Cerium-doped barium halide scintillators for x-ray and γ -ray detections

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Single crystals of Ce-activated BaCl_2 , BaBr_2 , and BaI_2 were investigated under x-ray and γ -ray excitation. The Ce^{3+} -related x-ray excited luminescence in BaBr_2 shifts significantly to longer wavelengths upon increasing the doping level from 0.1% to 1%. In Ce-activated BaCl_2 only a slight shift can be observed. BaI_2 does not show any Ce^{3+} -related emission. Scintillation decay time measurements show that the decay in BaBr_2 is delayed due to migration processes. Additional K doping has a large influence on the scintillation decay time properties but not on the overall efficiency. © 2007 American Institute of Physics. [DOI: 10.1063/1.2786714]

I. INTRODUCTION

Eu-activated fluorozirconate-based glass ceramics represent a promising class of x-ray scintillators.^{1,2} The scintillation in these glass ceramics is caused mainly by the emission of divalent europium incorporated in hexagonal barium chloride nanocrystals, which are formed in the glass matrix upon annealing at specified temperatures. Since research on fast scintillators has become important during the last decades, experiments with Ce-activated fluorozirconate glass ceramics have been performed, showing that cerium is an interesting alternative.^{3,4} Ce-activated single crystals like LaCl_3 (Ref. 5) or LaBr_3 (Ref. 6) are known as fast scintillators with a high light output. A short scintillation decay time is necessary for fast timing or high rate counting applications.

In order to get a better understanding of the scintillation mechanism in Eu- or Ce-activated barium halide nanocrystals, an investigation of the processes in the corresponding bulk material is essential. In Ref. 7 we reported on the scintillation properties of undoped and Eu-activated barium halides which were investigated by x-ray excited luminescence (XL), pulse height, and scintillation decay spectra. XL spectra of the Eu-activated barium halides show a single, Eu^{2+} -related emission while Ce-activated systems usually show the typical double band shape; the doublet is caused by the two levels of the split cerium ground state. In contrast to the Eu-activated barium halides, which have a single Eu^{2+} site in the Ba^{2+} position, the situation in the Ce-activated barium halides is more complicated; recent investigations on $\text{BaCl}_2:\text{Ce}^{3+}$ (Ref. 8) and $\text{BaBr}_2:\text{Ce}^{3+}$ (Ref. 9) showed that we are dealing with more than one Ce^{3+} site in BaBr_2 . This work studies the optical properties of Ce-activated barium halides upon x-ray and γ -ray excitation.

II. EXPERIMENTAL TECHNIQUES

A. Sample preparation and crystal structure

Ce^{3+} -doped and K^{+} -codoped single crystals of orthorhombic BaX_2 ($X=\text{Cl}, \text{Br}, \text{I}$) were grown at the University of Paderborn crystal growth laboratory using the Bridgman method. To prepare the samples, 0.1 or 1 mol % of CeX_3 and KX were added to BaX_2 powder in a quartz glass ampoule with a SiX_4 atmosphere. In the case of K codoping, the K concentration was the same as the Ce concentration. Prior to crystal growth the BaX_2 powder was dried in vacuum with subsequent melting in the SiX_4 atmosphere to reduce oxygen contamination. However, the silicon treatment did not work for the BaI_2 powder. The usual technique was completed by slow cooling through the cubic-orthorhombic phase transition near 920 °C for BaCl_2 (Ref. 10) and 800 °C for BaBr_2 .¹¹ The stable phase of BaX_2 crystals at room temperature (RT) has the orthorhombic PbCl_2 structure [space group $D_{2h}^{16}\text{-Pnma}$ (Ref. 10)]. The melting point of BaCl_2 , BaBr_2 , and BaI_2 is 958 °C, 850 °C, and 740 °C, respectively.^{12–14}

B. Experimental setup

The x-ray excited luminescence and afterglow spectra were recorded at the University of Paderborn using a 0.22-m double monochromator (Spex) in combination with a cooled photomultiplier (Hamamatsu R943–02) working in single-photon counting mode (HP 5370B Universal Time Interval Counter). All spectra were recorded at RT and not corrected for spectral sensitivity of the experimental setup. The x-ray irradiation was carried out with a mobile x-ray tube (Phillips MGC 01) using a tungsten anode at 60 kV and 15 mA.

Pulse height spectra were obtained at the Delft University of Technology with a Hamamatsu R1791 photomultiplier tube (PMT) with a box-type dynode structure connected to a preamplifier and an Ortec 672 spectroscopy amplifier inside an M-Braun UNILAB dry box with a moisture content less than one part per million. The crystals were mounted directly to the window of the PMT and covered with several Teflon layers to optimize the light collection. The photoelec-

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tron yield (LY_{phe} in photoelectrons per MeV) is obtained by comparing the peak position of the photopeak with that of the single-electron spectrum.¹⁵ The absolute light yield, LY_{ph} in photons per MeV (ph/MeV), is derived from LY_{phe} as follows¹⁶:

$$LY_{\text{ph}} = (1 - R_{\text{eff}})/(0.98QE_{\text{eff}})LY_{\text{phe}}. \quad (1)$$

The effective quantum efficiency QE_{eff} of the PMT was obtained from the manufacturer, and the PMT effective reflectivity R_{eff} was measured. Both are averaged over the spectral profile of the γ -ray excited scintillation spectrum. The effective reflectivity, R_{eff} , for $\text{BaCl}_2:\text{Ce}$, K-codoped $\text{BaCl}_2:\text{Ce}$, $\text{BaBr}_2:\text{Ce}$, K-codoped $\text{BaBr}_2:\text{Ce}$, and $\text{BaI}_2:\text{Ce}$ is 19.4, 18.9, 26.0, 20.9, and 31.8, respectively; the effective quantum efficiency QE_{eff} is 27.6, 28.8, 23.1, 28.6, and 12.5, respectively. The position and the energy resolution of the photopeak (full width at half maximum) was determined by fitting the photopeak with a Gaussian curve.

Scintillation decay time was measured at Delft University of Technology. The spectra were recorded by two methods. The first is the single-photon counting technique described by Bollinger and Thomas.¹⁷ For this method, scintillation decay time spectra were recorded at times up to 200 μs with XP2020Q PMTs, Ortec 934 constant fraction discriminators, an Ortec 567 time-to-amplitude converter (TAC), and an AD513A CAMAC analog-to-digital converter (ADC).

To record decay time spectra at times longer than 200 μs , the multihit method¹⁸ was used. The TAC and ADC in the single-photon counting technique were replaced by a Lecroy 4208 time-to-digital converter (TDC), which has a channel width of 1 ns. Using this method, the short decay component and its contribution to the total light yield are less accurately obtained than those using the single-photon counting technique.

III. RESULTS AND DISCUSSION

A. X-ray excited luminescence and integral x-ray scintillation efficiency

Figure 1 shows the normalized XL spectra of Ce-doped BaX_2 (solid curves) and Ce- and K-codoped BaCl_2 and BaBr_2 (dashed and dotted curves). The XL curves of Ce-doped BaCl_2 [Fig. 1(a), solid curve] and BaBr_2 [Figs. 1(b) and 1(c), solid curves] have the typical doublet for Ce luminescence. The double band shape is a result of the $4f$ ground state splitting, caused by the spin-orbit coupling. In BaCl_2 the Ce doublet is at 349 and 373 nm. For BaBr_2 the doublet shifts to 345 and 370 nm. In the case of BaI_2 [Fig. 1(d), solid curve] no Ce luminescence can be observed. The increase of an additional band from Cl via Br to I can be seen. While in the BaCl_2 host lattice the additional luminescence bands at 420 and 480 nm can only be observed in the expanded spectrum, in BaBr_2 they are almost as intense as the Ce doublet. For BaI_2 only a broad band at 550 nm can be seen. The additional bands agree with those of the corresponding undoped crystals.⁷ Besides the bands at 420 and 480 nm the expanded spectrum of $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) shows a peak at

FIG. 1. Normalized x-ray excited luminescence spectra of (a) $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%), (b) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (0.1%), (c) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%), and (d) $\text{BaI}_2:\text{Ce}^{3+}$ (0.1%). Parts of the spectrum of 0.1% Ce-doped BaCl_2 are expanded as indicated. In (d) the spectrum of undoped BaI_2 (Selling *et al.*⁷) is shown for comparison.

305 nm. This corresponds to a band observed in undoped BaCl_2 and is assumed to be a self-trapped exciton (STE).

The spectrum of $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) [Fig. 1(a), dashed curve] shows the same characteristic Ce doublet as found in the sample without potassium, but slightly (less than 5 nm) shifted to longer wavelength; the linewidth is slightly smaller. However, the additional weak bands at 420 and 480 nm as well as at 305 nm found in $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) are completely suppressed in the K-codoped sample. The fact that the position of the Ce^{3+} emission shifts slightly to longer wavelengths upon increasing the doping level from 0.1% to 1% agrees with findings by Li and Leskelä.¹⁹ They observed a shift in the emission wavelength from 340 to 356 nm, when the Ce doping level is increased from 0.05% to 5%.

In the case of BaBr_2 doped with 0.1% CeBr_3 and 0.1% KBr [Fig. 1(b), dotted curve], the ratio between the Ce doublet and the additional luminescence bands at 420 and 480 nm has changed in favor of the Ce doublet. The intensity of the Ce doublet in 0.1% Ce- and 0.1% K-codoped BaBr_2 is about twice that of the corresponding 0.1% Ce-doped crystal. In $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) [Fig. 1(c), dashed curve] the Ce

TABLE I. Integral x-ray scintillation efficiencies and XL-to-afterglow ratios of Ce-doped and K-codoped BaCl_2 , BaBr_2 , and BaI_2 . The scintillation efficiency was derived by comparing the integrated area under the XL curve of the corresponding barium halide to that of a CdWO_4 [28 000 photons/MeV (Ref. 20)] reference sample. The XL-to-afterglow ratio was detected at the wavelengths indicated.

Crystal	Integral x-ray scintillation efficiency with respect to CdWO_4 (photons/MeV)	XL-to-afterglow ratio (after 3 s)
$\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%)	4800 ± 480	2% at 305 nm 8% at 350/370 nm 5% at 420/480 nm
$\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%)	13000 ± 1300	35% at 350/370/420 nm 12% at 480 nm
$\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%)	36000 ± 3600	8% at 350/370 nm 0.5% at 420/480 nm
$\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (0.1%)	65000 ± 6500	—
$\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%)	54000 ± 5400	6% at 350/370/420 nm 2% at 480 nm
$\text{BaI}_2:\text{Ce}^{3+}$ (0.1%)	1800 ± 180	<0.1% at 550 nm

doublet is barely resolved and shifted by more than 30 nm to 375 and 410 nm. The additional bands at 420 and 480 nm are very weak and hardly noticeable.

The situation in Ce-doped BaBr_2 is more complicated than in Ce-doped BaCl_2 . There are (at least) three different Ce sites in BaBr_2 :⁹ (A) the so-called A-site (doublet at 349/373 nm) is attributed to Ce ions charge-compensated by a potassium impurity; (B) the B-site (420 nm) is assumed to be a Ce ion in the vicinity of any other impurity; and (C) the C-site (330/353 nm) can only be seen at low temperatures and is attributed to an unperturbed Ce site. This assignment by Corradi *et al.*⁹ is in good agreement with our XL results. Upon 0.1% K codoping [Fig. 1(b), dotted curve], the A-site to B-site ratio changes in favor of the A-site; for a Ce- and K-codoping level of 1% [Fig. 1(c), dashed curve] the B-site has completely disappeared while the A-site is shifted to longer wavelengths. The latter result is consistent with the findings for 1% Ce- and 1% K-codoped BaCl_2 [Fig. 1(a), dashed curve].

For a rating of the scintillation properties with regard to integral x-ray scintillation efficiency the barium halide single crystals were compared to the common scintillator CdWO_4 . The measurements were made using the same parameters for all crystals. The area under the XL curve is calculated and compared to that of a CdWO_4 reference sample (28 000 ph/MeV).²⁰ The results are given in Table I. The integral x-ray scintillation efficiencies of Ce-doped BaCl_2 and BaBr_2 have already been presented in Ref. 21.

B. Afterglow

Normalized afterglow spectra of 0.1% Ce-doped BaCl_2 and BaBr_2 are shown in Fig. 2 (solid curves); normalized afterglow spectra of 1% Ce- and 1% K-codoped samples are also shown (dashes and dotted curves). Ce-doped BaI_2 shows only a very weak afterglow, which makes the recording of the spectral behavior impossible. The afterglow spectra of the 0.1% Ce-doped as well as of the 1% Ce- and 1% K-codoped samples are dominated by the Ce doublet. The

420 and 480 nm bands, which have been observed in the XL spectra, are negligible in the afterglow spectra.

Figure 3 shows the temporal behavior of the XL/afterglow intensity of 0.1% Ce-doped (solid curves) and 1% Ce- and 1% K-codoped BaCl_2 and BaBr_2 (dashed curves) after switching on (for 5 min) and off the x-ray excitation at RT; the resolution of these measurements was 3 s, i.e., a data point was recorded every 3 s. The curves have been normalized for easier comparison. As seen in the afterglow spectra above, the afterglow is dominated by the Ce luminescence. The Ce^{3+} emission in 0.1% Ce-doped BaCl_2 [Fig. 3(a), solid

FIG. 2. Normalized afterglow spectra of (a) $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%), (b) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (0.1%), and (c) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%).

FIG. 3. Normalized temporal behavior of the XL/afterglow intensity of (a) $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) and (b) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) after switching on and off the x-ray excitation at RT. The (dashed) curves for $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) were horizontally displaced for clarity. The XL/afterglow intensity was detected at the wavelength indicated.

curves] has an afterglow of about 8%, i.e., the emission intensity drops down to 8% of its value after switching off the x-ray excitation. The additional luminescence bands have an afterglow between 2% (305 nm) and 5% (420 and 480 nm). The 1% Ce- and 1% K-codoped sample [Fig. 3(a), dashed curves] shows an afterglow of 35% for the Ce doublet and 12% at 480 nm. The Ce^{3+} emission in 0.1% Ce-doped BaBr_2 [Fig. 3(b), solid curves] has an afterglow of 8%, while the afterglow of the additional bands at 420 and 480 nm is less than 1%. The afterglow of the 1% Ce- and 1% K-codoped sample [Fig. 3(b), dashed curves] is 6% for the Ce emission and about 2% at 480 nm. Ce-doped BaI_2 shows an afterglow below 0.1%. The XL-to-afterglow ratios detected at the wavelengths indicated are listed in Table I.

C. γ -ray light yield and energy resolution

γ -ray light yields and energy resolution for 0.1% Ce-doped and 1% Ce- and 1% K-codoped BaCl_2 and BaBr_2 are derived from pulse height spectra under 662 keV γ -ray excitation of a ^{137}Cs source; the spectra are shown in Fig. 4. To determine the position of the photopeak and the energy resolution, the photopeaks were fitted by Gaussian curves. Besides the photopeak at 662 keV the spectra show the Compton continuum from the Compton edge at about 450 keV down to zero energy. The backscatter peak, which arises from scattering of the γ -rays from the photomultiplier and materials outside the system back into the scintillation crystals, is at 200 keV. The leftmost peak at 32 keV corresponds to the K_α x-rays of barium, which are also emitted in a ^{137}Cs

FIG. 4. Pulse height spectra of (a) $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) and (b) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) under 662 keV γ -ray excitation of a ^{137}Cs source. The spectra are measured with a shaping time of 10 μs .

decay. The values for 0.1% Ce-doped BaI_2 were obtained from pulse height spectra under 59.9 keV γ -rays of a ^{241}Am source (the spectra are not shown); Ce-doped BaI_2 did not show a photopeak under 662 keV γ -ray excitation. γ -ray light yields and energy resolution of all samples investigated are compiled in Table II.

0.1% Ce-doped BaBr_2 shows the highest γ -ray light yield of all Ce-doped barium halides investigated with $(13\,600 \pm 1350)$ ph/MeV. The values were obtained with a shaping time of 10 μs . Increasing the shaping time from 0.5 to 10 μs leads to an increase in the γ -ray light yield by a factor of about 3.5, which indicates the existence of a slow scintillation component in the μs range. This finding is confirmed by the scintillation decay time measurements (see below). The γ -ray light yield in BaCl_2 and BaI_2 —both samples showing a very low light yield—is approximately doubled by increasing the shaping time to 10 μs . Increasing the Ce-doping level to 1% (in combination with additional 1% K codoping) leads to a slight increase in γ -ray light yield. In BaCl_2 the 0.5 μs as well as the 10 μs value could be increased, whereas in BaBr_2 only the 0.5 μs value is found to be larger.

A comparison between the γ -ray light yield values obtained from the pulse height spectra (Table II) and the integral x-ray scintillation efficiencies obtained from the XL spectra (Table I) which were compared to CdWO_4 [28 000 ph/MeV (Ref. 20)] shows that the data do not agree with each other. Apart from Ce-doped BaI_2 , the integral x-ray scintillation efficiency is always significantly higher than the γ -ray light yield of the corresponding crystal. An explanation

TABLE II. γ -ray light yield, energy resolution, and scintillation decay of Ce-doped BaCl_2 , BaBr_2 , and BaI_2 . The light yield and energy resolution values for Ce-doped BaCl_2 and BaBr_2 were derived from pulse height spectra under 662 keV γ -ray excitation of a ^{137}Cs source; the values for Ce-doped BaI_2 were obtained from pulse height spectra under 59.9 keV γ -rays of a ^{241}Am source. The scintillation decay measurements for $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaI}_2:\text{Ce}^{3+}$ (0.1%) were carried out with the multihit method, and those for $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%), K-codoped $\text{BaCl}_2:\text{Ce}^{3+}$ (1%), and $\text{BaBr}_2:\text{Ce}^{3+}$ (1%) with the single-photon counting method.

Crystal	γ -ray light yield (photons/MeV)		Energy resolution (%)	Scintillation decay time (ns)	Relative contribution to total γ -ray light yield (for a shaping time of 10 μs)
	0.5 μs	10 μs			
$\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%)	1500 $\pm$ 150	3100 $\pm$ 300	14.0 $\pm$ 1.4	14 $\pm$ 1 90 $\pm$ 9 1400 $\pm$ 140	10% 40% 50%
$\text{BaCl}_2:\text{Ce}^{3+}$, K ⁺ (1%)	2000 $\pm$ 200	5200 $\pm$ 500	16.2 $\pm$ 1.5	7 $\pm$ 1 190 $\pm$ 20 1500 $\pm$ 150	6% 11% 83%
BaBr_2 (Ref. 7)	5100 $\pm$ 500	19300 $\pm$ 1950	5.4 $\pm$ 0.5	2200 $\pm$ 220	100% $\tau_{\text{rise}}=(200\pm 20)$ ns
$\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%)	3700 $\pm$ 350	13600 $\pm$ 1350	10.0 $\pm$ 1.0	1700 $\pm$ 170	100% $\tau_{\text{rise}}=(150\pm 15)$ ns
$\text{BaBr}_2:\text{Ce}^{3+}$, K ⁺ (1%)	5000 $\pm$ 500	10300 $\pm$ 1000	9.8 $\pm$ 1.0	80 $\pm$ 8 490 $\pm$ 50 2100 $\pm$ 210	27% 22% 51%
$\text{BaI}_2:\text{Ce}^{3+}$ (0.1%)	2600 $\pm$ 250	4600 $\pm$ 450	—	590 $\pm$ 60 2200 $\pm$ 200	71% 29%

for this observation lies in the method of recording the data: The γ -ray light yield values derived from the pulse height spectra were recorded with a maximum shaping time of 10 μs , whereas each data point of the XL spectra was obtained after 1–2 s of integration and was thus enhanced by afterglow effects. This is the reason why the values from the XL spectra of BaCl_2 and BaBr_2 are higher than that from the pulse height spectra. In addition, since the scintillation decay measurements have been recorded for a shaping time of only 10 μs , very slow decay time components in the range of several micro- or even milliseconds are difficult to detect. The last column of Table II shows that the relative contribution to the total light is often dominated by such slow components.

In contrast to BaCl_2 and BaBr_2 , the x-ray scintillation efficiency for 0.1% Ce-doped BaI_2 is smaller than the corresponding γ -ray light yield value obtained from pulse height measurements. BaI_2 is very hygroscopic and becomes opaque while performing the XL measurements, i.e., the scintillation intensity decreases during the measurement. This effect could be avoided for the pulse height measurements, which were performed inside a dry box.

D. Scintillation decay

Figure 5(a) shows the scintillation decay curves of 0.1% Ce-doped BaCl_2 , BaBr_2 , and BaI_2 . All samples were measured with both methods, TDC and TAC. The results of the two methods are the same within an error of 10%. The presented curve for BaBr_2 was measured with the single-photon counting method, whereas those for BaCl_2 and BaI_2 were

measured with the multihit method. The scintillation decay components are shown in Table II together with their relative contribution to the total γ -ray light yield.

In contrast to 0.1% Ce-doped BaCl_2 and BaI_2 , the decay curve of 0.1% Ce-doped BaBr_2 shows an initial rise in the scintillation intensity before a slow, monoexponential decay is observed. The normalized decay curve can be described by

$$I(t) = \underbrace{(1 - e^{-t/\tau_{\text{rise}}})}_{I_0} e^{-t/\tau}, \quad (2)$$

with the initial rise time τ_{rise} and the decay time τ for the monoexponential decay. A revised analysis of the scintillation decay in undoped BaBr_2 (decay curve already published in Ref. 7) showed that such an initial rise can be observed there as well. The initial rise times are listed in the last column of Table II.

K codoping of 1% Ce-doped BaCl_2 and BaBr_2 leads to significant changes in the scintillation decay [Figs. 5(b) and 5(c)]. The $\text{BaCl}_2:\text{Ce}^{3+}$, K⁺ (1%) and $\text{BaBr}_2:\text{Ce}^{3+}$, K⁺ (1%) decay curves can be fitted by assuming three components. The scintillation decay times of the K-codoped samples as well as the relative contribution of each component to the total γ -ray light yield are added to Table II.

The observation of an initial rise in the scintillation decay curve and the fact that there is no fast decay component (although there is significant contribution from Ce^{3+} emission) indicate that the Ce^{3+} excitation in 0.1% Ce-doped BaBr_2 is delayed, either due to energy migration processes or due to charge carrier migration processes from the ionization track to Ce^{3+} . Although we do not know what kind of migration process it is, it is clear that the observed scintillation decay is determined by both the Ce^{3+} 5d lifetime and the

FIG. 5. Normalized scintillation decay curves of (a) 0.1% Ce-doped BaCl_2 , BaBr_2 , and BaI_2 , (b) $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%), and (c) $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) under 662 keV γ -ray excitation of a ^{137}Cs source. The measurements for $\text{BaCl}_2:\text{Ce}^{3+}$ (0.1%) and $\text{BaI}_2:\text{Ce}^{3+}$ (0.1%) were carried out with the multihit method, and those for $\text{BaBr}_2:\text{Ce}^{3+}$ (0.1%), $\text{BaCl}_2:\text{Ce}^{3+}, \text{K}^+$ (1%), and $\text{BaBr}_2:\text{Ce}^{3+}, \text{K}^+$ (1%) with the single-photon counting method.

speed of migration/excitation. If the latter process is much slower than the $\text{Ce}^{3+} 5d$ lifetime then the scintillation decay is fully controlled by the migration/transfer process. We assume that the defects involved in the migration processes are the same as the ones responsible for the host-related emission bands at 420 and 480 nm [Figs. 1(b) and 1(c), solid curves]. The 1% K codoping, however, causes a significant change in the scintillation behavior. The additional emission bands assigned to host lattice emission bands at 420 and 480 nm disappear [Fig. 1(c), dashed curve] and a fast decay component of 80 ns can now be found in the corresponding scintillation decay curve [Fig. 5(c)]. It seems that the transfer from the host-related defects to the Ce ions is much enhanced by K codoping. The host emission is quenched by the fast transfer to Ce, which results in more intense and faster Ce scintillation decay. The decay is still controlled by the

migration/transfer process, but the lifetime of this process decreases to 80 ns. The intrinsic lifetime of the $\text{Ce}^{3+} 5d$ state is expected to be significantly shorter than 80 ns; we anticipate a lifetime of around 20–30 ns.

IV. CONCLUSION

The Ce-doped BaBr_2 samples show the highest γ -ray light yield of the barium halides investigated: The light yield of 0.1% Ce-doped BaBr_2 is 13 600 ph/MeV and 10 300 ph/MeV for 1% Ce- and 1% K-codoped BaBr_2 . Additional K doping did not (as expected) increase the γ -ray light yield but led to an even smaller value. Interestingly, in undoped BaBr_2 a light yield of 19 600 ph/MeV was found; this is significantly more than the values for the corresponding Ce-doped samples. However, the K codoping had a significant influence on the scintillation decay behavior: In 1% Ce- and 1% K-codoped BaBr_2 , a fast, medium, and slow decay time component could be observed, while the scintillation decay in undoped BaBr_2 and in 0.1% Ce-doped BaBr_2 consisted of only one slow component and the decay was delayed. The K codoping did not have a significant influence on the afterglow behavior or on the energy resolution under 662 keV γ -ray excitation of a ^{137}Cs source.

Both Ce-doped BaCl_2 and Ce-doped BaI_2 showed a very weak γ -ray light yield, which makes these systems less attractive for scintillation applications. Similar to the situation in Ce-doped BaBr_2 , increasing the Ce-doping level as well as additional K doping did not help very much to improve the scintillation properties of Ce-doped BaCl_2 .

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