Effects of Ce Concentration on Scintillation Properties of $LaBr_3$:Ce

J. Glodo, W. W. Moses, *Senior Member, IEEE*, W. M. Higgins, E. V. D. van Loef, P. Wong, S. E. Derenzo, *Senior Member, IEEE*, M. J. Weber, and K. S. Shah

***Abstract*—In this communication, we investigate the scintillation properties of $LaBr_3$:Ce as a function of Ce concentration. We have studied crystals nominally doped with 0.5%, 5%, 10%, 20%, and 30% Ce (by mole). Previous reports suggest that as the Ce content increases, there is a decrease in light output and little or no change in decay time constants. These results show that the light output does not change with Ce concentration up to 30% and depends mostly on the crystal quality. On the other hand we have found the timing properties to be a strong function of Ce concentration. As the Ce content increases, the principal decay time constant of scintillation decreases from ~ 26 ns for 0.5% Ce to ~ 17 ns for crystals with $> 5\%$ Ce. Moreover, there is a significant change in rise time constants. The rise time measured for a sample doped with 0.5% Ce is up to 9 ns, whereas for samples doped with $> 10\%$ Ce it is less than 0.5 ns. The change of rise time has a major effect on the timing properties of this scintillator, with timing resolution improving from 361 ps to less than 100 ps (full width at half maximum).**

***Index Terms*—$LaBr_3$, scintillation detectors, scintillators.**

I. Introduction

$LaBr_3$:Ce is a new, very promising scintillating material [1]–[3]. Samples of this material have shown excellent properties, such as high light output, fast decay, outstanding energy resolution, and excellent linearity. Those properties position it as a direct competitor to NaI:Tl, one of the most commonly used scintillators. $LaBr_3$:Ce is also considered for time-of-flight POSITION emission tomography [4]–[6].

The majority of experimental results published to date describe $LaBr_3$ samples activated with a relatively low level of Ce concentration (0.5%), since this level of activation appeared to provide the most efficient scintillation [2]. Initial reports also suggested that as the Ce concentration increases, the light output decreases and little or no change is observed in the decay time constant [2].

In this communication, we report on our investigation of $LaBr_3$:Ce and its properties in a function of Ce concentration. We have studied samples with Ce concentration ranging from 0.5% to 30%, extending our previous studies [7].

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J. Glodo, W. Higgins, E. van Loef, K. S. Shah, and P. Wong are with the Radiation Monitoring Devices, Watertown, MA 02472 (e-mail: kshah@rmdinc.com).

W. W. Moses, S.E. Derenzo, and M. J. Weber are with the Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8119, USA.

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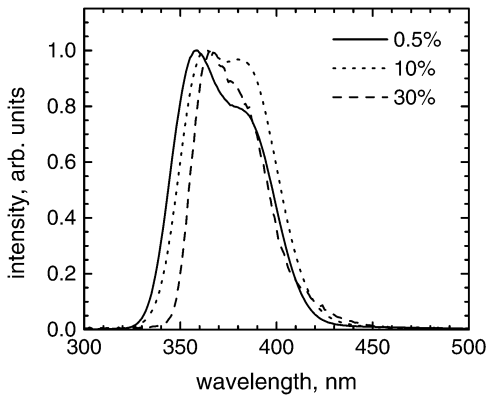

Fig. 1. Radioluminescence spectra measured with $LaBr_3$:Ce samples. The numbers on the graph indicate nominal Ce concentration. The samples were measured in reflection geometry.

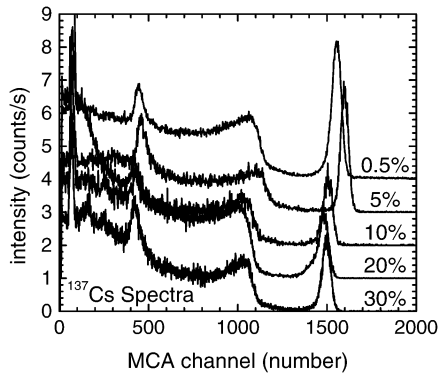

Fig. 2. ^{137}Cs energy spectra measured with $LaBr_3$:Ce samples. The numbers on the graph indicate nominal Ce concentration. The photopeak position is proportional to the light output. The relative peak positions are summarized in Table I.

II. Physical Properties and Crystal Growth

Crystals of $LaBr_3$:Ce have been grown at RMD (Watertown, MA) using the Bridgman method [7]. The nominal Ce concentration was: 0.5%, 5%, 10%, 20%, and 30% (by mole). A variety of samples with sizes ranging from 0.5 to 2.5 cm^3 were prepared, mostly with 0.5% Ce and only few with higher Ce concentrations. Since $LaBr_3$ is hygroscopic, some samples were packaged in a metal can with quartz window to prevent long-term exposure to moisture.

III. Emission

The emission wavelength of all investigated samples under X-ray excitation does not change significantly over the full

TABLE I EFFECTS OF Ce^{3+} CONCENTRATION ON LIGHT OUTPUT AND TIMING PROPERTIES OF $LaBr_3$:CE. SEE DESCRIPTION IN TEXT

Ce^{3+} Contr. %	Light Output %	Decay / Rise Times (intensity) ns/ns (%)	Effective Rise Time, ns	Timing Resolution		
				FWHM	$LaBr_3$:Ce	$\sqrt{(\tau / N)}$
				ps		
0.5	97	19/15 (56%), 15.2/2 (28%), 55 (16%)	9.4	390	361	83
5.0	100	15/0.38 (70%), 15/2.2 (27%), 55 (3%)	0.93	260	214	62
10.0	94	16.5/0.5 (89%), 4.5/0.5 (5%), 55 (6%)	0.5	182	106	67
20.0	92	17.5/0.16 (89%), 4.5/0.15 (5%), 55 (6%)	0.16	177	97	70
30.0	93	18/0.2 (91%), 2.5/0.2 (4%), 55 (6%)	0.20	165	73	70

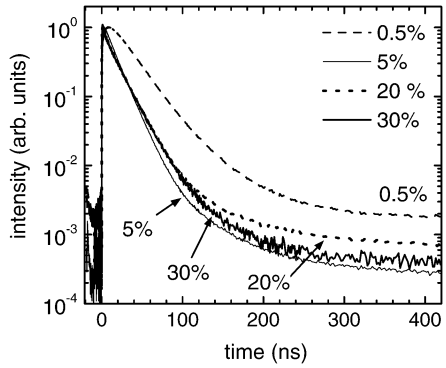

Fig. 3. Scintillation time profiles of $LaBr_3$:Ce samples doped with different Ce concentrations.

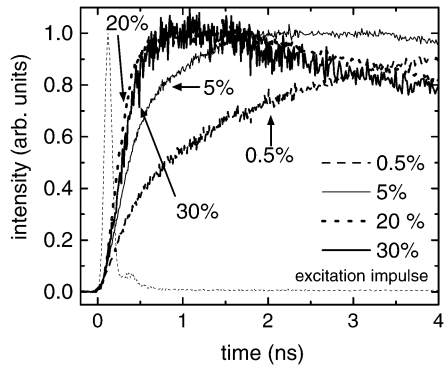

Fig. 4. Rising part of time profiles shown in Fig. 2. The numbers on the graph indicate nominal Ce concentration. On the far left an excitation impulse is shown. Note that the vertical scale is linear.

range of the Ce concentration, as it is shown in Fig. 1. However, as the Ce concentration increases, there is a small shift of the emission maximum in the direction of longer wavelengths that is related to reabsorption effects due to stronger overlap between absorption and emission bands.

IV. LIGHT OUTPUT

The light output measurements were performed by coupling the samples (unpackaged and Teflon wrapped) to a photomultiplier tube (Hamamatsu R2059) and irradiating them with a ^{137}Cs source (662 keV). Fig. 2 shows the recorded energy spectra. The highest light output (see Table I for summary of relative values) was measured for the 5% sample. The results show that light output does not change significantly with Ce

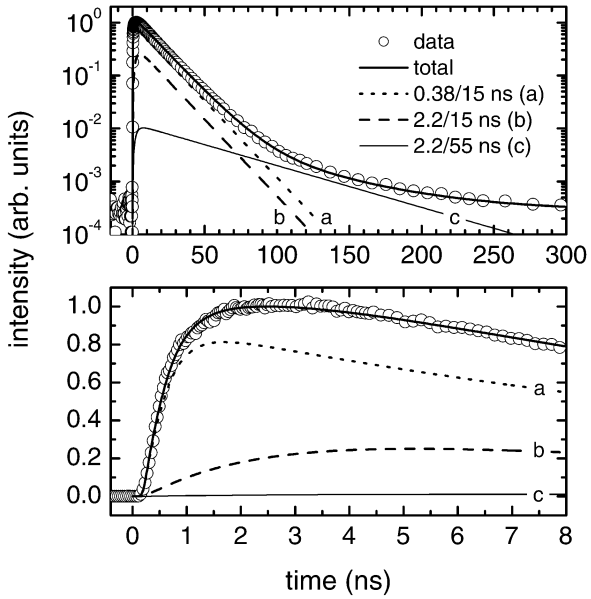

Fig. 5. Scintillation time profile of $LaBr_3$:5%Ce sample decomposed into three components. The numbers show rise/decay time value of each component. The letters on the graph indicate particular components.

concentration and stays within 10% range. Using a single photoelectron method [14] we estimated that the light output of the 5% sample is 74 000 photons/MeV (17200 photoelectrons/MeV and 23.2% QE).

V. TIME PROFILES

The scintillation time profiles of $LaBr_3$:Ce samples were measured using the delayed coincidence method at the LBNL Pulsed X-Ray Facility. The full width at half maximum (FWHM) of the excitation pulse of this setup is around 109 ps (including apparatus response). More detailed description of the setup can be found in [8]. Measured traces for 0.5%, 5%, 20%, and 30% samples are shown in Figs. 3 and 4 shows the rising part of the traces in detail. In order to describe the experimental data we used the following expression:

$$\sum_i a_i \left[\exp\left(-\frac{t}{\tau_{di}}\right) - \exp\left(-\frac{t}{\tau_{ri}}\right) \right] + b \qquad (1)$$

as a fitting function. This function was convoluted with the impulse response function shown in Fig. 4 (thin dotted line). The results of convolution were then compared with experimental data and adjusted accordingly. Equation (1) describes both the

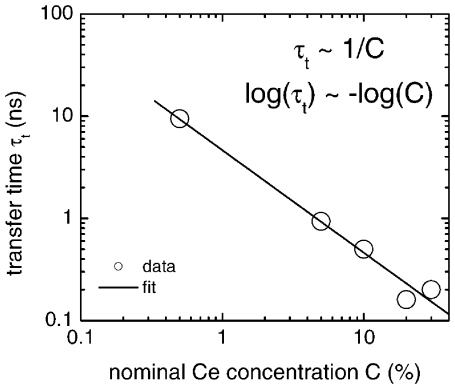

Fig. 6. Relation between Ce concentration and transfer time (rise time) for $LaBr_3$:Ce. Linear behavior indicates diffusion related energy transfer.

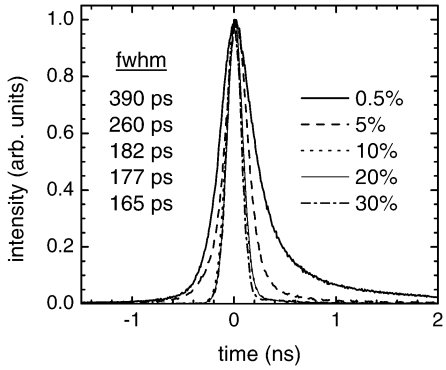

Fig. 7. Coincidence timing measurements for $LaBr_3$:Ce scintillators upon irradiation with 511 keV gamma ray pairs. The numbers show cerium concentration and respective timing resolution.

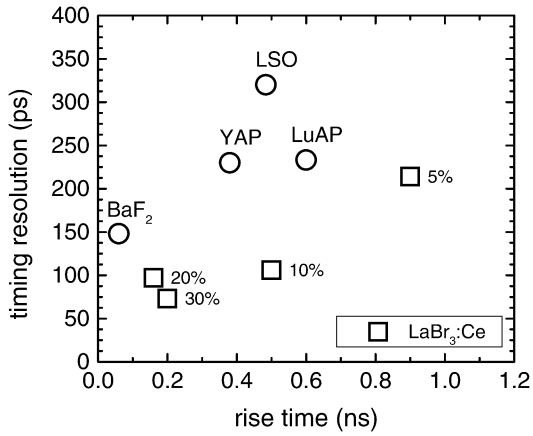

Fig. 8. Timing resolution versus rise time values for $LaBr_3$ samples doped with different Ce concentration. For reference also shown are values for BaF_2, YAP:Ce, LSO:Ce, and LuAP:Ce scintillators.

initial decay time (τ_{di}) and the rise time (τ_{ri}). Since it was difficult to use only single component $(i = 1)$ to match the data at the same time in both rising and decaying regions, we used a sum of three components $(i = 3)$ and a background. The first two components describe the fast rising and decaying parts of the traces, whereas the third component covers an additional decaying component characterized by τ_{d3} decay time of 55 ns (kept fixed). An example of the time profile decomposition into three components is shown in Fig. 5. The results are summarized in Table I.

The longest decay and rise time values were obtained for 0.5% sample. The majority of light is emitted within 15 ns rise time and 19 ns decay time component. This is a situation when the energy transfer time from the host to activator is longer than the radiative lifetime of the cerium ion hence the last defines the rise time. (The intrinsic lifetime of Ce^{3+} in the excited state in $LaBr_3$ was measured under optical excitation to be around 15 ns). The second component shows a shorter 2 ns rise time and 15 ns decay time. The average (weighted) value of rise times is 9.4 ns. If fitted with only a single component the decay time value for this trace is around 26 ns—a value that is usually quoted in other publications. As the Ce concentration increases to 5% the decay time of the main component quickly falls down to 15 ns. Its following slight increase with the further increase in concentration is most likely due to radiation trapping effects.

The changes with the Ce concentration can also be observed in rise time values. The rise time significantly decreases between 0.5% and 5% samples, from an average rise time of 9.4 to 0.93 ns. Even further decrease in rise times are observed for samples with higher Ce content. The average rise time values are 0.5, 0.16, and 0.2 ns for 10%, 20%, and 30% samples, respectively.

Rapid decrease of the rise time values with the Ce concentration indicates an efficient and fast energy transfer as well as excellent charge collection efficiency by cerium ions in $LaBr_3$. Observed changes in decay and particularly rise time values with the Ce concentration suggest that a diffusion of charge carriers in a form of self trapped holes (STH, V_k) or excitons (STE) is present. In the diffusion model, the transfer rate $k(\sim 1/\tau_r)$ depends on activator concentration. We can test this idea by plotting the rise time values against activator concentration. Fig. 6 shows that the relation between the logarithms of concentration and rise time is linear, supporting the diffusion model.

VI. Coincidence Timing Resolution

Coincidence timing experiments were performed at LBNL. The detailed description of the setup can be found in [9]. The measurements involved irradiation of BaF_2 (start) and packaged $LaBr_3$:Ce (stop) scintillators coupled to fast Hamamatsu H5321 photomultipliers (with 700 ps rise time and 160 ps FWHM transit time jitter) with 511 keV positron annihilation gamma ray pairs generated by a ^{68}Ga source. During the experiment the energy threshold for signal acceptance was set to about 250 keV. The reference measurement used two 1 cm cubes of BaF_2 detectors in coincidence with each other and yielded a timing resolution of 212 ps. This gives a timing resolution for a single BaF_2 channel a value of $148\ \text{ps}\ (= 212/\sqrt{2})$. One of the BaF_2 cubes was replaced with a $LaBr_3$:Ce sample and the coincidence timing resolution re-measured. These results are shown in Fig. 7 and FWHM values are summarized in Table I. Based on the reference value of BaF_2, we can calculate the timing resolution for a single $LaBr_3$:Ce channel using $t_{LaBr_3} = \sqrt{(t^2_{Exp} - t^2_{BaF_2})}$. The results are listed in $LaBr_3$:Ce column of Table I.

The experimental results show improvement in timing resolution as the Ce concentration increases up to 30%. Since the light output and decay time values of measured samples are comparable (for 5% and more samples) we associate changes

in timing resolution with the changes in rise times; as the rise time decreases the timing resolution improves. This dependence is shown in Fig. 8. The figure also shows results measured for a few other cerium-based scintillators, namely LuAP [10], YAP [11], and LSO [9], [12]. Care must be taken when interpreting these results, as the samples have different size, reflectors, and surface treatment and these factors can affect the timing resolution at the few hundred picoseconds level.

We also can calculate theoretical values of timing resolution following $\sqrt{(}\tau/N)$ equation given by Bengtson and Moszynski [13], where τ is a decay time constant and N is the number of generated photoelectrons. Decay time values are already given in Table I (we use only the smallest value). Since the number of photoelectrons per MeV is around 15600 (assuming light output of 74 000 ph/MeV, 90% collection efficiency, and 23% quantum efficiency of the tube) and the energy threshold was set to ~ 0.25 MeV, N is equal 3900 photoelectrons for $LaBr_3$:5%Ce. In our calculations we scaled the N value according to the light output of the samples. The results of calculations are shown in Table I in $\sqrt{(}\tau/N)$ column.

Since the calculated values were derived from a formula that does not take into account rise times, they differ from the measured values when samples exhibit longer rise times. This difference gradually decreases as the rise time values shorten. For a ~ 0.2 ns rise time (the 30% sample) the experimental results match the calculated value (~ 70 ps) very well.

VII. Summary

In this communication, we investigate $LaBr_3$ scintillation properties as a function of Ce concentration. The results show that the light output does not change significantly with Ce concentration for measured samples.

On the other hand we have found the timing properties to be a strong function of Ce concentration. As the Ce content increases, the principal decay time constant decreases from 26 ns for 0.5% Ce to about 17 ns for crystals with 5% and more of Ce. Moreover, there is also a significant change in rise time constants. The average rise time measured for samples doped with 0.5% are as long as 9 ns, whereas for a sample doped with 20% it reduces to less than 0.2 ns. The change of the rise time has a major effect on the timing properties of this scintillator, with its timing resolution improving from 361 to 73 ps.

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