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## Thermal quenching of $Ce^{3+}$ emission in $PrX_3$ (X = Cl, Br) by intervalence charge transfer

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#### Abstract

The cause of the relatively low scintillation light yield of PrBr<sub>3</sub>:Ce<sup>3+</sup> is investigated by means of optical spectroscopy, the temperature dependence of scintillation properties and the temperature dependence of optically excited decay curves of undoped and Ce<sup>3+</sup>-doped PrCl<sub>3</sub> and PrBr<sub>3</sub>. The integrated intensity of x-ray excited luminescence of PrBr<sub>3</sub>:5% Ce<sup>3+</sup> shows that the light yield at room temperature (RT) is two times less than at 80 K. The decay time of Ce<sup>3+</sup> emission optically excited to its 5d band in PrBr<sub>3</sub>:5% Ce<sup>3+</sup> has a single exponential decay of 11.0±1.1 and 6.0±0.6 ns at 10 K and RT, respectively. It is proposed that Ce<sup>3+</sup> emission is quenched by a metal-to-metal charge transfer of Ce<sup>3+</sup> + Pr<sup>3+</sup>  $\rightarrow$  Ce<sup>4+</sup> + Pr<sup>2+</sup> followed by 4f  $\rightarrow$  4f emission of Pr<sup>3+</sup> which is strongly concentration quenched.

#### 1. Introduction

There is a continued interest in the search for new scintillators for the detection of radiation. Much effort has already been devoted to the  $Ce^{3+}$ -doped lanthanide trihalide family. Among all investigated compounds,  $LaCl_3:Ce^{3+}$ ,  $LaBr_3:Ce^{3+}$  and  $LuI_3:Ce^{3+}$  show outstanding scintillation properties including high light yield, good energy resolution and fast decay time [1–3].

Besides Ce<sup>3+</sup>, there are also efforts to introduce the Pr<sup>3+</sup> ion as an optically active dopant [4]. Theoretically, the 5d  $\rightarrow$  4f emission in Pr<sup>3+</sup> should be a factor of two to three faster than in Ce<sup>3+</sup> due to the higher energy of the 5d  $\rightarrow$  4f emission of Pr<sup>3+</sup> compared to Ce<sup>3+</sup> [5]. Unfortunately, developing LaBr<sub>3</sub>:Pr<sup>3+</sup> as a new fast scintillator has not been successful. It does not show the anticipated 5d  $\rightarrow$  4f emission; instead, slow 4f  $\rightarrow$  4f emission is observed. The

charge transfer (CT) from the valence band to  $Pr^{3+}$  occurs at an energy below the energy of the  $5d \rightarrow 4f$  emission, and this quenches  $Pr^{3+}$  emission [6].

Recently, Nikl *et al* investigated the scintillation characteristics of  $PrF_3:Ce^{3+}$  [7]. This was the first scintillation study on a  $Ce^{3+}$ -doped praseodymium host. In  $PrF_3:Ce^{3+}$ , the energy transfer from the  $Pr^{3+}$  host to the  $Ce^{3+}$  via the  ${}^{1}S_0$  level of  $Pr^{3+}$  is efficient and  $Ce^{3+}$  doping can be accomplished at an arbitrary level because  $PrF_3$  and  $CeF_3$  are isostructural [7]. We decided to study the scintillation properties of  $Ce^{3+}$ -doped  $PrCl_3$  and  $PrBr_3$  [8]. Undoped  $PrCl_3$  and  $PrBr_3$  were previously studied for surface laser applications [9]. Studies of radiative and nonradiative transitions of  $Pr^{3+}$  in undoped  $PrCl_3$  and  $PrBr_3$  can be found in the works of German *et al* [10, 11].

We previously reported a scintillation light yield of  $PrBr_3:Ce^{3+}$  up to 21000 photons MeV<sup>-1</sup> [8]. This is three and a half times less than that of LaBr\_3:Ce<sup>3+</sup>. The cause of the relatively low scintillation light yield in  $PrBr_3:Ce^{3+}$  is interesting to investigate. In this work, optical spectroscopy, x-ray excited luminescence spectra and pulse height spectra as a function of temperature are presented in order to study the thermal quenching behaviour. A thermal quenching model is then proposed. Scintillation and optical properties of Ce<sup>3+</sup>-doped PrCl<sub>3</sub> are also presented.

#### 2. Experimental procedures

#### 2.1. Crystal growth and structure

Crystals of undoped and 5% Ce<sup>3+</sup>-doped PrCl<sub>3</sub> and PrBr<sub>3</sub> of  $5 \times 3 \times 2$  mm<sup>3</sup> were grown using the Bridgman technique. Starting materials of PrX<sub>3</sub> and CeX<sub>3</sub> (X = Cl, Br) were prepared from Pr<sub>6</sub>O<sub>11</sub> (Ultrafunction enterprise, 5N5), CeO<sub>2</sub> (Ultrafunction enterprise, 6N), NH<sub>4</sub>X (X = Cl, Br) (Merck, 99.9%), and HX (X = Cl, Br) (47% Merck, suprapur) by the ammonium halide method [12]. For the crystal growth, stoichiometric amounts of starting materials were sealed in silica ampoules under vacuum.

PrCl<sub>3</sub> and PrBr<sub>3</sub> show the UCl<sub>3</sub>-type structure with space group  $P6_3/m$  (no. 176) [13]. The structure can also be described as a hexagonal close packed arrangement of chains of edge-connected polyhedra (PrX<sub>9</sub>). The polyhedron can be viewed as a tricapped trigonal prism with the Pr<sup>3+</sup> ion in the centre. The nine Cl<sup>-</sup> or Br<sup>-</sup> ions are at an average distance of 292 or 307 pm from the central Pr<sup>3+</sup> ion, respectively. The calculated densities of PrCl<sub>3</sub> and PrBr<sub>3</sub> are 4.02 and 5.33 g cm<sup>-3</sup>, respectively, which is slightly larger than those of LaCl<sub>3</sub> (3.86 g cm<sup>-3</sup>) and LaBr<sub>3</sub> (5.07 g cm<sup>-3</sup>) [1, 2].

#### 2.2. Experimental techniques

X-ray excited luminescence spectra were excited with an x-ray tube with a Cu anode operating at 35 kV and 25 mA. The emission of the sample was dispersed by means of an Acton Research Corporation (ARC) VM-504 monochromator (blazed at 300 nm, 1200 grooves nm<sup>-1</sup>) and detected by a Hamamatsu R934-04 Photomultiplier Tube (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 emission measurements were performed between 80 and 600 K, using a JANIS VPF-700 Cryostat operated with a Model 331 LakeShore Temperature Controller.

The light yield at RT was determined from the 662 keV total absorption peak in the pulse height spectrum of a <sup>137</sup>Cs source detected with the scintillation crystal mounted directly on a Hamamatsu R1791 PMT recorded with 0.5 and 10  $\mu$ s shaping times. The yield, expressed



**Figure 1.** X-ray excited emission spectra of  $PrCl_{3}$ :5%  $Ce^{3+}$  and  $PrBr_{3}$ :5%  $Ce^{3+}$  at RT. The inset shows the x-ray excited emission spectrum of  $PrBr_{3}$ :5%  $Ce^{3+}$  between 500 and 750 nm on a 20 times enlarged scale. The increase in the intensity above 700 nm is due to second-order transmission.

in photoelectrons per MeV of absorbed  $\gamma$ -ray energy (phe MeV<sup>-1</sup>), was determined by comparison of the total  $\gamma$ -ray energy absorption peak with the single photoelectron peak. The light yield expressed in photons per MeV (photons MeV<sup>-1</sup>) is determined using the quantum efficiency and reflectivity of the PMT [14].

Scintillation decay curves under <sup>137</sup>Cs 662 keV  $\gamma$ -ray excitation were recorded at RT by the conventional delayed coincidence method described by Bollinger and Thomas [15]. For this method, scintillation decay time curves were recorded at timescales up to 200  $\mu$ s using Philips XP2020Q PMTs, Ortec 934 Constant Fraction Discriminators, an Ortec 567 Time to Analog Converter (TAC) and an AD413A CAMAC Analog to Digital Converter (ADC).

Time-resolved excitation and emission spectra at 10 and 300 K were recorded using synchrotron radiation at the SUPERLUMI station of the Synchrotron Strahlungslabor (HASYLAB) at the Deutches Electronen Synchrotron (DESY) in Hamburg (Germany). Details of this setup have been described elsewhere [16, 17].

Decay curves with selected excitation and emission wavelengths were recorded using a Model 5000 IBH coaxial flash lamp. The lamp was filled with hydrogen gas and operated at 7.0 keV and a frequency of 40 kHz. The excitation wavelength was dispersed using an ARC VM502 monochromator. The emission of the sample was selected using either the band or cutoff filters and detected by a Hamamatsu R934-04 PMT. Decay curves were obtained after deconvolution with the function of the system response. Temperature-dependent decay curves were recorded with the same cryostat and temperature controller as those of temperature-dependent  $\gamma$ -excited pulse height spectra is described in [18].

#### 3. Results

#### 3.1. Scintillation properties

X-ray excited emission spectra of  $PrCl_3:5\%$  Ce<sup>3+</sup> and  $PrBr_3:5\%$  Ce<sup>3+</sup> at RT are shown in figure 1. For both compounds, characteristic Ce<sup>3+</sup> 5d  $\rightarrow$  4f emission is observed. The maxima

**Table 1.** Scintillation light yields of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> and PrBr<sub>3</sub>:5% Ce<sup>3+</sup> under 662 keV  $\gamma$ -ray excitation. Those of LaCl<sub>3</sub>:4% Ce<sup>3+</sup> and LaBr<sub>3</sub>:5% Ce<sup>3+</sup> are added for comparison. Light yields were measured with 0.5 and 10  $\mu$ s shaping times.

	Light yield (ph <sup>137</sup> Csγ-1		
Compounds	0.5 μs	10 µs	Reference
PrCl <sub>3</sub> :5% Ce <sup>3+</sup> LaCl <sub>3</sub> :4% Ce <sup>3+</sup>	$18500 \pm 1900$ $37000 \pm 3700$	$20500 \pm 2100$ $49000 \pm 4900$	This work
PrBr <sub>3</sub> :5% Ce <sup>3+</sup> LaBr <sub>3</sub> :5% Ce <sup>3+</sup>	$\begin{array}{c} 14500\pm1500\\ 67000\pm6700\end{array}$	$\begin{array}{c} 16000\pm1600\\ 67000\pm6700\end{array}$	[8] [2]

are located at 340 and 365 nm for the chloride and at 366 and 395 nm for the bromide for the 5d  $\rightarrow {}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  transitions, respectively. Additionally, a broadband or a tail on the long-wavelength side of the Ce<sup>3+</sup> doublet is present in the x-ray excited emission spectrum of PrCl<sub>3</sub>:5% Ce<sup>3+</sup>. Similar bands were observed for LaCl<sub>3</sub>:Ce<sup>3+</sup> and K<sub>2</sub>LaX<sub>5</sub>:Ce<sup>3+</sup> (X = Cl, Br, I) [19, 20]. We attribute this band to self-trapped exciton (STE) emission. This emission is not observed in the x-ray excited emission spectrum of PrBr<sub>3</sub>:5% Ce<sup>3+</sup>. The STE emission was also not observed for LaBr<sub>3</sub>:5% Ce<sup>3+</sup> [20]. Pr<sup>3+</sup> 4f<sup>2</sup>  $\rightarrow$  4f<sup>2</sup> emission lines are present in the spectrum of PrBr<sub>3</sub>:5% Ce<sup>3+</sup>; see the inset in figure 1. These lines are not seen in the x-ray excited emission spectrum of PrCl<sub>3</sub>:5% Ce<sup>3+</sup>.

Table 1 shows scintillation light yields derived from the pulse height spectra of  $PrCl_3:5\%$  Ce<sup>3+</sup> and  $PrBr_3:5\%$  Ce<sup>3+</sup> at RT. The light yields of  $PrCl_3:5\%$  Ce<sup>3+</sup> and  $PrBr_3:5\%$  Ce<sup>3+</sup> are 42% and 24% of that of LaCl<sub>3</sub>:4% Ce<sup>3+</sup> and LaBr<sub>3</sub>:5% Ce<sup>3+</sup>, respectively [19, 2]; see column 3 in table 1.

Scintillation decay time curves of (a)  $PrCl_3:5\%$   $Ce^{3+}$ , (b)  $LaCl_3:4\%$   $Ce^{3+}$ , (c)  $PrBr_3:5\%$   $Ce^{3+}$  and (d)  $LaBr_3:5\%$   $Ce^{3+}$  at RT are shown in figure 2. The  $PrCl_3:5\%$   $Ce^{3+}$ decay curve was fitted with two exponential decay components of  $17 \pm 2$  and  $230 \pm 20$  ns with the contributions to the total light yield of 80 and 20%, respectively. The three decay components of  $LaCl_3:4\%$   $Ce^{3+}$  are  $25 \pm 3$ ,  $210 \pm 20$ , and  $1100 \pm 100$  ns with contributions to the total light yield of 18%, 25%, and 57%, respectively [19]. The fit of the  $PrBr_3:5\%$   $Ce^{3+}$ decay curve was already presented in Birowosuto *et al* [8]. For  $PrBr_3:5\%$   $Ce^{3+}$ , three decay processes were proposed. They are direct processes with a decay time constant of 6 ns and two delayed processes with transfer time constants of 1 and 9 ns [8]. The decay time constant of the direct process of 6 ns in [8] is faster than that of 16 ns for  $LaBr_3:5\%$   $Ce^{3+}$  reported by Bizarri *et al* [18].

#### 3.2. Luminescence characteristics

The excitation spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup>, 5% Ce<sup>3+</sup>-doped and undoped LaCl<sub>3</sub>, 5% Ce<sup>3+</sup>-doped and undoped PrBr<sub>3</sub>, LaBr<sub>3</sub>:5%Ce<sup>3+</sup> and LaBr<sub>3</sub>:0.5% Pr<sup>3+</sup> recorded at 10 K are shown in figure 3. The excitation spectrum of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> monitoring Ce<sup>3+</sup> emission at 336 nm shows several bands between 210 and 300 nm in spectrum (a) in figure 3. The bands between 230 and 290 nm in spectrum (a) in figure 3 are assigned to the interconfigurational Ce<sup>3+</sup> [Xe] 4f<sup>1</sup>  $\rightarrow$  [Xe] 5d<sup>1</sup> excitations. Compared with the excitation spectrum of LaCl<sub>3</sub>:5% Ce<sup>3+</sup> monitoring Ce<sup>3+</sup> emission at 350 nm in spectrum (c) in figure 3, the highest-energy 5d band of Ce<sup>3+</sup> in PrCl<sub>3</sub>:5% Ce<sup>3+</sup> is shifted 5 nm to longer wavelength. The 5d bands of Ce<sup>3+</sup> in LaCl<sub>3</sub>:5% Ce<sup>3+</sup> were previously identified by Guillot-Noël *et al* [1].



**Figure 2.** Scintillation decay curves of (a)  $PrCl_3:5\%$  Ce<sup>3+</sup>, (b) LaCl<sub>3</sub>:4% Ce<sup>3+</sup>, (c)  $PrBr_3:5\%$  Ce<sup>3+</sup> and (d) LaBr<sub>3</sub>:5% Ce<sup>3+</sup> at RT. The solid lines through the data and the dotted lines are the exponential fits and the corresponding background levels from each curve.

One band at 216 nm in spectrum (a) in figure 3 also appears in the excitation spectrum when monitoring the  ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$  transition line of  $Pr^{3+}$  at 490 nm; see the spectrum (b) in figure 3. This band is attributed to the lowest  $4f \rightarrow 5d$  excitation of  $Pr^{3+}$  [21]. Empirically, the energy of the lowest  $4f \rightarrow 5d$  transition of  $Pr^{3+}$  can be estimated from the lowest  $4f \rightarrow 5d$  transition of  $Ce^{3+}$  using [22].

$$E[\Pr^{3+}, 4f \to 5d_{\text{lowest}}] = E[\operatorname{Ce}^{3+}, 4f \to 5d_{\text{lowest}}] + 1.52 \pm 0.09 \text{ eV}.$$
(1)

From spectrum (a) in figure 3, the  $4f \rightarrow 5d_{lowest}$  transition of  $Ce^{3+}$  is located at 290 nm (4.28 eV). Then, the  $4f \rightarrow 5d_{lowest}$  transition of  $Pr^{3+}$  is expected at  $214 \pm 3$  nm (5.80  $\pm$  0.09 eV). This value agrees with the maximum at 216 nm in the excitation spectrum monitoring 490 nm emission; see spectrum (b) in figure 3. Additionally, a tail band between 160 and 206 nm is observed in the excitation spectrum monitoring 336 nm emission; see spectrum (a) in figure 3. This band can be attributed to host lattice excitation from the valence to conduction bands. In undoped LaCl<sub>3</sub>, the maximum of this host lattice excitation band was observed at 190 nm (6.53 eV); see spectrum (d) in figure 3.

The excitation spectrum of undoped PrBr<sub>3</sub> monitoring the  ${}^{3}P_{0} \rightarrow {}^{3}H_{4}$  line emission of Pr<sup>3+</sup> at 490 nm shows the host lattice excitation from valence to conduction bands; see spectrum (e) in figure 3. The fundamental absorption ( $E_{fa}$ ) at 217 nm (5.71 eV) is defined as the energy of the first sharp onset in the excitation spectra monitoring intrinsic emission. The first maximum ( $E_{ex}$ ) at 205 nm (6.05 eV) is tentatively attributed to the creation of excitons which can be regarded as bound electron-hole pairs. The edge of the conduction band ( $E_{VC}$ )



**Figure 3.** Excitation spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> monitoring (a) 336 and (b) 490 nm emission, (c) LaCl<sub>3</sub>:5% Ce<sup>3+</sup> monitoring 350 nm emission, (d) undoped LaCl<sub>3</sub> monitoring 400 nm emission, (e) undoped PrBr<sub>3</sub> monitoring 490 nm emission, (f) PrBr<sub>3</sub>:5% Ce<sup>3+</sup> monitoring 380 nm emission, (g) LaBr<sub>3</sub>:5% Ce<sup>3+</sup> monitoring 365 nm emission, and (h) LaBr<sub>3</sub>:0.5% Pr<sup>3+</sup> monitoring 535 nm emission. All spectra were recorded at 10 K.

estimated at 191 nm (6.50 eV) corresponds to the creation of free electrons in the conduction band and free holes in the valence band. This estimation is based on our assumption that the binding energy of the electron and hole pair in an exciton is about 8% of the exciton creation energy [23].

 $E_{\rm fa}$ ,  $E_{\rm ex}$ , and  $E_{\rm VC}$  in undoped LaBr<sub>3</sub> were previously reported by Dorenbos *et al* [6]. These energies can also be derived from spectrum (g) in figure 3. When we compare with spectrum (e) in figure 3,  $E_{\rm fa}$ ,  $E_{\rm ex}$ , and  $E_{\rm VC}$  in undoped PrBr<sub>3</sub> are  $0.59 \pm 0.06$  eV shifted to higher energy than those in undoped LaBr<sub>3</sub>.

The excitation spectrum of PrBr<sub>3</sub>:5% Ce<sup>3+</sup> monitoring Ce<sup>3+</sup> emission at 380 nm shows several bands between 220 and 330 nm; see spectrum (f) in figure 3. Some bands at wavelengths above 260 nm are assigned to interconfigurational Ce<sup>3+</sup> [Xe] 4f<sup>1</sup>  $\rightarrow$  [Xe] 5d<sup>1</sup> transitions. They are at  $\approx$ 277 (tentative), 288, 299, 312, and 328 nm. The 5d bands of Ce<sup>3+</sup> in PrBr<sub>3</sub>:Ce<sup>3+</sup> are shifted to longer wavelengths compared to those in LaBr<sub>3</sub>:Ce<sup>3+</sup>; see spectrum (g) in figure 3. We obtain energies for the total 5d Ce<sup>3+</sup> crystal field splitting and the 5d Ce<sup>3+</sup> centroid shift in PrBr<sub>3</sub>:Ce<sup>3+</sup> of 0.70 and 2.22 eV, respectively. The total 5d Ce<sup>3+</sup> crystal field splitting and the 5d Ce<sup>3+</sup> centroid shift are the energy difference between the highest and the lowest 5d Ce<sup>3+</sup> levels and the lowering of the average position of the 5d Ce<sup>3+</sup> levels in the crystal relative to the position in the free ion, respectively [24]. Both are due to the



**Figure 4.** Emission spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> excited at (a) 216 and (b) 280 nm recorded at 10 K, PrBr<sub>3</sub>:5% Ce<sup>3+</sup> excited at 285 nm recorded at (c) RT and (d) 10 K, (e) LaCl<sub>3</sub>:4% Ce<sup>3+</sup> excited at 245 nm recorded at 10 K, and (f) LaBr<sub>3</sub>:5% Ce<sup>3+</sup> excited at 295 nm recorded at 10 K. The spectra (a)–(d) between 450 and 800 nm are enlarged by a factor of five.

interaction with the crystalline environment. The energy for the total 5d  $Ce^{3+}$  crystal field splitting for  $PrBr_3:Ce^{3+}$  is almost identical with the 0.74 eV observed for  $LaBr_3:Ce^{3+}$ , whereas the energy for the 5d  $Ce^{3+}$  centroid shift for  $PrBr_3:Ce^{3+}$  is larger compared to the 1.97 eV for  $LaBr_3:Ce^{3+}$  [6].

A band at 240 nm (5.17 eV) in spectrum (f) in figure 3 is also observed in LaBr<sub>3</sub>:Pr<sup>3+</sup> when monitoring the  ${}^{3}P_{1} \rightarrow {}^{3}H_{5}$  line emission of Pr<sup>3+</sup> at 535 nm; see spectrum (h) in figure 3. This band is attributed to a valence band (VB)  $\rightarrow$  Pr<sup>3+</sup> CT transition [6]. The lowest 4f  $\rightarrow$  5d transition of Pr<sup>3+</sup> in PrBr<sub>3</sub>:Ce<sup>3+</sup> can be estimated from the lowest 4f  $\rightarrow$  5d transition of Ce<sup>3+</sup> using equation (1). It is expected at 234 ± 4 nm (5.30 ± 0.09 eV). The emission spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> and PrBr<sub>3</sub>:5% Ce<sup>3+</sup> recorded at 10 K and RT

The emission spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> and PrBr<sub>3</sub>:5% Ce<sup>3+</sup> recorded at 10 K and RT are shown in figure 4. All spectra show two overlapping bands peaking at 340 and 365 nm and 366 and 395 nm for PrCl<sub>3</sub>:5% Ce<sup>3+</sup> and PrBr<sub>3</sub>:5% Ce<sup>3+</sup>, respectively. These bands are attributed to transitions from the lowest 5d level to  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$  levels of Ce<sup>3+</sup>, which were also observed in the x-ray excited emission spectra of figure 1. This emission of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> and PrBr<sub>3</sub>:5% Ce<sup>3+</sup>, respectively; see spectra (e) and (f) in figure 4. Pr<sup>3+</sup> 4f  $\rightarrow$  4f emission lines are also present and originate from the  ${}^{3}P_{0}$  state. These emission lines were previously observed by German and co-workers [11]. They attributed the absence of the emission from the  ${}^{3}P_{1}$  state to the energy exchange with neighbouring Pr<sup>3+</sup> ions [11].



**Figure 5.** Decay curves of (a)  $PrCl_3:5\%$  Ce<sup>3+</sup> excited via the 5d band of Ce<sup>3+</sup> at 280 nm monitoring 336 nm emission, and  $PrBr_3:5\%$  Ce<sup>3+</sup> excited via (b) the 5d band of Ce<sup>3+</sup> at 300 nm and (c) the CT band of  $Pr^{3+}$  at 240 nm monitoring 366 nm emission. Decay curves with filled circles (•) were recorded at 10 K, whereas those with empty circles (•) were recorded at RT. Solid lines through the data are single exponential fits.

The emission spectra of PrCl<sub>3</sub>:5% Ce<sup>3+</sup> recorded at 10 K show that the Pr<sup>3+</sup> 4f  $\rightarrow$  4f lines appear only when we excite the 4f  $\rightarrow$  5d transition of Pr<sup>3+</sup> at 216 nm; see spectrum (a) in figure 4. This excitation is transferred to Ce<sup>3+</sup> since we also observe the Ce<sup>3+</sup> doublet emission. The emission spectrum of PrBr<sub>3</sub>:5% Ce<sup>3+</sup> excited via the 5d band of Ce<sup>3+</sup> at 285 nm recorded at RT shows the Pr<sup>3+</sup>4f  $\rightarrow$  4f lines, whereas that recorded at 10 K does not show the Pr<sup>3+</sup> 4f  $\rightarrow$  4f lines; see spectra (c) and (d) in figure 4. This means that there is a transfer from Ce<sup>3+</sup> to the <sup>3</sup>P<sub>0</sub> state of Pr<sup>3+</sup> at RT but not at 10 K.

Figure 5 shows decay curves of  $Ce^{3+}$  emission with different excitation of  $PrCl_3:5\% Ce^{3+}$ and  $PrBr_3:5\% Ce^{3+}$  recorded at 10 K and RT. All decay curves were fitted with a single exponential decay. Decay curves of the 5d<sub>1</sub> excited state of  $Ce^{3+}$  in  $PrCl_3:5\% Ce^{3+}$  both recorded at 10 K and RT show a decay time of  $12.0 \pm 2.0$  ns; see curves (a) in figure 5. This decay time is faster than the 16 ns decay time of the 5d $\rightarrow$  4f emission of  $Ce^{3+}$  in LaCl<sub>3</sub>:Ce<sup>3+</sup> [25]. Decay curves of  $PrBr_3:5\% Ce^{3+}$  show identical decay times when excited via the Ce<sup>3+</sup> 5d band and the CT band of  $Pr^{3+}$ ; see curves (b) and (c) in figure 5. Unlike the decay curves of  $PrCl_3:5\% Ce^{3+}$ , the decay curves of  $PrBr_3:5\% Ce^{3+}$  are temperature dependent. The decay times are  $11.0 \pm 1.1$  and  $6.0 \pm 0.6$  ns at 10 K and RT, respectively. This indicates the presence of thermal quenching of  $Ce^{3+}$  emission. The decay time at 10 K is still faster than the 15 ns decay time of the 5d excited state of  $Ce^{3+}$  in LaBr<sub>3</sub>:Ce<sup>3+</sup> [18].



**Figure 6.** Temperature dependence of (a) x-ray excited emission spectra, (b) decay curves of the 360 nm emission excited via the 5d band of  $Ce^{3+}$  at 280 nm, and (c) pulse height spectra under 662 keV  $\gamma$ -ray excitation from <sup>137</sup>Cs source recorded with 10  $\mu$ s shaping time of PrBr<sub>3</sub>:5% Ce<sup>3+</sup>.

#### 3.3. Temperature dependence

Figure 6(a) exhibits the x-ray excited emission spectra recorded between 300 and 500 nm, whereas figures 6(b) and (c) show the decay curves optically excited at the 5d state of  $Ce^{3+}$  and the  $\gamma$ -excited pulse height spectra recorded with 10  $\mu$ s shaping time as a function of temperature of PrBr<sub>3</sub>:5% Ce<sup>3+</sup>, respectively. The Ce<sup>3+</sup> x-ray excited emission intensity decreases from 80 to 400 K. This is accompanied by a shortening of the decay time of the Ce<sup>3+</sup> emission and a shift of the 662 keV photopeaks in the pulse height spectra towards lower channels. The corresponding photopeak position for each temperature is shown by the arrows; see figure 6(c). In order to analyse this Ce<sup>3+</sup> luminescence quenching, the integral of the x-ray excited emission spectra recorded between 300 and 500 nm, the decay time of Ce<sup>3+</sup> emission, and the light yields derived from the pulse height spectra as a function of temperature are shown in figure 7. All data exhibit the same type of thermal quenching behaviour.

The dotted curves through the data in figure 7 are model calculations. The integral of the x-ray excited emission spectra and the light yield of the luminescence are given by

$$I(T) = \frac{I_0}{1 + \Gamma_0 / \Gamma_v \exp(-\Delta E_q / kT)}$$
(2)

9



**Figure 7.** Temperature dependence of (a) the integral of the x-ray excited emission spectra recorded between 300 and 500 nm, (b) the decay time of  $Ce^{3+}$  emission and (c) scintillation yields of  $PrBr_3:5\%$   $Ce^{3+}$ . All data were derived from figure 6. The dotted lines through the data are model curves.

and the decay time is given by

1

$$\tau(T) = \frac{1/\Gamma_v}{1 + \Gamma_0/\Gamma_v \exp(-\Delta E_q/kT)}$$
(3)

where I(T) and  $\tau(T)$  are the integral of the light yield and the decay time at temperature T, respectively.  $I_0$  is the integral of the light yield at T = 0 K.  $\Gamma_0$  and  $\Gamma_v$ , respectively, are the thermal quenching rate at  $T = \infty$  (attempt rate) and the radiative  $Ce^{3+}$  5d  $\rightarrow$  4f transition rate.  $\Delta E_q$  is the activation energy for thermal quenching and k is the Boltzmann constant. From a fit to equations (2) and (3), fitting parameters are presented in figure 7. The thermal activation energy ( $\Delta E_q$ ) is around 0.15 eV for all temperature-dependence measurements. The radiative lifetime of  $Ce^{3+}$  5d  $\rightarrow$  4f transition ( $1/\Gamma_v$ ) of 11.0  $\pm$  0.3 ns and the light yield at T = 0 K ( $I_0$ ) of 28 100  $\pm$  300 photons MeV<sup>-1</sup> were obtained. Similar values of the attempt rate ( $\Gamma_0$ ) are derived from the values of  $\Gamma_0/\Gamma_v$  found in equations (2) and (3). These attempt rates are in the order of  $10^{10}$  Hz.

#### 4. Discussion

The lifetime of the  $Ce^{3+}$  5d state in compounds can be determined by different processes. First we have the spontaneous radiative lifetime of the 5d state determined by the oscillator strength. In addition, thermally excited interconfigurational system crossing from 5d to 4f or thermally excited 5d to conduction band ionization processes may occur. Lifetime shortening by means of energy transfer to neighbouring acceptor sites may also take place.

**Table 2.** Summary of the radiative decay parameter for  $Ce^{3+}$  in REX<sub>3</sub> (RE = La, Pr and X = Cl, Br). Values in brackets are the estimated values.

Host	τ <sub>r</sub> (ns)	λ (nm)	$ \langle 5d r 4f\rangle _{eff}$ (nm)	n	Reference
LaCl <sub>3</sub>	16	332	0.031	1.80	[31]
LaBr <sub>3</sub>	15	356	0.031	1.95	[31]
PrCl <sub>3</sub>	12	340	(0.022-0.034)	(2.38-1.89)	This work
PrBr <sub>3</sub>	11	366	(0.022–0.034)	(2.57-2.06)	This work

We have observed that the Ce<sup>3+</sup> decay times excited via the 5d state at 10 K of PrCl<sub>3</sub>:Ce<sup>3+</sup> and PrBr<sub>3</sub>:Ce<sup>3+</sup> are 11 and 12 ns, respectively. They are 4 ns faster than those of LaCl<sub>3</sub>:Ce<sup>3+</sup> and LaBr<sub>3</sub>:Ce<sup>3+</sup>, which are 15 and 16 ns, respectively. In part 1, we will discuss the possible causes of this reduced lifetime. In part 2, we will discuss the thermal quenching of Ce<sup>3+</sup> emission and, based on energy-level schemes derived in part 3, we will propose a new mechanism of 5d  $\rightarrow$  4f emission quenching for Ce<sup>3+</sup> in Pr-based compounds in part 4.

### 4.1. Radiative lifetimes of $Ce^{3+}$ in $PrCl_3:Ce^{3+}$ and $PrBr_3:Ce^{3+}$

In this part of the discussion, we will attend to explaining the faster radiative lifetimes of the  $Ce^{3+} 5d \rightarrow 4f$  transition in  $PrX_3:Ce^{3+} (X = Cl, Br)$  compared to those of  $LaX_3:Ce^{3+} (X = Cl, Br)$  by means of the spontaneous radiative emission rate.

The spontaneous radiative emission rate  $\Gamma_r$  of the electric dipole transition from a localized initial state  $\langle i |$  to a localized final state  $|f\rangle$  can be written as [26]

$$\Gamma_{\rm r} = \frac{64\pi^4}{3h} \chi v_{\rm if}^3 |\langle \mathbf{i}| - e\vec{r} \, |\mathbf{f}\rangle|^2 \tag{4}$$

where *h* is the Planck constant,  $v_{if}$  is the emission wavenumber,  $-e\vec{r}$  is the electric dipole moment between state (i) and |f), and  $\chi$  is an enhancement factor due to the dielectric medium. However, two models predict substantially different dependences of  $\chi$  on the refractive index *n*. They are the virtual- and real-cavity models [27]. Recently, Duan *et al* investigated the radiative lifetimes of Ce<sup>3+</sup> in different hosts and found that the observed dependence of the Ce<sup>3+</sup> decay rates in different compounds on the refractive index *n* favours the virtual-cavity models [28]. According to this model,  $\chi$  equals to  $n[(n^2 + 2)/3]^2$ .

In the same paper, Duan *et al* also simplified equation (4) with approximations for the  $5d \rightarrow 4f$  emission of Ce<sup>3+</sup> ions and the total spontaneous emission rate of the  $5d \rightarrow 4f$  Ce<sup>3+</sup> emission is given by [28]:

$$\Gamma_{\rm r} = \frac{1}{\tau_{\rm r}} = \frac{64\pi^4 e^2}{5h} \left(\frac{n(n^2+2)}{3}\right)^2 |\langle 5d|r|4f \rangle|_{\rm eff}^2 \overline{v}^3$$
(5)

where  $\tau_r$  is the radiative lifetime,  $\overline{v}$  is the average wavenumber, *n* is the refractive index, and  $|\langle 5d|r|4f \rangle|_{\text{eff}}$  is the effective electric dipole radial integral between 4f and 5d orbitals. For the Ce<sup>3+</sup> free ion,  $|\langle 5d|r|4f \rangle|_{\text{eff}}$  is 0.025 nm [29].

The lifetimes  $\tau_r$ , peak wavelengths of emission spectra  $\lambda$ , and refractive indices *n* of Ce<sup>3+</sup> in REX<sub>3</sub> (RE = La, Pr and X = Cl, Br) are summarized in table 2. Unfortunately, there is no information on the refractive index for PrCl<sub>3</sub> and PrBr<sub>3</sub>. With the known values of *n* for LaCl<sub>3</sub> and LaBr<sub>3</sub>, we obtain  $|\langle 5d|r|4f \rangle|_{\text{eff}} = 0.031$  nm; see column 4 in table 2. This value is larger than the free ion value of 0.025 nm, contrary to the expectation in [30] that it should be smaller than the free ion value. Duan *et al* obtained  $|\langle 5d|r|4f \rangle|_{\text{eff}}$  varying between 0.022 and 0.034 nm with an average of 0.028 nm from the data of various hosts and concluded that the values of  $Ce^{3+}$  effective radial integral  $|\langle 5d|r|4f\rangle|_{eff}$  are larger in crystals than in vacuum [28].

From the data of  $|\langle 5d|r|4f \rangle|_{eff}$  of various hosts, we assume that the values of  $|\langle 5d|r|4f \rangle|_{eff}$  for PrCl<sub>3</sub> and PrBr<sub>3</sub> should fall between 0.022 and 0.034. With these values, we calculate the ranges of the refractive indices for PrCl<sub>3</sub> and PrBr<sub>3</sub> as shown in column 5 of table 2. Table 2 shows that the decay times excited via the Ce<sup>3+</sup> 5d state at 10 K of PrCl<sub>3</sub>:Ce<sup>3+</sup> and PrBr<sub>3</sub>:Ce<sup>3+</sup> are not inconsistent with the spontaneous radiative emission rates derived from equation (4). However, there is also a possibility that the Ce<sup>3+</sup> emission is already quenched even at very low temperature.

#### 4.2. Quenching mechanisms of $Ce^{3+}$ emission

The 5d  $\rightarrow$  4f radiative emission process is often highly efficient. Multiphonon relaxation between the 5d and 4f states is usually unimportant because of the large energy separation between the 5d and 4f states. Nevertheless, the Ce<sup>3+</sup> emission is found to be completely quenched in a number of hosts, such as Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and La<sub>2</sub>O<sub>2</sub>S [32]. Our results show that Ce<sup>3+</sup> emission is thermally quenched in PrBr<sub>3</sub>:Ce<sup>3+</sup> with an activation energy of 0.15 eV; see figure 7. Several explanations have been put forward to explain the Ce<sup>3+</sup> quenching luminescence. These include the thermally excited interconfigurational system crossing from 5d to 4f of Ce<sup>3+</sup>, Förster–Dexter energy transfer from Ce<sup>3+</sup> to nearby centres, electron transfer and photoionization [32].

In the first case, the parabola offset can be estimated from the Stokes shift of the Ce<sup>3+</sup> emission. As far as we are aware, this Stokes shift is never large enough to explain Ce<sup>3+</sup> luminescence quenching of the Ce<sup>3+</sup> ion [32]. In the second case, the Ce<sup>3+</sup> ion loses its excitation energy by nonradiative energy transfer to nearby centres [33]. A high transfer rate requires an overlap between the emission spectrum of Ce<sup>3+</sup> with the absorption spectrum of the other centre. This type of transfer is well known in Ce<sup>3+</sup>-doped Gd<sup>3+</sup>-based compounds [34]. In the third case, the electron in the 5d state of Ce<sup>3+</sup> is promoted to one of its nearest or nextnearest neighbors. In the last case, the 5d electron of the excited Ce<sup>3+</sup> ion is promoted into the conduction band because of the proximity of the lowest 5d excited state of Ce<sup>3+</sup> to the lowest 5d Ce<sup>3+</sup> state and the host conduction band. This thermal quenching was previously observed in some Ce<sup>3+</sup>-doped oxides [35]. Recently, the absence of Ce<sup>3+</sup> luminescence at RT in LaI<sub>3</sub>:Ce<sup>3+</sup> was also attributed to this thermal quenching [36].

For PrBr<sub>3</sub>:Ce<sup>3+</sup>, the thermally excited interconfigurational system crossing from 5d to 4f of Ce<sup>3+</sup> is not possible. The Stokes shift of the Ce<sup>3+</sup> emission in PrBr<sub>3</sub>:Ce<sup>3+</sup> of 0.61 eV is similar to the 0.54 eV of LaBr<sub>3</sub>:Ce<sup>3+</sup>; see figures 3 and 4. Additionally, LaBr<sub>3</sub>:Ce<sup>3+</sup> does not show the Ce<sup>3+</sup> luminescence quenching. The Förster–Dexter energy transfer from Ce<sup>3+</sup> to nearby centres is also not possible in PrBr<sub>3</sub>:Ce<sup>3+</sup>. There is no overlap between the 5d  $\rightarrow$  4f Ce<sup>3+</sup> emission and the <sup>3</sup>H<sub>4</sub>  $\rightarrow$  <sup>3</sup>P<sub>2</sub> excitation at 448 nm (2.77 eV). This leaves the electron transfer to neighbouring ions or the photoionization as possible quenching mechanisms.

In this work, we first estimate the position of the  $Ce^{3+}$  emitting level relative to the conduction and valence bands in PrBr<sub>3</sub>: $Ce^{3+}$ . Next, based on these level positions, we propose a model for the thermal quenching of  $Ce^{3+}$  luminescence in PrBr<sub>3</sub>: $Ce^{3+}$ .

#### 4.3. Energy-level schemes in $LaBr_3:Ce^{3+}$ and $PrBr_3:Ce^{3+}$

The energy-level scheme of  $PrBr_3:Ce^{3+}$  is shown in figure 8. The scheme has been constructed with the information on the host lattice excitations,  $4f \rightarrow 5d$  excitations, and  $Pr^{3+}$  CT excitation



**Figure 8.** Energy-level schemes of (a)  $LaBr_3:Ce^{3+}/Pr^{3+}$  and (b)  $PrBr_3:Ce^{3+}$ .

energy. The scheme for LaBr<sub>3</sub>:Ce<sup>3+</sup> taken from Dorenbos *et al* is also presented [6]. The top of the bromide valence band is defined as the zero of energy. The bottom of the conduction bands  $(E_{\rm VC})$  of LaBr<sub>3</sub> and PrBr<sub>3</sub> is located at 5.90 ± 0.15 and 6.50 ± 0.15 eV, respectively. Arrows (a) and (b) indicate the energy differences  $(E_{\rm fd})$  between the lowest 4f and lowest 5d states of Ce<sup>3+</sup> in LaBr<sub>3</sub> and PrBr<sub>3</sub>, respectively.

Arrows (c) and (d) indicate the observed energy for CT from bromide to  $Pr^{3+}$  in LaBr<sub>3</sub> and PrBr<sub>3</sub> of 5.00 and 5.17 eV, respectively. The  $Pr^{3+}$  CT energies in LaBr<sub>3</sub> and PrBr<sub>3</sub> were obtained from [6] and the excitation spectrum (f) in figure 3, respectively. After CT,  $Pr^{3+}$  is converted to  $Pr^{2+}$  and the transferred electron is located in the 4f<sup>3</sup> ground state of  $Pr^{2+}$ .

In LaBr<sub>3</sub>, the 4f ground state of Ce<sup>3+</sup> is located at  $0.90 \pm 0.40$  eV above the top of the valence band [6]. This value, together with  $E_{\rm fd}$ , locates the lowest 5d state of Ce<sup>3+</sup> at 4.93  $\pm$  0.40 eV above the valence band, which is close to the location of the 4f<sup>3</sup> ground state of Pr<sup>2+</sup> in LaBr<sub>3</sub>. The lowest 5d state of Ce<sup>3+</sup> in LaBr<sub>3</sub> is at ~1 eV below the bottom of the conduction band. This large energy difference is consistent with the absence of Ce<sup>3+</sup> emission quenching in LaBr<sub>3</sub> even at a temperature of 600 K [18]. We expect that the location of the 4f ground state of Pr<sup>3+</sup> in PrBr<sub>3</sub> is not too much different from that in LaBr<sub>3</sub>, since both lattices share the same structure with similar lattice parameters. We also expect that the 4f ground state of Pr<sup>3+</sup> in PrBr<sub>3</sub> should not be too much different than that in LaBr<sub>3</sub>:Pr<sup>3+</sup>. The 4f ground state of Pr<sup>3+</sup> in LaBr<sub>3</sub>:Pr<sup>3+</sup> is located at 0.61  $\pm$  0.40 eV below the top of valence band [6]. We then arrive at a scheme shown in figure 8(b), which is very similar to that of LaBr<sub>3</sub>.

From this energy-level scheme, the distance between the  $Ce^{3+}$  lowest 5d excited state to the host conduction band is much larger than the 0.15  $\pm$  0.01 eV thermal activation energy found in figure 7. Therefore the thermal quenching of luminescence in PrBr<sub>3</sub>:Ce<sup>3+</sup> cannot be explained by ionization of the 5d electron to the conduction band.

#### 4.4. A model for the thermal luminescence quenching

We propose a new model for the thermal luminescence quenching in  $PrBr_3:Ce^{3+}$  that is based on electron transfer from  $Ce^{3+}$  to  $Pr^{3+}$ . Such transfer in solids is usually referred to as metalto-metal CT or intervalence CT [37]. The model is shown schematically in figure 9.

On excitation of the Ce<sup>3+</sup> 5d states at low temperature of 10 K, we have ordinary Ce<sup>3+</sup> 5d  $\rightarrow$  4f emission. When the temperature increases, thermal energy ( $\Delta E$ ) of



**Figure 9.** Schematic representation of the proposed model relating the thermal luminescence quenching in  $PrBr_3:Ce^{3+}$ . CB and VB are the conduction band and the valence band, respectively. The schemes are ordered alphabetically.

 $0.15 \pm 0.01$  eV is provided to the electron in the Ce<sup>3+</sup> excited 5d configuration. Since the Ce<sup>3+</sup> 5d state is close in energy to the empty 4f<sup>3</sup> state of Pr<sup>2+</sup>, the 5d electron can transfer to the empty 4f<sup>3</sup> state of Pr<sup>2+</sup>; see part (a) in figure 9. This is a metal-to-metal CT of the form:

$$(Ce^{3+})_{5d} + Pr^{3+} \to Ce^{4+} + Pr^{2+}.$$
 (6)

After CT,  $Ce^{4+}$  and  $Pr^{2+}$  are created and substantial lattice relaxation occurs; see arrow 1 in part (b) of figure 9. A large lattice relaxation in  $Pr^{2+}$  is shown by the inset in part (b) of figure 9. The electron in the relaxed  $4f^3$  state of  $Pr^{2+}$  cannot return to the  $Ce^{3+}$  5d state and jumps back to the ground state of  $Ce^{3+}$ . This process is indicated by arrow 2.

The energy of the recombination of the electron in the  $4f^3$  state of  $Pr^{2+}$  and the hole in the ground state of  $Ce^{4+}$  leaves  $Pr^{3+}$  in an excited state; see part (c) in figure 9. The excited  $Pr^{3+}$  relaxes, resulting in  $4f^2 \rightarrow 4f^2$  emission. This corresponds to the presence of the  $Pr^{3+} 4f^2 \rightarrow 4f^2$  transition lines at RT in the emission spectrum of  $PrBr_3:Ce^{3+}$  excited at the  $Ce^{3+} 4f \rightarrow 5d$  excitation band; see spectrum (c) in figure 4:

$$Pr^{2+} + Ce^{4+} \to (Ce^{3+})_{gs} + Pr^{3+*}$$
(7)

$$\Pr^{3+*} \to \Pr^{3+} + h\nu. \tag{8}$$

From the same emission spectrum, we observe that the intensity of the  $Pr^{3+} 4f^2 \rightarrow 4f^2$ emission lines is weak. This can be explained by part (d) in figure 9. This figure shows an energy transfer from one  $Pr^{3+}$  ion to its neighbouring  $Pr^{3+}$  ion. The excitation can migrate through the lattice until it meets a killer site and is then lost for luminescence. This phenomenon is often called concentration quenching. This quenching is indicated by the decrease of the decay time of  $Pr^{3+} 4f^2 \rightarrow 4f^2$  emission when the  $Pr^{3+}$  concentration increases, as reported previously by German and Kiel in LaCl<sub>3</sub>: $Pr^{3+}$  and LaBr<sub>3</sub>: $Pr^{3+}$  [11].

We did not observe a shortening of the decay time of the 5d state of  $Ce^{3+}$  in  $PrCl_3$  when the temperature increases from 10 K to RT; see curves (a) in figure 5. Apparently, the energy difference between the lowest 5d state of  $Ce^{3+}$  and the  $4f^3$  ground state of  $Pr^{2+}$  in  $PrCl_3$  is larger than in  $PrBr_3$ . The scintillation light yield of  $PrCl_3:Ce^{3+}$  in table 1 is 42% of that of  $LaCl_3:Ce^{3+}$ . The low light yield cannot be attributed to thermal quenching of  $Ce^{3+}$  emission, since that was not observed. Additionally, the light yield at T = 0 K for  $PrBr_3:Ce^{3+}$  of 28 100  $\pm$  300 photons  $MeV^{-1}$  is also 42% of the light yield for  $LaBr_3:Ce^{3+}$ ; see figure 7 and table 1. Both low light yields in  $PrCl_3:Ce^{3+}$  at RT and  $PrBr_3:Ce^{3+}$  at T = 0 K can be due to the less efficient energy transfer towards  $Ce^{3+}$  centre via energy migration over the 5d<sub>1</sub> state of  $Pr^{3+}$ , as reported previously in  $PrF_3:Ce^{3+}$  [7].

#### 5. Conclusion

We have investigated the scintillation properties and the luminescence characteristics of  $PrCl_3:Ce^{3+}$  and  $PrBr_3:Ce^{3+}$ . The scintillation light yield and the optically luminescence decay time of  $PrBr_3:5\%$  Ce<sup>3+</sup> are thermally quenched with an activation energy of  $0.15 \pm 0.01$  eV. A model of thermal luminescence quenching based on electron transfer from Ce<sup>3+</sup> to Pr<sup>3+</sup> has been proposed. We conclude that the thermal activation energy is related to the energy difference between the 4f<sup>3</sup> state of Pr<sup>3+</sup> and the lowest 5d state of Ce<sup>3+</sup>. However, the Ce<sup>3+</sup> emission quenching was not observed in PrCl<sub>3</sub>:Ce<sup>3+</sup>. This is due to the larger energy difference between the lowest 5d state of Ce<sup>3+</sup> and the 4f<sup>3</sup> ground state of Pr<sup>2+</sup> in PrCl<sub>3</sub> compared to that in PrBr<sub>3</sub>.

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