

# Ce<sup>3+</sup> activated LaBr<sub>3-x</sub>I<sub>x</sub>: High-light-yield and fast-response mixed halide scintillators

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Here, we report the scintillation properties of LaBr<sub>3-x</sub>I<sub>x</sub>:5%Ce<sup>3+</sup> with four different compositions of  $x$ , i.e.,  $x=0.75, 1.5, 2,$  and  $2.25$ . Radioluminescence spectra reveal a shift of the emission wavelength with the LaBr<sub>3</sub> to LaI<sub>3</sub> ratio. LaBr<sub>1.5</sub>I<sub>1.5</sub>:5%Ce<sup>3+</sup> shows the highest scintillation light yield of 58 000 photons/MeV, whereas LaBr<sub>0.75</sub>I<sub>2.25</sub>:5%Ce<sup>3+</sup> shows the fastest scintillation decay time of 12 ns under 662 keV  $\gamma$ -ray excitation. This decay time is faster than that of 16 ns in LaBr<sub>3</sub>:Ce<sup>3+</sup>. The temperature dependence of radioluminescence spectra is presented. The structures and lattice parameters of the materials were determined from powder x-ray diffraction. © 2008 American Institute of Physics. [DOI: 10.1063/1.2930884]

## I. INTRODUCTION

The search for new scintillators remains important in the past decade because of demands in the fields of medical diagnostics, nondestructive testing, homeland security, and many fields of physics and chemistry. One of the searching grounds for new scintillators is halide compounds.<sup>1</sup> Eu<sup>2+</sup> and Ce<sup>3+</sup> activated barium halide scintillators were recently discovered for x-ray and  $\gamma$ -ray detections.<sup>2,3</sup> Light yields of these materials are lower than 20 000 photons/MeV and decay times are slower than 80 ns. Among all investigated halides, Ce<sup>3+</sup> activated lanthanide trihalides are known as a scintillator family that often show high light yield and good energy resolution. One of its members, LuI<sub>3</sub>:Ce<sup>3+</sup>, is a scintillator with the highest scintillation light yield of 98 000 photons/MeV.<sup>4</sup>

In an attempt to search for better halide scintillators, we decided to investigate the scintillation and luminescence properties of mixed crystals of LaBr<sub>3-x</sub>I<sub>x</sub>:Ce<sup>3+</sup>. LaBr<sub>3</sub>:Ce<sup>3+</sup> is a scintillator with a fast decay time of 16 ns and a high light yield of 70 000 photons/MeV.<sup>5</sup> LaI<sub>3</sub>:Ce<sup>3+</sup> does not emit photons at room temperature (RT), which is attributed to the autoionization of the 5*d* electron of Ce<sup>3+</sup> to the conduction band. This autoionization of the 5*d* electron to the conduction band is related to the smaller band gap of 3.3 eV of LaI<sub>3</sub> than that of 5.9 eV of LaBr<sub>3</sub>.<sup>6,7</sup> The lowest 5*d* state of Ce<sup>3+</sup> in LaI<sub>3</sub> is only situated at 0.1–0.2 eV from the bottom of the conduction band.<sup>6</sup> With the mixed crystals, we anticipate that the band gap falls between the band gap of LaBr<sub>3</sub> and that of LaI<sub>3</sub>. This could possibly increase the light yield of the mixed crystal, as compared to that of LaBr<sub>3</sub>:Ce<sup>3+</sup>.

An early investigation on the scintillation properties of Ce<sup>3+</sup> activated LaBr<sub>3-x</sub>I<sub>x</sub> with polycrystalline structure was previously reported by Glodo *et al.*<sup>8</sup> The 1% Ce<sup>3+</sup> activated

sample shows a light yield of 24 100 photons/MeV with an energy resolution of 7%. In this publication, we report the scintillation properties of 5% Ce<sup>3+</sup> activated samples with improved crystal quality. The high light yield of 58 000 photons/MeV and the decay time of 12 ns are reported for these samples. This yield is competitive with 70 000 photons/MeV of LaBr<sub>3</sub>:Ce<sup>3+</sup> and this decay time is faster than 16 ns of LaBr<sub>3</sub>:Ce<sup>3+</sup>. Their crystal structures and lattice parameters were determined from powder x-ray diffraction (XRD).

## II. EXPERIMENTAL METHODS

### A. Crystal growth

Crystals of Ce<sup>3+</sup> activated LaBr<sub>3-x</sub>I<sub>x</sub> were grown by the Bridgmann method. The appropriate mixtures of LaBr<sub>3</sub>, LaI<sub>3</sub>, and CeBr<sub>3</sub> were sealed under vacuum in silica ampoules. Single crystals of four different compositions, i.e., LaBr<sub>2.25</sub>I<sub>0.75</sub>:5%Ce<sup>3+</sup>, LaBr<sub>1.5</sub>I<sub>1.5</sub>:5%Ce<sup>3+</sup>, LaBrI<sub>2</sub>:5%Ce<sup>3+</sup>, and LaBr<sub>0.75</sub>I<sub>2.25</sub>:5%Ce<sup>3+</sup>, were obtained (see Fig. 1).

The color of the crystals changes with increasing LaI<sub>3</sub> concentration from colorless to yellow. LaBr<sub>2.25</sub>I<sub>0.75</sub>:5%Ce<sup>3+</sup> is colorless as LaBr<sub>3</sub>:Ce<sup>3+</sup>. The hygroscopicity of the crystals increases with their LaI<sub>3</sub> contents too.

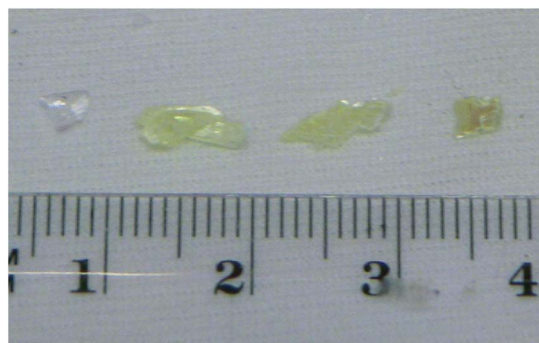


FIG. 1. (Color online) LaBr<sub>3-x</sub>I<sub>x</sub>:Ce<sup>3+</sup> crystals with different Br/I ratios. They are LaBr<sub>2.25</sub>I<sub>0.75</sub>:5%Ce<sup>3+</sup>, LaBr<sub>1.5</sub>I<sub>1.5</sub>:5%Ce<sup>3+</sup>, LaBrI<sub>2</sub>:5%Ce<sup>3+</sup>, and LaBr<sub>0.75</sub>I<sub>2.25</sub>:5%Ce<sup>3+</sup> from left to right, respectively.

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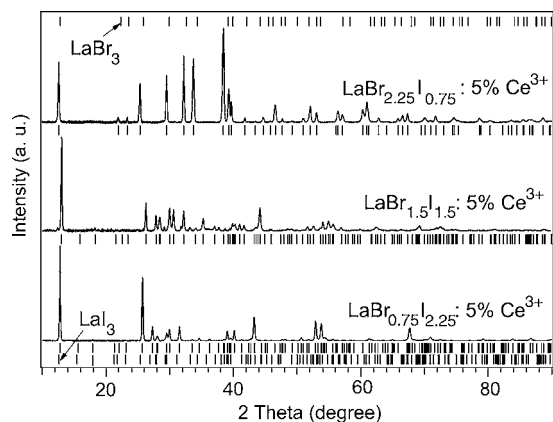


FIG. 2. XRD patterns of powder samples of  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ ,  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ , and  $\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$  at RT. Calculated XRD line positions are shown as vertical lines ( ) below the respective traces. Those of  $\text{LaBr}_3$  (top) and  $\text{LaI}_3$  (bottom) were obtained from Krämer *et al.* (Ref. 9) and Asprey *et al.* (Ref. 10), respectively.

The crystal growth of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  is difficult since  $\text{LaBr}_3$  and  $\text{LaI}_3$  differ in crystal structure.  $\text{LaBr}_3$  has a  $\text{UCl}_3$ -type structure, space group  $P6_3/m$  with a ninefold tri-capped trigonal prismatic coordination of  $\text{Br}^-$  around  $\text{La}^{3+}$ , whereas  $\text{LaI}_3$  has a  $\text{PuBr}_3$ -type structure, space group  $Cmcm$  with an eightfold bicapped trigonal prismatic coordination of  $\text{I}^-$  around  $\text{La}^{3+}$ .<sup>9,10</sup> The ionic radius of  $\text{Br}^-$ , 1.82 Å, is smaller than that of  $\text{I}^-$ , 2.06 Å.

## B. XRD

XRD pattern of powder samples were measured on a Stoe STADI P diffractometer at RT. A Bragg–Brentano reflection geometry was used with  $\alpha\text{-SiO}_2$  (101) monochromated  $\text{Cu } K\alpha_1$  radiation ( $\lambda=1.540598$  Å). The diffraction diagrams were recorded with a linear position-sensitive detector in a  $2\theta$  range of  $10^\circ$ – $100^\circ$  or  $150^\circ$  with a resolution of  $0.01^\circ$ . Since the materials are hygroscopic, the powders were measured in a gas tight cell with a Mylar window.

## C. Radioluminescence measurements

Radioluminescence spectra were recorded using an x-ray tube with Cu (XR) 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 groves/mm) and detected by a Hamamatsu R934-04 photomultiplier tube (PMT). The spec-

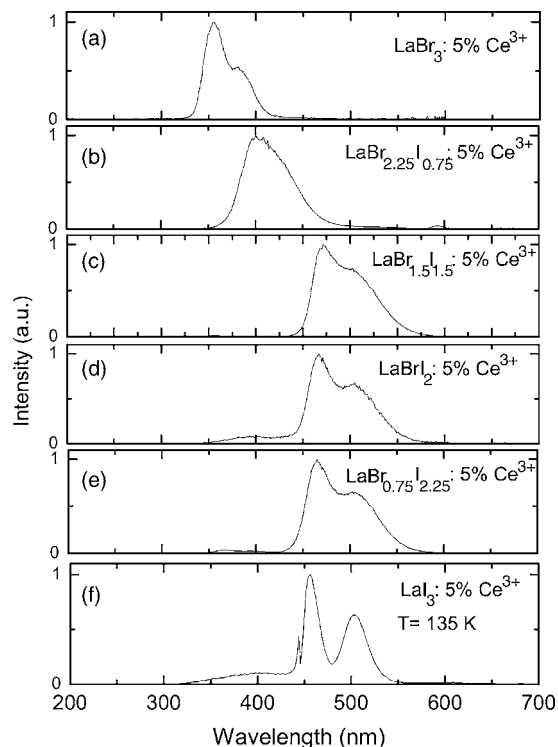


FIG. 3. Radioluminescence spectra of  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ ,  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ ,  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ , and  $\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$  at RT. Emission spectra of  $\text{LaBr}_3:5\%\text{Ce}^{3+}$  and  $\text{LaI}_3:5\%\text{Ce}^{3+}$  recorded at RT and 135 K, respectively, are added for comparison.

tra were corrected for the wavelength dependence of the photodetector efficiency as well as the monochromator transmission.

## D. Pulse height measurements

Pulse height spectra were recorded with a Hamamatsu R1791 PMT (cathode voltage= $-600$  V) with a box-type dynode structure connected to a preamplifier and an Ortec 672 spectroscopic amplifier. The crystals were mounted to the PMT window without an optical coupling and covered with several layers of Teflon tape for collection of scintillation light. The measurements were performed inside an M-Braun UNILAB dry box with a moisture content less than 1 ppm. The yield  $Y_{pe}$ , expressed in photoelectrons/MeV of absorbed  $\gamma$ -ray energy, was obtained by comparison of the peak position of the 662 keV photopeak relative to the position of the single-photoelectron peak. The absolute photon yield  $Y_{ph}$  in photons per MeV is derived from  $Y_{pe}$  as follows:<sup>11</sup>

TABLE I. Lattice parameters, calculated densities  $\rho_{cal}$ , and effective atomic numbers  $Z_{eff}$  of  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ ,  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ ,  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ , and  $\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$  at RT. The values for  $\text{LaBr}_3$  and  $\text{LaI}_3$  were obtained from Krämer *et al.* (Ref. 9) and Asprey *et al.* (Ref. 10), respectively.

$\text{LaBr}_{3-x}\text{I}_x$	Space group	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\rho_{cal}$ (g/cm <sup>3</sup> )	$Z_{eff}$
$\text{LaBr}_3$	$P6_3/m$	7.9648(5)	$=a$	4.5119(5)	5.07	46.90
$\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$	$P6_3/m$	8.111(1)	$=a$	4.5392(4)	5.47	48.79
$\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$	$Cmcm$	4.3297(5)	13.561(1)	9.698(1)	5.51	51.45
$\text{LaBrI}_2:5\%\text{Ce}^{3+}$	$Cmcm$	4.3105(7)	13.487(3)	9.647(2)	5.59	52.50
$\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$	$Cmcm$	4.3724(8)	13.8323(9)	9.904(1)	5.60	52.96
$\text{LaI}_3$	$Cmcm$	4.37(2)	14.01(2)	10.04(1)	5.61	54.20

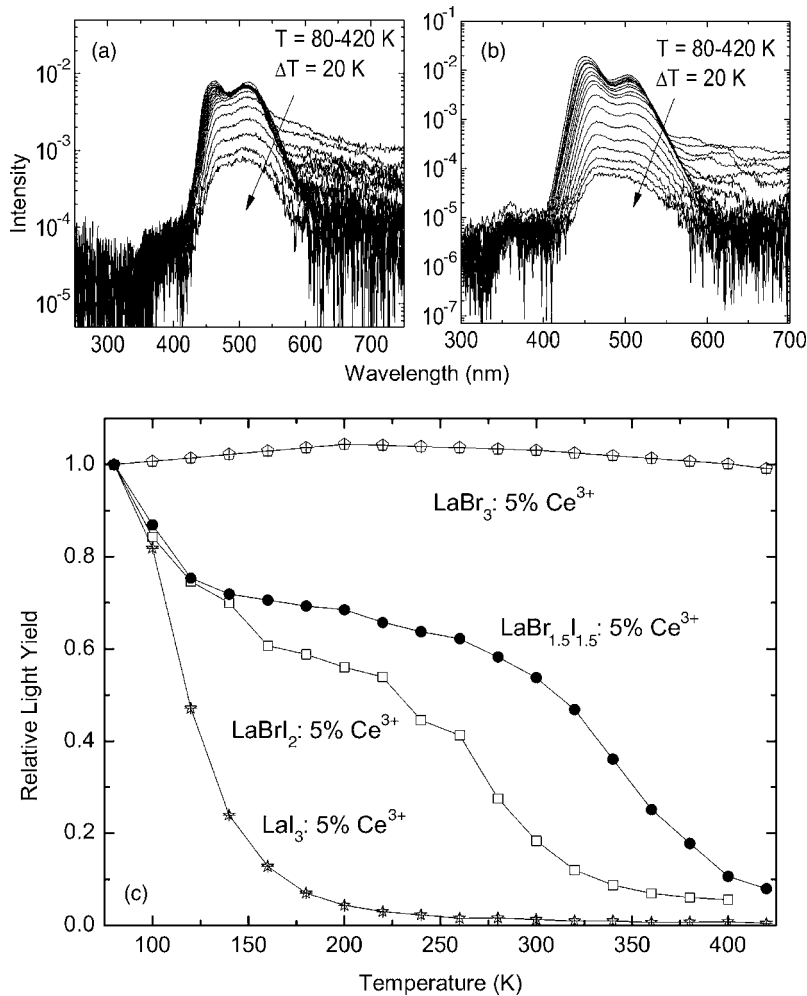


FIG. 4. Temperature dependence of radioluminescence spectra of (a)  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  and (b)  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$  from 80 to 420 K with an interval of 20 K. The temperature increases along the directions indicated by arrows. (c) Temperature dependence of the radioluminescence spectra of  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  and  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ . Those of  $\text{LaI}_3:5\%\text{Ce}^{3+}$  and  $\text{LaBr}_3:5\%\text{Ce}^{3+}$  were added for comparison and obtained from Bessiere *et al.* (Ref. 6) and Bizarri *et al.* (Ref. 15), respectively. Relative light yields were obtained by normalizing each integral of the radioluminescence spectrum with that recorded at 80 K.

$$Y_{\text{ph}} = Y_{\text{pc}} \frac{1 - R_{\text{eff}}}{R_{\text{PTFE}} Q E_{\text{eff}}}, \quad (1)$$

where  $Q E_{\text{eff}}$  is the effective quantum efficiency obtained from the manufacturer and  $R_{\text{eff}}$  is the PMT effective reflectivity previously measured by de Haas *et al.*<sup>11</sup> Both are averaged over the profile of the radioluminescence spectra. The reflection coefficient estimated for the 1 mm total thickness Teflon layer wrapping  $R_{\text{PTFE}}$  is 0.98.<sup>12</sup>

### E. Scintillation decay measurements

Scintillation decay spectra were recorded using the single photon counting method.<sup>13</sup> The crystal inside a quartz ampoule was mounted on an XP2020Q PMT acting as the start PMT. The quartz ampoule was covered with layers of Teflon tape. We made a hole in the Teflon tape, which allows few scintillation photons to reach the second XP2020Q PMT acting as the stop PMT. For electronics, an Ortec 934 constant fraction discriminator, an Ortec 567 time to amplitude converter, and an AD413 CAMAC analog to digital converter were used.

## III. RESULTS AND DISCUSSION

XRD patterns of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  are shown in Fig. 2. From these patterns, the structure types were determined and the lattice parameters were refined. The results are summa-

rized in Table I. As  $\text{LaBr}_3$ , the  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$  crystallizes in the  $\text{UCI}_3$  structure with space group  $P6_3/m$ . All other compounds with a higher  $\text{LaI}_3$  content adopt the  $\text{PuBr}_3$  structure with space group  $\text{Cmcm}$ .

The mass density  $\rho_{\text{cal}}$  in column 6 of Table I was calculated from the crystal structure. The effective atomic number  $Z_{\text{eff}}$  in column 7 of Table I depends on the  $\text{Br}^-/\text{I}^-$  ratio. The lattice parameters,  $\rho_{\text{cal}}$  and  $Z_{\text{eff}}$ , increase toward higher concentration.

Radioluminescence spectra of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  are shown in Fig. 3. All spectra are normalized to unity at the maximum of the emission spectra. All spectra are dominated by two bands assigned to the  $5d \rightarrow 4f$   $\text{Ce}^{3+}$  [ ${}^2F_{5/2}$ ,  ${}^2F_{7/2}$ ] doublet emission.

In  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ , the  $\text{Ce}^{3+}$  doublet emissions are peaked at 400 and 434 nm [see spectrum (b) in Fig. 3]. This emission is shifted 44 nm to longer wavelength, as compared to the  $\text{Ce}^{3+}$  doublet emissions in  $\text{LaBr}_3:5\%\text{Ce}^{3+}$  [see spectrum (a) in Fig. 3]. When the  $\text{LaI}_3$  concentration increases to 50% ( $x=1.5$ ), the  $\text{Ce}^{3+}$  doublet emissions are shifted to 472 and 500 nm [see spectrum (c) in Fig. 3]. If the concentration of  $\text{LaI}_3$  is above 50%, the spectra are similar to that of  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  [see spectra (d) and (e) in Fig. 3]. The  $\text{Ce}^{3+}$  doublet emissions in the  $\text{LaI}_3:5\%\text{Ce}^{3+}$  emission spectrum recorded at 135 K are peaked at shorter wavelengths of 452 and 502 nm [see spectrum (f) in Fig. 3]. At RT, these

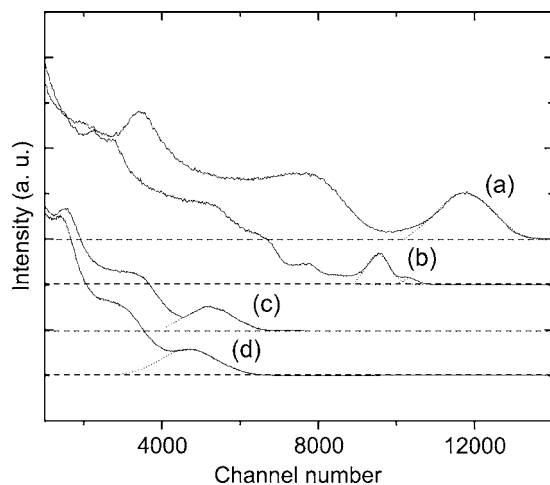


FIG. 5. Pulse height spectra under  $^{137}\text{Cs}$  662 keV  $\gamma$ -ray excitation of (a)  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ , (b)  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ , (c)  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ , and (d)  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$  recorded with a Hamamatsu R1791 PMT and a shaping time of 10  $\mu\text{s}$ . The dotted and the dashed lines correspond to Gaussian fits of the photopeaks and the background levels, respectively.

peaks may shift to the same wavelengths of those of  $\text{Ce}^{3+}$  doublet emission in  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  but, unfortunately,  $\text{Ce}^{3+}$  doublet emission in  $\text{LaI}_3:5\%\text{Ce}^{3+}$  is almost completely quenched at temperatures above 250 K.<sup>6</sup> The emission shift to longer wavelength with temperature increase was previously also observed in  $\text{LuI}_3:\text{Ce}^{3+}$  and was attributed to self-absorption effects.<sup>14</sup> Additionally, a weak broad band peaked at 390 nm is observed in spectra (d) and (e) in Fig. 3. This band can be assigned to the remnant of the self-trapped exciton emission, as previously observed in  $\text{LaI}_3:\text{Ce}^{3+}$  [see spectrum (f) in Fig. 3].<sup>6</sup>

Figure 4 shows temperature dependence of radioluminescence spectra of  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  and  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$  and the integrated emission intensity as a function of temperature of  $\text{LaBr}_3:5\%\text{Ce}^{3+}$ ,  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ ,  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ , and  $\text{LaI}_3:5\%\text{Ce}^{3+}$ . The  $5d \rightarrow 4f$   $\text{Ce}^{3+}$  [ $^2F_{5/2}$ ,  $^2F_{7/2}$ ] doublet emission is well resolved in the emission spectra of  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  and  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$  at 80 K [see Figs. 4(a) and 4(b)]. The origin of the band located around 600 nm at low temperatures is not clear. With the increase of temperature, the contribution from both  $\text{Ce}^{3+}$  emission band and the band peaked at 600 nm decreases.

The integrated radioluminescence intensity as a function of temperature is shown in Fig. 4(c). There is no decrease in light yield for  $\text{LaBr}_3:5\%\text{Ce}^{3+}$  from 80 to 420 K. When the

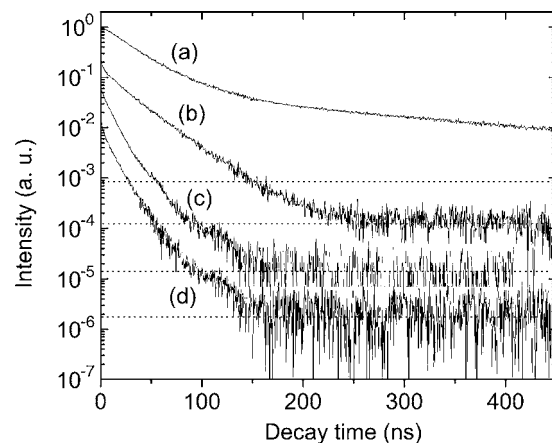


FIG. 6. Scintillation decay curves of (a)  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$ , (b)  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ , (c)  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$ , and (d)  $\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$  recorded using the single photon counting method at RT. The dashed lines correspond to the background levels for each decay curve.

$\text{LaI}_3$  concentration increases, one does observe quenching effects. At RT,  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$  and  $\text{LaBrI}_2:5\%\text{Ce}^{3+}$  show light yields of 54% and 18%, respectively, compared to the yield at 80 K, whereas  $\text{LaI}_3:5\%\text{Ce}^{3+}$  shows no luminescence at all.

Figure 5 shows the  $^{137}\text{Cs}$  source pulse height spectra of  $\text{LaBr}_{3-x}\text{I}_x:5\%\text{Ce}^{3+}$ . Light yields derived from the pulse height spectra are listed in Table II. The energy resolution  $R$  (full width at half maximum over the photopeak position) is obtained from the Gaussian fit of the photopeak. For the  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$  pulse height spectrum, we observe two photopeaks [see spectrum (b) in Fig. 5]. This is probably due to two regions in the crystals, which give two different light yields. Therefore, two light yields and energy resolutions of  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$  are listed in Table II.

Table II shows that the light yield does not change much when applying different shaping times and, therefore, the decay times are shorter than or equal to 500 ns. The highest light yield of 58 000 photons/MeV is found for  $\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$ . The light yield at 10  $\mu\text{s}$  shaping time decreases abruptly when  $x$  increases from 1.5 to 2 (see column 5 in Table II).

Scintillation decay curves of  $\text{LaBr}_{3-x}\text{I}_x:5\%\text{Ce}^{3+}$  are shown in Fig. 6. The decay curves were recorded using the single photon counting method at RT under  $^{137}\text{Cs}$   $\gamma$ -ray excitation.<sup>13</sup> The decay curve for  $\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$  has been fitted with two exponentials, whereas the other decay curves with a single exponential.

TABLE II. Photoelectron yield, light yield, and energy resolution derived from pulse height spectra of  $\text{LaBr}_{3-x}\text{I}_x:5\%\text{Ce}^{3+}$  under 662 KeV  $\gamma$ -ray excitation measured with a Hamamatsu R1791 PMT using shaping time of 0.5 and 10  $\mu\text{s}$ , and characteristic components of the scintillation decay curves. Values in the table have errors of  $\pm 10\%$ .

Compound	Photoelectron		Light yield		Energy resolution (%)	Decay components (relative contribution to total light yield) ns (%)
	( $10^3$ photoelectrons/MeV)		( $10^3$ photons/MeV)			
$\text{LaBr}_{3-x}\text{I}_x$	0.5 $\mu\text{s}$	10 $\mu\text{s}$	0.5 $\mu\text{s}$	10 $\mu\text{s}$		
$\text{LaBr}_{2.25}\text{I}_{0.75}:5\%\text{Ce}^{3+}$	13.8	14.9	42	45	4.1	31 (70), 244 (30)
	12.7	13.7	38	41	7.3	
$\text{LaBr}_{1.5}\text{I}_{1.5}:5\%\text{Ce}^{3+}$	15.9	16.9	55	58	14.6	28 (100)
$\text{LaBrI}_2:5\%\text{Ce}^{3+}$	6.6	7.5	22	25	25.9	13 (100)
$\text{LaBr}_{0.75}\text{I}_{2.25}:5\%\text{Ce}^{3+}$	6.6	6.7	22	22	35.9	12 (100)

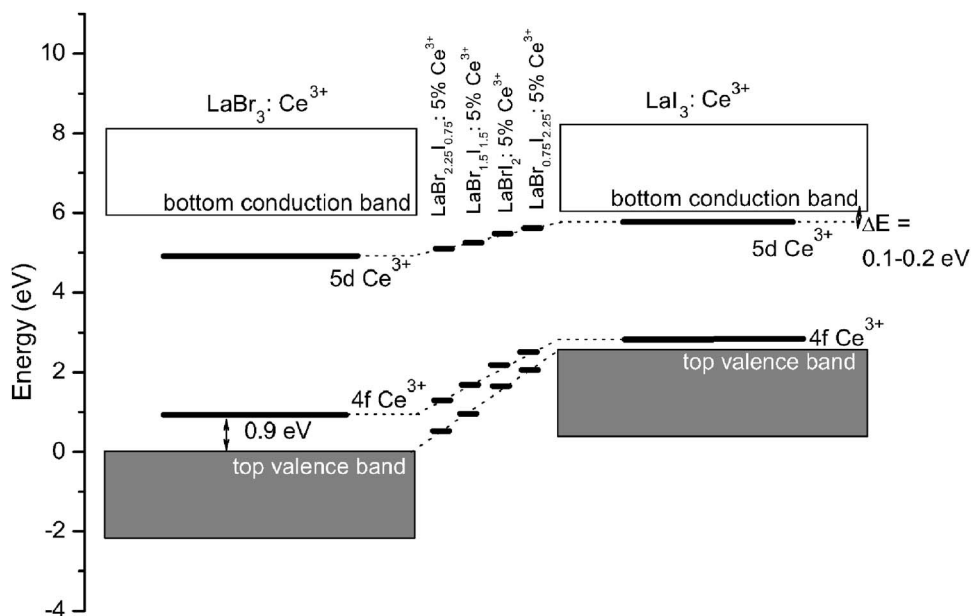


FIG. 7. Energy level schemes of  $\text{LaBr}_3:\text{Ce}^{3+}$ ,  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$ , and  $\text{LaI}_3:\text{Ce}^{3+}$ .

Decay components with their relative contribution to the total light yield are presented in Table II.  $\text{LaBr}_{2.25}\text{I}_{0.75}:\text{5\%Ce}^{3+}$  decay curve shows a fast component of 31 ns and a slow component of 244 ns. The fast component is 15 ns slower than the 16 ns intrinsic  $\text{Ce}^{3+}$  emission decay time of  $\text{LaBr}_3:\text{5\%Ce}^{3+}$ .<sup>15</sup> The presence of the slow component suggests a slow transfer of excitation energy from the host lattice to  $\text{Ce}^{3+}$ . This component disappears at higher  $\text{LaI}_3$  concentration and the fastest decay component of 12 ns was recorded for  $\text{LaBr}_{0.75}\text{I}_{2.25}:\text{5\%Ce}^{3+}$ .

The fast decay times of 13 and 12 ns and the low light yields of 25 000 and 22 000 photons/MeV were observed in  $\text{LaBrI}_2:\text{5\%Ce}^{3+}$  and  $\text{LaBr}_{0.75}\text{I}_{2.25}:\text{5\%Ce}^{3+}$ , respectively. The decay times are 2–3 ns faster than 15 ns of  $\text{LaBr}_3:\text{Ce}^{3+}$ , whereas the light yields are 45 000–48 000 photons/MeV of  $\text{LaBr}_3:\text{Ce}^{3+}$ .<sup>15</sup> In the integrated x-ray excited emission intensity as a function temperature, light yield of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  decreases as the temperature increases. Here, we will discuss the possible cause of these reduced decay times and light yields. We envisage a model for the thermal quenching of  $\text{Ce}^{3+}$  emission and estimate the position of the  $\text{Ce}^{3+}$  emitting level relative to the conduction and valence bands in  $\text{LaBr}_{3-x}\text{I}_x$ .

The energy level schemes of  $\text{LaI}_3:\text{Ce}^{3+}$ ,  $\text{LaBr}_3:\text{Ce}^{3+}$ , and  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  are shown in Fig. 7. The schemes of  $\text{LaI}_3:\text{Ce}^{3+}$  and  $\text{LaBr}_3:\text{Ce}^{3+}$  have been constructed with the information on the host lattice excitation and  $4f \rightarrow 5d$  excitations from Bessiere *et al.*<sup>6</sup> and Dorenbos *et al.*,<sup>7</sup> respectively. The top of the bromide valence band is defined as zero of energy, whereas the top of the iodide valence band is located at  $2.60 \pm 0.15$  eV. The bottom of the conduction bands of  $\text{LaBr}_3$  and  $\text{LaI}_3$  are located at  $5.90 \pm 0.15$  eV. The energy differences between the lowest  $4f$  and lowest  $5d$  states of  $\text{Ce}^{3+}$  ( $E_{fd}$ ) of  $\text{LaBr}_3$  and  $\text{LaI}_3$  are  $4.03 \pm 0.15$  and  $2.90 \pm 0.15$  eV, respectively.

In  $\text{LaBr}_3:\text{Ce}^{3+}$ , the  $4f$  ground state of  $\text{Ce}^{3+}$  is located at  $0.90 \pm 0.40$  eV above the valence band.<sup>7</sup> This value together with  $E_{fd}$  of  $\text{LaBr}_3:\text{Ce}^{3+}$  locates the  $5d$  state of  $\text{Ce}^{3+}$  at

$4.93 \pm 0.43$  eV above the valence band. The lowest  $5d$  state of  $\text{Ce}^{3+}$  is then at  $\sim 1$  eV below the bottom of the conduction band. This large energy difference is consistent with the absence of  $\text{Ce}^{3+}$  emission quenching in  $\text{LaBr}_3$  even at a temperature of 600 K.<sup>15</sup>

In  $\text{LaI}_3:\text{Ce}^{3+}$ , quenching of  $\text{Ce}^{3+}$  emission is due to the autoionization of an electron of the  $5d$   $\text{Ce}^{3+}$  to the conduction band because of the 0.1–0.2 eV small energy difference of the lowest  $5d$  state of  $\text{Ce}^{3+}$  with the conduction band.<sup>6</sup> Lifetime shortening and light yield loss in  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  when the temperature increases can be associated with the thermal luminescence quenching model in  $\text{LaI}_3:\text{Ce}^{3+}$ . In the case of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$ , we expect that the difference of the lowest  $5d$  state of  $\text{Ce}^{3+}$  with the conduction band is larger than 0.2 eV but smaller than that in  $\text{LaBr}_3$ . This difference decreases toward high  $\text{LaI}_3$  concentration. This assumption is based on the thermal quenching process from 150 to 450 K in the temperature dependence of integrated radioluminescence spectra of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  (see Fig. 4). However, we cannot derive the activation energies for  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  from the integrated intensity curves. The thermal quenching from 80 to 150 K in the curves of  $\text{LaBrI}_2:\text{5\%Ce}^{3+}$  and  $\text{LaBr}_{1.5}\text{I}_{1.5}:\text{5\%Ce}^{3+}$  can be associated with other quenching mechanisms.

#### IV. CONCLUSION

$\text{Ce}^{3+}$  activated  $\text{LaBr}_{3-x}\text{I}_x$  crystals were grown by the Bridgmann method. XRD patterns of crystals show that  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  crystals are of single phase.  $\text{LaBr}_{2.25}\text{I}_{0.75}:\text{5\%Ce}^{3+}$  has a  $\text{UCl}_3$  crystal structure with space group  $P6_3/m$ , whereas  $\text{LaBr}_{1.5}\text{I}_{1.5}:\text{5\%Ce}^{3+}$ ,  $\text{LaBrI}_2:\text{5\%Ce}^{3+}$  and  $\text{LaBr}_{0.75}\text{I}_{2.25}:\text{5\%Ce}^{3+}$  have a  $\text{PuBr}_3$  crystal structure with space group  $Cmcm$ . The scintillation properties of  $\text{Ce}^{3+}$  activated mixed halides  $\text{LaBr}_{3-x}\text{I}_x$  were also studied. The highest light yield of 58 000 photons/MeV was found for  $\text{LaBr}_{1.5}\text{I}_{1.5}:\text{5\%Ce}^{3+}$ , whereas the fastest decay time of 12 ns was found for  $\text{LaBr}_{0.75}\text{I}_{2.25}:\text{5\%Ce}^{3+}$ . The lower light yield and the faster decay time toward higher  $\text{LaI}_3$  concentration

are assigned to the quenching of  $\text{Ce}^{3+}$  emission, which is due to autoionization of the  $\text{Ce}^{3+}$   $5d$  electron to the conduction band.

Since  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  crystals have relatively high light yield and fast response, the application for  $\gamma$ -ray and x-ray detection is very promising. The  $0.40\text{--}0.53\text{ g/cm}^3$  higher mass density than  $5.07\text{ g/cm}^3$  of  $\text{LaBr}_3:\text{Ce}^{3+}$  is the advantage of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$ . This means that  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  is better than  $\text{LaBr}_3:\text{Ce}^{3+}$  with respect to high-energy detection efficiency. The energy resolution of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  is rather poor, and the pulse height spectrum of  $\text{LaBr}_{2.25}\text{I}_{0.75}:\text{5\%Ce}^{3+}$  even shows two photopeaks. Apparently, some part of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  crystals produce more photons or photons are collected more efficiently from one part than from another part due to crystal inhomogeneity. An improvement in the technology of  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  crystal growth may bring  $\text{LaBr}_{3-x}\text{I}_x:\text{Ce}^{3+}$  into a superior scintillator with a high light yield, good energy resolution, fast response, and high mass density.

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