Gij bereid hebt; Wat is de mens, dat Gij zijner gedenkt, en de zoon des mensen, dat Gij hem bezoekt?
(Ps 8:4,5)
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1 Introduction

In 1895 Röntgen discovered X-ray radiation. Very soon after this discovery, it was applied in medical diagnostics. Since then other types of ionising radiation have been discovered and utilised. Nowadays, ionising radiation is used in many fields, such as airport security, medical diagnostics and oil well logging.

Upon interaction of radiation with matter ionisations are produced in the material, as is shown schematically in the upper part of figure 1. For the prompt detection of the generated electrons and holes mainly two methods are used. These are illustrated in figure 1. If an electric field is applied as is shown in figure 1a, the electronic charges are separated and

\[ \text{FIGURE 1: Schematic of the prompt detection principle of ionising radiation. After absorption of the radiation, ionisations are produced. These charge carriers can be detected either, by (a) the collection of of the created charge carriers or by (b) the detection of the scintillation.} \]

Luminescence and scintillation properties of Ce\(^{3+}\) doped inorganic materials for gamma-ray detection © 1998 J.C. van 't Spijker, all rights reserved.
collected on the electrodes. The transported charge is a measure for the energy of the absorbed radiation. This method is mainly applied in gas and semiconductor based detectors. They are well suited to detect X-rays and low energetic γ-rays. The other detector principle is shown in figure 1 b. The electrons and holes, created after absorption of radiation, transfer their energy to a luminescence centre. The light emitted by the luminescence centre is detected by a photodiode, a photomultiplier tube or another light detector. The charge of the corresponding electric signal of the light detector is a measure for the absorbed energy. The light flash produced after absorption of ionising radiation is called scintillation and the detector material is called a scintillator. These words are derived from the word scintilla, which is Latin for spark. Scintillators are commonly used to detect high-energetic γ-quanta. The energy resolution of scintillators is worse than that of semiconductor detectors.

Scintillators were already applied soon after the discovery of ionising radiation. In fact, Röntgen used a scintillator for the discovery of X-ray radiation: the X-rays created an observable fluorescence in barium platinocyanide that was coated on a glass plate. Only a few months after the discovery of X-rays, Edison found the well-known calcium tungstate after an extensive study of several thousands of materials. Since then, numerous other scintillator materials have been discovered. Yet, there is still a need for scintillators with improved characteristics.

![Image of X-ray computed tomography](image)

**Figure 2:** Principle of X-ray computed tomography.

The investigations described in this thesis are focused on the search for new scintillator materials for γ-ray detection. From the technical point of view, new scintillator materials are of great interest, since the performance of many detector systems needs improvement. An example of a complex radiation detector system is presented in figure 2, showing the principle of computed tomography (CT). A patient is irradiated by X-rays from several directions. X-ray attenuation spectra are registered. From the recorded spectra a two-dimensional image is obtained. Some scintillators that are applied nowadays in these systems have serious drawbacks concerning afterglow, decay time and the matching between emission wavelength and light detector sensitivity. If the scintillator characteristics can be improved, the irradiation dose can be lowered and scanning times can be shortened, which is beneficial for the patient.

From the scientific point of view, scintillation materials are quite interesting as well. The scintillation process involves several complex phenomena: the absorption of ionising radiation, the multiplication and thermalisation of high-energetic electrons and holes, the energy transfer to the luminescence centre and the luminescence. Knowledge on these topics
gives mankind a somewhat better understanding of the observable world. Furthermore, insight in the scintillation mechanism is useful in the search for new scintillator materials with improved characteristics.

This thesis is organised as follows. Chapter 2 reviews the scintillator requirements for several applications and the properties of some scintillator materials. Attention is paid to the scintillation process and the choice of the studied compounds is motivated. The experimental methods that were used for investigations are discussed in chapter 3. Chapters 4 to 10 are devoted to the studied compounds. In chapter 4 the luminescence and scintillation properties of BaY$_2$F$_8$:Ce$^{3+}$ and pure and Ce$^{3+}$ doped BaLu$_2$F$_8$ are presented. For pure BaLu$_2$F$_8$, a luminescence with a decay time of ~1ns is observed under gamma-ray excitation, which is attributed to core-valence luminescence. Chapter 5 deals with the scintillation and luminescence in Cs$_3$LuCl$_6$:Ce$^{3+}$ and in the elpasolites Cs$_2$NaLaCl$_6$:Ce$^{3+}$, Cs$_2$NaCeCl$_6$ and Cs$_2$NaLuCl$_6$:Ce$^{3+}$. In chapter 6 attention is paid to the scintillation and luminescence in K$_2$LaCl$_3$:Ce$^{3+}$. The energy transfer is modelled. The results obtained for RbGd$_2$Cl$_7$:Ce$^{3+}$ and RbGd$_2$Br$_7$:Ce$^{3+}$ crystals are compiled in chapter 7. Both materials show high light yields. Under optical excitation efficient Gd$^{3+}$→Ce$^{3+}$ energy transfer is observed by energy migration on the Gd-sublattice. Under excitation by ionising radiation other energy transfer mechanisms are dominant. Chapter 8 deals with the recently discovered scintillator LuAlO$_3$:Ce$^{3+}$. The light yield of some crystals is determined. Another Lu-based compound, Lu$_2$S$_3$:Ce$^{3+}$, gains attention in chapter 9. It shows a high light yield and a fast scintillation decay time. Furthermore, it luminesces in the red, matching the sensitivity of silicium based light sensors. In chapter 10 the results on Ce$^{3+}$ doped Cs$_3$Lu$_2$Cl$_9$, LiLuSiO$_4$ and Gd$_2$Sc$_2$Al$_3$O$_{12}$ materials are briefly reported. Finally, in chapter 11 the thesis is summarised.
2 Scintillation materials

2.1 Introduction

Scintillators are applied in many detector systems in various fields. The demands for both old
and new applications on the scintillation properties are exigent. The applied scintillators do
not always meet the requirements of the detection systems. Consequently, there is a need for
new scintillators. In this chapter the pathway of the search for new compounds is discussed.
For that purpose an overview of the demands on scintillators and the shortcomings of the
currently applied scintillators is given. First the applications of scintillators for $\gamma$-ray detection
are reviewed. Information on other types of scintillator detectors, for example for electron or
neutron detection, can be found elsewhere [1]. Next, the currently known scintillators are
shortly discussed. Also attention is paid to the scintillation process, i.e. the way the $\gamma$-ray
energy is absorbed and transferred to luminescence centres. Knowledge on this subject gives
insight in the underlying physical processes determining the scintillation properties. Finally,
the need of new scintillating compounds is formulated and the selection of the compounds
studied in this thesis is motivated.

2.2 Application

The use of scintillators is manifold, varying from use in medical diagnostics to detector
systems for experiments in high energy physics (HEP). Two examples illustrate this variety.
The first example is positron emission tomography (PET). In this application, the
phenomenon that a positron recombines with an electron under collinear emission of two 511
keV photons is used to locate the point of recombination. A chemical compound containing a

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positron emitting radioactive tracer, a so-called radiopharmacon, is introduced into a patient. By detecting the 511 keV photons, an image of the patient's body or specific organs can be made. For this application most important prerequisites are a high 511 keV γ-quantum detection efficiency, a fast scintillation response and a high initial scintillation light intensity. The second example concerns the use of scintillators in HEP. At the large hadron collider (LHC), presently under construction at CERN, colliding proton beams will produce many particles, among which electrons with energies up to 100 GeV. For the detection of these electrons scintillators have to be used, which have a high stopping power and radiation hardness.

More detailed information on the scintillator requirements in the above examples and other applications can be found in table 1, as has been collected originally by Van Eijk [2]. For each application the specific needs on the density, effective atomic number, light yield, decay time and emission wavelength have been collected. The definition of the effective atomic number (Zeff) is discussed later on. Additional requirements are compiled in the 8th column. From table 1 it is clear that the to be detected γ-ray energy varies between several tens of keV to several hundreds of GeV. In most applications it is in the range of ~100 keV and ~1 MeV. Within this small γ-ray energy range, the demands on light yield and decay time may vary considerably. For example, the decay time is not of great importance for use in X-ray computed tomography (CT), whereas in positron lifetime detection a decay time of preferably less than 1 ns is needed. Actually, the demands presented in table 1 reflect the limitations of the currently used scintillators. Some detection principles are even not applied yet, simply because no scintillator can meet the stringent demands needed for practical application at this time. This concerns for example time-of-flight PET scanners. In such a device the 2 collinearly emitted 511 keV photons have to be detected as in conventional PET scanners, but also the time difference between the detection times of these photons. With this time-difference it is possible to localise the region of interest along the line of collinearity. For such systems a time resolution of ~500 ps (localisation 7.5 cm) or less is required, which can nowadays only be obtained by BaF₂ and CsF. Unfortunately, these scintillators have a too low γ-quantum attenuation coefficient to be used in practice.

2.3 Known scintillators

Table 2 presents the main characteristics for a number of scintillators, of which some have found practical application. In this table, the density, effective atomic number, light yield, decay time and emission wavelength are compiled. The main advantages and disadvantages of these materials are mentioned as well.

Each scintillator has its specific applicability. For example, for (sub)-nanosecond timing applications, CsF and BaF₂ are commonly used and for measurements involving high dose rates Gd₂SiO₅:Ce³⁺ is applied because of its radiation resistivity. Of the presented scintillators, the most used scintillators are CsI:Tl⁺ and NaI:Tl⁺ because of their high light yield and reasonably fast decay time and most importantly because of the low costs to grow these
2.4 Scintillation mechanism

Generally, the scintillation mechanism consists of four subsequent processes: i) the absorption of a $\gamma$-quantum, creating an energetic primary electron and hole, ii) the production of secondary electrons and holes and their subsequent thermalisation, iii) energy transfer of the thermalised electrons and holes to luminescence centres and iv) radiation emission by the luminescence centre. We will discuss these stages now in some more detail.

2.4.1 Absorption of $\gamma$-rays

In the interaction of electromagnetic radiation with matter, a quantum is completely or partially absorbed. The most important absorption processes in the range of several keV to several MeV are the photoelectric effect, Compton scattering and pair production. For a detailed treatment on these and other interaction mechanisms the reader is referred to [29]. In photoelectric absorption, a bound electron absorbs the $\gamma$-ray and an electron (mostly a K- or L-shell) is ejected from the atom. For energies larger than the K-absorption edge, the cross-section per atom, having atomic number $Z$, at an energy $E$ is proportional to $Z^n / E^k$ where $n$ varies between 4 and 5 and $k$ between 2 and 4. The cross-section for Compton scattering is proportional to $Z / E$. At energies above 1.02 MeV, the energy may be absorbed by pair production. Per atom the absorption cross-section, is proportional to $-Z^2 \ln(2E/m_e c^2)$, where $m_e c^2$ is the rest-mass energy of an electron (0.511 MeV).

The absorption coefficient of a compound that is constituted of different atoms is determined by the above mentioned cross-sections and the number of atoms per unit volume. For an element $i$ having an atomic mass $A_i$, this number is given by $N_A \rho w_i / A_i$. Here $N_A$ represents Avogadro's number, $\rho$ the density and $w_i$ the fraction by weight of the atoms in the chemical formula. This fraction is given by $m_i A_i / \sum m_i A_i$, where $m_i$ is the stoichiometric proportion in the chemical formula. Thus the absorption coefficient can be written as:
TABLE 1: Applications and requirements of scintillators for γ-ray detection. The abbreviations in the heading denote the energy (E), the density (ρ), the effective atomic number (Z_eff), the emission wavelength (λ) and the main scintillation decay time (τ). In the table abbreviations are used for integral scintillation intensity (I), temperature (T), dose rate (D_i) photomultiplier tube (PMT) and photodiode (PD).

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<td>&gt;70</td>
<td>&gt;8,000</td>
<td>&gt;300</td>
<td>&lt;100</td>
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<td>[3]</td>
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<td>varies</td>
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<td>&gt;4</td>
<td>&gt;50</td>
<td>&gt;15,000</td>
<td>&gt;450</td>
<td>&lt;10⁶</td>
<td>afterglow &lt; 1.10⁻² after 3ms ΔI/ΔT &lt; 0.6 %/C</td>
<td>[5],[6],[7]</td>
</tr>
<tr>
<td>Industrial</td>
<td>0.1</td>
<td>&gt;4</td>
<td>&gt;50</td>
<td>&gt;20,000</td>
<td>&gt;300</td>
<td>&lt;250</td>
<td></td>
<td>[8]</td>
</tr>
<tr>
<td>~10</td>
<td>&gt;7</td>
<td>&gt;60</td>
<td>&gt;8,000</td>
<td>&gt;300</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synchrotron</td>
<td>0.01-0.1</td>
<td>&gt;4</td>
<td>&gt;50</td>
<td>&gt;20,000</td>
<td>&gt;450</td>
<td>varies</td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>Positron life time</td>
<td>≥0.511</td>
<td>&gt;5</td>
<td>&gt;55</td>
<td>&gt;10,000</td>
<td>&gt;180</td>
<td>&lt;1</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>γ-camera</td>
<td>0.1-0.2</td>
<td>&gt;4</td>
<td>&gt;50</td>
<td>&gt;20,000</td>
<td>&gt;300</td>
<td>&lt;250</td>
<td>area &gt; 0.25 m²</td>
<td>[5],[6]</td>
</tr>
<tr>
<td>Positron emission tomography (PET)</td>
<td>0.511</td>
<td>&gt;7</td>
<td>~65</td>
<td>&gt;8,000 (PMT)</td>
<td>&gt;300</td>
<td>&lt;500</td>
<td>photoelectric fraction &gt; 0.30, absorption length &lt; 1.5 cm</td>
<td>[11]</td>
</tr>
<tr>
<td>Astrophysics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>Intern. energy physics</td>
<td>10⁻⁵</td>
<td>&gt;3.5</td>
<td>&gt;50</td>
<td>&gt;20,000</td>
<td>&gt;300</td>
<td>&lt;100</td>
<td>rugged</td>
<td>[12]</td>
</tr>
<tr>
<td>High energy physics</td>
<td>~10⁻³</td>
<td>&gt;7</td>
<td>&gt;70</td>
<td>&gt;200</td>
<td>&gt;450</td>
<td>&lt;30</td>
<td>rugged</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D_i &gt; 5.10⁶</td>
<td></td>
</tr>
<tr>
<td>scintillation material</td>
<td>$\rho$ [g/cm$^3$]</td>
<td>$Z_{\text{eff}}$</td>
<td>light yield [ph/MeV]</td>
<td>$\lambda$ [nm]</td>
<td>$\tau$ [ns]</td>
<td>main advantage</td>
<td>main disadvantage</td>
<td>Ref.</td>
</tr>
<tr>
<td>------------------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>----------------------</td>
<td>--------------</td>
<td>--------</td>
<td>----------------</td>
<td>------------------</td>
<td>-----</td>
</tr>
<tr>
<td>CsF</td>
<td>4.64</td>
<td>53.2</td>
<td>1900</td>
<td>390</td>
<td>2-4</td>
<td>short $\tau$</td>
<td>hygroscopic</td>
<td>[10]</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>4.88</td>
<td>52.7</td>
<td>1430</td>
<td>175-9500</td>
<td>0.8</td>
<td>short $\tau$</td>
<td>low $\rho +$ long $\tau$</td>
<td>[9]</td>
</tr>
<tr>
<td>CeF$_3$</td>
<td>6.16</td>
<td>53.3</td>
<td>4500</td>
<td>330</td>
<td>30</td>
<td>high dose rate resistivity</td>
<td>low LY</td>
<td>[15]</td>
</tr>
<tr>
<td>Lu$_2$Al$_2$O$_7$:Ce$^{3+}$</td>
<td>8.34</td>
<td>64.9</td>
<td>11,400</td>
<td>365</td>
<td>17</td>
<td>high initial intensity</td>
<td>crystal growing problems</td>
<td>[16]</td>
</tr>
<tr>
<td>Gd$_2$SiO$_4$:Ce$^{3+}$</td>
<td>6.71</td>
<td>59.4</td>
<td>10,000</td>
<td>430</td>
<td>56,600</td>
<td>high dose rate resistivity</td>
<td>brittle</td>
<td>[17]</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$:Ce$^{3+}$</td>
<td>7.4</td>
<td>66.4</td>
<td>27,000</td>
<td>420</td>
<td>40</td>
<td>high $\text{LY} +$ short $\tau$</td>
<td>crystal growing problems</td>
<td>[16]</td>
</tr>
<tr>
<td>Lu$_2$Al$_2$O$_7$:Sc $^u$</td>
<td>6.7</td>
<td>62.9</td>
<td>22,500</td>
<td>270</td>
<td>610</td>
<td>high $\text{LY}$</td>
<td>long $\tau$</td>
<td>[18]</td>
</tr>
<tr>
<td>CdWO$_4$</td>
<td>7.90</td>
<td>64.2</td>
<td>19,700</td>
<td>495</td>
<td>(2-15)$\times 10^2$</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>long $\tau$</td>
<td>[19],[20]</td>
</tr>
<tr>
<td>PbWO$_4$</td>
<td>8.28</td>
<td>75.6</td>
<td>$\sim 100$</td>
<td>$\sim 475$</td>
<td>$\sim 10$</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>low $\text{LY}$</td>
<td>[13]</td>
</tr>
<tr>
<td>Bi$_4$Ge$<em>3$O$</em>{12}$</td>
<td>7.13</td>
<td>75.2</td>
<td>8,200</td>
<td>505</td>
<td>300</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>low $\text{LY}$</td>
<td>[19]</td>
</tr>
<tr>
<td>TiCl$_3$</td>
<td>7.0</td>
<td>74.8</td>
<td>$\sim 1000$</td>
<td>465</td>
<td>200</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>low $\text{LY}$</td>
<td>[21]</td>
</tr>
<tr>
<td>NaI (77 K)</td>
<td>3.67</td>
<td>50.8</td>
<td>76,000</td>
<td>303</td>
<td>60</td>
<td>high $\text{LY} +$ short $\tau$</td>
<td>hygroscopic</td>
<td>[22]</td>
</tr>
<tr>
<td>NaI:Tl</td>
<td>3.67</td>
<td>50.8</td>
<td>43,000</td>
<td>415</td>
<td>230</td>
<td>high $\text{LY} +$ short $\tau$</td>
<td>hygroscopic + non-proportional response</td>
<td>[19],[17]</td>
</tr>
<tr>
<td>CsI:Na</td>
<td>4.51</td>
<td>54</td>
<td>43,000</td>
<td>420</td>
<td>630</td>
<td>high $\text{LY}$</td>
<td>long $\tau$</td>
<td>[17]</td>
</tr>
<tr>
<td>CsI:Tl</td>
<td>4.51</td>
<td>54</td>
<td>65,900</td>
<td>560</td>
<td>$10^3$</td>
<td>high $\text{LY}$</td>
<td>long $\tau$</td>
<td>[23]</td>
</tr>
<tr>
<td>CaI$_2$</td>
<td>3.96</td>
<td>51.1</td>
<td>86,000</td>
<td>410</td>
<td>550</td>
<td>high $\text{LY}$</td>
<td>very hygroscopic</td>
<td>[24]</td>
</tr>
<tr>
<td>HgI$_2$</td>
<td>6.38</td>
<td>68.8</td>
<td>6000</td>
<td>580</td>
<td>$2.1 \times 10^3$</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>low $\text{LY}$</td>
<td>[25]</td>
</tr>
<tr>
<td>Gd$_2$O$_2$:Pr,Ce, F</td>
<td>7.34</td>
<td>61.1</td>
<td>$\sim 40,000$</td>
<td>511</td>
<td>$3 \times 10^3$</td>
<td>high $\rho + Z_{\text{eff}}$</td>
<td>long $\tau$</td>
<td>[5]</td>
</tr>
<tr>
<td>ZnS:Ag</td>
<td>4.1</td>
<td>27.4</td>
<td>73,000</td>
<td>450</td>
<td>$10^5$</td>
<td>high $\text{LY}$</td>
<td>powder only</td>
<td>[26]</td>
</tr>
<tr>
<td>CdS:Te</td>
<td>4.8</td>
<td>48</td>
<td>17,000</td>
<td>640</td>
<td>$\sim 270-3000$</td>
<td>high $\text{LY}$</td>
<td>low $\rho + Z_{\text{eff}}$</td>
<td>[27]</td>
</tr>
</tbody>
</table>
\[ \mu = \sum_i (\kappa_{ai} + \sigma_{ai} + \tau_{ai}) \frac{N_A \rho w_i}{A_i} \]  

where \( \kappa_{ai} \), \( \sigma_{ai} \), and \( \tau_{ai} \) are respectively the absorption cross-section for atom \( i \) of the photoelectric effect, Compton scattering and pair production.

Considering the photoelectric effect only and neglecting its dependency on energy, equation (1) can be written as:

\[ \mu_\kappa = \rho N_A \sum_i \frac{w_i}{A_i} \kappa_{ai} \propto \rho \sum_i \frac{w_i Z_i^n}{A_i} \propto \rho \sum_i w_i Z_i^{n-1} \]  

where \( \mu_\kappa \) is the absorption coefficient for photoelectric absorption. In the last simplifying step the fact is used that for most elements the atomic mass is proportional to the atomic number. The last part of equation (2) can be redefined as:

\[ \mu_\kappa \propto \rho \sum_i w_i Z_i^{n-1} \equiv \rho Z_{\text{eff}}^{n-1} \quad \Rightarrow \quad Z_{\text{eff}} = \sqrt[\rho\sum w_i Z_i^{n-1}] \]  

In this way the compound can be represented as if it consists of only one type of atoms having atomic number \( Z_{\text{eff}} \). In this work will refer to \( \rho Z_{\text{eff}}^{n-1} \) as the photoelectric \( \gamma \)-quantum absorption power. Knowing that \( n \) varies between 4 and 5, equation (3) indicates that the photoelectric \( \gamma \)-quantum absorption power varies between \( \rho Z_{\text{eff}}^{1.2} \) and \( \rho Z_{\text{eff}}^{1.6} \).

In order to represent the \( \gamma \)-quantum absorption power for absorption by Compton interaction and pair production, similar expressions for \( Z_{\text{eff}} \) as that in equation (3) can be derived. One then finds that the absorption coefficient for Compton interaction and for pair production is proportional to \( \rho \) and \( \rho Z_{\text{eff}} \), respectively.

These simple formulas can be used as a rough measure for comparing the \( \gamma \)-quantum absorption power of compounds. Note that they serve only as a rough indication. It has to be realised that at energies between 100 keV and 1 MeV the absorption coefficient contains contributions of both Compton scattering and photoelectric absorption.

2.4.2 Multiplication and thermalisation of e-h pairs

After absorption of ionising radiation, the created high energetic primary electron and hole generate secondary electrons and holes. This avalanche of secondaries continues until the electrons and holes are not able to further ionise. The excess energy of these electrons and holes is lost by thermalisation. The time scale for these processes is believed to be in the order of 1 ps. Several theories have been developed to calculate the number of thermalised electron-hole pairs per unit of absorbed energy, given the bandgap energy. Rodnyi et al. reviewed and discussed these theories in detail [30]. As a rule of thumb, the energy needed for the creation of an electron-hole pair after absorption of high-energetic radiation number amounts two times the bandgap energy for materials having a small valence bandwidth and three times the bandgap energy for materials with a large valence bandwidth.
2.4.3 Energy transport

After thermalisation, the electrons and the holes have to transfer their energy to the luminescence centres. This stage is also called the energy migration stage. The electrons and holes may form excitons and in materials with mainly ionic bonding, holes and excitons may become self-trapped. This is likely to occur in halides. In such compounds a hole may become localised on a halide ion $X^-$, forming an $X^0$ atomlike defect. After polarisation of the lattice, it binds a neighbouring halide ion, forming a $X_i^-$ molecular like complex. Such a centre is called a $V_k$ centre. It is illustrated schematically in figure 1 for a rocksalt lattice. When such a centre captures an electron, a self-trapped exciton (STE) is formed. This and other centres are shown in figure 1 as well.

All these different types of (self-trapped) charge and energy carriers may either transfer their energy to luminescence centres, loose their energy non-radiatively or become lost by trapping near a defect or an (unwanted) impurity. The probability of occurrence of a certain process is dependent on numerous factors, such as the distance between the interacting carriers, the cross-section for interaction and temperature. As a consequence the scintillation properties may alter as the temperature and the concentration of luminescence centres varies. Furthermore, it has been found that the efficiency of the energy transfer is dependent on the electron-hole pair density, which is defined as the number of electrons and holes per mm of ionisation track length.
TABLE 3: Energy transfer processes in the migration stage

<table>
<thead>
<tr>
<th>Energy transfer (a)</th>
<th>Charge transfer (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>immobile donors (1)</td>
<td>-tunnelling of a charge carrier to a charge</td>
</tr>
<tr>
<td>-resonance energy transfer</td>
<td>recombination site</td>
</tr>
<tr>
<td>-radiative energy transfer</td>
<td></td>
</tr>
<tr>
<td>mobile donors (2)</td>
<td>- subsequent capture of a free electron and</td>
</tr>
<tr>
<td>-energy transfer by STE or</td>
<td>hole on the luminescence centre</td>
</tr>
<tr>
<td>exciton diffusion</td>
<td>- ( V_i ) diffusion to an electron trapped in the</td>
</tr>
<tr>
<td></td>
<td>vicinity of a luminescence centre</td>
</tr>
<tr>
<td></td>
<td>- thermal release of trapped charge carriers and</td>
</tr>
<tr>
<td></td>
<td>subsequent capture on a charge</td>
</tr>
<tr>
<td></td>
<td>recombination site</td>
</tr>
</tbody>
</table>

The complexity of these energy and carrier transfer processes makes it difficult to predict the efficiency and route of the migration stage. So this stage is by no means trivial and for most scintillators not yet understood. The time needed for migration to the luminescence centre may vary from \( \sim 10^{-12} \) to \( 10^{-3} \) seconds. Longer migration times are commonly referred to as scintillator afterglow.

In table 3, we have compiled schematically some possible interaction mechanisms. In this scheme, the transfer processes have been categorised in terms of the type of transfer (i.e. charge or energy transfer) and the mobility of the donor, defined as the centre that can transfer its energy or charge to another centre. With the help of the classification of table 3, the energy transfer processes in Gd₂SiO₅:Ce³⁺ and NaI:TI⁺ will be briefly discussed.

**Gd₂SiO₅:Ce³⁺** After absorption of a \( \gamma \)-quantum, the electrons and the holes, or excitons are captured by Gd³⁺ ions (process 2a/2b). The excited Gd³⁺ ions may transfer their energy by resonance energy migration on the Gd-sublattice (process 1a) and via the Gd-sublattice to Ce³⁺ ions (processes 1a) [31].

**NaI:TI⁺** The electrons and the holes, created after absorption of a \( \gamma \)-quantum, may be trapped on TI⁺ forming TI⁰ and TI²⁺ centres (process 2b) [32]. These centres may be excited by the diffusion of electrons and self-trapped holes (process 2b: \( TI^0 + V_i \rightarrow (TI^0)^* \rightarrow TI^+ + hv \), \( TI^{2+} + e \rightarrow (TI^{2+})^* \rightarrow TI^{+} + hv \) or detrapped again. Excitation of TI⁺ centres by STE diffusion (process 2a) has been observed as well [33].

### 2.4.4 Luminescence

The final stage of the scintillation process is the luminescence of the luminescence centre. The luminescence properties can be easily studied by optical excitation characterisation. For many optically active ions the quantum efficiency is high.

### 2.4.5 Scintillation efficiency and time response

The last three stages of the scintillation process determine the scintillation efficiency of a scintillator. These are the multiplication and the thermalisation of e-h pairs (dependent on the bandgap energy \( E_g \)), the energy transport (with efficiency S) and the luminescence of the optical centre (with efficiency Q). Accordingly, we can write for the light yield \( Y \) (in ph/MeV):
where $E_g$ is expressed in eV. The term in the denominator, $\beta E_g$, denotes the energy needed to create one electron-hole pair.

Equation (4) indicates that the light yield increases inversely proportional to $E_g$, provided that $S=1$ and $Q=1$. In order to illustrate this dependency, the light yields of efficient scintillators and cathode ray phosphors are shown in figure 2. Although for these materials the efficiency of energy migration is not known, it indicates that for very efficiently scintillating

![Figure 2: Light yield of efficient scintillators and cathode-ray phosphors as a function of the inverse of the bandgap energy.](image)

compounds, like CaF$_2$:Eu$^{2+}$, NaI (at 77 K) and CaS:Ce$^{3+}$, the light yield increases for smaller $E_g$. Theoretically, the highest obtainable light yield for a bandgap energy $E_g$ is given by $10^8/2E_g$ ph/MeV. This relationship is obtained from equation (4) for low thermalisation losses (i.e. $\beta=2$) and 100% energy transport and luminescence efficiency of the optical centre. In figure 2 this upper limit is shown by a dashed line.

The first two stages of the scintillation process, the absorption of a $\gamma$-quantum and the multiplication and thermalisation of the electrons and the holes occur within several ps. Hence, the time response of the scintillator is therefore determined by the last two stages, i.e. the energy migration stage and the decay time of the luminescence centre. If the energy migration is very fast compared to the decay time of the luminescence centre, then the decay time of the luminescence centre equals the decay time of the scintillation pulse.
2.5 Considerations for the search for new scintillators

Now we have presented an overview of the use (in table 1) and requirements of scintillators (in table 2), it is clear that it is not possible to formulate unambiguous demands on scintillators for all applications. Nevertheless, it is clear that a density larger than 4 g/cm$^3$, an effective atomic number higher than 50 are at least required. Densities larger than 7 g/cm$^3$ and effective atomic numbers larger than 70 are commendatory. For most applications a high light yield (say larger than 20,000 ph/MeV) and a short decay time (say shorter than 230 ns) are desired. Each of these demands will be discussed in this section in some more detail.

2.5.1 Decay time

The scintillation decay time is controlled by the speed of energy transfer by the thermalised electron-hole pairs created after absorption of a $\gamma$-ray, and the decay time of the luminescent centres. As was pointed out before, it is not possible to predict the speed of the energy transfer. Concerning the luminescent centre more is known. In order to obtain a fast luminescence decay, the optical transition should be spin and electric dipole allowed. Three types of luminescence transitions are of interest:

1. **exciton singlet-singlet transitions.** Such transitions are hardly observed in inorganic compounds. The most well known example of this type of luminescence is in pure NaI at 77 K, emitting around 300 nm and a decay time of 60 ns. At room temperature, singlet-singlet transitions in inorganic compounds are mostly quenched.

2. **core to valence luminescence (CVL).** If an electron is excited from the upper (cation) core band to the conduction band, the created core-hole may recombine with an electron from the (anion) valence band. Provided that the energy difference between the top of the core band and the bottom of the valence band is smaller than $E_{\chi}$ this luminescence can be observed. Unfortunately, the light yield of this type of luminescence is low.

3. **5d-4f luminescence.** Spin-allowed and electric dipole allowed $4f^n-5d-4f^o$ transitions of the rare earth ions have a decay time in the order of 10-70 ns, depending on the emission wavelength. The most well-known rare-earth ions, exhibiting this fast luminescence are Ce$^{3+}$ and Pr$^{3+}$ and to a lesser extent also Nd$^{3+}$. Dependent on the host lattice site, in which the Ce$^{3+}$ ion is incorporated, the luminescence is located within the whole spectral region from ultraviolet to the red. The difference between the lowest energy of the Ce$^{3+}$ 5d configuration and the highest energy of the Ce$^{3+}$ 4f configuration is quite large, so relaxation from the 5d to the 4f configuration is unlikely to occur. The Ce$^{3+}$ 4f-4f transitions are located in the infrared spectral region and are not detected by the light detectors as photodiodes and photomultiplier tubes. In some Pr$^{3+}$ and Nd$^{3+}$ doped compounds, the lowest energy level of the 5d configuration may be located close to a level of the 4f configuration, resulting in relaxation to this level. As a result the 5d-4f luminescence is quenched and only intraconfigurational 4f-4f transitions are observed, which have a decay time in the order of $>\mu$s. For the Pr$^{3+}$ and Nd$^{3+}$ ions these (unwanted) transitions are located in the visible and may be efficiently detected by light detectors. As a result, the detected
scintillation response will contain slow components due to these long 4f-4f decay
times. High light yields for Ce$^{3+}$ and Pr$^{3+}$ doped oxide material have been obtained.
The most well-known are Lu$_2$SiO$_5$:Ce$^{3+}$ and LuAlO$_3$:Ce$^{3+}$.

2.5.2 Light yield

According to equation (4) and figure 2, it is commendatory to study materials having a small
$E_g$. For materials being build of ions having a noble gas configuration, $E_g$ decreases roughly
along the series fluorides (9-12 eV), oxides (5-9 eV), chlorides (6-8 eV), bromides (5-7 eV),
iodides (4-6 eV), sulphides (2-5 eV) and selenides (2-4 eV). In the search for new scintillator
materials, mainly oxides and fluorides gained attention. Halides did not gain much attention,
probably due to the hygroscopicity of most of these compounds. If they are not too
hygroscopic application as a scintillator is well possible. This holds for example for the well-
known NaI:Tl$^+$. 

2.5.3 Gamma-quantum absorption power

As was pointed out before, a measure for the $\gamma$-quantum absorption power is given by
$\rho Z_{\text{eff}}^4$. Thus a high $Z_{\text{eff}}$ and $\rho$ are required. The effective atomic number $Z_{\text{eff}}$ is only
dependent on the stoichiometry of the compound. The density $\rho$ of a compound, however, is
dependent on numerous factors: the ionic radii of the anions and cations, the valence of the
ions and the lattice structure. Generally, the highest $\gamma$-quantum absorption power is obtained
for oxide compounds having a close-packed lattice structure.

It should be noted that the $\gamma$-quantum absorption power does not necessarily increase, if
an element in a compound is replaced by an isovalent element with larger atomic mass. We
will illustrate this by considering the $\gamma$-quantum absorption power of the lead halides. In table
4 the $\rho$ and $Z_{\text{eff}}$ of these materials are collected. $Z_{\text{eff}}$ was calculated using equation (3). In the

<table>
<thead>
<tr>
<th>compound</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$Z_{\text{eff}}$</th>
<th>$\rho Z_{\text{eff}}^4$ in $[10^6$ g/cm$^3$]</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$\rho Z_{\text{eff}}^4$ in $[10^6$ g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF$_2$</td>
<td>7.85</td>
<td>78</td>
<td>291</td>
<td>7.85</td>
<td>291</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>5.94</td>
<td>76.2</td>
<td>200</td>
<td>8.91</td>
<td>300</td>
</tr>
<tr>
<td>PbBr$_2$</td>
<td>6.83</td>
<td>71.5</td>
<td>178</td>
<td>11.73</td>
<td>306</td>
</tr>
</tbody>
</table>

fourth column of this table, $\rho Z_{\text{eff}}^4$ is given as a measure for the $\gamma$-quantum absorption power.
Of all lead halides, the highest $\gamma$-quantum absorption power is obtained for PbF$_2$. The $\gamma$-
quantum absorption power of the halides decreases along the series PbF$_2$, PbCl$_2$ and PbBr$_2$,
although the atomic mass of the halide ion increases. The cause for this decrease is the
lowering of the lead content per cm$^3$, which is a consequence of the larger chlorine and
bromine radii compared to that of fluorine. In order to illustrate that this is the case, the $\gamma$-
quantum absorption power was also calculated using the hypothetical density obtained under
the condition that the lead content per cm$^3$ for PbCl$_2$ and PbBr$_2$ equals that of PbF$_2$. This is
expressed as $\rho' Z_{\text{eff}}^*$ as presented in the last column. It shows a slight increase in $\gamma$-quantum absorption power for the heavier halides, due to the contribution of the halide ions.

Based on the above example, one could conclude that, of all halides, only the fluorides are useful to obtain a sufficient high $\gamma$-quantum absorption power. This does not hold as a general statement. Consider, for example, the $\gamma$-quantum absorption power of the Lu elpasolites, see table 5. By inspection, it is noted that the $\gamma$-quantum absorption power is

<table>
<thead>
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<th>compound</th>
<th>$\rho$ [g/cm$^3$]</th>
<th>$Z_{\text{eff}}$</th>
<th>$\rho Z_{\text{eff}}^*$ in [10$^6$ g/cm$^3$]</th>
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<td>4.60</td>
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quite low for Cs$_2$NaLuCl$_6$ and Cs$_2$NaLuBr$_6$, which is due to the small density of these materials. The $\gamma$-quantum absorption power of Cs$_2$NaLuI$_6$, however, is higher than that of Cs$_2$NaLuBr$_6$ and Cs$_2$NaLuCl$_6$, since the iodide ions contribute to the $\gamma$-quantum absorption power.

2.5.4 Emission wavelength

The most commonly used light detectors are photomultiplier tubes having bialkali photocathodes and solid-state detectors. The first type of detector has its maximum sensitivity of about 25% between ~250 and ~450 nm. Solid state detectors, such as photodiodes, have a detection efficiency of almost 80% between 450 and ~800 nm.

2.6 Choice of studied compounds

With the considerations set out in the previous section, we can motivate the choice of the studied materials. Let us start with the scintillation decay time, which should be shorter than 230 ns. As is discussed before, it is clear that the Ce$^{3+}$ 5d-4f transition is the most promising luminescence transition. Before the start of this work, the research was focused on the study of Ce$^{3+}$ doped fluorides and oxides. Other compounds such as chlorides and bromides have hardly been studied yet, despite the fact that they have smaller bandgap energies than most of the fluorides and oxides and are therefore candidates for high light yield scintillators. So, it is worthwhile to study Ce$^{3+}$ doped compounds other than fluorides and oxides as well.

In order to achieve the required $\gamma$-quantum absorption power, elements with high atomic numbers should be constituents of the host lattice. The elements having atomic numbers higher than 83 cannot be used, since they are radioactive. In order to avoid the presence of optical transitions in the ultraviolet or in the visible, it is commendatory to incorporate elements
having a noble gas configuration. A huge number of ions do not fulfil this requirement. This holds for the elements between Hf (atomic number 72) and Bi (atomic number 83). For some of these elements it is known that they quench the Ce$^{3+}$ luminescence. The ions Ti$^4+$, Pb$^{2+}$ and Bi$^{3+}$ have an s$^2$ configuration, showing optical transitions in the UV. Quenching of the Ce$^{3+}$ luminescence has been observed in lead compounds [28],[37]. This has been ascribed to proximity of the levels of the Ce$^{3+}$ 5d configuration to the levels of the Pb$^{2+}$ 6p configuration. As a consequence, photoionisation of Ce$^{3+}$ is likely to occur [28],[37]. In oxides of the transition metals, such as tantalates and niobates, having an empty d shell no Ce$^{3+}$ luminescence has been observed so far [38]. This has been, similarly as in the lead compounds, ascribed to photoionisation of Ce$^{3+}$ due to electron transfer to the metal ion [38]. A weak emission has been observed in LaTaO$_4$Ce$^{3+}$ [39] and LaTa$_2$O$_7$Ce$^{3+}$ [40], [39] but it is not known whether the observed luminescence can be attributed to Ce$^{3+}$ 5d-4f luminescence. Anyway, the light yield under γ-ray excitation is very low [39]. So far, experimental data lack on the luminescence or scintillation properties of Ce$^{3+}$ doped in inorganic compounds containing elements having atomic numbers between 74 and 81.

The heaviest elements that remain to be incorporated are Lu$^{3+}$ and La$^{3+}$. The Gd$^{3+}$ ion can also be used, since it has a stable half-filled shell. In many Gd compounds with Ce$^{3+}$ doping, Ce$^{3+}$ luminescence has been observed. Concluding, we arrive at the choice to study Ce$^{3+}$ doped Lu-, Gd- and La- compounds. In this thesis the attention is mainly focused on the study of Ce$^{3+}$ doped chlorides, since they did not gain much attention so far. Furthermore, in collaboration with the group of Prof. Güdel, Bern several congruently melting chlorides were selected. A consequence of the above choice is that it is not possible to achieve a density of 7 g/cm$^3$ and effective atomic numbers larger than 70.

REFERENCES

3 Experimental Techniques

3.1 Introduction

In this chapter the experimental techniques are discussed that have been used for studying scintillating materials. In order to study the properties of the optically active centres, standard luminescence spectroscopic methods are used. These are optical absorption, luminescence excitation and emission spectroscopy. They will be discussed first. Then the techniques used to study the luminescence under excitation by ionising radiation are considered. These concern recording of X-ray induced emission spectra, pulse height spectra and scintillation decay time spectra. Table 1 compiles the studied materials and their preparation method. Some materials that are studied in this work are hygroscopic. In order to minimise serious

<table>
<thead>
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<th>chapter</th>
<th>Compound</th>
<th>which laboratory</th>
<th>preparation technique</th>
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Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection © 1998 J.C. van 't Spijker, all rights reserved.
hydration of the samples, silicagel grains or solid NaOH pellets are used to dry the air during experimenting. Nevertheless, these precautions were not always sufficient to perform reproducible measurements. This holds especially for RbGd$_2$Br$_7$:Ce$^{3+}$ and RbGd$_2$Cl$_7$:Ce$^{3+}$. Therefore some samples were sealed inside small quartz cuvettes (Ø 0.65x-3 cm) under nitrogen atmosphere. This was done in Bern. These quartz-sealed samples have been used for the optical characterisation, X-ray induced emission measurements and the recording of scintillation decay time spectra.

3.2 Optical characterisation

Figure 1 displays the set-up that was used for optical characterisation and X-ray induced emission measurements. The equipment for the optical characterisation employs a 0.2 m ARC VM502 monochromator. It is equipped with MgF$_2$ windows and is operated in vacuum. The monochromator contains an aberration-corrected concave holographic grating (1200 grooves/mm and blazed at 250 nm) with an aperture ratio of f/4.5. A movable divertor mirror can direct the light either to the EMI photomultiplier tube (PMT) or to sample holder 2. Both sample holders can be evacuated and measurements can be performed down to 120 nm.

![Schematic of the experimental set-up for optical characterisation and X-ray induced emission measurements.](image)

**FIGURE 1:** Schematic of the experimental set-up for optical characterisation and X-ray induced emission measurements.

In order to record optical absorption spectra, the light of the lamp is fed through the sample under study that is mounted in sample holder 1. The light is monochromatised using the ARC VM502 monochromator and detected with the EMI PMT. The single photon counting technique is employed. Several light sources can be used. For measurements between 120 and 350 nm an ARC DS-775 deuterium discharge light source with a MgF$_2$...
window is used. The emission spectrum of this source consists of a continuum between 120 and 370 nm with a slight decrease in intensity at longer wavelengths. Superimposed are intense lines between 120 and 165 nm. In order to record absorption spectra at longer wavelengths, a light source having a tungsten filament is used. This lamp emits between 200 and 1000 nm.

Optical absorption spectra between 190 and 820 nm are also recorded using a Hewlett Packard 8452 diode-array spectrophotometer. In this system, a collimated light beam of a deuterium lamp passes through a sample holder and is dispersed by a concave grating on a diode array. The spectral resolution of this apparatus is about 2 nm. If not denoted otherwise, the spectral resolution of the optical absorption spectra presented in this thesis amounts to 0.5 nm full width at half maximum (FWHM) below 200 nm and to 2 nm (FWHM) above 200 nm.

Optical emission spectra were recorded by measuring the fluorescence spectrum at a fixed excitation wavelength. The excitation light is directed to sample holder 2 and focused with a 25 mm plano-convex MgF₂ lens on the sample, see figure 1. The emission of the sample is collected with a lens made of UV grade fused silica, having a focal length of 50 mm. The emission spectrum is recorded using a Jobin Yvon H10 UV monochromator and an XP2020 PMT. The monochromator has a focal length of 0.1 m and contains a holographic concave grating (grating 1200 grooves/mm, blazed at 250 nm) and an aperture ratio of f/3.5.

Excitation spectra were recorded in the same configuration as used for the recording of the emission spectra. The emission wavelength is fixed and the excitation wavelength is scanned. In order to suppress unwanted contributions due to second order transmission of light coming from the excitation monochromator, filters can be placed between the exit window of the ARC monochromator and sample holder 2. Instead of the Jobin Yvon monochromator also interference and cut-off filters can be used. Sodium salicylate is used as a reference to correct the excitation spectrum for the lamp spectrum, the transmission and the spectral sensitivity of the system.

Optical excitation and emission spectra have also been recorded using the spectrophotometer Quanta Master QM1 of Photon Technology International (PTI). This system consists of a 75 W Xenon lamp (PTI PowerArc™), a double excitation monochromator (model PTI 121 A, blazed at 300 nm, 1200 grooves/mm), quartz lenses, a sample box (MP-1) and an emission monochromator (model PTI 101 A, blazed at 500 nm, 1200 grooves/mm) with a PMT unit (model PTI 710). The monochromators are of the Czerny-Turner configuration, i.e. they consist of two (0.2 m) concave mirrors and one plane grating. The emission spectra are corrected for the wavelength dependency of the measurement device and spectral sensitivity of the light detector. Sodium salicylate and Rhodamine B are used as a reference to correct the excitation spectrum for the lamp spectrum, the transmission and the spectral sensitivity of the system. The spectral resolution of the excitation and emission spectra presented in this thesis amounts to 2 nm FWHM below 250 nm and to ~1 nm FWHM above 250 nm.

UV-excited decay time spectra are measured using an IBH System 5000 coaxial flashlamp, similar to the apparatus described in [1]. The discharge chamber can be filled with a variety of gases. The luminescence of the gas, excited by a spark discharge, is focused by a
plano-concave mirror on the output window. The pulse width is a few ns, dependent on the type of gas and pressure. Using an ARC VM502 monochromator the excitation wavelength is selected. The luminescence of the sample under study is selected by optical interference and cut-off filters and detected by an XP2020Q PMT. The decay time spectra are recorded with the single-hit method [2] using an Ortec 567 time to amplitude converter and Canberra 1326 D constant fraction discriminators. More information on the recording of decay time spectra can be found in the section on scintillation decay time measurements.

3.3 X-ray induced emission measurements

X-ray induced emission spectra are recorded using an X-ray tube with a Cu anode operated at 35 kV and 25 mA. The used set-up is similar to that presented in figure 1. The sample under study is mounted in sample holder 1 and the scintillation light is detected by ARC monochromators and the EMI PMT. The 0.39 meter ARC VM504 contains three plano diffraction gratings (blazed at 150, 300 and 750 nm, all 1200 grooves/mm) with an aperture ratio of 7/5.4. The monochromator is of the Czerny-Turner configuration. In order to perform measurements at other temperatures than room temperature, the sample can be mounted in a liquid nitrogen cryostat. Then X-ray induced spectra can be recorded between 100 and 400 K. All X-ray induced emission spectra presented in this thesis are recorded with a spectral resolution between 2 and 4 nm FWHM.

Two measurement modes are used. In the ‘single photon counting mode’, the number of photons detected by the EMI PMT is counted in a fixed time interval using 100 MHz LeCroy 821 discriminator and a 200 MHz Joerger SI-1 24 bits scaler. In the ‘current mode’ the PMT signal is integrated with a home-made integrating circuit.

For measurements using the ARC VM502 the recorded spectra are corrected for the transmission of the system and the QE of the PMT [3]. Once the spectra are corrected, the light yield is derived by comparison of the wavelength-integrated yield with that of a BaF$_2$ reference crystal measured under equal measurement conditions. The light yield of this reference crystal is $(11,000\pm1650)$ ph/MeV, as obtained from pulse height measurements [3]. Apart from the error in the light yield of the BaF$_2$ crystal, there are other errors that contribute to uncertainty in the light yield of the sample under study. These are due to the uncertainty in the detection efficiency of the measurement system (estimated to be 10 %) and the reproducibility of the mounting of the crystal in the sample holder (estimated to be 10 %). Furthermore, it is known that the light yield varies with the employed X-ray/γ-ray energy [4]. This will introduce an uncertainty as well. Since the energy spectrum of the X-ray tube is not exactly known and since the non-proportional response may be different than that of the employed BaF$_2$ reference crystal, the error may become quite large. We estimate the contribution of the non-proportional response to be 20 %. Finally, another error is introduced by a variation in light collection efficiencies e.g. due to a different quality of the crystal surface. The resulting uncertainty is estimated to be 10%. Altogether, the error in the light yield of the crystal under study is will be about 30%. So, the light yields derived from this method can be regarded as a rough indication. It is noted that in all cases above we use the 2σ-value (σ stands for standard deviation) for denoting the error.
3.4 Pulse height measurements

The use of pulse height spectra is well known in scintillation spectroscopy [5]. The set-up for recording such spectra is shown in figure 2. The crystal, optically coupled with a silicon grease (General Electric, viscosity 60,000 cst) and wrapped in 5 layers of 0.1 mm thick Teflon, is excited by γ-rays and/or X-rays of a radioactive source. The scintillation light is detected by an XP2020Q PMT (SN:40161). The corresponding output signal, denoted as (a) in figure 2, is integrated with a home-made charge sensitive pre-amplifier having an RC-time of 50 μs. The pulse shape of this signal is denoted in figure 2 as (b). Using an Ortec 572 or 672 spectroscopic amplifier this signal is further amplified and filtered using Gaussian shaping (see figure 2 (c)).

![Figure 2: Schematic of the set-up used to record pulse height spectra.](image)

![Figure 3: Pulse height spectrum of γ-rays and X-rays coming from a $^{137}$Cs source recorded with a CsI:Tl$^+$ crystal.](image)
An example of a pulse height spectrum is presented in figure 3 for γ-rays and X-rays of a $^{137}\text{Cs}$ source measured with a CsI:Tl$^+$ crystal. Several peaks are observed. Near channel 370 the 662 keV photopeak is shown. The energy resolution of the photopeak is defined as the ratio of the FWHM of this peak and the peak position. Further indicated in the figure are the Compton edge near channel 260, the backscatter peaks near channel 50-100 and a photopeak at channel 20 due to the photoelectric absorption of 32 keV X-rays emitted by the $^{137}\text{Cs}$ source.

3.4.1 Determination of light yield

The light yield, expressed as the number of collected photoelectrons per MeV of absorbed γ-ray energy (phe/MeV), is determined by comparing the peak position of the photopeak with that of the peak position of the single photoelectron spectrum. This spectrum is due to the thermal release of single photoelectrons from the photocathode and due to the detections of single photons from the scintillator crystals. In order to transform the number of photoelectrons/MeV into a light yield expressed in photons per MeV (ph/MeV), the scintillation light detection efficiency has to be known.

Knowing the wavelength dependence of the quantum efficiency (QE) of the PMT [3] and the Corning blue sensitivity, the absolute QE of the photocathode is known with an accuracy of 10%. In order to estimate the charge collection efficiency (CCE) of the photoelectrons coming from the photocathode, the light yield (in phe/MeV) of several crystals, luminescing between 250 and 500 nm, has been measured with the XP2020Q PMT and a Hamamatsu R1791 PMT. The QE of the Hamamatsu tube has been measured by the manufacturer. Furthermore, this tube is optimised for charge collection. Assuming a CCE of 0.95±0.05 for this PMT [6], we estimated the CCE for the XP2020Q tube to be 0.80±0.08. Knowing thus the detection efficiency of the XP2020Q PMT, the light yield in ph/MeV can be determined.

Further we have to take into account the light collection efficiency, that is the fraction of light generated in the crystal that reaches the photocathode. It is estimated to be 0.95±0.05. It is noted that in all cases above we use the 2σ-value (σ stands for standard deviation) for denoting the error.

If the light yield is determined with the above-described method, another type of error is also important. The peak position of the single electron spectrum is not necessarily equal to the average position of the single spectrum. This is a result of the asymmetric shape of the single electron peak caused by the Poisson distribution of the electrons coming from the first dynode of the PMT [7]. The other multiplication stages introduce a weak broadening of this peak. For the employed XP2020Q tube the mean gain of the first amplification stage is about 10-14, dependent of emission wavelength of the scintillator.

A typical single electron spectrum is shown in figure 4. In figure 4 the Poisson distribution for an amplification of 14 is shown in curve a. The presented spectrum is scaled to appropriate channel numbers and peak heights. It shows a good agreement with the measured single electron spectrum at channel numbers larger than 100. At smaller channel numbers the spectrum deviates. This may be due to contribution of inelastically backscattered electrons [8], non-uniformity of the dynodes or losses due to defocusing of the multiplied electron cloud [7]. Furthermore, at channel numbers lower than channel 20 the noise contribution of the preamplifier is dominant. Therefore, it is hard to estimate the exact single
electron distribution. If we assume that the Poisson distribution describes well the single electron spectrum the average peak position differs about 4% from the peak position. However, if we allow for the distribution shown in figure 4, curve b, this difference may be as large as 14%. The overall accuracy of the light yields reported in this thesis amount 16%.

3.4.2 Energy response

In order to measure the light yield as a function of the $\gamma$-quantum excitation energy, the crystal is mounted as described before. Instead of 5 layers of Teflon only 1 layer is used in order to prevent absorption of low energy X-rays in the Teflon layers. We used $\gamma$-rays and X-rays of $^{55}$Fe, $^{241}$Am, $^{133}$Ba, $^{51}$Cr, $^{57}$Co, $^{137}$Cs, $^{54}$Mn and $^{22}$Na sources to excite the crystal. An Amersham (AMC.2084) variable X-ray source was used as well. It contains $^{241}$Am, emitting X-rays and $\gamma$-rays that produce the characteristic K\(\alpha\) and K\(\beta\) X-rays of Cu, Rb, Mo, Ag, Ba and Tb targets. Using all these sources pulse height spectra are recorded at energies between of 5.9 keV and 1.2 MeV. Light yields are derived from the recorded spectra, as described above. During the recording of the spectra, all measurement conditions are kept equal, i.e. the crystal is not dismounted. In this way the error in the yield relative to that at 662 keV is only 3%.

3.5 Scintillation decay time measurements

Scintillation decay time spectra at time scales up to 200 $\mu$s were recorded using the multi-hit method described by Moses [2]. The experimental set-up is shown in figure 5. The sample under study is mounted on a 'start' tube and is excited by $\gamma$-rays of a radioactive source. Once a $\gamma$-ray is absorbed in the sample, the generated scintillation pulse is detected by the start PMT and, if the scintillation intensity is sufficiently high, a 'start' NIM pulse is generated by a
LeCroy 934 constant fraction discriminator (CFD). A few scintillation photons per scintillation event may pass through the slit and be detected by the stop tube. The PMT signal due to these detected photons is transformed into NIM pulses using Ortec 934 CFDs. The time differences between the start NIM pulse and the stop NIM pulses are digitised using a LeCroy 4208 Time to Digital Convertor and stored in a histogram. After the recording of a large number of scintillation events, such a spectrum shows the number of stops recorded in a time interval $t, t+dt$, where $dt$ is the TDC time resolution. If such a spectrum is normalised to the total number of recorded scintillation events, it expresses the chance that a photon is detected in a time interval $t, t+dt$. In fact, this time distribution equals the shape of the scintillation pulse.

In order to record the scintillation decay accurately, the number of stops per start should be lower than the maximum number the TDC can record. The employed TDC can detect at maximum 8 stops per start. Practically, in all our applications an average of 3.5 stops per start or less is commendatory. Also the dead time of the TDC should be considered. For the LeCroy 4208 TDC this amounts 3 ns.

For measurement on scintillation crystals having a low initial scintillation intensity, a small number of photoelectrons is present at the start of the scintillation. This will give rise to a jitter in the starting moment. Recently, a set-up has been built in which this jitter is prevented. The set-up is similar to that shown in figure 5, but instead of the crystal under study a BaF$_2$ crystal is mounted on the start PMT. The sample under study is mounted between the start tube and the slit. Between these crystals a $^{22}$Na source is placed. This source
3.5 Scintillation decay time measurements

generates a positron, which recombines with an electron under the emission of two collinearly emitted 511 keV photons. One of the 511 keV photons is detected by the BaF₂ crystal. The other 511 keV photon excites the crystal and some scintillation photons are detected by the ‘stop’ PMT. Because of the high initial scintillation intensity of the BaF₂ crystal, the jitter in the starting moment is much smaller than the 1 ns TDC time resolution.

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[8] Photomultiplier tubes, principles and applications, Philips Photonics, 1994, chapter 2 and 3
4 Luminescence and scintillation properties of BaY$_2$F$_8$:Ce$^{3+}$ and of pure and Ce$^{3+}$ doped BaLu$_2$F$_8$

4.1 Introduction

Crystals of BaF$_2$ are used as scintillators because of their scintillation emission near 200 nm with an 800 ps decay time [1],[2]. This luminescence, called core-valence luminescence (CVL) or cross-luminescence, is due to the radiative recombination of an electron from the F$^-$ 2p-valence band with a hole in the Ba$^{2+}$ 5p-core band. Some other compounds containing Ba cations and F anions show CVL as well when excited by ionising radiation. Among these compounds are LiBaF$_3$ [3], BaY$_2$F$_8$ [4], [5], [6] and BaLu$_2$F$_8$ [7].

In recent years the latter compound gained attention because of possible applications as a scintillator [7] and a laser host [8], [9]. In the framework of the search for new heavy scintillator materials with a fast response and a high light yield, we have studied the optical and the scintillation properties of pure and Ce$^{3+}$ doped BaLu$_2$F$_8$. BaLu$_2$F$_8$ has an effective atomic number of ~63. It crystallises either in a monoclinic (density 7.14 g/cm$^3$) or an orthorhombic structure (density 6.94 g/cm$^3$) [10]. The point symmetry for the rare earth site in the orthorhombic structure is C$_1$.

As a comparison, BaY$_2$F$_8$:Ce$^{3+}$ was also studied. Crystals of BaY$_2$F$_8$:Ce$^{3+}$ and BaY$_2$F$_8$:Nd$^{3+}$ have been studied in the search for fast responding scintillators [5], [11] and UV emitting lasers [12], [13]. BaY$_2$F$_8$ has a density of 4.97 g/cm$^3$ and an effective atomic number of 44. The crystal structure of BaY$_2$F$_8$ is monoclinic, equal to that of monoclinic BaLu$_2$F$_8$ [10]. The Y$^{3+}$ site, co-ordinated with 8 F$^-$ ions [14], [15], has a point symmetry C$_2$ [8].

Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
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4.2 Experimental

Pure and Ce$^{3+}$ doped BaLu$_2$F$_8$ and BaY$_2$F$_8$:Ce$^{3+}$ crystals were grown in carbon crucibles using the vertical Bridgman technique [8]. The BaY$_2$F$_8$:Ce$^{3+}$ crystals were grown from stochiometric amounts of BaF$_2$ (Merck, Optipur), YF$_3$ (Johnson and Mathey, purity 99.9 %) CeF$_3$, (Johnson and Mathey, purity 99.9 %) at about 1100 °C. The cylindrically shaped boules of the Ce$^{3+}$ doped BaY$_2$F$_8$ crystals, having a faintly purple colour, were cut into small pieces with plan parallel faces. The crystals, having a thickness of 1.45-2.45 mm, were subsequently sanded and polished. Similarly, polished colourless pure and Ce$^{3+}$ doped BaLu$_2$F$_8$ crystals with dimensions in the order of 5x5x5 mm$^3$ were obtained. X-ray powder diffraction was done on BaLu$_2$F$_8$. Unfortunately, the employed technique was not powerful enough to establish whether the structure is monoclinic or orthorhombic. The studied samples are listed in table 1. Most samples are transparent. Some of them contain small bubbles and/or inclusions. Crystal X1a is of poor quality, it is not transparent and cracks are visible.

Scintillation decays were inspected on a Tektronix TDS 380 digital oscilloscopy (bandwidth 400 MHz, samplerate 2GS/s).

4.3 Results

4.3.1 BaY$_2$F$_8$:Ce$^{3+}$

Under photon excitation the Ce$^{3+}$ ion in BaY$_2$F$_8$ shows a strong luminescence in the ultraviolet [13]. The optical absorption and excitation spectra of BaY$_2$F$_8$:0.7% Ce$^{3+}$ (H9)

![Figure 1: The optical absorption (a) and excitation (b) spectrum of BaY$_2$F$_8$:0.7% Ce$^{3+}$, measured at an emission wavelength of $\lambda_{em}$ = 360 nm between 250 and 350 nm and using a WG305 filter for the wavelengths below 250 nm. The emission spectrum (c) was measured under excitation of light with a wavelength of 250 nm.](image-url)
show three main bands located at ~200, 245 and 300 nm, while the first band has three components at 187, 196 and 214 nm, see figure 1. These bands have already been observed by Chernov et al. [13]. The excitation efficiency of the Ce$^{3+}$ luminescence between 140 and 190 nm is low, indicating that the absorption observed below 160 nm is not related to the 4f–5d transition of Ce$^{3+}$. It can not be attributed to the onset of the fundamental absorption band either, since that is located near 100-125 nm [4], [13]. Apparently, there is some uncontrolled impurity present. For almost all crystals a linear correlation in absorption coefficient of the Ce$^{3+}$ 4f-5d transitions is found with the concentration in the melt, except for H10. According to the measured absorption coefficient for this sample, the Ce$^{3+}$ concentration as put in the melt would correspond to 3%.

![Figure 2: X-ray induced emission spectra of BaY$_2$F$_8$:Ce$^{3+}$ with Ce$^{3+}$ concentrations of (a) 0.6%, (b) 2%, (c) 0.7%, (d) 9.9% and (e) 4.9%. In the inset the spectrum of BaY$_2$F$_8$0.7%Ce$^{3+}$ (H9) is shown. Note the logarithmic y-axis.](image)

X-ray induced emission spectra of BaY$_2$F$_8$:Ce$^{3+}$ crystals with different Ce$^{3+}$ concentrations are presented in figure 2. They show the characteristic doublet emission due to transitions from the lowest energy level of the Ce$^{3+}$ 5d configuration to the spin-orbit split $^2$F ground state of Ce$^{3+}$. Part of the Ce$^{3+}$ luminescence is re-absorbed by Ce$^{3+}$ ions due to the small Stokes shift between the Ce$^{3+}$ emission and absorption [13]. The emission bands at 230 nm and 270 nm are caused by the host lattice luminescence, see the inset of figure 2. It has almost 2 orders of magnitude less intensity than the Ce$^{3+}$ emission. In pure BaY$_2$F$_8$ it consists of CVL and luminescence due to the radiative recombination of self-trapped excitons (STEs) [5]. The STE emission consists of a band between 200 and 600 nm, peaking at 350 nm [5]. In the Ce$^{3+}$ doped samples in figure 2, part of the host lattice luminescence at 240 and 290 nm is absorbed by the Ce$^{3+}$ 4f-5d transitions. The scintillation emission is also partly absorbed by the X-ray induced defects that cause coloration. The absorption spectrum of the greenish coloured crystals resembles that measured by Kaminskii et al. [16]. This absorption is most pronounced between 320 and 375 nm, i.e. at the wavelength of the Ce$^{3+}$ luminescence. Light
yields, derived from X-ray induced emission spectra were corrected for this transmission loss. The yields are compiled in table 1 together with the light yields derived from pulse height spectra. The light yields are in the range of a few thousand ph/MeV.

<table>
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<th>Sample name</th>
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<th>Ce³⁺ conc. [at %]</th>
<th>Light yield X-ray [ph/MeV]</th>
<th>Light yield γ-ray (0.5 μs) [ph/MeV]</th>
<th>Light yield γ-ray (10 μs) [ph/MeV]</th>
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<td>500</td>
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<tr>
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<td>510</td>
<td>640</td>
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</tr>
<tr>
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<td>550</td>
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<td>780</td>
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</tbody>
</table>

Gamma ray induced decay time spectra are shown in figure 3. They consist of a fast decay time component of ~1 ns, a component of 36-44 ns and a non-exponential component extending into the μs regime, see the inset of figure 3.

![Graph showing scintillation decay curves](image)

**Figure 3**: Scintillation decay curves of BaY₂F₈:Ce³⁺ at Ce³⁺ concentrations of (a) 0.6 %, (b) 2 %, (c) 4.9 % and (d) 9.9 % excited by γ-rays of a ¹³⁷Cs source. In the inset the scintillation decay of BaY₂F₈:0.7 %Ce³⁺ in the first 20 μs is shown.
4.3 Results

The mean decay time in the interval from 20 to 120 ns after the start of the scintillation pulse becomes slightly longer with increasing Ce$^{3+}$ concentration (see table 1). Because of the low initial intensity at the start of the scintillation pulse, Cherenkov pulses produced in the PMT window, on which the crystal under study is mounted, could not be well discriminated. In the employed multi-hit method the average time response of a large number of scintillation events is recorded. As a result, the recorded decay time spectra show an artefact due to the detection of these Cherenkov pulses. By inspection of the time response of individual scintillation pulses on a fast digital oscilloscope in single-shot mode, only the BaY$_2$F$_8$:Ce$^{3+}$ crystals with the lowest Ce$^{3+}$ concentration show the presence of a $\sim$1 ns decay time component. We attribute this to CVL. For the other crystals with Ce$^{3+}$ concentrations in the melt of 2% and higher, no CVL was observed. Apparently, most of the CVL is emitted at same the wavelengths as the 4f-5d Ce$^{3+}$ absorption bands, i.e. below 310 nm (see figure 1 and 2). According to Kirikova et al. [5], a considerable part of CVL is emitted above 310 nm. This is not confirmed by our measurement results.

For sample H12 the CVL light yield was determined. From the measurements on the digital oscilloscope, we estimated that the intensity of the CVL is $\sim$3-4 larger than the initial intensity of the $\sim$40 ns decay time component. Using further the light yield derived from pulse height spectra recorded with a shaping time of 0.5 $\mu$s, the light yield of the CVL was estimated to be less than 20 ph/MeV.

4.3.2 BaLu$_2$F$_8$:Ce$^{3+}$ and BaLu$_2$F$_8$

The optical absorption and excitation spectra of Ce$^{3+}$ doped BaLu$_2$F$_8$ are presented in figure 4. The excitation bands at 183, 196, 225, 246 and 288 nm that are also observed in the

![Figure 4](image-url)

**Figure 4:** The optical absorption (a) and excitation spectrum (b) of BaLu$_2$F$_8$:1%Ce$^{3+}$ (X1b), measured at emission wavelength of $\lambda_{em}$ = 305 nm between 250 and 300 nm and using a WG305 filter for the wavelengths below 250 nm. The emission spectrum (c) was measured under excitation of light with wavelength of 280 nm.
absorption spectrum are attributed to 4f-5d transitions of Ce$^{3+}$. The absorption band between 140 and 170 nm is not observed in the excitation spectrum of the Ce$^{3+}$ luminescence. It is therefore not related to Ce$^{3+}$ 4f-5d transitions.

The emission spectrum in figure 4, curve c, consists of a band between 300 and 370 nm. At 308 nm (32,400 cm$^{-1}$) and 328 nm (30,500 cm$^{-1}$) the peaks are located corresponding with the transitions from the lowest level of the 5d configuration to the spin-orbit split $^2$F ground state. Note that this is at slightly shorter wavelengths than for BaY$_2$F$_8$:Ce$^{3+}$. The spin-orbit splitting of the $^2$F state amounts 1900 cm$^{-1}$, which is to be expected [17]. The Stokes shift amounts 2600±100 cm$^{-1}$.

The optical absorption spectrum of the undoped BaLu$_2$F$_8$ crystal consists of an absorption band starting below 220 nm with a tail extending to 280 nm. Excitation at 250 nm gives a weak broad luminescence band between 300 and 400 nm. The absorption band can not be attributed to the onset of the fundamental absorption band. For other barium fluoride compounds, containing ions with a noble gas electron configuration, the band gap corresponds with shorter wavelengths, e.g. in BaF$_2$ and BaY$_2$F$_8$ at 118 and 100 nm, respectively [4]. Therefore we attribute the 220 nm absorption band and the broad emission band to an impurity.

![Image of spectrum graph]

**Figure 5:** X-ray induced emission spectrum of (a) undoped BaLu$_2$F$_8$ (X2) and (b) BaLu$_2$F$_8$:Ce$^{3+}$ (X1b)

X-ray induced emission spectra of BaLu$_2$F$_8$ and BaLu$_2$F$_8$:Ce$^{3+}$ are presented in figure 5. Undoped BaLu$_2$F$_8$ shows a broad emission band between 180 and 480 nm. For BaLu$_2$F$_8$:Ce$^{3+}$ the emission is mainly due to Ce$^{3+}$ luminescence. During the recording of the X-ray induced emission spectra the crystals became yellowish. For both undoped BaLu$_2$F$_8$ and BaLu$_2$F$_8$:Ce$^{3+}$, the radiation induced absorption spectra appear similar. Light yields, derived from the X-ray induced emission spectrum and corrected for the transmission losses due to
the coloration, are compiled in table 1, together with the light yields derived from pulse height spectra. For these crystals low light yields are measured with a maximum of 1200 ph/MeV.

![Scintillation decay curves](image)

**Figure 6:** Scintillation decay curves of (a) BaLu₂F₈:Ce³⁺ and (b) undoped BaLu₂F₈ excited by γ-rays of a ¹³⁷Cs source. In the inset the decays in the first 5 μs are shown.

The scintillation decay curve of undoped BaLu₂F₈, shown in figure 6, consists of a fast emission with a decay time of ~ 1 ns and a tail extending in the μs range. The intensity of the fast luminescence is much higher than that of the Cherenkov light, as was deduced by inspecting the scintillation pulses on the Tektronix oscilloscope. We attribute it to CVL. The same fast component was observed by Weber et al. [7]. The tail is attributed to the radiative recombination of STEs. Doping BaLu₂F₈ with Ce³⁺ replaces the slow host lattice emission and most of the CVL by Ce³⁺ luminescence. The fast initial intensity in the recorded scintillation decay of BaLu₂F₈:Ce³⁺ (see figure 6) is due to Cherenkov light. Apparently, the emission spectrum of the CVL is mainly located at the absorption bands of Ce³⁺, i.e. below 300 nm (see figure 4).

Using the decay time spectrum and the pulse height spectrum of undoped BaLu₂F₈, the light yield of the CVL was calculated. From the decay curve, the ratio of the time-integrated yield of the CVL and the total time-integrated yield in the first 0.5 μs was estimated. Knowing the light yield, derived from the pulse height spectrum recorded with a shaping time of 0.5 μs, the light yield of the CVL was estimated to be 200±50 ph/MeV. It is possible that the actual yield of the BaLu₂F₈ CVL is higher, since part of the scintillation light may be absorbed by the absorption below 200 nm, caused by defects or impurities. Weber et al. [7] report a CVL light yield for BaLu₂F₈ to be about one-third of that of BaF₂, that is ~ 1400/3 = 460 ph/MeV [18]. Since the crystal structure of the studied samples and the one studied by Weber may be different, no comparison in light yields can be made.
4.4 Discussion

4.4.1 Ce$^{3+}$ levels in BaLu$_2$F$_8$

The peak positions of the Ce$^{3+}$ 4f-5d absorption and Ce$^{3+}$ 5d-4f emission bands in a compound are determined by the crystal field, which in turn depends on the type of ligands surrounding the Ce$^{3+}$ ion, the Ce$^{3+}$ to ligand distances, the coordination number, and the point symmetry. Due to this dependency on the surroundings, the spectral properties of the Ce$^{3+}$ ion will differ from one host lattice to another. Generally, for isostructural Y and Lu compounds, the peak positions of the absorption and emission bands are located within 5 nm at equal wavelengths. As examples we mention the similar spectroscopic properties in MF$_3$ [19], [20], M$_2$SiO$_5$ [21], LiMF$_4$ [22] and MAI0$_3$ [23], [24] (M=Y or Lu). The difference is due to a slightly smaller radius of the Lu$^{3+}$ ion compared to that of the Y$^{3+}$ ion [25].

When we compare the peak positions of the Ce$^{3+}$ 4f-5d absorption bands in BaY$_2$F$_8$ and BaLu$_2$F$_8$, we notice that they are at different wavelengths, see figure 1 and 4. One absorption band in BaY$_2$F$_8$:Ce$^{3+}$ is located at 214 nm, whereas in BaLu$_2$F$_8$:Ce$^{3+}$ it is located at 11 nm longer wavelength. Furthermore, in the lowest 4f-5d absorption band is located at 300 nm in BaY$_2$F$_8$:Ce$^{3+}$, whereas in BaLu$_2$F$_8$:Ce$^{3+}$ it is located at 12 nm shorter wavelength. This 12 nm shift in absorption bands location is much longer than the 5 nm shift normally observed in isostructural Y and Lu compounds. Apparently, the site symmetries of the Ce$^{3+}$ ion in BaLu$_2$F$_8$ and monoclinic BaY$_2$F$_8$ are different. This may be related with a different crystal structure.

From the optical excitation and emission spectra in figure 1 and 4 we can derive the 4f-5d energy centroid, defined as the energy difference between the energy of the Ce$^{3+}$ groundstate and the average energy of the Ce$^{3+}$ 5d configuration in these materials. It is located at 44,980±500 and 45,070±500 cm$^{-1}$ in BaY$_2$F$_8$ and BaLu$_2$F$_8$, respectively. The reduction of this 4f-5d energy centroid with respect to the 51,230 cm$^{-1}$ of the free ion [26], is called the nephelauxetic effect according to Aull et al. [27]. The main contributions in the lowering of this centroid energy are covalency and the coupling in the orbital motions of the ligand and metal electrons [27]. Within the fluorides there is a variation in the 4f-5d energy centroid: from 39,000 cm$^{-1}$ in Rb$_2$NaYF$_6$:Ce$^{3+}$ [28] to 45,600 cm$^{-1}$ in LaF$_3$ [22]. Nevertheless, the Ce$^{3+}$ 4f-5d centroid energy difference in BaLu$_2$F$_8$:Ce$^{3+}$ and BaY$_2$F$_8$:Ce$^{3+}$ are about equal. Apparently, in the framework of the model by Aull et al. [27], the contribution of covalency and the coupled orbital motion in the centroid difference are about equal in these materials. Not only the 4f-5d energy centroid in BaY$_2$F$_8$:Ce$^{3+}$ and BaLu$_2$F$_8$:Ce$^{3+}$ are comparable, but also the Stokes shifts.

4.4.2 Energy transfer

In general the energy needed for the creation of an e-h pair amounts roughly 2 to 3 times the band gap energy [29]. Since the bandgap is ~10-12 eV we assume that ~45,000 e-h pairs are created upon absorption of a 1 MeV $\gamma$-quantum. Assuming further that the luminescence quantum efficiency (QE) of Ce$^{3+}$ is 100%, the maximum obtainable light yield is 45,000 ph/MeV. Inspection of table 2 learns that the maximum light yield measured is much lower,
only 2,000 ph/MeV. Thus only 1 out of ~ 20 e-h pairs gives rise to Ce$^{3+}$ luminescence, indicating an inefficient energy transfer. In some other fluorides low scintillation efficiencies are reported as well. We mention LiLuF$_4$:Ce$^{3+}$ [22], LaF$_3$:Ce$^{3+}$ [30], CeF$_3$ [30], and LuF$_3$:Ce$^{3+}$ [31].

Both for BaY$_2$F$_8$:Ce$^{3+}$ and BaLu$_2$F$_8$:Ce$^{3+}$ the light yields under continuous X-ray excitation are roughly 2-3 times larger than those derived from pulse height spectra. This difference is partly caused by the presence of a decay time in the > 10 μs range. From scintillation decay time spectra recorded until 200 μs after the start of the scintillation pulse, we estimated that 0.6-0.7% of the yield is emitted in the 35-45 ns component and 0.3-0.4% in the remainder of the time interval. To this we have to add luminescence occurring at time > 200 μs. Another phenomenon may also play a role. Contrary to the γ-ray measurements, which are performed under low radiation intensity, during the X-ray induced emission measurements the crystals became coloured. The measured light yields represent then the yields of a surface layer containing radiation induced defects. Therefore the measured light yields under X-ray excitation can only be regarded as a crude estimate.

By inspection of table 1, we learn that the light yields of BaY$_2$F$_8$:Ce$^{3+}$, derived from pulse height spectra, tend to increase with Ce$^{3+}$ concentration. This trend is somewhat obscured, since the light yields for equal Ce$^{3+}$ concentration vary considerably, which is probably caused by uncontrolled impurities or a different crystal quality.

The Ce$^{3+}$ luminescence decay time becomes longer with increasing Ce$^{3+}$ concentration, see table 1. This can be explained in terms of radiative trapping. Due to the small Stokes shift, part of the Ce$^{3+}$ luminescence is absorbed and can be re-emitted at later time, resulting in a longer decay time. Since the absorption length near 300 nm is much shorter than the crystal thickness, we can expect an enhancement of the Ce$^{3+}$ luminescence decay time by a factor of 1/(1-f) [32] at maximum, with f the ratio in absorbed light yield relative to the total light yield. This fraction can be determined from optically induced and X-ray induced emission spectra. For crystal H12 hardly any scintillation light is reabsorbed, for H13 about 20% is reabsorbed. Hence we expect for crystal H13 a mean decay time of 36.8/0.8 = 46 ns, in agreement with the measured value.

Because of the very low transfer efficiency of e-h pairs to the Ce$^{3+}$ centre, it is well possible that the fast Ce$^{3+}$ luminescence is due to impact excitation of Ce$^{3+}$. After absorption of ionising radiation the anions and cations are excited due to inelastic scattering of secondary electrons and X-rays created after absorption of a γ-quantum or by ionisation by such secondaries and subsequent electron capture. Since Ce$^{3+}$ ions are incorporated into the host lattice, some of them will be excited, giving rise to Ce$^{3+}$ luminescence. Such a mechanism results in i) a scintillation decay time equal to the radiative Ce$^{3+}$ 5d-4f luminescence decay time, which is in the order of 2·10^-8 s [13], ii) low light yields in the order of a few hundred ph/MeV and iii) the yield to increase linearly with increasing Ce$^{3+}$ concentration.

These model predictions agree with experimental observations. Yet, not all the scintillation light is emitted by impact excitation of Ce$^{3+}$. A significant fraction (i.e. 30-40%) of the scintillation light is emitted at times >> 40 ns. The host lattice emission can not be
responsible for this, because its intensity is almost 2 orders of magnitude less intense than the Ce\textsuperscript{3+} luminescence, as can be derived from the X-ray induced emission spectra in Figure 2. Consequently, some slow energy transfer process plays also a role in exciting the Ce\textsuperscript{3+} ions.

### 4.5 Conclusions

The light yield of the studied Ce\textsuperscript{3+} doped crystals is low, since most of the luminescence is probably generated by impact excitation of the Ce\textsuperscript{3+} ions. For an undoped crystal of BaLu\textsubscript{2}F\textsubscript{8} an even lower light yield is measured. Therefore the studied materials are not suitable as new scintillator materials. Furthermore, if large Ce\textsuperscript{3+} doped crystals could be grown, part of the scintillation light would be lost or trapped radiatively by self-absorption.

### REFERENCES

5 Scintillation properties of Ce$^{3+}$ doped Cs$_3$LuCl$_6$ and the elpasolites Cs$_2$NaMCl$_6$ (M=La,Ce,Lu)

5.1 Introduction

Optical centres having a perfect octahedral point symmetry gain considerable attention, since the interaction of such a centre with the surrounding lattice can be described with only a few parameters. Elpasolites contain one lattice site with a perfect O$_6$ point symmetry. Therefore, they have been thoroughly studied. In these studies, major attention has been focused on the 4f-electron energy level location of rare earth ions in these lattices [1]. Resonance energy transfer between neighbouring sites has been investigated as well [2]. For practical applications, elpasolites gained interest as laser hosts [3], storage phosphors [4] and scintillators [5],[6]. The search for new radiation detectors resulted in a study on the use of indium elpasolites [5] for neutrino detection and chloride elpasolites, exhibiting core-valence luminescence [6].

In the framework of search for new scintillators having comparable or better scintillation performance than the well-known NaI:Tl$^+$, we studied the scintillation and luminescence properties of some Ce$^{3+}$ doped elpasolites. Cs$_3$LuCl$_6$:Ce$^{3+}$, which has a structure resembling that of the elpasolites, has been studied as well.

Figure 1 shows a schematic representation of part of the elpasolite lattice structure of Cs$_2$NaRECl$_6$ (RE=rare earth). In this close-packed cubic lattice, the Na$^+$ and RE$^{3+}$ ions form a rocksalt like lattice, in which the rare earth ions are octahedrally surrounded by 6 Cl$^-$ ions. The high-temperature phase of Cs$_3$LuCl$_6$ has also the elpasolite structure, but at room temperature it has the K$_3$MoCl$_6$ structure [7]. In this lattice single, the Lu$^{3+}$ ion is surrounded by a distorted octahedra of Cl$^-$ ions. There are two sites for the Lu$^{3+}$ ion. We compiled some

Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
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properties of the studied materials in table 1, together with those of the well-known scintillators CsI:Tl\(^+\) and NaI:Tl\(^+\).

![Diagram of Cs\(_2\)NaRECl\(_6\)](image)

**Figure 1**: Part of the unit cell of the elpasolite Cs\(_2\)NaRECl\(_6\) (RE stands for Rare Earth)

**Table 1**: The density (\(\rho\)), effective atomic number (\(Z_{\text{eff}}\)) and Ce\(^{3+}\) content of the studied materials. For comparison \(\rho\) and \(Z\) of NaI and CsI are listed as well. n.r. stands for not relevant.

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<thead>
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<th>compound</th>
<th>(\rho) [g/cm(^3)]</th>
<th>(Z_{\text{eff}})</th>
<th>[Ce(^{3+})] in at. %</th>
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</table>

**5.2 Experimental methods**

Cs\(_2\)NaRECl\(_6\);Ce\(^{3+}\) (RE=La, Ce, Lu) and Cs\(_2\)LuCl\(_6\);Ce\(^{3+}\) were grown by the Bridgman technique in the laboratory of Prof. Güdel in Bern. Unfortunately, we do not have detailed information on the crystal growth of Cs\(_2\)NaCeCl\(_6\) and Cs\(_2\)NaLaCl\(_6\);Ce\(^{3+}\). Crystals of Cs\(_2\)NaLuCl\(_6\);Ce\(^{3+}\) and Cs\(_2\)LuCl\(_6\);Ce\(^{3+}\) were grown from the purified binary alkali halides (all from Merck, suprapur, i.e. 99.5\%) and LuCl\(_3\), CeCl\(_3\) which were obtained from Lu\(_2\)O\(_3\) (purity 99.99\%) and CeO\(_2\) (Heraeus, purity mixed in stoichiometric amounts. The furnace temperature was set at 720 and 780 °C, respectively. For Cs\(_2\)NaLuCl\(_6\);Ce\(^{3+}\) a single crystal boule could be grown,
whereas only small crystals of Cs₂LuCl₆:Ce³⁺ were obtained. The structure of the Lu-crystals was checked by powder X-ray diffraction. The lattice parameters for Cs₂LuCl₆ are \(a=26.830\) Å, \(b=8.100\) Å, \(c=12.934\) Å, \(\beta=99.7°\) and \(Z=8\). Cutting, sanding and polishing of the crystals was done in paraffin oil. In this way samples with plan parallel faces having a thickness of several mm were obtained. The Lu samples were optically clear, free of scattering centres. The Ce and La-epasolite crystals, however, are not transparent due to extensive scattering. Furthermore, the La-epasolite has a greenish colour. For the doped crystals, the Ce³⁺ concentration of the weighted-in amounts added to the melt amounts 1 at. %. The actual Ce³⁺ concentration is only known for the Lu-samples. From a chemical analysis they were determined to be 0.35 at.% in Cs₂NaLuCl₆:Ce³⁺ and 0.81 at.% in Cs₂LuCl₆:Ce³⁺, respectively.

### 5.3 Results

#### 5.3.1 Optical characterisation

Only for Cs₂NaLuCl₆:Ce³⁺ we were able to record the absorption spectrum. It is presented in figure 2, curve a. We attribute the broad band at 340 nm and the doublet centered at 210 nm to the Ce³⁺ 4f-5d(t₂g) and 4f-5d(e₉) transitions. Unfortunately, the studied sample was too thick to observe an anticipated possible splitting of the \(^{2}T₂g\) level. The strong absorption band observed below 187 nm is attributed to the onset of the fundamental absorption edge.

![Figure 2](image)

**Figure 2:** (a) Optical absorption spectrum of Cs₂NaLuCl₆:Ce³⁺, (b) 320 nm excited emission spectrum of Cs₂NaLuCl₆:Ce³⁺ and (c) the excitation spectrum of the 425 nm luminescence in Cs₂NaLuCl₆:Ce³⁺.
Excitation at 320 nm yields a double humped emission band between 350 and 450 nm (see figure 2, curve b) that we assign to Ce\(^{3+}\) luminescence. The typical splitting of the Ce\(^{3+}\) 4f ground state of \(\sim 2000 \text{ cm}^{-1}\) can be clearly resolved. The excitation spectrum of this emission is shown in figure 2, curve c. It resembles the absorption spectrum. The peak near 310 nm is attributed to a Gd\(^{3+}\) impurity. The origin of the excitation band below 200 nm is not completely clear. Excitation in these bands yields only Ce\(^{3+}\) 5d-4f luminescence. At these wavelengths, electrons can be excited from the valence to the conduction band. The presence of this excitation band indicates an efficient energy transfer from the host lattice to the Ce\(^{3+}\) ion.

**Figure 3:** Excitation and emission spectra of Ce\(^{3+}\) luminescence in Cs\(_2\)NaMCl\(_6\)-Ce\(^{3+}\) (M=La,Ce,Lu). Presented are the excitation spectra of the 425 nm emission and the 320 nm excited emission spectra. In the inset the excitation spectrum between 200 and 250 nm is shown more in detail.

Figure 3 shows the excitation and emission spectra of the studied elpasolites. The excitation spectra of the La and Ce elpasolite resemble that of the Lu elpasolite, showing the characteristic Ce\(^{3+}\) 4f-5d transitions near 210 and 330 nm and the band below 200 nm, which is related with energy transfer from the host lattice to the Ce\(^{3+}\) centre. The Ce\(^{3+}\) 4f-5d\((e_g)\) transition is shown more in detail in the inset of figure 3. The origin of the high excitation efficiency between 230 and 300 nm, which is especially pronounced for the Ce elpasolite, is not known. Since the crystals of the La and Ce elpasolite are optically not clear, other phases might be present in the samples, causing the appearance of other excitation peaks. Knowing the positions of the Ce\(^{3+}\) 4f-5d\((e_g)\) and 4f-5d\((t_{2g})\) transitions, the average Ce\(^{3+}\) 4f-5d energy was calculated. For the elpasolites a value of 36,500±1000 cm\(^{-1}\) was obtained. The large uncertainty is mainly due to uncertainty in the energy of the 4f-5d\((t_{2g})\) transitions. Similarly, the energy difference between the \(t_{2g}\) and \(e_g\) centroids were derived. The values are compiled in table 2.
TABLE 2: Peak positions of the Ce$^{3+}$ luminescence due to transitions from the lowest energetic level of the Ce$^{3+}$ 5d configuration to the spin-orbit split $^2$F state and the ratio, $I(T_{2g} \rightarrow F_{5/2})/I(T_{2g} \rightarrow F_{7/2})$, of the luminescence intensities of the $^2T_{2g} \rightarrow F_{5/2}$ and $^2T_{2g} \rightarrow F_{7/2}$ transitions. In column 2, the rare earth – chlorine distance d(RE-Cl) is given.

<table>
<thead>
<tr>
<th>compound</th>
<th>d(RE-Cl) [Å]</th>
<th>$E(T_{2g} \rightarrow F_{5/2})$ [cm$^{-1}$]</th>
<th>$E(T_{2g} \rightarrow F_{7/2})$ [cm$^{-1}$]</th>
<th>$I(T_{2g} \rightarrow F_{5/2})/I(T_{2g} \rightarrow F_{7/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$NaLaCl$_6$</td>
<td>2.74</td>
<td>17,300±1000</td>
<td>27,167±40</td>
<td>24,918±40</td>
</tr>
<tr>
<td>Cs$_2$NaCeCl$_6$</td>
<td>2.73</td>
<td>16,400±1000</td>
<td>26,592±40</td>
<td>24,539±40</td>
</tr>
<tr>
<td>Cs$_2$NaLuCl$_6$</td>
<td>2.66</td>
<td>18,300±1000</td>
<td>26,787±40</td>
<td>24,610±40</td>
</tr>
</tbody>
</table>

The luminescence spectra in figure 3 show the typical double peaked Ce$^{3+}$ luminescence. When we transform the wavelength scale into an energy scale, we can reasonably well fit the spectra with Gaussian curves. We compiled the peak positions, as well as the ratio in luminescence intensities from the lowest 5d level to the spin-orbit split groundstate in table 2. Note that the emission spectra are not corrected for the spectral sensitivity of the set-up, so there is a systematic error in the thus obtained ratio.

After excitation with light of 280 nm a weak additional luminescence band was observed at 335 nm in all the elpasolites. The excitation spectrum of this emission shows a broad structureless band between 210 and 300 nm.

Such centres have also been found in fluoride elpasolite crystals [3],[5] and were attributed by the authors to Ce$^{3+}$ centres on a low symmetry site. We did not study the optical emission and excitation spectra for Cs$_2$LuCl$_6$;Ce$^{3+}$.

5.3.2 Results under excitation of ionising radiation

The X-ray induced emission spectra in figure 4 consist of the typical Ce$^{3+}$ 5d-4f luminescence. No other emission bands are present at room temperature.

![Figure 4: X-ray induced emission spectra of (a) Cs$_2$NaLaCl$_6$;Ce$^{3+}$, (b) Cs$_2$NaCeCl$_6$, (c) Cs$_2$NaLuCl$_6$;Ce$^{3+}$ and (d) Cs$_2$LuCl$_6$;Ce$^{3+}$. In the inset the X-ray induced emission spectra of Cs$_2$NaLuCl$_6$;Ce$^{3+}$ at 100 and 300 K are shown. The spectral resolution is 4 nm FWHM.](image-url)
Note, that the Ce$^{3+}$ luminescence in Cs$_2$LuCl$_6$:Ce$^{3+}$ is shifted to 4 nm longer wavelengths compared to that in Cs$_2$NaLuCl$_6$:Ce$^{3+}$. Light yields, derived from the X-ray induced emission spectra, are collected in table 3, together with the ones derived from the pulse height spectra. Because of the small Stokes shift, part of the scintillation light is possibly quenched due to self-absorption in the crystal. The given yields are not corrected for that.

**TABLE 3**: Light yields derived from the X-ray induced emission spectra and pulse height measurements. The error in the light yields as derived from X-ray induced emission and pulse height spectra is respectively 30 and 16 %, respectively. The light yields are not corrected for self-absorption of scintillation light.

<table>
<thead>
<tr>
<th>compound</th>
<th>light yield X-rays [ph/MeV]</th>
<th>light yield γ-rays $^{137}$Cs (τ=0.5 μs) [ph/MeV]</th>
<th>light yield γ-rays $^{137}$Cs (τ=10 μs) [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$NaLaCl$_6$:Ce$^{3+}$</td>
<td>9400</td>
<td>3200</td>
<td>6400</td>
</tr>
<tr>
<td>Cs$_2$NaCeCl$_6$</td>
<td>12,000</td>
<td>3000</td>
<td>13,000</td>
</tr>
<tr>
<td>Cs$_2$NaLuCl$_6$:Ce$^{3+}$</td>
<td>23,000</td>
<td>3800</td>
<td>6100</td>
</tr>
<tr>
<td>Cs$_2$LuCl$_6$:Ce$^{3+}$</td>
<td>24,000</td>
<td>3000</td>
<td>5200</td>
</tr>
</tbody>
</table>

We also recorded X-ray induced emission spectra of Cs$_2$NaLuCl$_6$:Ce$^{3+}$ at low temperature. Some are shown in the inset of figure 4. At 100 K a broad emission band appears between 250 and 500 nm, partly absorbed by Ce$^{3+}$ 4f-5d(τ$_2$g) transition, similar to that observed in Cs$_2$NaLaCl$_6$:Ce$^{3+}$ [6]. We attribute it to the radiative luminescence of a self-trapped exciton (STE). Due to a coloration of the samples at low temperature, we were not able to estimate the light yields of the STE and Ce$^{3+}$ luminescence.

**FIGURE 5**: Scintillation decay time spectra of (a) Cs$_2$NaLaCl$_6$:Ce$^{3+}$, (b) Cs$_2$NaCeCl$_6$, (c) Cs$_2$NaLuCl$_6$:Ce$^{3+}$ and (d) Cs$_2$LuCl$_6$:Ce$^{3+}$ induced with γ-rays of a $^{137}$Cs source. The peak in the scintillation decay curve of Cs$_2$LuCl$_6$:Ce$^{3+}$ at 15 ns after the start of the scintillation decay, is due to an experimental artefact. In the inset the scintillation decay of Cs$_2$NaLuCl$_6$:Ce$^{3+}$ on the timescale up to 100 μs is shown.
The scintillation decay time spectra are presented in figure 5. For Cs$_2$LuCl$_6$:Ce$^{3+}$ a fast luminescing component is observed having a decay time constant in the order of 1 ns. We attribute it to an experimental artefact due to Cherenkov light detection. It is not likely that this is due to core-valence luminescence. In caesium chlorides this emission is generally located below 300 nm [6],[9], but at these wavelengths no luminescence has been observed under X-ray excitation. We did also not observe core-valence luminescence in Cs$_2$NaLaCl$_6$:Ce$^{3+}$ and Cs$_2$NaCeCl$_6$, as has been observed before [6],[9]. Probably, this emission is absorbed by the Ce$^{3+}$ 4f-5d transitions. The time response of the scintillation is clearly non-exponential. It consists mainly of power law-like decay time components with tails extending into the μs range.

The inset of figure 5 displays the scintillation decay of Cs$_2$NaLuCl$_6$:Ce$^{3+}$. This graph shows that still scintillation light is emitted at times larger than 100 μs after absorption of a γ-quantum. This holds probably also for the other studied materials. Therefore, the difference in yields obtained from X-ray induced emission spectra and the pulse height spectra is probably due to the presence of long decay components (τ ≥ 10 μs).

5.4 Discussion

In the elpasolites, the rare-earth site has a perfect octahedral point symmetry [10],[11],[12]. Hence, the Ce$^{3+}$ 5d state is, in first approximation, split into $^2E_g$ and $^2T_{2g}$ levels. The $^2T_{2g}$ level is further split by spin-orbit interaction into a double degenerate $\Gamma_8$ and a singlet $\Gamma_6$. This has been observed in Cs$_2$NaYCl$_6$:Ce$^{3+}$ [13]. The $E_g$ level can not be split by spin-orbit interaction. Nevertheless, in Cs$_2$NaLaCl$_6$:Ce$^{3+}$ and Cs$_2$NaLuCl$_6$:Ce$^{3+}$ two bands are observed near 210 nm, which are separated by 1400 cm$^{-1}$. The origin of this splitting remains unclear. It may be either due to the presence of two slightly different Ce$^{3+}$ centres or by a distortion of the perfect O$_h$ point symmetry in the excited state.

There is also a peculiarity in the recorded emission spectra. The ratio in the emission intensities from the lowest energy level of the Ce$^{3+}$ 5d configuration to the $^2F_{7/2}$ and $^2F_{5/2}$ levels vary from one elpasolite to another, as can be seen in the last column in table 2. This is determined by the transition probabilities from the lowest energy of the Ce$^{3+}$ 5d configuration to the $^2F$ [14], which are split into 5 sublevels by spin-orbit interaction and the crystal field [1]. The transition probability between a certain 5d orbital and a certain 4f orbital depends on the refractive index, the emission wavelength and the electric dipole matrix element between these two orbitals. Since the emission wavelengths are about equal and since we can reasonably well assume that the refractive index does not vary in a great extent between 350 and 450 nm, the observed variation in the ratio of the emission intensities is probably due to a variation of the electric dipole matrix element. In turn, this depends on the point symmetry of the luminescence centre and the spatial extent of the 4f and 5d wavefunctions.
5.5 Conclusions and outlook

Because of the perfect octahedral point symmetry of the rare earth site in the elpasolites, the optical excitation and emission spectra of the Ce$^{3+}$ ion can be straightforwardly analysed. Nevertheless, not all luminescence properties are well understood. This concerns the variation of the crystal field strength and of the ratio in the Ce$^{3+}$ $^2T_{2g}$-$^2F_{5/2}$ and $^2T_{2g}$-$^2F_{7/2}$ emission intensities with the lattice constant. We recommend to study purer Cs$_2$NaLaCl$_6$:Ce$^{3+}$ and Cs$_2$NaCeCl$_6$ crystals.

Finally, from the point of view of the use as scintillators these materials will probably not find an application, since the stopping power is comparable with that of NaI:Tl$^+$, whereas the light yield is lower and the decay time is longer than NaI:Tl$^+$.

REFERENCES

6 Study of scintillation properties of $K_2LaCl_5$:Ce$^{3+}$

6.1 Introduction

Most attention in the field of scintillation and luminescence applications is paid to Ce$^{3+}$ doped oxide and fluoride materials. Chlorides gain less attention, probably because they are usually hygroscopic and thus require precautions in handling. Despite the difficulties in experimenting a wealth of data is available. As a result of the discovery of the scintillator NaI:Tl$^+$ the energy transport to impurity centres in doped alkali chlorides has been studied in detail, see for example [1],[2]. Recently, core-valence luminescence of elpasolite chlorides was studied [3]. In other luminescence applications chlorides also gained interest. We mention alkaline earth chlorides in the field of electroluminescent phosphors [4] and up-conversion in Er$^{3+}$ doped $K_2LaCl_5$ [5].

In the present study we report on the luminescence and scintillation properties of Ce$^{3+}$ doped $K_2LaCl_5$. The crystal structure of $K_2LaCl_5$ is orthorhombic [6],[7]. The La$^{3+}$ ions are co-ordinated by 7 Cl$^-$ ions forming a mono-capped trigonal prism. In this lattice the $[LaCl_7]$ polyhedra form a one-dimensional chain in the [010] direction. Crystals of $K_2LaCl_5$ have a density of 2.89 g/cm$^3$ and the effective atomic number is 44.1. $K_2LaCl_5$ is hygroscopic.

6.2 Experimental

Crystals have been grown by the Bridgman technique in the laboratory of Prof. Güdel in Bern starting with the purified binary halides KCl (Merck, suprapur, i.e. 99.5%), LaCl$_3$ and CeCl$_3$ mixed in stoichiometric amounts. The chlorides have been prepared from the oxides La$_2$O$_3$
and CeO₂ (both from Heraeus, purity 99.999 %). The crystal boules are cylindrically shaped, have 8 mm diameter and a typical length of ~10-20 mm. Cutting, sanding and polishing of the crystals was done in paraffin oil. In this way samples with plan parallel faces and a thickness of several mm were obtained.

The Ce³⁺ concentrations in most crystals were determined by ICPS (Induction Coupled Plasma Spectroscopy), in which a small part of the crystal was dissolved and subsequently sprayed into an argon plasma. From the characteristic luminescence intensities of the elements the Ce³⁺ content in the crystals was derived. This method was not applied to the sample with the highest Ce³⁺ concentration. By comparing its optical absorption coefficient with those of the other samples the Ce³⁺ content appeared to be at least 7%. We will refer to this sample as K₂LaCl₅:10%Ce³⁺, as calculated from the weight-in amounts in the melt. Hereafter, we will express the determined Ce³⁺ concentrations as x in K₂La₁₋ₓCeₓCl₅.

All experiments were done either in vacuum or in air dried by silicagel to prevent hydration of the crystals. If not mentioned otherwise, all experiments were performed at room temperature.

6.3 Results

6.3.1 Optical excitation

The Ce³⁺ luminescence in K₂LaCl₅ consists of a double peaked band between 340 and 380 nm, caused by the transitions from the lowest energy level of the Ce³⁺ 5d configuration to the

![Figure 1](image_url)

**Figure 1:** (a) Optical absorption spectrum, (b) excitation spectrum and (c) emission spectrum of K₂LaCl₅:0.23%Ce³⁺. The excitation spectrum was measured at a wavelength of 370 nm. The emission spectrum was measured under excitation of light with wavelength of 310 nm. The absorption above 5 mm⁻¹ is not reliable.
6.3 Results

spin-orbit split $^2F_{5/2}$ and $^2F_{7/2}$ levels, see figure 1. The peak positions are located at 347 nm (28,800 cm$^{-1}$) and 372 nm (26,900 cm$^{-1}$) respectively, with a splitting of 1900 cm$^{-1}$. The excitation and absorption spectrum in figure 1 consist of several bands, of which three are located at the wavelengths 221, 239 and 258 nm. The other band at 322 nm splits into 2 subbands at low temperature. Based on a C$_5$ symmetry we expect a 5 fold splitting. This is in agreement with the observed splitting in the absorption spectra. The difference of the average energy of the Ce$^{3+}$ 5d configuration and that of the $^2F_{5/2}$ ground state is 37,600 cm$^{-1}$. The Stokes shift amounts ~2000-3000 cm$^{-1}$.

The absorption below 200 nm, (i.e. 6.2 eV) may be attributed to the onset of the fundamental absorption band. For other lanthanide chlorides, similar values are reported [8]. Nevertheless, the strong absorption may also be related with the hygroscopicity of these materials. These measurements were performed in air and possible hydration of the surface layer may also be a likely cause for the absorption.

6.3.2 X-ray induced luminescence

The emission spectrum under X-ray excitation of K$_2$LaCl$_5$:Ce$^{3+}$ is shown in figure 2. Apart from the Ce$^{3+}$ luminescence, a broad emission band is observed between 250 and 500 nm, which we attribute to the luminescence of a self-trapped exciton (STE). STE emission is in general characterised by a large Stokes shift and a decay time in the order of μs-ms for triplet-singlet transitions [9]. Part of the STE and Ce$^{3+}$ luminescence is absorbed by the Ce$^{3+}$ 4f-5d absorption band near 320 nm.

![Graph showing X-ray induced emission spectra of K$_2$LaCl$_5$ doped with various concentrations of Ce$^{3+}$](image)

**Figure 2**: X-ray induced emission spectra of K$_2$LaCl$_5$ doped with (a) 0.001 % (b) 0.23%, (c) 0.7% and (d) 10% Ce$^{3+}$. In the inset the emission spectra are shown with a logarithmic y-axis.

When we transform the wavelength to an energy scale, the emission spectrum of the STE luminescence in K$_2$LaCl$_5$:0.001%Ce$^{3+}$ shows a Gaussian shaped band peaking at 3.10 eV with a full width at half maximum (FWHM) of 0.51 eV. Similar energies and FWHM-values have
been reported for e.g. alkali chlorides [9]. Light yields derived from the X-ray induced emission spectra are compiled in table 1.

<table>
<thead>
<tr>
<th>[Ce(^{3+})] in mol %</th>
<th>light yield of STE lum. [ph/MeV]</th>
<th>light yield of Ce(^{3+}) lum. [ph/MeV]</th>
<th>absorbed STE light yield [ph/MeV]</th>
<th>total light yield [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>37,400</td>
<td>6,500</td>
<td>2,200</td>
<td>41,700</td>
</tr>
<tr>
<td>0.23</td>
<td>16,700</td>
<td>15,100</td>
<td>2,100</td>
<td>29,700</td>
</tr>
<tr>
<td>0.7</td>
<td>9,800</td>
<td>17,400</td>
<td>1,400</td>
<td>25,800</td>
</tr>
<tr>
<td>10</td>
<td>900</td>
<td>49,300</td>
<td>200</td>
<td>50,000</td>
</tr>
</tbody>
</table>

With increasing Ce\(^{3+}\) concentration the intensity of the STE luminescence decreases and that of the Ce\(^{3+}\) luminescence increases. For K\(_2\)LaCl\(_5\):10%Ce\(^{3+}\), the Ce\(^{3+}\) emission intensity is almost two orders of magnitude higher than that of the STE. Assuming that the peak positions and the widths of the STE luminescence band remain equal for all Ce\(^{3+}\) concentrations, the light yield of both the STE and the Ce\(^{3+}\) luminescence were estimated. The results are shown in table 1. The STE light loss due to overlap between the STE luminescence and the Ce\(^{3+}\) absorption near 280-320 nm is also presented.

The temperature dependence of the STE and Ce\(^{3+}\) luminescence intensity was also measured for K\(_2\)LaCl\(_5\):0.23 % Ce\(^{3+}\) and K\(_2\)LaCl\(_5\):10%Ce\(^{3+}\). The results for

![Figure 3: Temperature dependence of the light yields of Ce\(^{3+}\) (denoted as •), STE (denoted as +) and total luminescence (denoted as ▲) in K\(_2\)LaCl\(_5\):0.23%Ce\(^{3+}\), derived from X-ray induced emission spectra. For points without error bar the error is in the same order as the point size. The dashed lines are drawn to guide the eye. The full curve is drawn according to a fit of an equation presented in the “Discussion”. In the inset the X-ray induced emission spectra are shown for (a) 140, (b) 298, (c) 345 and (d) 396 K.](image-url)
K$_2$LaCl$_5$:0.23%Ce$^{3+}$ are shown in figure 3. At 140 K the emission is mainly due to the STE luminescence as can be seen in the inset of figure 3. The light yield of this luminescence is about 30,000 ph/MeV, whereas that of the Ce$^{3+}$ luminescence amounts only ~5,000 ph/MeV.

When the temperature rises the Ce$^{3+}$ luminescence intensity is enhanced at the expense of the STE luminescence intensity and at 400 K the STE luminescence has negligible intensity. From 100 to 300 K the total light yield, i.e. that of the STE and Ce$^{3+}$ luminescence, remains constant. At higher temperatures the total light yield decreases drastically.

Contrary to the results for K$_2$LaCl$_5$:0.23%Ce$^{3+}$ we do hardly observe a change in Ce$^{3+}$ and STE luminescence yield for K$_2$LaCl$_5$:10%Ce$^{3+}$ at temperatures in the 100 -400 K range, see figure 4. We do observe another phenomenon, namely that of self-absorption and re-emission of scintillation light. Part of the luminescence is absorbed by the Ce$^{3+}$ absorption band at 300-340 nm, as is also apparent in figure 2.

![Figure 4](image)

**Figure 4:** X-ray induced emission spectra for K$_2$LaCl$_5$:10%Ce$^{3+}$ at temperatures of (a) 105 (b) 193 (c) 298 and (d) 399 K. In the inset the light yield of the STE and Ce$^{3+}$ luminescence is shown as a function of temperature.

At low temperatures the spectral overlap between absorption and emission bands is small and the transitions of the lowest energetic level of the Ce$^{3+}$ 5d configuration to the $^2$F$_{5/2}$ and $^2$F$_{7/2}$ levels are clearly resolved. When the temperature rises, the luminescence intensity of the transition from the lowest energetic level of the Ce$^{3+}$ 5d configuration to the $^2$F$_{5/2}$ state decreases, while the intensity of the transition to the $^2$F$_{7/2}$ state increases. At a temperature of 400 K the luminescence consists mainly of the latter transition. Note that the light yield remains constant in the temperature range between 100 and 400 K.

### 6.3.3 Pulse height measurements

Using $\gamma$-quanta from a $^{137}$Cs source, pulse height spectra were recorded. For K$_2$LaCl$_5$:10%Ce$^{3+}$ the pulse height spectrum is shown in figure 5. The background under the photopeak shows an exponential decrease in intensity with increasing energy, as is shown with a dotted line in the figure. This has two origins.
Figure 5: Pulse height spectrum of $^{137}$Cs $\gamma$-quanta recorded with $K_2LaCl_5$:10%Ce$^{3+}$ crystal coupled onto an XP2020Q PMT. The spectrum is measured with a shaping time of 10 $\mu$s. In the inset the fit of the full absorption peak is shown consisting of the photopeak and the K$\alpha$ and K$\beta$ escape peaks of La.

Firstly, the spectrum was recorded with a high interaction rate of $\gamma$-rays, which was necessary because of the low probability of photoelectric absorption. As a result some pileup could not be prevented. A second, more important

Table 2: Light yields of $K_2LaCl_5$:Ce$^{3+}$ derived from pulse height measurements under excitation by 662 keV $\gamma$-quanta. The errors in the yields are about $\pm 16\%$.

<table>
<thead>
<tr>
<th>Ce$^{3+}$ concentration in mol %</th>
<th>shaping time [\mu s]</th>
<th>light yield [phe/MeV]</th>
<th>light yield [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.5</td>
<td>760</td>
<td>4600</td>
</tr>
<tr>
<td></td>
<td>3</td>
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<td>15000</td>
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<td></td>
<td>10</td>
<td>3700</td>
<td>22600</td>
</tr>
<tr>
<td>0.23</td>
<td>0.5</td>
<td>770</td>
<td>4500</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1800</td>
<td>10500</td>
</tr>
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<td></td>
<td>10</td>
<td>2400</td>
<td>14000</td>
</tr>
<tr>
<td>0.70</td>
<td>0.5</td>
<td>1400</td>
<td>8000</td>
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<tr>
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<td>3</td>
<td>2900</td>
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<td>1</td>
<td>4500</td>
<td>25000</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4800</td>
<td>26700</td>
</tr>
<tr>
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<td>3</td>
<td>4900</td>
<td>27000</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5300</td>
<td>29200</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5500 (5700)</td>
<td>30000 (31300)</td>
</tr>
</tbody>
</table>

reason is the presence of $^{40}$K with a natural abundance of 0.01% in the samples. This radioactive isotope emits 1.46 MeV $\gamma$-rays and $\beta$-particles with an end point energy of 1.3
MeV. It is responsible for 26 disintegrations per second in one cm$^3$ of $K_2$LaCl$_5$ crystal. Light yields derived from pulse height spectra are compiled in table 2. They are quite high for all the crystals, though much lower than measured under X-ray excitation, see table 1. The actual light yields may be somewhat higher, since some hydrated parts may absorb the scintillation light. For $K_2$LaCl$_5$:10%Ce$^{3+}$ a yield of $\sim$30000 ph/MeV is measured. By carefully cleaning
the crystal surface a yield of 31,300 ph/MeV could be obtained, shown between brackets in table 2. The full energy peak in figure 5 is asymmetrically shaped due to escape of characteristic Kα and Kβ X-rays of La, giving lines at 33 and 38 keV below the photopeak, as shown in detail in the inset. The energy resolution of the photopeak is estimated to be 5.3 %. For other energies in the range between 300 keV and 1 MeV low energy resolutions are measured as well, see figure 6. At energies of 40 keV and lower we observe values of 10 % and higher.

Figure 7 presents the proportionality curve. Between ~10 keV and 1.2 MeV the light yield per MeV of absorbed γ-ray energy is constant within a few percent, even at the K-edge of La. Below ~10 keV the light yield decreases rapidly. Near the L-edge the light yield is only 80% of that at 662 keV.

6.3.4 Scintillation decay time spectra

Figure 8 shows the scintillation decay time spectra of K₂LaCl₅ as a function of the Ce³⁺ concentration. The inset shows the spectra in the first μs. The rising slope before t=0 is due to an experimental artefact and has no physical meaning.

![figure 8: scintillation decay curve](image)

For K₂LaCl₅:0.001%Ce³⁺ the scintillation decay is mainly exponential with a decay time of about 3.7 μs. We assume that it represents the radiative lifetime of the STE. For the other crystals this decay time component is also present and can be observed as a tail as the scintillation pulse at times larger than, say, 7 μs after the start of the scintillation decay. These tails have a slightly different slope: for K₂LaCl₅:0.23%Ce³⁺ it is 3.1 μs, for K₂LaCl₅:0.7%Ce³⁺ 2.4 and for K₂LaCl₅:10%Ce³⁺ 3.7 μs. For Ce³⁺ concentrations larger than 0.001%Ce³⁺ a clear non-exponential decrease in intensity is observed in the first 3 μs of the scintillation decay.
For K$_2$LaCl$_5$:10%Ce$^{3+}$ the scintillation decay in this region can reasonably well be described by a $(1+at)^{-1.85}$ dependence with $a = 10$ (µs)$^{-1}$ and an additional exponential with a decay in the order of 80 ns. We assume that the latter fast component contains the decay of promptly excited Ce$^{3+}$ ions. Thus for K$_2$LaCl$_5$:10%Ce$^{3+}$ most luminescence is emitted non-exponentially. Most of the scintillation light is emitted within 1 µs. This is well illustrated by figure 9. The solid line shows the integral of the scintillation decay curve. It is normalised to the light output measured as a function of the shaping time. Notice that the light yield still increases slightly beyond 10 µs.

![Figure 9: The integral light yield of K$_2$LaCl$_5$:10%Ce$^{3+}$ as derived from the scintillation decay curve from figure 8 (shown with solid line), together with the measured light yields as derived from pulse height measurements using different shaping times (denoted as o). The integral curve is normalised to the light output measured as a function of the shaping time.](image)

The spectra in figure 8 contain the decay of both STE and excited Ce$^{3+}$ centres. In order to separate their contributions in the scintillation decay, decay time spectra were recorded at 370 (mainly Ce$^{3+}$ luminescence) and 430 nm (STE luminescence). They are shown in figure 10. The scintillation decay of the STE luminescence is exponential with a decay constant of 2.9±0.2 µs for K$_2$LaCl$_5$:0.23%Ce$^{3+}$ and of 2.3±0.1 µs for K$_2$LaCl$_5$:0.7%Ce$^{3+}$. At 370 nm, however, the decay for the 0.7%Ce$^{3+}$ doped crystal is clearly non-exponential in the first 2 µs. Though the effect is weaker, a similar observation is made for the 0.23%Ce$^{3+}$ doped crystal. Therefore we conclude that the non-exponential part in the scintillation decay time spectra in figure 8 is due to Ce$^{3+}$ luminescence. At longer times the decay is exponential with a decay time equal to that of the STE luminescence. At this wavelength, both Ce$^{3+}$ and STE luminescence is emitted. The exponential tail in the spectra at 370 nm in figure 10 contains much more light than would be expected on basis of the STE intensity at 370 nm as derived from the X-ray induced emission spectra in figure 2. This implies that part of the Ce$^{3+}$ luminescence is emitted in this tail as well, at times > 5 µs.
6.4 Discussion

6.4.1 Light yields

The light yields derived from the X-ray induced emission spectra are about a factor 1.5-2 higher than those derived from the pulse height measurements, compare table 1 and 2. This difference can not be explained by a non-proportional response. Based on figure 7, we would expect a lower yield as derived from the emission spectra under the excitation of ~10 keV X-rays than from the 662 keV excitation used in pulse height measurements. Instead we observe a higher yield for X-ray excitation. The observed difference is better explained by the presence of scintillation light with very long decay time components, say > 10 μs, as can be seen in figure 9. It will not contribute to the light yield in the pulse height measurements, but it will be detected in X-ray induced emission measurements, recorded under continuous
excitation. The considerable afterglow, observed when a crystal is mounted onto a PMT directly after being continuously irradiated by X-rays indicates the presence of a slow seconds decay component. Afterglow disappears when the crystals are heated to 400 °C.

6.4.2 Energy resolution

Under excitation of 662 keV γ-rays, an energy resolution of 5.3 % has been obtained, see figure 5. It is worse than the 4.3 % measured for a 1 mm thick CsI:Tl§ crystal mounted on a silicon drift detector [11] and the 3.8 % for RbGd₂Br₇:Ce³⁺ [12], but better than the 5.6 % for NaI:Tl§ [13].

In the observed energy resolution (R) several contributions can be distinguished. These are the photomultiplier (R_M) and the scintillator resolution (R_S) [14]. Due to the spread in the detected number of photoelectrons (N_phe) and the relative variance in the photomultiplier gain (v_M), the first term can be described using Poisson statistics [14]: \[ R_M = 2.36 \sqrt{\frac{1 + v_M}{N_{phe}}} \] . For an XP2020Q PMT the variance in gain is ~0.09. On the average 3700 phe are collected at the first dynode of the employed PMT after absorption of a 662 keV γ-quantum. We thus expect an 662 keV energy resolution of 4.2 %. The remaining part, that is the scintillator resolution \( R_S = \sqrt{R^2 - R_M^2} \), amounts 3.2%. The contribution of non-proportionality effects to this energy resolution is assuming quite small, since figure 7 shows an energy response that is almost linearly dependent on energy. The decrease in light yield below 13 keV, especially near the L-edge of La, may be due to the non-proportional response of the scintillator, but at this low energy it will not affect the energy resolution in a great extent. It is due to imperfect crystal quality and variation in the light collection. Below 13 keV ionising radiation is absorbed within a ~100 μm thick surface layer. K₂LaCl₃ is hygroscopic and hydrated surface layers may cause the lower light yield. Obviously, this will also suffer the light transport properties and in a poor light collection if high energetic radiation is absorbed in this thin layer. The crystal quality may be not uniform, causing variation in light production and collection.

The relatively large energy resolutions in figure 6 at energies of 40 keV and lower can also not be attributed to non-proportionality effects either. Even for Lu₂SiO₅:Ce³⁺, which has a considerable light-yield dependence on the γ-quantum excitation energy, the non-proportionality effects on the energy resolution is only ~10% at 20 keV [15]. Imperfect crystal quality and variation in the light collection may be the cause for these large energy resolutions.

6.4.3 Energy transfer mechanism

In this section the energy transfer mechanism of the electron-hole pairs created upon absorption of ionising radiation to the luminescence centres is considered. First of all some mechanisms are excluded, then the possible models are considered. The main emphasis is put on the STE diffusion model.

Exclusion of possible mechanisms

Numerous energy transfer mechanisms are possible. Some can be excluded, such as energy transfer as described by Förster and Dexter [16]. In this type of transfer the energy of the
excited donor (in this case STE) is transferred to the acceptor (Ce$^{3+}$). The transfer rate is in first approximation not dependent on temperature. In second approximation, a temperature dependent spectral overlap between the STE luminescence and the Ce$^{3+}$ absorption bands may introduce a temperature dependent transfer energy. The STE emission band overlaps mainly the absorption band near 322 nm, see figure 1 and 2. Although the bandwidth of the absorption band will increase for higher temperatures, it will always overlap the STE luminescence band completely. Thus we would expect an almost temperature independent transfer rate, in disagreement with the measurement results.

Part of the Ce$^{3+}$ luminescence is emitted in a μs exponential tail, see figure 10. A possible explanation is radiative energy transfer from the STE luminescence to the Ce$^{3+}$ 4f-5d absorption bands. We do think that this contribution in the energy transfer process is small, because of the following reasons. Firstly, it can not explain the strong temperature dependency of the light yields of the STE and Ce$^{3+}$ luminescence for K$_2$LaCl$_5$:0.23%Ce$^{3+}$. Only a weak temperature dependency is expected based on the spectral overlap of the STE luminescence and Ce$^{3+}$ absorption bands. Secondly, in K$_2$LaCl$_5$:10%Ce$^{3+}$ most of the scintillation light is emitted within 1 μs in a non-exponential decay time component, in much shorter time than the STE radiative lifetime. Finally, it can not elucidate the shortening of the STE decay time with increasing Ce$^{3+}$ concentration at the lower Ce$^{3+}$ concentration.

Energy transfer by diffusion of self-trapped carriers

In order to explain the observed phenomena we propose a diffusion-limited reaction of self-trapped carriers. Ionising radiation produces electron-hole pairs, which will become self-trapped within a few ps in halide materials. The hole may become self-trapped, forming a a V$_k$ centre. Electron-hole pairs may become self-trapped forming a V$_k$ centre with a bound electron, which relax into an F-H pair [9]. Already at low temperatures these excitons can dissociate forming other self-trapped carriers such as F-, H- and V$_k$-centre, mostly stabilised near an impurity [17]. All these defects may move through the lattice by site-to-site hopping. This motion is activated by temperature with a specific activation energy for each carrier type. For some alkali halides the temperatures at which the carriers become mobile have been reported: a H- centre near 40 K [18],[17], STEs near 80-150 K [19],[20],[21] a V$_k$ centre near 150 K [22] and an F centre near room temperature [17]. These values may vary considerably from one compound to another and only serve as a rough indication. All these carriers may be involved in energy transport, making the analysis of the energy transfer processes rather complicated.

We assume that two types of energy transfer are most important, that of diffusion of STEs and binary electron-hole recombination. They will be discussed below.

Energy transfer by STE diffusion

The STE diffusion model is held dominant at low Ce$^{3+}$ concentrations, say below 1%Ce$^{3+}$. For K$_2$LaCl$_5$:0.23%Ce$^{3+}$ the luminescence at low temperatures is mainly due to the radiative recombination of an STE, see figure 3. As the temperature rises the STE mobility increases, and the energy is transferred to a Ce$^{3+}$ centre upon interaction. This transfer is in agreement with the observed anti-correlation of STE and Ce$^{3+}$ luminescence yields in figure 3 between
100 and 300 K. We can describe this type of energy transfer using a simplification of the model presented by Tanimura and Itoh [19].

The self-trapped exciton can be de-excited either by radiative recombination with a rate $k_r$, or transfer its energy to a Ce$^{3+}$ ion with a rate $k_\gamma$. The latter is given by $k_\gamma = 4\pi NR^2$ [19] containing the Ce$^{3+}$ concentration ($N$), the diffusion constant of the STEs ($D$) and the encounter distance ($R$). When the STE approaches a Ce$^{3+}$ ion within this distance $R$, the energy is transferred to the Ce$^{3+}$ ion. We will neglect losses due to thermal quenching of the STEs or transfer to non-luminescent impurities. Then the change in the number of STEs $n_{STE}$ and excited Ce$^{3+}$ ions $n_{Ce^*}$ is given by:

$$\frac{dn_{STE}}{dt} = -(k_r + k_\gamma)n_{STE} \quad (1)$$

$$\frac{dn_{Ce^*}}{dt} = k_\gamma n_{STE} - k_{Ce} n_{Ce^*} \quad (2)$$

where $k_{Ce}$ is the radiative transition probability of the Ce$^{3+}$ 5d-4f transition. After a pulsed excitation by ionising radiation with energy $E_\gamma$. It is assumed that STEs are created exclusively. The concentrations of STEs and excited Ce$^{3+}$ ions with time following excitation obtained by combining equations (1) and (2) yielding:

$$n_{STE}(t) = \eta E_\gamma e^{-(k_r + k_\gamma)t} \quad (3)$$

$$n_{Ce^*}(t) = \frac{k_\gamma \eta E_\gamma}{k_{Ce} - k_r - k_\gamma} \left( e^{-(k_r + k_\gamma)t} - e^{-k_r t} \right) \quad (4)$$

where $\eta$ is the number of STEs created per unit of absorbed $\gamma$-ray energy.

The time dependencies of the STE and Ce$^{3+}$ luminescence intensities are given by $k_\gamma n_{STE}(t)$ and $k_{Ce} n_{Ce^*}(t)$, respectively. Due to the delayed excitation of the Ce$^{3+}$ ions by the STE diffusion, the Ce$^{3+}$ luminescence intensity is at maximum at time $t_r$ after the moment when the ionising radiation is absorbed:

$$t_r = \frac{1}{k_{Ce} - k_r - k_\gamma} \ln \left( \frac{k_{Ce}}{k_r + k_\gamma} \right) \quad (5)$$

The total light yields of the STE and the Ce$^{3+}$ luminescence, $Y_{STE}$ and $Y_{Ce^*}$, are given by the time-integrated luminescence intensities:

$$Y_{STE} = k_\gamma \int n_{STE}(t) \, dt = \frac{k_\gamma \eta E_\gamma}{k_r + k_\gamma} \quad (6)$$

$$Y_{Ce^*} = k_{Ce} \int n_{Ce^*}(t) \, dt = \frac{k_\gamma \eta E_\gamma}{k_r + k_\gamma} \quad (7)$$

$$\eta E_\gamma = Y_{STE} + Y_{Ce^*} \quad (8)$$

---

1 Some formulas in [16] contain some (typing) errors. In equation (8) the term $\sqrt{\pi / A}$ should be changed into $\sqrt{\pi / A}$, and $a / A$ should be changed into $4\pi NR^2 / A$. In equation (12) and (13) the term $erfc(b / \sqrt{a})$ should be changed into $1 - erfc(b / \sqrt{a})$. Finally, $k_\beta$ in equation (13) should be changed into $k_r$. 
We will now evaluate the predictions of the presented model. Let us start with the observed time response. As long as \( k_{ce} >> k_r + k_i \), then according to equation (3) and (4), both the STE and Ce\(^{3+}\) luminescence should have an equal decay time. This is confirmed by the time responses presented in figure 10. The non-exponential decay in the first 2 \( \mu \)s of the in Ce\(^{3+}\) luminescence decay will be discussed later on. The rise time as predicted by formula (4) is not observed in the decay curves. Probably because it is masked by the contribution of the non-exponential decay in the first few \( \mu \)s.

**TABLE 3: Calculation of the transfer rate \( k_r \), based on the decay times (column 2) and the ratio of the Ce\(^{3+}\) luminescence yield and the total light yield (\( Y_{ce} / Y_{tot} \), column 3), corrected for the non-exponential part (\( Y_{non-exp} / Y_{tot} \), column 4).**

<table>
<thead>
<tr>
<th>[Ce(^{3+})] in %</th>
<th>( Y_{ce} / Y_{tot} )</th>
<th>( Y_{non-exp} / Y_{tot} )</th>
<th>( k_r \times 10^5 \mathrm{ s}^{-1} ) based on ( \tau )</th>
<th>( k_r \times 10^5 \mathrm{ s}^{-1} ) based on light yields</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.13±0.03</td>
<td>0.05±0.01</td>
<td>0</td>
<td>20±6</td>
</tr>
<tr>
<td>0.23</td>
<td>0.47±0.03</td>
<td>0.08±0.01</td>
<td>52±4</td>
<td>126±9</td>
</tr>
<tr>
<td>0.7</td>
<td>0.64±0.03</td>
<td>0.40±0.03</td>
<td>146±10</td>
<td>122±10</td>
</tr>
<tr>
<td>10</td>
<td>0.98±0.02</td>
<td>0.99±0.01</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The STE and Ce\(^{3+}\) luminescence decay time in the long time limit is given by \( \tau = 1/(k_r + k_i) \). Because \( k_r \) is proportional to the Ce\(^{3+}\) concentration, we expect \( \tau \) to shorten with increasing Ce\(^{3+}\) concentration as is indeed observed. The decay time decreases from 3.7 \( \mu \)s in K\(_2\)LaCl\(_3\):0.001%Ce\(^{3+}\) to 2.3 \( \mu \)s in K\(_2\)LaCl\(_3\):0.7%Ce\(^{3+}\). Yet, for K\(_2\)LaCl\(_3\):10%Ce\(^{3+}\) it is 3.7 \( \mu \)s, in disagreement with the expected shortening. When we assume that the observed decay time in K\(_2\)LaCl\(_3\):0.001%Ce\(^{3+}\) is comparable with the lifetime of the STE luminescence, we can calculate the transfer rate \( k_r \) for K\(_2\)LaCl\(_3\) with higher dopant concentrations. The results are compiled in table 3 (column 5). It shows that the transfer rate increases when the Ce\(^{3+}\) concentration increases from 0.23 to 0.7%. The expected proportionality between \( k_r \) and the Ce\(^{3+}\) concentration is indeed observed. For K\(_2\)LaCl\(_3\) doped with 0.23 and 0.7 % Ce\(^{3+}\) the ratio in transfer efficiencies is given by 52.3/146=0.36, which is close to the 0.32, expected on the ratio in Ce\(^{3+}\) concentrations.

The transfer rate can also be calculated in another way. Combining equation (7) and (8) the ratio of the Ce\(^{3+}\) luminescence light yield to the total light yield can be written as \( k_r / (k_r + k_i) = k_r \tau \). Using the STE and Ce\(^{3+}\) luminescence light yields from table 1, we can calculate the ratio in the Ce\(^{3+}\) luminescence light yield and the total light yield. They are shown in table 3, column 3. We note that uncertainty of the Ce\(^{3+}\) luminescence yield for K\(_2\)LaCl\(_3\):0.001%Ce\(^{3+}\) is rather large. This is caused by the fact that part of the STE luminescence is absorbed and may be radiatively transferred to Ce\(^{3+}\) ions. When we correct the obtained ratio (in column 3) with the part of the Ce\(^{3+}\) luminescence, which is emitted in the non-exponential tail (column 4), we can calculate the transfer rate \( k_r \). The obtained values are shown in the last column of table 3. The transfer rate increases with more than a factor of 6 when going from the 0.001% to 0.23% Ce\(^{3+}\). At higher concentrations the transfer rate drops.

The transfer rates \( k_r \), obtained with the two methods based on the STE luminescence decay time and the light yields are presented in the last two columns of table 3. They are not
in agreement. This is not surprising in view of the simplicity of the model. The presence of other energy transfer processes will affect the transfer rate calculated from the light yields.

Now, let us consider the temperature dependence of the intensites of the STE and Ce\(^{3+}\) luminescence in K\(_2\)LaCl\(_3\):0.23\%Ce\(^{3+}\), see figure 3. Between 100 and 300 K the total light yield remains constant, which is in accord with equation (8). Above 300 K the total light yield decreases, due to thermal quenching of the STE luminescence. The quenching rate can be described by \(n v e^{-E_q/kT}\) with a frequency factor \(v\) and an activation energy \(E_q\). The temperature dependence of the light yield can then be written as \(\eta E_q/(1 + \tau v e^{-E_q/kT})\). The fit of this equation is drawn in figure 3 by the solid curve.

The increase of the Ce\(^{3+}\) luminescence intensity at the expense of the STE luminescence intensity in figure 3 below 250 K can be explained by a temperature dependency of the diffusion constant \(D\) in the transfer rate \(k\). The diffusion constant at a temperature \(T\) can be written as \(D = ce^{-E_q/kT}/\sqrt{T}\) [23],[24] where \(c\) is a constant. We note that this dependency is based on some assumptions. These are: i) the electron-lattice coupling is linear ii) the lattice vibrations are harmonic iii) there is one effective phonon mode involved in the STE jump iv) this dependency is only valid in the high temperature approximation. Using equation (6) and (7) and knowing the temperature dependence of \(k\), we can calculate the activation energy \(E_q\) that promotes the STE jump. Based on the temperature dependent yields of the STE and Ce\(^{3+}\) luminescence in figure 3 between 100 and 250 K and the 3.7 \(\mu\)s STE luminescence lifetime, we derive \(E_q\) to be in the order of 60 meV. We only mention the order of magnitude, since the STE diffusion is not the only energy transfer process (see table 3, the ‘non-exponential’ contribution). One of the above mentioned assumptions is that the high temperature approximation holds. This implies that \(\hbar \omega_p / kT \lesssim 1\) with \(\omega_p\) the average phonon energy promoting the jump. If this is not the case, the estimated activation energy indicates an upper limit [23]. Since the fit is performed on the Ce\(^{3+}\) luminescence intensity at temperatures as low as 100 K, the phonon energy involved should be smaller than 8 meV to be in the high temperature regime. Yet, this energy is considerably lower than the highest vibrational mode of \(\sim 28\) meV in K\(_2\)LaCl\(_3\):Er\(^{3+}\)[5]. Nevertheless, Tanimura et al. [19] made it plausible that soft phonon modes are involved in the STE hopping. In NaCl they found that phonons with energy of \(\sim 12\) meV are involved. So, despite the apparently low phonon energy, it remains well possible that the high temperature approximation is still valid.

The activation energy of 60 meV is in range with those found for the STE hopping motion in NaCl (150 meV [19], 210 meV [20]) and in NaI (70 meV [21]). The STE in these materials consist of \(V_k\) centre together with a bound electron, which may further relax to an F-H pair. The hole centre in the STE can be either regarded as a displaced \(V_k\)-centre or a displaced H-centre. The axial shift of the hole centre in the STE with respect to the \(V_k\)-centre is called the off-centre shift. This off-centre shift is related to the activation energy for the STE hopping motion: the larger the off-centre shift, the larger the activation energy. This off-centre shift is related to the activation energy for the STE hopping motion. According to calculations performed by Chen and Song [25],[26], the most probable model for the STE motion consists of a succession of a F-H permutation and the hopping of the H centre. Most energy of the jump is required by the permutation. Furthermore, they showed that materials with a large off-centre shift, such as KCl, have rather large activation energy, viz. \(\sim 1\) eV, for the STE hopping motion [25]. The off-centre shift of the \(V_k\) centre in the STE affects also
other properties. These are: low temperature F-centre creation yield, triplet-singlet lifetimes at 
low temperature and the Stokes shift [26]. We can only discuss on the latter property, since no 
data are available for the others. A large off-centre shift will induce a substantial lattice 
relaxation, which will result in a large Stokes shift. In order to estimate the Stokes shift, the 
bandgap energy should be known. Unfortunately, this is not exactly known. From the optical 
measurements, we can reasonably well assume that it is located at 6.2 eV or larger. In any 
case, it will be much smaller than the largest band gap value of 9 eV in LiCl [9] reported for a 
chloride. Knowing that the peak position of the STE luminescence is located at 3.07 eV, we 
derive that the Stokes shift is located between 3.1 and 5.9 eV. Following Chen and Song [26], 
we can express it also as a relative Stokes shift \( S_r \), i.e. the Stokes shift divided by the \( n=1 \) 
exciton energy. When we assume that the latter is comparable to the onset of the bandgap, we 
arrive at \( 0.5 \leq S_r < 0.65 \) for \( \text{K}_2\text{LaCl}_3 \). It is in range with the value for NaCl [26] (\( S_r = 0.57 \)), but 
it is smaller than in KCl (\( S_r = 0.68 \)) and RbCl (\( S_r = 0.69 \)), in which the hole centre has a large 
off-centre shift. Thus the relative Stokes shift is in accord with the low activation energy.

Energy transfer by binary electron-hole diffusion

So far, the energy transfer by STE diffusion has been considered. For \( \text{K}_2\text{LaCl}_3:10\%\text{Ce}^{3+} \) we 
have to use another model to explain the results. Because of the high \( \text{Ce}^{3+} \) concentration, 
energy transfer via diffusion of STEs is not likely. Either the STE is already trapped near a 
\( \text{Ce}^{3+} \) ion or the STE has only to hop to the next nearest neighbour site to excite a \( \text{Ce}^{3+} \) centre. 
We propose that binary-electron hole diffusion is involved, since the scintillation decay can 
be well described by a \((1+at)^{1.85}\) dependence. This is close to the \( t^2 \) dependence expected for 
this type of bimolecular recombination. We presume that upon absorption of ionising 
radiation electrons (or holes) are trapped as F (or \( V_k \)) centres on or near a \( \text{Ce}^{3+} \) centre. The 
self-trapped holes (or electrons), have to migrate to the \( \text{Ce}^{3+} \) related traps. Upon their 
recombination the \( \text{Ce}^{3+} \) centre is excited. The efficiency of this energy transfer is only 
hampered when electrons (or holes) are trapped elsewhere. Therefore, the light yield is less 
dependent of temperature as in the case of STE diffusion. This can be seen in the inset in 
figure 4.

Limitations of the diffusion models

These two mechanisms are probably most important in energy transfer. For low \( \text{Ce}^{3+} \) 
concentration the STE diffusion mechanism is dominant. With increasing \( \text{Ce}^{3+} \) concentration 
the probability that an F (or \( V_k \)) centre is trapped in the vicinity of a \( \text{Ce}^{3+} \) ion increases and 
thus the contribution of binary electron-hole recombination will be enhanced. Even for 
\( \text{K}_2\text{LaCl}_3:0.23\%\text{Ce}^{3+} \) part of the luminescence is transferred via this mechanism, since a small 
part of the \( \text{Ce}^{3+} \) luminescence is emitted in a non-exponential decay (see figure 10a and table 
3).

The presented models give a rather simplified picture of the actual energy transfer 
processes. The use of the diffusion constant in the transfer rate as \( k_t = 4\pi ND \) [27] is based 
on spatially uniform distributions of the centres involved in the energy transfer. In the current 
study these are the \( \text{Ce}^{3+} \) ions and the self-trapped carriers, such as STEs and \( V_k \) centres. Non-
uniformity in their distribution will disturb the validity of the models. The presence of 
spatially correlated \( \text{Ce}^{3+} \) centres may disturb the uniformity of the \( \text{Ce}^{3+} \) concentration in the
crystal lattice. Such centres have been observed in BaF$_2$:Ce$^{3+}$ [28] at high dopant concentrations. These centres can be easily identified, since the position of the absorption and emission bands of Ce$^{3+}$ clusters will be at other wavelengths than those of a single Ce$^{3+}$ ion in a compound. To check whether these clusters are present in K$_2$LaCl$_3$, we compared the position of the Ce$^{3+}$ luminescence bands in K$_2$LaCl$_3$ for different Ce$^{3+}$ concentrations. Only one emission band is observed for all the Ce$^{3+}$ concentrations. So we do not expect that the concentration of Ce$^{3+}$ clusters is high compared to the Ce$^{3+}$ concentration in the crystals. There is another phenomenon that may disturb the uniform distribution of (self-)trapped carriers. After absorption of ionising radiation, electrons and holes are created in the crystal in an ionisation track. It is possible that they are trapped near an impurity in the vicinity of this track. We think that this is likely to occur. The diffusion length of hot holes as a function of the impurity concentration serves as an indication. For NaCl:Ag$^+$ [29], it has been observed that the hot hole diffusion length decreased from ~200 lattice distances in pure NaCl distances to about 55 in NaCl:0.1% Ag$^+$. So it is expected that for high impurity concentrations, that the charge carriers become spatially correlated. We do not know how this correlation affects the energy transfer process.

6.5 Conclusions

Despite the high light yields and the good energy resolution of the K$_2$LaCl$_3$:Ce$^{3+}$ crystals, it is not likely that K$_2$LaCl$_3$:Ce$^{3+}$ will be applied as a scintillator. Firstly, the density of the material and the effective atomic number are much lower than those of the well known and commonly used scintillator NaI:Tl$^+$. Consequently, for a 662 keV $\gamma$-quantum the absorption length in K$_2$LaCl$_3$ is 4.5 cm whereas for NaI it amounts only 3.6 cm. Secondly, due to the small Ce$^{3+}$ Stokes shift part of the scintillation light is absorbed and emitted at a later time. Especially large crystals will suffer from this. Finally, the crystals contain the radioactive isotope $^{40}$K, which causes a background in pulse height spectra.

We have proposed two main energy transfer mechanisms, that of STE diffusion and of binary electron-hole recombination. These models need further confirmation. The diffusion constants of STEs and other self trapped carriers are dependent on temperature. Thus the decay times will alter considerably as a function of temperature. This can be checked by recording temperature dependent scintillation decay time spectra. Furthermore, the concentrations of e.g. STEs and F-centres after absorption of ionising radiation could be monitored by measuring for example time-resolved absorption spectra.

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7 Scintillation properties and energy transfer in RbGd₂Cl₇:Ce³⁺ and RbGd₂Br₇:Ce³⁺

7.1 Introduction

In the field of γ-ray detection, Tl⁺ doped NaI and CsI are widely used as scintillators. These materials, which have been discovered in 1948 [1] and 1951 [2], show light yields of ≥ 43,000 ph/MeV [3],[4],[5] under γ-ray excitation. Such high yields have not been reported for other scintillators. The ~27,000 ph/MeV of Lu₂SiO₅:Ce³⁺ [6],[7] is the next least.

In order to obtain high light yields, the number of thermalised electron-hole pairs, created per unit of absorbed γ-ray energy, should be high. As a rule of thumb, this number is inversely proportional to the band gap energy of a compound [8]. So small band gap materials are commendatory. In the past 30 years, the search for new scintillator materials has been focused on fluorides and oxides. These compounds have in general much larger band gap energies than e.g. iodides. Thus, the relatively low light yields of most of the studied compounds are not surprising. Chlorides and bromides have smaller band gap energies than fluorides and most oxides and are thus possible candidates as high-light yield scintillators. Nevertheless, they hardly gained interest so far, probably because of the hygroscopicity of most of them.

New commercially attractive scintillators should not only have a higher light yield but also have better performances on stopping power, decay time and proportionality as compared to NaI:Tl⁺ and CsI:Tl⁺. Consequently, we study the luminescence and scintillation properties of Ce³⁺ doped chlorides and bromides. Due to the electric dipole-allowed 5d-4f transition of the Ce³⁺ ion, the Ce³⁺ luminescence has a radiative decay time of typically ~40 ns. Provided that the energy transport to the Ce³⁺ centres is fast and efficient, fast luminescing and high light yield scintillators can be obtained.

Luminescence and scintillation properties of Ce³⁺ doped inorganic materials for gamma-ray detection
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In order to obtain the required stopping power elements with a high atomic number should be incorporated into the host lattice. For that purpose the element Gd is of interest. It has a high atomic number (Z=64), which can account for the required density and effective atomic number of the compound. There are also other reasons to study Gd-based scintillators. Firstly, Ce³⁺ can be easily incorporated on a Gd³⁺ site. Secondly, if electrons and holes, created after absorption of ionising radiation excite the Gd³⁺ ions, their energy can be fast and efficiently transferred via the Gd-sublattice to the Ce³⁺ centres. For this type of energy transfer the following requirements have to be fulfilled [9]: i) the Gd³⁺-Gd³⁺ distance should be short, i.e. 4-6 Å, ii) the Gd³⁺ luminescence should overlap a Ce³⁺ absorption band and iii) the Ce³⁺ luminescence wavelength should be larger than 350 nm. For the well-known scintillators Gd₂SiO₅:Ce³⁺ and GdAlO₃:Ce³⁺ these prerequisites are satisfied.

In the present study we report on the luminescence and scintillation properties of Ce³⁺ doped RbGd₂Cl₇ and RbGd₂Br₇. They crystallise in the RbDy₂Cl₇ structure [10],[11], having two crystallographic sites for the Gd³⁺ atoms. Both are co-ordinated by a trigonal-monocapped prism of halide ions (C₃v symmetry). Slightly unequal Gd³⁺-halide distances determine the difference in these two sites. In this lattice the [GdX₇₋₋] (X=Cl,Br) polyhedra form a layer in the [100] direction and a honeycomb-like structure in the [010] plane. The 2-dimensional layers are held together by Rb⁺ ions. Due to the layered structure the crystals cleave quite easily along the [010] plane.

In RbGd₂Cl₇ the distance of Gd³⁺ to the nearest Gd³⁺ neighbours is 3.86 Å (1 neighbour) and 4.31 Å (2 neighbours), and the nearest intraplane Gd³⁺-Gd³⁺ distance is 6.47 Å. RbGd₂Cl₇ has a density of 3.74 g/cm³ and an effective atomic number of 53.9. Unfortunately, the unit cell dimensions of RbGd₂Br₇ are not known. Based on the crystallographic data on other lanthanide chlorides and bromides we estimate the lattice constant to increase with 5% when changing the chloride for bromide for isostructural compounds. Therefore, we estimate the Gd³⁺-Gd³⁺ distance in RbGd₂Br₇ to be 4.07 Å (1 neighbour), 4.54 Å (2 neighbours) and 6.82 Å (intraplane). The effective atomic number of RbGd₂Br₇ is 50.6 and the estimated density is 4.8 g/cm³.

7.2 Experimental

Crystals were grown in the laboratory of Prof. Güdel in Bern by the Bridgman technique with a moving furnace and a static vertical ampoule starting from stoichiometric amounts of the binary halides RbX, GdX₃ and CeX₃ sealed into silica ampoules under vacuum. RbX (Merck, 99.5% suprapur) was dried in vacuum at 500 °C and the rare earth halides (purity > 99.99%) were prepared from oxides. RbGd₂Cl₇ and RbGd₂Br₇ melt congruently. The Ce³⁺ concentrations in the crystals were determined by a chemical analysis, in which a small part of the crystal boule was dissolved and subsequently sprayed into an argon plasma. From the characteristic luminescence intensities of the elements the Ce³⁺ content in the crystals was derived. Hereafter, we will express the determined Ce³⁺ concentrations as x in RbGd₂(1- x)Ce₂ₓX₇. From a comparison of the measured Ce³⁺ concentrations and those put in the melt,
the distribution coefficients were found to be $0.46 \pm 0.05$ and $0.81 \pm 0.05$ for RbGd$_2$Cl$_7$:Ce$^{3+}$ and RbGd$_2$Br$_7$:Ce$^{3+}$, respectively.

The obtained crystals are rather hygroscopic. During experimenting, some RbGd$_2$Cl$_7$:Ce$^{3+}$ crystals were exposed to air, which was dried with NaOH pellets. Over a couple of months, the quality of the samples worsened slightly due to hydration of the surface. Other crystals of RbGd$_2$Br$_7$:Ce$^{3+}$, with typical dimensions of $2 \times 2 \times 2$ mm$^3$, were sealed into small quartz cuvettes ($\Theta$ 0.65x3 cm) under nitrogen atmosphere. These quartz-sealed samples have been used for the optical characterisation, X-ray induced emission measurements and the recording of the scintillation decay time spectra. Only for pulse height measurements unprotected crystals were used.

For measurements at temperatures lower than room temperature, the start tube and the sample under study were cooled with a Peltier cooling, model TE-102TS-RF of Products for Research Inc. The temperature of the sample was monitored using a chromel-alumel thermocouple.

If not mentioned otherwise, all experiments were performed at room temperature.

### 7.3 Results under optical excitation

Figure 1 shows the absorption spectra of a RbGd$_2$Br$_7$:0.88%Ce$^{3+}$ crystal that has a thickness

![Absorption Spectra](image)

**Figure 1:** Optical absorption spectrum of RbGd$_2$Br$_7$:0.88%Ce$^{3+}$ at 11 K (dashed line) and 296 K (solid line), recorded using a Cary 5 E spectrophotometer. The Gd$^{3+}$ 4f-4f transitions are indicated by arrows. The spectral resolution is 0.3 nm FWHM.
between 0.1 and 0.2 nm. At 11 K, the typical transitions of the Gd$^{3+} \,^8S_{7/2}$ ground state to $^6D_j$, $^6I_j, \,^6P_j$ levels are visible near 250, 275 and 310 nm. In addition, broad bands are observed near 260, 270, 310 nm and 345 nm. The latter consists of two sub-bands. We assign these 5 bands to Ce$^{3+}$ 4f-5d transitions. The strong absorption below 240 nm is attributed to the onset of the fundamental absorption.

At 296 K, the Ce$^{3+}$ absorption bands are broadened, as is to be expected due to the population of higher vibrational levels in the ground and excited states. More noteworthy is the shift of the absorption band from 270 nm to 280 nm. This phenomenon is commonly observed for optical centres having a strong electron-lattice coupling. As examples we mention LiYbF$_4$:Ce$^{3+}$ [12] and ns$^2$-nsnp impurities in alkali halides [13]. It may originate from a thermal lattice expansion or an anharmonicity in the vibrational motion of the optical centre. Also the onset of the fundamental absorption shifts to longer wavelengths when the temperature increases. This may be due to thermal expansion of the lattice as well. Another contribution results from a temperature enhanced electron-phonon interaction. It causes the conduction band electrons to be scattered into higher energetic band states. The interaction between different states causes a lowering of the lowest energetic band state [14].

![Graphical representation of absorption and emission spectra](attachment:image.png)

**Figure 2:** (a) $\lambda_{exc} = 350$ nm induced emission spectrum of RbGd$_2$Br$_7$:0.11%Ce$^{3+}$. (b) optical absorption spectrum (dotted line) of RbGd$_2$Br$_7$:0.88%Ce$^{3+}$ and (c) excitation spectrum recorded at 420 nm of RbGd$_2$Br$_7$:0.11%Ce$^{3+}$. In the inset the absorption and excitation spectra near 275 nm are shown.

When excited at 350 nm, a broad luminescence band is observed, extending from 350 to 550 nm, see figure 2, curve a. We attribute it to Ce$^{3+}$ luminescence. The decay time of this luminescence is 30 ±3 ns, a typical value for the lifetime of the excited state of Ce$^{3+}$. The expected splitting of 2,000 cm$^{-1}$ in the Ce$^{3+}$ $^2F$ ground state can not be resolved. When we transform the wavelength-scale into an energy scale, we estimate the transitions from the lowest level of the Ce$^{3+}$ 5d configuration to the groundstate to be located at 24,900±300 cm$^{-1}$ (401±5 nm) and 22,900±300 cm$^{-1}$ (436±5 nm), respectively. The Stokes shift is estimated to
be 3100 cm⁻¹. The excitation spectrum in figure 2, curve c, shows excitation peaks at 277 and 346 nm. These peaks are also observed in the absorption spectrum (see figure 2, curve b).

![Figure 3: Excitation and emission of Ce₁ and Ce₂ centres in RbGd₂Br₇:0.11%Ce³⁺. The excitation spectra are recorded at 420 nm (solid line) and 450 nm (dashed line). The emission spectra are recorded after excitation at λₑₓᶜ = 275 nm (solid line) and λₑₓᶜ = 313 nm (dashed line).](image)

Excitation at 275 and 313 nm yields two different Ce³⁺ emissions showing slightly shifted emission bands. This can be seen in figure 3. We will call the centres showing these emissions Ce₁-centre (peaking at 410 nm) and Ce₂-centre (peaking at 435 nm). The excitation spectrum of the Ce₁-centre is similar to that shown in figure 2, curve c. The excitation spectrum of the Ce₂-centre contains a broad excitation band near 310 nm, on which the Gd⁳⁺ ⁸S⁷/₂⁻⁶P₁ transitions are superimposed. This band is also observed in the absorption spectrum (see figure 2, curve b), though it is very weak compared to the other Ce³⁺ ⁴f-⁵d absorption bands. We do not know, whether these observed optical centres reflect the two different crystallographic lattice sites, in which the Ce³⁺ ion can be incorporated. The low absorption coefficient of the 310 nm band as compared to the 345 nm band suggests that the Ce₂-center may be a Ce⁵⁺ ion on a perturbed lattice site. Consequently, the five observed Ce³⁺ ⁴f-⁵d absorption bands observed in figure 1 are due to more than one Ce³⁺ centre. In view of the low point symmetry at the crystallographic sites on which the Ce³⁺ ion is incorporated, a five-fold splitting in the levels of Ce³⁺ ⁵d configuration is expected for each Ce³⁺ centre. When we further assume that the Ce³⁺ ²F₅/₂ groundstate is positioned in the band gap, it implies that part of the levels of the Ce³⁺ ⁵d configuration are located in the conduction band.

The Gd³⁺ ⁶I₇/₂⁻⁸S₇/₂ transitions overlap the Ce³⁺ absorption band near 275 nm, as can be clearly seen in figure 1, curves b and c. Hence, Gd³⁺ → Ce³⁺ energy transfer is likely to occur. Yet, these Gd³⁺ lines are not visible in the excitation spectrum of figure 2, curve c. The inset of figure 2 shows the absorption of excitation spectrum around 275 nm in some more detail. On close examination one observes dips in the excitation spectrum at wavelengths where the absorption coefficient peaks. We will discuss this phenomenon later on.
The Gd$^{3+} \rightarrow$ Ce$^{3+}$ energy transfer is nicely expressed by figure 4, showing the time response of the Ce$^{3+}$ luminescence after excitation at 275 nm into the Gd$^{3+}$ $^8S_{7/2} \rightarrow ^6I_1$ transition and the overlapping Ce$^{3+}$ $4f5d$ transition. Figure 4, curve a shows the decay recorded for RbGd$_2$Br$_7$:0.11%Ce$^{3+}$.

![Figure 4: Time response of the Ce$^{3+}$ luminescence in (a) RbGd$_2$Br$_7$:0.11%Ce$^{3+}$ and (b) RbGd$_2$Br$_7$:0.88%Ce$^{3+}$ after excitation at 275 nm.](image)

Two exponential decay times can be distinguished, one with a decay time of 30 ns and another with a decay time constant in the μs regime. The fast component is mainly due to direct excitation of Ce$^{3+}$ and the slow one is due to Gd$^{3+} \rightarrow$ Ce$^{3+}$ transfer by energy migration on the Gd-sublattice. For higher dopant concentrations, only the fast component is observed, as is shown for RbGd$_2$Br$_7$:0.88%Ce$^{3+}$. We will discuss the Gd$^{3+} \rightarrow$ Ce$^{3+}$ transfer later in more detail. The Gd$^{3+}$ $^5P_{7/2}$ $^8S_{7/2}$ transitions also overlap the Ce$^{3+}$ $4f5d$ transition near 310 nm, see figure 3. However, no Gd$^{3+} \rightarrow$ Ce$^{3+}$ energy transfer could be observed in the time response of the Ce$^{3+}$ luminescence after excitation into the Gd$^{3+}$ $^8S_{7/2} \rightarrow ^6P_j$ transitions. Apart from the Gd$^{3+} \rightarrow$ Ce$^{3+}$ energy transfer, also Ce$^{3+} \rightarrow$ Gd$^{3+}$ energy transfer is effective. When excited at the Ce$^3+$ absorption band near 265 nm, also Gd$^{3+}$ emission is observed.

Figure 5 shows the excitation and emission spectra of RbGd$_2$Cl$_7$:2.5%Ce$^{3+}$. We note that the surface of this sample has slightly been hydrated after air-exposure. Therefore the shapes of excitation and emission bands differ somewhat from unhydrated RbGd$_2$Cl$_7$:Ce$^{3+}$. In any case, the peak positions of the Ce$^{3+}$ luminescence and excitation bands are shifted somewhat to the blue compared to those in RbGd$_2$Br$_7$. We attribute this to a difference in ligand polarisabilities and covalent bonding [15]. The first factor is held dominant in these materials. The larger polarisability of the Br$^-$ ion (atomic polarisability of 4.5 Å$^3$ [16]) than that of the Cl$^-$ ion (atomic polarisability of 3 Å$^3$ [16]) lowers the mean energy of the levels of the Ce$^{3+}$ 5d configuration more in RbGd$_2$Br$_7$ than in RbGd$_2$Cl$_7$. Therefore, the Ce$^{3+}$ 4f5d absorption bands in RbGd$_2$Cl$_7$ overlap mainly the Gd$^{3+}$ 6P levels and not the Gd$^{3+}$ 6I levels as in RbGd$_2$Br$_7$:Ce$^{3+}$. We did not study the Gd$^{3+} \rightarrow$ Ce$^{3+}$ energy transfer in this compound.
7.4 Results under excitation by ionising radiation

7.4.1 X-ray induced luminescence

The X-ray induced luminescence spectrum of RbGd₂Br₇:Ce³⁺ is shown in figure 6. By
comparison with the light yields obtained from pulse height spectra, the y-axis has been expressed in ph/(MeV nm). The luminescence of RbGd₂Br₇:0.02%Ce⁴⁺ in figure 6, curve a, consists of the characteristic Gd⁴⁺ ⁶P₇/₂-⁸S₇/₂ luminescence at 313 nm and a very broad band between 350 and 600 nm. The band is attributed to self-trapped exciton (STE) luminescence together with a weak Ce³⁺ emission. For other bromides, such as RbBr and CsBr, similar peak positions and bandwidths have been observed for STE emission [17]. For Ce³⁺ concentrations of 0.11% and higher, the Ce³⁺ 4f-5d luminescence is dominant and an increase in light yield is observed with increasing Ce³⁺ concentration, as can be seen in figure 6, curves b-d.

![Figure 7: X-ray induced emission spectra of RbGd₂Br₇:0.02%Ce³⁺ recorded at 117 and 400 K. In the inset the temperature dependence of the Gd³⁺ luminescence (denoted as *) and the STE luminescence (denoted as △) light yields are shown.](image)

Figure 7 presents the X-ray induced emission spectrum of RbGd₂Br₇:0.02%Ce³⁺ at different temperatures. At 100 K the STE luminescence is quite intense. As the temperature increases, the STE intensity lowers considerably with increasing temperature and at 400 K the intensity of this luminescence is only one-tenth of that at 100 K. Meanwhile, the peak position of the STE luminescence is shifted from 450 nm at 117 K to 400 nm at 400 K. We attribute this blue shift to quenching of the STE emission, while a weak Ce³⁺ luminescence remains present. This explains also the slightly asymmetric shape of the emission spectrum at 400 K. Opposed to the decrease of STE emission intensity with temperature, the Gd³⁺ ⁶P₇/₂-⁸S₇/₂ luminescence intensity shows an increase. As a result, the Gd³⁺ ⁶P₇/₂-⁸S₇/₂ luminescence yield is tripled between 100 and 400 K. From the X-ray induced emission spectra of RbGd₂Br₇:0.02%Ce³⁺, recorded at temperatures between 100 and 400 K, we estimated the Gd³⁺ ⁶P₇/₂-⁸S₇/₂ and STE emission intensities. Since the spectra are not corrected for the spectral sensitivity of the set-up, the obtained light yields serve only as an order of magnitude. They are shown in the inset of figure 7 as a function of temperature.
The X-ray induced emission spectra of RbGd$_2$Br$_7$:0.11%Ce$^{3+}$ at various temperatures are presented in figure 8. In all spectra the Ce$^{3+}$ 5d-4f and Gd$^{3+}$ 6$P_{7/2}$-8$S_{7/2}$ luminescence is visible. At low temperature, the luminescence intensity at wavelengths longer than 500 nm is quite pronounced, see figure 8, curve a. It decreases drastically when the temperature raises (Figure 8, curves b and c).

![Figure 8: X-ray induced emission spectra of RbGd$_2$Br$_7$:0.11%Ce$^{3+}$ recorded at (a) 118 K, (b) 200 K and (c) 400 K. In the inset the temperature dependence of the light yields of the Gd$^{3+}$ luminescence (denoted as +), the Ce$^{3+}$ luminescence (denoted as o) and the STE luminescence (denoted as Δ) are shown.](image)

We identify this emission as the high-wavelength part of the STE luminescence, in view of the equal band shape of the host lattice emission in RbGd$_2$Br$_7$:0.02%Ce$^{3+}$. Knowing the envelope of this emission, the light yields of STE, Ce$^{3+}$ and Gd$^{3+}$ 6$P_{7/2}$-8$S_{7/2}$ luminescence were estimated. They are shown in the inset of figure 8. We stress that the presented light yields are rough estimates. While the light yield of the Ce$^{3+}$ luminescence remains constant, the STE and Gd$^{3+}$ 6$P_{7/2}$-8$S_{7/2}$ luminescence intensities behave similarly as in RbGd$_2$Br$_7$:0.02%Ce$^{3+}$.

For RbGd$_2$Br$_7$ doped with 0.88 and 4.1 % Ce$^{3+}$, only Ce$^{3+}$ luminescence is observed between 100 and 400 K. The light yield remains constant in this temperature range. Apparently, the energy transfer to the Ce$^{3+}$ centres is the most efficient in these samples.

The X-ray induced emission spectra of RbGd$_2$Cl$_7$:Ce$^{3+}$ are presented in figure 9. They consist mainly of the Ce$^{3+}$ 5d-4f luminescence. The displacement of the peak position to longer wavelengths for increasing Ce$^{3+}$ concentration can be explained by an increase in self-absorption at the low-wavelength side. From the X-ray induced emission spectrum, recorded with the set-up employing the ARC VM502 monochromator (see chapter 3) we obtained for RbGd$_2$Cl$_7$:0.42%Ce$^{3+}$ a light yield of (40±4)$\times$10$^3$ ph/MeV.
7.4.2 Pulse height measurements

Light yields derived from pulse height spectra are compiled in table 1. Of the studied samples RbGd₂Br₇:4.1%Ce³⁺ shows the highest light yield of 54,700 ph/MeV. This number is considerably higher than the 43,000 ph/MeV of the well-known NaI:Tl⁺ [3]. In the RbGd₂Br₇:Ce³⁺ samples, most of the scintillation light is emitted within 0.5 µs. An increase of only ~10-20% in light yield is obtained for larger shaping times. In contrast, a significant part of the scintillation light in RbGd₂Cl₇:Ce³⁺ is emitted after 0.5 µs: the light yield increases with a factor ~1.6 when the shaping time is increased from 0.5 to 10 µs.

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>[Ce³⁺] in %</th>
<th>shaping time [µs]</th>
<th>light yield [phe/MeV]</th>
<th>light yield [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbGd₂Br₇</td>
<td>0.02</td>
<td>0.5</td>
<td>300±30</td>
<td>1,800±290</td>
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<tr>
<td></td>
<td></td>
<td>3</td>
<td>350±35</td>
<td>2,100±340</td>
</tr>
<tr>
<td>RbGd₂Br₇</td>
<td>0.11</td>
<td>0.5</td>
<td>1,260±60</td>
<td>7,600±1,100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>1,400±100</td>
<td>8,400±1,300</td>
</tr>
<tr>
<td>RbGd₂Br₇</td>
<td>0.88</td>
<td>0.5</td>
<td>4,900±200</td>
<td>29,400±4,700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>5,500±200</td>
<td>33,000±5,300</td>
</tr>
<tr>
<td>RbGd₂Br₇</td>
<td>4.1</td>
<td>0.5</td>
<td>8,300±200</td>
<td>49,900±8,000</td>
</tr>
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<td></td>
<td></td>
<td>3</td>
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<td>54,700±8,700</td>
</tr>
<tr>
<td>RbGd₂Cl₇</td>
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<td>0.5</td>
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<td>20,000±3,200</td>
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<td></td>
<td></td>
<td>10</td>
<td>6,600±850</td>
<td>40,000±11,000</td>
</tr>
<tr>
<td>RbGd₂Cl₇</td>
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<td>0.5</td>
<td>5,100±250</td>
<td>29,100±4,700</td>
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<tr>
<td></td>
<td></td>
<td>10</td>
<td>7,300±800</td>
<td>43,000±11,000</td>
</tr>
</tbody>
</table>
The energy resolution of the as-received crystals is in the order of 5-6% at 662 keV. One of the samples was cleaved into two pieces. We mounted one piece, which has dimensions of 7.4x5.3x1.15 mm$^3$, to record pulse height spectra.

![Pulse height spectra](image)

**Figure 10:** Pulse height spectra recorded with RbGd$_2$Br$_7$:4.1%Ce$^{3+}$ of X-rays and $\gamma$-rays of (a) $^{55}$Fe, (b) $^{241}$Am and (c) $^{137}$Cs sources. The fits of some photopeaks are indicated with dashed lines. The dotted line in (b) represents the contributions due to backscattering and escape of the characteristic X-rays of Rb and Br.
On top of the Teflon wrapped crystal we placed a small copper plate with a pinhole, on which the radioactive source was placed. In this way we were able to irradiate a small part of the sample at low γ-ray energies. Within an hour, pulse height spectra were recorded for several γ-ray energies, of which some are shown in figure 10. Part of the photopeaks has been fitted by gaussian curves and the obtained energy resolutions are compiled in table 2.

**TABLE 2: Energy resolution [in %] of RbGd₂Br₇:4.1%Ce³⁺ at different excitation energies.** The second column the number of detected photoelectrons (N_{photo}) is presented. The measured energy resolution (R), the photomultiplier (R_{p}) and the scintillator resolution (R_{sc}) are shown in column 3-5.

<table>
<thead>
<tr>
<th>energy [keV]</th>
<th>N_{photo}</th>
<th>R</th>
<th>R_{p}</th>
<th>R_{sc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9</td>
<td>60</td>
<td>43.9</td>
<td>30.2</td>
<td>31.9</td>
</tr>
<tr>
<td>32.1</td>
<td>288</td>
<td>23.9</td>
<td>19.0</td>
<td>14.5</td>
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<tr>
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<tr>
<td>662</td>
<td>5960</td>
<td>3.8</td>
<td>2.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Some of the obtained fits are shown in figure 10 by dashed curves. Figure 10, curve b, shows the pulse height spectrum measured with γ-rays and X-rays from a ²⁴¹Am source. In addition to the characteristic photopeaks, we observe a rather broad band peaking at 45 keV. This band contains contributions of backscattering (at 48 keV) and the escape of the characteristic X-rays of Rb and Br. Unfortunately, we were not able to separate these contributions. The photopeak in figure 10, curve c, is accompanied with a satellite peak at somewhat lower energy. It is due to the escape of the characteristic X-rays of Gd. The full energy peak has an energy resolution of only 3.8%. Such a small value has never been obtained before. Even the 4.3 % for a CsI:Tl⁺ crystal mounted on a small silicon drift chamber, obtained only recently [18], is higher. In the range from 17.1 to 835 keV the light yield relative to that at 662 keV remains equal within a margin of 7%. So, the scintillation response is proportional to the γ-ray energy.

Due to the presence of radioactive ⁸⁷Rb in the samples, scintillation pulses are generated intrinsically. This isotope, having a natural abundance of 27%, emits β-particles with endpoint energy of 275 keV. Therefore, in the pulse height spectra a β-continuum will be present as a background. Per cm³ of RbGd₂Cl₇ and RbGd₂Br₇ this results in 430 and 340 counts/s, respectively.

### 7.4.3 Scintillation decay

Figure 11 and 12 shows the scintillation decay time spectra of Ce³⁺ doped RbGd₂Br₇. The rising slope in figure 11 before t=0 is due to an experimental artefact and does not represent a genuine part of the scintillation pulse. It is caused by the poor optical coupling of the quartz-sealed samples to the PMT-window, resulting in a low number of photoelectrons present at the start, giving rise to a jitter in the starting moment. The spectra consist of a weak build-up of scintillation intensity, an exponential decay component dominating at times shorter than 300 ns and a non-exponential decay extending beyond 2 µs. For Ce³⁺ concentrations larger
than 0.02% Ce$^{3+}$ the main exponential decay time shortens with increasing Ce$^{3+}$ concentration, see figure 11. Contrary to this Ce$^{3+}$ concentration dependence, the shape of the non-exponential tail remains the same. A reasonable fit of this tail could be obtained assuming a time dependence of $e^{-bt}$ ($b=0.11\pm0.01 \text{ (ns)}^{-1}$) and even better results were obtained with $(1+at)^{-a}$ ($a=4\pm2 \text{ (ns)}^{-1}$ and $a=2\pm0.1$). In table 3, we have compiled the main exponential decay times and the time in which 90% of the scintillation light is emitted. From the decay time spectra, we deduce that ~96% of the light is emitted within 3 µs.
TABLE 3: The main scintillation decay time (τ) and the time (t_{90\%}) in which 90% of the total light yield has been emitted for RbGd_{2}Br_{7}:Ce^{3+} and RbGd_{2}Cl_{7}:Ce^{3+}, as obtained from scintillation decay time spectra. If not denoted otherwise, the obtained values were derived from spectra measured at room temperature.

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>[Ce^{3+}]</th>
<th>τ [ns]</th>
<th>t_{90%} [ns]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>0.02</td>
<td>104±2</td>
<td>410</td>
</tr>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>0.11</td>
<td>132±4</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td></td>
<td>220±2 (T=273 K)</td>
<td></td>
</tr>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>0.88</td>
<td>87±3</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td></td>
<td>132±5 (T=254 K)</td>
<td></td>
</tr>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>2.05</td>
<td>91±2</td>
<td>550±50</td>
</tr>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>4.1</td>
<td>66±4</td>
<td>550</td>
</tr>
<tr>
<td>RbGd_{2}Br_{7}</td>
<td>9.8</td>
<td>65±6</td>
<td>470</td>
</tr>
<tr>
<td>RbGd_{2}Cl_{7}</td>
<td>1</td>
<td>405±30</td>
<td>6550</td>
</tr>
<tr>
<td>RbGd_{2}Cl_{7}</td>
<td>5</td>
<td>166±9</td>
<td>4450</td>
</tr>
</tbody>
</table>

Figure 13: (a) Scintillation decay time spectra of RbGd_{2}Br_{7} doped with (a) 0.11% and (b) 0.88% at room and lower temperature. In the inset the scintillation decays in the first 10 μs are shown on a log-log scale. The spectra are recorded using the conventional configuration.
7.5 Discussion

When the temperature decreases, the scintillation decay becomes slower, as can be seen in figure 13. The initial decay time increases with ~ 50% when the temperature is lowered with approximately 30 °C, see also table 3. Also the non-exponential scintillation component becomes longer as can be seen in the insets of figure 13.

The scintillation decay time spectra of RbGd₂Cl₇ are shown in figure 14. Compared to the scintillation response of RbGd₂Br₇:Ce³⁺ in figure 11, that of RbGd₂Cl₇:Ce³⁺ is much slower, a conclusion already drawn based on the light yields derived from pulse height spectra. Some properties are compiled in table 3.

![Figure 14](image_url)

Figure 14: (a) Scintillation decay time spectra of (a) RbGd₂Br₇:0.88%, (b) RbGd₂Cl₇:2.5%Ce³⁺ and (c) RbGd₂Cl₇:0.42%Ce³⁺. In the inset the scintillation decays in the first 20 μs are shown. Note the logarithmic x-axis. The spectra are recorded using the conventional configuration.

7.5 Discussion

In this section first the scintillation properties of RbGd₂Br₇:Ce³⁺ are discussed and compared with the well-known scintillators CsI:Tl⁺ and NaI:Tl⁺. Next we focus on the energy transfer mechanisms in RbGd₂Br₇:Ce³⁺. First the possibility of energy transfer via energy migration on the Gd-sublattice after optical excitation is discussed. After that the scintillation mechanism is discussed.

7.5.1 Scintillation properties

The light yield of the Ce³⁺ doped RbGd₂Br₇ samples is very high, with a maximum yield for RbGd₂Br₇:4.1%Ce³⁺. In order to calculate energy transfer efficiency, it is necessary to know the number of thermalised e-h pairs per MeV of absorbed γ-ray energy. This can be estimated,
knowing that for halides the energy needed for the creation of an e-h pair amounts ~2 times the band gap energy [8]. From the low temperature absorption spectrum in figure 1 the onset of the fundamental absorption edge is located at 5.2 eV. As a rough estimate we assume the band gap energy to be ~ 5.6 eV, which is in range 5-6 eV valid for other lanthanide bromides [19]. Accordingly, the number of created e-h pairs per MeV of absorbed γ-quantum energy will be ~89,000. Since the light yield of RbGd₂Br₇:4.1%Ce³⁺ amounts 54,700 ph/MeV, this implies that ~60 % of the e-h pairs excite a Ce³⁺ ion, that gives rise to Ce³⁺ luminescence.

Another noteworthy property is the 3.8 % energy resolution recorded with RbGd₂Br₇:4.1%Ce³⁺. The measured energy resolution (R) consists of the photomultiplier (Rₚ) and the scintillator resolution (Rₛ) [20]. The first term is due to the spread in the detected number of photoelectrons (Nₚₑₑ) and the variance in the photomultiplier gain (vₚₑₑ) and can be written as $Rₚ = 2.36(1 + vₚₑₑ)/Nₚₑₑ$. For an XP2020Q PMT the variance in gain is 0.09. In the PMT 5960 phe are detected after absorption of a 662 keV γ-quantum, see table 2. Thus $Rₚ$ is 3.2 %. The remaining part, the scintillator resolution $Rₛ = \sqrt{R^2 - Rₚ^2}$, amounts 2.1%. It contains the intrinsic and the scintillator resolution. Contributions due to the non-proportional response, the variation of reflectivity of the reflective coating, crystal inhomogeneities and non-uniformity of the photo-cathode are held responsible [20]. Since the light yield is proportional to the γ-ray energy, the non-proportionality is negligible. The fact that after cleavage of the original crystal piece the energy resolution decreased suggests that the contribution due to crystal inhomogeneity is the most important.

Let us consider the energy resolutions obtained at lower γ-ray excitation energy. Table 2 shows that the measured energy resolution (R) is much larger than one would expect based on the statistics in the number of detected photoelectrons (Rₚₑₑ). This implies that the scintillator resolution Rₛ is rather large, which can not be explained by an overall decrease in crystal quality during the measurement series. This is certainly clear, when we compare the scintillator resolutions of the 32.1 keV Ba X-ray and the 662 keV photopeak, which have been obtained from the same pulse height spectrum (Figure 10, curve c). The cause for this discrepancy lies in the different properties of the surface layer and the crystal bulk. For a 662 keV photon the absorption length is 2.8 cm, implying that the γ-rays are uniformly absorbed in the crystal bulk. For the lower energies they are considerably shorter: at 59.5 keV 0.36 mm, at 32.1 keV ~0.15 mm and at 5.9 keV ~9.5 μm. As a result, these low energetic photons are only absorbed in the surface layer of the crystal. Apparently, the crystal quality of this layer is not so homogeneous as of the crystal bulk. This is not surprising, considering the hygroscopicity of the samples. Despite the measures taken to lower the humidity of ambient air, hydration of the surface layer could not be completely prevented.

For a detailed comparison of the scintillation properties with those of NaI:Tl⁺ and CsI:Tl⁺, we compiled some features in table 4. The most important properties such as light yield and stopping power of RbGd₂Br₇:4.1%Ce³⁺ are similar to those of the other scintillators. The main advantages compared to the iodide scintillators concern the energy resolution and the short response time of the scintillator. Yet, RbGd₂Br₇:4.1%Ce³⁺ has some serious drawbacks. The material is rather hygroscopic and brittle. Moreover, the presence of the
radioactive isotope $^{87}$Rb in the lattice causes an unwanted background in pulse height spectra. Especially this disadvantage may limit the use of this material as a scintillator.

**Table 4:** Comparison of scintillation properties of RbGd$_2$Br$_7$:4.1%Ce$^{3+}$ with NaI:Tl$^+$ and CsI:Tl$^+$

<table>
<thead>
<tr>
<th></th>
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<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>density [g/cm$^3$]</td>
<td>3.67</td>
<td>4.51</td>
<td>4.79</td>
</tr>
<tr>
<td>effective atomic number</td>
<td>50.8</td>
<td>53.7</td>
<td>50.6</td>
</tr>
<tr>
<td>attenuation length in [cm] for a photon of 150 keV</td>
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<td>0.30</td>
<td>0.37</td>
</tr>
<tr>
<td>511 keV</td>
<td>2.92</td>
<td>2.30</td>
<td>2.27</td>
</tr>
<tr>
<td>emission maximum [nm]</td>
<td>415</td>
<td>540</td>
<td>420</td>
</tr>
<tr>
<td>light yield [ph/MeV]</td>
<td>43,000</td>
<td>66,800</td>
<td>54,700</td>
</tr>
<tr>
<td>energy resolution (%)</td>
<td>5.6</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td>primary decay time [ns]</td>
<td>230</td>
<td>~1000</td>
<td>66</td>
</tr>
<tr>
<td>$\tau_{50%}$ [ns]</td>
<td>680</td>
<td>~5000</td>
<td>580</td>
</tr>
<tr>
<td>number of background counts [count/s.cm$^2$]</td>
<td>0</td>
<td>0</td>
<td>340</td>
</tr>
<tr>
<td>cleavage plane</td>
<td>[100]</td>
<td>none</td>
<td>[100]</td>
</tr>
<tr>
<td>hygroscopic plane</td>
<td>yes</td>
<td>slightly</td>
<td>yes</td>
</tr>
</tbody>
</table>

7.5.2 Energy transfer: migration after excitation into the Gd$^{3+}\rightarrow$Ce$^{3+}$ transitions

After optical excitation into the $^8$S$_{7/2}\rightarrow$6$I_1$ transitions of Gd$^{3+}$ the energy is efficiently transferred to Ce$^{3+}$ centres, as can be clearly seen in figure 4. The presence of two exponential decay time components in this figure indicates that the energy migration on the Gd-sublattice is of the fast diffusion type. This means that the Gd$^{3+}\rightarrow$Gd$^{3+}$ energy transfer rate is much higher than the Gd$^{3+}\rightarrow$Ce$^{3+}$ energy transfer rate and other depopulation rates of the Gd$^{3+}$ $^6$I levels e.g. by radiative Gd$^{3+}$ luminescence. As a result the Gd$^{3+}$ ions act collectively. For such type of transfer, Suzuki et al. [21] modelled the time response of the Ce$^{3+}$ luminescence intensity after excitation into Gd$^{3+}$ 4f-4f transition and the overlapping Ce$^{3+}$ 4f-5d transition. This model has further been refined by Schaart et al. [22] by allowance for Ce$^{3+}\rightarrow$Gd$^{3+}$ backtransfer. Accordingly, the time response can be described as a summation of two exponential decays, one with a fast ($W_f$) and another ($W_s$) with a slow decay rate. These rates are given by:

$$W_f = W_{Ce} + W_{Ce\rightarrow Gd}C_{Gd}n \approx W_{Ce}$$  \hspace{1cm} (1)

$$W_s = W_{Gd} + W_{Gd\rightarrow Ce}C_{Ce}n \approx W_{Gd\rightarrow Ce}C_{Ce}n$$  \hspace{1cm} (2)

where $W_{Ce}$, $W_{Gd}$, $W_{Ce\rightarrow Gd}$, $W_{Gd\rightarrow Ce}$ are respectively the radiative decay rate of the Ce$^{3+}$ 5d-4f transition, the depopulation rate of the Gd$^{3+}$ 4f level other than due to transfer to Ce$^{3+}$, the Ce$^{3+}\rightarrow$Gd$^{3+}$ and the Gd$^{3+}\rightarrow$Ce$^{3+}$ resonance energy transfer rates. $C_{Gd}$ and $C_{Ce}$ denote the Gd$^{3+}$ and Ce$^{3+}$ concentrations and $n$ the number of next nearest Gd$^{3+}$ neighbours. For RbGd$_2$Br$_7$ $n$ equals 3. Note that $C_{Gd} = 1 - C_{Ce}$. Equation (1) can be simplified under the assumption that $W_{Ce\rightarrow Gd}C_{Gd}n \ll W_{Ce}$. This is shown in the last term of this equation (1). Similarly equation (2) can be simplified assuming that $W_{Gd} \ll W_{Gd\rightarrow Ce}C_{Ce}n$. 

W_{Gd} includes the radiative recombination rate of the Gd^{3+} 6I_{7/2} \rightarrow 8S_{7/2} luminescence, but also the transition rate to killer centres and non-radiative decay rate to the Gd^{3+} 6P level, see also figure 15. So, we can write for $W_{Gd}$:

$$W_{Gd} = W_{t \rightarrow P, nr} + W_{t \rightarrow k} + W_{t \rightarrow S, rad}$$

(3)

where $W_{t \rightarrow P, nr}$ is the non-radiative decay rate to the Gd^{3+} 6P state, $W_{t \rightarrow k}$ the transfer rate to killer centres, via energy migration on the Gd^{3+} 6I level and $W_{t \rightarrow S, rad}$ is the radiative recombination rate of the Gd^{3+} 6I_{7/2} \rightarrow 8S_{7/2} transition. Of these rates, $W_{t \rightarrow P, nr}$ is the largest, since the Gd^{3+} 6I_{7/2} \rightarrow 8S_{7/2} luminescence is absent and the transfer rate to Ce^{3+} centres is expected to be much larger than to killer centres.

By fitting the two exponential decay curves in figure 4 using equation (1) and (2), the transition and the energy transfer rates were estimated. The fast decay rate $W_f$ equals the $3.7 \times 10^7$ s$^{-1}$ radiative decay rate of the Ce$^{3+}$ 5d-4f transition and is independent of the Ce$^{3+}$ concentration. According to equation (1), this implies that $W_{Ce \rightarrow Gd}$ must be smaller than $5 \times 10^6$ s$^{-1}$. The slow decay rate $W_s$ appears to increase proportionally with the Ce$^{3+}$ concentration from $2 \times 10^6$ s$^{-1}$ in the 0.11%Ce$^{3+}$ doped sample to $16 \times 10^6$ s$^{-1}$ in RbGd$_2$Br$_7$-0.88% Ce$^{3+}$. By inspection of equation (2) this indicates that $W_{Ce \rightarrow Gd} \ll W_{Gd \rightarrow Ce,Ce,n}$. From these values, we obtain $W_{Gd \rightarrow Ce}$ to be $(6.0 \pm 0.3) \times 10^8$ s$^{-1}$ and $W_{Gd} < 5 \times 10^5$ s$^{-1}$. In table 5 we have compiled the obtained values for the transfer and transition rates. From the values presented in this table and using equation (2) it appears that for Ce$^{3+}$ concentrations $> 0.88\%$ the slow decay rate ($W_s$) has about the same order of magnitude as the radiative decay of the Ce$^{3+}$ 5d-4f transition ($W_{Ce}$). It can be shown with the equations presented in [22] that the slow decay component disappears and that $W_s \approx W_{Ce}$. This means that energy transfer via the Gd-sublattice is so fast, that it is almost instantaneously transferred to a Ce$^{3+}$ centre.
Now the transition rates are known, we can determine whether the energy migration on the Gd-sublattice is of the exchange type. For that purpose, the results obtained from a detailed study on the energy transfer process in Li(Y,Gd)F₄ can be used [23]. In this compound the Gd³⁺→Gd³⁺ migration is governed by exchange interaction. The migration rate via the Gd³⁺ 6I₇/₂ level is ~2.8×10⁷ s⁻¹. Knowing that the shortest Gd³⁺-Gd³⁺ distances in Li(Y,Gd)F₄ is 3.75 Å and in RbGd₂Br₇ 4.07 Å, we expect a Gd³⁺→Gd³⁺ transfer rate of ~2.8×10⁷ exp(-4.07/3.75) = ~9×10⁶ s⁻¹ for exchange interaction. In order to be in the fast migration regime, we recall that the Gd³⁺→Gd³⁺ transfer efficiency should be larger than the Gd³⁺→Ce³⁺ transfer rate of 6×10⁸ s⁻¹. Therefore, a transfer type other than by exchange interaction should be dominant. We can think of electric dipole-electric dipole resonance energy transfer. Such type of transfer is possible in RbGd₂Br₇, since the rare-earth site lacks inversion symmetry. As a result, Gd³⁺ 5d wavefunctions can be mixed into the Gd³⁺ 4f wavefunction. Similar conclusions were made for the Gd³⁺→Gd³⁺ interaction mechanism in gadolinium oxides [24].

The last part in this section is devoted to the dips in the excitation spectrum near 278 nm, see figure 2, curve c. It is not likely that these are due to surface quenching. This type of quenching is observed when the radiation has a small penetration depth, i.e. for high absorption coefficients [25]. Yet, the Gd³⁺ 4f-4f absorption strength is quite small. Furthermore, due to the fast energy diffusion on the Gd-sublattice, the excitation energy is efficiently transported into the crystal. Instead, it is better explained by the fact that not all energy that migrates on the Gd-sublattice is transferred to Ce³⁺ centres. In order to explain this, the observed excitation quantum efficiency will be calculated.

Yet, the Gd³⁺ 4f-4f absorption strength is quite small. Furthermore, due to the fast energy diffusion on the Gd-sublattice, the excitation energy is efficiently transported into the crystal. Instead, it is better explained by the fact that not all energy that migrates on the Gd-sublattice is transferred to Ce³⁺ centres. In order to explain this, the observed excitation quantum efficiency will be calculated.

For simplification we assume that Ce³⁺→Gd³⁺ backtransfer can be neglected and that all incident photons near 275 nm are absorbed. The latter is reasonable, since the excitation spectrum was measured on a RbGd₂Br₇:0.11%Ce³⁺ sample having a thickness of ~1mm. The former presumption is valid as well. We will show this below. Let us assume that only the Ce³⁺ ions are continuously excited. Part of the excitation energy will be transferred to Gd³⁺ ions. With the help of figure 13, the following steady-state equation can be written that describes the population of the Gd³⁺ 4f level:

<table>
<thead>
<tr>
<th>Transition probability</th>
<th>rate [s⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>WₐCe</td>
<td>3.7×10⁷</td>
</tr>
<tr>
<td>WₐGd</td>
<td>&lt;5×10⁴</td>
</tr>
<tr>
<td>WₐGd→Ce</td>
<td>(6.0±0.3)×10⁸</td>
</tr>
<tr>
<td>WₐCe→Gd</td>
<td>&lt;5×10⁶</td>
</tr>
</tbody>
</table>
\[-(W_{\text{Gd}} + W_{\text{Gd} \rightarrow \text{Ce}} nC_{\text{Ce}}) N_{\text{Gd}} + W_{\text{Ce} \rightarrow \text{Gd}} nC_{\text{Gd}} N_{\text{Ce}} = 0 \quad (4)\]

where \(N_{\text{Gd}}\) and \(N_{\text{Ce}}\) are the number of excited Gd\(^{3+}\) and Ce\(^{3+}\) ions. Using this equation, the ratio \(W_{\text{Gd}} N_{\text{Gd}} / W_{\text{Ce}} N_{\text{Ce}}\) can be written as \(W_{\text{Gd}} W_{\text{Ce} \rightarrow \text{Gd}} C_{\text{Gd}} / W_{\text{Ce}} W_{\text{Gd} \rightarrow \text{Ce}} C_{\text{Ce}}\). Using the values presented in Table 2, this ratio appears to be less than 10% for RbGd\(_2\)Br\(_7\)·0.11%Ce\(^{3+}\). So, the effect of Ce\(^{3+} \rightarrow\)Gd\(^{3+}\) backtransfer is negligible. Now, a simple expression for the observed excitation quantum efficiency can be derived. The fraction of the incident photon flux \(I_{ph}\) that excite the Gd\(^{3+}\) and Ce\(^{3+}\) ions is respectively \(\alpha_{\text{Gd}} / (\alpha_{\text{Ce}} + \alpha_{\text{Gd}})\) and \(\alpha_{\text{Ce}} / (\alpha_{\text{Ce}} + \alpha_{\text{Gd}})\), where \(\alpha_{\text{Gd}}\) and \(\alpha_{\text{Ce}}\) denote the absorption coefficients due to Gd\(^{3+}\) 4f-4f and Ce\(^{3+}\) 4f-5d transitions. For the observed excitation quantum efficiency \(L\) can then be written:

\[L \approx \frac{\eta_{\text{Ce}}}{\alpha_{\text{Ce}} + \alpha_{\text{Gd}}} \left(1 - \frac{W_{\text{Gd} \rightarrow \text{Ce}} nC_{\text{Ce}}}{W_{\text{Gd}} + W_{\text{Gd} \rightarrow \text{Ce}} nC_{\text{Ce}}}\right) \quad (5)\]

where \(\eta_{\text{Ce}}\) is the luminescence efficiency of the Ce\(^{3+}\) ion. The above equation is easy to understand: The first term indicates the fraction of the totally absorbed light that is absorbed directly by Ce\(^{3+}\) ions resulting in luminescence and the second part gives the fraction absorbed by Gd\(^{3+}\) ions that is transferred to Ce\(^{3+}\), subsequently resulting in luminescence.

By inspection of the absorption spectrum of RbGd\(_2\)Br\(_7\)·0.88%Ce\(^{3+}\) in figure 2, we have to realise that the Ce\(^{3+}\) absorption strength in RbGd\(_2\)Br\(_7\)·0.11%Ce\(^{3+}\) is a factor of 8 lower. As a consequence, almost all the 275 nm light will be absorbed by Gd\(^{3+}\) ions. If 100 photons are absorbed near 275 nm, we deduce from the inset of figure 2 that about 80-90 of them will be transferred to Ce\(^{3+}\) and give rise to luminescence. The other 10-20 photons are lost due to Gd\(^{3+}\) luminescence or transfer to killer centres. Since \(W_{\text{Gd} \rightarrow \text{Ce}} nC_{\text{Ce}}\) is known to be \(2 \times 10^6\) s\(^{-1}\) (see Table 2), we can roughly estimate \(W_{\text{Gd}}\) to be \((3 \pm 1) \times 10^5\) s\(^{-1}\). This is in agreement with the previously estimated \(W_{\text{Gd}} < 5 \times 10^5\) s\(^{-1}\).

7.5.3 Scintillation mechanism

In the previous section, the energy transfer on the Gd-sublattice was discussed after optical excitation. Under excitation of ionising radiation the energy transfer process may involve many other processes than the energy migration on the Gd-sublattice alone. These processes are considered in this section. The absorption of ionising radiation produces one or more high-energetic electrons, which generate secondary electrons and holes. In turn, these may produce secondary electrons and holes as well. When further ionisation is not possible, the electrons and holes will be either trapped near an impurity or will thermalise and they may become self-trapped as STEs and V\(_k\) centres. Part of the charge and energy carriers will excite the luminescence centres.

The role of the Gd\(^{3+}\) ions in the scintillation process

Let us first pay attention to the excitation mechanism of the Gd\(^{3+}\) ions. In RbGd\(_2\)Br\(_7\)·0.02%Ce\(^{3+}\) the STE luminescence intensity decreases with temperature, whereas the Gd\(^{3+}\) luminescence intensity increases, see figure 7. This anti-correlation of the STE and Gd\(^{3+}\) luminescence yields with temperature can not be due to transfer from STE energy, since
the energy of the STEs is much too low to excite the Gd$^{3+}$ ions. It is well known, that the STE formation at excitation energies much larger than the band gap energy consists of subsequent hole self-trapping, electron capture and further lattice relaxation [26]. The efficiency of this capture process decreases with temperature [27] and thus the chance that the electron is trapped elsewhere will increase. Such a mechanism may be efficient in RbGd$_2$Br$_7$;0.02%Ce$^{3+}$. Apparently, the STE formation efficiency decreases with temperature, resulting in a higher chance that an electron or hole is trapped on Gd$^{3+}$. The charge carrier of opposite charge diffuses to this Gd$^{3+}$-trapped carrier and upon recombination, the Gd$^{3+}$ ion is excited. This may explain the increase of the Gd$^{3+}$ luminescence yield with temperature.

The contribution of the Gd$^{3+}$ luminescence to the total light yield is negligibly small, whereas the scintillation efficiency of the Ce$^{3+}$ luminescence is very high. In fact, the role of the Gd$^{3+}$ ions as an energy transmitter to the Ce$^{3+}$ ions is of minor importance in the scintillation energy transfer. We have the following reasons for this hypothesis:

1. The Ce$^{3+}$ luminescence light yield increases considerably beyond the Ce$^{3+}$ concentration of 0.88 %, see table 1. This holds both for the exponential and the non-exponential part in the scintillation decay, see figure 11. Now, if most energy is transferred to Ce$^{3+}$ ions via Gd$^{3+}$ ions, only a slight increase in light yield is expected for Ce$^{3+}$ concentrations larger than 0.88%. Thence almost all excited Gd$^{3+}$ ions will transfer their energy to Ce$^{3+}$ centres; thus no excitation energy is lost (see previous section).

2. In RbGd$_2$Br$_7$;0.11 %Ce$^{3+}$ the light yield of the Ce$^{3+}$ luminescence remains constant with temperature, whereas the Gd$^{3+}$ luminescence intensity increases with temperature. Thus, the Ce$^{3+}$ ions can not be excited by energy migration on the Gd-sublattice, since then the light yield would be linearly dependent of the Gd$^{3+}$ luminescence intensity. We conclude that the energy transfer to the Ce$^{3+}$ ions is different than that to the Gd$^{3+}$ ions.

3. The main scintillation decay time shortens drastically with increasing Ce$^{3+}$ concentration, see figure 11 and table 3. This indicates that the energy transfer process of this fast component has no relationship with the energy migration on the Gd-sublattice. In case of energy transfer by energy migration on the sublattice, we would expect that the shape of the scintillation decay to be almost independent of the Ce$^{3+}$ concentration for Ce$^{3+}$ concentrations larger than 0.88%, as has been made clear in the previous section.

So we conclude that the role of Gd$^{3+}$ in the energy transfer process is negligibly small in RbGd$_2$Br$_7$;Ce$^{3+}$. A similar situation was reported by Welker et al. [28] in a study on the excitation mechanism in the cathode-ray phosphor GdOBr;Ce$^{3+}$. By contrast, in the well-known scintillators GdAlO$_3$;Ce$^{3+}$ and Gd$_2$SiO$_5$;Ce$^{3+}$, the role of Gd$^{3+}$ as energy transmitter in the energy transfer is held dominant. For these materials, it is assumed that part of electron-hole pairs is directly trapped by Ce$^{3+}$ and Gd$^{3+}$ ions. Accordingly, the scintillation decay is composed of the fast exponential Ce$^{3+}$ 5d-4f luminescence decay and of the slower Ce$^{3+}$ luminescence decay fed by energy migration on the Gd-sublattice. Ishibashi [29] explains the scintillation decay in Gd$_2$SiO$_5$;Ce$^{3+}$ as the diffusion of V$_k$ centres to Ce$^{3+}$ centres. Yet, only moderate agreement between the predicted and the measured scintillation decay was obtained using this model. Furthermore, for Gd$_2$SiO$_5$;Ce$^{3+}$ containing Ce$^{3+}$ concentrations of 0.1 mol%
and less, the light yields related to the obtained fits are much lower than the actual measured light yields. Therefore, it is unlikely that bimolecular diffusion is significant in Gd$_2$SiO$_5$:Ce$^{3+}$.

Exclusion of possible energy transfer mechanisms

We concluded that the Gd$^{3+}$ ions do not play an important role in the scintillation energy transfer. Still, numerous other energy transfer processes may be involved. Some of them can be excluded. These are radiative energy transfer between the STE and Ce$^{3+}$ and resonance energy transfer between the STE and Ce$^{3+}$. In the first mechanism the Ce$^{3+}$ ions are excited by absorption of STE luminescence. Then the low light yield of the STE luminescence would be measured, in disagreement with the observed high light yields. The second mechanism, the resonance energy transfer between an excited STE and a Ce$^{3+}$ ion, is possible since the Ce$^{3+}$ absorption band overlaps the STE emission. At room temperature the STE luminescence is partly quenched having a decay time of about 60 ns, see figures 11 and 12. Therefore it is rather unlikely that the Ce$^{3+}$ luminescence observed at a longer time, say longer than 300 ns is due to this type of energy transfer. The STE luminescence has then almost vanished and the lifetime of the Ce$^{3+}$ 5d-4f transition is too short to observe still considerable luminescence intensity. Nevertheless, it may still play a role at shorter times, i.e. < 200 ns in which most of the scintillation light is emitted. The energy transfer rate for resonance is determined by an interaction matrix element and the spectral overlap of the STE emission and Ce$^{3+}$ emission bands [30]. The overlap of these bands is located near 350 nm. When the temperature varies, this overlap will not change to a great extent, since the Ce$^{3+}$ absorption band will always overlap the STE emission band. This was checked by a simple model calculation. Therefore, the STE to Ce$^{3+}$ transfer rate will be almost independent of temperature. Now, let us pay attention to the temperature dependence of the STE and Ce$^{3+}$ luminescence yield of RbGd$_2$Br$_7$:0.11%Ce$^{3+}$ presented in the inset of figure 8. It shows that the Ce$^{3+}$ luminescence intensity remains constant, whereas the STE luminescence intensity decreases. In case of resonance energy transfer, we would expect that the Ce$^{3+}$ luminescence intensity increases as the STE luminescence intensity increases, provided that the Ce$^{3+}$ luminescence is not quenched. The Ce$^{3+}$ luminescence is not quenched in a great extent, since the light yield of RbGd$_2$Br$_7$:4.1%Ce$^{3+}$ remains 54,700 ph/MeV at temperatures between 100 and 400 K. Therefore, the energy is not transferred by resonance STE→Ce$^{3+}$ transfer in RbGd$_2$Br$_7$:0.11%Ce$^{3+}$. Still, this mechanism may be important for the RbGd$_2$Br$_7$ samples containing a higher Ce$^{3+}$ content.

Possible mechanisms

Summarising, we have made clear that Gd ions are not involved in the scintillation energy transfer. Radiative and resonance STE→Ce$^{3+}$ energy transfer are unlikely as well. Now that some possible energy transfer mechanisms in RbGd$_2$Br$_7$:Ce$^{3+}$ are excluded, we may hypothesise what type of energy transfer is most likely. We suppose that the energy-transfer is controlled either by the diffusion of self-trapped carriers or by the thermally activated release of carriers trapped in shallow traps. There are two grounds for this assumption. Firstly, the time-response of the scintillation is in the μs range, which can not be due to the recombination of free electrons and holes in halide lattices, which have disappeared on a timescale of 1 ns. Secondly, the energy transfer is activated by temperature (see figure 13) which indicates a defect-like motion. Self-trapped carriers may be regarded as such kind of defects.
Several models may explain the non-exponential decay component having the $t^2$ time dependence. These involve the recombination of charge carriers having opposite charges. In bimolecular diffusion a charge carrier (for example a $V_x$ centre) has to migrate to a counter charge carrier (for example an electron trapped near or on Ce$^{3+}$ ion). Upon recombination, the Ce$^{3+}$ ion is excited. The recombination rate is proportional to the concentration of the diffusing charge and that of the trapped counter charges and thus a $t^2$ time dependence is observed. When the transfer is controlled by the thermal release of trapped carriers two mechanisms may explain this time dependence as well. Suppose that a charge carrier (for example a hole) is captured in the vicinity of a Ce$^{3+}$ ion and that the charge carrier having the opposite charge (for example an electron) is trapped somewhere else. Upon release by thermal activation, this may either recombine with the charge carrier captured by Ce$^{3+}$ or become trapped again. Provided that the chance of retrapping is much larger than that of recombination with the hole, also a $t^2$ is to be expected. If the traps have an exponential trap-depth and if released carriers recombine directly on Ce$^{3+}$, then such time dependence is observed. Let us turn to the fast exponential component observed in the first 200 ns. figure 11 and 12 indicate that part of the Ce$^{3+}$ ions is almost instantaneously excited after absorption of a $\gamma$-quantum and that this number increases with increasing Ce$^{3+}$ concentration. It is possible that part of the e-h pairs is almost instantaneously captured by Ce$^{3+}$ or that the Ce$^{3+}$ ions are excited by a neighbouring STE. We need more information on the energy or charge carriers involved in the energy transfer processes to make a more detailed analysis. Furthermore, the actual energy transfer processes are generally much more complicated than those mentioned here. Even in the well-known scintillators NaI:Tl$^+$ and CsI:Tl$^+$, which have been discovered more than 40 years ago, not all transfer processes are well understood [31].

In the last part of this section, we will pay attention to the possibility of a diffusion mechanism controlling the energy transfer. If we assume that diffusion controls the energy transfer, the much slower scintillation response times of RbGd$_2$Cl$_2$:Ce$^{3+}$ compared to RbGd$_2$Br$_7$:Ce$^{3+}$ might indicate that the diffusion constant is much smaller in the chloride compound. Before we pay attention to this halide dependency, we will first consider the migration of a self-trapped carrier. A charge carrier in a polarisable crystal distorts the lattice, thereby creating a potential well in which it is trapped. When the lattice distortion is confined to the dimensions of one lattice cell or less, such a charge carrier is called a small polaron. The motion can be described by a random hopping to neighbouring sites, thereby dragging the lattice deformation. For a jump to an adjacent site a potential barrier has to be overcome by thermal activation. A general theory for such a motion was developed in the late fifties to explain the conductivity in NiO and LaMnO$_3$ [32]. Song [33],[34] used it to explain the diffusion of a $V_x$ centre in alkali halides. The diffusion constant $D$ is given by $D = a^2\nu$, where $a$ is the length of the hop and $\nu$ the transition probability of the hopping process. This probability is given by:

$$\nu = \frac{|J|^2}{2\hbar} \left( \frac{\pi}{E_c kT} \right)^{1/2} e^{-E_c / kT}$$

(6)

where $J$ is the transfer energy between the two adjacent polaron wavefunctions for the jump from $R_m$ to $R_{m+1}$. It is expressed as $<\psi(r-R_m)|H|\psi(r-R_{m+1})>$, in which $\psi(r-R)$ denotes the
wavefunction at lattice site \( R \) and \( H \) the potential energy of the polaron in the field of all ions, except that of the polaron. \( E_a \) is the activation energy needed for the jump. So, the decisive parameters for the polaron motion are the energies \( E_a \) and \( J \). The activation energy \( E_a \) represents the energy difference between the ground state of the polaron and the saddle-point, which it has to cross for the jump. A detailed knowledge of the lattice relaxation is required to estimate this energy. The transfer energy \( J \) depends on the lattice potential and the overlap of two adjacent polaron wavefunctions, which in turn depends on the crystal structure, the lattice constant and the diffuseness of the polaron wavefunctions.

Because of the complexity of factors that determine \( E_a \) and \( J \), it is not easy to predict or calculate general trends [33]-[39]. Nevertheless, when we confine our attention to the alkali halides, there is a tendency that \( E_a \) of a compound MX decreases in the series X=Cl, I. This can be seen in table 6, where we compiled some experimentally determined values. By inspection, it is noted that the room temperature diffusion constant may vary considerably, due to a difference of only a few tenths of eV in activation energy. This holds for example for KCl and KI, for which the diffusion constants are respectively \( 2.5 \times 10^{-12} \) and \( 1 \times 10^{-7} \) cm\(^2\)/s, due to a variation of 0.27 eV in \( E_a \).

### TABLE 6: Experimental activation energies (\( E_{a,exp} \)), the transfer energy (\( J_{exp} \)) and the room temperature diffusion constant (\( D \)) of STEs and \( V_\text{k} \) centres in alkali halides. The values indicated with * should be regarded as an order of magnitude.

<table>
<thead>
<tr>
<th>compound</th>
<th>( V_\text{k} ) centre</th>
<th>( E_{a,exp} ) [eV]</th>
<th>( J_{exp} ) [eV]</th>
<th>( D ) [cm(^2)/s]</th>
<th>( E_{a,exp} ) [eV]</th>
<th>( J_{exp} ) [eV]</th>
<th>( D ) [cm(^2)/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.44(^*)</td>
<td></td>
<td></td>
<td></td>
<td>0.15(^b)</td>
<td>0.022(^b)</td>
<td>2.10(^{-5})</td>
</tr>
<tr>
<td>NaI</td>
<td>0.18(^c)</td>
<td>0.08(^e)</td>
<td>1.10(^{-5})</td>
<td></td>
<td>0.07(^d)</td>
<td>0.09(^d)</td>
<td>2.10(^{-2})</td>
</tr>
<tr>
<td>KCl</td>
<td>0.54(^d)</td>
<td>0.3(^d)</td>
<td>2.5.10(^{-12})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>0.27(^e)</td>
<td>0.3(^e)</td>
<td>1.10(^{-7})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Ref [40]; \(^b\)Ref [41]; \(^c\)Ref [42]; \(^d\)Ref [43]

Finally, let us estimate the diffusion constant of the carriers in RbGd\(_2\)Br\(_7\) and RbGd\(_2\)Cl\(_7\) assuming that the diffusion of self-trapped carriers controls the energy transfer. For that purpose, the recorded scintillation decay time spectra can be used. As can be seen in figure 11, 12 and 14, the decay time spectra of RbGd\(_2\)Br\(_7\):Ce\(^{3+}\) contains components in the range of 300 ns, whereas in RbGd\(_2\)Cl\(_7\):Ce\(^{3+}\) it is in the range of 3 \( \mu \)s. Assuming for simplicity that the Gd\(^{3+}\)-Gd\(^{3+}\) distance in RbGd\(_2\)Br\(_7\) and RbGd\(_2\)Cl\(_7\) is on the average 5 \( \AA \) and that the Ce\(^{3+}\) concentration is \( \sim 1\% \), the distance from the carrier to the nearest Ce\(^{3+}\) ion, amounts on the average \( \sqrt[3]{100 \cdot (5/2)^3} =11.6 \) \( \AA \). The time \( t \) required for travelling a distance \( l \) is given by \( t = \sqrt{Dt} \), where \( D \) is the diffusion coefficient. For \( D=10^{-12}, 10^{-9}, 10^{-7} \) and \( 10^{-5} \) cm\(^2\)/s this gives respectively typical travelling times of 13 ms, 13 \( \mu \)s, 130 ns and 1.3 ns. Based on these considerations, we estimate the room temperature diffusion constant to be \( 10^{-7} \) cm\(^2\)/s in RbGd\(_2\)Br\(_7\):Ce\(^{3+}\) and \( 10^{-8} \) cm\(^2\)/s in RbGd\(_2\)Br\(_7\):Ce\(^{3+}\), respectively, i.e. the diffusion constant in RbGd\(_2\)Cl\(_7\):Ce\(^{3+}\) is about a factor of 10 lower than in RbGd\(_2\)Br\(_7\):Ce\(^{3+}\). In K\(_2\)LaCl\(_5\):Ce\(^{3+}\) and the Ce\(^{3+}\) doped elpasolites we observed scintillation decay time components in the order of 1-10 \( \mu \)s, in range with that of RbGd\(_2\)Cl\(_7\):Ce\(^{3+}\). If the energy transfer is controlled by some kind of a
diffusion process, it indicates that the diffusion constant in bromides is larger than in chlorides. This may be in line with the observations that in alkali halides the diffusion constant of STEs and $V_\kappa$ centres increases for the heavier halides, see table 6.

7.6 Conclusions and outlook

The studied RbGd$_2$Br$_7$:Ce$^{3+}$ and RbGd$_2$Cl$_7$:Ce$^{3+}$ show light yields comparable to those of CsI:Tl$^+$ and NaI:Tl$^+$. Advantageous are the fast scintillation response and the small energy resolution for 662 keV $\gamma$-rays. Yet, the hygroscopicity and the presence of $^{87}$Rb in the samples may limit practical use.

The overlap of the energy of the Gd$^{3+}$ and Ce$^{3+}$ transitions results in efficient Gd$^{3+}$→Ce$^{3+}$ energy transfer via the Gd-sublattice by fast energy migration. For low Ce$^{3+}$ concentrations, i.e. ≤0.11%, part of the energy is lost due to transfer to killer centres or due to Gd$^{3+}$ luminescence.

The role of the Gd$^{3+}$ ions in the energy transfer process under ionising radiation is negligible. Instead, the energy transfer is probably controlled by diffusion of self-trapped carriers to Ce$^{3+}$ centres or by the release of trapped carriers. For further clarification of the energy transfer process the knowledge of the type of involved carriers is required. This information can be derived by recording time-resolved absorption or EPR spectra following pulsed excitation of ionising radiation.

The scintillation decay is much faster in RbGd$_2$Br$_7$:Ce$^{3+}$ than in RbGd$_2$Cl$_7$:Ce$^{3+}$. It is worthwhile to study the origin of this halide dependency and to check whether it holds also for other halide compounds.

REFERENCES

8 Light yield estimation of LuAlO$_3$:Ce$^{3+}$ crystals

8.1 Introduction

In the research program on new $\gamma$-ray scintillator materials, the scintillation properties of LuAlO$_3$:Ce$^{3+}$ are also under study. Its development, started in 1994 [1], is a logical consequence of the efficient scintillation in isostructural YAlO$_3$:Ce$^{3+}$ [2] and the discovery of efficient lutetium oxide scintillators like Lu$_2$SiO$_5$:Ce$^{3+}$ [3] and LuPO$_4$:Ce$^{3+}$ [4]. The advantage of the LuAlO$_3$:Ce$^{3+}$ scintillator with respect to other Lu based scintillators is its higher density (8.34 g/cm$^3$ [5]) and shorter main scintillator decay time (~18 ns [5]). The high density is due to the close-packed perovskite-like structure of this material. It is therefore a potential candidate for use in e.g. medical-diagnostic applications.

The 4f-5d excitation transitions of Ce$^{3+}$ are grouped in 2 main bands near 225 and 290 nm [6]. The former consists of three and the latter two sub-bands. The 5d-4f luminescence of Ce$^{3+}$ at room temperature consist of a structureless band between 330 and 430 nm [6]. At liquid nitrogen temperature the typical splitting of the $^7F$ ground state can be resolved clearly. When excited by X- or $\gamma$-rays, two additional luminescence bands are observed: one near 280 nm and another near 650 nm [6]. The former is attributed to the radiative recombination of a self-trapped exciton (STE) and the latter is related with defects.

Upon absorption of ionising radiation, free electrons and free holes are created in the material. In the transfer of excitation energy to the Ce$^{3+}$ luminescence centres two mechanisms have been distinguished, based on luminescence excitation spectra in the range of 4-50 eV [6]. These are energy transport via excitons and hole-electron capture. As a result, rise times of about, respectively, 2 ns and 900 ps are introduced. For the hole-electron capture mechanism, the luminescence decay is somewhat longer than the 17 ns radiative lifetime of excited Ce$^{3+}$ due to the transport times of electrons and holes to the Ce$^{3+}$ ions. The presence of a rise time and long decay time components are also observed in scintillation decay. In the

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Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
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first 200 ns, Moszynski et al. [7] observe a rise time of 600 ps, a main decay time of 17.4±0.3 ns and a slow decay time of 88.0±1.9 ns.

In the framework of the Crystal Clear Collaboration the luminescence and scintillation properties of LuAlO3:Ce3+ crystals have also been studied. Our aim is to obtain an accurate estimate of the light yield of these crystals. For that purpose we used several techniques. Firstly, we compared the wavelength-integrated yield derived from X-ray induced emission spectra with that of a crystal with a known light yield. Secondly, we recorded pulse height spectra. Further insight in the light yields of several decay time components was acquired from scintillation decay time spectra.

8.2 Experimental methods

LuAlO3:Ce3+ crystals have been grown by A.G. Petrosyan using the vertical Bridgman technique. Details on the crystal growth can be found in [8]. The 60 mm long crystal rods, obtained with this technique, were optically clear and free of cracks. The boules were cut, sanded and polished. Due to the smaller ionic radius of Lu3+ compared to that of Ce3+, only 17% of Ce3+ ions present in the melt is incorporated in the crystal lattice [8]. Two types of samples were studied: large sized samples, having dimensions of 5x5x10 mm³, and thin samples with thickness up to 900 μm. In table 1 the codes, dimensions and the actual Ce3+ concentration of the studied crystals are compiled.

<table>
<thead>
<tr>
<th>crystal name</th>
<th>Ce3+ concentration [%]</th>
<th>dimensions [mm³]</th>
<th>thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4</td>
<td>0.13</td>
<td>5x5x10</td>
<td></td>
</tr>
<tr>
<td>P5</td>
<td>0.19</td>
<td>5x5x10</td>
<td></td>
</tr>
<tr>
<td>P6</td>
<td>0.47</td>
<td>5x5x10</td>
<td></td>
</tr>
<tr>
<td>P7</td>
<td>0.28</td>
<td>5x5x10</td>
<td></td>
</tr>
<tr>
<td>#6/49</td>
<td>0.13</td>
<td></td>
<td>130</td>
</tr>
<tr>
<td>Polish 2-21h</td>
<td>0.17±0.04</td>
<td></td>
<td>950</td>
</tr>
<tr>
<td>#1/2</td>
<td>0.2</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td>#6/1</td>
<td>0.28</td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>P7_s (part of P7)</td>
<td>0.28</td>
<td></td>
<td>700</td>
</tr>
<tr>
<td>No 76</td>
<td>0.47</td>
<td></td>
<td>600</td>
</tr>
<tr>
<td>No 159</td>
<td>0.9</td>
<td></td>
<td>540</td>
</tr>
<tr>
<td>No 163</td>
<td>0.9</td>
<td></td>
<td>550</td>
</tr>
</tbody>
</table>

The faces of the large sized crystals were defined as follows: The top and bottom faces with dimensions of 5x5 mm² are numbered as face 1 and 2. The others have the numbers 3-6. Crystal P7 is not completely transparent; very clearly a greyish milky region is visible. Sample P7_s is cut from crystal P7 and 2-21h was not grown by A.G. Petrosyan, but by Litton Airtron using the Czochralski technique (also indicated as the Polish crystal). The Ce3+
8.3 Results

In this section first the experimental results for the large samples will be discussed, next the results for the thin samples.

8.3.1 Results for the large crystals

X-ray induced emission

The X-ray induced emission spectra of P4-P7 are presented in figure 1. They consist of the

![Graph showing X-ray induced emission spectra of P4-P7](image-url)

**Figure 1:** X-ray induced emission spectra of P4-P7. The numbers 1 and 3 refer to the irradiated face.
Ce\textsuperscript{3+} 5d-4f luminescence between 330 and 430 nm. Light yields derived from these spectra are presented in Table 2. By inspection, we observe that the light yield is in the order of 10,000 ph/MeV for all crystals, independent of the Ce\textsuperscript{3+} concentration. By exciting crystal P7 on face 1 in the milky spot, a lower light yield is observed (denoted between brackets in Table 2). The light yield is reduced by a factor of 2 compared to that of the transparent part.

Table 2: Light yields derived from the X-ray induced emission spectra. The light yields are not corrected for self-absorption in the crystal. The error in the yields is 10%. The light yields are not corrected for self-absorption in the crystal.

<table>
<thead>
<tr>
<th>crystal</th>
<th>[Ce\textsuperscript{3+}]</th>
<th>irradiated at face</th>
<th>light yield [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4</td>
<td>0.13 %</td>
<td>1</td>
<td>12,000</td>
</tr>
<tr>
<td>P4</td>
<td>0.13 %</td>
<td>2</td>
<td>12,500</td>
</tr>
<tr>
<td>P4</td>
<td>0.13 %</td>
<td>3,4,5,6</td>
<td>12,200</td>
</tr>
<tr>
<td>P5</td>
<td>0.19 %</td>
<td>1</td>
<td>9,300</td>
</tr>
<tr>
<td>P5</td>
<td>0.19 %</td>
<td>2</td>
<td>8,500</td>
</tr>
<tr>
<td>P5</td>
<td>0.19 %</td>
<td>3,4,5,6</td>
<td>10,700</td>
</tr>
<tr>
<td>P6</td>
<td>0.19 %</td>
<td>1</td>
<td>11,900</td>
</tr>
<tr>
<td>P6</td>
<td>0.19 %</td>
<td>2</td>
<td>11,300</td>
</tr>
<tr>
<td>P6</td>
<td>0.47 %</td>
<td>3</td>
<td>10,300</td>
</tr>
<tr>
<td>P6</td>
<td>0.47 %</td>
<td>4</td>
<td>12,800</td>
</tr>
<tr>
<td>P6</td>
<td>0.47 %</td>
<td>5</td>
<td>11,000</td>
</tr>
<tr>
<td>P6</td>
<td>0.47 %</td>
<td>6</td>
<td>12,000</td>
</tr>
<tr>
<td>P7</td>
<td>0.28 %</td>
<td>1</td>
<td>8,900 / (4,300 on spot)</td>
</tr>
<tr>
<td>P7</td>
<td>0.28 %</td>
<td>2</td>
<td>8,000</td>
</tr>
<tr>
<td>P7</td>
<td>0.28 %</td>
<td>3,4,5,6</td>
<td>8,600</td>
</tr>
</tbody>
</table>

Part of the scintillation light is absorbed due to overlap of the emission band with an absorption band. This can be clearly seen after comparison of Figure 1 and 2.

![Figure 2: The transmission spectra for P4-P7, corrected for reflection losses.](image-url)
When the crystals are excited on face 1 the distance the light has to travel in the crystals to the other side is about 5 mm longer than when excited on face 3. As a result, the absorption of the short-wavelength emission is more pronounced for face 1 than for face 3 irradiation. Especially in P5 and P7 this loss is considerable, see figure 2. So the actual light yields may be higher. The presence of such absorption has been observed before [12],[13]. It has been attributed to the presence of defects [12],[14].

Pulse height spectra

The light yields derived from pulse height spectra are shown in table 3. Note that the light yields are not corrected for self-absorption. By inspection of this table the light yield tends to increase with increasing Ce³⁺ concentration. Due to the possible presence of a parasitic absorption in the crystal, this dependence is not always obvious.

<table>
<thead>
<tr>
<th>crystal</th>
<th>[Ce³⁺]</th>
<th>source</th>
<th>shaping time [μs]</th>
<th>light yield [ph/MeV] when irradiation incident on face</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>P4</td>
<td>0.13 %</td>
<td>^137Cs</td>
<td>0.5</td>
<td>2120</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>2840</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^57Co</td>
<td>0.5</td>
<td>2160</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>3000</td>
</tr>
<tr>
<td>P5</td>
<td>0.19 %</td>
<td>^57Co</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>2450</td>
</tr>
<tr>
<td>P7</td>
<td>0.28 %</td>
<td>^137Cs</td>
<td>0.5</td>
<td>1820</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>2360</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^57Co</td>
<td>0.5</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>2240</td>
</tr>
<tr>
<td></td>
<td>^241Am</td>
<td></td>
<td>0.5</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>1890</td>
</tr>
<tr>
<td>P6</td>
<td>0.47 %</td>
<td>^137Cs</td>
<td>0.5</td>
<td>3240</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>4070</td>
</tr>
<tr>
<td></td>
<td></td>
<td>^57Co</td>
<td>0.5</td>
<td>3310</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>4340</td>
</tr>
<tr>
<td></td>
<td>^241Am</td>
<td></td>
<td>10</td>
<td>3200</td>
</tr>
</tbody>
</table>

Scintillation decay

The scintillation decay spectrum for P7 is shown in figure 3. It shows a fast decay time of 18.5 ns, persisting over 2 decades in intensity. Furthermore, a tail in the range of 100 ns and a long non-exponential decay component in the μs- ms range are observed. For the other crystals similar decay time spectra are recorded. From the recorded decay time spectra it is deduced that about 75% of the scintillation light in the first 3 μs is emitted within 100 ns.
8.3.2 Results for thin samples

X-ray induced emission

Figure 4 shows the X-ray induced emission spectra of the thin samples. Apart from the Ce$^{3+}$ luminescence, other emission bands are observed. The band near 200 nm, indicated with an arrow, is an experimental artefact.
Near 250 nm the host lattice luminescence is observed [6]. The intensity of this band tends to decrease as the absorption due to Ce$^{3+}$ 4f-5d transitions increases. This is especially pronounced near 300 nm, where the lowest Ce$^{3+}$ 4f-5d absorption band is located. Note that the mentioned absorption increases both with the Ce$^{3+}$ absorption coefficient and with sample thickness. The emission band between 550 and 600 nm is due to the defect-type luminescence, as has been observed before [6]. The contribution of second order transmission of the monochromator of the host lattice emission near 250 nm is negligible. In fact, the real intensity of this emission is higher since the QE of the PMT and the transmission of the monochromator drops dramatically above 450 nm. It is possible that the intensity of this emission in the Polish crystal is somewhat less in comparison with that in the Petrosyan crystals.

Table 4: Light yields derived from the X-ray induced emission spectra. The error in the yields is 10%. The light yields are not corrected for self-absorption in the crystal.

<table>
<thead>
<tr>
<th>crystal</th>
<th>Ce$^{3+}$ concentration [%]</th>
<th>light yield [plv/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#6/49</td>
<td>0.13</td>
<td>10,400</td>
</tr>
<tr>
<td>2-21h</td>
<td>0.17</td>
<td>14,700</td>
</tr>
<tr>
<td>#1/2</td>
<td>0.2</td>
<td>10,000</td>
</tr>
<tr>
<td>P7_s</td>
<td>0.28</td>
<td>9500</td>
</tr>
<tr>
<td>#6/1</td>
<td>0.28</td>
<td>9100</td>
</tr>
<tr>
<td>No 76</td>
<td>0.47</td>
<td>10,000</td>
</tr>
<tr>
<td>No 159</td>
<td>0.9</td>
<td>9100</td>
</tr>
<tr>
<td>No 163</td>
<td>0.9</td>
<td>9400</td>
</tr>
</tbody>
</table>

Although the crystals are rather thin, almost all X-rays will be absorbed. Even for a 100 μm thick crystal the absorption amounts 98%. Light yields derived from the X-ray induced emission spectra are compiled in table 4. Note that the light yield of crystal 2-21h is much higher than that of the others. The correction for the transmission of the monochromator and the QE of the PMT could only be performed in the wavelength range of 150-500 nm, so the light yield between 550 and 600 nm could not be estimated.

Pulse height spectra

In table 5 the light yields derived from pulse height spectra are shown. Note that the measured light yields of #6/49 (10 μs) differ about 20%, dependent on the employed radioactive source. This difference is due to the broadness of the photopeak in the recorded spectra for this crystal. The light yield as a function of the Ce$^{3+}$ concentrations for all thin crystals is shown in figure 5.

Inspection shows that for the Petrosyan crystals, the light yields measured for 0.5 and 10 μs shaping time increase roughly with the Ce$^{3+}$ concentration. There is a large difference in light yields for P7_s and #6/1 although they have the same Ce$^{3+}$ concentration. This is unexpected since in P7_s there is an absorption for the scintillation emission in the crystal. The light yield of the Polish crystal is higher than those of the other crystals, except for crystal No 159.
For sample P7_s pulse height spectra at γ-ray energies between 8 and 60 keV were recorded. The light yields at 13.3 keV and 60 keV, whereas at 8 keV the light yield is considerably lower.

Scintillation decay

For all decay curves a fast decay time was found of 18.5 ns. Furthermore a tail in the range of 100 ns and a long non-exponential decay component in the μs-ms range is observed, similarly to the obtained results for the large crystals. In order to check whether the slow component is related to the Ce₃⁺ emission between 330 and 500 nm, measurements were performed on the No 163 sample using 350 and 370 nm interference filters. A slow component is still observed in these spectra. At these wavelengths the ratio of the time-integrated yield in the first 100 ns and that in the first 3 μs is in the range of 70-80%. This is about the same fraction for the measurements performed without filters.

The scintillation response upon switching on and off the X-ray irradiation was measured as well. Upon switching on, the maximum scintillation intensity was reached within a few μs for almost all samples, except for sample P7_s. Before P7_s was irradiated, it was annealed 5 minutes at 500 °C. After irradiation we observed a 10% light yield increase in the first 200 s, as is shown in figure 6.
FIGURE 6: The ingrowth of the scintillation intensity of P7_s after switching on X-ray irradiation. Before irradiation, the sample was annealed 5 minutes at 500 °C.

Upon switching off, there was still scintillation light emitted, as can be seen in figure 7. The afterglow spectra of the Petrosyan samples consist of an afterglow decay time component of about 0.8 s. Similar afterglow spectra as shown in figure 7, curves a-c, have been recorded for the other Petrosyan samples. Yet, the Polish sample shows a higher initial intensity, see figure 7, curve d. The afterglow decay time is about 1.2 s, somewhat longer than that of the Petrosyan samples.

FIGURE 7: The time response of the scintillation intensity upon switching off the X-ray irradiation of (a) P7_s (b) #6/49 (c) #1/2 and (d) 2-21h.
8.4 Discussion

8.4.1 Difference in light yields obtained from several methods

There is a clear difference between the light yields derived from X-ray induced emission spectra and those derived from pulse height spectra. The mean light yield under X-ray irradiation is $\sim 10,000$ ph/MeV, whereas the light yield found in the pulse height measurements is 4,000-9,000 ph/MeV. The difference is ascribed to the presence of long decay time components containing a considerable part of the total light yield. The light yields present in these components do contribute to the light yields derived from X-ray induced emission spectra, but not to those obtained from pulse height spectra, where maximum shaping times of 10 $\mu$s are used. From the recorded scintillation decay time and afterglow spectra, the presence of such components extending to times much larger than the $\mu$s range is rather obvious.

The presence of a long decay time component has been observed before. Mares et al. [15] showed that a contamination of Gd$^{3+}$ introduces long decay time components in the Ce$^{3+}$ luminescence decay. In the here studied samples a Gd$^{3+}$ impurity is present [6]. Long decay times are possibly also introduced by the presence of electron and hole traps [6].

8.4.2 Comparison with other obtained light yields

There is a considerable variation in the light yields reported in the literature. The yields reported so far are collected in table 6. The reported values have been separated according to the employed measurement techniques.

By inspection, we notice that the light yields reported in the first three rows are about a factor of 2-3 higher than for the other cases. This could imply a considerably better crystal quality compared to other crystals. Unfortunately, most authors do not give a detailed description how the light yield was determined. So, the accuracy of the most reported light yields is difficult to judge. We suppose that the light yield estimations that are obtained using a Bi$_4$Ge$_2$O$_{12}$ (BGO) crystal as a reference are too high, because of the following reasons. Firstly, the light yield is dependent on the crystal thickness [16] and crystal quality [7]. Mostly the light yield of 8,200 ph/MeV [17] is used as a reference, although it is known that some crystals have two times lower yield [16]. Secondly, the emission wavelength of LuAlO$_3$:Ce$^{3+}$ crystals is near 350 nm, much shorter than the BGO luminescence between 400 and 600 nm. As a result, inaccuracies in the shape of the emission spectra and in the QE of the PMTs introduce large errors in the light yields. When bi-alkali photocathodes are used, the error may be rather high, since the QE drops dramatically above 450 nm [16], [18]. Instead of a BGO crystal, we use a BaF$_2$ crystal as a reference, of which the light yield has been
### Table 6: Comparison with light yields reported in the literature.

<table>
<thead>
<tr>
<th>measured by</th>
<th>Ce(^{3+}) conc. [%]</th>
<th>crystal growth technique</th>
<th>light yield (derived from X/γ-ray induced emission) [ph/MeV]</th>
<th>light yield (derived from pulse height spectra) [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lempicki et al [5]</td>
<td>0.12(^1)</td>
<td>Czochralski, Ir crucibles</td>
<td>32,000(^2)</td>
<td>-</td>
</tr>
<tr>
<td>Mares et al [19]</td>
<td>≤0.02</td>
<td>Czochralski</td>
<td>11,000(^*)</td>
<td>-</td>
</tr>
<tr>
<td>Moses et al [20]</td>
<td>0.1-0.3</td>
<td>from the melt, Mo crucibles</td>
<td>-</td>
<td>26,000(^*)</td>
</tr>
<tr>
<td>Moses et al [20]</td>
<td>0.1-0.3</td>
<td>powder</td>
<td>9,600(^3)</td>
<td>-</td>
</tr>
<tr>
<td>Moses et al [20]</td>
<td>0.12(^1)</td>
<td>unknown</td>
<td>-</td>
<td>7,600(^*)</td>
</tr>
<tr>
<td>Shah et al [21]</td>
<td>0.12(^1)</td>
<td>Czochralski</td>
<td>-</td>
<td>17,000(^*)</td>
</tr>
<tr>
<td>Moszynski et al [7]</td>
<td>0.105</td>
<td>Czochralski, Ir crucibles(^4)</td>
<td>-</td>
<td>11,400±1500</td>
</tr>
<tr>
<td>this study</td>
<td>0.47</td>
<td>Bridgman, Mo crucibles</td>
<td>12,800±1,000</td>
<td>5680±600</td>
</tr>
<tr>
<td>this study</td>
<td>0.9</td>
<td>Bridgman, Mo crucibles</td>
<td>9100±900</td>
<td>9270±1900</td>
</tr>
</tbody>
</table>

\(^1\)The light yield was determined using a BGO reference crystal
\(^2\)The Ce\(^{3+}\) concentration is estimated from that put in the melt
\(^3\)The actual measurement method is not known
\(^4\)The light yield was obtained by comparing the wavelength-integrated yield with that of a powdered YAlO\(_3\);Ce\(^{3+}\) sample, measured under equal experimental circumstances.

\(^*\)It was assumed that the crystals are from the same source as reported in [5]

Determined accurately [9]. Furthermore, BaF\(_2\) and LuAlO\(_3\);Ce\(^{3+}\) have about equal emission wavelengths. Therefore, we estimate the error in the light yield as measured to be only 10 %.

A reliable estimate of the light yield can be derived from pulse height spectra, which are compiled in the last column of table 6. The absolute light yield, as measured by Moszynski et al. [7] for a Czochralski grown crystal, is higher than the highest light yield of the Bridgman grown crystals reported in this chapter. Recently, the light yield of the Petrosyan crystals has been increased by the use of a new Mo crucible. For a crystal with 0.2 % Ce\(^{3+}\) concentration about the same light yield is measured as for the 0.17% Ce\(^{3+}\) doped Polish crystal.

It should be noted that the light yields presented in this chapter are not corrected for losses due to absorption of scintillation light. A correction is difficult to perform in the large sized crystals, since the light transport in the crystals is not known. Even for the light yields of thin crystals were not corrected for self-absorption, since it is not known whether the absorbed light is re-emitted at a later time.
8.5 Conclusions

The light yields derived from X-ray induced emission spectra are about 10,000 ph/MeV. The light yields derived from pulse height spectra are generally lower, at maximum 9270 ph/MeV. Although obscured by the presence of an absorption band overlapping the Ce$^{3+}$ luminescence, the light yields derived from pulse height spectra increase with increasing Ce$^{3+}$ concentration.

The difference in light yields obtained under continuous and pulsed excitation are explained by the presence of long decay time components. The light yields of the studied samples are somewhat lower than reported by others. This is probably related with the purity of the used Mo crucible or the crystal growth technique.

REFERENCES

[10] Photomultiplier Tube, Principle to Application, Hamamatsu Photonics K.K., Data Process Laboratory K.K., 1994, chapter 3
9 Luminescence and scintillation properties of Lu$_2$S$_3$:Ce$^{3+}$

9.1 Introduction

In recent years several interesting Lu based scintillators were found, with Ce$^{3+}$ as the luminescent centre. Examples are Lu$_2$SiO$_4$:Ce$^{3+}$ [1] and LuAlO$_3$:Ce$^{3+}$ [2]. These kind of scintillators interact with γ-rays efficiently, because of the high atomic number of Lu and the high density of the compounds. Electrons and holes created in the crystal, upon X-ray or γ-ray interaction can transfer their energy fast and efficiently to Ce$^{3+}$ centres and scintillation decay times in the order of 30 ns can be achieved because of the allowed 5d-4f dipole transition in this dopant.

So far the search for new scintillators has been focused mainly on fluoride and oxide host materials. Sulfides did not gain much attention, despite the fact that they are well known in other luminescence applications. For example, impurity doped alkali sulfides [3],[4], thioaluminates and -gallates [5] are used in cathode ray tubes and in electroluminescent devices.

Here we present the optical and scintillation properties of Lu$_2$S$_3$:Ce$^{3+}$. The host lattice belongs to the binary, non-hygroscopic, rare earth sesquisulfides (sesqui=$1\frac{1}{2}$). These materials have been studied since the past 30 years, gaining a continuously growing attention [6]. The practical interest is mainly focused on optical and luminescence applications, for example in the development of new pigments [7], laser hosts for rare earth ions [8],[9], infrared transmission filters [10], and lamp phosphors [11].

For RE$_2$S$_3$ (RE= yttrium or a rare earth element) several crystal structures are known. The sulfides of the elements La-Nd and Sm, Gd, Tb and Dy crystallise in the orthorhombic α-RE$_2$S$_3$ form [12],[13]. For almost all these elements the β-RE$_2$S$_3$ structure is known as well, which is stabilised by a small amount of O$^2-$ in the lattice. Crystalisation in the monoclinic δ-RE$_2$S$_3$ form occurs for Y and Ho-Tm [12],[13]. For the heavy rare earths Tm, Yb and Lu the ε-RE$_2$S$_3$ structure is known [12],[14]. For all rare earth sulfides the cubic γ-form exists as

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Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
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well, however only at high temperatures and pressures. It crystallises in a $\text{Th}_3\text{P}_4$ defect type structure, i.e. as $\text{RE}_{8/3}\square_{1/3}\text{S}_4$ (RE=rare earth, $\square$ representing a vacant cation site). Some other structure types exist as well, but they are rarely reported [12]. All rare earth sulfides are not hygroscopic.

We will discuss the known structures for lutetium sulfide in some more detail. Apart from the sesquisulfides other stoichiometries have also been obtained. Cubic Lu$_2$S$_x$ exists with $x$ between 0.75-1.3 [15]. Another phase is formed by decomposition of $\varepsilon$-Lu$_2$S$_3$, heated near the melting temperature of 1750 °C. It decomposes into Lu$_2$S$_4$, which has a defect Sc$_2$S$_3$ type structure [16]. At elevated pressures an orthorhombic modification is also known as Lu$_2$S$_3$-III [17].

9.2 Experimental

Ce$^{3+}$ doped Lu$_2$S$_3$ crystals were grown by the method of chemical vapour transport at the laboratory of Prof. Huber in Hamburg, Germany [9],[18]. The rare earth sulfides were prepared from the rare earth oxides (purity > 99,999 %, Auer-Remy). Stoichiometric amounts of Lu$_2$S$_3$ and Ce$_2$S$_3$ powder were mixed into a quartz ampoule filled with iodide gas. Upon heating at ~1100 °C, vapour of rare earth iodides is formed in reaction with the sulfides. At cooler parts in the ampoule, the rare earth sulfides are created by the reverse reaction and crystallisation takes place. In this way irregularly shaped crystals with dimensions in the order of 1x1x1 mm$^3$ are obtained. A disadvantage of this crystal growth method is the contamination with iodide, oxygen and silicium impurities. For La$_2$S$_3$ and Gd$_2$S$_3$ crystals prepared with the same crystal growth technique iodide impurities were detected in concentrations of 20-50 ppm in the crystal bulk [18]. At the surface the iodide impurity concentration is as high as 0.3% [18]. The concentration of other impurities is not known.

The crystal structure, determined by diffraction analysis, is of the $\varepsilon$-phase [14], with the corundum structure and space group $R\overline{3}c$. The co-ordination of the rare earth atoms is trigonal anti-prismatic with co-ordination number 6 and point symmetry $C_{3v}$. The effective atomic number is 66.8 and the density 6.25 g/cm$^3$.

The emission spectrum under X-ray excitation was measured with an X-ray tube with a Cu anode operated at 35 kV and 25 mA. The generated luminescence was detected by a red-sensitive Philips XP2254/B photomultiplier tube (PMT) and a H10 Jobin Yvon monochromator (grating 1200 grooves/mm, blazed at 250 nm). Using a cryostat, X-ray induced emission spectra were recorded between 100 and 400 K with an ARC VM504 monochromator (grating 1200 grooves/mm blazed at 300 nm), using a Hamamatsu R 943 PMT.

The optical absorption spectrum is measured using a light source with tungsten filament, an ARC VM504 monochromator and a Thorn EMI type 9426 PMT.

Light yields were derived from pulse height spectra, using three different light detectors: Philips XP2020Q and XP2254/B PMTs, and a Hamamatsu S5345 Avalanche Photodiode (APD). The crystals were mounted on a light detector with a coupling liquid and were wrapped in 5 layers of 0.1 mm thick Teflon tape. They were excited by $^{241}$Am and $^{137}$Cs $\gamma$-quanta and a variable X-ray source (Amersham source (AMC.2084)). Standard spectroscopic
techniques were used to record the pulse height spectra. In pulse height measurements with the PMTs the peak position of the photopeak was compared with that of the single electron spectrum. Thus the photo electron yield per absorbed γ-ray energy (phe/MeV) was deduced. Using the quantum efficiencies (QEs) these yields were converted into photons/MeV (ph/MeV). The QEs of the XP2020Q and the XP2254/B PMT were determined with the method described in [19]. In order to determine the light yield from a pulse height spectrum measured with the APD, at first the preamplifier and spectroscopic amplifier were calibrated with pulses of known charges. The number of generated e-h pairs can then be calculated from the photopeak position, knowing that the gain for a detected photon in the visible is about 12.8 (at a bias voltage of -260 V). For the QE of the APD we used the data presented by the manufacturer.

9.3 Results

9.3.1 Luminescence under optical excitation

The 5d-4f luminescence of Ce$^{3+}$ in Lu$_2$S$_3$ consists of a broad emission between 500 and 750 nm, see figure 1, curve a. Transforming wavelength to energy, the emission can reasonably well fitted

![Graph showing luminescence properties](attachment:image.png)

**Figure 1:** (a) The $\lambda_{exc}=450$ nm excited emission spectrum of Lu$_2$S$_3$:Ce$^{3+}$, (b) optical absorption spectrum, (c) the excitation spectrum measured at $\lambda_{em}=580$ nm and (d) X-ray induced emission spectrum of Lu$_2$S$_3$:Ce$^{3+}$. Curve (a) is corrected for the transmission of the optical system and the QE of the PMT. The X-ray induced emission spectrum is not corrected for the transmission of the measurement system and the QE of the XP2254/B PMT. The peak at 650 nm indicated with an arrow is an artefact.
by two gaussian shaped peaks, located at 16770±80 cm\(^{-1}\) (2.08±0.01 eV) and 14760±80 cm\(^{-1}\) (1.83±0.01 eV). The two emission bands are due to the transition from the lowest 5d level to the 2010±110 cm\(^{-1}\) spin-orbit split \(^{2}\)F ground state, which is typical for Ce\(^{3+}\) [20].

The optical absorption spectrum of Lu\(_2\)S\(_3\);Ce\(^{3+}\) in figure 1, curve b, consists of a strong absorption below 330 nm, a tail between 330 and 400 nm and a broad absorption band peaking at 460 nm. This spectrum strongly resembles the absorption spectrum of \(\beta\)-La\(_2\)S\(_3\);Ce\(^{3+}\) [8]. The onset of the fundamental absorption band starts at 330 nm. The corresponding bandgap energy of 3.8 eV is −0.6 eV higher than that reported by Schevciw et al. [21]. Assuming that the absorption peak cross section for Ce\(^{3+}\) in Lu\(_2\)S\(_3\) is equal to that in \(\beta\)-La\(_2\)S\(_3\);Ce\(^{3+}\) we estimated the Ce\(^{3+}\) concentration in Lu\(_{2-2x}\)Ce\(_{2x}\)S\(_3\) as \(x=0.005\). When we use the Ce\(^{3+}\) 4f-5d absorption cross-section of 6.8×10\(^{-18}\) cm\(^2\), as estimated by Scharmer [18], we arrive at a somewhat smaller concentration. The Stokes shift amounts 4960 ± 160 cm\(^{-1}\).

Based on the C\(_{3v}\) point symmetry at the rare earth site, we expect a three fold splitting of the Ce\(^{3+}\) 5d level. Spin-orbit interactions will cause a further splitting into 5 levels. Yet, only one 4f-5d transition is observed. Hence, we presume that the other 5d energy levels are located in the conduction band.

The excitation spectrum of the Ce\(^{3+}\) emission is given in figure 1, curve c. It consists of several broad bands located at 460, 380 and a 20 nm wide band peaking at 310 nm. The 460 nm band has already been observed in the absorption spectrum and is attributed to a Ce\(^{3+}\) 4f-5d transition. The hump near 380 nm may be assigned to an excitation of a Ce\(^{3+}\) 4f electron into a higher 5d level. For excitation wavelengths shorter than 330 nm, electrons may be excited both from the valence to the conduction band and from the 4f Ce\(^{3+}\) level into the higher 5d levels. This makes the analysis rather complicated. The narrowness of the 310 nm band suggests an excitonic origin. The corresponding estimate of the bandgap energy is 4.0 eV.

### 9.3.2 Luminescence under X-ray and \(\gamma\)-ray excitation

The X-ray induced luminescence, presented in figure 1, curve d, consists of the 5d-4f Ce\(^{3+}\) luminescence between 500 and 750 nm. In the range of 100 to 400 K no other luminescence bands were observed.

The temperature dependence of the wavelength-integrated yields derived from the X-ray induced emission spectra is shown in figure 2. It presents a constant yield between 100 and \(\sim\)300 K and a decrease at higher temperatures. At 400 K the yield is reduced to 47 % of that at room temperature. Allowing for a temperature dependent quenching rate \(v e^{-E_a/4T}\) with a frequency factor \(v\) and an activation energy \(E_a\), we can find a fit of the data using \(v\) in the order of \(7\times10^{11}\) Hz and \(E_a = 0.34 ± 0.10\) eV. A dashed line represents this fit in figure 2.
The scintillation decay is presented in figure 3. It shows a main decay time of 32 ns, persisting over almost 2 decades of intensity. This short scintillation decay time corresponds to the 34 ns life time of the Ce$^{3+}$ 5d-4f dipole allowed transition in Lu$_2$S$_3$ [18]. Thus the energy transfer process of the electrons and holes, created by ionising radiation, to the Ce$^{3+}$ centres is...
very fast compared to the radiative decay time of the Ce\textsuperscript{3+} 5d-4f transition. Similarly fast energy transfer processes are reported for some other Lu based scintillators, such as Lu\textsubscript{2}SiO\textsubscript{5}:Ce\textsuperscript{3+} [1] and LuAlO\textsubscript{3}:Ce\textsuperscript{3+} [2].

### 9.3.3 Pulse height measurements

A main reason for performing pulse height measurements is to derive an accurate estimation of the scintillation light yield. For that purpose, the photoelectron yields of 10 different Lu\textsubscript{2}S\textsubscript{3}:Ce\textsuperscript{3+} crystals were measured with the XP2254/B PMT using the 59.5 keV γ-rays from a \textsuperscript{241}Am source. All crystals were grown with the same technique. The mean yield at 0.5 μs shaping time amounts 3100 phe/MeV with a standard deviation of 340 phe/MeV. Since the crystals are small and irregularly shaped, there is a possible loss in light yield due to the non-optimal coupling of the crystal to the detector. After sanding and polishing an irregularly shaped crystal into one with plan parallel faces an increase of ~20% in light yield was observed. The crystal, with dimensions of 0.2x0.4x2 mm\textsuperscript{3}, showing the highest yield, was used to further study with three different scintillation-light sensors. The light yield, measured under equal experimental conditions, remains constant within approximately 10% for γ-ray energies between 13 and 662 keV. It varies for low γ-ray energies, depending on the position of the radioactive source relative to that of the crystal.

![Pulse height spectrum](image)

**Figure 4:** Pulse height spectrum of \textsuperscript{137}Cs γ-rays recorded with Lu\textsubscript{2}S\textsubscript{3}:Ce\textsuperscript{3+} coupled onto an XP2254/B tube. The spectrum is measured with a shaping time of 0.5 μs. The fits of the photopeak and the escape peaks are shown with dashed and solid lines. In the inset the total pulse height spectrum is shown on a logarithmic γ-axis.

Figure 4 shows the pulse height spectrum of 662 keV γ-quanta of a \textsuperscript{137}Cs source, measured with the crystal coupled onto an XP2254/B PMT. The contribution of β- and γ-quanta due to the natural abundance of radioactive \textsuperscript{176}Lu in the Lu\textsubscript{2}S\textsubscript{3}:Ce\textsuperscript{3+} crystal to this spectrum is negligible. In the pulse height spectrum, the characteristic escape peaks of the Kα
and Kβ Lu X-rays arise 54 and 62 keV below the 662 keV photopeak. Considering the almost 100% X-ray fluorescence yield of Lu, and that the linear attenuation coefficient is \( \sim 2 \text{ mm}^{-1} \) for a 54 keV X-ray, we expect escape from the 0.2 mm thick crystal in \( \sim 65\% \) of the cases when we have absorption by the photoelectric effect. In figure 4 the ratio in peak intensity of the photopeak and the escape peak is about \( \frac{1}{2} \), thus consistent with the expectations. The energy resolution of the fitted full energy peak is 9 %. Based on the 3900 phe/MeV light yield one would expect an energy resolution of 5%. We attribute the large energy resolution to a non-uniform crystal quality and a non-optimal coupling of the crystal on the PMT. In the inset of figure 4 the complete pulse height spectrum is presented, showing also the photopeak of the 32 keV \(^{137}\text{Ba}\) X-rays originating from the \(^{137}\text{Cs}\) source.

![Figure 5: Pulse height spectrum of \(^{241}\text{Am}\) X-rays and \(\gamma\)-rays recorded with \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) coupled to the APD. The spectrum is measured with a shaping time of 0.5 \(\mu\text{s}\).](image)

The pulse height spectrum of \(\gamma\)-rays and X-rays of a \(^{241}\text{Am}\) source recorded for a \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) crystal mounted on the APD is shown in figure 5. In this spectrum the 59.5 keV scintillation peak in \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) is located at channel 580. The peaks at channel 1660, 2060 and 2370 are due to the direct detection of X-rays of \(^{237}\text{Np}\) in the APD. Knowing the amplification of the APD for visible light [22], the e-h pair yield of the \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) crystal measured with the calibrated set-up amounts 21,100 e-h pairs/MeV. A simple method to obtain the number of e-h pairs per MeV of absorbed radiation in the \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) crystals is by comparison of position of the 59.5 keV photopeak of the scintillation in the \(\text{Lu}_2\text{S}_3:\text{Ce}^{3+}\) crystal with that of the direct detection of the 13.9 keV X-rays in the APD, considering that the e-h production requires 3.62 eV. We then derive a light yield of 22,700 e-h pairs/MeV. Allowing for a correction of 7 % because the APD-amplification for visible light is somewhat higher than for X-rays [22], also a yield of 21,100 e-h pairs/MeV results.
TABLE 1: The light yields of the 0.2x0.4x2 mm$^3$ Lu$_2$S$_3$:Ce$^{3+}$ crystal, measured with three different light detectors. The QE in column 4 represents the mean QE at the scintillation emission of Lu$_2$S$_3$:Ce$^{3+}$. It includes the collection efficiency of the charge carriers generated in the light detector.

<table>
<thead>
<tr>
<th>light detector</th>
<th>Shaping time [μs]</th>
<th>Measured light yield [phe/MeV]</th>
<th>[e-h pairs/MeV]</th>
<th>QE at Lu$_2$S$_3$:Ce$^{3+}$ emission [%]</th>
<th>light yield [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S5345 APD</td>
<td>0.5</td>
<td>21,100±400</td>
<td>79 ± 2</td>
<td>26,700 ± 2,600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23,700±400</td>
<td></td>
<td>30,000 ± 3,000</td>
<td></td>
</tr>
<tr>
<td>XP2020Q</td>
<td>0.5</td>
<td>291±10</td>
<td>1.8 ± 1</td>
<td>21,200±12,800</td>
<td></td>
</tr>
<tr>
<td>XP2254/B</td>
<td>0.5</td>
<td>3922±60</td>
<td>13 ± 2</td>
<td>30,100±5,500</td>
<td></td>
</tr>
</tbody>
</table>

The measured light yields of the 0.2x0.4x2 mm$^3$ crystal are compiled in table 1. In this table the error in light yields in column 5, are due to the uncertainty in peak position of the photopeak and single electron peak (column 3), the error in the mean QE at the scintillation emission (column 4) and the inaccuracy in the value for the light collection, which is estimated to be 10%. The light yield, measured with the XP2254/B PMT and the APD is ∼28,000 ph/MeV. In the XP2254/B error contributions for QE and mounting inaccuracy are of the same order of magnitude. In the APD the main error is the inaccuracy in mounting. The light yield measured with the XP2020Q PMT seems to be somewhat lower, i.e., ∼21,200 ph/MeV, but the error is much larger. The uncertainty in the mean QE of the XP2020Q at the Lu$_2$S$_3$:Ce$^{3+}$ emission is quite large, because of the low QE of the bialkali photocathode at 600 nm. Upon an increase in shaping time from 0.5 to 10 μs, the light yields measured with the PMTs remain constant. Recently [23] we reported an increase of the light output of 15% with increasing shaping time. It appeared now that this increase was caused by a malfunctioning of the shaping amplifier. Meanwhile the calibration of the measurement set-up has been improved. For the APD we observe an increase of 10% when going from 0.5 to 3 μs shaping time. The reason for this discrepancy between the PMT and the APD measurements remains unclear.

Scharmer [18] measured a cathode ray energy efficiency of 3.8%. We can transform this efficiency into light yield. From the Ce$^{3+}$ luminescence spectrum in figure 1, the mean energy of an emitted photon is estimated to be 1.9 eV. Consequently, the corresponding light yield is 20,000 photons per MeV. This is ∼30% less than the ∼28,000 ph/MeV derived from pulse height spectra (see table 1).

9.4 Discussion

9.4.1 Absence or presence of Ce$^{3+}$ luminescence

It has been suggested that for small bandgap materials the lowest level of the Ce$^{3+}$ 5d configuration is located in or close to the conduction band and therefore quenching due to photoionisation is likely to occur [20]. In order to prevent such type of quenching, Blasse et
al. [20], [24] argues that Ce$^{3+}$ should be incorporated in wide optical bandgap materials. Yen et al. [25] extended this hypothesis. Based on the absence or presence of Ce$^{3+}$ luminescence in some fluoride and oxide host lattices, they predicted that efficient Ce$^{3+}$ luminescence is only observed when the bandgap energy is $\sim 6$ eV or higher. Contrary to this prediction, efficient Ce$^{3+}$ luminescence is observed in Lu$_2$S$_3$ with a bandgap of only $\sim 4$ eV. This is no exception. Also for other sulfides with bandgap energies as low as 2.7 eV, efficient Ce$^{3+}$ luminescence has been observed [8]. Clearly, the 6 eV threshold rule does not hold as a general statement, though it may be valid for oxides. One should also reconsider the suggestion, that efficient Ce$^{3+}$ luminescence in sulfide host lattices can only be obtained when it is incorporated on a divalent cation site [20]. This idea was used to explain the efficient luminescence in the Ce$^{3+}$ doped alkali earth sulfides. Yet, also in trivalent lanthanide sulfides efficient Ce$^{3+}$ emission is observed. Apparently, it is not easy to predict the absence or presence of Ce$^{3+}$ luminescence in sulfides.

In order to correlate the Ce$^{3+}$ luminescence efficiency with the bandgap energy, we can use the simple rule, that for efficient Ce$^{3+}$ luminescence it is at least required that the lowest level of the Ce$^{3+}$ 5d configuration is located below the conduction band, as has been noticed before [25]. This condition can be expressed more explicitly by:

$$E_{\text{host}} > E_{\text{VB-4f}} + E_{4f-5d,i}$$  \hspace{1cm} (1)

where $E_{\text{host}}$ is the energy of the fundamental host absorption, $E_{\text{VB-4f}}$ the energy of the Ce$^{3+}$ ($^{2}F_{5/2}$) ground state relative to the top of the valence band and $E_{4f-5d,i}$ the energy difference between the lowest level of the Ce$^{3+}$ 5d configuration and the Ce$^{3+}$ ground state.

An energy level diagram is shown in figure 6. With the help of this figure, equation (1) can be written as:

$$E_{\text{host}} > E_{\text{VB-4f}} + E_{4f-5d} - E_{5d,i-5d}$$  \hspace{1cm} (2)

where $E_{4f-5d}$ is the difference between the average (centroid) energy of the levels of the Ce$^{3+}$ 5d configuration and that of the Ce$^{3+}$ ground state and $E_{5d,i-5d}$ the difference between the average energy level of Ce$^{3+}$ 5d configuration and that of the lowest level of the Ce$^{3+}$ 5d configuration. In the following discussion, we will use experimental results from which the position of the Ce$^{3+}$ energy levels can be derived. The attention is especially focused on oxides, because the Ce$^{3+}$ luminescence efficiency in these materials varies between zero and almost unity. Finally, we discuss the possibility of efficient Ce$^{3+}$ luminescence in sulfide host lattices.
Figure 6: Energy level diagram of the Ce$^{3+}$ centre and host lattice configurations. In the scheme $E_{VB}$ and $E_{CB}$ denote respectively the energy of the top of the valence and the bottom of the conduction bands and $E_{host}$ the energy of the fundamental host absorption. $E_{5d_{1}}$ and $E_{5d_{2}}$ are respectively the energy of the lowest level and average (centroid) energy of the levels of the Ce$^{3+}$ 5d configuration, and $E_{4f}$ the energy of the Ce$^{3+}$ ground state. The abbreviations Eq. 1 and Eq. 2 refer to the equations in the text.

$E_{VB-4f}$ is determined by the binding energy of a Ce$^{3+}$ 4f electron and that of a valence band electron. These energies are dependent on numerous electron-lattice interaction effects, such as the attractive electrostatic interaction between cations and anions, the repulsion between adjacent electron clouds, covalent contributions in the bonding and the lattice relaxation around the Ce$^{3+}$ ion when incorporated on a non-equivalent cation site. Unfortunately, only sparse experimental information is available on $E_{VB-4f}$ in materials. Several measurement techniques can be used to determine $E_{VB-4f}$, such as (soft) X-ray photoelectron spectroscopy (XPS), photoconductivity (PC) and excited state absorption (ESA). Only with the first technique the position of the level of the Ce$^{3+}$ 4f configuration can directly be determined relative to the valence band. With the other techniques, the position of a level of a Ce$^{3+}$ 4f or 5d configuration relative to conduction band can be recorded. If the energy of the fundamental host absorption is known, the position of the Ce$^{3+}$ $^{2}F_{5/2}$ state can be estimated. The interpretation of the spectra from which $E_{VB-4f}$ can be derived is not unambiguous, since the location of Ce$^{3+}$ ground state is dependent on the definition of the valence band and conduction band edges. In the present study we used the following definitions. For (S)XPS spectra we defined the energy of the top of the valence band as the difference of the energy of the (gaussian shaped) band closest to the top of the valence band and the standard deviation $\sigma$ of that peak, as indicated in figure 6. Using PC and ESA, we recall that we use the energy of the fundamental host absorption. Hence, for the positions of the levels of the Ce$^{3+}$ 4f and 5d configuration, the low-energy side of the PC and ESA peaks are used as the energy difference between the Ce$^{3+}$ level under study and the conduction band. In table 2 we compiled the energy position of the Ce$^{3+}$ ground state in a number of oxide compounds obtained from literature. Because of the definitions described above, in some
cases other results are obtained than mentioned in the references. By inspection of table 2, we note a considerable variation in $E_{\text{VB}-4f}$ for the oxides, varying from 0.5 eV for Ce$_2$(WO$_4$)$_3$ to 3.1 eV for Lu$_2$O$_3$; $E_{\text{CB}}^{4+}$.

**TABLE 2:** The energy difference $E_{4f-VB}$ between the energy level position of the Ce$^{3+}$ ($^2F_{5/2}$) ground state and the top of the valence band in some oxide materials (column 6). The experimental energies from which $E_{4f-VB}$ is derived are shown in column 2-5. They denote respectively the onset of the fundamental absorption edge ($E_{\text{hbm}}$), the energy level position of the Ce$^{3+}$ 4f or 5d configuration with respect to the conduction band ($E_{4f-CB}$ and $E_{5d-CB}$) and the energy difference between the levels of the Ce$^{3+}$ 4f and the Ce$^{3+}$ 5d configuration under study ($E_{4f-5d}$). Column 7 shows the used measurement techniques. (S)XPS stands for (soft) X-ray photoelectron spectroscopy, PC for photoconductivity and ESA for excited state absorption. The absence or presence of Ce$^{3+}$ luminescence is mentioned as well.

<table>
<thead>
<tr>
<th>compound</th>
<th>$E_{\text{hbm}}$ [eV]</th>
<th>$E_{4f-CB}$ [eV]</th>
<th>$E_{5d-CB}$ [eV]</th>
<th>$E_{4f-5d}$ [eV]</th>
<th>$E_{4f-VB}$ [eV]</th>
<th>measurement technique</th>
<th>Ce$^{3+}$ luminescence</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$(WO$_4$)$_3$</td>
<td>2.4</td>
<td>1.9</td>
<td>-0.5</td>
<td>no</td>
<td>[26]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$_2$O$_3$; Ce$^{3+}$ / Lu$_2$O$_3$; Ce$^{3+}$</td>
<td>5.6</td>
<td>2.5</td>
<td>3.1</td>
<td>PC</td>
<td>5</td>
<td>[25]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeAlO$_3$</td>
<td>unknown</td>
<td>6.55</td>
<td>0.45</td>
<td>3.44$^1$</td>
<td>2.7</td>
<td>PC</td>
<td>yes</td>
<td>[28]</td>
</tr>
<tr>
<td>Lu$_2$SiO$_5$; Ce$^{3+}$</td>
<td>6.55</td>
<td>3.75</td>
<td>2.8</td>
<td>PC</td>
<td>yes</td>
<td>[31]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y$_2$AlO$_4$; Ce$^{3+}$</td>
<td>6.3</td>
<td>1.24</td>
<td>2.55</td>
<td>2.5</td>
<td>ESA</td>
<td>yes</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>Ce$_2$O$_4$</td>
<td>6.3</td>
<td>3.8</td>
<td>2.5</td>
<td>PC</td>
<td>yes</td>
<td>[30]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeF$_3$</td>
<td>8.7</td>
<td>1.7$\pm$0.3</td>
<td>SXPS</td>
<td>yes</td>
<td>[27]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ We use 3.44 eV instead of 3.29 eV mentioned by Yen et al. [31], since the 4f-5d transition is located at 360 nm, which is corresponding to 3.44 eV.

The second term in formula (2), $E_{4f-5d}$, expresses the difference between the average (centroid) energy of the Ce$^{3+}$ 5d configuration and the energy of the Ce$^{3+}$ ground state. The reduction of this energy difference with respect to the 6.4 eV of the free ion [32], is called the nephelauxetic effect. The origin lies in the delocalised nature of both the Ce$^{3+}$ 5d and the ligand wavefunctions. In a semi-empirical approach Aull and Jenssen [33] described the crystal field effects on $E_{4f-5d}$. According to them, the most important contributions are the ‘correlation crystal field’ and covalent bonding. The first effect is due to the polarisability of the ligands. The displacement of a Ce$^{3+}$ 4f or 5d electron will induce multipole moments on the ligands. Due to the resulting polarisation of the ligand, the electric field felt by the Ce$^{3+}$ 4f or 5d electron will be altered. As a result, the potential energy for the Ce$^{3+}$ 4f and 5d electrons will be lowered. Due to the difference in spatial extent of the 4f and 5d orbitals, also $E_{4f-5d}$ is lowered. The covalent contribution is due to charge transfer between the ligands and the Ce$^{3+}$ ion. This causes a mixing in the wavefunctions of the Ce$^{3+}$-ligand complex, in which the antibonding wavefunctions consist mainly of the Ce$^{3+}$ 5d wavefunctions. Part of the ligand electrons will reside some time on the Ce$^{3+}$ ion, thereby increasing $E_{4f-5d}$. Other contributions to $E_{4f-5d}$ shift, including for example exchange and the classical overlap, have only a minor net effect. Experimentally, $E_{4f-5d}$ can be derived from Ce$^{3+}$ 4f-5d excitation and absorption spectra, provided that they are not obscured by the fundamental host absorption. From the current available experimental data it is found that in fluorides $E_{4f-5d}$ varies between 5.0 eV (for Rb$_2$NaYF$_5$; Ce$^{3+}$[35]) and 5.7 eV (for LaF$_3$; Ce$^{3+}$[36]), in oxides between
4.2 eV (for LuBO₃:Ce³⁺ [37] (vaterite structure)) and 5.6 eV (in La₅O₁₄:Ce³⁺ [27]). Low values are obtained in sulfide host lattice materials. For example in MgS:Ce³⁺, \( E_{4f-5d} \) is only 3.5 eV [38].

The last term in formula (2) is \( E_{5d_{-5d}} \), the difference between the mean energy of the Ce³⁺ 5d configuration and that of lowest level of the Ce³⁺ 5d configuration. This is determined by the crystal field strength. The energy location of the levels of the Ce³⁺ 5d configuration is determined by several crystal field effects, such as the point symmetry at the lattice site on which the Ce³⁺ ion is incorporated, the Ce³⁺-ligand distances, the polarisability of the ligands and the contribution of covalent bonding. For an octahedral complex they are discussed by Aull and Jenssen [33]. Experimentally, \( E_{5d_{-5d}} \) can be derived from Ce³⁺ 4f-5d excitation and absorption spectra. Typically, in oxide materials \( E_{5d_{-5d}} \) varies between ~0.8 eV (in LuBO₃:Ce³⁺ [37] (vaterite structure)) and 1.7 eV (in Y₂Al₂O₁₂:Ce³⁺ [39]).

Let us return to the prediction of Yen et al. [25]. The data presented in table 2 seem to confirm the hypothesis that in oxide materials no Ce³⁺ luminescence is observed if the fundamental host absorption energy is lower than 6 eV, like in Y₂O₃:Ce³⁺ and Ce₂(WO₄)₃. Nevertheless, we consider this threshold as rather premature. The threshold energy is based the Ce³⁺ luminescence efficiency in only a few oxide materials: 7 compounds in table 2 and 6 compounds in the table presented by Yen et al. [25]. Furthermore, in the preceding paragraphs it has been made clear that subtle crystal field and electron-lattice interaction effects determine the exact energy locations of the levels of the Ce³⁺ 4f and 5d configurations.

Next, let us discuss the efficiency of Ce³⁺ luminescence in sulfides. In table 3 the data of some relevant rare earth and yttrium sulfide host matrices doped with Ce³⁺ are compiled. The fundamental host absorption energy is in the range of 1.7-3.8 eV. By inspection, for α-La₂S₃ and SrGd₂S₄ a discrepancy between the data reported by several authors is noted. In these compounds, the lowest energy of the Ce³⁺ 4f-5d transition is larger than the reported bandgap energy. Nevertheless, efficient Ce³⁺ luminescence is observed. This contradiction is due to underestimated bandgap energy values reported by Schevciw et al. [21], like we noticed for Lu₂S₃ in a preceding section. Despite the small bandgap energy, in most sulfides the lowest level of the Ce³⁺ 5d configuration is still located below the conduction band. The lowest energy of the Ce³⁺ 4f-5d transitions, \( E_{4f-5d} \), varies from 2.3 eV in β-La₂S₃:Ce³⁺ to ~3.0 eV in I-LaLuS₃:Ce³⁺. This small energy is mainly due to the strong nephelauxetic effect in these materials. In order to explain the presence of Ce³⁺ luminescence in most of the sulfides in table 3, the energy difference between the Ce³⁺ ground state and the top of the valence band, \( E_{\gamma-4f} \), must be quite small. In β-La₂S₃:Ce³⁺, for example, \( E_{\gamma-4f} \) may be at maximum 0.47 eV in order to fulfill the luminescence condition of equation (1). For γ-Ce₂S₃ the energy of the Ce³⁺²F⁵/₂ state can be derived from XPS and PC spectra. Based on the XPS spectra presented in [7], \( E_{\gamma-4f} \) is found to be 0±0.5 eV. The interpretation of the PC spectra presented in [40] is not unambiguous. Dependent on the interpretation of the spectra, \( E_{\gamma-4f} \) may vary from 0.05 to ~0.9 eV. In this compound no Ce³⁺ luminescence is observed.
### Table 3: The absence or presence of Ce$^{3+}$ luminescence in sulfide host lattices containing trivalent cations. Column 2 presents the onset of the fundamental absorption. The indirect bandgap energy is shown between brackets. The presence or absence of Ce$^{3+}$ luminescence is shown in the last column

<table>
<thead>
<tr>
<th>Host lattice</th>
<th>$E_{host}$ [eV]</th>
<th>$E_{4f-5d,l}$ [eV]</th>
<th>Ce$^{3+}$ luminescence</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-LaLu$_3$S$_6$</td>
<td>&lt;2$^a$</td>
<td>no$^a$</td>
<td></td>
</tr>
<tr>
<td>G-LaYS$_3$</td>
<td>&lt;2$^a$</td>
<td>no$^a$</td>
<td></td>
</tr>
<tr>
<td>α-GdS$_3$</td>
<td>1.72(1.02)$^a$</td>
<td>no$^a$</td>
<td></td>
</tr>
<tr>
<td>SrGd$_2$S$_4$</td>
<td>2.70$^b$</td>
<td>2.8$^c$</td>
<td>yes</td>
</tr>
<tr>
<td>α-La$_2$S$_3$</td>
<td>2.7$^b$</td>
<td>3.1$^c$</td>
<td>yes$^a$</td>
</tr>
<tr>
<td>β-La$_2$S$_3$</td>
<td>2.77(1.46)$^a$</td>
<td>2.30$^a$</td>
<td>yes</td>
</tr>
<tr>
<td>SrLa$_2$S$_4$</td>
<td>2.82$^b$</td>
<td>2.5$^c$</td>
<td>yes</td>
</tr>
<tr>
<td>δ'-Y$_2$S$_3$</td>
<td>2.85(1.69)$^a$</td>
<td>2.38$^a$</td>
<td>yes, below 77 K</td>
</tr>
<tr>
<td>SrY$_2$S$_4$</td>
<td>3.1$^b$</td>
<td>2.5$^d$</td>
<td>yes</td>
</tr>
<tr>
<td>CaLa$_2$S$_4$</td>
<td>3.1$^d$</td>
<td>2.6$^d$</td>
<td>yes</td>
</tr>
<tr>
<td>γ-Ce$_2$S$_3$</td>
<td>3.3 (2.75)$^c$</td>
<td>no, impurity-bound exciton, below 77 K$^f$</td>
<td></td>
</tr>
<tr>
<td>I-LaLuS$_3$</td>
<td>3.5$^a$</td>
<td>3.00$^a$</td>
<td>yes</td>
</tr>
<tr>
<td>ε-Lu$_2$S$_3$</td>
<td>3.8</td>
<td>2.70</td>
<td>yes</td>
</tr>
</tbody>
</table>

$^a$ Ref [18]; $^b$ Ref [21]; $^c$ Ref [11], $^d$ Ref [41], $^e$ Ref [7], $^f$ Ref [42]

* The origin of the luminescence is not clear, since the Stokes shift amounts 9000 cm$^{-1}$. So the luminescence may also originate from the recombination of an impurity-bound exciton.

Table 3 also indicates that there is no clear correlation between the fundamental host absorption energy and the Ce$^{3+}$ luminescence efficiency. By inspection, it is found for the compounds presented in this table that below fundamental host absorption energies of 2 eV the Ce$^{3+}$ luminescence is quenched and above 3.5 eV efficient Ce$^{3+}$ luminescence is observed. In the intermediate region there is no correlation between the fundamental host absorption energy and the Ce$^{3+}$ luminescence efficiency. In some cases the luminescence is efficient as in β-La$_2$S$_3$:Ce$^{3+}$ ($E_{host} = 2.7$ eV), but in other cases it is quenched as in γ-Ce$_2$S$_3$ ($E_{host} = 3.3$ eV). In this context, it is noticed that other quenching mechanisms may be effective as well. This holds for concentration quenching, as has been noticed already by Blasse et al. [20], and for quenching by energy transfer to other luminescence centres. In GdF$_3$:Ce$^{3+}$, for example, the Ce$^{3+}$ luminescence is lost by Gd$^{3+}$→Ce$^{3+}$ energy transfer [43].

### 9.4.2 Decay time

The observed Ce$^{3+}$ 5d-4f radiative decay time of ~ 32 ns in Lu$_2$S$_3$ is much shorter than the 60 ns in Y$_3$Al$_5$O$_{12}$ [44], luminescing at about the same wavelength. The radiative life time $\tau$ (in ns) for an electric dipole allowed transition [45] can be expressed as:

$$\tau = 1.5 \cdot 10^{-5} \frac{\lambda^2}{f(1/3n^2 + 2)n}$$  \hspace{1cm} (3)

where $f$ is the oscillator strength, $n$ the refractive index and $\lambda$ the wavelength of emission (in nm).
The factor \( \left( \frac{1}{3 \eta^2 + 2} \right)^{-2} \) represents the correction for the macroscopic electric field by the local electric field at the Ce\(^{3+}\) site. This correction factor can only be used for sites with a high point symmetry.

Now we will compare the radiative decay times of the Ce\(^{3+}\) 5d-4f luminescence in Y\(_3\)Al\(_5\)O\(_{12}\) and Lu\(_2\)S\(_3\). The emission wavelength in Y\(_3\)Al\(_5\)O\(_{12}\):Ce\(^{3+}\) is located at 550 nm [44], which is a slightly shorter wavelength than the 590 nm in Lu\(_2\)S\(_3\):Ce\(^{3+}\). A variation in lifetime can thus only be explained by different material properties, giving rise to different refractive indeces or oscillator strengths. Unfortunately, the oscillator strengths are not known. The refractive index in Y\(_3\)Al\(_5\)O\(_{12}\) is 1.83 [29]. That of Lu\(_2\)S\(_3\) is not known, but we assume that it is comparable to that of other rare earth sesquisulfides, i.e. between 2.5 and 2.8 [6]. This high value is probably due to the high polarisability of this material. Using equation (3), the ratio in radiative decay times of the two compounds can be expressed as \( \tau(Lu_2S_3)/\tau(Y_3Al_5O_{12}) = (0.29\pm0.05)/(Y_3Al_5O_{12})/(Lu_2S_3) \). Although the oscillator strength and (or) the local field correction factor may not be equal in the two compounds, it is clear that the radiative decay time in Lu\(_2\)S\(_3\):Ce\(^{3+}\) can be shorter than in Y\(_3\)Al\(_5\)O\(_{12}\):Ce\(^{3+}\), due to the different polarisabilities of the host materials resulting in different refractive indices. Anyway, it is obvious that the ~32 ns decay time is not necessarily due to quenching of the Ce\(^{3+}\) 5d-4f luminescence.

### 9.4.3 Energy transfer

Upon absorption of ionising radiation, electrons and holes are created in the material. In the thermalisation phase of the electrons and holes, part of the absorbed energy is lost. For small bandgap materials like Lu\(_2\)S\(_3\):Ce\(^{3+}\) the energy needed for the creation of an e-h pair amounts 2-3 times the bandgap energy [46]. The bandgap for Lu\(_2\)S\(_3\) is ~4 eV. Then the energy needed for the creation for an e-h pairs is at most ~12 eV, implying that per MeV absorbed radiation energy \( \geq 83,000 \) e-h pairs are created. The maximum light yield we measured is ~28,000 ph/MeV, so only \( \leq 35\% \) of the e-h pairs eventually gives rise to radiative recombination on Ce\(^{3+}\). Inspite of the high light yield, we therefore conclude that a considerable fraction of the e-h pairs is lost for luminescence. At temperatures above 300 K the scintillation intensity decreases further. This quenching may have several causes, viz. thermal quenching of Ce\(^{3+}\) luminescence or a decrease in the energy transport efficiency to the Ce\(^{3+}\) centres.

### 9.4.4 Comparison with other Lu based scintillators

In table 4 some properties of Lu\(_2\)S\(_3\):Ce\(^{3+}\) are compared with those of Lu\(_2\)SiO\(_5\):Ce\(^{3+}\) and Lu\(_2\)O\(_3\):Ce\(^{3+}\). Lu\(_2\)S\(_3\) has a ~30% longer absorption length than Lu\(_2\)O\(_3\):Ce\(^{3+}\) and the light yield of the new scintillator is approximately equal to that of Lu\(_2\)SiO\(_5\):Ce\(^{3+}\).

The main advantage of the Lu\(_2\)S\(_3\):Ce\(^{3+}\) scintillator is its emission in the red. Thus, the scintillation light can be efficiently detected by silicon detectors. The light-detection efficiency for these detectors is ~80%, whereas for PMTs with bi-alkali photocathodes it is only ~25% at maximum. Consequently, the number of detected photons will be less when PMTs are used instead of silicon based photodetectors. Because of the high QE of solid state light detectors, smaller energy resolution can be achieved than with PMTs, provided that the crystal quality and the coupling to the light detector are improved.
TABLE 4: A comparison of the scintillation properties of Lu₂S₃:Ce³⁺ with other Lu based scintillators

<table>
<thead>
<tr>
<th>Properties</th>
<th>Lu₂SiO₅:Ce³⁺ [1],[47]</th>
<th>LuAlO₃:Ce³⁺ [47]</th>
<th>Lu₂S₃:Ce³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>density [g/cm³]</td>
<td>7.4</td>
<td>8.34</td>
<td>6.25</td>
</tr>
<tr>
<td>effective atomic number</td>
<td>66.4</td>
<td>65</td>
<td>66.7</td>
</tr>
<tr>
<td>attenuation length for</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a 511 keV photon [cm]</td>
<td>1.14</td>
<td>1.05</td>
<td>1.35</td>
</tr>
<tr>
<td>photoelectric fraction at 511 keV</td>
<td>0.34</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>emission maximum [nm]</td>
<td>420</td>
<td>365</td>
<td>592</td>
</tr>
<tr>
<td>light yield [ph/MeV]</td>
<td>27,000</td>
<td>11,400/∼10,000*</td>
<td>∼28,000</td>
</tr>
<tr>
<td>decay time [ns]</td>
<td>42</td>
<td>17.5</td>
<td>32</td>
</tr>
<tr>
<td>refractive index</td>
<td>1.81</td>
<td>1.95</td>
<td>2.5–2.8**</td>
</tr>
<tr>
<td>number of background counts due to the presence of $^{176}$Lu [count/s.cm³]</td>
<td>318</td>
<td>323</td>
<td>270</td>
</tr>
</tbody>
</table>

* The crystal growth technique of LuAlO₃:Ce³⁺ is not yet optimised. It is well possible that the light yield increases for better crystal quality.

** The refractive index for Lu₂S₃:Ce³⁺ is not known, we assume that it is comparable with other rare earth sulfides, i.e. between 2.5 and 2.8 [6]

The refractive index of Lu₂S₃ is probably equal to that of other sesquisulfides, viz. in the range of 2.5 and 2.8 [6]. This is slightly higher than that of other high-density scintillators, such as Bi₄Ge₃O₁₂ and CdWO₄, which have a refractive index of 2.15 and 2.3 respectively. Since standard photodetectors and coupling liquids only have a refractive index around 1.5, a large part of the generated scintillation light might be reflected on the crystal–photodetector interface. If clear crystals can be obtained, possible light losses can be minimised using highly reflective coatings. From transmission measurements on the small crystals we observed that self-absorption of the scintillation light in the crystal does not pose a problem.

9.5 Conclusions and outlook

For many applications the scintillation properties of Lu₂S₃:Ce³⁺ appear quite good. Further improvements can be made by optimising the Ce³⁺ concentration. However, the results presented were obtained on small crystals. We do not know, whether efficient Lu₂S₃:Ce³⁺ scintillation crystals with sizes of e.g. 1x1x1 cm³ can be grown. So far, only small Lu₂S₃ crystals have been grown [13],[14]. The crystal growth of other rare earth sesquisulfides with sizes larger than 1x1x1 mm³ is rarely reported [7],[48]. Decomposition of Lu₂S₃ near the melting point may limit the growth of large, say 1x1x1 cm³, crystals. For the crystal growth of La₂S₃ crystals, a similar problem was solved by controlling the pressure of the sulphur vapour [49].

Ce³⁺ doped sulfides and other chalcogenides like selenides and tellurides deserve further attention in the search for new scintillators. Compared to rare earth sulfides, rare earth
selenides and tellurides will have smaller optical phonon energies and bandgap energies. Provided that the energy transport and the Ce$^{3+}$ luminescence are efficient, scintillators with a high luminosity may be obtained. As long as the emission wavelength remains below ~800 nm, this light can be efficiently detected by means of silicon based light detectors.

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9.5 Conclusions and outlook


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10 Luminescence and scintillation properties of other $\text{Ce}^{3+}$ doped compounds

In this chapter the main results obtained for $\text{Ce}^{3+}$ doped $\text{Cs}_3\text{Lu}_2\text{Cl}_9$, $\text{LiLuSiO}_4$ and $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ materials are presented. On some of them research is continuing.

10.1 $\text{Cs}_3\text{Lu}_2\text{Cl}_9:\text{Ce}^{3+}$

The crystal structure of $\text{Cs}_3\text{Lu}_2\text{Cl}_9$ is of the $\text{Cs}_3\text{Ti}_2\text{Cl}_9$ type [1]. $\text{Cs}_3\text{Lu}_2\text{Cl}_9$ has a density of 4.01 g/cm$^3$ and an effective atomic number of 58.6. Because of the closed-packed structure and the high Lu content, this material has a much higher $\gamma$-quantum stopping power than the chlorides discussed in the previous chapters.

10.1.1 Experimental

$\text{Cs}_3\text{Lu}_2\text{Cl}_9$ melts incongruently. Nevertheless, crystals have been grown using the Bridgman technique in Bern from the purified binary halides $\text{CsCl}$ (merck suprapur, purity 99.5%), $\text{LuCl}_3$ and $\text{CeCl}_3$. The rare earth chlorides were prepared from the oxides $\text{Lu}_2\text{O}_3$ (purity 99.99%) and $\text{CeO}_2$ (Heraeus 99.999%) In the starting mixture the ratio of the elements $\text{Cs}$ to $\text{Lu}$ is 3:2:5. The $\text{Ce}^{3+}$ concentration as obtained from the weight-in amounts put in the melt is 1 at%. From a chemical analysis, the $\text{Ce}^{3+}$ content incorporated in the host lattice was found to be only 0.09 at%.

10.1.2 Results

Figure 1 shows the X-ray induced emission spectrum of $\text{Cs}_3\text{Lu}_2\text{Cl}_9:\text{Ce}^{3+}$. It consists of a structureless band between 350 and 550 nm, peaking at 409 nm, which may be due to radiative recombination of a self-trapped exciton (STE) and/or the $\text{Ce}^{3+}$ 5d-4f luminescence. The characteristic spin-orbit splitting of the groundstate $^2\text{F}$ of $\text{Ce}^{3+}$ can not be observed.

Luminescence and scintillation properties of $\text{Ce}^{3+}$ doped inorganic materials for gamma-ray detection © 1998 J.C. van 't Spijker, all rights reserved
Near 310 nm a weak luminescence is visible due to the presence of a Gd$^{3+}$ impurity. From the recorded X-ray induced emission spectrum a light yield of 7500 ph/MeV is obtained, whereas from pulse height spectra a light yield of 650 ph/MeV for 10 µs shaping time was obtained. The difference in these yields is caused by the slow scintillation response. The scintillation pulse contains decay time components in the range of several tens of µs to ms, as was observed by inspection of the scintillation pulses recorded with a PMT and displayed on an oscilloscope. It was not possible to record the slow scintillation decay with the multi-hit method.

10.2 LiLuSiO$_4$:Ce$^{3+}$

Recently the scintillation and storage properties of LiYSiO$_4$:Ce$^{3+}$ were reported [2]. For that material the light yield was estimated to be $1 \times 10^4$ photons per MeV of absorbed γ-ray energy. Here we present the scintillation properties of the isostructural LiLuSiO$_4$:Ce$^{3+}$. The measurements are performed on powder. In order to achieve a good estimate of the light yield, several experiments have been performed. The accuracy of the obtained values is discussed.

10.2.1 Experimental

LiLuSiO$_4$:2at.%Ce$^{3+}$ powder was prepared by a solid state reaction of stoichiometric proportions of Li$_2$CO$_3$, Lu$_2$O$_3$, CeO$_2$ and SiO$_2$ in a reducing atmosphere. The powder was mixed, homogenised in ethyl alcohol, dried and pressed into a pill form. Synthesis in solid form was performed at a temperature of 1200 °C during 30 hours. Then the pills were ground, again pressed and the same heating procedure was repeated. The powders were checked by X-
ray diffraction analysis. Presence of some Lu$_2$SiO$_5$ is not excluded, however it can be at most 2 percent. The X-ray diffraction spectrum resembles that of the isostructural LiYSiO$_4$, which has the olivine structure. The density of LiLuSiO$_4$ is 5.61 g/cm$^3$ and the effective atomic number is 63.4.

X-ray induced emission measurements were done using an X-ray tube with a Cu anode, operated at 35 kV and 25 mA. The X-rays are filtered by a 0.5 mm thick Be window. The powder is pressed into a 4 mm diameter sampleholder. The side facing the monochromator window is covered with a quartz window. The side facing the X-ray tube is covered with a 0.2 mm thick reflecting Al foil. The intensity of the scintillation emission was measured using ARC VM502 and ARC VM504 monochromators and a Thorn EMI 9426 photomultiplier tube (PMT). The emission spectra are corrected for the transmission of the measurement system and the quantum efficiency (QE) of the PMT. The yield, calculated as the wavelength integrated emission intensity, of LiLuSiO$_4$:Ce$^{3+}$ is compared with that of BaF$_2$ powder, which has a light yield of $\sim$11,000 ph/MeV. Part of the X-rays incident on the powder is not absorbed in the powder. The yields are corrected for this transmission loss.

Pulse height spectra of powders were recorded with an XP2020Q PMT and standard spectroscopic amplifiers. Powder was put directly on the PMT window, i.e. without using a coupling grease, which is normally used to measure light yields of crystals. The PMT window with powder was completely covered with 5 layers of 0.1 mm thick Teflon. Gamma rays from an $^{241}$Am source were used to excite the powder. For the determination of the light yield the standard procedure was followed.

10.2.2 Results

The excitation and emission spectrum of the Ce$^{3+}$ emission is shown in figure 2. The excitation spectrum consists of two main bands at 353 and 315 nm with a shoulder below 300

![Figure 2: (a) Excitation spectrum of LiLuSiO$_4$:Ce$^{3+}$ measured at the emission wavelength of 400 nm (b) The 350 nm excited emission spectrum. (c) X-ray induced emission spectrum. Both emission and excitation spectra are measured with a resolution of 1 nm.](image-url)
nm. The emission consists of a band between 370 and 490 nm, peaking at 405 nm. The typical splitting of 2000 cm\(^{-1}\) in the transitions of the lowest level of the Ce\(^{3+}\) 5d configuration to the spin-orbit split \(^{2}\)F levels cannot be resolved. The peak positions and the shape of the excitation and emission spectra resemble those of LiYSiO\(_4\):Ce\(^{3+}\) [2].

The X-ray induced emission spectrum of LiLuSiO\(_4\):Ce\(^{3+}\) is also shown in figure 2, curve c. It coincides with the Ce\(^{3+}\) 5d-4f emission between 370 and 470 nm. The wavelength-integrated yield was measured as a function of powder layer thickness (in mg/mm\(^2\)), to study the light scattering losses. Figure 3 displays the yields of BaF\(_2\) and LiLuSiO\(_4\):Ce\(^{3+}\) as a function of powder layer thickness. It shows a decrease in light yield with increasing layer thickness, with equal logarithmic slopes for BaF\(_2\) and LiLuSiO\(_4\):Ce\(^{3+}\). This indicates a light loss proportional to powder weight. So the loss seems to be only dependent on layer thickness. The light yield of LiLuSiO\(_4\):Ce\(^{3+}\) powder is 2.3-4.2 times higher than that of BaF\(_2\) powder. Accordingly, we estimate the light yield of LiLuSiO\(_4\):Ce\(^{3+}\) to be \((3\pm1)\times10^4\) ph/MeV.

The \(^{241}\)Am \(\gamma\)-ray induced pulse height spectrum of LiLuSiO\(_4\):Ce\(^{3+}\) powder is shown in figure 4. It consists of two bands located at 55 phe and 270 phe. The latter is shown on a linear scale in the inset of figure 4. They are attributed to the scintillation upon photoelectric absorption in LiLuSiO\(_4\):Ce\(^{3+}\) of the 13.9 keV and 17.8 keV X-rays of Np and to 59.5 keV \(\gamma\)-ray photopeak, respectively. To check on this, pulse height spectra were recorded with 2 mm thick aluminium plate placed between the \(^{241}\)Am source and the powder. The recorded pulse height spectrum is similar to that shown in figure 4, except that the intensity of the photopeak near 55 phe has decreased considerably, due to absorption of the low energetic X-rays by the aluminium. The QE at the Ce\(^{3+}\) emission in LiLuSiO\(_4\) being \(\sim\)22 % and assuming a collection efficiency of 0.76 (see chapter 3), the light yield is estimated to be 27,000 ph/MeV. Upon an increase in shaping time from 0.5 to 10 \(\mu\)s an increase of 20 % in light yield is observed. This
implies a decay time component in the \( \mu \)s range or larger. The light yield of LiLuSiO\(_4\):Ce\(^{3+}\) under \( \alpha \)-particle excitation is estimated to be \((4\pm2)\times10^3\) ph/MeV \( \alpha \) particle energy.

The main scintillation decay time is \(41\pm1\) ns, persisting over almost 2 decades. This is typical for Ce\(^{3+}\). A slower non-exponential decay time component in the \( \mu \)s range was also observed. The origin of the \( \mu \)s component is not clear. It can be a material property of the compound itself. Since the measurements are performed on powders, which have a much larger surface-volume ratio than say a 1x1x1 cm\(^3\) sized crystal, surface effects might slow down the scintillation decay as well.

10.2.3 Discussion

The main uncertainties in light yields derived from the X-ray induced emission measurements are the uncertainties in light losses and the absorbed fraction of X-ray energy incident on the sample. The latter was estimated in the following way. The total energy absorption of X-rays was calculated in the narrow beam geometry, which is a simplification of the measurement configuration. Effects like build up, multiple scattering of X-rays in the powder layer and non-homogeneity of the layer thickness are not taken into account. For 4 mg of BaF\(_2\) and LiLuSiO\(_4\) powder respectively only 65 and 78 % of the total X-ray energy is absorbed. For 10 mg of BaF\(_2\) and LiLuSiO\(_4\) these numbers are 87 and 93%. Errors like non-homogeneity of the powder layer will be most pronounced for a layer thickness of 0.32 mg/mm\(^2\) and are estimated to be \(~50\%\). The error for samples of 0.80 mg/mm\(^2\) and thicker is expected to be negligible. For these layer thicknesses the light loss of the generated scintillation light due to scattering and absorption by the powder grains is most pronounced as can be seen in figure 3. It is dependent of layer thickness, grain size, presence of surface traps and homogeneity of the surface layer thickness [6]. This loss will be minimal for samples with powder weights of \(~0.32\) mg/mm\(^2\). The error in the expected light loss is \(~20\%\). Thus we estimate the total error
in light yield derived from X-ray induced emission measurements to be in the order of ~ 50%. From pulse height measurements a more accurate light yield can be derived. Upon absorption of a γ quantum by the photoelectric effect a photoelectron is created and in addition an X-ray or an Auger electron with an energy close to the binding energy of the released photoelectron is generated. To minimise possible losses due to X-ray escape, the energy of the γ-ray should be chosen slightly below that of the K binding energy of the atom responsible for photoelectric absorption. For Lu in LiLuSiO₄:Ce³⁺ the binding energy is 63 keV, which is slightly higher than the 59.5 keV of ²⁴¹Am used in these experiments.

The estimated light yield of LiLuSiO₄:Ce³⁺ is comparable to that of Lu₂SiO₅:Ce³⁺, of which a small amount may be present as an impurity in the LiLuSiO₄:Ce³⁺ powder. Thus the question arises whether the measured scintillation could be due to Lu₂SiO₅:Ce³⁺. Since the fraction of Lu₂SiO₅:Ce³⁺ in LiLuSiO₄:Ce³⁺ is at most a few percent, its contribution to the observed light yield in the X-ray excited spectrum can only be a minor one. Therefore it should be attributed to the scintillation of LiLuSiO₄:Ce³⁺.

10.3 Gd₃Sc₂Al₃O₁₂:Ce³⁺

Gd₃Sc₂Al₃O₁₂ crystallises in the garnet structure. In this structure, the scandium ions are octahedrally and the aluminium ions tetrahedrally surrounded by oxygen atoms. The rare-earth ions are co-ordinated by 8 oxygens in a dodecahedron [7]. Gd₃Sc₂Al₃O₁₂ has a density of 5.56 g/cm³ and an effective atomic number of 55.5. Practically, rare earth garnets gained a considerable attention as laser host materials. We mention Y₃Al₅O₁₂:Ce³⁺, Y₃Al₅O₁₂:Nd³⁺, Gd₃Ga₅O₁₂:Cr³⁺. As scintillators Y₃Al₅O₁₂:Ce³⁺, Lu₃Al₅O₁₂:Ce³⁺, Lu₃Al₅O₁₂:Sc₃Pr³⁺ have been studied. Kling et al. [8] reported on the scintillation properties of Gd₃Sc₂Al₃O₁₂:Ce³⁺.

10.3.1 Experimental

Crystals of Gd₃Sc₂Al₃O₁₂:Ce³⁺ were kindly provided by N.N. Ryskin and E.V. Zharkov of General Physics Institute, Moscow, Russia. The studied samples have a thickness of ~ 2 mm and are optically clear and free of cracks. The Ce³⁺ concentrations as derived from the weight-in amounts in the melt are respectively 0.33, 1 and 3.3 at %. From a comparison of optical absorption spectra, the relative Ce³⁺ concentrations were found to be 0.62, 1 and 1.55. In this study, the Ce³⁺ concentrations are expressed accordingly, using 1 at.% Ce³⁺ as the norm.

Because the scintillator luminesces in the red, X-ray induced emission spectra were recorded using a Jobin Yvon H10 UV monochromator (grating 1200 grooves/mm) and a red sensitive XP2254/B PMT. The X-ray induced emission spectra were corrected for the transmission of the monochromator and the spectral dependence of the QE of the PMT. In order to estimate the light yield, the wavelength-integrated yield was compared with that of a BaF₂ reference crystal being 11,000 ph/MeV. Absolute light yields are obtained from pulse height spectra recorded with the XP2254/B PMT using standard techniques. At the synchrotron facility at Daresbury luminescence decay time spectra were recorded using the single-hit method.
10.3.2 Results

Figure 5 displays the absorption spectrum of Gd₃Sc₂Al₅O₁₂:Ce³⁺. In this spectrum the narrow absorption lines due to Gd³⁺ ⁸S₇/₂→⁶H₇/₂ and ⁸S₇/₂→⁶P₇/₂ transitions are clearly visible near 275 and 310 nm. In addition, broad bands are observed peaking at 230, 340 and 455 nm, which have to be attributed to Ce³⁺ 4f-5d transitions and not to Gd³⁺ 4f-5d transitions as was done by Kling et al. [8]. Also in other garnets, like Y₃Al₅O₁₂:Ce³⁺ [10], [11], the absorption bands due to Ce³⁺ 4f-5d transitions are located at comparable wavelengths. The strong crystal field at the rare earth site in these materials results in a low energy absorption band at 455 nm. This band is responsible for the yellowish colour of the Ce³⁺ doped Gd₃Sc₂Al₅O₁₂. Kling et al. [8] estimate the onset of the fundamental absorption band to be located near 240 nm. This onset, however, has to be attributed to the low-wavelength shoulder of a Ce³⁺ 4f-5d absorption band, similarly as is in Y₃Al₅O₁₂:Ce³⁺. The onset of the fundamental absorption is probably located near 200 nm, as in other rare earth aluminate garnets [12],[13].

As can be seen in figure 5, the Gd³⁺ 4f-4f transition near 275 nm overlap with a Ce³⁺ 4f-5d absorption band. The characteristic Gd³⁺ 4f-4f transitions near 240 and 200 nm are not observed. They are apparently obscured by the Ce³⁺ 4f-5d absorption bands. Gd³⁺→Ce³⁺ resonance energy transfer may be possible via these levels. In order to study this transfer, the decay of the Ce³⁺
luminescence was recorded after pulsed excitation into the Ce\textsuperscript{3+} 4f-5d and Gd\textsuperscript{3+} 4f-4f absorption bands. The results are shown in figure 6. After excitation at 240 nm into the Gd\textsuperscript{3+} \( ^8S_{7/2} \rightarrow ^6D_J \) and overlapping Ce\textsuperscript{3+} 4f-5d transition, an almost exponential decay is observed with a main decay time constant of 52 ns and another of \( \sim 15 \) ns having less intensity, see figure 6, curve a. We attribute this to the decay of the Ce\textsuperscript{3+} 5d-4f transition. Apparently, the number of excited Gd\textsuperscript{3+} ions is negligibly small compared to the number of excited Ce\textsuperscript{3+} ions. The main decay time compares well to the 60 ns of the Ce\textsuperscript{3+} 5d-4f transitions in \( Y_2Al_5O_{12}:Ce^{3+} \) [13]. The decay curves in figure 6, curves b and c, consist of an initial build-up followed by an exponential decay. We attribute this ingrowth to the feeding of the Ce\textsuperscript{3+} luminescence via energy migration on the Gd-sublattice. This will be discussed later on.

So far, the optical properties have been characterised. Next, the scintillation properties will be considered. Under excitation of ionising radiation, the luminescence consists of the Ce\textsuperscript{3+} 5d-4f emission between 500 and 700 nm, as can be seen in figure 5. No other emissions bands are observed. Light yields obtained from the X-ray induced emission spectra are collected in table 2, together with the light yields derived from pulse height spectra. By inspection, it is noted that the light yields derived under continuous X-ray irradiation are \( \sim 8 \) times higher than those derived from pulse height measurements. We attribute this to the presence of afterglow components, which do not contribute to light yields derived from pulse height spectra. Kling et al. [8] report the light yield to be 30% of that of NaI:Tl\textsuperscript{+}, i.e. 12,600 ph/MeV. This yield is considerably higher than the highest yield of 8,800 ph/MeV reported in this work.
TABLE 2: Light yields of Gd₃Sc₂Al₅O₁₂:Ce³⁺ derived from the X-ray induced emission spectra and pulse height measurements. The errors in the numbers is about 30 %.

<table>
<thead>
<tr>
<th>[Ce³⁺]</th>
<th>light yield X-rays [ph/MeV]</th>
<th>shaping time [μs]</th>
<th>light yield γ-rays ^137Cs [ph/MeV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62</td>
<td>7000</td>
<td>2</td>
<td>710</td>
</tr>
<tr>
<td>1</td>
<td>8000</td>
<td>3</td>
<td>1130</td>
</tr>
<tr>
<td>1.55</td>
<td>8800</td>
<td>3</td>
<td>980</td>
</tr>
</tbody>
</table>

Figure 7 presents the scintillation decay of Gd₃Sc₂Al₅O₁₂:1at.%Ce³⁺. It resembles the Ce³⁺ luminescence decay after excitation into the Gd³⁺ levels, see figure 6 curve b. This suggests that after absorption of ionising radiation the created electrons and holes are almost instantaneously captured by Gd³⁺ ions from where the energy is transferred to Ce³⁺ ions by energy transfer via the Gd-sublattice.

![Figure 7: Scintillation decay time spectrum of Gd₃Sc₂Al₅O₁₂:1at.%Ce³⁺.](image)

The scintillation properties of Gd₃Sc₂Al₅O₁₂:Pr³⁺ have been studied as well. figure 8 shows the X-ray induced emission spectrum of Gd₃Sc₂Al₅O₁₂:Pr³⁺. The luminescence is mainly due to the 4f-4f Pr³⁺ transitions as is indicated in the figure. In addition, a weak luminescence band is observed between 300 and 400 nm, peaking at ~350 nm.
10.3.3 Discussion

For efficient and fast Gd$^{3+}$→Ce$^{3+}$ resonance transfer it is required that i) the Ce$^{3+}$ emission wavelength is located at wavelengths > 350 nm in order to prevent Ce$^{3+}$→Gd$^{3+}$ backtransfer, ii) the Gd$^{3+}$ 4f-4f emission overlaps a Ce$^{3+}$ 4f-5d absorption band and iii) the distance between two neighbouring Gd$^{3+}$ ions is short, i.e. shorter than the critical distance of ~5 Å in gadolinium oxides [14]. Prerequisites i) and ii) are fulfilled, see figure 5. In Gd$_3$Sc$_2$Al$_5$O$_{12}$ the Gd$^{3+}$-Gd$^{3+}$ distance it is only 3.793 Å [7]. So prerequisite iii) is also fulfilled. The experimental results confirm that efficient Gd$^{3+}$→Ce$^{3+}$ transfer via migration over the Gd-sublattice occurs. The presence of the exponential decays indicates that the energy is transferred via fast energy migration on the Gd-sublattice. For such type of transfer the energy transfer rate between two neighbouring Gd$^{3+}$ ions should be much larger than the Gd$^{3+}$→Ce$^{3+}$ energy transfer rate and other depopulation rates of the Gd$^{3+}$ levels. When the Ce$^{3+}$→Gd$^{3+}$ back transfer is neglected, the time response of the Ce$^{3+}$ luminescence, $I_{Ce}(t)$ after pulsed excitation into the Gd$^{3+}$ levels and underlying Ce$^{3+}$ level, can be written as [15]:

$$I_{Ce}(t) = W_{Ce} \left[ N_{Gd} e^{-W_{Ce} t} + \frac{W_{Gd→Ce}}{W_{Ce} - W_{Gd} - W_{Gd→Ce}} N_{Gd0} \left( e^{-(W_{Gd} + W_{Gd→Ce}) t} - e^{-W_{Ce} t} \right) \right]$$

(1)

where $W_{Ce}$, $W_{Gd→Ce}$, $W_{Gd}$ are the transition rates of the Ce$^{3+}$ 5d-4f transition, the transfer of Gd$^{3+}$ to Ce$^{3+}$ and the deexcitation rate the Gd$^{3+}$ level, respectively. $N_{Gd0}$ and $N_{Gd0}$ are the initial numbers of excited Gd$^{3+}$ and Ce$^{3+}$ ions. The decay curves b and c in figure 6 were fitted using equation (1). In the fitting it was assumed that $W_{Gd} \ll W_{Gd→Ce}$. The obtained values are compiled in table 1.
10.3 Gd₃Sc₂Al₃O₁₂:Ce³⁺

TABLE 1: Transition rates in Gd₃Sc₂Al₃O₁₂:Ce³⁺. \( W_{\text{Gd,G→Ce}} \) and \( W_{\text{Gd,I→Ce}} \) denote respectively the transfer rates from Gd³⁺ 6G and 4I levels to overlapping Ce³⁺ levels.

<table>
<thead>
<tr>
<th>transition probability</th>
<th>rate [1/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( W_{\text{Ce}} )</td>
<td>19.2 \times 10⁶</td>
</tr>
<tr>
<td>( W_{\text{Gd,G→Ce}} )</td>
<td>(15±2) \times 10⁶</td>
</tr>
<tr>
<td>( W_{\text{Gd,I→Ce}} )</td>
<td>(17±1) \times 10⁶</td>
</tr>
</tbody>
</table>

Finally, the luminescence in Gd₃Sc₂Al₃O₁₂:Pr³⁺ will be discussed. The weak luminescence band observed around 350 nm in figure 8 is probably not due to host lattice luminescence, since in Y₃Al₅O₁₂:(Sc) and Lu₃Al₅O₁₂:(Sc) the peak position of this luminescence is located at much shorter wavelengths [16],[17],[18]. It is probably due to Pr³⁺ 5d-4f luminescence. In other garnets like Lu₃Al₅O₁₂:Sc,Pr³⁺ the Pr³⁺ 5d-4f luminescence is located at comparable wavelengths, as is shown with a dotted line in the figure. Yet, it is rather surprising that the Pr³⁺ 5d-4f luminescence is almost completely quenched, while it is not in other Pr³⁺ doped garnets [17],[19],[20]. The cause for the absence of the Pr³⁺ 5d-4f luminescence is probably either due to energy transfer from the lowest energy level of the Pr³⁺ 5d configuration to a level of the Gd³⁺ 4f configuration by lattice relaxation or due to a Förster-Dexter type transfer by the overlap of the Pr³⁺ 5d-4f luminescence with the Gd³⁺ ⁸S₇/₂-⁸P₇ absorption peaks near 310 nm. As a consequence, the energy of a state of the Pr³⁺ 5d configuration is lost due to efficient transfer to the Gd-sublattice and subsequent transport to quenching centres. Such type of luminescence quenching has also been observed in GdOCl:Pr³⁺[21],[22].

REFERENCES


Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection

Summary and conclusions

Ionising radiation is being used in many applications. For the detection of this radiation several methods are applied. In one of those scintillators are used. These are materials, mostly crystals, in which a light flash is produced upon absorption of the radiation. The generated luminescence is detected by e.g. a photodiode or a photomultiplier tube. Despite the fact that many scintillator materials are known since a long time, there is still a need for a scintillator with improved properties. The investigations described in this thesis are focused on the search for new scintillator materials for $\gamma$-ray detection. Scintillation materials are also interesting from scientific point of view. After absorption of radiation some complicated and interesting phenomena take place, before the scintillation is generated. The subject is introduced in chapter 1.

In order to discern what scintillator features need to be improved, the scintillator requirements dictated by detection systems and the specifications of currently applied scintillators are reviewed. This is presented in chapter 2. Furthermore, the energy transfer from the absorbed $\gamma$-quantum to the luminescence centre is described. Next the choice of the studied compounds is motivated. The attention is focused on the study of Ce$^{3+}$ doped compounds with an emphasis on Ce$^{3+}$doped chlorides.

The experimental methods that are used to study the selected compounds are discussed in chapter 3. Chapters 4 to 10 are devoted to the investigations of the selected compounds. In table 1 their main scintillation properties are compiled.
Table 1: Scintillation properties of the investigated materials. Presented are the Ce<sup>3+</sup> concentration, the effective atomic number (Z<sub>eff</sub>), the density (ρ), the peak wavelength (λ) of the transition from the lowest level of the 5d configuration to the Ce<sup>3+</sup> groundstate (λ), the light yield (LY) as derived from X-ray induced emission spectra on pulse height measurements (phm) and the scintillation decay time (τ). The used shaping times for the light yields derived from pulse height spectra are shown between brackets.

<table>
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<tr>
<th>Compound</th>
<th>Ce&lt;sup&gt;3+&lt;/sup&gt; at. %</th>
<th>Z&lt;sub&gt;eff&lt;/sub&gt;</th>
<th>ρ [g/cm&lt;sup&gt;3&lt;/sup&gt;]</th>
<th>λ [nm]</th>
<th>LY (ph/MeV) (X-ray)</th>
<th>LY (ph/MeV) (phm)</th>
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<td>6.94</td>
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<td>550</td>
<td>~8000</td>
<td>1100 (3 µs)</td>
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</table>

<sup>a</sup>The given concentration is the one as put in the melt.
<sup>*</sup>It is not sure whether the emission is due to Ce<sup>3+</sup> luminescence.

In chapter 4 the study of the scintillation and luminescence properties of BaY<sub>2</sub>F<sub>8</sub>:Ce<sup>3+</sup> and BaLu<sub>3</sub>F<sub>8</sub>:Ce<sup>3+</sup> crystals is presented. For pure BaLu<sub>3</sub>F<sub>8</sub>, a luminescence with a decay time of ~ 1ns is observed under γ-ray excitation, which is attributed to core-valence luminescence. The scintillation efficiency of the studied crystals is rather low.

Chapter 5 deals with the optical and scintillation properties of Cs<sub>2</sub>LuCl<sub>6</sub>:Ce<sup>3+</sup> and some Ce<sup>3+</sup> containing elpasolites. In the elpasolites, the site on which the Ce<sup>3+</sup> ion is incorporated has a perfect O<sub>4h</sub> point symmetry. Unexpectedly, the levels of the Ce<sup>3+</sup> 5d(e<sub>2g</sub>) configuration appear to be split. The scintillation decay consists mainly of power-law decay time components with µs tails.

Scintillation and luminescence properties of K<sub>2</sub>LaCl<sub>5</sub>:Ce<sup>3+</sup> are presented in chapter 6. Under X-ray excitation self-trapped exciton (STE) luminescence and Ce<sup>3+</sup> luminescence are observed. With increasing Ce<sup>3+</sup> concentration, the STE luminescence intensity decreases.
along with an increase of the Ce\(^{3+}\) luminescence intensity. Of the studied samples, the highest light yield is measured for K\(_2\)LaCl\(_5\);10% Ce\(^{3+}\) (see Table 1). For this sample an energy resolution of 5.3 % is recorded at 662 keV \(\gamma\)-ray energy. In order to explain the energy transfer STE diffusion and bimolecular recombination are proposed. For low Ce\(^{3+}\) concentration the energy transfer is mainly governed by STE diffusion, whereas for high Ce\(^{3+}\) concentration the bimolecular recombination process is held dominant. A simple model for the STE diffusion is presented and compared with the experimental results. Reasonable agreement is obtained.

Chapter 7 describes the luminescence and scintillation of RbGd\(_3\)Cl\(_7\);Ce\(^{3+}\) and RbGd\(_3\)Br\(_7\);Ce\(^{3+}\) crystals. In RbGd\(_3\)Br\(_7\);Ce\(^{3+}\) the Gd\(^{3+}\) \(^{6}\)I\(_{11/2}\) luminescence overlaps a Ce\(^{3+}\) 4f-5d absorption band. After excitation into the Gd\(^{3+}\) \(^{6}\)I\(_1\) levels, efficient Gd\(^{3+}\) →Ce\(^{3+}\) energy transfer is observed by fast energy migration on the Gd-sublattice. The energy migration is discussed quantitatively. It is concluded that an interaction other than exchange interaction is dominant.

Under excitation by X-rays and \(\gamma\)-rays RbGd\(_3\)Br\(_7\); Ce\(^{3+}\) and RbGd\(_3\)Cl\(_7\); Ce\(^{3+}\) show both high light yields (see Table 1). For undoped RbGd\(_3\)Br\(_7\) the characteristic Gd\(^{3+}\) 4f-4f luminescence is observed together with a weak broad band emission, that is attributed to STE luminescence. For increasing Ce\(^{3+}\) concentration, the Gd\(^{3+}\) 4f-4f luminescence and the STE emission intensities decrease along with an increase of Ce\(^{3+}\) luminescence intensity. For RbGd\(_3\)Br\(_7\);4.1% Ce\(^{3+}\) an energy resolution of 3.8% at a \(\gamma\)-ray energy of 662 keV was derived. In the scintillation energy transfer at least two mechanisms can be identified, one giving rise to an exponential decay in the first few hundred nanoseconds, another giving rise to a non-exponential scintillation decay in the \(\mu\)s range. The importance of the former increases considerably with increasing Ce\(^{3+}\) concentration. In the energy transfer from the thermalised electrons and holes to the Ce\(^{3+}\) centres the role of the Gd\(^{3+}\) ions is negligible. Instead, the energy transfer is either controlled by diffusion of self-trapped carriers or by the thermally activated release of trapped electrons and holes.

LuAlO\(_3\);Ce\(^{3+}\) is known as a promising scintillator material. Some crystals have been studied in order to achieve an accurate estimate of the light yield. The results are described in chapter 8. Under X-ray excitation light yields of about 10,000-12,000 ph/MeV are obtained, independent of the Ce\(^{3+}\) content in the crystals. Yet, the light yields as derived from pulse height spectra are lower. These increase with increasing Ce\(^{3+}\) concentration. The difference in light yields obtained by the two methods is explained by the presence of slow decay time components. In most of the samples an absorption band is found overlapping the scintillator emission. This means that the actual light yields may be higher.

Luminescence and scintillation properties of Lu\(_2\)S\(_3\);Ce\(^{3+}\) crystals are described in chapter 9. The emission spectrum is between 550 and 700 nm. Consequently the scintillation light can be very efficiently detected by means of silicon photodiodes. The red Ce\(^{3+}\) luminescence is due to the strong nephelauxetic effect in this material. Opposed to previous predictions, efficient Ce\(^{3+}\) luminescence is observed. The requirements for efficient Ce\(^{3+}\) luminescence are reviewed. Also the Ce\(^{3+}\) 5d-4f luminescence decay time is discussed. The 32 ns decay time is rather short at the relatively long emission wavelength. This is probably due to the high polarisability of this material, which gives rise to a high refractive index. The combination of a
high light yield, a short scintillation decay time and the red Ce$^{3+}$ luminescence make this a promising scintillator material.

In chapter 10 the main results obtained for Ce$^{3+}$ doped Cs$_3$Lu$_2$Cl$_6$, LiLuSiO$_4$ and Gd$_2$Sc$_2$Al$_5$O$_{12}$ materials are summarised. Of all the studied chlorides, Cs$_3$Lu$_2$Cl$_6$ has the highest density and effective atomic number (see Table 1). Unfortunately, it has a low light yield and a long scintillation decay time.

Powder of LiLuSiO$_4$:Ce$^{3+}$ has been studied. In order to estimate the light yield of this material, two methods were used. Firstly, the wavelength-integrated yield obtained under X-ray excitation is compared with that of BaF$_2$ powder. Secondly, the photoelectron yield is derived from pulse height spectra employing a $^{241}$Am source. The obtained light yields are compiled in Table 1. The accuracy of the employed methods is discussed.

The Ce$^{3+}$ luminescence in Gd$_2$Sc$_2$Al$_5$O$_{12}$:Ce$^{3+}$ is located in the red due to the strong crystal field effect. Under optical excitation into the Gd$^{3+}$ levels, efficient Gd$^{3+}$→Ce$^{3+}$ energy transfer is observed by fast energy migration on the Gd-sublattice. The scintillation decay resembles the Ce$^{3+}$ luminescence decay after excitation into the Gd$^{3+}$ levels. This suggests that after absorption of ionising radiation the created electrons and holes are almost instantaneously captured by Gd$^{3+}$ ions from where the energy is transferred to Ce$^{3+}$ ions by fast energy migration on the Gd-sublattice.

Some Pr$^{3+}$ doped Gd$_2$Sc$_2$Al$_5$O$_{12}$ doped samples were studied as well. They show only Pr$^{3+}$ 4f-4f luminescence under X-ray excitation. The Pr$^{3+}$ 5d-4f luminescence is quenched, probably either due to energy transfer from the lowest Pr$^{3+}$ 5d state to a Gd$^{3+}$ state by lattice relaxation or due to a Föster-Dexter type transfer by the overlap of the Pr$^{3+}$ 5d-4f luminescence with the Gd$^{3+}$ $^8S_{7/2}$→$^6P_J$ absorption peaks near 310 nm.

In this thesis much attention has been focused on the study of Ce$^{3+}$ doped chlorides. These show high light yields under X-ray excitation. The scintillation time response spectra show components in the range of $\sim$100 ns to $\mu$s or longer. So, the energy transfer to the Ce$^{3+}$ centres is efficient, but at least for a considerable fraction slow. For K$_2$LaCl$_5$:Ce$^{3+}$ and RbGd$_2$Br$_7$:Ce$^{3+}$ it is shown that the transfer is activated by temperature. Self-trapped carriers or carriers trapped in shallow traps are probably involved. For further clarification of the energy transfer process the knowledge of the type of involved carriers is required. This information can be derived by recording time-resolved absorption or EPR spectra following pulsed excitation by ionising radiation.

It is further noted that the light yields of the currently studied Ce$^{3+}$ doped chlorides are much higher than most of the studied Ce$^{3+}$ doped fluorides, for which often light yields in the order of 1,000-5,000 ph/MeV are measured. This does not hold as a general rule. For BaF$_2$:Ce$^{3+}$, for example, a light yield of 20,000 ph/MeV has been measured.

It is interesting to study the energy transfer to the Ce$^{3+}$ centres in halide compounds more fundamentally. Suitable host lattices are the elpasolites Cs$_2$NaMX$_6$ (M=La, Gd, Lu, X=F,Cl,Br,I). These have a cubic structure, with a perfect $O_h$ point symmetry for the site on which the Ce$^{3+}$ ion is incorporated for almost all halides. Using several experimental techniques, it is possible to study e.g. the dependence of the energy transfer efficiency on the type of the halide ion and the ionic radius of the rare earth site. Furthermore, experimental results may be compared with theoretical calculations, which can easily be performed because of the cubic structure and the high point symmetry at the Ce$^{3+}$ site.
Luminescentie en scintillatie van Ce$^{3+}$ gedoteerde anorganische materialen voor gammastralingsdetectie

Samenvatting en conclusies

Ioniserende straling wordt gebruikt in een groot aantal toepassingen. Voor de detectie van deze straling kan een aantal methoden worden toegepast. In één van deze worden scintillatorengem gebruikt. Dit zijn materialen, meestal kristallen, waarin een scintillatie, dat is een lichtflitsje, wordt geproduceerd ten gevolge van absorptie van straling. De gegenereerde luminescentie kan worden gedetecteerd met een lichtdetector, bijvoorbeeld een fotodiode of een fotomultiplicatorbuis. Ondanks het feit, dat er al veel scintillatormaterialen ontdekt zijn, is er nog steeds vraag naar een scintillator met verbeterde eigenschappen. Het onderzoek dat in dit proefschrift beschreven staat is er op gericht om nieuwe scintillatorengem te vinden die geschikt zijn om γ-straling te kunnen detecteren. Daarnaast zijn scintillatiematerialen ook interessant vanuit wetenschappelijk gezichtspunt. Na absorptie van straling vindt een aantal ingewikkelde en interessante processen plaats, voordat de scintillatie gegenereerd wordt. Dit alles staat beschreven in hoofdstuk 1.

Voor een goed begrip van de scintillatoreigenschappen die verbeterd kunnen worden, moet er kennis zijn over de eisen die aan scintillatorengem gesteld worden in detectiesystemen en de specificaties van de tegenwoordig toegepaste scintillatorengem. Dit komt ter sprake in hoofdstuk 2. Verder wordt de energieoverdracht van de geabsorbeerde γ-straling naar de luminescentiecentra beschreven. Daarna wordt de keuze van de gekozen materialen besproken. De aandacht is gericht op de studie van Ce$^{3+}$ gedoteerde materialen, waarbij de nadruk valt op chloriden als gastmaterialen.

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Luminescence and scintillation properties of Ce$^{3+}$ doped inorganic materials for gamma-ray detection
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De experimentele technieken die gebruikt zijn om de materialen te onderzoeken, staan beschreven in hoofdstuk 3. In hoofdstuk 4 tot en met 10 staat het onderzoek aan de geselecteerde materialen beschreven. In tabel 1 staan de bestudeerde materialen en de belangrijkste scintillatie-eigenschappen vermeld.

### Tabel 1: Scintillatieeigenschappen van de bestudeerde materialen

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<tr>
<th>Verbinding</th>
<th>Ce$^{3+}$ at. %</th>
<th>Z$_{eff}$</th>
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<th>$\lambda$ [nm]</th>
<th>LO (fotonen/MeV)</th>
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<td>592</td>
<td>28,000</td>
<td>28,000 (0.5 μs)</td>
</tr>
<tr>
<td>hoofdstuk 10:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs$_2$Lu$_2$Cl$_6$</td>
<td>0.09</td>
<td>58.6</td>
<td>4.01</td>
<td>409*</td>
<td>7500</td>
<td>650 (10 μs)</td>
</tr>
<tr>
<td>LiLu$_2$SiO$_4$</td>
<td>2*</td>
<td>69.4</td>
<td>5.61</td>
<td>405</td>
<td>(3±1)×10$^4$</td>
<td>23,000 (0.5 μs)</td>
</tr>
<tr>
<td>Gd$_3$Sc$_2$Al$<em>5$O$</em>{12}$</td>
<td>1*</td>
<td>55.5</td>
<td>5.56</td>
<td>550</td>
<td>~8000</td>
<td>1100 (3 μs)</td>
</tr>
</tbody>
</table>

*a De gegeven concentratie zoals aanwezig in de smelt
* Het is niet zeker of de emissie toe te schrijven is aan Ce$^{3+}$ luminescentie

In hoofdstuk 4 worden de scintillatie en luminescentie eigenschappen van BaY$_2$F$_8$:Ce$^{3+}$ en BaLu$_2$F$_8$(Ce$^{3+}$) besproken. Onder excitatie van gammastraling vertoont ongedoteerd BaLu$_2$F$_8$ een luminescentie met een vervaltijd van ~1 ns, die toegeschreven wordt aan "core-valence" luminescentie. De scintillatie efficiëntie van de bestudeerde kristallen is nogal laag.
In hoofdstuk 5 komen de optische en scintillatie eigenschappen van Cs$_2$LuCl$_6$:Ce$^{3+}$ en enkele Ce$^{3+}$ gedoteerde elpasolithen aan de orde. In de elpasolithen is het Ce$^{3+}$ ion ingebouwd op een rooster positie met een perfecte O$_h$ puntsymmetrie. Het niveau van de 5d(e$_g$) configuratie is onverwacht opgesplitst. Het scintillatieverval bestaat uit $r^0$ type vervaltijdcomponenten ($r$ stelt de tijd voor).

De scintillatie en luminescentie eigenschappen van K$_2$LaCl$_5$:Ce$^{3+}$ worden besproken in hoofdstuk 6. Na excitatie met röntgen straling vertoont dit materiaal "self-trapped exciton" (STE) luminescentie en Ce$^{3+}$-emissie. Met toenemende Ce$^{3+}$ concentratie daalt de STE-luminescentieintensiteit, terwijl de Ce$^{3+}$-luminescentieintensiteit toeneemt. De hoogste lichtopbrengst wordt gemeten voor K$_2$LaCl$_5$:10%Ce$^{3+}$ (zie tabel 1). Voor dit sample wordt een energieresolutie van 5.3 % gemeten bij een $\gamma$-stralingsenergie van 662 keV. Om de energieverdracht te verklairen worden STE diffusie en bimoleculaire recombinatie voorgesteld. Bij lage Ce$^{3+}$ concentraties wordt de energieverdracht hoofdzakelijk bepaald door STE diffusie, terwijl bij hoge Ce$^{3+}$ concentraties bimoleculaire recombinatie het belangrijkst is. Een eenvoudig model voor STE diffusie wordt gepresenteerd en vergeleken met de experimentele resultaten. Het gepresenteerde model voldoet redelijk.

Hoofdstuk 7 beschrijft de luminescentie- en scintillatieeigenschappen van RbGd$_2$Cl$_7$:Ce$^{3+}$ en RbGd$_2$Br$_7$:Ce$^{3+}$. In RbGd$_2$Br$_7$:Ce$^{3+}$ overlap de Gd$^{3+}$ 4f-5d absorptie band. Na excitatie in de Gd$^{3+}$ 4f niveau, wordt er efficiënte Gd$^{3+}$-Ce$^{3+}$ energieverdracht geobserveerd door snelle energiemigratie over het Gd-subsrooster. De energieverdracht wordt kwantitatief besproken. De interactie die verantwoordelijk is voor de energieverdracht kan niet worden toegeschreven aan "exchange" interactie.

RbGd$_2$Cl$_7$:Ce$^{3+}$ en RbGd$_2$Br$_7$:Ce$^{3+}$ hebben beiden een hoge lichtopbrengst (zie tabel 1). In ongedoteerd RbGd$_2$Br$_7$ bestaat de emissie uit de karakteristieke Gd$^{3+}$ 4f-4f luminescentie en een breedbandige emissie, die toegeschreven wordt aan STE luminescentie. Met toenemende Ce$^{3+}$ concentratie, neemt de Gd$^{3+}$ 4f-4f en STE luminescentieintensiteit af, terwijl de Ce$^{3+}$ emissieintensiteit sterk toeneemt. Voor RbGd$_2$Br$_7$:4.1%Ce$^{3+}$ wordt een energieresolutie van 3.8 % gemeten bij een $\gamma$-stralingsenergie van 662 keV. In de overdracht van geabsorbeerde $\gamma$-stralingsenergie naar de luminescentiecentra zijn er minimaal twee mechanismen te onderscheiden. Eén is verantwoordelijk voor een snel exponentieel verval in de eerste paar honderd ns van het scintillatieverval, de andere is verantwoordelijk voor een niet-exponentieel verval dat plaats heeft in het $\mu$s bereik. Het eerstgenoemde mechanisme is dominant voor hoge Ce$^{3+}$ concentraties. De rol van Gd$^{3+}$ ionen in de energieverdracht van de gethermaliseerde elektronen en gaten naar de Ce$^{3+}$ centra is verwaarloosbaar klein. De energieverdracht wordt gecontroleerd door de thermisch geactiveerde vrijlating van ingevangen elektronen en gaten.

LuAlO$_2$:Ce$^{3+}$ is een veelbelovende scintillator. Er is een aantal kristallen bestudeerd om de lichtopbrengst nauwkeurig te bepalen. Onder röntgenexcitatie wordt een lichtopbrengst van ongeveer 10,000-12,000 fotonen/MeV verkregen, onafhankelijk van de Ce$^{3+}$ concentratie in de kristallen. De lichtopbrengsten zoals bepaald uit de pulshoogtespectra zijn echter een stuk lager en met toenemende Ce$^{3+}$ concentratie wordt de lichtopbrengst nu wel groter. Het verschil in de lichtopbrengsten die met deze twee methoden bepaald zijn kan worden
verklaard door de aanwezigheid van langzame scintillatievervaltijdcomponenten. In de meeste samples is er een absorptieband die met de scintillatieemissie gedeeltelijk samenvalt. Dit betekent dat de werkelijke lichtopbrengsten hoger kunnen zijn.

De luminescentie- en scintillatieeigenschappen van Lu₂S₄:Ce³⁺ kristallen staan beschreven in hoofdstuk 9. De emissie is tussen 550 en 700 nm. Daardoor kan het licht erg efficiënt worden gedetecteerd door middel van silicium fotodetectoren. De rode Ce³⁺ luminescentie wordt veroorzaakt do het sterke nphelauxetische effect in dit materiaal. In tegenstelling tot eerdere voorspellingen, wordt er efficiënte Ce³⁺ luminescentie geobserveerd. De vereisten voor efficiënte Ce³⁺ luminescentie worden besproken. Ook de Ce³⁺ 5d-4f luminescentie vervalt kon ter sprake. De 32 ns vervaltijd is nogal kort, gezien de lange emissiegolf. Dit is waarschijnlijk het gevolg van de grote polariseerbaarheid van dit materiaal, die ook verantwoordelijk is voor de hoge brekingsindex. De combinatie van een hoge lichtopbrengst, een korte vervaltijd en de rode Ce³⁺ emissie maken dit materiaal tot een veelbelovende scintillator.

In hoofdstuk 10 staan de belangrijkste resultaten die verkregen zijn voor Ce³⁺ gedoteerd Cs₂Lu₂Cl₆, LiLu₄O₄ en Gd₃Sc₂Al₂O₁₂.

Van alle bestudeerde chlorides heeft Cs₂Lu₂Cl₆:Ce³⁺ de hoogste dichtheid en het hoogste effectief atoomnummer. Helaas vertoont dit materiaal een lage lichtopbrengst en een lange scintillatie vervaltijd.

Van LiLu₄O₄:Ce³⁺ is alleen poeder bestudeerd. Om de lichtopbrengst te kunnen afslachten zijn er twee methoden gebruikt. Ten eerste, wordt de golfbreuk-integreerde opbrengst vergeleken met die van BaF₂ poeder. Ten tweede, wordt de lichtopbrengst bepaald uit pulshoogte spectra die zijn gemeten met hulp van een ²⁴¹Am bron. De verkregen resultaten staan vermeld in tabel 1. De nauwkeurigheid van de gebruikte methoden wordt beduidend.

De Ce³⁺ luminescentie in Gd₃Sc₂Al₂O₁₂ is rood gekleurd do het sterke kristalveld effect. Onder optische excitatie in de Gd³⁺ niveaus, wordt er efficiënte Gd³⁺-Ce³⁺ energieoverdracht geobserveerd door snelle energiemigratie over het Gd-subrooster. Het scintillatieverval lijkt op het verval van de Ce³⁺ luminescentie na excitatie in de Gd³⁺ niveaus. Dit suggereert dat na absorptie van ioniserende straling, de gecreëerde elektronen en gaten bijna instantaan worden ingevangen door de Gd³⁺ ionen, waaraan de energie wordt overgedragen door efficiënte energiemigratie over het Gd-subrooster.

Een aantal Pr³⁺ gedoteerde Gd₃Sc₂Al₂O₁₂ kristallen is ook bestudeerd. Onder X-ray excitatie wordt er alleen Pr³⁺ 4f-4f luminescentie geobserveerd. De Pr³⁺ 5d-4f luminescentie is afwezig, waarschijnlijk door energieoverdracht van de laagste Pr³⁺ 5d toestand naar het Gd³⁺ ⁸S₇/₂ niveau door roosterrelaxatie of door een Förster-Dexter type overdracht door de overlap van de Pr 5d-4f luminescentie met de Gd³⁺ absorptiebanden bij 310 nm.

De aandacht in dit proefschrift was gevestigd op de studie van Ce³⁺ gedoteerde chlorides. Zij vertonen in het algemeen hoge lichtopbrengsten onder röntgenexcitatie. De scintillatievervals tijdens zijn in het µs gebied. Dat betekent, dat de energieoverdracht naar de Ce³⁺ centra efficiënt is, maar op zijn minst voor een belangrijk deel traag. Voor K₂LaCl₅:Ce³⁺ en RbGd₂Br₇:Ce³⁺ is aangetoond dat de overdracht wordt geactiveerd do de temperatuur.
Energie- of ladingsdragers die gevangen zijn in ondiepe defectcentra zijn waarschijnlijk betrokken in de energieoverdracht. Om verdere duidelijkheid te verkrijgen is de kennis van het defectcentrum nodig. Deze informatie kan worden verkregen door het meten van tijdopgeloste absorptie of EPR spectra na gepulste excitatie van ioniserende straling.

Verder is het opmerkelijk dat de lichtopbrengsten van de bestudeerde Ce³⁺ gedoteerde chloriden veel hoger zijn dan die van de meeste Ce³⁺ gedoteerde fluoriden, waarvoor vaak lichtopbrengsten veelal tot in de orde grootte van 1,000 fotonen/MeV worden gemeten. Hierbij wordt aangetekend dat dit niet geldt als een algemene regel. Voor BaF₂:Ce³⁺, bijvoorbeeld, is een lichtopbrengst van 20,000 fotonen/MeV gemeten.

Het is interessant om de energieoverdrachtsefficiëntie naar de Ce³⁺ centra en de snelheid van energieoverdracht in halide verbindingen fundamenteel te bestuderen. Geschikte gastroosters zijn de elpasolieten Cs₂NaMX₆:Ce³⁺ (M=La,Gd,Lu, X=F,Cl,Br,I). Deze materialen hebben een kubische kristalstructuur, met een perfecte O₈ symmetrie voor de roosterplek waarin het Ce³⁺ ion is ingebouwd. Met gebruikmaking van verschillende meettechnieken, kan bijvoorbeeld de afhankelijkheid van de energieoverdrachtsefficiëntie van het type halide ion en van de ionische straal van het zeldzame aardion worden bestudeerd. Verder kunnen de experimentele resultaten worden vergeleken met berekeningen, die relatief eenvoudig kunnen worden uitgevoerd vanwege de kubische structuur en de hoge puntsymmetrie op de roosterpositie waar het Ce³⁺ ion is ingebouwd.
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Nu u dit boekje in ogenschouw hebt genomen en het één en ander in wijsheid hebt overdacht, dan begrijpt u wel dat het toetstandkomen van zo’n proefschrift een heidens karwei is. Gelukkig heeft een groot aantal mensen mij geholpen. Ik wil hen hier bedanken.

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Tenslotte dank ik mijn ouders, broers, zus en vrienden voor hun steun, interesse en betrokkenheid.
Curriculum vitae

The author of this thesis was born the 15th of May 1969 in Zwolle. After graduation from the VWO at the Baudartius College in Zutphen, he started the study Electrical engineering at the University of Twente in Enschede. His graduation work took place in the section Light Wave Devices Group, department of Transducers and Materials. In 1992 he graduated on an experimental study of the AC Kerr effect in semiconductor doped glass. From December 1993 he has been working on the Radiation Detection Group at the Interfaculty Reactor Institute (TU Delft). There he investigated some Ce$^{3+}$ doped materials in the search for new efficient scintillators for $\gamma$-ray detection. The results of these investigations are presented in this thesis. Since January 1999 he is working as a postdoc in the field of solar cells at the Laboratory for Applied Inorganic Chemistry, Faculty of Chemical Technology, TU Delft.
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J.C. van 't Spijker, P. Dorenbos, C.W.E. van Eijk, J.E.M. Jacobs, H.W. den Hartog, N. Korolev, *Luminescence and scintillation properties of BaY$_2$F$_8$:Ce$^{3+}$ and of pure and Ce$^{3+}$ doped BaLu$_2$F$_8$*, to be published

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Other publications to which was contributed


