

Scintillation properties and anomalous Ce^{3+} emission of $\text{Cs}_2\text{NaREBr}_6:\text{Ce}^{3+}$ (RE = La, Y, Lu)

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Abstract

We report the optical and scintillation properties of the Ce^{3+} -doped bromoelpasolites $\text{Cs}_2\text{NaREBr}_6$ (RE = La, Y, Lu). The γ -ray scintillation light yield of these materials varies from 6000 to 17 000 photons per MeV absorbed γ -ray energy. At room temperature (RT), the γ -ray scintillation decay curves for all compounds show a fast component of 61 ns, whereas the intrinsic Ce^{3+} decay time is 30 ns. The scintillation mechanism in elpasolites is addressed. In $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$, we observe for the first time the so-called Ce^{3+} anomalous emission in bromide compounds. This emission previously observed for chloride compounds is an ultrafast Ce^{3+} emission with a selective excitation mechanism. The decay time of the anomalous emission at 10 K in bromide compounds (~ 7.80 ns) is faster than that in chloride compounds (~ 9.90 ns). Two bands of the anomalous emission are resolved for the first time. The mechanism behind this emission is discussed.

1. Introduction

Elpasolites have been thoroughly studied for applications such as laser hosts [1] and storage phosphors [2]. Recently, many Ce^{3+} -doped elpasolites have been investigated for use as inorganic scintillators, in particular for thermal neutron detection [3–5].

In Ce^{3+} -doped elpasolites, the Ce^{3+} ions occupy a high O_h symmetry site which splits the Ce^{3+} 5d levels into a lower triplet $5d_{t_{2g}}$ and an upper doublet $5d_{e_g}$. As in the case of the closely related perovskites, variants with lower symmetry occur, depending on composition, temperature or pressure. So far, elpasolites have shown less attractive scintillation properties than the lanthanum trihalides. The light yield in $\text{LaBr}_3:\text{Ce}^{3+}$ is 70 000 photons MeV^{-1} , whereas that in $\text{Cs}_2\text{LiYBr}_6:\text{Ce}^{3+}$ is 25 000 photons MeV^{-1} [6, 7]. The question why elpasolites

show a lower light yield has remained open, due to lack of in-depth knowledge about the scintillation mechanism.

Van Loef *et al* reported the influence of the anion on the scintillation mechanism of Ce^{3+} -doped Cs_2LiYX_6 ($X = \text{Cl}, \text{Br}$) [4]. Van't Spijker *et al* have previously studied the scintillation properties of Ce^{3+} -doped $\text{Cs}_2\text{NaRECl}_6$ ($\text{RE} = \text{La}, \text{Lu}$) [8]. The optical and scintillation properties of Ce^{3+} -doped $\text{Cs}_2\text{NaREBr}_6$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$) are investigated in this work. The influences of the RE^{3+} ions on the host properties and on the spectroscopic behaviour of Ce^{3+} are discussed. Scintillation mechanisms, i.e. radiative transfer from a self-trapped exciton (STE) to Ce^{3+} , STE migration, and binary vacancy (V_k) and electron diffusion, are addressed.

A so-called anomalous Ce^{3+} emission was observed recently in $\text{Cs}_3\text{LuCl}_6:\text{Ce}^{3+}$, $\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{LiLuCl}_6:\text{Ce}^{3+}$ [9–11]. The anomalous Ce^{3+} emission with a decay time of 10 ns is only observed when the $5d_e$ level is excited. It does not appear when the host lattice is excited. The application of this emission can be useful as a selective ultraviolet (UV) sensor. In the present paper, the same type of anomalous emission is observed for the first time in bromide compounds. Also for the first time, the emission shows clearly two bands that can be associated with the transitions to the $^2F_{5/2}$ and $^2F_{7/2}$ states of Ce^{3+} . The temperature dependence of the intensity and the decay times of the anomalous emission are presented, too.

2. Experimental techniques

2.1. Crystal growth

$\text{Cs}_2\text{NaREBr}_6$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$) crystals were grown by the vertical Bridgman method using stoichiometric amounts of CsBr, NaBr and REBr_3 ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$). CeBr_3 was used to prepare the Ce^{3+} -doped compound. $\text{Cs}_2\text{NaLaBr}_6:0.5\% \text{Ce}^{3+}$, $\text{Cs}_2\text{NaYBr}_6:0.3\% \text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:0.5\% \text{Ce}^{3+}$ were grown. These crystals are hygroscopic and were sealed under argon atmosphere in small quartz ampoules to prevent hydration of the surfaces.

$\text{Cs}_2\text{NaYBr}_6$ and $\text{Cs}_2\text{NaLuBr}_6$ have the cubic elpasolite structure with four formula units in the unit cell ($\text{Cs}_2\text{NaYBr}_6$ with $a = 11.30 \text{ \AA}$; $\text{Cs}_2\text{NaLuBr}_6$ with $a = 11.23 \text{ \AA}$). $\text{Cs}_2\text{NaLaBr}_6$ is tetragonal ($a = 11.52 \text{ \AA}$ and $c = 11.61 \text{ \AA}$) [12]. In $\text{Cs}_2\text{NaLaBr}_6:\text{Ce}^{3+}$, two La^{3+} sites can be occupied by Ce^{3+} . The space group of $\text{Cs}_2\text{NaLaBr}_6$ is $P4/nbm$ (No. 125) and that of $\text{Cs}_2\text{NaYBr}_6$ and $\text{Cs}_2\text{NaLuBr}_6$ is $Fm\bar{3}m$ (No. 225).

2.2. Equipment

X-ray excited emission spectra were recorded using an x-ray tube with Cu anode operated at 35 kV and 25 mA. The emission was dispersed with an ARC VM504 monochromator, blazed at 300 nm with 1200 grooves mm^{-1} , and measured with a Hamamatsu R934-04 photomultiplier tube (PMT). The spectra were corrected for the transmittance of the monochromator and the quantum efficiency of the PMT.

Time-resolved excitation and emission spectra with high resolution at temperatures between 10 and 300 K were recorded at the SUPERLUMI vacuum ultraviolet (VUV) station of Hamburger Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY) facility in Hamburg, Germany. Emission spectra were recorded with an ARC Spectropro 300I monochromator, blazed at 500 nm with 300 grooves mm^{-1} , and a Hamamatsu R6358 PMT. Excitation spectra were recorded using a 0.3 nm resolution McPherson monochromator with a working range of 50–330 nm. Photons were counted within a time window of 20 ns, 6 ns after following the start of the excitation synchrotron pulse. Another 65 ns wide time window starting after 85 ns delay was used to discriminate between

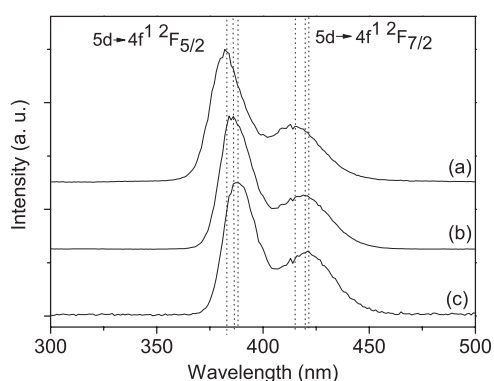


Figure 1. X-ray excited emission spectra at RT of (a) Cs₂NaLaBr₆:0.5% Ce³⁺, (b) Cs₂NaYBr₆:0.3% Ce³⁺ and (c) Cs₂NaLuBr₆:0.5% Ce³⁺. The dotted lines indicate the peak maxima of the 5d¹ → 4f¹ ²F_{5/2} and 5d¹ → 4f¹ ²F_{7/2}Ce³⁺ emissions.

fast and slow luminescence components. Integral spectra comprising all emitted light were also recorded. With the same setup, we recorded decay time curves. Details about the SUPERLUMI station were published by Zimmerer [13]. Ultraviolet/visible (UV/VIS) excitation and emission spectra measured at RT with an observation of wavelengths longer than 330 nm were performed with a spectrophotometer (Quanta Master QM1, Photon Technology International).

Pulse height spectra under γ -ray excitation from a ¹³⁷Cs source were recorded with a Hamamatsu R1791 PMT with a box type dynode structure connected to a pre-amplifier and an Ortec 672 spectroscopy amplifier. The quartz ampoules containing the crystals were optically coupled onto the PMT window with Viscasil 60 000 cSt from General Electric. The quartz ampoules were covered with several layers of 0.1 mm UV reflecting Teflon tape for better light collection. The yield, expressed as photoelectrons per MeV (phe/MeV) of absorbed γ -ray energy, was obtained by comparison of the peak position of the 662 keV photopeak in the pulse height spectra with the peak position of the single photoelectron response. The light yield, expressed in photons MeV⁻¹, is determined by correcting for the quantum efficiency and the reflectivity of the PMT [14].

Scintillation decay time curves under ¹³⁷Cs 662 keV γ -ray excitation were recorded with the multi-hit method. A description about the experimental setup can be found elsewhere [15, 16].

3. Results

3.1. X-ray excited emission spectra

X-ray excited emission spectra of Ce³⁺-doped Cs₂NaREBr₆ (RE = La, Y, Lu) are shown in figure 1. The maximal intensity for each spectrum has been normalized and vertically shifted with respect to each other for clarity.

Characteristic 5d → 4f Ce³⁺[²F_{5/2}, ²F_{7/2}] doublet emission is well resolved in the spectra. The 5d → ²F_{5/2} emission is peaked at 382, 385, and 389 nm for Cs₂NaLaBr₆:Ce³⁺, Cs₂NaYBr₆:Ce³⁺ and Cs₂NaLuBr₆:Ce³⁺, respectively. The 5d → ²F_{7/2} emission is peaked at 414, 420, and 422 nm for Cs₂NaLaBr₆:Ce³⁺, Cs₂NaYBr₆:Ce³⁺ and Cs₂NaLuBr₆:Ce³⁺, respectively. In the x-ray excited emission spectra of Cs₂LiYCl₆:Ce³⁺, Cs₂LiLuCl₆:Ce³⁺ and Cs₂LiYBr₆:Ce³⁺, an additional low intensity emission band was observed at shorter wavelength [4, 10, 11]. This band was attributed to a remnant of STE emission. We do not observe such a band in the x-ray excited emission spectra of Cs₂NaREBr₆:Ce³⁺ (RE = La, Y, Lu) recorded at RT; see figure 1.

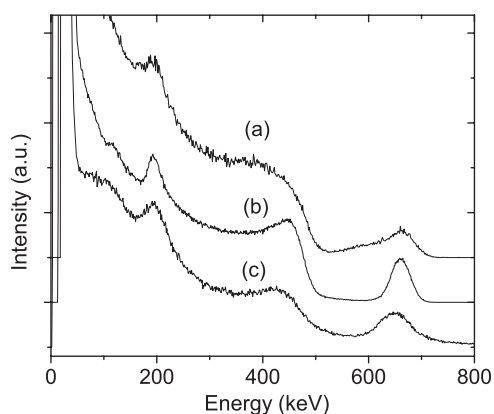


Figure 2. Pulse height spectra under ^{137}Cs 662 keV γ -ray excitation of (a) $\text{Cs}_2\text{NaLaBr}_6:0.5\% \text{Ce}^{3+}$, (b) $\text{Cs}_2\text{NaYBr}_6:0.3\% \text{Ce}^{3+}$ and (c) $\text{Cs}_2\text{NaLuBr}_6:0.5\% \text{Ce}^{3+}$ recorded with a Hamamatsu R1791 PMT and a shaping time of $10 \mu\text{s}$. The spectra are stacked for clarity.

Table 1. Light yield and energy resolution derived from pulse height spectra of $\text{Cs}_2\text{NaLaBr}_6:0.5\% \text{Ce}^{3+}$, $\text{Cs}_2\text{NaYBr}_6:0.3\% \text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:0.5\% \text{Ce}^{3+}$ under 662 keV γ -ray excitation measured with a Hamamatsu R1791 PMT. Energy resolution was recorded with a shaping time of $10 \mu\text{s}$ at the 662 keV photopeak.

Compound	Light yield (10^3 photons MeV^{-1})			Energy resolution R (%)
	$0.5 \mu\text{s}$	$3 \mu\text{s}$	$10 \mu\text{s}$	
$\text{Cs}_2\text{NaLaBr}_6:\text{Ce}^{3+}$	9.0 ± 0.9	14.0 ± 1.4	17.0 ± 1.7	11.3 ± 1.1
$\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$	5.0 ± 0.5	6.8 ± 0.7	9.5 ± 1.0	6.3 ± 0.6
$\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$	5.2 ± 0.5	5.6 ± 0.6	5.8 ± 0.6	10.5 ± 1.1

3.2. Gamma spectroscopy

The ^{137}Cs 662 keV γ -ray pulse height spectra of Ce^{3+} -doped $\text{Cs}_2\text{NaREBr}_6$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$) are presented in figure 2. Light yields derived from the pulse height spectra are compiled in table 1. $\text{Cs}_2\text{NaLaBr}_6:\text{Ce}^{3+}$ has the highest light yield of 17000 photons MeV^{-1} . The yield decreases when RE^{3+} changes from La^{3+} to Y^{3+} to Lu^{3+} . Such a decrease was not observed for Ce^{3+} -doped $\text{Cs}_2\text{NaRECl}_6$ ($\text{RE} = \text{La}, \text{Lu}$) but it was observed for $\text{Cs}_2\text{LiRECl}_6:\text{Ce}^{3+}$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$) [3, 7, 8, 11]. The contribution of the fast components (within $0.5 \mu\text{s}$ shaping time) to the total light yield of $\text{Cs}_2\text{NaLaBr}_6:\text{Ce}^{3+}$, $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ is 53, 53 and 90%, respectively. The energy resolutions of these materials are still far from the best energy resolution of 2.8% recorded for $\text{LaBr}_3:\text{Ce}^{3+}$; see column 5 in table 1 [6].

3.3. Scintillation and intrinsic Ce^{3+} emission decay times

Figure 3 shows scintillation and optical excited Ce^{3+} emission decay curves of Ce^{3+} -doped $\text{Cs}_2\text{NaREBr}_6$ ($\text{RE} = \text{La}, \text{Y}, \text{Lu}$). The scintillation decay curves were recorded at RT, whereas the Ce^{3+} emission decay curves were recorded at 10 K and RT. The Ce^{3+} emission decay curves of $\text{Cs}_2\text{NaLaBr}_6:\text{Ce}^{3+}$ were excited at 330 nm and the emission monitored at 384 nm, whereas those of $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ were excited at 328 nm and the emission monitored at 380 nm.

The scintillation decay curves are characterized by three decay components: a fast, an intermediate and a slow component. In table 2, the three decay components are presented as well as their relative contribution to the total light output of the crystals. Intrinsic decay times of the Ce^{3+} emission at 10 K and RT are also presented. They are obtained from single exponential fits of the decay curves after excitation of the $5d_1$ state.

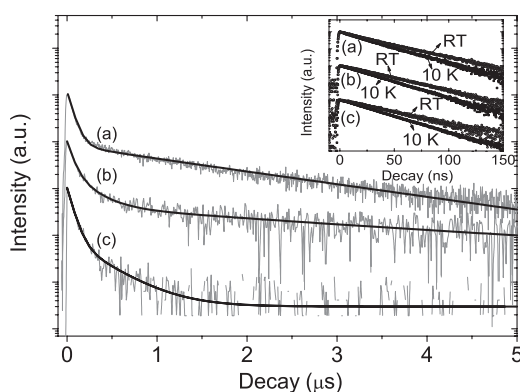


Figure 3. Scintillation decay curves under ¹³⁷Cs 662 keV γ -ray excitation recorded at RT and Ce³⁺ decay curves excited in the 5d_i state recorded at 10 K and RT (inset) of (a) Cs₂NaLaBr₆:0.5% Ce³⁺, (b) Cs₂NaYBr₆:0.3% Ce³⁺, and (c) Cs₂NaLuBr₆:0.5% Ce³⁺ in a semi-logarithmic representation. The spectra are stacked for clarity. The solid lines drawn through the data are summed exponential fits.

Table 2. Characteristics of the scintillation decay curves and intrinsic decay times of Ce³⁺ of Cs₂NaLaBr₆:0.5% Ce³⁺, Cs₂NaYBr₆:0.3% Ce³⁺ and Cs₂NaLuBr₆:0.5% Ce³⁺ at RT. Intrinsic decay times of Ce³⁺ were recorded at 10 K and RT.

Compound	Decay components (relative contribution to total light yield)			Intrinsic Ce ³⁺ decay times 10 K/RT (ns)
	Fast (ns)	Intermediate (ns)	Slow (μ s)	
Cs ₂ NaLaBr ₆ :Ce ³⁺	61 \pm 6 (32%)	450 \pm 50 (11%)	1.9 \pm 0.2 (57%)	24/30
Cs ₂ NaYBr ₆ :Ce ³⁺	61 \pm 6 (26%)	350 \pm 40 (23%)	2.7 \pm 0.3 (51%)	24/30
Cs ₂ NaLuBr ₆ :Ce ³⁺	61 \pm 6 (65%)	350 \pm 40 (35%)	(Not observed)	24/30

The fast component of the scintillation decay remains 61 ns when changing the cation from La³⁺ to Y³⁺ to Lu³⁺ but there are differences for the intermediate and slow components. The optically excited decay curves at 10 K exhibit the same 24 ns Ce³⁺ emission decay time; see the inset in figure 3. At RT, these decay times increase to 30 ns. A similar decay time increase with temperature is reported for Ce³⁺ emission in other compounds [17].

3.4. Spectroscopy

The optically excited emission spectra of Ce³⁺-doped Cs₂NaREBr₆ (RE = La, Y, Lu) at 10 K are shown in figure 4. The spectra were normalized to each other in order to demonstrate best the different contributions. Slow (i) and fast (ii) emission spectra were excited into the host lattice absorption and the Ce³⁺ 4f \rightarrow 5d_e bands, and are shown as dotted and full lines, respectively, in figures 4(a)–(c).

The fast emission spectra excited into the Ce³⁺ 4f \rightarrow 5d_e band exhibit two bands of the characteristic 5d \rightarrow 4f Ce³⁺ doublet emission around 400 nm. The ²F spin-orbit splittings of the Ce³⁺ ground state in Cs₂NaLaBr₆:Ce³⁺, Cs₂NaYBr₆:Ce³⁺, and Cs₂NaLuBr₆:Ce³⁺ are 2023, 2165, and 2010 cm⁻¹ (0.25, 0.27, and 0.25 eV), respectively. Two other fast doublet emissions with maxima at 282 and 285 nm are observed for Cs₂NaYBr₆:Ce³⁺ and Cs₂NaLuBr₆:Ce³⁺, respectively. Similar high energy emissions under excitation in

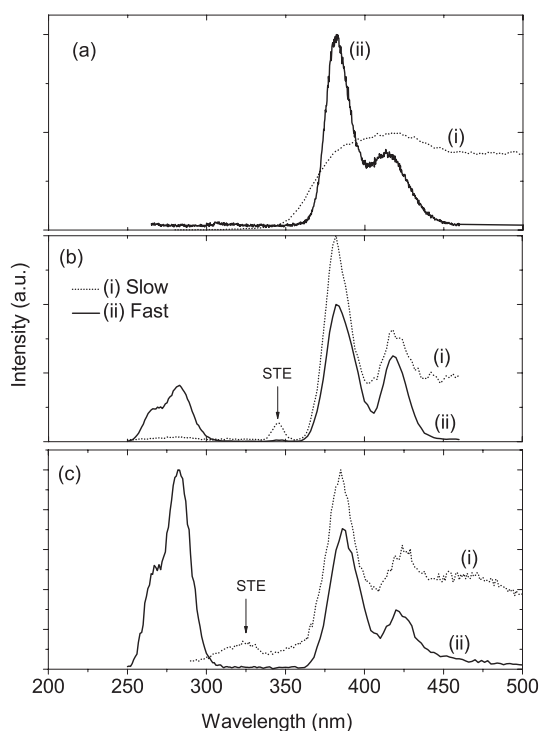


Figure 4. Emission spectra of (a) $\text{Cs}_2\text{NaLaBr}_6:0.5\% \text{Ce}^{3+}$ excited at 209 (i) and 230 nm (ii), (b) $\text{Cs}_2\text{NaYBr}_6:0.3\% \text{Ce}^{3+}$ excited at 200 (i) and 225 nm (ii), and (c) $\text{Cs}_2\text{NaLuBr}_6:0.5\% \text{Ce}^{3+}$ excited at 190 (i) and 222 nm (ii). All spectra were recorded at 10 K.

$5d_e$ were previously observed in the chloride compounds $\text{Cs}_3\text{LuCl}_6:\text{Ce}^{3+}$, $\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}$, and $\text{Cs}_2\text{LiLuCl}_6:\text{Ce}^{3+}$ [9–11], where they were called anomalous Ce^{3+} emissions. For the bromoelpasolites in figure 4, we observe a clear doublet structure of this emission that was not observed before. The doublets are separated by 2055 and 2022 cm^{-1} (0.25 and 0.25 eV) for $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$, respectively. Considering of an error of 10%, these energy differences correspond to the spin–orbit splittings between ^2F states.

Beside the normal and anomalous Ce^{3+} emission, the slow emission spectra excited into the host lattice absorptions show emissions at 345 and 325 nm for $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$, respectively. These emissions are attributed to a remnant of STE emission. Such emissions were often observed in other elpasolites [9–11].

The excitation spectra of the STE emission remnants at 360, 345, and 325 nm for $\text{Cs}_2\text{NaLaBr}_6$, $\text{Cs}_2\text{NaYBr}_6$ and $\text{Cs}_2\text{NaLuBr}_6$, respectively, are shown as curves (ii) in figures 5(a)–(c). From those spectra, properties of the host compounds which are compiled in table 3 were derived. The fundamental absorption (E^{fa}) is the energy of the first sharp onset in the slow excitation spectra of the STE emission. The first maximum (E^{ex}) is attributed to the creation of excitons which can be regarded as bound electron hole pairs. The edge of the conduction band (E_{VC}) corresponds to the creation of free electrons in the conduction band and free holes in the valence band. We estimate the bottom of the conduction band at 8% higher energy than E^{ex} (i.e., the binding energy of the electron–hole pair in the exciton is about 8% of the exciton creation energy).

The integral excitation spectra of the $5d \rightarrow 4f \text{Ce}^{3+}$ emission recorded at RT show the $\text{Ce}^{3+} 4f \rightarrow 5d$ excitation bands. For elpasolites, we expect the $5d_t$ levels at lower energy and the $5d_e$ levels at higher energy due to the octahedral crystal field splitting. Most of the $4f \rightarrow 5d$ bands overlap. The level positions were determined by fitting multiple Gaussians to the $5d_e$ and

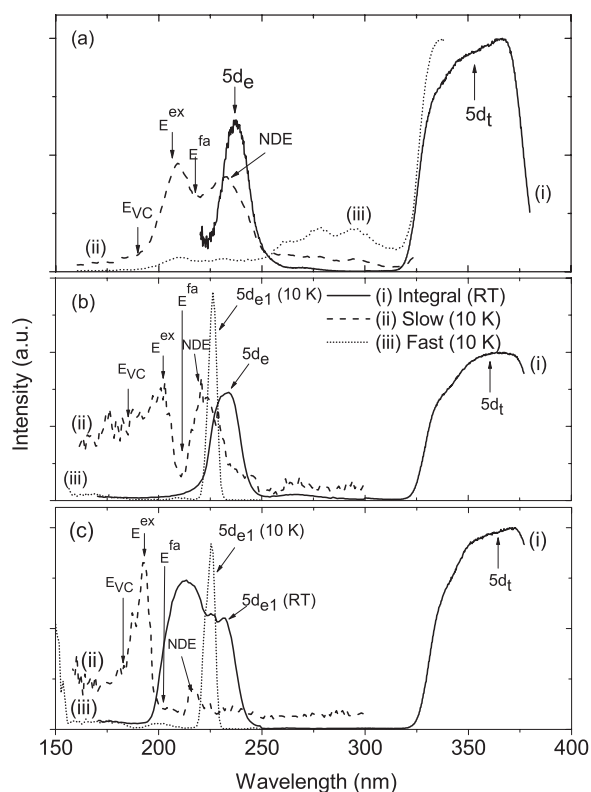


Figure 5. Excitation spectra of (a) $\text{Cs}_2\text{NaLaBr}_6:0.5\% \text{Ce}^{3+}$ monitoring 407 (i), 360 (ii), and 384 nm (iii) emissions, (b) $\text{Cs}_2\text{NaYBr}_6:0.3\% \text{Ce}^{3+}$ monitoring 390 (i), 345 (ii), and 282 nm (iii) emissions, and (c) $\text{Cs}_2\text{NaLuBr}_6:0.5\% \text{Ce}^{3+}$ monitoring 390 (i), 325 (ii), and 285 nm (iii) emissions. The integral spectra (full lines) were recorded at RT, whereas slow (dotted lines) and fast spectra (broken lines) were recorded at 10 K.

Table 3. Host properties of $\text{Cs}_2\text{NaLaBr}_6$, $\text{Cs}_2\text{NaYBr}_6$, and $\text{Cs}_2\text{NaLuBr}_6$. Energies are given in eV.

Compound	E^{fa} (eV)	E^{ex} (eV)	E_{VC} (eV)
$\text{Cs}_2\text{NaLaBr}_6$	5.71	5.95	6.43
$\text{Cs}_2\text{NaYBr}_6$	5.88	6.16	6.70
$\text{Cs}_2\text{NaLuBr}_6$	6.21	6.46	6.85

the $5d_t$ bands. In the excitation spectrum of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$, see figures 5(c)(i), a splitting of the $5d_e$ levels is observed. We refer to the high energy band at 225 nm as $5d_{e2}$ and to the low energy one at 233 nm as $5d_{e1}$. The fitted energies of the $5d$ levels of Ce^{3+} are compiled in table 4. We observed another fast excitation band at 212 nm for $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$. Although it is connected to the $5d \rightarrow 4f$ Ce^{3+} emission, this band is not attributed to the $\text{Ce}^{3+} 4f \rightarrow 5d$ excitation. This band is related to the fast transfer to Ce^{3+} but we do not know its exact mechanism.

The fast excitation spectra at 10 K monitoring the anomalous emission of $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ show a $\text{Ce}^{3+} 4f \rightarrow 5d_e$ excitation band; see figures 5(b)(iii) and c(iii). The $\text{Ce}^{3+} 4f \rightarrow 5d_{e1}$ excitation band is shifted from 233 and 235 nm

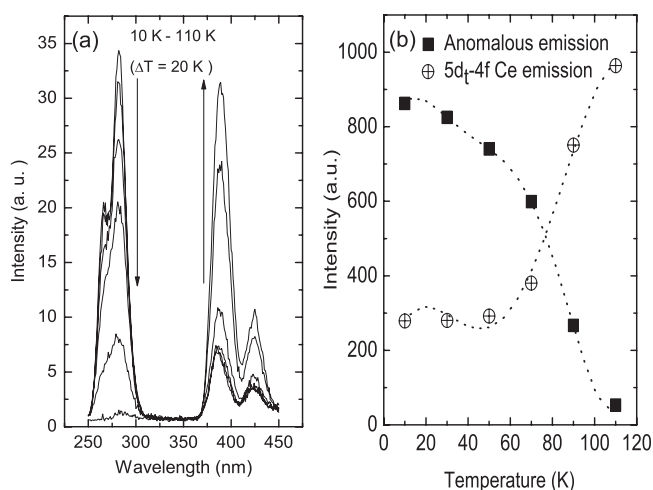


Figure 6. Temperature-dependent emission spectra of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ excited via the $4f \rightarrow 5d_{e1}$ Ce^{3+} band at 226 nm (a) and integrated intensities of the emission bands (b). Solid curves in (b) are drawn to guide the eye.

Table 4. Spectroscopic and crystallographic properties of Ce^{3+} -doped $\text{Cs}_2\text{NaREBr}_6$ (RE = La, Y, Lu) at RT. ($N:R_{\text{avg}}$) represents the anion coordination number and the average distance to the anion (pm). The polyhedron (poly) at the Ce^{3+} site is a *trigonal antiprism* (tap) or *octahedron* (octa). ϵ_c and ϵ_{cfs} are the centroid shift and the crystal field splitting, respectively. λ_{em} and ΔS_{or} are the $5d \rightarrow {}^2F_{5/2}$ emission wavelength and the Stokes shift, respectively. Values between brackets are estimated values.

Ce^{3+} -doped	($N:R_{\text{avg}}$)	(poly)	5d-excitation bands (nm)	ϵ_c (cm^{-1})	ϵ_{cfs} (cm^{-1})	λ_{em} (nm)	ΔS_{or} (eV)
$\text{Cs}_2\text{NaLaBr}_6$	(6:285)	(tap)	$2 \times (238), 333, 347, 367$	(17200)	(14770)	382	0.13
$\text{Cs}_2\text{NaYBr}_6$	(6:276)	(octa)	230, 235, 336, 352, 372	17010	16600	385	0.11
$\text{Cs}_2\text{NaLuBr}_6$	(6:273)	(octa)	225, 233, 338, 351, 373	16780	17780	389	0.14

at RT to 226 nm at 10 K for $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$, respectively. This anomalous excitation band has a cut off on the short wavelength side. If we excite at the $4f \rightarrow 5d_{e2}$ Ce^{3+} band, this does not lead to anomalous emission. The anomalous emission is also absent in the x-ray excited emission spectra; see figure 1. This means that there is no energy transfer from the host lattice to the anomalous emitting state.

Besides $4f \rightarrow 5d$ Ce^{3+} and host lattice excitation bands, we observed some other bands. Two bands at 217 and 222 nm for $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$, respectively, are tentatively assigned to a kind of near defect exciton (NDE); see figures 5(b)(ii) and c(ii). NDEs are excitons created in the near vicinity of an impurity. We also observed three fast bands at 262, 279 and 295 nm in the excitation spectrum of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$; see figure 5(a)(iii). Although they are fast and connected to Ce^{3+} emission, the origin of these bands is not clear.

3.5. Temperature dependence of anomalous emission

Figure 6 shows the emission spectra of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ excited into the $4f \rightarrow 5d_{e1}$ Ce^{3+} band (226 nm) and their integrals as a function of temperature. With increasing temperature, the anomalous emission quenches and fully disappears at 110 K. At the same time, the $5d_i \rightarrow 4f$ Ce^{3+} emission increases.

Figure 7(a) shows the decay time curves of the anomalous emission at 282 nm excited in the $4f \rightarrow 5d_{e1}$ band of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ at 226 nm as function of temperature. All spectra show a single exponential decay. The decay time of 7.83 ns is constant up to about 60 K;

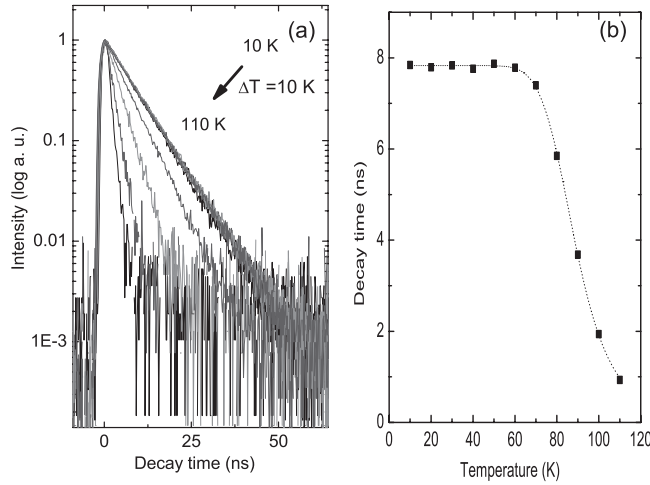


Figure 7. Semi-logarithmic plot of the decay time curves of the 282 nm anomalous emission of Cs₂NaLuBr₆:Ce³⁺ excited via the 4f → 5d_{e1} band (a) and the decay time of the anomalous emission as function of temperature (b). The dotted line through the data is from a model calculation.

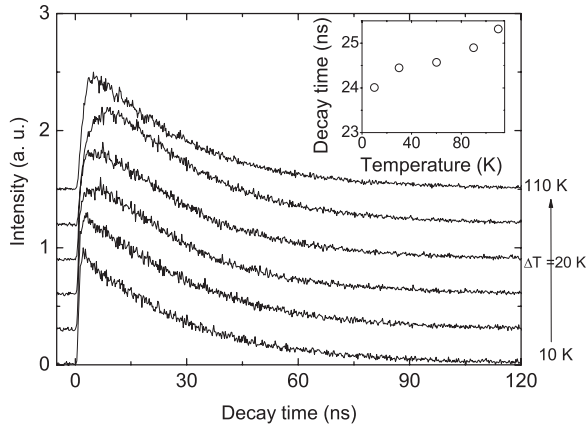


Figure 8. Temperature dependence of the decay curves of the 385 nm 5d₁ → 4f emission of Ce³⁺ in Cs₂NaLuBr₆:Ce³⁺ excited into 4f → 5d_e band at 226 nm and plotted on a linear scale. The decay time τ_d of the 380 nm 5d₁ → 4f Ce³⁺ emission excited at 333 nm is shown in the inset as function of temperature.

see figure 7(b). It drops at higher temperature. The temperature at which the decay time of the anomalous emission decreases more or less corresponds to the temperature where the anomalous emission intensity decreases and the Ce³⁺ 5d₁ → 4f emission intensity increases; see figure 6. This anticorrelation between anomalous emission and Ce³⁺ 5d₁ → 4f emission was also observed for Cs₃LuCl₆:Ce³⁺, Cs₂LiYCl₆:Ce³⁺, and Cs₂LiLuCl₆:Ce³⁺ [9–11].

The dotted line through the data in figure 7(b) is a fit by equation (1) used to describe the thermal luminescence quenching. The decay time of anomalous emission (τ_a^q) is calculated as [10]

$$\tau_a^q(T) = \frac{1}{\frac{1}{\tau_a} + \Gamma_0 \exp\left(\frac{-\Delta E_q}{kT}\right)} \quad (1)$$

where τ_a is the 7.83 ns radiative decay time of anomalous emission assumed to be temperature independent. Γ_0 is the thermal quenching rate at $T = \infty$ K (attempt rate), ΔE_q is the activation energy for thermal quenching, and k is the Boltzmann constant. A fit to equation (1) yields values of $\Gamma_0 = 3.21 \times 10^{12}$ Hz and $\Delta E_q = 0.08$ eV.

The decay curves of the Ce³⁺ 5d₁ → 4f emission at 385 nm in Cs₂NaLuBr₆:Ce³⁺ into the 4f → 5d_{e1} excited at 226 nm are shown in figure 8 on a linear scale. The decay curves in figure 8 show different features than those of the anomalous emission in figure 7.

The decay time becomes slower when the temperature increases; see figure 8. Between 50 and 110 K, the curves show a slow rise time in the first 3–10 ns leading to a delayed $5d_t \rightarrow 4f$ emission. The delay is most prominent at 90 K. For higher temperatures, the rise time becomes faster and the decay tends to return to single exponential with a decay time close to that of the $Ce^{3+} 5d_t \rightarrow 4f$ emission under direct $4f \rightarrow 5d_t$ excitation.

The inset in figure 8 shows the decay time τ_d of the Ce^{3+} emission upon $4f \rightarrow 5d_t$ excitation at 333 nm as a function of temperature. The corresponding decay time curve at 10 K was already shown as inset in figure 3. Some values are also listed in table 6. τ_d increases from 24.0 ns at 10 K to 25.3 ns at 110 K.

4. Discussion

4.1. Host properties

Table 3 compiles the host properties E^{fa} , E^{ex} and E_{VC} of $Cs_2NaREBr_6$ (RE = La, Y, Lu). The tabulated energies increase in the series La^{3+} to Y^{3+} to Lu^{3+} . We expect that the bottom of the conduction band is formed by the lanthanide orbitals. The ionic radius of La^{3+} is 13 pm larger than that of Y^{3+} and 17 pm larger than that of Lu^{3+} , leading to larger $La^{3+}-Br^-$ distances; see table 4 [18]. The negative Madelung potential at RE^{3+} site increases with smaller RE^{3+} size, resulting in the increase of the energies in table 3.

4.2. Ce^{3+} spectroscopy

The energy to excite a Ce^{3+} ion from its 4f ground state to the lowest energy 5d state in a free ion is $51\,230\text{ cm}^{-1}$. When Ce^{3+} ions are placed in a crystalline environment, this energy becomes smaller. It is determined by (i) the crystal field splitting ϵ_{cfs} of the 5d configuration and (ii) the centroid shift ϵ_c [19]. The spectroscopic and crystallographic properties of Ce^{3+} -doped $Cs_2NaREBr_6$ (RE = La, Y, Lu) are shown in table 4.

The crystal field splitting is controlled by the size and shape of the bromide ion polyhedron coordinating the Ce^{3+} ion. The size of the polyhedron is approximated by the average distance R_{av} of the cation to the N coordinating anions with a correction of $0.6\Delta R$ accounting for lattice relaxation [20]. ΔR is defined as the difference in ionic radius between Ce^{3+} and the cation it substitutes for. It amounts to 2, -11 , and -15 pm for La^{3+} , Y^{3+} , and Lu^{3+} , respectively. ϵ_{cfs} is empirically modelled by equation (2) [20]:

$$\epsilon_{cfs} = \beta_{poly} \left(\frac{1}{N} \sum_{i=1}^N (R_i - 0.6\Delta R) \right)^{-2} \quad (2)$$

where β_{poly} is a constant that depends on the type of coordination polyhedron. Figure 9 shows the crystal field splitting data of some elpasolites. The dotted curve through the data is a fit to equation (2). From this fit, we obtained $\beta_{elpasolite} = 1.33 \times 10^9\text{ pm}^2\text{ cm}^{-1}$. It corresponds well with β values of compounds with octahedral coordination ($1.35 \times 10^9\text{ pm}^2\text{ cm}^{-1}$) reported previously by Dorenbos [21].

In table 4, ϵ_{cfs} increases in the sequence La^{3+} to Y^{3+} to Lu^{3+} . A similar trend is also observed for $Cs_2NaRECl_6:Ce^{3+}$ (RE = La, Y, Lu); see figure 9. It shows that the smaller the cation site occupied by Ce^{3+} is the larger is ϵ_{cfs} . A larger ϵ_{cfs} shifts the Ce^{3+} emission towards longer wavelengths; see figures 1 and 4.

The centroid shift is the lowering of the average position (barycentre) of the 5d levels of Ce^{3+} in a host crystal. From table 4, ϵ_c decreases in the sequence La^{3+} to Y^{3+} to Lu^{3+} by about 400 cm^{-1} as a result of increasing 5d-ligand covalency. Compared to the increase of the crystal field splitting in the sequence La^{3+} to Y^{3+} to Lu^{3+} , this decrease has a smaller influence on the energy of the $Ce^{3+} 4f \rightarrow 5d$ transition.

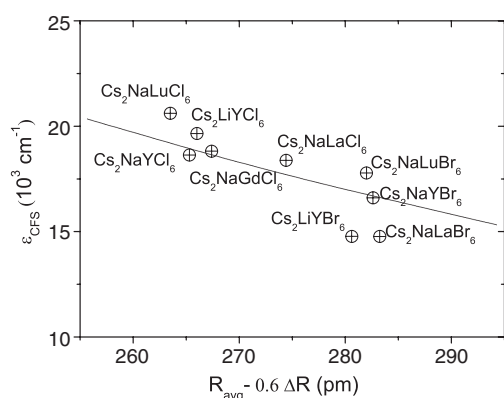


Figure 9. Crystal field splitting of Ce³⁺ as function of the average distance to neighbouring anions in the relaxed lattice. Data on the other elpasolites were added from [22].

The Stokes shift in the bromoelpasolites is smaller than that in the chloroelpasolites, see column 8 in table 4, and is ~ 0.18 eV for Cs₂LiYCl₆:Ce³⁺ and Cs₂LiLuCl₆:Ce³⁺ [4, 11]. It is caused by the shorter bond length shifts as a consequence of a smaller vibrational frequency in the bromoelpasolites than in the chloroelpasolites [23].

4.3. Scintillation mechanism

Scintillation mechanisms in elpasolites crystals have been previously discussed by Dorenbos [24]. Different energy transfer mechanisms to Ce³⁺ occur at different timescales and with different probabilities. Radiative transfer through reabsorption of STE emission by Ce³⁺, STE migration, and binary V_k centre and electron diffusion are possible mechanisms. It was suggested that an energy transfer by direct electron–hole capture does not occur in elpasolites. For direct capture, one would expect a decay component of 30 ns, similar to the decay for optical excitation of the 5d state at RT. However, the fast decay component for γ -excitation is 61 ns for all the elpasolites; see table 2. This implies that there is a delayed transfer to Ce³⁺ that does not depend on the type of RE³⁺ ions.

For Ce³⁺-doped Cs₂NaREBr₆ (RE = La, Y, Lu), the radiative energy transfer from STE to Ce³⁺ is not an important excitation mechanism because of the absence of the STE emission in the x-ray excited emission spectra; see figure 1.

Additional mechanisms might be the non-radiative energy transfers from STE to Ce³⁺, i.e. *STE diffusion*, or the *binary electron–hole recombination on Ce³⁺*. In the first case, the transfer rate from STE to Ce³⁺ increases with temperature and results in an increased Ce³⁺ luminescence on the expense of STE luminescence [25]. In the second case, after the creation of an STE, the bound electron and hole separate again and form an F–H and F–V_k pair [26]. For rising temperature, the number of loosely bound electrons (F centres) and holes (H or V_k centre) increases. At a certain temperature, they start to migrate through the lattice and a V_k centre can be trapped or stabilized near a Ce³⁺ ion. The recombination with an electron will excite Ce³⁺. It is also possible that first the electron is trapped by Ce³⁺, and subsequently the V_k diffuses and recombines with the (Ce³⁺–e[−]) centre to yield Ce³⁺ luminescence. We propose that *this binary electron–hole recombination on Ce³⁺* plays the important role in energy transfer.

4.4. Anomalous emission

Figure 10 shows a configuration coordinate diagram for anomalous emission in Cs₂NaLuBr₆:Ce³⁺. A very similar diagram was used to explain anomalous emission in

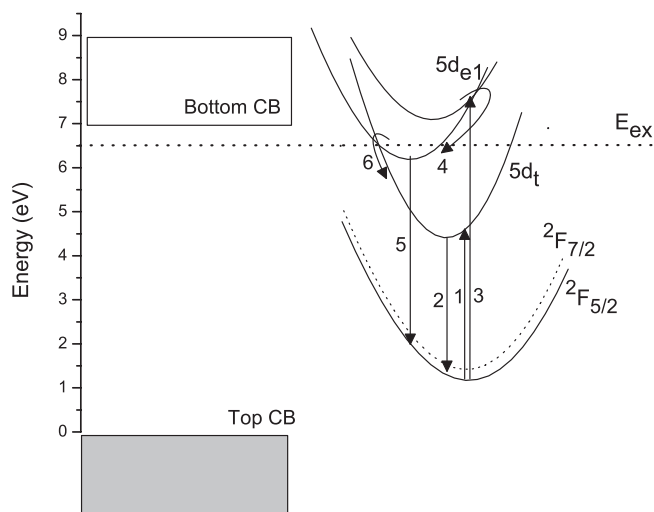


Figure 10. Energy level scheme of $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ and a configuration coordinate diagram illustrating the mechanism for the anomalous emission. The transitions indicated by the numbered arrows are explained in the text.

$\text{Cs}_3\text{LuCl}_6:\text{Ce}^{3+}$ [9] and later in $\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}$ [10] and $\text{Cs}_2\text{LiLuCl}_6:\text{Ce}^{3+}$ [11]. The anomalous emission is only observed when an electron is excited from the 4f ground state to the 5d_{e1} or small part of the 5d_{e2} levels. In the following discussion, we only consider the mechanism involving the 5d_{e1} excitation with the assumption that the mechanism for the 5d_{e2} excitation is the same.

Arrow 1 in figure 10 symbolizes the 4f → 5d_t excitation. It leads to the normal doublet 5d_t → 4f $\text{Ce}^{3+} [^2\text{F}_{5/2}, ^2\text{F}_{7/2}]$ emission symbolized by arrow 2. For this emission, a decay time of 24 ns was recorded at 10 K; see figure 3. The 4f → 5d_{e1} excitation indicated by arrow 3 can be followed by different steps. The 5d_{e1} state may decay through multi-phonon relaxation to the 5d_t states followed by normal 5d_t → 4f emission (arrow 2). This relaxation is not likely for chloroelpasolites due to a large energy gap of 2.07–2.50 eV between the 5d_{e1} and 5d_t states and the small maximum phonon frequency [9, 11]. In $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$, the energy gap of 1.65 eV between the 5d_{e1} and 5d_t states is smaller than in $\text{Cs}_2\text{LiLuCl}_6:\text{Ce}^{3+}$ and $\text{Cs}_3\text{LuCl}_6:\text{Ce}^{3+}$. However, the multi-phonon relaxation in $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ is still not favourable due to the smaller maximum phonon frequency. Instead the following return transition from 5d_{e1} to Ce^{3+} was proposed [9–11].

An electron in the 5d_{e1} state auto-ionizes to the conduction band indicated by arrow 4. This electron, somehow, remains localized in the attractive Coulomb potential of the Ce^{4+} ion left behind. The electron relaxes to the ground state of this anomalous state located below the conduction band by an amount similar to the binding energy of the electron to Ce^{4+} . We predict that this energy has the same order as the exciton binding energy (0.5 eV). The radiative recombination of the electron in the anomalous state with the hole left behind on Ce^{4+} leads to the fast 0.81 eV Stokes shifted emission at 265 nm indicated by arrow 5. The doublet splitting of the anomalous emission of 0.25 eV is consistent with the 0.25 eV splitting between $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ states of Ce^{3+} . This splitting was not previously observed for chloride compounds. In order to further analyse this splitting, the widths of the Ce^{3+} emission bands (full width at half maximum (FWHM)) in chloroelpasolites and bromoelpasolites are compiled in table 5.

Table 5. Widths of the Ce³⁺ emission bands in chloride and bromoelpasolites (FWHM). Values are derived from the emission spectra recorded at 10 K.

Compounds	Widths of the Ce ³⁺ emission bands (eV)				Reference
	Ordinary Ce ³⁺ emission		Anomalous Ce ³⁺ emission		
	² F _{5/2}	² F _{7/2}	² F _{5/2}	² F _{7/2}	
Cs ₂ LiYCl ₆ :Ce ³⁺	0.338	0.489	—	—	[10]
Cs ₂ LiLuCl ₆ :Ce ³⁺	0.339	0.480	—	—	[11]
Cs ₂ NaYBr ₆ :Ce ³⁺	0.252	0.240	0.346	0.460	This work
Cs ₂ NaLuBr ₆ :Ce ³⁺	0.273	0.261	0.361	0.485	This work

Table 6. The decay times (ns) and decay rates (10⁹ Hz) from experiment and modelling curves of Cs₂NaLuBr₆:Ce³⁺. τ_d is the decay time of the 5d_t state, τ_a^{tot} and $1/\Gamma_t$ are the decay time for anomalous emission and the transfer rate calculated with equation (1). The data in column 5 and 6 are from fits of equation (6) to the 5d_t → 4f decay curves of Ce³⁺ excited in the 5d_{e1} state. $N_a(0)/N_d(0)$ is the ratio in initial populations of the anomalous and 5d_t states.

T (K)	τ_d	τ_a^{tot}	$1/\Gamma_t$	$1/(\Gamma_a + \Gamma_t)$	$N_a(0)\Gamma_t/N_d(0)$	$N_a(0)/N_d(0)$
10	24.0	7.83	5.64×10^{35}	27.70	0.011	Maximum
30	24.5	7.83	3.81×10^9	15.13	0.014	5.32×10^7
60	24.6	7.77	1091	6.75	0.040	44.34
90	24.9	3.75	7.19	3.57	0.180	1.29
110	25.3	1.01	1.16	1.00	0.087	0.101

From table 5, we observe that the ordinary Ce³⁺ emission bands in bromoelpasolites are narrower than in chloroelpasolites. The difference is larger for the 5d → ²F_{7/2} Ce³⁺ emission. The narrower emission band is attributed to the smaller breathing mode vibrational frequencies in bromoelpasolites (~200 cm⁻¹) than in chloroelpasolites (~300 cm⁻¹) [23]. This is also related with the anomalous Ce³⁺ emission. Thus, the splitting of the anomalous emission is resolved in bromoelpasolites but not in chloroelpasolites.

In figure 6, the anomalous emission intensity decreases with increasing temperature which is accompanied by an increase of the 5d_t → 4f emission. This is explained by a temperature-activated energy transfer from the anomalous state to the 5d_t emitting state symbolized by arrow 6 in figure 10. The thermal activation energy of 0.08 eV calculated for this process, see equation (1), is attributed to the energy difference between the bottom of the anomalous state and the crossing point in the configurational coordinate diagram with the parabola of the 5d_t in figure 10.

This whole energy transfer mechanism was modelled by a set of rate equations in [9–11]. Here we will use the same model. $N_a(t)$ is the number of populated anomalous states that has a rate $\Gamma_a(T)$ for decreasing radiatively by anomalous emission and a rate $\Gamma_t(T)$ for decreasing by transfer to the 5d_t state due to thermal activation. The change in $N_a(t)$ is given by

$$\frac{dN_a(t)}{dt} = -\Gamma_a(T)N_a(t) - \Gamma_t(T)N_a(t). \quad (3)$$

$N_d(t)$ is the number of populated 5d_t states with a rate $\Gamma_d(T)$ for decreasing by radiative transitions to the 4f ground state. The time derivative of $N_d(t)$ is given by

$$\frac{dN_d(t)}{dt} = -\Gamma_d(T)N_d(t) + \Gamma_t(T)N_a(t). \quad (4)$$

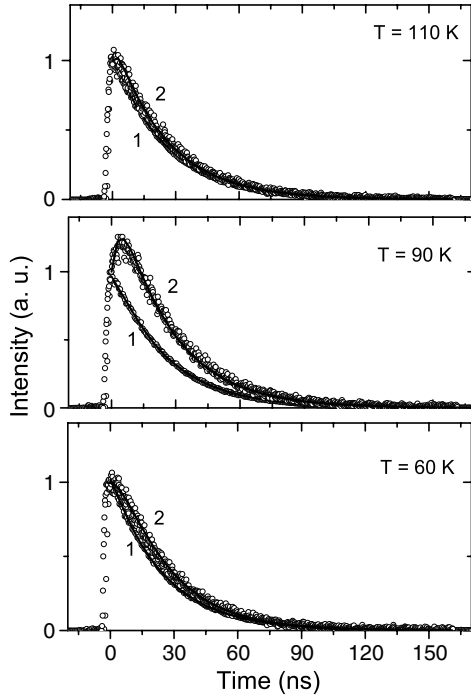


Figure 11. Decay curves of 380–385 nm $5d_t \rightarrow 4f$ emission in $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ excited directly in the $5d_t$ state (curves 1) and in the $4f \rightarrow 5d_{e1}$ state (curves 2) at 60, 90, and 110 K. The solid lines through the data represent the model curves. Parameter values are shown in table 6.

From both equations, the solutions are given by

$$N_a(t) = N_a(0)e^{-(\Gamma_a(T)+\Gamma_t(T))t} \quad (5)$$

and

$$N_d(t) = N_d(0)e^{-\Gamma_d(T)t} + \frac{\Gamma_t(T)N_a(0)}{\Gamma_a(T) + \Gamma_t(T) - \Gamma_d(T)}(e^{-\Gamma_d(T)t} - e^{-(\Gamma_a(T)+\Gamma_t(T))t}) \quad (6)$$

where $N_a(0)$ and $N_d(0)$ are the initial population at $t = 0$ of the anomalous and $5d_t$ states, respectively. $\Gamma_d(T) = 1/\tau_d$ is known from experiment, see figure 8(b), and compiled in table 6. $\Gamma_a(T) + \Gamma_t(T)$ and $\Gamma_t(T)N_a(0)$ are treated as the unknown parameters of equation (6).

Figure 11 shows the decay curves of Ce^{3+} $5d_t \rightarrow 4f$ emission excited in the $5d_{e1}$ state and in the $5d_t$ state for 60, 90, and 110 K. Curves excited in the $5d_t$ state are normalized to 1 at time $t = 0$, and are fitted with a single exponential with the decay times $\tau_d(T)$ listed in table 6. The curves excited in the $5d_{e1}$ level were modelled using equation (6) with the same $\Gamma_d(T)$ values and $N_d(0) = 1$. Values for $\tau_a^{\text{tot}} = 1/(\Gamma_a + \Gamma_t)$ and $1/\Gamma_t$ in columns 3 and 4 in table 6 were calculated with the Γ_0 and ΔE_q parameter of equation (1). The values obtained from the fit for $1/(\Gamma_a + \Gamma_t)$ and $\Gamma_t N_a(0)/N_d(0)$ are compiled in columns 5 and 6 of table 6, respectively. The model yields a good simulation for the observed decay curves.

For temperatures above 60 K, column 3 agrees satisfactorily with column 5. This is the proof that the anomalous emission is quenched by means of energy transfer to the $5d_t$ state of Ce^{3+} . There are disagreements for temperatures below 60 K. The values are larger than 7.83 ns; see column 5 in table 6. Presumably, besides excitation of the $5d_{e1}$ state, other centres are also excited at 226 nm that may transfer energy to Ce^{3+} [11]. Multiplying column 4 with column 6 in table 6 provides $N_a(0)/N_d(0)$ in column 7. The larger values at lower temperatures suggest that upon excitation of the $5d_{e1}$ state, the relaxation to the anomalous state at low temperature is more probable than to the $5d_t$ state.

Table 7. Anomalous emission properties; decay time (τ_a), average emission wavelength ($\bar{\lambda}_{an}$), Stokes shift (ΔS_{an}), ratio between the decay time and the average emission wavelength of the anomalous and ordinary Ce³⁺ emissions ($\frac{\tau_a}{(\bar{\lambda}_{an})^3} / \frac{\tau_{or}}{(\lambda_{or})^3}$), thermal activation energy (ΔE_q), quenching temperature at which the anomalous Ce³⁺ emission intensity has dropped to 50% of the low temperature value ($T_{0.5}$) and attempt rate (Γ_0) in all studied elpasolites. Values for $\bar{\lambda}_{an}$ and ΔS_{an} are derived from the excitation and emission spectra recorded at 10 K.

Ce ³⁺ -doped	τ_a (ns)	$\bar{\lambda}_{an}$ (nm)	ΔS_{an} (eV)	$\frac{\tau_a}{(\bar{\lambda}_{an})^3} / \frac{\tau_{or}}{(\lambda_{or})^3}$	ΔE_q (eV)	$T_{0.5}$ (K)	Γ_0 (Hz)	Reference
Cs ₃ LuCl ₆	10.50	281	1.40	0.98	—	80	—	[9]
Cs ₂ LiYCl ₆	9.80	270	1.07	0.99	0.14	180	5.80×10^{11}	[10]
Cs ₂ LiLuCl ₆	9.40	267	0.99	0.98	0.36	300	9.02×10^{13}	[11]
Cs ₂ NaYBr ₆	7.74	273	0.81	0.89	—	—	—	This work
Cs ₂ NaLuBr ₆	7.83	273	0.81	0.91	0.08	80	3.21×10^{12}	This work

We compare the quenching parameters for Cs₂NaYBr₆:Ce³⁺ and Cs₂NaLuBr₆:Ce³⁺ with those of the previously studied chloride compounds in table 7. The decay time of the anomalous emission (τ_a) in the bromoelpasolites (~ 7.80 ns) is faster than that in chloride compounds (~ 9.90 ns); see column 2 in table 7. The average anomalous emission wavelength ($\bar{\lambda}_{an}$) ranges from 267 to 281 nm. For the following discussion, the relation between the decay time τ and the emission wavelength λ of an electric dipole allowed transition is given by [27, 28]

$$\frac{1}{\tau} \propto \frac{n}{\lambda^3} \left(\frac{n^2 + 2}{3} \right)^2 \sum_f |\langle f | \mu | i \rangle|^2 \quad (7)$$

where n is the refractive index. The summation over the matrix element connecting an initial state $|i\rangle$ with a final state $|f\rangle$ via the dipole operator μ gives the oscillator strength [28].

The ratio of τ/λ^3 between the anomalous Ce³⁺ emission and the ordinary Ce³⁺ emission is close to unity; see column 5 in table 7. This means that the anomalous Ce³⁺ emission is an electric dipole allowed transition. The slightly lower values than unity can be related with the difference between the oscillator strength of the anomalous and that of the ordinary Ce³⁺ emissions. From equation (7), the faster decay time of anomalous emission in bromoelpasolites than in chloride compounds can be related to the larger refractive index in bromide than in chloride compounds.

The Stokes shift (ΔS_{an}) relates to the energy difference between the 5d_{e1} and the anomalous states. The Stokes shift decreases towards the larger anion. This means that the 5d_{e1} which is inside in the conduction band gets closer to the bottom of the conduction band. All Stokes shifts are larger than those of the ordinary Ce³⁺ emission; see column 8 in table 4.

We cannot find a relationship between the Stokes shift and the thermal activation energy (ΔE_q). ΔE_q of Cs₂NaLuBr₆:Ce³⁺ is the smallest among the investigated elpasolites. This causes a lower quenching temperature ($T_{0.5}$) in Cs₂NaLuBr₆:Ce³⁺ (80 K) than those of Cs₂LiYCl₆:Ce³⁺ (180 K) and Cs₂LiLuCl₆:Ce³⁺ (300 K). The attempt rates (Γ_0) for all elpasolites are in the order of 10¹²–10¹⁴ Hz.

5. Conclusion

Cs₂NaREBr₆:Ce³⁺ (RE = La, Y, Lu) are new bromoelpasolites scintillators. Cs₂NaLaBr₆:Ce³⁺ emits under x-ray and γ -ray excitation the highest light yield among these compounds (17 000 photons MeV⁻¹), whereas Cs₂NaLuBr₆:Ce³⁺ has the lowest light yield (5800 photons MeV⁻¹). Scintillation decay curves of bromoelpasolites show a fast 61 ns compo-

ment with the presence of slow components. We propose that the scintillation mechanism in $\text{Cs}_2\text{NaREBr}_6:\text{Ce}^{3+}$ (RE = La, Y, Lu) is a binary electron–hole recombination.

$\text{Cs}_2\text{NaYBr}_6:\text{Ce}^{3+}$ and $\text{Cs}_2\text{NaLuBr}_6:\text{Ce}^{3+}$ show anomalous emission under $4f \rightarrow 5d_{e1}\text{Ce}^{3+}$ excitation. This is the first report on anomalous emission in bromoelpasolites and also the first time that two bands of the anomalous emission are observed. These bands are attributed to the transitions from the anomalous state to the ${}^2\text{F}_{5/2}$ and ${}^2\text{F}_{7/2}$ states of Ce^{3+} .

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