Temperature Dependent Scintillation and Luminescence Characteristics of GdI₃: Ce³⁺

M. Danang Birowosuto, Pieter Dorenbos, G. Bizarri, Carel W. E. van Eijk, Member, IEEE, Karl W. Krämer, and Hans U. Güdel

Abstract—We investigated scintillation and luminescence properties of GdI₃:1% Ce³⁺. It shows a light yield of 47 000 photons/MeV recorded with a Hamamatsu R1791 photomultiplier tube (PMT). Using an Advanced Photonix 630-70-73-510 avalanche photodiode (APD), the light output of this sample is 44 000 electron-hole pairs/MeV. The best energy resolution at 662 keV of 4.7% was recorded at 10°C with the APD with a shaping time of 0.5 μs. At room temperature (RT), the γ-scintillation decay curve of GdI₃:1% Ce³⁺ shows a fast component of 45 ns, which is the same as the intrinsic Ce³⁺ decay time, and that contributes 70% to the total light yield. GdI₃:1% Ce³⁺ shows no afterglow at RT. Temperature dependence ranging from 80 to 600 K of X-ray excited emission spectra, pulse height spectra, scintillation decay curves and optically excited decay curves of Ce³⁺ emission are also presented.

Index Terms—Decay time, GdI₃:Ce³⁺, light yield, scintillator.

I. INTRODUCTION

IODIDE scintillators doped with Ce³⁺ were studied for the past four years [1]. These iodides that posses the smallest band gap in the halide family of compounds catch a lot of attention since high light yield scintillators may theoretically be found in small band gap compounds [2].

LuI₃: Ce³⁺ as one of the iodides has a light yield of 98 000 photons/MeV [3]–[5]. This is hitherto the highest light yield ever reported for a lanthanide halide scintillator. On the other hand, LaI₃: Ce³⁺ shows no luminescence at RT but it does luminesce at temperatures below 200 K [6]. The thermal quenching is attributed to a small energy difference of 0.1–0.2 eV between the Ce³⁺ lowest 5d state and the conduction band of the host. Ce³⁺ doped ternary cesium rare-earth iodides have a relatively low light yield of 1 500–22 800 photons/MeV [7]. Unlike LaI₃: Ce³⁺, the low light yield is due to a small efficiency of electron-hole transport to the optical center. Though most of the investigated iodides show low light yields, the search for the iodide scintillators with high light yield continues.

The first report by Glodo et al. on the scintillation properties of GdI₃:2% Ce³⁺ shows a high light yield of 58 000 photons/MeV and a fast decay time of 39 ns [8]. Potential applications as γ or neutron scintillator were proposed in the same paper. The scintillation mechanism was not discussed in detail.

In this work, we report scintillation and luminescence characteristics at RT and temperature dependent measurements of GdI₃:1% Ce³⁺. Its scintillation mechanism is also addressed.

II. EXPERIMENTAL

Single crystals of GdI₃:1% Ce³⁺ were grown by the Bridgmann technique using a moving furnace and a static vertical ampoule. GdI₃ and CeCl₃ were used as starting materials. Both were prepared from the elements and sublimated for purification. GdI₃: Ce³⁺ is easier to grow than LuI₃: Ce³⁺ since its melting point of 1200 K is lower than 1323 K of LuI₃: Ce³⁺. This means that GdI₃: Ce³⁺ has a better heat and mass transfer in the melts during crystal growth compared to those of LuI₃: Ce³⁺. Like other iodides, GdI₃: Ce³⁺ is very hygroscopic at RT and therefore some measurements were performed with a small crystal of 8 mm³ size sealed inside a quartz ampoule, see Fig. 1(a). Both crystal and the emission color under ultraviolet (UV) excitation are yellow [8]. A bare crystal of 120 mm³ size was used for measurements performed inside a dry box (M Braun), which was kept at a H₂O level less than one part per million. The same crystal was also used for measurements inside a clean vacuum sample chamber.

GdI₃: Ce³⁺ is isostructural with LuI₃: Ce³⁺. The crystal lattice of GdI₃ with parameters a = 7.55 ± 0.01 Å and c = 20.80 ± 0.02 Å belong to the BiI₃-type structure with space group R-3 (no. 148)[9]. The calculated density ρ is the effective atomic number Z_eff are 5.22 g/cm³ and 56.90, respectively. When GdI₃ is doped with Ce³⁺, the 7 pm larger Ce³⁺ ions occupy Gd³⁺ sites at Wyckoff position 6c with C₃ point symmetry.
and Gd-I distances of 305 and 308 pm. The polyhedron may be viewed as a GdI$_6^-$ octahedron with a small distortion, see Fig. 1(b).

X-ray excited emission spectra were recorded in reflection using an X-ray tube with a Cu-anode. The anode was operated at 35 kV and 25 mA. The emission of the sample was dispersed by an Acton Research Corporation (ARC) VM-504 monochromator (blazed at 300 nm, 1200 grooves/mm) and detected by a Hamamatsu R934-04 PMT. The spectra in this study were corrected for the wavelength dependence of the photodetector quantum efficiency as well as monochromator transmission. The afterglow spectra were recorded with the same setup after the crystals were exposed to X-rays for 60 s.

γ-ray pulse height spectra were recorded with bare crystals mounted on a 16 mm diameter Advanced Photonix 630-70-73-510 APD. The APD was operated at a bias voltage where the electronic noise and gain are optimum (1600 V) [10]. In order to avoid gain drift, the APD was stabilized at 10°C. The crystals were mounted without optical coupling on a quartz window placed on top of the APD. The crystals were covered with pressed Teflon powder to optimize the light collection. Other pulse height spectra were recorded with a Hamamatsu R1791 PMT. The crystals were directly mounted to the window of the PMT without optical coupling and covered with several layers of 0.1 mm UV reflecting Teflon tape. Both types of pulse height measurements were performed inside an M-Braun UNILAB dry box. The number of electron-hole pairs created in the APD was obtained through the comparison of the 662 keV photopeak position relative to the 17.8 keV peak of characteristic K X-rays from Np decay product of $^{241}$Am directly detected by the APD whereas the number of photoelectron emitted by the PMT photocathode was determined by comparison of the 662 keV photopeak position relative to the position of the mean value of the single electron response. The light yield derived from the photoelectrons of the PMT expressed in photons per MeV is determined using the quantum efficiency and reflectivity of the PMT [11].

Scintillation decay time curves were recorded using the single-photon counting technique described by Bollinger and Thomas [12]. For this method, scintillation decay time spectra were recorded at time ranges up to 200 $\mu$s with XP2020Q PMTs, Ortec 934 Constant Fraction Discriminators, Ortec 567 Time to Amplitude Converter (TAC) and AD413A CAMAC Analog to Digital Converter (ADC).

Optical excitation and emission spectra at RT in the 220–800 nm wavelength range were recorded using the spectrophotometer Quanta Master QM1 of Photon Technology International (PTI). Decay curves with selected excitation and emission wavelengths were recorded using a PicouQuant PDL 808 Sepia pulsed diode laser. Laser heads with wavelengths ranging from UV to infrared were used to excite the sample. The emission was filtered by a band filter and detected by a Philips XP2020Q PMT. Decay curves were obtained after deconvolution of the system response function.

Temperature dependent X-ray excited emission and optical excited decay curves measurements were performed between 80 and 600 K, using a JANIS VPF-700 Cryostat operated with Model 331 LakeShore Temperature Controller whereas the setup of temperature dependent recording of γ-excited pulse height spectra is described in Bizzari et al. [13]. The PMTs in both setups were kept in RT.

### III. RESULTS AND DISCUSSION

#### A. Scintillation and Luminescence Properties at RT

The X-ray excited emission spectrum of GdI$_3$:1% Ce$^{3+}$ is shown in Fig. 2. Those for LuI$_3$:1% Ce$^{3+}$ and LaI$_3$:5% Ce$^{3+}$ are added for comparison. The emission spectrum of GdI$_3$:1% Ce$^{3+}$ shows a broad band between 450 and 700 nm attributed to the characteristic 5d$_{x^2-y^2}$ → 4f Ce$^{3+}$ emission. Similar emission was also reported for GdI$_3$:2% Ce$^{3+}$ [8]. The 5d$_{x^2-y^2}$ → 4f Ce$^{3+}$ emission is shifted towards longer wavelengths compared to that of LuI$_3$:1% Ce$^{3+}$ and LaI$_3$:5% Ce$^{3+}$.

GdI$_3$: Ce$^{3+}$ has the same crystal structure as LuI$_3$: Ce$^{3+}$ but the Gd$^{3+}$ site is larger than the Lu$^{3+}$ site. One then expects a smaller crystal field interaction leading to smaller splitting between Ce$^{3+}$ 5d states in GdI$_3$ and a higher energy Ce$^{3+}$ emission than in LuI$_3$ [14]. In Fig. 2, the Ce$^{3+}$ emission in GdI$_3$ is still unknown reason at lower energy than that of LuI$_3$.

Two weak emission bands peaked at 290 and 390 nm are also observed in the emission spectrum of GdI$_3$:1% Ce$^{3+}$, see Fig. 2. A band at 390 nm is present in the emission spectrum of LaI$_3$:5% Ce$^{3+}$, see Fig. 2. Here we will designate the emission band in GdI$_3$: Ce$^{3+}$ at 290 nm as the short-wavelength luminescence (SWL) and that at 390 nm as the long-wavelength luminescence (LWL). They can be tentatively attributed to self-trapped-exciton (STE) emission or other defects.

Fig. 3 shows optical excitation and emission spectra and the decay curve recorded at RT of GdI$_3$:1% Ce$^{3+}$. The excitation spectrum of GdI$_3$:2% Ce$^{3+}$ in the work of Glodo et al. shows better resolved structures [8]. The excitation spectrum monitoring 500 nm emission shows a broad band between 225 and 490 nm, see spectrum (a) in Fig. 3. This broad band is due to the overlap between the host lattice and the 5d Ce$^{3+}$ excitations as previously identified by Glodo et al. [8]. In the same work, the...
host lattice excitation from valence to conduction band $E_c$ and the band gap $E_g$ were estimated at 4.7 and 5.1 eV, respectively.

The decay curve excited at 377 nm and monitoring 475–600 nm emission of GdI$_3$:1% Ce$^{3+}$ has been fitted with a single exponential, see curve (c) in Fig. 3. From the fit, the decay time of the Ce$^{3+}$ emission in GdI$_3$ at RT is 45 ± 4 ns. This decay time is 12 ns slower than the 33 ± 3 ns decay time of Ce$^{3+}$ emission in LuI$_3$ [15]. For an electric dipole allowed 5d → 4f transition, the lifetime of the 5d state of Ce$^{3+}$, $\tau_{Ce}$, is proportional to the third power of the emission wavelength $\lambda_{Ce}$ [2]

$$\tau_{Ce} \propto \lambda_{Ce}^{-3}. \quad (1)$$

From Fig. 2, $\lambda_{Ce}$ for LuI$_3$: Ce$^{3+}$ and GdI$_3$: Ce$^{3+}$ is 475 and 560 nm, respectively. This gives a ratio of $\tau_{Ce}/\lambda_{Ce}^3$ for LuI$_3$: Ce$^{3+}$ and GdI$_3$: Ce$^{3+}$ of 3.08 ± 0.28 and 2.56 ± 0.28 · 10$^{-7}$ ns nm$^{-3}$, respectively. Both ratios are not inconsistent with each other and the 12 ns slower decay time for GdI$_3$: Ce$^{3+}$ is therefore attributed with the longer emission wavelength.

The $^{137}$Cs γ source pulse height spectra measured with the PMT and the APD of GdI$_3$:1% Ce$^{3+}$ are presented in Fig. 4. Both pulse height spectra show a clear 662 keV photopeak. Photon yield, electron-hole pair yield and energy resolution derived from both pulse height spectra are presented in Table I. Energy resolution [full width at half maximum (FWHM)] is obtained from a Gaussian fit of the photopeak.

The photon yield of GdI$_3$:1% Ce$^{3+}$ recorded with the PMT is 47 000 ± 5 000 photons/MeV. This light yield is lower than the 58 000 photons/MeV of GdI$_3$:2% Ce$^{3+}$ reported by Glodo et al. [8]. The electron-hole pair yield recorded with the APD is 44 000 ± 4 000 electron-hole pairs/MeV. The photon yield derived from this value is identical with that derived from the PMT since the effective quantum efficiency of the APD is about 95–100% [11]. The photon yield at a shaping time of 0.5 µs compared to that at 10 µs is about 94%. This means that most of the photons are emitted fast. The energy resolution recorded with the PMT is 5.7 ± 0.6%. This energy resolution is better than the 8.7% previously reported for GdI$_3$:2% Ce$^{3+}$ [8]. The best energy resolution of 4.7 ± 0.5% is observed for the pulse height spectrum recorded with the APD at 10°C and a shaping time of 0.5 µs.

Fig. 5 shows the scintillation decay curve of GdI$_3$:1% Ce$^{3+}$ at RT. The curve has been fitted with three exponentials. The decay components from the fit are 45, 250, and 2000 ns with
Fig. 6. (a) X-ray excited emission spectra recorded between 80 and 600 K with 20 K interval and (b) $^{137}$Cs pulse height spectra with a shaping time of 10 $\mu$s recorded at 100, 300, and 600 K.

contributions to the total light yield of 70, 24, and 6%, respectively.

B. Temperature Dependence

The temperature dependence of X-ray excited emission and pulse height spectra recorded with a Philips XP2020 PMT with 10 $\mu$s shaping time is shown in Fig. 6. As previously seen in Fig. 2, the X-ray excited emission spectra show SWL and LWL bands peaked respectively at 290 and 390 nm and Ce$^{3+}$ doublet emission bands peaked at 560 nm. With the increase of temperature, the SWL band disappears. For the pulse height spectra recorded at 100, 300, and 600 K, the 662 keV photopeak is located at channel number of 5270 and 5580, respectively. The energy resolution of the pulse height spectra is 6.8%. This is poorer than 5.7% of the pulse height spectrum recorded with a Hamamatsu R1791 PMT, see Table 1. The degradation is due to less effective scintillation light collection in the temperature dependence setup [13].

Light yields as a function of temperature of GdI$_3$:1% Ce$^{3+}$ in Fig. 7(a) were derived from the integral of each X-ray excited emission spectrum and from pulse height spectra measured between 80 to 600 K. The y-axis for the integral of the X-ray excited emission spectra has been calibrated in such a way that the integral at RT is equal to the value of the absolute light yield expressed in photons per MeV as found from the analysis of the pulse height spectra recorded at RT. Later in this work, we will report that no afterglow is observed at RT, and therefore the light yield at RT derived from the pulse height spectra with a shaping time of 10 $\mu$s represents that derived from the integral of X-ray excited emission spectrum.

The yields derived from X-ray excited emission spectra show that it decreases at 300 K by 33% from that recorded at 80 K. When the temperature increases higher than 300 K, the yield is rather constant, see Fig. 7(a). From the same diagram, the yield under X-ray excitation at 80 K equals 70 000 photons/MeV. This is close to the theoretical light yield limit of $10^3/(2-3)E_g = 81 500 \pm 16 500$ photons/MeV where the band gap $E_g$ is estimated 5.1 eV for GdI$_3$: Ce$^{3+}$.

The light yield derived from pulse height spectra shows that it is constant from 80 to 600 K, see Fig. 7(a). In the region 80 to 300 K, there is a discrepancy with the yield derived from the integral of the X-ray excited emission spectra. One explanation is related with the recording time of the data. The light yields from the pulse height spectra were recorded with a shaping time of 10 $\mu$s whereas those from the X-ray excited emission spectra were recorded in a DC scanning mode integrating all decay components. If afterglow is present in GdI$_3$: Ce$^{3+}$, it increases the intensities of the X-ray excited emission spectra. Additionally, one may not exclude differences in yield due to the nonproportional response of scintillators with excitation energies.
The temperature dependence of the Ce$^{3+}$, LWL and SWL yields in GdI$_3$:1% Ce$^{3+}$ are shown in Fig. 7(b). The X-ray excited emission spectra were fitted with four Gaussians. The yields were derived from the integrals of the Gaussian fits corresponding to Ce$^{3+}$, SWL and LWL bands. The Ce$^{3+}$ and the LWL yields are relatively constant from 80 to 600 K whereas the SWL yield is completely quenched at 400 K.

Fig. 8 shows the temporal behavior of the X-ray excited luminescence/afterglow intensity of GdI$_3$:1% Ce$^{3+}$ after switching on for 60 s and off the X-ray excitation at 80 K and RT. Data points were recorded every 0.1 s. The background level for both curves is identical and shown by the dotted line. GdI$_3$:1% Ce$^{3+}$ shows no significant afterglow at RT while 10 s integral of the afterglow intensity at 80 K is about 8% from that of X-ray excited emission intensity. This afterglow contributes to the difference between the light yields derived from the integral of the X-ray excited emission spectra and those derived from the pulse height spectra at low temperatures as observed in Fig. 7(a).

Fig. 9(a) shows decay time curves of the Ce$^{3+}$ emission at 475–600 nm upon 4$f$ → 5$d$ excitation at 377 nm and recorded at 100, 300 and 600 K in GdI$_3$:1% Ce$^{3+}$. All decay curves were fitted with a single exponential decay. The characteristic decay time is shown as a function temperature between 80 and 600 K with 20 K interval in Fig. 9(b). The decay time increases from 33 to 45 ns when the temperature increases from 80 to 300 K. It is then followed by a 9 ns decrease of decay time when the temperature increases to 600 K. A similar decay time behavior was observed for LuI$_3$: Ce$^{3+}$ [15].

The temperature dependence of scintillation decay curves of GdI$_3$:1% Ce$^{3+}$ under γ-ray excitation is shown in Fig. 10. Decay curves do not decay single exponentially but are composed of different decay components. In order to analyze the data, decay curves up to 5 μs were fitted with three exponential decay components.

Table II shows the decay time of three components with their relative contribution to the photon yield within 5 μs. The fast components at 100 and 200 K are about 20 ns slower than the Ce$^{3+}$ intrinsic lifetime in GdI$_3$ measured under optical excitation, see Fig. 9(b). When temperature increases from 300 to 600 K, the fast component of decay is similar to the intrinsic Ce$^{3+}$ emission lifetime in GdI$_3$ for each temperature. The intermediate and the slow components become faster with the increase of the temperature. The contribution of the fast component significantly increases from 30% to 70% when the temperature increases from 100 to 300 K and it becomes relatively constant of about 80% at temperatures above 300 K.

We may distinguish different energy transfer processes leading to scintillation light emission in GdI$_3$: Ce$^{3+}$. The first process is the prompt sequential electron-hole capture. The free electron and hole from the ionization track are sequentially captured within 1 ns by Ce$^{3+}$ ion leading to 4$f$ → 5$d$ excitation. This mechanism is followed by 5$d$ → 4$f$ emission. The 70–80% contribution of the fast component in the scintillation
energy resolution at 662 keV recorded with the APD of 4.7% were reported in GdI$_3$:1% Ce$^{3+}$ at RT. The fast component of 45 ns with a contribution of 70% from the photon yield in the scintillation decay curve of GdI$_3$:1% Ce$^{3+}$ is important for fast counting applications. GdI$_3$:1% Ce$^{3+}$ also shows no afterglow at RT. The location of the Ce$^{3+}$ doublet emission of GdI$_3$: Ce$^{3+}$ in the 450–800 nm region is highly advantageous for the applications using the APD since it is perfectly matched with the sensitivity of the APD.

The temperature dependence of X-ray excited emission spectra, pulse height spectra, scintillation decay curves and optically excited decay curves of Ce$^{3+}$ emission were presented in this work. The energy transfer processes in GdI$_3$: Ce$^{3+}$ were also discussed.

### IV. SUMMARY

We have reported the scintillation and luminescence properties of GdI$_3$:1% Ce$^{3+}$ at RT and as a function of temperature. The relatively high light yield of 47 000 photons/MeV and the decay curves recorded between 300 and 600 K implies that the prompt capture and other fast transfer processes dominate at temperatures above 300 K, see column 2 in Table II.

A second process is often the prompt creation of a STE that may luminesce by itself or transfer its excitation energy to Ce$^{3+}$ ions by thermal activated migration and/or transfer. This process is important at 100 K as the contribution of the intermediate and the slow components is 54% and 16%, respectively.

### REFERENCES