

Scintillation Properties of $\text{LaCl}_3:\text{Ce}^{3+}$ Crystals: Fast, Efficient, and High-Energy Resolution Scintillators

E. V. D. van Loef, P. Dorenbos, C. W. E. van Eijk, *Member, IEEE*, K. Krämer, and H. U. Güdel

Abstract—The scintillation properties of LaCl_3 doped with different Ce^{3+} concentrations studied by means of optical, X-ray, and γ -ray excitation are presented. Under optical and γ -ray excitation, Ce^{3+} emission is observed peaking at 330 and 352 nm. For LaCl_3 doped with 2%, 4%, 10%, and 30% Ce^{3+} and pure CeCl_3 , we measured a light yield of $46\,000 \pm 3\,000$ photons per MeV of absorbed γ -ray energy. The scintillation decay curve can be described by three decay components: short ($\tau = 25$ ns), intermediate ($\tau = 200 - 800$ ns), and long ($\tau = 0.8-14$ μs). The contribution of the short decay component to the total light yield increases with Ce^{3+} concentration: ranging from 10% for $\text{LaCl}_3: 2\% \text{Ce}^{3+}$ to 69% for pure CeCl_3 . An energy resolution (full-width half-maximum over peak position) for the 662-keV full energy peak of $3.5 \pm 0.4\%$, $3.5 \pm 0.4\%$, $3.1 \pm 0.3\%$, $3.3 \pm 0.3\%$, and $3.4 \pm 0.3\%$, respectively, was observed for $\text{LaCl}_3: 2\%, 4\%, 10\%, 30\% \text{Ce}^{3+}$ and pure CeCl_3 .

Index Terms—Energy resolution, Gamma-detection, $\text{LaCl}_3:\text{Ce}$, PACS: 29.40 Mc; 2930 Kv; 78.55 Hx, rare-earth trihalides, scintillators.

I. INTRODUCTION

THE Search for new inorganic scintillators with a high light yield, a short decay time, and good energy resolution has resulted in the discovery of scintillating materials like $\text{K}_2\text{LaCl}_5:\text{Ce}^{3+}$ [1], [2] and $\text{RbGd}_2\text{Br}_7:\text{Ce}^{3+}$ [3], [4]. $\text{K}_2\text{LaCl}_5:\text{Ce}^{3+}$ scintillates efficiently with a photon yield of 28 000 photons per MeV (ph/MeV). It shows a good energy resolution of 5.1% for 662 keV γ -quanta. $\text{RbGd}_2\text{Br}_7:\text{Ce}^{3+}$ has an even higher light output of 56 000 ph/MeV in addition to an excellent energy resolution of 4.1% at 662 keV. Recently, the scintillation properties of $\text{LaCl}_3:\text{Ce}^{3+}$ 0.57% were published by Guillot-Noël *et al.* [5]. Unfortunately, both the timing resolution and the energy resolution of this compound left much to be desired. Nevertheless, it was thought that the scintillation properties, and especially the scintillation decay, could be improved by increasing the cerium concentration. In this paper, we investigated the optical and scintillation properties of LaCl_3 crystals doped with different Ce^{3+} concentrations under X-ray and γ -ray excitation.

Manuscript received October 24, 2000; revised January 18, 2001. This work was supported by the Netherlands Technology Foundation (STW), the Swiss National Science Foundation, and Crismatec, France.

E. V. D. van Loef, P. Dorenbos, and C. W. E. van Eijk are with the Radiation Technology Group, Interfaculty Reactor Institute, Delft University of Technology, Delft 2629JB, The Netherlands.

K. Krämer and H. U. Güdel are with the Department of Chemistry and Biochemistry, University of Bern, Bern 3000, Switzerland.

Publisher Item Identifier S 0018-9499(01)04761-X.

II. EXPERIMENTAL

Crystals of pure LaCl_3 , $\text{LaCl}_3: 2\%, 4\%, 10\%, 30\% \text{Ce}^{3+}$ and pure CeCl_3 were grown by the Bridgman technique using a moving furnace and a static vertical ampoule. The preparation has already been described in [5]. LaCl_3 and CeCl_3 crystallize in the UCl_3 type structure [6], space group $\text{P6}_3/\text{m}$ (no. 176). The lattice is not layered and does not cleave easily. LaCl_3 and CeCl_3 melt at about 872 °C. The Ce^{3+} concentrations in the crystals were determined by induction-coupled plasma spectroscopy.

LaCl_3 and CeCl_3 crystals are hygroscopic but less sensitive than RbGd_2Br_7 or NaI . Samples of both LaCl_3 and NaI were exposed to air, and after a few hours, the quality of the LaCl_3 sample worsened slightly due to hydration of the surface. By that time, the NaI crystal had already become deliquescent. To avoid such deterioration, the studied crystals were sealed into small quartz ampoules under nitrogen atmosphere.

X-ray excited optical luminescence spectra were recorded with a Cu anode operating at 35 kV_p and 25 mA. The spectra were obtained with an ARC VM504 monochromator (blazed at 300 nm, 1200 grooves/mm) and an EMI 9462 photomultiplier (PMT). The spectra in this study were corrected for the wavelength dependence of the photodetector quantum efficiency as well as monochromator transmission. Temperature-dependent X-ray excited optical luminescence measurements were performed between 100 and 400 K using a Cryospec model 20A Joule-Thomson Miniature Refrigerator operated with 99.999% purity nitrogen gas at 120 bar. The temperature resolution is typically 0.1 K. The temperature measurements, in absolute terms, are limited by experimental factors such as the thermal coupling between the control stage and the sample.

Pulse-height spectra were recorded with a Hamamatsu R1791 PMT with a box-type dynode structure. It was connected to a homemade preamplifier and an Ortec 672 spectroscopic amplifier. The quartz ampoules containing the crystal are optically coupled onto the window of the PMT with Viscasil 60 000 cSt from General Electric. To minimize the losses in light yield, the ampoules were covered with several layers of 0.1-mm ultraviolet-reflecting Teflon tape. The light yield, expressed in collected photoelectrons per MeV of absorbed γ -ray energy (phe/MeV), was determined by comparing the peak position of the 662-keV photopeak in the pulse-height spectra with that of the spectrum of single photoelectrons. To determine the position of the photopeak, we fitted it, when necessary, with a sum of several Gaussian-shaped bands. In general, when the photopeak was not symmetrical, due to the presence of unresolved X-ray escape peaks, an additional error in the

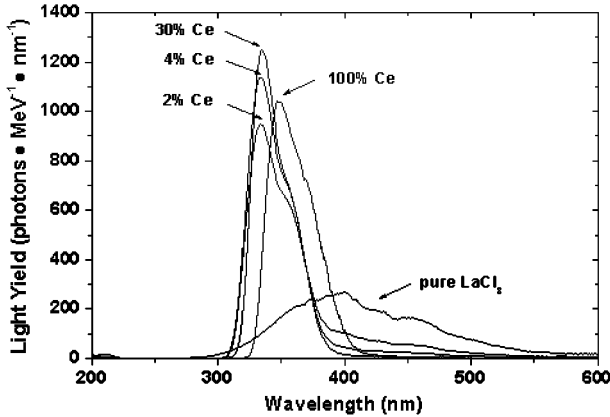


Fig. 1. X-ray excited optical luminescence spectrum of pure LaCl_3 , LaCl_3 : 2%, 4%, 10%, 30% Ce^{3+} and pure CeCl_3 at room temperature. The y -axis has been calibrated using the light yields derived from pulse-height measurements.

position was taken into account. The error made in the number of photoelectrons, caused by errors in the determination of the relative gain of the PMT and the position of the photopeak, is typically 2%.

The absolute light yield, expressed in photons per MeV of absorbed γ -ray energy (ph/MeV), was determined from the detection efficiency $\eta_d(\lambda)$ of the PMT. The detection efficiency is given by

$$\eta_d(\lambda) = \eta_q(\lambda)\eta_c\eta_l \quad (1)$$

where

- $\eta_q(\lambda)$ quantum efficiency of the PMT;
- η_c charge collection efficiency of the photoelectrons originating from the photocathode;
- η_l fraction of light generated in the crystal that reaches the photocathode.

The manufacturer provided the detection efficiency of the R1791 Hamamatsu tube. The charge collection efficiency of PMTs with box-type dynodes is close to optimal, and in this work, we assume $\eta_c = 0.95 \pm 0.05$. The light collection efficiency η_l is estimated to be 0.95 ± 0.05 .

Scintillation decay time spectra at time scales up to 200 μs were recorded using the conventional multihit method [7] with XP2020Q PMTs, an Ortec 934 Constant Fraction Discriminators, and a Lecroy 4208 time-to-digital converter having a channel width of 1 ns.

III. RESULTS

A. X-Ray Excited Optical Luminescence

The X-ray excited optical luminescence spectra of pure LaCl_3 , LaCl_3 : 2%, 4%, 30% Ce^{3+} and pure CeCl_3 are shown in Fig. 1. Each spectrum has been corrected for the wavelength dependence of the photodetector quantum efficiency as well as monochromator transmission. Each spectrum is normalized such that the integral over all wavelengths is equal to the value for the absolute light yield in photons per MeV, as found from

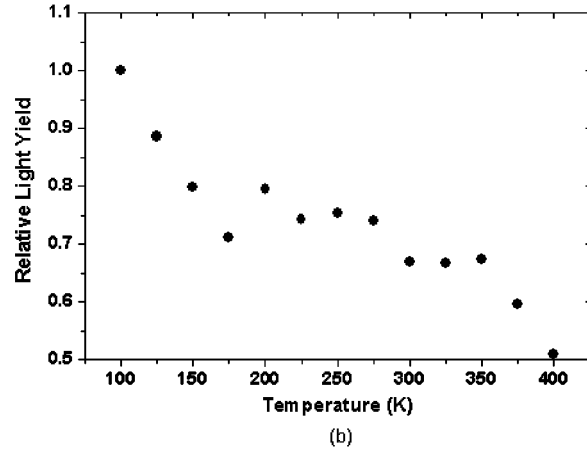
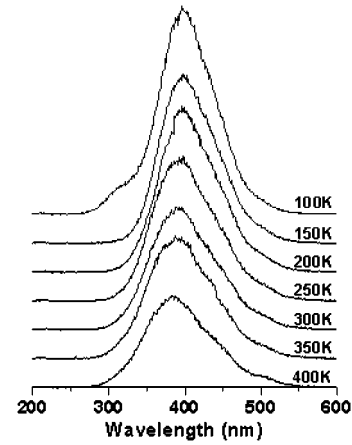


Fig. 2. (a) X-ray excited optical luminescence spectra of pure LaCl_3 between 100 and 400 K, recorded in steps of 50 K. (b) Temperature dependence of the total light yield, derived from X-ray excited optical luminescence spectra. The errors are in the same order as the point size.

pulse-height spectra recorded with a shaping time of 10 μs (see Section III-B).

For pure LaCl_3 , the X-ray excited optical luminescence spectrum at room temperature consists of a broad band located between 250 and 600 nm and is attributed to self-trapped-exciton (STE) luminescence. For other chlorides [8] and pure LaF_3 [9], similar bands have been observed and were readily assigned to STE luminescence.

Temperature-dependent X-ray excited optical luminescence spectra of pure LaCl_3 , measured between 100 and 400 K in steps of 50 K are shown in Fig. 2. For pure LaCl_3 , the total light yield decreases when the temperature increases from 100 to 400 K. The total light yield at 400 K with respect to that at 100 K is about 50%. This is probably due to quenching of STE luminescence. In the X-ray excited optical luminescence spectrum at 100 K, a weak band can be observed near 317 nm next to the main peak at 398 nm. At elevated temperatures, the 317-nm band has completely disappeared. Thermoluminescent glow curves of pure LaCl_3 irradiated with X-rays at 77 K reveal a main peak at 111 K that is attributed to the release of self-trapped holes [10]. Possibly, the peak at 317 nm in the X-ray excited optical luminescence spectrum of pure LaCl_3 is associated with this detrapping of the self-trapped holes. Note

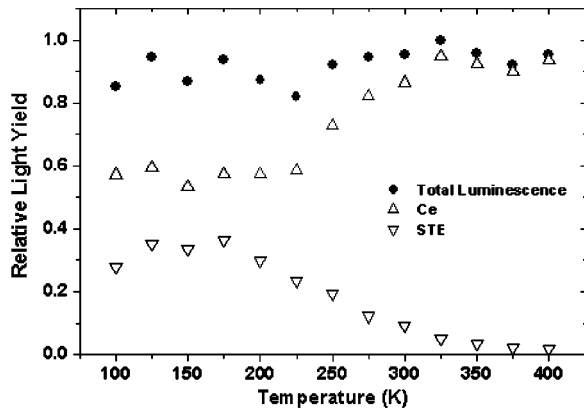


Fig. 3. Temperature dependence of the light yields of Ce^{3+} , STE, and total luminescence in $\text{LaCl}_3: 4\% \text{Ce}^{3+}$ derived from X-ray excited luminescence spectra. The errors are in the same order as the point size.

that from 100 to 400 K, the maximum of the STE luminescence shifts to shorter wavelengths (higher energy).

The X-ray excited optical luminescence spectra of the cerium-doped LaCl_3 crystals are dominated by a broad emission band located between 300 and 400 nm. It is attributed to Ce^{3+} luminescence. In addition, a weak emission band can be observed between 400 and 550 nm. It is not present under optical excitation and is probably due to some residual STE luminescence. The X-ray excited optical luminescence of pure CeCl_3 [11] is located at longer wavelengths (lower energy) compared to the luminescence of the cerium-doped LaCl_3 samples. Note that when the Ce^{3+} concentration is increased, the intensity of the Ce^{3+} emission band increases, whereas the intensity of the (residual) STE luminescence decreases.

From 100 to 400 K, the total light yield under X-ray excitation of $\text{LaCl}_3: 2\%$, 4% , and $10\% \text{Ce}^{3+}$ remains almost constant. However, as the temperature rises, the Ce^{3+} luminescence intensity is enhanced at the expense of STE luminescence intensity, revealing an anticorrelation between these two types of emissions. In order to quantitatively separate the contributions of Ce^{3+} and STE luminescence to the total light yield, the wavelength scale of the X-ray excited optical luminescence spectra was transformed to an energy scale, and spectra were fitted with three Gaussian-shaped bands. From these fits, the contribution of Ce^{3+} and STE luminescence to the total light yield can be determined. As an example, Fig. 3 shows the temperature dependence of the light yields of Ce^{3+} , STE, and total luminescence output under X-ray excitation in $\text{LaCl}_3: 4\% \text{Ce}^{3+}$.

The anticorrelation between Ce^{3+} and STE luminescence has been observed before by Guillot-Noël *et al.* in $\text{LaCl}_3: 0.57\% \text{Ce}^{3+}$. At 135 K and lower temperatures, the contributions of the STE and Ce^{3+} luminescence to the total light yield of $\text{LaCl}_3: 0.57\% \text{Ce}^{3+}$ were almost equal [5]. However, for $\text{LaCl}_3: 2\%$, 4% , and $10\% \text{Ce}^{3+}$, the contribution of STE luminescence to the total light yield at 135 K is significantly lower compared to that of Ce^{3+} . In these compounds, STE luminescence might already be quenched at 135 K. Both $\text{LaCl}_3: 30\% \text{Ce}^{3+}$ and pure CeCl_3 show a gradual decrease in the total light yield as the temperature is increased from 100 to 400 K. For $\text{LaCl}_3: 30\%$

TABLE I
LIGHT YIELDS DERIVED FROM PULSE-HEIGHT SPECTRA AND THE ENERGY RESOLUTION R OF PURE LaCl_3 , $\text{LaCl}_3: 2\%$, 4% , 10% , $30\% \text{Ce}^{3+}$ AND PURE CeCl_3 UNDER ^{137}Cs 662 KeV γ -RAY EXCITATION

Host	[Ce^{3+}] (%)	Photon yield (10^3 ph/MeV)			Energy resolution R (%)
		0.5 μs	3 μs	10 μs	
LaCl_3	-	-	-	34 ± 1	4.7 ± 0.2
LaCl_3	2	-	44 ± 1	49 ± 1	3.5 ± 0.4
LaCl_3	4	37 ± 1	47 ± 1	49 ± 1	3.5 ± 0.4
LaCl_3	10	45 ± 1	49 ± 1	49 ± 1	3.1 ± 0.3
LaCl_3	30	42 ± 1	43 ± 1	43 ± 1	3.3 ± 0.3
CeCl_3	-	44 ± 1	46 ± 1	46 ± 1	3.4 ± 0.3

Ce^{3+} and pure CeCl_3 , the total light yield at 400 K with respect to that at 100 K is 85% and 72%, respectively.

B. Pulse-Height Experiments

Light yields derived from pulse-height spectra under ^{137}Cs 662-keV γ -ray excitation are compiled in Table I. All light yields of Table I are obtained with crystals in quartz ampoules.

The pulse-height spectrum of $\text{LaCl}_3: 10\% \text{Ce}^{3+}$ is shown in Fig. 4. In order to determine the position of the photopeak and the energy resolution of the studied compounds, the photopeak was fitted with several Gaussian curves. In many cases, the photopeak is accompanied by satellite peaks at lower energy, due to the escape of characteristic K_{α} , K_{β} X-rays of lanthanum or cerium.

Of all studied compounds, pure LaCl_3 seems to have the lowest light output with $34\,000 \pm 1000$ ph/MeV, obtained with a shaping time of 10 μs (see Table I). As shown in Fig. 1, the light yield of pure LaCl_3 is mainly due to STE luminescence. For LaCl_3 doped with different Ce^{3+} concentrations and pure CeCl_3 , we measured light yields on the order of 43 000 to 49 000 ph/MeV of absorbed γ -ray energy. The absolute light yield of powder samples of pure CeCl_3 has been reported before by Derenzo *et al.* [12]. However, they reported a lower light yield of 28 000 ph/MeV under X-ray excitation.

Energy resolutions R (full-width half-maximum over peak position) for the 662-keV full energy peak are between 3.1 and 3.5%. These energy resolutions are the best for inorganic scintillator detectors ever reported in the literature [13].

C. Scintillation Decay

Scintillation decay time spectra of $\text{LaCl}_3: 2\%$, 4% , $10\% \text{Ce}^{3+}$ and pure CeCl_3 at room temperature under ^{137}Cs γ -ray excitation are shown in Fig. 5. At first sight, the decay curves are not single exponential and have a long decay component extending into the microsecond region. The overall decay time decreases when the cerium concentration is increased. The only compound that seems to have a single exponential decay is pure LaCl_3 . Its luminescence has a decay time of 3.5 μs . The irregularity in curve (d) is due to after pulses in the PMT.

To characterize the decay curves more accurately, three decay components were assumed. This assumption has no physical

TABLE II
CHARACTERISTIC COMPONENTS OF THE SCINTILLATION DECAY CURVES OF PURE LaCl_3 , LaCl_3 : 2%, 4%, 10%, 30% Ce^{3+} AND PURE CeCl_3 . THE COMPONENTS CALLED "INTERMEDIATE" ARE NONEXPONENTIAL

Host	[Ce^{3+}] (%)	Decay components		
		Short (ns)	Intermediate (ns)	Long (μs)
LaCl_3	-	-	-	3.48 ± 0.02 , 100%
LaCl_3	2	26.8 ± 0.9 , 10%	229 ± 2 , 18%	1.76 ± 0.01 , 72%
LaCl_3	4	25.0 ± 0.1 , 18%	213 ± 1 , 25%	1.14 ± 0.01 , 57%
LaCl_3	10	25.5 ± 0.1 , 41%	213 ± 2 , 29%	0.80 ± 0.02 , 30%
LaCl_3	30	24.3 ± 0.1 , 65%	379 ± 5 , 11%	2.7 ± 0.2 , 24%
CeCl_3	-	25.1 ± 0.1 , 69%	861 ± 22 , 8%	14 ± 4 , 23%

IV. DISCUSSION

In order to propose a scintillation mechanism for $\text{LaCl}_3:\text{Ce}^{3+}$, it is necessary to survey the mechanisms that could play a role in the scintillation process. Already in the paper by Guillot-Noël [5], the three most important mechanisms to consider were described and explained:

- 1) energy transfer by direct electron-hole capture on Ce^{3+} ;
- 2) energy transfer by binary electron-hole recombination;
- 3) energy transfer by STE diffusion.

In all samples, the relatively short decay component is probably due to *direct capture of electron-hole pairs* on Ce^{3+} . The observed decay time of ~ 25 ns is typical for Ce^{3+} luminescence. When the Ce^{3+} concentration is increased, the contribution of this component to the total light yield is expected to increase as well. Indeed, from LaCl_3 : 2% Ce^{3+} to LaCl_3 : 30% Ce^{3+} , the contribution of this component to the total light yield increases from 10% to 65% (see Table II).

The long decay component is probably due to STE luminescence. The decay time of this component, which is on the order of a few microseconds, is typical for self-trapped excitons [8]. As for LaCl_3 : 0.57% Ce^{3+} [5], we observed an anticorrelation between Ce^{3+} luminescence and STE luminescence for LaCl_3 : 2%, 4%, 10% Ce^{3+} . Consequently, it is assumed that *energy transfer by STE diffusion* is an important mechanism in these samples. The shortening of the decay time of STE luminescence is consistent with this model: if the Ce^{3+} concentration is increased, the diffusion path length of STE to cerium is shortened, as well as the decay time of the STE. For LaCl_3 : 30% Ce^{3+} and CeCl_3 , we did not observe an anticorrelation between STE and Ce^{3+} luminescence. Considering the high Ce^{3+} concentration in these samples, the STE is actually next to a certain Ce ion. Consequently, no STE to Ce^{3+} diffusion is present. The long decay component is probably due to impurity (Ce^{3+}) trapped STE luminescence.

In addition to these simple exponential components, a substantial part of the decay curves of LaCl_3 : 2%, 4%, 10%, 30% Ce^{3+} is nonexponential. This nonexponential component is probably due to *binary electron-hole recombination*. Previous papers have shown that in several lanthanide trihalides [5], $\text{K}_2\text{LaCl}_5:\text{Ce}^{3+}$ [2] and $\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}$ [14] binary electron-hole recombination could explain the observed nonexponential component in the decay curve under γ -ray excitation.

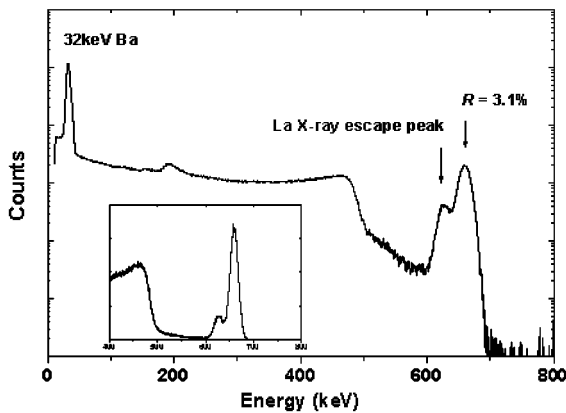


Fig. 4. Pulse-height spectrum of LaCl_3 : 10% Ce^{3+} under ^{137}Cs γ -ray excitation, recorded with a shaping time of $10 \mu\text{s}$.

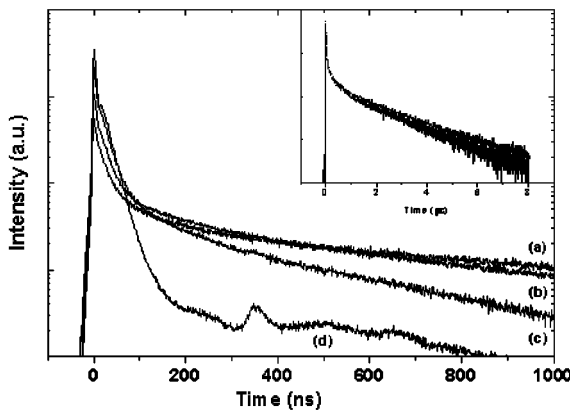


Fig. 5. Scintillation decay time spectra of (a) LaCl_3 : 2% Ce^{3+} , (b) LaCl_3 : 4% Ce^{3+} , (c) LaCl_3 : 10% Ce^{3+} , and (d) pure CeCl_3 . The inset shows the decay time spectrum of LaCl_3 : 2% Ce^{3+} on a longer time scale. The fit of the spectrum is indicated by a white dotted line.

meaning but is used to analyze the data. In Table II, the three decay components are presented as well as their relative contribution to the total light yield of the crystals. The components marked "intermediate" are nonexponential and have been approximated by an exponential fit. For simplicity, the components will be addressed as "short," "intermediate," and "long" in the following discussion.

In addition, it is known from the literature that in alkali fluorides and chlorides, STEs are not easily formed and are more likely to form a localized F-H pair [15]. To give a more definitive judgement on this type of energy transfer in these compounds, more experiments like electron-paramagnetic resonance and temperature-dependent decay time measurements have to be performed.

REFERENCES

- [1] J. C. van't Spijker, P. Dorenbos, J. T. M. de Haas, C. W. E. van Eijk, H. U. Güdel, and K. Krämer, "Scintillation properties of K_2LaCl_5 with Ce doping," *Rad. Meas.*, vol. 24, no. 4, pp. 379–381, 1995.
- [2] J. C. van't Spijker, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel, "Scintillation and luminescence properties of Ce^{3+} doped K_2LaCl_5 ," *J. Lumin.*, vol. 85, pp. 1–10, 1999.
- [3] P. Dorenbos, J. C. van't Spijker, O. W. V. Frijns, C. W. E. van Eijk, K. Krämer, H. U. Güdel, and A. Ellens, "Scintillation properties of $\text{RbGd}_2\text{Br}_7:\text{Ce}^{3+}$ crystals; fast, efficient and high density scintillators," *Nucl. Instrum. Meth. Phys. Res. B*, vol. 132, pp. 728–731, 1997.
- [4] O. Guillot-Noël, J. C. van't Spijker, J. T. M. de Haas, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel, "Scintillation properties of $\text{RbGd}_2\text{Br}_7:\text{Ce}$ advantages and limitations," *IEEE Trans. Nucl. Sci.*, vol. 46, pp. 1274–1284, Oct. 1999.
- [5] O. Guillot-Noël, J. T. M. de Haas, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel, "Optical and scintillation properties of cerium-doped LaCl_3 , LuBr_3 and LuCl_3 ," *J. Lumin.*, vol. 85, pp. 21–35, 1999.
- [6] B. Morosin, *J. Chem. Phys.*, vol. 49, no. 7, p. 3007, 1968.
- [7] W. W. Moses, "A method to increase optical timing spectra measurement rates using a multi-hit TDC," *Nucl. Instrum. Meth.*, vol. A336, pp. 253–265, 1993.
- [8] K. S. Song and R. T. Williams, "Alkali halides," in *Self-Trapped Excitons*. ser. Solid-State Sciences no. 105, M. Cardona, Ed. New York: Springer-Verlag, 1993, ch. 4 and 5.
- [9] E. Radzhabov and A. I. Nepomyashikh, "Exciton emission on LaF_3 crystals," *Mater. Sci. For.*, vol. 239–241, pp. 275–278, 1997.
- [10] S. M. Kuzakov, "Electron-hole traps and thermoluminescence of the $\text{LaCl}_3:\text{TR}$ single crystals," *Rad. Protect. Dosim.*, vol. 33, no. 1, pp. 115–117, 1990.
- [11] A. S. Voloshinovskii, P. A. Rodnyi, O. T. Antonyak, and N. S. Pidzyrailo, "Luminescence properties of cerium chloride," *Phys. Solid-State*, vol. 36, no. 2, pp. 239–242, 1994.
- [12] S. E. Derenzo and W. W. Moses, "Experimental efforts and results in finding new heavy scintillators," in *Proc. Crystal 2000 Int. Workshop "Heavy Scintillators for Scientific and Industrial Application"*, F. De Notaristefani, P. Lecoq, and M. Schneegans, Eds, 1993, pp. 125–135.
- [13] E. V. D. van Loef, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel, "High-energy-resolution scintillator: Ce^{3+} activated LaCl_3 ," *Appl. Phys. Lett.*, vol. 77, pp. 1467–1468, Sept. 2000.
- [14] C. M. Combes, P. Dorenbos, C. W. E. van Eijk, K. Krämer, and H. U. Güdel, "Optical and scintillation properties of pure and Ce^{3+} -doped $\text{Cs}_2\text{LiYCl}_6$ and $\text{Li}_3\text{YCl}_6:\text{Ce}^{3+}$ crystals," *J. Lumin.*, vol. 82, pp. 299–305, 1999.
- [15] K. S. Song and R. T. Williams, "Alkali halides," in *Self-Trapped Excitons*. ser. Solid-State Sciences no. 105, M. Cardona, Ed. New York: Springer-Verlag, 1993, p. 133.